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

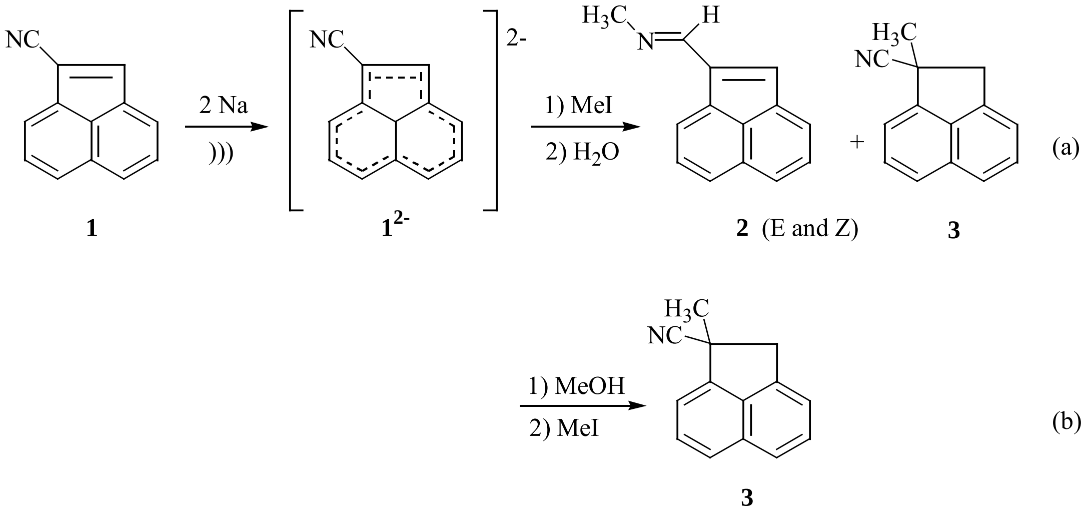
8.2.1 Reductive methylation

1-Cyanoacenaphthylene

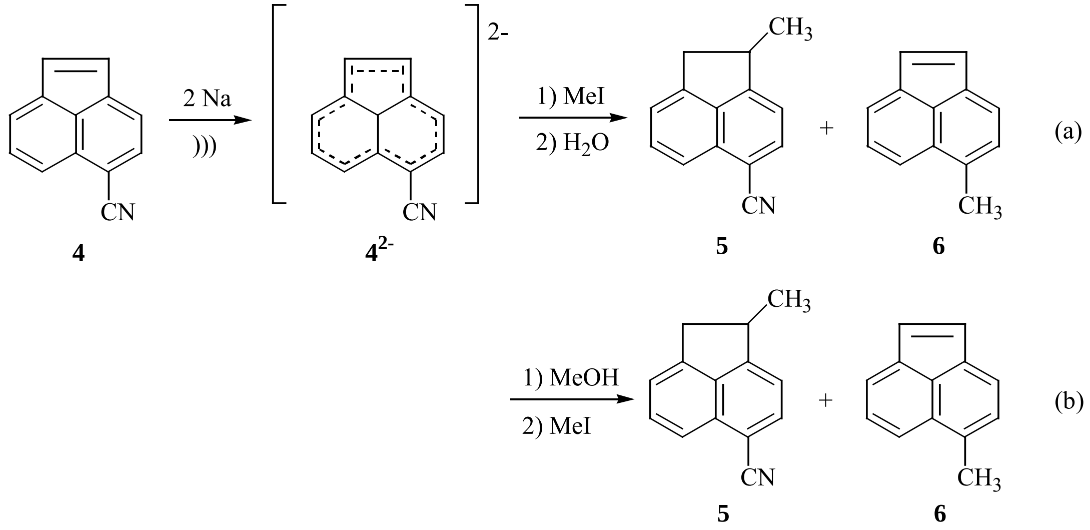
1-Cyanoacenaphthylene (**1**) was converted into its dianion (**1^{2-}**) according to the procedure described earlier (Chapter 2). The reaction mixture was cooled to -70ºC, one equivalent of methyl iodide was added and the solution was stirred at room temperature for 15 minutes. Quenching with water 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 $\mathbf{1}^{2-}$, $\mathbf{7}^{2-}$ and **1** in ppm and the differences in chemical shift between neutral form and dianion for $\mathbf{1}^{2-}$ and $\mathbf{7}^{2-}$.*

carbon atom	δ ($\mathbf{1}^{2-}$)	δ ($\mathbf{7}^{2-}$)	δ (**1**)	δ (**1**) - δ ($\mathbf{1}^{2-}$)	δ (7) - δ ($\mathbf{7}^{2-}$)
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)-$\mathbf{1}^{-}$)

The hydroanion of 1-cyanoacenaphthylene ((2H)-$\mathbf{1}^{-}$) was prepared from the dianion $\mathbf{1}^{2-}$ by addition of one equivalent of methanol to a solution of $\mathbf{1}^{2-}$ 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)-$\mathbf{1}^{-}$). The official name for (2H)-$\mathbf{1}^{-}$ 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)-$\mathbf{1}^{-}$ 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.

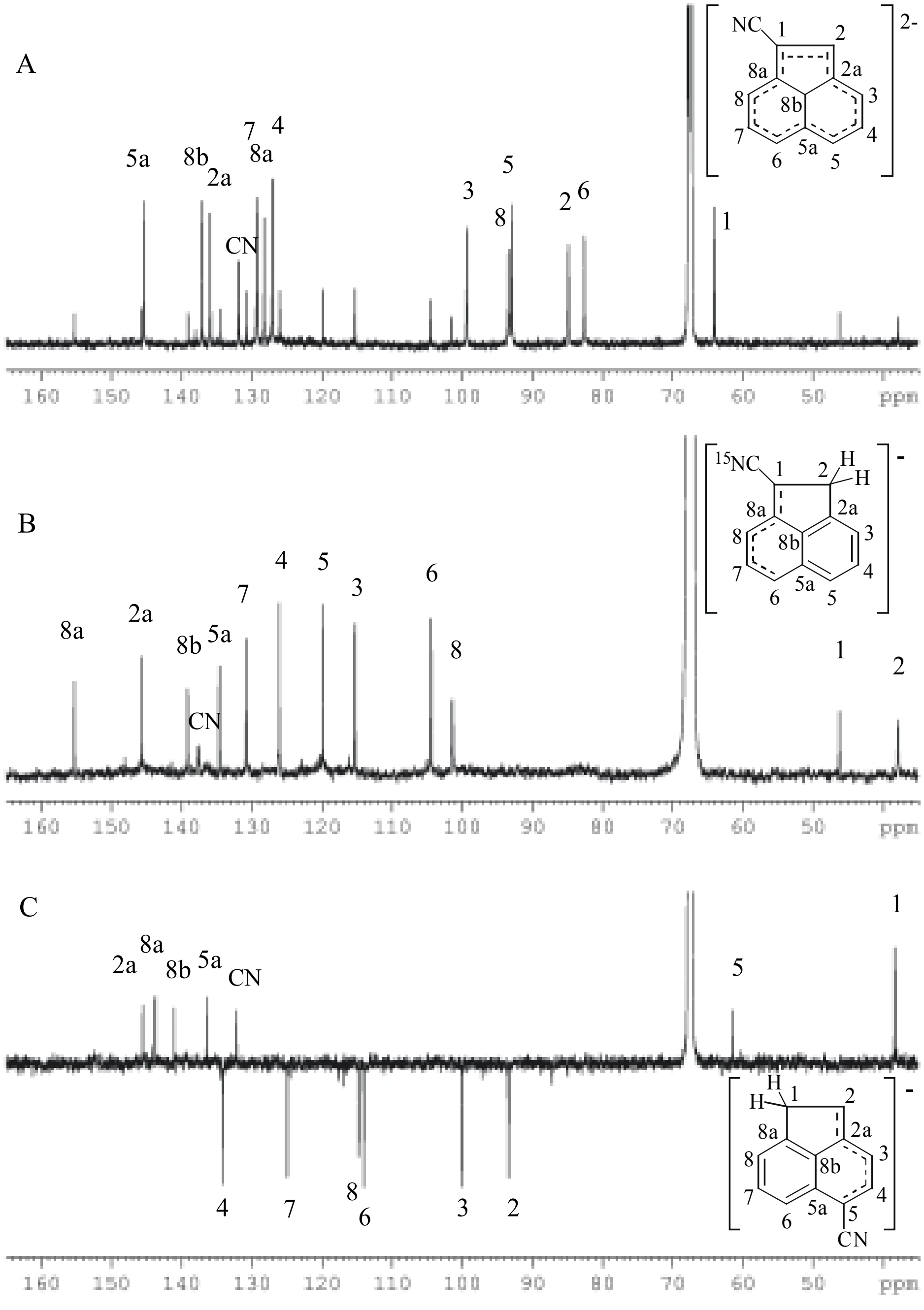


Figure 1: *^{13}C NMR spectra of A: the 1-cyanoacenaphthylene dianion (**1^{2-}**),B: the 1-cyano-2-hydroacenaphthylene anion ((2H)-**1^{-}**), and C: the 5-cyano-1-hydroacenaphthylene anion ((1H)-**4^{-}**) (A and C: 150 MHz, B: 75 MHz, 20ºC, the spectrum of **1^{2-}** contains some (2H)-**1^{-}**).*

*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 (**1**$^{2-}$) could be prepared in THF using sodium and ultrasonic vibration (see Chapter 7). In the experiments in which **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 (**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 **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 **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.

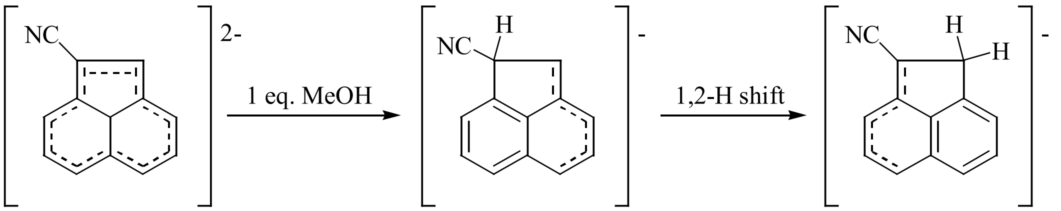
According to the calculations, carbon atoms 1 and 5 would be the carbon atoms with the highest charge. Because in the reaction of **1** with methyl iodide the π-electrons are involved in the bond formation process, the π-electron density should be regarded. The highest concentration of π-electrons is also found at carbon atoms 1 and 5. Although the HOMO coefficient on carbon atom 1 is not extremely large, the reaction of **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 **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 -70°C.



$\mathbf{1}^{2-}$

Kinetic product

Green

(2H)-$\mathbf{1}^-$

Thermodynamic product

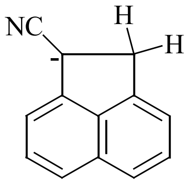
Brown

***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 KC^{15}N 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 ($\mathbf{1}^{2-}$) 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 ($\mathbf{4}^{2-}$) 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, $J_{2,\mathrm{Me}}$ = 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) : $\delta = 2.5$ (m, 1H, H-3), 1.25 (m, 2H, H-4), 1.85 (m, 1H, H-2) (broad signals).

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

^{15}N NMR (THF-d_8) : $\delta = 253.4$.

Crotonitrile

^{15}N NMR ($CDCl_3$) : $\delta = 265.1$ (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 ($CDCl_3$) : $\delta = 8.14$ (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 ($CDCl_3$) : $\delta = 149.9$ (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): $\delta = 265.5$ (SR DMSO = -62.8).

p-Methoxybenzonitrile

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

Benzonitrile

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

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