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^{1}H NMR CHEMICAL SHIFTS OF [14]ANNULENES AND THEIR DIANION SALTS. A COMBINED EXPERIMENTAL AND THEORETICAL APPROACH.[#]

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Abstract - The bridged [14]annulene 2 was reduced into its dianion and the structure of the dianion salt was proven by chemical and spectroscopic means. The ^{1}H NMR spectroscopic properties of 2 are similar to those of the structurally related bridged [14]annulene 1, whereas the corresponding dianions 2^{2-} and 1^{2-} are strikingly different. The geometries of 1 and 2 and their dianions were studied by means of a modified π-SCF force field approach. Almost planar perimeters without significant bond length alternation are obtained for the neutral annulenes 1 and 2, whereas their dianions are characterized by structures with reduced symmetry. The ^{1}H chemical shifts of the bridged [14]annulenes and of the related non-cyclic conjugated compounds 3 and 4 were calculated by taking into account ring current, local anisotropic, and charge density contributions. It is shown that the transformation of the diatropic neutral systems 1 and 2 into the paratropic dianions $1^{2-}/2K^+$ and $2^{2-}/2K^+$ is due to the sign inversion of the ring current contribution. Furthermore we demonstrate that a satisfactory assessment of ^{1}H NMR chemical shifts in the paratropic systems $1^{2-}/2K^+$ and $2^{2-}/2K^+$ can be achieved only if the interaction between the π-systems of the annulenes and the counterions is explicitely taken into account.

[14]Annulene is characterized by severe non-bonded interactions of the inner hydrogens and so considerable ring distortions are encountered.[1-3] On the contrary, the bridged [14]annulenes trans-10b,10c-dialkyldihydropyrene (1a: $R=CH_3$; 1b: $R=(CH_2)_2CH_3$)[4] and trans-10b,10c-dihydro-10b,10c-dialkyldicyclopenta[ef,kl]-heptalene (2a: $R=R'=CH_3$; 2b: $R=CH_3$, $R'=(CH_2)_3CH_3$; 2c: $R=CH_3$, $R'=(CH_2)_7CH_3$)[4-6] possess essentially planar [14]perimeters according to X-ray analysis.[5,7] Therefore, they are more suitable models for studying the physical and chemical properties of [4m+2]annulenes which are diatropic compounds[2] due to their proton NMR spectra. Upon reduction with potassium 1 has been reported[6] to yield the paratropic dianion salt $1^{2-}/2K^+$. According to Winstein's notation[8] this reduction process transforms a (4m+2)π(4m+2)C- into a (4m')π(4m+2)C-annulene with m'=m+1.

The diatropism of neutral [4m+2]annulenes can be rationalized by the conceptually simple ring current (RC) model.[9,10] The paratropism of (4m')π-(4m+2)C-annulenes has been predicted by analogy to the (4m)π(4m)C-annulenes[11,12] and has been attributed to a paramagnetic RC effect.[13] However, the RC model cannot be applied straightforwardly in case of (4m')π(4m+2)C-annulenes due to the degeneracy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO) in the Hückel picture. This degeneracy is even encountered if the perimeter exhibits bond lengths alternation[10] in contrast to neutral [4m]annulenes. Recently we could show[14] that the RC model also accounts qualitatively for the paratropism of [4m+2]annulene dianions if the HOMO/LUMO degeneracy is lifted by introducing appropriate perturbations into the perimeter.

We report on the preparation and NMR spectroscopic characterization of the dianion $2a^{2-}$ and the related species $2b^{2-}$ (potassium salts) and describe the quenching reaction of $2a^{2-}/2K^{+}$ to afford the dihydro derivatives 4 and 5.

While the annulenes 1a and 2a exhibit a striking similarity in their ring geometry and spectroscopic properties, this finding being also valid for the corresponding radical anions[15] $1a^{\overset{\bullet}{-}}$ and $2a^{\overset{\bullet}{-}}$, the dianions differ significantly in their NMR resonances. A theoretical investigation of the annulene title compounds, therefore, appeared highly promising. We present the first approach to a quantitative assessment of ^{1}H chemical shifts in neutral and ionic annulenes by means of semiempirical quantum chemical methods. Toward this end it was necessary to determine theoretically the geometries of the bridged annulenes 1a and 2a as well of their corresponding dianions. The determination of the geometries with the aid of an ab-initio approach is not feasible due to the size of the compounds of interest and the necessity to go beyond the mean-field approximation in the case of annulenes.[16,17] Also the ab-initio calculation of chemical shifts for the neutral and especially the negatively charged bridged annulenes is prohibitive and could not fill the gap between the simple RC model and the experimental facts.

Experimental[18,19] and preliminary theoretical[20,21] studies lead to the conclusion that the counterions significantly affect the NMR spectra of charged paratropic annulenes. Therefore, we also investigate the counterion effect on chemical shifts in $1a^{2-}/2K^{+}$ and $2a^{2-}/2K^{+}$ by explicitely taking into account the electrostatic and covalent interactions within the ion pair. Our combination of experimental and calculated results should lead to a better understanding of ion pair structures and of the importance of counterion effects in paratropic annulenes.

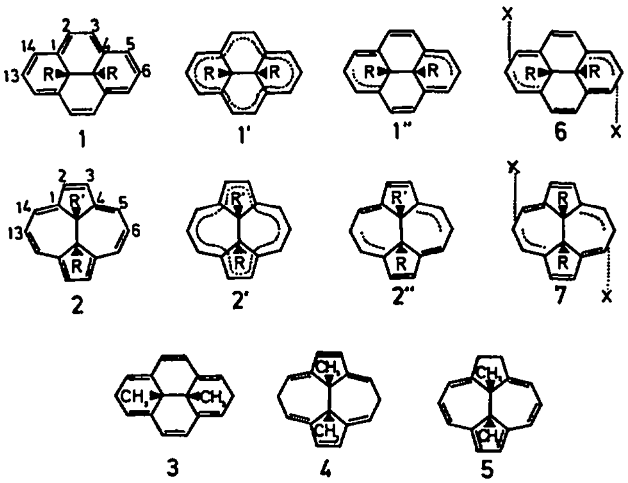

Figure 1. Survey of compounds under study (R and R' are identified in the text).

Experimental Section

Compounds 2a, 2b and 2c (see Table 1) were prepared according to the procedure given by us in the literature.[6,23]

Reduction of the annulenes 2. 5 mg of the neutral annulene (2a or 2b) were placed at the bottom of a 5mm-diameter NMR-tube and 0.5 ml dry [D_8]tetrahydrofuran were distilled in under vacuum. After degassing the solution by repeated freeze and thaw cycles a large excess of potassium was sublimed in from a side arm and deposited in the upper part of the tube as a mirror. The tube was sealed and the ^{1}H NMR spectrum of the neutral compound was recorded. The solution was then contacted with the metal at -78°C and the progress of the reduction monitored by ESR and NMR spectroscopy. The final deep green solution of $2a^{2-}/2K^+$ gave rise to well resolved NMR signals (see Table 2). In order to prevent decomposition of the sample the tube had to be kept at temperatures below -20°C.

Protonation of the dianion $2a^{2-}/2K^+$. 23 mg (0.1 m mol) annulene 2a were reduced with potassium in THF (20 ml) at -78°C according to the above technique. The reaction was carried out in a sealed ampoule. Dianion formation was complete after ca. 1 day. The ampoule was opened under argon and 1 ml of dry, degassed methanol added. The colour of the solution instantaneously turned from deep green to pale yellow. The mixture was allowed to warm to room temperature and extracted with water/hexane. The organic layer was dried with magnesium sulfate, and the solvent evaporated. One obtained a quantitative yield of a pale yellow residue. The ^{1}H NMR spectrum of the raw material indicated the formation of 4:

^{1}H NMR (60 MHz, $CDCl_3$) δ 6.12 (4H,s,2,3,9,10-H), 5.47 (4H,t,5,7,12,14-H), 3.25 (4H,t,6,6',13,13'-H), 1.29 (6H,s,15a-H,16a-H).

The product always contained a few per cent of 2a (2a is formed slowly upon contact with air).

All attempts to separate 2a and 4 via column chromatography failed. Separation via preparative GC (Carlo Erba, Fractovab 2300, OV 17, 220°C) gave a surprising result since the isolated dihydroannulene was identified as the isomer 5: m.p. 120°C (yellow needles); ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.04 (2H,s), 5.84 (4H,m), 5.32 (2H,dd), 2.52 (4H,m), 1.79 (3H,s), 1.75 (3H,s); MS (70eV), m/e 234 (35%), 219 (100%), 202 (58%); absolute mass: 234.138; calcd. for $C_{18}H_{16}$ 234.140.

Computational Procedures

1) Geometries. The X-ray structures of neutral 1a and 2a are known,[5,7] however, not those of the corresponding dianions $1a^{2-}/2K^+$ and $2a^{2-}/2K^+$. Therefore, we needed a procedure for obtaining reliable geometries since they are of great importance for the magnitude of the RC effect in paratropic compounds. Both ab-initio and semiempirical all-valence methods within the frame-work of the Hartree-Fock mean-field approximation are unsuitable for the study of geometries of annulenes since electron correlation is crucial for the structure of [4m+2]-annulenes.[16,17] The same applies to π-SCF force-field methods like those of Allinger et al.[3] and Lindner[24] since they utilize the Dewar-Sabelli/Ohno-Klopman formula[25] for the two-centre electron repulsion integrals which leads to Hartree-Fock instabilities[16,26] in [n]annulenes already with small n and favours first-order bond fixation.[27] The correct D_{6h} structure for [18]annulene is obtained if the π-bond orders used for the geometry optimization in the π-SCF force-field method of Lindner[24] are corrected by configuration interaction within a second-order perturbation approach.[28] However, such a procedure is very laborious. Electron correlation can be taken into account in a semiempirical method if the Dewar-Sabelli/Ohno-Klopman formula is replaced by the Mataga-Nishimoto formula[29] which leads to smaller and hence more dressed two-centre integrals. Then it proved necessary to use the bond order (P_{st}) - bond length (r_{st}) - relationship $r_{st}=1.5305-0.1971P_{st}$ which was chosen in order to reproduce the experimental bond lengths in trans-butadiene. Such a modified π-SCF force-field procedure yields the correct π-bond delocalized structures for [18]annulene as well as for 1 and 2.

Whereas the formula for the two-centre repulsion integrals turns out to be crucial in case of the [4m+2]annulenes this is not true with olefinic systems like [4m]annulenes, acyclic polyenes or with benzenoid systems.

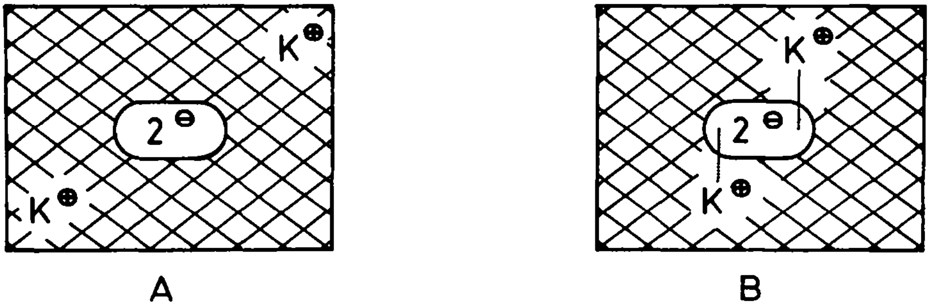

Figure 2. Schematical representation of a SIP (A) and a CIP (B).

2) Counterions. There is ample evidence[18,19] that annulene dianions and their counterions form equilibria of solvent separated ion pairs (SIP's) and contact ion pairs (CIP's). A SIP is characterized by electrostatic interaction between the ions whereas additional covalent interaction is possible between the conterions and the π-system of the annulene in case of a CIP, see Fig. 2. Clearly, such a complex system cannot be treated fully theoretically, but the important features of a SIP should be described by an electrostatic solvation model[30] where the counterion is represented by a point charge simulated by an empty 1s orbital with infinitely large core energy (pseudoproton). The electric field is transmitted through the two-centre electron repulsion integral γ_{sP} between atom s of the perimeter and pseudoproton P. A pseudoproton modifies the diagonal part of the π-SCF operator by the additional term $-\Sigma_s \gamma_{sP}$ where a posi-tive unit charge is assumed in order to simulate a single positively charged counterion.

A simple approach for the description of a CIP is obtained if counterion (we consider here alkali atoms, however, a generalization is straightforward) and annulene are treated as a supermolecule. Alkali atoms possess an empty ns orbital which can interact with the π-system of the annulene. It is adequate also to take the unoccupied alkali np orbitals into consideration since they are only slightly higher in energy. The ion pair is surrounded by the solvent, and so we can assume that the counterion interacts covalently with one or more solvent molecules. For example, an X-ray study[31] of conjugated dianions with Li^+ counterions in N,N,N',N'-tetramethylethylenediamine (TMEDA) revealed that Li and the two nitrogen atoms of TMEDA form an angle of about 120°. Thus, we can consider Li as sp^2-hybridized where two hybrid orbitals are used for the binding of the solvent molecules. The remaining hybrid orbital which points toward the annulene interacts with the π-system. Also the non-hybridized np orbital, which lies in a plane parallel to the conjugated system, can interact, however, less effectively. It is conceivable that the counterion exhibits a higher coordination number with respect to the solvent molecules. Then we can consider the counterion as effectively sp^3-hybridized so that only one hybrid orbital can interact with the π-system. In that case we can simulate this hybrid orbital simply by a ns orbital of the counterion and we arrive at the CIP(s) model in contrast to the CIP(sp) model, where the full valence shell of the alkali atom is utilized. Also in case of the cyclooctatetraene dianion the X-ray structure[32] reveals that the K^+ counterions are complexed by the solvent diglyme so that the interaction between the counterion and the π-system can be simulated by the CIP(s) model. Further computational details for SIP's and CIP's are given in Appendix I.

We want to emphasize that our SIP and CIP models represent only simplified treatments of the ion pair structure of charged annulenes. Nevertheless, our results demonstrate that these models are sufficient in order to understand RC effects and hence proton chemical shifts in such systems. Furthermore, at present it appears prohibitive to design a practicable theoretical approach where all ion pair features are fully taken into account.

3) ^{1}H Chemical Shifts. ^{1}H chemical shifts δ (see Tables 1 and 2) are calculated utilizing the procedure of Ref.[33] according to the formula $\delta = \delta^{RC} + \delta^{LA} + \delta^{q} + \delta^{o}$. δ^{RC} is the RC contribution of the π-system, δ^{LA} the local anisotropic (LA) contribution of π- and σ-system. δ^{o} defines the zero of the π-scale. δ^{q} is the shift arising from net charges q on the carbon atom which is bonded to the proton in question. It has been shown[34,35] that $\delta^{q} \approx a \cdot q$ with $a \approx 10.6$ ppm/electron.

Table 1. Calculated (δ^{RC}, δ^{LA}, δ) and experimental (δ_{exp}) ^{1}H chemical shifts (ppm) of the bridged annulenes 1a, 1b, 2a and 2b and the related compounds 3 and 4.

Compound	proton[a]	δ^{RC}	δ^{LA}	δ	δ_{exp}		ref
1a/1b	6	1.69	1.36	8.15	8.11[b]		53
	5	2.00	1.36	8.46	8.59		
	3	2.10	1.37	8.57	8.67		
	α	-4.10		-3.13[c]	-4.25	-4.03[d]	
	β	-1.46		-0.49		-1.67	
		-1.01		-0.04		-0.65	
3	5	0.	0.48	5.58	5.70		53
	3	0.	1.16	6.26	5.96		
	α	0.			0.97		
2a/2b	6	1.97	1.39	8.46	8.04[e]		5,22
	5	2.28	1.41	8.79	8.77		
	3	1.83	1.30	8.23	8.74		
	α	-4.08		-2.79[c]	-4.53	-4.70[f]	
	β	-1.84		-0.55		-1.8	
		-1.00		0.29		-0.71	
	δ	-0.59		0.70		0.1	
4	5	0.	0.48	5.58	5.47		g
	3	0.	1.16	6.26	6.12		
	α	0.			1.29		

[a] Proton numbering of ring protons see Figure 1. α-δ denote the protons of the alkyl substituent R (1a, 1b, 3) and R' (2a, 2b, 4). [b] Values of 1a. [c] Obtained as a sum of δ^{RC} and the δ_{exp} values for H-α of 3 and 4. [d] Values of 1b. [e] Values of 2a. [f] Values of 2b. [g] This work.

Although the perimeters of 1, 2 and their dianions are nearly planar, δ^{RC} has to be calculated as the mean value of its x-, y-, and z-component. The formulae for calculating δ^{LA} given in Ref.[33] are only valid for planar conjugated systems. Therefore, we calculated δ^{LA} for planar perimeters, but utilizing the correct bond lengths. Nevertheless, we expect that the obtained LA terms are of the correct order of magnitude.

RC contributions are connected with cyclic conjugation. If our models are applied to a CIP, where the counterion is explicitely taken into account, this has to be included in the calculation of δ^{RC} since the counterion introduces new conjugation cycles. However, this aspect does not present any problems due to the use of the London approximation[10] in the evaluation of δ^{RC}.

Results and Discussion

1) Structure Proof and ^{1}H NMR Spectra of the Annulene Dianions. The structure proof of the dianion $\underline{2a}^{2-}/2K^+$ follows from chemical and spectroscopic evidence. Upon protonation $\underline{2a}^{2-}/2K^+$ transforms into the dihydro derivative $\underline{4}$ (see below). The intact molecular framework of the dianion can also be deduced from the number of ^{1}H resonances, which prove a C_{2h} symmetry of the π-system within the time scale of the NMR experiment, and from the pronounced paratropic effect, which can only originate from a π-perimeter.

Upon going from the neutral annulenes, $\underline{2a}$ and $\underline{2b}$, to the corresponding dianions the bridge (ring) protons suffer from an extreme deshielding (shielding) (see Table 1). The assignment of the signals of the ring protons follows readily from the splitting patterns. The assignment of the bridge protons within $\underline{2b}$ and $\underline{2b}^{2-}/2K^+$ is based upon the splitting patterns and the assumption that the anisotropic RC effects decrease with increasing distance from the π-system.

It can be inferred from the sequence of ^{1}H NMR chemical shifts in e.g. $\underline{2a}^{2-}/2K^+$ that the π-centers C-6 and C-13 accept the highest π-charge. This finding is in agreement with the mode of spin density distribution in the corresponding radical anion and can readily be explained by the nodal properties of the HOMO of both $\underline{2a}^{2-}$ and $\underline{2a}^{-}$ (see below). Not surprisingly, therefore, the protonation of $\underline{2a}^{2-}/2K^+$ in a regioselective manner gives rise to the dihydro derivative $\underline{4}$. Obviously, the kinetically controlled attack of the electrophile proceeds at the position of the highest π-charge.

The most striking outcome from the experimental shift data given in Tables 1 and 2 is the similarity of the neutral annulenes $\underline{1a}$ and $\underline{2a}$, on the one hand, and the difference of the dianions, on the other hand.

2) Geometric and Electronic Structures. The X-ray analysis of a derivative of $\underline{1a}$[7] and of $\underline{2a}$[5] revealed that these compounds possess almost planar perimeters without significant bond lengths variation and so $\underline{1a}$ and $\underline{2a}$ are best represented by formulae $\underline{1'}$ and $\underline{2'}$ (cf. Fig. 1). These structures are reproduced by our π-SCF force-field calculations which provide additional evidence that the geometries of $\underline{1a}$ and $\underline{2a}$ are not significantly influenced by the alkyl substituents R and R'. Also for the corresponding dianions $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ essentially planar perimeters are calculated, however, parts of them are characterized by significant bond lengths alternation as is indicated by formulae $\underline{1''}$ and $\underline{2''}$ in Fig. 1. The latter structures exhibit reduced symmetry with respect to $\underline{1'}$ and $\underline{2'}$. Such a symmetry reduction was encountered also with other (4m')π(4m+2)C-annulenes[20] and a (4m')π(4m+3)C-annulene.[36]

Within the framework of Hückel theory with tight-binding approximation the HOMO and LUMO of a dianion of a [4m+2]annulene are degenerate even in the presence of bond lengths alternation in the sense of Ref. 10. This prevents the application of a simple orbital description of such compounds. In a π-SCF approach the explicit shape of the perimeter is taken into account. Therefore, HOMO and LUMO are no longer degenerate in $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ with perimeter structures $\underline{1'}$ and $\underline{2'}$. However, the resulting wave functions are not an adequate representation of the electronic structure of these compounds since they do not constitute stable Hartree-Fock solutions.[26] On the contrary, the perimeter geometries $\underline{1''}$ and $\underline{2''}$ yield π-SCF wave functions for $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ which can be considered adequate descriptions of their electronic structures. Still the HOMO/LUMO gaps of $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ are only

2.8 eV, thus, being more than 2 eV smaller than those of the corresponding neutral bridged annulenes 1a and 2a.

The frontier orbitals Φ_8 (HOMO) and Φ_9 (LUMO) of 1^{2-} are displayed in Fig. 3. The corresponding orbitals of $2a^{2-}$ exhibit analogous nodal properties. Although the symmetry is reduced in $1a^{2-}$ and $2a^{2-}$ their HOMO and LUMO are uniquely related to the two degenerate Hückel orbitals Φ_8 and Φ_9 of a planar [14]perimeter. Thus it is in accordance with ESR studies[15] that the HOMO derives from the symmetric and the LUMO from the antisymmetric Hückel orbital.

The inductive and hyperconjugative effect of the alkyl bridges in 1a and 2a is not taken into account in our numerical procedure. Our results reveal that the HOMO/LUMO gap in the dianions $1a^{2-}$ and $2a^{2-}$ is not caused mainly by the influence of the bridges. The inductive effect can be simulated by increasing the core energy of bridgehead carbon atoms by 1.4 eV.[37] In the case of the neutral annulenes 1a and 2a this does not yield any significant change in the electronic structure. The HOMO/LUMO gap of $1a^{2-}$ and $2a^{2-}$ is reduced by only 0.3 eV and the charge distribution is affected only slightly. It was shown[15] that the hyperconjugative effect increases the HOMO/LUMO gap in contrast to the inductive one. Therefore, we expect only a small influence of the alkyl bridges on the properties of the studied annulenes. This is also corroborated by studies of the excited states of 1.[38]

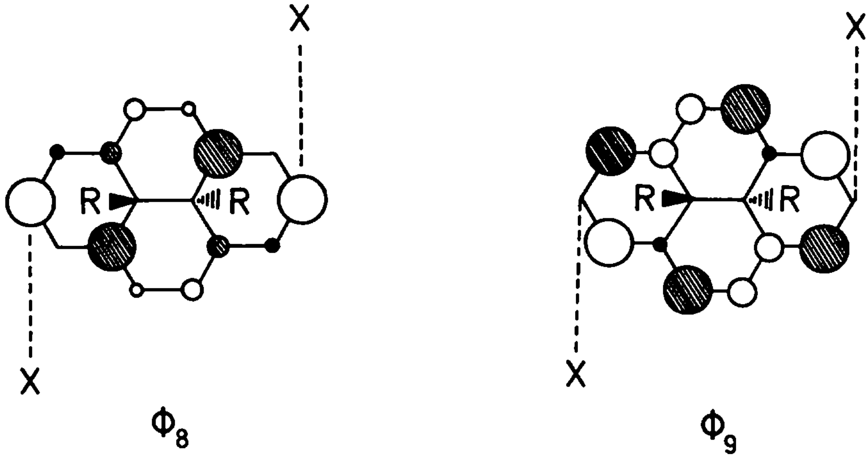

Figure 3. Frontier orbitals Φ_8 (HOMO) and Φ_9 (LUMO) of 1^{2-} and assumed position of counterions X.

3) ^{1}H Chemical Shifts. The calculated and experimental proton chemical shifts of the bridged annulenes 1 and 2 and the related acyclic conjugated compounds 3 and 4 are given in Table 1. 1a and 2a are diatropic due to the diamagnetic RC effect, i.e. $\delta^{RC}>0$ for the outer protons at the 14-ring and $\delta^{RC}<0$ for the internal protons located at the alkyl bridges. The deshielding caused by δ^{RC} for the ring protons is enhanced by the LA term. We determine $\delta^{o}=5.1$ as the mean of $(\delta_{exp}-\delta^{RC}-\delta^{LA})$ utilizing the experimental shifts of 1a and 3. This value is approximately the average of the δ^{o} values given in Ref. 33 for benzenoid and olefinic protons and it is used for all calculated shifts of ring protons in this paper.

The sequence of proton signals in 1a and 3 is correctly reproduced by our calculation. The mean numerical error is only 0.1 ppm and does not exceed 0.3 ppm although the alkyl bridges were not taken into account in the computation of RC and LA terms. Obviously, inductive and hyperconjugative effects of the bridges are either negligible or cancel out with respect to chemical shifts. The inductive effect alone yields a small decrease of all shifts of 1a by about 0.1 ppm.

In contrast to 1a our calculations do not reproduce the correct order of protons in 2a with respect to the proton chemical shifts. Furthermore, the mean error of calculated shifts for 2a and 4 is 0.2 ppm and hence larger than for 1a and 3. This cannot be ascribed to the neglect of the alkyl bridges in the calculation of shifts since MO considerations have shown[15] that inductive and hyperconjugative effects are not significantly different in 1a and 2a. The inductive effect alone leads to rather small changes of the calculated shifts analogous to 1a. Possibly the larger errors in calculated shifts for 2a with respect to 1a are due to the fact that the LA terms have been calculated by assuming[33] sp^2-hybrids in the σ-core and hence 120° bond angles. This is a sufficient approximation for 1 as in the case of benzenoid hydrocarbons but not for 2 where the 5- and 7-rings in the carbon skeleton enforce bond angles considerably different from 120°.

A large shielding is observed for the methyl protons H-α of 1a and 2a which corresponds to strongly negative δ^{RC} values. With increasing distance from the [14]perimeter the shielding of the protons decreases, cf. H-α of 1b and 2b, which derives from the numerical decrease of the RC terms. We can interpret the experimental shifts for H-α of 3 and 4 as an approximate value of $(\delta^{O}+\delta^{LA})$ for H-α to H-δ of 1a, 1b, 2a, and 2b and so we obtain calculated shifts δ which are about 1 ppm larger than the observed ones. This is due to an underestimation of the RC contribution to the chemical shift of protons which are not located in the plane of the π-network.[39]

The small deviations of the perimeters of 1 and 2 from planarity do not significantly influence the RC terms. A geometry 1' or 2' with a planar perimeter leads to nearly identical calculated shifts. On the other hand, the absence of significant bond lengths alternation in 1 or 2 is important for the magnitude of δ^{RC} since a geometrical model with alternating bond lengths ($r_{C=C}/r_{C-C}$=134/146 pm) yields RC contributions which are smaller by about 1 ppm. The same applies for the resulting shifts δ because the LA terms are not significantly affected by bond lengths alternation.

The experimental shifts of the protons of the paratropic dianions $1a^{2-}$, $1b^{2-}$, $2a^{2-}$, and $2b^{2-}$ are given in Table 2 together with corresponding calculated values. Our quantum chemical approach qualitatively reproduces the observed shielding of the outer protons and the deshielding of the internal protons at the alkyl bridges. However, the calculated shifts turn out to be numerically too large which is obviously due to exaggerated RC terms. The effect of the paramagnetic RC on the ring protons is slightly reduced by the LA contribu-tions. On the other hand, the negative charge leads to shielding contributions δ^{q} of varying size according to the non-uniform charge distribution.

The magnitude of the RC terms depends sensitively on details of the electronic structure.[20,40] Nevertheless it is unlikely that the large differences between calculated and observed proton chemical shifts derive from inadequacies in the structures 1'' and 2'' which have been determined by the π-SCF force-field procedure for $1a^{2-}$ and $2a^{2-}$ since 1'' and 2'' already exhibit important bond lengths alternation. The same applies to the neglect of the alkyl bridges in the computation of shifts since the HOMO/LUMO gap which is important for the magnitude of the paramagnetic RC effect,[14] is not changed significantly by the inductive and hyperconjugative influence of the bridges.

Table 2. Experimental ^1H chemical shifts δ_{exp} of $1a^{2-}/2K^+$, $1b^{2-}/2K^+$, $2a^{2-}/2K^+$, and $2b^{2-}/2K^+$ and corresponding calculated values δ^{RC}, δ^{LA}, δ^q, δ for the FI's and the SIP and CIP models (all values in ppm).

		FA				SIP	CIP(s)	CIP(sp)			
compound	proton[a]	δ^{RC}	δ^{LA}	δ^q	δ	δ	δ	δ	δ_{exp}		ref
$1a^{2-}/1b^{2-}$	6	-18.8	0.75	-3.03	-16.0	-7.63	-3.46	-0.61	-3.19[b]		6
	5	-22.4	1.22	-0.59	-16.7	-6.21	-1.28	1.12			
	3	-23.5	1.15	-0.70	-18.0	-6.57	-4.41	-0.06	to		
	2	-23.3	0.93	-1.64	-18.9	-7.32	-4.96	-0.60			
	14	-22.4	1.14	-1.34	-17.5	-6.49	-3.22	0.89	-3.96		
	α	45.7			46.7[c]	25.0[c]	20.6[c]	12.1[c]	21.0	21.24[d]	
	β	16.3			17.3					12.59	
	γ	11.3			12.3					5.51	
$2a^{2-}/2b^{2-}$	6	-31.4	0.76	-3.11	-28.7	-9.90	-6.36	-1.18	-0.85[e]	-0.79[f]	g
	5	-36.6	1.20	-0.71	-31.0	-8.45	-5.39	0.45	0.17	0.20-0.26	
	3	-29.0	0.87	-1.50	-24.5	-5.80	-4.88	0.30	0.05	0.15/	
	2	-29.2	1.02	-0.86	-23.9	-6.12	-4.88	0.08	0.05	0.16	
	14	-36.7	1.26	-0.53	-30.9	-8.62	-4.71	0.13	0.17	0.20-0.26	
	α	65.3			66.6[c]	26.4[c]	24.1[c]	13.0[c]	11.96	13.68	
	β	32.1			33.4					7.33	
	γ	16.0			17.3					4.39	
	δ	9.41			10.7					2.38	

[a] See footnote a in Table 1. [b] Values of $1a^{2-}/2K^+$. [c] See footnote c in Table 1. [d] Values of $1b^{2-}/2K^+$. [e] Values of $2a^{2-}/2K^+$. [f] Values of $2b^{2-}/2K^+$. [g] This work and Ref. 23.

Thus far the chemical shifts have been calculated by assuming that annulene dianion and counterions form free ions (FI's) without any specific interaction between the ions. However, FI's are not present appreciably in solution of negatively charged conjugated hydrocarbons,[18] rather one encounters equilibria between SIP's and CIP's which depend on the choice of temperature, solvent, and counterion. Furthermore, there is experimental evidence[19,41] that the ion pairing has a pronounced effect on the proton shifts in paratropic annulene dianions. One could argue that the temperature dependence of NMR signals of annulene dianions with a given choice of solvent and counterion does not result from an equilibrium between different ion pairs but from an equilibrium between different aggregates of the ionic hydrocarbon.[42] A significant interaction between the π-systems of the annulene dianions is achieved only in a sandwich arrangement. However, the alkyl bridges prevent a close contact of the hydrocarbons. We studied sandwich dimers of $\underline{1}^{2-}$ and $\underline{2}^{2-}$ with a transannular distance of 350 ppm and obtained a numerical reduction of δ^{RC} by about 0.5 ppm only. Thus the pairing of the annulene dianion cannot rationalize the large differences between calculated and observed proton shifts in these paratropic species.

4) Counterion Effects. The annulene dianions $\underline{1a}^{2-}$, $\underline{1b}^{2-}$, $\underline{2a}^{2-}$, $\underline{2b}^{2-}$, and $\underline{2c}^{2-}$ have been obtained only with K^+ as counterion which is known[18] to form preferentially CIP's. The mutual orientation of annulene dianion and counterions is unknown. Even an X-ray analysis would not necessarily lead to a definitive conclusion on the ion pairing in solution, since a definite ion pair arrangement will occur in the solid state but not in solution. This is due to the expected rather flat energy surface for a movement of the counterion above the π-system. The alkyl bridges prevent a half-sandwich structure as was found by X-ray analysis[32] for the cyclooctatetraene dianion/$2K^+$ system and by ab-initio calculations[43] for the cyclopentadienyl anion/Li^+ salt. A close contact between counterions and bridges is avoided in the ion pair arrangements $\underline{6}$ and $\underline{7}$ for $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ which should be energetically favourable since the counterions are situated over the C-atoms 6 and 13 with the largest negative net charges, cf. δ^q values for FI's of $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ in Table 2. We fixed the distance between counterion K^+ and the mean molecular plane in a CIP at 237.5 ppm which were formed in other related charged annulenes.[32] The same distance was used in the SIP. Ion pair structures where the counterion is bonded directly to the perimeter, thus, interrupting the π-conjugation can be excluded since they could not rationalize the large shifts which are observed in the NMR spectra of the dianions.

The calculated proton shifts for the annulene dianions assuming an ion pair structure $\underline{6}$ and $\underline{7}$ in a SIP or CIP are given in Table 2. The assumption of a SIP leads to a considerable numerical reduction of the calculated proton chemical shifts δ with respect to the FI's. This is mainly due to the numerical decrease of the RC terms δ^{RC} since the negative charge on the perimeter is preserved in a SIP although the polarizing effect of the counterion changes the net charges and hence the δ^q shielding contributions up to 0.6 ppm. Probably the effect of a SIP is overestimated here due to the chosen mean distance between counterion and perimeter.

A further numerical decrease of δ is encountered for the CIP's, especially for the sp-model where the full valence shell of the counterion can interact with the π-system of the annulene. Both the numerical reduction of δ^{RC} and of δ^q is responsible for the change of proton shifts in a CIP with respect to a FI or SIP. The covalent interaction between the ion pair induces a charge transfer from the annulene to the counterion, thus, reducing the charge on the perimeter to values between -1.0 and -1.5. Hence also the average δ^q of the CIP's is numerically smaller (δ^q=0.1 to -0.7 ppm) than that of the FI's or SIP's ($\delta^q \approx$ -1.4 ppm). It is interesting to note that in the CIP's even positive net charges are encountered, e.g. at C-atoms 2 of $1a^{2-}$ and $2a^{2-}$ and 5 of $2a^{2-}$, which yield a deshielding δ^q up to 1 ppm. There is indeed experimental evidence[41] for the occurence of positive net charges in the carbon skeleton of negatively charged annulenes. Despite the reduction of the effective negative charge on the annulene in a CIP the largest negative net charges are still found at C-atoms 6 and 13 as in the FI's and the SIP.

The calculated proton shifts for the 14-ring protons and the bridge protons are of the same order of magnitude as the experimental ones for the CIP (s) model for $1a^{2-}$ and the CIP (sp) model for $2a^{2-}$. However, one should not derive conclusions out of this on the kind of solvation of the counterion since the precise ion pairing is unknown. Furthermore, eventual changes of the bond lengths induced by the covalent interaction between the ions were not taken into account in our calculations. Therefore, we do not know if the observed equality of NMR signals for protons 5 and 14 or 2 and 3 of $2a^{2-}$ is due to (almost) equal shifts or to a dynamic process, e.g. a motion of the counterions or an equilibrium between structure 2'' and the related one which is obtained if 2'' is rotated by 180° with respect to the axis through C-atoms 6 and 13. Our calculated shifts for $1a^{2-}$ and $2a^{2-}$ demonstrate that both the electrostatic and the covalent interaction between annulene dianion and counterions greatly reduce the paramagnetic RC effect. It is obvious that only the consideration of the whole ion pair leads to a quantitative assessment of the observed proton shifts in paratropic annulene dianions.

The charge on the counterion in a SIP leads to a decrease $-\Sigma_P \gamma_{sP}$ of the diagonal elements of the π-SCF Fock matrix. γ_{sP} denotes the Coulomb repulsion integral with respect to the π-basis function χ_s and the pseudoproton, cf. Appendix I. This causes a change of energies ϵ_i of molecular orbitals $\Phi_i = \Sigma_s c_{is} \chi_s$ by $\delta\epsilon_i = -\Sigma_P \Sigma_s c_{is}^2 \gamma_{sP}$ within first-order perturbation theory. Consequently, the HOMO/LUMO gap which determines[14] crucially the magnitude of the paramagnetic RC term δ^{RC} changes according to $\delta(\epsilon_{LUMO} - \epsilon_{HOMO}) = \Sigma_P \Sigma_s (c_{LUMOs}^2 - c_{HOMOs}^2) \gamma_{sP}$. From the nodal properties of HOMO and LUMO for $1a^{2-}$ (they are displayed in Figure 3, those of $2a^{2-}$ are similar) and $2a^{2-}$ it follows immediately that $\delta(\epsilon_{LUMO} - \epsilon_{HOMO}) > 0$ for the assumed arrangements 6 and 7. Thus, the electrostatic interaction between annulene dianion and counterions increases the HOMO/LUMO gap, and, consequently, the paramagnetic RC effect is reduced in the SIP with respect to FI's.

In a CIP the virtual orbitals of the K^+ counterions mix covalently with the occupied π-orbitals of the annulene. This is necessarily connected with a transfer of negative charge to the counterion. The remaining positive charge on the counterions increases the HOMO/LUMO gap similar as in the SIP. The ion pair arrangement 6 and 7 and the nodal properties of HOMO and LUMO (cf. Figure 3) allow significant interaction of the virtual orbitals of the counterions only with the HOMO. Consequently, mainly the HOMO is stabilized but not the LUMO and so the HOMO/LUMO gap is further enhanced. Thus, the combined effect of electrostatic and covalent interactions causes the larger depression of the paramagnetic RC in a CIP with respect to a SIP.

Conclusion

The bridged [14]annulenes 2a and 2b could be transformed into their dianion salts. The NMR spectroscopic properties of the dianions $2a^{2-}/2K^+$ and $2b^{2-}/2K^+$ are strikingly different from those of the structurally related species $1a^{2-}/2K^+$ and $1b^{2-}/2K^+$. Therefore, we performed model calculations of the differently bridged compounds 1a, 2a, and their dianions $1a^{2-}$, $2a^{2-}$. A modified π-SCF force-field procedure reproduces the near-planarity and the absence of significant bond lengths alternation in the perimeter of the neutral 1a and 2a. For the corresponding dianions $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ we obtained structures $\underline{1''}$ and $\underline{2''}$ which are characterized by symmetry reductions and bond lengths alternation in subunits of the perimeters. By means of a π-electronic method we calculated ^1H chemical shifts by taking into account RC, LA, and net charge contributions. The agreement between calculated and experimental proton chemical shifts is good for $\underline{1a}$ and satisfactory for $\underline{2a}$. The somewhat larger errors in the calculated shifts of $\underline{2a}$ are most likely due to LA contributions which derive from the strained geometry of $\underline{2a}$.

The reduction of the annulenes $\underline{1a}$ and $\underline{2a}$ into their dianions $\underline{1a}^{2-}$ and $\underline{2a}^{2-}$ transforms diatropic into paratropic species. This is correctly reflected by the sign inversion of calculated RC terms. Simple RC models[10,13,20] do not allow conclusions on the RC effect in these dianions due to the HOMO/LUMO degeneracy within the Hückel picture, even if bond lengths alternation[10,13] is introduced. However, the calculated paramagnetic RC effect for FI's turns out to be exaggerated.

We, therefore, proposed a simple approach for the simulation of both a SIP and a CIP in order to study the effect of the counterions on proton chemical shifts. The interaction between the π-system of the annulene and the counterions in a SIP and even more so in a CIP is responsible for the great reduction of the paramagnetic RC effect if the counterions are placed in the proximity of the largest negative net charges on the carbon skeleton. The calculated proton chemical shifts for $\underline{1b}^{2-}$ and $\underline{2b}^{2-}$ exhibit the correct order of magnitude with respect to the observed values of the K^+ salts if a CIP is assumed. This is in agreement with experimental findings[18] that K^+ forms predominantly CIP's. Consequently, we present the first satisfactory quantum chemical assessment of proton chemical shifts in paratropic $(4m')\pi(4m+2)$C-annulenes. We want to emphasize that we cannot deduce from our calculations the actual mutual arrangements of the ions in the CIP. They would be elucidated only by energy and structure studies which are not feasible at present for such large systems.

In this paper we investigated monocyclic conjugated neutral and negatively charged hydrocarbons. Therefore, it seems interesting to study ion pairing effects on observables like proton chemical shifts also in the case of polycyclic conjugated systems.[44] A corresponding theoretical study is in progress.

Appendix I

In a CIP we compute the resonance integrals $\beta_{s\mu}$ between the basis functions χ_s of the π-systems and χ_μ (ns or np orbitals) of the counterion according to the Wolfsberg-Helmholtz formula[45] $\beta_{s\mu}=K\ S_{s\mu}(U_s+U_\mu)$ with the core energies U_s and U_μ. $S_{s\mu}$ denote the overlap integrals over Slater type orbitals.[46] The integral parameters of the π-SCF procedure[33] which is used for the calculation of chemical shifts are related to an orthonormal basis set.[47] The resonance integrals between the π-system and the counterion with respect to an orthonormal basis are given as $\beta_{s\mu}=(K - \frac{1}{2})S_{s\mu}(U_s+U_\mu) - \frac{1}{2}\Sigma_{t\neq s}S_{t\mu}\cdot\{\beta_{st}+S_{st}[K - \frac{1}{2})(U_s+U_\mu)+K(U_t-U_s)]\}$ if we utilize the formula given in Ref.[49] and neglect all overlap integrals S_{st} between π-basis functions at non-bonded atoms a and t. β_{st} are the resonance integrals in the π-systems. No matrix elements are used between counterions.

We use the following parameters for potassium as counterion (notation as in Ref.[33] $U_{K,4s}$=-3.77 eV, $U_{K,4P}$=-2.16 eV, $_{KK}$=3.65 (one-centre repulsion integral) and 2.18 eV (used in the Mataga-Nishimoto formula[29] for the two-centre integrals). The U values have been obtained from ionization potentials I[49] taking U=I+C where $C=U_{s,sp^2}-I_{C,2p}$ and the parameters are obtained from g values[50] by reducing with the factors f=0.986 (one-centre) and 0.589 (two-centre) which have been determined as $f=\gamma_{CC}/g_{CC}$. The parameter K was fixed at K=1.75.[51]

The two centre repulsion integrals in the pseudoproton model for a SIP are calculated by means of the Mataga-Nishimoto formula[29] with the one-centre repulsion integral γ_{pp}=20.408 eV[52] for the pseudoproton.

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References and Notes

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