

The Homotropylium Ion and Homoaromaticity

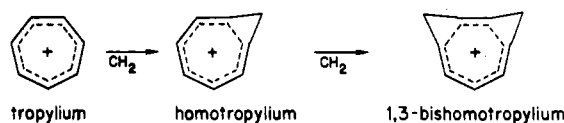
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Saul Winstein first introduced the concept of homoaromaticity in a generalized way in 1959.¹ In the ensuing 25 years there has been an impressive amount of work in this area and a large variety of systems have been deemed homoaromatic.² The importance of homoaromatic delocalization in molecules and ions has been continually questioned,³ however; recently two groups in particular have suggested that homoaromaticity is only important with a limited number of medium ring cations.⁴ In view of these suggestions it is appropriate to examine the evidence for the importance of homoaromaticity even with these cations. In undertaking this reexamination one is mindful of the strident calls that have been made for the abolition of the term aromatic⁵ and the considerable difficulties in defining just what is an aromatic molecule.⁶

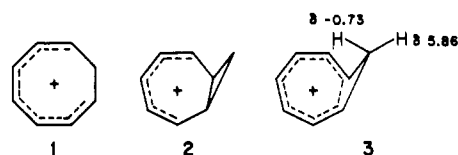
A homoaromatic molecule or ion can be conceptually derived by homologation of an aromatic molecule or ion.¹ Thus the homotropylium ion, or more correctly the monohomotropylium ion, can be derived by the insertion of a CH₂ group into the seven-membered ring of the tropylium ion. Likewise bishomotropylium ions can be derived by the insertion of two CH₂ groupings. The important feature of these homologated systems is that the aromatic properties of the parent system are maintained. In other words a cyclic array of $4n + 2 \pi$ electrons is considered to be involved in an homoaromatic molecule with a "through space" interaction projected between the noncontiguous π centers flanking the bridging methylene group.



The homotropylium cation is a particularly important example of homoaromaticity. While it was not the first example, it early became the pièce de résistance for proponents of homoaromaticity and it has certainly received more attention than any other homoaromatic molecule or ion. For example, at this present time over 40 substituted derivatives of the homotropylium cation have been reported,⁷ and more are implicated as transients in the electrophilic additions to cyclooctatetraene.⁸

Pettit and co-workers first isolated the parent homotropylium ion as a stable salt in 1962 by reacting cyclooctatetraene with strong acids.⁹ The salt obtained by this reaction was characterized by a variety of techniques, but the key evidence used to propose its structure was the ¹H NMR spectrum.¹⁰ This was remarkable in that the resonances corresponding to the

two protons of a methylene group were separated by 5.86 ppm with one resonance occurring at -0.73 ppm, a strikingly high-field position for a proton on a carbocation. On the basis of this NMR spectrum, Pettit rejected the classical cyclooctatrienyl cation 1 from consideration and instead suggested that the data was consistent with a bicyclo[5.1.0]octadienyl structure 2, in which extensive delocalization of the internal cyclopropane bond had taken place. Pettit further represented this ion as 3 to indicate that the delocalization was cyclic, involving six electrons. This formulation, which will be used throughout this Account, stressed the relationship of the ion to the aromatic tropylium ion. As a result of this electronic structure, it was suggested that a ring current was induced when the ion was in a magnetic field, resulting in the large chemical shift difference between the exo and endo C₈ proton resonances.



Subsequent work enhanced the original suggestions for the electronic structure of the homotropylium ion. High-field ¹H NMR and ¹³C NMR studies of the homotropylium ion have been reported, and comparison of the observed chemical shifts with those of the appropriate model compounds supported the delocalized model for the homotropylium ion.^{10,11} The NMR spectra of metal carbonyl complexes 4 and 5 were particularly important in reinforcing the homoaromatic view of the electronic structure of 3.¹² The molybde-

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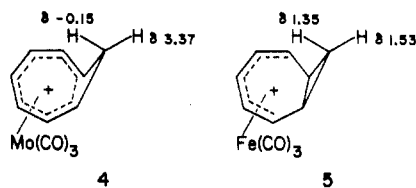
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Ronald F. Childs obtained a B.Sc. in Applied Chemistry in 1963 from the University of Bath, England. Moving to Nottingham, he worked with Alan W. Johnson on an azepine problem for a Ph.D. He spent 2 years at UCLA working with Saul Winstein before taking a position at McMaster University as an Assistant Professor in 1968. He is currently Professor of Chemistry and Dean of the Faculty of Science at McMaster and his research interests span the gamut from carbenium ions through solar energy storage to desalination.

num complex 4 with the six-electron demand of the metal was suggested to be homoaromatic while a localized structure was proposed for the iron complex 5 in which only four electrons are donated to the iron. The ^1H NMR spectra of 4 and 5 were in accord with these suggestions. The diamagnetic susceptibility exaltation of the homotropylium ion was found to be large and comparable in magnitude to that of the tropylium ion.¹³



The question arises as to what is the most appropriate criterion for homoaromatic delocalization. In terms of aromaticity itself, several criteria have been proposed. These include molecular structure, molecular energetics, and various spectroscopic and particularly magnetic properties. There has been extensive discussion on the most appropriate criterion and it will not be repeated here.⁶ Suffice it to say that the presence of an induced ring current in a molecule, whether it be detected in its ^1H NMR spectrum or determined directly with diamagnetic susceptibility measurements,¹⁴ is but one and indeed a relatively poor criterion of aromaticity.¹⁵ For example, several years ago we determined the volume diamagnetic susceptibilities and susceptibility exaltations of 7-substituted cycloheptatrienes.¹⁶ The disturbing feature of these results was that the exaltations were in some cases larger (more negative) than those found for benzene itself! Thus 7-*tert*-butylcycloheptatriene had an exaltation of $-14.8 \times 10^{-6} \text{ cm}^3/\text{mol}$ as compared to that of benzene of $-13.7 \times 10^{-6} \text{ cm}^3/\text{mol}$. On this magnetic criteria 7-*tert*-butylcycloheptatriene should be classified as a homobenzene, it seemingly being as aromatic as benzene. On the other hand, examination of the energetics¹⁷ and molecular geometry¹⁸ of related cycloheptatrienes suggests that cyclic delocalization is not important in determining the properties of these molecules.

As was indicated above, essentially all the evidence used to substantiate the claim that the homotropylium cation is homoaromatic lies in its magnetic properties and it is hard to find additional types of information. The stereoselective deuterations of cyclooctatetraene and its derivatives and their subsequent ring inversion processes are understandable in terms of the homo-

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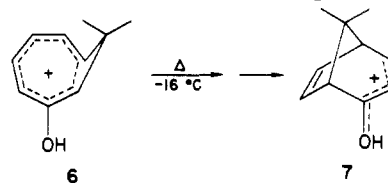
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aromatic formulation but in their own right do not establish the electronic structure of these ions.^{19,20} Solvolytic studies on a dibenzobicyclo[5.1.0]octyl system have been reported, but the interpretation of these is difficult because of the conformational properties of these systems.²¹ Feldman and Flythe have attempted to measure the reduction potential of the homotropylium ion although again the results are not definitive.²²

Perhaps the most important non-NMR experiment is the determination of the UV spectra of these ions.¹⁹ The absorption maxima of the homotropylium ion occur at considerably shorter wavelengths than would be expected either for the cyclooctatrienyl cation, 1, or a bicyclo[5.1.0]octadienyl cation with a fully formed cyclopropane bond.²³ Instead the UV spectrum is much more closely akin to that of the tropylium ion. On the basis of the long-wavelength absorption band and HMO treatment of the homotropylium ion, Winstein estimated the 1,7 bond order to be 0.56. This can be compared to a π bond order of 0.64 for the tropylium ion. It must be remembered, however, that UV spectra are generally not considered to be a good criterion of aromaticity let alone homoaromaticity.⁶

This heavy reliance on magnetic properties to define the electronic structure of a molecule or ion is not unique to the homotropylium cation. The same situation can be found with the majority of other supposedly homoaromatic systems. In fact, in most cases the *only evidence* presented to substantiate the claim of homoaromaticity is an analysis of the ^1H NMR spectrum of the species in question. Indeed, in his recent review, Paquette goes further than this and implicitly defines a homoaromatic molecule or ion as being one which can maintain some form of ring current.^{2c}

To compound the unease we had about the almost exclusive use of magnetic criteria for homoaromaticity, we were surprised to find recently that the substituted homotropylium cation 6 was less stable than the non-aromatic cation 7.²⁴ The ^1H NMR spectrum of 6 was



quite consistent with the presence of an induced ring current; however, the rearrangement suggested at first glance that there is no large thermodynamic stability associated with the homotropylium cation. In summary, we felt that the question of the homoaromaticity of the homotropylium cations merited renewed attention and embarked on a more quantitative approach to resolving this situation.

More Recent Work

Structural Studies. Molecular geometry has long been used as a criterion for aromaticity. Attention is

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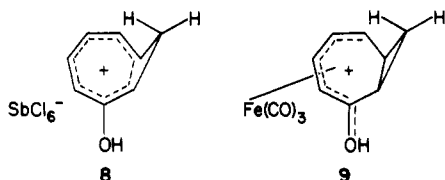
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usually given to the planarity of the ring atoms and degree of alternation of bond lengths in a cyclic polyene.^{25,23}

The adaptation of such criteria to a homoaromatic system is not straightforward. Bond equalization in the polyenyl segment of the molecule or ion would still be expected. However, in contrast to a regular aromatic molecule, a marked nonplanarity of the basal plane is required in order to optimize interaction of the cyclopropane internal bond with the polyenyl system.²⁷ The internal cyclopropane bond should be longer than encountered for a normal cyclopropane and the lengthening of this bond should be accompanied by a corresponding shortening of C-C bonds between the cyclopropyl carbons and the first atoms of the polyenyl system.

Two complimentary approaches have been used to determine the structure of homotropylium cations. These involve the experimental approach of X-ray diffraction techniques applied to isolated salts²⁸⁻³⁰ and theoretical calculations.^{27,31-34}

Crystallographic Studies. Recently we have been able to obtain the crystal structure of 2-hydroxyhomotropylium hexachloroantimonate (8).²⁸ This ion exhibits a similar type of ¹H NMR spectrum to that of the parent ion although the chemical shift difference between the C₆ exo and endo protons is only 3.10 ppm.^{24,35} While this chemical shift difference is smaller than that of the parent ion, it is still substantial when compared to that of the iron complex 9 where the two C₈ protons have the same chemical shift.^{24,35} The reduction in the chemical shift difference of the C₈ protons of 8 as compared to 3 results from a partial removal of the positive charge from the ring system onto the oxygen atom.⁷



The structure of 8 is shown in Figure 1.³⁷ It exists with the basal carbons forming a shallow boat and with the bridging carbon tipped over this ring. This nonplanar arrangement of the basal carbons of 8 is consistent with earlier suggestions based on a coupling constant analysis.¹⁰ The C₁-C₇ bond distance of 1.626 Å (8) is significantly longer than that of a normal cy-

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(37) The cation is disordered in the crystal lattice, and the structure was solved by assuming the ion to be bisected by a minor plane through C₄, C₈ and the midpoint of the C₁-C₇ bond.

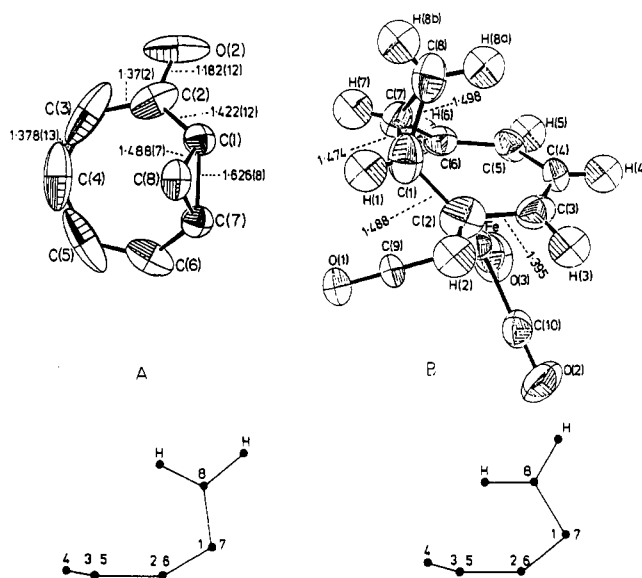
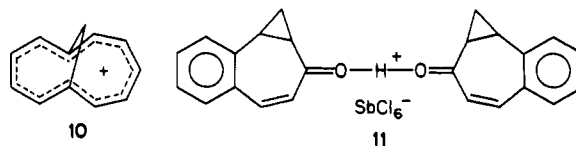


Figure 1. Structures of (A) 2-hydroxyhomotropylium hexachloroantimonate (3) and (B) bicyclo[5.1.0]octadienyliron tricarbonyl tetrafluoroborate (8).

clopropane (1.510 Å),³⁸ whereas the external C₁-C₉ (C₇-C₈) bond distance is shorter. These interatomic distances indicate involvement of the C₁-C₇ bond and not the external cyclopropane bonds in charge delocalization in 8. The shortened C₁-C₂ (C₆-C₇) bonds in 8 also support this suggestion. Solid-state CPMAS ¹³C NMR spectra of crystalline samples of 8 were found to be essentially identical with those obtained for the cation in solution, indicating the cation has the same structure and charge distribution in both phases.²⁸

To compare the structure of 8 with a comparable nonhomoaromatic cation, we have also determined the structure of 5 as its BF₄⁻ salt.³⁰ From NMR evidence it was concluded that this had a bicyclo[5.1.0]octadienylum structure and this is fully borne out by the X-ray crystallographic study (Figure 1). The marked difference in the C₁-C₇ bond distances in 8 and 5 is quite consistent with homoaromatic delocalization in the former cation.

The only other structure determination of a potential homotropylium ion is that reported for 10 by Simonetta and co-workers.²⁹ This ion, which was formulated by Vogel and co-workers to be a perturbed [11]annulenium system³⁹ and by Masamune and co-workers to be a benzohomotropylium system,⁴⁰ was found to have a long C₁-C₆ interatomic distance (2.293 Å). This large separation coupled with a rather flat peripheral carbon system suggested that transannular interactions in this cation are not important.



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Up to the present time we have not been able to obtain suitable crystals of the parent homotropylium for X-ray diffraction studies. Attempts to prepare other crystalline derivatives have met with some surprises. For example, the unusual salt 11 was isolated in attempts to crystallize the corresponding 4,5-benzo-2,3-homotropone.⁴¹

Theoretical Studies. The other approach used to investigate the structure of the homotropylium cation involves theoretical calculations.^{27,30-34} The most complete examination of the homotropylium energy surface is that reported by Haddon.²⁷ The minimum-energy geometry of **3** calculated by Haddon and that obtained experimentally for **8** are remarkably similar. The C₁-C₇ bond was again found to be relatively long for a cyclopropane (1.578 Å STO-2G; 1.621 Å MINDO-3). A further energy minimum was found on the homotropylium cation surface by Haddon with a somewhat longer (2.303 Å) C₁-C₇ bond distance. This species, which some 6-10 kcal/mol less stable than the former structure, was suggested would be favored by electron-donating substituents at C₁ and C₃.

Bader and co-workers have recently applied their topological theory of molecular structure to homoaromaticity and the homotropylium ion in particular.³³ Two points of note emerge from their treatment. First, the critical points of the C₁-C₇ bond and cyclopropane ring are very close. This means that stretching of this bond rapidly leads to its rupture, in contradiction with the second minimum-energy structure found by Haddon on the homotropylium energy surface. Second, the C₁-C₈ and C₇-C₈ bonds have lost most of their cyclopropane character in **3** and can be regarded best as conventional C-C single bonds.

The agreement between the measured and calculated structures of these homotropylium ions is remarkable and suggests that the structures found are likely to be general for these cations. The structures of **3** and **8** fully meet the structural criteria outlined earlier for homoaromaticity.

Validity of the Ring-Current Criterion for Homoaromaticity

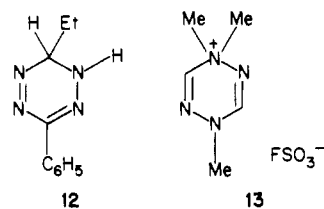
With the geometry of the homotropylium ion defined, it is appropriate to see whether a ring current model can adequately account for the chemical shifts of the C₈ protons. Both Winstein¹⁹ and Pettit⁴² have carried out such calculations, but in each case a planar arrangement of the basal carbons in the "seven-membered" ring was assumed.

Both an induced ring current and local anisotropy are important in determining the chemical shifts of protons abutting an aromatic ring.⁴³ In the present case, the local anisotropies of the ring carbons of a homotropylium cation have not been measured and instead the local anisotropies of the tropylium ring carbons were used in the calculations.⁴⁴ Making this assumption and using a full six-electron ring current, the chemical shift difference between the exo and endo C₈ protons was

calculated to be 6.9 ppm.⁴⁵ Local anisotropy contributed 3.0 ppm (43%) and the ring current 3.9 ppm (57%) to this total difference. The agreement between this calculated chemical shift difference and the 5.86 ppm observed experimentally is reasonable considering the approximations made.

Despite the reasonable agreement between the calculated and observed chemical shift differences, we were disturbed to find that *the calculations indicated that both the endo and exo protons were shielded*. With the conditions specified above, the endo proton was shielded by -8.4 ppm and the exo by -1.5 ppm. This is surprising as the conventional view is that the large separation in chemical shifts of the C₈ protons arises from a shielding of the endo and deshielding of the exo proton resonances. Taking the argument one stage further, it means that the intrinsic shift of the C₈ protons in the absence of this shielding due to the ring current is about 6 ppm, an anomalously low-field position. This shift is comparable to that of the CH₂ group of a benzenium ion,⁴⁶ suggesting that the special magnetic properties normally associated with a cyclopropane ring are lost in the homotropylium ion. This conclusion supports the findings of Bader and co-workers mentioned above.

Overall the results of these ring-current calculations suggest that considerable caution should be used in the use of chemical shifts as a criterion of homoaromaticity. The large contribution of local anisotropies to the chemical shift difference and the unexpected shielding of both protons clearly indicate the dangers of the simplistic use of an induced ring current model. In this context it is instructive to consider the heterocycles **12** and **13**. Proton chemical shifts were used initially to suggest that these molecules were homoaromatic. Recent structural work would clearly seem to refute these claims in as much as in both species the homoconjugate distances are very large.⁴⁷



Energetics

Molecular energetics are a further widely used criterion of aromaticity.⁶ Qualitatively, an aromatic molecule is expected to possess "unusual stability". Quantitatively, there are difficulties in applying thermodynamic data to define aromaticity, particularly in the choice of appropriate reference compounds. Such difficulties are of course not unique to a thermochemical approach.

One approach to the molecular energetics of the homotropylium cation has been to compare its energy relative to the unknown, planar, nonaromatic cyclooctatrienyl cation, **14**. Homotropylium cations undergo

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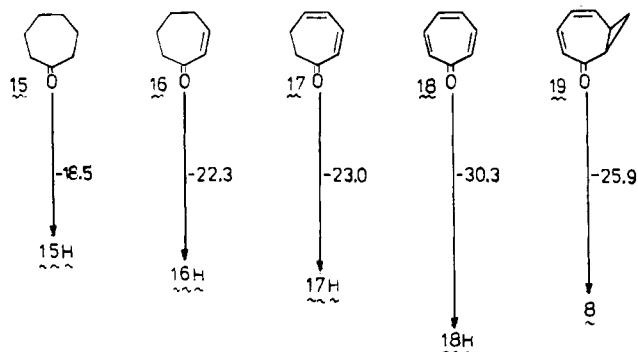
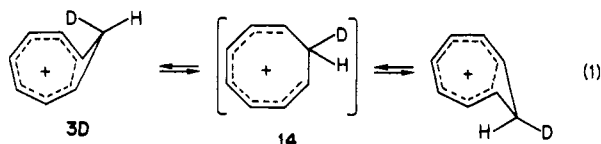


Figure 2. Heats of transfer of various ketones from CCl_4 to FSO_3H . All values shown are in kilocalories/mole.

a molecular rearrangement that interconverts C_8 exo and endo substituents.^{19,23,48-52} This process has been amply demonstrated to involve a ring inversion rather than a more complex pathway, and as such the planar species 14 cannot be lower in energy than the transition state for this rearrangement.



The activation barrier (ΔG^\ddagger) for the isomerization of 3D (eq 1) is 22.3 kcal/mol.²¹ Thus the homotropylium ion is at least 22.3 kcal/mol more stable than 14. However, before attributing all of this difference in stability to resonance stabilization of 3, it should be remembered that other factors such as the difference in strain energies of 3 and 14 have to be taken into account. This also has to be done of course in the case of 6 and 7 discussed earlier. The barrier for this reaction is substituent dependent with electron-donating substituents at C_1 lowering the barrier while electron-donating substituents at C_2 and C_4 raise the barrier as compared to the 22.3 kcal/mol observed for the parent system.^{24,48-52} These substituent effects are understandable in terms of the relative openness of the homoconjugate bond in the ground states of the homotropylium cations and the relative stabilities of the planar cyclooctatrienyl cations involved in the inversion reactions. In contrast to the effect of ring substituents, groups at C_8 have little effect on the barrier to inversion, confirming that there is little positive charge at this carbon in homotropylium cations.⁴⁹ Large substituents at C_8 normally prefer to be in the exo position.

In a more direct approach to measuring the energetics of homoaromaticity in homotropylium ions, we have measured the heats of protonation of a series of unsaturated ketones.⁵³ The heats of transfer (ΔH_{tr})⁵⁴ from CCl_4 to FSO_3H of some seven-membered ring ketones

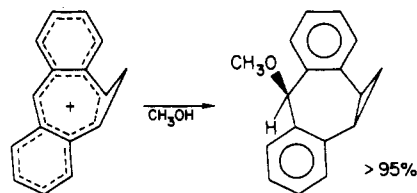
are summarized in Figure 2. A typical series of results can be seen with the ketones 15, 16, 17, and 18. The introduction of the first double bond into the seven-membered ring results in a substantial increase in ΔH_{tr} . A further modest increase is observed on going to the dienone 17. In the absence of any special stability of the ion 18H, the introduction of the third double bond in this series should produce only a further very modest increase in ΔH_{tr} . Instead, as can be seen, a very large increase was observed. This discontinuity in behavior is naturally associated with the aromaticity of 18H. A similar pattern is observed with the series 15, 16, 17, and 19. The marked discontinuity in this latter series indicates that 8 is more stable than would have been expected in the absence of homoaromatic stabilization of the ion. The magnitude of the increase in ΔH_{tr} observed on introduction of the cyclopropyl (17 \rightarrow 19) is some 40% of that observed between 17 and 18. Thus, while in the homotropylium series homoaromaticity has a measurable thermodynamic effect, it does not seem to be as important a factor as aromaticity itself.

In closing this section it should be remembered that the homotropylium ion is but one energy minimum on the C_8H_9^+ energy surface and there are many other possible isomeric cations. Jefford has examined part of this energy surface using MINDO-3 calculations.⁵⁵

Further Comments on the Electronic Structure of Homotropylium Ions

Further insight into the structure, stability, and charge distribution of homotropylium ions can be obtained from a consideration of some of their reactions. These reactions will not be exhaustively summarized here, but rather two types will be singled out that are particularly informative about the electronic structure of these ions.

Nucleophilic capture of homotropylium ions could be regarded as a trivial reaction; however, an important feature of these reactions is that irrespective of whether attack occurs at C_1 , C_2 , or C_4 , the nucleophile approaches the cation from the more hindered endo side.^{21,49,56} The preference for attack of the nucleophile from the most hindered side of the ring system suggests that the symmetric electron distribution at the C_1 - C_7 bridge is reflected at the remaining carbons of the homotropylium ring.



Degenerate Rearrangements. There are two types of degenerate rearrangements that occur with homotropylium ions. The first is the ring inversion process that has been mentioned earlier. The second type of degenerate rearrangement encountered with homotropylium cations is a circumambulation of C_8 around the "seven-membered" ring of these cations.⁵⁷ In

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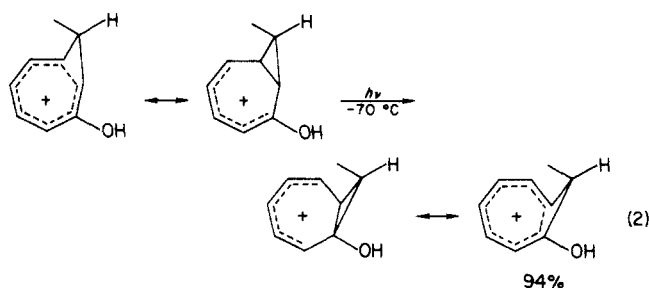
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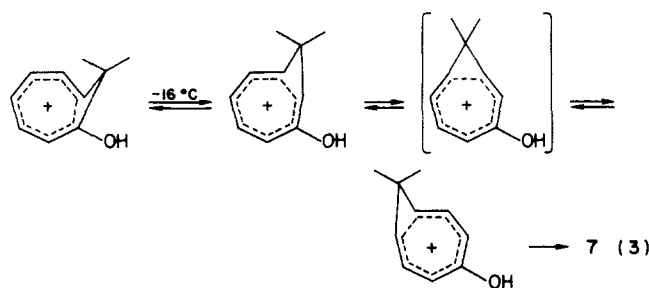
contrast to the extremely facile perambulations of the cyclopropyl around the bicyclo[3.1.0]hexenyl cations, this type of reaction does not occur readily with homotropylium cations. Indeed, Berson and Jenkins have shown that the barrier to such a circumambulation in the parent cation must be greater than 26–27 kcal/mol.⁴⁸

There are two reasons why this type of circumambulatory rearrangement is difficult in the homotropylium cations. First, the transition state for the migration involves the complete formation of a bond between C₁ and C₇ of the homotropylium ring and the development of a substantial fraction of the positive charge at C₈. This involves a disruption of the homoaromatic nature of the ion in contrast to the situation with the bicyclo[3.1.0]hexenyl cations where the internal C₁–C₅ bond is already formed and positive charge is delocalized to C₆ in the ground state. A second reason for the high barrier is that the process if it were to occur would involve a suprafacial 1,6 sigmatropic shift with retention of configuration at C₈ during the migration. This motion that has the effect of interconverting the relative positions of the exo and endo substituents is a non-least-motion process.

This orbital-symmetry/least-motion restriction to circumambulation should be lifted in the first excited state as is illustrated in the stereoselective reaction shown in eq 2.^{51,24}



Hehre has suggested on the basis of calculations that the barrier to thermally induced circumambulations could be substantially reduced by the presence of charge-stabilizing substituents at C₈.³³ This is indeed the case as is shown by the example in eq 3.²⁴ No such thermal reactions take place with simple systems in the absence of the *gem*-dimethyl group at C₈. Scott and Brunsvold have reported one example where a C₈ unsubstituted ion undergoes migration, but in this case the reaction appears to be helped by steric factors associated with a three-carbon bridge between C₁ and C₇.⁵⁸



No stereochemical information is known about any of these thermally induced circumambulations. Hehre's calculations indicate that there is a considerable preference for the migration to occur by the least motion allowed, orbital symmetry forbidden, inversion mechanism.³¹

Charge Distribution. These circumambulatory walk reactions allow the charge distribution in the homotropylium ring to be examined experimentally. By allowing a circumambulation to occur in a substituted ion, the various site preferences for the substituent can be obtained. Such an approach is complicated by the occurrence of further isomerization reactions to other bicyclic cations, but results are available with methyl and hydroxy substituents on the "seven-membered ring" and a dimethyl grouping at C₈ to permit circumambulation. In each case the charge stabilizing methyl or hydroxy substituents prefers to reside at C₂(C₆) or C₄. The C₁(C₇) and C₃(C₅) substituted isomers are a minimum of 1 kcal/mol less stable than the C₂ and C₄ isomers.^{7,24,59} These experimental results stand in direct opposition to the early suggestion of Winstein based on HMO calculations.^{2a}

Concluding Remarks

At the outset of this Account attention was drawn to the limited amount of definitive information available to support the importance of homoaromatic delocalization in determining the properties of a molecule or ion. At least for the homotropylium ion recent work has changed this position and there is now a considerable amount of experimental and theoretical information that all indicates that this cation can indeed be formulated as being homoaromatic. Homoaromatic delocalization in the homotropylium cation and its derivatives has measurable effects on the structure, energy, and reactions of these ions.

On the other hand, it has also been shown from a detailed investigation of the chemical shifts of the bridging methylene protons of the homotropylium cation that only 60% of the chemical shift difference between the exo and endo proton resonances can be accounted for on the basis of an induced ring current. In addition, in contrast to all previous expectations, both proton resonances were found to be shielded. It is clear that extreme caution should be exercised in the use of magnetic properties as criteria of homoaromaticity and a much broader range of techniques should be used to substantiate the claims for homoaromaticity in other systems. Hopefully a more cautious approach to homoaromaticity will result in fewer "recalls" in the future.

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