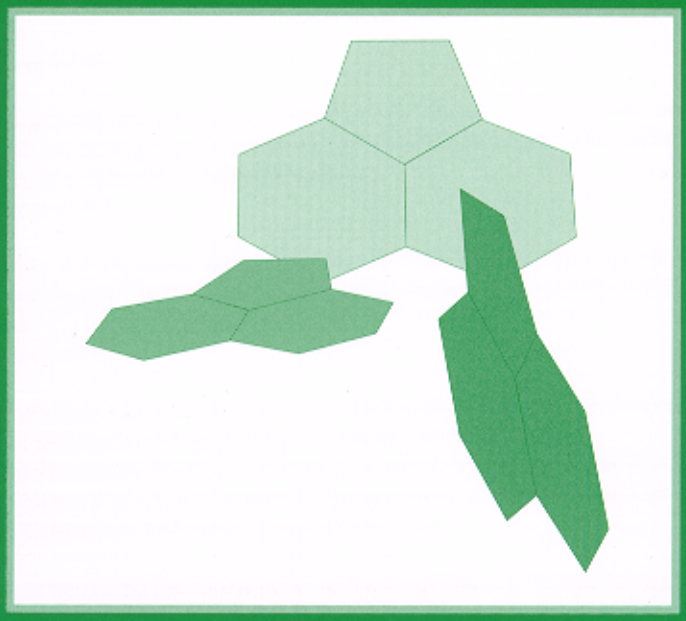
Anions of Acenaphthylene

Reactions, NMR Spectroscopy and Quantum Chemical Calculations



M.E. Van Loo

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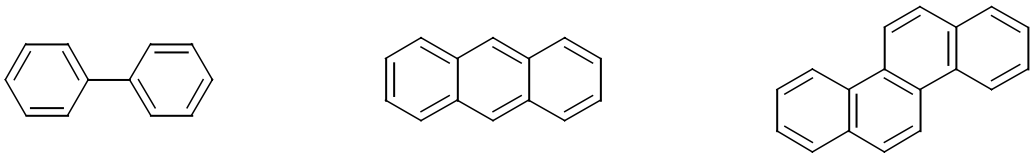
1

Introduction

1.1 General introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic molecules, which consist of two or more unsaturated rings. The five-, six- or seven-membered rings can be linked together in three manners giving the following categories: polyaryls, *ortho*-fused PAHs and *ortho*- and *peri*-fused PAHs. In polyaryls (Figure 1) two rings are connected by a single bond (e.g. biphenyl), in *ortho*-fused PAHs two rings share a common C-C bond (e.g. anthracene, chrysene) and in *ortho*- and *peri*-fused PAHs three rings share a common C-C bond and a common central C-atom (e.g. pyrene, acenaphthylene).[1]



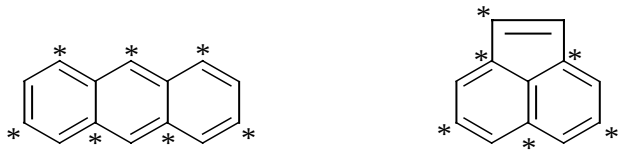
1 **2** **3**

4 **5**

Figure 1*: Examples of PAHs: biphenyl* ***(1)****, anthracene* ***(2)****, chrysene* ***(3)****, pyrene* ***(4)*** *and acenaphthylene* ***(5)****.*

A second classification among PAHs is the division into alternant and non-alternant PAHs. In alternant PAHs, the carbon atoms can be assigned as starred (*s*) and unstarred (*u*) with each *s*-carbon having only *u* neighbours and *vice versa* (Figure 2).[2] In non-alternant PAHs either two adjacent *s*-carbons or *u*-carbons are present. Alternant PAHs are constituted of even-membered rings only,

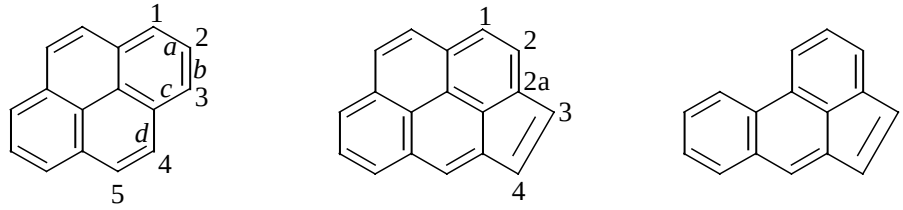
whereas in non-alternant PAHs at least one odd-membered ring is present. The difference between alternant and non-alternant PAH is exhibited properly in the positions of the π-molecular orbital energy levels in HMO calculations: in alternant PAHs these levels are symmetrically positioned about the α level (α = 0 by definition), in non-alternant PAHs they are not.



2 **5**

***Figure 2**: Alternant and non-alternant PAHs.*[2]

IUPAC has formulated rules for naming, numbering and orientation of PAHs.[3-6] PAHs which have no accepted trivial name are named by prefixing to the name of a component ring (system) designations of the other components. For example, the prefixes cyclopenta and ace in cyclopenta[*cd*]pyrene (**6**) and acephenanthrylene (**7**) point to the presence of a five-membered ring (Figure 3). The PAH is oriented so that the greatest number of rings is in a horizontal row and a maximum number of rings are above and to the right of the horizontal row.[7] Letters and/or numbers indicate at which position a ring or substituent is located. The system is numbered in a clockwise direction commencing with the carbon not engaged in a ring-fusion in the most counter-clockwise position of the uppermost ring. Atoms common to two or more rings are designated by adding roman letters "a", "b", "c", etc., to the number of the position immediately preceding. The peripheral sides of the base component are lettered *a*, *b*, *c*, etc., beginning with "*a*" for the side "1,2", "*b*" for "2,3" or "2,2a" and so on.



4 **6** **7**

***Figure 3**: Pyrene (**4**), cyclopenta[*cd*]pyrene (**6**) and acephenanthrylene (**7**).*

Polycyclic aromatic hydrocarbons are widely spread in the environment and are predominantly formed by incomplete combustion of organic material.[8-13] Natural sources (volcanic activity, forest fires, and biosynthesis)[14-17] account partly for the distribution. However, the majority of PAHs

results from human activities such as the burning of fossil fuels for power and heat generation, in power plants, industrial processes and engines of aeroplanes and automobiles.[18-23] Significant levels of PAHs have been detected in food, air and drinking water[24-26] but also in the interstellar medium,[27-34] thanks to the development of sensitive detection techniques.[35]

PAHs can enter the human body by inhalation of contaminated air (e.g. tobacco smoke or exhaust-gases from cars)[36-38] or by eating food containing PAHs (grilled meat).[39] This exposure to PAHs has a variety of consequences for health: some PAHs are known to have toxicological effects or they may even act as mutagens or carcinogens, leading to tumours of lungs, stomach, kidneys and liver.[40-43]

Although PAHs are widely spread in the environment it is not possible to separate the complicated mixtures into their single components. Therefore, pure, well characterised PAHs are necessary as reference materials for the analysis of PAHs as environmental pollutants and, of course, for the study of their biological properties.[44-47]

Establishing the structure-activity relationships is important for the elucidation of the mechanism of cancer induction and for the prediction of the properties of new PAHs.[48,49] The presence and position of an extra benzene ring, methyl group[50] or nitro group[51-55] can make the difference between a harmless chemical and a highly mutagenic/carcinogenic one. Pyrene, for example, is not carcinogenic whereas benzo[*a*]pyrene[56] and some nitropyrene derivatives have been shown to be carcinogenic.[1,57-63] Similarly, the introduction of one or more fused five-membered rings to the carbon skeleton of a PAH can increase the mutagenic potency as in cyclopenta[*cd*]pyrene and aceanthrylene.[64-66]

Not only the biological but also the physical properties of PAHs are interesting. Some PAHs are used as fluorescent probes either linked to a frame[67-71] for the study of biological processes or by themselves in environmental monitoring[72]and in polymer research.[73] The aromaticity of PAHs allows their application in conducting polymers,[74,75] organic (photo)conductors[76,77] and solar cell research.[78,79] Frequent use of PAHs is observed in pigments for dyes.[80,81]

Apart from these noble reasons, the structures of PAHs invite research groups all over the world to build such beautiful molecules.

1.2 Aromaticity

The term aromaticity is indissolubly connected to benzene. Since in benzene the delocalisation of the π-electrons is complete, benzene is the prototype of an aromatic system. Before the idea of the special stability of aromatic systems, the term aromaticity was associated with chemical reactivity. Unlike other unsaturated systems, aromatic compounds undergo substitution rather than addition.

In polycyclic aromatic compounds the delocalisation is not as ideal as in benzene. The fusion of two or more aromatic rings causes a perturbation in the delocalisation of the electrons. This leads to the question to which degree PAHs are aromatic. Criteria for aromaticity are based on theory and on experimental data. Regarding the following theories it is obvious that there still is much discussion about what aromaticity is and when a PAH can be designated as aromatic.

Theoretical criteria

According to Hückel a planar, monocyclic, completely conjugated system is aromatic when the ring contains (4n + 2) π-electrons.[82,83] In benzene the six p-atomic orbitals are linearly combined to molecular orbitals with energies given in terms of α, the Coulomb integral of an electron in a carbon 2p atomic orbital, and β, the resonance integral, expressing the interaction energy between two neighbouring 2p orbitals. Three orbitals are lower in energy than the atomic orbitals from which they are derived and they are the bonding orbitals (Figure 4). The three orbitals that are higher in energy are the antibonding orbitals. The six π-electrons of benzene can be placed pairwise into the bonding orbitals and this results in a stabilisation of 2 β with respect to the individual atomic orbital energies. This stabilisation energy, also called delocalisation energy, is the cause of the special stability of benzene.

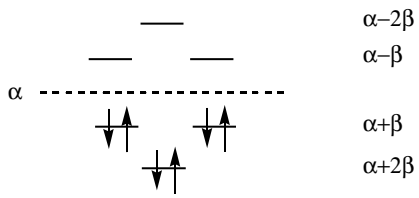
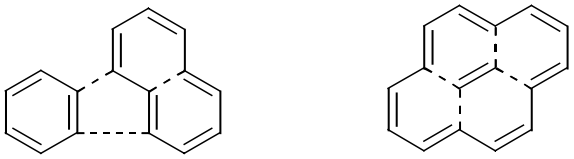


***Figure 4**: HMO-scheme for benzene.*

The resonance energies according to Hückel (HRE) are equivalent to the delocalisation energies. Comparison of the HRE gives an estimation of the relative stability of aromatic molecules. However, because the HRE is used to evaluate the energy of the electron delocalisation rather than the cyclic electron (bond) delocalisation, this method is not very suitable for the determination of aromaticity.[84]

Extrapolation of the Hückel theory to polycyclic aromatic hydrocarbons is more difficult. Application of the rules would lead to the conclusion that fluoranthene (**8**) and pyrene (**4**) should be antiaromatic compounds, which disagrees with their known chemical properties. A possible solution for this problem is the examination of the PAH as conjugated cyclic polyenes which are internally cross-linked and/or linked to other cyclic polyenes (fluoranthene) or double bonds (pyrene) (Figure 5).[85]



8 **4**

***Figure 5**: Aromaticity of fluoranthene and pyrene regarded as cross-linked polyenes.*[85]

In Dewar's definition aromatic molecules have a cyclic π-electron delocalisation which reduces the energy content of the systems relative to that of the corresponding model compounds without cyclic delocalisation.[86] In antiaromatic systems the cyclic π-electron delocalisation leads to a strong destabilisation with respect to the acyclic analogues. The resonance energy according to Dewar, DRE, is found as the difference between the atomisation enthalpies of a given conjugated molecule and the classical Kekulé reference structure.[87] *Ab initio* calculations have confirmed the additivity for linear polyenes and thus justified the basis of this calculation method.

Hess and Schaad applied the DRE calculation method within the HMO method, with the important expansion of making a distinction between different types of C-C bonds.[88-91] Their calculation method confirmed the importance of the correct choice of the reference structure, because even if they used the less sophisticated HMO method, they obtained better results than Dewar. A further improvement was made by Moyano and Paniagua, who parameterised the π-bond energies, based on the localised molecular π-orbitals.[92]

Due to progress in the computer techniques many methods for the calculation of resonance energies have been developed and this has led to a simplification of the calculations.[93-96]

A simple and practical method to understand the aromatic stability and behaviour of PAHs was developed by Clar.[97] In Clar's model the π-electrons are localised favourably in sextets, as in benzene rings. The stability of the structure increases with the number of π-electron sextets. PAHs which can be regarded as cross-linked purely benzenoid partial systems, such as triphenylene, are the most stable PAHs known.[98] In contrast with the HMO-model, aromaticity is not a molecular property but localised in distinct rings. Clar's model predicts many of the chemical and physical

properties of PAH, e.g. reactive positions in electrophilic aromatic substitution and bond lengths, correctly.

The conjugated circuits' model (CC model) as proposed by Randic uses the Kekulé valence structures.[99,100] In the individual Kekulé structures the regular alternations of carbon carbon single and double bonds form the so-called conjugated circuits.[101] PAHs are viewed as a superposition of conjugated circuits instead of as a collection of Kekulé valence forms. In all Kekulé structures conjugated circuits of six, ten or more (4n+2) bonds are determined and if the number of conjugated circuits is also (4n + 2) the PAH is aromatic.[102]

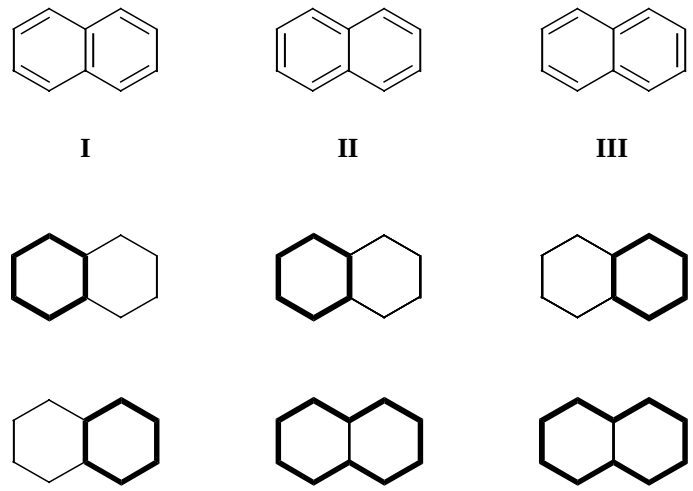


***Figure 6**: Aromaticity of naphthalene according to the conjugated circuits' model.*[102]
There are three Kekulé valence structures for naphthalene I, II and III. Structure I consists of two Kekulé formulae of benzene (fused across the double bond). In structures II and III, next to one Kekulé benzene formula, a second circuit can be observed of ten carbons, representing a regular alternation of five single and five double bonds. From the total of 6 circuits it can be concluded that naphthalene is an aromatic structure.

The resonance energy can be calculated by summation of the energies of the individual circuits.[103] For the comparison of the aromaticity of PAHs the resonance energy per π-electron should be calculated. In Figure 6 this theory is worked out for naphthalene. A classification of PAH according to their degree of benzene character, i.e. their benzoidicity, can be made using the conjugated circuits' model.[103] The results are in agreement with the predictions made by Clar. A statistical approach of the CC model can give a good estimation of the aromaticity for large PAH.[104]

Platt suggested the peripheral criterion based on the free-electron theory, treating cross-links and inner sp^2 carbons as small perturbations.[105] A cyclic or polycyclic system has aromatic character if it

has (4n + 2) π-electrons in its periphery. 4n π-Electrons would lead to anti-aromaticity and systems with (4n + 1) or (4n + 3) π-electrons in its periphery would be estimated as nonaromatic. Now pyrene (**4**) and fluoranthene (**8**) are estimated to be aromatic and non-aromatic, respectively.

Experimental criteria

A criterion that refers to experimentally observable phenomena is based on magnetic anisotropy.[106-109] Aromatic compounds are defined as cyclic or polycyclic systems which sustain a diamagnetic ring current and consequently exhibit a total diatropic, low-field ^{1}H NMR chemical shift relative to that of olefinic protons. Nonaromatic compounds give rise to characteristic olefinic ^{1}H NMR patterns, while in antiaromatic species the paramagnetic ring current results in a high-field ^{1}H NMR band displacement.[106,110-112]

A second experimentally based criterion for aromaticity uses bond lengths. Aromatic compounds reveal a low degree of bond length alternation around the characteristic bond length (1.38-1.40 Å) in contrast with nonaromatic compounds.[113] The bond lengths can be determined by electron diffraction and X-ray diffraction.

Finally, reactions of aromatic compounds differ from those of alkenes. Alkenes undergo additions with for example bromine and dienes (Diels-Alder), whereas aromatic compounds preferably react in substitution reactions. The relative heats of reaction towards for example hydrogenation can be used to determine the degree of aromaticity of aromatic molecules.[84]

A related index for the structural stability is the value of the HOMO-LUMO energy gap. In reactions in which the HOMO and LUMO take part in driving the reaction, aromatic compounds with a high HOMO-LUMO energy gap are more stable and will show lower reactivity.[84]

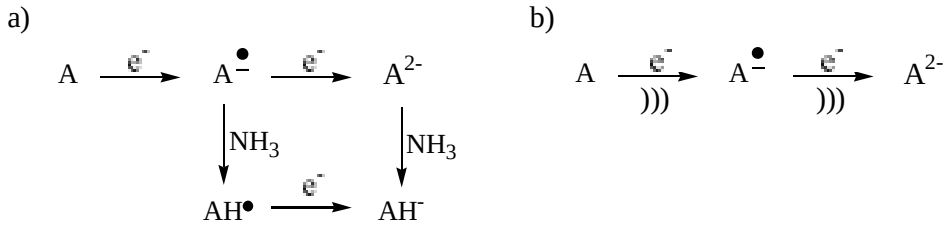
1.3 Reduction and reductive alkylation of PAHs

For the syntheses of PAHs a broad scale of chemical reactions can be used, ranging from electrophilic aromatic substitution to photochemical reactions, from pyrolysis to Diels-Alder reactions. One reaction that converts PAHs very effectively into useful derivatives is the dissolving metal reduction.[114-116] In this reaction anions of PAHs are generated by electron transfer from an alkali metal to the PAHs.[117] These anions react readily with electrophiles, such as protons and alkyl halides, often with remarkable regioselectivity.[118-120] Therefore, the reaction products often are valuable intermediates in the preparation of specifically substituted PAHs[121-126] and other polycyclic compounds.[127,128] In contrast to electrophilic aromatic substitution, in which a relatively unreactive PAH is treated with an activated electrophile, this mild method permits the use of less reactive electrophiles, e.g. alkyl halides instead of acyl chlorides in combination with a Lewis acid.

In the classical dissolving metal reduction, the Birch reduction, the PAH and an alkali metal are dissolved in liquid ammonia.[129,130,] In the first step, one electron is transferred from the alkali metal

to the PAH, resulting in a radical anion $\mathbf{A^{\bullet -}}$ (Scheme 1).[131] This radical anion can be observed by ESR spectroscopy. The second step depends on the size and the stability of the radical anion.[132] Small or less stable radical anions are often protonated by ammonia, thus forming a neutral radical $\mathbf{AH^{\bullet}}$. A second electron transfer leads to the monohydroanion. Otherwise, the radical anion may accept a second electron, generating a dianion $\mathbf{A^{2-}}$. The dianion may persist, or it may be protonated by the solvent (ammonia), leading to the monohydroanion $\mathbf{AH^{-}}$. Phenanthrene is already protonated by ammonia at the stage of the radical anion and a hydroanion is formed after a second electron transfer. Anthracene and pyrene follow the second reaction path, resulting in the anthracene dianion and the 5-hydropyrene anion, respectively.

Apart from the protonation of initially formed radical anions or dianions by ammonia, and the overreduction, due to repeated electron transfer to neutral reduction products,[133] the use of ammonia as a solvent in laboratories should be reconsidered for safety reasons as well as because of the complicated procedures and equipment needed for this low temperature reaction. A more convenient method for the preparation of dianions is the reduction in strictly aprotic solvents.[134,135] In contrast to the reduction in ammonia, in which the metal dissolves and thus the solvated electrons are transferred easily to the PAH, the reaction without ammonia is a solid surface reaction and therefore slow. Sonication facilitates the reaction[136] and reduces the reaction time to a few hours.



Scheme 1*: a) Dissolving metal reduction of PAHs; b) aprotic reduction of PAHs.*

The structure of the aromatic dianions and hydroanions can be elucidated by ^{1}H and ^{13}C NMR spectroscopy techniques such as 2D NMR and decoupling experiments.

Apart from the structure elucidation, NMR chemical shifts afford further information on π-charge densities, charge delocalisation patterns and the anisotropy of the system.[136] It is known that shielding of hydrogen and carbon atoms in charged conjugated systems varies linearly with the corresponding π-electron density[137-143] and can be formulated as follows:

$$\delta_H = \delta_N - K_H \Delta q_\pi \qquad (1)$$

$$\delta_C = \delta_N - K_C \Delta q_\pi \qquad (2)$$

With: δ_H = chemical shift of the proton in the charged species

δ_C = chemical shift of the carbon in the charged species

δ_N = the corresponding shift for the neutral precursor

q_π = the quantity of π-charge
K = proportionality factor

Of course these equations should be used with caution. The proportionality factors K depend on several molecular parameters such as the molecular structure and the hybridisation of the carbon atoms. Generally, 10.7 ppm per electron is taken for K_H and 160 ppm per electron is a good value for K_C.[136] These correlations enable estimation of the charge at the individual atoms and the total charge in the molecule. Because proton shifts are strongly influenced by induced magnetic fields, carbon shifts are preferred for the determination of the local π-charge density.

A second method for the determination of the charge distribution in conjugated anions is a study of the regioselectivity of protonation and alkylation of the anions. The atoms with a high electron density are most susceptible to kinetically controlled electrophilic attack.[144,145,146]

Finally, these experimentally observed data can be supported by charge density calculations.[147]

1.4 Acenaphthylene

Berthelot[148,149] discovered acenaphthylene in 1867 and gave the compound the name derived from its synthesis i.e. the reaction of naphthalene with acetylene (or ethylene) in a hot tube oven. In 1873 Behr and Van Dorp synthesised acenaphthylene by the oxidation of acenaphthene with lead(II) oxide.[150-152]

Since the discovery of acenaphthylene it has been isolated from charcoal,[153] pyrolysis of natural gas,[154] cigarette smoke and shale oil.[155] Acenaphthylene itself is not carcinogenic or mutagenic, but it can give rise to irritations in contact with eyes, skin and respiratory system.[156]

Acenaphthylene is one of the smallest PAHs and because it is commercially available, it can well be used as a building block for the synthesis of larger PAHs such as fluoranthene[157] and acephenanthrylene.[158]

Aromaticity in acenaphthylene and its dianion

Application of the simple Hückel rules to acenaphthylene would lead to the conclusion that it is antiaromatic with its 12 π-electrons. Therefore, acenaphthylene can better be regarded as the aromatic naphthalene linked to a double bond (Figure 7A). This structure is confirmed by most of the theoretical and experimental criteria. Clar predicts the olefinic bond character of the bond between C-1 and C-2 (Figure 7B). Reactions with acenaphthylene show the aromatic and the olefinic character of the naphthalene skeleton and the double bond, respectively. The double bond character is confirmed by the addition reaction with bromine and by photodimerisation.[159]

When conjugated circuit counts are made, acenaphthylene has the same conjugation content as naphthalene, because the external C(1)-C(2) double bond can never be involved in a conjugated circuit.[102]

According to Platt's model acenaphthylene should be depicted as a perturbed [11]annulene, or as a (4n + 3) π conjugated system (n=2), with an inner carbon atom acting as a weak perturbation to the annulene skeleton.[160] Consequently, acenaphthylene is expected to reveal a nonaromatic, polyvinylic character (Figure 7C). This is not in accordance with the other criteria and the experimental results.

The protons at C-1 and C-2 appear in the ^{1}H NMR spectrum near 7 ppm, separate from the signals of the naphthalene moiety. This points to the presence of only a small amount of aromatic character in the five-membered ring of acenaphthylene.

Also on the basis of bond length considerations, acenaphthylene can best be described as a naphthalene weakly conjugated with an outer double bond. The C(1)-C(2) bond was calculated to have a value typical for a double bond, the connecting bonds (C(1)-C(8a) and C(2)-C(2a)) are substantially longer than the aromatic bonds (Figure 7D). From neutron diffraction experiments the double bond appears to be somewhat longer than a normal double bond, and in this way may reflect the strain imposed by the naphthalene framework on the double bond.[161]

From theoretical calculations it is known that the RE of acenaphthylene is only slightly higher than the RE of naphthalene, indicating that the aromatic character mainly comes from the naphthalene skeleton.[162,163]

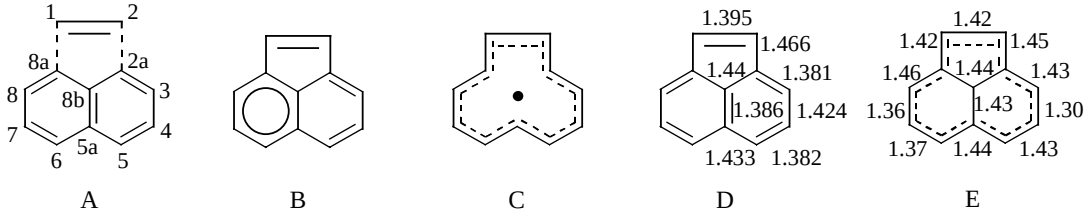


***Figure 7**: Aromaticity in acenaphthylene according to: A. Hückel, B. Clar and C. Platt's model; Bond lengths: D. acenaphthylene, E. acenaphthylene dianion.*

The acenaphthylene dianion has 14 π-electrons and would, using Hückel rules, be considered as aromatic. Similarly to the neutral species it depends on the participation of the C(1)-C(2) bond in the delocalisation if the dianion is really aromatic.

In the conjugated circuits' model negative charge is counted as a double bond, based on the structure of the cyclopentadienyl anion.[102] Similarly to the neutral systems, Kekulé structures should be drawn and the resonance energies calculated. Comparison of the resonance energies of acenaphthylene and its dianion gives a reduction of the aromaticity for the latter with 26%.[102]

However, the decrease in resonance energy is less than in the hypothetical naphthalene dianion. Therefore, it can be concluded that the outer double bond contributes more to the conjugation of the dianion than in the case of the neutral compound.

For the estimation of the aromatic character of the acenaphthylene dianion according to the peripheral criterion, it is important how the 14 π-electrons are distributed over the 12 carbon atoms. The two extra electrons can be inserted into the periphery resulting in an [11C-13π] system or one of the extra electrons is located on the inner carbon C-8b and the other in the periphery resulting in an [11C-12π] system.[160] The latter would be expected to have antiaromatic character. By means of ^{13}C NMR spectroscopy it has been established that little charge is located at the central carbon and thus that the two electrons are distributed over the outer carbons resulting in a nonaromatic structure.[160]

This conclusion was confirmed by bond length determination from the dilithium complex of the acenaphthylene dianion by X-ray crystallography (Figure 7E). The decrease of the C(1)-C(8a) bond distance and increase of the C(1)-C(2) bond length indicate that the C(1)-C(2) bond is now part of the delocalisation pattern. It should be noted that also the C(3)-C(4) bond shortens and that the structure is less symmetric.[164] Calculations of the charge density and the HOMO-LUMO gap and comparison with the experimental ^{1}H and ^{13}C NMR data indicate also that the five-membered ring double bond is part of the electron delocalisation, in contrast to the neutral system.[165]

Reduction of acenaphthylene

Acenaphthylene can be reduced in a Birch-reduction like procedure. The product depends on whether the radical anion or the dianion is protonated: The radical anion gives acenaphthene while the dianion yields 1,5-dihydroacenaphthylene.[166] The protonation of the acenaphthylene dianion in ammonia seemed to depend on the counter ion. To avoid undesired protonation, the acenaphthylene dianion could be prepared in aprotic solvents using sonication of the solution in the presence of an alkali metal[167] or by deprotonation of acenaphthene. [168,169]

The acenaphthylene dianion and the 5-hydroacenaphthylene anion were prepared in NMR tubes and spectra were recorded.[170,171] From these spectra some predictions about the reactivity of the reactive species were made.[172] These were in accordance with the protonation experiments.

From the reactions of the acenaphthylene dianion with dihaloalkanes it was concluded that the acenaphthylene dianion does not react selectively with electrophiles.[173] In other cases the dianion was concluded to react very selectively based on 100 MHz ^{1}H NMR spectra![168,169] In Chapter 2 a more detailed discussion of the literature on the acenaphthylene anions and their reaction products is given. It is obvious from these examples that the relationship between structure and reactivity of the anions of acenaphthylene towards electrophiles requires a more detailed study.

1.5 Purpose of this investigation

In this thesis two important aspects in the reactivity of anions of PAH are investigated:
1: The influence of electrophiles on the mechanism of the reductive alkylation of acenaphthylene (Part I: Chapters 2-6).
2: The influence of substituents on the reactivity of anions of acenaphthylene (Part II: Chapters 7-9).
For the first aspect acenaphthylene can be taken as a model compound for non-alternant PAH. In spite of its small size it is easily converted into its dianion. Both the dianion and the hydroanion are subjected to reactions with electrophiles. Analysis of the reaction products in combination with NMR spectroscopy and calculations of the intermediate anions will help us to understand the reaction pathway of electrophiles with anions of PAH.

A second point of interest is the use of the reductive alkylation in the synthesis of larger PAH. Therefore, electrophiles with a second functionality were used in order to find a general route for the extension of the PAH skeleton.

In the second part the influence of electron-withdrawing and electron-donating groups on the reaction of the acenaphthylene anions with simple electrophiles will be discussed. NMR spectroscopy, cyclic voltammetry, alkylation experiments and calculations will be used to study the substituted anions. The effect of the substituent will be dependent on its electronic properties as well as on its position at the acenaphthylene skeleton. Next to the understanding of the influence of substituents on the reactivity of PAH in reductive alkylation experiments, this part provides routes for the selective synthesis of disubstituted acenaphthenes.

A general conclusion is given in Chapter 10. This thesis is concluded with summaries in English and Dutch.

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Part I

Reductive alkylation of

Acenaphthylene

2

The acenaphthylene dianion and 5-hydroacenaphthylene anion

2.1 Introduction

The investigation of the reactivity of the acenaphthylene dianion starts with the use of simple electrophiles: a proton donor (methanol and/or water) and methyl iodide. With these reagents the reactive positions in the anionic intermediates can be determined. The results will be correlated to NMR data and compared to the results of quantum chemical calculations. In these calculations, the charge and HOMO coefficient distributions in the dianion and the hydroanion are used to predict the most reactive positions. Because reactions of anions of PAH with electrophiles normally are fast and thus have an early transition state, this initial state approximation might give a good insight in the reaction process.

2.2 Results

2.2.1 Reactions with electrophiles

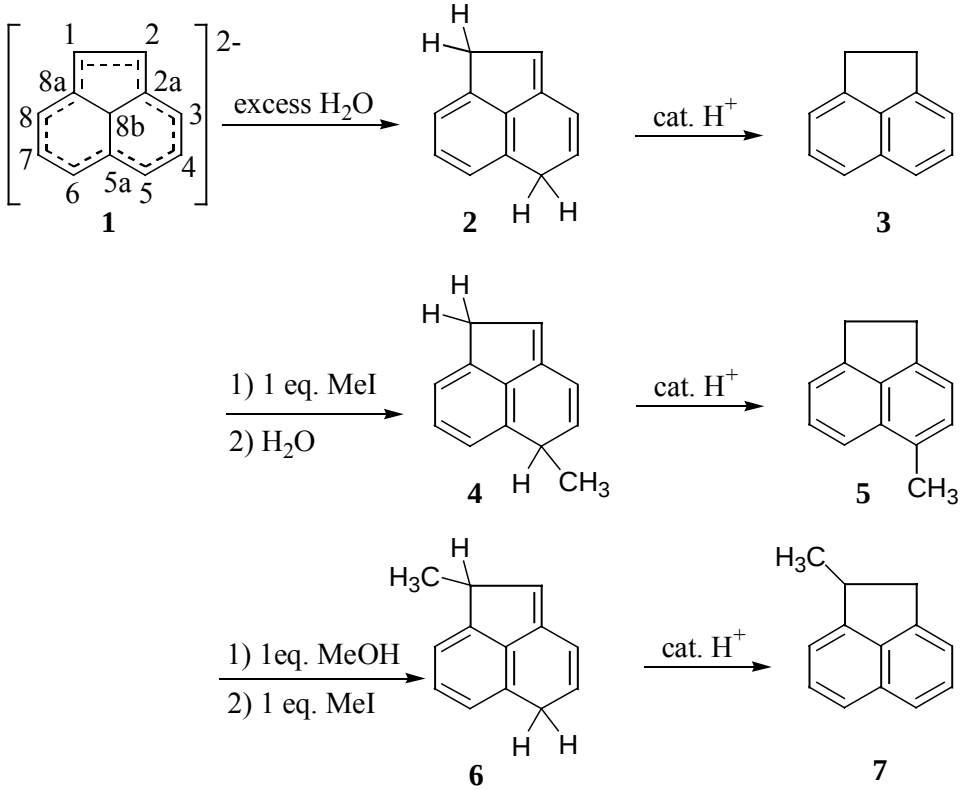
The dianion of acenaphthylene was prepared by dissolving the hydrocarbon (0.5-5 g) and 2.2 equivalents of sodium in anhydrous THF, and exposing the solution to ultrasonic vibration. Within 3-5 hours the colour of the solution turned deep green, indicating that the dianion (**1**) (Scheme 1) had been formed.[1]

The solution of **1** was treated at -70ºC with excess water and stirred for 15 minutes at room temperature. After extraction with light petroleum (boiling range 40-60ºC) and work-up, 1,5-dihydroacenaphthylene (**2**) was obtained quantitatively. Upon dissolving **2** in acetone and adding a few drops of concentrated HCl, a rearrangement took place, resulting in the formation of the stable acenaphthene (**3**) in 98% yield (Scheme 1).

In the next experiment one equivalent of methyl iodide was added to **1** at -70ºC, and the mixture was stirred for 30 minutes at room temperature. The solution was again cooled to –70ºC and excess water was added. 1,5-Dihydro-5-methylacenaphthylene (**4**) was isolated after extraction with light petroleum (boiling range 40-60ºC) and work-up in more than 95% yield. This compound appeared to be unstable upon storage at room temperature; under slightly acidic conditions it rearranges to 5-methylacenaphthene (**5**) quantitatively (Scheme 1).

If the sequence of addition of the electrophiles to the dianion was reversed i.e., with the addition of one equivalent of proton donor (methanol) followed by one equivalent of methyl iodide, the procedure described above yielded 1,5-dihydro-1-methylacenaphthylene (**6**) almost quantitatively. 1-Methylacenaphthene (**7**) was obtained after exposure of the product to slightly acidic conditions (Scheme 1).

When two equivalents of methyl iodide, or one equivalent of ethyl iodide followed by one equivalent of methyl iodide, were added to the acenaphthylene dianion, a mixture of mono-, di- and multisubstituted products was obtained.



***Scheme 1**: Reaction of the acenaphthylene dianion with electrophiles.*

2.2.2 ^{1}H and ^{13}C NMR spectroscopy

*Acenaphthylene dianion (**1**)*

The dianion of acenaphthylene was prepared in THF-d_8 in an NMR tube, using the procedure described by Van Dijk (See experimental).[2] The measured spectra (^{1}H and ^{13}C) were nearly identical to those reported previously.[1,3-8] Small deviations in chemical shifts can be ascribed to differences in conditions. The spectra were assigned using H-H and C-H COSY techniques. The signals in the ^{1}H NMR spectrum are broad. This might be due to the temperature (20ºC) and the

high concentration. The protons H-5 and H-6 have the highest chemical shift value (5.93 ppm) and this means that a large amount of charge is located at C-5 and C-6.

The signals in the ^{13}C NMR spectrum are very sharp, indicating that no more radical anion is present. It can also be concluded that the acenaphthylene dianion is a diamagnetic and symmetric particle. The ^{13}C NMR shift values strongly depend on the temperature and on the counter ion.[4,5,8] At room temperature the signals of C-5/C-6 appear at the highest field (82.6 ppm), followed by C-1/C-2 (85.9 ppm) and C-3/C-8 (96.9 ppm). The average shift over all carbon atoms due to the lower temperature was 0.34 ppm per carbon atom downfield. Lowering of the temperature to -80ºC results in a downfield shift for C-5/C-6 to 83.7 ppm whereas C-1/C-2 undergo an upfield shift to 84.7 ppm.

***Table 1**: ^{13}C NMR chemical shifts of **1** and acenaphthylene (ANY) in ppm, the difference in chemical shift between neutral and dianion and the charge derived from this difference.*

Carbon atom	δ ^{13}C (20ºC)	δ ^{13}C (-80ºC)	δ ^{13}C ANY	δ (**1**) - δ (ANY)	charge
1,2	85.9	84.7	129.7	-43.8	-0.36
3,8	96.9	96.1	128.7	-31.8	-0.26
4,7	126.7	126.9	124.3	+2.4	+0.02
5,6	82.6	83.4	127.9	-45.3	-0.38
2a, 8a	123.4	122.9	140.0	-16.6	-0.14
5a	149.2	148.6	128.4	+20.8	+0.17
8b	137.7	137.0	127.4	+10.3	+0.09

The ^{13}C chemical shifts can be used as measure for the charge distribution in the acenaphthylene dianion.[8] The shielding of the carbon atoms is supposed to vary linearly with the corresponding π-electron density (see Chapter 1). The ^{13}C NMR signals are paratropically shifted with respect to the signals of the neutral compound by a total of 239.1 ppm. This is considerably less than would be expected for the induction by two electrons (320 ppm). A possible explanation for the low K_c is a reduced average excitation energy and consequently an increased paramagnetic shielding in the dianion.[4] This might also be the explanation for the variation of K_c with different combinations of cation, solvent and temperature. Because also other PAH gave variations of K_c, system-specific K_c-values should be used.[4]

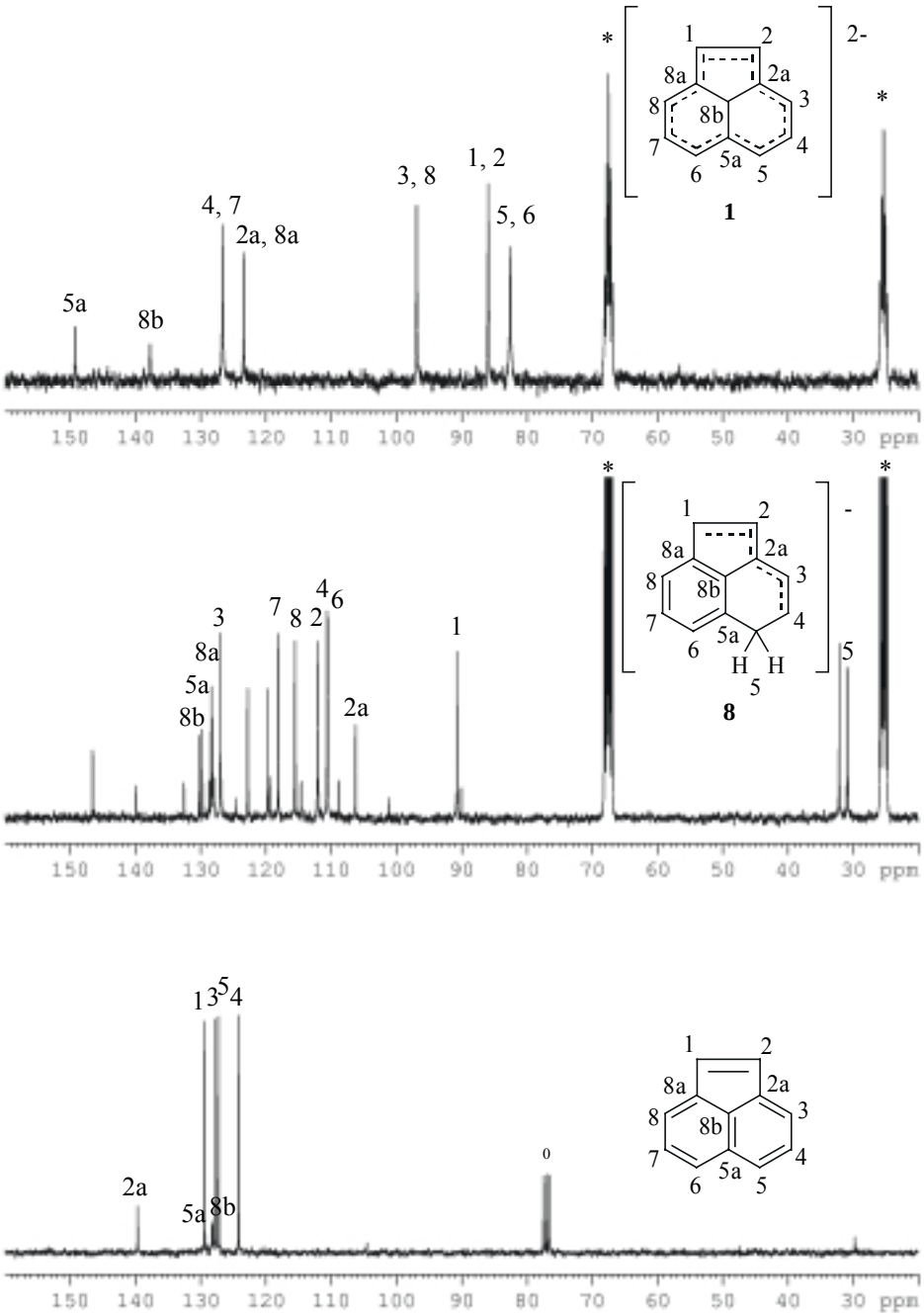


Figure 1: *^{13}C NMR spectra of the acenaphthylene dianion (**1**), the 5-hydroacenaphthylene anion (**8**) and acenaphthylene (75 MHz, 20ºC, * = THF, º = $CDCl_3$, the spectrum of **8** contains some acenaphthene).*

The difference in chemical shifts between the neutral and dianionic system was used to estimate the charge on the carbon atoms (Table 1, column 6). Despite the fact that the five-membered ring tends to attract the charge to its carbon atoms it appears that the highest charge is found at carbon atoms 5 and 6. Also a high charge is located at carbon atoms 1 and 2, although less than expected.[7] The carbon atoms 4 and 7 are predicted to bear even a positive charge. The carbon atoms with the highest charge are the ones from which the ^{13}C NMR shifts are most affected by the temperature. More detailed NMR studies showed that in the case of lithium one cation is linked to the five-membered ring while the other appears as a solvated ion at positions 5 and 6.[8]

*5-Hydroacenaphthylene anion (**8**)*

The 5-hydroacenaphthylene anion (**8**) was prepared in THF-d_8 and transferred into an NMR tube. The measured spectra (^1H and ^{13}C) were similar to those recorded by Müllen and co-workers.[6] The small deviations in chemical shifts can be ascribed to differences in temperature, counter ion (Na *versus* Li), proton donor (methanol *versus* ammonia) and concentration. The ^1H and ^{13}C NMR spectra were assigned completely using H-H and C-H inverse COSY techniques. The ^1H spectrum (see experimental section) consists of 7 broad signals forming an ABC pattern for protons H-6, H-7 and H-8, an AB pattern for H-1 and H-2 and an ABX_2 pattern for H-3, H-4 and H-5. H-6 and H-8 could be distinguished by measuring NOEDIFF.

From the chemical shifts in the ^{13}C NMR spectrum (Table 3) the charge distribution in the hydroanion can be determined.[8] It is obvious that the highest charge is located at C-1. However, attention should be paid to C-2a, which has a noteworthy shift upfield, indicating that also a substantial amount of charge is located at this carbon atom.

Although in ^1H NMR H-4 is found at relatively high field (4.78 ppm), the ^{13}C NMR chemical shift indicates that much less charge is located at C-4 than at C-1. Because in ^1H NMR other factors such as ring current contribute to the shielding of hydrogens, an indication of the charge distribution should preferably be based on ^{13}C NMR.Furthermore it should be noted that C-3 appears at very low field and thus has very little negative charge or even is positively charged. This is in accordance with the charge alternation concept as proposed by Rabinovitz and co-workers.[7]

*1,5-Dihydroacenaphthylene (**2**), 1,5-dihydro-5-methylacenaphthylene (**4**) and 1,5-dihydro-1-methylacenaphthylene (**6**)*

The ^1H NMR spectrum of 1,5-dihydroacenaphthylene (**2**) was identical to that reported earlier.[9]

The ^1H NMR spectrum of 1,5-dihydro-5-methylacenaphthylene (**4**) closely resembles that of **2** and consists of an ABX and an $ABMX_3$ pattern for the non-aromatic part of the molecule and an ABC pattern for the three aromatic protons. The methyl group shows couplings with H-5 and H-4.

The ^{1}H NMR spectrum of 1,5-dihydro-1-methylacenaphthylene (**6**) is similar to the spectrum of 1,5-dihydro-5-methylacenaphthylene (**4**). The non-aromatic protons gave an ABX_2 and an AMX_3 pattern. In this case the methyl group gave only coupling with H-1.

*5-Methylacenaphthene (**5**) and 1-methylacenaphthene (**7**)*

After rearrangement of **4**, the methyl group has become benzylic and shifts to 2.61 ppm. The rest of the spectrum of 5-methylacenaphthene (**5**) closely resembles that of acenaphthene.

The aromatic part of the ^{1}H NMR spectrum of 1-methylacenaphthene (**7**) is almost identical to that of acenaphthene. The methyl group induces chirality at C-1. The protons at C-2 can be distinguished on the basis of their different couplings with H-1; the H-H cis-coupling is 8.0 Hz whereas the trans-coupling is 3.2 Hz.

2.2.3 *Ab initio* calculations

Quantum chemical calculations can give additional information for the understanding of chemical reactions and NMR spectra. Therefore, the charge distribution, the HOMO coefficients and the shielding constants were calculated with *ab initio* methods for the acenaphthylene dianion (**1**) and the 5-hydroacenaphthylene anion (**8**). The calculations were carried out with the GAUSSIAN 94 suites of programs.[10] The geometries were fully optimised without symmetry restriction at the HF level by using the 6-31G(d,p) basis set, and characterised by frequency calculations. The shielding constants for the ^{13}C NMR spectrum were calculated and they correlate well with the experimental data.

The experimental and calculated ^{13}C NMR chemical shifts as well as the Mulliken sum charges (hydrogens included) and the HOMO coefficients are given for the acenaphthylene dianion(**1**) and for the 5-hydroacenaphthylene anion (**8**) in Table 2 and in Table 3, respectively. It should, however, be realised that several factors, such as counter ion and solvent, have been neglected in the calculations. Therefore, the calculations should only be ussed as an indication of the most reactive positions. A pictorial representation is given in Figure 2.

***Table 2**: Experimental and calculated ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), Mulliken sum charge distribution and HOMO coefficients of acenaphthylene dianion (**1**).*

Carbon atom	δ ^{13}C (20ºC)	δ ^{13}C (calc.)	Charge	HOMO
1,2	85.9	76.4	-0.302	0.323
3,8	96.9	86.2	-0.254	0.354
4,7	126.7	124.8	-0.086	0.124
5,6	82.6	67.0	-0.356	-0.425
2a, 8a	123.4	118.2	+0.022	-0.273
5a	149.2	152.1	+0.171	0.000
8b	137.7	127.1	-0.219	0.000

***Table 3**: Experimental and calculated ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), Mulliken sum charge distribution and HOMO coefficients of 5-hydroacenaphthylene anion (**8**).*

Carbon atom	δ ^{13}C (20ºC)	δ ^{13}C (calc.)	Charge	HOMO
1	90.7	84.0	-0.207	-0.275
2	112.1	114.4	-0.099	0.033
3	127.0	130.7	+0.028	-0.047
4	110.6	96.7	-0.168	-0.210
5	32.1	27.4	-0.016	0.049
6	110.5	104.0	-0.159	-0.136
7	118.1	111.0	-0.092	0.123
8	115.5	111.8	-0.092	0.144
2a	106.2	93.0	-0.123	0.303
5a	129.7	126.3	+0.028	-0.136
8a	128.2	124.9	+0.080	-0.115
8b	130.3	126.4	-0.109	0.088

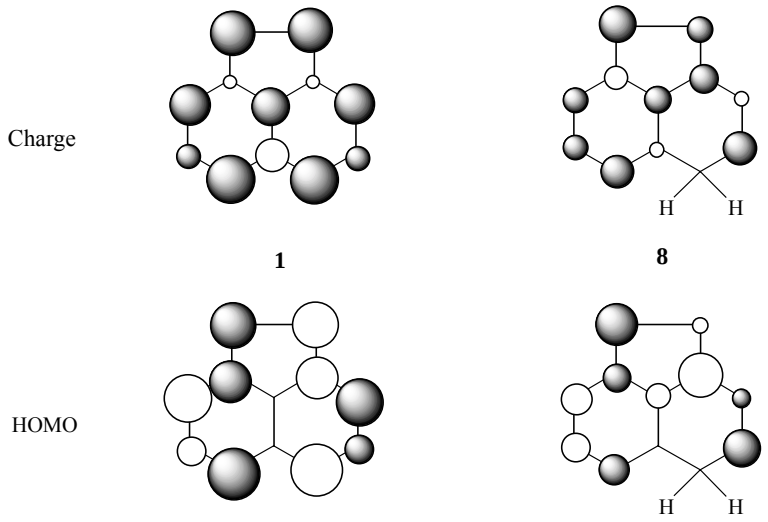


***Figure 2**: Charge distribution and HOMO coefficients of dianion **1** and hydroanion **8**.*

2.3 Discussion

The dianion of acenaphthylene can be prepared under Birch reduction conditions, using an alkali metal in a mixture of liquid ammonia and THF.[5,6,11] Using lithium in this reduction results in protonation of the acenaphthylene dianion by the solvent. To avoid this, the dianion **1** can better be prepared using pure THF as solvent. Efficient electron transfer from sodium to the PAH can be accomplished by using metal mirrors. A more convenient procedure uses ultrasonic vibration to accelerate the electron transfer.[4,12] We could perform the reduction of acenaphthylene to acenaphthene via its dianion on 10 gram scale using this procedure.

Experiments in which **1** is treated with a proton donor (hard electrophile) show that the first equivalent of proton reacts at position 5, resulting in the 5-hydroacenaphthylene anion **8**. This is subsequently protonated at position 1, resulting in 1,5-dihydroacenaphthylene (**2**).[9,13,14] Methyl iodide (soft electrophile) also reacts selectively at position 5 of **1**. Protonation of the resulting anion gives 1,5-dihydro-5-methylacenaphthylene (**4**) almost quantitatively. No dimethyl derivatives were obtained. A similar experiment was performed by Müllen and co-workers. They obtained, after dehydrogenation, 5-methylacenaphthylene as the sole product.[11] The high selectivity in the alkylation of the dianion provides a simple synthesis for 5-alkylated acenaphthenes and acenaphthylenes.

If the reaction of the acenaphthylene dianion (**1**) with methyl iodide proceeds via the S_N2 mechanism, the reaction is expected to proceed at the carbon with the highest charge and a high HOMO coefficient. The charge distribution in the acenaphthylene dianion can be derived from the differences in chemical shifts in the ^{13}C NMR spectrum of **1** with respect to that of neutral

acenaphthylene (Table 1). C-5 and C-6 are the carbon atoms with the largest upfield shift and thus the carbons with the highest charge. The calculated chemical shift values correlate very well with the experimental data. The *ab initio* calculations showed that the highest charge density and the highest HOMO-coefficient are located at C-5 (Table 2, Figure 2). This is in accordance with the ^{13}C NMR spectrum and the observed reactivity at position 5.

In the crystal structure of **1** the bond lengths differ for both sides of the molecule.[15] In solution, NMR gives no evidence for the existence of more than one species. So if there is an equilibrium between the different structures, this is so fast that they cannot be distinguished by NMR. The calculations give a fully symmetric structure for **1**, indicating that opposite carbons are identical. Remarkable is that the C-3-C-4 bond is rather short (1.37 Å) and has a high bond order (1.62). A second high bond order is found for C-2-C-2a (1.61), although this bond is not very short (1.40 Å). These high bond orders disfavour the reactivity at positions 1 (2) and 3 (8), and thus direct the substitution to take place at carbon atom 5 (6).

Reversal of the sequence of addition of methyl iodide and proton donor to the dianion, thus first one equivalent of methanol followed by one equivalent of methyl iodide, leads to protonation at position 5, giving the 5-hydroacenaphthylene anion (**8**), which in turn is methylated at position 1.

Similarly, the selectivity of the 5-hydroacenaphthylene anion (**8**) in the reaction with protons and methyl iodide can be explained by the presence of the highest charge and a high HOMO coefficient at C-1 (Table 3, Figure 2). From the ^{13}C chemical shifts it can be concluded that C-1 has the highest charge. *Ab initio* calculations predict the order of the chemical shifts very well (Table 3). Although C-2a has a very high HOMO coefficient, no reaction takes place at this position. This might be due to the smaller amount of charge at C-2a and the fact that quaternary centres are formed more difficultly in S_N2 reactions. The calculated high bond order (1.66) and the short bond length of the C-3-C-4 bond (1.34 Å) indicate that the C-3-C-4 bond already has a considerable amount of double bond character before interaction with the electrophile and this might cause the low reactivity of C-4 towards electrophiles. Based on the ^{13}C NMR spectrum and the quantum chemical calculations, the 5-hydroacenaphthylene anion (**8**) can be considered as a combination of a phenyl ring and a pentadienyl anion.

Both substituted 1,5-dihydroacenaphthylenes rearrange under acidic conditions to the corresponding acenaphthene derivatives. These structures have a higher degree of aromaticity and are therefore more stable.

Experiments have been reported in which two equivalents of electrophiles (D_2O, methyl iodide, CO_2, benzophenone) in the reaction with **1** yielded 1,5-disubstituted products exclusively.[16,17] The procedure described in this chapter was used to introduce two alkyl groups selectively at positions 1 and 5 in acenaphthylene. However, NMR spectroscopy showed that the reaction of **1** with two equivalents of methyl iodide led to a complex mixture of mono-, di- and polysubstituted products. Similar results were obtained for the reaction of **1** with two different electrophiles, e.g. ethyl iodide

followed by methyl iodide. The aselectivity of the reaction may have been the result of equilibration between products and reactants: e.g., 1,5-dihydro-1,5-dimethylacenaphthylene may transfer a proton to 5-hydro-5-methylacenaphthylene anion, to give a disubstituted hydroanion and a monosubstituted product (see Chapter 3). Another possibility might be that the methyl group at position 5 in the hydroanion does not affect the reactivity of the hydroanion towards protons, but does so towards alkyl halides. A third explanation for the difference with the literature data might be the advance in spectroscopic techniques, which enabled us to discriminate between mono- and polysubstituted products.

2.4 Conclusions

The dianion of acenaphthylene can easily be prepared on gram scale in THF, using ultrasonic vibration to activate the sodium. This dianion can be substituted with alkyl halides selectively at positions 1 or 5, depending on the sequence of addition of electrophiles. The resulting 1- or 5-substituted 1,5-dihydroacenaphthylenes rearrange under slightly acidic conditions to the corresponding acenaphthenes. The reactive positions in the acenaphthylene dianion and the 5-hydroacenaphthylene anion correlate well with the results of *ab initio* calculations and with the ^{13}C NMR data.

2.5 Experimental section

General: Acenaphthylene (75%) was obtained from Aldrich and purified by treatment with DDQ and filtration over silica. Methyl iodide was obtained from Acros and used without further purification. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3A, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra.

Reduction of acenaphthylene:

Into a dry 250 ml three-necked round-bottomed flask THF (125 ml) was distilled under an atmosphere of argon. Acenaphthylene (0.761 grams, 5 mmol) was added, together with freshly cut sodium (0.3 g, 13 mmol). Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0ºC, a deep green solution was obtained. The flask was then

cooled in an ethanol-nitrogen bath to -70ºC and water was added. The colour of the mixture changed via red to yellow-brown. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. Addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. Immediate analysis by NMR spectroscopy showed mainly 1,5-dihydroacenaphthylene.[9] This product was not stable to air and could, with a small amount of HCl in acetone, easily be converted into acenaphthene (Yield: 98%).

1,5-Dihydroacenaphthylene

^{1}H NMR ($CDCl_3$, TMS) δ 7.28 (d, $J_{7,8}$ = 7.2, 1H, H-8), 7.15 (dd, $J_{7,8}$ = 7.2, $J_{6,7}$ = 7.6, 1H, H-7), 7.04 (d, $J_{6,7}$ = 7.6, 1H, H-6), 6.59 (dt, $J_{3,4}$ = 10.0, $J_{3,5}$ = 2.4, 1H, H-3), 6.03 (dt, $J_{3,4}$ = 10.0, $J_{4,5}$ = 3.8, 1H, H-4), 5.95 (t, $J_{1,2}$ = 2.2, 1H, H-2), 3.70 (dd, $J_{4,5}$ = 3.8, $J_{3,5}$ = 2.4, 2H, H-5), 3.47 (d, $J_{1,2}$ = 2.2, 2H, H-1).

Reaction of the acenaphthylene dianion with methyl iodide:

According to the procedure described above, acenaphthylene (0.761 g, 5 mmol) was converted into the dianion and treated with methyl iodide (0.311 ml, 5 mmol) at -70°C. After stirring for 15 minutes at room temperature, the mixture was cooled again and quenched with water. After extraction, 1,5-dihydro-5-methylacenaphthylene was obtained in more thatn 95% yield.

1,5-Dihydro-5-methylacenaphthylene

^{1}H NMR ($CDCl_3$, TMS) δ 7.24-7.14 (m, 3H, H-6, H-7, H-8), 6.50 (dd, $J_{3,4}$ = 10.0, $J_{3,2}$ = 6.0, 1H, H-3), 5.95-5.90 (m, 2H, H-2, H-4), 3.65 (m, 1H, H-5), 3.45-3.43 (m, 2H, H-1), 1.30 (dd, $J_{Me,5}$ = 7.6, $J_{Me,4}$ = 2.6, 3H, CH_3).

Rearrangement to 5-methylacenaphthene was achieved by stirring for two hours in acetone with a few drops of HCl. The conversion was complete and 5-methylacenaphthene was isolated after extraction with light petroleum (boiling range 40-60ºC), drying over $MgSO_4$ and concentration quantitatively.

5-Methylacenaphthene

^{1}H NMR ($CDCl_3$, TMS) δ 7.64 (dd, $J_{6,7}$ = 8.3, $J_{6,8}$ = 0.9, 1H, H-6), 7.45 (dd, $J_{7,6}$ = 8.3, $J_{7,8}$ = 6.8, 1H, H-7), 7.27 (dd, $J_{8,7}$ = 6.8, $J_{8,6}$ = 0.8, 1H, H-8), 7.23 (dd, $J_{3,4}$ = 6.9, $J_{3,2}$ = 0.8, H-3), 7.15 (dd, $J_{3,4}$ = 7.0, $J_{4,Me}$ = 1.3, H-4), 3.39-3.31 (m, 4H, H-1, H-2), 2.61 (d, $J_{Me,4}$ = 0.9, CH_3).

^{13}C NMR ($CDCl_3$) δ 146.2 (C-2a or C-8a), 143.7 (C-2a or C-8a), 139.0 (C-8b), 129.8 (C-5a), 129.8 (C-3), 127.8 (C-7), 119.5 (C-6), 119.0 (C4 or C8), 118.9 (C4 or C8), 30.6 (C1 or C2), 29.8 (C1 or C2), 17.9 (CH_3), C-5 was not observed.

Reaction of the acenaphthylene dianion with methanol followed by methyl iodide:
According to the procedure described above, acenaphthylene (0.761 g, 5 mmol) was converted into the dianion and allowed to react with methanol (0.146 ml, 5 mmol) at -70°C. After stirring for 15 minutes at room temperature, the mixture was cooled again to -70°C; methyl iodide (0.311 ml, 5 mmol) was added and stirring was continued at room temperature for 30 minutes. The reaction was quenched with water. This resulted, after work-up, in the isolation of 1,5-dihydro-1-methylacenaphthylene in more than 95% yield.

1,5-Dihydro-1-methylacenaphthylene
^{1}H NMR ($CDCl_3$, TMS) δ 7.18-7.08 (m, 3H, H-6, H-7, H-8), 6.50 (dt, $J_{3,4}$ = 10.0, $J_{3,5}$ = 2.1, 1H, H-3), 5.95 (dt, $J_{4,3}$ = 10.0, $J_{4,5}$ = 3.8, 1H, H-4), 5.85 (d, $J_{1,2}$ = 1.9, 1H, H-2), 3.61-3.52 (m, 3H, H-1, H-5), 1.26 (d, $J_{Me,1}$ = 7.3, 3H, CH_3).

Rearrangement to 1-methylacenaphthene was achieved by stirring for two hours in acetone with a few drops of HCl. The conversion was complete and 1-methylacenaphthene was isolated after extraction with light petroleum (boiling range 40-60ºC), drying over $MgSO_4$ and concentration in >95% yield.

1-Methylacenaphthene
^{1}H NMR ($CDCl_3$, TMS) δ 7.57 (d, J = 8.2, 2H, H-5 and H-6), 7.45-7.39 (m, 2H, H-4 and H-7), 7.21 (d, $J_{7,8 = 3,4}$ = 6.9, 1H, H-3, H-8), 3.70 (m, 1H, H-1), 3.59 (dd, $J_{2,2}$ = 16.9, $J_{2,1}$ = 8.0, 1H, H-2_{trans}), 2.95 (d, $J_{2,2}$ = 16.9, $J_{2,1}$ = 3.2, 1H, H-2_{cis}), 1.45 (d, $J_{Me,1}$ = 6.9, CH_3).
^{13}C NMR ($CDCl_3$) δ 150.8 (C-2a or C-8a), 144.5 (C-2a or C-8a), 138.2 (C-8b), 131.4 (C-5a), 127.8 (C-4 and C-7), 122.4 (C-5 or C-6), 122.2 (C-5 or C-6), 119.1 (C3 or C8), 118.3 (C3 or C8), 39.7 (C2), 37.9 (C1), 21.7 (CH_3).

Generation of the acenaphthylene dianion in an NMR tube:
In a glove bag under an atmosphere of argon, acenaphthylene (ca. 0.1 g), THF-d_8 (0.75 ml) and sodium wire (ca. 2 cm) were transferred into an NMR tube. After three freeze-pump-thaw cycles, the NMR tube was sealed under vacuum. After three hours of ultrasonic vibration the formation of the dianion was complete.

Acenaphthylene dianion (**1**)
^{1}H NMR (THF-d_8, 20ºC) δ = 7.63 (2 H, H-4 and H-7), 7.08 (2 H, H-1 and H-2), 7.06 (2 H, H-3 and H-8), 5.93 (2 H, H-5 and H-6).
^{13}C NMR (THF-d_8, 20ºC) : δ = 149.2 (C-5a), 137.7 (C-8b), 126.7 (C-4 and C-7), 123.4 (C-2a and C-8a), 96.9 (C-3 and C-8), 85.9 (C-1 and C-2), 82.6 (C-5 and C-6).
^{13}C NMR (THF-d_8, -80ºC) : δ = 148.6 (C-5a), 137.0 (C-8b), 126.9 (C-4 and C-7), 122.9 (C-2a and C-8a), 96.1 (C-3 and C-8), 84.7 (C-1 and C-2), 83.4 (C-5 and C-6).

Generation of the 5-hydroacenaphthylene anion in an NMR tube:

The acenaphthylene dianion (1 mmol) was prepared in THF-d_8 (1 ml) according to the general procedure. At room temperature one equivalent of methanol was added and the solution was transferred to an NMR tube and sealed.

5-Hydroacenaphthylene anion (**8**)

^{1}H NMR (THF-d_8) : δ = 6.84 (d, $J_{7,8}$ = 7.8, 1H, H-8), 6.86-6.33(m, 2H, H-3 and H-7), 6.17 (m, 1H, H-2), 6.03 (d, $J_{6,7}$ = 6.4, 1H, H-6), 5.55 (d, $J_{1,2}$ = 2.1, 1H, H-1), 4.78 (m, 1H, H-4), 3.93 (m, 1H, H-5).

^{13}C NMR (THF-d_8) : δ = 130.3 (C-8b), 129.7 (C-5a), 128.2 (C-8a), 127.0 (C-3), 118.1 (C-7), 115.5 (C-8), 112.1 (C-2), 110.6 (C-4), 110.5 (C-6), 106.2 (C-2a), 90.7 (C-1), 32.1 (C-5).

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3

Reactivity of the 5-hydroacenaphthylene anion towards alkyl bromides

3.1 Introduction

In Chapter 2 it has been demonstrated that the acenaphthylene dianion reacts with one equivalent of proton selectively at position 5, resulting in the 5-hydroacenaphthylene anion (**1**).[1] Reaction of hydroanion **1** with one equivalent of methyl iodide results in the formation of 1-methyl-1,5-dihydroacenaphthylene in more than 90% yield (Chapter 2).[2]

In this chapter we use the 5-hydroacenaphthylene anion (**1**) in reactions with allyl bromide, 3,3-dimethylallyl bromide, propargyl bromide and (bromomethyl)cyclopropane. This extension to allylic systems leads to introduction of functional groups at position 1 in acenaphthene and to the synthesis of novel compounds. Another reason for using these electrophiles is the possibility to study the mechanism of the reaction of the 5-hydroacenaphthylene anion with alkyl bromides.

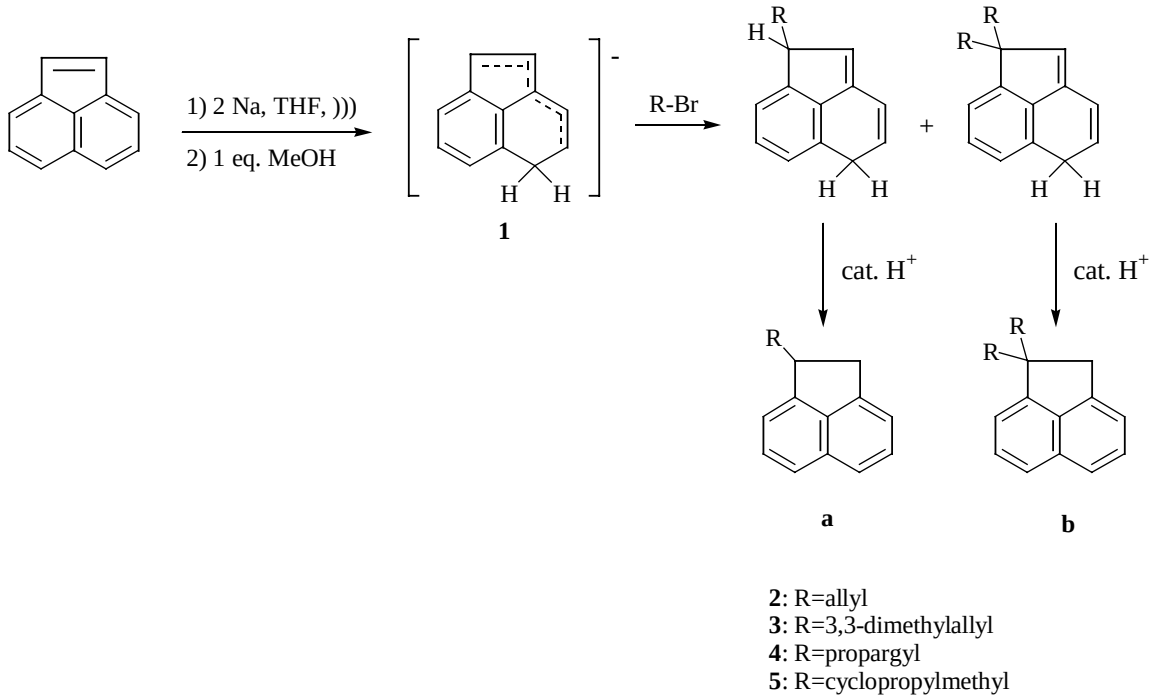
3.2 Results

The 5-hydroacenaphthylene anion was prepared with the procedure outlined in Chapter 2, starting from acenaphthylene, which was converted into its dianion using 2.2 equivalents of sodium in anhydrous THF and ultrasonic vibration. Within 3-5 hours the colour of the solution turned deep green, indicating that the acenaphthylene dianion had been formed. The reaction mixture was cooled to -70ºC and exactly one equivalent of anhydrous methanol was added. The reaction mixture was stirred for a further 15 minutes at room temperature. After cooling the solution to -70ºC, one equivalent of allyl bromide was added to the hydroanion and the mixture was stirred at room temperature during a further 30 minutes. After extraction with light petroleum (boiling range 40-60ºC) and work-up, 1-allylacenaphthene (**2a**) was obtained as the major product (60% of product mixture). The initially formed product, 1-allyl-1,5-dihydroacenaphthylene, is very unstable and rearranges easily to the acenaphthene derivative − under slightly acidic conditions, even on a silica gel column, or at elevated temperatures − and could not be isolated. GC-MS analyses of the crude product showed the presence of acenaphthene, a mono- and a diallylated acenaphthene in the ratio of 1:3:1 (Table 1). These products could not be separated by means of chromatography over a silica

gel column. Kugelrohr distillation of the product mixture gave rise to polymerisation reactions. Therefore, preparative gas chromatography was used to separate the products and sufficient amounts of pure products were isolated to measure NMR. By means of NMR techniques the alkylation products were identified as 1-allylacenaphthene (**2a**) and 1,1-diallylacenaphthene (**2b**) (Scheme 1).

The same procedure was used with 3,3-dimethylallyl bromide as electrophile. 1-(3-Methyl-2-butenyl)acenaphthene (**3a**) and 1,1-bis(3-methyl-2-butenyl)acenaphthene (**3b**) were formed in a 3:1 ratio (Table 1). The products could easily be separated by preparative GC and were characterized by NMR.

Use of propargyl bromide gave similar results. The products, 1-propargylacenaphthene (**4a**) and 1,1-dipropargylacenaphthene (**4b**), were separated by preparative GC and could be isolated in a 3:1 ratio (Table 1).



***Scheme 1**: Reaction of **1** with alkyl halides.*

With (bromomethyl)cyclopropane only the monoalkylated product was formed next to acenaphthene in a 1:2 ratio (Table 1). Separation was performed by crystallisation of the acenaphthene followed by Kugelrohr distillation of the resulting oil and 1-(cyclopropylmethyl)-acenaphthene (**5a**) was obtained.

***Table 1**: Results of the reaction of the 5-hydroacenaphthylene anion with electrophiles. A = acenaphthene, R = substituent*

Electrophile	Overall yield	ratio A : 1-R-A : 1,1-diR-A
Allyl bromide	96%	1 : 3 : 1
3,3-Dimethylallyl bromide	93%	1 : 3 : 1
Propargyl bromide	95%	1 : 3 : 1
(Bromomethyl)cyclopropane	96%	2 : 1 : 0

3.3 ^{1}H and ^{13}C NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra of the products were assigned using H-H and C-H inverse COSY techniques. The ^{1}H NMR spectrum of 1-allylacenaphthene (**2a**) (Figure 1) consists of 6 aromatic, 3 olefinic, 3 benzylic and 2 allylic protons.

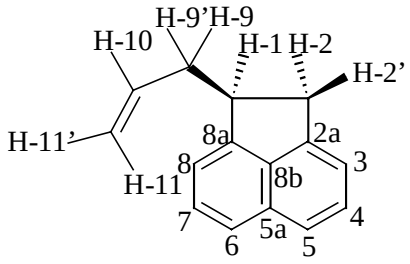


***Figure 1**: 1-Allylacenaphthene (**2a**).*

The aromatic part of the spectrum consists of two separated ABC patterns. Next to the expected ortho and meta couplings H-3 and H-5 show additional small couplings, which could be ascribed to coupling with H-2 and H-2'. A similar coupling can be observed between H-1 and H-6 and between H-1 and H-8. These couplings were confirmed by long-range H-H-COSY and decoupling experiments. The non-aromatic part shows an ABCMNXYZ pattern. The two protons at C-2, with a large negative geminal coupling constant, have different coupling constants with H-1, the cis-coupling being the larger one. H-1 also couples with the distinguishable protons at C-9. This difference between H-9 and H-9' is induced by the chirality at C-1, but the assignment of the individual protons on the basis of a molecular model and these NMR results is not possible. Selective substitution of H-9 or H-9' with deuterium is necessary to discriminate between both protons.[3,4] The dddd's from H-9 and H-9' are due to the coupling with H-10 and allylic coupling with H-11 and H-11'. H-11 and H-11' have coupling constants of 16.8 and 10.3 Hz with H-10, and can be assigned as E and Z respectively, because J(Z)<J(E). For the determination of the coupling constants we used the simulation program PERCH. The ^{13}C NMR spectrum was consistent with this structure.

The spectra of the other 1-substituted acenaphthenes were similar to the spectrum described above and all expected couplings were found. In the case of 1-(3-methyl-2-butenyl)acenaphthene (**3a**) the methyl groups showed allylic couplings with the olefinic proton. The aliphatic part in the spectrum of 1-(cyclopropylmethyl)acenaphthene (**5a**) was too complex to obtain all the coupling constants.

In the 1,1-disubstituted acenaphthenes the molecules have a plane of symmetry. Therefore, both H-2's are identical. The same might be expected for H-9 and H-9', but although the signals moved towards each other and the coupling between them decreased, they were still separated. This might be the result of steric interactions.

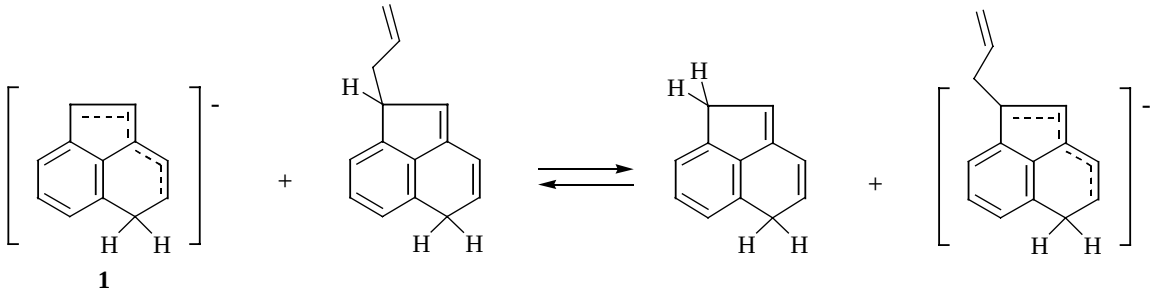
In 1,1-dipropargylacenaphthene (**4a**) a remarkable shift of H-8 towards lower field is observed. This is probably caused by the influence of the π-electrons of propargyl-substituents at C-1. A second deviation from the other spectra are the coupling constants between H-6 and both H-7 and H-8. $J_{6,8}$ increased to 7.0 Hz, $J_{6,7}$ however decreased to 2.0 Hz.

3.4 Discussion

The 5-hydroacenaphthylene anion (**1**) can easily be prepared by addition of one equivalent of methanol to the dianion. The hydroanion reacts with methyl iodide at position 1 to give 1-methyl-1,5-dihydroacenaphthylene as the sole product. This unstable product rearranges under slightly acidic conditions to 1-methylacenaphthene. Allyl bromide is expected to react in the same way with **1**, thus giving 1-allylacenaphthene. In our experiments three products were formed: acenaphthene and 1,1-diallylacenaphthene (**2b**) were isolated next to the expected 1-allylacenaphthene (**2a**). Obviously, the proton at position 1 of 1-allyl-1,5-dihydroacenaphthylene can easily be abstracted to give a 1-substituted 5-hydroanion. This hydroanion can react with a second allyl bromide to give the doubly substituted product. Two bases are present in the reaction mixture: one equivalent of methoxide, generated by the reaction of methanol with the dianion, and unreacted 5-hydroacenaphthylene anion. If the latter acts as a base this results in the formation of acenaphthene. Addition of two equivalents of allyl bromide gave approximately the same product ratio as in the experiment using only one equivalent of allyl bromide. If methoxide would be the most important base, a substantially larger amount of 1,1-diallylacenaphthene (**2b**) should be formed and less acenaphthene. Because the product ratio did not change, it may be concluded that the hydroanion is the strongest base in this process (Scheme 2). Addition of potassium *t*-butoxide, after addition of two equivalents of allyl bromide, did not result in more dialkylated product. Similarly, when a solution of 1,5-dihydroacenaphthylene was first treated with one equivalent of sodium methoxide and subsequently with excess electrophilic reagent, no substitution product could be detected. This also confirms the assumption that the 5-hydroacenaphthylene anion is a stronger base than methoxide. Apparently the 1-propynyl anion is a stronger base than 5-

hydroacenaphthylene anion, because otherwise the reaction with propargyl bromide would yield much more acenaphthene, since the acetylenic moiety would be a proton donor for the 5-hydroacenaphthylene anion. The acidity of 1,5-dihydroacenaphthylene is expected to be in the vicinity of that of indene ($pK_a = 20$). The results of the reaction are in agreement with this estimated pK_a compared with the acidity of methanol ($pK_a = 15.2$) and acetylene ($pK_a = 25$).

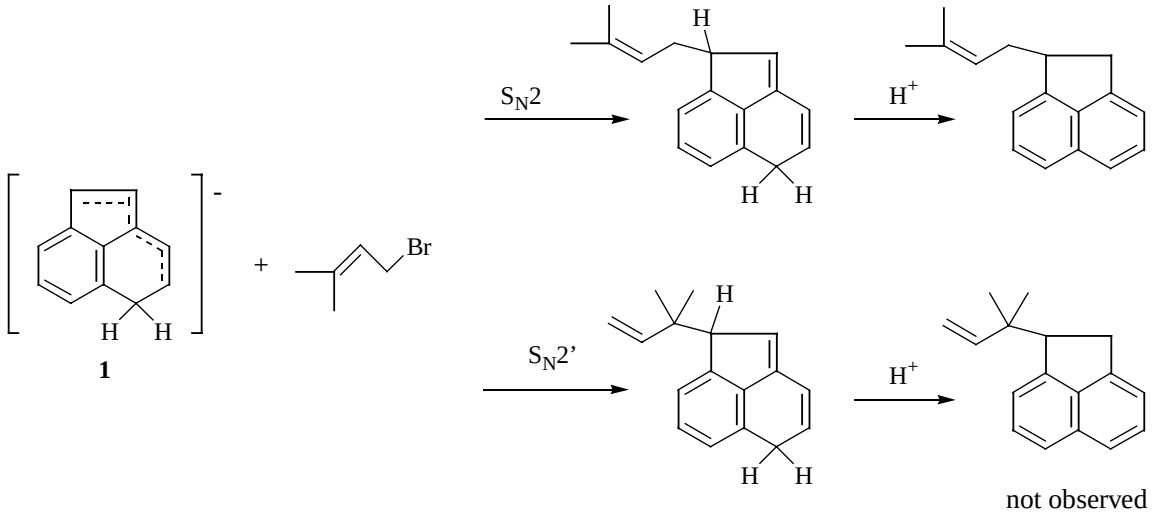
In the reaction with methyl iodide no doubly alkylated product is formed. A possible explanation is that methyl iodide is more reactive towards the hydroanion, thus converting all the hydroanion immediately to the neutral compound and quenching further reaction. The higher reactivity of methyl iodide is in agreement with the influence of the leaving group (iodide vs. bromide) and the substituent (methyl vs. allyl).[5,6]



1

***Scheme 2**: Equilibrium in the reaction of **1** with allyl bromide.*

Allyl bromide can react via three mechanisms with nucleophiles: S_N2, S_N2' or single electron transfer (SET). From the results of the reaction of the hydroanion with 3,3-dimethylallyl bromide it can be concluded that the S_N2' mechanism does not play a significant role (Scheme 3). In the SET mechanism one electron is transferred from the hydroanion to the allyl bromide. The latter radical anion splits into an allyl radical and a bromide ion. The allyl radical will react at C-1 and at C-3, differently substituted in 3,3-dimethylallyl bromide. However, occurrence of the SET mechanism is unlikely because of the absence of products with methyl groups at C-9 (S_N2'-product). The reaction products indicate that the S_N2 mechanism must be the most important one.



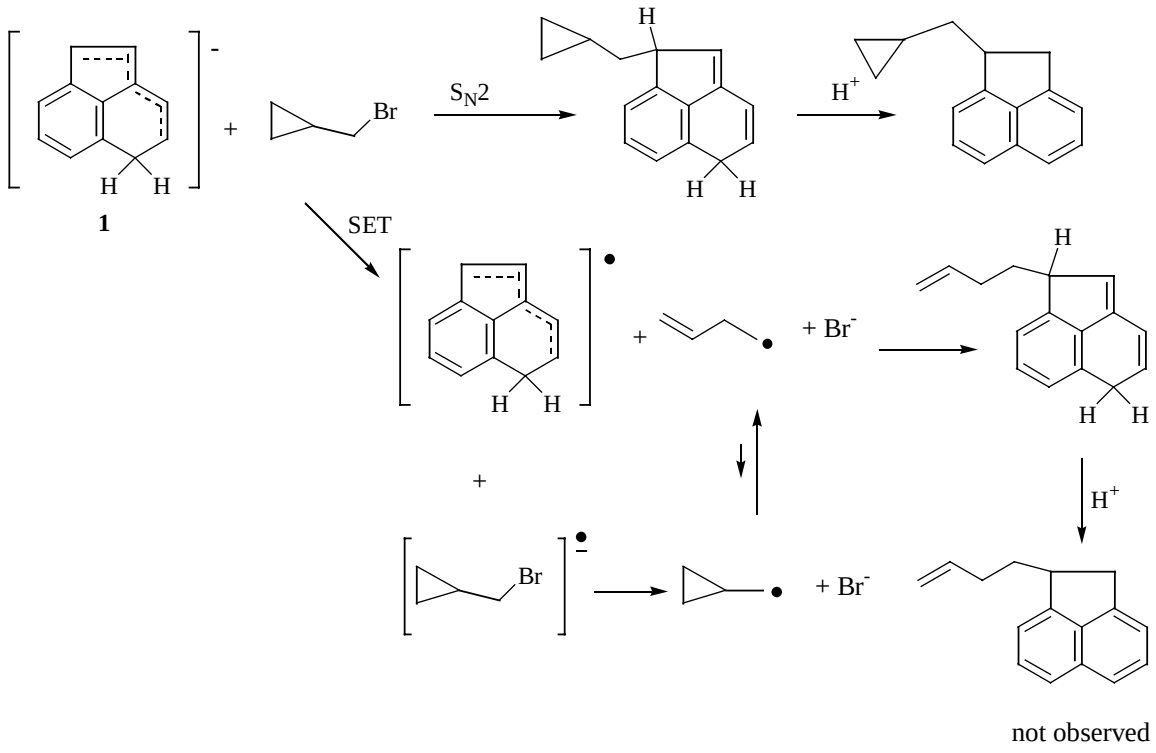
***Scheme 3**: S_N2 and S_N2' mechanism of the reaction of 3,3-dimethylallyl bromide with **1**.*

A similar conclusion can be drawn for the reaction of **1** with (bromomethyl)cyclopropane: if electron transfer were part of the substitution, the cyclopropylmethyl radical would be opened immediately to a butenyl radical (Scheme 4). 1-(3-Butenyl)acenaphthene (**6**) was, however, not observed. The yield of 1-(cyclopropylmethyl)acenaphthene (**4**) was relatively low (30%) in comparison with methyl iodide. This may be explained by the lower reactivity of (bromomethyl)cyclopropane compared to methyl iodide.

These experiments show that the reaction of **1** with alkyl bromides, such as allyl bromide, proceeds via an S_N2 mechanism. The selectivity of this reaction is in accordance with the charge distribution as predicted from the ^{13}C NMR spectrum and quantum mechanical calculations (Chapter 2).

3.5 Conclusions

Reaction of the 5-hydroacenaphthylene anion with unsaturated alkyl bromides provides an easy route to introduce functional groups at position 1. In the case of allyl bromide, 3,3-dimethylallyl bromide and propargyl bromide a considerable amount of 1,1-dialkylated product could be isolated. This is the first route to obtain these disubstituted products selectively. The mechanism was shown to be S_N2 by reaction with dimethylallyl bromide and (bromomethyl)cyclopropane.



***Scheme 4**: Possible pathways for the raction of (bromomethyl)cyclopropane with **1**.*

3.6 Experimental section

General: Acenaphthylene (75%) was obtained from Aldrich and purified by treatment with DDQ and filtration over silica. Allyl bromide, 3,3-dimethylallyl bromide, propargyl bromide and (bromomethyl)cyclopropane were obtained from Acros and used without further purification. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3A, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. The 600 MHz ^{1}H spectrum of 1-propargylacenaphthene was recorded on a Bruker AM-600 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Coupling constants in the range 1.2-0.5 Hz were determined by simulation with the program PERCH[7] and give an indication of the real value with a deviation of ±0.2 Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra. The numbering of the hydrogen and carbon atoms is indicated in Figure 1.

Preparative GC was performed on an ATI Unicam 610 series gas chromatograph equipped with an SE 15% 3 m column with the following temperature profile: 10 min. 100°C, 10°C/min. to 160°C, 15 min. 160°C.

Mass spectra were recorded on a Finnigan MAT 900 mass spectrometer, equipped with a direct insertion probe (EI-MS, 70 eV) or on a Finnigan MAT ITD 700 (EI, 70 eV) coupled to a Packard 438A gas chromatograph equipped with a Chrompack 25 m fused silica column (CP-Sil-5CB; 0.25 mm i.d.) (GC-MS).

General procedure:

Into a dry 250 ml three-necked round-bottomed flask THF (125 ml) was distilled under an atmosphere of argon. Acenaphthylene (0.76 g, 5 mmol) were added, together with freshly cut sodium (0.3 g, 13 mmol). Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0°C, a deep green solution was obtained. The flask was then cooled in an ethanol-liquid nitrogen bath to -70°C and methanol (0.15 ml, 5 mmol) was added. The colour of the mixture turned red-brown. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. The mixture was cooled again to -70°C and 5 mmol of alkyl bromide were added. Stirring was continued at room temperature for 30 minutes after which period the reaction was quenched with water. Addition of light petroleum (40-60), extraction with water, washing with brine, drying over $MgSO_4$ and evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. With a small amount of HCl in acetone, all the products were converted into acenaphthene derivatives. A fraction of each product mixture was separated by means of preparative GC in order to obtain pure material for NMR spectroscopy.

Reaction of the 5-hydroacenaphthylene anion with allyl bromide:

To the 5-hydroacenaphthylene anion, prepared following the general procedure, allyl bromide (0.87 ml, 5 mmol) was added. Column chromatography over silica using light petroleum as eluent gave a mixture of mono- and dialkylated products. The mass recovery was 96%.

1-Allylacenaphthene (**2a**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.61 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$ = 0.7, $J_{6.8}$ = 1.1 ,1H, H-6), 7.60 (dddd, $J_{4,5}$ = 8.4, $J_{2.5}$ = $J_{2',5}$ = 1.2, $J_{3,5}$ = 0.7, 1H, H-5), 7.46 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1H, H-7), 7.45 (dd, $J_{3,4}$ = 6.7, $J_{4,5}$ = 8.4, 1H, H-4), 7.30 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 1.6, $J_{6.8}$ = 1.1, 1H, H-8), 7.26 (dddd, $J_{3,4}$ = 6.7, $J_{2,3}$ = 0.9, $J_{2',3}$ = 1.0, $J_{3,5}$ = 0.7, 1H, H-3), 5.89 (dddd, $J_{10,11}$ = 16.8, $J_{10,11'}$ = 10.3, $J_{9,10}$ = 6.5, $J_{9',10}$ = 7.1, 1H, H-10), 5.13 (dddd, $J_{11,11'}$ = -2.2, $J_{10,11}$ = 16.8, $J_{9,11}$ = $J_{9',11}$ = 1.3, 1H, H-11), 5.07 (dddd, $J_{11,11'}$ = -2.2, $J_{10,11'}$ = 10.3, $J_{9,11'}$ = $J_{9',11'}$ = 1.4, 1H, H-11') 3.78 (dddddd, $J_{1,2}$ = 8.8, $J_{1,2'}$ = 4.2, $J_{1,9}$ = 4.7, $J_{1,9'}$ = 8.4, $J_{1,8}$ = 1.6, $J_{1,6}$ = 0.7 1H, H-1), 3.54 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2}$ = 8.8, $J_{2.5}$ = 1.2, $J_{2,3}$ = 0.9, 1H, H-2), 3.10 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2'}$ = 4.2, $J_{2',5}$ = 1.2, $J_{2',3}$ = 1.0, 1H, H-2'), 2.67 (dddd, $J_{9,9'}$ = -14.6, $J_{1,9}$ = 4.7, $J_{9,10}$ = 6.5 $J_{9,11}$ = 1.3, $J_{9,11'}$ = 1.4, 1H, H-9), 2.54 (dddd, $J_{9,9'}$ = -14.6, $J_{1,9'}$ = 8.4, $J_{9',10}$ = 7.1 $J_{9',11}$ = 1.3, $J_{9',11'}$ = 1.4, 1H, H-9').

^{13}C NMR ($CDCl_3$) **:** δ = 148.8 (C-2a or C-8a), 144.5 (C-2a or C-8a), 138.7 (C-8b), 136.5 (C-10), 131.5 (C-5a), 127.8 (C-4 or C-7), 127.7 (C-4 or C-7), 122.7 (C-5 or C-6), 122.3 (C-5 or C-6), 119.2 (C-3 or C-8), 118.9 (C-3 or C-8), 116.5 (C-11), 42.6 (C-1), 40.6 (C-9), 36.9 (C-2).
Exact mass calculated for $C_{15}H_{14}$: 194.1096 m/z; found: 194.1087 m/z. MS m/z (%): 194 (17), 165 (6), 153 (100), 127 (1), 89 (2).

1,1-Diallylacenaphthene (**2b**)
^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.63 (dd, $J_{6,7}$ = 8.1, $J_{6.8}$<0.7 ,1H, H-6), 7.61 (dddd, $J_{4,5}$ = 8.5, $J_{2.5}$ = 1.0, $J_{2',5}$ = 0.8, $J_{3,5}$<0.7, 1H, H-5), 7.48 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 7.0, 1H, H-7), 7.45 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.5, 1H, H-4), 7.24 (dd, $J_{7,8}$ = 7.0, $J_{6.8}$<0.7, 1H, H-8), 7.22 (dddd, $J_{3,4}$ = 6.9, $J_{2,3}$ = 1.4, $J_{2',3}$ = 0.9, $J_{3,5}$<0.7, 1H, H-3), 5.57 (dddd, $J_{10,11}$ = 16.6, $J_{10,11'}$ = 10.3, $J_{9,10}$ = 6.4, $J_{9',10}$ = 8.1, 2H, H-10), 5.04 (dddd, $J_{11,11'}$ = -3.0, $J_{10,11}$ = 16.6, $J_{9,11}$ = $J_{9',11}$ = 1.2, 2H, H-11), 4.94 (dddd, $J_{11,11'}$ = -3.0, $J_{10,11'}$ = 10.3, $J_{9,11'}$ = $J_{9',11'}$ = 1.3, 2H, H-11'), 3.27 (dd, $J_{2.5}$ = 1.0, $J_{2,3}$ = 1.4, 1H, H-2), 3.26 (dd, $J_{2',5}$ = 0.8, $J_{2',3}$ = 0.9, 1H, H-2'), 2.55 (ddd, $J_{9,9'}$ = -1.8, $J_{9,10}$ = 6.4, $J_{9,11}$ = 1.2, $J_{9,11'}$ = 1.3, 2H, H-9), 2.53 (ddd, $J_{9,9'}$ = -1.8, $J_{9',10}$ = 8.1, $J_{9',11}$ = 1.2, $J_{9',11'}$ = 1.3, 2H, H-9').
^{13}C NMR ($CDCl_3$) **:** δ = 150.7 (C-2a or C-8a), 143.4 (C-2a or C-8a), 138.4 (C-8b), 134.6 (C-10), 131.2 (C-5a), 127.9 (C-4 or C-7), 127.7 (C-4 or C-7), 123.0 (C-5 or C-6), 122.3 (C-5 or C-6), 119.1 (C-3 or C-8), 118.4 (C-3 or C-8), 117.7 (2 C-11), 50.5 (C-1), 45.4 (C-9), 41.4 (C-2).
Exact mass calculated for $C_{18}H_{18}$: 234.1408 m/z; found: 234.1389 m/z. MS m/z (%): 234 (15), 193 (100), 152 (17).

Reaction of the 5-hydroacenaphthylene anion with 3,3-dimethylallyl bromide:
To the 5-hydroacenaphthylene anion, prepared following the general procedure, 3,3-dimethylallyl bromide (0.58 ml, 5 mmol) was added. Column chromatography over silica using light petroleum as eluent gave a mixture of mono- and dialkylated product. The mass recovery was 93%.
1-(3-Methyl-2-butenyl)acenaphthene (**3a**)
^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.61 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$ = 0.6, $J_{6.8}$ = 1.0 ,1H, H-6), 7.60 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$ = $J_{2',5}$ = 1.1, $J_{3,5}$ = 1.0, 1H, H-5), 7.45 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1H, H-7), 7.44 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.2, 1H, H-4), 7.29 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 0.8, $J_{6.8}$ = 1.0, 1H, H-8), 7.26 (dddd, $J_{3,4}$ = 6.9, $J_{2,3}$ = $J_{2',3}$ = 1.1, $J_{3,5}$ = 1.0, 1H, H-3), 5.28 (ddqq, $J_{10,Me}$ = 1.4, $J_{10,Me'}$ = 1.5, $J_{9,10}$ = 7.1, $J_{9',10}$ = 7.1, 1H, H-10), 3.71 (dddddd, $J_{1,2}$ = 8.0, $J_{1,2'}$ = 3.6, $J_{1,9}$ = 6.1, $J_{1,9'}$ = 8.4, $J_{1,8}$ = 0.8, $J_{1,6}$ = 0.6, 1H, H-1), 3.54 (dddd, $J_{2,2'}$ = -17.4, $J_{1,2}$ = 8.0, $J_{2.5}$ = 1.0, $J_{2,3}$ = 1.1, 1H, H-2), 3.04 (dddd, $J_{2,2'}$ = -17.4, $J_{1,2'}$ = 3.6, $J_{2',5}$ = $J_{2',3}$ = 1.1, 1H, H-2'), 2.59 (dddqq, $J_{9,9'}$ = -14.1, $J_{9,10}$ = 7.1, $J_{1,9}$ = 6.1, $J_{9,Me}$ = 0.7, $J_{9,Me'}$ = 0.9, 1H, H-9), 2.36 (dddqq, $J_{9,9'}$ = -14.1, $J_{9',10}$ = 7.1 $J_{1,9'}$ = 8.4, $J_{9',Me}$ = 0.7, $J_{9',Me'}$ = 0.9, 1H, H-9'), 1.73 (ddd, $J_{10,Me}$ = 1.4, $J_{9,Me}$ = 0.7, $J_{9',Me}$ = 0.7, 3H, Me), 1.61 (ddd, $J_{10,Me'}$ = 1.5, $J_{9,Me'}$ = 0.9, $J_{9',Me'}$ = 0.9, 3H, Me')
^{13}C NMR ($CDCl_3$) **:** δ = 148.8 (C-2a or C-8a), 144.5 (C-2a or C-8a), 138.7 (C-8b), 131.5 (C-5a), 128.6 (C-4 and C-7), 123.4 (C-10), 123.3 (C-5 or C-6), 123.0 (C-5 or C-6), 119.9 (C-3 or C-8), 119.6 (C-3 or C-8), 44.5 (C-Me, 2x) 41.2 (C-1), 38.9 (C-9), 36.5 (C-2), C-11 was not observed.
Exact mass calculated for $C_{17}H_{18}$: 222.1408 m/z; found: 222.1476 m/z. MS m/z (%): 222 (27), 184 (8), 153 (100), 127 (5).

1,1-Bis(3-methyl-2-butenyl)acenaphthene (**3b**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.61 (dd, $J_{6,7}$ = 8.2, $J_{6.8}$ = 0.6 ,1H, H-6), 7.60 (ddt, $J_{4,5}$ = 8.0, $J_{2.5}$ = 0.9, $J_{3,5}$ = 0.5, 1H, H-5), 7.46 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 7.0, 1H, H-7), 7.44 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.0, 1H, H-4), 7.23 (dd, $J_{7,8}$ = 7.0, $J_{6.8}$ = 0.6, 1H, H-8), 7.19 (ddt, $J_{3,4}$ = 6.9, $J_{2,3}$ = 1.2, $J_{3,5}$ = 0.5, 1H, H-3), 5.01 (ddqq, $J_{10,Me}$ = $J_{10,Me'}$ = 1.4, $J_{9,10}$ = 7.9, $J_{9',10}$ = 6.7, 2H, H-10), 3.18 (dd, $J_{2,3}$ = 1.2, $J_{2,5}$ = 0.9, 2H, H-2), 2.50 (ddqq, $J_{9,9'}$ = -14.6, $J_{9,10}$ = 7.9, $J_{9,Me}$ = 0.7, $J_{9,Me'}$ = 0.9, 2H, H-9), 2.41 (ddqq, $J_{9,9'}$ = -14.6, $J_{9',10}$ = 6.7, $J_{9',Me}$ = 1.2, $J_{9',Me'}$ = 1.5, 2H, H-9'), 1.59 (ddd, $J_{10,Me}$ = 1.4, $J_{9,Me}$ = 0.7, $J_{9',Me}$ = 1.2, 6H, Me), 1.54 (ddd, $J_{10,Me'}$ = 1.4, $J_{9,Me'}$ = 0.9, $J_{9',Me'}$ = 1.5, 6H, Me').

Reaction of the 5-hydroacenaphthylene anion with propargyl bromide:

To the 5-hydroacenaphthylene anion, prepared following the general procedure, propargyl bromide (0.45 ml, 5 mmol) was added. Column chromatography over silica using light petroleum as eluent gave a mixture of mono- and alkylated product. The mass recovery was 95%.

1-Propargylacenaphthene (**4a**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.64 (ddd, $J_{6,7}$ = 8.1, $J_{1,6}$ = 0.7, $J_{6.8}$ = 0.7 ,1H, H-6), 7.61 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$ = $J_{2',5}$ = 1.1, $J_{3,5}$ = 0.8, 1H, H-5), 7.47 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 6.9, 1H, H-7), 7.46 (dd, $J_{3,4}$ = 6.8, $J_{4,5}$ = 8.2, 1H, H-4), 7.41 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 1.2, $J_{6.8}$ = 0.7, 1H, H-8), 7.28 (dddd, $J_{3,4}$ = 6.8, $J_{2,3}$ = $J_{2',3}$ = 1.1, $J_{3,5}$ = 0.8, 1H, H-3), 3.90 (dddddd, $J_{1,2}$ = 8.1, $J_{1,2'}$ = 3.5, $J_{9',1}$ = 8.0, $J_{9,1}$ = 6.2, $J_{1,8}$ = 1.2, $J_{1,6}$ = 0.7, 1H, H-1), 3.67 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2}$ = 8.1, $J_{2.5}$ = $J_{2,3}$ = 1.1, 1H, H-2), 3.22 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2'}$ = 3.5, $J_{2',5}$ = $J_{2',3}$ = 1.1, 1H, H-2'), 2.72 (ddd, $J_{9,9'}$ = -16.7, $J_{9,1}$ = 6.2, $J_{9,11}$ = 2.6, 1H, H-9), 2.55 (ddd, $J_{9,9'}$ = -16.7, $J_{9',1}$ = 8.0, $J_{9',11}$ = 2.7, 1H, H-9), 1.98 (dd, $J_{9,11}$ = 2.6, $J_{9',11}$ = 2.7, 1H, H-11).

^{13}C NMR ($CDCl_3$) **:** δ = 148.8 (C-2a or C-8a), 143.7 (C-2a or C-8a), 138.7 (C-8b), 131.4 (C-5a), 127.9 (C-4 or C-7), 127.8 (C-4 or C-7), 123.3 (C-5 or C-6), 122.4 (C-5 or C-6), 119.3 (C-3 or C-8), 119.1 (C-3 or C-8), 69.2 (C-11), 42.2 (C-1), 37.4 (C-2), 25.4 (C-9).

Exact mass calculated for $C_{15}H_{12}$: 192.0939 m/z; found: 192.0933 m/z. MS m/z (%): 192 (18), 153 (100), 126 (2).

1,1-Dipropargylacenaphthene (**4b**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.69 (ddd, $J_{6,7}$ = 2.0, $J_{6.8}$ = 7.0 ,1H, H-6), 7.65 (ddt, $J_{4,5}$ = 8.5, $J_{2.5}$, $J_{3,5}$, 1H, H-5), 7.51 (dd, $J_{6,7}$ = 2.0, $J_{7,8}$ = 7.0, 1H, H-7), 7.50 (ddd, $J_{7,8}$ = 7.0, $J_{6.8}$ = 7.0 , 1H, H-8), 7.49 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.5, 1H, H-4), 7.30 (ddt, $J_{3,4}$ = 6.9, $J_{2,3}$, $J_{3,5}$, 1H, H-3), 3.46 (s, 2H, H-2), 2.83 (dd, $J_{9,9'}$ = -16.7, $J_{9,11}$ = 2.6, 2H, H-9), 2.75 (dd, $J_{9,9'}$ = -16.7, $J_{9',11}$ = 2.6, 2H, H-9'), 1.98 (dd, $J_{9,11}$ = $J_{9',11}$ = 2.6, 2H, H-11).

^{13}C NMR ($CDCl_3$) **:** δ = 128.0 (C-4 or C-7), 127.7 (C-4 or C-7), 124.0 (C-5 or C-6), 122.7 (C-5 or C-6), 119.5 (C-3 or C-8), 118.9 (C-3 or C-8), 70.4 (C-11, C11'), 43.4 (C-2), 31.5 (C-9), quaternary carbon atom signals were not observed.

Exact mass calculated for $C_{18}H_{14}$: 230.1095 m/z; found: 230.1083 m/z. MS m/z (%): 230 (24), 191 (100), 152 (24).

Reaction of the 5-hydroacenaphthylene anion with (bromomethyl)cyclopropane:

To the 5-hydroacenaphthylene anion, prepared following the general procedure using acenaphthylene (0.46 g, 3 mmol) and methanol (0.121 ml, 3 mmol), (bromomethyl)cyclopropane (0.36 ml, 3 mmol) was added. The crude product was filtered through silica with light petroleum as eluent. The product mixture consisted of acenaphthene and 1-(cyclopropylmethyl)acenaphthene in a 2:1 ratio. The mass recovery was 96%. The major part of the acenaphthene could be removed by crystallisation from light petroleum. Kugelrohr distillation of the oil gave 187 mg (0.9 mmol, 30%) of >90% pure 1-(cyclopropylmethyl)acenaphthene in the second fraction.

1-(Cyclopropylmethyl)acenaphthene (**5a**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.59 (d, $J_{6,7}$ = 8.2, 1H, H-6), 7.58 (d, $J_{4,5}$ = 8.2, 1H, H-5), 7.44 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.8, 1H, H-7), 7.43 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.8, 1H, H-4), 7.26 (d, $J_{7,8}$ = 6.8, 1H, H-8), 7.25 (d, $J_{3,4}$ = 6.8, 1H, H-3), 3.76 (m, 1H, H-1), 3.60 (dd, $J_{2,2'}$ = -17.2, $J_{1,2}$ = 8.0, 1H, H-2), 3.17 (d, $J_{2,2'}$ = -17.2, $J_{1,2'}$ = 3.5, 1H, H-2), 1.72 (ddd, $J_{9,9'}$ = -13.5, $J_{9,10}$ = 7.2, $J_{1,9}$ = 5.5, 1H, H-9), 1.63 (ddd, $J_{9,9'}$ = -13.5, $J_{9',10}$, $J_{1,9'}$ = 6.33, 1H, H-9'), 0.89 (m, 1H, H-10), 0.51 (ddd, 2H, H-11), 0.19 (ddd, 2H, H-12).

^{13}C NMR ($CDCl_3$) **:** δ = 149.5 (C-2a or C-8a), 144.8 (C-8a or C-2a), 138.6 (C-8b), 131.4 (C-5a), 127.8 (C-6 or C-5), 127.7 (C-5 or C-6), 122.5 (C-7 or C-4), 122.2 (C-4 or C-7), 119.1 (C-8 or C-3), 118.9 (C-3 or C-8), 44.0 (C-1), 41.5 (C-9 or C-2), 37.5 (C-2 or C-9), 9.4 (C-10), 4.9 (C-11 or C-12), 4.8 (C-12 or C-11).

GC-MS showed one product with mass 208. MS m/z (%): 208 (100), 166 (17), 153 (70).

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4

Reactivity of the 5-hydroacenaphthylene anion towards electrophiles: single electron transfer *vs.* S_N2

4.1 Introduction

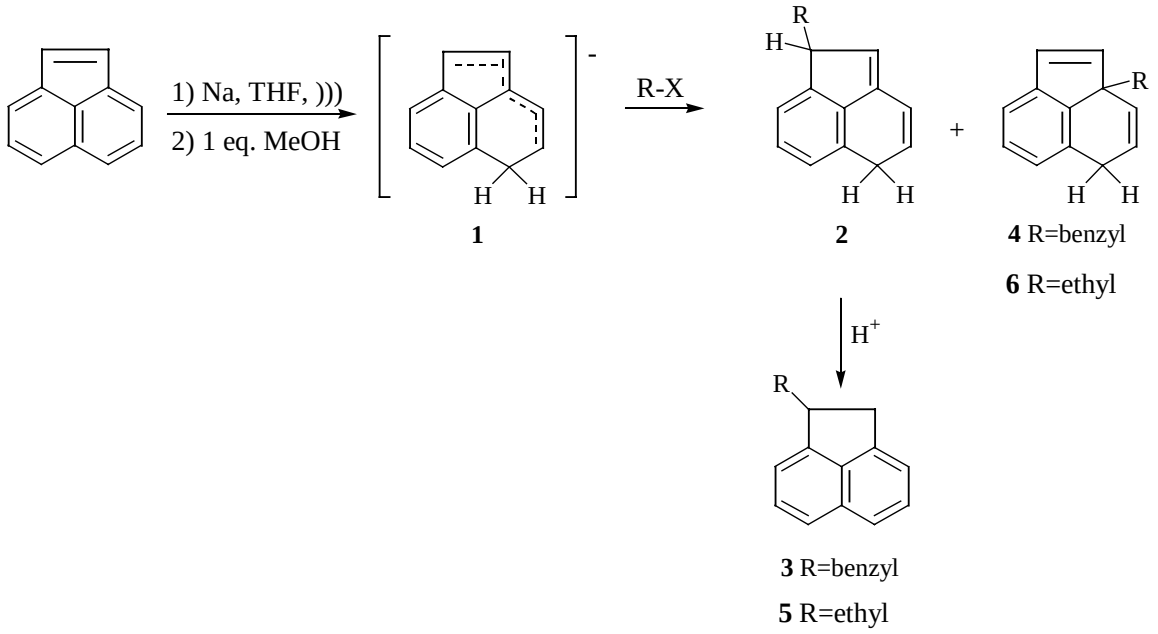
With alkyl halides such as methyl iodide and allyl bromide the 5-hydroacenaphthylene anion (**1**) reacts exclusively at position 1, resulting, after acidic work-up, in 1-substituted acenaphthenes (Chapters 2 and 3).[1,2] The next extension of the investigation of the reactivity of **1** involved the use of benzyl halides. From a synthetic organic point of view, coupling of the acenaphthene skeleton to a benzyl group would open the way to larger PAH: ring closure by means of irradiation[3,4,5] or metal-catalysed cyclodehydrogenation[6,7] might lead to e.g. cyclopenta[*def*]chrysene.

Preliminary results of the reaction of **1** with benzyl bromide as electrophile showed however that reaction took place not only at position 1 but also at position 2a.[2] The hardness or softness of the electrophile was presumed to be the cause of the different behaviour towards the 5-hydroacenaphthylene anion. In this chapter we study the reaction of the 5-hydroacenaphthylene anion with various benzyl halides (iodide, bromide, chloride and also tosylate) and for comparison also with ethyl halides (iodide, bromide and also tosylate) in order to obtain more evidence about the reaction mechanism. The results of these experiments required further mechanistic investigations. These include the use of sterically hindered electrophiles (isopropyl iodide and *tert*-butyl bromide), as well as the search for possible intermediates using *p*DNB (as electron scavenger) and radical scavengers (e.g., TEMPO). Furthermore, methods for the separation of the pure products have been developed.

4.2 Results

Acenaphthylene was converted into its 5-hydroanion (**1**) according to the procedure described earlier (Chapters 2 and 3).[1,2] The reaction mixture was cooled to -70ºC, one equivalent of benzyl bromide was added and the solution was stirred at room temperature during 30 minutes. Quenching with water and extraction with light petroleum (boiling range 40-60ºC) and the usual work-up, during which the initially formed 1-benzyl-1,5-dihydroacenaphthylene (**2**) rearranges to 1-benzylacenaphthene (**3**), gave **3** and 2a-benzyl-2a,5-dihydroacenaphthylene (**4**) as the major

products (more than 90% based on acenaphthylene) (Scheme 1). Acenaphthene and dibenzylated products were the only side products (less than 10%) observed.



***Scheme 1**: Reaction of the 5-hydroacenaphthylene anion with benzyl and ethyl halides (R = benzyl, ethyl, X = I, Br, Cl, OTs).*

Compounds **3** and **4** could not be separated by column chromatography over silica gel or silica gel impregnated with caffeine, by normal phase HPLC or by preparative gas chromatography. Therefore, the product mixture was treated with 3-chloroperoxybenzoic acid (*m*CPBA) in dichloromethane, which led to the selective epoxidation of **4**. Subsequent removal of the oxidation product by means of silica gel column chromatography allowed the isolation of 1-benzylacenaphthene (**3**).

If the trisubstituted double bond, present in the initially formed 1-substituted product (**2**), is more reactive towards *m*CPBA than the double bonds in **4**, selective epoxidation of this bond would afford an isolation procedure for **4**. In order to avoid rearrangement of **2**, *m*CPBA was added to the reaction mixture before work-up. However, because of the competitive epoxidation of **4** it was not possible to obtain pure **4**. Eventually, 2a-benzyl-2a,5-dihydroacenaphthylene **4** was obtained pure by treatment of the product mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and removal of the 1-benzylacenaphthylene formed from **3** by subsequent column chromatography over silica impregnated with 10% caffeine.

The alkylation of the 5-hydroacenaphthylene anion **1** was also performed with benzyl chloride, benzyl iodide and benzyl tosylate, following the procedure as described for benzyl bromide. **3** and **4**

were obtained as major products. The ratios of **3** and **4** in these reactions, determined by NMR spectroscopy, are given in Table 1.

Treatment of **1** with one equivalent of ethyl iodide gave substitution at positions 1 and 2a in a 5:1 ratio (Table 1) and a mixture of 1-ethylacenaphthene **5** and 2a-ethyl-2a,5-dihydroacenaphthylene **6** was isolated. The use of one equivalent of ethyl bromide resulted in the formation of more 1-substituted product. However, use of the harder ethyl tosylate gave a 1:1 mixture of **5** and **6**. **5** could be isolated by the method described above. It was however not possible to oxidise **5** selectively by DDQ to obtain pure **6**.

Table 1*: Reaction of the 5-hydroacenaphthylene anion with benzyl and ethyl halides.*

Electrophile	ratio **3** : **4**	Electrophile	ratio **5** : **6**
Benzyl tosylate	1:0.6	Ethyl tosylate	1:1
Benzyl chloride	1:0.9	Ethyl chloride	N.D.
Benzyl bromide	1:1.2	Ethyl bromide	7:1
Benzyl iodide	1:1.0	Ethyl iodide	5:1

Reaction of **1** with one equivalent of isopropyl iodide gave a product mixture which contained, according to NMR, 30% acenaphthene, 35% 1-(2-propyl)acenaphthene and 35% 2a,5-dihydro-2a-(2-propyl)acenaphthene. Treatment of **1** with one equivalent of *tert*-butyl bromide gave only 20% substitution products, which contained *tert*-butyl groups at positions 1 and 2a in a 1:1 ratio, and almost 80% acenaphthene.

The reaction of **1** with benzyl bromide was also performed in the presence of the electron scavenger *para*-dinitrobenzene (*p*DNB) and radical scavengers (di-*tert*-butyl nitroxide and TEMPO), following the general procedure. The product ratios, which were determined with NMR, are given in Table 2. A similar experiment was performed with ethyl iodide in the presence of TEMPO (Table 2).

Table 2: *Effect of addition of electron or radical scavengers on the reaction of* ***1*** *with benzyl bromide and ethyl iodide.*

Electrophile	Additive	1-subst. prod. (%)	2a-subst. prod.(%)	acenaphthene (%)
Benzyl bromide	none	46	46	8
	0.5 eq. *p*DNB	24	24	48
	1 eq. di-*t*BuNO	33	33	32
	1 eq. TEMPO	24	24	51
Ethyl iodide	none	80	16	4
	1.5 eq. TEMPO	75	8	15

4.3 ^{1}H and ^{13}C NMR spectroscopy

The ^{1}H NMR spectrum of 1-benzylacenaphthene (**3**) consists of 11 aromatic and 5 benzylic protons. The aromatic part of the spectrum consists of two separate ABC patterns for the acenaphthene part and one A_2B_2C pattern for the phenyl group. In addition to the expected ortho- and meta-couplings in the naphthalene skeleton, H-3 and H-5 show small couplings with H-2 and H-2'. Similar couplings can be observed between H-6 and H-1 and between H-8 and H-1. These couplings were confirmed by H-H-COSY and decoupling experiments. The non-aromatic part shows an ABCDE pattern. The two protons at C-2, with a large negative geminal coupling constant, have different coupling constants with H-1, the cis-coupling being the larger one. H-1 also couples with the distinguishable protons at C-9 (see experimental section). This difference between H-9 and H-9' is induced by the chirality at C-1, but the assignment of the individual protons on the basis of a molecular model and these NMR results is not possible. Selective substitution of H-9 or H-9' with deuterium is necessary to discriminate between both protons.[8,9] The ^{13}C NMR spectrum was consistent with the structure of **3**.

In the spectrum of 2a-benzyl-2a,5-dihydroacenaphthylene (**4**) 8 aromatic protons, 4 olefinic and 4 benzylic protons can be recognised. The aromatic part of the spectrum consists of an ABC pattern for H-6, H-7 and H-8 and one A_2B_2C pattern for the phenyl group. H-1 and H-2 appear in a doublet at relatively low field, as can be expected by comparison with the ^{1}H NMR spectrum of styrene. The other olefinic protons H-3 and H-4 give together with H-5 and H-5' an ABX_2 pattern. In the boat-shaped six-membered ring, H-5 (pseudo-equatorial) and H-5' (pseudo-axial) can be clearly distinguished (see experimental section) by their different couplings with H-3 and H-4, due to the different dihedral angles. The benzylic protons H-9 and H-9' have different chemical shifts induced by chirality, but cannot be assigned on the basis of the molecular structure of **4**. The ^{13}C NMR spectrum was consistent with the structure of **4**.

The spectra of **5** and **6** were similar to the spectra discussed above.

4.4 Discussion

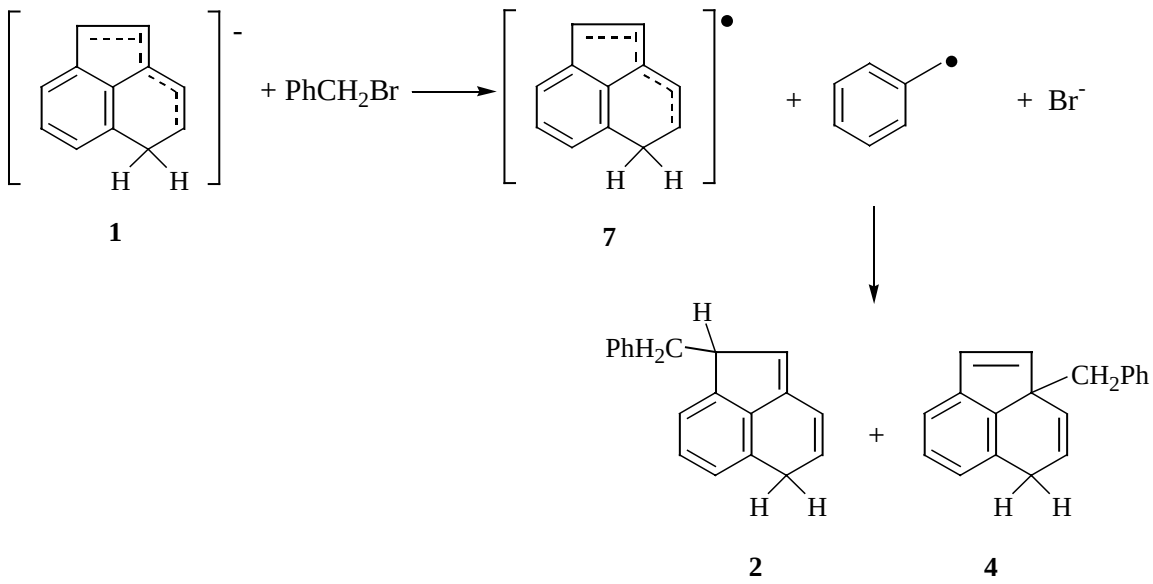
Reaction of the 5-hydroacenaphthylene anion **1** with alkyl halides such as methyl iodide and allyl bromide occurs at carbon atom 1. This may be due to the presence of the highest charge and a high HOMO coefficient at this carbon atom (Chapter 2).[1]

The charge distribution in **1** can be inferred from its ^{13}C NMR chemical shifts. From the order of these shifts (see Chapter 2, Table 2) C-1 appears to have the highest charge, in agreement with the calculations. A substantial amount of charge is also found at C-2a, less charge is present at C-4. In semiempirical (PM3)[2] and *ab initio* calculations (Chapter 2) the carbon atoms with the highest charge are C-1 (-0.21), C-4 (-0.17), C-6 (-0.16) and C-2a (-0.12). The highest HOMO coefficient is, however, found at C-2a (0.303), followed by C-1 (-0.275) and C-4 (-0.210).

In the reaction of benzyl bromide with **1** substitution takes place at position 1 as well as at 2a, in a ratio of 1:1. Such a change in regioselectivity with change in electrophile has been reported in the literature for the reaction of the 5-hydropyrenyl anion with soft electrophiles such as benzyl iodide and *n*-propyl iodide.[10,11] In this case the results were rationalised by the assumption that these electrophiles are soft and react at the position with the highest HOMO. In parallel, the hard-softness of electrophiles might be an important factor in determining at which position of **1** alkylation takes place. Therefore, **1** was treated with benzyl iodide, benzyl bromide, benzyl chloride and benzyl tosylate in order to investigate the influence of the nature of the leaving group.[12] Surprisingly, the leaving group did hardly affect the product distribution in the case of iodide, bromide and chloride (Table 1). The reaction of **1** was also performed with ethyl iodide, ethyl bromide and ethyl tosylate. Now, the hardest electrophile of the three, ethyl tosylate, gave the largest percentage of substitution at position 2a (Table 1). This is a strong indication that the hard-soft effect of the leaving group is not a major factor in determining the product distribution.

The following question now arises: which factors do determine the reactivity of the various positions in the hydroanion towards alkyl halides? If an S_N2 reaction would be possible at position 2a, thus creating a quaternary carbon atom, this must certainly be found for the small methyl iodide. But in the reaction of **1** with methyl iodide, absolutely no 2a-substituted product was observed. Bulkier electrophiles than methyl iodide do react at position 2a and this indicates that the reaction at 2a does not follow the S_N2 pathway. The mode of attack must be related to the nature of the interaction between nucleophile and electrophile.

In reactions with electron-rich nucleophiles, the single electron transfer (SET) mechanism can be competitive with the S_N2 mechanism. If **1** reacts via electron transfer, the 5-hydroacenaphthylene radical **7** will be an intermediate (Scheme 2).



***Scheme 2**: Reaction of the 5-hydroacenaphthylene anion with benzyl bromide via electron transfer.*

The recombination of the benzyl radical and **7** will take place at the positions with the highest spin densities (Figure 1), which are positions 1 and 2a according to *ab initio* calculations (ROHF/6-31G(d,p), restricted open shell, see Experimental section). The product ratio of **3** and **4** is 1:1, although carbon atom 1 has a lower spin density than carbon atom 2a. Positiion 1 is however more easily accessible for the electrophile. Apparently, the spin density at C-4 is not high enough to be able to compete with the other two carbon atoms.

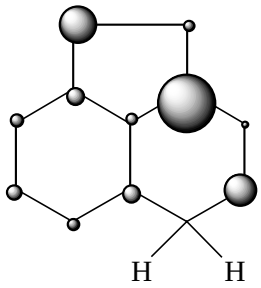


***Figure 1**: Total atomic spin densities in the 5-hydroacenaphthylene radical (**7**).*

The nature of the halide is one factor upon which the competition between S_N2 and SET in a substitution reaction with an alkyl halide depends. The transition states of both reactions will be influenced to a different degree by a change of leaving group.[13,14,15] The electron-acceptor ability (reduction potential) of the alkyl halide is an important factor in determining the possibility of SET and it increases in the order OTs <Cl<Br<I.[16,17,18,19] The order of reactivity observed in S_N2 reactions with primary alkyl halides is OTs>I>Br>Cl.[20] Therefore, reactions of alkyl tosylates are

more likely to proceed via an S_N2 mechanism whereas those of alkyl iodides will favourably proceed by SET.

In the case of simple alkyl halides, including benzyl halides, concerted electron transfer-bond breaking prevails, resulting in an alkyl radical and an halide ion.[21,22,23] Thus, the reactive intermediate after SET is identical for all leaving groups and reaction of this species will therefore result in the same substitution pattern for all leaving groups if SET is the exclusive mechanism.[24]

In the S_N2 mechanism primary alkyl halides will react more rapidly than more crowded derivatives. Decrease of reaction rate due to steric hindrance is less pronounced in the SET mechanism. To understand this inequality the transition states (TS) for both reaction pathways should be regarded.[25,25,26] Increase of steric hindrance in the transition state will result in bond loosening and will increase the TS barrier more for S_N2 than for SET.[27,28] In addition to steric factors, inhibition or hindering of the coupling process by electronic or geometric factors will result in a preference for the SET pathway.[25]

The benzyl group lowers the reduction potential with respect to simple alkyl groups and will therefore more easily undergo electron transfer.[29] More sterically hindered alkyl halides can also be more easily reduced and will therefore give more SET than their linear analogues. [18,30] This influence of the bulkiness of the reagent was confirmed by experiments with (aromatic radical anions and) a variety of alkyl halides.[14,15,17,31]

Applying this knowledge to the reaction of the 5-hydroacenaphthylene anion with benzyl halides demonstrates that the SET mechanism is consistent with the data. The product distribution is rather independent of the leaving group for iodide, bromide and chloride. This implies that the reaction pathway is the same for each halide and is in accordance with the assumption that in these cases SET is the principal reaction pathway. For benzyl tosylate the product distribution shifts towards more 1-substituted products. This may be due to the higher reactivity of tosylates in S_N2 reactions and their lower reactivity in SET reactions in relation to the other halides, because of their higher reduction potential. Ethyl iodide gives more 2a-substituted products than ethyl bromide but less than the benzyl halides. Ethyl halides have higher reduction potentials than the corresponding benzyl halides and will thus tend to give less SET products. Ethyl tosylate is an exception in its reactivity towards the hydroanion. However, it should be realised that the tosylate group is bulky and that the S_N2 reaction with the bulky hydroanion will therefore be seriously hindered.

To obtain further experimental evidence for the SET mechanism the following experiments were performed:

*1) Reaction of **1** with isopropyl iodide and tert-butyl bromide.*

These electrophiles were chosen because they are known to favour the electron transfer mechanism in their reaction with nucleophiles because of their steric proportions.[18,25,30] Isopropyl iodide gave substitution at both positions 1 and 2a, in a 1:1 ratio.
The reaction of the hydroanion with *tert*-butyl bromide gave, next to acenaphthene, circa 20% substitution products; the products formed were C-1 and C-2a substituted acenaphthenes in a 1:1 ratio. The reluctance of isopropyl iodide and *tert*-butyl bromide to undergo S_N2 reactions and the 1:1 ratio of the C-1 and C-2a substituted products validate the assumption that when exclusive SET reaction takes place substitution occurs to the same extent at positions 1 and 2a. Furthermore it should be noted that the bulkiness of the electrophile influences the reaction path (S_N2 *versus* SET), but does not affect the substitution ratios, which depend, in the case of SET, on the spin density distribution in **7**.

*2) Reaction of **1** with benzyl bromide in the presence of the electron scavenger para-dinitrobenzene.*
0.5 Equivalents of *para*-dinitrobenzene (*p*DNB) were added to the mixture of **1** and benzyl bromide in order to investigate if electron transfer is possible from the hydroanion to an electron scavenger.[20] In comparison with the reaction without electron scavenger, less benzylated products were found in the product mixture and more acenaphthene. From the decrease of the amount of substitution products we may conclude that electrons from the hydroanion were transferred to *p*DNB and thus that SET is possible. The resulting 5-hydroacenaphthylene radical is converted by hydrogen transfer into a dihydroacenaphthylene derivative, which rearranges to acenaphthene. The ratio of C-1 and C-2a benzylated products, determined by comparison of the characteristic NMR integrals, was unchanged. This indicates that either the two processes are delayed to the same extent or only electron transfer takes place.

*3) Reaction of **1** with alkyl halides in the presence of the radical scavengers di-tert-butyl nitroxide and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).*
An attractive possibility to discriminate between the S_N2 and SET mechanism is to investigate if free radical intermediates are present during the course of action. Because of the sensitivity of the reaction mixture to moisture and air it is difficult to perform the reaction in an EPR spectrometer. Therefore radical scavengers were used.[20,28]

Di-*tert*-butyl nitroxide (1 equivalent) was added to the reaction mixture of the hydroanion with benzyl bromide, following the general procedure. After the usual work-up the product mixture was analysed by NMR spectroscopy. The yield of substitution products was decreased, in favour of acenaphthene, but the **3** : **4** ratio did not change. The decrease of substitution products and the formation of acenaphthene indicates that radicals were present and thus that electron transfer has taken place. The yield of substitution products is lowered but not zero. Evidently the efficiency of the reaction with the radical scavenger is not so high that all the radicals are captured. The products

derived from the reaction of the radical scavenger with the benzyl radicals could not be isolated, due to the instability of the radical coupling products. The addition product of the radical scavenger to the 5-hydroacenaphthylene radical is probably converted into acenaphthene. If the S_N2 mechanism would be part of the reaction pathway, substitution at C-1 would not be hampered and thus the substitution ratio would have changed. The unchanged product ratio is a strong indication that the reaction of the hydroanion with benzyl bromide proceeds exclusively via SET.

Experiments were also performed with another radical scavenger: TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). Addition of TEMPO (1 equivalent) to the mixture of the 5-hydroacenaphthylene anion and benzyl bromide gave similar results as with di-*tert*-butyl nitroxide.

However, the use of TEMPO (1.5 equivalents) in the reaction of the 5-hydroacenaphthylene anion with ethyl iodide gave a change in the product distribution: **4** and **5** were now formed in the ratio 1 : 0.1 instead of 1 : 0.2. From the total amount of isolated product it could be concluded that the yield of **4** had not dramatically decreased. The decrease in yield of **5** leads to the conclusion that **5** must be formed in an SET reaction. Because the radical scavenger will not hinder S_N2 substitution, it is expected that the amount of product formed by S_N2 substitution will not be diminished. Therefore, the 1-substitution product in the reaction of the 5-hydroacenaphthylene anion with ethyl iodide is predominantly formed via an S_N2 mechanism.

These mechanistic investigations confirm the occurrence of electron transfer in the reaction of the 5-hydroacenaphthylene anion with electrophiles that are capable to accept electrons. In pure S_N2 reactions substitution takes place only at position 1 and in pure SET reactions substituents are found at positions 1 and 2a in a ratio of 1:1. The reaction of the 5-hydroacenaphthylene anion with ethyl iodide gives reaction products derived from both S_N2 and SET reactions. Alternatively, these results may be explained by assuming that the reaction type is intermediate between S_N2 and SET (continuum model).[13,14,24,32]

4.5 Conclusions

The reaction of the 5-hydroacenaphthylene anion **1** with electrophiles such as benzyl halides takes place at both positions 1 and 2a. 1-Benzylacenaphthene and 2a-benzyl-2a,5-dihydroacenaphthylene can be isolated by selective oxidation of the undesired isomer and subsequent separation by chromatography. The reactivity at position 2a cannot be ascribed to hardness-softness of the electrophile, but is more likely to be the result of electron transfer. The SET reaction takes place at position 1 as well as at 2a in a 1:1 ratio. After transfer of one electron, the 5-hydroacenaphthylene radical will react at the positions with the highest spin density. The observed product ratios from the reactions of electrophiles with **1** are in accordance with the electron affinities.

The use of electron scavengers (*p*DNB), radical scavengers (TEMPO) and more sterically hindered electrophiles corroborates the occurrence of the SET mechanism in the reaction of the 5-hydroacenaphthylene anion with electrophiles such as benzyl halides.

4.6 Experimental section

General: Acenaphthylene (Aldrich, 75%) was purified by treatment with DDQ and filtration over silica. Benzyl bromide, benzyl chloride, and ethyl tosylate were obtained from Acros and used without further purification but dried over molecular sieves (3Å, 8-12 mesh). Ethyl iodide was purchased from Acros and was extracted with a saturated sodium sulfite solution, predried over calcium chloride, distilled at atmospheric pressure and stored over molecular sieves (3Å, 8-12 mesh). Benzyl iodide was prepared from benzyl bromide by bromine-iodine exchange with potassium iodide in acetone. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3Å, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra. For the determination of the coupling constants we used the simulation program PERCH.[33]

General procedure:

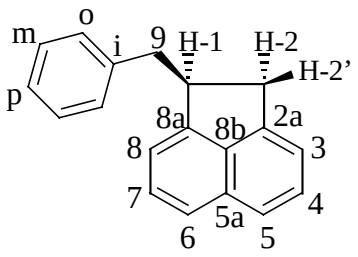
Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. Acenaphthylene (0.76 g,5 mmol) was added, together with freshly cut sodium (0.3 g, 13 mmol). Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0ºC, a deep green solution was obtained. The flask was then cooled in an ethanol-liquid nitrogen bath to -70ºC and methanol (0.15 ml, 5 mmol) was added. The colour of the mixture turned red-brown. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. The mixture was cooled again to -70ºC and alkyl halide (5 mmol) was added. Stirring was continued at room temperature for 30 minutes after which period the reaction was quenched with water. The addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. Yields of substitution products are generally between 90 and 100%, depending on the humidity of the air in the laboratory and the reactivity of the electrophile. The composition of the mixture was determined by means of NMR spectroscopy. In the reaction with benzyl chloride 20 equivalents were used to accelerate the reaction.

Reaction of the acenaphthylene hydroanion with benzyl bromide:

To the 5-hydroacenaphthylene anion (5 mmol), prepared according to the general procedure, benzyl bromide (0.595 ml, 5 mmol) was added. Column chromatography over silica gel using light petroleum as eluent gave two fractions; the first consisted of acenaphthene (less than 10%) and benzyl bromide, the other contained the substitution products. Kugelrohr distillation gave a mixture of 1-benzylacenaphthene (**3**) and 2a-benzyl-2a,5-dihydroacenaphthylene (**4**). The residue contained a trace of at least two disubstituted products.

*Isolation of 1-benzylacenaphthene (**3**):*

To a mixture of **3** and **4** (ca. 5 mmol) in dichloromethane (25 ml) *m*-chloroperbenzoic acid (0.43 g, 2.5 mmol) was added and the reaction mixture was stirred overnight. Dichloromethane-water extraction, washing with Na_2SO_3-solution, followed by drying over $MgSO_4$ and evaporation of the solvent gave a mixture of **3** and (ep)oxidised **4**. Silica gel column chromatography with light petroleum gave 1-benzylacenaphthene as a light yellow oil. The oxidation products were not isolated and characterised. The yield of **3** varied between 40 and 50%, based on acenaphthylene.



1-Benzylacenaphthene (**3**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.61 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1H, H-5), 7.60 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$, $J_{6.8}$,1H, H-6), 7.43 (dd, $J_{3,4}$ = 6.7, $J_{4,5}$ = 8.2, 1H, H-4), 7.41 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.6, 1H, H-7), 7.23 (dddd, $J_{3,4}$ = 6.7, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1H, H-3), 7.20-7.12 (m, 5H, H-phenyl), 7.05 (ddd, $J_{7,8}$ = 6.6, $J_{1,8}$, $J_{6.8}$, 1H, H-8), 4.02 (dddddd, $J_{1,2}$ = 8.1, $J_{1,2'}$ = 2.3, $J_{9',1}$ = 8.9, $J_{9,1}$ = 7.5, $J_{1,8}$, $J_{1,6}$, 1H, H-1), 3.47 (dddd, $J_{2,2'}$ = -17.0, $J_{1,2}$ = 8.1, $J_{2.5}$, $J_{2,3}$, 1H, H-2), 3.19 (dd, $J_{9,9'}$ = -14.0, $J_{9,1}$ = 7.5, 1H, H-9), 3.10 (dddd, $J_{2,2'}$ = -17.0, $J_{1,2'}$ = 2.3, $J_{2',5}$, $J_{2',3}$, 1H, H-2'), 2.89 (dd, $J_{9,9'}$ = -17.0, $J_{9',1}$ = 8.9, 1H, H-9). $J_{1,6}$, $J_{6.8}$, $J_{1,8}$, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$ were observed but could not exactly be determined.

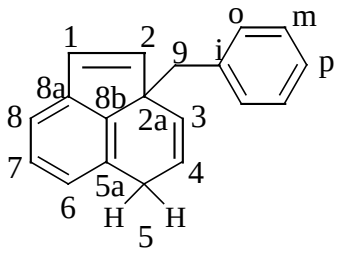
^{13}C NMR ($CDCl_3$) **:** δ = 148.5 (C-2a or C-8a), 144.1 (C-2a or C-8a), 140.3 (C-8b), 131.5(C-5a), 130.5 (C-ipso), 129.1 (2C-meta), 128.3 (2C-ortho), 127.8 (C-4 or C-7), 127.6 (C-4 or C-7), 126.1 (C-para), 122.8 (C-6), 122.3 (C-5), 119.2 (C-3 or C-8), 119.1 (C-3 or C-8), 44.5 (C-1), 42.6 (C-9), 37.3 (C-2).

$C_{19}H_{16}$: calcd. 244.1252; found 244.1276. MS; *m/z* (%): 244 (13), 165 (7), 154 (12), 153 (100), 91 (29), 65 (11).

*Isolation of 2a-benzyl-2a,5-dihydroacenaphthylene (**4**):*

To a mixture of **3** and **4** (ca. 5 mmol) in toluene 0.5 equivalent DDQ was added and the reaction mixture was stirred for 36 hours at room temperature. Filtration over hyflo, washing with a saturated sodium sulfite solution, drying over $MgSO_4$ and concentration was followed by chromatography

over silica impregnated with 10% caffeine. The first fraction, detected by an iodine bath, contained pure **4**. The oxidation products were not isolated and characterised.



2a-Benzyl-2a,5-dihydroacenaphthylene (**4**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ 7.19 (dd, $J_{7,8}$ = 7.3, $J_{6,7}$ = 7.6,1H, H-7), 7.18 (d, $J_{o,m}$ = 5.0, 2 H, H-o), 7.18 (d, $J_{p,m}$ = 5.0, 1 H, H-p), 7.16 (dd, $J_{7,8}$ = 7.3, $J_{6.8}$, 1H, H-8), 6.98 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$, 1H, H-6), 6.97 (dd, $J_{o,m}$ = $J_{m,p}$ = 5.0, 2 H, H-m), 6.67 (d, $J_{1,2}$ = 5.5, 1H, H-1), 6.59 (d, $J_{1,2}$ = 5.5, 1H, H-2), 6.19 (ddd, $J_{3,4}$ = 9.2, $J_{3,5}$, $J_{3,5'}$ = 3.1, 1H, H-3), 6.14 (ddd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 5.5, $J_{4,5'}$ = 1.8, 1H, H-4), 3.12 (ddd, $J_{5,5'}$ = -19.6, $J_{3,5}$, $J_{4,5}$ = 5.5, 1H, H-5), 3.02 (ddd, $J_{5,5'}$ = -19.6, $J_{3,5'}$ = 3.1, $J_{4,5'}$ = 1.8, 1H, H-5'), 2.89 (d, $J_{9,9'}$ = -12.7, 1H, H-9), 2.62 (d, $J_{9,9'}$ = -12.7, 1H, H-9'), $J_{6.8}$ and $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$)**:** δ = 148.7, 140.7, 138.2, 133.6 (C-8b, C-8a, C-5a, C-ipso), 142.5 (C-2), 130.4 (2 C-meta), 130.1 (C-1), 129.5 (C-4), 128.7 (C-3), 127.4 (2 C-ortho), 127.0 (C-7), 126.1 (C-para), 123.1 (C-6), 119.2 (C-8), 56.5 (C-2a), 46.2 (C-9), 29.7 (C-5)

$C_{19}H_{16}$: calcd. 244.1252; found 244.1209. MS; *m/z* (%): 244 (12), 152 (100), 91 (58), 65 (30).

Reaction of the acenaphthylene hydroanion with ethyl iodide:

To the 5-hydroacenaphthylene anion (3 mmol), prepared according to the general procedure, ethyl iodide (0.25 ml, 0.47 g, 3 mmol) was added. The products could not be separated using column chromatography over silica gel. Acenaphthene could be removed by Kugelrohr distillation or by crystallisation from methanol, yielding a mixture of 1-ethylacenaphthene (**5**) and 2a-ethyl-2a,5-dihydroacenaphthylene (**6**) (90-100%).

*Isolation of 1-ethylacenaphthene (**5**):*

To a mixture of **5** and **6** (5 mmol) in dichloromethane (25 ml) was added *m*-chloroperbenzoic acid (0.43 g, 2.5 mmol) and the reaction mixture was stirred overnight. Dichloromethane-water extraction, washing with Na_2SO_3-solution, followed by drying over $MgSO_4$ and concentration gave a mixture of **5** and (ep)oxidised **6**. Silica gel column chromatography with light petroleum gave **5** as a light yellow oil. The oxidation products were not isolated and characterised. The yield of **5** varies between 40 and 50%, based on acenaphthylene.

1-Ethylacenaphthene (**5**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.58 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$, $J_{6.8}$,1H, H-6), 7.57 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1H, H-5), 7.43 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.7, 1H, H-7), 7.42 (dd, $J_{3,4}$ = 5.9, $J_{4,5}$ = 8.2, 1H, H-4), 7.23 (ddd, $J_{7,8}$ = 6.7, $J_{1,8}$, $J_{6.8}$, 1H, H-8), 7.23 (dddd, $J_{3,4}$ = 5.9, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1H, H-3), 3.57 (m, 1H, H-1), 3.53 (dddd, $J_{2,2'}$ = -17.7, $J_{1,2}$ = 8.3, $J_{2.5}$, $J_{2,3}$, 1H, H-2), 3.02 (dddd, $J_{2,2'}$ = -17.7, $J_{1,2'}$ = 2.7, $J_{2',5}$, $J_{2',3}$, 1H, H-2'), 1.94 (ddq, $J_{9,9'}$ = -16.0, $J_{9,1}$ = 4.8, $J_{9,10}$ = 7.5, 1H, H-9), 1.64 (ddq, $J_{9,9'}$ = -16.0, $J_{9',1}$ = 8.9, $J_{9',10}$ = 7.5, 1H, H-9'), 1.02 (dd, $J_{9,10}$ = $J_{9',10}$ = 7.5, 3 H's, H-10). $J_{1,6}$, $J_{6.8}$, $J_{1,8}$, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) **:** δ = 149.4 (C-2a or C-8a), 144.8 (C-2a or C-8a), 138.4 (C-8b), 131.4 (C-5a), 127.7 (C-4 and C-7), 122.5 (C-5 or C-6), 122.2 (C-5 or C-6), 119.0 (C-3 or C-8), 118.7 (C-3 or C-8), 44.9 (C-1), 37.0 (C-2), 29.1 (C-9), 11.8 (C-10).

$C_{14}H_{14}$: calcd. 182.1095; found 182.1105. MS; *m/z* (%): 182 (26), 153 (100), 140 (6), 84 (8), 60 (6), 51 (10).

2a-Ethyl-2a,5-dihydroacenaphthylene (**6**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.32-7.23 (m, 2H, H-7 and H-8), 7.06 (m, 1H, H-6), 6.81 (d, $J_{1,2}$ = 5.5, 1H, H-1), 6.67 (d, $J_{1,2}$ = 5.5, 1H, H-2), 6.37 (ddd, $J_{3,4}$ = 9.2, $J_{3,5}$, $J_{3,5'}$ = 3.2, 1H, H-3), 6.16 (ddd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 5.8, $J_{4,5'}$ = 1.7, 1H, H-4), 3.50 (m, 1H, H-5), 3.25 (ddd, $J_{5,5'}$ = -19.5, $J_{4,5'}$ = 1.7, $J_{3,5'}$ = 3.2, 1H, H-5'), 1.49 (m, 1H, H-9), 1.37 (m, 1H, H-9'), 0.92 (dd, $J_{9,10}$ = $J_{9',10}$ = 7.4, 3H, H-10), $J_{3,5}$ was observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) **:** δ = 142.3 (C-2), 134.8 (C-3), 130.6 (C-1), 128.3 (C-4), 128.1 (C-7), 123.1 (C-6), 119.0 (C-8), 33.3 (C-9), 30.4 (C-5), 10.6 (C-10), the quaternary C's were not observed.

Mechanistic investigations:

*Reaction of **1** with isopropyl iodide:*

To the 5-hydroacenaphthylene anion (3 mmol), prepared according to the general procedure, isopropyl iodide (0.60 ml, 1.02 g, 6 mmol) was added. From the NMR data it was concluded that the reduction was complete (no acenaphthylene) and the oil consisted of acenaphthene (30%), 1-(2-propyl)acenaphthene (35%) and 2a,5-dihydro-2a-(2-propyl)acenaphthene (35%). The total yield was 94%.

*Reaction of **1** with and* tert-*butyl bromide:*

To the 5-hydroacenaphthylene anion (3 mmol), prepared according to the general procedure, *tert*-butyl bromide (0.70 ml, 0.82 g, 6 mmol) was added. From the NMR data it was concluded that the reduction was complete (no acenaphthylene) and the oil consisted of acenaphthene (80%), 1-(*tert*-butyl)acenaphthene (10%) and 2a,5-dihydro-2a-(*tert*-butyl)acenaphthene (10%). The total yield was 97%.

Reaction in the presence of para-*dinitrobenzene (*p*DNB):*

The 5-hydroacenaphthylene anion was prepared according to the general procedure. At -60°C 0.5 equivalents of pDNB and 1 equivalent of benzyl bromide were added simultaneously to the reaction mixture. Stirring was continued at room temperature for 60 minutes after which the reaction was quenched with water. The addition of light petroleum (40-60), extraction with water, washing with brine, drying over $MgSO_4$ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. This oil was analysed by NMR spectroscopy and consisted of acenaphthene (50%), **2** (25%) and **3** (25%). The total yield was 96%.

Reaction in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, free radical):

The 5-hydroacenaphthylene anion was prepared according to the general procedure. At -60°C 1.5 equivalents of TEMPO and 1 equivalent of ethyl iodide were added simultaneously to the reaction mixture. Stirring was continued at room temperature for 60 minutes after which period the reaction was quenched with water. The addition of light petroleum (40-60), extraction with water, washing with brine, drying over $MgSO_4$ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. This oil was analysed by NMR spectroscopy and consisted of acenaphthene (15%), **4** (77%) and **5** (8%). The total yield was 97%.

Computational details

The calculations were carried out with the GAUSSIAN 94 suites of programs.[34] The geometry of radical **7** was fully optimised without symmetry restriction at the ROHF (restricted open shells) level by using the 6-31G(d,p) basis set.

5-Hydroacenaphthylene radical (**7**)*:*

Total atomic spin densities: 1 (0.192), 2 (0.012), 2a (0.489), 3 (0.004), 4 (0.141), 5 (0.001), 5a (0.037), 6 (0.015), 7 (0.027), 8 (0.019), 8a (0.036), 8b (0.013).

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5

Reactivity of the 5-hydroacenaphthylene anion towards electrophiles containing an additional functional group

5.1 Introduction

A useful tool in the synthesis of PAH is the reductive alkylation with electrophiles containing a second functional group. These compounds, such as an ester, a nitrile, a halide or a ketone, can be used in a second step for extension of the PAH skeleton, e.g. by cyclisation. Examples of this strategy are the syntheses of cyclopent[*hi*]aceanthrylene[1] and cyclopenta[*cd*]pyrene.[2] The sodium salt of bromoacetic acid was used as electrophile in the reaction of the anthracene dianion and the 5-hydropyrene anion. The resulting acids could easily be cyclised leading to an additional five-membered ring in an internal Friedel-Crafts acylation. Also, electrophiles with a nitrile or ester group can be used as precursors for ring closure reactions via acid chlorides. Methyl groups can now be introduced easily by using methylated electrophiles or by reaction of the resulting ketones with methyllithium.[3]

In the synthesis of benzo[*ghi*]perylene and coronene, bromoacetaldehyde diethyl acetal was reacted with the dianions of perylene and benzo[*ghi*]perylene to give expansion of the original PAH skeleton with 2 carbon atoms and, after ring closure, extension of the original structure with a six-membered ring.[4]

A third class of electrophiles which can be used for the expansion of PAHs via reductive alkylation are the dihaloalkanes. In a one-pot reaction the dihaloalkanes react twice with a PAH anion resulting in the addition of a (spiro-fused) ring to the anionic system.[5] Reactions with the phenalene anion[6] and the 5-hydropyrene anion[7] gave high yields of cyclised products. In a subsequent step spiro-fused rings can be rearranged to ortho- or meta-fused rings, either photochemically or via a thermal reaction.[6] The use of methyl-substituted dihaloalkanes leads directly to the methyl derivatives of the larger PAHs.[8]

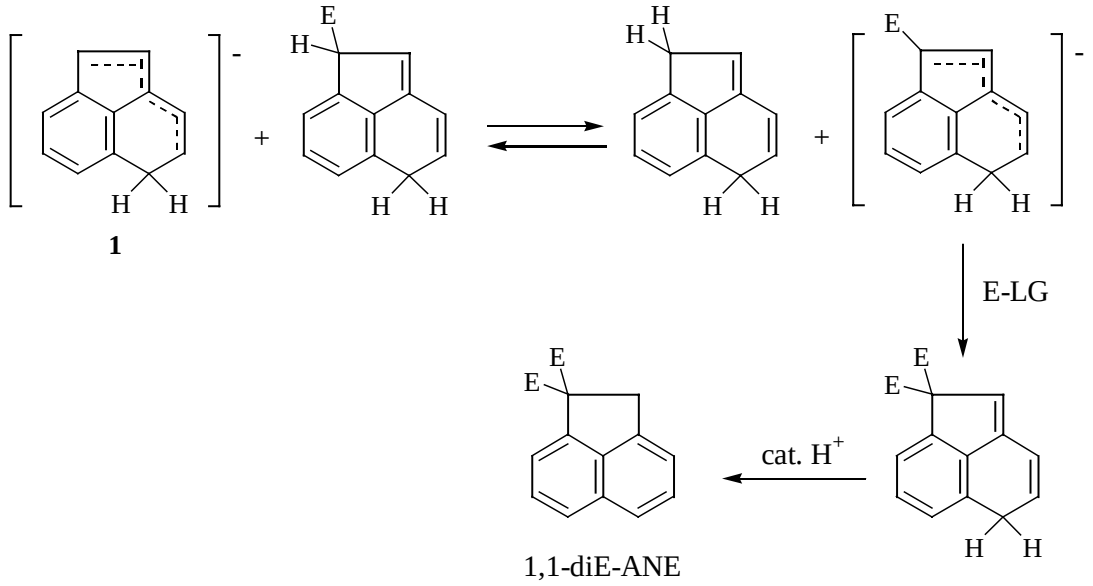
For the synthesis of PAHs containing heteroatoms such as sulfur and nitrogen, the direct formation of a carbon atom-heteroatom bond would open the way to novel PAHs.

In this chapter, reactions of the 5-hydroacenaphthylene anion are performed with a variety of electrophiles. In this manner substituents containing a functional group can be introduced or carbon-sulfur bonds can be created.

5.2 Results and discussion

The 5-hydroacenaphthylene anion **1** was prepared as described in Chapter 2. At -60ºC one equivalent of electrophile was added (unless stated otherwise) and the reaction mixture was stirred for 15 minutes, after which the reaction was quenched with water. Extraction with diethyl ether, drying over magnesium sulfate and concentration *in vacuo* gave the substitution products.

The general reaction will predominantly give 1-substituted acenaphthenes, but in some cases also 1,1-disubstituted products are found (Scheme 1). In Table 1, the electrophiles that were used in the reactions with **1** are listed.



1

Scheme 1*: Formation of disubstitution products in the reaction of* ***1*** *with electrophiles (E = electrophile, LG = leaving group, ANE = acenaphthene).*

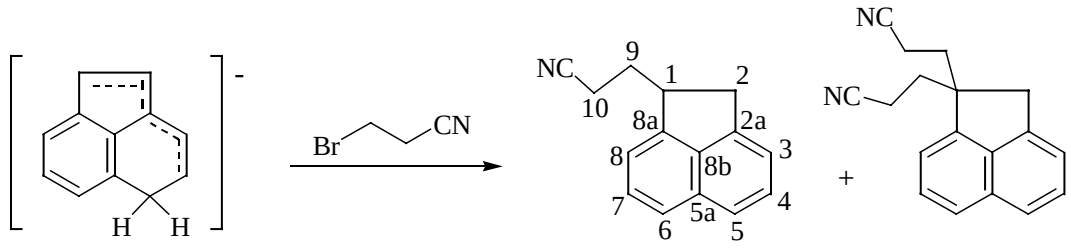
The products were characterised by NMR spectroscopy, infrared spectroscopy and GC-MS. In the NMR spectra the patterns of the acenaphthene moiety of the mono-substituted and 1,1-disubstituted acenaphthenes resemble those of 1-allyl- and 1,1-diallylacenaphthene (Chapter 3).

***Table 1**: Products of the reactions of **1** with electrophiles.*

Electrophile	1-E-ANE	1,1-diE-ANE
3-Bromopropionitrile	**2**	**2a**
3-Iodopropionitrile	**2**	**2a**
Ethyl bromoacetate	**3**	
Ethyl iodoacetate	**3**	
Ethyl 3-bromopropanoate	**4**	
Ethyl 3-iodopropanoate	**4**	
Methyl thiocyanide	**5**	**5a**
Diphenyl disulfide		**6a**
1,4-Dibromobutane		**7a**
1,4-Diiodobutane		**7a**
1,5-Dibromopentane		**8a**
1,5-Diiodopentane		**8a**

In contrast to the reactions with methyl iodide, allyl bromide and benzyl bromide, the reactions of **1** with the more polar electrophiles gave lower yields of substitution products and also gave more side-products. In many reactions considerable amounts of acenaphthene were formed. One explanation is that the electrophiles are more hygroscopic than the alkyl halides and thus contain a larger amount of water. Therefore, the electrophiles should be carefully purified and dried before use to obtain the best results. The formation of side-products may be due to the presence and the reactivity of the second functional group.

ω-Halonitriles



1 **2** **2a**

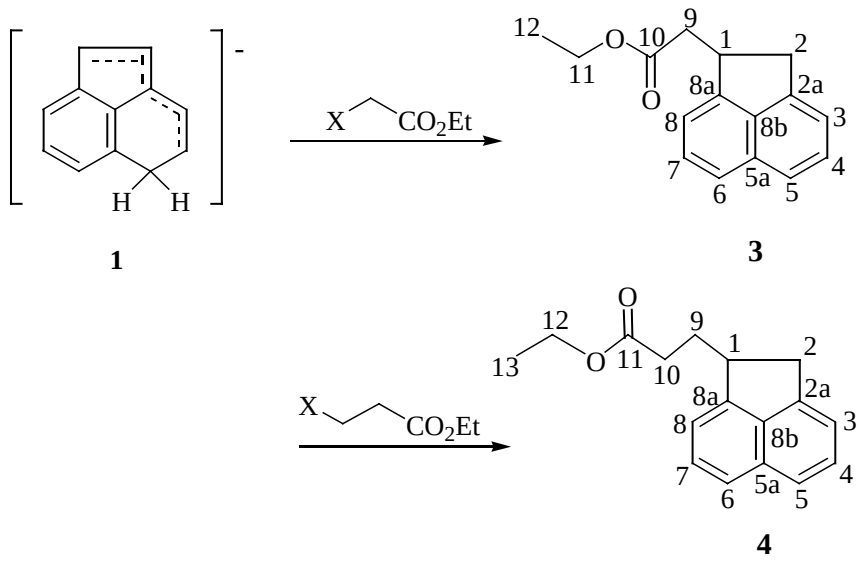
***Scheme 2**: Reaction of **1** with 3-bromopropionitrile.*

The reaction of **1** with 3-bromopropionitrile gives mono- as well as disubstitution products in 20-60% and 5-50% yield, respectively (Scheme 2). The formation of disubstitution products can be explained by the reaction sequence shown in Scheme 1 (see also Chapter 3). The ratio of mono- and

di-substitution products depends strongly on the concentration of 3-bromopropionitrile: more electrophile leads to more disubstitution products. If only 1-(2-cyanoethyl)acenaphthene (**2**) is required, the reaction should be performed with only 0.5 equivalents of 3-bromopropionitrile. This product can easily be separated from acenaphthene by silica gel column chromatography. Next to the mono- and di-substitution products, traces of side-products containing olefinic protons are present. These could not be identified as 2a-substitution products (see Chapter 4) or as 1,5-dihydro-1-substituted acenaphthylenes. No further attempts were made to characterise these products.

The use of 3-iodopropionitrile instead of 3-bromopropionitrile leads to even more disubstitution product. This might be due to the fact that alkyl iodides react faster than alkyl bromides in S_N2 reactions.

Halo-esters



***Scheme 3**: Reaction of **1** with ethyl haloacetate and ethyl 3-halopropanoate (X = Br, I).*

The reaction of **1** with ethyl bromoacetate (Scheme 3) gives ethyl acenaphthene-1- acetate **3** in relatively high yields (up to 90%). No di-substitution products were observed. The side-products with olefinic protons were not stable towards exposure to air. They might include the initial 1-substituted 1,5-dihydroacenaphthylene. The use of ethyl iodoacetate gave the same substitution pattern, but yielded more acenaphthene, which is probably caused by traces of water in the ethyl iodoacetate.

Ethyl acenaphthene-1-acetate (**3**) can easily be hydrolysed into the corresponding acid quantitatively. The synthesis of this acid was reported before, starting from 1-acenaphthenol.[9] In three steps the alcohol was converted via the bromide and the malonic acid derivative to the acid in

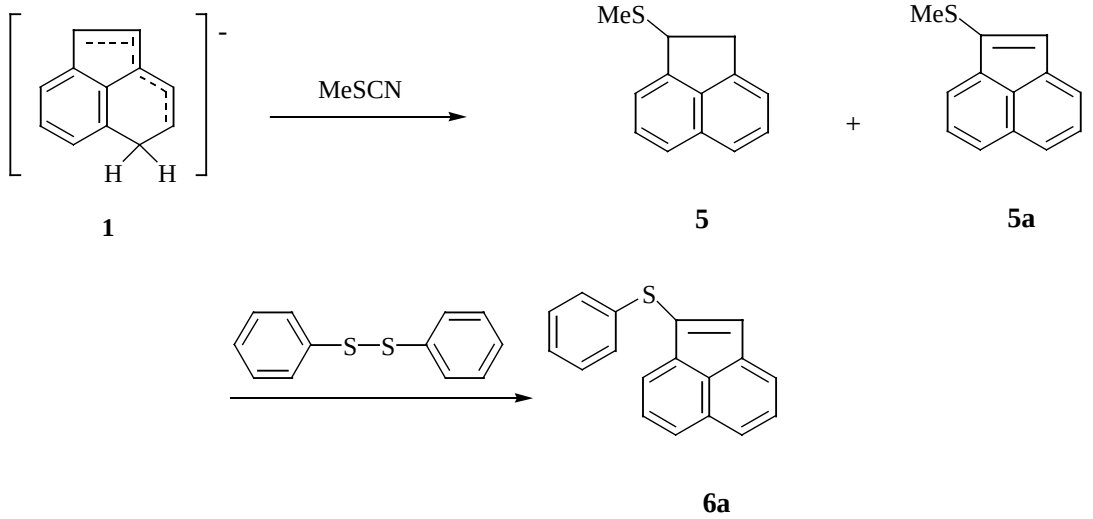
70% yield. 1-Acenaphthenol, however, is rather expensive (25 g, ca. NLG 200) compared to acenaphthylene (100 g, ca. NLG 70,00). Therefore, our shorter route is preferable to the synthesis reported earlier.

Ethyl acenaphthene-1-propanoate (**4**) is the major product from the reaction of **1** with ethyl 3-bromopropanoate and could be isolated in 30-60% yield. Again, side-products containing olefinic protons are observed. The yield of the reaction is considerably lower than in the case of the reaction of ethyl bromoacetate. A possible explanation is that the side-chain of **4** is deprotonated by **1**. The side products could not be characterised. Remarkable is the presence of traces of carboxylic acids in the product mixture.

The yield of ethyl acenaphthene-1-propanoate (**4**) could be elevated by changing from ethyl 3-bromo- to ethyl 3-iodopropanoate. Now, less side-products and more **4** were isolated. Conversion from the ester into the acid could be accomplished by dissolving the ester in ethanol and boiling under reflux for several hours with KOH. Certainly, this synthesis is much more convenient than the synthesis from acenaphthene-1-acetic acid as proposed by Bachmann and Sheehan.[9] Acenaphthene-1-propanoic acid can be cyclised via a Friedel-Crafts acylation and converted into cyclopenta[*def*]phenanthrene.[9]

Bromoacetaldehyde diethylacetal is expected to react via the SET mechanism[10,11] with **1** and thus products with substituents at position 2a should be found. However, reaction of **1** with bromoacetaldehyde diethylacetal gave only low yields of substitution products which were not further isolated and characterised.

Sulfur electrophiles



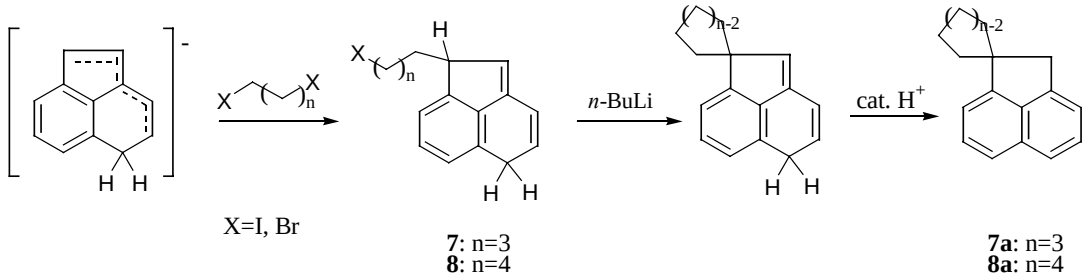
1 **5** **5a** **6a**

***Scheme 4**: Reaction of **1** with methyl thiocyanate and diphenyl disulfide.*

Reaction of **1** with methyl thiocyanide gave 1-(methylthio)acenaphthene (**5**) and 1-(methylthio)acenaphthylene (**5a**) in equal amounts (both in 25% yield) (Scheme 4). Oxidation of 1-(methylthio)acenaphthene (**5**) to 1- (methylthio)acenaphthylene (**5a**) is not likely to occur, because **5** could be isolated by silica gel column chromatography and was stable towards exposure to air for several weeks without conversion into **5a**. Therefore, elimination of methanethiol from the 1,1-bis-(methylthio)acenaphthene seems the most reasonable explanation for the formation of **5a**. Variation in the amount of methyl thiocyanide added to the reaction mixture would give conditions for the more selective synthesis of one of the two products.

A similar reaction was performed using diphenyl disulfide as electrophile. One major reaction product was obtained: 1-(phenylthio)acenaphthylene **6a** in 43% yield (Scheme 4). The formation of **6a** can again be explained by the elimination of thiophenol from 1,1-bis(phenylthio)acenaphthene. It can also be concluded that under these conditions no monosubstituted acenaphthene is formed. Probably the acidity of 1-(phenylthio)-1,5-dihydroacenaphthylene is higher than that of 1,5-dihydroacenaphthylene, resulting in the formation of the substituted hydroanion in high yields. If 1-(phenylthio)acenaphthene is desired, the reaction of **1** should be performed with a lower concentration of diphenyl disulfide.

α,ω-Dihaloalkanes



7: n=3
8: n=4

7a: n=3
8a: n=4

Scheme 5*: Reaction of* ***1*** *with dihaloalkanes.*

The reaction of **1** with 1,4-dihalobutane and 1,5-dihalopentane gave predominantly substitution at position 1. When 1,1-disubstitution occurred, the internal reaction was always favoured over reaction with a second dihaloalkane: no 1,1-di(haloalkane)-acenaphthenes were isolated. The yield of the so-formed spiro-fused rings could be elevated by the addition of *n*-butyllithium to the reaction mixture (Scheme 5).

Following this procedure spiro[acenaphthene-1,1'-cyclopentane] **7a** and spiro[acenaphthene-1,1'-cyclohexane] **8a** could be isolated in 35% and 40% yield, respectively. Because of the difficult silica gel chromatography separation of monosubstitution products and cyclised products, the former were not isolated, but directly used in the reaction with *n*-butyllithium. The reactions with

diiodoalkanes, especially with 1,2-diiodoethane and 1,3-diiodopropane, gave small amounts of 2a-substituted products. In these reactions the SET mechanism plays a more important role (see Chapter 4). The products were identified by NMR spectroscopy but no attempts for further isolation and characterisation were performed. It was remarkable that no cyclisation products of the reactions with 1,2-dihaloethane were observed.

5.3 Conclusions

The reaction of the 5-hydroacenaphthylene anion with electrophiles containing a second functional group proceeds at position 1 and provides an easy and fast route to 1-substituted acenaphthenes. These new 1-substituted acenaphthenes can be used for the synthesis of higher derivatives of acenaphthene. 3-Bromopropionitrile, 1,4-dibromobutane and 1,5-dibromopentane, and their iodo-analogues, give rise to 1,1-disubstitution products, in the case of the dihaloalkanes resulting in spiro-fused rings. In the reaction of **1** with diphenyl disulfide and methyl thiocyanide a carbon-sulphur bond is created. In these reactions the disubstituted products undergo an elimination reaction resulting in 1-substituted acenaphthylenes.

5.4 Experimental section

General: Acenaphthylene (Aldrich, 75%) was purified by treatment with DDQ and filtration over silica. The electrophiles were obtained from Acros, Aldrich and Merck and used without further purification but dried over molecular sieves (3A, 8-12 mesh). 3-Iodopropionitrile, ethyl iodoacetate and ethyl 3-iodopropanoate were prepared from the corresponding bromides by bromine-iodine exchange with potassium iodide in acetone. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3A, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra. For the determination of the coupling constants we used the simulation program PERCH.[12]

General procedure:

Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. Acenaphthylene (0.76 g, 5 mmol) was added, together with freshly cut sodium (0.3 g, 13 mmol). Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After five hours of sonication, during

which the temperature was kept at 0°C, a deep green solution was obtained. The flask was then cooled in an ethanol-nitrogen bath to -70°C and methanol (0.146 ml, 5 mmol) was added. The colour of the mixture turned red. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. The mixture was cooled again to -70°C and 5 mmol of electrophile were added. Stirring was continued at room temperature for 30 minutes after which period the reaction was quenched with water. The addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. Yields of substitution products are variable, generally between 30 and 90%, depending on the humidity of the air in the laboratory and the reactivity of the electrophile. The composition of the mixture was determined by means of NMR spectroscopy.

*Reaction of **1** with 3-bromopropionitrile:*

To a solution of **1** (5 mmol) 3-bromopropionitrile (0.45 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded two products: 1-(2-cyanoethyl)acenaphthene (20-60%) and 1,1-bis(2-cyanoethyl)acenaphthene (5-50%).

1-(2-Cyanoethyl)acenaphthene (**2**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.63 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.60 (dddd, $J_{4,5}$ = 8.1, $J_{2,5}$, $J_{2',5}$, $J_{3,5}$, 1 H, H-5), 7.46 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 7.1**,** 1 H, H-7), 7.45 (dd, $J_{4,5}$ = 8.1, $J_{3,4}$ = 7.1, H-4), 7.26 (d, $J_{3,4}$ = 7.1, $J_{2,3}$, $J_{2',3}$, 1 H, H-3), 7.24 (ddd, $J_{7,8}$ = 7.1, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 3.79 (dddddd, $J_{1,2}$ = 8.2, $J_{1,2'}$ = 4.2, $J_{1.9}$ = 4.5, $J_{1.9'}$ = 8.7, $J_{1,6}$, $J_{1,8}$,1 H, H-1), 3.60 (dddd, $J_{1,2}$ = 8.2, $J_{2,2'}$ = -17.5, $J_{2,3}$, $J_{2,5}$, 1 H, H-2), 3.00 (dddd, $J_{1,2'}$ = 4.2, $J_{2,2'}$ = -17.5, $J_{2',3}$, $J_{2',5}$, 1 H, H-2'), 2.40 (dd, $J_{9,10}$ = 7.3, $J_{9',10}$ = 7.2, 2 H, H-10), 2.20 (ddt, $J_{9,9'}$ = -14.4, $J_{1.9}$ = 4.5, $J_{9,10}$ = 7.3, 1 H, H-9), 1.97 (ddt, $J_{9,9'}$ = -14.4, $J_{1.9'}$ = 8.7, $J_{9',10}$ = 7.2, 1 H, H-9'), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) δ: 146.7 (C-2a or C-8a), 143.2 (C-2a or C-8a), 138.3 (C-8b), 131.4 (C-5a), 128.0 (C-7), 127.7 (C-4), 123.3 (C-6), 122.5 (C-5), 119.5 (CN), 119.5 (C-3),118.9 (C-8), 42.0 (C-1), 36.7 (C-2), 31.6 (C-9), 14.9 (C-10).

1,1-Bis(2-cyanoethyl)acenaphthene (**2a**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.72 (ddd, $J_{6,7}$ = 8.9, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.67 (dddd, $J_{4,5}$ = 8.8, $J_{2,5}$, $J_{2',5}$, $J_{3,5}$, 1 H, H-5), 7.54 (dd, $J_{6,7}$ = 8.9, $J_{7,8}$ = 6.9**,** 1 H, H-7), 7.51 (dd, $J_{4,5}$ = 8.8, $J_{3,4}$ = 6.9, H-4), 7.31 (dddd, $J_{3,4}$ = 6.9, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$, 1 H, H-3), 7.19 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 3.30 (s, 2 H, H-2), 2.21 (dd, $J_{9,10}$ = 8.5, $J_{9',10}$ = 7.8, 4 H, H-10), 2.06 (dt, $J_{9,9'}$ = -16.2, $J_{9,10}$ = 8.5, 2 H, H-9), 1.86 (dt, $J_{9,9'}$ = -16.2, $J_{9',10}$ = 7.8, 2 H, H-9'), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) δ: 145.3 (C-2a or C-8a), 140.8 (C-2a or C-8a), 138.2 (C-8b), 131.4 (C-5a), 128.6 (C-4 or C-7), 128.1 (C-4 or C-7), 124.6 (C-5 or C-6), 123.2 (C-5 or C-6), 120.0 (C-3 or C-8), 119.3 (CN), 118.3 (C-3 or C-8), 50.1 (C-1), 40.6 (C-2), 36.7 (2 C-10), 12.7 (2 C-9).

IR (pure liquid) cm^{-1} : 3040, 2970, 2920, 2860, 2240, 1600, 1480, 1460, 1420, 1380, 1350, 1290, 1120, 915, 810, 780, 730, 645.
MS m/z (%): 54 (8), 75 (3), 87 (2), 100 (1), 115 (1), 165 (100), 178 (3), 206 (28), 219 (1), 260 (15).

*Reaction of **1** with ethyl bromoacetate:*

To a solution of **1** (5 mmol) ethyl bromoacetate (0.554 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded ethyl acenaphthene-1-acetate (40-90%).

Ethyl acenaphthene-1-acetate (**3**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.56 (dddd, $J_{4,5}$ = 8.1, $J_{2,5}$, $J_{2',5}$, $J_{3,5,}$ 1 H, H-5), 7.54 (ddd, $J_{6,7}$ = 8.1, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.39 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 7.4, 1 H, H-7), 7.38 (dd, $J_{4,5}$ = 8.1, $J_{3,4}$ = 7.4, 1 H, H-4), 7.19 (dddd, $J_{3,4}$ = 7.4, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1 H, H-3), 7.19 (ddd, $J_{7,8}$ = 7.4, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 4.15 (q, $J_{11,12}$ = 7.1, 2 H, H-11), 4.05 (dddddd, $J_{1,2}$ = 8.1, $J_{1,2'}$ = 3.6, $J_{1,9}$ = 5.6, $J_{1.9'}$ = 9.4, $J_{1,6}$, $J_{1,8}$, 1 H, H-1), 3.63 (dddd, $J_{1,2}$ = 8.1, $J_{2,2'}$ = -17.5, $J_{2,3}$, $J_{2,5}$, 1 H, H-2), 3.02 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2'}$ = 3.6, $J_{2',3}$, $J_{2',5}$, 1 H, H-2'), 2.80 (dd, $J_{9,9'}$ = -15.8, $J_{1,9}$ = 5.6, 1 H, H-9), 2.52 (dd, $J_{9,9'}$ = -15.8, $J_{1.9'}$ = 9.4, 1 H, H-9'), 1.21 (t, $J_{11,12}$ = 7.1, 3 H, H-12), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) δ: 172.2 (C-10), 147.4 (C-2a or C-8a), 143.7 (C-2a or C-8a), 138.1 (C-8b), 131.3 (C-5a), 127.8 (C-4 or C-7), 127.6 (C-4 or C-7), 122.9 (C-5 or C-6), 122.2 (C-5 or C-6), 119.2 (C-3 or C-8),118.6 (C-3 or C-8), 60.3 (C-11), 40.7 (C-9), 39.3 (C-1), 37.7 (C-2), 14.1 (C-12).

IR (pure liquid) cm^{-1} : 2840, 1710, 1665, 1600, 1490, 1460, 1425, 1355, 1270, 1230, 1020.

GC-MS m/z = 240 is major product.

*Reaction of **1** with ethyl bromopropanoate:*

To a solution of **1** (5 mmol) ethyl 3-bromopropanoate (0.650 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded Ethyl acenaphthene-1-propanoate (30-60%).

Ethyl acenaphthene-1-propanoate (**4**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.57 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.55 (dddd, $J_{4,5}$ = 8.2, $J_{3,5}$, $J_{2,5}$, $J_{2',5}$, 1 H, H-5), 7.41 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 7.0, 1 H, H-7), 7.40 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.9, H-4), 7.24 (ddd, $J_{7,8}$ = 7.0, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 7.20 (dddd, $J_{3,4}$ = 6.9, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$, 1 H, H-3), 4.10 (q, $J_{12,13}$ = 7.2, 2 H, H-12), 3.64 (dddddd, $J_{1,2}$ = 8.3, $J_{1,2'}$ = 3.6, $J_{1.9}$ = 5.0, $J_{1.9'}$ = 6.1, $J_{1,6}$, $J_{1,8}$, 1 H, H-1), 3.50 (dddd, $J_{2,2'}$ = -17.2, $J_{1,2}$ = 8.3, $J_{2,3}$, $J_{2,5}$, 1 H, H-2), 2.97 (dddd, $J_{2,2'}$ = -17.2, $J_{1,2'}$ = 3.6, $J_{2',3}$, $J_{2',5}$, 1 H, H-2'), 2.38 (dd, $J_{9,10}$ = 6.6, $J_{9',10}$ = 7.1, 2 H, H-10), 2.20 (ddt, $J_{9,9'}$ = -15.3, $J_{1.9}$ = 5.0, $J_{9,10}$ = 6.6, 1 H, H-9), 1.94 (ddt, $J_{9,9'}$ = -15.3, $J_{1.9'}$ = 6.1, $J_{9',10}$ = 7.1, 1 H, H-9'), 1.20 (t, $J_{12,13}$ = 7.2, 3 H, H-13), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) δ: 173.3 (C-11), 148.1 (C-2a or C-8a), 143.9 (C-2a or C-8a), 138.4 (C-8b), 131.3 (C-5a), 127.7 (C-4 or C-7), 127.6 (C-4 or C-7), 122.7 (C-5 or C-6), 122.2 (C-5 or C-6), 119.7 (C-3 or C-8), 119.1 (C-3 or C-8), 60.2 (C-12), 42.4 (C-1), 35.2 (C-2), 31.8 (C-9), 31.1 (C-10), 14.1 (C-13).

IR (pure liquid) cm^{-1} : 3040, 2980, 2940, 2920, 1730, 1600, 1495, 1440, 1370, 1300, 1255, 1175, 1030, 800, 770.
MS m/z (%): 42 (8), 63 (4), 89 (2), 115 (2), 167 (100), 209 (12), 225 (1), 254 (90).

*Reaction of **1** with methyl thiocyanide:*

To a solution of **1** (5 mmol) methyl thiocyanide (0.34 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded two products: 1-(methylthio)acenaphthene (25%) and 1-(methylthio)acenaphthylene (25%).

1-(Methylthio)acenaphthene (**5**)

^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ: 7.68 (d, $J_{4,5}$ = 8.2, 1 H, H-5), 7.63 (d, $J_{6,7}$ = 8.2, 1 H, H-6), 7.48 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.7, 1 H, H-7), 7.44 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.7, 1 H, H-4), 7.37 (d, $J_{3,4}$ = 6.7, 1 H, H-3), 7.24 (d, $J_{7,8}$ = 6.7, 1 H, H-8), 3.88-3.77 (m, 3 H, H-1 and H-2), 2.12 (s, 3 H, -SMe).
^{13}C NMR ($CDCl_3$) δ: 140.3 (C-2a and C-8a), 136.1 (C-8b), 131.5 (C-5a),128.1 (C-4 or C-7), 127.9 (C-4 or C-7), 124.7 (C-5 or C-6), 123.0 (C-5 or C-6), 119.4 (C-3 or C-8),119.2 (C-3 or C-8), 63.0 (C-1), 49.2 (C-2), 15.8 (-SMe).

1-(Methylthio)acenaphthylene (**5a**)

^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ: 7.78 (d, $J_{4,5}$ = 8.2, 1 H, H-5), 7.68 (d, $J_{6,7}$ = 5.5, 1 H, H-6), 7.62 (dd, $J_{6,7}$ = 5.5, $J_{7,8}$ = 3.9, 1 H, H-7), 7.51 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.9, 1 H, H-4), 7.43 (d, $J_{3,4}$ = 6.9, 1 H, H-3), 7.42 (d, $J_{7,8}$ = 3.9, 1 H, H-8), 6.56 (s, 1 H, H-2), 2.60 (s, 3 H, -SMe).

*Reaction of **1** with diphenyl disulfide:*

To a solution of **1** (5 mmol) diphenyl disulfide (1.09 g, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded 1-(phenylthio)acenaphthylene (43%).

1-(Phenylthio)acenaphthylene (**6a**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.70 (d, $J_{4,5}$ = 8.1, 1 H, H-5), 7.65 (d, $J_{6,7}$ = 7.8, $J_{6,8}$ = 1.1, 1 H, H-6), 7.52-7.35 (m, 6 H, H-4, H-7, H-3, H-8, and H-o or H-m), 7.25-7.17 (m, 3 H, H-p and H-o or H-m), 6.90 (s, 1 H, H-2).
^{13}C NMR ($CDCl_3$) δ: 138.4 (C-2a and C-8a), 135.8 (C-8b), 134.9 (C-5a), 130.5 (C-o or C-m), 129.7 (C-2), 129.0 (C-o or C-m), 127.9 (C-1 and C-i), 127.8 (C-4 or C-7), 127.7 (C-5), 127.5 (C-4 or C-7), 126.9 (C-p), 126.8 (C-6), 123.1 (C-3 or C-8), 123.0 (C-3 or C-8).

*Reaction of **1** with 1,4-dibromobutane:*

To a solution of **1** (5 mmol) 1,4-dibromobutane (0.60 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes at room temperature. The solution was cooled again to -60ºC and *n*-butyllithium (3.1 ml, 1.6 M in hexane, 5 mmol) was added. The reaction mixture was stirred for a

further 30 minutes and then quenched with water. After normal work-up, purification by silica gel column chromatography yielded spiro[acenaphthene-1,1'-cyclopentane] (35%).

Spiro[acenaphthene-1,1'-cyclopentane] (**7a**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.55 (dd, $J_{6,7}$ = 8.2, $J_{6,8}$, 1 H, H-6), 7.52 (dddd, $J_{4,5}$ = 8.2, $J_{3,5}$, $J_{2,5}$, 1 H, H-5), 7.41 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1 H, H-7), 7.38 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.7, H-4), 7.19 (dddd, $J_{3,4}$ = 6.7, $J_{3,5}$, $J_{2,3}$, 1 H, H-3), 7.12 (dd, $J_{7,8}$ = 6.9, $J_{6,8}$, 1 H, H-8), 3.16 (dd, $J_{2,3}$, $J_{2,5}$, 2 H, H-2), 1.90-1.79 (m, 8 H, H-cyclopentyl), $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{3,5}$ were observed but could not exactly be determined.

*Reaction of **1** with 1,5-dibromopentane:*

To a solution of **1** (5 mmol) 1,5-dibromopentane (0.68 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes at room temperature. The solution was cooled again to -60ºC and *n*-butyllithium (3.1 ml, 1.6 M in hexane, 5 mmol) was added. The reaction mixture was stirred for a further 30 minutes and then quenched with water. After normal work-up, purification by silica gel column chromatography yielded spiro[acenaphthene-1,1'-cyclohexane] (40%).

Spiro[acenaphthene-1,1'-cyclohexane] (**8a**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.61 (dd, $J_{6,7}$ = 8.2, $J_{6,8}$, 1 H, H-6), 7.61 (dddd, $J_{4,5}$ = 8.2, $J_{3,5}$, $J_{2,5}$, 1 H, H-5), 7.48 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1 H, H-7), 7.46 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.7, H-4), 7.27 (dddd, $J_{3,4}$ = 6.7, $J_{3,5}$, $J_{2,3}$, 1 H, H-3), 7.22 (dd, $J_{7,8}$ = 6.9, $J_{6,8}$, 1 H, H-8), 3.28 (dd, $J_{2,3}$, $J_{2,5}$, 2 H, H-2), 1.80 (m, 4 H, H-10 and H-12), 1.71 (m, 2 H, H-11), 1.57 (m, 4 H, H-9 and H-13), $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) δ: 148.1 (C-2a or C-8a), 143.9 (C-2a or C-8a), 138.4 (C-8b), 131.3 (C-5a), 127.9 (C-4 or C-7), 127.8 (C-4 or C-7), 122.6 (C-5 or C-6), 122.2 (C-5 or C-6), 119.2 (C-3 or C-8), 117.5 (C-3 or C-8), 48.5 (C-1), 42.5 (C-2), 38.7 (C-10 and C-12), 25.8 (C-11), 23.5 (C-9 and C-13).

IR (pure liquid) cm^{-1} : 3040, 1730, 1480, 1030, 800, 770, 730.

MS m/z (%): 42 (8), 63 (4), 89 (2), 115 (2), 167 (100), 209 (12), 225 (1), 254 (90).

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6

Reactions of the acenaphthylene dianion

6.1 Introduction

The acenaphthylene dianion **1** reacts with protons and methyl iodide selectively at position 5 (Chapter 2). The latter reaction is supposed to proceed via an S_N2 mechanism. However, in Chapter 4 we have seen that the 5-hydroacenaphthylene anion **2** can react via S_N2 as well as via single electron transfer (SET). The reaction path depends on the ability of the electrophile to accept an electron. A lower reduction potential and more steric bulk of the electrophile contribute to more SET character of the reaction. Because the electron-donating capacity of **1** is even higher than that of **2**, the probability of the occurrence of the SET mechanism is expected to be higher. In this chapter we study the reaction of **1** with a variety of electrophiles in order to elucidate the mechanism of the reductive alkylation of acenaphthylene.

6.2 Results

The acenaphthylene dianion (**1**) was prepared starting from acenaphthylene using 2.2 equivalents of sodium in anhydrous THF and ultrasonic vibration (see Chapter 2).

At -70 ºC one equivalent of electrophile was added to the reaction mixture and the solution was stirred at room temperature for 30-60 minutes. After cooling to -70 ºC the reaction was quenched with water. Addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. These oils were analysed by means of GC-MS and NMR techniques.

Most electrophiles gave complex mixtures of products upon reaction with **1**. In several cases these mixtures could not be separated into their components and the products could thus not be identified and characterised. When (bromomethyl)cyclopropane and allyl bromide were used, product isolation and identification turned out to be possible and conclusions about the reactivity of the dianion could be drawn. In other cases, the NMR and GC-MS data of the crude products mixtures provided indications about the interaction between the acenaphthylene dianion and the electrophile.

When one equivalent of (bromomethyl)cyclopropane was added to the acenaphthylene dianion (**1**), 5-(cyclopropylmethyl)acenaphthene was the major product (>90%) that could be isolated.

Addition of one equivalent of allyl bromide to the dianion **1** led, after work-up, to the isolation of a mixture of substitution products. This mixture could be separated with preparative gas chromatography. The major substitution products were identified by means of NMR as 1-allylacenaphthene (**3a**) (39% of substitution products), 5-allylacenaphthene (**3b**) (21%), 1,2-diallylacenaphthene (**3c**, one isomer, probably trans) (17%) and 1,5-diallylacenaphthene (**3d**) (12%). Next to these products probably 1-allylacenaphthylene (**3e**) (5%) and a third diallylacenaphthene (**3f**) (6%) were present. Because only one equivalent of allyl bromide was added, acenaphthene and acenaphthylene were also formed.

Reaction of **1** with 3,3-dimethylallyl bromide also gave a complex mixture of products. Comparison of the ^{1}H NMR spectrum with those of compounds **3** learned that the methyl groups were present at the olefinic as well as the allylic position.

Reaction of **1** with electrophiles containing a second functional group − in particular bromoacetonitrile, acetyl chloride, benzyl chloride, ethyl bromoacetate, diphenyl disulfide and methyl thiocyanide − gave acenaphthylene as the major product. Traces of substitution products were detected using GC-MS.

Reaction of bromoacetaldehyde diethylacetal with **1** gave a complex mixture of mono- and disubstitution products. The substitution pattern was similar to that in the reaction of **1** with allyl bromide. Next to the expected 5-substituted acenaphthene also 1-, 1,2-di- and 1,5-disubstitution products were observed. The monosubstitution products could be separated from the disubstitution products with silica gel column chromatography. However, the isolation of the individual isomers was not possible in this way. Therefore, no exact characterisation could be made for the isomers.

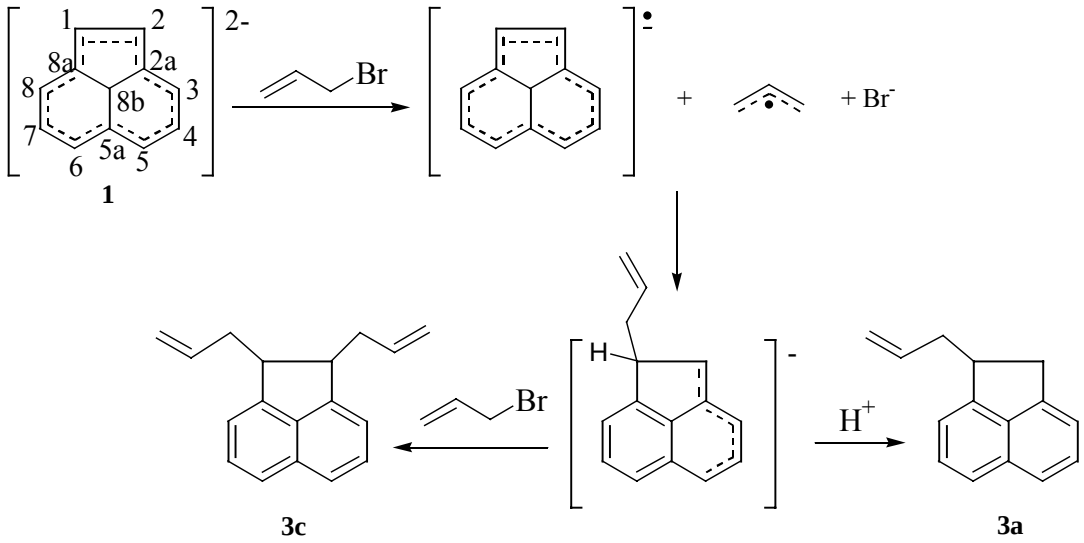
Reaction of **1** with one equivalent of bromobenzene resulted in a mixture of substitution products. GC-MS analysis showed three monophenylacenaphthenes and two monophenylacenaphthylenes. Next to these products a bromo-phenylacenaphthene was observed. The product mixture could not be separated by silica gel column chromatography, HPLC or preparative gas chromatography. Because of the presence of so many isomers and the complexity of the NMR spectrum (all peaks in the aromatic region), the products could not be identified with NMR spectroscopy.

The same reaction was performed with *p*-bromotoluene as electrophile. GC-MS analyses showed that this reaction also gave three mono(methylphenyl)acenaphthenes and one bromine containing derivative. In this case no acenaphthylene derivatives were observed. Remarkable was the presence of dimethylbiphenyl.

In the reaction of **1** with E/Z β-bromostyrene GC-MS showed the presence of one major substitution product (monosubstituted) and two side products (one mono- and one disubstitution product).

6.3 Discussion

The reaction of the acenaphthylene dianion with simple alkyl halides takes place selectively at position 5. The mechanism of this reaction is expected to be S_N2. However, single electron transfer (SET) may also play a role in the mechanism because of the high reactivity of the acenaphthylene dianion. To obtain evidence for the occurrence of SET in the reaction of **1** with simple alkyl halides, (bromomethyl)cyclopropane was used. If SET would be part of the mechanism, butene-substituted acenaphthenes should be present in the reaction mixture (see Chapter 3). Because no such products were found it may be concluded that (bromomethyl)cyclopropane and probably also other alkyl bromides, react with the acenaphthylene dianion via the S_N2 mechanism. Next to 5-(cyclopropylmethyl)acenaphthene, small amounts of acenaphthene and 5-(cyclopropylmethyl)-acenaphthylene were detected with GC-MS (<5%).



***Scheme 1**: Reaction of **1** with allyl bromide via SET.*

Allyl bromide reacts with the 5-hydroacenaphthylene anion (**2**) via S_N2 (Chapter 3). If the reaction of the dianion would proceed via S_N2 only, 5-allylacenaphthene should be obtained as the only product. However, the reaction gives a mixture of products, in which 1-allylacenaphthene is the major substitution product. Because allyl bromide is more easily reduced than simple alkyl halides such as methyl iodide and (bromomethyl)cyclopropane, the reaction of **1** with allyl bromide might proceed via SET. In the SET reaction one electron is transferred from the dianion to allyl bromide (Scheme 1). In a concerted electron transfer-bond breaking mechanism, allyl bromide dissociates into an allyl radical and a bromide ion. The allyl radical and the resulting acenaphthylene radical anion will combine to a substituted acenaphthylene hydroanion. This anion can react a second time with allyl bromide (now via S_N2) or it can become protonated during work-up.

If the reaction of **1** with allyl bromide takes place via SET, the position at which substitution occurs, is not determined by the charge distribution and HOMO coefficients in the dianion but by those in the radical anion. In non-alternant PAH the most reactive position in the radical anion can be different from that in the dianion. The dianion reacts preferably at position 5, whereas the highest reactivity in the radical anion is found at position 1.[1] This was proven by the reaction of the radical anion and the dianion with water: the radical anion gave acenaphthene (1,2-dihydroacenaphthylene) as the only product, whereas the protonation product of the dianion is 1,5-dihydroacenaphthylene.[1] Because the reaction of **1** with allyl bromide gave predominantly substitution at position 1, it can be concluded that the radical anion was an intermediate and thus that SET plays a role in the mechanistic pathway. After the first substitution, the resulting 1-allyl-1-hydroacenaphthylene anion might react a second time. The most likely position for this second substitution is position 2, thus giving the 1,2-diallylacenaphthene. The formation of 5-allylacenaphthene **3b** might be the result of reaction via an S_N2 pathway or an SET reaction. It would be interesting to perform the reaction of **1** with allyl bromide in the presence of a radical scavenger in order to investigate the mechanism by which **3b** is formed (see Chapter 4). Compound **3d** might result from reaction of the 5-allyl-5-hydroacenaphthylene anion with a second equivalent of allyl bromide at position 1. Alternatively, the 1-allyl-1-hydroacenaphthylene anion might react also at position 5, resulting in **3d**. The latter pathway is less likely, because substitution at position 2, resulting in an aromatic naphthalene skeleton, is energetically more favorable.

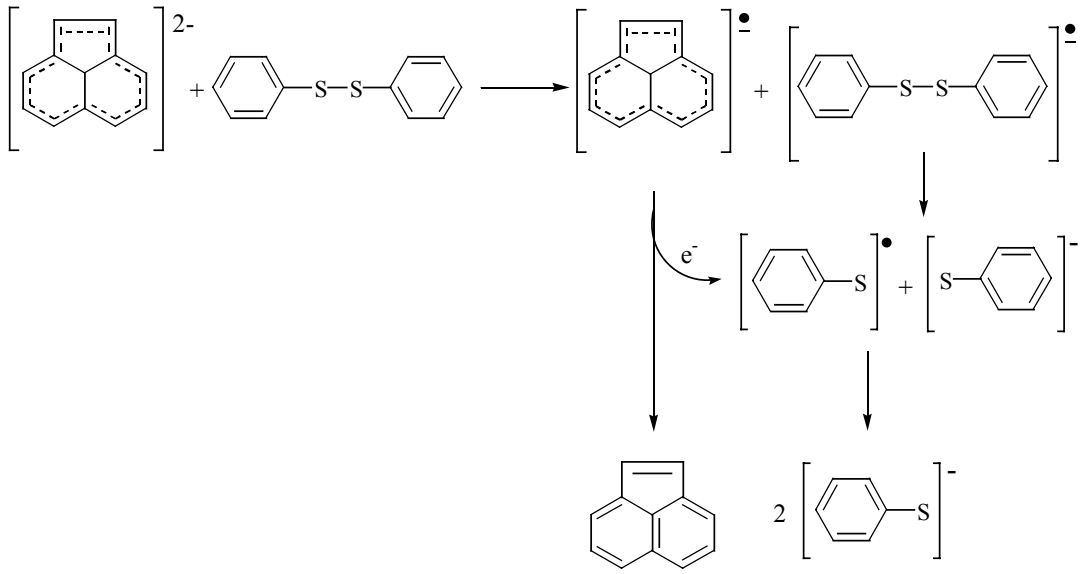
The occurrence of the SET mechanism was confirmed by the reaction of **1** with 3,3-dimethylallyl bromide. In the case of electron transfer the allyl radical now has two different reactive positions and thus may give rise to coupling products with the methyl groups at position 1 or at position 3 of the allyl chain (see Chapter 3). Two different methyl groups are indeed observed by NMR spectroscopy. Therefore, it can be concluded that SET does indeed play a role in the reaction of **1** with allylic bromides.

Bromoacetaldehyde diethylacetal is an electrophile which is known to react via electron transfer.[2,3] In the reaction with **1** a substitution pattern similar to that of allyl bromide is found.

Based on these results the observations of Neumann and Müllen can be understood.[4] These authors found that the reaction of the acenaphthylene dianion with 1,ω-dichloroalkanes was not regioselective, in contrast to the reaction with methyl iodide. The product distribution is similar to the one we found for the reaction of **1** with allyl bromide. Therefore, it seems likely that this reaction also proceeds via SET and thus that the regioselectivity is not determined by **1** but by the radical anion.

Reaction of the dianion with alkyl halides containing functional groups such as ethyl bromoacetate, however, results in oxidation of the dianion. This can be rationalised by the assumption that a double electron transfer is responsible for the conversion into the starting material. In Scheme 2 this double electron transfer is shown for the reaction of **1** with diphenyl

disulfide. Only a small percentage (<10%) of addition products was detected in reactions with these electrophiles.



***Scheme 2**: Double electron transfer from **1** to diphenyl disulfide.*

Reaction of **1** with bromobenzene gives a mixture of substitution products. Because bromobenzene cannot give an S_N2 reaction with nucleophiles, the mechanism must be different. The most important mechanism for nucleophilic aromatic substitution is addition-elimination. However, the presence of strongly electron-demanding groups is required to give a fast reaction. A second possibility is the benzyne mechanism. This substitution occurs on aryl halides that have no activating groups. For this reaction a very strong base, such as KNH_2, is required.[5] The acenaphthylene dianion might be strong enough to abstract a proton from bromobenzene. The resulting 5-hydroacenaphthylene anion will then react with benzyne, most likely at position 1. This reaction therefore does not explain the formation of a complex mixture of products. Next to a strong base, the acenaphthylene dianion is also a strong electron donor. Therefore, bromobenzene might be substituted via the $S_{RN}1$ mechanism.[6-9] This mechanism, depicted in eq 1-4, is initiated by electron transfer to substrate ArX from a suitable electron donor. This ET (eq 1) can occur under the influence of light,[10-13] electrochemically[14-16] or by free electrons.[17,18]

$$ArX + e^- \longrightarrow ArX^{\bullet -} \qquad (1)$$

$$ArX^{\bullet -} \longrightarrow Ar^{\bullet} + X^- \qquad (2)$$

$$Ar^{\bullet} + Nu^- \longrightarrow ArNu^{\bullet -} \qquad (3)$$

$$ArNu^{\bullet -} + ArX \longrightarrow ArNu + ArX^{\bullet -} \qquad (4)$$

The radical anion thus formed dissociates (eq 2) to give an aryl radical and a halide anion. The aryl radical combines with the nucleophile to form an adduct (eq 3), which is a radical anion. In a next step (eq 4) the extra electron is transferred to a haloarene and the resulting radical anion will continue the chain (eq 2 and eq 3). This chain process can be terminated by coupling of two radicals or by reduction of the adduct.[6,19] In the reaction of **1** with bromobenzene the dianion (A^{2-}) can act as the electron source. In the first step one electron is transferred to bromobenzene (eq 5) resulting in an acenaphthylene radical anion and a bromobenzene radical anion. The latter dissociates (eq 2) into a phenyl radical and a bromide anion. Then the acenaphthylene radical anion combines with the phenyl radical (eq 6). This anion ($Ar\text{-}A^-$) is protonated in the work-up procedure by water. In contrast to the chain process in the $S_{RN}1$ reaction, the reaction of **1** with bromobenzene is in principle a one-to-one reaction.

$$ArX + A^{2-} \longrightarrow ArX^{\bullet -} + A^{\bullet -} \qquad (5)$$

$$ArX^{\bullet -} \longrightarrow Ar^{\bullet} + X^- \qquad (2)$$

$$Ar^{\bullet} + A^{\bullet -} \longrightarrow Ar\text{-}A^- \qquad (6)$$

The position where the addition takes place depends on the properties of the acenaphthylene radical anion. There is an attractive MO interaction between the benzene radical and the carbanion nucleophile: the strongest interaction occurs at the nucleophilic position with the highest HOMO coefficient.[20] In the acenaphthylene radical anion the positions 1 (2) and 5 (6) are those with the highest SOMO coefficients. The relative rate of an $S_{RN}1$ reaction is not only controlled by the stability of the product radical ions but also by the strength of the incipient carbon-carbon bond.[21] This latter factor might also influence the substitution pattern.

Reaction of **1** with *para*-bromotoluene gave a similar substitution pattern as in the case of reaction with bromobenzene. In this case no oxidised products were detected. However, a product with mass 182 was found with GC-MS. This must be dimethylbiphenyl that is formed by coupling of two methylphenyl radicals. Normally, this coupling product is not observed in $S_{RN}1$ reactions, because of the low concentration in which it is present. In our reaction the concentration of toluene radicals is relatively high and thus this termination step will take place.

A third electrophile which cannot give S_N2 reaction is β-bromostyrene. With GC-MS one major addition product and traces of other mono- and disubstitution products are detected. Obviously, also in this case the reaction starts with electron transfer. In recent years Rappoport and co-workers have found that vinyl halides can react in an $S_{RN}1$ reaction.[22-25] They encountered, however, problems with side-reactions, such as addition-elimination. In the case of the reaction of **1** with bromostyrene

these side-reactions will probably not interfere with the $S_{RN}1$ reaction. Although GC-MS showed one major substitution product, the ^{1}H NMR spectrum was too complicated to identify the product. It might also be a mixture of isomers, which cannot be separated by GC.

6.4 Conclusions

The acenaphthylene dianion reacts with bromomethylcyclopropane via the S_N2 mechanism and this occurs selectively at position 5. The SET mechanism plays an important role in the reaction of **1** with allyl bromide. Due to the role of the acenaphthylene radical anion as reaction intermediate, a mixture of 1-allyl-, 5-allyl-, 1,2-diallyl- and 1,5-diallylacenaphthenes was obtained. The occurrence of the SET mechanism was confirmed by the reaction of **1** with 3,3-dimethylallyl bromide. A double electron transfer occurs if more readily reducible electrophiles, such as diphenyl disulfide and ethyl bromoacetate are used. Bromobenzene, *para*-bromotoluene and β-bromostyrene give an $S_{RN}1$-type reaction with **1** and complex product mixtures are obtained.

6.5 Experimental section

General: Acenaphthylene (75%) was obtained from Aldrich and purified by treatment with DDQ and filtration over silica. The electrophiles were obtained from Acros, Aldrich and Merck and used without further purification. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3A, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra.

Preparative GC was performed on an ATI Unicam 610 series gas chromatograph equipped with an SE 15% 3 m column with the following temperature profile: 10 min. 100°C, 10°C/min. to 160°C, 15 min. 160°C.

Mass spectra were recorded on a Finnigan MAT 900 mass spectrometer, equipped with a direct insertion probe (EI-MS, 70 eV) or on a Finnigan MAT ITD 700 (EI, 70 eV) coupled to a Packard 438A gas chromatograph equipped with a Chrompack 25 m fused silica column (CP-Sil-5CB; 0.25 mm i.d.) (GC-MS).

General procedure:

Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. Acenaphthylene (0.76, 5 mmol) was added, together with freshly cut sodium (0.3 g, 13 mmol). Directly after the addition, the flask was evacuated and sonicated for a period of

40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0ºC, a deep green solution was obtained. The flask was then cooled in an ethanol-liquid nitrogen bath to -70ºC and the electrophile (5 mmol) was added. The mixture was allowed to warm to room temperature and stirred for a further 30-60 minutes, after which period the reaction was quenched with water. Addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oils.

*Reaction of **1** with allyl bromide:*

To a solution of **1** (5 mmol), allyl bromide (0.43 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography a mixture of products was obtained (mass recovery more than 90%). This mixture was separated by preparative gas chromatography. Next to acenaphthene and acenaphthylene the following products were found: 1-allylacenaphthene **3a** (39%), 5-allylacenaphthene **3b** (21%), 1,2-diallylacenaphthene **3c** (17%), 1,5-diallylacenaphthene **3d** (12%),1-allylacenaphthylene **3e** (5%) and another diallylacenaphthene **3f** (6%) (Figure 1). **3e** and **3f** could not be characterised by NMR. From **3e** no GC-MS spectrum was measured.

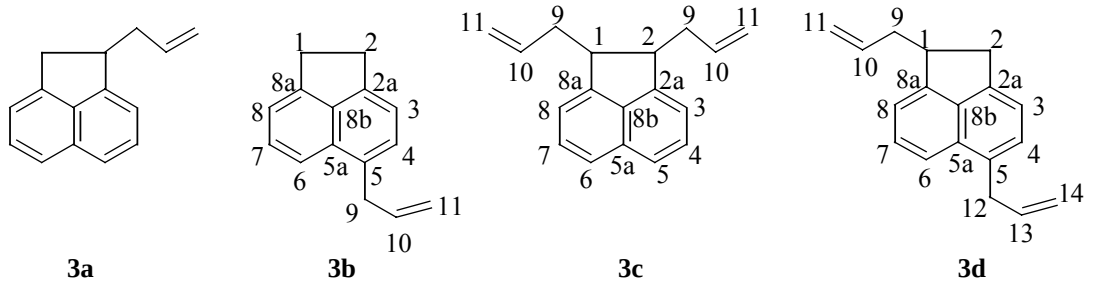


***Figure 1**: Isolated products from the reaction of **1** with allyl bromide.*

1-Allylacenaphthene (**3a**)*:see Chapter 3*

5-Allylacenaphthene (**3b**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.69 (ddt, $J_{6,7}$ = 8.3, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.45 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.9**,** 1 H, H-7), 7.27 (ddt, $J_{7,8}$ = 6.9, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 7.27 (d, $J_{3,4}$ = 6.9, H-4), 7.21 (dt, $J_{3,4}$ = 6.9, $J_{2,3}$, 1 H, H-3), 6.09 (m, 1 H, H-10), 5.11 (m, 1 H, H-11), 5.07 (m, 1 H, H-11'), 3.76 (ddd, $J_{9,10}$ = 6.3, $J_{9,11}$, $J_{9,11'}$, 2 H, H-9), 3.38-3.36 (m, 4 H, H-1 and H-2), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{9,11}$, $J_{9,11'}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) δ: 137.3 (C-10), 127.6 (C-7), 127.5 (C-4), 119.4 (C-6), 119.0 (C-3 and C-8), 115.7 (C-11), 36.4 (C-9), 30.5 (C-1 or C-2), 29.8 (C-1 or C-2), quaternary C's not observed.
GC-MS m/z (%): 194 (100), 179 (11), 165 (13), 153 (5).

1,2-Diallylacenaphthene (**3c**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.62 (d, $J_{4,5}$ = $J_{6,7}$ = 8.2, 2 H, H-5 and H-6), 7.46 (dd, $J_{4,5}$ = $J_{6,7}$ = 8.2, $J_{3,4}$ = $J_{7,8}$ = 6.9**,** 2 H, H-4 and H-7), 7.28 (d, $J_{3,4}$ = $J_{7,8}$ = 6.9, 2 H, H-3 and H-8), 5.84 (m, 2 H, H-10), 5.09 (m, 2 H, H-11), 5.05 (m, 2 H, H-11'), 3.45 (t, $J_{1,9}$ = $J_{2.9}$ = 5.8, 2 H, H-1 and H-2), 2.54 (m, $J_{9,10}$ = 6.3, $J_{9,11}$, $J_{9,11'}$, 4 H, H-9).
^{13}C NMR ($CDCl_3$) δ: 137.3 (C-10), 128.6 (C-4 and C-7), 123.6 (C-5 and C-6), 120.0 (C-3 and C-8), 117.5 (C-11), 49.7 (C-1 and C-2), 41.2 (C-9), quaternary C's not observed.
GC-MS m/z (%): 234 (48), 193 (100), 178 (21), 165 (23), 152 (4).

1,5-Diallylacenaphthene (**3d**)

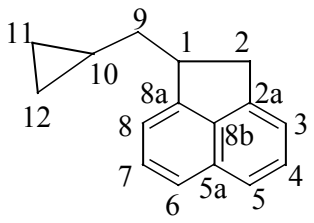
^{1}H NMR ($CDCl_3$, TMS) δ: 7.72 (d, $J_{6,7}$ = 8.3, 1 H, H-6), 7.48 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.9, 1 H, H-7), 7.31-7.18 (m, 3 H, H-3, H-4 and H-8), 6.09 (m, 1 H, H-13), 5.89 (m, 1 H, H-10), 5.15-5.05 (m, 4 H, H-11 and H-14), 3.79-3.74 (m, 3 H, H-1 and H-12), 3.50 (dd, $J_{2,2'}$ = -16.9, $J_{1,2}$ = 7.8, 1 H, H-2), 3.06 (dd, $J_{2,2'}$ = -16.9, $J_{1,2'}$ = 2.9, 1 H, H-2'), 2.66 (m, 1 H, H-9), 2.42 (m, 1 H, H-9').
GC-MS m/z (%): 234 (100), 193 (73), 178 (12), 165 (18).

Third disubstituted product (**3f**)

GC-MS m/z (%): 234 (68), 193 (100), 178 (21), 165 (24), 152 (5).

*Reaction of **1** with (bromomethyl)cyclopropane:*

To a solution of **1** (3 mmol) (bromomethyl)cyclopropane (0.29 ml, 3 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography 5-(cyclopropylmethyl)acenaphthene was obtained as the major product (>90%). GC-MS analysis showed that also some acenaphthene and 5-(cyclopropylmethyl)acenaphthylene were present.



5-(Cyclopropylmethyl)-acenaphthene (**4**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.69 (ddt, $J_{6,7}$ = 8.3, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.45 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.9, 1 H, H-7), 7.27 (ddt, $J_{7,8}$ = 6.9, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 7.27 (d, $J_{3,4}$ = 6.9, H-4), 7.21 (dt, $J_{3,4}$ = 6.9, $J_{2,3}$, 1 H, H-3), 3.38-3.36 (m, 4 H, H-1 and H-2), 2.91 (d, $J_{9,10}$ = 6.2, 2 H, H-9), 1.14 (m, 1 H, H-10), 0.53 (m, 2 H, H-11/12), 0.25 (m, 2 H, H-11/12).

^{13}C NMR ($CDCl_3$) δ: 146.3 (C-2a or C-8a), 143.9 (C-2a or C-8a), 133.8 (C-5a), 126.9 (C-4 and C-7), 119.3 (C-6), 119.0 (C-3 or C-8), 118.9 (C-3 or C-8), 36.2 (C-9), 30.5 (C-1 or C-2), 29.8 (C-1 or C-2), 11.3 (C-10), 5.1 (C-11 or C-12), 5.0 (C-11 or C-12).

Exact mass calculated for $C_{16}H_{16}$: 208.1252 m/z; found: 208.1252. MS m/z (%): 208 (100), 193 (23), 179 (20), 167 (74), 165 (60), 152 (31)139 (2), 115 (2), 89 (5).

*Reaction of **1** with bromobenzene:*

To a solution of **1** (5 mmol), bromobenzene (0.537 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography a mixture of phenylacenaphth(yl)enes was obtained (yield: 60-90%). GC-MS analysis showed 6 products in the following ratio: A (20%), B (13%), C (18%), D (7%), E (19%), F (23%)

A: GC-MS m/z (%): 230 (100), 152 (22).
B: GC-MS m/z (%): 228 (100), 202 (11), 113(10).
C: GC-MS m/z (%): 230 (100), 202 (6), 153 (8), 113 (5).
D: GC-MS m/z (%): 228 (100), 113 (11).
E: GC-MS m/z (%): 230 (100), 215 (15), 153 (7).
F: GC-MS m/z (%): 308/310 (100/92), 229 (70), 153 (8), 113 (13), 101 (10).

*Reaction of **1** with para-bromotoluene:*

To a solution of **1** (5 mmol), *p*-bromotoluene (0.62 ml, 5 mmol) was added at -60ºC and the solution was stirred for a further 30 minutes. After normal work-up and purification by silica gel column chromatography a mixture of methylphenylated acenaphthenes was obtained. GC-MS analysis showed next to dimethylbiphenyl four products in the following ratio: A (26%), B (15%), C (35%), D (24%)

A: GC-MS m/z (%): 244 (100), 229 (96), 152 (58).
B: GC-MS m/z (%): 244 (100), 229 (25), 153(12).
C: GC-MS m/z (%): 244 (100), 229 (40), 152 (5).
D: GC-MS m/z (%): 322/324 (100/93), 243 (38), 228 (41), 152 (4).

*Reaction of **1** with E/Z bromostyrene:*

To a solution of **1** (3 mmol), E/Z β-bromostyrene (0.40 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography, styrylacenaphthene was obtained. GC-MS analysis showed one major product.
GC-MS m/z (%): 256 (43), 165 (100), 91 (8), 43 (10).

6.6 References

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Part II

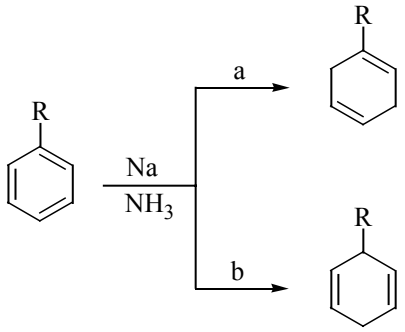
Substituted acenapphthylenes

7

Synthesis, reduction and electrochemistry of substituted acenaphthylenes

7.1 Introduction

In Part I of this thesis (Chapters 2-6) the reactivities of the acenaphthylene dianion and the 5-hydroacenaphthylene anion towards electrophiles were discussed. The regioselectivity of the protonations and the alkylations depends on the charge distribution in the anionic intermediates. The charge distribution and thus the regioselectivity of the reduction may be influenced by substituents. For example, electron-releasing groups deactivate the ring in the Birch reduction of benzene derivatives and direct protonation to unsubstituted 2,5-positions (Scheme 1, path a) while electron-withdrawing groups have the opposite effect, promoting 1,4-reduction (path b).[1,2] The trimethylsilyl group induces a similar effect in the reduction of naphthalene.[3]



***Scheme 1**: Birch reduction of substituted benzenes: a: R=NR_2, OR, alkyl, b: R=COOMe, $CONH_2$, $Si(CH_3)_3$, phenyl.*

Not only the nature of the substituent but also its position determines how the reduction potential and the charge distribution change.[4] The effect of a substituent on the charge distribution can be studied by NMR spectroscopy of the anionic intermediate.[5] Using this method, the effects of various substituents on the charge distribution in the phenalene anion have been examined.[6,7] Pyrene is the only compound for which the effect of substituents on the dianion has been studied.[8]

In the next part of this thesis the influence of substituents on the physical properties and on the reactivities of substituted acenaphthylene dianions and hydroanions will be investigated. The introduction of substituents will lead to a change in the energy levels of the neutral acenaphthylene and will therefore influence the reduction potential. A similar reasoning applies to the reduction from radical anion to dianion.

The reduction potentials can be measured by cyclic voltammetry. Furthermore, the substituents will affect the charge density distribution in the neutral as well as in the dianionic particle. These effects can be measured by NMR spectroscopy, observed in the reactivity towards electrophiles and calculated by *ab initio* methods. This study will be the main topic of the next two chapters (Chapters 8 and 9).

In the present chapter the syntheses of the substituted acenaphthylenes will be discussed. These substituted acenaphthylenes will be converted into their dianions and subsequently be treated with water in order to investigate if the corresponding dianions have been formed. Cyclic voltammetry will be used to compare the reduction potentials and thus the ease of formation of the dianions.

7.2 Results and discussion

7.2.1 Synthesis of 1- and 5-substituted acenaphthylenes

Acenaphthylene can be substituted at positions 1 and 5 rather easily. These positions are also the most interesting ones, because in the acenaphthylene dianion the highest charge density and HOMO coefficients are found at these carbon atoms. The effects of substituents at positions 3 (8) and 4 (7) will probably be smaller and will therefore not be considered in this study. Next to the weakly electron-donating methyl group, the methoxy group is studied as an electron donor. As examples of electron-withdrawing groups, bromide (weak), cyanide (strong) and nitro (very strong) were chosen.

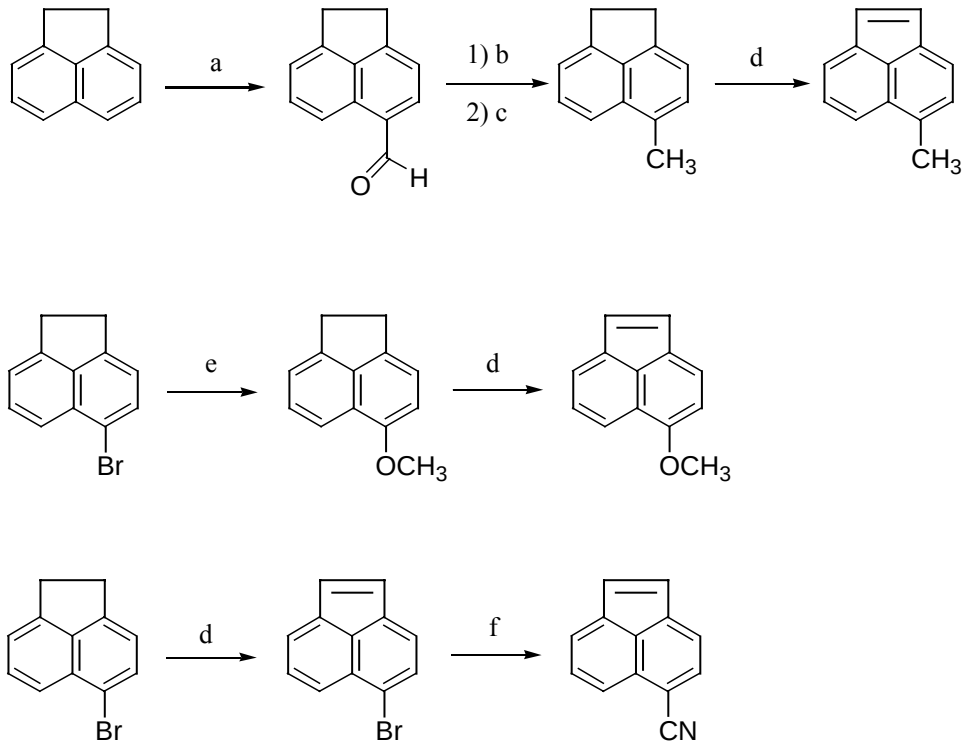
Acenaphthene was formylated selectively at position 5 using dichloromethyl methyl ether and titanium(IV) chloride. Wolff-Kishner reduction of the formyl group followed by dehydrogenation gave 5-methylacenaphthylene (Scheme 2).

The commercially available 5-bromoacenaphthene was converted into 5-methoxyacenaphthene by treatment with sodium methanolate in dimethylformamide using copper(I) iodide as a catalyst. The product could be easily oxidised with DDQ and 5-methoxyacenaphthylene was obtained (Scheme 2).

Direct oxidation of 5-bromoacenaphthene gave 5-bromoacenaphthylene in high yield. The latter could also be converted into 5-methoxyacenaphthylene, but in that case copper(I) oxide should be used as a catalyst (Scheme 2).

Treatment of 5-bromoacenaphthylene with potassium cyanide and copper(I) iodide gave 5-cyanoacenaphthylene (Scheme 2).

5-Nitroacenaphthylene was prepared by dehydrogenation of 5-nitroacenaphthene.[9] Due to the presence of the nitro group, oxidation with DDQ failed. Therefore, 5-nitroacenaphthene was oxidised by treatment with chromium trioxide in acetic acid. The two products, 1-oxo-5-nitroacenaphthene and 2-oxo-5-nitroacenaphthene, were reduced with sodium borohydride in a methanol/dichloromethane mixture to the corresponding alcohols. The alcohols were dehydrated using a catalytic amount of p-toluenesulfonic acid in refluxing toluene and 5-nitroacenaphthylene was obtained in 44% overall yield.



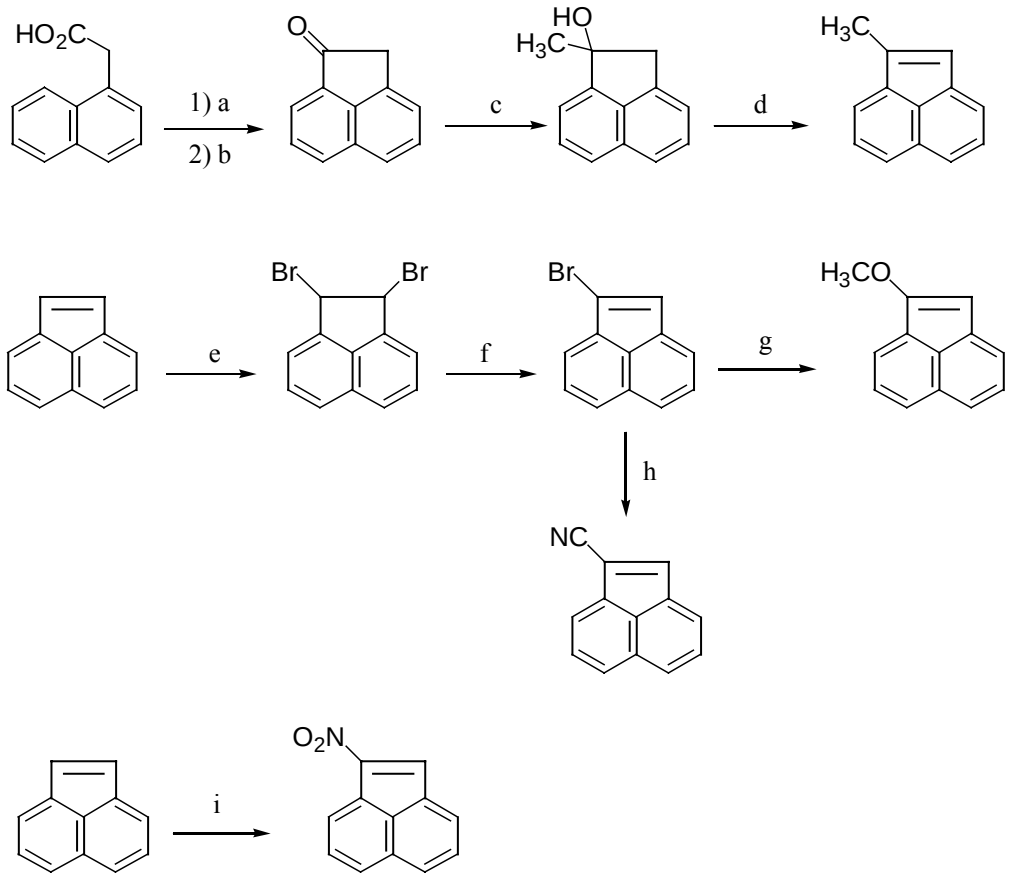
***Scheme 2**: Syntheses of 5-substituted acenaphthylenes, a: Cl_2CHOCH_3, $TiCl_4$, b: H_2NNH_2, diethylene glycol, c: KOH, d: DDQ, e: CuI, NaOMe, f: CuI, KCN.*

The introduction of a methyl group at position 1 can be accomplished using reductive alkylation with methyl iodide. However, oxidation of 1-methylacenaphthene with DDQ yielded many side-products, in which the methyl group was converted into an aldehyde or acid. Therefore, the synthesis of 1-methylacenaphthylene was started by cyclisation of naphthalene-1-acetic acid via the acid chloride by a Friedel-Crafts procedure. The resulting ketone was treated with methyllithium. Dehydration with a catalytic amount of *p*-toluenesulfonic acid gave 1-methylacenaphthylene (Scheme 3).

The 1-methoxy- and 1-cyanoacenaphthylenes could be prepared starting with 1-bromoacenaphthylene following the procedures as described for the 5-substituted equivalents. 1-

Bromoacenaphthylene can be synthesised by bromination of acenaphthylene and subsequent dehydrobromination (Scheme 3).

For the synthesis of 1-nitroacenaphthylene, acenaphthylene was treated with silver nitrate, sodium nitrite and iodine in acetonitrile. The product is, however, very sensitive to light, heat and moisture and should be used immediately after preparation.

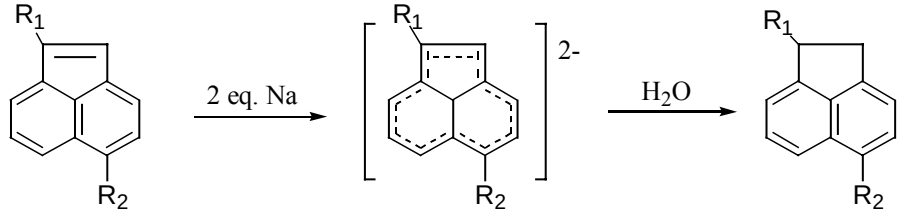


***Scheme 3**: Syntheses of 1-substituted acenaphthylenes, a: ClCOCOCl, b: $AlCl_3$, c: MeLi, d: p-TSA, e: Br_2, f: KOH, g: CuI, NaOMe, h: CuI, KCN i: $AgNO_3$, $NaNO_2$, I_2.*

7.2.2 Reduction of 1- and 5-substituted acenaphthylenes

The 1- and 5-substituted acenaphthylenes were converted into the corresponding dianions using the same procedure as for the acenaphthylene dianion (Chapter 2).[10] The compounds were dissolved in anhydrous THF and exposed to 2.2 equivalents of sodium under ultrasonic vibration. Within 3-6 hours the colour of the solution changed and the dianions were formed. The reaction mixture was cooled to –70ºC and quenched with water. After extraction with light petroleum (boiling range 40-60ºC) or diethyl ether and work-up, the thermodynamically most stable products were obtained. These were characterised by NMR.

Using this procedure it was possible to reduce 5-methyl-, 5-methoxy-, 5-cyano-, 1-cyano- and 1-methylacenaphthylene to the corresponding acenaphthene derivatives via their dianions (Scheme 4).



***Scheme 4**: Reduction of substituted acenaphthylenes, R_1=H, R_2=CN, OMe, Me and R_1=CN, Me, R_2=H.*

5-Methyl- and 1-methylacenaphthene gave dark green solutions of their dianions within 5 hours. The corresponding acenaphthenes were isolated in more than 95% yield.

The reactions with 5-methoxy- and 1-methoxyacenaphthylene were considerably slower (7 hours). In the case of 5-methoxyacenaphthylene, 5-methoxyacenaphthene was obtained as the only product. The reaction with 1-methoxyacenaphthylene was less successful: either many side-products or much starting material was observed. Probably, this compound should better be reduced using another method.

The reductions of the cyano-substituted acenaphthylenes were much faster: within 3 hours the colour of the solution had changed to dark orange. The corresponding acenaphthenes were isolated in high yields (>90%).

5-Bromo- and 1-bromoacenaphthylene were debrominated during the reduction procedure and finally gave acenaphthene. The bromide ion might be split off at the stage of radical anion or dianion. After release of the bromide the resulting radical (anion) takes up a hydrogen atom from the solvent and is finally converted into the acenaphthylene dianion. The latter is protonated during work-up giving acenaphthene.

In the reactions with 1- and 5-nitroacenaphthylene, either starting material (no colour change) or undefinable products were isolated. Apparently, the nitroacenaphthylenes could not be converted into their dianions under these conditions. This may be due to the fact that the nitro group itself can also be reduced in this procedure.

7.2.3 Cyclic voltammetry

General:

The reduction process of polycyclic aromatic hydrocarbons can be studied by cyclic voltammetry experiments. Although much attention has been paid to larger PAH, only little is known about acenaphthylene.[11-14] In this section the electrochemical properties of acenaphthylene and its substituted derivatives concerning the reduction process are studied.

In cyclic voltammetry, the potential of the working electrode is changed linearly in time starting from a value where no electrode reaction occurs, and moving to potentials where reduction of the compound does take place. At a certain potential, the energy of the electrons at the electrode is higher than the energy level of the LUMO of the compound under study, and electrons will be transferred. This results in an electric current response. When all the reactant in the diffusion layer is reduced, the current diminishes. Reversal of the potential sweep should give oxidation of the reduced product. The typical reduction-oxidation wave can only be observed when the system is electrochemically reversible.

The average of the anodic (oxidation, E_{pa}) and cathodic (reduction) peak potential (E_{pc}), the halfwave potential ($E_{½}$), is closely related to the standard reduction potential and can be used as a measure for the ease of reduction. In a reversible redox system, the anodic (i_{pa}) and the cathodic (i_{pc}) peak currents should be equal. According to Nernst's law, the difference between oxidation and reduction potential should be about 60 mV for a one-electron process. In less ideal circumstances, e.g. smaller conductivity of the solvent or slower diffusion at the electrode, the difference may be larger. In the cases that the process is not electrochemically reversible at the time scale of the experiment ($\Delta E>60$ mV), the process should be chemically reversible and electrochemically quasi-reversible. The intermediates are chemically stable if repeated measurements give identical signals. The reduction-oxidation wave of a redox couple is quasi-reversible when the observed peak current is related linearly to the square root of the scan rate.

Results:

In order to study the electrochemical behaviour of acenaphthylene, solutions of acenaphthylene in anhydrous THF, DMSO, DMF and acetonitrile were measured at a scan rate of 0.1 V/s (Table 1). In all cases the difference between reduction and oxidation potential (ΔE) was more than 60 mV. In THF and DMSO this difference is extremely large. A second important point derived from the experiments with different solvents is the dependence of the reduction potential on the solvent. In THF and acetonitrile, $E_{½}$ is 0.13 V higher than in DMSO and DMF. For THF this observation might be explained by its low dielectric constant (7.6) in comparison with the other solvents (36.7-46.7). The advantage of using THF as solvent is that much lower reduction potentials can be measured (down to –4.5 V). Furthermore, in this solvent the electrochemical reduction resembles the chemical reduction with sodium, which is also performed in THF. Because of the high ΔE, the values of $E_{½}$

should be interpretated with care. Therefore, both $E_{½}$ and E_{pc} are given as a measure for the ease of reduction.

***Table 1**: Electrochemical reduction-oxidation behaviour of acenaphthylene in various solvents.*

Solvent	E_{pc} (V)	E_{pa} (V)	$E_{½}$ (V)	ΔE (V)
THF	-2.14	-1.27	-1.71	0.87
DMSO	-1.90	-1.25	-1.58	0.65
DMF	-1.75	-1.40	-1.58	0.35
Acetonitrile	-1.82	-1.59	-1.70	0.23

The substituted acenaphthylenes were dissolved in THF and measured using the same procedure as for acenaphthylene (Table 2). When the potential scan was reversed after the addition of the first electron, the current-voltage trace had the stable, symmetrical form, characteristic of a reversible process (Figure 1). Although the differences between E_{pc} and E_{pa} were again very large (>60 mV), the values of E_{pc} and $E_{½}$ showed the same trend for the reduction of substituted acenaphthylenes.

***Table 2**: Half wave reduction potentials for substituted acenaphthylenes measured in THF at 0.1 V/s.*

Compound	1^{st} $E_{½}$ (V)	1^{st} E_{pc} (V)	LUMO (eV)
5-Nitroacenaphthylene	-0.99	-1.54	-1.93
5-Cyanoacenaphthylene	-1.38	-1.90	-1.59
1-Cyanoacenaphthylene	-1.47	-2.16	-1.60
1-Bromoacenaphthylene	-1.63	-1.93	-1.27
Acenaphthylene	-1.71	-2.14	-1.06
5-Methylacenaphthylene	-1.73	-2.18	-1.05
1-Methylacenaphthylene	-1.87	-2.20	-1.03
5-Methoxyacenaphthylene	-1.96	-2.64	-0.97

As expected, the acceptor substituents (nitro and cyano) lower the reduction potential of acenaphthylene. This effect is highest for the strongest electron-accepting substituent. Comparison of 5-cyano- and 1-cyanoacenaphthylene learns that not only the nature of the substituent influences the reduction potential but also its position. The largest effect is found for the cyano group at position 5, the carbon atom with the highest charge in the (unsubstituted) acenaphthylene radical anion and dianion.

Bromoacenaphthylene is also more readily reduced than acenaphthylene itself. The reduction process is quasi-reversible at the cyclic voltammetric time scale. This means that no chemical

reaction takes place and thus that the bromine atom remains attached to the acenaphthylene skeleton during this process.

The reduction potential is less dramatically influenced by donor substituents. A similar trend was observed in the reduction of substituted naphthalenes and anthracenes.[15] However, the effect of the position of the methyl group is larger than that of the cyano group.

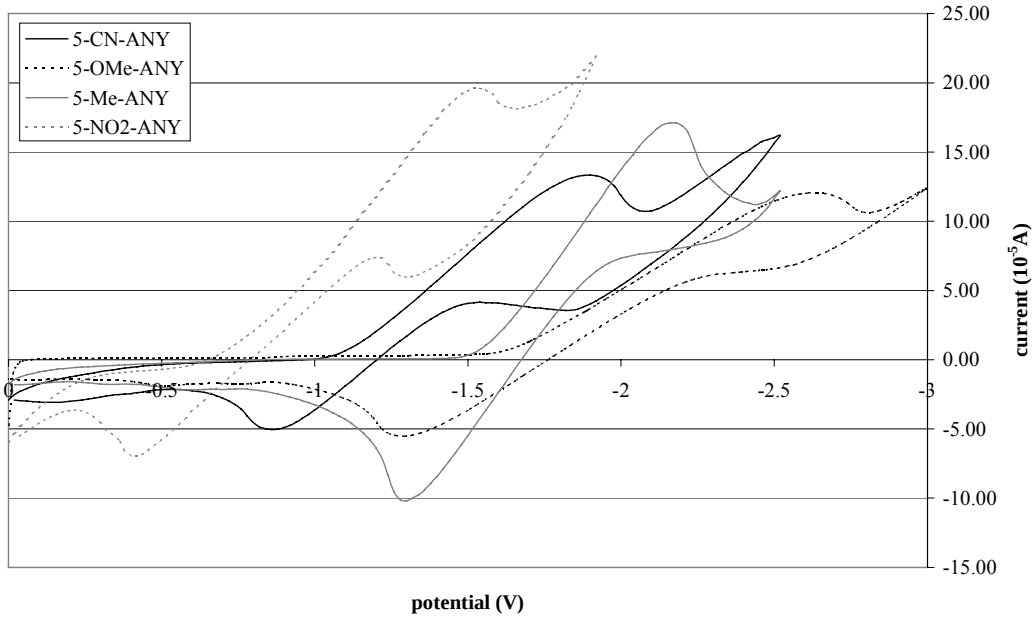


***Figure 1**: Reduction-oxidation waves for 5-methoxyacenaphthylene, 5-methylacenaphthylene, 5-cyanoacenaphthylene and 5-nitroacenaphthylene.*

The ease of reduction depends on the energy level of the LUMO, which is lowered by electron-withdrawing groups. Therefore, these compounds are more easily reduced. The LUMO energies were calculated semi-empirically using the PM3 calculation method in MOPAC93 (Table 2). In Figure 2 it is shown that the half wave reduction potentials are indeed linearly related to the calculated LUMO energies.

In linear free energy relationships (LFER) the effects of substituents on chemical reactions are described. In order to find a LFER for the reduction of substituted acenaphthylenes, the half wave reduction potentials were plotted against various Hammett constants (R^-, σ_p, σ_p^-, F).[16,17] However, no linear relation could be detected.

For the substituted acenaphthylenes it was very difficult to measure the second reduction-oxidation wave. Next to irreversible side-reactions, the position of the second E_{pc} was often unclear. The trend seemed to be similar as for the first reduction-oxidation wave.

The use of higher potentials clearly showed how important it is to work under anhydrous conditions. Traces of water already destruct the second oxidation wave. Instead, an oxidation wave at low potential was observed. Comparison with the work of Dietz and Peover[12] indicates that the dianion is protonated forming a hydroanion, which is oxidised at this potential.

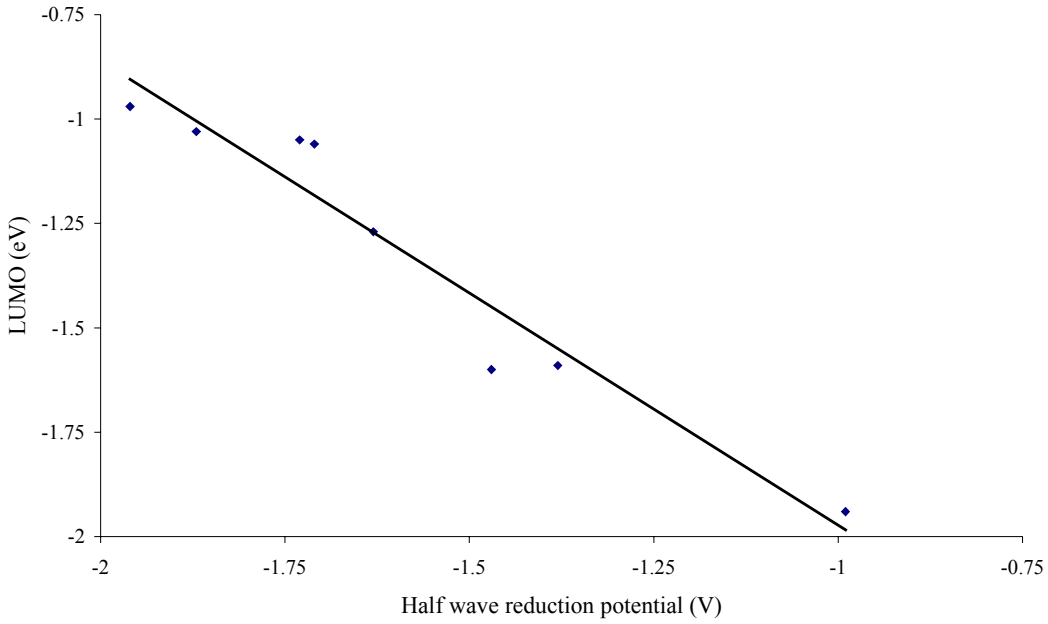


***Figure 2**: Relation between the half wave potential and the LUMO energy.*

7.3 Conclusions

Acenaphthylenes with electron-withdrawing (cyano, nitro) and electron-donating (methyl, methoxy) groups were synthesised and used in reductions with sodium in THF. 5-Methyl-, 1-methyl-, 5-methoxy-, 1-methoxy-, 5-cyano- and 1-cyanoacenaphthylene were converted into the corresponding acenaphthenes. Both 1-bromoacenaphthylene and 5-bromoacenaphthylene were debrominated and gave acenaphthene as the final product. The nitroacenaphthylenes could not be converted into stable dianions.

Cyclic voltammetry showed that electron-withdrawing substituents, such as a nitro and a cyano group, lower the reduction potential with respect to the unsubstituted acenaphthylene. The electron-donating methoxy and methyl groups make reduction more difficult. The relation between the half wave reduction potential and the LUMO energy, calculated by the PM3 method, was established to be linear.

7.4 Experimental section

General: Acenaphthylene (Aldrich, 75%) was purified by treatment with DDQ and filtration over silica. All reagents were obtained from Acros, Aldrich or Fluka and used without further purification. Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra. For the determination of the coupling constants we used the simulation program PERCH.[18]

The electrochemistry measurements were performed with an Autolab Pgstat10 potentiostat controlled by GPES4 software. A three electrode system was used, containing a glassy carbon (GC) working electrode, a platinum (Pt) auxiliary electrode and a Ag/AgCl reference electrode. The experiments were carried out in THF, acetonitrile, DMSO and DMF at room temperature under an argon atmosphere with tetrabutylammonium hexafluorophosphate as electrolyte. Because the radical anions and dianions are very sensitive towards oxygen, the solutions were purged with argon for 10 minutes before starting the measurements. Under these conditions, the ferrocenium-ferrocene couple was located at +0.44 V. The peak separations were different for the different solvents, with the highest value in THF. To determine whether the processes are quasi-reversible, several runs with different scan rates were performed. The observed peak current was plotted versus the square root of the scan rate and in all cases a straight line was obtained.

Synthesis of 5-formylacenaphthene

To a solution of acenaphthene (8.30 g, 53.9 mmol) in dichloromethane (250 ml) dichloromethyl methyl ether (5.9 ml, 65 mmol) was added under an atmosphere of nitrogen. The solution was cooled to 0°C and titanium(IV) chloride (25.0 ml, 228 mmol) was added. The solution immediately turned black and vigorous stirring was necessary to dissolve all the solids. After 2 hours stirring at room temperature, all starting materials had disappeared (TLC, dichloromethane as eluent). The solution was cooled again to 0°C and water was added carefully. The dark green-black reaction mixture was extracted with dichloromethane. The organic layer was washed with saturated sodium hydrogen carbonate and dried over $MgSO_4$. Evaporation of the solvent followed by flash chromatography (silica; dichloromethane/light petroleum (boiling range 40-60ºC) (1:1)) gave 9.50 g (52.2 mmol, 97%) of light grey solid product.

^{1}H NMR ($CDCl_3$, TMS) δ: 10.0 (s, 1H, CHO), 8.60 (d, 1H, $J_{6,7}$ = 8.2, H-6), 7.46 (m, 2H, H-4, H-7), 7.10 (d, 1H, $J_{7,8}$ = 6.9, H-8), 6.98 (d, 1H, $J_{3,4}$ = 7.2, H-3), 2.99 (m, 4H, H-1, H-2).

Synthesis of 5-methylacenaphthene

A suspension of 5-formylacenaphthene (9.50 g, 52.2 mmol) in di(ethylene glycol) (250 ml) was prepared. Hydrazine monohydrate (25.0 ml, 515 mmol) was added while stirring under an argon atmosphere. Upon heating, the starting material dissolved. After 1 hour, potassium hydroxide (29.3 g, 586 mmol) was added and the reaction mixture was heated at gentle reflux (210°C) until all starting material had disappeared (TLC, petroleum ether as eluent, 4½ hours). The solution was cooled down to room temperature and water (400 ml) was added. The mixture was extracted twice with diethyl ether. The combined organic layers were washed with water and dried over $MgSO_4$. Evaporation of the solvent and flash chromatography (silica; light petroleum (boiling range 40-60ºC)) yielded 8.40 g (50.0 mmol, 96%) 5-methylacenaphthene as a white solid (m.p. 82–84°C).
The ^{1}H NMR spectrum was identical to the one obtained earlier (Chapter 2).

Synthesis of 5-methylacenaphthylene

5-Methylacenaphthene (8.25 g, 49.1 mmol) was dissolved in dry toluene (250 ml) under an argon atmosphere. The solution was degassed and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 13.4 g, 59.0 mmol) was added. The reaction mixture was heated at 65°C for 3 hours under an argon atmosphere and then stirred at room temperature for one night. Work-up consisted of filtering over hyflo, washing twice with a saturated solution of Na_2SO_3 and twice with a saturated solution of sodium chloride and drying over $MgSO_4$. Evaporation of the solvent yielded a dark brown-red oil. Flash chromatography followed by column chromatography (silica; light petroleum) yielded 3.86 g (23.3 mmol, 47%) of 5-methylacenaphthylene as a yellow oil.
^{1}H NMR ($CDCl_3$, TMS) δ: 7.58 (d, 1H, $J_{6,7}$ = 8.3, H-6), 7.38 (d, 1H, $J_{7,8}$ = 6.8, H-8), 7.24 (d, $J_{3,4}$ = 7.0, 1H, H-3), 7.21 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.8, 1H, H-7), 6.94 (d, 1H, $J_{3,4}$ = 7.0, H-4), 6.85 (d, 1H, $J_{1,2}$ = 5.2, H-2), 6.83 (d, 1H, $J_{1,2}$ = 5.2, H-1), 2.42 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$) δ: 139.9 (C-2a or C-8a), 137.7 (C-2a or C-8a), 136.0 (C-5), 129.1 (C-2), 128.5 (C-5a), 128.3 (C-1), 128.1 (C-8b), 127.5 (C-4), 127.0 (C-7), 124.1 (C-3), 123.9 (C-6), 123.6 (C-8), 17.6 (CH_3).
Exact mass calculated for $C_{13}H_{10}$: 166.0782 m/z; found: 166.0782.

Synthesis of 5-methoxyacenaphthene

Sodium methanolate (0.34 mmol) was prepared by dissolving sodium (7.9 g, 0.34 mmol) in dry methanol (30 ml) under a nitrogen atmosphere and evaporation of the excess methanol. Under an argon atmosphere the sodium methanolate was dissolved in dry dimethylformamide and 13.0 g (68.2 mmol) copper(I) iodide and 8.02 g (34.4 mmol) of 5-bromoacenaphthene were added. The reaction mixture was heated at reflux temperature (153°C) for 7 hours, during which time most of the starting material disappeared (TLC, toluene). The solution was allowed to cool down to room temperature and water and dichloromethane were added. After filtration over hyflo the two layers were separated. The water layer was extracted with dichloromethane and the combined organic

layers were washed with brine and dried over $MgSO_4$. Evaporation of the solvent and flash chromatography yielded 5.40 g (29.3 mmol, 85%) of white solid 5-methoxyacenaphthene.
^{1}H NMR ($CDCl_3$, TMS): δ = 8.26 (d, 1H, $J_{6,7}$ = 8.2, H-6), 7.68 (dd, 1H, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, H-7), 7.43 (d, 1H, $J_{7,8}$ = 6.9, H-8), 7.26 (d, 1H, $J_{3,4}$ = 7.6, H-3), 6.79 (d, 1H, $J_{3,4}$ = 7.6, H-4), 3.99 (s, 3H, OCH_3), 3.39 (m, 4H, H-1, H-2).

Synthesis of 5-methoxyacenaphthylene

5-Methoxyacenaphthene (5.40 g, 29.3 mmol) was dissolved in dry toluene (250 ml) under an argon atmosphere. The solution was degassed and DDQ (8.50 g, 37.4 mmol) was added. The reaction mixture was heated at 60°C for 2 hours under an argon atmosphere and then allowed to cool to room temperature. Another 2.0 g (8.8 mmol) of DDQ were added and the solution was stirred for 2 days. Work-up consisted of filtering over hyflo, washing twice with a saturated solution of Na_2SO3 and twice with a saturated solution of sodium chloride and drying over $MgSO_4$. Evaporation of the solvent and subsequent purification by column chromatography (silica; petroleum ether) yielded 3.36 g (18.5 mmol, 59%) of yellow solid 5-methoxyacenaphthylene.
^{1}H NMR ($CDCl_3$, TMS) δ: 8.04 (d, 1H, $J_{6,7}$ = 8.1, H-6), 7.64 (d, 1H, $J_{7,8}$ = 6.9, H-8), 7.52 (d, $J_{3,4}$ = 7.6, 1H, H-3), 7.48 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 6.9, 1H, H-7), 6.98 (d, 1H, $J_{1,2}$ = 5.2, H-2), 6.93 (d, 1H, $J_{1,2}$ = 5.2, H-1), 6.68 (d, 1H, $J_{3,4}$ = 7.6, H-4), 3.94 (s, 3H, OCH_3).
^{13}C NMR ($CDCl_3$): 158.1 (C-5), 139.3 (C-2a or C-8a), 132.1 (C-2a or C-8a), 129.5 (C-8b), 128.9 (C-2), 127.3 (C-1), 126.7 (C-7), 125.5 (C-3), 124.0 (C-8), 121.8 (C-6), 121.4 (C-5a), 105.1 (C-4), 55.7 (OCH_3).

Synthesis of 5-bromoacenaphthylene

5-Bromoacenaphthene (5.01 g, 21.5 mmol) was dissolved in dry toluene (300 ml) under an argon atmosphere. The solution was degassed and DDQ (5.38 g, 23.7 mmol) was added. The reaction mixture was heated at 111°C for 2 hours under an argon atmosphere and then allowed to cool to room temperature. Another 2.0 g (8.8 mmol) of DDQ were added and the reaction mixture was boiled under reflux for 2 hours. Work-up consisted of filtering over hyflo, washing twice with a saturated solution of Na_2SO_3 and twice with a saturated solution of sodium chloride and drying over $MgSO_4$. Evaporation of the solvent gave a brown-red oil. Flash chromatography (silica; petroleum ether) yielded 2.53 g (11.0 mmol, 51%) of yellow solid 5-bromoacenaphthylene.
^{1}H NMR ($CDCl_3$, TMS) δ: 7.78 (d, $J_{6,7}$ = 8.2, 1H, H-6), 7.51 (d, $J_{3,4}$ = 7.3, 1H, H-4), 7.43 (d, $J_{7,8}$ = 6.3, 1H, H-8), 7.34 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.3, 1H, H-7), 7.18 (d, $J_{3,4}$ = 7.3, 1H, H-3), 6.83 (d, $J_{1,2}$ = 5.3, 1H, H-1), 6.78 (d, $J_{1,2}$ = 5.3, 1H, H-2).
^{13}C NMR ($CDCl_3$) δ: 139.8 (C2a or C-8a), 139.1 (C-2a or C-8a), 130.6 (C-4), 129.5 (C-5a), 129.3 (C-1), 129.0 (C-2), 128.5 (C-7), 128.1 (C-8b), 126.1 (C-6), 124.7 (C-8), 124.5 (C-3), 122.8 (C-5).

Synthesis of 5-cyanoacenaphthylene

To a solution of 5-bromoacenaphthylene (1.17 g, 5.07 mmol) in dry dimethylformamide under an argon atmosphere copper(I) iodide (1.89 g, 9.92 mmol) and potassium cyanide (0.385 g, 5.91 mmol) were added. The reaction mixture was heated at reflux (153°C) for 7 hours. The mixture was allowed to cool down to 70°C and a solution of iron(III) chloride hexahydrate (3.0 g, 11 mmol) and concentrated hydrogen chloride (3.0 ml) in water (15.0 ml) was added carefully. The mixture was stirred for 1 hour at 70ºC and then allowed to cool down to room temperature. Diethyl ether and water were added. The solution was filtered over hyflo and the layers were separated. The water layer was extracted with diethyl ether. The combined organic layers were washed with a saturated solution of potassium carbonate, a saturated solution of sodium chloride and water. The solution was dried over $MgSO_4$ and the solvent was evaporated. Column chromatography (silica; petroleum ether/toluene (5:1)) yielded 0.75 g (4.2 mmol, 84%) of yellow solid 5-cyanoacenaphthylene.

^{1}H NMR ($CDCl_3$, TMS) δ: 7.92 (d, $J_{6,7}$ = 8.3, 1H, H-6), 7.83 (d, $J_{3,4}$ = 7.2, 1H, H-4), 7.63 (d, $J_{7,8}$ = 6.8, 1H, H-8), 7.58 (d, $J_{3,4}$ = 7.2, 1H, H-3), 7.56 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.8, 1H, H-7), 7.12 (d, $J_{1,2}$ = 5.3, 1H, H-1), 6.95 (d, 1H, $J_{1,2}$ = 5.3, H-2).

^{13}C NMR ($CDCl_3$) δ: 144.0 (C-2a or C-8a), 139.6 (C-2a or C-8a), 134.2 (C-4), 132.8 (C-1), 129.8 (C-7), 128.9 (C-2), 127.8 (C-5a), 127.1 (C-8b), 125.7 (C-8), 124.7 (C-6), 122.7 (C-3), 117.5 (CN), 108.8 (C-5).

Synthesis of 1-acenaphthenone

To a solution of naphthalene-1-acetic acid (3.72 g, 20 mmol) in dry dichloromethane (60 ml) was added oxalyl chloride (2.6 ml, 30 mmol) under nitrogen atmosphere. After stirring for three hours, the solvent was evaporated. The residue was dissolved in carbon disulphide (40 ml), and, after cooling to 0ºC, $AlCl_3$ (5.6 g, 42 mmol) was added in portions. The solution was stirred for 1 hour at 0ºC and then heated at reflux temperature for 10 minutes. The solution was allowed to cool down to room temperature and poured into ice water containing 4 ml of concentrated HCl. Extraction with dichloromethane, followed by washing with aqueous NaOH and work-up gave 1 g of cyclised product.

Synthesis of 1-methylacenaphthylene

1-Acenaphthenone (1.90 g, 12.8 mmol) was dissolved in dry THF (15 ml) under an argon atmosphere. The solution was cooled with an ethanol-liquid nitrogen bath to -70ºC and MeLi (8.0 ml, 1.6 M in Et_2O) was added with a syringe. The solution turned red and was stirred for 1 hour at 0ºC. A saturated NH_4Cl solution was slowly added. Extraction with diethyl ether and work-up gave 1-hydroxy-1-methylacenaphthene. The crude product was dissolved in toluene (50 ml) and a catalytic amount of *p*-toluenesulfonic acid (*p*-TSA) was added. The reaction mixture was heated under reflux for 45 minutes under an argon atmosphere, cooled to room temperature and washed with an aqueous $NaHCO_3$ solution. After the usual work-up the product was purified by means of column chromatography (silica gel; light petroleum).

^{1}H NMR ($CDCl_3$, TMS) δ: 7.76 (d, $J_{6,7}$ = 7.9, 1H, H-6), 7.67 (dd, $J_{4,5}$ = 7.5, $J_{3,5}$ = 1.3, 1H, H-5), 7.61 (d, $J_{7,8}$ = 6.6, 1H, H-8), 7.53 (dd, $J_{3,4}$ = 7.2, $J_{3,5}$ = 1.3, 1H, H-3), 7.48 (dd, $J_{7,8}$ = 6.6, $J_{6,7}$ = 7.9, 1H, H-7), 7.45 (dd, $J_{3,4}$ = 7.2, $J_{4,5}$ = 7.5, 1H, H-4), 6.68 (d, $J_{2,Me}$ = 1.5, 1H, H-2), 2.41 (d, $J_{2,Me}$ = 1.5, 3H, -CH_3).
^{13}C NMR ($CDCl_3$) δ: 141.0 (C-8a), 140.3 (C-2a), 139.7 (C-1), 128.9 (C-5a), 127.8 (C-8b), 127.7 (C-7), 127.3 (C-4), 127.1 (C-5), 125.8 (C-6), 125.2 (C-2), 122.3 (C-8), 121.7 (C-3), 13.1 (-CH_3).

Synthesis of 1,2-dibromoacenaphthene

To a solution of acenaphthylene (4.57 g, 30 mmol) in tetrachloromethane (100 ml) was added bromine (1.55 ml, 30 mmol) in tetrachloromethane (15 ml) in 90 minutes. The solution was stirred for 18 hours. Extraction with dichloromethane and water and usual work-up gave a mixture of cis- and trans-1,2-dibromoacenaphthene (8.29 g, 90%).
^{1}H NMR ($CDCl_3$, TMS) δ: 7.74 (m, 2H, H-5 and H-6 cis or trans), 7.69 (m, 2H, H-5 and H-6 cis or trans), 7.57-7.50 (m, 4H, H-3, H-4, H-7, H-8), 5.97 (m, 2H, H-1 and H-2 cis or trans), 5.94 (m, 2H, H-1 and H-2 cis or trans).

Synthesis of 1-bromoacenaphthylene

A solution of 1,2-dibromoacenaphthene (8.29 g, 26.5 mmol) and potassium hydroxide (8.00 g, 140 mmol) in ethanol (200 ml) was heated at reflux temperature for 18 hours. The solution was allowed to cool down to room temperature. Ethyl acetate-water extraction, followed by the usual work-up gave 1-bromoacenaphthylene. Purification was performed by silica gel column chromatography with light petroleum.
^{1}H NMR ($CDCl_3$, TMS) δ: 7.78 (d, $J_{4,5}$ = 8.1, 1H, H-5), 7.70 (d, $J_{6,7}$ = 8.2, 1H, H-6), 7.63 (d, $J_{3,4}$ = 6.7, 1H, H-3), 7.53 (d, $J_{7,8}$ = 7.0, 1H, H-8), 7.52 (dd, $J_{3,4}$ = 6.7, $J_{4,5}$ = 8.1, 1H, H-4), 7.43 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 7.0, 1H, H-7), 7.08 (s, 1H, H-2), $J_{6,8}$, $J_{2.3}$, $J_{2,5}$, and $J_{3,5}$ were observed but not exactly determined.
^{13}C NMR ($CDCl_3$) δ: 138.1 (C-2a or C-8a), 137.9 (C-2a or C-8a), 129.0 (C-5a), 128.8 (C-2), 128.4 (C-5), 128.2 (C-8b), 127.8 (C-7), 127.5 (C-4), 127.4 (C-1), 127.0 (C-6), 123.6 (C-8), 123.4 (C-3).

Synthesis of 1-cyanoacenaphthylene

1-Cyanoacenaphthylene was prepared starting from 1-bromoacenaphthylene using the procedure as described for 5-cyanoacenaphthylene.
^{1}H NMR ($CDCl_3$, TMS) δ: 7.95 (d, $J_{4,5}$ = 8.2, 1H, H-5), 7.87 (d, $J_{6,7}$ = 8.2, 1H, H-6), 7.82 (d, $J_{3,4}$ = 7.5, 1H, H-3), 7.81 (d, $J_{7,8}$ = 6.9, 1H, H-8), 7.62 (s, 1H, H-2), 7.60 (dd, $J_{3,4}$ = 7.5, $J_{4,5}$ = 8.2, 1H, H-4), 7.57 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1H, H-7), $J_{6,8}$, $J_{2.3}$, $J_{2,5}$, and $J_{3,5}$ were observed but not exactly determined.
^{13}C NMR ($CDCl_3$) δ: 139.7 (C-2), 136.6 (C-1), 135.8 (C-2a), 135.7 (C-8a), 130.7 (C-5), 129.0 (C-6), 128.3 (C-4), 128.1 (C-5a), 128.0 (C-7 and C-8), 126.8 (C-8b), 124.4 (C-3), 115.8 (-CN).

Synthesis of 1-nitroacenaphthylene

$AgNO_3$ (3.53 g, 20.8 mmol) and $NaNO_2$ (9.71 g, 140.7 mmol) were added to a stirred solution of acenaphthylene (1.85 g, 12.2 mmol) in dry acetonitrile (250 ml). The mixture was cooled to 0ºC and I_2 (5.16 g, 20.3 mmol) was added. After stirring for 2 hours, during which the colour of the solution turned dark red, water was added and the remaining I_2 was destroyed with $NaSO_3$. Extraction with dichloromethane and the usual work-up gave 1-nitroacenaphthylene as orange crystals. Like many other nitro-PAH, the product is sensitive to light, heat and moisture.

^{1}H NMR ($CDCl_3$, TMS) δ: 7.71-7.67 (m, 2H, H-5 and H-6), 7.42-7.39 (m, 4H, H-3, H-4, H-7, H-8), 6.61 (s, 1H, H-2).

Synthesis of 1-methoxyacenaphthylene

1-Bromoacenaphthylene was converted into 1-methoxyacenaphthylene using the procedure as described for 5-methoxyacenaphthene.

^{1}H NMR ($CDCl_3$, TMS) δ: 7.73 (d, $J_{4,5}$ = 8.1, 1H, H-5), 7.65 (d, $J_{3,4}$ = 6.9, 1H, H-3), 7.53 (dd, $J_{6,7}$ = 8.0, $J_{6,8}$=1.0, 1H, H-6), 7.45 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.1, 1H, H-4), 7.36 (dd, $J_{7,8}$ = 6.7, $J_{6,7}$ = 8.0, 1H, H-7), 7.32 (dd, $J_{6,8}$ = 1.0, $J_{7,8}$ = 6.7, 1H, H-8), 5.83 (s, 1H, H-2), 3.89 (s, 3H, -OCH_3).

^{13}C NMR ($CDCl_3$) δ: 162.9 (C-1), 138.2 (C-8a), 134.1 (C-2a), 127.7 (C-5a), 128.0 (C-5 and C-7), 127.0 (C-4), 126.0 (C-8b), 124.0 (C-6), 120.9 (C-3), 120.7 (C-8), 97.3 (C-2), 57.4 (-OCH_3).

Reduction of substituted acenaphthylenes

General procedure: Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. The substituted acenaphthylene (5 mmol) was added, together with 0.3 g (13 mmol) of freshly cut sodium. Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately became dark-coloured, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0°C, the dianions were obtained. The flask was then cooled in an ethanol-liquid nitrogen bath to -70°C and the reaction was quenched with water. The addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil.

Reduction of 5-cyanoacenaphthylene

According to the general procedure 5-cyanoacenaphthylene (0.53 g, 3.00 mmol) was converted into its dianion and the reaction was quenched with water at -70ºC. The usual work-up gave 5-cyanoacenaphthene (0.35 g, 2.0 mmol, 65%, white crystals) as the only product.

5-Cyanoacenaphthene

^{1}H NMR ($CDCl_3$, TMS) : δ = 7.78 (d, $J_{6,7}$ = 8.3, 1H, H-6), 7.75 (d, $J_{3,4}$ = 7.4, 1H, H-4), 7.58 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 7.0, 1H, H-7), 7.36 (d, $J_{7,8}$ = 7.0, 1H, H-8), 7.24 (d, $J_{3,4}$ = 7.2, 1H, H-3), 3.37 (m, 4H, H-1 and H-2).
^{13}C NMR ($CDCl_3$): δ = 152.6 (C-2a), 146.7 (C-8a), 138.6 (C-8b), 134.4 (C-4), 131.7 (C-5a), 130.2 (C-7), 120.9 (C-8), 119.8 (C-6), 118.7 (C-3), 118.0 (CN), 104.9 (C-5), 30.7 (C-1 or C-2), 30.1 (C-1 or C-2).
Exact mass calculated for $C_{13}H_9N$: 179.0734 m/z; found: 179.0735. MS m/z (%): 179 (100), 151 (22).

Reduction of 5-methoxyacenaphthylene

According to the general procedure 5-methoxyacenaphthylene (0.487 g, 2.68 mmol) was converted into its dianion (dark green) and the reaction was quenched with water at -70ºC. The usual work-up gave 5-methoxyacenaphthene (0.15 g, 0.82 mmol, 31%, a yellow oil) as the only product. The NMR spectrum was identical to that reported earlier.
Exact mass calculated for $C_{13}H_{12}O$: 184.0888 m/z; found: 184.0888.

Reduction of 5-methylacenaphthylene

According to the general procedure 5-methylacenaphthylene (0.4091 g, 2.46 mmol) was converted into its dianion and the reaction was quenched with water at -70ºC. The usual work-up gave 5-methylacenaphthene as the only product. The NMR spectra were identical to those reported in Chapter 2.
Exact mass calculated for $C_{13}H_{12}$: 168.0939 m/z; found: 168.0939. MS m/z (%): 168 (100), 153 (56), 139 (4), 69 (9).

Reduction of 1-cyanoacenaphthylene

According to the general procedure 1-cyanoacenaphthylene was converted into its dianion and the reaction was quenched with water at -70ºC. The usual work-up gave 1-cyanoacenaphthene as the only product.

1-Cyanoacenaphthene

^{1}H NMR ($CDCl_3$, TMS) δ: 7.72 (ddd, $J_{6,7}$ = 8.3, $J_{1,6}$, $J_{6,8}$,1H, H-6), 7.66 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1H, H-5), 7.52 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 7.0, 1H, H-7), 7.51 (ddd, $J_{7,8}$ = 7.0, $J_{1,8}$, $J_{6.8}$, 1H, H-8), 7.49 (dd, $J_{3,4}$ = 7.0, $J_{4,5}$ = 8.2, 1H, H-4), 7.30 (dddd, $J_{3,4}$ = 7.0, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1H, H-3), 4.57 (dddd, $J_{1,2}$ = 9.2, $J_{1,2'}$ = 4.8, $J_{1,6}$, $J_{1,8}$, 1H, H-1), 3.84 (dddd, $J_{1,2}$ = 9.2, $J_{2,2'}$ = -17.2, $J_{2.3}$, $J_{2,5}$, 1H, H-2), 3.70 (dddd, $J_{2,2'}$ = -17.2, $J_{1,2'}$ = 4.8, $J_{2',3}$, $J_{2',5}$, 1H, H-2'), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2.3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, and $J_{3,5}$ were observed but not exactly determined.
^{13}C NMR ($CDCl_3$) δ: 140.6 (C-2a or C-8a), 138.6 (C-2a or C-8a), 137.4 (C-8b), 131.5 (C-5a), 128.4 (C-4), 128.0 (C-7), 124.8 (C-6), 123.3 (C-5), 120.7 (CN), 120.2 (C-8), 120.0 (C-3), 36.5 (C-2), 32.0 (C-1).
Exact mass calculated for $C_{13}H_9N$: 179.0735 m/z; found: 179.0692. MS m/z (%): 179 (100), 178 (48), 152 (24), 87 (13), 74 (12), 63 (13), 50 (18).

Reduction of 1-methylacenaphthylene

According to the general procedure 1-methylacenaphthylene was converted into its dianion and the reaction was quenched with water at -70ºC. The usual work-up gave 1-methylacenaphthene as the only product. The NMR spectra were identical to those reported in Chapter 2.

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8

Substituent induced perturbation of the charge distribution in acenaphthylene anions: the cyano group

8.1 Introduction

In Chapter 7 it was shown that 1-cyanoacenaphthylene and 5-cyanoacenaphthylene can be reduced to the corresponding acenaphthene derivatives via their dianions. In this chapter the influence of the cyano substituent on the charge distribution will be examined more closely. In order to determine the most reactive positions in the dianions and hydroanions these particles were used in reactions with methyl iodide. A second method to obtain information about the charge distribution was recording the ^{13}C NMR spectra of the dianions and hydroanions. Finally, the results are compared with the data obtained from *ab initio* calculations.

8.2 Results

8.2.1 Reductive methylation

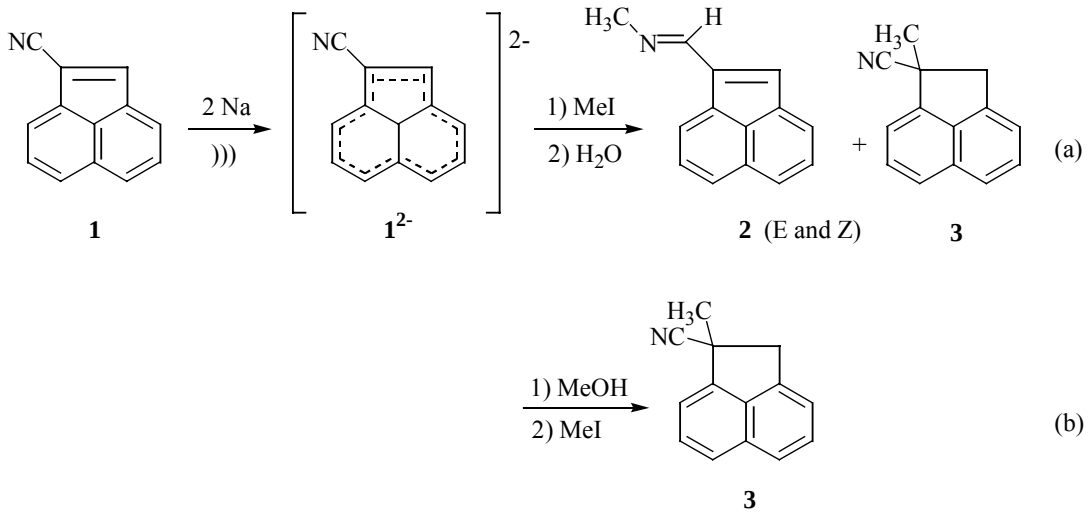
1-Cyanoacenaphthylene

1-Cyanoacenaphthylene (**1**) was converted into its dianion ($\mathbf{1}^{2-}$) according to the procedure described earlier (Chapter 2). The reaction mixture was cooled to -70ºC, one equivalent of methyl iodide was added and the solution was stirred at room temperature for 15 minutes. Quenching with water and extraction with diethyl ether and the usual work-up gave a mixture of 2 products: N-(1-acenaphthylenylmethylene)methanamine (**2**) (10-20%) and 1-cyano-1-methylacenaphthene (**3**) (50-80%) (Scheme 1).

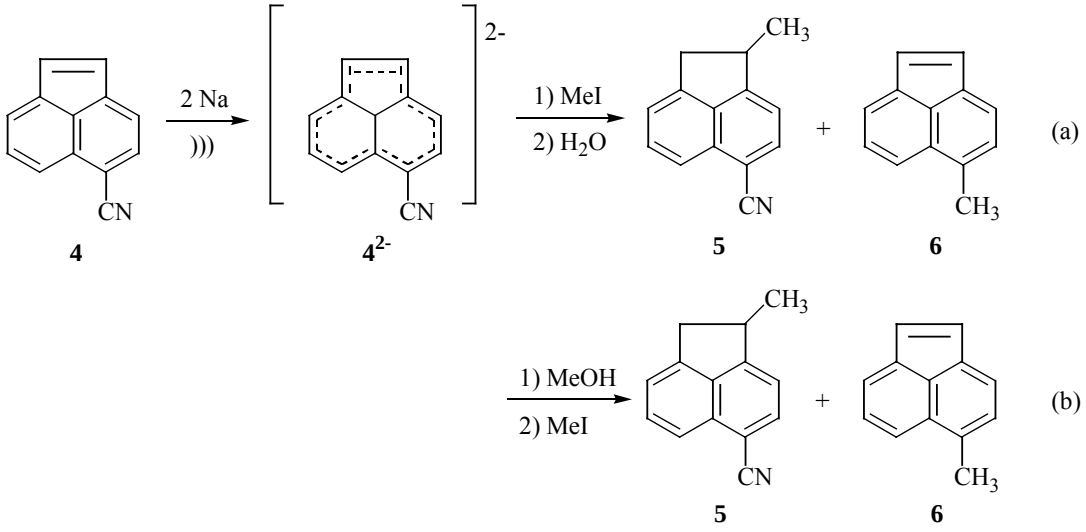
Compound **3** could easily be characterised by NMR techniques. The characterisation of **2** was more difficult. From the number and integrals of the signals in the ^{1}H NMR spectrum it could be concluded that the compound was monosubstituted. The characteristic benzylic signals for the acenaphthene skeleton were missing. The high Rf-value (0.95 in toluene) combined with the absence of the vibrations of a cyano group in the infrared spectrum pointed towards substitution of the nitrogen of the cyano group. The characteristic ^{1}H NMR signals for the Z- and E-methyl groups in the formylidene methyl imine group were observed at 3.39 and 3.25 ppm, respectively. The proton at the C=N resonates in the same region as H-5 and H-6 and could not be separately

observed. The ^{13}C NMR spectrum was also consistent with the proposed structure. GC-MS analysis led to decomposition of the compound.

Reversal of the sequence of addition of the electrophiles, i.e. first one equivalent of proton donor (methanol) followed by one equivalent of methyl iodide gave 1-cyano-1-methylacenaphthene (**3**) as the major product (Scheme 1). Small amounts of 1-cyanoacenaphthene were isolated as a minor product (less than 10%).



***Scheme 1**: Reaction of the 1-cyanoacenaphthylene dianion with a) methyl iodide and water; b) methanol followed by methyl iodide.*



***Scheme 2**: Reaction of the 5-cyanoacenaphthylene dianion with a) methyl iodide and water; b) methanol followed by methyl iodide*

5-Cyanoacenaphthylene

The same experiments were performed with the dianion of 5-cyanoacenaphthylene (**4**$^{2-}$). Both experiments gave 5-cyano-2-methylacenaphthene (**5**) and 5-methylacenaphthylene (**6**) in a 3:1 ratio (Scheme 2). The official name of **5** is 6-cyano-1-methylacenaphthene, but for the sake of comparison the numbering and orientation of the parent compound have been retained.

8.2.2 ^{1}H and ^{13}C NMR spectroscopy

*1-Cyanoacenaphthylene dianion (**1**$^{2-}$)*

The dianion of 1-cyanoacenaphthylene was prepared according to the general procedure in THF-d_8 and transferred into an NMR tube. The ^{1}H and ^{13}C NMR spectra were recorded at room temperature. The spectra were assigned using H-H COSY and C-H COSY techniques (see Table 1 and Figure 1). The signals in the ^{1}H NMR spectrum are broad, as in the case of the unsubstituted acenaphthylene dianion. The protons H-5 and H-6 resonate at the highest field (4.28 and 3.76 ppm, respectively), but also H-8 and H-2 show a large chemical shift. The signals in the ^{13}C NMR spectrum are very sharp (Figure 1), indicating that no radical anion is present in the solution. For the exact assigment of C-1 and CN, 1-cyanoacenaphthylene was prepared with a ^{13}C-label in the cyano group and converted into its dianion. Due to the introduction of this label, a coupling of 87.2 Hz could be observed between C-1 and CN.

The ^{13}C NMR chemical shifts can be used as measure for the charge distribution in the 1-cyanoacenaphthylene dianion (**1**$^{2-}$) (see Chapter 2). Because in **1**$^{2-}$ charge is also located at the nitrogen of the cyano group, the charge distribution cannot be calculated from the differences in chemical shifts between neutral and dianionic particle. The total paratropic shift with respect to the signals of the neutral compound (**1**) is 236.5 ppm. Although this value is considerably less than would be expected (320 ppm for two electrons), it is of the same magnitude as the one for unsubstituted acenaphthylene (**7**) (239.1 ppm). In Table 1, the ^{13}C chemical shifts and the chemical shift differences with the neutral parent compounds of **1**$^{2-}$ and of **7**$^{2-}$ are given. The largest effect of the cyano group is observed on the chemical shift of carbon atom 1: from 85.9 ppm to 64.0 ppm. The difference in chemical shift between the neutral and the dianionic system increased from 43.8 in acenaphthylene to 72.6 ppm in 1-cyanoacenaphthylene. This indicates that a large part of the charge is now located at the carbon attached to the cyano group. Carbon atoms 5 and 2a are found at lower field with respect to the unsubstituted acenaphthylene dianion. Consequently, less charge will be found at these positions. Obviously, the cyano group draws the charge into the five-membered ring.

***Table 1**: ^{13}C NMR shift values for **1**$^{2-}$, **7**$^{2-}$ and **1** in ppm and the differences in chemical shift between neutral form and dianion for **1**$^{2-}$ and **7**$^{2-}$.*

carbon atom	δ (**1**$^{2-}$)	δ (**7**$^{2-}$)	δ (**1**)	δ (**1**) - δ (**1**$^{2-}$)	δ (**7**) - δ (**7**$^{2-}$)
1	64.0	85.9	136.6	72.6	43.8
2	84.8	85.9	139.7	54.9	43.8
3	99.3	96.9	124.4	25.1	31.8
4	127.0	126.7	128.3	1.3	-2.4
5	92.0	82.6	130.7	38.7	45.3
6	82.6	82.6	129.0	46.4	45.3
7	129.3	126.7	128.0	-1.3	-2.4
8	93.4	96.9	128.0	34.6	31.8
2a	135.8	123.4	135.8	0	16.6
5a	145.2	149.2	128.1	-17.1	-20.8
8a	128.2	123.4	135.7	7.5	16.6
8b	137.0	137.7	126.8	-10.2	-10.3
C(N)	131.8		115.8	-16.0	

*1-Cyano-2-hydroacenaphthylene anion ((2H)-**1**$^{-}$)*

The hydroanion of 1-cyanoacenaphthylene ((2H)-**1**$^{-}$) was prepared from the dianion **1**$^{2-}$ by addition of one equivalent of methanol to a solution of **1**$^{2-}$ in THF-d_8 and the solution was transferred into an NMR tube. The ^{1}H and ^{13}C NMR spectra were assigned using H-H COSY and C-H COSY techniques (see Table 3 and Figure 1). The hydroanion was characterised as 1-cyano-2-hydroacenaphthylene anion ((2H)-**1**$^{-}$). The official name for (2H)-**1**$^{-}$ is 2-cyano-1-hydroacenaphthylene anion, referring to the carbon-hydrogen skeleton, but for the sake of comparison the numbering of the parent compound has been retained.

The ^{13}C NMR chemical shift values indicate that most of the charge is located at carbon atom 1, which has an extremely large upfield shift to 46.2 ppm. The chemical shifts of carbon atoms 6 and 8 are about 20 ppm lower than in 1-cyanoacenaphthene, which implies that a small amount of charge is located on these carbons. However, the chemical shifts of the other carbon atoms are found at relatively low field (115.3-155.2), which indicates that only a minor amount of charge is located in the residual naphthalene skeleton.

(2H)-**1**$^{-}$ was also prepared with a ^{15}N-label in the cyano group. The ^{1}H and ^{13}C NMR spectra were identical to those of the unlabelled anion, except the coupling of -17.9 Hz for the cyano carbon. In the ^{15}N NMR spectrum the signal of the cyano nitrogen was found at 241.6 ppm. In the discussion, this value is compared to the chemical shift values of other systems and related to the charge on the nitrogen atom.

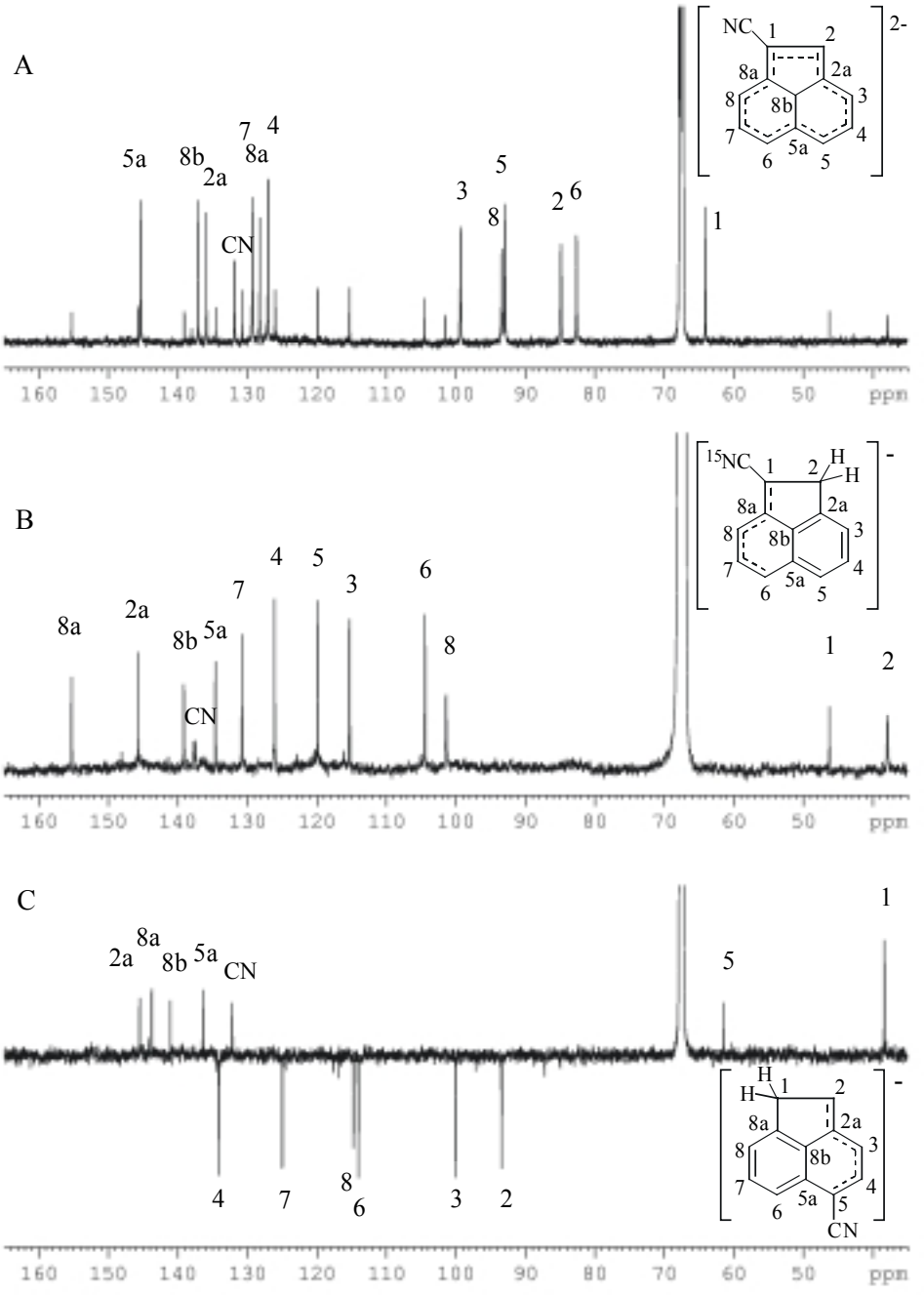


Figure 1: *^{13}C NMR spectra of A: the 1-cyanoacenaphthylene dianion (**1**$^{2-}$),B: the 1-cyano-2-hydroacenaphthylene anion ((2H)-**1**$^{-}$), and C: the 5-cyano-1-hydroacenaphthylene anion ((1H)-**4**$^{-}$) (A and C: 150 MHz, B: 75 MHz, 20°C, the spectrum of **1**$^{2-}$ contains some (2H)-**1**$^{-}$).*

*5-Cyano-1-hydroacenaphthylene anion ((1H)-**4**$^-$)*

The hydroanion of 5-cyanoacenaphthylene ((1H)-**4**$^-$) was prepared from 5-cyanoacenaphthylene following the procedure as described for (2H)-**1**$^-$. Attempts to prepare a stable solution of the dianion of 5-cyanoacenaphthylene failed and resulted in the formation of (1H)-**4**$^-$. The ^{1}H and ^{13}C NMR spectra were assigned using H-H COSY and C-H COSY techniques (see Table 4 and Figure 1) and the introduction of a ^{13}C label in the cyano group. Assignment of the spectra showed 5-cyano-1-hydroacenaphthylene anion ((1H)-**4**$^-$) to be the only product present (Figure 1, Table 4).

The introduction of the ^{13}C label in the cyano group resulted in an extra coupling in the ^{13}C NMR spectrum of 89 Hz between C-5 and the carbon of the cyano group. The ^{13}C chemical shift values of the carbon atoms 5, 2 and 3 are now found at the highest field. Thus, it can be predicted that much charge is located at these carbon atoms. The difference in shifts between C-5, C-2 and C-3 is smaller than for (2H)-**1**$^-$, which indicates that in (1H)-**4**$^-$ the charge is more evenly spread over the molecule.

Also (1H)-**4**$^-$ was prepared with a ^{15}N label in the cyano group. The effect of charge on the cyano group in the ^{15}N NMR spectrum will be discussed in the last part of the discussion.

8.2.3 Quantum chemical calculations

In order to obtain additional information for understanding the chemical reactions and the NMR spectra of the anions of 1-cyano- and 5-cyanoacenaphthylene, quantum chemical calculations were performed. *Ab initio* methods were used to calculate the charge distribution, the HOMO coefficients and the shielding constants for the 1-cyanoacenaphthylene dianion (**1**$^{2-}$), the 1-cyano-2-hydroacenaphthylene anion ((2H)-**1**$^-$), the 5-cyano-1-hydroacenaphthylene anion ((1H)-**4**$^-$), and the 5-cyanoacenaphthylene dianion (**4**$^{2-}$) (Tables 2-5).

The calculations were carried out with the GAUSSIAN 94 suites of programs.[1] The geometries were fully optimised without symmetry restriction at the HF level by using the 6-31G(d,p) basis set, and characterised by frequency calculations. The shielding constants for the ^{13}C NMR spectra of **1**$^{2-}$, (2H)-**1**$^-$ and (1H)-**4**$^-$ were calculated and compared to the experimental data. The trends predicted by the calculations correlate well with those observed (Tables 2-4).

***Table 2**: Experimental and calculated ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), natural charges with the hydrogens summed into heavy atoms, natural π-electron charges and HOMO coefficients of 1-cyanoacenaphthylene dianion (**1**$^{2-}$).*

Carbon atom	δ ^{13}C (exp.)	δ ^{13}C (calc.)	Charge	π-el. charge	HOMO
1	64.0	54.9	-0.38	-0.36	-0.178
2	84.8	80.0	-0.18	-0.25	+0.213
3	99.3	82.5	-0.24	-0.26	-0.221
4	127.0	130.5	-0.01	+0.02	-0.055
5	92.0	66.4	-0.34	-0.39	+0.245
6	82.6	78.0	-0.28	-0.31	-0.208
7	129.3	125.6	-0.02	0	+0.061
8	93.4	88.5	-0.20	-0.22	+0.198
2a	135.8	123.8	-0.07	-0.03	+0.128
5a	145.2	149.5	+0.05	+0.12	-0.009
8a	128.2	136.6	-0.01	+0.03	-0.105
8b	137.0	127.4	-0.10	-0.10	-0.033
C(N)	131.8	122.1	+0.41	+0.16	-0.043
N			-0.63	-0.34	-0.132

Initially, the charges were calculated by the Mulliken Population Analysis (MPA) method. The MPA is in widespread use because it is conceptually simple and straightforward and it is easily coded into computer programs. In the MPA the electrons are distributed according to the atomic orbital occupancy. The charge distribution is derived from the gross atomic population, which is the sum of the net atomic population and half the overlap with all other atoms.[2] The calculated charges were, however, not in accordance with the observed and calculated chemical shifts. E.g., much negative charge (-0.24) was found in **1**$^{2-}$ at the center carbon atom 8b, although only a minor amount of charge should be present according to the ^{13}C NMR chemical shift. The unexpected high positive charge (+0.17) at carbon atom 5a could also not be rationalised. These errors in the calculations are probably caused by the arbitrary division of the overlap population equally between two atoms, regardless of possible differences in the coefficients, atom types, electronegativities, etc., involved.

***Table 3**: Experimental and calculated ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), natural charges with the hydrogens summed into heavy atoms, natural π-electron charges and HOMO coefficients of 1-cyano-2-hydroacenaphthylene anion ((2H)-**1**$^-$).*

Carbon atom	δ ^{13}C (exp.)	δ ^{13}C (calc.)	Charge	π-el. charge	HOMO
1	46.2	39.3	-0.43	-0.46	+0.340
2	37.8	33.5	+0.02		-0.048
3	115.3	105.5	-0.09	-0.11	+0.127
4	126.0	124.6	0	0	+0.006
5	119.9	112.3	-0.06	-0.08	-0.105
6	104.4	89.1	-0.18	-0.22	+0.242
7	130.7	136.0	+0.06	+0.07	+0.036
8	101.4	88.1	-0.18	-0.22	-0.243
2a	145.6	149.0	+0.04	+0.08	+0.015
5a	134.5	136.3	0	+0.06	-0.011
8a	155.2	161.2	+0.10	+0.14	-0.037
8b	139.1	131.7	-0.09	-0.06	-0.124
C(N)	137.5	115.5	+0.37	+0.15	+0.027
N			-0.55	-0.32	-0.191

An improved method, Natural Population Analysis (NPA), is less basis set dependent than the MPA and takes into account spatial components.[2] The NPA method attempts to define atomic orbitals depending on the chemical environment: the density matrix is used to calculate natural atomic orbitals (NAOs).[3] Summing the atomic populations over all NAOs centered on a particular atom gives the natural atomic population. In the determination of the charge distribution the contributions of the hydrogens were summed into the heavy atoms. The charges calculated with NPA (natural charges) correspond better with the chemical shifts.

In the calculation of the charge distribution both σ- and π-electrons are involved. However, in the chemical reactions of the anions, the σ-electrons play only a minor role. Therefore, the π-electron density should be used as a measure for the most reactive positions. For the sake of comparison the π-electron charges (= π-electron density - 1) are given in Tables 2-5.

***Table 4**: Experimental and calculated ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), natural charges with the hydrogens summed into heavy atoms, natural π-electron charges and HOMO coefficients of 5-cyano-1-hydroacenaphthylene anion ((1H)-**4**$^-$).*

Carbon atom	Δ ^{13}C (exp.)	δ ^{13}C (calc.)	Charge	π-el. charge	HOMO
1	38.3	33.7	-0.01		-0.038
2	93.4	77.6	-0.18	-0.26	+0.274
3	100.0	86.1	-0.20	-0.24	-0.240
4	134.1	144.1	+0.13	+0.11	-0.028
5	61.5	55.2	-0.41	-0.40	+0.303
6	114.0	110.2	-0.05	-0.08	-0.120
7	124.9	124.7	0	0	+0.040
8	114.7	105.0	-0.10	-0.11	+0.144
2a	145.4	148.8	+0.02	+0.09	+0.048
5a	136.4	140.9	+0.04	+0.09	-0.050
8a	143.7	145.0	+0.02	+0.06	-0.013
8b	141.0	132.6	-0.09	-0.06	-0.144
C(N)	132.1	115.9	+0.37	+0.15	+0.025
N			-0.53	-0.29	-0.167

***Table 5**: Calculated ^{13}C NMR chemical shifts (in ppm, given relative to TMS), natural charges with the hydrogens summed into heavy atoms, natural π-electron charges and HOMO coefficients of of 5-cyanoacenaphthylene anion (**4**$^{2-}$).*

Carbon atom	δ ^{13}C (calc.)	Charge	π-el. charge	HOMO
1	76.3	-0.25	-0.28	-0.199
2	89.8	-0.18	-0.19	+0.140
3	98.3	-0.15	-0.15	-0.170
4	124.8	0	-0.01	-0.121
5	47.6	-0.44	-0.43	+0.229
6	78.2	-0.26	-0.30	-0.210
7	119.9	-0.05	-0.03	+0.092
8	95.0	-0.17	-0.17	+0.186
2a	109.2	-0.15	-0.12	+0.195
5a	149.1	+0.08	+0.12	-0.055
8a	120.8	-0.10	-0.06	-0.136
8b	124.6	-0.10	-0.10	+0.016
C(N)	124.2	+0.40	+0.15	+0.057
N		-0.64	-0.36	-0.132

8.3 Discussion

1-Cyanoacenaphthylene

The dark orange dianion of 1-cyanoacenaphthylene ($\mathbf{1}^{2-}$) could be prepared in THF using sodium and ultrasonic vibration (see Chapter 7). In the experiments in which $\mathbf{1}^{2-}$ was treated with one equivalent of methyl iodide followed by water, two products were isolated: 1-cyano-1-methylacenaphthene (**3**) (50-80%) and N-(1-acenaphthylenylmethylene)methanamine (**2**) (10-20%). In the major product **3**, substitution had occurred at position 1.

In the reaction of the unsubstituted acenaphthylene dianion ($\mathbf{7}^{2-}$) with methyl iodide the reaction took place selectively at position 5. The cyano group thus has an extremely large effect on the reactivity of the dianion! The reaction of $\mathbf{7}^{2-}$ with methyl iodide was proven to proceed via the S_N2 mechanism and not via SET (see Chapters 2 and 4). The electron-demanding cyano group lowers the energy of the dianion and therefore diminishes the possibility that a reaction with an electrophile proceeds via the SET mechanism. It is therefore likely that the reaction of $\mathbf{1}^{2-}$ with methyl iodide will follow the S_N2 pathway.

Generally, this reaction occurs at the position bearing the highest charge and a high HOMO coefficient. From the ^{13}C NMR chemical shift values it can be concluded that carbon atom 1 is the carbon with the highest upfield shift and the highest difference in chemical shift compared to the neutral compound (Table 1). This indicates that carbon atom 1 is the position with the highest charge. Carbon atoms 2, 3, 5, 6 and 8 have also relatively low chemical shifts, which are in the order of 82.6-99.3 ppm.

The chemical shifts are rather well predicted by the *ab initio* calculations. The calculated values are somewhat lower than those experimentally observed. Only in the case of carbon atom 5 a large difference (25.6 ppm) with the experimental value was found.

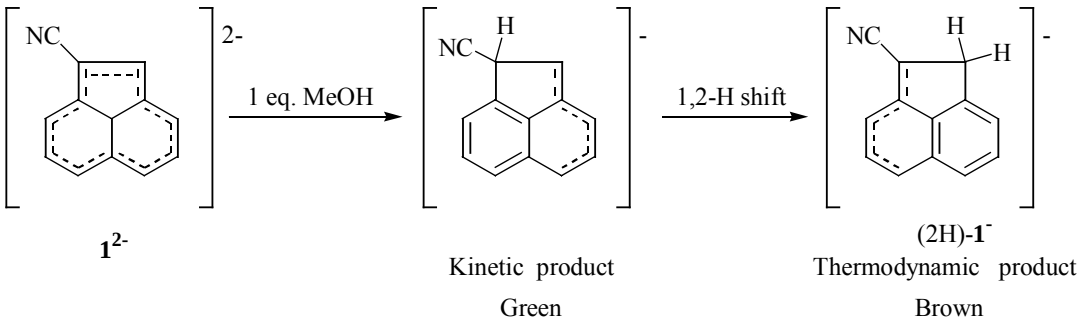
According to the calculations, carbon atoms 1 and 5 would be the carbon atoms with the highest charge. Because in the reaction of **1** with methyl iodide the π-electrons are involved in the bond formation process, the π-electron density should be regarded. The highest concentration of π-electrons is also found at carbon atoms 1 and 5. Although the HOMO coefficient on carbon atom 1 is not extremely large, the reaction of $\mathbf{1}^{2-}$ with methyl iodide takes place selectively at this carbon atom. The calculations might predict reaction to take place at position 5, but this is not observed. Probably, the cyano group has a larger effect on the charge distribution in the acenaphthylene dianion than can be predicted by these *ab initio* calculations.

The second product of the reaction of $\mathbf{1}^{2-}$ with methyl iodide is the result of reaction at the nitrogen of the cyano group. This is the first time that this kind of reductive alkylation is observed. The reaction can be rationalised by a large charge at the nitrogen atom. Although the HOMO-coefficient is rather low, the high charge will direct methylation to this position. More evidence for the charge at the nitrogen atom is given by ^{15}N NMR spectroscopy (see below).

The effect of the cyano group in $\mathbf{1}^{2-}$ can be compared with that in the 1-cyanophenalenyl anion. The introduction of a cyano group at position of the phenalenyl anion also caused an enormous upfield shift of carbon atom 1.[4] From the downfield shift of the other carbon atoms, it was concluded that charge shifted from the phenalenyl moiety to carbon atom 1 and the cyano group. However, semi-empirical calculations gave a lower charge and a lower HOMO coefficient at this carbon atom than was expected.

In the next experiment, one equivalent of methanol was added to $\mathbf{1}^{2-}$ followed by one equivalent of methyl iodide. Surprisingly, 1-cyano-1-methylacenaphthene (**3**) was again found as the major product. To understand the formation of **3**, the intermediate hydroanion was prepared in THF-d_8 and measured with NMR techniques. These NMR measurements identified the intermediate hydroanion as the 1-cyano-2-hydroacenaphthylene anion ((2H)-$\mathbf{1}^-$). However, in view of the previous experiment and the ^{13}C NMR chemical shifts, protonation of the dianion was expected to proceed at carbon atom 1. If the initial protonation does indeed take place at carbon atom 1, the formation of (2H)-$\mathbf{1}^-$ must be the result of a 1,2-H shift (Scheme 3). An explanation for this shift is that the kinetically formed hydroanion is converted into its thermodynamically more stable isomer.

Experimental evidence for this shift is a rapid double colour change after addition of the methanol. The orange solution of dianion changes to dark green if one equivalent of methyl iodide is added. The addition of methanol also results in a change to dark green, but this is immediately followed by a change to dark brown. This second colour change is almost instantaneous at room temperature, but takes up to 60 seconds at -70ºC.

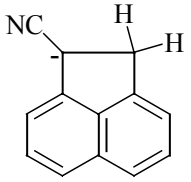


Scheme 3: *Formation of (2H)-$\mathbf{1}^-$ from $\mathbf{1}^{2-}$.*

Methylation of (2H)-$\mathbf{1}^-$ proceeds at position 1. Examination of the ^{13}C NMR spectrum of (2H)-$\mathbf{1}^-$ learns that C-1 is found at extremely high field (46.2 ppm). Therefore, much charge will be located at this carbon atom. Also the *ab initio* calculations predict a low chemical shift value for carbon atom 1. Although the calculations give lower chemical shift values for the carbons with the most charge than those observed experimentally, the order of appearance in the spectrum is correctly given.

The difference between experimental and calculated value is highest for carbon atoms 6 and 8, which are carbon atoms with relatively much charge. The charge, the π-electron charge and the HOMO coefficient distribution predict that carbon atom 1 is the most reactive. This is in agreement with the methylation experiment. Based on the calculated charge distribution (2H)-**1**$^-$ might be visualised with the charge located at carbon atom 1 and an uncharged naphthalene skeleton (Figure 2).

Although also much charge is found at the nitrogen atom of the cyano group, no reaction is observed at this position in (2H)-**1**$^-$. In contrast to the reaction of **1**$^{2-}$ at the nitrogen atom, in which a stable anion is formed, the reaction of (2H)-**1**$^-$ gives an energetically less favorable ketenimine. Reaction at position 1 gives directly the stable naphthalene skeleton. A second reason why **1**$^{2-}$ reacts at the nitrogen atom, in spite of a low HOMO coefficient, is that the difference in the amount of charge between C-1 and the nitrogen atom is larger in **1**$^{2-}$ than in (2H)-**1**$^-$.



(2H)-**1**$^-$

Figure 2: *Alternative representation of (2H)-**1**$^-$.*

5-Cyanoacenaphthylene

The hydroanion of 5-cyanoacenaphthylene ((1H)-**4**$^-$), was prepared and transferred into an NMR tube using the procedure as described for the hydroanion of 1-cyanoacenaphthylene. The hydroanion was identified to be the 5-cyano-1-hydroacenaphthylene anion ((1H)-**4**$^-$). The ^{13}C NMR spectrum shows that the signal of carbon atom 5 appears at high field (61.5 ppm). The signals of carbon atoms 2 and 3 are also found at relatively high field (93.4 and 100.0 ppm, respectively). The *ab initio* calculations predict the trend in the chemical shifts very well. Also in this case, the calculated values are lower than the experimental ones.

The *ab initio* calculations indicate that most charge is found at the nitrogen of the cyano group (-0.53), followed by carbon atoms 5 (-0.41), 3 (-0.20) and 2 (-0.18). The HOMO coefficients at these carbon atoms are also high: 0.303, -0.240 and 0.274, respectively. Reaction of the hydroanion of 5-cyanoacenaphthylene with methyl iodide takes place at positions 2 and 5 in a ratio of 3:1. Although carbon atom 5 has a higher charge and a higher HOMO coefficient than carbon atom 2, the reaction takes place preferentially at position 2. The reason might be that the reaction at position 2 gives a product with an acenaphthene skeleton, which is energetically profitable.

If the reaction takes place at position 5, 5-cyano-5-methyl-1,5-dihydroacenaphthylene is the initial product. 1,5-Dihydroacenaphthylenes rearrange easily into acenaphthene derivatives (see Chapter 2 and 3). In this case, there is no hydrogen at position 5 to move. However, the cyano group is a rather good leaving group. Elimination of HCN leads to the fully aromatic 5-methylacenaphthylene. This elimination of HCN under the basic conditions of the reaction, has been observed before in the reduction of benzonitriles.[5]

A solution of the dianion of 5-cyanoacenaphthylene was treated with one equivalent of methyl iodide. Surprisingly, the same products as in the reaction of (1H)-**4**$^-$ with methyl iodide, 5-cyano-2-methylacenaphthene (**5**) and 5-methylacenaphthylene (**6**), were isolated. This might lead to the conclusion that the dianion also reacts at positions 2 and 5.

Unfortunately, the dianion of 5-cyanoacenaphthylene **4**$^{2-}$ could not be prepared in an NMR tube. *Ab initio* calculations indicate that the highest charges and HOMO coefficients are located at carbon atoms 1, 5 and 6. Reaction at carbon atom 2 seems therefore very unlikely.

Because 5-cyano-1-hydroacenaphthylene anion is formed in the reaction of the dianion of 5-cyanoacenaphthylene with one equivalent of methanol, the most reactive position in the acenaphthylene dianion is position 1. Protonation at position 1 results in a pentadienyl anion structure stabilised with a cyano group at position 5. Therefore, methylation of the dianion would also be expected to proceed at carbon atom 1. This product was however not isolated.

Reaction at position 5 would, after release of a cyanide ion, result in 5-methylacenaphthylene **6**. Because the ratio between **5** and **6** is 3:1, it is very unlikely that the dianion is involved in the methylation process. This leads to the conclusion that the dianion is protonated even before methyl iodide is added and that the 5-cyano-1-hydroacenaphthylene anion ((1H)-**4**$^-$) is the reactive intermediate in the reaction with methyl iodide. This protonation might be the result of extreme sensitivity towards moisture of **4**$^{2-}$ or the hygroscopy of **4**.

^{15}N NMR spectroscopy

The *ab initio* calculations show that much charge is present on the nitrogen atoms of the cyano groups in both dianions and hydroanions of 1-cyano- and 5-cyanoacenaphthylene. To obtain experimental evidence for the charge on the nitrogen atoms, ^{15}N NMR spectroscopy was performed. [^{15}N]-1-cyanoacenaphthylene and [^{15}N]-5-cyanoacenaphthylene were prepared from the corresponding bromoacenaphthylenes with K^{15}CN and copper(I) iodide as a catalyst in DMF. Both compounds were converted into hydroanions and transferred into NMR tubes. ^{15}N NMR chemical shift values of the neutral and the hydroanionic systems are given in Table 6.

The ^{15}N chemical shift of the 1-cyano-2-hydroacenaphthylene anion ((2H)-**1**$^-$) is 241.6 ppm, at 23.3 ppm higher field than that of the neutral 1-cyanoacenaphthylene. The same shift to higher field is observed for 5-cyanoacenaphthylene ((1H)-**4**$^-$). The presence of charge on the nitrogen atom induces a shift to higher field.

To obtain experimental evidence for the upfield shift of a charged nitrogen, the allyl cyanide anion was used as a model compound. In this anion the cyano group is conjugated with an allyl moiety, comparable to the conjugation of the cyano group in (2H)-**1**$^-$ and (1H)-**4**$^-$. This anion must be compared with crotonitrile, in which the cyano group is conjugated with the double bond. The ^{15}N NMR chemical shift due to charge migration to the cyano group was determined. ^{15}N-labelled allyl cyanide was prepared from allyl bromide with KC^{15}N. The compound was converted into the allyl cyanide anion (^{15}N) by dissolving it in THF-d_8 and adding one equivalent of sodium hydride. Also in this case the signal of nitrogen shifts to higher field. This indicates that a ^{15}N shift to higher field is indeed an indication for the presence of negative charge at nitrogen.

A second system to study the effect of charge on the nitrogen of the cyano group is benzonitrile. The ^{15}N NMR chemical shifts of *para*-nitrobenzonitrile, benzonitrile and *para*-methoxybenzonitrile were found to appear at 265.5, 258.9 and 254.2 ppm, respectively. In *para*-nitrobenzonitrile, the electron-demanding nitro group will attract charge and thus the nitrogen of the cyano group will be more positively charged than in benzonitrile. The reverse effect, induced by a methoxy group, leads to more charge on the nitrogen and thus a shift to higher field.

Comparison of the results of the model compounds with those of 1-cyano-2-hydroacenaphthylene anion and 5-cyano-1-hydroacenaphthylene anion learns that in the hydroanions indeed more charge is present on the nitrogen atom than in the neutral systems. Our calculations predict a high charge at the nitrogen atom of the cyano group. This is in accordance with the ^{15}N NMR data. The calculated charge at the nitrogen atom in the 1-cyanophenalenyl anion was of the same order as those at the carbon atoms, indicating that only a small amount of charge was drawn to the nitrogen atom.[4]

Table 6: *^{15}N chemical shifts of cyano compounds in ppm, externally referenced to NH_3 (liq.), in $CDCl_3$.*

Compound	δ ^{15}N (exp.)
1-Cyanoacenaphthylene	264.93
1-Cyano-2-hydroacenaphthylene anion*	241.62
5-Cyanoacenaphthylene	263.95
5-Cyano-1-hydroacenaphthylene anion*	240.58
Allyl cyanide	250.4
Crotonitrile	265.1
Allyl cyanide anion*	253.4
p-Methoxybenzonitrile	254.2
Benzonitrile	258.9
p-Nitrobenzonitrile	265.5

* in THF-d_8

Pagani et al.[6] and Gao et al.[7] have studied the effect of the cyano group in carbanions. Both research groups conclude that the cyano group has only a weak charge demand and thus only a small amount of charge would reside at the nitrogen atom. However, the exact role of the cyano group is very difficult to understand. The large effect of the cyano group in the acenaphthylene anions might be due to conjugation with the π-electron system.

8.4 Conclusions

The charge distribution in the 1-cyanoacenaphthylene dianion is influenced strongly by the presence of the cyano group: reaction with methyl iodide takes place at position 1 and, to a less extent, at the nitrogen of the cyano group. Also ^{13}C NMR spectroscopy shows that the highest charge is found at carbon atom 1. The chemical shifts are rather well predicted by *ab initio* calculations. The natural charge distribution and the π-electron densities can be used to understand the chemical reactivity and the ^{13}C NMR chemical shifts. The HOMO coefficients are less in accordance with the experiments. It should be mentioned that the calculations ignore the effects of solvent, counter ion, temperature and concentration. Possibly, the cyano group has a stronger effect than can be predicted by the calculations. Protonation of $\mathbf{1}^{2-}$ takes place initially at position 1, but the hydroanion rearranges via a 1,2-H shift to the thermodynamically more stable 1-cyano-2-hydroacenaphthylene anion ((2H)-$\mathbf{1}^-$). (2H)-$\mathbf{1}^-$ reacts with methyl iodide selectively at position 1. This is also the carbon atom with the highest charge according to ^{13}C NMR and *ab initio* calculations.

In the 5-cyanoacenaphthylene dianion the charge distribution is also influenced by the cyano group. Protonation with one equivalent of methanol leads to 5-cyano-1-hydroacenapthylene anion ((1H)-$\mathbf{4}^-$). (1H)-$\mathbf{4}^-$ reacts with methyl iodide at positions 2 and 5, resulting in the formation of 5-cyano-2-methylacenaphthene and, after elimination of HCN, 5-methylacenaphthylene, respectively. ^{13}C NMR spectroscopy of (1H)-$\mathbf{4}^-$ predicts the highest charge at carbon atoms 2, 3 and 5, which is in accordance with the calculations.

^{15}N NMR spectroscopy of (2H)-$\mathbf{1}^-$ and (1H)-$\mathbf{4}^-$ shows that more charge is present on the nitrogen atom in the hydroanions than in the neutral parent compounds.

8.5 Experimental section

General: Acenaphthylene (Aldrich, 75%) was purified by treatment with DDQ and filtration over silica. The reagents were obtained from Acros, Aldrich and Merck and used without further purification. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3A, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. The 600 MHz ^{1}H NMR spectra and 150 MHz ^{13}C NMR spectra were recorded on a Bruker 600-DMX spectrometer. All chemical shift data (δ) are given in ppm relative to

tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra. For the determination of the coupling constants we used the simulation program PERCH.[8]

General procedure: Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. The substituted acenaphthylene (5 mmol) was added, together with 0.3 g (13 mmol) of freshly cut sodium. Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0°C, the dianions were formed.

Reaction of the 1-cyanoacenaphthylene dianion with methyl iodide:
The 1-cyanoacenaphthylene dianion (**1**$^{2-}$) was prepared according to the general procedure. The orange solution was cooled to -70ºC and methyl iodide (0.31 ml, 5 mmol) was added. After stirring for 15 minutes at room temperature the solution was cooled to -70ºC again and quenched with water. After normal work-up a mixture of two products was obtained. Silica gel column chromatography (light petroleum, boiling range 40-60ºC and toluene) gave N-(1-acenaphthylenylmethylene)methanamine (**2**) (10-20%) and 1-cyano-1-methylacenaphthylene (**3**) (50-80%).

*N-(1-acenaphthylenylmethylene)methanamine (**2**)*
^{1}H NMR ($CDCl_3$, TMS) : δ = 7.62-7.59 (m, 3H, H-5, H-6 and H-C=NMe), 7.50-7.44 (m, 2H, H-4 and H-7), 7.26-7.19 (m, 2H, H-3, H-8 and H-2), 3.39 (s, 3H, Me-Z), 3.25 (s, 3H, Me-E).
^{13}C NMR ($CDCl_3$) : δ = 127.9 (2C), 127.8, 122.6, 122.4, 119.3, 117.0, 29.7 (quaternary C-s were not observed).
IR (pure): 3020, 2940, 2900, 2870, 1600, 1590, 1450, 1360, 800, 780.
GC-MS: not possible because of decomposition of the product.

*1-cyano-1-methylacenaphthene (**3**)*
^{1}H NMR ($CDCl_3$, TMS) : δ = 7.73 (dd, $J_{6,7}$ = 7.8, $J_{6.8}$ = 1.0, 1H, H-6), 7.67 (d, $J_{4,5}$ = 8.3, 1H, H-5), 7.53 (dd, $J_{6,7}$ = 7.8, $J_{7,8}$ = 7.3, 1H, H-7), 7.51 (dd, $J_{3,4}$ = 7.2, $J_{4,5}$ = 8.3, 1H, H-4), 7.49 (dd, $J_{7,8}$ = 7.3, $J_{6.8}$ = 1.0, 1H, H-8), 7.30 (d, $J_{3,4}$ = 7.2, 1H, H-3), 4.01 (d, $J_{2,2'}$ = -17.2, 1H, H-2), 3.46 (d, $J_{2,2'}$ = -17.2, 1H, H-2), 1.78 (s, 3H, Me).
^{13}C NMR ($CDCl_3$) : δ = 144.5 (C-2a or C-8a), 139.8 (C-2a or C-8a), 139.3 (C-8b), 131.4 (C-5a), 128.5 (C-4), 128.1 (C-7), 124.9 (C-6), 123.3 (C-5), 120.1 (C-3), 118.9 (C-8), 45.8 (C-2), 40.6 (C-1), 28.2 (Me), CN was not observed.
Exact mass calculated for $C_{14}H_{11}N$: 193.0898 m/z; found: 193.0892. MS m/z (%): 193 (48), 178 (100), 165 (10), 151 (14).

Reaction of the 1-cyanoacenaphthylene hydroanion with methyl iodide:
The 1-cyanoacenaphthylene dianion (**1**$^{2-}$) was prepared according to the general procedure. The orange solution was cooled to -70ºC and methanol (0.15 ml, 5 mmol) was added. After stirring for 15 minutes at room temperature, the solution was again cooled to -70ºC; methyl iodide (0.31 ml, 5 mmol) was added and stirring was continued at room temperature for 30 minutes. The reaction was quenched with water. After normal work-up the crude product was obtained. Silica gel column chromatography (light petroleum, boiling range 40-60ºC and toluene) gave 1-cyano-1-methylacenaphthylene (**3**) (60-90%).

Reaction of the 5-cyanoacenaphthylene hydroanion with methyl iodide:
The 5-cyanoacenaphthylene dianion (**4**$^{2-}$) was prepared according to the general procedure. The orange solution was cooled to -70ºC and methanol (0.15 ml, 5 mmol) was added. After stirring for 15 minutes at room temperature, the solution was again cooled to -70ºC; methyl iodide (0.31 ml, 5 mmol) was added and stirring was continued at room temperature for 30 minutes. The reaction was quenched with water. After normal work-up a mixture of two products was obtained. Silica gel column chromatography (light petroleum, boiling range 40-60ºC and toluene) gave 5-methylacenaphthylene (**6**) (15-20%) and 5-cyano-2-methylacenaphthene (**5**) (45-60%) in a ratio of 1:3. *5-Methyl-acenaphthylene (**6**):* See Chapter 7

*5-Cyano-2-methylacenaphthene (**5**)*
^{1}H NMR ($CDCl_3$, TMS) : δ = 7.75 (d, $J_{6,7}$ = 8.2, 1H, H-6), 7.75 (d, $J_{3,4}$ = 7.2, 1H, H-4), 7.54 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 7.0, 1H, H-7), 7.30 (d, $J_{7,8}$ = 7.0, 1H, H-8), 7.19 (d, $J_{3,4}$ = 7.2, 1H, H-3), 3.65 (m, 1H, H-2), 3.59 (dd, $J_{1,1'}$ = -16.8, $J_{1,2}$ = 7.8, 1H, H-1), 2.90 (dd, $J_{1,1'}$ = -16.8, $J_{1',2}$ = 3.2, 1H, H-1'), 1.39 (d, $J_{2,Me}$ = 7.4, 3H, Me).
^{13}C NMR ($CDCl_3$): δ = 157.0 (C-2a), 145.1 (C-8a), 137.2 (C-8b), 134.3 (C-4), 130.4 (C-5a), 130.2 (C-7), 120.8 (C-8), 119.6 (C-6), 117.8 (CN), 117.7 (C-3), 104.4 (C-5), 39.2 (C-1), 38.1 (C-2), 20.8 (Me).
Exact mass calculated for $C_{14}H_{11}N$: 193.0898 m/z; found: 193.0891. MS m/z (%): 193 (68), 178 (100), 165 (8), 151 (22).

Synthesis of ^{15}N and ^{13}C labelled compounds:
To a solution of (1- or) 5-bromoacenaphthylene (5.0 mmol) in dry dimethylformamide under an argon atmosphere copper(I) iodide (10.0 mmol) and potassium cyanide with either a ^{13}C or ^{15}N label (5.0 mmol) were added. The reaction mixture was heated at reflux (153°C) for 7 hours. The mixture was allowed to cool down to 70°C and a solution of iron(III) chloride hexahydrate (3.0 g, 11 mmol) in hydrogen chloride (35%, 30 ml) and water (15 ml) was added carefully. The mixture was stirred for 1 hour at 70ºC and then allowed to cool down to room temperature. Diethyl ether and water were added. The solution was filtered over hyflo and the layers were separated. The water layer was extracted with diethyl ether. The combined organic layers were washed with a saturated solution of potassium carbonate, a saturated solution of sodium chloride and water. The solution

was dried over magnesium sulphate and the solvent was evaporated. Column chromatography (silica; petroleum ether/toluene (5:1)) yielded (1- or) 5-cyanoacenaphthylene in 70-95% yield.

1-([^{13}C]cyano)acenaphthylene

1-Bromoacenaphthylene (1.02 g, 4.42 mmol) was converted into 1-([^{13}C]cyano)acenaphthylene (0.67 g, 3.8 mmol, 86%) using the procedure described above.

The ^{1}H NMR spectrum was identical to that of 1-cyanoacenaphthylene (Chapter 7).

^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 139.3 (C-2), 136.6 (d, $J_{1,CN}$ = 45, C-1), 135.5 (d, $J_{2a,\ CN}$ = 7, C-8a), 135.4 (C-2a), 130.4 (C-5), 128.7 (C-6), 128.1 (C-4), 127.8 (C-5a), 127.7 (C-7 and C-8), 126.5 (C-8b), 124.0 (C-3), 115.6 (-CN).

1-([^{15}N]cyano)acenaphthylene

1-Bromoacenaphthylene (1.10 g, 4.46 mmol) was converted into 1-([^{15}N]cyano)acenaphthylene (0.77 g, 4.4 mmol, 91%) using the procedure described above.

The ^{1}H NMR and ^{13}C NMR spectra were identical to the spectra of the unlabelled 1-cyanoacenaphthylene (**1**). However in the ^{13}C NMR spectrum the following extra coupling constants were observed due to the introduction of the ^{15}N label: $J_{C\text{-}N}$ = -18.4, $J_{1,CN}$ = 7.9.

^{15}N NMR: δ = 264.93

5-([^{13}C]cyano)acenaphthylene

5-Bromoacenaphthylene (1.09 g, 4.42 mmol) was converted into 5-([^{13}C]cyano)acenaphthylene (0.75 g, 4.2 mmol, 90%) using the procedure described above.

The NMR spectra were identical to those of the unlabelled 5-cyanoacenaphthylene (**4**). The following extra couplings due to the ^{13}C-label were found:

^{1}H NMR: $J_{4,CN}$ = 6.5.

^{13}C NMR: $J_{5,CN}$ = 82, $J_{3,CN}$ = 6, $J_{5a,CN}$ = 5.

5-([^{15}N]cyano)acenaphthylene

5-Bromoacenaphthylene (1.10 g, 4.4 mmol) was converted into 5-([^{15}N]cyano)acenaphthylene (0.72 g, 4.1 mmol, 86%) using the procedure described above.

The ^{1}H NMR and ^{13}C NMR spectra were identical to the spectra of the unlabelled 5-cyanoacenaphthylene (**4**). However in the ^{13}C NMR spectrum the following extra coupling constants were observed due to the introduction of the ^{15}N label: $J_{C\text{-}N}$ = -17.7, $J_{5,CN}$ = 2.8.

^{15}N NMR: δ = 263.95.

Preparation of the 1-cyanoacenaphthylene dianion in an NMR tube:

The 1-cyanoacenaphthylene dianion (**1**$^{2-}$) was prepared in THF-d_8 under argon using the general procedure. The solution was allowed to warm to room temperature before transferring it with a

syringe into an NMR tube. The tube was sealed with a rubber stopper and parafilm. The whole procedure must be performed with carefully dried equipment and under argon. Traces of water already protonate the dianion converting it into the hydroanion.

Dianion of 1-cyanoacenaphthylene (**1**$^{2-}$)*:*

^{1}H NMR (THF-d_8) : δ = 5.60 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 6.1, 1H, H-4), 5.44 (dd, $J_{6,7}$ = 6.6, $J_{7,8}$ = 7.6, 1H, H-7), 5.11 (d, $J_{3,4}$ = 7.2, 1H, H-3), 4.53 (s, 1H, H-2), 4.51 (d, $J_{7,8}$ = 7.6, 1H, H-8), 4.28 (d, $J_{4,5}$ = 6.1, 1H, H-5), 3.76 (d, $J_{6,7}$ = 6.6, 1H, H-6).

^{13}C NMR (THF-d_8) : δ = 145.2 (C-5a), 137.0 (C-8b), 135.8 (C-2a), 131.8 (CN), 129.3 (C-7), 128.2 (C-8a), 127.0 (C-4), 99.3 (C-3), 93.4 (C-8), 92.0 (C-5), 84.8 (C-2), 82.6 (C-6), 64.0 (C-1).

Dianion of 1-([^{13}C]cyano)acenaphthylene:

The ^{1}H NMR and ^{13}C NMR spectra were identical to the spectra of the unlabeled 1-cyanoacenaphthylene dianion. In the ^{13}C NMR spectrum an extra coupling between C-1 and ^{13}CN was observed. $J_{1,\,CN}$ = 87.2 Hz.

Preparation of the hydroanion of 1-cyanoacenaphthylene in an NMR tube.

The 1-cyanoacenaphthylene dianion (**1**$^{2-}$) was prepared in THF-d_8 under argon using the general procedure. At 0ºC one equivalent of methanol was added and the solution was stirred for a further 15 minutes. The solution was allowed to warm to room temperature before transferring it with a syringe into an NMR tube. The tube was sealed with a rubber stopper and parafilm. The whole procedure must be performed with carefully dried equipment and under argon.

*1-Cyano-2-hydroacenaphthylene anion ((2H)-**1**$^{-}$)*

^{1}H NMR (THF-d_8) : δ = 6.93-6.85 (m, 2H, H-4 and H-5), 6.73-6.68 (m, 2H, H-3 and H-7), 6.01 (d, $J_{6,7}$ = 7.8, 1H, H-6), 5.85 (d, $J_{7,8}$ = 7.1, 1H, H-8), 3.80 (s, 2H, H-2).

^{13}C NMR (THF-d_8) : δ = 155.2 (C-8a), 145.6 (C-2a), 139.1 (C-8b), 137.5 (CN), 134.5 (C-5a), 130.7 (C-7), 126.0 (C-4), 119.9 (C-5), 115.3 (C-3), 104.4 (C-6), 101.4 (C-8), 46.2 (C-1), 37.8 (C-2).

[^{15}N]-1-cyano-2-hydroacenaphthylene anion

The ^{1}H NMR and ^{13}C NMR spectra were identical to the spectra of the unlabelled 1- cyano-2-hydroacenaphthylene anion*((2H)-**1**$^{-}$)*. In the ^{13}C NMR spectrum no coupling between C-1 and C^{15}N was observed. J_{CN} = -17.9.

^{15}N NMR (THF-d_8) : δ = 241.62

Preparation of the 5-cyanoacenaphthylene dianion and 5-cyano-1-hydroacenaphthylene anion in an NMR tube:

The 5-cyanoacenaphthylene dianion was prepared in THF-d_8 under argon using the general procedure. The solution was allowed to warm to room temperature before tranferring it with a syringe into an NMR tube. The tube was sealed with a rubber stopper and parafilm. Although the whole procedure was performed with carefully dried equipment and under argon, the dianion became protonated to result in the 5-cyano-1-hydroacenaphthylene anion.

The 5-cyano-1-hydroacenaphthylene anion was also prepared by adding one equivalent of methanol to a solution of 5-cyanoacenaphthylene dianion at 0ºC. The solution was allowed to warm to room temperature before transferring it with a syringe into an NMR tube.

*1-Hydro-5-cyanoacenaphthylene anion ((1H)-**4**$^-$):*

^{1}H NMR (THF-d_8) : δ = 6.53 (m, 1H, H-7), 6.37-6.35 (m, 2H, H-6 and H-8), 6.02 (d, $J_{3,4}$ = 8.5, 1H, H-4), 4.99 (d, $J_{3,4}$ = 8.5, 1H, H-3), 4.20 (t, 1H, H-2), 3.08 (d, 2H, H-1), $J_{1,2}$ was observed but could not be determined.

^{13}C NMR (THF-d_8) : δ = 145.4 (C-2a), 143.7 (C-8a), 141.0 (C-8b), 136.4 (C-5a), 134.1 (C-4), 132.1 (CN), 124.9 (C-7), 114.7 (C-8), 114.0 (C-6), 100.0 (C-3), 93.4 (C-2), 61.5 (C-5), 38.3 (C-1).

1-Hydro-5-([^{13}C]cyano)acenaphthylene anion:

The ^{1}H NMR and ^{13}C NMR spectra were identical to the spectra of the unlabelled 1-hydro-5-cyanoacenaphthylene anion *((1H)-**4**$^-$)*. In the ^{1}H NMR spectrum a small coupling of the ^{13}C with H-4 is observed. In the ^{13}C NMR spectrum no couplings between C-5a and ^{13}CN and between C-3 and ^{13}CN were observed. $J_{5,\,CN}$ = 89 Hz.

1-Hydro-5-([^{15}N]cyano)acenaphthylene anion:

The ^{1}H NMR and ^{13}C NMR spectra were identical to the spectra of the unlabelled 1-hydro-5-cyanoacenaphthylene anion *((1H)-**4**$^-$)*. In the ^{13}C NMR spectrum no coupling between C-5 and C^{15}N was observed.

^{15}N NMR (THF-d_8) : δ = 240.58.

Allyl [^{15}N]cyanide:

Allyl bromide was converted into allyl [^{15}N]cyanide using the procedure of Van Liempt et al.[9] The ^{1}H NMR and ^{13}C NMR spectra were similar to those reported previously.

^{15}N NMR ($CDCl_3$) : δ = 250.4.

Preparation of allyl [^{15}N]cyanide anion:

Allyl cyanide (0.24 ml, 3 mmol) was dissolved in anhydrous THF-d_8 (1 ml) under an argon atmosphere and sodium hydride (0.14 g, 3.5 mmol) was added at 0ºC. After stirring for 30 minutes, the solution was transferred into an NMR tube and sealed under argon.

Allyl [^{15}N]cyanide anion

^{1}H NMR (THF-d_8) : δ = 2.5 (m, 1H, H-3), 1.25 (m, 2H, H-4), 1.85 (m, 1H, H-2) (broad signals).

^{13}C NMR (THF-d_8) : δ = 30.6 (C-4), 18.9 (C-3), 14.4 (C-1).

^{15}N NMR (THF-d_8) : δ = 253.4.

Crotonitrile

^{15}N NMR ($CDCl_3$) : δ = 265.1 (natural abundance).

Synthesis of 4-nitrobenzo[^{15}N]nitrile:

4-Bromonitrobenzene (0.3017 g, 1.49 mmol) was converted into 4-nitrobenzo[^{15}N]nitrile with potassium [^{15}N]cyanide (0.1120 g, 1.69 mmol) using the procedure as described above, yielding 0.212 g (1.43 mmol, 96%) of 4-nitrobenzo[^{15}N]nitrile.

4-Nitrobenzo[^{15}N]nitrile

^{1}H NMR ($CDCl_3$) : δ = 8.14 (d, $J_{2,3} = J_{5,6} = 8.9$, 2H, H-2 and H-6), 8.35 (d, $J_{2,3} = J_{5,6} = 8.9$, 2H, H-3 and H-5).

^{13}C NMR ($CDCl_3$) : δ = 149.9 (C-1), 134.1 (C-3 and C-5), 124.3 (C-2 and C-6), 117.3 (d, $J_{CN} = -15.4$, CN), 117.2 (d, $J_{4,N} = 5.5$, C-4).

^{15}N NMR (DMSO-d_6): δ = 265.5 (SR DMSO = -62.8).

p-Methoxybenzonitrile

^{15}N NMR ($CDCl_3$) : δ = 254.2 (natural abundance).

Benzonitrile

^{15}N NMR ($CDCl_3$) : δ = 258.9 (natural abundance).

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9

Some effects of the methyl group on the acenaphthylene dianion

9.1 Introduction

Alkali metal reduction of substituted acenaphthylenes in pure THF gives the corresponding acenaphthenes in high yields (Chapter 7). In this reduction process the parent compound is converted into its dianion with sodium in THF and subsequently protonated by water. Cyclic voltammetric experiments showed that substituents have a large effect on the reduction potential of acenaphthylene: introduction of a cyano group results in a lower reduction potential whereas a methyl group increases the reduction potential.

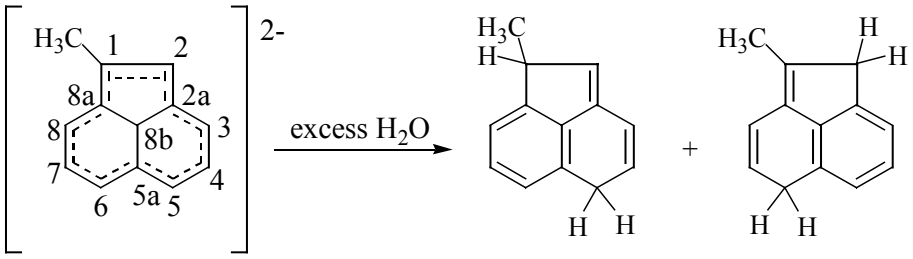
An electron-withdrawing substituent also has a large effect on the reactivity and the charge distribution of the dianion of acenaphthylene (see Chapter 8). The anions of 1- and 5-cyanoacenaphthylene were thoroughly studied by means of methylation experiments, NMR spectroscopy and *ab initio* calculations. It can be expected that the influence of electron-donating groups on the reactivity and the properties of the anions differs from that of electron-withdrawing groups.

In this chapter the initial results of a comparative study of the perturbation of the conjugated anions by methyl groups are described for 1-methylacenaphthylene (**1**) and 5-methylacenaphthylene (**5**).

9.2 Results and discussion

9.2.1 1-Methylacenaphthylene

The dianion of 1-methylacenaphthylene ($\mathbf{1}^{2-}$) was prepared according to the method described before (Chapter 2). $\mathbf{1}^{2-}$ was treated with water at -70ºC and the work-up procedure was performed very carefully, i.e. the temperature was kept below 30ºC. The major products were the 1,5-dihydroacenaphthylene derivatives: 1-methyl-1,5-dihydroacenaphthylene (**2**) and 1-methyl-2,6-dihydroacenaphthylene (**3**) in a ratio of 5:3 (Scheme 1). The official name of **3** is 2-methyl-1,5-dihydroacenaphthylene, but for the sake of comparison the numbering of the parent compound is retained. Initially, only traces of 1-methylacenaphthene (**4**) were present in the product mixture, but after exposure to air larger amounts of **4** were observed.

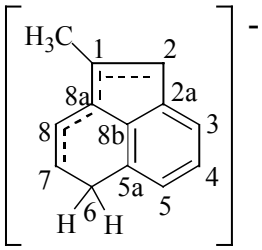


1^{2-} **2** **3**

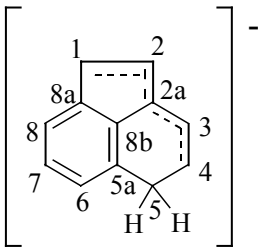
Scheme 1: *Reaction of the 1-methylacenaphthylene dianion with water.*

The protonation of **1**$^{2-}$ thus takes place at both positions 5 and 6, the same as where the reaction proceeds in the unsubstituted acenaphthylene dianion (**7**$^{2-}$). This result suggests that the methyl group at position 1 does not cause an extensive redistribution of charge in the acenaphthylene dianion (**7**$^{2-}$). In **7**$^{2-}$ the positions 5 and 6 are equivalent. Introduction of a methyl group at position 1 induces asymmetry in the structure. If the methyl group did not have any effect on the reaction of **1**$^{2-}$ with protons, **2** and **3** would be formed in equal amounts. However, the yield of **2** is almost twice that of **3**, indicating that the methyl group does indeed have a small effect on the reactivity of **1**$^{2-}$.
Attempts to prepare **1**$^{2-}$ in THF-d_8 and transfer the solution into an NMR tube failed. In these cases only the hydroanion of 1-methylacenaphthylene was formed. Addition of one equivalent of methanol to a solution of **1**$^{2-}$ and subsequent transfer into an NMR tube also resulted in the formation of the hydroanion. The measured NMR spectra (^{1}H and ^{13}C) were similar to those of the 5-hydroacenaphthylene anion ((5H)-**7**$^{-}$) (Chapter 2). The ^{1}H and ^{13}C NMR spectra were assigned completely using H-H and C-H inverse COSY techniques. Surprisingly, only one of the two expected isomers was observed: the 1-methyl-6-hydroacenaphthylene anion ((6H)-**1**$^{-}$) (Figure 1). A small amount of **4** was also present in the solution. This can be explained by the presence of excess protons in the reaction mixture.

The difference between the reaction with excess water and the reaction with one equivalent of methanol is that in the former reaction the kinetic products are formed. After addition of one proton, the resulting hydroanion immediately reacts with a second proton. In the case of the reaction with one equivalent of methanol, the initially formed hydroanions are converted into the thermodynamically most stable isomer. Comparison of the two possible isomers of the 5-hydroacenaphthylene anion, with the methyl group at position 1 or at position 2, indicates that (6H)-**1**$^{-}$ will have the lowest energy because the electron-donating methyl group is then located at an uncharged carbon atom. During the NMR measurements only this hydroanion is observed.



(6H)-**1**$^-$



(5H)-**7**$^-$

Figure 1: *6-Hydro-1-methylacenaphthylene anion (6H)-**1**$^-$ and 5-hydroacenaphthylene anion (5H)-**7**$^-$.*

Table 1: *Experimental ^{13}C NMR chemical shifts of (6H)-**1**$^-$ compared to the corresponding shifts of the 5-hydroacenaphthylene anion ((5H)-**7**$^-$) (in ppm, given relative to the 25.3 ppm signal of THF).*

(6H)-**1**$^-$		(5H)-**7**$^-$	
Carbon atom	δ ^{13}C (exp.)	Carbon atom	δ ^{13}C (exp.)
1	122.7	2	112.1
2	91.9	1	90.7
3	114.0	8	115.5
4	117.3	7	118.1
5	110.0	6	110.5
6	32.0	5	32.1
7	108.8	4	110.6
8	125.1	3	127.0
2a	127.7	8a	128.2
5a	128.4	5a	129.7
8a	104.9	2a	106.2
8b	130.7	8b	130.3
CH_3	13.4		

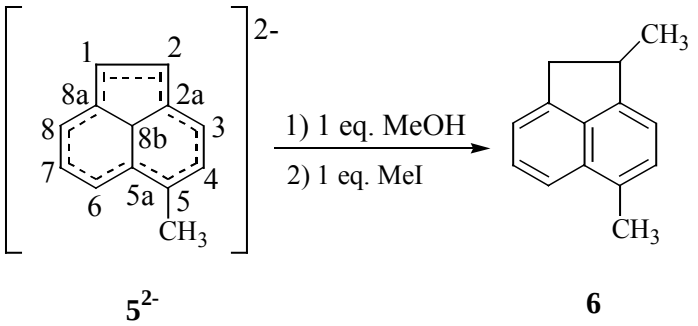
Comparison of the ^{13}C NMR chemical shifts of (6H)-**1**$^-$ with those of (5H)-**7**$^-$ learns that the shifts only differ 0.1-2.2 ppm (See Table 1)! (Of course carbon atom 1 is shifted more to lower field, due to its quaternary character.) This implies that the charge distribution in (6H)-**1**$^-$ is equal to that of (5H)-**7**$^-$ and thus that the methyl group at C-1 barely perturbs the conjugated system. This small effect of a methyl group at an uncharged position in an anion was observed earlier in the case of the phenalene anion.[1] In the case of the 2-methylphenalene anion the positions *ortho* to the methyl group are more reactive than the other charged positions. It would be interesting to study the

reactivity of (6H)-**1**$^-$ in the reaction with alkyl halides and see if methylation takes place at positions 2 and 8a.

The next step would be methylation experiments with **1**$^{2-}$ and (6H)-**1**$^-$. It is expected that **1**$^{2-}$ will react at both positions 5 and 6 in almost the same ratio as was observed in the protonation experiment. Reaction of (6H)-**1**$^-$ with methyl iodide will probably result in the selective formation of 1,2-dimethylacenaphthene.

9.2.2 5-Methylacenaphthylene

5-Methylacenaphthylene (**5**) was converted with two equivalents of sodium into its green dianion (**5**$^{2-}$). Treatment of **5**$^{2-}$ with one equivalent of methanol, followed by one equivalent of methyl iodide gave 2,5-dimethylacenaphthene (**6**) (original numbering retained) as the only product (Scheme 9.2). Reaction of **5**$^{2-}$ with one equivalent of methyl iodide, followed by water, gave also **6**. It is likely that the dianion was already protonated before the methyl iodide was added, because the colour of the solution turned from dark brownish green to brown after addition of the methyl iodide, indicating that no more anion is present.

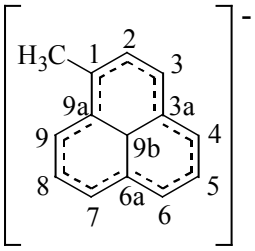


5^{2-} **6**

Scheme 2: *Reaction of* **5**$^{2-}$ *with one equivalent of methanol followed by one equivalent of methyl iodide.*

The initial step in the formation of **6** is the protonation of **5**$^{2-}$. Then the resulting hydroanion reacts with methyl iodide at position 2 selectively. If the charge distribution in the acenaphthylene dianion is not much perturbed by the introduction of the methyl group at position 5, protonation may proceed at position 5 or position 6. Because the reaction of the resulting hydroanion with methyl iodide proceeds selectively at carbon atom 2, **5**$^{2-}$ must be protonated at position 6 exclusively. Next to the charge and HOMO coefficient distribution, steric factors must be taken into account in the case of reactions with substituted carbanions. Steric hindrance by the methyl group in **5**$^{2-}$ will have a negative effect on the reactivity of carbon atom 5, which is bearing the methyl group.

The reactivity of $\mathbf{5}^{2-}$ can be compared to that of the 1-methylphenalene anion ($\mathbf{8}^{-}$, Figure 2). In $\mathbf{8}^{-}$, the carbon atom attached to the methyl group (C-1) did not undergo alkylation. In contrast to C-6 in $\mathbf{5}^{2-}$, the carbon atom at the *peri* position (C-9) in $\mathbf{8}^{-}$ was also less reactive towards alkylation than the unhindered atoms (C-3, C-4, C-6, C-7).[1] The higher reactivity of C-6 in $\mathbf{5}^{2-}$ than that of C-9 in $\mathbf{8}^{-}$ might be the result of a different geometry of the *ipso* and *peri* carbon atoms in $\mathbf{5}^{2-}$, caused by the five-membered ring. A second important point is that the positions in the unsubstituted phenalene anion are identical but that C-5 and C-6 have a much higher reactivity than the other carbon atoms in the unsubstituted acenaphthylene dianion and thus that C-6 will be more reactive in $\mathbf{5}^{2-}$ in comparison with the other carbon atoms.



$\mathbf{8}^{-}$

Figure 2: *1-Methylphenalene anion.*

The 5-methylacenaphthylene dianion was prepared in THF-d_8 and transferred into an NMR tube as described before (Chapter 8). The ^{1}H NMR spectrum consisted of very broad signals. The ^{13}C NMR spectrum (APT) was however very sharp and clearly showed the presence of 5 quaternary carbon atoms and 8 carbon atoms bonded to 1 or 3 hydrogen atoms. This indicates that the dianion is indeed formed. The ^{13}C NMR spectrum of the hydroanion would contain an extra C_q or CH_2 (C-6, in case of the 5-hydroanion) or an extra CH or CH_3 (C-5, in case of the 6-hydroanion), which is not observed.

Assignment of the spectra was very difficult, because the broadness of the signals made it impossible to obtain relevant information from the H-H COSY and C-H inverse COSY spectra. Complete assignment based on comparison with the spectra of the unsubstituted acenaphthylene dianion and the calculated NMR spectrum was therefore not possible. The only carbon atoms which could be assigned with certainty are C-6 (44.35), C-5 (99.1) and the methyl group (15.3). Although steric interaction with the methyl group already induces an upfield shift for the *peri* carbon atom, as was already observed in $\mathbf{8}^{-}$,[1] the very high upfield shift of carbon atom 6 indicates that much charge is present at this position. This is in accordance with the proposed reaction path for the reaction of $\mathbf{5}^{2-}$ with one equivalent of methanol followed by one equivalent of methyl iodide.

In order to obtain additional information about $\mathbf{5}^{2-}$, quantum chemical calculations were performed. *Ab initio* methods were used to calculate the charge distribution, the HOMO coefficients and the shielding constants for the 5-methylacenaphthylene dianion ($\mathbf{5}^{2-}$) (Table 2). The calculations

were carried out with the GAUSSIAN 94 suites of programs.[2] The geometries were fully optimised without symmetry restriction at the HF level by using the 6-31G(d,p) basis set, and characterised by frequency calculations. As was already discussed in Chapter 8, better results would be obtained if the calculation were performed using the NPA instead of the MPA. However, this charge distribution can be used as a rough indication where much charge is present. The highest charge is located at carbon atoms 1, 2 and 6. The highest HOMO coefficients are found at carbon atoms 5 and 6. It is thus very likely that the most reactive position is carbon atom 6.

The calculated ^{13}C NMR chemical shifts of C-5 and C-6 deviate appreciably from those observed experimentally. The calculated values closely resemble those of the unsubstituted acenaphthylene dianion (**7**$^{2-}$) (Chapter 2, Table 1). Obviously, the influence of the methyl group is underestimated in the calculations. This underestimation of a substituent effect was already seen in the cyano-substituted dianions (Chapter 8). The calculated charge distribution indicates, however, that C-6 bears much more charge than C-5 and should be found at higher field. On the basis of the experimentally determined spectrum, it may be concluded that the methyl group at C-5 pushes a substantial amount of charge to carbon atom 6.

***Table 2**: Mulliken charges with the hydrogens summed into heavy atoms, HOMO coefficients, calculated ^{13}C NMR chemical shifts (in ppm, given relative to TMS, respectively) and experimental ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF) of 5-methylacenaphthylene dianion (**5**$^{2-}$).*

Carbon atom	Charge	HOMO	δ ^{13}C (calc.)	δ ^{13}C (exp.)
1	-0.30	+0.18	75.7	
2	-0.30	-0.18	75.7	
3	-0.25	+0.21	84.1	
4	-0.10	+0.08	126.0	
5	-0.17	-0.24	63.0	99.1
6	-0.34	+0.22	65.5	44.4
7	-0.09	-0.08	122.5	
8	-0.24	-0.19	88.0	
2a	+0.02	-0.15	116.0	
5a	+0.14	-0.00	148.4	
8a	+0.02	+0.16	115.6	
8b	-0.21	-0.03	125.6	
CH_3	-0.19		19.4	15.3

Further experiments which should be performed are ^{13}C NMR of the hydroanion of 5-methylacenaphthylene (to obtain information about the charge distribution) and reaction of **5**$^{2-}$ with one equivalent of methyl iodide.

9.3 Conclusions

Reaction of the 1-methylacenaphthylene dianion (**1**$^{2-}$) with water takes place at positions 5 and 6 in a ratio of 5:3. If however only one equivalent of proton donor (methanol) is added, the thermodynamically most stable hydroanion, 6-hydro-1-methylacenaphthylene anion ((6H)-**1**$^{-}$), is formed exclusively. ^{13}C NMR spectroscopy shows that the chemical shifts of (6H)-**1**$^{-}$ are almost identical to those of the unsubstituted 5-hydroacenaphthylene anion. The methyl group thus has little influence on the charge distribution in the hydroanion.

The ^{13}C NMR spectrum of 5-methylacenaphthylene dianion (**5**$^{2-}$) indicates that much charge is located at carbon atom 6. Reaction of **5**$^{2-}$ with one equivalent of methanol and subsequently one equivalent of methyl iodide results in the selective formation of 2,5-dimethylacenaphthene. This is in accordance with the assumption that carbon atom 6 is the most reactive position in **5**$^{2-}$.

9.4 Experimental section

General: The reagents were obtained from Acros, Aldrich and Merck and used without further purification. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3Å, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra.

General procedure: Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. The substituted acenaphthylene (5 mmol) was added, together with 0.3 g (13 mmol) of freshly cut sodium. Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0°C, the dianions were formed.

Reaction of the 1-methylacenaphthylene dianion with water:

The 1-methylacenaphthylene dianion was prepared according to the general procedure. The green solution was cooled to -70ºC and quenched with water. Fast work-up (temperatures carefully kept under 30ºC), gave a mixture of 1-methyl-1,5-dihydroacenaphthylene and 2-methyl-1,5-dihydroacenaphthylene in a ratio of 5 : 3. After exposure to air, the formation of 1-methylacenaphthene was observed.

*1-Methyl-1,5-dihydroacenaphthylene (**2**)*: see Chapter 2

*1-Methyl-2,6-dihydroacenaphthylene (**3**)*

^{1}H NMR ($CDCl_3$, TMS): δ = 7.18-6.93 (m, 3H, H-3, H-4 and H-5), 6.53 (dt, $J_{7,8}$ = 10.1, $J_{6,8}$ = 2.0, 1H, H-8), 6.02 (dt, $J_{7,8}$ = 10.1, $J_{6,7}$ = 3.8, 1H, H-7), 3.60-3.67 (m, 4H, H-2 and H-6), 2.03 (s, 3H, Me).

*Preparation of the 1-methylacenaphthylene dianion (**1**$^{2-}$) and 1-methyl-6-hydroacenaphthylene anion ((6H)-**1**$^-$) in an NMR tube.*

The 1-methylacenaphthylene dianion was prepared in THF-d_8 under argon using the general procedure. The solution was allowed to warm to room temperature before transferring it with a syringe into an NMR tube. The tube was sealed with a rubber stopper and parafilm. Although the whole procedure was performed with thouroughly dried equipment and under argon, the dianion was already protonated to result in the 1-methyl-6-hydroacenaphthylene anion. Addition of one equivalent of methanol to the reaction mixture before transfer into the NMR tube also resulted in formation of the 1-methyl-6-hydroacenaphthylene anion.

*1-Methyl-6-hydroacenaphthylene anion ((6H)-**1**$^-$)*

^{1}H NMR (THF-d_8): δ = 6.68 (d, $J_{3,4}$ = 7.3, 1H, H-3), 6.35 (d, $J_{7,8}$ = 9.1, 1H, H-8), 6.26 (m, 1H, H-4), 5.94 (m, 1H, H-5), 5.34 (s, 1H, H-2), 4.69 (m, 1H, H-7), 3.87 (m, 2H, H-6), 2.24 (s, 3H, Me).

^{13}C NMR (THF-d_8): δ = 130.7 (C-8b), 128.4 (C-5a), 127.7 (C-2a), 125.1 (C-8), 122.7 (C-1), 117.3 (C-4), 114.0 (C-3), 110.0 (C-5), 108.8 (C-7), 104.9 (C-8a), 91.9 (C-2), 32.0 (C-6), 13.4 (Me).

*Reaction of the 5-methylacenaphthylene dianion (**5**$^{2-}$) with 1 equivalent of methanol, followed by one equivalent of methyl iodide:*

The 1-methylacenaphthylene dianion (**5**$^{2-}$) (1.83 g, 11.0 mmol) was prepared according to the general procedure. The green solution was cooled to -70ºC and methanol (0.69 ml, 11 mmol) was added. After stirring for 15 minutes at room temperature the solution was again cooled to -70ºC and methyl iodide (0.69 ml, 11 mmol) was added. After stirring for a further 15 minutes the reaction was quenched with water at -70ºC. After normal work-up a yellow oil was obtained. Silica gel column chromatography (light petroleum, boiling range 40-60ºC and toluene) gave pure 2,5-dimethylacenaphthene (**6**) (0.711 g , 3.9 mmol, 36%).

*2,5-Dimethylacenaphthene (**6**)*

^{1}H NMR ($CDCl_3$, TMS): δ = 7.56 (dddd, $J_{6,7}$ = 8.2, $J_{6,8}$, $J_{1,6}$, $J_{1',6}$, 1H, H-6), 7.36 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1H, H-7), 7.16 (d, $J_{3,4}$ = 6.9, 1H, H-4), 7.12 (dddd, $J_{7,8}$ = 6.9, $J_{6,8}$, $J_{1,8}$, $J_{1',8}$, 1H, H-8), 7.03 (dd, $J_{3,4}$ = 6.9, $J_{2,3}$, 1H, H-3), 3.56 (m, 1H, H-2), 3.48 (dddd ($J_{1,1'}$ = -16.7, $J_{1,2}$ = 8.0, $J_{1,6}$, $J_{1,8}$, 1H, H-1), 2.81 (dddd, $J_{1,1'}$ = -16.7, $J_{1',2}$, $J_{1',6}$, $J_{1',8}$, 1H, H-1'), 2.52 (s, 3H, 5-Me), 1.32 (d, $J_{2,Me}$ = 6.9, 3H, 2-Me), $J_{1,6}$, $J_{1,8}$, $J_{1',2}$, $J_{1',6}$, $J_{1',8}$, $J_{6,8}$, $J_{2,3}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$): δ = 148.5 (C-2a), 144.5 (C-8a), 139.1 (C-8b), 138.2 (C-5), 129.9 (C-5a), 128.1 (C-4), 127.5 (C-7), 119.3 (C-6), 118.8 (C-8), 117.7 (C-3), 39.8 (C-1), 37.2 (C-2), 21.7 (2-Me), 17.8 (5-Me).

Preparation of the 5-methylacenaphthylene dianion (5^{2-}) in an NMR tube.

The 5-methylacenaphthylene dianion was prepared in THF-d_8 under argon using the general procedure. The solution was allowed to warm to room temperature before transferring it with a syringe into an NMR tube. The tube was sealed with a rubber stopper and parafilm.

5-Methylacenaphthylene dianion (5^{2-})

^{1}H NMR (THF-d_8): δ = 6.84 (1H), 6.35 (1H), 6.26 (2H), 5.66 (1H), 5.42 (1H), 4.59 (1H, H-6), 2.18 (s, 3H, Me).

^{13}C NMR (THF-d_8): δ = 127.2, 124.8 (q), 121.5 (q), 119.3 (q), 116.5 (q), 114.0, 109.6, 104.9, 100.8, 99.1 (C-5), 85.2, 44.4 (C-6), 15.3 (Me).

9.5 References

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10

General conclusions and prospects

10.1 The acenaphthylene dianion

Acenaphthylene can, despite its small size, easily be converted into its dianion with sodium in THF using ultrasonic vibration. It was shown that the dianion can be selectively methylated at position 1 or at position 5, depending on the order of addition of the proton donor and methyl iodide. The most reactive position in the dianion, C-5, is the carbon atom with the highest charge and the largest HOMO coefficient, according to ^{13}C NMR spectroscopy and quantum chemical calculations.

The 5-hydroacenaphthylene anion can be prepared quantitatively from the dianion by addition of one equivalent of methanol. Reaction of the 5-hydroacenaphthylene anion with methyl iodide occurs selectively at position 1.

Until now the acenaphthylene dianion was studied only by NMR spectroscopy. In this thesis the research is extended to the reactivity towards electrophiles and the influence of substituents on the properties of the acenaphthylene dianion.

10.2 Mechanistic aspects

Both the acenaphthylene dianion and the 5-hydroacenaphthylene anion can react via two different mechanisms with electrophiles: S_N2 and SET. The reaction path depends on the HOMO energy of the nucleophile and the LUMO energy of the electrophile. The higher the energy of the HOMO of the nucleophile and the lower the energy of the LUMO of the electrophile, the greater the possibility for SET to occur.

The acenaphthylene dianion reacts selectively with protons and methyl iodide at carbon atom 5 via the S_N2 mechanism. If however an electrophile is used with a lower LUMO energy, such as benzyl bromide or allyl bromide, single electron transfer occurs. Now the reactive particle is the acenaphthylene radical anion. Because acenaphthylene is a non-alternant PAH, the reactivity of the radical anion is different from that of the dianion. The reactivity is now determined by the spin density and the charge density. The substitution via SET is not regioselective and a mixture of products is isolated. The reported lack of selectivity in the reaction of the acenaphthylene dianion with dihaloalkanes by Neumann and Müllen can now be explained as the result of electron transfer.[1]

The reaction of the acenaphthylene dianion with bromobenzene is a unique example of a chemically driven $S_{RN}1$ reaction. After transfer of one electron from the acenaphthylene dianion to

the bromobenzene and subsequent dissociation of the ensuing radical anion into a bromide ion and a benzene radical, the resulting acenaphthylene radical anion couples with the benzene radical under formation of phenyl substituted acenaphthenes.

The 5-hydroacenaphthylene anion reacts with most alkyl bromides via the S_N2 mechanism. Substitution proceeds selectively at position 1 in the acenaphthylene skeleton. If however the reduction potential of the electrophile is low enough, SET can occur. An SET reaction, such as with benzyl bromide, results, next to the 1-substituted acenaphthene, in the formation of the novel 2a-substituted product. The products are formed in a 1:1 ratio.

The reaction of the 5-hydropyrene anion with benzyl iodide and *n*-propyl iodide gave also substitution at the quaternary position C-3a. [2,3] The hardness-softness of the electrophiles was assumed to be the cause of the change in regioselectivity. However, also in this reaction electron transfer might play an important role.

Prospects:

The reactions of the acenaphthylene dianion and the 5-hydroacenaphthylene anion with a variety of electrophiles have provided a much better insight into the mechanism of reductive alkylation. Electrophiles can now be ordered with respect to their possibility to give electron transfer. Comparison with other electrophiles allows to predict how a reaction will proceed. A similar approach can be used to study the reductive alkylation of other PAHs and to predict the reactivity of their anions towards electrophiles.

It will be worthwhile to further investigate the use of dianions of PAHs in $S_{RN}1$ reactions.

10.3 Influence of substituents

For the first time the effects of substituents on the reduction and reductive alkylation of acenaphthylene have been studied. Electron-withdrawing substituents as the cyano or the nitro group lower the reduction potential, whereas methyl and methoxy groups (electron donors) increase the reduction potential. Next to the character of the substituent, its position influences the ease of reduction of the acenaphthylene derivative.

The cyano group has an enormous influence on the charge distribution and the reactivity of 1- as well as 5-cyanoacenaphthylene. In the 1-cyanoacenaphthylene dianion the charge is drawn into the five-membered ring. This is established by ^{13}C NMR and *ab initio* calculations. The reaction with methyl iodide takes place at position 1 and, surprisingly, at the nitrogen of the cyano group. Protonation of the 1-cyanoacenaphthylene dianion results, via a 1,2-H-shift, in the thermodynamically most stable hydroanion: 1-cyano-2-hydroacenaphthylene anion.

The charge distribution in the 5-cyanoacenaphthylene dianion is also perturbed by the cyano group and protonation takes place at position 1 exclusively. The resulting 5-cyano-1-

hydroacenaphthylene anion reacts at positions 2 and 5. Reaction at carbon atom 5 leads, after elimination of HCN, to the formation of 5-methylacenaphthylene.

The methyl group exerts a much smaller effect on the reactivity of the acenaphthylene dianion. In both 1- and 5-methylacenaphthylene dianion the highest charge remains located at carbon atoms 5 and 6. However, the methyl group induces asymmetry in the acenaphthylene dianion and this leads to a difference in reactivity of the formerly equivalent positions.

Prospects:

The cyano group has a large effect on the reactivity of the acenaphthylene dianion. It will be interesting to investigate the influence of the cyano group on dianions of other PAHs. Also, the investigation of the effect of less electron-withdrawing groups on the acenaphthylene dianion would help to obtain a better understanding of reductive alkylations. The introduction of a methoxy group might have a larger effect than that of a methyl group. Next to influencing the charge distribution, the methoxy group might increase the energy of the HOMO of the dianion so much that already with methyl iodide an SET reaction would occur.

10.4 Synthetic aspects

The 5-hydroacenaphthylene anion was used in reactions with a wide variety of electrophiles and in this way many novel compounds were synthesised. Alkyl, allyl, propargyl, benzyl, cyanoalkyl, alkyl esters and alkylthio substituents could easily be introduced at position 1 of acenaphthene. The selective synthesis of 1,1-disubstituted acenaphthenes is now possible by using less reactive electrophiles (e.g., allyl bromide) or by addition of a strong base to the reaction mixture.

Reaction of the acenaphthylene dianion was used for the synthesis of interesting compounds such as phenylacenaphthylenes. Although mixtures of products are formed, many of these products cannot be prepared in other ways.

Reactions of the dianions and hydroanions of substituted acenaphthylenes with methyl iodide provide an easy way for the synthesis of novel substituted products, which cannot be prepared selectively by any classical synthetic route. Examples of these products are 1-cyano-1-methylacenaphthene and 5-cyano-2-methylacenaphthene.

Prospects:

The use of a wider variety of electrophiles combined with the use of substituted acenaphthylenes in reductive alkylations will lead to the selective synthesis of a wide range of novel products. The bifunctional electrophiles can be used to extend the existing acenaphthylene skeleton with a new ring.

10.5 Quantum chemical calculations

The development of new easy-to-use computer programs makes it possible for every organic chemist to perform quantum chemical calculations. However, if the results of semiempirical calculations for anions of PAHs are compared to the experimental results, it must be concluded that these calculations can only be used as rough estimations. This might be due to the complex structure of the anions with an excess of electrons. Better results are obtained with *ab initio* calculations. Comparison of experimental and calculated chemical shifts learns that the calculations give a good estimation of the ^{13}C NMR chemical shifts. The charge distribution can be determined by the Mulliken Population Analysis. However, in the MPA the overlap integral is divided equally over two neighbouring carbon atoms and this gives large deviations for the quaternary carbon atoms. Therefore, it is advisable to use the Natural Population Analysis (NPA).

Prospects:

For an even better estimation of the electron density and thus the charge distribution, the calculations should include configuration-interaction, larger basis sets, and diffuse functions. Furthermore, many factors, such as counter ions, solvent, concentration and temperature, which have hitherto been neglected in the calculations should be considered. Progress in computer capacity and calculation systems makes it easier to take these factors into account in the future.

In the calculation, only the starting situtation is regarded. The charge and HOMO coefficient distributions in the dianion or hydroanion are used to predict the most reactive positions. However, also the final state and the transition state may play an important role in the reaction path. Therefore, attempts should be made to calculate the entire reaction path.

10.6 References

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Summary

Acenaphthylene is one of the smallest polycyclic aromatic hydrocarbons (PAHs). In contrast to much other PAHs, acenaphthylene is not mutagenic or carcinogenic. Because PAHs are widely spread in the environment it is important to synthesise PAHs and establish the relation between structure and reactivity. Acenaphthylene can be used as building block in the synthesis of larger PAHs. A very useful and efficient step in the synthesis is the reductive alkylation. In this reaction a PAH is converted into its dianion or hydroanion and subsequently reacted with an electrophile. In this thesis the influence of electrophiles (Part I) and substituents (Part II) on the reactivity of the acenaphthylene anions is extensively studied.

Despite its small size, acenaphthylene can be easily converted into its dianion. Because in liquid ammonia protonation can occur, the acenaphthylene dianion is prepared in pure THF using ultrasonic vibration to activate the sodium. The dianion can be converted into the 5-hydroacenaphthylene anion by addition of one equivalent of methanol. In Chapter 2, the reactivity of the acenaphthylene dianion and the 5-hydroacenaphthylene anion towards methyl iodide is related to the ^{13}C NMR spectra and quantum chemical calculations. The acenaphthylene dianion reacts with methyl iodide selectively at position 5, the 5-hydroacenaphthylene anion is methylated at carbon atom 1.

In Chapter 3 the reactions of the 5-hydroacenapthylene anion with allyl bromide, propargyl bromide and (bromomethyl)cyclopropane are described. Next to the major product, 1-substituted acenaphthenes, 1,1-disubstituted acenaphthenes are isolated. The formation of these products was ascribed to the equilibrium of 5-hydroacenaphthylene anion and 1-allyl-5-hydroacenaphthyleneanion. The reaction with (bromomethyl)cyclopropane proved that the reaction proceeds via the S_N2 mechanism.

The reaction of the 5-hydroacenaphthylene anion with benzyl bromide proceeds at both positions 1 and 2a in a ratio of 1:1. In Chapter 4 the mechanism of this reaction was investigated. The product ratio was independent of the leaving group (Cl, Br, I) and could thus not be the result of the hard-soft effect of the leaving group. The results were however consistent with the single electron transfer (SET) reaction mechanism. After transfer of one electron to the electrophiles, the resulting 5-hydroacenaphthylene radical reacts at the positions with the highest spin density.

Electron scavengers (*p*DNB), radical scavengers (di-*tert*-butylnitroxide, TEMPO) and more sterically hindered electrophiles were used to obtain experimental evidence for the SET mechanism. In case of a 100% SET reaction substitution occurs at positions 1 and 2a in a ratio of 1:1. Reaction of the 5-hydroacenaphthylene anion with ethyl bromide and ethyl iodide proceed via S_N2 as well as SET in a ratio of 3:1 and 2:1, respectively.

In Chapter 5 reactions of the 5-hydroacenaphthylene anion with electrophiles containing a second functional group are described. These reactions provide easy and fast routes to novel 1-substituted acenaphthenes. These acenaphthene derivatives containing cyano alkyl, ester alkyl and alkyl bromides can be used for the synthesis of larger PAHs. 3-Bromopropionitrile, 1,4-dibromobutane and 1,5-dibromopentane, and their iodo-analogs, gave rise to 1,1-disubstitution products, in the case of the dihaloalkanes resulting in spiro-fused rings. The use of diphenyl disulfide and methyl thiocyanide as electrophiles lead to the creation of carbon-sulfur bonds. The disubstitution products undergo spontaneous elimination of thiophenol or methane thiol yielding the 1-substituted acenaphthylene derivatives.

The reactivity of the acenaphthylene dianion towards a variety of electrophiles is examined in Chapter 6. The dianion reacts with (bromomethyl)cyclopropane via the S_N2 mechanism selectively at position 5. With more readily reducable electrophiles such as allyl bromide the reaction proceeds via the SET mechanism and gives, due to the role of the acenaphthylene radical anion as reaction intermediate, rise to the formation of 1-, 5-, 1,2-di- and 1,5-disubstitution products. Electrophiles containing a second functional group (e.g., ethyl bromoacetate, diphenyl disulfide) undergo a double electron transfer, resulting in acenaphthylene and the reduced electrophile. When bromobenzene was used as electrophile in the reaction with the acenaphthylene dianion, a mixture of phenyl substituted acenaphthene was isolated. This is the result of the occurence of a chemically driven $S_{RN}1$ reaction. It is the first time that this kind of reaction is documented for dianions of PAHs.

The syntheses of acenapthylenes with electron-withdrawing (cyano, nitro) and electron-donating (methyl, methoxy) groups at position 1 or 5 are described in Chapter 7. Using the procedure described for acenaphthylene, 5-methyl-, 1-methyl-, 5-methoxy-, 1-methoxy-, 5-cyano- and 1-cyanoacenaphthylene were converted into the corresponding acenaphthenes via the dianion. Both 1- and 5-bromoacenaphthylene

were debrominated during the formation of the dianion and yielded acenaphthene after work-up. The nitroacenaphthylene could not be converted into stable dianions. With cyclic voltammetry the effect of substituents on the reduction potential of acenaphthylene was examined: electron-withdrawing groups lower the reduction potential, whereas electron donors result in an increase of the the reduction potential. A linear correlation between the half wave reduction potential and the calculated LUMO energy of the substituted acenaphthylenes was found.

In Chapter 8 the reactivities of the dianions of 1- and 5-cyanoacenaphthylene are related to the ^{13}C NMR spectra and *ab initio* calculations. Introduction of the cyano group at position 1 of the acenaphthylene dianion changes the reactivity towards methyl iodide to position 1 and, to a less extent, to the nitrogen of the cyano group. ^{13}C NMR spectroscopy and *ab initio* calculation indicate that the highest charge is found at carbon atom 1. The very high charge at the nitrogen counts for the reaction at this position. Protonation of the 1-cyanoacenaphthylene dianion takes place initially at position 1, but the hydroanion rearranges via a 1,2-H-shift to the thermodynamically more stable 2-hydro analog. The 1-cyano-2-hydroacenaphthylene anion reacts with methyl iodide slectively at position 1. This is in accordance with the predictions based on ^{13}C NMR and *ab initio* calculations of the hydroanion.

Protonation of the 5-cyanoacenaphthylene dianion proceeds selectively at position 1, resulting in the 5-cyano-1-hydroacenaphthylene anion. Reaction of the latter with methyl iodide gives substitution at positions 2 and 5, yielding 5-cyano-2-methylacenaphthene and, after elimination of HCN, 5-methylacenaphthylene. This is, again, in accordance with the ^{13}C NMR of the hydroanion and the calculations. ^{15}N NMR spectroscopy was used to show that indeed more charge is present on the nitrogen atom of the cyano group in the hydoanion than in the neutral parent compound.

The influence of the methyl group on the charge distribution in the dianion is less pronounced than the effect of the cyano group (Chapter 9). Although initial protonation of the 1-methylacenaphthylene dianion takes place at position 5 and 6 in a ratio of 5:3, the 6-hydro-1-methylacenaphthylene anion is formed selectively after addition of one equivalent of methanol. In the 5-methylacenaphthylene dianion the highest charge is located at position 6. This high charge in combination with steric hindrance at carbon atom 5 results in protonation at position 6 and, after addition of methyl iodide in the selective synthesis of 2,5-dimethylacenaphthene.

Samenvatting

Polycyclische aromatische koolwaterstoffen (PAKs) komen overal in het milieu voor en van vele is bekend dat zij mutaties in DNA of kanker kunnen veroorzaken. Het is daarom belangrijk zuivere PAKs te synthetiseren die als referentiemateriaal kunnen dienen om de relatie tussen structuur en biologische activiteit te bepalen. Acenaftyleen is één van de kleinste PAKs. Acenaftyleen zelf is niet mutageen of carcinogeen, maar het kan worden gebruikt om grotere of gesubstitueerde PAKs te maken. Een zeer geschikte en efficiënte synthesemethode is reductieve alkylering. In deze reactie wordt een PAK omgezet in zijn dianion of hydroanion en vervolgens behandeld met een elektrofiel. In dit proefschrift worden de invloeden van elektrofielen (Deel I) en substituenten (Deel II) op de reactiviteit van de anionen van acenaftyleen bestudeerd.

Ondanks het feit dat acenaftyleen klein is, kan het gemakkelijk worden omgezet in zijn dianion. Het acenaftyleen-dianion werd gemaakt in zuivere THF, met behulp van ultrasone vibratie om het natrium te activeren, omdat in vloeibare ammoniak protonering kan optreden,. Het dianion kan worden omgezet tot het 5-hydro-acenaftyleen-anion door het toevoegen van één equivalent methanol. In hoofdstuk 2 wordt de reactiviteit van het acenaftyleen-dianion en het 5-hydroacenaftyleen-anion ten opzichte van methyljodide gerelateerd aan de ^{13}C NMR spectra en aan kwantum-chemische berekeningen. Het acenaftyleen-dianion reageert met methyljodide selectief op positie 5, het 5-hydroacenaftyleen-anion wordt gemethyleerd op koolstof-atoom 1.

In hoofdstuk 3 worden de reacties van het 5-hydroacenaftyleen-anion met allylbromide, propargylbromide en (broommethyl)cyclopropaan beschreven. Naast de hoofdproducten, 1-gesubstitueerde acenaftenen, worden 1,1-digesubstitueerde acenaftenen geïsoleerd. De vorming van deze producten wordt toegeschreven aan het evenwicht van het 5-hydroacenaftyleen-anion en het 1-allyl-5-hydroacenaftyleen-anion. Uit de reactie met (broommethyl)cyclopropaan blijkt dat deze via het S_N2 mechanisme verloopt.

De reactie van het 5-hydroacenaftyleen-anion met benzylbromide vindt zowel plaats op positie 1 als op positie 2a, in een verhouding van 1:1. In hoofdstuk 4 wordt het mechanisme van deze reactie onderzocht. De productverhouding is onafhankelijk van de vertrekkende groep (Cl, Br, I) en kan dus niet het gevolg zijn van het hard-zacht effect. De resultaten zijn echter in overeenstemming met het één-elektron-overdracht (SET) reactiemechanisme. Na overdracht van één elektron aan het elektrofiel reageert het overblijvende 5-hydroacenaftyleen-radicaal op de posities met de hoogste spindichtheid. Elektronvangers (*p*DNB), radicaalvangers (di-*tert*-butylnitroxide, TEMPO) en sterisch gehinderde elektrofielen zijn gebruikt om het

optreden van het SET-mechanisme experimenteel aan te tonen. Als de reactie 100% via SET gaat, vindt de substitutie op posities 1 en 2a in een verhouding van 1:1 plaats. De reactie van het 5-hydroacenaftyleen-anion met ethyljodide en ethylbromide gebeurt zowel via S_N2 als via SET in een verhouding van 3:1, respectievelijk 2:1.

In hoofdstuk 5 worden reacties van het 5-hydroacenaftyleen-anion met elektrofielen die een tweede functionele groep hebben, beschreven. Hiermee is het mogelijk om snel en gemakkelijk nieuwe 1-gesubstitueerde acenaftenen te synthetiseren. Deze acenafteenderivaten met een cyaanalkyl-, esteralkyl- of broomalkylsubstituent kunnen worden gebruikt in de synthese van grotere PAKs. 3-Broompropionitril, 1,4-dibroombutaan en 1,5-dibroompentaan, en hun jodiumanaloga, geven tevens 1,1-digesubstitueerde producten, die, in het geval van de dihaloalkanen, spiro-gefuseerde ringen bevatten. Het gebruik van difenyldisulfide en methylthiocyanide als elektrofiel leidt tot de vorming van koolstof-zwavel-bindingen. De digesubstitueerde verbindingen ondergaan spontane eliminatie van thiofenol of methaanthiol resulterend in 1-gesubstitueerde acenaftyleenderivaten.

De reactiviteit van het acenaftyleen-dianion ten opzichte van verschillende elektrofielen wordt onderzocht in hoofdstuk 6. Het dianion reageert met (broommethyl)cyclopropaan via het S_N2 mechanisme selectief op positie 5. Met gemakkelijker te reduceren elektrofielen, zoals allylbromide, vindt de reactie plaats via het SET mechanisme en geeft aanleiding, door het optreden van het acenaftyleen-radicaalanion als reactie-intermediair, tot de vorming van 1-, 5-, 1,2-di- en 1,5-disubstitutieproducten. Elektrofielen met een tweede functionele groep (b.v. ethylbroomacetaat, broompropionitril) ondergaan een dubbele elektronoverdracht, hetgeen resulteert in acenaftyleen.

Als broombenzeen wordt toegepast als elektrofiel in de reactie met het acenaftyleen-dianion, wordt een mengsel van fenyl-gesubstitueerde acenaftenen geïsoleerd. Dit is het resultaat van het optreden van een thermische $S_{RN}1$ reactie. Het is de eerste keer dat een dergelijke reactie voor dianionen van PAKs wordt beschreven.

De syntheses van acenaftylenen met elektronenzuigende (cyaan, nitro) en elektronenstuwende (methyl, methoxy) groepen op positie 1 of 5 worden beschreven in hoofdstuk 7. Gebruikmakend van de procedure zoals beschreven voor het acenaftyleen-dianion, worden 5-methyl-, 1-methyl-, 5-methoxy-, 1-methoxy-, 5-cyaan- en 1-cyaanacenaftyleen via hun dianionen gereduceerd tot de overeenkomstige acenaftenen. Zowel 1- als 5-broomacenaftyleen worden gedebromeerd tijdens de vorming van het dianion, hetgeen na het opwerken tot de isolatie van acenafteen leidt. De nitroacenaftylenen konden niet worden omgezet in stabiele dianionen.

Met cyclische voltammetrie worden de effecten van substituenten op de reductiepotentiaal van acenaftyleen onderzocht: elektronenzuigende groepen verlagen

de reductiepotentiaal, terwijl elektronenstuwers een verhoging van de reductiepotentiaal tot gevolg hebben. Er is een lineaire correlatie tussen de reductiepotentiaal en de berekende LUMO energie van de gesubstitueerde acenaftylenen.

In hoofdstuk 8 worden de reactiviteiten van de dianionen van 1- en 5-cyaanacenaftylenen gerelateerd aan de ^{13}C NMR spectra en *ab initio* berekeningen. De introductie van de cyaangroep op positie 1 van het acenaftyleen-dianion stuurt de reactie met methyljodide naar positie 1 en, in mindere mate, naar de stikstof van de cyaangroep. ^{13}C NMR spectroscopie en *ab initio* berekeningen duiden erop dat de hoogste lading wordt gevonden op koolstofatoom 1. De zeer hoge lading op stikstof zorgt ervoor dat ook op deze positie reactie plaatsvindt. Protonering van het 1-cyaanacenaftyleen-dianion vindt oorspronkelijk plaats op positie 1, maar het gevormde hydroanion legt via een 1,2-H-verhuizing om naar het thermodynamisch meer stabiele 2-hydroanalogon. Het 1-cyaan-2-hydroacenaftyleen-anion reageert met methyljodide selectief op positie 1. Dit is in overeenstemming met de voorspellingen gebaseerd op ^{13}C NMR spectroscopie en *ab initio* berekeningen voor het hydroanion.

Protonering van het 5-cyaanacenaftyleen-dianion gebeurt selectief op positie 1, hetgeen resulteert in de vorming van het 5-cyaan-1-hydroacenaftyleen-anion. Reactie van het hydroanion met methyljodide geeft substitutie op posities 2 en 5 en dit leidt tot 5-cyaan-2-methylacenafteen en, na eliminatie van HCN, tot 5-methylacenaftyleen. Dit is wederom in overeenstemming met het ^{13}C NMR spectrum van het hydroanion en met de kwantumchemische berekeningen.

Met ^{15}N NMR spectroscopie werd aangetoond dat er inderdaad meer lading aanwezig is op het stikstofatoom van de cyaangroep in het hydroanion dan in het neutrale molecuul.

De invloed van de methylgroep op de ladingsverdeling in het dianion is minder uitgesproken dan het effect van de cyaangroep (hoofdstuk 9). Ofschoon protonering van het 1-methylacenaftyleen-dianion in eerste instantie plaatsvindt op posities 5 en 6 in een verhouding van 5:3, wordt het 6-hydro-1-methylacenaftyleen-anion selectief gevormd na het toevoegen van één equivalent methanol.

In het 5-methylacenaftyleen-dianion bevindt zich de hoogste lading op positie 6. Deze grote lading in combinatie met sterische hindering op koolstofatoom 5 leidt tot protonering op positie 6. Na toevoegen van methyljodide aan het gevormde hydroanion wordt selectief 2,5-dimethylacenafteen gevormd.

Curriculum Vitae

Marcia Van Loo werd op 5 juli 1971 geboren te Heerlen. Na het behalen van het Gymnasium diploma aan het Bisschoppelijk College Schöndeln te Roermond in 1989, begon zij in september van dat jaar met de studie Scheikundige Technologie aan de Technische Universiteit Eindhoven. In december 1994 werd deze studie voltooid met een afstudeeronderzoek (“On the way to regioregular polypyrroles”) binnen de vakgroep Organische Chemie onder leiding van prof. dr. E.W. Meijer. Het in dit proefschrift beschreven onderzoek werd verricht van januari 1995 tot april 1999, onder leiding van prof. dr. J. Cornelisse en prof. dr. J. Lugtenburg. In januari 1997 werd deelgenomen aan de Winter School on Organic Reactivity (WISOR) in Bressanone, Italië. In november 1997 werd met steun van SON/NWO en de Shell reisbeurs deelgenomen aan het 16th International Symposium on Polycyclic Aromatic Compounds in Charlotte, North Carolina, USA. Vanaf december 1999 is de auteur van dit proefschrift werkzaam bij Diosynth te Oss.

Nawoord

Tot slot wil ik graag een aantal mensen noemen die ieder op eigen wijze hebben bijgedragen aan de totstandkoming van dit proefschrift. Allereerst Bart van Dongen, die altijd opgewekt aan de slag ging om er vervolgens achter te komen dat in de kolf weer zwarte muk zat. Onze lijfspreuk in die tijd was niet voor niets “All I want is a little reaction”. Samen met Marilyn van de Bulk heb ik de eerste stappen in de goede richting gezet. Sjoerd Ypma, Milroy van de Bor, Mehmet Tektaş en Mesut Yildirim hebben tijdens hun (hoofdvak)stages geleerd dat naast een goede dosis gezond verstand ook veel inzet nodig is om mooie resultaten te bereiken. Last, but not, least Theo Smit. Onvermoeibaar en superenthousiast leverde hij een enorme bijdrage aan de laatste hoofdstukken van dit proefschrift.
Als voorlopig laatste AIO in de werkgroep Polycyclische Aromaten heb ik vele goede contacten gehad met de AIO’s en studenten van de Bio-Organische Fotochemie en de Organische Fotochemie. De Boffers hebben er toe bijgedragen dat ik een onvergetelijke tijd in Leiden heb gehad. Aan de werkbesprekingen bij fotochemie en de EHBO bij rekenproblemen denk ik met veel plezier terug. Ook bij Gerrit kon ik te allen tijden binnenvallen met lastige vragen. Ineke heeft de aanzet gegeven voor de semi-empirische berekeningen. Later, bij de *ab initio* berekeningen mocht ik op de deskundige hulp van Johanna rekenen. Frans heeft mij ingewijd in de geheimen van het argonorgel. Joke heeft geduldig de preparatieve scheidingen met behulp van gaschromatografie verricht. De altijd vrolijke Jos stond mij met raad, daad en belangstelling ter zijde bij de IR en UV-VIS metingen. Cees Erkelens en Fons Lefeber waren de reddende engelen als ik weer eens problemen met de NMR spectrometers had. En natuurlijk vergeet ik ook de glasblazers, de ama’s, de computerdienst, de veiligheidsdienst, de magazijnmedewerkers, de technische dienst enz. enz. niet.
Tenslotte wil ik mijn ouders en René noemen. Ook al zaten jullie “ver weg”, altijd kon ik op jullie begrip, liefde en steun rekenen.

Stellingen

Behorende bij het proefschrift

Anions of Acenaphthylene
Reactions, NMR Spectroscopy and Quantum Chemical Calculations

1. Uitspraken over de oorzaak van selectiviteit in de reacties van anionen van polycyclische aromatische koolwaterstoffen (PAKs) met elektrofielen kunnen pas gedaan worden als het reactiemechanisme bekend is.
   Dit proefschrift

2. Het heeft alleen zin om een lineaire relatie tussen de lading en de chemische verschuiving in ^{13}C NMR voor anionen van PAKs aan te nemen indien koolstofatomen die deel uitmaken van dezelfde ring(en) met elkaar vergeleken worden.
   Dit proefschrift

3. Bij het gebruik van het begrip "lading op een atoom" onderschatten veel organisch chemici het belang van de keuze van de methode om deze lading af te leiden uit de berekende elektronendichtheidsverdeling.
   Dit proefschrift

4. De keuze van vloeibare ammoniak als referentie voor de bepaling van de chemische verschuiving in ^{15}N NMR spectroscopie bevordert de vergelijkbaarheid met ^{13}C NMR spectra.
   Dit proefschrift

5. Het ontbreken van acenaftyleen in de boekwerken van Clar en Harvey doet onrecht aan het polycyclische aromatische karakter van acenaftyleen.
   E. Clar *Polycyclic Hydrocarbons (Vol. 1 and 2)* **1964**, Academic Press Inc., London.
   R.G. Harvey *Polycyclic Aromatic Hydrocarbons, Chemistry and Carcinogenicity* **1991**, Cambridge University Press, Cambridge.

6. Het is te betreuren dat Lewis *et al*. hebben nagelaten te concluderen dat het voorgestelde mechanisme voor de fotochemische cis-transisomerisatie van 11,19-ethano-11-*cis*-retinal, waarbij rotatie om de C12-H binding plaatsvindt, ook van toepassing is op de fotochemische cis-transisomerisatie van rhodopsine zelf.
   M. Sheves, A. Albeck *J. Am. Chem. Soc.* **1986**, *108*, 6440-6441
   A.E. Asato, M. Denny, R.S.H. Liu *J. Am. Chem. Soc.* **1986**, *108*, 5032-5033
   J.W. Lewis, I. Pinkas, M. Sheves, M. Ottolenghi, D.S. Kliger *J. Am. Chem. Soc.* **1995**, *117*, 918-923

7. De naamsverandering van benzo[*a*]pyreen in benzo[*pqr*]tetrafeen zal tot veel verwarring leiden, vooral onder niet-chemici.
   Pure Appl. Chem. **1998**, *70*, 143-216

8. Het is aan te bevelen eerst onderzoek te doen naar het effect van substituenten in een gemodificeerd retinal chromofoor op de binding aan het eiwit, voordat een uitspraak gedaan wordt over de chiraliteit van retinal in zijn natuurlijke vorm.
   J. Lou, M. Hashimoto, N. Berova, K. Nakanishi *Organic Letters* **1999**, *1*, 51-54
   V. Buss, K. Kolster, F. Terstegen, R. Vahrenhorst *Angew. Chem. Int. Ed. Eng.* **1998**, *37*, 1893-1895

9. Het is te betreuren dat de synthese van nieuwe polycyclische aromatische koolwaterstoffen in Leiden uitsluitend door hoogleraren wordt voortgezet.

10. Een cursus EHBO zou in het curriculum voor scheikundestudenten moeten worden opgenomen.

11. Het gebruik van suiker in diëten zal tot betere resultaten bij het afslanken leiden.
    Cosun magazine **1998**, nr. 8

12. Hoffelijkheid van heren, zoals die bijvoorbeeld blijkt uit het openhouden van deuren, wordt juist door geëmancipeerde vrouwen zeer gewaardeerd.

Leiden, 3 februari 2000 Marcia Van Loo