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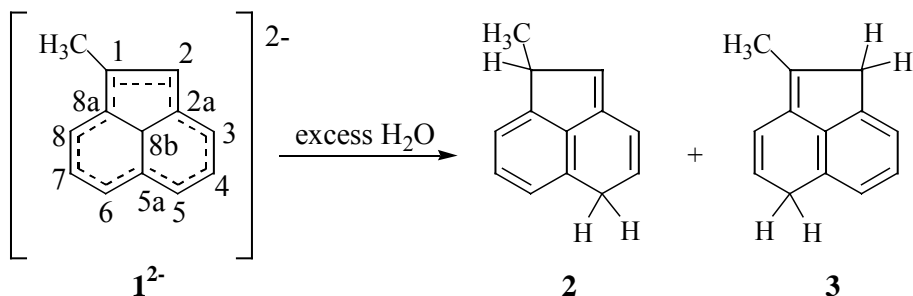
Scheme 1: *Reaction of the 1-methylacenaphthylene dianion with water.*

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.
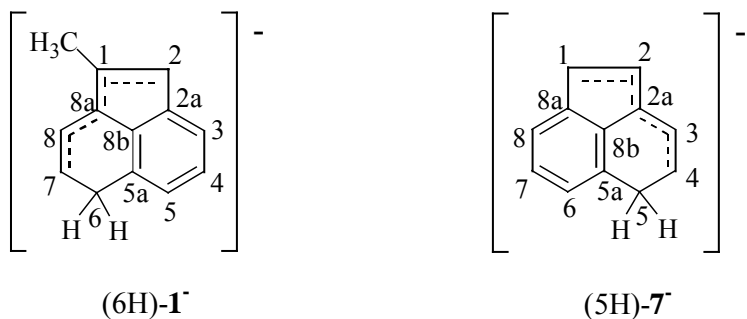
(6H)-**1**⁻   (5H)-**7**⁻

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	$\delta\ ^{13}C$ (exp.)	Carbon atom	$\delta\ ^{13}C$ (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
CH₃	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 **1²⁻** and (6H)-**1**⁻. It is expected that **1²⁻** 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 (**5²⁻**). Treatment of **5²⁻** 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 **5²⁻** 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.
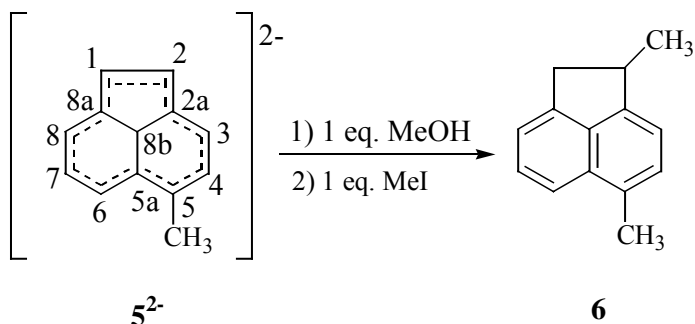
Scheme 2: *Reaction of **5²⁻** with one equivalent of methanol followed by one equivalent of methyl iodide.*

The initial step in the formation of **6** is the protonation of **5²⁻**. 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, **5²⁻** 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 **5²⁻** will have a negative effect on the reactivity of carbon atom 5, which is bearing the methyl group.

The reactivity of 5^{2-} can be compared to that of the 1-methylphenalene anion (8^-, Figure 2). In 8^-, the carbon atom attached to the methyl group (C-1) did not undergo alkylation. In contrast to C-6 in 5^{2-}, the carbon atom at the *peri* position (C-9) in 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 5^{2-} than that of C-9 in 8^- might be the result of a different geometry of the *ipso* and *peri* carbon atoms in 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 5^{2-} in comparison with the other carbon atoms.
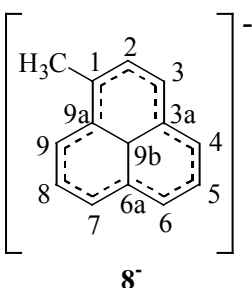

8^-

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 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 5^{2-} with one equivalent of methanol followed by one equivalent of methyl iodide.

In order to obtain additional information about 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 (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 ($\mathbf{1^{2-}}$) 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 (($6H$)-$\mathbf{1^-}$), is formed exclusively. ^{13}C NMR spectroscopy shows that the chemical shifts of ($6H$)-$\mathbf{1^-}$ 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 ($\mathbf{5^{2-}}$) indicates that much charge is located at carbon atom 6. Reaction of $\mathbf{5^{2-}}$ 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 $\mathbf{5^{2-}}$.

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 -70°C and quenched with water. Fast work-up (temperatures carefully kept under 30°C), 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

1 M.A. Hempenius, W. Heinen, P.P.J. Mulder, C. Erkelens, H. Zuilhof, J. Lugtenburg, J. Cornelisse *J. Phys. Org. Chem.* **1994**, *7*, 296-302

2 Gaussian 94, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, J.A. Peterson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioşlowski, B. Stefanov, A. Nanayakhara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian Inc., Pittsburg, PA, **1995**