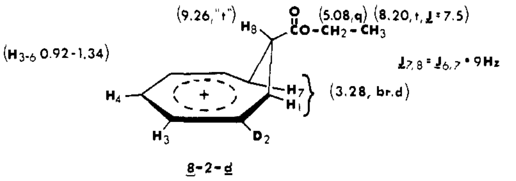
reported[5-7] for **2** prepared by protonation of cyclooctatetraene. The spectrum of the deuterio analog **2**-*4-d* is again identical except for the absorptions at lowest field (near τ 1.5) due to H_{2-6}. The intensity of this group decreases from 5 units in the spectrum of **2** to 4 in the spectrum of **2**-*4-d*, and the multiplicity is simplified to a sharp five-line pattern (doublet + pseudotriplet). Spin decoupling by irradiation at τ 3.6, where absorption due to $H_{1,7}$ occurs, causes the H_{2-6} multiplet of **2**-*4-d* to collapse to an AB quartet ($\Delta\tau_{2,3} = 0.18$ ppm; $J_{2,3} \sim 8.6$ Hz), in agreement with values found[7] on the undeuterated cation **2** by analysis of the 251-MHz nmr spectrum.

At equilibrium, after a large number of sequential circumambulatory steps, the rearrangement shown in Scheme I would have spread the deuterium label equally over sites 1–7. Thus, in the H_{1-7} absorption region, the nmr proton spectrum would be six-sevenths as intense as that of the undeuterated analog **2**, but more significantly, the clean doublet + pseudotriplet pattern of H_{2-6} of **2**-*4-d* would have returned to the unsymmetrical multiplet pattern of **2** (slightly broadened because of deuterium coupling). The latter multiplet contains strong lines that occur in absorption "windows" of the **2**-*4-d* pattern and thus provides a means to detect scrambling significantly in excess of a few per cent. The conservative estimate that 50% scrambling would not escape notice, and the observation that the τ 1.5 multiplet remains unchanged even when solutions of **2**-*4-d* are heated almost to complete destruction of the cation (75 min at 65° in FSO_3H, 75 min at 80° in H_2SO_4), place a lower limit of 26–27 kcal/mol on $\Delta F^{\ddagger}$ for the rearrangement. By exclusion, the most likely mechanism for the 8-endo–8-exo hydrogen interchange ($\Delta F^{\ddagger} = 22.3$ kcal/mol) is the previously postulated[5] conformational isomerization.

The ring-deuterated 8-*exo*-carboethoxyhomotropylium ion (**8**-*2-d*) (nmr chemical shifts shown in τ units), prepared from the known[13] 8-*exo*-carboethoxybicyclo[5.1.0]octa-3,5-dien-2-one, does not rearrange after 100 min at 60° in FSO_3H–SO_2ClF, so that again $\Delta F^{\ddagger} > 26$ kcal/mol.



8-**2**-*d*

The billion-fold retardation of circumambulatory rearrangement in homotropylium ion **2** as compared to bicyclo[3.1.0]hexenyl ion **1** presumably results from two causes. The first operates in the ground state, which must sacrifice its homoaromaticity in order to cyclize (**2**-*4-d* → **4**, Scheme I) in preparation for rearrangement. This factor, anticipated on qualitative grounds, also is suggested by *ab initio* molecular orbital calculations.[14] The second is the rather inefficient orbital overlap which would be imposed upon the transition state by the twisting motion of the migrating carbon in the "allowed" pathway. The relative importance of these factors is not known.

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(15) National Science Foundation Postdoctoral Fellow, 1970–1971.

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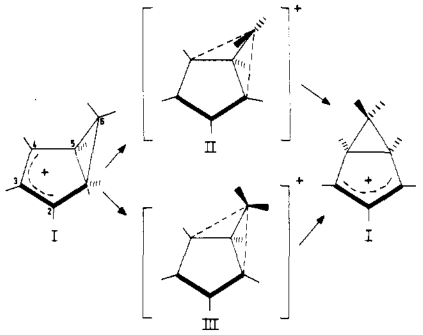
Circumambulatory Degenerate Rearrangements in Polyenyl Cations

Sir:

The bicyclo[3.1.0]hex-3-en-2-yl cation **1** undergoes facile degenerate rearrangement in which the three-membered ring circumambulates above the cyclic polyene[1] (Scheme I). The positional identity of the polyene is completely lost as a result of such a process, but the two methylene hydrogens retain their endo–exo integrity, implying first that the rearrangement proceeds through a bisected II (as opposed to eclipsed III) transition state or intermediate, in accordance with orbital symmetry considerations for a suprafacial [1,4*N*] (*N* = 1) sigmatropic shift,[2] and second that inversion through a planar benzenium ion (and hence scrambling of the endo–exo hydrogens) is not energetically competitive. As pointed out in the work of Berson and Jenkins,[3] however, the situation is entirely different for the corresponding [1,4*N* + 2] (*N* = 1) degenerate rearrangement in the homotropylium ion IV (Scheme II). No scrambling of the polyene skeletal positions is observed, suggesting that neither the symmetry "forbidden" bisected V nor the "allowed" eclipsed VI transition states (intermediates) are energetically realizable. A low-energy pathway to scrambling of the methylene hydrogens is available, presumably through the planar cyclooctatrienyl cation.[4]

Scheme I



In this communication we report our preliminary

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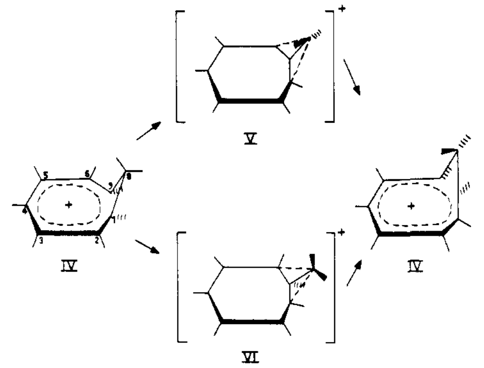
Scheme II



studies on the structures of the bicyclo[3.1.0]hex-3-en-2-yl and homotropylium carbocations and on the possible modes of degenerate circumambulatory rearrangement. Two levels of single determinant *ab initio* molecular orbital theory have been applied. The STO-3G basis[5] involves the use of an expansion of Gaussian functions closely simulating a minimal set of Slater-type orbitals. It is inexpensive enough that a significant amount of exploration of molecular potential surfaces, even on species of the size considered here, is possible. The extended 4-31G basis functions[6] give superior estimates of relative molecular energies. They are, however, more costly to apply and only a limited number of calculations at specific points on the STO-3G surface have been performed, and only on the smaller bicyclohexenyl systems. All calculations were carried out using the GAUSSIAN 70 series of programs.[7]

The bicyclo[3.1.0]hex-3-en-2-yl cation I is a minimum on the $C_6H_7^+$ potential surface, stable with respect to the circumambulatory motion of the cyclopropane, in agreement with nuclear magnetic resonance data on the parent[1f] and substituted molecules.[1a–e] The preliminary geometrical structure we report (full details will be given in a forthcoming paper) incorporates a five-membered ring resembling much more closely that of the cyclopentenyl cation rather than the antiaromatic polyenyl cation of cyclopentadiene (Table I). Consistent with this most of the positive charge (Mulliken analysis[8]) is localized on positions 2, 3, and 4. Both theoretical methods predict the bisected II rather than the eclipsed III form of cyclopentadienyl carbinyl to be the favored transition state for circumambulatory rearrangement. The minimal STO-3G set overestimates the barrier to rearrangement, consistent with its known behavior to favor tight (cyclic) structures; the extended 4-31G functions predict an activation energy in moderate agreement with the experimental (solution phase) estimate of 15 kcal mol^{-1} (see Table II).[1f] The structure we find for the bisected (and eclipsed) cyclopentadienylcarbinyl transition state contains a five-membered ring of almost identical geometry with that of neutral cyclopentadiene. Consistent with this most of the positive charge is localized on the external methylene.

Table I. Theoretical (STO-3G) Geometry of Bicyclo[3.1.0]hex-3-en-2-yl Cation[a]

$r(C_1C_2) = 1.46$ Å
$r(C_1C_5) = 1.48$ Å
$r(C_1C_6) = 1.62$ Å
$r(C_2C_3) = 1.39$ Å
$\angle(C_1C_2C_3) = 110°$
$\angle(C_1C_6C_5) = 55°$
$\angle(C_2C_1C_5) = 105°$
$\angle(C_2C_3C_4) = 109°$
$\angle(\alpha)^b = 105°$
$\angle(\beta)^c = 155°$

[a] C–H bond lengths set at 1.10 Å; bond C_1–H bisects angle $C_2C_1C_5$; C_2–H, angle $C_1C_2C_3$; C_3–H, angle $C_2C_3C_4$; HC_6H, angle set at 120°. [b] Angle between the planes formed by the two rings. [c] Angle between the C_1–H bond and the plane of the five-membered ring.

Table II. Theoretical Energies of Degenerate Circumambulatory Rearrangement in Bicyclo[3.1.0]hex-3-en-2-yl Cation (kcal mol^{-1})

	STO-3G	4-31G
Bicyclo[3.1.0]hex-3-en-2-yl (I)	0	0
Bisected cyclopentadienylcarbinyl (II)	38	20
Eclipsed cyclopentadienylcarbinyl (III)	47	32

Much less searching of the geometrical potential surface of homotropylium was possible than was for the bicyclohexenyl cation. Several interesting features are to be found in the preliminary structures we report. In contrast with the bicyclo[3.1.0]hexenyl cation, the external methylene in homotropylium is positioned almost directly over a carbon–carbon bond, leading to but a slight distortion of the C_7H_7 ring system from planarity. Also, the cyclopropane ring in homotropylium is more open than that in the bicyclo[3.1.0] cation, consistent with experimental predictions (see Table III).[1f,9] The transition state to degenerate circumambulatory rearrangement is indeed the orbital symmetry predicted eclipsed form of cycloheptatrienyl carbinyl VI; however, the symmetry-forbidden bisected structure V is but 3 kcal mol^{-1} higher in energy (Table IV). Although extended basis 4-31G calculations are not feasible on systems of this complexity at the present time, we may estimate their effect by using our experience on the related bicyclohexenyl molecules. Thus we would anticipate the barrier to degenerate circumambulatory rearrangement proceeding through an eclipsed cycloheptatrienylcarbinyl to be reduced from the STO-3G value by some 15 kcal mol^{-1}, to approximately 37 kcal mol^{-1}, consistent with the experi-

Table III. Theoretical (STO-3G) Geometry of the Homotropylium Cation[a]

$r(C_1C_2) = 1.45$ Å
$r(C_1C_7) = 1.49$ Å
$r(C_1C_8) = 1.56$ Å
$r(C_2C_3) = 1.37$ Å
$r(C_3C_4) = 1.46$ Å
$\angle(C_1C_8C_7) = 57°$
$\angle(C_2C_3C_4) = 125°$
$\angle(C_3C_4C_5) = 136°$
$\angle(\alpha)^b = 93°$
$\angle(\beta)^c = 164°$

[a] Angles $C_7C_1C_2$ and $C_1C_2C_3$ set at 128.6° ($5\pi/7$); C–H bond lengths set at 1.10 Å; bond C_1–H bisects angle $C_1C_7C_2$; C_2–H, angle $C_1C_2C_3$; C_3–H, angle $C_2C_3C_4$; C_4–H, angle $C_3C_4C_5$; H-C_8H angle set at 120°. [b] Angle between the planes formed by the two rings. [c] Angle between the C_1–H bond and the plane of the seven-membered ring.

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Table IV. Theoretical (STO-3G) Energies of Degenerate Circumambulatory Rearrangement in the Homotropylium Cation (kcal mol^{-1})

Homotropylium (IV)	0
Eclipsed cycloheptatrienylcarbinyl (VI)	52
Bisected cycloheptatrienylcarbinyl (V)	55

mental lower bound (26 kcal mol^{-1}) placed on the process by Berson and Jenkins.[3] As was the case for the transition-state structures in the bicyclohexenyl degenerate rearrangement, both bisected and eclipsed forms of cycloheptatrienylcarbinyl (V and VI) show alternation of single and double bonds, much what one might expect from neutral planar cycloheptatriene.

Ex post facto it appears possible to rationalize the difference in activation energies for the two rearrangement processes primarily on account of the ground-state properties of the bicyclohexenyl and homotropylium carbocations. The former has a choice of being structured on the base of either the antiaromatic cyclopentadienyl cation or the classical (charge localized) cyclopentenyl ion. The lesser of the two evils is chosen, resulting in an ion not expecially stable, but resembling to a great extent the eventual transition state to circumambulatory rearrangement. The situation is different for homotropylium. Here the aromatic (charge localized) tropylium ion is the chosen base. Rearrangement *via* the classical cycloheptatrienylcarbinyl cation requires a significant change in geometry.

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Lanthanide Shift Reagents. X-Ray Structure of the Seven-Coordinate 3,3-Dimethylthietane 1-Oxide (1) Complex with Tris(dipivalomethanato)europium(III), Eu(dpm)$_3$·(1), and Its Implication on Pseudocontact Shift Calculations

Sir:

Exceptionally wide interest has been shown in the paramagnetic lanthanide shift reagents.[1] Their presence in solution often produces large isotropic shifts, which generally spread out the chemical shifts, frequently reducing the spectrum to first order, and thereby facilitating analysis. The Eu(III) and Pr(III) chelate complexes of 2,2,6,6-tetramethylheptane-3,5-dione and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione have proven to be the most popular shift reagents because of their favorable shift to line broadening characteristics.[1,2]

In addition to spectral simplification, there is evidence that the magnitudes of the shifts (and perhaps the line broadening as well)[3] can be interpreted in terms of the molecular geometry of the complex.[1] If this holds true, then the technique would be extremely important for the determination of molecular stereochemistry. In most cases it is clear that the shifts are a consequence of through-space dipolar interactions. The spatial dependence of the shifts for axially symmetric complexes is given by eq 1,[4] where ΔH_i is the change in field

$$\frac{\Delta H_i}{H} = f\left(g_{\parallel}, g_{\perp}, K, \frac{1}{T}\right)\frac{(3\cos^2\theta_i - 1)}{r_i^3} \qquad (1)$$

strength at nuclei i, r_i is the distance between the paramagnetic metal and nucleus i, and θ_i is the angle between the principal magnetic axis of the complex and the vector r_i.

In applying eq 1 to structural problems, a large number of authors have chosen to interpret the observed shifts using only an r^{-n} term.[2a] The exponent n has either been taken to be equal to 3 or adjusted to improve the fit between calculated and observed shifts. The distance r_i has been estimated in a number of ways. Some authors have chosen to set it equal to the distance between the site of coordination, Q, and nucleus i. Most have, however, estimated r_i by positioning the lantanide (Ln) at some predetermined distance from Q and calculating the Ln–(i) distance accordingly. Distances for Ln···Q ranging from the van der Waals radius of Q to roughly one and one-half times the sum of the covalent radii of Ln and Q have been employed. Usually this distance is adjusted to improve the fit of the calculated to the observed shifts.

There are a few examples in the literature where the full form of eq 1 has been used.[5] This generally results in fits which are significantly better[6] than those obtainable using only a distance parameter.

Several difficulties arise, however, when one attempts to use eq 1. The first is that in order to calculate a shift, it is necessary to average the calculated shifts over all orientations of the shift complex. The various conformations of the shift complex are unknown, as are their populations. A second difficulty is that the shift eq 1, strictly speaking, is only applicable to axially symmetric complexes.[7] Third, the angle θ_i is defined as the angle between the vector r_i and the principal magnetic axis. The location of this axis is unknown but has generally been taken along the Ln···Q axis.

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