78. ^{1}H- and ^{13}C-NMR Study of the Dilithium Naphthalene and its TMEDA Complex

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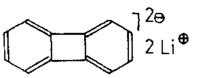
Dilithium naphthalene (**2**) and its TMEDA complex **3** have been prepared, and their ^{1}H- and ^{13}C-NMR spectra were analyzed in terms of chemical shifts and coupling constants. From its Q value, **2** is characterized as delocalized [4*n*] π system and the ^{1}H- as well as the ^{6}Li-NMR shifts classify the ion as strongly paratropic. For the quarternary C-atoms, a *down-field* shift of 30.4 ppm is observed. The conclusions drawn from the NMR parameters are compared with the results of MNDO calculations for naphthalene and biphenylene and their ions.

Introduction. – Recently, we reported on the complete NMR analysis of dilithium biphenylene (**1**), obtained by Li reduction of the hydrocarbon in THF at −78° [1]. A similar study for the well-known dilithium naphthalene (**2**), which can be stabilized as *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) complex (**3**) [3], seemed rewarding for several reasons. Firstly, an X-ray analysis of **3** is available, and an NMR investigation of this species should allow an interesting comparison between the structure of the organic ligand in the solid state and in solution. Secondly, strong shielding was reported for the ^{1}H resonances of **2** [4], which indicates the presence of molecular paramagnetism in the ion. The transformation of a 10π electron system into a 12π-electron system, thus, constitutes an intriguing test for our Q-value method [5] and allows at the same time a comparison with the 12π→14π transformation realized in the case of **1**. Finally, the results for **2** were needed as important reference data for a new species obtained by Li reduction of benzo[*b*]biphenylene [6].



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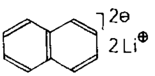

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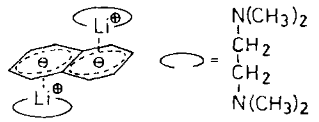

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Results. – Treatment of naphthalene with Li sand in (D_8)THF at −78° under Ar, using mechanical vibration of the reaction vessel (a 5-mm NMR tube) and 10% biphenylene as reduction catalyst yielded a dark blue/black suspension which was stored at −30°. The reduction progress was monitored by ^{1}H-NMR spectroscopy. After 4 weeks, the 400-MHz ^{1}H-NMR spectrum, which originally showed only broadened resonances, displayed several sharp signals, among them two *'triplets'* at 3.09 and 1.27 ppm, typical for the *AA′XX′* spin system expected for **2** *(Fig. 1a)*. The corresponding ^{13}C-NMR spectrum yielded resonances at 163.65, 112.93, and 82.70 ppm, respectively, which were character-

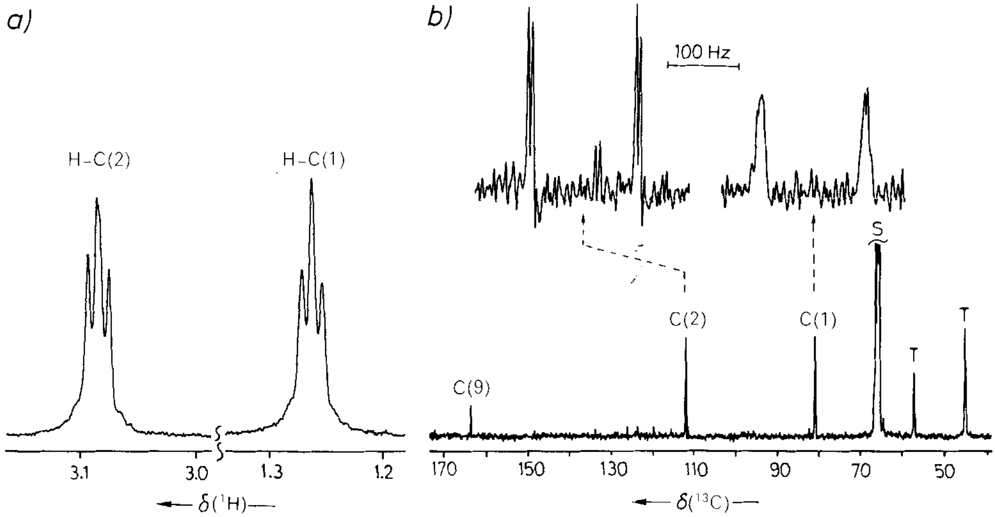


Fig. 1. a) *400-MHz ^1H-NMR spectrum of* **2**; b) *100 MHz ^{13}C-NMR spectrum of* **3** *with ^1H-coupled multipletts* ('fingerprints') [7] *for C(1) and C(2)* (S = solvent (D_8)THF, T = TMEDA signals)

ized by the 'fingerprints' observed in the ^1H-coupled spectrum [7] as belonging to the quarternary and tertiary C-atoms C(2) and C(1), respectively. ^1H-NMR assignment was achieved through reduction of partially deuterated $(1,4\text{-}^2H_2)$naphthalene, where the intensity of the high-field triplet in the ^1H-NMR spectrum was diminished by 33%. These results were confirmed by a two-dimensional $^1H,^{13}C$-shift correlation [8] *(Fig. 2a)*. The

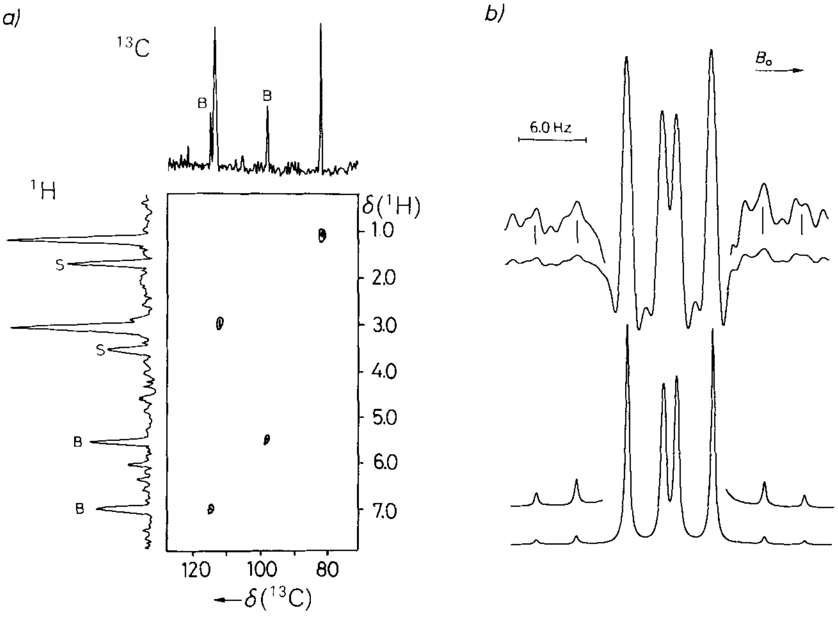


Fig. 2. a) *$^{13}C,^1H$-shift correlation for* **2** (S = (D_7)THF, B = biphenylene, *cf.* text); b) AA′ *part of the ^1H-spin system of* **2** *observed* (above, after *Gaussian* multiplication of the time domain function) *and calculated* (below)

complex **3** was prepared as described in [3] and investigated in (D$_8$)THF solution. Assignment of ^{13}C and ^{1}H resonances was again achieved by the fingerprint method [7] *(Fig. 1b)* and a 2D-^{13}C,^{1}H-shift correlation.

The ^{1}H-spin system of **2** was treated as *AA'XX'* system, thus neglecting interring couplings. While this procedure presented problems in the case of naphthalene, which could only be solved by synthesis of the 1,2,3,4-tetradeutero compound and its analysis using ^{2}H decoupling [9], or, more recently, by the complete analysis of the 8-spin system [10], the reduced resolution obtained for the ionic species due to inherent line-broadening allowed the simplified treatment as 4-spin system *(Fig. 2b)*. The complete results, together with the $^1J(^{13}$C,^{1}H) data determined for **2** and the ^{6}Li resonance of **3** are collected in *Table 1*, which also contains the relevant data of the parent hydrocarbon naphthalene (**4**) for comparison.

Table 1. *^{1}H and ^{13}C Chemical Shifts* (δ [ppm] relative to TMS), *and ^{1}H,^{1}H- and ^{13}C,^{1}H-Coupling Constants* [Hz] *of* **2**, **3**, *and* **4**

^{1}H-NMR (400.13 MHz)						
	δ(H–C(1))	δ(H–C(2))	J(1,2)	J(1,3)	J(1,4)	J(2,3)
2[a]	1.266	3.088	6.15	1.36	1.86	9.48
3[b]	1.167	3.071	–	–	–	–
4[c]	7.70	7.34	8.28	1.24	0.74	6.85

^{13}C-NMR (100.61 MHz)					
	δ(C(1))	δ(C(2))	δ(C(9))	^1J(1,H)	^1J(2,H)
2	82.70	112.93	163.65	148.8	152.0
3[d]	82.10	113.23	163.78	150.4	153.5
4[e][f]	127.7	125.6	133.3	158.8	159.5

^{6}Li-NMR (58.88 MHz): **3** –1.87 ppm (–30°) relative to 1M LiCl in THF

[a] RMS error of interative analysis 0.03 Hz.
[b] TMEDA signals at δ 2.565 (CH$_2$) and 2.508 (CH$_3$).
[c] [9].
[d] TMEDA signals at δ 58.54 (CH$_2$) and 46.56 (CH$_3$).
[e] Chemical shifts: [11].
[f] Coupling constants: [12].

Discussion. – An inspection of *Table 1* allows the immediate conclusion that the electronic properties of the organic moiety have profoundly changed in going from the hydrocarbon to the ionic compound. It is also apparent that the species identified after alkali-metal reduction of naphthalene is indeed the dianion **2**, since the same spectral data are derived for **3**. It is not clear, however, if in (D$_8$)THF solution TMEDA complexation of the lithium cations in **3** is replaced by complexation through the solvent, and this aspect requires further studies.

Coupling Constants. The vicinal ^{1}H,^{1}H-coupling constants J(1,2) and J(2,3) of **2** indicate a bonding arrangement which differs from that in naphthalene, as far as $J(1,2) < J(2,3)$ is found, whereas in the hydrocarbon the reverse ratio holds. This is in accord with the X-ray results for **3** which yielded the bond lengths given in *Table 2*. With the $^3J/R_{\mu,\nu}$ relation derived for six-membered rings [9] we calculate $R_{1,2} = 143.6$ and $R_{2,3} = 134.4$ pm in excellent agreement with the experimental results for the solid, con-

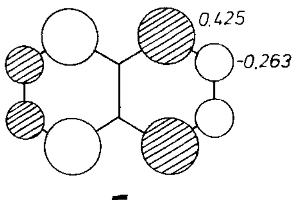
Table 2. A) *Bond Lengths* $R_{1,2}$ *and* $R_{2,3}$ [pm] *for* **2**, **3**, *and Biphenylene* (**1**°), *and its Ions* $\mathbf{1}^{2-}$ *and* $\mathbf{1}^{2+}$ *as Calculated from the Vicinal* $^1H,^1H$*-Coupling Constants Using the Empirical Equation* $R_{\mu,\nu} = (56.65 - {}^3J)/35.10^{a)}$; *Experimental Data for Comparison* (Italics); B) *Empirical* (*Eqn. 1*) *and Calculated (PPP) π-Bond Orders* $P_{\mu,\nu}$ *for* **2** *and* **4** *and Derived Q Value* $P_{1,2}/P_{2,3}$

A)	$R_{1,2}$	$R_{2,3}$		$R_{1,2}$	$R_{2,3}$		$R_{1,2}$	$R_{2,3}$
2	143.9	134.4	**1**°	141.8	137.6	$\mathbf{1}^{2-}$	139.3	144.2
3	*143.3*[b])	*134.3*[b])		*142.8*[c])	*137.0*[c])	$\mathbf{1}^{2+}$	138.2	143.2

B)	$P^{emp}_{1,2}$	$P^{emp}_{2,3}$	Q^{emp}	$P^{calc}_{1,2}$	$P^{calc}_{2,3}$	Q^{calc}
2	0.520	0.866	0.600	0.492	0.747	0.659
4	0.741	0.592	1.252	0.741	0.587	1.262

[a]) [9]. [b]) X-Ray results from [3]. [c]) Electron-diffraction results from [14].

sidering an error of 1–2 pm in the data derived from the NMR coupling constants. The results of similar bond-lengths calculations for biphenylene and its ions are also given. As the change in the bond lengths [3], the change in the ^3J values observed in going from **4** to **2** can be equally well rationalized in terms of the HMO-LUMO of **4** (**5**) [13], which is the doubly occupied HOMO of the dianion. Thus, an increase of *antibonding* character between the C(1) and C(2) is accompanied by an increase of *bonding* character between the C(2) and C(3).



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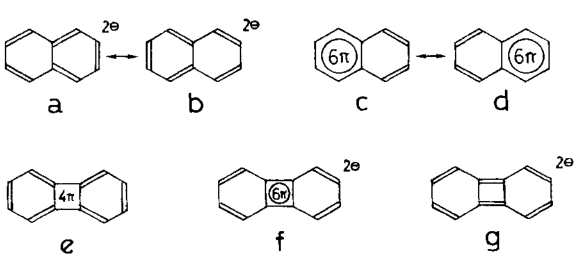
Turning to the Q-value method, our empirical *Eqn. 1* [5] yields *Pople-Pariser-Parr* SCF-π-bond orders for **2** that are given in *Table 2*. The value $Q = P_{1,2}/P_{2,3}$ calculated from these data characterizes **2** as delocalized [4*n*] π-system. For the neutral benzo[8]annulene, a Q value of 0.930 was predicted [5].

$$P_{\mu,\nu}(\text{SCF}) = 0.104\,{}^3J_{\mu,\nu} - 0.120 \qquad (1)$$

Thus, in terms of resonance theory, structures like **a** and **b** appreciably contribute to the resonance hybrid of the dianion, while in the hydrocarbon **c** and **d** are important. In the



case of biphenylene, on the other hand, the reduction of the hydrocarbon to the dianion shifts the importance from resonance structure **e** to **f** or **g**. In other words and in line with our model [5], a [4*n*]annulene induces a bonding situation in the annellated benzene ring, where exocyclic double bonds at the annulene ring are favoured.

Chemical Shifts. The interpretation of the chemical shifts observed for **2** and **3** is less straightforward, since work on polycyclic ions has shown over the years (for reviews, see [15]) that the simple linear π-charge-density/chemical-shift correlations [16], which were established in the early days of ^{1}H- and ^{13}C-NMR using a limited number of monocyclic charged species, can hardly be expected to hold for more complicated situations (for a recent discussion, see [17]). In the present context, two aspects are of importance:

1) The breakdown of the simple one-electron MO model for the prediction of spin and charge densities in ionic species of certain alternant hydrocarbons. Here, negative spin density is found in the radical anions [18] and partial positive charge in the dianions [4] at positions where the one-electron wave function for the HOMO has nodes. As a consequence, downfield ^{1}H- and ^{13}C-chemical shifts may be induced at these positions which, if not compensated by upfield contributions at other positions, lead to reduced proportionality constants for the charge-density/chemical-shift correlations mentioned above.

2) Observations made for a number of polycycles where reduction of $[4n + 2]\ \pi$ systems leads to $[4n]\ \pi$ systems have led to the proposal [19] that in these cases a further paramagnetic contribution to the ^{13}C screening constant arises which, in addition to the partial positive charges, may lead to extra downfield shifts in the negative ions. The proportionality constants K_c for the well-known *Spiesecke-Schneider* relation *(Eqn. 2)* [16c, d]

$$\Delta\delta = K_c \cdot \Delta\rho_\pi \qquad (2)$$

are then again considerably smaller than the original value of 160 ppm. This effect may be attributed to changes in certain terms of the *Karplus-Pople* equation [20] for the paramagnetic contribution to the total ^{13}C screening constant σ.

In addition, *van-der-Waals-*, electric-field- and neighboring anisotropy effects may play a role [21], but these aspects are of minor importance in the present case. We will also neglect any influence resulting from ion-pair formation, since the temperature and concentration dependence of the ^{1}H and ^{13}C shifts of **2** were not studied.

For the protons in **2** as in the case of other [4*n*] dianions of benzenoid hydrocarbons [22], a strong paramagnetic contribution to the ^{1}H shielding [23] is expected and indeed evident from the observed high-field shift ($\Delta\delta$(H–C(1)) –6.43, $\Delta\delta$(H–C(2)) –4.25 ppm) which totals 42.7 ppm! Since the two added electrons, according to the empirical rule [16] $\Delta\delta = 10.7\ \Delta\rho_\pi$, could give rise to a maximum of only 21.4 ppm shielding, there must be a second shielding mechanism. Within the limits of the one-electron model, the π-charge densities expected from **5** (1.361, 1.138), yield 3.86 and 1.48 ppm to the shielding of H–C(1) and H–C(2), respectively. This leaves high-field shifts of 2.57 and 2.77 ppm in these positions for the contribution of the paramagnetic ring-current effect, if the hydrocarbon is used as reference *(cf. Table 1)*. Since the ^{1}H,^{1}H-NMR coupling constants (see above) as well as the ESR hyperfine splittings [24] and the NMR contact shifts [25] in naphthalene radical anion are fairly well explained on the basis of **5**, our analysis has some support, despite the reservations made above. PPP-SCF calculations [18] are in line with these results, as the bond orders and the Q value given in *Table 2* demonstrate. As discussed below, a more realistic picture is obtained by the PPP model for the charge density situation at C(9) and C(10).

The induced shifts for the ^{13}C resonances of C(1) and C(2) in **2** (45.0 and 12.7 ppm, respectively) follow again the calculated HMO and PPP π-charge-density changes at these positions (0.361, 0.138, and 0.357, 0.165, respectively), but they are smaller than expected on the basis of *Eqn. 2,* and a proportionality constant $K_c = 160$ ppm, which yields upfield shifts of 57.8 and 22.1 ppm, respectively. As in related cases [4] [26], there is a large downfield shift for the quarternary C-atoms which conforms with the partial positive charge at these positions calculated by the PPP method (π-charge density 0.956) as well as by the CNDO method (gross atomic charges at C-atoms are: C(1) −0.256, C(2) −0.054, C(9) +0.072 [3]). While the total upfield shift for all protonated C-atoms amounts to 230.8 ppm, the deshielding found C(9) and C(10) reduces this value to only 170.0 ppm which leads to $K_c = 85$ for the proportionality constant of *Eqn. 2.* This type of analysis, which is in widespread use, in fact compares the centers of gravity for the ^{13}C chemical shifts in the dianion and the neutral species and assumes that partial positive charges at certain centers of the perimeter should in turn increase the negative charge at other positions in order to maintain a total π-charge increase of 2 negative units. It neglects that appreciable negative charge can also be transferred to the H-atoms, in the case of **2** as much as 42% (gross atomic charges at H-atoms are: H–C(1) −0.094, H–C(2) −0.132 [3]). The paramagnetic-ring-current shift derived above for the protons may, thus, be partly due to this effect and the decrease in the proportionality constant K_c results in part from a charge deficiency at the perimeter C-atoms¹).

If uncertainties are attached to the theoretical concepts used for the interpretation of experimental data, a comparison of two experimental quantities sometimes allows a conclusion with regard to the physical origin of the observed phenomena. For the

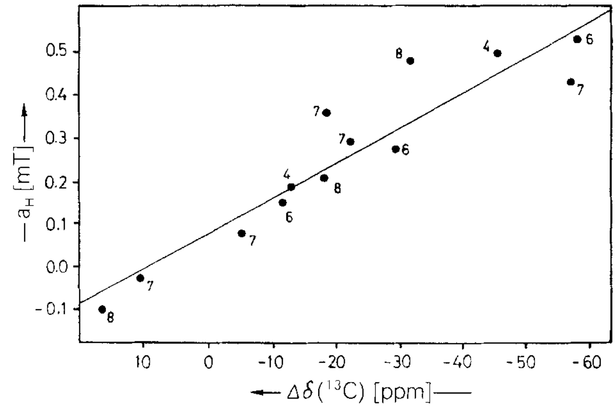


Fig. 3. *Correlation between ESR hyperfine coupling constants* a_H [28] (mT) *and* ^{13}C $\Delta\delta$ *values* (ppm, from the refs. cited below) *for the radical anions and the dianions, respectively, of naphthalene* (**4**, this work), *anthracene* (**6**) [4], *phenantrene* (**7**) [29], *and pyrene* (**8**) [30] (the regression yields a_H [mT] = 0.0759 − 0.0084 × $\Delta\delta$(^{13}C)).

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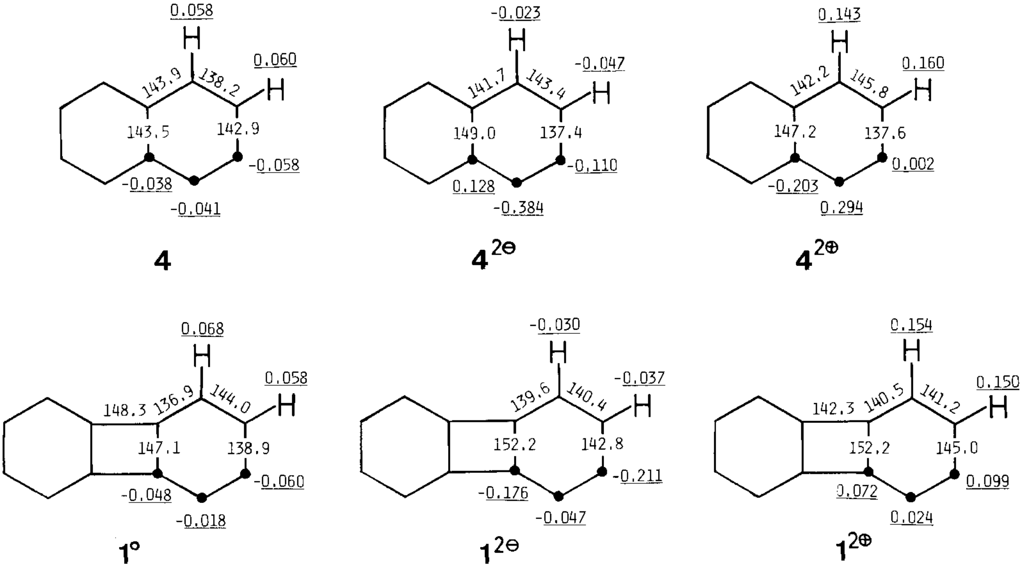
¹) This aspect remains unnoticed in a pure π-electron treatment as used in [19]; thus, in the PPP model the partial positive charge at C(9), C(10) is compensated by an increase of negative charges at the β-C-atoms.

dianions of benzenoid hydrocarbons, the corresponding radical anions are obviously species of related structure and, as was pointed out elsewhere [15a] [26a], a comparison of the $\Delta\delta(^{13}C)$ values with the ESR hyperfine coupling constants should reveal this similarity as far as the tertiary C-positions are concerned. As *Fig. 3* shows for the relevant data of the mono- and dianions of naphthalene, anthracene, phenanthrene, and pyrene, there is indeed a linear correlation between these two parameters, and the slope of the regression is similar to that found for other polycyclic systems [26a]. Since the ESR data depend only on spin densities, one can conclude that the ^{13}C shifts at the CH positions in the dianions are also dominated by the charge distribution.

Another interesting probe for the electronic structure of Li salts of cyclic π systems is provided by the ^6Li or ^7Li chemical shift, since distinct shielding ranges are observed for dia- and paratropic systems. From a compilation of ^7Li-NMR data for 13 different dianions [27], one expects the Li resonance for species with $[4n + 2]$ π electrons between -4 and -8 ppm and for those with $[4n]$ π electrons between 0 and -1.1 ppm (external reference 1M $LiCl/H_2O$). For comparison, σ-bound Li in compounds like PhLi resonates at much lower field (~ 2 ppm). The value of -1.87 ppm found for **3** is, thus, at relatively high field, but compares well with the value found for dilithium anthracene (-1.15 ppm) and characterizes **2** again as paratropic $[4n]$ π system. In contrast, for the diatropic dilithium biphenylene, we measured -7.3 ppm [1].

MNDO Calculations. To compare the structural information derived from the NMR data for **2** and earlier for **1** and $\mathbf{1}^{2+}$ [1] with theoretical predictions, we have performed MNDO calculations [31] with geometry optimization within the constraint of a planar structure with D_{2h} symmetry, even if only the gas-phase structures of the isolated species are obtained. The relevant results for the hydrocarbons, the dianions, and the dications are given in *Fig. 4* (for a MINDO/3 calculation of **2**, see [32]).



4 $\mathbf{4}^{2\ominus}$ $\mathbf{4}^{2\oplus}$

$\mathbf{1}^{0}$ $\mathbf{1}^{2\ominus}$ $\mathbf{1}^{2\oplus}$

Fig. 4. *C–C bond lengths* (pm) *and local total charges* (underlined) *for naphthalene, and biphenylene, and their ions from MNDO calculations*

With respect to the C(1)–C(2) and C(2)–C(3) bond lengths and the π-bond dominance in the C(1)–C(4) bond fragments, there is excellent agreement with the conclusions drawn from the ^{1}H,^{1}H-coupling constants. In addition, the calculations show a considerable weakening of the cross ring bonds in the ions, where a peripherical π-electron loop is apparently preferred. This is also borne out by the X-ray results (**3**: 144.7 pm [3]; **4**: 141.8 pm [33]). $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$ may then be regarded as dianion and dication, respectively, of a perturbed [12]annulene, and resonance structure **g** is supported. A similar trend is predicted by PPP calculations and was recently found even by HMO calculations using ω and variable β techniques [34]. Certainly, the situation for the four-membered-ring partial structure of these ions is quite distinct from that predicted theoretically for the dianion and dication of cyclobutadiene [35] [36].

The total charge densities parallel the ^{13}C shifts, and the partial positive and negative charge at C(9), C(10) of the naphthalene ions is especially noteworthy, as is the charge transfer to the H-atoms. This factor accounts for part of the ^{1}H-shielding and deshielding observed in the dianions and dications, respectively. It may be responsible for the difference derived for the ring current contributions to the ^{1}H chemical shifts in $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$ on the basis of a simple π-electron analysis [1]. Thus, more charge-induced ^{1}H shielding in the dianion and ^{1}H deshielding in the dication with respect to the ^{1}H data of the hydrocarbon would seemingly diminish the diamagnetic ring-current effect in the former species and attenuate this effect in the latter (for a MNDO study of **2**, see [37]).

Experimental. – *Reduction of Naphthalene* (**4**). An NMR tube of 5 mm o. d. was flushed with dry Ar and subsequently charged with *ca.* 20 mg (2.9 mmol) of Li sand, and fitted with a septum; 12 mg (0.094 mmol) of freshly sublimed **4** and 1.6 mg (0.011 mmol) of biphenylene, dissolved in 0.5 ml of dry (D_8)THF were added with a syringe at −78°. The initial blue colour changed to dark blue/black. The tube was sealed and transferred to the rod of a mechanical vibrator and vigorously shaken during 2 h at −30°. Thereafter, the tube was kept at this temp. and the reduction progress followed by sporadically recording the ^{1}H-NMR spectrum. The addition of biphenylene as reduction catalyst was indicated by the empirical observation that in some cases Li reductions of π systems were promoted by the presence of biphenylene dianion, which is easily formed. A systematic investigation of this effect was, however, not attempted.

The complex **3** was prepared from 3.3 mmol of 1,4-dihydronaphthalene and BuLi according to *Stucky* and coworkers [3]. Crystals of **3** were isolated under Ar, washed with dry pentane, and dried at r.t. A sat. soln. of **3** in (D_8)THF was used for the NMR measurements (sealed 5-mm o. d. NMR tube).

NMR spectra were run on a *Bruker WH-400 Fourier*-transform NMR spectrometer at the frequencies given in *Table 1*, using standard *Bruker* software and routine parameters for the 2D-^{13}C,^{1}H-shift correlation [8]. Iterative spectral annalysis was performed with the program PANIC, a version of the LAOCN procedure [38]. The MO calculations were performed with the QCPE programs No. 76 (PPP, parameters as in [5] and No. 353 (MNDO)).

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