Part II

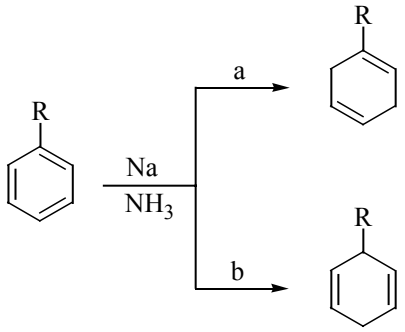
Substituted acenapphthylenes

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.

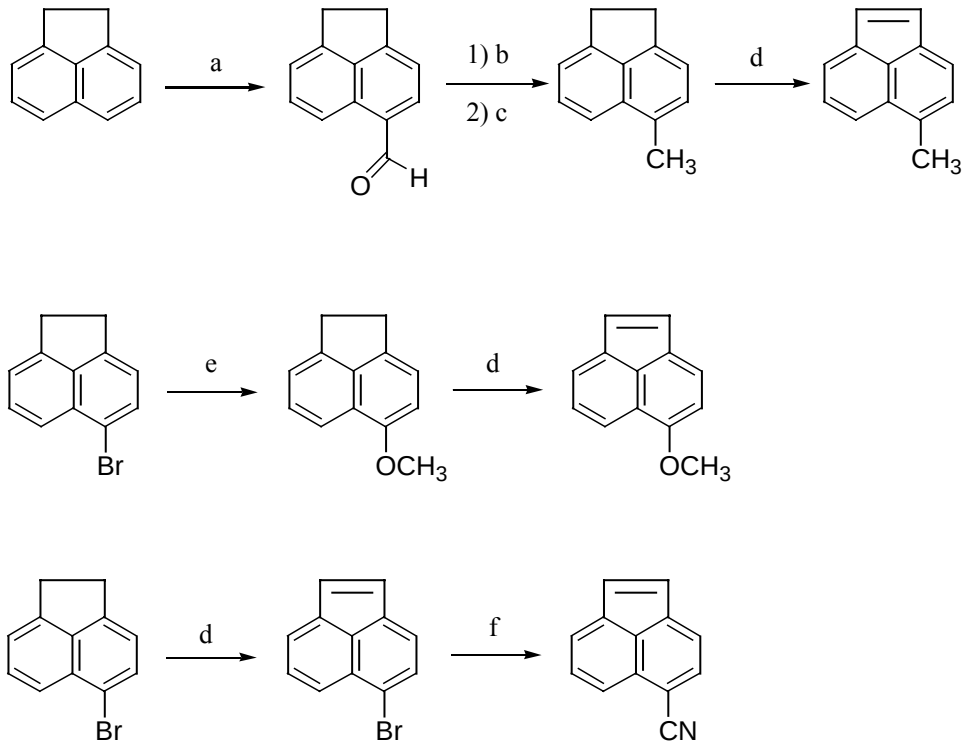
Acenaphthene was formylated selectively at position 5 using dichloromethyl methyl ether and titanium(IV) chloride. Wolff-Kishner reduction of the formyl group followed by dehydrogenation gave 5-methylacenaphthylene (Scheme 2).

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.



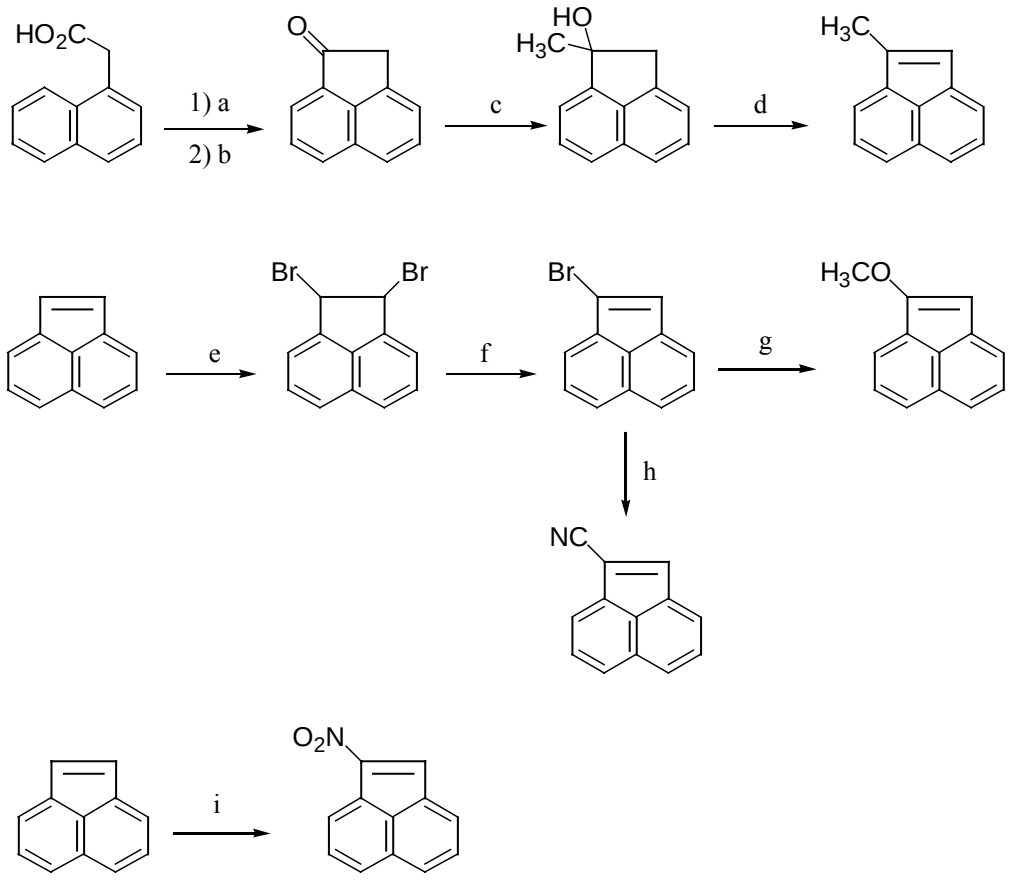
***Scheme 2**: Syntheses of 5-substituted acenaphthylenes, a: Cl_2CHOCH_3, $TiCl_4$, b: H_2NNH_2, diethylene glycol, c: KOH, d: DDQ, e: CuI, NaOMe, f: CuI, KCN.*

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.

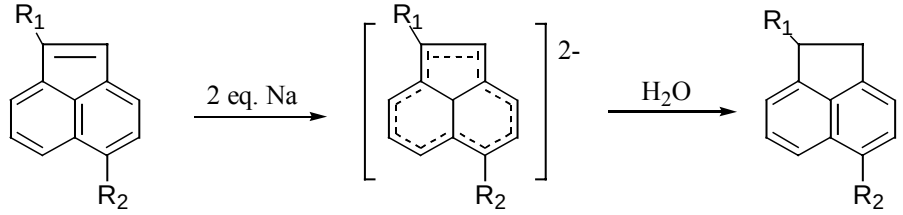


***Scheme 3**: Syntheses of 1-substituted acenaphthylenes, a: ClCOCOCl, b: $AlCl_3$, c: MeLi, d: p-TSA, e: Br_2, f: KOH, g: CuI, NaOMe, h: CuI, KCN i: $AgNO_3$, $NaNO_2$, I_2.*

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.

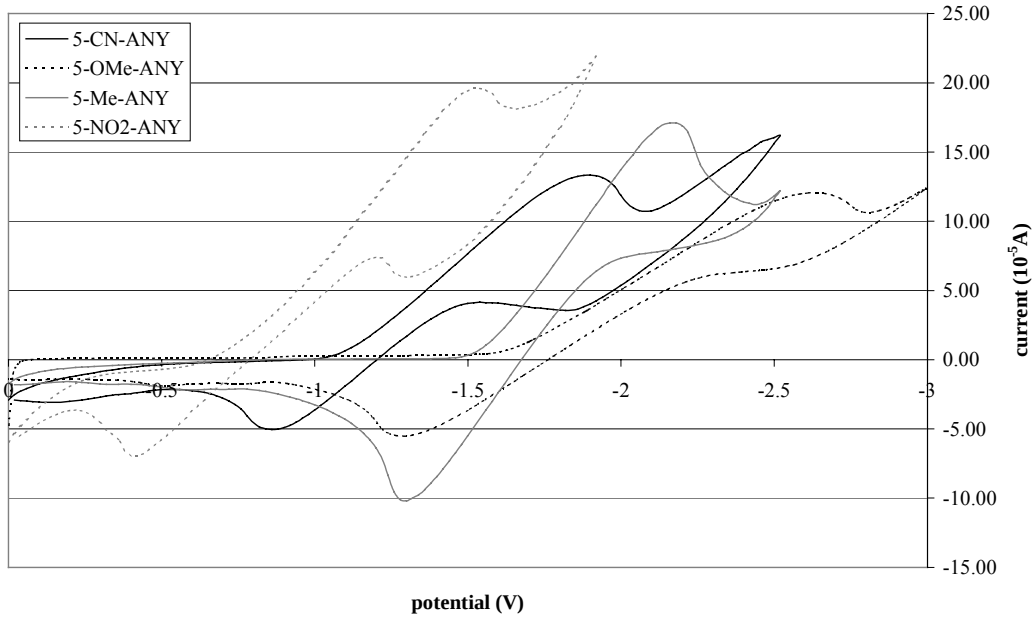


***Figure 1**: Reduction-oxidation waves for 5-methoxyacenaphthylene, 5-methylacenaphthylene, 5-cyanoacenaphthylene and 5-nitroacenaphthylene.*

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.

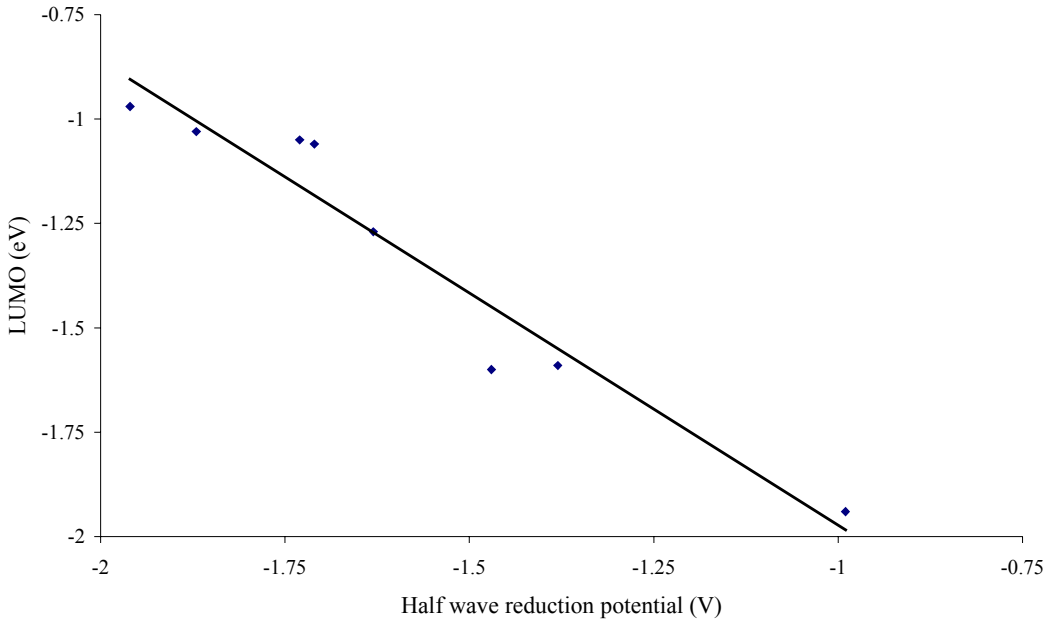


***Figure 2**: Relation between the half wave potential and the LUMO energy.*

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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