

Ring Currents, NMR Chemical Shifts, and Homoaromaticity: The Homotropylium Ion Revisited¹

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Abstract: The large chemical shift difference between the exo and endo methylene proton resonances in the NMR spectrum of the homotropylium ion is normally rationalized on the basis of an induced ring current. It is shown here that the ring current model can only account for this chemical shift difference provided that a loop separation and large H-C₈-H angle are assumed. There is no justification for the use of a loop separation in these calculations, and it is shown that local anisotropic contributions are an important factor accounting for more than 40% of the total chemical shift difference. One startling feature of these calculations is that both the endo and the exo protons are found to be shielded. This surprising result means that the intrinsic shift of these protons in the absence of an induced ring current would be at ca. 5.5 ppm. The position of this intrinsic shift is discussed in terms of various model cations. The effect of a systematic variation in the magnitude of the ring current has been examined experimentally by the preparation of various Lewis acid complexes of 2,3-homotropone.

The homotropylium cation, **1**, is the archetype of homoaromatic systems in general.² Despite this, until recently most of the evidence for the formulation of **1** as being homoaromatic rested on its ¹H NMR spectrum and particularly the need to invoke an induced diamagnetic ring current³ to account for the very large difference in chemical shift between the exo and endo C₈ proton resonances.^{4,5} The existence of an induced diamagnetic ring current is not in question when **1** is placed in a magnetic field. Thus Dauben and co-workers⁶ have measured the diamagnetic susceptibility exaltation of **1** and some of its derivatives and shown that the exaltation is comparable in magnitude to that of the tropylium ion. The question arises, however, whether the induced ring current can adequately account for the very large chemical shift difference of the C₈ proton resonances of **1** ($\Delta\delta = 5.86$) (Figure 1).⁷ The answer to this question has particular significance to the whole area of homoaromaticity inasmuch as the observation of similarly large chemical shift differences for substituents on the bridging carbon is considered to be diagnostic for and, indeed in most cases, is the sole criterion used in denoting a system as being homoaromatic.

Some years ago Winstein reported a ring current calculation on the homotropylium ion; however, he assumed a planar C₁-C₇ carbon atom framework.⁸ Our recent structural work⁹ and the theoretical calculations of Haddon¹⁰ indicate that this has been a false assumption, and consequently it is of interest to repeat this type of ring current calculation to see whether the model is still valid for a nonplanar geometry. We show here that although it is possible to use a widely invoked ring current model to account for most of the large chemical shift difference between the resonances of the exo and endo protons, one must consider the somewhat unrealistic tenets on which this model is based. Local anisotropic contributions have been estimated and are an important

Table I. Calculated Ring Current Contribution (δ') to the Chemical Shifts for Methylene Protons in **1** with a "Planar Geometry"^a

loop separation, Å	δ' for H _{endo}	δ' for H _{exo}	$\Delta\delta$
0.00	-4.81	0.03	4.84
0.94	-5.41	0.31	5.72
1.00	-5.49	0.34	5.83
1.02	-5.52	0.36	5.88
1.28	-5.95	0.99	6.94

^aNegative sign indicates shielding. Coordinates used are shown in Figure 2.

contributor to this chemical shift difference.

Results and Discussion

Ring Current Calculations. In his early attempts to account for the low-field shift of the benzene protons relative to that of the nonaromatic system 1,3-cyclohexadiene, Pople^{11,12} used a dipolar approximation. This approach was superseded by the model introduced by Waugh and Fessenden¹³ who calculated the magnetic field components due to the current in a circular loop with radius equal to that of the benzene ring. By this method it was demonstrated that protons in the plane of the benzene ring would resonate at low field since the induced field at the nucleus augments the applied field. In contrast, protons situated above or inside an aromatic system (such as in [10]paracyclophane¹⁴ or [18]annulene,¹⁵ respectively) are shielded since the induced field opposes the applied field. A six-electron current in the plane of the arene ring of radius 1.39 Å leads to a deshielding of 2.78 ppm for the benzene protons. This was considered to be too large since the difference between the shifts of the protons in benzene and of the vinylic protons of 1,3-cyclohexadiene is only 1.5 ppm. Thus the ring current was empirically separated into two loops symmetrically disposed above and below the ring plane and their separation varied until the desired 1.5 ppm incremental shift was achieved; this empiricism is the origin of the 1.28-Å loop separation used in the Johnson-Bovey tabulations¹⁶ which are based on the Waugh-Fessenden model.^{13,17}

We have briefly summarized the historical development of the semiclassical ring current model since, although the widespread

(1) This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

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

(3) For a comprehensive review of the various approaches to calculating ring currents, see: Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 303.

(4) Rosenberg, J. L., Jr.; Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 2842. Winstein, S.; Kreiter, C. G.; Brauman, J. I. *Ibid.* **1966**, *88*, 2047. Keller, C. E.; Pettit, R. *Ibid.* **1966**, *88*, 606.

(5) Winstein, S.; Kaesz, H. D.; Kreiter, C. G.; Freidrich, E. C. *J. Am. Chem. Soc.* **1965**, *87*, 3267.

(6) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *Nonbenzenoid Aromat.* **1971**, *2*, 167.

(7) Warner, P.; Harris, D. L.; Bradley, C. H.; Winstein, S. *Tetrahedron Lett.* **1970**, 4013.

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(10) Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608 and earlier papers.

(11) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111.

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(13) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846; **1958**, *80*, 6697.

(14) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204 and references therein.

(15) Sondheimer, F. *Pure Appl. Chem.* **1963**, *7*, 363.

(16) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(17) Different values of loop separation have been chosen by other workers. For example, in an analysis of a series of polycyclic aromatics a 1.63-Å separation was used: Barfield, M.; Grant, D. M.; Ikenberry, D. *J. Am. Chem. Soc.* **1975**, *97*, 6956.

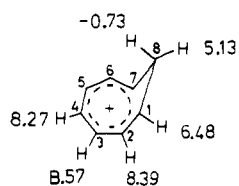
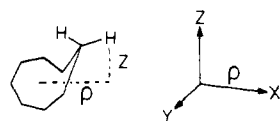


Figure 1. Experimental ^1H NMR chemical shifts (ppm) of the homotropylium ion (**1**) in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ measured at 5.97 T (251 MHz). Data from ref 7.



Coordinates		
Proton	P(x)	Z
H_{endo}	0.81	1.70
H_{exo}	2.60	1.37

Ring radius $\delta = 1.6 \text{ \AA}$

Figure 2. Coordinates used by Winstein for homotropylium ion with assumed geometry (ref 8).

usage of the Johnson–Bovey tables¹⁷ over the last 25 years has almost bestowed an imprimatur upon them, they tend to be used somewhat indiscriminately with little appreciation of the simplicity and empirical nature of the concept. It is well established that for protons positioned almost directly above the benzene rings the incremental shifts predicted by this model are moderately reliable; however, for nuclei in the deshielding region of the arene ring the correlation between predicted and measured chemical shifts is usually rather poor.³ In contrast, the quantum mechanically derived ring current tabulations of Haigh and Mallion¹⁸ work well for protons in the plane of the arene but seriously underestimate the shielding of protons above the ring.^{3,19} Recently it has been shown that these two approaches can be reconciled by first evaluating the local anisotropic contributions to the chemical shift and then the residual shift is nicely accounted for by using either the quantum mechanical approach or the semiclassical (Waugh–Fessenden–Johnson–Bovey) model with no loop separation.²⁰ In other words, if the local anisotropic contributions for a system are known, there is no need to invoke the empirical loop separation technique to account for the chemical shifts of protons abutting an aromatic ring.

Calculations for a “Planar” Homotropylium Ion. As few details are available for the calculation carried out by Winstein on the homotropylium ion,⁸ we repeated it assuming a planar arrangement of the seven-carbon “tropylium” fragment. The coordinates used were those reported by Winstein for the C_8 exo and endo protons together with a ring radius of 1.6 Å.⁸ The coordinate system is shown in Figure 2, and the ring current contributions to the chemical shifts of the two methylene protons for various loop separations are shown in Table I. In the original report of Winstein there is no indication as to whether a loop separation was used. We found it was possible to duplicate Winstein’s results when a loop separation of approximately 1 Å was used (Table I).²¹

Before leaving this unrealistic geometry it should be noted that not only is there no justification for the use of a loop separation for conventional aromatic systems but it is particularly hard to justify the use of such a separation with a homoaromatic system

(18) Haigh, C. W.; Mallion, R. B. *Org. Magn. Reson.* **1974**, *4*, 203.

(19) Haigh, C. W., personal communication.

(20) Agarwal, A.; Barnes, J. A.; Fletcher, J. L.; McGlinchey, M. J.; Sayer, B. G. *Can. J. Chem.* **1977**, *55*, 2575. Agarwal, A.; McGlinchey, M. J. *Ibid.* **1978**, *56*, 959.

(21) All calculations were carried out with the program LARC (Local Anisotropy Ring Current): Agarwal, A. M.Sc. Thesis, McMaster University, Hamilton, Ontario, Canada, 1976.

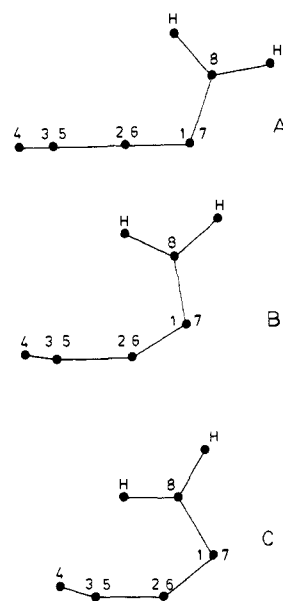
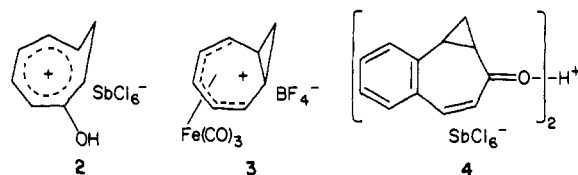


Figure 3. Side projections showing conformations of the carbon framework of the homotropylium ion as assumed by Winstein⁸ (A), “nonplanar” conformation used here, (B), and that of the $\text{Fe}(\text{CO})_3$ complex **3** (C).

such as **1**. Clearly there has to be an asymmetric π electron distribution between the two faces of **1**, and cyclic delocalization of the electrons via a π -type overlap would seem to occur only on the face opposite to the bridging methylene group.

Geometry of Homotropylium Ions. The most important problem with Winstein’s calculation⁸ is the assumption of a planar geometry for the seven ring carbons of **1**. Detailed NMR studies by Warner et al.⁷ have shown that a nonplanar conformation is preferred; furthermore, calculations by Haddon^{10,22} at the MINDO-3 and STO-2G level indicate that the seven ring carbons of **1** form a shallow boat with C_8 , the bridging carbon, being in a pseudoaxial position. The correctness of this structure has been shown by an X-ray diffraction study on the 2-hydroxyhomotropylium ion **2**⁹



in which a very similar geometry to that calculated by Haddon was found. It was also shown that there is no major change in charge distribution or conformation on dissolution of **2** in various nonnucleophilic solvents. Further confirmation of this nonplanar conformation of **1** comes from structural work on the related ions **3** and **4** in which very similar conformations of the ring were obtained.^{23,24} Side projections showing the conformations of **1** and **3** are shown in Figure 3.

Calculations for the “Nonplanar” Homotropylium Ion. In view of the similarities in the calculated structure of **1** and the measured X-ray crystallographic structure of **2**, it was decided to use the geometry of the latter ion as the basis of the ring current calculations for **1**. The C_8 hydrogen atoms were not found in the X-ray study, and standard 1.08-Å C–H bond lengths and a H–C–H bond angle of 114° were assumed. The crystallographic coordinates calculated for these hydrogens were transformed to orthogonal Cartesian coordinates with respect to the crystallographic (heavy-atom) origin. These coordinates were then referred to the

(22) Haddon, R. C. *Tetrahedron Lett.* **1975**, 863.

(23) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Ummat, P.; Varadarajan, A., unpublished results.

(24) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Varadarajan, A. *Acta Crystallogr.*, in press.

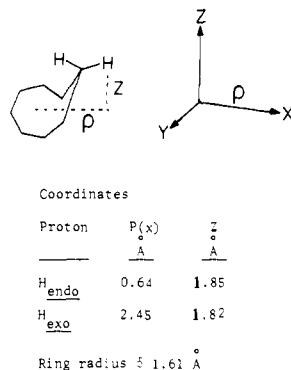


Figure 4. Coordinates used for "nonplanar" homotropylium ion.

Table II. Calculated Ring Current Contribution (δ') to the Chemical Shifts for the Methylene Protons of **1** with a "Nonplanar Geometry"^a

loop separation, Å	δ' for H _{endo}	δ' for H _{exo}	$\Delta\delta$
0	-4.48	-0.55	3.93
1.28	-5.44	-0.25	5.19

^aNegative sign indicates shielding. Coordinates used are shown in Figure 4.

center of the seven-membered ring which was used as the origin for the ring current calculation.

For the nonplanar seven-membered ring the midpoint of the line joining C₄ and A (the midpoint of the line joining C₁ and C₇) was considered to represent the "center" of the seven-membered ring. The coordinates of the hydrogens on C₈ were then tabulated with respect to this new origin. The radius (r) of the circular loop inscribing the (nonplanar) seven-membered ring was calculated as the average distance of the carbon atoms C₁ to C₇ from the center of the ring. These values are summarized in Figure 4. Due to the crystallographic mirror-plane symmetry restriction imposed to solve the crystal structure, the y coordinates of these hydrogens were zero (C₄, O, A, H_{endo}, and H_{exo} lie in the xz plane). These data were then used to calculate the ring current contribution to the incremental shifts for the C₈ protons. A 1.28-Å loop separation was also tried, and the results are given in Table II.

The evaluation of local anisotropic contributions to the shift of protons proximate to an aromatic ring system is relatively straightforward. In the simplest model, one can envisage three mutually orthogonal current loops about each aromatic carbon atom. The radius of each of these current loops is taken as the expectation value of a carbon 2p orbital (0.47 Å), while the relative magnitudes of the line currents requires a knowledge of the three principal components of the ¹³C chemical shielding tensor. These data are derivable either from an analysis of the spinning sidebands of the solid-state ¹³C NMR spectrum²⁵ or more directly from measurements on oriented single crystals.²⁶ The theory of this approach to local anisotropic effects and its application to several systems is presented elsewhere;^{17,20} local anisotropic and ring current shifts were evaluated by the program LARC written for this purpose.²¹

Since the methylene protons of **1** are symmetrically disposed relative to the C₁ and C₇ atoms, it was assumed that their local anisotropies affect the exo and endo protons equally, and so only the contributions from the carbon atoms at positions 2-6 are presented in Table III. The tensor components used are those recently reported for the tropylium cation.²⁷ The net result is a shielding of the endo proton relative to its exo partner of 3.01 ppm. This, together with the 3.93 ppm shielding calculated for an in-plane six-electron ring current, leads to a predicted chemical

Table III. Calculated Local Anisotropic Contribution (δ') to the Chemical Shifts for the Methylene Protons of **1** with a "Nonplanar Geometry"^a

ring carbon atom	δ' for H _{endo}	δ' for H _{exo}	$\Delta\delta$
C _{2,6}	-0.930	-0.485	0.445
C _{3,5}	-0.593	-0.046	0.547
C ₄	-0.844	+0.183	1.027

^aNegative sign indicates shielding. Coordinates used are shown in Figure 4.

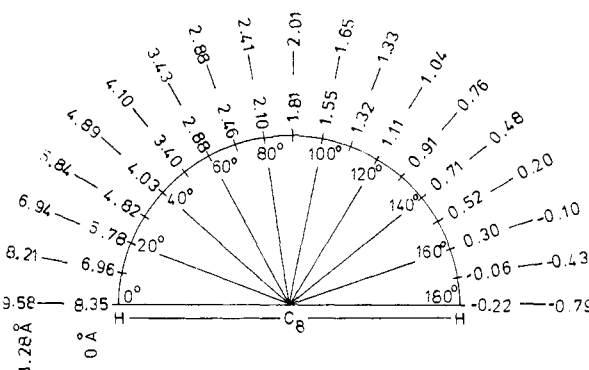


Figure 5. Profile map of shielding of C₈ protons of the homotropylium ion as a function of bond angle. Inner circle, zero loop separation. Outer circle, 1.28-Å loop separation.

shift difference of ~6.9 ppm between the methylene protons, somewhat larger than the experimentally observed separation of 5.86 ppm.

A possible criticism of the ring current model is that a planar loop was used while in the real molecule the seven carbon atoms of the ring form a shallow boat. In principle, nonplanar systems can be handled by using an approach in which the calculation of the magnetic field at any point in space, arising from a linear current flowing between specified points, is based on the Biot-Savart Law.²⁸ That is, the field due to the current flowing in a polygon is the sum of the contributions from the edges. This idea was originally proposed by Longuet-Higgins and Salem²⁹ and was subsequently invoked by Haddon³⁰ in a comprehensive study of the annulenes. Such calculations involve merely a composite geometric factor (the position of the proton relative to each of the polygonal edges must be evaluated), the area of the polygon, and the experimentally measured molar diamagnetic anisotropy χ_{π} .

When the boat-shaped geometry already described is used in conjunction with the observed χ_{π} value for the homotropylium ion (-72×10^{-6})⁶ it transpires that the endo and exo protons are shielded by 8.22 and 0.63 ppm, respectively, leading to a chemical shift difference at 7.59 ppm. This value is considerably larger than the observed value, but this is typical of this approach to the estimation of induced chemical shifts. We note that Longuet-Higgins and Salem obtained a value for benzene that was considered too large, and so they chose only to use ratios of chemical shifts.²⁹ Likewise, Haddon preferred not to use the benzene shift as a single calibrant but instead carried out a regression analysis on a large number of annulenes and obtained the best fit for a Biot-Savart model with a split loop separated by 1.2 Å.³⁰ No further work was carried out with the Biot-Savart approach in this work in view of its poor quantitative reliability.

It is clear on comparison of the results given in Tables II and III that the local anisotropic component of the overall difference is very substantial. Some 3.01 ppm (43%) of the calculated 6.94 ppm difference comes from this effect. The overall calculated chemical shift difference is somewhat greater than the observed 5.86 ppm.

(25) Marleq, M. M.; Waugh, J. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 6902 and references therein.

(26) Pausak, S.; Tegenfeldt, J.; Waugh, J. S. *J. Chem. Phys.* **1974**, *61*, 1338.

(27) Strub, H.; Beeler, A. J.; Grant, D. M.; Michl, J.; Cutts, P. W.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 3333.

(28) Atkins, K. R. "Physics"; Wiley: New York, 1966; pp 301-313.

(29) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1960**, *A257*, 445.

(30) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613.

Table IV. ¹H NMR Chemical Shifts of the Lewis Acid Complexes of **5**

Lewis acid	value of OLA ^a	chemical shifts, ^b ppm					Δδ ^c
		vinyl	bridgehead	H _{endo}	H _{exo}		
none		6.43, 5.76	2.34, 1.90	1.45	1.90	0.45	
SnCl ₄	0.52	7.08, 6.68, 6.32	2.95	1.04	2.95	1.91	
TiCl ₄	0.66	7.92, 7.26	3.98	0.49	3.98	3.49	
BF ₃	0.77	7.22, 6.85, 6.48	3.43	0.86	3.43	2.57	
SbCl ₅	0.85	7.65, 7.31, 6.93	3.79	0.59	3.79	3.20	
BCl ₃	0.93	7.52, 6.86	3.77	0.58	3.73	3.16	
BBr ₃	1.00	7.71, 7.12	3.96	0.40	3.96	3.56	

^a Values taken from ref 32. ^b In CD₂Cl₂ at -80 °C using 10-fold molar excess of Lewis acid. Chemical shifts referred to CDHCl₂ taken as δ 5.3. ^c Chemical shift difference between H_{endo} and H_{exo}.

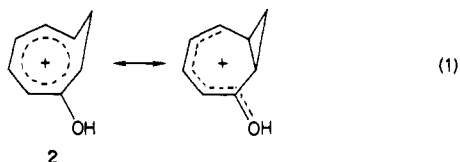
It is possible that the assumption of a regular cyclopropyl geometry for the H-C-H bond angle used in the calculation of the coordinates of the hydrogens is incorrect. To test the effect of variation in this bond angle, a profile map was traced for the protons on C₈. This profile took the shape of a semicircle with C₈ as the center and the C-H bond length (1.08 Å) as the radius. Shielding contributions from the ring current (for zero loop separation and for a 1.28-Å separation) were calculated at positions corresponding to 10° increments with respect to the reference line (which is parallel to the C₄-O-A axis shown in Figure 4). The results are summarized in Figure 5. Local anisotropic contributions were not calculated for each of these geometries, but it is assumed that they will follow the shifts due to the induced ring current.

As can be seen from Figure 5, the magnitude of the shielding experienced by the endo C₈ proton is very sensitive to its position. Movement of this proton down toward the center of the "tropylium" ring causes a very large upfield shift of this proton resonance. On the other hand, the corresponding exo proton is much less sensitive to positional changes. With minor geometric modification at C₈ it would be possible to match the observed chemical shift difference.

It is clear from these calculations on the nonplanar homotropylium cation that it is possible to reproduce approximately the chemical shift difference between the exo and endo protons. *It should be emphasized, however, that for the nonplanar geometry used here both protons are predicted to experience shielding irrespective of the model used.* Such a result is surprising inasmuch as conventional wisdom in the area generally suggests that the large chemical shift difference in the homotropylium ion, and indeed other homoaromatic ions, results from a shielding of the endo and deshielding of the exo bridging protons.

Variation in the Magnitude of the Ring Current. The shielding experienced by a proton due to an induced diamagnetic ring current is directly proportional to the magnitude of the ring current. In all the above calculations, a full six-electron ring current was assumed. Reduction of this ring current will thus directly attenuate the magnitude of the shielding experienced by the C₈ protons. Keller and Pettit³¹ recognized this factor in their early work on substituted homotropylium ions where they noted there was a correlation between the chemical shifts of the methylene protons and the difference (Δδ) in these shifts.

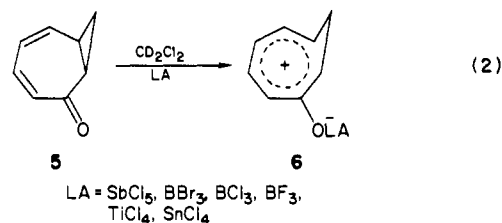
An electron-donating substituent on a homotropylium ring will have the effect of reducing the relative importance of homoaromatic cyclic delocalization. Thus, for example, the 2-hydroxyhomotropylium ion, **2**, would be expected to have a significant fraction of the positive charge residing on the oxygen atom (eq 1). As a result the homoconjugate bond in **2** will be more



(31) Keller, C. E.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 606.

the parent ion. This tendency toward bond fixation should reduce the magnitude of the ring current and hence the chemical shift difference between the C₈ methylene protons. In fact Δδ for **2** is only some 3.28 ppm as compared to 5.86 ppm in **1**.

To probe systematically the effect of variation in the electron-donating properties of substituents on the homotropylium ring, we have treated 2-homotropone with a series of Lewis acids (eq 2). The -O-LA⁻ group is an electron donor; however, the



relative ability of this group to donate an electron pair to a cationic center is determined by the Lewis acid used. An empirical scale of donor abilities of these groupings has recently been established.³² As ketones react readily with strong Lewis acids to form stable complexes, this approach offers a very simple method of producing a series of closely related ions with a systematic variation in the charge-stabilizing ability of one substituent.³³

In the present case, **5** was treated at low temperature in CD₂Cl₂ solution with various Lewis acids to form the complexes **6**. The complexes were characterized by their ¹H NMR spectra (Table IV). From the data given in Table IV, it can be seen that both the absolute chemical shifts and also the differences in the shifts of the C₈ protons show considerable variation as the Lewis acid is changed. If it is assumed that the geometry of these complexes remains essentially the same throughout the series, then it would be expected that the chemical shifts of the C₈ methylene protons would be directly dependent on the Lewis acid used as the fraction of positive charge induced on the carbon framework and hence the magnitude of the ring current is dependent on the donor properties of the O-LA⁻ group. That this is indeed the case can be seen from Figure 6 where the chemical shifts of the C₈ protons are plotted against the Lewis acid scale.³² Apart from the TiCl₄ complex,³⁴ remarkably good correlations are obtained which when extrapolated back to no Lewis acid give shifts which are in reasonable agreement with those of the starting homotropone. Extrapolation of these lines in the other direction enables the chemical shifts of the parent ion to be predicted. Assuming a 5.86 ppm separation in these two resonances, an endo proton resonance at δ 5.36 and exo proton resonance at δ -0.50 are estimated. This is in remarkably good agreement with values of δ 5.13 and -0.73 found experimentally in FSO₃H and confirms the validity of this analysis.

(32) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

(33) This approach to systematic variation of the donor properties of an oxygen function adjacent to a carbenium ion center should be of general applicability. Its advantage over the more generally used para-substituted aryl groups lies in the need to only prepare a single precursor of the series of ions and the simplicity of the reactions with the various Lewis acids.

(34) TiCl₄ can coordinate with either one or two ketones. The discrepancy found here could reflect different types of complexes formed in the reactions of 2,3-homotropone and the model ketones used in setting up the scale.

like a regular cyclopropane bond than the corresponding bond in

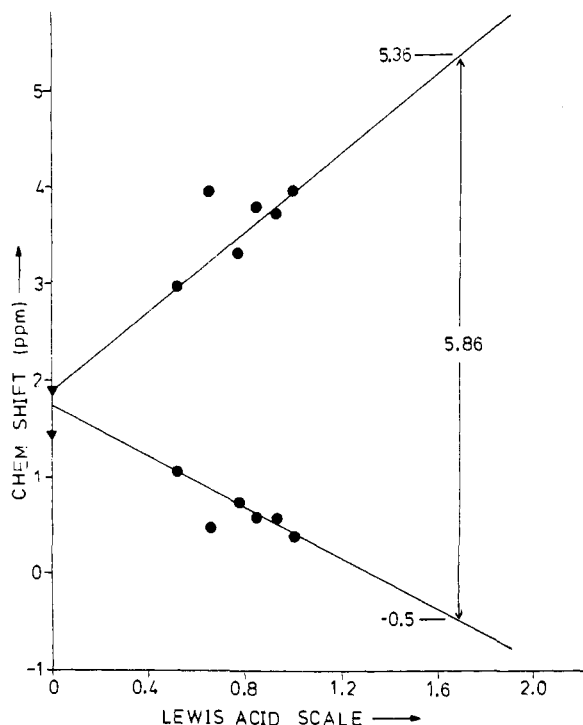
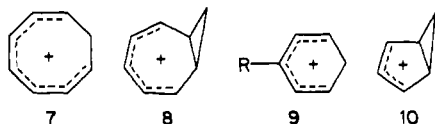


Figure 6. Chemical shift of H_8 protons of Lewis acid complexes of 2,3-homotropone vs. Lewis acid scale (●). 2,3-Homotropone with no Lewis acid (▼).

It is evident from this correlation that as progressively more positive charge is induced on the seven-membered ring this will result in less cyclopropane character and concomitant greater delocalization of the electrons in the C_1 - C_7 bond; hence the magnitude of the ring current is increased and the difference in chemical shift ($\Delta\delta$) between the endo and exo protons is also increased. As was pointed out above, the effect of this ring current should be to shield both protons; however, as can be seen from Figure 6 the exo proton moves downfield about twice as rapidly as the endo proton moves upfield. The obvious conclusion that must be drawn is that there is an additional factor over and above the ring current/local anisotropic terms which systematically varies in this series and acts to deshield both of these methylene protons.

Estimation of the Intrinsic Shift for the Methylene Protons. If it is assumed that the methylene protons of **1** would have the same intrinsic shift in the absence of a ring current effect, then these proton resonances would be expected to occur at ca. δ 5.5.³⁵ This appears to be an anomalously low-field position for such methylene protons; however, great care must be taken in choosing model compounds for comparison.

Two extreme models can be considered for the intrinsic shift of the methylene protons of **1**. These are the hypothetical cations **7** and **8** in which no cyclic delocalization occurs. Neither of these



cations exists, but the chemical shifts of the methylene protons of each can be estimated by comparison with related systems. Thus the benzenium cations **9** can be considered as models for **7**. Cation **9**, $R = Me$, where it is possible to get a completely frozen spectrum, exhibits a methylene proton resonance at 5.05 ppm.³⁶ This is not a perfect model as it is a dienyli rather than

(35) The exo proton, which is found at δ 5.13, is calculated to be shielded by ca. 0.2 ppm. This gives an intrinsic shift at δ 5.3.

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a trienyli cation. On the other hand, the bicyclo[3.1.0]hexenyli cations **10** can be considered as models for **8**. There is some charge delocalization into the two external cyclopropane bonds of these cations, but the internal bond is not delocalized.³⁷ The methylene protons of the parent ion **10** are reported to resonate at 3.73 and 4.03 ppm.³⁸ Bearing in mind that this bicyclic system has an allyli rather than pentadienyli cation and that there is charge leakage to C_6 , it is clear that the ca. 5.5 ppm intrinsic shift observed for **1** cannot be accounted for on the basis of a fully formed cyclopropane bond. It would appear that the most appropriate model for the chemical shift of the C_8 protons in the absence of a ring current is the open rather than a closed form of the cation.

Conclusions

We have shown it is possible to account for the chemical shift differences of the C_8 methylene proton resonances of the homotropylium ion on the basis of two models. Local anisotropic effects are nearly as important as the induced ring current in determining the chemical shift differences of these methylene protons.

Importantly, we have shown that both protons are shielded as a result of the induced ring current. This surprising result means that the intrinsic shift of these protons in the absence of an induced ring current is at low field. To account for this shift it is necessary to assume that the lengthening of the C_1 - C_7 bond in the homotropylium ion causes a loss of any cyclopropane character of the C_8 methylene group. As the magnitude of the charge induced on the system varies and the homoaromatic type delocalization of the cyclopropane bond is increased, then it would appear that there is a systematic loss of the characteristic properties associated with the three-membered ring.

Finally, we would note that, while it is possible to account for the NMR spectrum of the homotropylium cation, the situation is complex, even in this case where the geometry is known with certainty. We would urge caution in the complete reliance on NMR properties of a system to classify it as being homoaromatic. Safer criteria for homoaromaticity are those based on structural and thermochemical studies.^{39,40}

Experimental Section

¹H NMR spectra were obtained with a Bruker WP-80 spectrometer. The Lewis acids were purified by distillation under vacuum prior to use, and all manipulations with them were carried out under an argon blanket.

Preparation of Lewis Acid Complexes of 2. Carefully purified 2,3-homotropone (**2**) was weighed into a dried NMR tube (typically 12–15 mg) and CD_2Cl_2 (1 mL) added. The solution was cooled to $-78^\circ C$ and the appropriate Lewis acid added from a weighed 100- μL syringe. The weight of Lewis acid used was adjusted so that a 10-fold molar excess of the acid was present. Gaseous Lewis acids were condensed directly into the cooled NMR tubes. The samples were mixed and the NMR spectra recorded at $-80^\circ C$ shortly after preparation.

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Registry No. **1**, 32731-02-5; **2**, 61333-71-9; **5**, 3818-97-1; **5-SnCl₄**, 91606-82-5; **5-TiCl₄**, 91606-83-6; **5-BF₃**, 91606-84-7; **5-SbCl₅**, 91606-85-8; **5-BCl₃**, 91606-86-9; **5-BBr₃**, 91606-87-0.

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(40) In this regard it is of interest to note the conflicting evidence reported for 1,6-dihydro-1,2,4,5-tetrazines. From ¹H NMR studies⁴¹ it was concluded that these tetrazines are neutral homoaromatic systems with π -overlap between N_1 and N_5 . Subsequent X-ray diffraction studies showed that the distance between these two atoms was too large for there to be any significant interaction.⁴²

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