Highly Reduced Annulenes. Novel Probes for Spectroscopy and Theory

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Abstract: A homologous series of [4n + 2]annulenes has been reduced with alkali metals to yield (4n)π dianions and stable (4n + 2)π tetraanions. The structural proof of the highly charged products is based on quenching experiments (addition of electrophiles), an analysis of the ^{1}H and ^{13}C NMR spectra, the kinetics of the reduction, i.e., the appearance and disappearance of the respective NMR and ESR spectra, as well as polarographic evidence. A careful control of the electron-transfer processes is necessary to obtain and spectroscopically characterize the intermediate dianions. The π charge distribution within the anions, which can be evaluated by experimental ^{13}C shift data and simple MO models, exhibits characteristic variations along the homologous series. A systematic change of experimental conditions (counterions, solvents, temperature) was performed in order to describe the ion-pairing phenomena. The most obvious spectroscopic consequences of the reduction processes are, clearly, the dramatic ring current effects on ^{1}H chemical shifts. While the (4n)π dianions appear as paratropic systems, the tetraanions can be convincingly characterized as diatropic π-bond delocalized annulene species. Proton resonances, which have been corrected for the specific influences of molecular geometry, π charge, and ion pairing, provide a reliable experimental measure of ring current effects. As the latter are known to reflect the π-bonding situation, the novel dianions and tetraanions appear as useful model compounds for structural considerations, particularly in the study of ring-size influence.

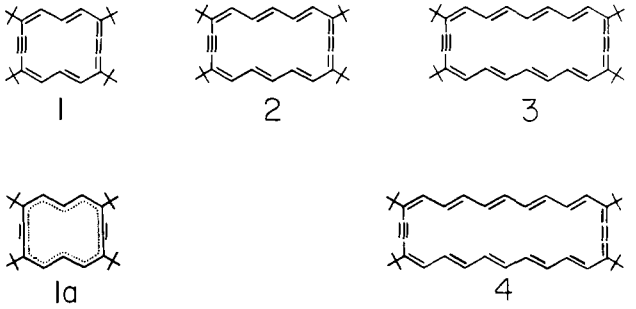
1. Introduction

During the last 2 decades annulenes have served as most appropriate subjects for investigating the electronic structure of conjugated π systems: (i) the fundamental alternative of π-bond delocalization vs. π-bond localization has been tested for both (4n + 2)π and (4n)π perimeters, and (ii) the number of electrons has been varied by constructing monocycles of different ring size.[1–6] Systematic studies of electronic stabilization effects would demand a homologous series of annulenes with identical molecular architecture. Increasing the ring size of the molecules, however, may at the same time modify both ring configurations and conformations.

One possibility of circumventing the resulting inconsistencies is the transformation of neutral annulenes into ionic derivatives, which approach follows the pioneering work of Katz[8] as well as of Oth,[9,10] Sondheimer,[10,11] Boekelheide,[12] and Paquette.[13] Dianion formation by a two-electron reduction process, for example, allows one to readily interconvert (4n)π and (4n + 2)π systems within a given molecular framework.

In order to gain deeper insight into the nature of π-bond delocalization, it is even more interesting to compare monocyclic (4n + 2)π species with *different* number of electrons (n values), but *identical* geometry. Transforming a neutral [4n + 2]annulene into its tetraanion salt (this idea has actually been our starting point) would generate a new (4n + 2)π system which might exist as a diatropic and π-bond delocalized species, the spectroscopic properties of which could readily be compared with those of the neutral educt. Having recently succeeded in preparing "supercharged" tetraanion salts of polycyclic π systems,[14–17] we describe herein the extension of this work to the annulene field. The orbital scheme of a [4n + 2]annulene comprises a degenerate or nearly degenerate LUMO pair separated by a large energy gap from the degenerate or nearly degenerate HOMO pair. In the course of a reduction experiment, dianion formation will generate a π system expected to possess low-lying electronically excited states—with the well-known consequences of π-bond fixation and of paratropic effects. Subsequent tetraanion formation should increase the HOMO/LUMO gap, thus creating a situation similar to the one in the neutral compound.

Compounds **1–4** possess essentially planar, π-delocalized, rigid



monocycles with an analogous series of double-bond configurations.[7] Perturbations which are significant in other types of annulenes, such as the steric hindrance of inner hydrogens or the transannular interaction of certain π centers, are of minor importance. Firm evidence has been compiled that the existence of two relatively short bonds between sp-hybridized centers does not seriously influence the cyclic π conjugation. Structure **1a** will,

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thus, constitute an adequate representation of the prevailing π-bonding situation.[7]

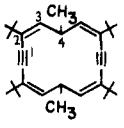
It turns out that, in contrast to other annulenes, the bisdehydro derivatives can be reduced both to dianions and tetraanions so that one obtains the desired model compounds for systematic NMR spectroscopic studies. Above all, one will consider the potential diatropism of annulenes and their tetraanions as well as the paratropism of the dianions. Within the homologous series, however, a consistent NMR spectroscopic comparison has to take account of those effects which may additionally influence the NMR chemical shifts and which cannot be assumed constant. Thus, it will be shown that the ionic species differ both in the mode of π-charge distribution and of ion pairing.

2. Experimental Section

Compounds **1–4** have been prepared according to the procedures given in the literature[7] and freshly purified prior to use by chromatography and subsequent recrystallization.

Without careful purification of the substrates the reduction experiments proceed relatively slowly or give rise to increased amounts of decomposition products. Dianions and tetraanions were prepared by reduction of the neutral annulenes at −78 °C in sealed NMR tubes using absolute tetrahydrofuran-d_8 (THF), dimethoxyethane-d_{10} (DME), diethyl-d_{10} ether (DEE), mixtures of THF and hexamethylphosphoric-d_{18} triamide (HMPT), or mixtures of THF and DEE as solvents. Alkali metals served as reducing agents. Lithium was inserted into the tube as freshly prepared wire; sodium, potassium, and cesium were present as highly active mirrors generated after repeated sublimation in vacuo. Formation of the ionic products was frequently accompanied by small amounts of side products giving rise to ^{1}H resonances between δ 1 and 2. This is mostly due to the unavoidable rewarming of the rest of the solution remaining in the upper part of the sample tube when it is turned around for spectroscopic measurements.

As will become obvious below, it is most important to monitor the reduction by recording ^{1}H NMR and ESR spectra after controlled periods of time. Thus, the ^{1}H signals of the neutral annulene (**1**) broaden into the base line after contacting the solution of the compound with the alkali metal for a few seconds. This is the consequence of a rapid electron-exchange process between **1** and the radical anion $\mathbf{1}^{\cdot-}$, the latter species being detectable by its ESR spectrum. After prolonged metal contact the ^{1}H NMR signals of a diamagnetic product appear. Analysis of its ^{1}H and ^{13}C NMR spectra (see below) as well as quenching experiments permit its identification as the alkali metal salt of a dianion $\mathbf{1}^{2-}$. On addition of dimethyl sulfate to the cold dianion solution, the deep red-green color disappears instantaneously. Evaporation of the solvent and filtration (alox, hexane) provides a dimethyl adduct (mp 243–244 °C; ^{1}H NMR δ 5.72 (H-3), 4.67 (H-4), 1.24 (H-*t*-Bu), 1.13 (H-CH_3); ^{13}C NMR: δ 94.1 (C-1), 133.3 (C-2), 136.6 (C-3), 39.4 (C-4), 35.9 (q, *t*-Bu), 29.9 (CH_3, *t*-Bu), 23.0 (CH_3)) to which we ascribe structure **5**.



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Thus, we obtain firm chemical evidence for the nature of the reduction product.[18]

The solution of the dianion is stable for weeks when kept in sealed NMR tubes at low temperatures; moreover, no change of the spectrum is observed when allowing the solution to be in metal contact for long periods of time.

The experimental procedure appears much more complicated in the case of the higher membered ring homologues **2**, **3**, and **4**. Reductive formation of the corresponding dianions is complete after very short contact times (about 1 min for reduction with potassium). NMR spectroscopic monitoring of the reaction is inevitable since renewed metal contact causes the dianion signals to broaden and, finally, disappear. That the reduction indeed proceeds to more highly charged anions can be demonstrated by ESR spectroscopy through the detection of the tri-

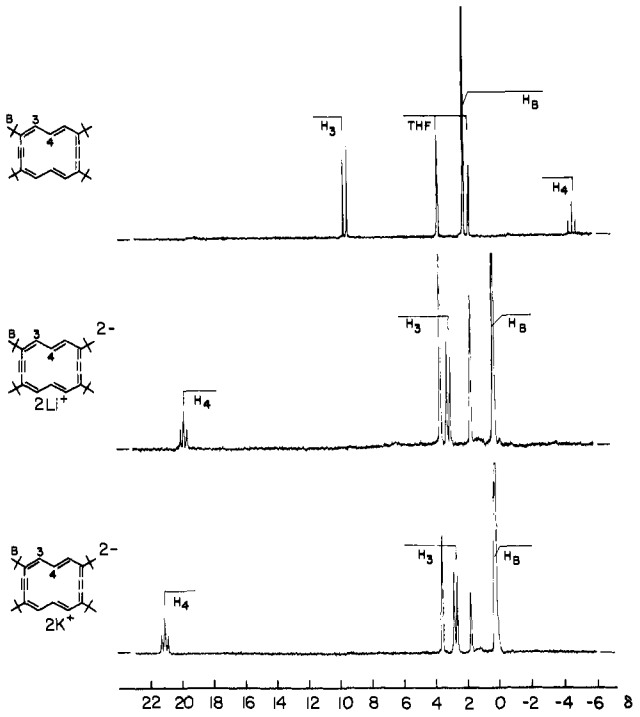

Figure 1. ^{1}H NMR spectra (60 MHz, FT, THF-d_8) of **1** (35 °C) and $\mathbf{1}^{2-}$ (Li and K salts, −42 °C).

anion radicals.[19] On further reduction the trianions transform again to diamagnetic products which are characterized by NMR spectroscopy as constituting quadruply charged annulene compounds.

Methylation to yield isomeric mixtures of tetramethyl adducts[20] verifies this conclusion which is also supported by the fact that reoxidation (O_2, I_2) at any stage of the reduction affords only the starting compounds. This finding excludes the occurrence of rearrangement and protonation processes which would result in a destruction of the perimeter framework. The formation of the tetraanions is also obvious from electrochemical evidence. While the detailed results of the latter study are being published separately,[21] we describe here one significant reduction experiment. The cyclic voltammogram of **3** (THF, 0.1 M $NaBPh_4$, E_{app} vs. Ag as quasi-reference electrode) shows a broad wave between −2.14 and −2.42 V which from the measured current intensity is ascribed to a four-electron transfer. This finding is supported by the digital simulation of the current–voltage curve. The small differences in the potentials of the single reduction steps (<80 mV) do not allow a resolution of the cathodic voltammogram. The anodic sweep indicates the occurrence of irreversible electron transfers.

In order to study the ion pairing that prevails in solutions of the reduction products, it is necessary to change both the counterions (Li, Na, K, Cs) and the solvents (THF, DME, DEE, THF/HMPT, THF/DEE) as well as the temperature. Various experimental difficulties are encountered during such a study; rapid decomposition is observed above −20 °C, which situation becomes increasingly serious with the dianion and tetraanion salts of the larger alkali metal ions. Thus, we could not prepare the ions $\mathbf{3}^{4-}$ and $\mathbf{4}^{4-}$ as Cs salts. Furthermore, adding a small amount of hexamethylphosphoric triamide to the THF solution of $\mathbf{1}^{2-}$ (lithium salt) causes rapid decomposition.

An interpretation of the ^{1}H NMR spectra of annulene dianions and tetraanions (see Figures 1 and 2 as well as Table I) will, of course, require reliable signal assignments, in particular, a differentiation of signals being due to either "inner" and "outer" ring protons. This goal can be achieved in a straightforward manner from the splitting patterns and the relative signal intensities. Inspection of formula **1** indicates the existence of four outer and two inner ring protons. Consequently, in the spectrum of $\mathbf{1}^{2-}$

(18) The specific attack of the quenching agent at the "central" positions 4 and 11 of the perimeter is remarkable. This finding can readily be explained, however, as a charge-controlled addition of the electrophile: one concludes from the ^{13}C NMR spectra of $\mathbf{1}^{2-}$ that the π charge distribution is largely nonuniform with the highest local charge at the carbons 4 and 11. For other examples of preparatively useful "reductive alkylations", see: Huber, W.; Meul, T.; Lex, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 391.

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(20) The tetramethyl adduct is obtained as the major product only under the conditions of inverse quenching, i.e., if the tetraanion solution is slowly added to a large excess of dimethyl sulfate in THF. Addition of the quenching agent to the tetraanion solution produces, as is inferred from mass spectrometric evidence, a mixture of extremely labile di-, tetra-, and hexamethyl adducts. In the latter case, electron-transfer processes compete with the addition of the electrophile. Thereby, the highly charged ions are able to further reduce intermediate methylation products.

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Table I. ^{1}H Chemical Shifts (δ_H) of Neutral, Dianionic, and Tetraanionic Annulenes[a]

δ_H	solvent	temp, °C	color	H-3	H-4	H-5	H-6	H-7	H-*t*-Bu
1	$CHBr_3$	36		9.32	−4.44				1.94
1^{2-} ($2Li^+$)	THF	−82	red-green	2.89	19.84				0.29
1^{2-} ($2Li^+$)	THF	6		3.22	18.88				0.37
1^{2-} ($2K^+$)	THF	−82		2.65	20.89				0.20
1^{2-} ($2Cs^+$)	THF	−35		2.77	23.27				0.20
1^{2-} ($2K^+$)	DME	−80		2.50	21.76				0.17
1^{2-} ($2Li^+$)	DME	−75		1.85	24.37				−0.01
1^{2-} ($2Li^+$)	THF/HMPA 10:1	−40		*b*	23.11				0.16
2	$CHBr_3$	36		9.32	−3.64	9.82			1.91
2^{2-} ($2Li^+$)	THF	−42	red-green	1.50	23.33	1.04			−0.12
2^{2-} ($2Li^+$)	THF	−82		1.04[c]	24.88	1.04[c]			−0.11
2^{2-} ($2K^+$)	THF	−60		2.07	21.50	1.57			0.07
2^{2-} ($2K^+$)	DME	−75		2.05	24.51	*b*			−0.19
2^{4-} ($4Li^+$)	THF	−40	dark red	7.95	−8.97	9.85			2.12
3	$CHBr_3$	36		8.76	−0.82	9.21	−0.82		1.82
3^{2-} ($2Li^+$)	THF	−80	red-violet	1.15	24.80	−0.29	23.23		−0.29
3^{2-} ($2K^+$)	THF	−45		1.95	21.29	1.22	19.84		−0.06
3^{4-} ($4Li^+$)	THF	−45	red	9.03	−10.67	10.61	−9.50		2.29
3^{4-} ($4K^+$)	THF	−45		9.00	−10.50	10.58	−9.07		2.33
4	$CHBr_3$	+36		7.93	1.95	8.23	1.82	8.23	1.61
4^{2-} ($2Li^+$)[d]	THF	−80	red-violet	1.20	23.39 (21.35)	0.18	21.35 (23.39)	0.18	−0.20
4^{2-} ($2K^+$)[d]	THF	−80		1.70[e]	21.58 (19.72)	1.50	19.72 (21.58)	1.50	−0.09
4^{4-} ($4Li^+$)[d]	THF	−45	red	9.84	−10.17 (−11.27)	11.49	−11.27 (−10.17)	11.49	2.44
4^{4-} ($4K^+$)[d]	THF	−45		9.80	−9.83 (−11.16)	11.47	−11.16 (−9.83)	11.47	2.45

[a] δ_H values have been taken with respect to the solvent signals and then referred to Me_4Si. Counterions in parentheses. [b] Covered by the signal of an impurity. [c] The estimated error is relatively high (±0.2 ppm) owing to the overlap of the signals of H-4 and H-5 with the signal of an impurity. [d] It is not possible to discriminate between the signals of H-4 and H-6, from experimental evidence. [e] Covered by solvent-signals.

the low-field triplet (2 H) is assigned to H-4 and H-11, while the doublet at high field must be due to H-3, H-5, H-10, and H-12. Similarly, in the case of 2^{2-} the triplet (4 H) at low field is ascribed to H-4, H-6, H-13, and H-15. The equivalent outer protons H-3, H-7, H-12, and H-16 give rise to a (high-field) doublet; the outer nuclei H-5 and H-14 appear as a (high-field) triplet. All assignments are supported by homonuclear decoupling experiments. Similar arguments hold for the ^{1}H spectra of 2^{4-} as well as the higher membered dianions and tetraanions. In the case of 3^{2-}, for example, the resonances of H-3 and H-5 differ by their splitting patterns (doublet and triplet, respectively) whereas the (triplet) signals of H-4 and H-6 can easily be discriminated by considering the relative signal intensities. Obviously, for the dianion and tetraanion of **4** it is not possible from experimental evidence to differentiate the triplet signals of the inner protons H-4 (H-10, H-17, H-23) and H-6 (H-8, H-19, H-21).

In spite of the limited stability and solubility of the ionic species, one can obtain good quality ^{13}C NMR spectra. Signal assignments are achieved from ^{1}H off-resonance-decoupled spectra and from selective ^{1}H decoupling experiments, the latter being particularly straightforward owing to the large shift difference of the respective ^{1}H resonances. The results of the ^{13}C measurements for neutral, dianionic, and tetraanionic species are presented in Table II and Figure 3.

During the ^{1}H NMR measurements the concentrations of the starting materials were always lower than 2×10^{-2} M. Normally, for a single experiment between 30 and 50 scans have to be accumulated. The locking was provided by the deuterated solvent. For experimental reasons (stability, solubility) the chemical shifts could not be measured with respect to the resonances of an internal hydrocarbon or Me_4Si reference. δ values were taken with respect to the solvent lines and converted to the Me_4Si basis by means of the appropriate increments. ^{1}H NMR spectra (FT mode) were taken on a Bruker WP60-spectrometer equipped with a homemade system for sample cooling; ^{13}C NMR spectra were recorded on a Bruker HX90-spectrometer. The temperature which is believed to be constant within ±1.5 °C was measured before and after any experiment by means of a Pt resistance thermometer.

3. Discussion

a. Structure Proof of the Anions and Qualitative Interpretation of Their NMR Spectra. The structure of the dianions and tetraanions is proven by the following. (i) Quenching experiments (via the number of added electrophiles) indicate the number of charges in the anions; moreover, together with reoxidation experiments, they reveal the existence of intact molecular frameworks. (ii) The kinetics of the reduction, i.e., the appearance and disappearance of the respective NMR and ESR spectra, characterizes the sequence of successive electron transfers. (iii) The ^{1}H and ^{13}C NMR spectra, besides being significant for the relevant π-bonding situation, indicate the intact monocyclic π systems and show the number of electrons having been transferred. (iv)

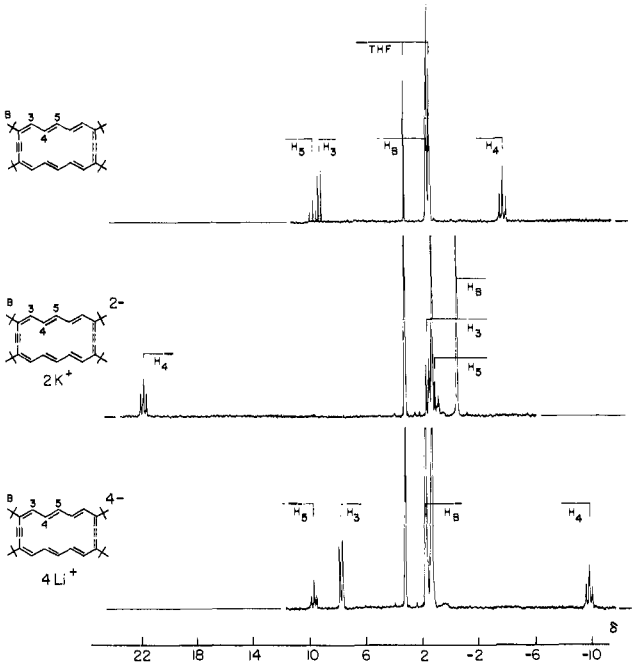

Figure 2. ^{1}H NMR spectra (60 MHz, FT, THF-d_8) of **2** (35 °C), 2^{2-} (K salt, −40 °C), and 2^{4-} (Li salt, −45 °C).

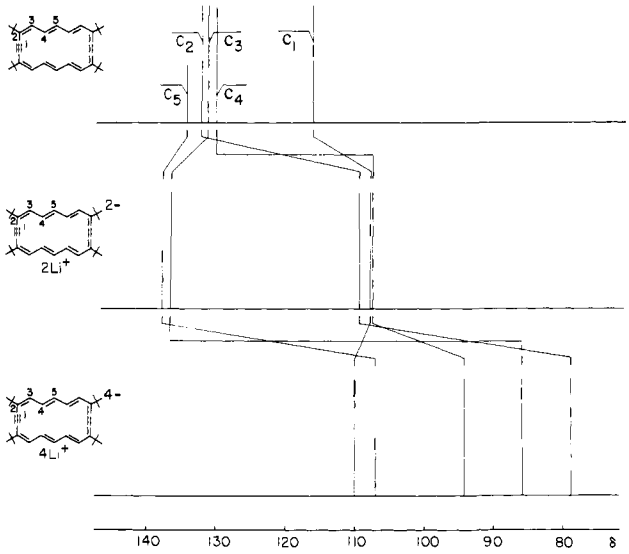

Figure 3. ^{13}C NMR spectra (schematic representation of the olefinic part; 22 MHz, FT, THF-d_8, −30 °C) of **2**, $\mathbf{2}^{2-}$ (Li salt), and $\mathbf{2}^{4-}$ (Li salt).

Voltammetric experiments provide the number of separate one-electron reduction steps as well as the relevant reduction potentials.

As is known from ample experience the diatropism of [4n + 2]annulenes induces a deshielding of nuclei outside and a shielding of nuclei inside the ring. For the example of annulenes **1**–**4** this feature is documented by the resonances given in Table I as well as by the spectra in Figures 1 and 2. Formation of the $(4n)\pi$ dianions creates a situation with low-lying electronically excited states whose interaction with the ground state gives rise to paramagnetic ring current effects superimposed on the diamagnetic ones.

As a result, outer ring protons should be strongly shielded and inner protons deshielded. It is, therefore, most instructive to note that the resonances of inner protons in $\mathbf{1}^{2-}$–$\mathbf{4}^{2-}$ appear at $\delta \sim +23$ and, thus, shifted downfield by more than 25 ppm (see Table I). When the dianion accepts two additional electrons on further reduction, a low-lying MO is going to be occupied. The expected diatropism of the resulting tetraanionic $(4n+2)\pi$ systems $\mathbf{2}^{4-}$–$\mathbf{4}^{4-}$ is proven by the extreme low-field resonances of outer and high-field resonances of inner protons. The shift differences of both types of nuclei are about 20 ppm and, thus, exceed even those in the corresponding neutral annulenes.[22] The characterization of tetraanionic [4n + 2]annulenes as stable and essentially diatropic species is, certainly, a basic result. Furthermore, one can now systematically analyze homologous series of neutral, dianionic, and tetraanionic annulenes.

b. π Charge Distribution. Since ^1H resonances are known to reflect both charge and ring current effects,[23-25] one needs independent information on the π charge distribution, information which can be obtained either from calculated π charge densities or from experimental ^{13}C chemical shifts.[26,27]

From our recent ^{13}C NMR spectroscopic studies[14-17,25] on diamagnetic multi-charged π systems, we could conclude the following (see Figure 3).

(22) While the large shift differences of inner and outer ring protons in dianions and tetraanions are certainly the most important piece of evidence, it should be noted that resonances of different outer (or inner) protons within specific anions are more apart from each other than in the corresponding neutral compounds.

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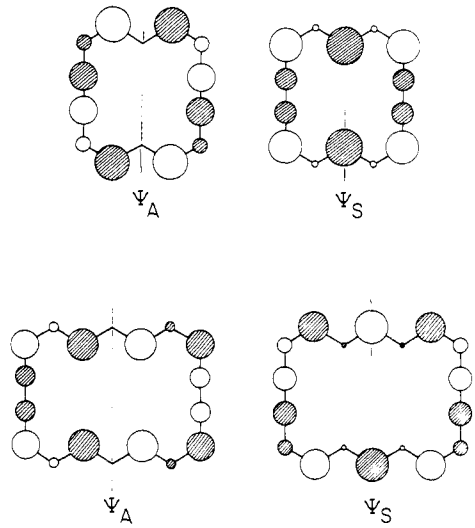

Figure 4. Schematic representation of the two low-lying Hückel molecular orbitals of **1** and **2**.

(1) The sequence of ^{13}C chemical shifts of individual nuclei within a dianion or tetraanion qualitatively reflects the order of π charge densities.

(2) For many cases the spin density distribution in the intermediate radical anions, as deduced from ESR hyperfine coupling constants, provides a suitable basis for predicting the π charge distribution within the higher charged diamagnetic anions.

(3) The π charge distribution within ions can be grossly nonuniform; in some cases one even observes downfield shifts of ^{13}C signals when going from the neutral to the dianionic species. This outcome can be ascribed to some partial positive π charge on the corresponding π centers as a consequence of π,π charge polarization.[25]

By comparing the ^{13}C NMR spectra of **1** and **2** with those of the corresponding dianions $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ we could determine charge-induced signal shifts of individual nuclei. It is obvious for the pair of compounds $\mathbf{1}/\mathbf{1}^{2-}$ that the signal of the central carbon C-4 is strongly shifted upfield, while that of C-3 actually suffers a slight downfield shift. The situation in the $\mathbf{2}/\mathbf{2}^{2-}$ pair is different, since here one observes the most pronounced upfield shift for the resonance of C-4 and a downfield shift for the resonances of C-3 and of the central carbon C-5. This striking difference in behavior can easily be rationalized when considering a simple orbital scheme (see Figure 4).[29] The degeneracy of the two LUMO's, which is expected for an ideal [14]- or [18]annulene, is destroyed in the present distorted perimeters. Among the perturbations that are to be encountered, the occurrence of two "short" acetylenic bonds is certainly the most serious one. Simulating the shortening of the C–C bonds by increasing the corresponding β values lifts the degeneracy of the LUMO pair. Interestingly, however, while in **1** the orbital Ψ_S becomes more stable than Ψ_A, the sequence in **2** is reversed (note the relative signs of the AO coefficients at the "acetylenic" bonds). This characteristic feature can be found to be generally valid, since the energetic sequence of the MO's Ψ_A and Ψ_S alternates along the homologous series. As a result the LUMO in **2** and **4**, i.e., the orbital accepting the excess charge in the dianion, possesses a nodal plane through the central ring carbons [C-5, C-14 in **2**, C-7, C-20 in **4**].

On the basis of this information the different behavior of $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$, obvious from the above ^{13}C measurements, can readily be explained.

The calculated (SCF–PPP[30]) changes in π charge densities of individual carbons, $\Delta q_\pi'$, which are predicted on going from the neutral compounds to either the dianions or tetraanions, are presented in Table II. Another strategy of quantitatively de-

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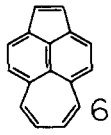
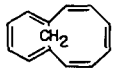
scribing the mode of π charge distribution might make use of the proportionality between the measured upfield shifts of individual ^{13}C signals ($\Delta\delta_C$) and the changes of local π charge densities (Δq_π). The $\Delta\delta_C$ data, when divided by a suitably chosen constant K_C, would provide "experimental" Δq_π values ($\Delta q_\pi''$).[31] The basic problem here is the choice of the constant K_C.

O'Brien, Hart, and Russell obtained a linear shift/π charge density relationship when they plotted the average ^{13}C chemical shifts of various cyclic and acyclic anions against the average π charge densities.[31] The satisfying correlation obtained from *average* chemical shifts within species of *nonuniform* charge distribution led them to conclude that the local π charge density is, indeed, the main factor influencing the individual ^{13}C chemical shifts.

We determined "compound-specific" proportionality constants $K_C = \Delta\langle\delta_\pi\rangle/\Delta\langle q_\pi\rangle$ by dividing the charge-induced upfield shift of the center of gravity of the ^{13}C signals by the average change of the π charge densities (e.g., 4/18 in the case of $\mathbf{2}^{4-}$). The K_C constants for the tetraanions $\mathbf{2}^{4-}$ and $\mathbf{3}^{4-}$ are 154.1 and 164.5 (ppm/unit charge), respectively. These values are close to the ones that have been given in the literature for various monoanions.[26,31] The K_C values of the dianions $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$, which are calculated in the same fashion, are 112.0 and 93.6 (ppm/unit charge), respectively.

In empirically dealing with the marked contrast of annulene dianions and tetraanions we considered other examples of ionic $(4n+2)\pi$ and $(4n)\pi$ systems.[32a] A similarly low proportionality constant is observed by us for the dianions of differentialy bridged [14]annulenes.[33] Even in the case of polycyclic π systems such as **6**, we observed that the diatropic tetranion $\mathbf{6}^{4-}$, but not the


6



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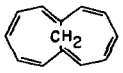

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paratropic dianion $\mathbf{6}^{2-}$, possesses a normal K_C value.[15] On the other hand, when we prepared and analyzed dianions of [4*n*]annulenes, e.g., $\mathbf{7}^{2-}$ and $\mathbf{8}^{2-}$,[34] the latter ions again representing $(4n + 2)\pi$ systems, we arrived at a K_C value of about 169 [ppm/unit charge]. On the basis of the above results we could proceed to determine "experimental" changes of π charge densities, $\Delta q_\pi''$, from the observed upfield shifts $\Delta\delta_C$ of individual signals and from the specific constants K_C. The results are included in Table II for both dianions and tetraanions. It appears that the $\Delta q_\pi'$ values, obtained from MO calculations, are in reasonable agreement with the experimental $\Delta q_\pi''$ values. For the centers 4 and 5 of $\mathbf{2}^{4-}$ and for the centers 5 and 6 of $\mathbf{3}^{4-}$, both methods provide a similar but small difference (note that the corresponding hydrogens are considered for analyzing ring current effects). Therefore, the differences of the relevant ^1H chemical shifts, which result from inhomogeneities in the π charge distribution, can be taken into account reliably (see section 3.d).[32b]

In the case of the dianions, the SCF π charge densities $\Delta q_\pi'$ indicate a more uniform distribution than the corresponding $\Delta q_\pi''$ values. In particular, the former do not reproduce the observed downfield shifts of certain carbon signals. As concerns the proton-bearing centers significant for the ^1H NMR analysis of ring current effects it becomes obvious that the π charge distribution is much less uniform than in the tetraanions.

Before we proceed now to calculate "charge-corrected" ^1H chemical shifts, we have to investigate the influence of ion pairing.

c. Effects of Ion Pairing. Both ^1H and ^{13}C chemical shifts are known from ample experience to reflect changes in the mode of ion pairing.[35-40] Most NMR studies of ion-pairing phenomena have dealt with singly charged species which offer the advantage of being stable over a large temperature range. The present annulene anions, while being less easily accessible, allow one to modify both the size and the electronic configuration of the organic anion systematically.

(i) Dianions. From extended studies of various ionic π species[35-40] one has obtained firm evidence for an equilibrium of solvent-separated and contact ion pairs. In characterizing the homologous series of dianions $\mathbf{1}^{2-}$–$\mathbf{4}^{2-}$ we varied the counterions (Li, Na, K, Cs), the solvent (THF, DME, DEE, THF/HMPT, THF/DEE), and the temperature.

In accordance with findings well established in the literature, we could generally conclude that solvent-separated ion pairs are favored by: smaller metal ions, low temperatures, large annulene rings, and more polar solvent systems, e.g., THF/HMPT instead of THF, or solvents of higher cation-coordinating ability, i.e., DME/K^+ instead of THF/K^+. In the case of $\mathbf{1}^{2-}$/THF, when the counterion is varied from Li^+ to Na^+, K^+, and Cs^+, the value of $|\Delta[\delta(H_0) - \delta(H_i)]|$ $\{=|\Delta[\delta(H\text{-}3) - \delta(H\text{-}4)]|\}$ increases from about 16 to 20 ppm, and the resonance of H_i (=H-4) shifts from δ_i +19 to +23. No temperature dependence is observed except for the lithium salt where the absolute values of both $\delta(H_i)$ and $\Delta[\delta(H_0) - \delta(H_i)]$ increase on lowering the temperature. We conclude that the dianion salts of K and Cs exist solely as contact ion pairs (with the smallest "perturbation" induced by the large Cs^+ ion) and that a certain amount of solvent-separated species is present in the lithium case. The contribution of the latter increases on lowering the temperature.

The results obtained on a change of the solvent system are also characteristic. When for the ion pairs $\mathbf{1}^{2-}/2K^+$ and $\mathbf{1}^{2-}/2Li^+$ the solvent THF is replaced by DME, both the absolute values of $\delta(H_i)$ and $\Delta[\delta(H_0) - \delta(H_i)]$ are increased. As can be seen from Table I this effect is particularly drastic for the lithium salt. Obviously, the fraction of solvent-separated ion pairs becomes greater, this tendency being further enhanced by lowering the temperature. Considering the competition of anion and solvent for the counterion one would conclude that within an appropriate series of anions the fraction of contact ion pairs should decrease with increasing anion size.

In the case of $\mathbf{2}^{2-}$–$\mathbf{4}^{2-}$ the absolute values of $\delta(H_i)$ and $\Delta[\delta(H_0) - \delta(H_i)]$ are always greater for $2Li^+$/THF than for $2K^+$/THF. This situation clearly differs from the one prevailing in $\mathbf{1}^{2-}$/THF. Furthermore, while no temperature dependence is observed for the systems $\mathbf{2}^{2-}/2K^+$/THF and $\mathbf{4}^{2-}/2Li^+$/THF, the above shift values increase with decreasing temperature for the systems $\mathbf{2}^{2-}/2Li^+$/THF and $\mathbf{4}^{2-}/2K^+$/THF. It follows that the lithium salt of $\mathbf{4}^{2-}$, the largest dianion considered, gives rise to a solvent-separated ion pair, while its corresponding potassium salt exists as an equilibrium of contact and solvent-separated ion pairs.

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(32) (a) Discussing the abnormal K_C values of annulene dianions, as well as the downfield shifts of specific carbon signals within the realm of a π-MO model, is certainly a crude approach. A more sophisticated treatment will have to consider the role of the σ core and of the orthogonal "acetylene-type" π system. (b) The above procedure for calculating "compound-specific" proportionality constants $K_C = \Delta\langle\delta_\pi\rangle/\Delta\langle q_\pi\rangle$ and "experimental" changes of individual π charge densities $\Delta q_\pi'' = \Delta\delta_C/K_C$ should not be confused with the method generally applied in the literature. In his basic work O'Brien,[31] when correlating ^{13}C chemical shifts and π charge densities of ionic π systems, arrived at the following equation: $\langle\delta\rangle^{ion} = 289.5 - 156.3\langle q_\pi\rangle$. It is interesting to note that the chemical shifts of $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ satisfy this equation in spite of the "normal" value of the porportionality constant. However, the $\Delta q_\pi''$ values calculated via this equation upon going from average to individual chemical shifts do not add up to the total π charge. The discrepancy follows from the choice of the second constant (289.5) and, thus, indirectly from the choice of the chemical shifts of the neutral compounds.

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(40) Smid, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 112. Murdoch, J. R.; Streitwieser, A. *Intra-Sci. Chem. Rep.* **1973**, *7*, 45.

Table II. ^{13}C Chemical Shifts (δ_C) of Neutral, Dianionic, and Tetraanionc Annulenes; Changes of Local π Charge Densities ($\Delta q_\pi'$, $\Delta q_\pi''$) That Result from Ion Formation[a]

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-2a	C-2b	
$\delta_C(1)$	117.2	131.9	131.1	129.6				37.9	32.4	$\langle\delta_\pi\rangle = 127.1$
$\delta_C(1^{2-}\ 2Li^+)$	106.0	100.0[b]	137.4	90.7				32.3	30.2	$\langle\delta_\pi\rangle = 111.1$
$\delta_C(\mathbf{1}^{2-}\ 2K^+)$	107.6[b]	98.2[b]	138.5	94.7				31.9	29.9	$\langle\delta_\pi\rangle = 111.9$
$\Delta[\delta_C(1) - \delta_C(1^{2-}\ 2Li^+)] = \Delta\delta_C$	11.2	31.9	−6.3	38.9						$\Delta\langle\delta_\pi\rangle = 16.0$
$\Delta q_\pi'[(1)/(\mathbf{1}^{2-})]$	0.07	0.24	0.06	0.26						$K_C = 112$
$\Delta q_\pi''[(\mathbf{1})/(1^{2-})]$	0.10	0.28	−0.06	0.35						
$\delta_C(2)$	116.3	132.2	131.3	130.1	134.3			38.4	32.3	$\langle\delta_\pi\rangle = 128.2$
$\delta_C(\mathbf{2}^{2-}\ 2Li^+)$	107.9	109.4	136.5	107.6	137.7			31.5	28.7	$\langle\delta_\pi\rangle = 117.8$
$\Delta[\delta_C(2) - \delta_C(2^{2-})] = \Delta\delta_C$	8.4	22.9	−5.2	22.5	−3.4					$\Delta\langle\delta_\pi\rangle = 10.4$
$\Delta q_\pi'[(2)/(2^{2-})]$	0.02	0.19	0.04	0.20	0.02					$K_C = 93.6$
$\Delta q_\pi''[(2)/(2^{2-})]$	0.09	0.24	−0.06	0.24	−0.04					
$\delta_C(2^{4-}\ 4Li^+)$	110.1[b]	79.0[b]	85.9	94.4	107.1			37.3	34.5	$\langle\delta_\pi\rangle = 94.0$
$\Delta[\delta_C(2) - \delta_C(2^{4-})] = \Delta\delta_C$	6.2	53.2	45.4	35.7	27.2					$\Delta\langle\delta_\pi\rangle = 34.2$
$\Delta q_\pi'[(2)/(2^{4-})]$	0.18	0.29	0.24	0.18	0.23					$K_C = 154.1$
$\Delta q_\pi''[(2)/(2^{4-})]$	0.04	0.35	0.29	0.23	0.18					
$\delta_C(3)$	116.5	132.1	134.5 (131.3)	130.8	131.3 (134.5)	132.1		37.9	31.6	$\langle\delta_\pi\rangle = 129.3$
$\delta_C(3^{4-}\ 4Li^+)$	108.6[b]	83.6[b]	109.4 (94.3)	97.5	94.3 (109.4)	106.2		38.0	35.4	$\langle\delta_\pi\rangle = 99.4$
$\Delta[\delta_C(3) - \delta_C(3^{4-})] = \Delta\delta_C$	7.9	48.5	25.1	33.3	37.0	25.9				$\Delta\langle\delta_\pi\rangle = 29.9$
$\Delta q_\pi'[(3)/(3^{4-})]$	0.16	0.25	0.20	0.15	0.18	0.13				$K_C = 164.5$
$\Delta q_\pi''[(3)/(3^{4-})]$	0.05	0.29	0.15	0.20	0.22	0.16				
$\Delta q_\pi'[(3)/(3^{2-})]$	0.05	0.15	0.03	0.15	0.02	0.16				
$\Delta q_\pi'[(4)/(\mathbf{4}^{2-})]$	0.04	0.13	0.02	0.15	0.01	0.16	0.00			
$\Delta q_\pi'[(4)/(4^{4-})]$	0.10	0.21	0.13	0.18	0.15	0.16	0.16			

[a] Measurements have been performed in THF-d_8 at −30 °C; δ_C values have been taken with respect to the solvent signals and then referred to Me_4Si. $\Delta q_\pi'$ = changes of local π charge densities that result from ion formation; values have been obtained from SCF-PPP calculations.[30] Annulene **4** was too large to be handled by the SCF program available to us. The corresponding values of 4, 4^{2-}, and 4^{4-} have, therefore, been obtained from a HMO treatment. Thereby, the two "acetylenic" bonds have been simulated by a resonance integral of $\beta = 1.5$; $\Delta q_\pi''$ = changes of π charge densities that result from ion formation, values have been calculated from the ratio $\Delta\delta_C/K_C$, whereby $\Delta\delta_C$ is the experimental signal shift and K_C is the system-specific proportionality constant. [b] Assignments have been made from calculated π charge densities.

Supporting evidence in favor of these arguments can be obtained from the lithium and potassium salts of $\mathbf{2}^{2-}$ when substituting THF by DME; the NMR spectroscopic criteria indicate that the solvent change increases the contribution of solvent-separated ion pairs.

The above results create some inconsistencies: $\mathbf{1}^{2-}$ exists preferentially as a contact ion pair; the higher homologues preferentially exist as solvent-separated ion pairs. Clearly, when comparing the different dianions, we want to come as close as possible to the situation of an "unperturbed" $(4n)\pi$ species. Accordingly, we focus on the lithium salts, which are measured at the lowest possible temperature in THF (DME for the particular case of $\mathbf{1}^{2-}$). These experimental conditions are expected to comprise predominantly solvent-separated ion pairs. The resulting ^{1}H chemical shifts are given in Table III.

Finally we consider the redistribution of the π charge which can be induced by changing the counterion. The ^{13}C chemical shifts of $\mathbf{1}^{2-}/2Li^+$ and $\mathbf{1}^{2-}/2K^+$ are revealing. As has been mentioned already and in accordance with related experience,[41,42] the center of gravity of the ^{13}C resonances suffers from only a slight change (<1 ppm). The signal of C-4, the center which is known to accept the greatest π charge, is shifted upfield by 4 ppm when going from the potassium to the lithium counterion. This particular effect is larger than those observed for the other resonances. Obviously, the higher polarizing ability of the lithium ion causes the π charge distribution to become less uniform by attracting the π charge toward the centers of originally high charge density. From what has been said above (see section 3.b), it is also clear that the charge effects exerted by the counterions are much too small to adequately explain the corresponding changes of ^{1}H resonances.[41,42]

A detailed study of ion-pair structures in annulene species, in particular, on the correlation of ion pairing and ring current effects, will be published separately.[43] Therefore, only those findings have been given here which are essential for a consistent comparison of ^{1}H chemical shifts.

(ii) Tetraanions. In the same context a consideration of the tetraanionic species turns out to be much simpler and to require no corrections accounting for the influence of ion pairing. The ^{1}H chemical shifts of the tetraanions are not significantly influence by either a change of counterion (Li, K), of solvent (THF, DEE) or of temperature. Therefore, the data given in Table I can directly be used for further analysis.

d. Ring Current Effects as a Function of Ring Size. Coming back to the combined analysis of ^{13}C and ^{1}H spectra we conclude that ^{13}C and MO data succeed in creating a consistent view of the π charge distribution in the present ions, but that the approach of quantitatively correcting ^{1}H chemical shifts for the effects of charge is certainly a crude one. This feature, however, should not seriously inhibit the intended discussion of anisotropic effects; consider, for example, the case of dianion $\mathbf{2}^{2-}$. The observed shift difference of inner and outer protons $\Delta[\delta(\text{H-4}) - \delta(\text{H-5})]$ is 22 ppm. This value is greater by a factor of about 10 than the charge-induced shift difference of about 2 ppm. The changes of π charge densities, $\Delta q_\pi'$ and $\Delta q_\pi''$, which are induced by ion formation, are reported in Table II. By using a proportionality constant of $K_H = 10.7$ one can now easily obtain the charge-induced shifts, $\Delta\delta_H'$ and $\Delta\delta_H''$, for individual protons. Subtracting the latter values from the experimentally observed shifts of ^{1}H signals, $\Delta\delta_H$, provides the "charge-corrected" signal shifts, $\Delta\delta_H'^{(RC)}$ and $\Delta\delta_H''^{(RC)}$. These data can be used for considerations of ring current effects. The results of the above procedure are given in Table III.

Two further aspects have to be encountered when comparing ring current effects within annulenes of different size: the influence of geometry and the local anisotropic effects. A classical treatment of the deshielding of protons in polycyclic benzenoid hydrocarbons

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Table III. Experimental ^{1}H Chemical Shifts (δ_H) of Neutral Annulenes and Their Ionic Derivatives; Calculation of Charge-Induced and Ring-Current-Induced Signal Shifts (See Text)[a]

	H-3	H-4	H-5	H-6	H-7	H-*t*-Bu
$\delta_H(1)$	9.32	−4.44				1.94
$\delta_H(1^{2-})$	1.85	24.37				−0.01[b]
$\Delta[\delta_H(1^{2-}) - \delta_H(1)] = \Delta\delta_H$	−7.47	28.81				−1.95
$\Delta\delta_H'$	−0.64	−2.78				
$\Delta\delta_H''$	0.64	−3.75				
$\Delta\delta_H'^{(RC)}$	−6.83	31.59				
$\Delta\delta_H''^{(RC)}$	−8.11	32.56				
$\delta_H(2)$	9.32	−3.64	9.82			1.91
$\delta_H(2^{2-})$	1.04	24.88	1.04			0.12[c]
$\Delta[\delta_H(2^{2-}) - \delta_H(2)] = \Delta\delta_H$	−8.28	28.52	−8.78			−2.03
$\Delta\delta_H'$	−0.43	−2.14	−0.21			
$\Delta\delta_H''$	0.64	−2.57	0.43			
$\Delta\delta_H'^{(RC)}$	−7.85	30.66	−8.57			
$\Delta\delta_H''^{(RC)}$	−8.92	31.09	−9.21			
$\delta_H(2)$	9.32	−3.64	9.82			1.91
$\delta_H(2^{4-})$	7.95	−8.97	9.85			2.12[d]
$\Delta[\delta_H(2^{4-}) - \delta_H(2)] = \Delta\delta_H$	−1.37	−5.33	0.03			0.21
$\Delta\delta_H'$	−2.57	−1.93	−2.46			
$\Delta\delta_H''$	−3.10	−2.46	−1.93			
$\Delta\delta_H'^{(RC)}$	1.20	−3.40	2.49			
$\Delta\delta_H''^{(RC)}$	1.73	−2.87	1.96			
$\delta_H(3)$	8.76	−0.82	9.21	−0.82		1.82
$\delta_H(3^{2-})$	1.15	24.80	−0.29	23.23		−0.29[e]
$\Delta[\delta_H(3^{2-}) - \delta_H(3)] = \Delta\delta_H$	−7.61	25.62	−9.50	24.05		−2.11
$\Delta\delta_H'$	−0.32	−1.61	−0.21	−1.71		
$\Delta\delta_H'^{(RC)}$	−7.29	27.23	−9.29	25.76		
$\delta_H(3)$	8.76	−0.82	9.21	−0.82		1.82
$\delta_H(3^{4-})$	9.03	−10.67	10.61	−9.50		2.29[f]
$\Delta[\delta_H(3^{4-}) - \delta_H(3)] = \Delta\delta_H$	0.27	−9.85	1.40	−8.68		0.47
$\Delta\delta_H'$	−2.14	−1.61	−1.93	−1.39		
$\Delta\delta_H''$	−1.61	−2.14	−2.35	−1.71		
$\Delta\delta_H'^{(RC)}$	2.41	−8.24	3.33	−7.29		
$\Delta\delta_H''^{(RC)}$	1.88	−7.71	3.75	−6.97		
$\delta_H(4)$	7.93	1.95	8.23	1.82	8.23	1.61
$\delta_H(4^{2-})$	1.20	23.39	0.18	21.35	0.18	−0.20[g]
$\Delta[\delta_H(4^{2-}) - \delta_H(4)] = \Delta\delta_H$	−6.73	21.44	−8.05	19.53	−8.05	−1.81
$\Delta\delta_H'$	−0.21	−1.61	−0.01	−1.71	0.00	
$\Delta\delta_H'^{(RC)}$	−6.52	23.05	−8.04	21.24	−8.05	
$\delta_H(4)$	7.93	1.95	8.23	1.82	8.23	1.61
$\delta_H(4^{4-})$	9.84	−10.17	11.49	−11.27	11.49	2.44[h]
$\Delta[\delta_H(4^{4-}) - \delta_H(4)] = \Delta\delta_H$	1.91	−12.12	3.26	−13.09	3.26	0.83
$\Delta\delta_H'$	−1.39	−1.93	−1.61	−1.71	−1.71	
$\Delta\delta_H'^{(RC)}$	3.30	−10.19	4.87	−11.38	4.97	

[a] δ_H = experimental ^{1}H resonances; $\Delta\delta_H$ = shifts of individual proton signals which are experimentally observed on going from the neutral annulenes to their ionic derivatives; $\Delta\delta_H'$, $\Delta\delta_H''$ = "charge-induced" shifts of individual ^{1}H signals (these data have been calculated from the changes in π charge densities, $\Delta q_\pi'$ and $\Delta q_\pi''$ (see Table II) by adopting a proportionality constant of $K_H = 10.7$); $\Delta\delta_H'^{(RC)}$, $\Delta\delta_H''^{(RC)}$ = "charge-induced" shifts of individual ^{1}H signals (these data are obtained as the difference $\Delta\delta_H - \Delta\delta_H' = \Delta\delta_H'^{(RC)}$ or $\Delta\delta_H - \Delta\delta_H'' = \Delta\delta_H''^{(RC)}$). [b] $2Li^+$/DME (−75 °C). [c] $2Li^+$/THF (−80 °C). [d] $2Li^+$/THF (−40 °C). [e] $2Li^+$/THF (−80 °C) [f] $2Li^+$/THF (−45 °C). [g] $2Li^+$/THF (−80 °C). [h] $2Li^+$/THF (−45 °C).

performed by Barfield, Grant, and Ikenberry[44] reveals that the nonspherical electronic environments of carbons cause a local magnetic anisotropy which, within the chemical shift scale, can dominate the "nonlocal" ring current effects. The unique structural features of [4*n* + 2]annulenes, however, create a somewhat different situation, since the contribution of delocalized shielding terms is much more important.

In a quantum mechanical approach Vogler[30,45] has analyzed the shielding phenomena of the present bisdehydroannulenes, thereby taking into account both the ring current ($\Delta\delta^{(RC)}$) and local contributions ($\Delta\delta^{(LC)}$). The latter comprise the effects of the perimeter π system and of the orthogonal (acetylene-type) π system as well as the σ framework. For outer protons the term $\Delta\delta^{(LC)}$ amounts to about 1 ppm and is significantly smaller than $\Delta\delta^{(RC)}$, both contributions resulting in some deshielding; for inner protons the major role of $\Delta\delta^{(RC)}$ is even more pronounced, the shielding effect of $\Delta\delta^{(RC)}$ being slightly diminished by the influence of $\Delta\delta^{(LC)}$. Extension of this work to the dianions and tetraanions[46] reveals that $\Delta\delta^{(LC)}$ values of individual positions are again of the order of 1 ppm, indicating a large domination by nonlocal effects. Moreover, when comparing dianions (or tetraanions) of different ring size, $\Delta\delta^{(LC)}$ turns out to be essentially constant. Therefore, if one considers the experimental ^{1}H chemical shifts as a function of ring size, one can safely regard the local anisotropic contributions as constant. In our empirical treatment we may approximately identify the (charge-corrected) shifts of specific proton signals, which are induced by anion formation, as a ring current effect. The main consequence of such ring current effects in neutral, dianionic, and tetraanionic annulenes is the large chemical shift difference of inner and outer ring protons. It is advantageous, therefore, to determine the difference $\Delta[\delta(H_o) - \delta(H_i)]^{(RC)}$ (see Table IV) which in Figure 6a is plotted as a function of ring size.

On the other hand, within an analysis of ring current effects it is clear that the secondary magnetic field at a particular proton depends not only on the ring current intensity per unit applied field but also on the location of the proton and the shape of the perimeter.[47] Various procedures, both in the classical[48–51] and

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Table IV. ^{1}H Chemical Shift Differences of Inner and Outer Ring Protons[a]

	$\Delta[\delta_o - \delta_i]^b$	$\Delta[\delta_o - \delta_i]'^{(RC)\,c}$	$\Delta[\delta_o - \delta_i]''^{(RC)\,d}$	$\Delta[\delta_o - \delta_i]'^{(RC)}/S^e$	$\Delta[\delta_o - \delta_i]''^{(RC)}/S^e$
1	13.76			6.88	
2	13.46			4.49	
3	10.03			2.51	
4	6.41			1.28	
1^{2-}	−22.52	−24.66	−26.91	−12.33	−13.46
2^{2-}	−23.84	−25.77	−26.84	−8.59	−8.95
3^{2-}	−23.52	−25.02		−6.26	
4^{2-}	−21.17	−22.88		−4.58	
2^{4-}	18.82	19.35	18.29	6.45	6.10
3^{4-}	20.11	20.65	20.75	5.16	5.19
4^{4-}	22.76	22.76		4.55	

[a] $\delta_o = \delta$ (H_o), $\delta_i = \delta$ (H_i); (1) H_o = H-3, H_i = H-4; (2) H_o = H-5, H_i = H-4; (3) H_o = H-5, H_i = H-6; (4) H_o = H-7, H_i = H-6. [b] Calculated from the experimental resonances (δ_H) given in Tables I and III. [c] Calculated from the ring-current-induced signal shifts of individual protons ($\Delta\delta_H'^{(RC)}$; see Table III. [d] Calculated from the ring-current-induced signal shifts of individual protons ($\Delta\delta_H''^{(RC)}$; see Table III. [e] S = ring area.

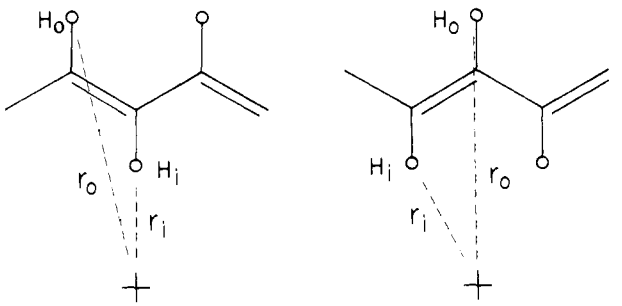

Figure 5. The position of inner and outer hydrogens in bisdehydroannulenes.

quantum-mechanical treatments,[52-54] have been put forward to account for these spatial factors. In an approximate equation[55] the ring-current-induced shift of a particular proton resonance is proportional to the product of ring current intensity, the area of the ring, and the inverse-cube distance of the nucleus from the center of the ring. Considering the situation that prevails in the present annulenes (see Figure 5), it turns out that the variation of the ring size does not significantly change the distance of inner and outer protons from the center of the ring. We can, therefore, take the charge-corrected shift difference of inner and outer protons, $\Delta[\delta(H_o) - \delta(H_i)]$, divided by the respective ring area S, as an empirical measure of the ring current effect (see Table IV). When the area of a hypothetical bisdehydro[10]annulene is taken as unity, it follows that the areas of **1**, **2**, **3**, and **4** are 2, 3, 4, and 5, respectively. The above method has successfully been applied to the neutral annulenes **1–4**;[7] for the sake of comparison it is also adopted (see Figure 6b) in our present description of the anions.

The following features are obvious. (i) On going from **1** to **2** the value $|\Delta[\delta(H_o) - \delta(H_i)]|$ remains unchanged; it decreases only for **3** and **4**. In $\mathbf{2}^{2-}$ it is larger than in $\mathbf{1}^{2-}$ and suffers from only a slight decrease in $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$. In the case of the tetraanions this difference increases significantly along the homologous series. (ii) In the neutral compounds the ratio $[\Delta[\delta(H_o) - \delta(H_i)]]/S$, the "diamagnetic ring current effect", decreases with increasing ring size, so that the plot in Figure 6b gives a smoothly decay curve. (iii) A similar trend is observed for the paramagnetic ring current effect in the corresponding dianions, the decay appearing more rapid than in the corresponding neutral annulenes. (iv) Diamagnetic ring current effects in the tetraanions are always greater than in the corresponding neutral annulenes.

These results provide the first systematic description of the change of ring current effects in neutral, dianionic, and tetraanionic

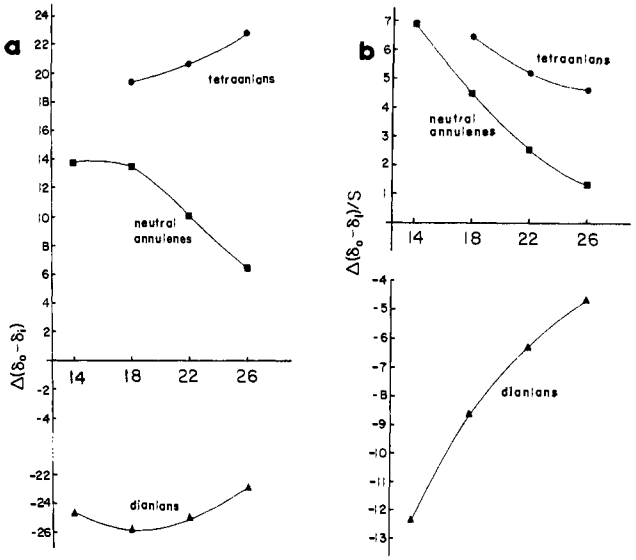

Figure 6. Plot of diamagnetic and paramagnetic ring current effects vs. ring size (see text): (a) $\Delta[\delta(H_o) - \delta(H_i)]$, (b) $\Delta[\delta(H_o) - \delta(H_i)]/S$.

annulenes which have different ring size but identical perimeter type.

e. π-Bonding Situation of Ionic Annulenes. Pople and Untch[56] described both the diamagnetic ring current effect in $[4n + 2]$-annulenes and the paramagnetic ring current effect in $[4n]$-annulenes as being partly quenched by π-bond alteration. It has also been predicted by various authors[57] that the tendency toward π-bond delocalization falls off for larger annulenes. Thus, the decrease of diatropism in the series of neutral annulenes **1–4** can compellingly be ascribed to the occurrence of π-bond fixation.

It is most instructive at this point to extend this reasoning to the $(4n + 2)\pi$ tetraanions.[47,56,58] As mentioned already the diatropism of the tetraanions exceeds that one of the neutral annulenes. Obviously, the tendency of the excess charge to be uniformly distributed over the entire π system strongly reinforces the π-bond delocalization. Further support of this naive view is obtained when comparing the different tetraanions. Their diatropism, if measured by the term $\Delta[\delta(H_o) - \delta(H_i)]/S$, becomes smaller in the larger rings, this "quenching effect", however, being much less severe than in the neutral species.

In an empirical approach one might consider two features as relevant for the existence of stable annulene tetraanions:[59] the

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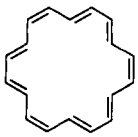
(59) It is clear that any restriction to the properties of the pure π system constitutes a rather crude approach. See: Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7928, and references cited therein.

achievement of a $(4n + 2)\pi$ system[60,61] and the compensation of electron–electron repulsion. Cyclic voltammetry shows a small difference in the potentials (<80 mV) of the redox step $3^{3-}\cdot/3^{4-}$, on the one hand, and of the mono-, di-, and trianion formation, on the other hand. Under the assumption that the entropy changes of the single redox reactions are of similar magnitude and that there is no dramatic change of the solvation effects, this finding might, indeed, indicate some electronic stabilization in the tetraanion. Furthermore, the failure of **1** to provide a tetraanion points out that there is a minimum perimeter size which will be necessary for tetraanion formation and, thus, for the minimization of electron–electron Coulomb repulsion.[62]

For the dianion, constituting $(4n)\pi$ monocycles, a discussion of π-bond fixation[47,56] is different, since such species will tend to alternate their bond lengths even in the absence of a magnetic field. A characteristic feature can be revealed when comparing the dianion 2^{2-} with the isoelectronic dianion of the parent [18]annulene (9^{2-}) which has been prepared by Oth and So-



9

ndheimer.[10] In 9^{2-} the shift difference of inner and outer protons is much greater than in 2^{2-}. Within the realm of a simple MO model one will expect a decreasing HOMO/LUMO gap to increase the paramagnetic effects, i.e., the admixture of electronically excited states to the zero-field ground state. As has been mentioned already, the degeneracy of the two LUMO's in the neutral annulene **2** is destroyed because of the present perturbations. These two annulene MO's are degenerate as long as a C_3 axis is maintained; this situation is expected to prevail in **9**. According to this simple approach, one will, indeed, predict the paratropism of 9^{2-} to be more pronounced than in 2^{2-}.[63]

The question arises for the present dianions, if, in addition to first-order double-bond fixation, a second-order fixation process occurs which will lower the symmetry of the molecular framework.[64] The ^{1}H and ^{13}C spectra of the title dianions have been measured at temperatures as low as −115 °C, but fail to provide any evidence in favor of distorted structures. This is particularly obvious from the signal of the *tert*-butyl protons which always appear as a sharp singlet. Accordingly, either the D_{2h} symmetry of the perimeter must be maintained or a π-bond shift process must occur which rapidly interconverts species of lower symmetry.

4. Conclusion

The well-established model character of annulenes for investigations of electronic structure is expected to gain a further significant aspect by the inclusion of the dianionic $(4n)\pi$ and tetraanionic $(4n + 2)\pi$ species which have been introduced here. It appears from detailed spectroscopic studies that the ions may adequately be described as typical π-delocalized species, the charge distribution being predictable from elementary π-MO models.

In view of the strongly increased diatropism of the tetraanions—the most spectacular outcome of this work—the somewhat trivial fact might be recalled that, clearly, the π-delocalization energy of the tetraanions is greater than that of the isoelectronic neutral species.[65] This is just because one would compare the former with a π-bond localized (and charge-localized) reference structure.

Contact ion pairs, whose π systems suffer from symmetry distorsions due to specific interactions with the metal, do not contribute significantly to the ground state of the ions. On the other hand, experimental evidence clearly indicates that ion-pair formation is a major reason for the existence of the stable tetraanions. Consequently, any structural scrutiny will have to consider the role of the σ core in accommodating with four extra charges as well as the preferred locations of the counterions with respect to the π system. We are currently investigating these structural features.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. H. Vogler for stimulating discussions and for making available unpublished results. Thanks are also due to Professor G. Hohlneicher for helpful suggestions.

Registry No. 1, 38941-87-6; $1^{2-}(2L_i^+)$, 82666-39-5; $1^{2-}(2K^+)$, 82666-41-9; $1^{2-}(2Cs^+)$, 82666-43-1; **2**, 38937-12-1; $2^{2-}(2Li^+)$, 82666-45-3; $2^{2-}(2K^+)$, 82666-47-5; $2^{4-}(4Li^+)$, 82666-49-7; **3**, 38671-95-3; $3^{2-}(2Li^+)$, 82666-51-1; $3^{2-}(2K^+)$, 82666-53-3; $3^{4-}(4Li^+)$, 82666-55-5; $3^{4-}(4K^+)$, 82679-02-5; **4**, 39124-78-2; $4^{2-}(2Li^+)$, 82679-04-7; $4^{2-}(2K^+)$, 82666-57-7; $4^{4-}(4Li^+)$, 82666-59-9; $4^{4-}(4K^+)$, 82666-61-3; **5**, 82679-00-3.

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