

# Theoretical Approaches to Rearrangements in Carbocations. II. Degenerate Rearrangements in Bicyclo[3.1.0]hexenyl and Homotropylium Cations. On the Stability of Homoaromatic Molecules<sup>1,2</sup>

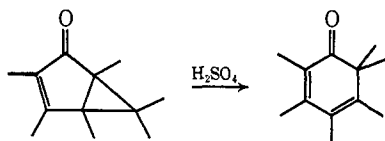
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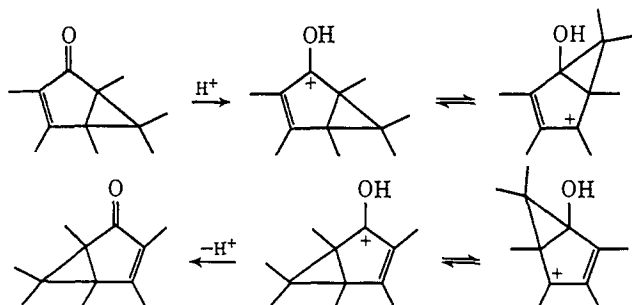
**Abstract:** *Ab initio* molecular orbital theory has been used to investigate the energetics of circumambulatory degenerate rearrangement in the bicyclo[3.1.0]hexenyl and homotropylium carbocations. In agreement with experiment and with orbital symmetry considerations, rearrangement in bicyclohexenyl system proceeds with inversion at the migrating carbon. Circumambulation in homotropylium has not been detected experimentally but according to symmetry conservation arguments should proceed with opposite stereochemistry to the analogous process in bicyclohexenyl. The theoretical calculations confirm such behavior. The difference in energetics between the two symmetry allowed rearrangements (circumambulation in bicyclohexenyl being very much the more facile process) is rationalized in terms of a difference in stabilities in the ground-state molecules rather than having much to do with the transition-state structures themselves. Thus the bicyclo[3.1.0]hexenyl cation displays antiaromatic character and is destabilized relative to its rearrangement transition state, while homotropylium is stabilized through aromaticity. The effects of substituents in altering the energetics of these two rearrangement processes are considered. Two models for the stability of homoaromatic arrangements are presented. The first is a restatement of the ideas put forth by Winstein over a decade ago while the alternative approach considers the possibility of participation in the cyclic conjugation of the electrons of the interrupting group. It is suggested that the geometry of the polyene may be used to distinguish between the two alternative modes of conjugation and we have examined the theoretical structures for bicyclohexenyl and homotropylium cations keeping this in mind.

Our interest in and entry into the area of homoaromatic molecules was catalyzed by a parallel set of experimental observations, the results of which were annoyingly dissimilar.

Perhaps credit for the first recognition of degenerate rearrangement in the bicyclo[3.1.0]hexenyl cation (I) belongs to Swatton and Hart.<sup>4</sup> Confronted with the rearrangement

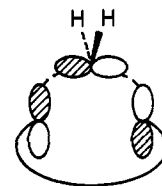


these authors invoked circumambulation of the cyclopropane about the five-membered ring as one possible path, and by use of deuterium labeling eventually established the facility of migration about four of the five ring base positions. That the rearrangement proceeds

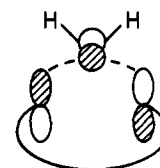


with inversion at the migrating center (upper pathway

of Figure 1 rather than retention (lower pathway) was first clearly established by Childs and Winstein,<sup>5</sup> in their nmr observations on the heptamethylbicyclo[3.1.0]hexenyl cation. Here it was noted that the methyl group hydrogens on the external methylene maintain their exo-endo integrity throughout the rearrangement indicating intervention of a *bisected* cyclopentadienyl-carbinyl transition state or intermediate (II) as opposed to an *eclipsed* form (III). This is in keeping with orbital symmetry considerations<sup>6</sup> for a suprafacial [1,4]-sigmatropic shift where progression through a *bisected* transition state (or intermediate) maintains continuity of orbital overlap throughout, while passage *via* an



*eclipsed* ion necessitates a break at one point or another.<sup>7</sup>



(5) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968).

(6) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

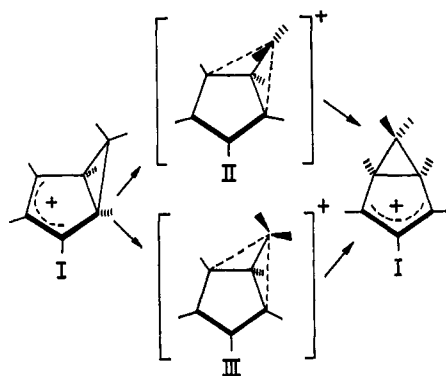
(7) What we have pictured here (and below) is the hypothetical interaction between the *highest* (doubly) *occupied molecular orbital* (HOMO) on a butadiene fragment and an empty orbital of *p* symmetry on the migrating group. As two electrons are involved in the total interaction, it is net *stabilizing* and maintenance of positive overlap is energetically beneficial.

(1) Paper I: W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **96**, 2665 (1974).

(2) Portions of this work have already appeared as preliminary communications.<sup>3</sup>

(3) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 8908 (1972); **95**, 5807 (1973).

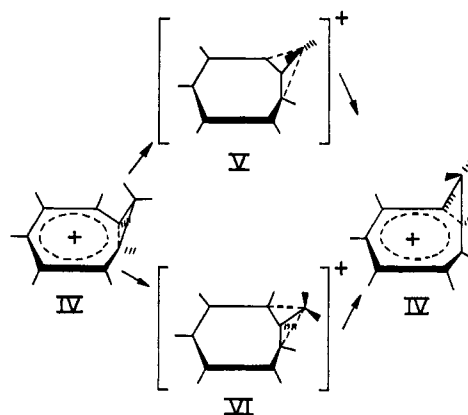
(4) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967).



**Figure 1.** Degenerate circumambulation in bicyclo[3.1.0]hexenyl cation: I  $\rightarrow$  II  $\rightarrow$  I, Woodward-Hoffmann allowed; I  $\rightarrow$  III  $\rightarrow$  I, Woodward-Hoffmann forbidden.

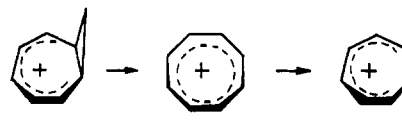
Several studies on alkyl substituted bicyclohexenyl cations<sup>8-10</sup> preceded the eventual observation of degenerate circumambulation in the parent species itself<sup>11</sup> where an activation energy ( $\Delta G^\ddagger$ ) of  $15 \pm 1$  kcal/mol (for the symmetry allowed rearrangement mode) has been assigned.

Ring circumambulation in the next higher system, homotropylium (IV) should reverse the above trend and proceed through an *eclipsed* (VI) as opposed to *bisected* (V) intermediate structure (Figure 2). Applying the same symmetry conservation rules as before, this time for a suprafacial [1,6] process, we see that now the orbitals on the diene termini are of the same sign and that in order to maintain orbital continuity the migrating group must be of local *s* symmetry. Whereas a *bisected* intermediate form does not satisfy this need,



**Figure 2.** Degenerate circumambulation in homotropylium cation: IV  $\rightarrow$  V  $\rightarrow$  IV, Woodward-Hoffmann forbidden; IV  $\rightarrow$  VI  $\rightarrow$  IV, Woodward-Hoffmann allowed.

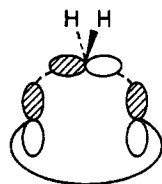
ambulatory rearrangement processes are known. It is a pity that such a rearrangement—accompanied not only by the scrambling of the seven tropylium positions but also of the endo-exo integrity of the positions on the external methylene—cannot be observed experimentally, for it would serve as a beautiful test of the Woodward-Hoffmann predictions to complement the work on the bicyclohexenyl cation. Unfortunately a second process, inversion through a probable planar cyclooctatrienyl cation, intervenes<sup>16</sup> thereby scrambling the endo-exo methylene positions and



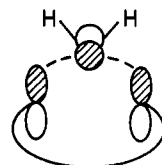
eliminating the possibility of stereochemical classification of the circumambulation process. Using deuterium labeling of the tropylium positions Berson and Jenkins<sup>15</sup> have, however, been able to set a lower bound of 27 kcal/mol on any possible ring circumambulation process.

In this paper we analyze in some detail the rearrangement surfaces for the bicyclo[3.1.0]hexenyl and homotropylium carbocations, using theoretical *ab initio* molecular orbital techniques. A comparison between theory and experiment on the energetics of degenerate circumambulation in the bicyclo[3.1.0]hexenyl cation should provide us with a level of confidence by which we may be able to judge the quality of the predictive aspects of the work. Of particular interest will be the difference in required activation between the allowed rearrangement processes in the two ions ( $E_a(\text{homotropylium}) > E_a(\text{bicyclo[3.1.0]hexenyl cation})$ ). Here we will seek a simple rationalization. We shall also look at the forbidden transition states for the two methylene migrations, in order to obtain a feeling for the amount of energy required to violate orbital symmetry considerations. The effects of simple alkyl substituents on the parent reaction surfaces will be

(16) Ring inversion in parent homotropylium requires 22.3 kcal/mol (S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Amer. Chem. Soc.*, **88**, 2047 (1966)); for a related study on chlorohomotropylium, see G. Boche, W. Hechtel, H. Huber, and R. Huisgen, *ibid.*, **89**, 3344 (1967); see also ref 14. An interesting parallel may be drawn between the transition state to inversion in homotropylium and that for symmetry allowed antarafacial [1,6]-sigmatropic migration.



an *eclipsed* arrangement would appear to be perfectly



suited. Unfortunately even though the homotropylium ion has been around for well over a decade,<sup>12-15</sup> neither the stereochemistry nor the energetics of possible circum-

(8) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968).

(9) V. H. Koptyug, L. T. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 389 (1969).

(10) R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970).

(11) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

(12) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 1411 (1969), and references therein. See also: P. R. Story, and B. C. Clark Jr., in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972, p 1007.

(13) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970), and references therein.

(14) (a) R. Huisgen and J. Gasteiger, *Tetrahedron Lett.*, 3661 (1972); (b) J. Gasteiger and R. Huisgen, *ibid.*, 3665 (1972).

(15) J. A. Berson and J. A. Jenkins, *J. Amer. Chem. Soc.*, **94**, 8907 (1972).

studied. Our hope here is to suggest ways in which to stabilize the homotropylium rearrangement transition state so that it might be brought into view experimentally. We will also probe the possibility of reducing the gap between symmetry allowed and forbidden migration pathways.

In hope of a more thorough understanding of the origins of homoaromatic stability and the consequences resulting from it we will turn to a simpler—and perhaps more informative—level of theory. Using arguments derived from a simple perturbation treatment of interacting orbitals we can construct a pair of alternative descriptions for the enhanced stability of homopolyene arrangements, one of which is essentially equivalent to Winstein's original formulation, the other fundamentally different. In addition we will explore the charge-transfer effects arising from the interaction of orbital arrays and use these to rationalize the (theoretically) observed geometrical distortions in the homoaromatic cations. Here we will see that the crude—but seemingly reliable—model leads to insight unavailable from the quantitative calculations. In a forthcoming paper we will extend out treatment to consider the structural and energetic consequences of multiple interruptions of the base polyene and of intervening alkyl chains more than a single methylene unit in length. Also deferred to future publications are discussions of our theoretical investigations on the structures, stabilities, and rearrangement mechanisms of a third class of homopolyene systems, the mono-, bis-, and trishomocyclopropenyl cations. Although smaller than the molecules under consideration in the present work, they pose a number of fascinating complications leading to largely unexpected behavior.

### Quantum Mechanical Methods

For the computational aspects of this work single determinant *ab initio* molecular orbital theory has been used throughout. We employ the minimal STO-3G basis functions,<sup>17</sup> primarily to establish theoretical equilibrium and transition-state geometries, and the split valence shell set, 4-31G<sup>18</sup> to more accurately assess relative molecular energetics at selected interesting points on the STO-3G potential surface. Such tactics have been found economical and reliable in prior studies.<sup>19</sup> All *ab initio* calculations reported herein have been performed using the GAUSSIAN 70 series of computer programs.<sup>20</sup>

### Results and Discussion

Theoretical (STO-3G) energies for all molecules considered in this paper are presented in Table I. Equilibrium- and transition-state geometries for the parent molecules have been optimized at the STO-3G level and are fully detailed in text. For the methyl-substituted cations theoretical geometries are those of the parent ions with "standard" CH<sub>3</sub> groups<sup>21</sup> attached at the

(17) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(18) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(19) For example, see W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, **11**, 175 (1974).

(20) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, Program No. 236.

(21) Tetrahedral, C-H = 1.09 Å, connecting bond length to trigonal carbon = 1.50 Å, to tetrahedral carbon = 1.52 Å.

Table I. Theoretical Energy Data (hartrees)

Cation	STO-3G	4-31G
Cyclopentadienyl	-189.59995	-191.61514
Bicyclo[3.1.0]hexenyl	-228.21903	-230.62194
Bisected cyclopentadienylcarbinyl	-228.15960	-230.59156
Eclipsed cyclopentadienylcarbinyl	-228.14519	-230.57222
6,6-Dimethylbicyclo[3.1.0]hexenyl	-305.38648	
Bisected dimethylcyclopentadienylcarbinyl	-305.35494	
Eclipsed dimethylcyclopentadienylcarbinyl	-305.36695	
Tropylium	-265.66771	
Homotropylium	-304.19104	
Bisected cycloheptatrienylcarbinyl	-304.08490	
Eclipsed cycloheptatrienylcarbinyl	-304.09396	
8,8-Dimethylhomotropylium	-381.35112	
Bisected dimethylcycloheptatrienylcarbinyl	-381.30650	
Eclipsed dimethylcycloheptatrienylcarbinyl	-381.27887	

same bond angles as the hydrogens replaced. Where possible 4-31G calculations have been performed to supplement the STO-3G data and these are also listed.

**A. Degenerate Circumambulation in Parent Cations.** We indeed find that methylene circumambulation in the bicyclo[3.1.0]hexenyl cation (I) proceeds preferentially through a *bisected* cyclopentadienylcarbinyl transition state (II), the theoretical activation energy of 20 kcal/mol (4-31G) overestimating somewhat the experimental *solution phase* value of 15 kcal/mol (Table II). Migra-

Table II. Degenerate Rearrangement in Bicyclo[3.1.0]hexenyl Cation (kcal/mol)

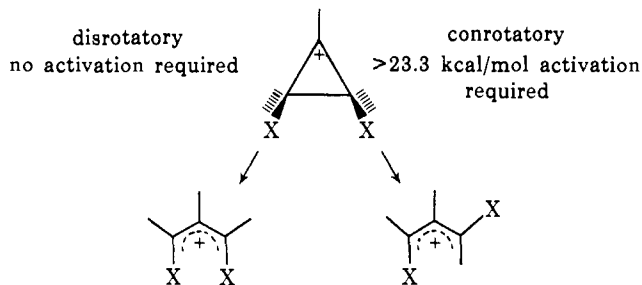
	STO-3G	4-31G	Expt <sup>a</sup>
Bicyclo[3.1.0]hexenyl (I)	0	0	0
Bisected cyclopentadienylcarbinyl (II)	38	20	15
Eclipsed cyclopentadienylcarbinyl (III)	47	32	

<sup>a</sup> Reference 11.

tion of the methylene in a manner in which orbital symmetry is not conserved (*i.e.*, passage through the *eclipsed* transition state (III)) requires an additional boost of 12 kcal/mol. Thus, it is not surprising that the rearrangement does indeed proceed stereospecifically with inversion.

It is of interest at this point to compare our (12 kcal/mol) value for the energy required to violate orbital symmetry in the bicyclo[3.1.0]hexenyl sigmatropic rearrangement with whatever experimental estimates exist and with theoretical studies on this and other symmetry controlled processes. Childs and Winstein<sup>5</sup> early concluded that the symmetry forbidden (*eclipsed*) transition state to degenerate rearrangement in heptamethylbicyclo[3.1.0]hexenyl cation was at least 5.7 kcal/mol higher in energy than the allowed. Given that methyl substitution is likely to stabilize the charge localized forbidden transition state structure more than it is the allowed form where positive charge is dispersed throughout the molecular skeleton, this would imply that the difference noted here represents a *lower bound* for that in the parent system. Related is work by Radom,

Hariharan, Pople, and Schleyer<sup>22</sup> on the conversion of cyclopropyl to allyl cation. While conversion along the Woodward–Hoffmann allowed disrotatory pathway proceeds without activation, a considerable energy boost (>23.3 kcal/mol at the 4-31G level) is required for passage in a symmetry forbidden conrotatory manner.



Smaller differences (as low as 3.5 kcal/mol) between symmetry allowed and forbidden alternatives were reported by Hehre, Willcott, and Salem<sup>23</sup> in their recent theoretical investigation of the mechanism of methylenecyclopropane degenerate rearrangement. These were rationalized in terms of overlap of orbitals other than those valence functions considered explicitly in the Woodward–Hoffmann model.<sup>24</sup>

STO-3G calculations indicate that ring circumambulation in homotropylium (IV) is a far less facile process (Table III). Thus, the symmetry allowed process—this

Table III. Degenerate Rearrangement in Homotropylium Cation (kcal/mol)

	STO-3G	4-31G <sup>a</sup>	Expt <sup>b</sup>
Homotropylium (IV)	0	0	0
Eclipsed cycloheptatrienyl-carbinyl (VI)	61	(43)	>27
Bisected cycloheptatrienyl-carbinyl (V)	67	(52)	

<sup>a</sup> Estimated values, see text. <sup>b</sup> Reference 15.

time passage through an *eclipsed* cycloheptatrienyl-carbinyl transition state (VI)—requires 61 kcal/mol compared with only 38 kcal/mol for the same level of theory for degenerate rearrangement in bicyclo[3.1.0]hexenyl cation. Although we have been unable to perform extended basis 4-31G level calculations on homotropylium and its rearrangement transition states, we can anticipate their conclusions by direct analogy with our STO-3G and 4-31G data on the bicyclo[3.1.0]hexenyl system. Thus, relative to parent bicyclo[3.1.0]hexenyl cation, the energies of the *bisected* and *eclipsed* transition state structures improve by 18 and 15 kcal/mol, respectively, corrections which when applied to homotropylium results in energies for the symmetry allowed and forbidden processes of 43 and 52 kcal/mol, respectively. These values too are included in Table III, as is the experimental lower bound (presumably

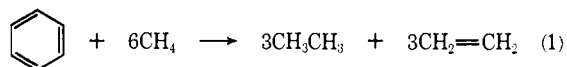
(22) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973).

(23) W. J. Hehre, L. Salem, and M. R. Willcott, *J. Amer. Chem. Soc.*, **96**, 4328 (1974).

(24) Such an extension has been termed *Subjacent Orbital Control* by its original discoverers (J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972); J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972)). Recent examples include: J. A. Berson and R. W. Holder, *J. Amer. Chem. Soc.*, **95**, 2037 (1973); S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *ibid.*, **95**, 3807 (1973); A. J. P. Devaquet and W. J. Hehre, *ibid.*, **96**, 3644 (1974).

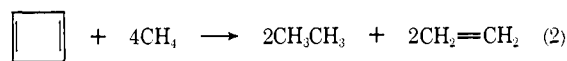
related to the allowed process) of 27 kcal/mol.<sup>15</sup> Note that the energy required to violate orbital symmetry in the homotropylium migration process is in keeping with our earlier contentions (see above), the small reduction over that found in the bicyclo[3.1.0]hexenyl system (9 kcal/mol instead of 12) possibly being due to the increased size of the base polyene.

We begin to understand the dissimilar energetics of these two seemingly comparable degenerate circumambulatory rearrangements if we consider the difference in ground-state stabilities of the individual parent ions. This can be readily accomplished by comparing them to “standards,” that is to say systems which we can conveniently label as possessing aromatic or antiaromatic character. Let us consider benzene as an example of a typical (if not the typical) aromatic molecule. Here we might define the stability gain due to aromaticity as the energy required to separate the molecule into its simplest component bonds. In the case of benzene, which we have written in terms of single valence structure, that is its energy relative to those of three isolated single bonds and three isolated double bonds, as given by the *isodesmic* bond separation reaction<sup>25</sup> (eq 1). We would expect the reaction to be



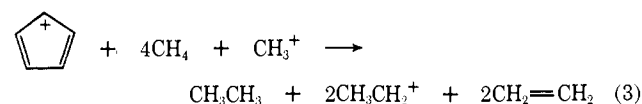
highly endothermic.

Correspondingly the antiaromatic character of the 4π-electron cyclic 1,3-cyclobutadiene is likewise portrayed by reaction 2. This time expectations tell us to

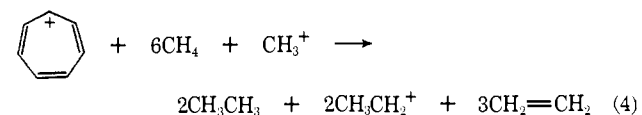


be on the lookout for an exothermic process.

It is simple to extend our treatment to include the related cationic systems. For example, planar cyclopentadienyl cation, which forms the polyene base for the bicyclo[3.1.0]hexenyl system is also formally a 4π-electron cyclic and thus is antiaromatic. The energy of reaction 3 should contain this information, while that

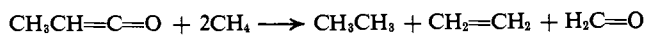


of the bond-separation reaction (eq 4) for the tropylium



ion, on which homotropylium is formed, should tell

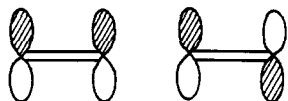
(25) The *isodesmic* bond separation process involves separating all formal bonds between heavy atoms into the simplest molecules with the same type of bond. For example, the bond separation reaction for methylketene would be written in such a way as to compare the incor-



porated C—C, C=C, and C=O linkages to those in ethane, ethylene, and formaldehyde, respectively. Here the two molecules of methane are added to the left-hand side to achieve stoichiometric balance. Experience has shown that the energies of such processes are well described by simple levels of single determinant molecular orbital theory: (a) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970); see also (b) L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 289 (1971); (c) L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971).

that this molecule, like benzene, is stabilized by aromaticity.

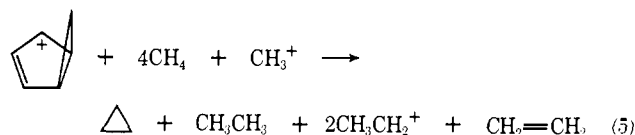
The scheme may be generalized one step further to include exactly those bicyclic systems, the degenerate rearrangements of which concern us here. All we need do is to consider one of the double bonds in the cyclic polyenyl cation (cyclopentadienyl or tropylium) to be replaced by a cyclopropane ring. The overall similarity of the highest occupied  $\pi$  and lowest unoccupied  $\pi^*$  orbitals on an unsaturated linkage, say ethylene, to the



occupied valence pair of (Walsh) orbitals on cyclopropane<sup>26</sup> suggests the logic behind such a move.



While the comparison between the ethylenic  $\pi$  orbital and the symmetric Walsh component is wholly justified, it must be emphasized that although the ethylene  $\pi^*$  orbital is formally empty, its analog in cyclopropane (the antisymmetric member of the Walsh duo) is doubly occupied. We will use this fundamental difference to develop a description of homoaromatic stability alternative to that proposed by Winstein.<sup>12</sup> Returning we see that the bicyclo[3.1.0]hexenyl cation is, in such a manner, formally related to cyclopentadienyl and might be expected to show some of its antiaromatic character.



Correspondingly, homotropylium (as its name implies) is the homoaromatic derived from aromatic tropylium.

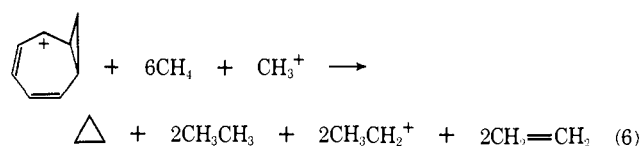


Table IV displays theoretical (and where available, experimental) energies of the *isodesmic* reactions 1–6. The reasonable agreement between theory and experiment in those cases where the latter is known, together with our considerable past experience on the ability of simple *ab initio* methods to adequately describe the energies of *isodesmic* processes<sup>25</sup> such as these, gives us enough confidence to proceed. The bond separation energy of benzene is as expected large and positive, indicating a considerable stability gain due to aromatic association. On the contrary, that of 1,3-cyclobutadiene is equally large, but negative.<sup>27</sup> Although the

(26) For a discussion, see R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).

(27) Note, however, that single determinant molecular orbital theory is not well suited to the description of the lowest singlet states of species such as cyclobutadiene and the energy of the *isodesmic* bond separation process 2 represents a lower bound. For a discussion of the problems involved here and the use of limited mixing of electronic configurations in their resolution, see A. Krantz, C. Y. Lin, and M. D. Newton, *J. Amer. Chem. Soc.*, **95**, 2744 (1973), and references therein; W. J. Hehre and J. A. Pople, *ibid.*, manuscript to be submitted.

Table IV. Bond Separation Energies of Cyclic Polyenes and Homopolyenes (kcal/mol)<sup>a</sup>

	STO-3G	4-31G	Expt
Benzene (1)	+70	+64	+61 <sup>b</sup>
1,3-Cyclobutadiene (2)	-66	-68	
Tropylium cation (3)	+99		+73 <sup>c</sup>
Cyclopentadienyl cation (4)	+10	-3	-16, <sup>c</sup> 0 <sup>c</sup>
Homotropylium cation (5)	+56		
Bicyclo[3.1.0]hexenyl cation (6)	+27	+26	

<sup>a</sup> Energies of the *isodesmic* reactions 1–6. Theoretical data from Table I and: Methyl cation, methane, ethylene, ethyl cation, ethane, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 808 (1970); cyclopropane, W. A. Lathan, L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971); benzene, W. J. Hehre and J. A. Pople, *ibid.*, **94**, 6901 (1972); (singlet) cyclobutadiene, W. J. Hehre and J. A. Pople, *ibid.*, submitted for publication. <sup>b</sup> Experimental thermochemical data (at 0°K and including corrections for zero-point vibrational energy) summarized in ref 25a. <sup>c</sup> Experimental thermochemical data (at 298°K, uncorrected for zero-point vibrational energy) from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26, 53, 66 (1969).

6 $\pi$ -electron cyclic, tropylium, is actually stabilized more than is benzene itself (an effect due for the most part on the instability of the ethyl cation which appears on the right-hand side of (4)), antiaromatic destabilization in the cyclopentadienyl cation is somewhat less effective than in neutral 1,3-cyclobutadiene, its bond-separation energy being approximately zero. More interesting are the results for the antihomoaromatic bicyclo[3.1.0]hexenyl and homoaromatic homotropylium cations, where the bond-separation energies fall intermediate between the limiting values set by antiaromatic cyclopentadienyl and aromatic tropylium cations. Thus, homotropylium is indeed stabilized by aromaticity but not nearly as effectively as is tropylium. Conversely the bicyclo[3.1.0]hexenyl cation does not suffer from antiaromatic destabilization to the extent shown by the parent polyene.

It is interesting to note that the difference in bond-separation energies between homotropylium and bicyclo[3.1.0]hexenyl cations (29 kcal/mol at STO-3G) is nearly the same as the difference in activation energies required for the two circumambulatory degenerate rearrangement processes (23 kcal/mol). Thus, if we ignore any differences in the energetics of the (symmetry allowed) transition-state structures,<sup>28</sup> and concentrate on the stabilities of the ground-state ions, we arrive at a simple rationale for the experimentally observed—and theoretically confirmed—difference in activation for the two rearrangement processes. We see in Figure 3 that the bicyclo[3.1.0]hexenyl cation, which is destabilized by (anti) aromatic conjugation, has only a small barrier to surmount in order to reach its rearrangement transition state, while homotropylium, an aromatic and hence stabilized, has much further to climb.

Our notions here may be generalized to tell us something about required activation for degenerate circumambulation—or other symmetry controlled processes

(28) This we would expect to be reasonable as the allowed transition state for either process is aromatic (M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 781 (1971)). It is only the ground-state ions which, in a formal sense, differ in aromatic character.

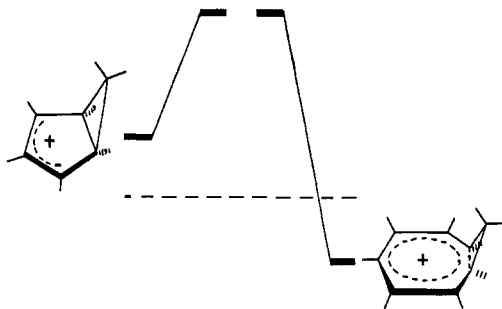
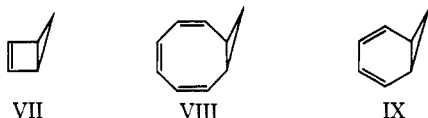


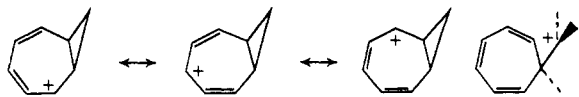
Figure 3. Rearrangement in bicyclo[3.1.0]hexenyl and homotropylium cations.

where the allowed transition states are always aromatic—in other systems. Thus we would expect thermally induced methylene circumambulation to be facile in bicyclo[2.1.0]pentene (VII)<sup>29</sup> and bicyclo-



[6.1.0]nonatriene (VIII)<sup>30</sup> (formally antiaromatic in their ground states) and more difficult in norcaradiene (IX).<sup>31</sup>

**B. Substituent Effects on the Energetics of Degenerate Rearrangement in Bicyclo[3.1.0]hexenyl and Homotropylium Cations.** Although degenerate circumambulatory rearrangement in parent homotropylium cation is not facile enough to be observed by current (nmr) experimental tactics (as outlined in the previous section the best theoretical estimate for the symmetry allowed process being 43 kcal/mol to be compared with the experimental *lower bound* of 27 kcal/mol), it should be possible to reduce this activation barrier by selective substitution. Thus, in the best of all possible worlds, we would like to be able to stabilize the transition state—an *eclipsed* cycloheptatrienylcarbiny cation—either without affecting at all or perhaps even better destabilizing the parent ion. Regarding the simple resonance structures for the homotropylium ground-state and cycloheptatrienylcarbiny transition-state ions, the direction in which we must proceed becomes clear. In homotropylium itself the positive charge (formally)



resides on the seven-membered ring, and we must avoid the use of any potentially stabilizing substituents here. For the same reason substitution on the external methylene here should have little effect. In the transition-state structure the trend is precisely reversed and by the same arguments all positive charge rests on the migrating methylene. Thus it would appear that a

(29) Unobserved because of facile (27 kcal/mol) interconversion to cyclopentadiene: D. M. Golden and J. I. Brauman, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).

(30) Occurs with stereochemical inversion at the migrating carbon;  $\Delta G^\ddagger = 29$  kcal/mol: F. G. Klärner, *Angew. Chem., Int. Ed. Engl.*, **11**, 832 (1972); see also M. B. Sohn, M. Jones, and B. Fairless, *J. Amer. Chem. Soc.*, **94**, 4774 (1972).

(31) Occurs with an activation in the range of 50 kcal/mol; stereochemistry unknown: J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966).

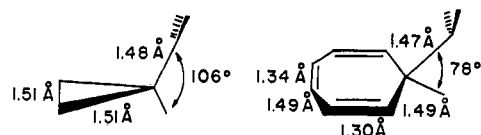
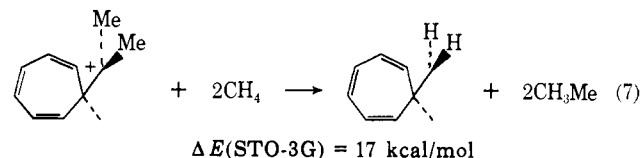


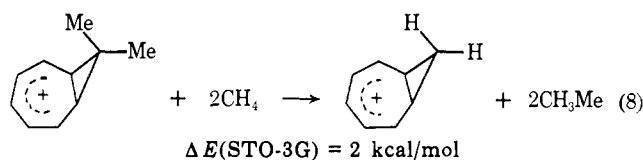
Figure 4. Theoretical (STO-3G) structures for *eclipsed* cyclopropylcarbiny and *eclipsed* cycloheptatrienylcarbiny.

maximum reduction in rearrangement energy would be expected for substitution (by groups able to delocalize positive charge) at the eight positions.

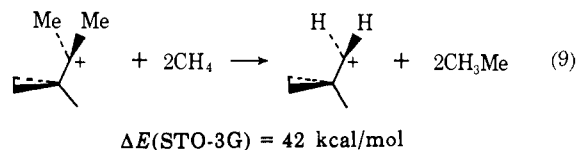
The stabilizing effect of a pair of 8,8'-methyl substituents on cycloheptatrienylcarbiny cation is given by the energy of the *isodesmic* process (eq 7). Diminished



by the lesser stabilization afforded by the same duo of methyls on parent homotropylium (reaction 8) it



represents the energy lowering (over the parent) anticipated for methylene migration. Thus, the calculations suggest that dimethylhomotropylium requires 28 kcal/mol for methylene migration with stereochemical retention (that is *via* an *eclipsed* dimethylcycloheptatrienylcarbiny cation) most likely still too high a barrier for the process to be characterized experimentally. In light of our experience with methyl substitution on related cations, the calculated stabilization here is somewhat less than this author would have expected. Thus, for example, an equivalent pair of methyls stabilize *eclipsed* cyclopropylcarbiny by 42 kcal/mol as measured by the heat of the *isodesmic* process (9).<sup>32</sup>



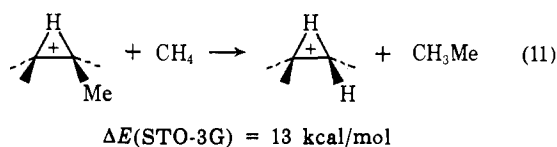
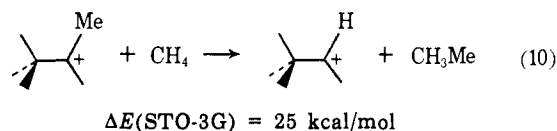
A comparison of the pertinent aspects of the calculated molecular geometries of the *eclipsed* parent cycloheptatrienylcarbiny and cyclopropylcarbiny cations (Figure 4) suggests a rationale for this startling difference in (di) methyl stabilization energies. The molecular geometry of *eclipsed* cyclopropylcarbiny resembles to a great extent that which is implied by its classical valence structure ( $\text{CH}_2^+$  bonded to cyclopropane). That is to say, we expect the greater part of the positive charge to be localized on the external methylene. The calculated structure for *eclipsed* cycloheptatrienylcarbiny, however, does not allow us to conclude similarly. Rather than being best represented by a trigonally coordinated (and positively charged) carbon attached

(32) (a) W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, **96**, 302 (1974); (b) P. C. Hiberty, Thèse de Troisième Cycle, Université de Paris Sud, Orsay, France, 1973.

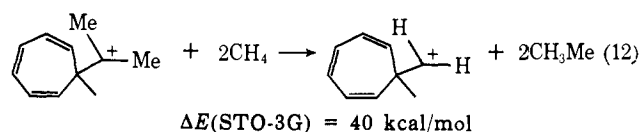
to neutral cycloheptatriene, the calculated geometry seems to suggest that the ion is best represented in terms of a (partially) hydrogen-bridged and hence charge-delocalized structure.<sup>33</sup> Experience with model systems



has indeed suggested the obvious: that alkyl groups directly bonded to centers of high (positive) charge concentration play far more effective roles than those attached at some point on  $\sigma$ - or  $\pi$ -delocalized structures.<sup>1,34</sup> Thus, for example, a single methyl substituent is much more effective in stabilizing the localized positive charge on the open ethyl cation than it is in lowering the energy of the charge-delocalized hydrogen-bridged form (reactions 10 and 11, respectively).



Stabilization afforded by dimethyl substitution to the *bisected* form of the cycloheptatrienylcarbinyl transition state (reaction 12) is more in keeping with the idea that



the parent is best represented as we have drawn it, a charge localized classical ion. The hefty stabilization noted here, together with the rather small methyl substituent effect discussed previously for eclipsed cycloheptatrienylcarbinyl, is enough to reverse the rearrangement stereochemistry suggested by the quantitative calculations (and predicted by the Woodward-Hoffmann orbital symmetry arguments) in parent homotropylium. Indeed, the calculations suggest that a "mere" 13 kcal/mol activation is required for 8,8-dimethylhomotropylium to undergo degenerate circumambulatory rearrangement through a symmetry forbidden *bisected* transition state some 14 kcal/mol less than what is needed for passage in an allowed mode. The former (symmetry disallowed) process should now be of low enough energy as to be amenable to experimental characterization.

Table V summarizes available experimental activation energies for ring circumambulation in the methyl-substituted bicyclo[3.1.0]hexenyl cations, relative to the 15

(33) The (STO-3G) energy we find for methyltropylium ( $-304.25431$ ) is significantly below that of *eclipsed* cycloheptatrienylcarbinyl. This hints at the possibility that thermal isomerization of homotropylium to the thermodynamically more stable methyltropylium ion is almost as facile a process as degenerate rearrangement.

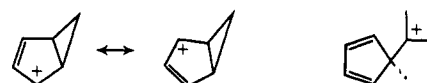
(34) For recent examples from the theoretical literature, see (a) W. J. Hehre and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 5837 (1973); (b) C. F. Wilcox, Jr., L. M. Loew, R. G. Jesaitis, S. Belin, and J. N. C. Hsu, *ibid.*, **96**, 4061 (1974); (c) W. J. Hehre and P. v. R. Schleyer, *ibid.*, to be submitted for publication.

Table V. Effects of Methyl Substitution on Degenerate Rearrangement in Bicyclo[3.1.0]hexenyl Cation

Methyl substituents at positions	Rearrangement energy relative to parent (kcal/mol)
1, 2, 4, 5	$\geq 3.6^a$
1, 2, 3, 4, 5, 6 (exo)	$-3.0^b$
1, 2, 3, 4, 5, 6 (endo)	$\geq 0.4^b$
1, 2, 3, 4, 5, 6 (exo + endo)	$-6.0^c$

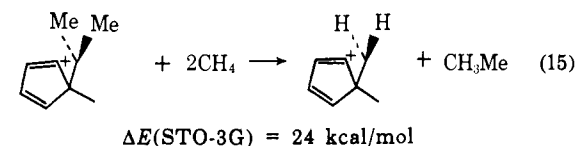
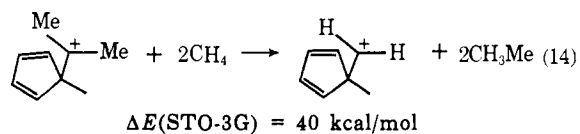
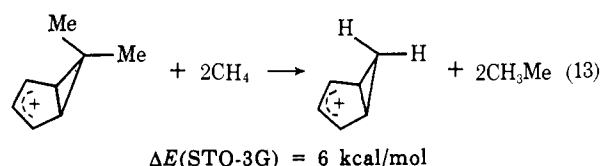
<sup>a</sup> Reference 10. <sup>b</sup> Reference 9. <sup>c</sup> Reference 5.

kcal/mol value reported for rearrangement of the parent. Here, as in homotropylium, cursory consideration of the "classical" valence structure representation of bicyclo[3.1.0]hexenyl cation and of its cyclopentadienylcarbinyl rearrangement transition state provides easy rationalization of (most) what is experimentally observed. Thus, methyl substitution on the five-membered ring alone, results in stabilization of the ground-state



bicyclo[3.1.0]hexenyl cation, but offers very little in the way of energetic assistance to the cyclopentadienylcarbinyl transition-state structure. The barrier to methylene circumambulation increases, as the results of Childs and Parrington<sup>10</sup> on rearrangement in 1,2,4,5-tetramethylbicyclo[3.1.0]hexenyl cation attest. Except for the strange case of a single endo (methyl) substituent, either one or two methyl groups placed at the 6 position(s) of bicyclo[3.1.0]hexenyl cation are sufficient to outweigh the effects of basal (methyl) groups in altering the rearrangement energetics. Thus, heptamethylbicyclo[3.1.0]hexenyl cation undergoes degenerate methylene migration with an activation of only 9 kcal/mol, some 6 kcal/mol less than that observed for the parent.

We limit our theoretical treatment to a single example, that of dimethyl substitution on the three-membered ring. The STO-3G energies of the isodesmic process (13-15) when combined with our best theoretical



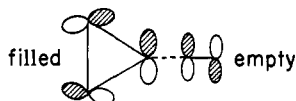
estimate of 20 kcal/mol (32 kcal/mol *via* the symmetry forbidden pathway) for rearrangement in parent bicyclo[3.1.0]hexenyl cation (or with Berson and Jenkins' experimental value of 15 kcal/mol)<sup>15</sup> show the expected effects. Indeed, the substituted cation is predicted by the theory to undergo symmetry allowed rearrangement (*i.e.*, *via* a *bisected* cyclopentadienylcarbinyl type struc-

ture) with a required activation of only 2 kcal/mol. In view of the apparent closeness in energy of ground (bicyclo[3.1.0]hexenyl)- and transition (cyclopentadienyl-carbinyl)-state structures here, and of the considerable limitations inherent to the theoretical model, it is quite conceivable that in actual fact their roles might be interchanged. (Indeed if we use Berson and Jenkins' experimental value for rearrangement in the parent, this is the conclusion.) Methyl substitution in *eclipsed* cyclopentadienylcarbinyl is more effective than on the *bisected* structure—not unexpected in view of experience with methyl substituent effects on *bisected* and *eclipsed* cyclopropylcarbinyl. Indeed stabilization of the *eclipsed* ion is so great as to bring its energy below not only that of the *bisected* form but also that of dimethylbicyclo[3.1.0] cation itself. Experimental investigation would be of great interest.

It is interesting to speculate on the effects of substitution on yet another rearrangement process common to the bicyclo[3.1.0]hexenyl and homotropylium systems; that is ring opening to produce cyclohexadienyl (benzenium) and cyclooctatrienyl cations, respectively. Hoffmann has recently put forth a model to explain the observed effects of substituents on the thermodynamics of cycloheptatriene–norcaradiene equilibrium.<sup>35</sup> Here, interaction between the lowest unoccupied molecular orbital on a ( $\pi$ ) withdrawing R sub-

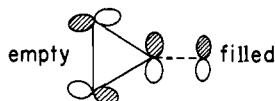


stituent (say the  $\pi^*$  orbital on a cyano group) and the highest filled Walsh cyclopropane component (on norcaradiene) results in electron transfer from the small ring to the substituent. Although bonding



electron density is removed from two of the cyclopropane linkages, leading to their weakening, the third ring-fused bond is actually strengthened as a result of the withdrawal. That is to say, as far as this linkage is concerned, the electrons removed from the three-membered ring came from an antibonding orbital.<sup>36</sup>

The effects of  $\pi$ -donating groups (the halogens, for example) arise due to delocalization of the high-lying (lone-pair) electrons on the substituent into the lowest unoccupied Walsh cyclopropane orbital. As a result, all three of the small ring linkages are weakened.

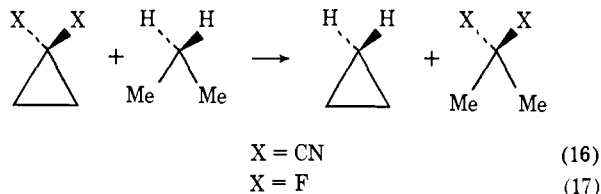


(35) (a) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); see also (b) H. Günther, *ibid.*, 5173 (1970).

(36) Hoffmann has commented on geometry changes in the three-membered ring due to substitution. Whereas  $\pi$ -withdrawing groups lead to a lengthening of two of the cyclopropane bonds and a shortening of the third (observed, for example, in structural investigations on 2,5-dimethyl-7,7-dicyanonorcaradiene<sup>37a</sup>) substitution by  $\pi$  donors is suggested to lead to a lengthening of all three ring bonds. The experimentally determined structure of 1,1-dichlorocyclopropane<sup>37b</sup> and STO-3G geometry of 1,1-difluorocyclopropane<sup>37c</sup> show the expected trends (see text following).

(37) (a) C. J. Fritchie, Jr., *Acta Crystallogr.*, 20, 27 (1966). (b) W. H. Flygare, A. Narath, and W. D. Gwinn, *J. Chem. Phys.*, 36, 200 (1962); (c) R. Bianchi, G. Morosi, A. Mugnoli, and M. Simonetta, *Acta Crystallogr., Sect. B*, 29, 1196 (1973).

Hoffmann's implication that increase or decrease in the bonding character of the ring fused cyclopropane linkage in norcaradiene (by  $\pi$ -withdrawing and donating substituents, respectively) results in a shift in thermodynamic equilibrium to and away from the bicyclic may easily be tested theoretically (or experimentally if appropriate thermochemical data were available) by consideration of the energies of the *isodesmic* processes (16) and (17). Indeed, STO-3G calculations<sup>38</sup> do indi-



cate that whereas a geminal pair of  $\pi$ -accepting (cyano) substituents stabilize cyclopropane (relative to the equivalently sized acyclic hydrocarbon) by 6.0 kcal/mol, destabilization of the small ring (by 2.3 kcal/mol) actually results by corresponding substitution of two donating (fluoro) substituents.

It would be of use to apply these same arguments—in a qualitative manner—in order to see what control one might possibly exercise over the thermodynamic equilibrium between the bicyclo[3.1.0]hexenyl–cyclohexadienyl (benzenium) and homotropylium–cyclooctatrienyl cation pairs. The latter is of special importance, for it is cyclooctatrienyl cation which is envisioned not as a stable ion but rather as a low energy transition state to “ring-flipping” in homotropylium. Recall that it was exactly such a process, leading to the scrambling of endo–exo methylene positions in homotropylium, which interfered with the experiment's ability to assign stereochemistry to possible rearrangement modes. We might suggest, therefore, that  $\pi$ -electron acceptor groups attached to the methylene positions in homotropylium would stabilize it over forms of cyclooctatrienyl cation, thereby increasing the barrier to pseudorotation from the 22.3 kcal/mol value observed experimentally in the parent. Unfortunately these same acceptor substituents (cyano, for example), while leading to net stabilization in homotropylium, would certainly play havoc with the energy of the circumambulation transition state, the *eclipsed* cycloheptatrienylcarbinyl cation, making degenerate rearrangement processes all the more difficult to observe. A happy compromise is not evident to this author at the present time.

### C. Orbital Models for Homoaromatic Stability.

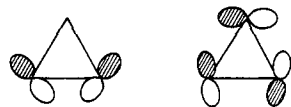
Let us now consider the origin of the stabilization due to aromaticity (and destabilization due to antiaromaticity) in the homotropylium and bicyclo[3.1.0]hexenyl cations. As mentioned in section A one way to visualize our bicyclic homo- and antihomoaromatic systems is to consider them as derivatives of the aromatic and antiaromatic polyenes, formed by the replacement of one double bond by a cyclopropane ring. That is to say, that instead of considering the external methylene

(38) Substituents attached to the optimum STO-3G structures of cyclopropane and propane<sup>39</sup> at the same bond angles as the hydrogens which have been replaced. C–F = 1.36 Å; C–C = 1.46 Å, C≡N = 1.16 Å.

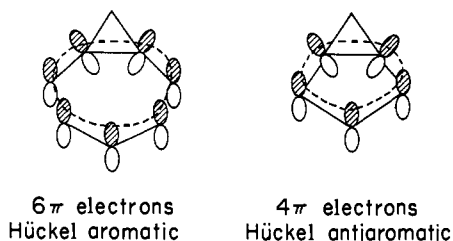
(39) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 93, 5339 (1971).



as an isolated entity, we treat it together with its two CH neighbors as part of a cyclopropane ring. The degenerate pair of valence orbitals (highest occupied molecular orbitals) of cyclopropane are well known<sup>26</sup> and the striking resemblance of the symmetric compo-



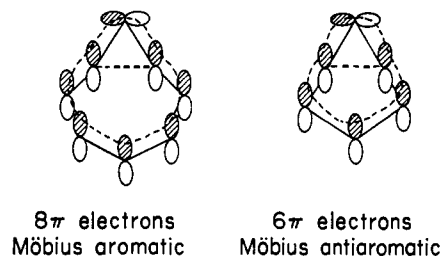
nent to the  $\pi$  orbital of an ethylenic double bond is reflected in a markedly similar chemical behavior of unsaturated and small ring molecules.<sup>40</sup> As visualized by Winstein<sup>12</sup> the two electrons occupying the symmetric Walsh orbital should be able to delocalize over the ring (but certainly less effectively than those in an ethylenic  $\pi$  bond), the resulting (homoaromatic) polyene being of the same structure as its (aromatic) parent, and containing the identical number of electrons in cyclic conjugation. This we would expect to be a satisfactory description in those cases where the cyclopropane was fully closed; that is, for example, in the hypothetical "classical" structures for the bicyclo[3.1.0]hexenyl and homotropylium cations, the orbital basis descriptions for which would incorporate the symmetric Walsh orbital of cyclopropane.



Alternatively we might visualize a situation with a relatively open cyclopropane moiety, thus effectively ruling out transmission of conjugation along the ring-fused bond, and necessitating the involvement of the basis orbitals of the external methylene. In this instance *two factors distinguish the resulting homoaromatic from its parent*. The number of electrons in the cycle has *increased by two*. Homotropylium now has eight electrons in conjugation, the bicyclo[3.1.0]hexenyl cation six. At the same time, however, electron delocalization through the valence orbitals of cyclopropane, has *increased by one* the number of nodes present in the atomic orbital basis of the cyclic polyene. That is to say that the increase in number of electrons in cyclic conjugation (for example, from six in tropylium to eight in homotropylium, and from four to six for the cyclopentadienyl–bicyclo[3.1.0]hexenyl cation pair) has been paralleled by a change from a Hückel to a Möbius ring structure. Thus both homotropylium and bicyclo[3.1.0]hexenyl cations may be thought of as Möbius molecules,<sup>41</sup> with an odd number of nodes in their atomic orbital representation. Below we show the sequence of *atomic orbitals* which form the Möbius array. The enhanced stability (or instability) of this homoaromatic arrangement follows directly from the

(40) For a readable account, see F. J. McQuillin, "Alicyclic Chemistry," Cambridge University Press, New York, N. Y., 1972.

(41) Other representatives include cyclopropane itself, trimethylene-methane, barrelene, and the cumulenes with an odd number of carbons; see ref 42.



theories of Heilbronner,<sup>42</sup> Dewar,<sup>43</sup> and Zimmermann.<sup>44</sup> Homotropylium with its eight electrons in cyclic conjugation is a Möbius aromatic while the six-electron bicyclo[3.1.0]hexenyl cation might equally well be termed Möbius antiaromatic.

It should be noted that the two alternative descriptions lead to the same conclusion. Thus, homotropylium is stabilized through aromatic conjugation, either *via* six electrons in a Hückel ring or eight in a Möbius arrangement. Correspondingly, applying either model, bicyclo[3.1.0]hexenyl cation is seen to suffer in stability from its antiaromatic character. The description of choice would seem to rest heavily upon geometrical arguments (see below), that is a fully formed cyclopropane ring favoring a Hückel polyene, a more open structure, the Möbius arrangement. In actual practice both models for electron delocalization are no doubt operative.

The detailed theoretical (STO-3G) structure for the bicyclo[3.1.0]hexenyl cation is presented in Table VI.

Table VI. Theoretical (STO-3G) Equilibrium Geometry of Bicyclo[3.1.0]hexenyl Cation<sup>a</sup>

$r(\text{C}_1\text{C}_2) = 1.463 \text{ \AA}$	$r(\text{C}_1\text{C}_5) = 1.483 \text{ \AA}$
$r(\text{C}_1\text{C}_6) = 1.617 \text{ \AA}$	$r(\text{C}_2\text{C}_3) = 1.391 \text{ \AA}$
$\angle(\text{C}_5\text{C}_1\text{C}_2) = 105.4^\circ$	$\angle(\text{C}_1\text{C}_2\text{C}_3) = 110.2^\circ$
$\angle(\text{C}_2\text{C}_3\text{C}_4) = 108.7^\circ$	$\angle(\text{C}_3\text{C}_5\text{C}_1) = 54.6^\circ$
$\angle(\alpha)^\dagger = 104.4^\circ$	$\angle(\text{HC}_1\text{C}_2) = 120.9^\circ$
$\angle(\text{HC}_1\text{C}_5) = 125.8^\circ$	$\angle(\text{HC}_2\text{C}_1) = 124.3^\circ$
$\angle(\text{HC}_6\text{C}_1\text{C}_5)^\ddagger, \text{d} = 122.2^\circ$	$\angle(\text{HC}_6\text{C}_1\text{C}_5)^\ddagger, \text{e} = 120.7^\circ$

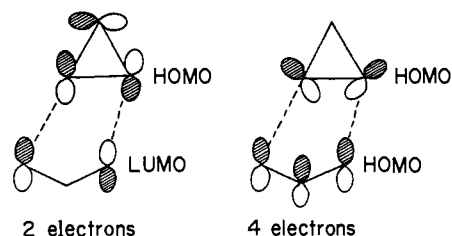
<sup>a</sup> Base five-membered ring, except for hydrogens 1 and 5, constrained to be planar; C–H bond lengths set at 1.10 Å. <sup>b</sup> Intersection angle of the planes formed by the five- and three-membered rings. <sup>c</sup>  $\text{C}_6\text{C}_1\text{C}_5$  is the line bisecting the three-membered ring. <sup>d</sup> Endo H. <sup>e</sup> Exo H.

Of importance to note is the local geometry of the incorporated three-membered ring. Here two of the bonds show a drastic lengthening (with respect to the normal (STO-3G) cyclopropane value of 1.50 Å) while the third, the ring-fused linkage, displays a slight shortening. These effects can easily be rationalized by considering the consequences of interaction of the valence  $\pi$  orbitals of an allyl cation with the degenerate pair of Walsh orbitals on cyclopropane, two fragments which can be visualized as the parents of the bicyclo[3.1.0]hexenyl system (Figure 5). Two interactions are im-

(42) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).

(43) (a) M. J. S. Dewar, *Tetrahedron, Suppl.*, 8, 75 (1966); (b) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, 10, 761 (1971).

(44) H. E. Zimmerman, *Accounts Chem. Res.*, 4, 272 (1971).

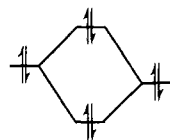


**Figure 5.** Interaction of the valence orbitals of allyl cation with the highest occupied symmetric and antisymmetric Walsh components on cyclopropane.

portant.<sup>45</sup> The two-electron term between the lowest unoccupied molecular orbital (LUMO) on the allyl cation and the antisymmetric Walsh component on cyclopropane, results in charge transfer (from cyclopropane to the allyl cation), the net effect of which is the loss of bonding electron density in two of the small ring linkages and of antibonding density in the third (ring-fused) one. Charge-transfer effects resulting from the four-electron interaction<sup>46</sup> (between the highest occupied allyl cation orbital (HOMO) and symmetric Walsh component) are generally of less importance, but should tend in the direction of increasing the bonding electron density in the ring-fused cyclopropane linkage. Little effect on the other pair of cyclopropane bonds is expected. Thus, overall, it would appear that the simple model does indeed well account, in a qualitative manner at least, for the theoretically observed lengthening of the apical pair of cyclopropane bonds and for lesser shortening of the basal linkage.

The STO-3G structure for homotropylium (Table VII) shows no significant changes in local geometry of the incorporated three-membered ring from that found in cyclopropane, an observation which at first glance would seem to be in contradiction to the predictions of simple charge-transfer model. Thus, as depicted in Figure 6, the two-electron interaction between the pentadienyl cation LUMO and the symmetric Walsh orbital would be expected to drain bonding electron density from the latter, and hence lead to a significant lengthening of the ring-fused cyclopropane bond. As before the four-electron interaction—between the highest occupied molecular orbitals of both fragments—should lead to lesser geometrical distortions, in this instance, a slight shortening of the apical cyclopropane linkages due to a piling up of bonding electron density in these regions. Neither of these anticipated changes is actually observed.<sup>47</sup> Although we might be tempted

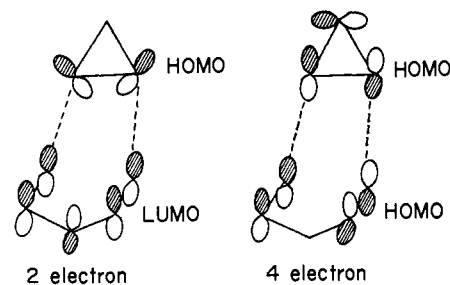
(45) We employ the arguments of perturbation theory. Upon interaction, energy levels split, that is to say, one is lowered, the other raised. It is important to note that the magnitude of energy raising (destabilization) is greater than that of lowering (stabilization). If in total two



electrons are involved, net stabilization results. Net destabilization results from the interaction of two doubly occupied orbitals—four electrons in total. For an enlightening discussion of a variety of consequences of orbital interaction, see R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

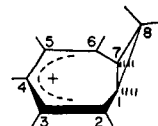
(46) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968); K. Muller, *Helv. Chim. Acta*, **53**, 1112 (1970).

(47) It is possible that had we allowed distortion from a planar seven-membered ring, or had we not insisted on a bisecting plane the anticipated geometrical distortions would have resulted.



**Figure 6.** Interaction of the valence orbitals of pentadienyl cation with the highest occupied symmetric and antisymmetric Walsh components on cyclopropane.

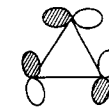
**Table VII.** Theoretical (STO-3G) Equilibrium Geometry for Homotropylium Cation<sup>a</sup>



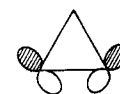
$r(\text{C}_1\text{C}_2) = 1.471 \text{ \AA}$	$r(\text{C}_1\text{C}_7) = 1.512 \text{ \AA}$
$r(\text{C}_1\text{C}_8) = 1.510 \text{ \AA}$	$r(\text{C}_2\text{C}_3) = 1.361 \text{ \AA}$
$r(\text{C}_3\text{C}_4) = 1.438 \text{ \AA}$	
$\angle(\text{C}_2\text{C}_1\text{C}_2) = 127.6^\circ$	$\angle(\text{C}_1\text{C}_2\text{C}_3) = 128.5^\circ$
$\angle(\text{C}_2\text{C}_3\text{C}_4) = 126.7^\circ$	$\angle(\text{C}_3\text{C}_4\text{C}_5) = 134.5^\circ$
$\angle(\text{C}_7\text{C}_8\text{C}_1) = 60.1^\circ$	$\angle(\alpha)^b = 103.0^\circ$
$\angle(\text{H}_1\text{C}_1\text{C}_2) = 116.3^\circ$	$\angle(\text{H}_1\text{C}_1\text{C}_2) = 112.8^\circ$
$\angle(\text{H}_2\text{C}_2\text{C}_1) = 114.6^\circ$	$\angle(\text{H}_3\text{C}_3\text{C}_2) = 115.8^\circ$
$\angle(\text{H}_8\text{C}_8\text{C}_7)^c, d = 121.9^\circ$	$\angle(\text{H}_9\text{C}_9\text{C}_8)^c, e = 121.4^\circ$

<sup>a</sup> Base seven-membered ring, except for hydrogens 1 and 7, constrained to be planar; C-H bond lengths set at 1.10 Å. <sup>b</sup> Interaction angle of the planes formed by the seven- and three-membered rings. <sup>c</sup> C<sub>8</sub>H<sub>17</sub> is the line bisecting the three-membered ring. <sup>d</sup> Endo H. <sup>e</sup> Exo H.

to ignore the disagreement between the simple perturbational treatment and the quantitative *ab initio* calculations regarding the geometrical distortions resulting from the (four-electron) HOMO-HOMO interaction, experience with the bicyclo[3.1.0]hexenyl system has clearly demonstrated that the structural consequences of two-electron interaction are significant and should be observable. Hoffmann has provided a plausible solution to the dilemma, in pointing out the detailed shapes of each of the degenerate pair of highest occupied molecular orbitals of cyclopropane (the Walsh orbitals).<sup>48</sup> Whereas the functions which make up the antisymmetric Walsh component are oriented approximately perpendicular to the ring-fused carbon-carbon bond, and hence are able to overlap optimally with pentadienyl terminal  $\pi$  orbitals, those which form the symmetric member are tilted considerably from this



preferred orientation. Overlap, and hence interaction,



with the diene termini is vastly reduced. As we have seen, the two-electron interaction in the bicyclo[3.1.0]-

(48) R. Hoffmann, private communication, Oct 4, 1973.

hexenyl cation involves the antisymmetric Walsh orbital, and it is not at all surprising that it—and its geometrical consequences—is significant. The symmetric Walsh component participates only in the relatively unimportant (geometrically speaking) four-electron interaction. In homotropylium, however, the roles of the two cyclopropane valence orbitals are reversed, and in view of what we have said about effectiveness of orbital overlap it perhaps should not be surprising that the resulting geometrical distortions are of a lesser magnitude. There are other possible causes for the seeming inability of the simple perturbational model to properly account for the calculated geometrical structure of homotropylium. Consider a comparison of the orbital interaction pattern for the bicyclo[3.1.0]hexenyl and homotropylium systems (Figure 7). As pointed out earlier the (geometrically) important interaction in the former system is the two-electron term between the allyl cation LUMO and the antisymmetric Walsh orbital on cyclopropane. A similar interaction is indeed possible between the two fragments which go to make up homotropylium; this time involving the lowest unfilled orbital of the pentadienyl cation with the symmetric Walsh component. Two differences in this crucial two-electron term in the two systems, bicyclo[3.1.0]hexenyl and homotropylium cations, are evident by a comparison of interaction diagrams and either or both may contribute toward the apparent lack of potency noted in the latter system. For one the pentadienyl LUMO is higher in energy than the analogous function on the allyl system, which means that according to simple perturbational arguments it interacts less with the appropriate valence Walsh orbital on cyclopropane. A second factor whose implications are not entirely obvious to this author, is that while the two-electron interaction between the allyl cation LUMO and the occupied Walsh component on cyclopropane (to make up the bicyclo[3.1.0]hexenyl cation) occurs without interference from the remainder of the valence orbital manifold, the corresponding interaction in homotropylium (this time between the lowest empty function on pentadienyl cation and the Walsh symmetric component) has competition. That is to say, perhaps we need to consider the overall interaction here as one involving three orbitals (both occupied high lying as well as the lowest unoccupied pentadienyl cation orbitals interacting with the symmetric Walsh component) and a total of four electrons. Thus one is tempted to visualize a cycle in which electrons transferred from the cyclopropane Walsh orbital to the pentadienyl cation LUMO are channeled back through (four electron) interaction of the two occupied members of the trio.

### Conclusion

We have concerned ourselves in this paper with the

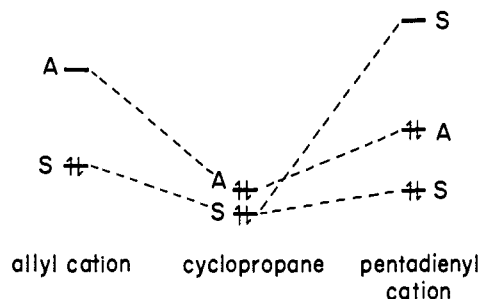


Figure 7. Comparison of allyl and pentadienyl cation interactions with the cyclopropane Walsh orbitals.

structures and stabilities of the bicyclo[3.1.0]hexenyl and homotropylium carbocations, and with the energetics of their degenerate circumambulatory rearrangements. Our instrument has been *ab initio* molecular orbital theory. The following general conclusions have emerged.

Both ions display to some extent the enhanced stability (or instability) of the parent aromatic (or antiaromatic) systems. Thus homotropylium (like tropylium) benefits from cyclic conjugation while the bicyclo[3.1.0]hexenyl cation (based on the antiaromatic cyclopentadienyl) suffers from it. The experimentally observed difference in activation required for degenerate rearrangement in the two ions is rationalized on this basis; that is aromatic stabilization of homotropylium, making passage through its rearrangement transition state a costly process, and antiaromatic destabilization of the bicyclo[3.1.0]hexenyl cation, facilitating its rearrangement.

Both parent ions undergo degenerate circumambulation in the manner dictated by symmetry conservation arguments for suprafacial [1,4] and [1,6] shifts. Dimethyl substitution on the external methylene positions significantly decreases rearrangement barriers in both ions, and in the case of homotropylium is suggested by the calculations to lead to a favoring of the Woodward–Hoffmann forbidden pathway over the allowed.

Both homotropylium and bicyclo[3.1.0]hexenyl cations exhibit geometrical structures consistent with normal Hückel polyene arrangements, just as found in the base aromatic and antiaromatic systems. Möbius arrangements, in which cyclic conjugation significantly involves the orbitals and electrons of the external methylene, would seem to be of lesser importance.

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