J. Am. Chem. Soc. **1982**, *104*, 2452-2456

Structure of the 2-Hydroxyhomotropylium Cation. Unequivocal Evidence for Homoaromatic Delocalization[1]

Ronald F. Childs,*[2a] Aravamuthan Varadarajan,[2a] Colin J. L. Lock,*[2a] Romolo Faggiani,[2a] Colin A. Fyfe,*[2b] and Roderick E. Wasylishen[2b]

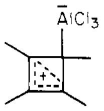
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada, and Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph University, Guelph, Ontario N1G 2W1, Canada. *Received September 16, 1981*

Abstract: The structure of 2-hydroxyhomotropylium hexachloroantimonate, **4**, has been determined. Monoclinic crystals of **4** were obtained on recrystallization from methylene chloride. The compound has a space group $A2/m$ with cell dimensions $a = 8.893$ (4) Å, $b = 11.093$ (6) Å, $c = 18.811$ (9) Å, and $\beta = 128.32$ (3)° and has four formula units in the unit cell. Intensities were measured by using Mo Kα radiation and a Syntex P2_1 diffractometer at −68 °C. The crystal structure was determined by standard methods and was refined to $R_1 = 0.0448$ and $R_2 = 0.0696$ on the basis of 2086 independent reflections. The cation is disordered, but the refinement is sufficiently good to say that the internal cyclopropane bond is longer than normal (1.626 (8) Å) and the other cyclopropane bonds shorter than normal (1.488 (7) Å). These bond distances are fully in accord with what would be expected for a homoaromatic cation. The ^{13}C NMR spectra of **4** were obtained in solution by conventional techniques and of the crystalline solid by using magic angle spinning methods. As the ^{13}C chemical shifts obtained by the two methods were very similar, it was concluded that the structure of **4** is the same in both solution and the crystalline state. The structure of **4** closely resembles that calculated by Haddon for the homotropylium cation by using MINDO/3.

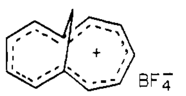
The concept of homoaromaticity was first advanced in a generalized form by Winstein over 20 years ago.[3] Since that time many different types of systems have been claimed to be homoaromatic, supposedly exhibiting cyclic delocalization and consequent enhanced stability.[4] More recently many of these claims have been questioned and it has been suggested on the basis of theoretical calculations that homoaromatic stabilization is only of importance with cationic systems.[5]

A worrying feature about the experimental evidence for homoaromaticity is its very paucity. The most generally used criterion is the ^{1}H NMR spectrum of the species being investigated and the need to involve an induced ring current in order to account for the various proton chemical shifts. At best such arguments are only as good as the model systems chosen for comparative purposes and are rendered somewhat tenuous in light of the continued discussion of the origin of ring currents.[6]

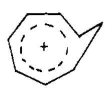
The clearest way of establishing whether a system is homoaromatic or not is to directly determine its structure.[7] While there might be some technical difficulties in sample handling, X-ray diffraction methods could provide these much needed data. Surprisingly very little work has been reported in this area. As far as we are aware the only relevant studies are those on the structures of the aluminum chloride complex of tetramethylcyclobutadiene **1**[9] and the bridged undecapentadienyl cation **2**.[10]



1



2



3

The four-membered ring of zwitterion **1** is nonplanar which is consistent with its formulation as a homocyclopropenium cation. It should be borne in mind, however, that the thermal chemistry of **1** is different from other cyclobutenylcations,[11] and consequently it is not clear whether the structure found for **1** is characteristic of this type of cation. In the case of **2**, the large transannular distance between C_1 and C_6 (2.30 Å) shows that homoaromatic delocalization is not important in this ion.

The homotropylium cation, **3**, was one of the earliest claimed examples of an homoaromatic system.[12] It has been examined by a somewhat larger range of techniques than the average homoaromatic system. These include UV spectra,[10d] diamagnetic susceptibility,[12e] ^{1}H and ^{13}C NMR spectroscopy,[12a-e] and a variety of theoretical methods.[13,14] Despite this no definitive structural work has been reported for this ion. In a broad ranging program on the structural aspects of carbenium ions, we have examined several homotropylium cations and report here the results of a single-crystal X-ray diffraction study of the 2-hydroxyhomotropylium cation which unambiguously defines its molecular structure and a high-resolution solid-state ^{13}C NMR study which relates this structure directly to that found in solution.

---

(1) R.E.W., C.A.F., C.J.L.L., and R.F.C. acknowledge NSERC for grants in aid of research and last three for a Co-op grant for structural investigations of carbonium ions. R.E.W. thanks the University of Winnipeg for sabbatical leave.

(2) (a) McMaster University. (b) Guelph University.

(3) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524.

(4) For reviews see: (a) Winstein, S. *Q. Rev., Chem. Soc.* **1969**, *23*, 141. (b) Warner, P. M. *Top. Nonbenzenoid Aromat. Chem.* **1976**, 2. Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.

(5) Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1372. Kaufmann, E.; Mayr, H.; Chandrasekhar, J.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1981**, *103*, 1375.

(6) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012. Haigh, C. W.; Mallion, R. B. *Org. Magn. Reson.* **1972**, *4*, 203. Agarawal, A.; Barnes, J. A.; Fletcher, J. L.; McGlinchey, M. J.; Sayer, B. G. *Can. J. Chem.* **1977**, *55*, 2575.

(7) Binsch has pointed out that there is an inherent difficulty associated with any criterion for aromaticity.[8] This stems from the difficulty of defining the concept itself. In general a parallelism seems to exist between a structural approach such as used here and one based on energetics. Ultimately, however, as Binsch reminds us, a structure tells nothing about other molecular properties unless it is interpreted.

(8) Binsch, G. *Naturwissenschaften* **1973**, *60*, 369.

(9) Krüger, C.; Roberts, P. J.; Tsay, Y.-H.; Koster, J. B. *J. Organomet. Chem.* **1974**, *78*, 69.

(10) Destro, R.; Simonetta, M. *Acta Crystallogr.* **1979**, *B35*, 1846.

(11) Koptyug, V. A.; Shleider, I. A.; Isaev, I. S. *J. Org. Chem.* **1971**, *7*, 864. Shleider, I. A.; Isaev, I. S.; Koptyug, V. A. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 1357. Hogeveen, H.; Jorritsma, H.; Wade, P. A. *Tetrahedron Lett.* **1974**, 3915. Hogeveen, H.; Driessen, P. B. J. *J. Am. Chem. Soc.* **1978**, *100*, 1193.

(12) (a) Rosenberg, J. L.; Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 2842. Keller, C. E.; Pettit, R. *Ibid.* **1966**, *88*, 604, 606. (b) Warner, P.; Harris, D. L.; Bradley, C. H.; Winstein, S. *Tetrahedron Lett.* **1970**, 4013. (c) Paquette, L. A.; Broadhurst, M. J.; Warner, P.; Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1973**, *95*, 3386. Olah, G. A.; Staral, J. S.; Liang, G. *Ibid.* **1974**, *96*, 6233. Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *Ibid.* 1975, *97*, 5489. Oth, J. F. M.; Smith, D. M.; Prange, U.; Schröder, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 327. (d) Winstein, S.; Kreiter, C. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1966**, *88*, 2047. (e) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *Nonbenzenoid Aromat.* **1971**, *2*, 167.

(13) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 8908; **1974**, *96*, 5207. Haddon, R. C. *Tetrahedron Lett.* **1975**, 863; *Tetrahedron Lett.* **1974**, 2797; *Aust. J. Chem.* **1977**, *30*, 1. Jorgensen, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 6784.

(14) Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.

0002-7863/82/1504-2452$01.25/0 © 1982 American Chemical Society

Table I. ^{13}C NMR Chemical Shifts of 4

solvent or phase	chem shift,[b] ppm							
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
D_2SO_4	52.5[a]	199.0	127.0	155.6	119.6	152.5	56.3[a]	28.4
CD_2Cl_2	51.2[a]	199.7	126.9	154.9	120.5	152.0	56.0[a]	28.2
solid	54.5	194.1	127.7	157.0	119.1	151.9	60.4	30.2

[a] Assignment may be reversed. [b] Chemical shifts are referred to CD_2Cl_2 (δ 53.6) in CD_2Cl_2; $CDCl_3$ (internal, δ 76.95) in D_2SO_4 and CH_3OH (external, δ 49.17) for the solid.

Experimental Section

Solution NMR spectra were obtained by using Bruker WP80 and WH 400 instruments. ^{13}C CPMAS spectra of the solid salt were obtained at 22.6 MHz on a Bruker CXP100 pulse spectrometer with a "home-built" probe and spinner assembly. Proton spin locking and decoupling fields of ~40 kHz were used. The spinner design was of the Andrew-Beams type utilizing Kel-F spinners of ~450 μL capacity driven by air and operated at spinning rates of approximately 3 kHz. The sample was sealed and protected in the spinner from air and moisture by Teflon tape wound on the threads of the spinner cap.

All solvents were distilled from P_2O_5 before use. The $SbCl_5$ was distilled in vacuo and the 2,3-homotropone purified by column chromatography on neutral alumina.

2-Hydroxyhomotropylium Hexachloroantimonate (4).[15] The synthesis was carried out in a two-limbed reaction vessel in which the limbs were separated by a sintered frit. The vessel was flame dried on a vacuum line before use. With use of a glove bag, $SbCl_5$ (1.12 g) and nitromethane (10 mL) were introduced into one limb of the reaction vessel. The solution was cooled to −11 °C and anhydrous HCl introduced to the vessel by way of a vacuum line until no more was taken up by the solution. The vessel was closed and removed from the vacuum line. With dry nitrogen passing through the vessel, a solution of 2,3-homotropone (0.448 g) in CH_3NO_2 (5 mL) was added slowly at −11 °C. The resulting yellow solution was stirred for 1.5 h before dry benzene (100 mL) was added slowly. The precipitated salt was filtered by using the sintered frit and dried under a vacuum. Further crops of the salt were obtained from the filtrate. The salt was recrystallized from CH_2Cl_2 at −20 °C: Raman (sealed sample −196 °C), 171, 180, 282, 290, 330, 361 cm^{-1}; ^{13}C NMR data are given in Table I.

ORD (optical rotatory dispersion) measurements in CH_2Cl_2 for the starting ketone **5**, bulk salt **4**, and a single-crystal of **4** showed no measurable rotations. In the latter case the solution concentration was ca. 1.5×10^{-3} M as a result of the size of the crystal used.

Collection of the X-ray Data. Because the compound was unstable in air, a crystal, which appeared suitable when examined under a stereomicroscope, was mounted and sealed in a Lindemann glass capillary tube. Precession photographs confirmed that the crystal was single and revealed it was monoclinic. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections for each compound in the range $14 < 2\theta < 20°$ recorded on a Syntex $P2_1$ diffractometer using Mo Kα radiation (λ = 0.710 96 Å at 22 °C). Crystal data and other numbers related to data collection are summarized in Table II. No density was measured because of the instability of the sample. Intensity data were also recorded on a Syntex $P2_1$ diffractometer using a coupled θ(crystal)-2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[16,17] Corrections were made for Lorentz-polarization effects but not for absorption. This will make a maximum error in F of 5.6%.

Solution of the Structure. The systematic absences were consistent with the space groups *A*2, *Am*, and *A*2/*m* (nonstandard settings of the corresponding C-centred cell). Some difficulty was experienced in the choice of space group. A three-dimensional Patterson synthesis revealed the antimony atoms and a difference synthesis revealed chlorine atoms which were consistent with the *A*2 or *A*2/*m* space group. Since $Z = 4$ and the cation was asymmetric, *A*2 was chosen and the structure was solved in this space group. Subsequently, because of certain obvious symmetry relationships (see below), final refinement was done in *A*2/*m*. A series of full-matrix, least-squares refinements, followed by three-dimensional electron density difference syntheses, revealed all the nonhydrogen atoms. At this stage the temperature factors of all atoms were made anisotropic. Tests were made at each stage to show the use of increased parameters was justified.[18] Further refinement using full-matrix least-squares minimizing $\sum w|F_o| - |F_c|)^2$ was terminated when the maximum shift/error was <0.01. Corrections for secondary extinction were made by using the method of Larson.[19] Throughout the refinement, the scattering curves were taken from ref 20, and anomalous dispersion corrections from ref 21 were applied to the curves for antimony and chorine.

Table II. Crystal Data

compd	$[C_8H_8OH^+][SbCl_6^-]$
fw	455.62
cryst size, mm	rough cylinder, $r = 0.15$, $l = 0.50$
systematic absences	h,k,l, $k + l = 2n + 1$
space group[a]	A2/m
unit-cell parameters[a]	
a, Å	8.893 (4)
b, Å	11.093 (6)
c, Å	18.811 (9)
β, deg	128.32 (3)
V, $Å^3$	1456 (1)
Z	4
ρ_{calcd}, g cm^{-3}	2.078
linear abs coeff, cm^{-1}	29.80
max 2θ, quadrant	45°, $h,k,\pm l$
std reflctns (esd, %)	3,0,−4 (1.1%), −3,−3,9 (0.5%)
temp, °C	−65 (1)
no. of independent reflctns	2086
no. with $I > 3\sigma(I)$	1690
$3\sigma(I) > I > 0$	246
$I < 0$, rejected	150
final R_1,[b] R_2[b]	0.0448, 0.0696
final shift/error (max), average	0.0040, 0.0006
g(secondary extinction	5.48×10^{-8}
final diff map	
highest peak (e/$Å^3$): location	1.2; 0.10, 0.05, 0.15
lowest valley (e/$Å^3$); location	−2.0; 0.40, 0.50, 0.0
weighting	$w = (\sigma^2 + (0.06F_o)^2)^{-1}$
error in an observn of unit weight	1.060

[a] The cell can be transformed to the standard *C*2/*m* cell by the matrix (001/0-10/100). [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$.

As noted above the initial structure solution was made in space group *A*2 and a fairly satisfactory refinement was obtained ($R_1 = 0.047$, $R_2 = 0.071$). Nevertheless, there were disturbing features. First, there were obvious symmetry relationships between certain pairs of chlorine atoms and of carbon atoms, and two chlorine atoms and C(8) and C(5) had values very close to 0.5. Second, the salt was obtained from a racemic mixture of the starting ketone, and there was no obvious reason why one enantiomer should have been isolated. Moreover there were some differences in bond distances which were expected to be nearly equivalent. Because reversal of the signs of all atoms' parameters made no difference to the refinement and because an ORD spectrum of a solution made from the crystal showed no optical activity, we concluded that the space group was *A*2/*m*, in which case the asymmetric cation had to be disordered since the restriction of $Z = 4$ meant that the cation was bisected by a mirror plane. The disorder arises primarily from the oxygen atoms which in *A*2/*m* must have half occupancy in a site either side of the mirror plane. Various methods of treating the disorder were attempted by using refinements with (a) two overlying cations, both of half-occupancy, related by the mirror plane, (b) C(8) and C(4) lying on the mirror plane but two separate sets of C(1), C(2), C(3), C(5), C(6), C(7), and O(2), of half-occupancy, related by the mirror plane, and (c) only O(2) of half-occupancy. In the end only c gave a satisfactory solution. Correlation effects did not allow a satisfactory solution of a or b. Nevertheless disorder does exist as shown in the temperature factors of C(3), C(4), and O(2), and this limits the accuracy of the structure. Efforts were made to locate the hydrogen atoms, and two or three peaks were found in the final difference map in chemically acceptable positions, but more peaks of equal magnitude were found in unacceptable positions and ultimately hydrogen atoms were not included in the refinement. The atom parameters for nonhydrogen atoms are listed in Table III.[22] De-

---

(15) Holmes, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 2531.

(16) Hughes, R. P.; Krishnamachari, J.; Lock, C. J. L.; Powell, J.; Turner, G. *Inorg. Chem.* **1977**, *16*, 314.

(17) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1978**, *17*, 2971.

(18) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

(19) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(20) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1964; Vol. IV, Table 2.2A, p 72 ff.

(21) Cromer, D. T., ref 18, Table 2.3.1, pp 149–150.

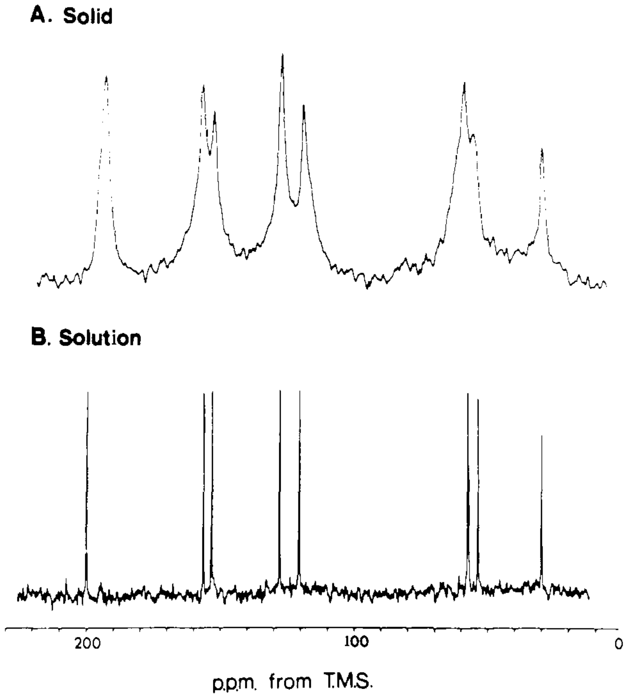
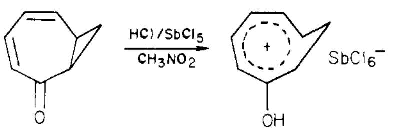


Figure 1. Solution and magic angle spinning solid-state ^{13}C NMR spectra of 4.

spite the disorder discussed above, the positions of the carbon atoms of the cyclopropane ring are well-defined.

Results

The 2-hydroxyhomotropylium cation 4 was prepared as its $SbCl_6^-$ salt in a similar manner to that described by Pettit by adding 2-homotropone, 5, to $HCl/SbCl_5^-$ in nitromethane.[15] The yellow salt was precipitated by the addition of benzene and recrystallized from dry CH_2Cl_2. The ^1H NMR spectrum of this salt dissolved in SO_2 was identical with that of 5 when protonated in H_2SO_4.



5 4

The ^{13}C NMR spectrum of 4 was obtained both in solution (CD_2Cl_2 and D_2SO_4) and as a crystalline solid by using a magic angle spinning technique. The solution spectrum was assigned by selective proton decoupling. The results are given in Table I.

Single crystals of 4 were obtained by a slow recrystallization from CH_2Cl_2 at −20 °C. The crystals were thermally stable at room temperature in the absence of moisture. The structure of 4 was determined by using X-ray diffraction as outlined in the Experimental Section.

Discussion

In terms of the usually used proton chemical shift criterion of homoaromaticity, 4 can be classified as being homoaromatic. The chemical shift difference between the 8-exo and 8-endo proton resonances is substantial, $\Delta\delta = 3.10$ ppm. This difference is somewhat smaller than that of the homotropylium cation itself ($\Delta\delta = 5.86$ ppm)[12b] but much greater than the comparable difference of the noncyclically delocalized iron complex 6 ($\Delta\delta = 0.0$ ppm).[23]

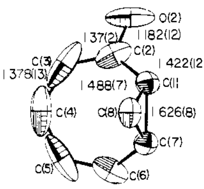


Figure 2. The cation $C_8H_8(OH)^+$ showing the atom numbering.

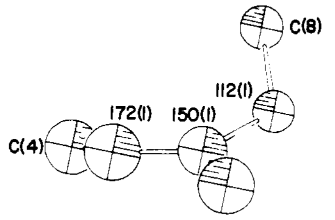
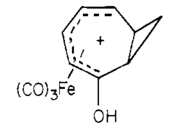


Figure 3. The cation $C_8H_8(OH)^+$ showing the dihedral angles between planes of atoms (temperature factors are isotropic for simplicity).



6

The narrow-line ^{13}C NMR spectrum of the solid salt (Figure 1) obtained under magic angle spinning conditions gives isotropic chemical shifts. As can be seen from Table I and Figure 1, there is a very close similarity between the ^{13}C spectrum of the solid cation salt and its solution spectrum, the broadness of the solid-state spectrum being probably due to quadrupolar interactions with the chlorines in the counterion. The maximum difference observed between the two spectra is ca. 6 ppm for the C_2, resonance and the other differences are substantially smaller. *This means that there are no substantial differences in the structure or charge distribution of 4 as a crystalline solid or as a solution in CH_2Cl_2.* In other words, on the basis of the NMR data, we can directly link the structure determined crystallographically in the solid state with all of the solution parameters previously measured.

The structure of the molecular cation is illustrated in Figures 2 and 3, and selected interatomic distances and angles are given in Table IV. It can be seen that the "seven-membered" ring of the cation exists as a shallow boat with the bridging C_8 carbon held right over this ring.

A notable feature of this structure is the bond lengths of the formal cyclopropane. *The bridging C_1–C_7 distance of 1.626 (8) Å is significantly* longer *than in a free cyclopropane (1.510 Å).*[24] *On the other hand, the C_1–C_8 distance of 1.488 (7) Å is shorter than that of a normal cyclopropane.* It must be emphasized that the disorder observed with the cation does not significantly affect these measured bond distances. The disorder encountered with the cation does result in large errors for the C_1–C_2, C_2–C_3, and C_3–C_4 distances (Table IV), although it is interesting that the C_1–C_2 (or C_6–C_7) distance (1.422 (12) Å) is significantly shorter than would be anticipated for the average of two single bonds.[25]

Taken together these bond distances and angles clearly indicate that cation 4 can be regarded as being homoaromatic. The lengthening of the C_1–C_7 and shortening of the C_1–C_8 distances from those of a normal cyclopropane and substantial shortening of the C_1–C_2 distance from a regular single bond are exactly in

---

(22) All calculations were carried out on CDC-6400 or CYBER 170/730 computers. The programs DATCO5 and DATRDN from the X-RAY 76 program were used for preliminary data treatment. The structure was solved by using the SHELX package, and final refinement used the internally written programs CUDLS and SYMFOU by J. S. Stephens and J. S. Rutherford, respectively. Planes calculations used NRC-22 (M. E. Pippy and F. R. Ahmed), and diagrams were prepared using ORTEP-II (Johnson, C. K. U.S. Atomic Energy Commission Report, ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1976).

(23) Childs, R. F.; Rogerson, C. V. *J. Am. Chem. Soc.* **1980**, *102*, 4159.

(24) Haddon, R. C.; Williams, G. R. J. *Chem. Phys. Lett.* **1976**, *42*, 453.

(25) *Spec. Publ.—Chem. Soc.* **1958**, *No.* 11; **1965**, *No. 18*. Faggiani, R.; Lock, C. J. L.; Pollock, R. J.; Rosenberg, B.; Turner, G. *Inorg. Chem.* **1981**, *20*, 804 and references therein.

Table III. Atomic Positional Parameters (×10^4) and Temperature Factors (Å^2; ×10^4 for Sb and Cl, ×10^3 for C and O)

	x	*y*	*z*		*x*	*y*	*z*
Sb(1)	0	0	0	C(1)	1440 (8)	4267 (5)	2688 (3)
Sb(2)	5000	5000	0	C(2)	1771 (10)	3607 (6)	2149 (4)
Cl(11)	1527 (3)	0	1569 (1)	C(3)	2977 (12)	3873 (11)	1950 (4)
Cl(12)	2123 (2)	−1493 (1)	214 (1)	C(4)	3595 (13)	5000	1927 (7)
Cl(21)	2054 (2)	5000	−241 (1)	C(8)	2973 (11)	5000	3478 (5)
Cl(22)	3826 (2)	3493 (1)	−1120 (1)	O(2)[a]	890 (19)	2700 (8)	1844 (7)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	255 (3)	243 (3)	255 (3)		155 (2)	
Sb(2)	232 (3)	244 (3)	177 (3)		123 (2)	
Cl(11)	496 (10)	836 (16)	277 (8)		235 (8)	
Cl(12)	471 (7)	597 (10)	665 (9)	238 (7)	245 (7)	−123 (7)
Cl(21)	258 (1)	489 (6)	292 (7)		175 (6)	
Cl(22)	384 (6)	491 (7)	412 (6)	−68 (5)	222 (5)	−224 (5)
C(1)	50 (3)	40 (3)	37 (3)	1 (2)	30 (2)	4 (2)
C(2)	72 (4)	55 (4)	31 (3)	24 (3)	20 (3)	4 (2)
C(3)	77 (5)	161 (10)	36 (3)	74 (6)	30 (3)	10 (4)
C(4)	35 (5)	197 (17)	33 (5)		22 (4)	
C(8)	39 (4)	70 (5)	26 (3)		20 (3)	
O(2)	147 (11)	29 (4)	50 (5)	3 (6)	41 (6)	−4 (4)

[a] Atom given half-occupancy in this position. Anisotropic temperature factors given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}\lambda 12 + \ldots)]$ where a*, b*, and c* are the reciprocal lattice vectors (Å^2).

Table IV. Selected Interatomic Distances (Å) and Angles (Deg)

		Interatomic Distances			
Sb(1)–Cl(11)	2.363 (2)	Sb(1)–Cl(12)	2.350 (2)	Sb(2)–Cl(21)	2.365 (2)
Sb(2)–Cl(22)	2.365 (1)	C(1)–C(2)	1.422 (12)	C(2)–C(3)	1.368 (16)
C(3)–C(4)	1.378 (13)	C(1)–C(8)	1.488 (7)	C(1)–C(7)	1.626 (8)
C(2)–O(2)	1.182 (12)				
		Possible Hydrogen Bonds			
O(2)···Cl(22)[a]	3.292 (9)	O(2)···Cl(11)	3.15 (1)	O(2)···Cl(12)[b]	3.332 (9)
		Interatomic Angles			
Cl(11)–Sb(1)–Cl(12)	90.4 (1)	Cl(11)–Sb(1)–Cl(12)[a]	89.6 (1)	Cl(12)–Sb(1)–Cl(12)[a]	90.4 (1)
C(12)–Sb(1)–Cl(12)[c]	89.6 (1)	Cl(21)–Sb(2)–Cl(22)	90.3 (1)	Cl(21)–Sb(1)–Cl(21)[d]	89.7 (1)
Cl(22)–Sb(2)–Cl(22)[d]	90.1 (1)	Cl(22)–Sb(2)–Cl(22)[e]	89.9 (1)	C(8)–C(1)–C(2)	121.8 (3)
C(1)–C(2)–C(3)	128.9 (7)	C(2)–C(3)–C(4)	127 (1)	C(3)–C(4)–C(5)	130 (1)
C(7)–C(1)–C(2)	127.0 (7)	C(8)–C(1)–C(7)	56.9 (3)	C(1)–C(8)–C(7)	66.2 (4)
C(1)–C(2)–O(2)	115 (1)	C(3)–C(2)–O(2)	117 (1)		

[a–f] Atoms are related to those given in Table II: *a*, −*x*, *y*, −*z*; *b*, *x*, −*y*, *z*; *c*, −*x*, −*y*, −*z*; *d*, 1 − *x*, *y*, −*z*; *e*, 1 − *x*, 1 − *y*, −*z*; *f*, *x*, 1 − *y*, *z*. C(5), C(6), and C(7) are related to atoms C(3), C(2), and C(1) respectively by *f*.

Table V. Comparison of Calculated Interatomic Distances and Angles of 3 with Those Found for 5

		dist, Å					dihedral angle, deg	
cation	method	C_1–C_8	C_1–C_7	C_1–C_2	C_2–C_3	C_3–C_4	*a*	*b*
5	X-ray	1.488	1.626	1.42 (1)	1.37 (2)	1.38 (2)	152 (1)	110 (1)
3	MINDO/3[c]	1.498	1.621	1.449	1.387	1.412	164.5	117.9
3	STO-2G[c]	1.516	1.578	1.479	1.379	1.425	158.1	108.5

[a] $C_2C_3C_5C_6$–$C_1C_2C_5C_7$ dihedral angle. [b] $C_1C_2C_5C_6$–$C_1C_7C_8$ dihedral angle. [c] Reference 14.

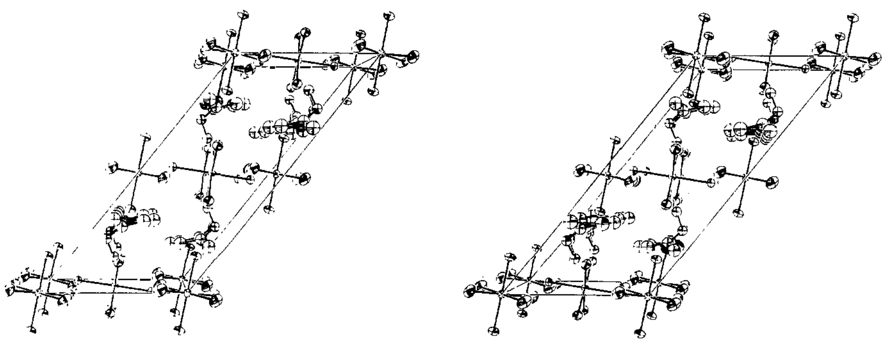


Figure 4. The packing of $[C_8H_8(OH)^+][SbCl_6^-]$ within the unit cell. The two oxygen atoms (each of half-occupancy) of the disordered cation are shown. The view is down *b*, and *a* and *c** are parallel to the bottom and side of the page, respectively (temperature factors of the cation are isotropic for simplicity).

accord with a delocalization which involves only the internal cyclopropane bond.

The bond distances and angles we observe here for **4** are in remarkably good agreement with those calculated by Haddon using MINDO/3 for the parent homotropylium cation **3**.[14] This is shown by the compilation of data in Table V. The cation **4** is a little more bent than the calculations indicated for **3** while the agreement between calculated and observed bond lengths is excellent. This agreement is all the more remarkable in as much as a substantial part of the positive charge of **4** would be on the hydroxy group and the importance of cyclic delocalization reduced.

It is possible to estimate a bond order for the C_1,C_7 bond of **4** using the distance found here (1.626 (8) Å) and the empirical bond valence method developed by Brown.[26] With use of this method, which for C,C bonds essentially consists of establishing a relationship beween the lengths and bond orders of single, double and triple bonds, a bond order of 0.76 is found. This compares to a value of 0.56 estimated by Winstein from UV spectra for the bond order of the C_1,C_7 bond of the parent homotropylium.[4a]

The packing is shown in Figure 4. The structure comprises of alternate layers of anions (at $z = 0, {}^1/_2$) and cations (at roughly $z = {}^1/_4, {}^3/_4$) parallel to the *ab* planes. Within the cation layer, disordered cations are arranged in paired chains. Thus a cation, which resembles a half-closed hand, is related to another in the adjacent chain as though the hands were interlinked fingertips to finger tips but displaced along *b* because of the 2_1 operation. The cation is hydrogen bonded to the $SbCl_6^-$ ions through either O(2)···Cl(22) or the bifurcated system O(2)···Cl(11), Cl(12).

The anions form a regular array, but there is no regular close packing of halogen ions within the layer. The perturbation appears to be caused by the interactions of the cation and anion layers. These are Cl(21) alternating with the C(2)C(3)C(5)C(6)O(2) portion of the cation along the *b* direction and a similar alternation of Cl(22) and Cl(22)^f pairs with C(8) along the *b* direction. All interactions appear to be weak ionic or van der Waals forces, and thus packing considerations do not appear to be important in determining the conformation of the cation. This is in accord with the conclusions reached previously from a comparison of the solution and solid-state ^{13}C NMR spectra.

Conclusion

The results we have described above show that protonated 2,3-homotropone, **5**, has the same structure in both the solid state and solution. Moreover, the bond lengths of this cation as determined by X-ray diffraction are fully in accord with it having a homotropylium structure. These results fully substantiate the concept of homoaromaticity as it was originally developed by Winstein some 20 years ago.

Further structural work on related systems will be reported shortly.

Registry No. 4, 80976-39-2; **5**, 3818-97-1.

Supplementary Material Available: A listing of structure factor amplitudes for $[C_8H_8OH^+][SbCl_6^-]$ (9 pages). Ordering information is given on any current masthead page.

---

[26] (26) Brown, I. D. "Structure and Bonding in Crystals"; O'Keeffe, M.; Navvotsky, A., Eds.; Academic Press: New York, in press.

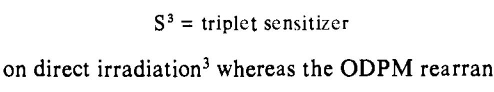
Singlet-Triplet Reactivity of a β,γ-Unsaturated Ketone: Mechanistic Studies in Photochemistry[1]

Richard S. Givens,* Woo Ki Chae, and Bogdan Matuszewski

Contribution from the Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045. *Received January 12, 1981*

Abstract: The photochemistry of bicyclo[3.2.1]oct-2-en-7-one (**1**) and four halogen-substituted derivatives is reported. The parent ketone **1** undergoes a 1,3-acyl shift (1,3-AS) with an efficiency of 0.42 on direct irradiation. Introduction of a chlorine atom at the bridgehead (ketone **9**) or on the double bond (ketone **5**) reduces the 1,3-AS efficiency to 0.11 and 0.14, respectively. Bromine atom substituents (ketones **8** and **4**) lower the 1,3-AS efficiencies even farther to 0.088 and 0.062. However, this loss in singlet reactivity does not result in successively more efficient intersystem crossing to the ketone triplet state, for no oxadi-π-methane (ODPM) products, the triplet rearrangement products, are found on direct irradiation for any of the ketones examined. The oxadi-π-methane products are formed upon sensitized irradiations with the triplet sensitizers acetone and acetophenone. As with the direct irradiations, the efficiencies of the sensitized ODPM reactions decrease monotonically with heavy-atom introduction, i.e., ODPM: 0.08 (H); 0.0062 and 0.03 (Cl); 0.0033 and 0.007 (Br); triplet sensitized 1,3-AS: 0.048 (H); 0.0041 and 0.009 (Cl); 0.0036 and 0.0029 (Br). The disappearance efficiencies reflect the same trend for heavy-atom substitution. It is concluded that introduction of the heavy atom increases the radiationless decay rate for the triplet state. Acetophenone and benzophenone phosphorescence quenching studies indicated that energy transfer from bromo ketone **4** was slower than the diffusion-controlled rate, indicating excited state complex formation between the sensitizer and **4**. Furthermore, a combined acetophenone sensitization-piperylene quenched reaction gave a nonlinear Stern-Volmer plot from which was derived a 6-ns lifetime for the complex. It was concluded that the heavy-atom effect was to increase the importance of the radiationless decay processes for the triplet complex.

The photochemistry of β,γ-unsaturated ketones has received extensive attention.[2] Particular interest has been directed toward the nature of the two major rearrangement reactions, the 1,3-acyl shift (1,3-AS) and the oxadi-π-methane (ODPM) rearrangement (eq 1). With a few notable exceptions, the 1,3-AS rearrangement occurs on direct irradiation[3] whereas the ODPM rearrangement



(1)

S^3 = triplet sensitizer

---

[1] (1) A preliminary report has appeared: Givens, R. S.; Chae, W. K. *J. Am. Chem. Soc.* **1978**, *100*, 6278-6280. Taken in part from the Ph.D. thesis of W. K. Chae, University of Kansas, 1977.

[2] (2) Reviews: (a) Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531-551. (b) Houk, K. N. *Ibid.* **1976**, *76*, 1-74. Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73-114. Recent leading references: (c) Henne, A.; Siew, N. P. Y.; Schaffner, K. *Helv. Chim. Acta* **1979**, *62*, 1952-1965; *J. Am. Chem. Soc.* **1979**, *101*, 3671-3673. (d) Schaffner, K. *Tetrahedron* **1976**, *32*, 641-653.

[3] (3) Sensitized 1,3-AS reaction have been noted: (a) Schexnayder, M. A.; Engel, P. S. *Tetrahedron Lett.* **1975**, 1153-1156. (b) Engel, P. S.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 145-153. (c) See ref 1.

0002-7863/82/1504-2456$01.25/0