the NH and β-pyrrolic hydrogens.

(iv) The observed substituent effects do not follow a known substituent scale, possibly due to steric interactions between the β-pyrrolic substituent and the peri phenyl ring.

(v) β-Substitution is predicted to modify chemical reactivities at the various pyrrolic positions; i.e., those involved in the major delocalization pathway should exhibit greater aromatic-type reactivity, while those on the localized double bond should be more susceptible to electrophilic attack.

Acknowledgment. We thank the Australian Research Grants Committee for financial support (to M.J.C.) and the Australian Government for a Commonwealth Postgraduate Award (to M. M.H.).

Structure of 1-Ethoxyhomotropylium Hexachloroantimonate: A Nonaromatic Homotropylium Cation[1]

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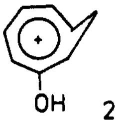
Abstract: Cycloocta-2,4,6-trienone, **4**, was reacted with Et$_3$O$^+$SbCl$_6^-$ to yield 1-ethoxyhomotropylium hexachloroantimonate, **5**. NMR spectra of solutions of this salt are consistent with the ion sustaining an induced ring current. Pale-yellow, near cubic crystals of **5** were obtained on recrystallization from CH$_2$Cl$_2$. The CPMAS ^{13}C NMR spectrum of the crystalline sample was very similar to its solution spectrum, indicating that there was no difference in the structure of the cation in the two phases. The crystal structure of **5** was determined by using X-ray diffraction. The cation has adopted an open conformation which was predicted by Haddon, with a large C$_1$, C$_7$ internuclear distance (2.284 (5) Å). A more detailed examination of the structure of **5** shows that the cation can best be regarded as a linear 1-ethoxyoctatrienyl cation and that on structural grounds this cation cannot be regarded as being homoaromatic. This conclusion is at odds with the NMR evidence and points to the need for caution in the use of the latter techniques as a criterion of homoaromaticity.

A major thrust of our current work has been the attempt to define more precisely the importance of homoaromaticity in medium ring cations such as the homotropylium ion, **1**.[2] To do this we have used a combination of structure determinations using X-ray crystallography,[3] thermochemical measurements,[4] and both solution and solid-state NMR spectroscopy. In this latter area we have carried out a detailed analysis of the ring current criterion of homoaromaticity for some homotropylium cations and have shown that the large chemical shift difference of the exo and endo protons of the bridging methylene group of these ions is consistent with the presence of an induced ring current.[5] The conclusion reached from this multifaceted approach to a more rigorous definition of homaromaticity is that the original homoaromatic formulation of the structure of the 2-hydroxyhomotropylium cation, **2**, is correct.[6,2] The question arises as to how general is this conclusion.


1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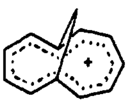
3

Haddon, in a detailed theoretical investigation of the homotropylium cation, has concluded that there are two minima on the potential energy surface.[7] The lowest energy of these, which corresponds closely to the structure found experimentally for **2**, has a calculated homoconjugate internuclear distance of 1.621 Å (MINDO-3). The second unsuspected energy minimum, which occurs along the pathway for the ring inversion process of the homotropylium cation,[8] was calculated to be some 6–10 kcal/mol less stable than the former conformation. The major distinguishing structural feature of this second conformation is the very long C$_1$,C$_7$ homoconjugate distance of 2.303 Å.

Scheme I

There are only two reported structure determinations of potential homotropylium cations. The first is **2**, mentioned above, and the second is the bridged annulene **3** reported by Simonetta et al.[9] This latter cation with a very long homoconjugate internuclear distance of 2.229 Å can formally be thought of as corresponding to the second, open conformation predicted by Haddon. However, this ion is also an annulenium cation with a 10 π-electron periphery and as such it is not clear how typical this structure is in terms of simpler homotropylium ions lacking the second carbon bridge.[10]

The relative energies of the two conformations of the homotropylium cation should depend on the position and nature of any substituents.[7] This is readily apparent from a consideration of the resonance structures of the homotropylium cation, Scheme I. Electron donor groups at C$_1$, C$_3$, C$_5$, and C$_7$ should favor the cyclooctatrienylium resonance structures as positive charge is maximized at these carbons in the open form of the cation. Conversely, donor substituents at C$_2$, C$_4$, and C$_6$ would be most effective in stabilizing the cation when it is in the closed bicyclo[5.1.0]octadienyl form. Substituents at C$_8$ might be expected

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[1] This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, Imperial Oil Ltd., and the Science and Engineering Research Board at McMaster University.

[2] Childs, R. F. *Acc. Chem. Res.* **1984**, *17*, 347–352.

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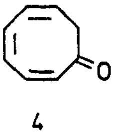
0002-7863/86/1508-3613$01.50/0

to have a similar effect on the structure of a homotropylium cation to those reported for the cycloheptatriene/norcaradiene and bridged annulene systems.[11]

In principle, in view of the relatively small energy difference between the two conformations, it should be possible by the appropriate placement of substituents to invert their relative energies so that the open form becomes the lowest energy and preferred conformation. Such a proposal is open to direct experimental test by preparing a stable derivative of 1 with an electron-donating substituent at C_1, or the related carbons, and to determine the structure of such a system directly. In an attempt to do this we selected the 1-ethoxyhomotropylium cation as both a likely candidate and also a cation which was relatively easy to prepare. We report here the results of this study and indeed show that it is possible to prepare a simple homotropylium cation which has an open conformation.

Results and Discussion

Preparation and Characterization of the 1-Ethoxyhomotropylium Cation. Reaction of cyclooctatrienone, 4, with $Et_3O^+SbCl_6^-$ in CH_2Cl_2 led to the formation of 5. The stable salt was isolated as a solid and was fully characterized spectroscopically and by elemental analysis. It was recrystallized from CH_2Cl_2 to give single crystals that were suitable for X-ray diffraction studies.



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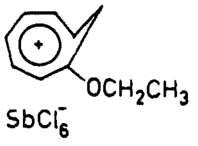
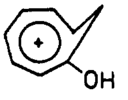


5

The ^1H NMR spectral data of solutions of 5 are given in Table I. At 250 MHz most of the proton resonances of 5 were resolved and it was possible to obtain the proton/proton coupling constants. One feature of the spectrum is the magnetic inequivalence of the two methylene protons of the ethoxy group which gives rise to an ABX_3 pattern for the ethyl protons. A further aspect of the ^1H NMR spectrum of 5 is the chemical shift difference (3.12 ppm) between the C_8 exo and endo protons. This difference is comparable in magnitude to that found for 2 (3.10 ppm).[3]

^{13}C NMR spectra of 5 were obtained both in solution and in the solid state by using CPMAS techniques. As can be seen from the data in Table II, the positions of all the resonances of 5 are very similar in both the solution and the solid-state spectra. The maximum difference that exists is a little more than 5 ppm for the CH_3 resonance, and in most instances the agreement is much closer than this. Clearly, there is a very close similarity of 5 in the two phases, and it is unlikely that there are any major structural differences in the cation in the solid phase as compared to solution.

Comparison of the data given in Tables I and II for 5 and the corresponding hydroxy and methoxy cations 6 and 7, respectively, indicates that these ions are very similar spectroscopically.[12,13] It would seem likely that the properties and structures of these ions will also be similar.



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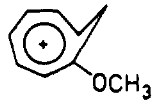

7

The structure of 5 was determined as outlined in the Experimental Section, Figure 1. Atomic positional parameters and temperature factors are given in Table III, and key interatomic distances and angles are summarized in Table IV. Before the structure of 5 is examined in detail, it is important to look for any specific cation–anion interactions which could lead to possible geometric distortions. As was already indicated above, this was not expected on the basis of the ^{13}C NMR evidence and indeed no carbon/chlorine contacts were found with an internuclear distance of less than 3.5 Å. There were some hydrogen/chlorine contacts which were just below 3.0 Å, particularly with the hydrogens of the ethyl group, but overall there is no reason to suspect that the structure of the cationic portion of 5 should be perturbed by the presence of the anion.

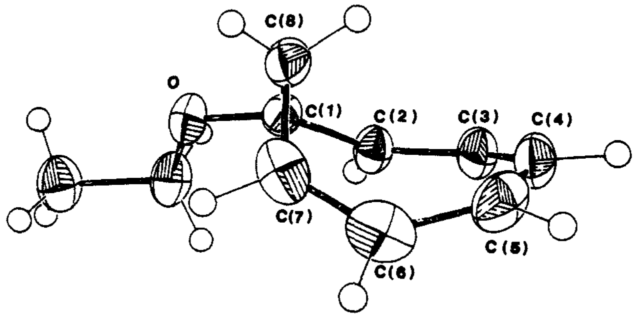

Figure 1. Structure of 1-ethoxyhomotropylium cation.

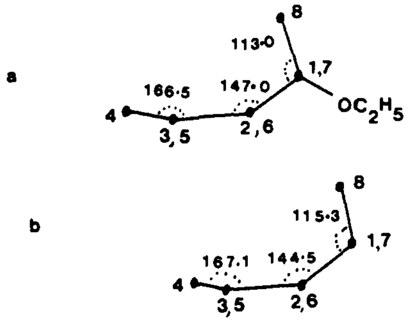

Figure 2. (a) Conformation of 1-ethoxyhomotropylium cation (interplanar angles). (b) Conformation calculated by Haddon for the second higher energy form (interplanar angles).

The conformation of 5 is shown in Figure 2a. The eight ring carbons can be broken down into a series of planes: 1, $C_{1,7,8}$; 2, $C_{1,2,6,7}$; 3, $C_{2,3,5,6}$; and 4, $C_{3,4,5}$. Plane 3 shows the maximum deviation of carbons from a plane with an average deviation of 0.047 Å. The angles formed between these planes are shown in Figure 2a, and for comparison, the conformation calculated by Haddon of the second, higher energy form is also shown, Figure 2b. The agreement between the two is remarkable. It is worth noting that the angles formed between the various planes in cation 5 are similar to those encountered in the 2-hydroxyhomotropylium cation,[3] and this would seem to be a general shape for these cations.

The structural feature of 5 which stands out immediately on examination of the various internuclear distances is the long C_1,C_7 distance of 2.284 (5) Å. This is very much greater than the comparable internuclear distance of the 2-hydroxyhomotropylium cation and directly comparable to the value calculated by Haddon for the second open form of the homotropylium cation. It is clear that the presence of an ethoxy group on C_1 of the homotropylium ring is sufficient to tip the balance between the two conformations and make the open form the lowest in energy.

In terms of a more detailed look at the structure of 5, it is apparent that there is a progressively increasing bond alternation present on proceeding from C_1 around the unsaturated portion of the ring. In fact, the C_5,C_6 and C_6,C_7 bond distances in 5, 1.429 (7) and 1.337 (5) Å, respectively, are the same as those normally encountered for single and double bonds in polyenes[14] or polye-

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(13) Brookhart, M. S.; Atwater, M. A. M. *Tetrahedron Lett.* **1972**, 4399–4402.

(14) For example, the single and double bond distances in 1,3-cyclohexadiene are 1.468 and 1.339 Å, respectively: Dallinga, G.; Toneman, L. H. *J. Mol. Struct.* **1968**, *1*, 11–23.

Table I. ^1H NMR Data[a]

		chemical shifts. ppm											
compd	solvent	H_1	H_2	H_3	H_4	H_5	H_6	H_7	$H_{8(exo)}$	$H_{8(endo)}$	$-OCH_2$[c]	$-CH_3$	$-OCH_3$
5[b]	CD_2Cl_2		7.57 dd	8.45 dd	7.50 m	8.03 dd	7.47 m	6.07 dt	4.46 dq	1.34 t	4.96 dq 4.73 dq	1.61 t	
6[12]	FSO_3H/SO_2		8.15–7.45 m	8.15–7.45 m	8.15–7.45 m	8.15–7.45 m	8.15–7.45 m	5.95 q	4.40 dq	1.32 t			
7[13]	FSO_3H		8.60–7.35 m	8.60–7.35 m	8.60–7.35 m	8.60–7.35 m	8.60–7.35 m	6.03 m	4.55 m	1.35 t			4.45 s
8[25]	FSO_3H	8.57 d	6.79 m	8.08 t	6.92 t	7.83 t	6.79 m	7.18 m				2.17 d	

[a] Referenced to methylene chloride at 5.31 ppm. t = triplet. m = multiplet(s). q = quartet. dq = doublet of quartets. [b] Coupling constants in hertz: $J_{2,3}$ = 11.5. $J_{3,4}$ = 9.1. $J_{4,5}$ = 11.6. $J_{5,6}$ = 6.5. $J_{6,7}$ = 9.3. $J_{7,8(endo)}$ = 9.4. $J_{7,8(exo)}$ = 7.7. $J_{8endo,exo}$ = 10.8. [c] $-OCH_2CH_3$. ABX_3 pattern. $J_{H'H''}$ = 10.7.

Table II. ^{13}C NMR Data[a]

		chemical shifts. ppm						
compd	solvent or phase	C_1	C_2–C_7			C_8	$-OCH_2$	$-CH_3$
5	CF_3SO_3H	185.8	155.4	147.6	139.2	39.5	75.2	13.2
			134.0	132.5	126.4			
5	solid	183.9	157.2	148.7	141.6	43.3	76.7	18.8
			138.8	133.9	126.6			
6	FSO_3H	186.3	155.5	148.0	139.7	39.5		
			133.2	133.2	129.4			
8	FSO_3H	190.9	183.5	171.9	164.1	21.0		
			134.4	132.1	122.2			

[a] Chemical shifts are referred to CD_2Cl_2 (internal. δ 53.6) in FSO_3H and CF_3SO_3H. Adamantane (external δ 38.57 and 29.5) for solid.

Table III. Atomic Positional Parameters and Temperature Factors (Å^2)

atom	10^4x	10^4y	10^4z	10^3U_{eq}
C(1)	3286 (3)	-2295 (3)	5064 (3)	28 (2)
C(2)	3220 (4)	-3236 (3)	4503 (3)	30 (2)
C(3)	3014 (4)	-4263 (3)	4768 (3)	35 (2)
C(4)	2387 (5)	-4719 (3)	5449 (3)	39 (2)
C(5)	1420 (5)	-4304 (4)	5861 (3)	43 (2)
C(6)	917 (5)	-3220 (4)	5861 (3)	46 (2)
C(7)	1688 (5)	-2318 (3)	5934 (3)	39 (2)
C(8)	3266 (4)	-2328 (3)	6088 (3)	34 (2)
C(9)	3197 (5)	-1132 (3)	3704 (3)	36 (2)
C(10)	3132 (5)	61 (3)	3574 (4)	41 (2)
O	3409 (3)	-1337 (2)	4747 (2)	33 (2)
Sb	2273.6 (2)	1498.3 (2)	7166.8 (1)	20.6 (1)
Cl(1)	2933 (1)	2077 (1)	8809 (1)	31.8 (4)
Cl(2)	4179 (1)	242 (1)	7606 (1)	31.8 (4)
Cl(3)	3807 (1)	2803 (1)	6808 (1)	32.8 (4)
Cl(4)	1668 (1)	901 (1)	5548 (1)	43.6 (5)
Cl(5)	760 (1)	177 (1)	7502 (1)	38.1 (4)
Cl(6)	415 (1)	2769 (1)	6786 (1)	44.9 (4)

[a] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

nones,[15] suggesting that the C_6,C_7 *bond is not significantly involved in the delocalization of the positive charge in the system.* In this regard it is interesting to examine the various torsional angles between adjacent C(sp^2)–C(sp^2) bonds around the seven basal carbons of **5**. With one exception, these torsional angles are relatively small (<23°) and should not interfere with π-delocalization. The exception is the $C_{4,5}$–$C_{6,7}$ torsion angle for which a value of 38.9° is found. This approaches the 45–55° torsion angle limit to effective π-delocalization which has been found in the bridged annulenes.[16] This relatively large value of the $C_{4,5}$–$C_{6,7}$ torsion angle reinforces the suggestion made above that the C_6,C_7 double bond is not extensively involved in the delocalization of the positive charge.

The suggestion that the structure of the unsaturated part of **5** can be best regarded as an 1-ethoxydienyl or twisted trienyl cation raises the question as to how it compares with other comparable linear cations. Unfortunately, at this point we know of no other reported structure determination of a 1-alkoxy- or hydroxy-substituted trienyl or dienyl cation which could serve as an example. There have been many theoretical studies of the structure of protonated carbonyl compounds, but most of these have involved relatively simple systems,[17] and there is a marked lack of detailed calculations on protonated polyenones.

While there is a lack of direct structural information for protonated polyenones, from other types of less direct evidence there is reason to expect increased bond alternation on proceeding away from the alkoxy or hydroxy substituent. For example, it is well-known that there is a fall off in the effectiveness of increased conjugation in stabilizing a protonated carbonyl compound as the unsaturated chain is extended. This shows up in the acidities of the conjugate acids of the carbonyl compounds[18] and also in their related heats of protonation.[4,19] Similarly, NMR studies on protonated polyenones suggest that while the greatest fraction of the positive charge resides on the odd-numbered carbons, the fraction of this charge on any carbon diminishes with distance from the carbonyl.[20] It would seem likely that these diminishing effects of extending the conjugation would be reflected in the structures of alkoxy and hydroxy carbenium ions.

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(15) For example, the comparable bonds in all *trans*-retinal have distances of 1.460 and 1.336 Å, respectively: Hamanaka, T.; Mitsui, T.; Ashida, T.; Kakudo, M. *Acta Crystallogr.* **1972**, *28*, 214–222.

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

C(1)–C(2)	1.407 (5)	C(2)–C(3)	1.359 (5)	C(3)–C(4)	1.420 (5)
C(4)–C(5)	1.364 (6)	C(5)–C(6)	1.429 (7)	C(6)–C(7)	1.337 (5)
C(7)–C(8)	1.506 (6)	C(8)–C(1)	1.480 (5)	C(1)···C(7)	2.284 (5)
C(1)–O	1.289 (4)	O–C(a)	1.474 (5)	C(9)–C(10)	1.487 (6)
Sb–Cl(1)	2.365 (1)	Sb–Cl(2)	2.377 (1)	Sb–Cl(3)	2.370 (1)
Sb–Cl(4)	2.346 (1)	Sb–Cl(5)	2.357 (1)	Sb–Cl(6)	2.354 (1)
C(8)–C(1)–C(2)	122.4 (3)	C(7)···C(1)–C(2)	112.4 (3)	O–C(1)–C(2)	123.5 (3)
C(7)···C(1)–C(8)	40.5 (2)	O–C(1)–C(8)	114.1 (3)	O–C(1)···C(7)	111.0 (2)
C(1)–C(2)–C(3)	126.8 (3)	C(2)–C(3)–C(4)	131.4 (3)	C(3)–C(4)–C(5)	130.8 (3)
C(4)–C(5)–C(6)	129.8 (3)	C(5)–C(6)–C(7)	126.3 (4)	C(6)–C(7)–C(8)	123.0 (3)
C(6)–C(7)···C(1)	115.8 (3)	C(8)–C(7)···C(1)	39.7 (2)	C(1)–C(8)–C(7)	99.8 (3)
C(1)–O–C(9)	121.2 (3)	O–C(9)–C(10)	106.7 (3)	Cl(1)–Sb–Cl(2)	88.3 (1)
Cl(1)–Sb–Cl(3)	90.3 (1)	Cl(1)–Sb–Cl(4)	178.7 (1)	Cl(1)–Sb–Cl(5)	90.6 (1)
Cl(1)–Sb–Cl(6)	89.8 (1)	Cl(2)–Sb–Cl(3)	89.9 (1)	Cl(2)–Sb–Cl(4)	90.4 (1)
Cl(2)–Sb–Cl(5)	89.5 (1)	Cl(2)–Sb–Cl(6)	178.0 (1)	Cl(3)–Sb–Cl(4)	89.5 (1)
Cl(3)–Sb–Cl(5)	178.9 (1)	Cl(3)–Sb–Cl(6)	89.9 (1)	Cl(4)–Sb–Cl(5)	89.6 (1)
Cl(4)–Sb–Cl(6)	91.5 (1)	Cl(5)–Sb–Cl(6)	90.8 (1)		

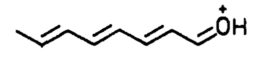
If indeed the structure of **5** can be best regarded as a 1-ethoxytrienyl system, this is tantamount to saying that from a structural perspective, **5** is not cyclically delocalized. Other features of the structure support this view. The very long C_1,C_7 internuclear distance indicates that any bonding between these carbons will be very weak. In terms of a bond order, this internuclear distance corresponds to a value of ca. 0.12[21] and corresponds quite closely to the estimated bond orders of the comparable bonds in cycloheptatrienes.[22] Bader et al.[23] in their analysis of the closed conformation of the homotropylium cation using the topological theory of molecular structure concluded that the homoaromatic bond between C_1 and C_7 is labile as a result of its low bond order, substantial ellipticity, and proximity of the ring and bond critical points. Thus while at the relatively short C_1,C_7 distance corresponding to those found for **2** (1.626 Å) there is a characterizable bond between these two carbons, no bond exists at a distance of 2.3 Å corresponding to that found here for **5**.

The C_1,C_8,C_7 bond angle in **5** is 101.1 (0.6)°. This is smaller than the tetrahedral angle, suggesting perhaps that there is a bonding interaction between C_1 and C_7. However, if this were so then it would be expected that C_1 and C_7 would both be distorted from a trigonal geometry. This is not the case for C_1 since this atom lies exactly in the plane defined by C_8, C_2, and O. Similarly, within the error limits of the positions of the various atoms, C_7 lies within a plane defined by C_6, C_8, and H_7. The 101° bond angle at C_8 and the planarity of the "bridging" carbons C_1 and C_7 mean that the interaction formally involves two p lobes on these carbons, the axes of which intersect at an angle of 80.3° to each other, 1.77 Å from each carbon. With this spatial arrangement of C_1 and C_7, any interaction between these two carbons will be very weak.

One question which arises is how much charge in cation **5** is located on the oxygen substituent, particularly as it was necessary to place an electron-donating substituent on the ring in order to obtain this open conformation of the homotropylium ring? One point to note is that the C_1O bond distance of 1.289 (9) Å is considerably longer than a regular C=O bond distance, and this would point to there being a substantial transfer of the positive charge onto the ring carbons. The bond distance found here seems to be fairly typical of the value found in the limited number of other protonated or alkylated carbonyl compounds whose structures have been determined.[24]

Further Consideration of the NMR Spectra of 5. The most widely used criterion of homoaromaticity is an analysis of the ^{1}H NMR spectrum of a species in question, and most frequently this analysis comes down to an examination of the chemical shift difference of the exo and endo protons of the methylene bridge. In the case of **5** this difference is fairly large, 3.12 ppm, and as has been shown for **2**, which has a comparable conformation and chemical shift difference,[3,5] this difference would suggest that **5** sustains an induced diamagnetic ring current. This observed chemical shift difference for the methylene protons in **5** is larger than can be accounted for in the absence of a ring current.[3]

It is informative to compare the NMR spectra of **5** with those of the linear protonated trienal **8**.[25] With the exception of H_7, all the ring proton resonances of **5** are shifted further downfield than those of **8**. There is, however, a similarity in the pattern of the shifts, with the odd-numbered proton resonances being further downfield than those of the even-numbered protons. Moreover, there is a steady progression in the magnitude of the downfield shifts of these odd-numbered protons, with H_3 being shifted the furthest downfield. The largest difference in the ^{1}H NMR spectra of **5** and **8** is in the positions of the resonances of H_7. In **5** the H_7 resonance is more than 1 ppm further upfield than the comparable resonance of **8**. This might be regarded as evidence for bridging between C_1 and C_7, with these carbons having a hybridization somewhere between sp^2 and sp^3 and the C–H bonds of these atoms thus having a higher p character than those of a completely trigonal carbon. This is not the case, however, for **5**, as was shown above, and the upfield shift as compared to **8** is due either to the limited conjugation of the C_6,C_7 bond with the rest of the charged unsaturated system or to the positioning of this proton with respect to an induced ring current. Overall, the NMR spectra of **5** are consistent with the ion having the open conformation found here but which, nevertheless, sustains an induced ring current. Structurally, however, this interaction is not apparent, and this raises the question of whether there is other evidence to support the homoaromatic formulation.



8

Some thermochemical studies have been reported for the corresponding 1-hydroxyhomotropylium cation, 6, and these would seem to indicate that there is little thermodynamic reason to suggest that there is a significant resonance stabilization of 6 resulting from cyclic delocalization. Thus the 8,8-dimethyl derivative of 6 was found to be thermodynamically less stable than the comparable derivative of **2** by ca. 1 kcal/mol.[26] The heat of transfer of cyclooctatrienone into FSO_3H would seem to be typical of that expected for a trienone and did not exhibit any anomaly which could be attributed to homoaromatic stabilization.[4] These thermochemical results are consistent with the conclusions

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Table V. Crystal Data

compd	$[C_7H_8OC_2H_5]^+[SbCl_6^-]$, $C_{10}H_{13}Cl_6OSb$
fw	483.7
cryst shape, size near cube (mm)	0.30 × 0.30 × 0.35
systematic absences	$h0l$, $l = 2n + 1$, $0k0$, $k = 2n + l$
space group	$P2_1/c$(no. 14)
unit cell	
a, Å	9.864 (2)
b, Å	12.370 (2)
c, Å	14.386 (3)
β, deg	107.15 (1)
vol, $Å^3$	1677.3 (5)
Z	4
temp, °C	−67
ρ calcd, g cm^{-3}	1.915
linear abs coeff, cm^{-1}	25.9
reflctns collected, max 2θ	$h,k,\pm l$, 65°
std reflctn, esd %	1 7 1, 0.9; −3 0 −6, 0.9
no. of reflctns measd	6665
no. of independent reflctns	5651
R merg.	0.018
no. with $I > 0$, used	5200
final R_1, R_2[a]	0.052, 0.043
final shift error max, av	0.178, 0.020
x (secondary extinctn)	0.000 59
final difference map, max, min, e $Å^{-3}$	0.96, −0.93
weighting scheme	$\omega = (\sigma_F^2 + 0.000359F_o^2)^{-1}$
error in an observtn of unit wt	1.162

[a] $R_1 = (\Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{1/2}$.

reached on the basis of the structure of **5** that this cation is not homoaromatic.

In conclusion, it is quite clear from these results that we have succeeded in inverting the relative energies of the two conformations of the homotropylium ring and that Haddon's prediction of a second energy minimum is quite correct. However, there is no apparent need to invoke a homoconjugative interaction between C_1 and C_7 of **5** in order to account for its observed structure or indeed thermochemistry, and rather, the structure would seem to correspond with an ethoxy-substituted dienyl or twisted trienyl cation. As far as the structure of **5** is concerned, it is very hard to justify designating this cation as homoaromatic. On the other hand, the NMR spectrum of **5** can be understood best in terms of an induced ring current. Haddon has shown that resonance energies and ring currents are related for at least the annulenes;[27] however, it would seem that such a relationship does not hold in this present case and that in view of the structural information now available for **5** the magnetic criteria alone are insufficient to classify a molecule or ion as being homoaromatic. Instead we suggest that molecules or ions which exhibit an induced diamagnetic ring current but do not have structural or thermochemical properties consistent with a homoaromatic designation continue to be designated as being diatropic.[28] The 7-substituted cycloheptatrienes are another group of molecules which fall into the same category, being diatropic but not homoaromatic.[29]

Two further general observations can be made. First, the barriers to ring inversion of the known 1-substituted homotropylium cations are all comparable in magnitude. This would suggest that they all have similar structures corresponding to the open conformation found here for **5**. Second, it is interesting to note the relationship of **5** to the related bridged annulenium cation **3** and indeed the wider range of bridged annulenes whose structures have been determined. For example, in the case of **3** it has been concluded that the homoconjugative interaction is small and only has a small effect on the structure of the cation.[9,10] It was possible to understand the NMR spectrum of **3** in terms of the larger annulene-type electron delocalization and in particular to account for the positions of the bridging methylene protons on this basis.[30] In this present case of **5**, such a large ring current is not possible, yet there is still an induced ring current. It would seem that further studies of homotropylium cations will be informative in terms of the origin of the spectral shifts in bridged annulenes.

Experimental Section

Solution NMR spectra were obtained by using Bruker WP80 and WM250 instruments. ^{13}C CPMAS spectra of the solid salt were obtained at 50.3 MHz on a Bruker CXP200 spectrometer. All solvents were distilled from P_2O_5 before use.

1-Ethoxyhomotropylium Hexachloroantimonate (5). A solution of triethyloxonium hexachloroantimonate (2.4 g, 5.5 mmol) in dichloromethane (15 mL) was added dropwise to a solution of cycloocta-2,4,6-trienone[31] (600 mg, 5 mmol) under dry nitrogen atmosphere. The reaction mixture was allowed to stand at room temperature for 2 h, and the precipitated salt **5** was filtered. The salt was recrystallized from CH_2Cl_2 at −20 °C: 1.60 g, 43.8%, mp 103–104 °C. Anal. Calcd for $C_{10}H_{13}OSbCl_6$: C, 24.78; H, 2.71. Found: C, 25.00; H, 2.74.

Collection of the Crystal Data. A pale-yellow, near cubic crystal was sealed in a Lindemann tube and used for data collection. Precession photographs showed that the crystal was monoclinic, and unit cell parameters were obtained from a least-squares fit of x, ϕ, and 2θ for 15 reflections for the compound in the range $21° < 2\theta < 28°$ recorded on a Syntex P2 diffractometer with use of graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at low temperature. Crystal data and other numbers related to data collection are given in Table V. The density was not determined because of the air instability of the crystals. Intensities were also recorded on the Syntex P2 diffractometer at low temperature with a coupled θ(crystal)–2θ(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[32,33] Corrections were made for Lorentz-polarization effects but not absorption. This will introduce a maximum error in F_o of <10%.

Solution of the Structure. The coordinates of the antimony atom were found from a three-dimensional Patterson synthesis, and a series of full-matrix least-squares refinements followed by three-dimensional electron density synthesis revealed all the atoms. At this stage the temperature factors of all non-hydrogen atoms were made anisotropic, and further full-matrix least-squares refinement, which minimized $\sum\omega(|F_o| - |F_c|)^2$, was terminated when the maximum shift/error was less than 0.2. Corrections were made for secondary extinction by the method in SHELX.[34] Throughout the refinement the scattering curves were from ref 35, and anomalous dispersion corrections from ref 36 were applied to the curves for Sb and Cl. The atom parameters for non-hydrogen atoms are listed in Table III.

Supplementary Material Available: Anisotropic temperature factors, hydrogen atom positional parameters, bond lengths and angles involving hydrogen atoms, and F_o and F_c values (32 pages). Ordering information given on any current masthead page.

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