102. A Comparative ^{1}H- and ^{13}C-NMR Study of the Dianion and Dication of Biphenylene

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Biphenylene dianion has been prepared by Li reduction of the parent hydrocarbon. It is stable below –30° and was characterized by its ^{1}H- and ^{13}C-NMR spectra. A comparison of these data with those of the dication indicates the existence of ion pairs in the dianion case which are responsible for a different charge distribution. The diamagnetic ring currents of both ions, however, are of comparable magnitude, and both are more diatropic than the parent hydrocarbon. Predictions of the π-charge-density effect on ^{1}H chemical shifts are improved by calculations that use the linear and quadratic electric-field effect equation instead of the simple *Spiesecke-Schneider* relation.

Cyclic conjugated π systems containing [4n]π electrons can be transformed to [4n + 2]π systems either by oxidation to the dication or by reduction to the dianion [1]. In general, such transformations should be accompanied by a gain in delocalization energy. Thus, they are of particular interest in the case of the unstable cyclobutadiene [2], the smallest member of the neutral [4n]annulene family.

While experiments to generate substituted cyclobutadiene dications were successful [3], analogous attempts to synthesize substituted cyclobutadiene dianions were less rewarding [4] [5]. For example, in the case of 3,4-diphenylbenzocyclobutadiene dianion as well as tetraphenylcyclobutadiene dianion, it was concluded – mainly on the basis of the NMR data – that the negative charge is predominantly residing in the phenyl substituents, thereby rendering olefinic character to the central four-membered ring [5]. Similar results seemed to hold for biphenylene (**1**), where $\mathbf{1}^{2+}$ was well-characterized by ^{1}H- and ^{3}C-NMR measurements [6], while equally clear data for $\mathbf{1}^{2-}$ were still missing [7]. On the other hand, however, strong support for the diatropic nature of $\mathbf{1}^{2-}$ came from ^{7}Li-NMR measurements [8], where an upfield shift of 6.1 ppm relative to external aq. LiCl was observed.

We now conducted a clean reduction of biphenylene with Li sand in THF at –78° by ultrasonic treatment. A quantitative conversion to the dianion, formed as a deep copper-brown suspension, was achieved in less than 2 h. We could then determine the complete H- and ^{13}C-NMR data for $\mathbf{1}^{2-}$, and these results are reported in the present communication. In addition, we compare the results for the dianion with those obtained earlier for the dication [6], which we supplemented by an analysis of the ^{1}H-NMR-*AA'XX'* system.

Results. – *Spectra.* The dianion $\mathbf{1}^{2-}$ yielded, at 400 MHz, an *AA'XX'* system for the aromatic protons that was analyzed by standard procedures [9]. The assignment of the 1 – ^{1}H and 2 – ^{1}H resonances was unambiguously achieved through observation of the ^{13}C satellites in the ^{1}H-NMR spectrum [10]. The ^{13}C-NMR spectrum was assigned from the 'fingerprints' observed in the off-resonance decoupled spectrum [11] as well as by a two-dimensional ^{1}H,^{13}C-shift correlation [12]. Similar treatment was applied for $\mathbf{1}^{2+}$ which was prepared according to *Olah* and *Liang* [6b]. All results are collected in *Table 1*, some spectra are shown in the *Figure*.

Stability. Contrary to the general assumptions [4], $\mathbf{1}^{2-}$ was found stable for several hours at temperatures below 0°. Above 0°, 2,2'-dilithiobiphenyl (**2**) is formed by a ring-opening reaction as shown by quenching experiments with H_2O and diphenyl ketone.

Table 1. *^1H and ^{13}C Chemical Shifts* δ [ppm] *relative to TMS and ^1H, ^1H- and ^{13}C, ^1H-Coupling Constants* [Hz] *of* **1**, $\mathbf{1}^{2-}$, *and* $\mathbf{1}^{2+}$

	^{1}H-NMR								
	$\delta(1)$	$\delta(2)$	$J(1,2)$	$J(1,3)$	$J(1,4)$	$J(2,3)$	Temp.	Solvent	Ref.
1	6.59	6.69	–	–	–	–	r.t.	(D_8)THF	This work
	–	–	6.87	0.82	1.04	8.34	r.t.	(D_6)Aceton/CCl_4 (12:1)	[13]
$\mathbf{1}^{2-}$	6.926	5.467	7.74	0.85	1.22	6.05	–40°	(D_8)THF	This work
$\mathbf{1}^{2+}$	10.00	10.37	8.13	0.76	1.52	6.39	–20°	SO_2ClF/SbF_5	This work

	^{13}C-NMR							
	$\delta(1)$	$\delta(2)$	$\delta(4a)$	$^1J(1,H)$	$^1J(2,H)$	Temp.	Solvent	Ref.
1	117.9	128.9	152.2	–	–	r.t.	(D_8)THF	This work
	–	–	–	163.33	159.81	r.t.	(D_6)Aceton/CCl_4 (12:1)	[13]
$\mathbf{1}^{2-}$	113.7	97.3	97.9	148.9	151.2	–40°	(D_8)THF	This work
$\mathbf{1}^{2+}$	135.5	169.9	177.7	190.4	186.9	–20°	SO_2ClF/SbF_5	[6b]

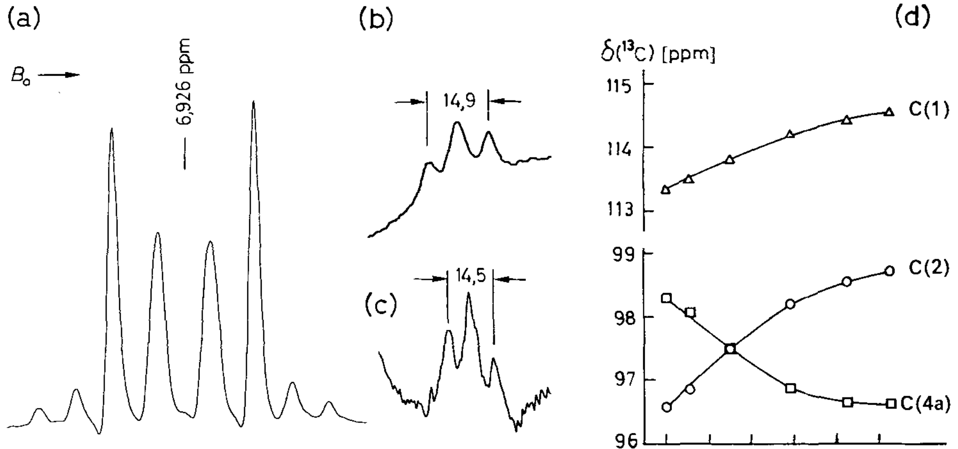
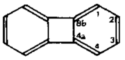


Fig. (a) *Low-field part of the* AA'XX' *system of the ^1H-NMR spectrum of* $\mathbf{1}^{2-}$ *at 400 MHz;* (b) *^{13}C satellite of the low-field part of the* AA'XX' *^1H-NMR spectrum of* $\mathbf{1}^{2+}$ *at 400 MHz* (splitting in Hz); (c) *^{13}C satellite of the high-field part of the* AA'XX' *^1H-NMR spectrum of* $\mathbf{1}^{2-}$ *at 400 MHz* (splitting in Hz); (d) *temperature dependence of the ^{13}C-NMR signals of* $\mathbf{1}^{2-}$

From ^{7}Li-NMR measurements, where **1**$^{2-}$ and **2** showed signals at -7.3 and $+2.22$ ppm relative to external aq. LiCl, a half life of *ca.* 1.7 h was estimated for **1**$^{2-}$ at 25°. Oxidation by air at $-30°$ led to biphenylene and *ca.* 30% biphenyl as by-product, while quenching with H_2O yielded benzocyclooctene (54%) as in the case of K reduction of **1** [7d].

Discussion. – If compared with the data of **1**, the vicinal coupling constants in the ions (*Table 1*) clearly indicate the different nature of these π systems. In terms of resonance theory, the major contribution of the resonance structure **1** to the hydrocarbon resonance hybrid has now been replaced by the contribution of **3** and **4** to the resonance hybrid of the charged species. Both, the vicinal as well as the long-range coupling constants are in agreement with this tendency, characterized by the relation $^3J(1,2) > {}^3J(2,3)$ and $^5J > {}^4J$ [14].



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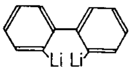

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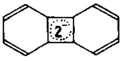

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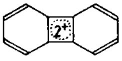

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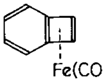
Using the Q value method [15] to gain insight into the electronic structure of **1**$^{2-}$ and **1**$^{2+}$, we found, from the ^3J values, the empirical π-bond orders given in *Table 2*. Since strain effects in annelated benzene rings influence vicinal ^{1}H,^{1}H-coupling constants [16], the experimental results (*Table 1*) had to be corrected for this effect. Increments of $+0.18$ Hz for $J(1,2)$ and -0.24 Hz for $J(2,3)$ were derived from a comparison of the relevant data of benzocyclobutene and benzene [17].

Table 2. *Vicinal ^{1}H,^{1}H-Coupling Constants* [Hz] *of* **1**, **1**$^{2-}$, *and* **1**$^{2+}$ *Corrected for Strain Effects, Empirical and Calculated PPP π-Bond Orders, and Q Values*

	$J(1,2)_{\text{corr.}}$	$J(2,3)_{\text{corr.}}$	$P^{\text{emp.}}_{1,2}$	$P^{\text{calc.}}_{1,2}$	$P^{\text{emp.}}_{2,3}$	$P^{\text{calc.}}_{2,3}$	$Q = P^{\text{emp.}}_{1,2}/P^{\text{emp.}}_{2,3}$
1	7.05	8.10	0.613	0.623	0.722	0.697	0.849
1^{2-}	7.92	5.81	0.704	0.699	0.484	0.507	1.455
1^{2+}	8.31	6.15	0.744	0.699	0.520	0.507	1.431

The calculated Q values again demonstrate $[4n + 2]\pi$ character for the central four-membered ring of **1**$^{2-}$ and **1**$^{2+}$ (n = 1 and 0, respectively) which then must hold a considerable amount of charge[1]). This is particularly well-demonstrated, if we compare the Q value of **1**$^{2-}$ with that of the dianion of 3,4-diphenylbenzocyclobutadiene (Q = 1.05 [5]). A further interesting comparison is possible with the irontricarbonyl complex of benzocyclobutadiene (**5**), where the ^{1}H coupling constants [18] lead to a Q value of 1.42, again after correction for strain effects. Since the diene character of the double bonds in the six-membered ring of **5** is sufficiently developed to allow the addition of a second irontricarbonyl group [19], considerable diene character must also be present in **1**$^{2-}$ and **1**$^{2+}$.



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[1]) By definition, the Q value of a benzoannulene characterizes the π system annelated to the benzene ring [15].

Information on the charge distribution in $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$ is best obtained from the ^{13}C chemical shifts [20]. Compared to the parent hydrocarbon, the overall shift for $\mathbf{1}^{2-}$ is 360.4 ppm, while for $\mathbf{1}^{2+}$ 342.4 ppm was found [6]. The proportionality constants K in the well-known *Spiesecke-Schneider* relation $\Delta\delta(^{13}C) = K\Delta\rho$ [21] between ^{13}C chemical shifts and charge-density changes are thus 180.2 and 171.2 ppm, respectively, and are close to the general accepted value of 160–180 ppm found for diatropic systems [22] [23]. With these constants, we calculate individual charge densities for $\mathbf{1}^{2-}$ in good agreement with the simple HMO predictions *(Table 3)*. For $\mathbf{1}^{2+}$, the HMO and the experimental data differ. The experiment indicates considerably less positive charge in the four-membered ring and more positive charge at C(1). In fact, in the dianion 60% of the charge is located in the four-membered ring, while only 30% of the charge is found in these positions in the dication. Here, nearly 50% charge is located at C(2), C(3), C(6), and C(7).

The deviation of the dication charges from the predictions of the simple one-electron picture suggests that *Coulomb* repulsion is responsible for a more even charge distribution: 0.89, 0.76, and 0.85 at C(1), C(2), and C(4a), respectively, instead of 0.95, 0.82, and 0.73 as calculated. In $\mathbf{1}^{2-}$, such an effect is apparently absent, because the small counter ions Li^+ situated above and below the four-membered ring strongly favor charge localization at C(4a). As a consequence, the qualitative agreement is better between experimental charges and HMO charges, *i.e.* using a MO formalism where electron repulsion is not accounted for. This interpretation finds strong support from the results of PPP calculations *(Table 3)*, where the inclusion of electron repulsion leads to a good agreement with the empirical charge densities of $\mathbf{1}^{2+}$. For $\mathbf{1}^{2-}$, on the other hand, the now existing deviation from the PPP predictions must originate from the counter-ion effect. Evidence for contact-ion pairs in $\mathbf{1}^{2-}$ with the cations above and below the four-membered ring is obtained from the ^{7}Li-NMR results mentioned above as well as from the temperature dependence of the ^{13}C chemical shifts *(Figure)*, which show a levelling tendency above 0°. Shielding of C(4a) increases with temperature, indicating charge polarization to the four-membered ring in accord with increasing concentration of the contact-ion pairs *vs.* solvent-separated ion pairs [24]. At low temperature, on the other hand, where the concentration of solvent-separated ion pairs is raised, the charge density at C(4a) is decreasing, while it is increasing at C(1) and C(2).

Assuming that the ^{13}C-NMR shifts in the ions relative to the parent hydrocarbon are only due to charge-density changes, the ^{1}H shifts can be corrected for charge-density contributions on the basis of the experimentally determined charge densities at the C-atom of the respective C–H bond, ρ_i, and the empirical relation [21]

$$\Delta\delta(^{1}H) = 10.6\,\Delta\rho_i \qquad (1)$$

Within this approximation, the resulting shifts $\delta(^{1}H)_{\text{corr.}}$ should now reflect the ring-current effect in $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$. The corresponding data are collected in *Table 3*. Both compounds show the expected downfield shift with respect to **1**, and they are, thus, characterized as more diatropic. There are, however, a number of significant differences. In $\mathbf{1}^{2+}$, the ring-current contributions $\Delta\delta_{RC}$ to the ^{1}H chemical shifts are in the expected order of $\Delta\delta_{RC}$ (1 – H) > $\Delta\delta_{RC}$ (2 – H), while in $\mathbf{1}^{2-}$ the reverse order holds. Furthermore, $\mathbf{1}^{2+}$ with δ values > 7.5 ppm seems to sustain a stronger ring current than $\mathbf{1}^{2-}$. This is especially surprising, since in the simple ring-current model, the ring-current intensity is a function of the number of electrons involved, and a quantum mechanical calculation [25] has

Table 3. *^{13}C Chemical Shifs $\Delta\delta$* [ppm], *and Empirical and Calculated Excess Charge Density of* **1**$^{2-}$ *and* **1**$^{2+}$ *Relative to* **1**; *Charge Density and Ring-Current Contributions to ^{1}H Chemical Shifts* [ppm] *in* **1**$^{2-}$ *and* **1**$^{2+}$

	1^{2-}			**1**$^{2+}$		
	C(1)	C(2)	C(4a)	C(1)	C(2)	C(4a)
$\Delta\delta(^{13}C)$	–4.2	–31.6	–54.3	18.4	41.2	26.0
$\rho_{emp.}$	–0.023	–0.175	–0.301	+0.107	+0.242	+0.151
[%]	5	35	60	21	49	30
ρ_{HMO}	–0.054	–0.178	–0.272	+0.054	+0.178	+0.27
[%]	11	35	54	11	35	54
ρ_{PPP}	–0.086	–0.224	–0.191	+0.086	+0.224	+0.191
[%]	17	45	38	17	45	38
a) Calculations using *Eqn. 1*						
$\Delta\delta(^{1}H)_{\rho}$	–0.24	–1.86	–	+1.13	+2.57	–
$\delta(^{1}H)_{corr.}$	7.18	7.33	–	8.87	7.81	–
$\Delta\delta(^{1}H)_{RC}$	+0.59	+0.64	–	+2.28	+1.12	–
b) Calculations using *Eqn. 2*						
$\Delta\delta(^{1}H)_{\rho}$	–1.50	–2.01	–	+1.69	+2.07	–
$\delta(^{1}H)_{corr.}$	8.43	7.48	–	8.31	8.30	–
$\Delta\delta(^{1}H)_{RC}$	+1.84	+0.79	–	+1.72	+1.61	–

shown that the reduced ring current as well as the resonance energy are essentially the same for the dianion and dication of [12]annulene, which may be considered as models for **1**$^{2-}$ and **1**$^{2+}$.

Considering the well-known fact that ^{1}H chemical shifts are also subject to linear and quadratic electric-field effects from charges residing at neighbouring C-atoms [26], it seemed reasonable to perform an alternative calculation of the $\Delta\delta(^{1}H)_{\rho}$ values using a model that makes allowance for these effects. In particular, the relatively high charge density located at the central four-membered ring of both ions suggested that this approach should give a more realistic picture of the charge-induced polarization of the C–H bond electron density and the resulting effect for the ^{1}H chemical shifts than the simple *Eqn. 1,* which accounts for these additional effects in an empirical way[2]).

Using *Eqn. 2* [27]

$$\Delta\delta[\mathrm{ppm}] = -12.5\,\Sigma(\Delta\rho_i/R_i^2)\cos\theta_i + 17.0\,(\Sigma\Delta\rho_i/R_i^2)^2 \tag{2}$$

where $\Delta\rho_i$ is the charge-density change at position, i, R_i the distance vector between i and the proton of interest, and θ_i the angle between R_i and the C–H bond, we now derive $\Delta\delta(^{1}H)_{\rho}$ values that lead to charge-density-corrected chemical shifts and ring-current contributions $\Delta\delta_{RC}$ relative to the parent hydrocarbon which – considering the different experimental conditions used for the generation of the ions and the fact that the electric field effect of Li^{+} on the ^{1}H chemical shifts of **1**$^{2-}$ was omitted – are similar for both systems *(Table 3)*. Since only a minor deshielding (< 0.3 ppm) can be expected due to the Li^{+} effect in **1**$^{2-}$ [28], we can conclude that **1**$^{2+}$ and **1**$^{2-}$ sustain ring currents of comparable magnitude, in agreement with theory [25] and an other experimental result [23]. Here, the diatropic ring currents for the dianion and dication of 1,6;9,14-bismethano[16]annulene

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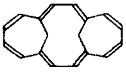
[2]) By using simple, cyclic ionic species to derive the proportionality constant in *Eqn. 1*, the charge-density effect of neighboring positions is automatically included.

(**6**), a 18π- and 14π-electron system, respectively, were compared and found to be of similar magnitude. The ion pairing that exists in $\mathbf{1}^{2-}$ (see above), thus, does not significantly quench its diatropic behavior, a conclusion which is in line with theoretical results on other charged [4n + 2]π systems [29].



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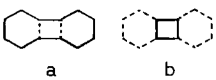

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A closer inspection of the data of *Table 3* shows that in $\mathbf{1}^{2-}$ $\Delta\delta_{RC}$ (1 – H) is considerably larger than $\Delta\delta_{RC}$ (2 – H), while in $\mathbf{1}^{2+}$ both increments are of equal magnitude. Also, $\Delta\delta_{RC}$ (2 – H) in $\mathbf{1}^{2-}$ is only 50% of the corresponding value in $\mathbf{1}^{2+}$. Notwithstanding the possibility that these differences arise through the affects mentioned above (different experimental conditions, neglecting Li^+ field effect), it is tempting to relate this finding to the idea that the total diamagnetic ring current arises from contributions of various subcircuits [30]. From the substructures **7a** and **7b**, a stronger contribution of **7b** in the case of $\mathbf{1}^{2-}$ and **7a** in the case of $\mathbf{1}^{2+}$ would be in line with our data as well as with the relatively strong ^{7}Li-shielding effect found in $\mathbf{1}^{2-}$.

Recently, *Vogler* [31] has calculated charge density and ring-current contributions to ^{1}H chemical shifts in $\mathbf{1}^{2-}$. For $\Delta\delta_{RC}$, he found 0.76 and 0.53 ppm for 1 – H and 2 – H, respectively, relative to the parent hydrocarbon. Since these calculated values are derived for the free ion, the agreement with our experimental data can be considered as good.

In conclusion, the increased diatropicity of $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$ relative to the parent hydrocarbon is well-documented. Counter-ion effects are shown to be present in $\mathbf{1}^{2-}$, which affect the charge-density distribution as known from other cases [32]. The diamagnetic ring-current intensity in both ions is comparable, while the contribution of individual subcircuits seems to differ. The application of *Eqn. 2* for the calculation of charge-density effects on ^{1}H chemical shifts should be considered, if one is dealing with small-ring compounds and systems with uneven charge distribution. Since the different charge densities as well as the different bond orders found for $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$, respectively, can be attributed to the effect of ion pairing in the Li salt of $\mathbf{1}^{2-}$, a violation of the pairing theorem [33] must not be involved, a conclusion which is in line with ESR results [34].

Experimental. – *Reduction of Biphenylene* (**1**). An NMR tube of 10-mm o.d. was flushed with dry Ar and subsequently charged with *ca.* 60 mg of Li sand, and fitted with a septum; 20 mg of **1** dissolved in 1.8 ml of dry (D_8)THF was added with a syringe at –78° and the suspension was subjected to ultrasonic treatment at this temp. for 90 min. The color changed from blue to copper-brown. The mixture was subsequently investigated by NMR at – 40°. Spectra of $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$, prepared according to [6b] in SO_2ClF, were run on *Bruker WH-400* and *WM-250 Fourier*-transform NMR spectrometers using standard *Bruker* software. The rms error for the iterative analysis of the ^{1}H spectra was 0.09 and 0.14 Hz for $\mathbf{1}^{2-}$ and $\mathbf{1}^{2+}$, respectively, and the exp. error in the NMR parameters is of the same magnitude.

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