

128. The Dianions of Phenanthrene and 1,2,3,4-Dibenzocyclooctatetraene

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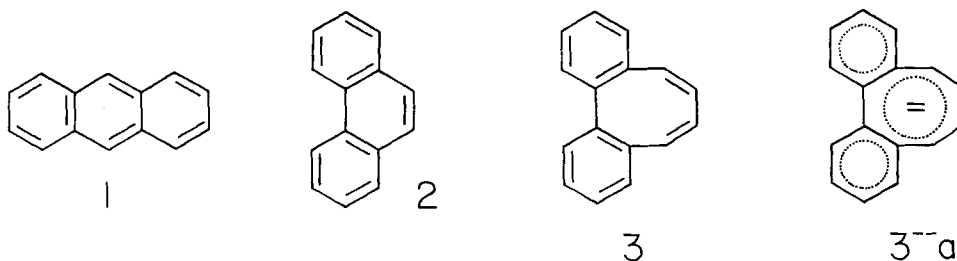
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Summary

The dianions of phenanthrene and 1,2,3,4-dibenzocyclooctatetraene have been prepared by metal reduction of the neutral compounds and characterized via the study of their ^1H - and ^{13}C -NMR. spectra. A description of the charge distribution can be achieved which is consistent with both MO-models and the spin density distribution of the corresponding radical anions. Thus, the dianion of 1,2,3,4-dibenzocyclooctatetraene appears as a π -bond delocalized species having its excess charge mainly localized in the eight membered ring.

1. Introduction. - In a recent paper we have compared the bonding situations in anthracene (**1**) and its corresponding dianion 1^{2-} and dication 1^{2+} via the study of their ^{13}C - and ^1H -NMR. spectra [1]. It appears that the charge distribution in the ionic species is largely non-uniform and that ring current effects have to be invoked to satisfactorily explain the ^1H -chemical shifts of both the 16π -dianion 1^{2-} and the 12π -dication 1^{2+} . We now describe the NMR. spectroscopic properties of the phenanthrene dianion 2^{2-} and of the 1,2,3,4-dibenzocyclooctatetraene dianion



3^{2-} [2]. Clearly, **2** differs from its isoelectronic analogue **1** only by the mode of condensation of the benzene rings whereas **2** and **3** have in common a diphenyl moiety whose 2 and 2' positions are linked by an ethylene or butadiene fragment, respectively. Compound **3** incorporates a cyclooctatetraene ring the latter being known to form an 'aromatic' 10π -dianion [3].

Accordingly, when studying the dianions one will have to focus on two questions: (i) how does the different topology of 1^{2-} and 2^{2-} influence the charge distribution and (ii) does structure 3^{2-} contribute significantly to the ground-state of 3^{2-} ?

2. Experimental and results. - The dianions 2^{2-} and 3^{2-} have been generated by bringing solutions of **2** and **3** in tetrahydrofuran- d_8 at -80° into contact with lithium. The radical anions which were first formed could be detected by means of their ESR. spectra. When reduction was complete the dianions gave rise to well resolved ^1H - and ^{13}C -NMR. signals.

A description of the bonding situations in 2^{2-} and 3^{2-} can be obtained *via* a comparison of the chemical shifts of neutral and dianionic species for any individual nucleus. Care was therefore taken to achieve reliable signal assignments in both the ^1H - and ^{13}C -NMR. spectra.

The ^1H -NMR. spectrum of 2^{2-} exhibits five well separated signals of equal intensity, one singlet at highest field and, towards lower field, two doublets and two triplets whose chemical shifts are given in the *Table*. Irradiation at the position of one triplet signal ($\delta = 1.51$ ppm) causes the triplet at $\delta = 2.69$ ppm and the doublet at $\delta = 0.71$ ppm to collapse to a doublet and singlet, respectively. From the observed splitting patterns the absorptions of H-C(7), H-C(3) (or H-C(6)) and H-C(4) (or H-C(5)) can be assigned in a straightforward manner. With this information selective $\{^1\text{H}\}$ - ^{13}C -decoupling experiments permit the identification of the corresponding ^{13}C -signals. Differentiation between the signals of C(1) and C(2), C(3) and C(6) (H-C(3)) and H-C(6)) as well as C(4) and C(5) (H-C(4) and H-C(5)), respectively, is not possible from the existing experimental evidence. Therefore, in those particular ^{13}C - and ^1H -signal assignments use has been made of the fact that the amount of upfield shift of the individual dianion- ^{13}C -signals closely parallels the π -charge densities, q_π , which we have calculated for 2^{2-} by the CNDO-method [4] (see *Table*).

As in the case of the phenanthrene dianion the ^1H -resonances of 3^{2-} exhibit 'first-order' splitting patterns (*Fig. 1*) which provide ready signal assignments. On irradiation with the frequency of one triplet signal ($\delta = 6.33$ ppm) the doublet at $\delta = 7.58$ ppm changes to a singlet and the triplet at $\delta = 5.75$ ppm to a doublet. Analogous modifications can be induced for the doublet at $\delta = 7.81$ ppm and the triplet at $\delta = 6.33$ ppm on irradiating the absorption of the high field triplet ($\delta = 5.75$ ppm). Consequently, these four signals of equal intensity are assigned to the 'benzene' protons, and therefore the singlet signal at $\delta = 5.71$ ppm corresponds to the four protons of the cyclooctatetraene moiety. In differentiating the 'ortho'- (H-C(3) and H-C(6)) and the 'meta'-protons (H-C(4) and H-C(5)) and in assigning the related ^{13}C -signals the same steps have been taken as for 2^{2-} .

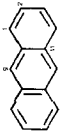
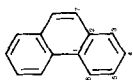
The chemical shifts of the neutral compounds **2** and **3** have been determined under the same experimental conditions as those used for the dianion work.

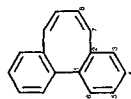
For compound **2** those signal assignments (^1H , ^{13}C) have been adopted which are reported in [5] [6]. The signal assignments in the ^{13}C -spectrum of **3** are based on selective decoupling experiments and on a comparison of analogous C,H-coupling constants ($^1J_{\text{CH}}$, $^2J_{\text{CH}}$, $^3J_{\text{CH}}$) in both **2** and **3**. It should be noted that while the $^1J_{\text{CH}}$ -values in **2** and **3** are approximately 160-161 Hz for positions 3, 4 and 5, the value for position 6 is diminished to 154.6 Hz in **2** and 157.1 Hz in **3**. The NMR. data thus obtained are presented in the *Table*¹⁾.

When investigating the charge distribution in the dianionic species inspection of the spin density distribution within the corresponding radical anions appears to be an adequate starting point. We have therefore measured the proton hyperfine

1) Note that within the *Table* and the *Figures* the numbering of the individual π -centers is chosen in such a way as to allow a meaningful comparison of the title compounds **2** and **3**.

Table. ^{13}C - and ^1H -NMR. chemical shifts (δ_{C} , δ_{H}) of **1**, **2** and **3** as well as of their corresponding dianions (δ -values are given in ppm))

	1	2	3	4	5	6	7	8	9	11
										
$\delta_{\text{C}}(\mathbf{1})$	130.1	125.5							132.6	132.2
$\delta_{\text{C}}(\mathbf{1}^{2-})$	101.1	114.2							75.1	150.0
$\Delta\delta_{\text{C}}[(\mathbf{1})-(\mathbf{1}^{2-})]$	29.0	11.3							57.5	- 17.8
$\Delta\delta_{\text{H}}[(\mathbf{1})-(\mathbf{1}^{2-})]$	4.61	3.18							6.56	
										
$\delta_{\text{C}}(\mathbf{2})$	132.7	130.9	128.9	126.9	126.9	123.2	127.3			
$\delta_{\text{C}}(\mathbf{2}^{2-})$	139.7	163.6	110.7	137.6	104.8	118.2	70.7			
$\Delta\delta_{\text{C}}[(\mathbf{2})-(\mathbf{2}^{2-})]$	- 7.0	- 32.7	18.2	- 10.7	22.1	5.0	56.6			
$\delta_{\text{H}}(\mathbf{2}^{2-})^{\text{a}}$			- 3.87	\pm 0.52	- 2.98	0.59	- 4.63			
q_{H}^{b}	1.055	0.949	- 1.292	0.973	1.298	1.079	1.352			
$\delta_{\text{H}}(\mathbf{2})$			7.68	7.35	7.41	8.46	7.50			
$\delta_{\text{H}}(\mathbf{2}^{2-})$			0.53(d)	2.69(t)	1.51(t)	0.71(d)	- 1.25(s)			
$\Delta\delta_{\text{H}}[(\mathbf{2})-(\mathbf{2}^{2-})]$			7.15	4.66	5.90	7.75	8.75			



$\delta_C(\mathbf{3})$	142.5	138.1	130.9 ^{f)}	127.3 ^{d)}	126.8 ^{d)}	128.3 ^{e)}	133.2	130.3
$\delta_C(\mathbf{3}^{\cdot-})$	111.5 ^{e)}	117.7 ^{e)}	136.9 ^{f)}	115.1	103.9	131.7 ^{e)}	81.6	92.5
$\Delta\delta_C[(\mathbf{3})-(\mathbf{3}^{\cdot-})]$	31.0	20.4	-	12.2	22.9	-3.4	51.6	37.8
$a_H(\mathbf{3}^{\cdot-})$	-	-	0.98	-0.65	-1.64	0.58	-3.90	-1.92
$a_H(\mathbf{3}^{\cdot-})^b)$	-	-	0.75	-0.45	-1.55	0.27	-4.59	-2.24
$\delta_H(\mathbf{3})$	-	-	7.24 ^{b)}	7.03 ^{b)}	7.03	7.24	6.60	5.97
$\delta_H(\mathbf{3}^{\cdot-})$	-	-	7.58 (d)	6.33 (t ⁱ⁾)	5.75 (t ^{j)})	7.81 (d)	5.71	5.71
$\Delta\delta_H[(\mathbf{3})-(\mathbf{3}^{\cdot-})]$	-	-	0.34	0.70	1.28	-0.57	0.89	0.26
$J_{CH}(\mathbf{3})^k)$	160.0	161.3	160.6	161.3	160.6	157.1	161.0	158.0
$J_{CH}(\mathbf{3}^{\cdot-})$	149.2	153.0	156.0	153.0	156.0	151.2	143.2	144.0

a) Experimental ^1H -hyperfine coupling constants of the radical anion (counterion: potassium, dimethoxyethane, -90°) in Gauss.

b) π -charge densities, q_π , of the dianion as calculated by a CNDO-model [4]. Thereby an idealized planar geometry with equal bond lengths is assumed.

c)^{d)} Tentative assignments.

e)^{f)} Assignment made by correlation of chemical shifts with calculated π -charge densities.

g) These ^1H -hyperfine coupling constants have been calculated by means of the *McLachlan*-procedure assuming $\beta_{\mu\nu} = 1$, $\lambda = 1.2$ and $Q = -25$ Gauss [7] [8].

h)ⁱ⁾ Tentative assignments.

k) One-bond C, H-coupling constants.

l) The chemical shifts are measured with respect to the solvent resonances and then referred to TMS.

coupling constants of the phenanthrene radical anion 2^- and of the as yet unknown radical anion 3^- (counterion: potassium, solvent: dimethoxyethane, -90°). These data are also presented in the *Table*.

The assignment of the hyperfine coupling constants, a_H , to the individual positions of 3^- is based on the correlation with a simple MO-model. A calculation of a_H by the *McLachlan*-procedure ($\lambda=1.2$) [7] and the *McConnell*-relation ($Q=-25$ G) [8], thereby assuming all resonance integrals to be equal ($\beta_{uv}=1$), provides the following results: the two largest couplings are observed for the protons H-C(7) and H-C(8), whereas among the (smaller) couplings of the 'benzene' protons the largest one corresponds to H-C(5) (see below).

3. Discussion. - It has been pointed out by several authors that the ^{13}C -chemical shifts δ_C are not significantly influenced by ring current effects if the carbon atoms are within the unsaturated ring [9]. On the other hand, since δ_C -values depend on the local π -charge densities [10] they can be expected to adequately reflect the charge distribution within ionic π -systems. Accordingly, it appears relevant that the ^{13}C -chemical shifts of 2^- cover a range of more than 90 ppm, this value being much greater than the corresponding ones in the isoelectronic analogue 1^- (~ 75 ppm) and the non-benzenoid dianion 3^{2-} (~ 55 ppm). Moreover, when going from the neutral compound **2** to the doubly charged species 2^{2-} the signals of C(1), C(2) and C(4) experience downfield shifts amongst which the value $\Delta\delta(\text{C}(2)) = -32.7$ ppm is certainly the most remarkable one. It becomes quite clear from inspection of the *Table* that both the sign and the relative magnitude of these shift differences can correctly be predicted on the basis of the π -charge densities which we obtain from CNDO-calculations [4]. One can thus safely conclude that the π -charge distribution in 2^{2-} is extremely non-uniform: the carbon atoms C(7), C(5) and C(3) (following this sequence) accept the greatest portion of the excess charge while centers C(1), C(2) and C(4) bear a partial 'positive' charge. The latter finding corresponds to the observation of a negative spin density on those π -centers of radical anions which possess small or zero AO-coefficients in the singly occupied molecular orbital. Both phenomena can be termed polarization effects arising from the interaction of the π -electrons. While an inspection of ^{13}C -chemical shifts proves to be a powerful tool for elucidating the charge distribution within dianions no attempt has been made herein, *e.g.* by consideration of electronically excited states, to further improve the correlation between the δ_C -values of individual nuclei and calculated π -charge densities.

The same qualitative approach provides an insight into the bonding situation of the dianion 3^{2-} : comparing the individual ^{13}C -chemical shifts of **3** and 3^{2-} (see *Table*) the carbon signals of the 8-membered ring can clearly be seen to undergo a much greater upfield shift than the others. While for C(7) and C(8) the ^{13}C -data are supported by the values of the ESR. hyperfine coupling constants, the upfield shift of the quaternary carbon signals (C(1), C(2)) is somewhat unexpected and strikingly different from the shifts of the corresponding centers in 2^{2-} . Consequently, the excess charge is essentially localized in the 8-membered ring thereby creating a bonding situation which approaches the border-line structure 3^{2-a} . It has been shown recently that conversion of cyclic π -systems to their corresponding dianions

is accompanied by a marked decrease of the one-bond C,H-coupling constants [11]. The data presented in the *Table* are in accordance with this finding. The effect is, however, most pronounced for positions 7 and 8. This fits nicely with the trend observed for the ^{13}C -chemical shifts.

Further evidence in favour of the bonding scheme outlined above can be obtained from inspection of the ^1H -NMR. parameters. While on conversion from **3** to **3⁻** the ^{13}C -signals of nuclei within the cyclooctatetraene moiety experience the greatest upfield shift this is no longer true for the corresponding ^1H -signals. Thus, in **3⁻** the 'cyclooctatetraene' protons H-C(7) and H-C(8) absorb only at slightly higher field than the 'benzene' protons H-C(4) and H-C(5). Considering the charge effect alone and keeping in mind that the π -centers C(7) and C(8) accept an appreciable negative charge, one would have expected a marked upfield shift of their proton signals [12]. One is thus brought to the conclusion that the charge induced upfield shift is compensated by the opposing influence of a diamagnetic ring current which is built up on dianion formation. The low field positions of the resonances of H-C(3) and H-C(6) are in line with this argument: the diamagnetic ring current *e.g.* causes an additional deshielding of proton H-C(3) which is positioned outside the eight membered ring. A 'perimeter-model'

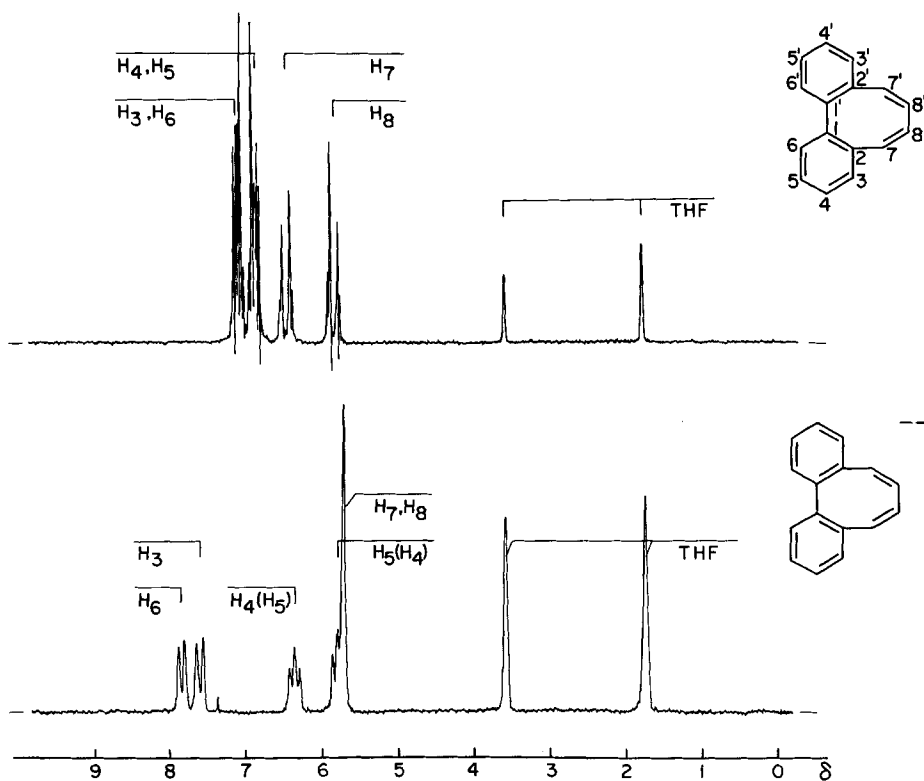


Fig. 1. ^1H -NMR. spectra (100 MHz, FT-mode) of **3** and **3⁻** (THF- d_8 , -30°)

comprising the formation of a cyclic 18π -system within the periphery of 3^{2-} could, in principle, not be excluded from the $^1\text{H-NMR}$. data, but does not fit either with the ^{13}C -results or with theoretical considerations [13].

From the 'aromatic' character of the cyclooctatetraene dianion one might have, indeed, anticipated that structure 3^{2-} is stabilized by π -bond delocalization within the 8-membered ring. On the other hand, the existence of benzene fragments condensed with the central $(4n+2)\pi$ -perimeter as well as the appreciable steric strain opposing any flattening of the molecule are both expected to introduce some π -bond fixation [14], and this will decrease the energy gain associated with π -bond delocalization. If from the ^{13}C -data one assumes a significant contribution of structure 3^{2-} to the ground-state of the dianion, one may also conclude the following: in spite of the opposing effects the stabilization energy suffices to override the electrostatic energy required for the 'localization' of the charge.

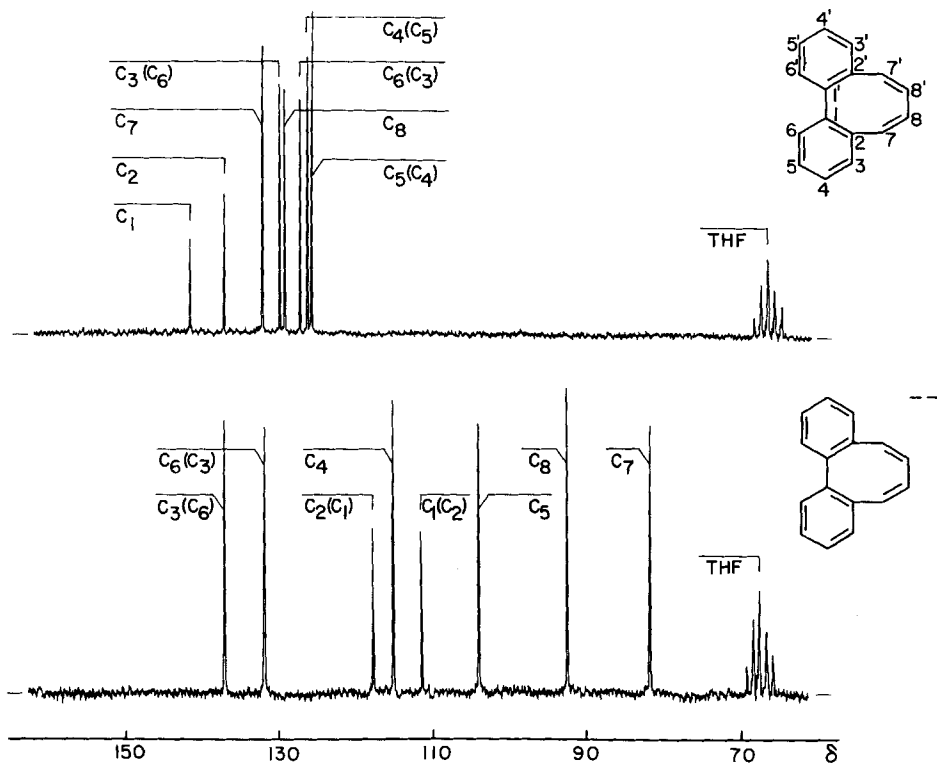


Fig. 2. $^{13}\text{C-NMR}$. spectra (25.2 MHz, FT-mode) of 3 and 3^{2-} (THF-d_8 , -30°)

Although the geometry of 3 has not yet been determined the 8-membered ring is expected to adopt a tub-like conformation. There should thus exist a considerable twist around the formal single bonds, including the 1, 1'-bond of the diphenyl moiety. Having established the existence of π -bond delocalization in the

butadienyl part of 3^{2-} one might well ask whether this bonding situation is accompanied by some flattening of the central ring. Unfortunately, due to the small chemical shift difference of H-C(7) and H-C(8) (H-C(7') and H-C(8')) an exact analysis of the relevant $AA'BB'$ -spin system and subsequent interpretation of the vicinal H,H-coupling constants in terms of geometrical factors proved to be impossible. Alternatively, one may try to derive from the ESR. coupling constants information concerned with the geometry of the corresponding radical anion $3^{\cdot-}$. Within the simple MO-model mentioned above one can simulate any twist around the single bonds by reducing the corresponding resonance integrals [15]. It appears, however, that the calculated ^1H -hyperfine coupling constants are not sensitive to such variations.

On the other hand, hyperfine coupling constants of non-planar π -systems are known to differ substantially from those values that are calculated on the basis of the *McLachlan*/HMO-procedure [16]. Thus, as the experimental hyperfine coupling constants of H-C(7) and H-C(8) are only slightly smaller than the calculated data one might expect the butadiene moiety of $3^{\cdot-}$ to be not far from planarity. Since, according to the HMO-model, the LUMO of **3** is bonding with respect to the four linkages 1-1', 2-2', 2'-7' and 8-8' this trend might well be enhanced when going from $3^{\cdot-}$ to 3^{2-} .

The significance of ring current effects, which is born out from an interpretation of the ^1H -chemical shifts of 3^{2-} , is equally well documented from the ^1H -NMR. spectra of 1^{2-} and 2^{2-} . In fact, the most striking result being obtained from the ^1H -NMR. spectrum of 2^{2-} is the extreme high field position of the resonance signals [e.g. $\delta_{\text{H}}(\text{C}(7)) \cong -1.3$ ppm]. Assuming the two extra charges in 2^{2-} to be uniformly distributed and applying the well established relation between the π -charge density and the ^1H -chemical shift [12] one will predict for the center of gravity of the ^1H -absorptions an upfield shift of $\Delta\delta = 10.7 \times 2/14 \cong 1.5$ ppm. Taking into account the partial 'positive' charge of the quaternary centers by correlating local π -charge densities and corresponding ^1H -chemical shifts is, of course, a more realistic approach, but still does not suffice to explain the experimental data. It is therefore tempting to ascribe the additional upfield shift of the proton resonances to the occurrence of a paramagnetic ring current in the periphery of the polycyclic 16π -system 2^{2-} . Quite the same argument could be shown to hold in the case of the anthracene dianion 1^{2-} [1] which is isoelectronic with 2^{2-} . It does, however, not follow clearly from this simple model why the center of gravity of the ^1H -signals moves to higher field by ~ 2.5 ppm when going from 1^{2-} to 2^{2-} . One possible explanation might be the stronger charge separation among the π -centers of 2^{2-} . As far as the paramagnetic ring current is concerned it has to be noticed that according to the CNDO-calculation the highest occupied molecular orbital is at much higher energy in 2^{2-} than in 1^{2-} . The occurrence of paramagnetic ring currents essentially depends on the existence of electronically excited states whose symmetry and energy allow a distinct interaction with the ground-state [17]. One might therefore assume from the above finding that, since the contribution of excited states is expected to be greater in 2^{2-} , the effect of the paramagnetic ring current is more pronounced.

As can readily be concluded from the description of the title dianions the sequence of the ^{13}C -chemical shifts parallels both the relative magnitude of the calculated π -charge densities and of the ESR. coupling constants in the corresponding radical anions. Deviations observed for the ^1H -chemical shifts have been rationalized on the basis of ring current effects. While these results appear to create a consistent picture of the bonding situations in the dianions one observation is worth of further comment. On conversion from **3** to 3^{2-} the center of gravity of the ^{13}C -signals is shifted upfield by 20.8 ppm which value is close to the one predicted from the usual charge density/chemical shift correlation ($160 \times 2/16 = 20$ ppm) [10]. In contrast, the corresponding value observed for the $2/2^{2-}$ pair is 7.4 ppm. Consequently, in the latter case one will expect the counterions and/or the σ -orbitals of the dianion to be involved in the delocalization of the excess charge²⁾. This outcome, on the other hand, does obviously not affect the validity of simple π -orbital considerations in qualitatively predicting the charge distribution.

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2) The ^1H - and ^{13}C -chemical shifts of 2^{2-} can be satisfactorily rationalized by assuming the existence of an ion pair. A species with covalently bonded lithium, e.g. in positions 7 and 7', should give rise to a ^{13}C -signal of two 'aliphatic' carbon atoms at rather high field in addition to the signals of a diphenyl moiety.