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Dications of Tetrabenzofulvalenes. Paratropicity and σ Donation in Perpendicular Antiaromatic Systems

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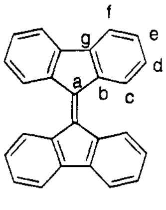
We are interested in the preparation of unusually unstable dications that might assume novel bonding arrangements including hypervalency in order to minimize their instability.[1] The oxidation to a dication of a sterically strained olefin might be aided by relief of that steric strain, making possible the formation of these particularly unstable species. For example, oxidation of 9-(9*H*-fluoren-9-ylidene)-9*H*-fluorene (tetrabenzo[5.5]fulvalene, **1**) could result in the formation of two antiaromatic cations linked by a single bond. To examine this possibility, and to put it into context, the oxidations of **1** and related fulvalenes **2** and **3** were examined.



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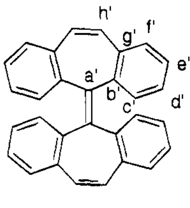

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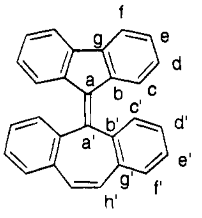

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Oxidation of fulvalenes **1**−**3** with SbF_5 in SO_2ClF gave dications, whose ^1H NMR spectral data are reported in Figure 1 and ^{13}C spectral data in Table 1. Assignments for the ^{13}C NMR spectrum of $\mathbf{1}^{2+}$ were made by a combination of heteronuclear correlation (HETCOR) spectroscopy, off-resonance decoupled ^{13}C NMR spectroscopy, and a consideration of the coupling and chemical shift in the ^1H NMR spectrum. Specifically, the protons with the largest chemical shifts, a doublet at 5.43 ppm and a triplet at 5.87 ppm, were assigned to the protons on carbons bearing the largest amount of positive charge, carbons c and e, respectively, based on resonance arguments. HETCOR spectroscopy allowed the assignment of carbons c through f and their neighbors, b and g. The carbon shifts show the expected pattern of charge alternation,[2,3] with the carbons with positive charge appearing further downfield than those not bearing charge, taking into account position on the ring and substitution. For example, carbons c and f are "partners", and c is further downfield. The furthest downfield carbon, at 188.6 ppm, was assigned to a, the carbenium carbon. Long-range HETCOR spectroscopy focusing on three-bond couplings validated the assignments based initially on the prediction of the effect of charge on proton chemical shifts.

The assignments for the ^{13}C NMR spectrum of $\mathbf{2}^{2+}$ could be made in an analogous manner with the following difference. The proton on h′ is the only singlet in the ^1H NMR spectrum, allowing unambiguous assignment of the chemical shift for h′. Long-range HETCOR spectroscopy allowed assignment of g′ and ultimately the connectivity of all carbons. This allowed the assignment then of the ^1H NMR spectrum, with confirmation of the accuracy of the proton assignments given by the splitting in the ^1H NMR spectrum.

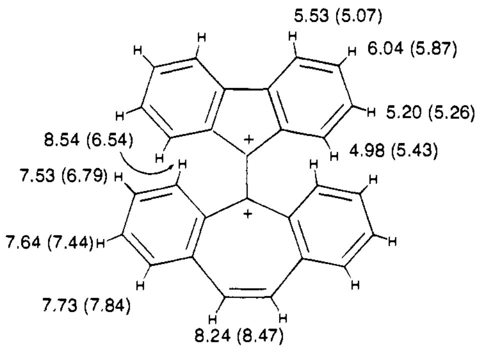

Figure 1. ^1H NMR chemical shifts for $\mathbf{3}^{2+}$ ($\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ in parentheses).

Table 1. Chemical Shifts for Dications $\mathbf{1}^{2+}-\mathbf{3}^{2+}$ [a,b]

	^{13}C chemical shifts							
	a[c]	b[c]	c[d]	d[d]	e[d]	f[d]	g[c]	h[d]
$\mathbf{1}^{2+}$	188.6	145.8	144.8	136.0	158.9	130.4	152.5	
$\mathbf{3}^{2+}$ (5-mem ring)	210.5	146.8	144.7	135.2	156.9	129.0	151.0	
$\mathbf{3}^{2+}$ (7-mem ring)	159.7	133.1	134.2	135.3	142.6	137.2	146.3	146.8
$\mathbf{2}^{2+}$	174.3	137.2	137.0	134.6	141.4	137.1	146.7	147.0

[a] All shifts reported at −50 °C in SbF_5/SO_2ClF, referenced to TMS and locked to d_6−acetone in a capillary tube. [b] Positions should be primed on the seven-membered rings and unprimed on the five-membered rings. [c] Singlet. [d] Doublet.

The assignment of the ^{13}C NMR spectrum of $\mathbf{3}^{3+}$ was again made using HETCOR spectroscopy in conjunction with the ^1H NMR spectrum. The ^1H chemical shifts fall into two groups. One is centered at 5.44 ppm and contains two doublets and two triplets, which is consistent with protons on the five-membered ring; the other is centered at 7.94 ppm and is consistent with peaks expected for protons on the seven-membered ring. There is an extremely good correlation between the chemical shift in the ^{13}C NMR spectrum for the carbons of $\mathbf{1}^{2+}$ and the five-membered ring of $\mathbf{3}^{2+}$, without including carbon a, and between the chemical shift in the ^{13}C NMR spectrum for the carbons of $\mathbf{2}^{2+}$ and the seven-membered ring of $\mathbf{3}^{2+}$, again without including carbon a′. The assignments for the ^1H NMR spectra of $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ follow from the assignments of the ^{13}C chemical shifts.

The ^{13}C chemical shifts for $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$ are all consistent with dicationic systems on the basis of the chemical shift difference between charged and neutral systems[4] (428 ppm for $\mathbf{1}^{2+}$,[5] 322 ppm for $\mathbf{2}^{2+}$,[6] and 378 ppm for $\mathbf{3}^{2+}$ [7]). The ^1H NMR spectra for $\mathbf{1}^{2+}$ and the five-membered ring of $\mathbf{3}^{2+}$ are consistent with ring systems with an appreciable paratropic ring current and are therefore considered antiaromatic.[8] The center of gravity for the proton shifts of $\mathbf{1}^{2+}$ is 5.41 ppm, substantially upfield from the center of gravity for the neutral precursor (7.75 ppm)[5] and also substantially upfield from the center of gravity for substituted fluorenyl cations (≈7.4 ppm).[9] The fluorenyl cation has recently been reinterpreted as not antiaromatic.[10] A similar

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[7] ^{13}C NMR shifts for neutral **3** (300 MHz, $CDCl_3$): δ 119.2, 125.1, 125.4, 126.4, 127.0, 127.4, 127.8, 129.6, 130.8, 133.5, 137.8, 137.9, 138.0, 140.6, 144.6.

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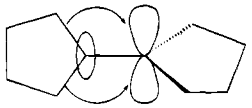
upfield shift is seen for $\mathbf{3}^{2+}$ with a center of gravity of 5.44 for the five-membered ring compared to a shift of 7.05 ppm for the center of gravity for the five-membered ring of the neutral precursor.[11] Total chemical shift per charge (K_C) was defined by Eliasson *et al.*,[12] and correlated with the degree of diatropicity/paratropicity in doubly charged ions. K_C for $\mathbf{1}^{2+}$ is 214 ppm; that for the five-membered ring of $\mathbf{3}^{2+}$ is 256 ppm. The most paratropic dication examined by Eliasson, the dication of pyrene, had $K_C = 235$ ppm.

The ^{1}H NMR spectra for $\mathbf{2}^{2+}$ and the seven-membered ring of $\mathbf{3}^{2+}$ are consistent with ring systems with an appreciable diatropic ring current. The center of gravity for $\mathbf{2}^{2+}$ is 7.42 ppm, in comparison with 6.96 ppm for the neutral system.[6] A similar downfield shift is seen for the seven-membered-ring system of $\mathbf{3}^{2+}$ with a center of gravity of 7.94 ppm, compared to 7.40 ppm for the neutral system.[11] The chemical shift difference for the proton on carbon h′ is even more pronounced, $\Delta\delta_{h}{}' = 1.37$ ppm for $\mathbf{2}^{2+}$ and 1.21 for $\mathbf{3}^{2+}$ ($\delta_{\text{cation}} - \delta_{\text{neutral}}$). Again, consideration of K_C gives confirmation to the prediction of diatropicity. K_C for $\mathbf{2}^{2+}$ is 161 ppm; that for the seven-membered ring of $\mathbf{3}^{2+}$ is 122 ppm. The most diatropic system examined by Eliasson, the dication of dibenzo[*a,d*]cyclooctatetraene, had $K_C = 154$ ppm. At the current time, we are focusing on the general magnitude of K_C, not the relative magnitude, because the correlation between diatropicity/paratropicity and K_C was made for systems which are planar (see below).

The proton chemical shifts are summarized in Figure 1, which shows the chemical shift for each proton of $\mathbf{3}^{2+}$ followed by the chemical shift for the corresponding proton of $\mathbf{1}^{2+}$ or of $\mathbf{2}^{2+}$ in parentheses. Analysis of the differences in chemical shifts for protons in the five-membered-ring systems is complicated because an increase in positive charge causes a downfield shift, while the presence of a paratropic ring current causes a shift to higher field. Proton f is least influenced by these effects and shows $\mathbf{1}^{2+}$ to be slightly more paratropic than $\mathbf{3}^{2+}$. This is also true for proton e. However, protons c and d in $\mathbf{1}^{2+}$ show a downfield shift in $\mathbf{1}^{2+}$ compared to $\mathbf{3}^{2+}$. The simplest explanation for this difference assumes that in both $\mathbf{1}^{2+}$ and $\mathbf{3}^{2+}$ the two ring systems once connected by a double bond are now perpendicular. Thus the "ortho" and "meta" protons of $\mathbf{1}^{2+}$ are in the diatropic shielding cone of the paratropic system perpendicular to them. Analogously, the "ortho" and "meta" protons of $\mathbf{3}^{2+}$ are in the paratropic shielding cone of the diatropic system of the seven-membered ring.

A similar analysis for the seven-membered-ring system shows $\mathbf{2}^{2+}$ to be slightly more diatropic than $\mathbf{3}^{2+}$ by consideration of the shifts of protons f′ and h′. The chemical shift for proton c′ on $\mathbf{3}^{2+}$ should be a combination of downfield shifts from positive charge through resonance, diatropicity of the aromatic ring system, and the presence of the diatropic shielding cone of the perpendicular paratropic five-membered ring. These combine to make the chemical shift of c′ dramatically downfield, the largest downfield shift of any proton attached to a benzene ring on the systems studied. Analogously, the shift for proton c′ on $\mathbf{2}^{2+}$ should be influenced by the paratropic cone of the perpendicular diatropic seven-membered ring and does indeed possess a chemical shift particularly far upfield for a carbon predicted to be positively charged by resonance arguments.

The postulation of perpendicular ring systems for $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$ also helps rationalize the great difference in the ^{13}C NMR shift for carbons a and a′. The fluorenyl[9] and dibenzotropylium[13] cations serve as reasonable models for the anticipated shift for a and a′ in systems without perpendicular π-systems. The chemical shift for the carbon corresponding to carbon a in substituted fluorenyl cations is $\approx$226 ppm; that for the analogous carbon in substituted dibenoztropylium cations is $\approx$185 ppm. The carbenium carbon in $\mathbf{1}^{2+}$ has a shift of 188.6 ppm; that of the five-membered ring in $\mathbf{3}^{2+}$ is 210.5 ppm. Both show an upfield shift, indicating a decrease in positive charge over the fluorenyl cation. One rationalization for this decrease consistent with the perpendicular geometry would be donation of electron density to carbon a through the electrons in the σ bonds. As is shown below, the empty p orbital of one system would lie in the plane of the other system, allowing the appropriate geometry for σ donation. This type of σ–π interaction has been described as *cross-hyperconjugation.*[14] Calculations of a number of dications suggest that the stabilization offered through an orthogonal geometry is substantial.[15,16] Analogously, the shift for carbon a′ of $\mathbf{2}^{2+}$ of 174.3 ppm and that of the seven-membered ring of $\mathbf{3}^{2+}$ of 159.7 ppm are further upfield than that of substituted dibenzotropylium cations. Again, a perpendicular geometry would allow donation of electron density from the σ bonds into the empty p orbital on a′. The upfield shift is greatest for $\mathbf{1}^{2+}$ and $\mathbf{3}^{2+}$, strongly suggesting more effective donation from five-membered-ring systems. Presumably, the fluorenyl system has less conformational flexibility than the dibenzotropylium system and is able to donate electron density more effectively. Alternatively, calculations on the triafulvalene dication containing two aromatic cationic systems linked by a single bond suggest that hyperconjugative stabilization in the orthogonal system is not as important as it is for systems not possessing aromatic rings.[17]



We are continuing to probe both the σ donation and the paratropicity of these systems by examining the effects of substituents on both the structure and electronic character of these and other systems.

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