

where v is the local velocity going through the crossing seam. In our case the simple Landau-Zener theory is not adequate since the position of the crossing seam depends on vibration, but we do see a rapid drop in the cross section with increasing translational energy as is predicted by the theory. Because the crossing seam depends on vibration, the cross section can be expected to depend on the initial vibrational energy, although it is difficult to predict which way the dependence will go.

The fragmentation results present other interesting problems. According to the modified stripping model which works well for the energy distributions of the products, any translational energy in excess of the vertical threshold goes into translational energy of the product ions. This implies that the product ions are formed with a constant internal energy ($E_{\text{vert}} - E_{\text{ad}}$) independent of the initial translational energy. The fragment ratios should then be independent of translational energy. The results in ref 11 which confirm this model were done on $\text{SbF}_5 + \text{TDMAE}$ at energies below 6.1 eV, below the lowest energies in Figure 7. It is possible that the much higher ionization potential of TBBA requires a much harder collision for the reaction to occur. In the case of TBBA the energy required for dissociation of the ion product is quite small so only a small fraction of the initial translational energy is required. The fact that reactant vibrational energy does not affect the dissociation may indicate that the dissociation occurs immediately after the electron transfer in a direct process. Since

the amount of vibrational energy in the reactants is much smaller than the amount of translational energy, we may simply not be able to see the effect. It may be that the choice of products depends on more than one ionic surface. Thus the system can miss the first jump, remain on the covalent surface, and then jump to an ionic surface which is dissociative asymptotically. It is very difficult to estimate the absolute cross section for out reactions, but we guess that it is in the range of 10^{-3} – 10^{-1} Å² depending on the system and energy. This is small enough so that many nonionic processes can occur at the same time as the electron-transfer reaction.

Our experimental results fall into a simple pattern which is in qualitative agreement with what is known about charge transfer and chemical dynamics. The results are quite different from those obtained for the halide transfer reaction 1. The cross sections for the halide transfer may be very sensitive to vibration near the threshold but are insensitive at higher energies. When fragmentation occurs, the product ratios depend very strongly on vibrational energy in the reactants.

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Homotropylium Cation Revisited: POAV and 3D-HMO Analysis

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Abstract: Homoconjugate bonding was characterized as: "... orbital overlap of a type intermediate between σ and π ", by Winstein over 30 years ago. Nevertheless, the concept has remained controversial and the molecular and electronic structure of the homotropylium cation (**1**, the *prima facie* example of this phenomenon) remains in doubt. Previous theoretical calculations and experimental studies of derivatives of the molecule have produced evidence for two minima on the potential surface, with homoconjugate bond distances $R_{1,7} = 1.6$ and 2.3 Å. In the present paper we report the results of Hartree-Fock (HF) geometry optimizations of the molecular structure of **1**. At the HF level the same two minima are located, but when electron correlation effects are included in the wave function, the potential surface is totally transformed and a single minimum results with an $R_{1,7}$ value of 1.7–2.0 Å. The structures obtained by calculation are further analyzed with the POAV and 3D-HMO theories. This allows the development of a unified picture of homoaromatic character as embodied in **1**. The results of the analysis provide a natural explanation of the molecular and electronic structure of the homotropylium cation, the distance dependence of the homoconjugate bond, the electronic spectrum, and the ring current as observed in the NMR chemical shifts and diamagnetic susceptibility exaltation. The concept of homoaromatic character as embodied in the homotropylium cation is supported by this study. The present analysis differs with all previous experimental interpretations and calculations as to the details.

Homoaromatic character has proved to be a particularly enduring concept in organic chemistry.¹ Qualitative molecular orbital theories²⁻⁴ provided a satisfactory account of the occurrence

(and nonoccurrence) of this phenomenon some time ago, but quantitative data have proved elusive.

The best characterized homoaromatic species at the present time is probably the homocyclopropenylium cation.⁵ An X-ray crystal structure⁶ of a simple derivative yielded a homoaromatic bond length of 1.775 Å, and an NMR study⁷ of the parent system provided a bridge-flipping barrier of 8.4 kcal/mol. These parameters were fairly well reproduced by semiempirical MINDO

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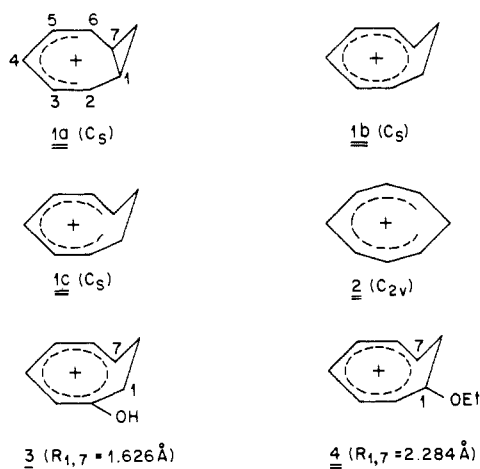
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calculations,^{4c,8} but not by the early nonempirical studies. A flexible basis set together with allowance for electron correlation effects were found to be essential ingredients in achieving a satisfactory description of the potential energy surface of the homocyclopropenylium cation.⁹

Nevertheless, it is generally agreed that the *prima facie* example of homoaromatic character is provided by the homotropenylium cation (**1**).^{1,10,11} The ion provides clear evidence of a substantial diamagnetic ring current,¹⁰⁻¹³ an electronic spectrum characteristic of the tropenylium cation,^{11a} and a large barrier to ring inversion (22.3 kcal/mol).^{11a} The first structural investigations of **1** employed molecular orbital calculations, and a value of about 1.6 Å was found for the length of the 1-7 homoconjugate linkage ($R_{1,7}$).^{2c,3} Subsequently, a second minimum was found on the potential surface with a calculated 1-7 distance of about 2.3 Å,¹⁴ presumably corresponding to the cyclooctatrienylium cation (**1c**).



Nevertheless, it was not until the work of Childs and co-workers^{14,15,16} that an experimental determination of the structure of a homotropenylium cation became available. These workers succeeded in structurally characterizing salts of the 2-hydroxyhomotropenylium cation (**3**, $R_{1,7} = 1.626$ Å)¹⁵ and the 1-ethoxyhomotropenylium cation (**4**, $R_{1,7} = 2.284$ Å).¹⁶ The drastic change in the homoconjugate bond distance is apparently in accord with previous predictions on the effect of electron-donating substituents on the potential energy surface of the homotropenylium cation.^{14,16} If two limiting structures are considered for the homotropenylium cation, then it is clear that the cyclopropane/pentadienyl cation structure (**1a**) will be favored by electron-donating substituents at the 2, 4, and 6 positions; conversely the heptatrienyl cation structure (**1c**) will be preferentially stabilized by substitution at the 1, 3, 5, and 7 positions. In spite of the gross structural differences between these two cations, quite large ring currents were inferred for both of these compounds on the basis of the proton NMR chemical shifts.¹⁵⁻¹⁷

In the present paper we report the results of a nonempirical molecular orbital study of the homotropenylium cation. The derived structures are analyzed with the π -orbital axis vector

(POAV) method and the 3D-HMO theory which shed new light on the homotropenylium cation and homoaromatic character in general.

Computational Section

Theoretical Structures and Energies. The selection of a theoretical technique for the quantitative assessment of the structures and energies of potentially homoaromatic molecules is critical. An important feature of homoaromaticity is the energy balance between a double bond and a three-membered ring (3-MR). An estimate of the performance of theoretical methods in this regard may be deduced from the calculated relative energies of propene and cyclopropane. For the reaction $\text{CH}_3\text{CH}=\text{CH}_2 \rightarrow (\text{CH}_2)_3$, the energies are as follows: 2 kcal/mol (MINDO/3),¹⁸ -4 (HF/STO-3G),¹⁹ 13 (HF/4-3G),²⁰ 8 (HF/6-31G*),²¹ 7 (exptl).²² It is therefore clear at the outset that MINDO/3 and minimal basis sets (STO-3G) will favor structures with a closed cyclopropane, whereas extended basis sets (4-31G) will emphasize those geometries with an open cyclopropane unit. Reference to the literature on the calculations reported for the homotropenylium cation shows this to be the case, and extended basis set calculations on this molecule find no minimum on the potential surface in the vicinity of 1.6 Å.¹⁴

The situation is more complicated in the case of the homocyclopropenylium cation where both minimal and extended basis sets greatly underestimate the strength of the homoconjugate bond.⁹ Most of the structural inadequacies of these calculations are rectified when polarization functions are included in the basis set, and the results at the HF/6-31G* level of theory are in fairly good accord with the experimental information on this system.⁹ However, the homoaromatization energy (for bridge flipping) remains seriously underestimated. In order to achieve a good description of the energetic aspects of the potential energy surface, the inclusion of correlation effects was found to be mandatory; to obtain quantitatively reliable data the energies had to be evaluated at the MP3/6-31G* level of theory.⁹ The sensitivity of delocalization and aromatic character to the inclusion of electron correlation effects in the wave function has been discussed by a number of authors, and it is clear that these effects are underestimated at the HF level of theory.²³⁻²⁸ The semiempirical MINDO/3 method provides a fairly good general picture of the potential surfaces of both molecules.^{2c,4c,14}

Much of the current controversy regarding homoaromatic character may be traced back to the application of inadequate calculational techniques; as emphasized herein, a particularly high level of theory is required for quantitative assessments of homoaromatic character.

In the present study, all geometries were calculated at the HF/6-31G+5D level of theory.^{21,29} Optimized structures were obtained at 0.1-Å (or less) intervals along the homoconjugate bond length ($R_{1,7}$) for the range $1.6 \text{ \AA} \geq R_{1,7} \geq 2.6 \text{ \AA}$. These geometries were then used for single-point MP2 and MP3 calculations^{29,30}

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Table I. Energies for **1** at HF Optimized Geometries Obtained with the 6-31G+5D Basis Set

1-7 distance (Å)	total (hartrees)			relative (kcal/mol)		
	HF	MP2	MP3	HF	MP2	MP3
1.60	-307.882 01	-308.875 39	-308.918 83	-14.5	-29.0	-23.2
1.62	-307.882 19	-308.876 64	-308.919 61	-14.6	-29.8	-23.6
1.64	-307.882 30	-308.878 24	-308.920 57	-14.7	-30.8	-24.2
1.660 ^a	-307.882 32	-308.879 45	-308.921 25	-14.7	-31.6	-24.7
1.70	-307.882 29	-308.881 80	-308.922 51	-14.7	-33.1	-25.5
1.80	-307.882 28	-308.886 11	-308.924 70	-14.7	-35.6	-26.8
1.90	-307.883 21	-308.887 85	-308.925 83	-15.2	-36.9	-27.6
2.00	-307.884 87	-308.886 85	-308.925 82	-16.3	-36.2	-27.5
2.10	-307.886 85	-308.884 35	-308.925 25	-17.5	-34.7	-27.2
2.20	-307.888 36	-308.881 15	-308.924 17	-18.5	-32.7	-26.5
2.290 ^a	-307.888 82	-308.877 61	-308.922 42	-18.8	-30.4	-25.4
2.40	-307.887 73	-308.872 61	-308.919 26	-18.1	-27.3	-23.4
2.50	-307.884 80	-308.866 92	-308.914 92	-16.2	-23.7	-20.7
2.60	-307.879 81	-308.859 93	-308.908 99	-13.1	-19.3	-17.0
2.684 ^{a,b}	-307.858 93	-308.829 10	-308.881 92	0.0	0.0	0.0

^a HF minimum. ^b Constrained to C_{2v} symmetry.

and were further analyzed with the POAV³¹ and 3D-HMO³² models.

Results and Discussion

Structure and Energetics. The total and relative energies for **1** are collected in Table I, and summarized in Figure 1. Two minima were located on the potential surface through geometry optimization at the HF/6-31G+5D level of theory. The homoconjugate bond lengths ($R_{1,7}$) of 1.660 and 2.290 Å compare favorably with previous calculations^{2c,14} and with X-ray crystal structures of substituted derivatives (**3** and **4**)^{15,16} of the homotropylium cation.

However, as may be seen in Figure 1 the potential energy surface is completely transformed by the inclusion of electron correlation effects in the wave function (MP2 and MP3). Single minima result in both cases at $R_{1,7}$ values of 1.913 Å (MP2) and 1.949 Å (MP3). The fact that the geometries were not fully optimized with allowance for electron correlation effects is of some concern, particularly in view of the fact that in the range $1.6 \text{ Å} \leq R_{1,7} \leq 2.4 \text{ Å}$ the MP3 energy changes by less than 5 kcal/mol. This serves to reemphasize the statement that:¹⁴ "the very existence of homoaromaticity is a matter of a few kcal/mol." Thus the potential surface is extremely flat—to the point that experimental determination of the structure of **1** may be difficult. In the case of the homocyclopropenylium cation, optimization of the structure with inclusion of electron correlation effects led to a further shortening of the homoconjugate distance,⁹ and if the same effects are operative in the present instance we might expect an $R_{1,7}$ value for the homotropylium cation in the range 1.8–2.0 Å, although the confidence level of this estimate must be regarded as low.

We have previously suggested a double minimum potential surface for **1**,¹⁴ and this possibility has received support from the elegant structural studies reported by Childs and co-workers.^{15,16} The present results suggest that a new interpretation of the homotropylium cation potential surface is in order. If Figure 1 is taken at face value, then there is but one minimum on the potential surface of **1**, with a homoconjugate bond length intermediate between those found previously. The low force constant for stretching the homoconjugate bond suggests that the molecular structure will be extremely polarizable along this coordinate. It is therefore possible that the long and short homoconjugate bond lengths found experimentally in 1- and 2-substituted derivatives reflect the extreme sensitivity of the molecular geometry to electronic effects.

One-Center POAV Analysis.^{31,32} The results of the analysis of the conjugated atoms of **1** are summarized in Figure 2 in the form of the pyramidalization angle ($\theta_{\sigma\pi} - 90$)° ($\theta_{\sigma\pi}$ is the common angle

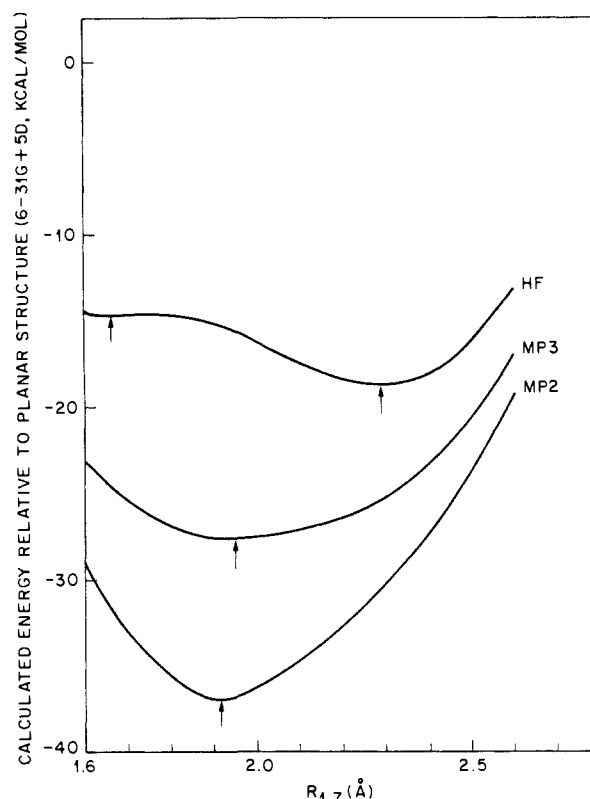


Figure 1. Energies for **1** at HF optimized geometries obtained with the 6-31G+5D basis set as a function of the homoconjugate distance. Minima are indicated by arrows; the MP2 and MP3 values were calculated by quadratic interpolation.

made by the σ orbitals to the π orbital, POAV1) and the s character m in the π orbital ($s^m p$, POAV2). The bridge carbon atoms C-1 (and C-7) show strong rehybridization from pure p ($m = 0$) π character toward sp^3 ($m = 1/3$), at $R_{1,7} = 1.6 \text{ Å}$ in reflection of the relatively intact cyclopropane unit. As the homoconjugate linkage lengthens, however, C-1 rapidly approaches sp^2 hybridization, and at large values of $R_{1,7}$ this atom exhibits the highest degree of planarization. The behavior of the other atoms is more complex, and it is apparent that in the opening of the cyclopropane ring, maximization of homoaromatic character and progression toward the cyclooctatrienylium cation is intimately linked to the state of rehybridization of all of the conjugated atoms. The furthest atom from the bridge, C-4, undergoes the most complicated rehybridization pathway and also exhibits the largest average degree of rehybridization. Similar behavior was previously noted in the bridged [10]annulenes.³¹

Two-Center POAV2/3D-HMO Analysis.³² The results of this analysis are collected in Figure 3 in the form of the ρ values (which

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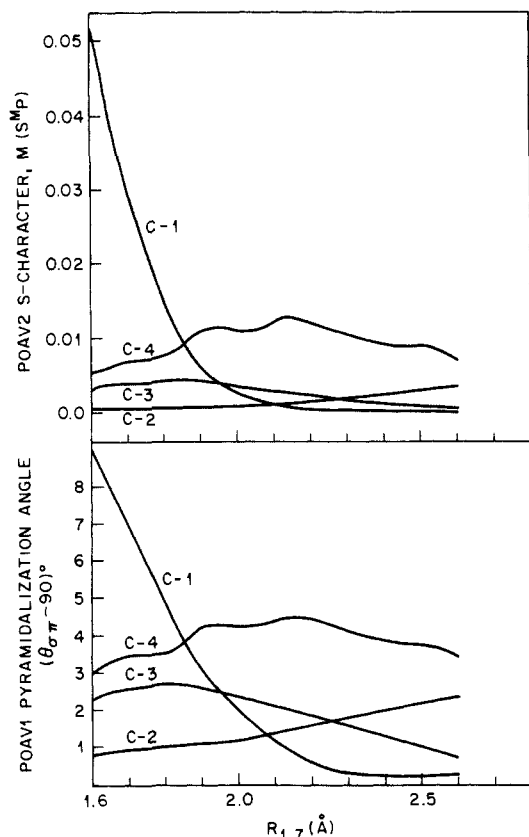


Figure 2. POAV analysis of the conjugated carbon atoms in **1** as a function of the homoconjugate distance.

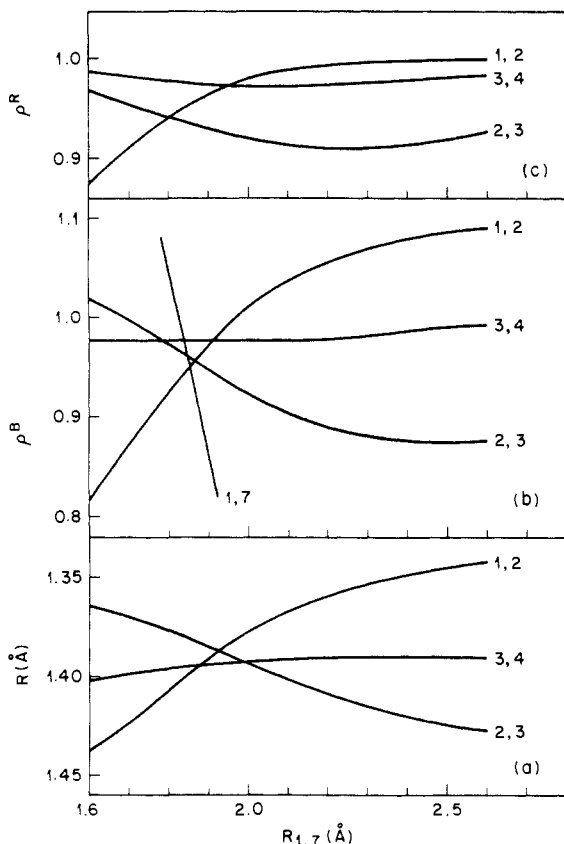


Figure 3. Conjugated bond lengths (a) and 3D-HMO reduced resonance integrals (b and c) in **1** as a function of the homoconjugate distance.

provide reduced resonance integrals $\rho\beta$ which are suitable for use in an HMO calculation), together with the calculated ring bond lengths (R). There are two sets of ρ_{ij} values: (i) those where the

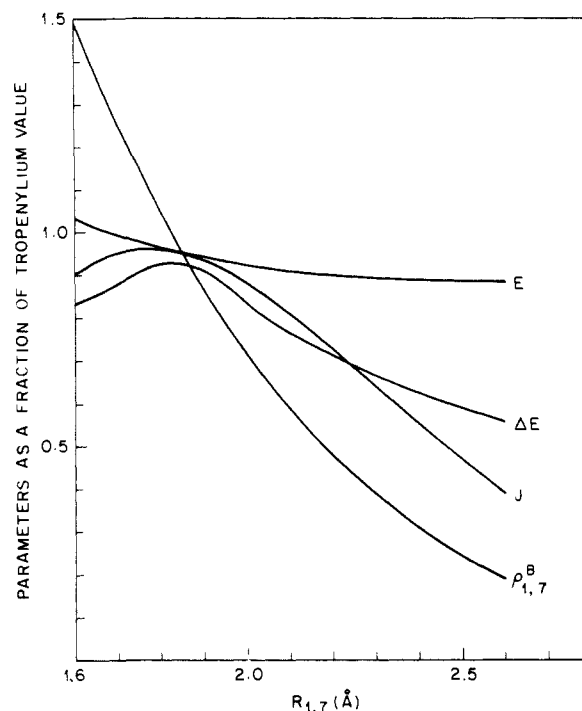


Figure 4. 3D-HMO values of the homoconjugate reduced resonance integral ($\rho_{1,7}^B$), total π -electron energy (E), HOMO-LUMO energy gap (ΔE), and ring current (J) calculated for **1** using ρ^R values, as a function of the homoconjugate distance.

calculated overlap integral (S_{ij}) is scaled by the nearest-neighbor p_π , p_π overlap integral in benzene (S^B), $\rho_{ij}^B = S_{ij}/S^B$, and (ii) those obtained by scaling with the p_π , p_π overlap integral (S^R) calculated at the bond length in question (R_{ij}), $\rho_{ij}^R = S_{ij}/S^R$. In the case of homoconjugate bonds, ρ^B is the only choice, but for conjugated bonds which possess the usual associated σ bond, either ρ^B or ρ^R may be employed. We have utilized ρ^R values in previous publications for reasons of simplicity and in order to make contact with the large body of HMO data in which the resonance integral was not adjusted for bond length.

Not surprisingly these three measures of bond strength show a strong correlation (Figure 3), but even more striking is the convergence exhibited by all three parameters in the range $R_{1,7} = 1.8$ – 2.0 Å. It is apparent that for these values of the homoconjugate bond length there is a high degree of bond length and reduced resonance integral equalization among the conjugated atoms and that this occurs at values quite typical of normal planar aromatic systems. The exception to the bond length equalization, of course, is provided by the homoconjugate linkage itself. However, considered from the standpoint of the ρ^B values of the 3D-HMO theory (Figure 3b) it may be seen that the π -orbital resonance integrals of all the bonds achieve a high degree of equalization in the range $R_{1,7} = 1.8$ – 2.0 Å.

Molecular Properties. The calculated 3D-HMO [ρ^R] total π -electron energy (E), ring current (J), HOMO-LUMO energy gap (ΔE), and $\rho_{1,7}^B$ values are given in Figure 4 (expressed as a fraction of the tropanylium cation values). The $\rho_{1,7}^B$ results indicate that the homoconjugate linkage is the strongest π bond in the molecule at $R_{1,7}$ distances less than 1.8 Å. This results from the superior orbital overlap properties of the σ components in this bond.³²

The idea that the homoconjugate bond can be stronger than a normal π bond flies in the face of the prevailing dogma,^{1,2} which has always held that a homoconjugate bond is a weakened (perturbed) π bond; nevertheless, the conclusion seems inescapable. Furthermore, the homoconjugate bond remains significant for large values of $R_{1,7}$ for the same reasons (as was found in the bridged annulenes³²).

The total fractional π -electron energy (E) does not exhibit a strong dependence on the homoconjugate distances ($R_{1,7}$). It has been shown that the resonance energy (involving a suitably scaled

π -electron energy) provides a better measure of aromatic character.³³⁻³⁹ Nevertheless, E does exhibit the same general dependence on $R_{1,7}$ that is shown by $\rho_{1,7}^B$. Furthermore, the total π -electron energy exceeds that of the tropylium cation for $1.6 \text{ \AA} \leq R_{1,7} \leq 1.7 \text{ \AA}$. The fractional π -electron energy shows a monotonic decrease as the homoconjugate bond lengthens (π -electrons destabilized). Of course, the σ -electrons will be stabilized by the opening of the apical bond angle of the incipient 3-MR. As Figure 1 indicates, the potential energy surface is a particularly delicate balance of these two factors.

The remaining two molecular properties (J and ΔE) exhibit a different dependence on $R_{1,7}$. Unlike $\rho_{1,7}^B$ and E , the ring current (J) and the energy gap (ΔE) do not exhibit a monotonic dependence on the value of $R_{1,7}$. We ascribe this dichotomy to the fact that the former quantities are ground-state properties, whereas the ring current and energy gap exhibit some dependence on excited states.^{2c} Both of these quantities obtain their maximum values around $R_{1,7} = 1.8 \text{ \AA}$, which corresponds to the region where the ρ values attain their largest degree of equalization (Figure 3). It would therefore seem that these properties are most sensitive to the extent of delocalization and provide a useful index of the degree of (homo)aromatic character. Thus, although the total π -electron energy is increased by greater values of $\rho_{1,7}^B$, the presence of one disproportionately large resonance integral serves to inhibit delocalization and apparently this is reflected in the behavior of the ring current and energy gap.

The calculated ring current is surprisingly large over the whole range of $R_{1,7}$ values; even at $R_{1,7} = 2.6 \text{ \AA}$ the ring current is 39% of that of the tropylium cation. For the range $1.6 \text{ \AA} \leq R_{1,7} \leq 1.95 \text{ \AA}$ the ring current is more than 90% of the tropylium cation value.

In relating the calculated ring current to experiment, a further factor must be considered and this relates to the relative area (S). The quantity J in Figure 4 is the bond current,⁴⁰ and for rings of equal area this would be directly proportional to the ring current (as observed in an NMR chemical shift), and to the diamagnetic susceptibility. However, the areas are as follows: **1** ($R_{1,7} = 1.660 \text{ \AA}$), 1.029; **1** ($R_{1,7} = 2.290 \text{ \AA}$), 1.102, relative to the value for the tropylium cation (benzene, $R = 1.3964 \text{ \AA}$).⁴¹ The ring current chemical shift is directly proportional to the area (S), whereas

the ring current diamagnetic susceptibility is proportional to S^2 . These factors serve to further enhance the ring current effects at large values of $R_{1,7}$.

The above considerations (perhaps taken together with the particular properties of cyclopropane)^{24,42} provide a satisfactory rationalization for the large ring current chemical shifts^{10,11,13} and diamagnetic susceptibility exaltation¹² observed for the parent homotropylium cation.

The results also offer an explanation for the similarity in ring current chemical shifts observed for the structurally characterized 2-hydroxyhomotropylium cation ($R_{1,7} = 1.626 \text{ \AA}$) and 1-ethoxyhomotropylium cation ($R_{1,7} = 2.284 \text{ \AA}$).^{15,16} From Figure 4 it may be seen that these homoconjugate bond lengths give rise to fractional ring currents of $J = 0.84$ and $J = 0.66$, respectively. These values should be corrected for area and substituent. Given the fact that the ring current geometric factors will also be different, the agreement is probably satisfactory. It is therefore concluded that the ring current effects in the homotropylium cation are satisfactorily rationalized by the present analysis.

Finally we turn to a consideration of the electronic spectrum of the homotropylium cation.^{11a} Winstein concluded that the experimental spectrum was best explained with an HMO excitation energy of 1.45β from which he derived $\rho_{1,7}^B = 0.73$.^{1a,11a} The observed energy corresponds to $\Delta E = 0.86$ in Figure 4, which would be fit by our calculations at both $R_{1,7} = 1.65$ and 1.97 \AA . In fact, the analysis presented in Figure 4 is within 10% of the experimental ΔE value for $1.6 \text{ \AA} \leq R_{1,7} \leq 2.1 \text{ \AA}$. Within this interval, however, $\rho_{1,7}^B$ varies from 1.5 to 0.6.

The present analysis suggests that the degree of inhibition of resonance in **1** is small and uniformly distributed among all of the bonds in the molecule. This interpretation differs from the conventional Winstein picture in which cyclic delocalization was only considered to be interrupted at the homoconjugate bond.

Conclusion

A complete theory of the homotropylium cation has been presented. The analysis suggests a $\rho_{1,7}^B \sim 1.0$ at the equilibrium geometry of the homotropylium cation ($R_{1,7} = 1.7\text{--}2.0 \text{ \AA}$) and thus the homoconjugate resonance integral is of much the same strength as a normal π -bond. The homotropylium cation therefore sets the standard against which other homoconjugated species may be measured: $\rho_{\text{homo}}^B \sim 1.0$. Thus the homotropylium cation emerges as an excellent approximation to the ideal homoaromatic species.

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