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DOUBLY CHARGED IONS OF BRIDGED [4n]ANNULENES. AN EVALUATION OF DIATROPIC RING CURRENT EFFECTS.

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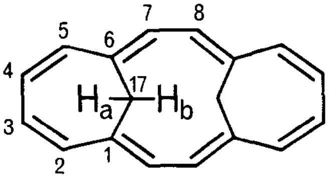
Summary: [4n]Annulenes are transformed into doubly charged ions (dianion, dication) and characterized NMR spectroscopically. The diatropic character of the ionic (4n+2)π-systems is studied as a function of the number of π-electrons.

The reduction and oxidation of annulenes have proven model experiments for bond theory and spectroscopy since they allow the ready interconversion of (4n)- and (4n+2)π-systems [1]. The successful transformation of the rigid [4n]annulene $\underline{1}$[2] into both its dianion, $\underline{1}^{2-}$, and dication, $\underline{1}^{2+}$, provides the unique opportunity of comparing different electronic configurations within one and the same molecular framework [3]. In a complementary approach one can compare the dianions $\underline{2}^{2-}$, $\underline{1}^{2-}$ and $\underline{5}^{2-}$ which constitute a series of structurally related (4n+2)π-systems with different ring sizes.

The dianion $\underline{1}^{2-}$ has been prepared by reacting degassed solutions of the 1,6:9,14-bismethano[16]-annulene $\underline{1}$ in tetrahydrofuran (THF) with highly active lithium in vacuo. The salt $\underline{1}^{2-}/2\ Li^+$ crystallizes from the solvent as violet needles, is stable at room temperature (THF-solution, exclusion of air) and can be reoxidized to $\underline{1}$ upon reaction with dry oxygen. The dication $\underline{1}^{2+}$ is obtained by oxidation of $\underline{1}$ with antimony pentafluoride in fluorosulfurylchloride at -80°C. The structural proof of the ions rests upon an analysis of their ^1H and ^{13}C NMR spectra (see Table and Figure) [4].



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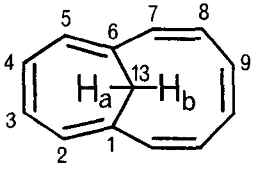

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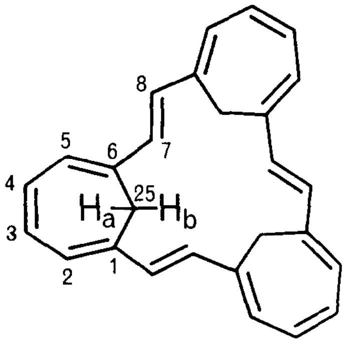

$\underline{5}$

The most remarkable spectroscopic result is the large upfield shift observed for the resonances of the bridge protons upon going from the neutral compound to the dianion ($\Delta\delta$ = -14.3) or the dication ($\Delta\delta$ = -10.9). The signals of the ring protons in $1^{2-}/2\ Li^+$ are markedly downfield from those in 1, despite the expected charge-induced shielding; similarly, the analogous signals of $1^{2+}/2\ SbCl_6^-$ are at much lower field than predicted from the charge effect alone. The deshielding (shielding) of the ring (bridge) protons in both the dianion and dication must be ascribed to a pronounced ring current effect: i.e. the paratropic neutral [4n]annulene 1 is transformed into strongly diatropic (4n+2)π-systems. The number of ^{13}C NMR resonances of 1^{2-} and 1^{2+} indicates that the ions preserve the original molecular framework, and must be regarded as π-bond delocalized species. The individual ^{13}C chemical shifts also reflect the local π-charge densities [1]. The proportionality constants $K_c = \Delta\delta_C/\Delta q_\pi$ which are calculated from the average charge-induced signal shifts of the ring carbons and from the mean π-charge density, are 186 ppm/e for

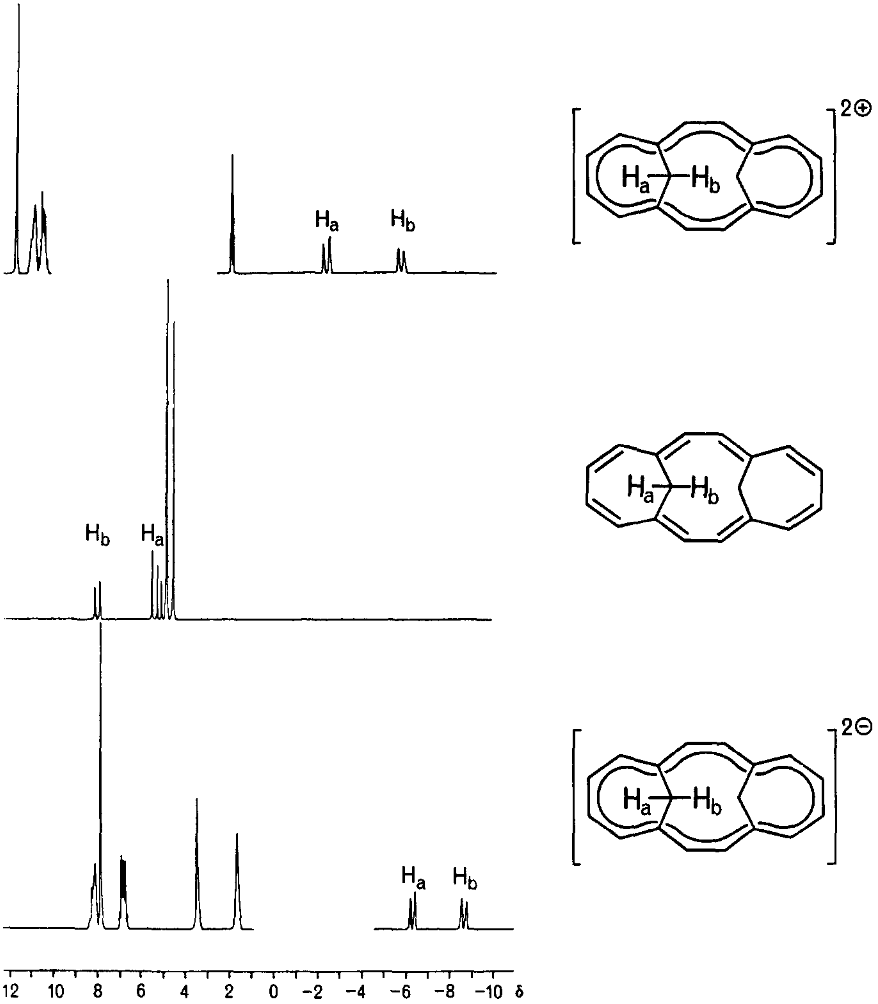

Figure ^{1}H NMR spectra (60 MHz) of the neutral annulene 1 as well as of its corresponding dianion ($1^{2-}/2\ Li^+$) and dication ($1^{2+}/2\ SbCl_6^-$) (see text).

$\underline{1}^{2-}$ and 175 ppm/e for $\underline{1}^{2+}$. These values are typical for diatropic ions [5]. Also indicative of the π-bonding in the ions are the vicinal H,H-coupling constants ($^3J_{HH}$) of the ring protons [4] which can be correlated with the corresponding π-bond orders. Thus, while $\underline{1}$ must be regarded as a π-bond localized species with a strong preference for the "diene-type" structure indicated in the formula, the ions are π-bond delocalized. While a syn-configuration of the bridges within $\underline{1}^{2-}$ and $\underline{1}^{2+}$ cannot be rigorously excluded, the analogy with the behaviour of the neutral compound is best explained by ion structures with a planar perimeter and anti-positioned methylene-groups. Moreover, the bending of a perimeter with syn-configurated bridges would significantly weaken the diatropism of the ions.

Table 1 ^1H (δ_H) and ^{13}C (δ_H) NMR chemical shifts and vicinal H,H-coupling constants (J [Hz]) of neutral, dianionic, and dicationic annulenes [a)]

	1	2	3	7	bridge H_b	 H_a	J (H-2, H-3)	J (H-3,H-4)
$\delta_H(\underline{1})$ [b)]		5.09	5.03	4.77	8.30	5.68	10.73	8.74
$\delta_H(\underline{1}^{2-})$ [c)]		8.24	6.93	7.92	-8.52	-6.20	8.94	8.71
$\delta_H(\underline{1}^{2+})$ [d)]		11.02	10.56	11.81	-5.71	-2.29	9.45	9.99
$\delta_H(\underline{2}^{2-})$		7.56	6.51	5.5 [e)]	-6.08	-5.52	8.3	8.5
$\delta_H(\underline{5}^{2-})$ [f)]		7.40 [g)] 8.99	7.12 [h)] 7.13	-3.91	-3.27	-2.42	8.6 [i)]	8.7
$\delta_C(\underline{1})$ [j)]	140.3	135.8	126.6	131.4	39.0			
$\delta_C(\underline{1}^{2-})$ [k)]	114.1	115.7	103.5	107.7	21.3			
$\delta_C(\underline{1}^{2+})$ [l)]	154.3	154.3	148.8	164.2	24.8			

a) Dianions as Li^+-salts, dications as SbF_6^--salts; b) 300 MHz, CD_2Cl_2, 20°C; c) 60 MHz, THF-d_8, 10°C; d) 60 MHz, SO_2ClF, 0°C; CD_3COCD_3, ext.; no correction for the differences of diamagnetic susceptibilities; e) H-7, H-8, H-9; f) H-8: $\delta = 6.99$; J(H-7, H-8) = 13.3; g) H-2, H-5; h) H-3, H-4; i) J(H-2, H-3) = J(H-4, H-5); j) 75 MHz, $CDCl_3$, 20°C; k) 75 MHz, THF-d_8, -20°C; l) 75 MHz, SO_2ClF, 0°C; CD_3COCD_3, ext.

In order to rationalize the ring current phenomena in $\underline{1}^{2-}$ and $\underline{1}^{2+}$ the experimental ^1H chemical shifts must be corrected for the influence of the π-charge upon the ring protons and for the electric field effect of the π-charge upon the bridge protons [1,6]. The resulting ring current induced deshielding (shielding) of ring protons (outer bridge protons) amounts to $\Delta\delta = +4.0$ ($\Delta\delta = -10.4$) in $\underline{1}^{2-}$ and to $\Delta\delta = +4.8$ ($\Delta\delta = -9.4$) in $\underline{1}^{2+}$. One concludes that the diamagnetic ring current effects in the 18π- and in the 14π-system are of similar magnitude. We point out that the pair $\underline{1}^{2-}/\underline{1}^{2+}$ is the first example of two geometrically identical (4n+2)π-systems with a difference of four π-electrons and that the above experimental result is in agreement with the theoretical prediction of Pople and Untch [7] as well as Haddon [8].

This outcome must be contrasted with the well-known fact that in a homologous series of neutral [4n+2]-annulenes the measurable ring current effect [9,10] decreases with ring size due to the increasing tendency toward π-bond fixation. That this trend is, indeed, much less pronounced for ionic (4n+2)π-systems has been demonstrated by us for a homologous series of [4n+2]annulene tetraanions[11] and can also be inferred from a comparison of $\underline{1}^{2-}/2\,\mathrm{Li}^{+}$ with the dianion of the structurally related [12]annulene $\underline{2}$[12]. The diatropic character is only slightly larger in the higher homologue. Including, finally, structurally related [14]- and [18]annulenes which are isoelectronic with $\underline{1}^{2+}$ and $\underline{1}^{2-}$, respectively, it follows that the diatropism of the ions is much more pronounced; this outcome is readily explained by the strong tendency toward π-bond delocalization in the charged species.

It was along this line of argument that we reduced the non-planar [24]annulene $\underline{5}$[13] into its dianion. The ^{1}H NMR data, in particular the number of (i) independent resonances, (ii) the high-field absorption of the bridge protons and (iii) the large shift-difference of the outer and inner protons (H-7, H-8) at the trans-double bond, leave no doubt that $\underline{5}^{2-}/2\,\mathrm{Li}^{+}$ adopts a structure with a C_3-axis, is not conformationally labile[14] and is strongly diatropic. The formation of a π-bond delocalized, diatropic 26π-dianion must be contrasted with both the olefinic character of the neutral [24]annulene $\underline{5}$ and the weak diatropism of neutral [26]annulenes[10] and is in full accord with the description of the lower-membered dianions $\underline{1}^{2-}$ and $\underline{2}^{2-}$.

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