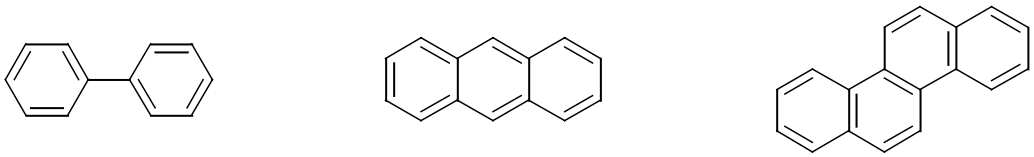
1

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.

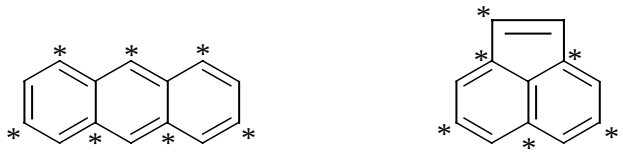


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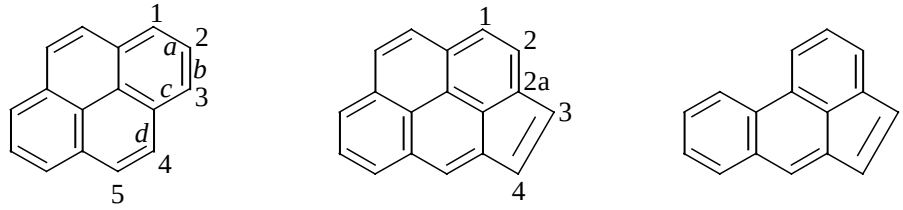
***Figure 2**: Alternant and non-alternant PAHs.*[2]

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.

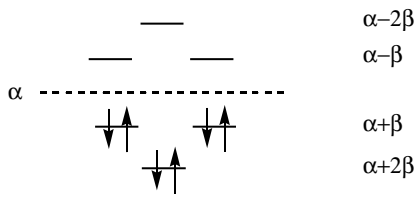


***Figure 4**: HMO-scheme for benzene.*

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]

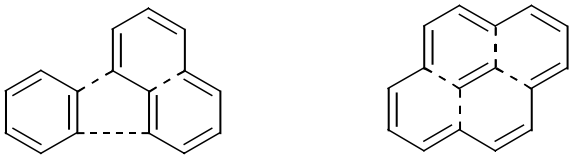


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***Figure 5**: Aromaticity of fluoranthene and pyrene regarded as cross-linked polyenes.*[85]

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]

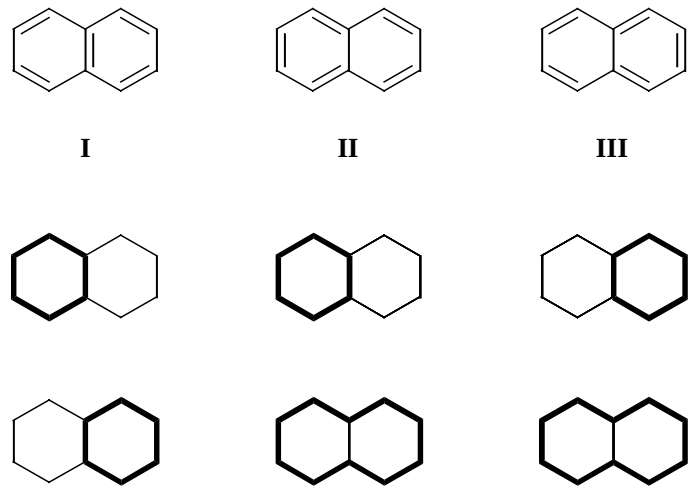


***Figure 6**: Aromaticity of naphthalene according to the conjugated circuits' model.*[102]
There are three Kekulé valence structures for naphthalene I, II and III. Structure I consists of two Kekulé formulae of benzene (fused across the double bond). In structures II and III, next to one Kekulé benzene 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]

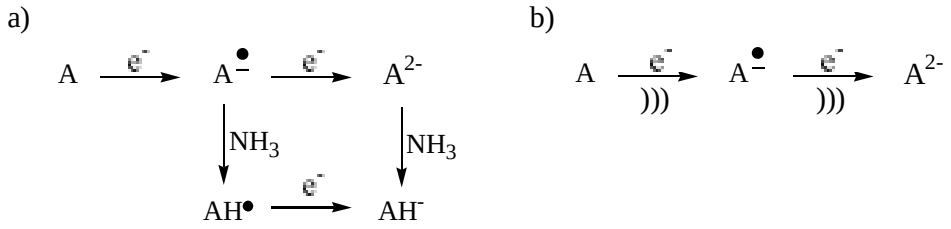
1.3 Reduction and reductive alkylation of PAHs

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]

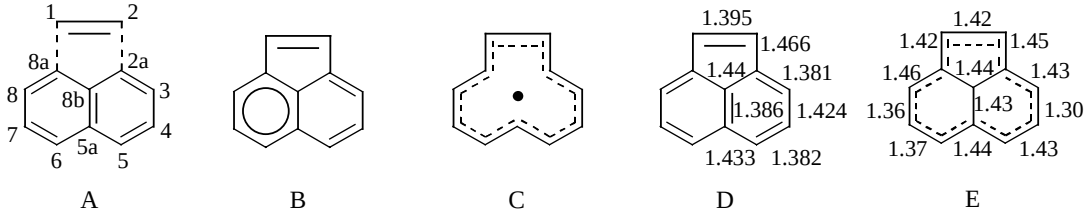


***Figure 7**: Aromaticity in acenaphthylene according to: A. Hückel, B. Clar and C. Platt's model; Bond lengths: D. acenaphthylene, E. acenaphthylene dianion.*

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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