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THE STRUCTURE OF THE HOMOTROPENYLIUM CATION

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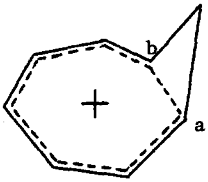
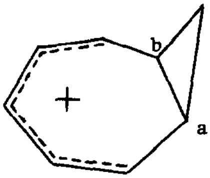
In previous publications[1] we have used a perturbational approach based on frontier orbitals to investigate the phenomenon of homoaromaticity. One of the predictions arising from this study[1] concerned the length of the homoconjugate linkage (a-b) in such molecules as the homotropenylium cation (1). For this case, it was found that the attachment of the pentadienyl cation to a cyclopropane ring (to give 1), leads to the removal of electron density from the a-b bond; hence a lengthening of the cyclopropane bond would be expected, leading to the Winstein[2] picture of an "open" cyclopropane unit (1a).



1a



1b

Recently, on the basis of *ab initio* calculations at the STO-3G level, Hehre[3] has formulated homotropenylium as the bicyclo[5.1.0]octadienyl cation (1b). It is difficult to rationalise the physical properties of homotropenylium[2,4-6] on the basis of structure 1b, and for this reason we have re-investigated the equilibrium geometry of 1 using the MINDO/3 method[7], with full geometry optimisation[8,9] .

In Table I we report the MINDO/3 geometries for 1 which were obtained at two levels of optimisation: planar (all atoms were constrained to the plane of the sevenmembered ring, with the exception of the hydrogen atoms of the homoconjugate linkage, and the bridging methylene group[3]), and nonplanar. In addition the C-H bonds were set equal to 1.1 A°; with these assumptions the planar case corresponds to the optimisation scheme used in the *ab initio* study[3]. In Table II we report the MINDO/3 energies[10] (with and without C-H bond length optimisation), together with the STO-3G energies[10,11] resulting from a single calculation on the structures derived from the MINDO/3 optimisation.

In the planar case, the *ab initio*[3] and MINDO/3 structures are in good agreement, with the exception of the geometry around the homoconjugate linkage; of particular interest is the

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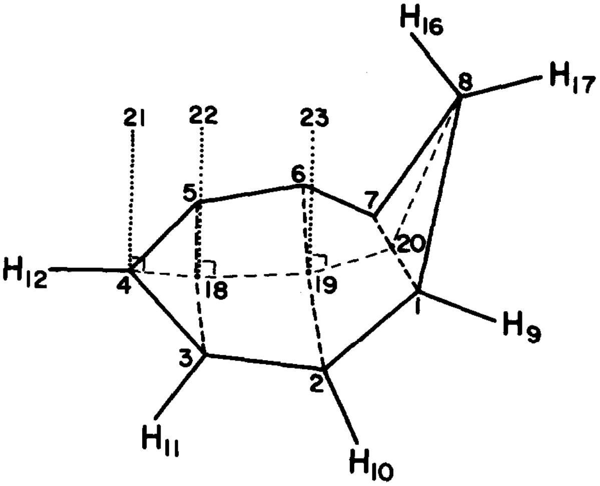
Table I. Calculated Geometries of the Homotropenylium Cation (1).



Bond Lengths (a-b)[a], Bond Angles (a-b-c)[b], Dihedral Angles (a-b-c-d; clockwise)[b]	STO-3G[c] Planar	MINDO/3 Planar	MINDO/3 Nonplanar
1-7	1.512	1.579	1.621
1-2	1.471	1.465	1.449
2-3	1.361	1.380	1.387
3-4	1.438	1.416	1.412
1-8	1.510	1.502	1.498
<2-1-7	127.6	124.4	122.8
<1-2-3	128.5	131.8	133.9
<2-3-4	126.7	128.4	128.5
<3-4-5	134.5	130.9	129.5
<1-8-7	60.1	63.4	65.5
<8-20-19	103.0	115.7	117.9
<18-19-23	90	90	74.5
<4-18-22	90	90	84.1
<16-8-20	121.9	126.3	126.4
<17-8-20	121.4	124.3	124.2
<2-1-9	112.8	109.6	111.2
<1-2-10	114.6	112.3	112.5
<2-3-11	115.8	116.4	116.0
<12-4-21	90	90	98.1
<9-1-2-19	201.5	218.1	221.7
<10-2-1-20	90	90	156.9
<11-3-2-19	90	90	171.1

[a] In angstroms. [b] In degrees. [c] Ref 3.

Table II. Calculated Energies for the MINDO/3 Geometries of the Homotropenylium Cation (1).

	MINDO/3		STO-3G
	ΔHf[a]	Relative Energies[a,b]	
Planar (C-H opt)	213.43	3.27	3.15
Planar (C-H=1.1A°)	213.81	3.28	1.67
Nonplanar (C-H opt)	210.16	0	-0.31
Nonplanar (C-H=1.1A°)	210.53	0	-1.81

[a] Kcals/mole. [b] STO-3G energies are relative to the value of -304.19104 hartrees obtained by Hehre[3].

homoconjugate bond length (0.07 A° longer with MINDO/3).

However, one of the most important findings to emerge from this study is the marked nonplanarity[12] of the sevenmembered ring in 1 (the deformation from planarity results in an energy gain of over 3 kcal/mole). Nonplanarity also leads to a lengthening of the homoconjugate bond length (by 0.04 A°) calculated with MINDO/3. This effect may be ascribed to the improved overlap between the pπ orbitals at the termini of the incipient pentadienyl cation and the highest occupied symmetric Walsh orbitals of cyclopropane[1,4c,13]. The convex deformation induced in the sevenmembered ring and the out-of-plane bending of the C-H bonds, evidently operate in concert to facilitate this interaction.

Clearly the homoconjugate bond length[14] found by the MINDO/3 method (1.621 A°, as against the calculated[7] (free) cyclopropane bond length of 1.504 A°), and not necessarily contradicted by the <u>ab initio</u> method, is better accommodated in terms of structure 1a as opposed to 1b. For this and other reasons[1,2,4-6] it would seem premature to abandon the Winstein[2] picture of homoaromaticity in the homotropenylium cation and other similarly constituted species.

References and Notes

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8. Using a gradient search procedure developed for MINDO/3 by M.J.S. Dewar, H.W. Kollmar, D.H. Lo, H. Metiu, P.J. Student and P.K. Weiner. The geometrical parameters are reliably calculated to high accuracy by this method (bond lengths to 0.001 A° and bond angles to 0.1 A°).
9. Although we allowed the relaxation of the bisecting plane through 1, no favourable distortion of this kind could be found and the ion apparently has C_s symmetry.
10. Calculations were carried out on the UNIVAC 1108 operated by the ANU Computer Center. Running times: 32 min for a full MINDO/3 optimisation of 1 in C_s symmetry (25 geometrical parameters); 35 min for a single STO-3G calculation.
11. GAUSSIAN 70, W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton and J.A. Pople, QCPE Program No. 236. The author is grateful to Dr L. Radom for supplying a copy of his version of this program.
12. Nonplanarity was originally suggested by Winstein and co-workers[4c] on the basis of the coupling constants found from the pmr spectrum of 1.
13. Professor R. Hoffmann, private communication, October, 1974. See also the discussion of this point by Hehre (ref 3).
14. Apparently, the only known homoaromatic bond length, is the value of 1.65 A° found for the complex of tricyclo[4.3.1.$0^{1,6}$]deca-2,4-diene with chromium tricarbonyl[15], by X-ray crystallographic analysis[16].
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