early discussions[20] of this possibility, as well as more recent experimental evidence[21] for excited-state pathways in the mass spectrometer.

Acknowledgment. We thank Florence Fiquet-Fayard for a stimulating discussion.

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On the Properties of Fused 4*n* π-Electron Systems. The 8,9-Benzobicyclo[5.2.0]nonatetraenyl Anion

Sir:

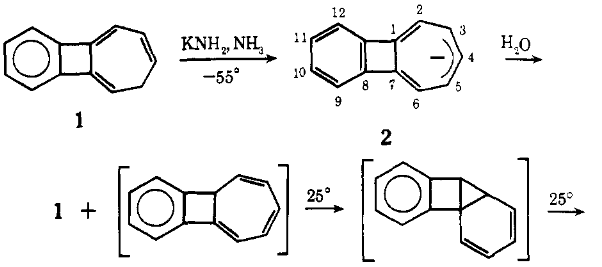
One of the more intriguing problems in connection with the concept of aromaticity concerns the electronic ground state character of $4n + 2$ π-electron systems which formally result from the fusion of two $4n$ π-electron systems. A variety of systems have been investigated but relatively little evidence bearing on the aforementioned question has been obtained for planar delocalized compounds.[1-10] We now report the preparation of the title anion, the first $4n + 2$ π-electron analogue of biphenylene, and present evidence which indicates that this compound displays properties characteristic of both $4n$ and $4n + 2$ π-electron systems.

Table I. Proton NMR Data and Charge Densities (q) Calculated by the HMO ω-Technique (ω = 1.4) for Anion **2** and Cation **5**

Position	δ (**2**)[a] (ppm)	q (**2**)[b]	δ (**5**)[c] (ppm)	q (**5**)[d]
2	6.49	−0.008	7.56	+0.087
3	4.20	−0.138	8.20	+0.130
4	5.79	−0.008	7.67	+0.090
9	7.93	−0.045	7.2	+0.043
10	7.34	−0.073	7.2	+0.034

[a] Potassium salt in liquid ammonia at −55° with trimethylamine as internal standard; $J_{2,3} = J_{5,6} = 7.60 \pm 0.07$, $J_{3,4} = J_{4,5} = 9.87 \pm 0.07$, $J_{2,4} = J_{4,6} = 0.98 \pm 0.04$, $J_{9,10} = J_{11,12} = 8.00 \pm 0.02$, $J_{10,11} = 7.06 \pm 0.02$, $J_{9,11} = J_{10,12} = 0.73 \pm 0.02$, $J_{9,12} = 1.51 \pm 0.02$ Hz. [b] $q_1 = -0.123$, $q_8 = -0.110$. [c] Reference 11; $J_{2,3} = 9.0$, $J_{3,4} = 9.9$ Hz. [d] $q_1 = +0.139$, $q_8 = +0.021$.

Treatment of **1**[11] with potassium amide in liquid ammonia at −55° cleanly afforded a brown solution of anion **2.** A ca. 5:1 mixture of fluorene (**4**) and **1** was obtained in 50% yield when **2** was quenched with water and the product mixture never warmed above room temperature prior to analysis by NMR spectroscopy. This result suggests that **2** is protonated primarily at C_1, the position of highest calculated charge density. (Structure **2** emphasizes bond orders rather than charge densities.) Thus the previously suggested rearrangement of **3** to **4**[11] occurs in less than 30 min at room temperature.



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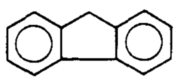

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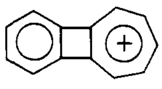

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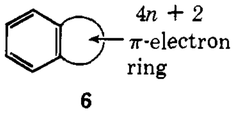
NMR data and self-consistent HMO charge densities are given in Table I. The calculated π-charge densities at C_3 and C_4 satisfactorially account for the difference in chemical shifts for H_3 and H_4[12] (which should experience similar ring current effects) in **2** and the corresponding cation **5**.[11]

Cyclic systems containing $4n$ or $4n + 2$ π-electrons have been characterized in several ways by NMR spectroscopy: (a) by the presence of a paramagnetic or diamagnetic ring current,[13,14] respectively, and (b) by the degree and direction of π-bond fixation in the ring itself or in an adjacent benzo group.[15,16] In the absence of major perturbations resulting from bond angle strain and/or steric interactions between peri hydrogens, π-bond fixation has been found to occur in the benzo ring of benzannelated $4n + 2$ and $4n$ π-electron annulenes as in **6**[16] and **7**,[16,17] respectively.



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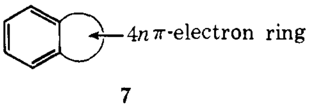

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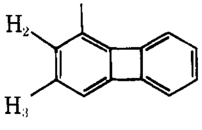
Analysis of the AA′XX′ pattern for the benzo protons of **2** yielded $J_{9,10} = 8.00$ and $J_{10,11} = 7.06$ Hz.[18] This indicates a bond fixation in the direction of **6** and contrasts with that in biphenylene (**8**) ($J_{1,2} = 6.89$, $J_{2,3} = 8.23$ Hz)[19] and several of its analogues.[20] Anion **2** is the first biphenylene analogue in which the four-membered ring exists in the dimethylenecyclobutene form rather than the tetramethylenecyclobutane form.[21] When one takes into account the strain of the four-membered ring,[22] the bond fixation in the benzo ring of **2** is comparable to that in naphthalene[23] and is clearly characteristic of a benzannelated $4n + 2$ π-electron system. In contrast, the degree of bond fixation (or distortion) in the seven-membered ring of **2** ($J_{2,3} = 7.60$ Hz) is more characteristic of a $4n$ π-electron ring than of a $4n + 2$ π-electron ring (such as in **5**, where $J_{2,3} = 9.0$ Hz[11]).



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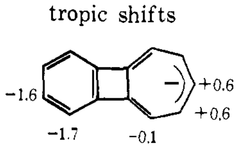

9

The influence of ring currents is most clearly illustrated by the downfield shift of H_9 and H_{10} in **2** compared to **5** despite the large increase in π-electron density in the former compound. The change in chemical shifts caused by net changes in ring currents which occur on adding two electrons to the lowest unoccupied molecular orbital (LUMO) in cation **5** to give anion **2** are termed "tropic shifts".[17] These result from the quenching of any paramagnetic ring currents associated with the LUMO in **5** and from the net diamagnetic or paramagnetic ring currents associated with the LUMO and the highest occupied molecular orbital in **2**. Tropic shifts (see **9**) are given by the difference between the charge-induced chemical shifts for **2** (calculated by correcting the chemical shifts in **5** for the change in π-electron density on going from **5** to **2**) and the observed chemical shifts for **2**. The large diatropic shifts (negative values) at H_9 and H_{10} can be explained by a quenching of a peripheral paramagnetic ring current in **5** coupled with a significant peripheral diamagnetic ring current in **2**. Interestingly, H_3 and H_4 suffer small paratropic shifts which can be attributed to the dominant influence of a paramagnetic ring current in the seven-membered ring of **2**. The significance of these shifts lies in their contrast with the large diatropic shift observed for H_{10} and indicate a local paramagnetic ring current of *over 2 ppm* in the seven-membered ring of **2**.

In summary, anion **2** behaves as *both* a peripheral $4n + 2$ π-electron system and as a local $4n$ π-electron system. This anion is therefore an example of that rare class of compounds which display properties characteristic of both aromatic and antiaromatic π-electron systems.[2a]

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(24) Gillette Research Foundation Fellow, 1972–1973.

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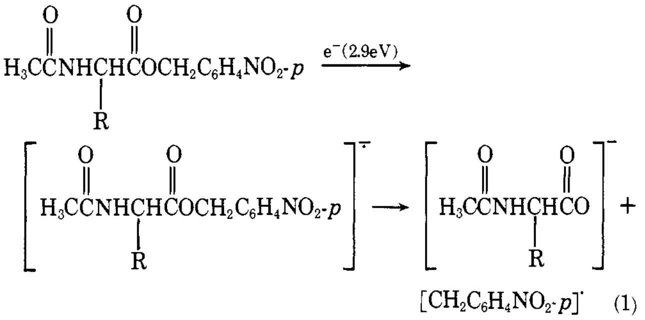
Gas Phase Carboxylate Anions from *N*-Acetyl-*p*-nitrobenzyl Amino Acid Esters

Sir:

Gas phase carboxylate anions of the *N*-acetyl derivatives of alanine, valine, and proline have been efficiently generated in a mass spectrometer. The process involves the dissociative resonance capture[1] of 2.9-eV electrons by the *p*-nitrobenzyl-*N*-acetyl amino acid derivative as illustrated in eq 1 below. The *p*-nitrobenzyl group is utilized to increase the electron affinity of the molecule and thereby enhance the efficiency of the initial electron capture which gives the anion radical intermediate postulated in eq 1. The subsequent cleavage of the carbon oxygen bond of the ester occurs almost exclusively to give the carboxylate anion and not the *p*-nitrobenzyl anion. This is shown in Table I by the relative intensities of the *m/e* 136 and the M − 136 peaks. At this electron voltage[2] (2.9 eV), the *m/e* 136 peak representing the *p*-nitrobenzyl anion was only 11% as large as the carboxylate anion (represented by the *m/e* 130 peak) in the alanine derivative and was not observed in the proline derivative. Thus, disregarding the *m/e* 46 peak (NO_2^-), the *N*-acetyl carboxylate anion represents over half the total ion current in each of the derivatives.



$$H_3C\overset{O}{\overset{\|}{C}}NH\underset{R}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}OCH_2C_6H_4NO_2\text{-}p \xrightarrow{e^-(2.9\,eV)}$$

$$\left[H_3C\overset{O}{\overset{\|}{C}}NH\underset{R}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}OCH_2C_6H_4NO_2\text{-}p\right]^{\cdot-} \longrightarrow \left[H_3C\overset{O}{\overset{\|}{C}}NH\underset{R}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}O\right]^- + [CH_2C_6H_4NO_2\text{-}p]^{\cdot} \quad (1)$$

The sensitivity of the instrumental technique and the simplicity of the experimental procedure are illustrated by the fact that only 1 μg of the derivatives was necessary to obtain the observed data in Table I. The esterification and acetylation were carried out in the same reaction vial using 5–10 μg of the free amino acids and no further purification was necessary.[3]

The specific electron energy (2.9 eV) used to generate the *N*-acetyl carboxylate anions was determined by obtaining