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ION-PAIRING AND RING CURRENT EFFECTS

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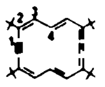
Abstract—A homologous series of [4n + 2] annulenes reduced with alkali metals yields paratropic (4n)π-dianions. ^{1}H NMR chemical shifts are most significant for a description of the relevant π-electron structures. However, the shift data turn out to reflect sensitively the ion-pairing. Therefore, the experimental conditions (counterion, solvent, temperature, organic ion) have been varied systematically, and a consistent description of the existing contact-solvent-separated ion pair equilibria (e.g. as a function of ring size, π-charge distribution etc) has been obtained. The interdependence of ion-pairing and ring current effects is discussed.

NMR spectroscopic studies of ion-pairing effects, amply described in the literature, have dealt preferentially with mono-charged aromatic species or their condensed benzene derivatives.[1-5] Such ions offer the advantage of being easily accessible and stable over a large temperature range. The experimental evidence compiled points toward equilibria of solvent-separated and contact ion pairs the relative weights of which are sensitively influenced by the choice of solvent, temperature and counterion. Similar investigations of highly charged organic ions (dianions, tetraanions) have been rare although these species might be particularly relevant in view of the occurring Coulomb-interactions.

During our continuing attempts at preparing novel ionic π-systems[6,7] we have recently transformed neutral [4n + 2]annulenes into (4n)π-dianions and, subsequently, into (4n + 2)π-tetraanions, the resulting ions exhibiting remarkable spectroscopic properties.[8] Ion formation brings about large changes of the ring current effects which are most significant for structural considerations and the verification of theoretical predictions. It has recently been established by us that a detailed evaluation of ring current phenomena on the basis of ^{1}H NMR chemical shifts requires significant "correction" terms accounting for the variable effects of the π-charge and of the mode of ion-pairing. It is the immediate consequence of this finding that the protons attached to annulene ions should experience the influence of a counterion in three ways: (a) via the (direct) electric field effect along the C–H-axis; (b) via the induced modification of the local π-charge densities; and (c) by the perturbed electronic structure and magnetic anisotropy of the entire π-system.

Consequently, one might expect the ^{1}H chemical shifts of ionic annulenes to constitute most sensitive probes for the description of ion pair structures. The interaction of the counterion or the solvent on the one hand with the organic substrate on the other hand will, apart from the above-mentioned experimental factors, also depend on the size of the organic ion.[1] It is, therefore, another promising feature that we have available a complete series of homologous annulenes **1**–**4**[8] with identical ring configurations and ring conformations. Our study of ion-pairing effects in annulenes thus implies a systematic variation not only of the counterion, the solvent and the temperature, but also of the size of the organic ion.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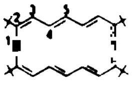
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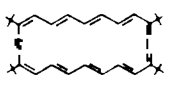
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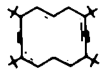
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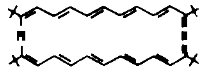
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EXPERIMENTAL

The synthesis of the neutral compounds, the method of obtaining solutions of pure dianions or tetraanions as well as the structure proof of the resulting species, are given elsewhere.[8] Representative experimental aspects necessary for the interpretation of the present NMR results are described.

All experiments were performed in sealed NMR tubes with alkali metals (Li, Na, K, Cs) as reducing agents in degassed deuterated etheral solvents [tetrahydrofuran (THF), dimethoxyethane (DME), diethylether (DEE), mixtures of THF and DEE or mixtures of ethers with hexamethylphosphoric triamide (HMPT)]. The reactions were performed at −78° while the temperature of the NMR measurements was varied between −80° and 0° (see below). In order to avoid decomposition of the starting materials, the solvents and the metals must be purified with extreme care.

When contacting a solution of the [14]annulene **1** with metal the original ^{1}H resonances are broadened into the baseline. This is a consequence of a rapid electron-transfer between **1** and the radical anion $\mathbf{1}^{\dot{-}}$. The latter can be identified by its ESR. After several hours of further metal contact, ESR measurements indicate the absence of paramagnetic species while at the same time the ^{1}H and ^{13}C spectra indicate the formation of a diamagnetic dianion $\mathbf{1}^{2-}$. The tremendous shifts of the ^{1}H resonances observed upon going from **1** to $\mathbf{1}^{2-}$ (see Table 1) leave no doubt that the diatropic (4n + 2)π-annulene has been transformed into a paratropic (4n)π-dianion—a finding which is in perfect accord with theoretical considerations of the π-structures.[8]

In the case of the higher-membered annulenes **2**–**4** a

Table 1. ^{1}H-chemical shifts (δ_H) of neutral, dianionic and tetraanionic annulenes[a]; counterions, solvents and temperatures are indicated

			H-3	H-4	H-5	H-6	H-7	H-t-but
$\delta_H(1)$	$CHBr_3$	+36°C	9.32	-4.44				1.94
$\delta_H(1)^{2-}(2Li^+)$	THF	+ 6°C	3.22	18.88				0.37
		-42°C	3.10	19.19				0.35
		-75°C	2.95	19.66				0.30
		-82°C	2.89	19.84				0.29
$\delta_H(1)^{2-}(2Li^+)$	DME	-10°C	2.52	21.24				0.18
		-45°C	2.18	22.60				0.11
		-75°C	1.85	24.37				-0.01
$\delta_H(1)^{2-}(2K^+)$	THF	+11°C	2.74	20.96				0.22
		-42°C	2.68	20.98				0.21
		-75°C	2.66	20.94				0.21
		-82°C	2.65	20.89				0.20
$\delta_H(1)^{2-}(2K^+)$	DME	- 5°C	2.63	21.37				0.19
		-45°C	2.61	21.41				0.19
		-80°C	2.50	21.76				0.17
$\delta_H(1)^{2-}(2Cs^+)$	THF	-35°C	2.77	23.27				0.20
$\delta_H(1)^{2-}(2Li^+)$	THF/ HMPT 10:1	-40°C	b)	23.11				0.16
$\delta_H(2)$	$CHBr_3$	+36°C	9.32	-3.64	9.82			1.91
$\delta_H(2)^{2-}(2Li^+)$	THF	-15°C	b)	22.47	b)			-0.12
		-42°C	1.50	23.33	1.04			-0.12
		-75°C	b)	24.56	b)			-0.11
		-82°C	$1.04^{c)}$	24.88	$1.04^{c)}$			-0.11
$\delta_H(2)^{2-}(2K^+)$	THF	-15°C	b)	21.10	b)			0.06
		-45°C	b)	21.22	b)			0.06
		-60°C	2.07	21.50	1.57			0.07
		-80°C	2.02	21.65	b)			0.07
$\delta_H(2)^{2-}(2K^+)$	DME	-25°C	b)	22.41	b)			-0.04
		-75°C	2.05	24.51	b)			-0.19
		-80°C	b)	24.68	b)			-0.19
$\delta_H(2)^{4-}(4Li^+)^{d)}$	THF	-40°C	7.95	- 8.97	9.85			2.12
$\delta_H(2)^{4-}(4K^+)$	THF	-40°C	7.40	-10.30	8.90			1.70
$\delta_H(2)^{4-}(4K^+)$	DME	-40°C	7.07	-10.54	8.91			1.97
$\delta_H(3)$	$CHBr_3$	+36°C	8.76	- 0.82	9.21	-0.82		1.82
$\delta_H(3)^{2-}(2Li^+)$	THF	-15°C	b)	24.20	b)	22.70		-0.25
		-45°C	b)	24.80	b)	23.20		-0.29
		-80°C	1.15	24.80	-0.29	23.23		-0.29

Table 1. (*Contd*)

			H 3	H 4	H-5	H-6	H 7	H 1 out
$\delta_H(3)^{2-}(2K^+)$	THF	-45°C	1.95	21.29	1.22	19.84		-0.06
$\delta_H(3)^{2-}(2K^+)$	THF/ DEE 1:1	+ 4°C	2.16	20.24	b)	18.90		0.01
		-15°C	2.07	20.45	1.45	19.06		0.01
		-45°C	1.93	20.84	1.26	19.47		-0.02
		-80°C	1.78	21.90	b)	20.40		-0.17
$\delta_H(3)^{2-}(2K^+)$	THF/ DEE 1:2	- 4°C	2.21	20.05	1.70	18.74		0.03
		-19°C	2.19	20.13	b)	18.71		0.03
		-40°C	2.08	20.41	b)	18.97		0.00
		-70°C	1.92	20.89	b)	19.46		-0.09
$\delta_H(3)^{4-}(4Li^+)$	THF	-45°C	9.03	-10.67	10.61	- 9.50		2.29
$\delta_H(3)^{4-}(4K^+)$	THF	-45°C	9.00	-10.50	10.58	- 9.07		2.33
$\delta_H(4)$	$CHBr_3$	+36°C	7.93	1.95	8.23	1.82	8.23	1.61
$\delta_H(4)^{2-}(2Li^+)^{e)}$	THF	-15°C	b)	23.28 (21.35)	0.18	21.35 (23.28)	0.18	-0.20
		-45°C	b)	23.32 (21.37)	b)	21.37 (23.32)	b)	-0.20
		-80°C	1.20	23.39 (21.35)	0.18	21.35 (23.39)	0.18	-0.20
$\delta_H(4)^{2-}(2K^+)^{e)}$	THF	-15°C	2.08	20.41 (18.71)	b)	18.71 (20.41)	b)	-0.18
		-45°C	b)	20.91 (19.14)	b)	19.14 (20.91)	b)	-0.09
		-80°C	1.70	21.58 (19.72)	1.50	19.72 (21.58)	1.50	-0.09
$\delta_H(4)^{4-}(4Li^+)^{e)}$	THF	-45°C	9.84	-10.17 (-11.27)	11.49	-11.27 (-10.17)	11.49	2.44
$\delta_H(4)^{4-}(4K^+)^{e)}$	THF	-45°C	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 TMS.

[b] Covered by the signal of an impurity or of the solvent.

[c] The estimated error is relatively high (± 0.2 ppm) due to the overlap of the signals of H-4 and H-5 with the signal of an impurity.

[d] For ease of comparison the data of the diatropic tetraanions have also been included.

[e] It is not possible from experimental evidence to discriminate between the signals of H-4 and H-6.

detection of the corresponding dianions turns out to be extremely difficult since the reduction proceeds beyond the two-electron stage to yield both radical trianions and tetraanions. As before, these ionic products can be characterized by ESR and NMR, respectively. The intermediate dianions, however, are detectable only by their NMR spectra when present as sole products. Accordingly, the reduction (formation of the dianions is complete within a few minutes) has to be performed in short time-intervals and carefully monitored by recording the respective ESR and NMR spectra.

Apart from problems inherent in the reduction kinetics, a NMR spectroscopic study of the dianions and tetraanions was severely inhibited by their low solubility and limited thermal stability. In some cases, decomposition started at temperatures above −20° so that we could not cover the full temperature range.

These problems are particularly severe for the larger counterions (it was not possible to obtain Cs salts of the tetraanions). Additional difficulties were encountered when changing the solvent system. Thus, the lithium salt of 1^{2-} decomposed rapidly when going from THF to a 10:1-mixture of THF/HMPT.

The energy terms relevant to a discussion of the existence of annulene dianions and tetraanions have been extensively examined by us in a separate paper.[8] It is clear that the stability of highly charged π-species essentially depends on the ion ion interaction with the metal; increasing cation-coordinating ability of the solvent system is observed to destabilize the organic anion. The above difficulties should be kept in mind when considering (see Table 1) that not every possible combination of organic substrate, counterion, solvent (and temperature) has been realized experimentally.

During ^{1}H NMR measurements the concentrations of the starting materials were always lower than 2×10^{-2} M. Dianion concentrations higher than 5×10^{-2} M could not be obtained for solubility reasons. On the other hand, when the original THF-solution of $1^{2-}/2Li^+$ was diluted and the concentration thus lowered from 2×10^{-2} M to about 7×10^{-3} M, the individual ^{1}H resonances are shifted by less than 0.1 ppm. This value is believed to represent the margin of error for the ^{1}H NMR chemical shifts given in Table 1.

Normally, for a single spectrum one has to accumulate between 30 and 50 scans. The locking was provided by the deuterated solvent. For experimental reasons (stability and solubility of the ions) the NMR chemical shifts could not be measured with respect to the resonances of an internal hydrocarbon or TMS reference; instead of, δ-values have therefore been taken with respect to the solvent lines and converted to the TMS-basis by means of the appropriate increments. ^1H NMR spectra (FT-mode) have been recorded at a Bruker WP60-spectrometer which is equipped with a home-made system for sample cooling. The temperature is believed to be kept constant within ± 1.5°. ^{13}C NMR spectra have been recorded on a Bruker HX90-spectrometer. ^1H and ^{13}C signal assignments (see Tables 1 and 2) have been extensively discussed elsewhere.[8]

4. RESULTS AND DISCUSSION

The existence of large ring current effects within the annulene anions (see Table 1), which is obvious from the extreme shift difference of inner and outer ring protons, provides firm evidence for a cyclic π-conjugation. Moreover, the excess π-charge appears to be delocalized over the entire π-systems with the π-charge distribution being correctly predictable on the basis of simple MO-models. The charged annulenes thus constitute the type of ionic systems for which, by analogy with various other examples,[1-5] one would expect an equilibrium of solvent-separated and contact ion pairs.

It is, certainly, a good starting point to develop a feeling as to the order of magnitude of chemical shift changes (in the following called the "ion pair shift") that can be brought about by modifying the type of ion-pairing. In their careful study of the indenylion, Velthorst and Gooijer,[9] when exchanging the counterion or when varying the temperature in a range of 60°, observed shifts of the respective ^1H resonances by not more than 0.2 ppm. Similar results are reported for related ion pairs.[3,5]†

A brief inspection of Table 1 will readily demonstrate that, in the case of annulene dianions, the analogous effects are much greater: for the lithium (THF) and potassium (THF/DEE 1:2) salts of 3^{2-} the absorptions of proton H-4 differ by 4.4 ppm and for the system $3^{2-}/2K^+/THF/DEE$ (1:1) the resonance of H-4 is shifted by about 1.5 ppm when the temperature is changed by 60°.

The drastic signal shifts which are induced by ion-pairing effects have to be contrasted with the finding that ^1H resonances of the dianion salts do not show a significant concentration dependence (see Experimental). Obviously, under the prevailing conditions, an eventual aggregation of ion pairs does not markedly affect the NMR chemical shifts.

Furthermore, the temperature-changes while severely affecting the ^1H-chemical shifts do not cause significant line broadening. One can therefore safely exclude that the temperature-dependent chemical shifts are due to the existence of thermally accessible triplet-states of the dianions. The following discussion will have two major subjects. The first one is to establish the principal analogy of the annulene dianions with the above-mentioned ionic reference compounds. The second subject is to investigate the origin of the extremely large ion pair shifts in annulene dianions. Of particular significance is the correlation of ion-pairing and ring current effects.

The protons inside (H_i) or outside (H_0) the paratropic monocycle are known to resonate at extremely low or high field, respectively. Therefore, the absolute values of δ-H_i and of $\Delta(\delta\text{-}H_0 - \delta\text{-}H_i)$ are expected to constitute appropriate criteria for the description of the present ion pair structures.

When for the system 1^{2-}/THF the counterion is varied (Li^+, Na^+, K^+, Cs^+), the value of $|\Delta(\delta\text{-}H_0 - \delta\text{-}H_i)|$ [= $\Delta(\delta$-H-3 − δ-H-4)] increases from about 16 to 20 ppm, at the same time the resonance of H_i (= H-4) moves from δ_i = 19 to

Table 2. ^{13}C-chemical shifts (δ_C) of neutral and dianionic annulenes[a]; counterions, solvents and temperatures are indicated

			C-1	C-2	C-3	C-4	C-5	C-2a	C-2b
$\delta_C(1)$			117.2	131.9	131.1	129.6		37.9	32.4
$\delta_C(1)^{2-}(2Li^+)$	THF	-1.5°C	108.9[b]	100.3[b]	137.3	90.6		32.2	30.2
		-30.0°C	106.0	100.0	137.4	90.7		32.3	30.2
		-85.0°C	106.2	99.5	137.6	91.9		32.3	30.2
$\delta_C(1)^{2-}(2K^+)$	THF	-30.0°C	107.6[b]	98.2[b]	138.5	94.7		31.9	29.9
$\Delta[\delta_C(1) - \delta_C(1)^{2-}(2Li^+)] = \Delta\delta_C$[c]			11.2	31.9	-6.3	38.9			
$\delta_C(2)$			116.3	132.2	131.3	130.1	134.3	38.4	32.3
$\delta_C(2)^{2-}(2Li^+)$	THF	-30.0°C	107.9	109.4	136.5	107.6	137.7	31.5	28.7
$\Delta[\delta_C(2) - \delta_C(2)^{2-}(2Li^+)] = \Delta\delta_C$			8.4	22.9	-5.2	22.5	-3.4		

[a] δ_C-values have been taken with respect to the solvent signals and then referred to TMS.
[b] Assignments have been made from calculated π-charge densities.
[c] δ_C-values at − 30°.

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†Not surprisingly, a temperature dependence of ^1H chemical shifts, i.e. an upfield shift of the signals of outer and a downfield shift of the signals of inner ring protons with increasing temperature, is also observed for the neutral annulenes.[8] It follows from these gradients, which are much smaller than those observed in the dianions, that one would not necessarily expect temperature-independent ^1H resonances for solutions of pure contact or solvent-separated ion pairs.

$\delta_t = 23$. Furthermore, the resonances of the K- and Cs-salts are essentially temperature independent, while for the Li-salt the absolute values of both δ-H$_i$ and $\Delta(\delta\text{-H}_0 - \delta\text{-H}_i)$ increase on lowering the temperature.

It is straightforward to assume that the K- and Cs-salts exclusively exist as contact ion pairs. Thereby the largest counterion (Cs) exerts the smallest perturbation, and the paramagnetic ring current effect is most pronounced. Not unexpectedly from related experience,[1] the tendency toward solvent-separated ion pairs can be increased when using Li as counterion; we conclude from the temperature-dependent ^{1}H resonances of $\mathbf{1}^{2-}$/2Li$^+$ that there exists an equilibrium of both structures which at lower temperatures is shifted toward the solvent-separated ion pair.

Additional evidence in favour of the above interpretation is obtained when exchanging THF by DME or when adding HMPT to the THF-solution. The latter systems are known to possess better cation-solvating abilities than THF and thus to favour solvent-separated ion pairs. Not unexpectedly, therefore, the resonance of H$_i$ is shifted from 18.9 to 23.1 and 24.4 when THF is replaced by THF/HMPT (10:1) or by DME, respectively.

Analogous consequences of such a solvent-change are obtained for the $\mathbf{1}^{2-}$/2K$^+$-pair. Furthermore, while for the system $\mathbf{1}^{2-}$/2K$^+$/DME no temperature-dependence of δ-H$_i$ is observed between 0° and −50°, the parameters $|\delta\text{-H}_i|$ and $|\Delta(\delta\text{-H}_0 - \delta\text{-H}_i)|$ increase on further lowering the temperature.

The above arguments can now be independently checked for the higher-membered dianions. The most striking outcome in a study of the dianions $\mathbf{2}^{2-}$, $\mathbf{3}^{2}$ and $\mathbf{4}^{2}$ (THF as solvent) is that the absolute values of δ-H$_i$ and $\Delta(\delta\text{-H}_i - \delta\text{-H}_0)$ are always greater for the Li-salts than for the K-salts. This situation clearly contrasts with the one prevailing in the ion pairs of $\mathbf{1}^{2}$. Thus, while the (4n)π-system of $\mathbf{1}^{2}$ seems to be more strongly perturbed by the lithium than by the potassium cations, this relation is inverted for the higher-membered systems; one is tempted to conclude that for the lithium salts of the latter the contribution of solvent-separated ion pairs is increased. The marked temperature-dependence of the ^{1}H resonances of $\mathbf{2}^{2}$ /2Li$^+$ would, in fact, indicate an equilibrium of both structures.

As for the case of $\mathbf{1}^{2}$ a change of counterions and solvents is revealing. While the systems $\mathbf{2}^{2}$ /2Li$^+$/THF and $\mathbf{2}^{2}$ /2K$^+$/THF obviously behave in quite a different fashion, this is no longer true when the potassium salt is measured in DME; the ^{1}H chemical shifts are slightly temperature-dependent and closely resemble those of the Li/THF-experiment.

The increasing fraction of solvent-separated lithium salts upon going from $\mathbf{1}^{2}$ to the larger organic anions becomes most obvious from the behaviour of the dianion $\mathbf{4}^{2}$, the largest member of the present series. As mentioned already, the values of $|\delta\text{-H}_i|$ and $|\Delta(\delta\text{-H}_i - \delta\text{-H}_0)|$ indicate the ring current effect to be more distinct in the lithium than in the potassium ion pair. Moreover, while the resonances of the combination $\mathbf{4}^{2}$ /2Li$^+$/THF no longer vary with temperature, the above parameters indicate a stronger ring current effect when the potassium salt is measured at increasingly low temperature.

A complementary experiment can be performed for the ion-pair $\mathbf{3}^{2}$ /2Li$^+$ in THF/DEE (1:1) which solvent system is expected to increase the fractions of contact ion pairs: the values of $|\delta\text{-H}_i|$ and $|\Delta(\delta\text{-H}_0 - \delta\text{-H}_i)|$ are, indeed, significantly diminished. This tendency is predicted to be further enhanced when potassium is introduced as counterion; the ^{1}H chemical shifts of $\mathbf{3}^{2-}$/2K$^+$ measured in both THF/DEE (1:1) and THF/DEE (1:2) (see Table 1) support this view. Moreover, in the THF/DEE-mixtures one observes a temperature-dependence of the resonances both for the Li- and K-salts, which finding indicates the increasing fraction of contact ion pairs at higher temperatures. For the system $\mathbf{3}^{2-}$/2K$^+$/THF/DEE (1:2) one approaches constant chemical shifts at about 0°.

It is straightforward to identify the corresponding data, δ_c, as those of the contact ion pair. In contrast, the predominance of the solvent-separated ion pair can be realized for the lithium, but not for the potassium case (see Table 1). Adopting in a crude approximation[10] the resonances thus obtained as δ_s-values of a solvent-separated potassium salt, we are now in a position to determine the equilibrium constants K for the contact-solvent-separated ion pair equilibrium from the well known equation[10,4]

$$K = \frac{\delta_c - \delta}{\delta - \delta_s}.$$

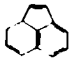
Thereby, δ represents the ^{1}H chemical shift of a single proton measured at a particular temperature. Using the temperature dependent K-values of the $\mathbf{3}^{2}$ /2K$^+$-salt [measured in THF/DEE (1:1)] we determine, from a plot of ln K vs reciprocal temperature, the thermodynamic parameters as $\Delta H^\circ = -14.5$[kJ · mol^{-1}] and $\Delta S^\circ = 74.8$[J · mol^{-1} · K^{-1}].

Clearly, the NMR-technique of determining such data suffers from various deficiencies and is less accurate than methods based on absorption spectroscopy. One would even conclude from the instability of the title dianions and, thus, from the limited temperature range being accessible, that the determination of the "borderline" values δ_s and δ_c is particularly critical for the annulene case.[4] Yet, it seems noteworthy that the enthalpy and entropy obtained for the contact-solvent-separated ion pair equilibrium of a doubly charged annulene are rather close to those cited for various monoanions.[10]

We conclude that the above investigation succeeds in creating a consistent view of the mode of ion-pairing in annulene dianions. The analogy with the well-known monoanions, e.g. the cyclopentadienylium type, is established by the obvious fact that larger counterions, higher temperatures and solvents with lower cation-solvating ability favour the contact ion pairs. Moreover, the contrasting behaviour of the dianions $\mathbf{1}^{2-}$ and $\mathbf{4}^{2}$ convincingly demonstrates the influence of the anion size.

We return finally to the observation that annulene dianions, while in a qualitative fashion behaving similarly to the aromatic monoanions, exhibit extremely large ion pair shifts. In order to rationalize this "enhancement" we might consider four significant features: (a) the higher total charge of the annulene ions; (b) the potential redistribution of the π-charge which is induced by the cation (this has been termed the "indirect cation effect"[9,11]); (c) the electric field effect of the cation upon the hydrogen (this is called the direct cation effect); (d) the ring current phenomena.[12]

In an independent study we have investigated the structures of dianions derived from the polycyclic π-systems 5–7.[13] By using different counterions and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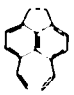
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by systematically varying the temperature we could determine from ^1H and ^{13}C NMR spectroscopic evidence the preferred locations of the counterions with respect to the polycycles. When present in THF solutions the Li- and K-salts of 5^{2-} and 6^{2-} exist predominantly as contact ion pairs. The ^1H resonances of the ion pair $5^{2-}/2Li^+$ are shifted by about 0.4 ppm when introducing potassium as counterion. Accordingly, the ion pair shifts turn out to be much smaller than in the present annulene case. Obviously, the ion-pairing effects in the polycyclic dianions, as detected by ^1H NMR spectroscopy, appear more similar to those in, e.g. indenyl or fluorenyl monoanions, than in annulene dianions.

These relatively small ^1H NMR effects, however, are in striking contrast to the finding that the corresponding changes of particular ^{13}C resonances, e.g. in 5^{2-}, are larger than 10 ppm. The observation that a change of the counterion influences the ^{13}C chemical shifts of the ions 5^{2-}, 6^{2-} and 7^{2-} to a much larger extent than the ^1H chemical shifts calls for a similar study of the annulene dianions.

We do not touch upon the problems inherent in correlating local π-charge densities with ^1H or ^{13}C chemical shifts.[14,15] We just mention the unequivocal results of independent studies that ^{13}C chemical shifts can be applied to describe changes of local π-charge densities and that they can be used in a subsequent step to determine "charge-induced" shifts of the corresponding proton signals. This is possible because carbon atoms within the periphery of the π-systems do not suffer significantly from ring current induced shielding effects.[16]

Let us consider as a typical example the ^{13}C NMR spectra[17] of the ion pairs $1^{2-}/2Li^+$ and $1^{2-}/2K^+$ (see Table 2). In complete accord with related experience the centre of gravity of the ^{13}C resonances experiences only a slight shift (< 1 ppm).[9,18] The absorption of C-4 is moved upfield by 4 ppm when potassium is substituted by lithium, the shifts of the other signals being much smaller.

One realizes from the experimental ^{13}C chemical shifts and also from MO-calculations[8] that the centre C-4 accepts the greatest π-charge. Obviously, the higher polarizing ability of the (smaller) lithium ion causes the π-charge distribution to become less uniform since it attracts the π-charge toward the centres of originally high π-charge density.

Having in mind the temperature dependence of the ^1H resonances of $1^{2-}/2Li^+$ we measured the corresponding ^{13}C NMR spectra in the same temperature range (i.e. 0–80°). It is remarkable in view of the large gradients of the ^1H chemical shifts that no carbon resonance was shifted by more than 1 ppm.

The importance of ^{13}C measurements for different counterions and temperatures becomes clear when referring to the proportionality of π-charge densities and ^1H or ^{13}C chemical shifts, respectively. The variations of particular ^{13}C resonances which are induced by a change of either the counterion or the temperature reflect the redistribution of the local π-charge densities. In a subsequent step one can now easily determine the charge effect upon the corresponding ^1H resonances from the equation $\Delta\delta_H = (\Delta\delta_C/K_C) \cdot K_H$. Thereby $K_C = (\Delta\delta_C/\Delta q_\pi)$ and $K_H = (\Delta\delta_H/\Delta q_\pi)$ are the proportionality constants giving the "charge-induced" shift of individual ^{13}C or ^1H signals per unit π-charge. Considering for the particular case of 1^{2-} the ^1H and ^{13}C resonances within a temperature range of $-80°$ to $-20°$, it follows that the "charge-induced" changes of ^1H chemical shifts will not exceed a value of about 0.1 ppm.

The "indirect" cation effect, which influences the polarization of the C–H-bond via a redistribution of the π-charge, does not explain the experimental results.

The "direct" cation effect upon the proton shielding, i.e. the polarization exerted by the electric field of the cation along the C H-bond, depends on the relative arrangement of the counterion and the organic anion. It is therefore straightforward that the induced shielding effects also reflect the contact-solvent-separated ion pair equilibrium and that they vary with temperature. Velthorst and Gooijer, when studying the indenyl anion, determined the indirect effect from ^{13}C data and visualized the direct effect by subtracting the temperature-dependent contribution of the indirect effect from the ^1H data.[9] Via this technique the authors obtained firm evidence that in the contact ion pair of the indenyl salt the counterion is localized over the five-membered ring.

Clearly, we cannot rigorously exclude the possibility that the pronounced ion pair shifts in the annulene dianions are due to extremely large ("direct") polarizing effects of the counterion. This might, in principle, result from the particular locations of the counterion with respect to the peripheral π-system of the perimeter. In the ionic macrocycles, however, one encounters large ion pair shifts for protons far apart from each other. Referring again to the contact ion pairs of indenyl and of 5^{2-}–7^{2-} it seems hard to believe that the outstanding shielding effects observed for annulene protons comes from the close proximity of the counterion and, therefore, their "direct" polarizing effect. We propose instead that the sensitive dependence of the ^1H chemical shifts on the mode of ion-pairing is a consequence of the large peripheral ring current effects. As is well known, the secondary magnetic field at a particular proton is not only due to the ring current per unit applied field but also due to spatial factors.[12,19] Of particular importance is the distance of the nucleus under consideration from the centre of the ring. Consequently, the resonance of protons inside the annulene ring should reflect a change of the ring current in a more sensitive way than that of outer protons.

It is significant for a description of annulene dianions that the protons inside the ring are observed to suffer much larger ion pair shifts than the nuclei outside.† This finding is true irrespective of the particular π-charge distribution: in the dianion salts $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ the signals of the inner nuclei (H-4) are most strongly shifted, due to the ion-pairing effects; the corresponding carbon centres adopt a very high π-charge density in $\mathbf{1}^{2-}$ and a very low π-charge density in $\mathbf{2}^{2-}$.

Moreover, as can be seen from Table 1, all the effects known to enhance the tendency toward solvent-separated ion pairs cause a further deshielding of inner and a (smaller) shielding of outer protons. This trend is, again, independent of the mode of π-charge distribution. Likewise, in the contact ion pairs $\mathbf{1}^{2-}/2\mathrm{K}^+$ and $\mathbf{1}^{2-}/2\mathrm{Cs}^+$, the smaller cation (with higher polarizing ability) diminishes the ring current effect to a larger extent.

Within our empirical approach we are therefore led to conclude that an increasing perturbation of doubly charged annulenes by their counterions decreases the measurable paramagnetic ring current effects. This feature, on the other hand, allows the detection of subtle ion-pairing effects.

CONCLUSION

The present study of annulene ions reveals, despite considerable experimental difficulties, new aspects of ion-pairing phenomena: (a) ring current effects enhance the measurable consequences of ion-pairing; and (b) the structure of the ion pairs sensitively depends on the size of the particular homologue.

It is well known, on the other hand, that ionic annulene species are important model compounds for theoretical considerations and that NMR spectroscopic criteria are extensively applied for a description of the prevailing π-bonding. In view of the above results it appears a prerequisite of this approach that the experimental conditions should be carefully defined and controlled.

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†An important structural problem, in view of the anisotropy of the ring current effects, concerns the geometry of the anionic π-system. Variation of the conformation of the perimeter (see Ref. 10) or of the C–C- and C–H-bond lengths is, indeed, expected to influence the measurable ring current effects. It is hard to believe, however, that such geometric variations, e.g. upon changing the counterion, could be responsible for the observed ion pair shifts.

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