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FURTHER EVIDENCE ON THE NATURE OF THE MONOHOMOTROPYLIUM ION[1]

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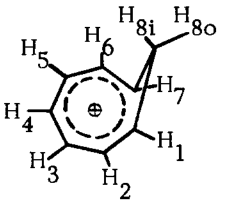
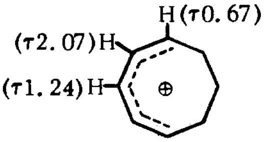
A considerable amount of attention has been recently focused on the subject of homoaromaticity,[4] especially on a multitude of homotropylium ions.[5] In view of this latter fact, we thought it would be interesting to further elucidate some of the details of the nmr spectrum of the unsubstituted monohomotropylium ion, $C_8H_9^+$ (I).[6] As will be seen, this has allowed a better understanding of the electronic structure of I.



I

Ia



II

When the 251 MHz[7] nmr spectrum of I in FSO_3H-SO_2ClF (1:1, v/v) was recorded at -60°, the five low field vinyl protons (H_2-H_6) appeared in three resolved, essentially first order, groups (Fig. 1). This enabled the complete assignment of all the protons of I; the chemical shifts and coupling constants are compiled in Table I.

From the coupling constant data for the vinyl protons of I, it is possible to conclude that the planar C_3-C_4-C_5 segment is slightly tilted with respect to the plane formed by C_1-C_2-H_2 (or C_7-C_6-H_6) such that the dihedral angle between H_3 (H_5) and H_2 (H_6) is different from zero. A similar statement can be made about the dihedral angle between H_2 (H_6) and H_1 (H_7). An examination of models suggests that the C_3-C_4-C_5 segment is tilted in the direction of C_8, whereby better overlap of the orbitals at C_1 and C_2 (C_7 and C_6) is apparently obtained.

The order of the chemical shifts of the vinyl protons allows some interesting inferences into the electronic structure of I. Previously,[6] the description of I as a homoaromatic species rested upon the large chemical shift difference between H_{8o} (deshielded)

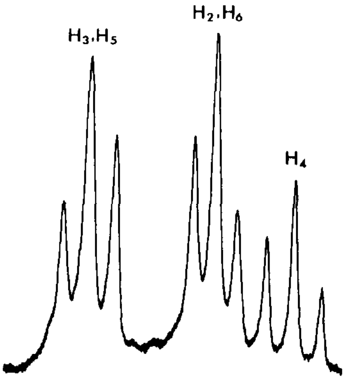


Figure 1. 251 MHz nmr spectrum of the vinyl region of I which resonates 1100-1250 Hz downfield of the internal lock signal (CH_2ClCH_2Cl).

Table I. Proton Nmr Data for the Monohomotropylium Ion (I).

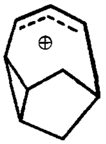
Proton	Chem. Shift[a]	Coupling Constants (Hz)
H_1, H_7[b]	3.52	$J_{1,2} \equiv J_{6,7} = 7.4 \pm 0.4$
H_2, H_6	1.61	$J_{2,3} \equiv J_{5,6} = 8.6 \pm 0.4$
H_3, H_5	1.43	$J_{3,4} \equiv J_{4,5} = 10.1 \pm 0.4$
H_4	1.73	
H_{8o}	4.87	$J_{8i,8o} = J_{1,8o} \equiv J_{7,8o} = 7.2 \pm 0.1$[c] $J_{^{13}C,H_{8o}} = 162.0 \pm 0.5$
H_{8i}	10.73	$J_{1,8i} \equiv J_{7,8i} = 9.8 \pm 0.3$ $J_{^{13}C,H_{8i}} = 155.5 \pm 0.5$

[a] Reported in τ, relative to internal CH_2ClCH_2Cl (τ6.28) which was referenced to CH_2Cl_2 (τ4.70). [b] Contrary to our previous report,[5c] we now find that H_1 and H_7 appear as a doublet of triplets. [c] Previously reported as 6.5 Hz.[5c]

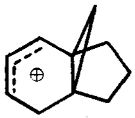
and H_{8i} (shielded), as well as on the contrast between I-Mo(CO)$_3$ and I-Fe(CO)$_3$. Deno,[8] however, has suggested that I be written as a pentadienyl cation with "normal" cyclopropyl conjugation (Ia). That the charge distribution over C_2-C_6 in I is not that expected for a pentadienyl cation can be seen by comparing the data for H_2-H_6 in I with that for the cyclooctadienyl cation, II.[9] However, it might be argued that the cyclopropane ring strangely affects the charge distribution, thereby invalidating the comparison with II. But examination of model systems, such as III[10] and IV,[11] containing allyl systems conjugated with a cyclopropane ring in a symmetrical or nearly symmetrical bisected fashion, reveals that by far the most charge is located at the carbon adjacent to the cyclopropyl moiety. In contrast, I has the most charge located at the position β to the cyclopropane ring (C_3, C_5).

Another way of examining the nature of the interaction between the cyclopropane ring and the other five carbons is to study the coupling constant data for the methylene group. For the nearly symmetrical bisected cyclopropylcarbinyl ion, IV, the $|J_{gem}^{cyclopropyl}| = 3.2$ Hz[11] is significantly smaller than the corresponding $|J_{8i,8o}| = 7.2$ Hz in I. Another indication of the qualitative difference between simple cyclopropylcarbinyl ions and I is obtained from the comparison of $J_{^{13}C,H}$'s. Thus $J_{^{13}C,H}(CH_2) = 180$ Hz in V[12] is much larger than the average of the $J_{^{13}C,H}(CH_2) = 159$ Hz in I.[13]

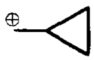
The apparently more open cyclopropane ring in I resembles that found in the "homoallylic" 2-phenylbicyclo[2.2.1]hepta-5-enyl cation, VI.[14] From this observation, together with the unusual charge distribution in I, we conclude that its electron delocalization involves a homoallylic participation by the cyclopropane ring. The essential difference between cyclopropylcarbinyl type ions such as III, IV and V and homoallylic ions such as I and VI is that the former utilize at least two bonds of the cyclopropyl group in a nearly symmetrical manner for electron delocalization, while the latter use only one of the cyclopropyl bonds to an appreciable extent. Indeed, other evidence[11] suggests that it is difficult to force a bisected ion over to the homoallylic mode of electron delocalization; in I, this difficulty is overcome by homoaromaticity.



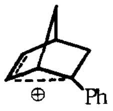
III



IV



V



VI

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1. Research supported in part by the National Science Foundation.
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