be obtained in the case of IA from the reported[7,30] energy of its lowest triplet state, which is also believed to correspond to $1 \rightarrow -1$ excitation. The singlet-triplet splitting is $2K_{1,-1} = 4800\ \text{cm}^{-1}$, to be compared with $13\,700\ \text{cm}^{-1}$ in naphthalene ($^1L_a - {}^3L_a$).[31] A similar situation has already been noticed for azulene and discussed in detail.[32] It probably prevails throughout the A and P families discussed here.

In summary, we believe that low-lying electronic states of the two title families of nonalternant hydrocarbons are now reasonably well understood. Some simple interpretations can be made even for higher states of certain of the compounds, but they are not generally applicable throughout the series, since they involve orbitals which are too profoundly modified by the various attached fragments and transitions whose description in terms of ordinary MO's requires considerable configuration mixing, and thus are of less interest for a simple classification scheme.

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Structure of Transition States. 4. MINDO/2 Study of Rearrangements in the C_6H_{10} System

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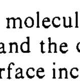
Abstract: A portion of the potential energy surface for C_6H_{10} is examined using the MINDO/2 molecular orbital method. The reactions include [3,3] sigmatropic shifts, double methylene isomerization of 1,5-hexadiene, and the cleavage and inversion of bicyclo[2.2.0]hexane. The calculations involve the location of 16 stationary points on this surface including geometries that characterize reactants, products, intermediates, and transition states for the various isomerizations. From the calculated force constants and vibrational modes together with the use of group theoretical theorems governing the symmetries of reaction paths, a picture of this energy surface is constructed and mechanistic information is deduced and compared to available experimental evidence. The various isomerizations are divided into two sets of HOMOmeric reactions corresponding to two molecular orbital energy surfaces in such a way that reaction paths between two structures on different surfaces are LUMOmeric.

Introduction

One of the earliest studied isomerizations of C_6H_{10} is the [3,3] sigmatropic shift or Cope rearrangement[2] of 1,5-hexadiene. The now classic experimental work of Doering and Roth suggested that the most facile route for this rearrangement involved a four-centered (chair-like) transition state.[3] The kinetic parameters for this "chair" rearrangement were subsequently determined.[4] More recently, the kinetic parameters for a Cope rearrangement involving a "boat-like" transition state have been obtained,[5] as have also the parameters for the inversion and stereospecific cleavage of bicyclo[2.2.0]hexane.[6] There is some controversy concerning the detailed mechanism of the latter.[7]

In the above investigations the species 1,4-cyclohexylene (**1**)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emerges as the central structure involved in these reactions. In particular, one can assign detailed structures to **1** such as chair, boat, twist-boat, or planar, analogous to the cyclohexane system, and one can also identify these structures with isotopically or stereochemically distinct reactions.[8]

If one is working within the context of transition state theory, it becomes useful and meaningful to ask what are the energies and structures of **1** and what role do they play in the above-mentioned reactions. Specifically one would like to characterize these structures as transition states, intermediates, or other stationary points on the many-dimensional potential energy surface and in this way construct a "picture" of this surface. Although experimental investigations have been highly successful in determining the stereochemistry of these reactions, a convenient and potentially fruitful approach is through the computational investigation of the C_6H_{10} stationary structures on approximate potential energy surfaces.

An attempt to extract useful information from computations on systems of the size and type dealt with here demands caution and necessitates the use of approximate methods. Regardless of the method used to obtain energies, one cannot currently reach the "one kilocalorie" limit desired for chemical accuracy for systems of this size. Closed-shell molecular orbital methods, although moderately reliable for stable closed-shell molecules, fail when comparison is made between diradicals and stable structures. The computational expense of accurate ab initio methods currently precludes the optimization of geometries and the evaluation of force constants for realistic chemical systems the size of C_6H_{10}. We have, therefore, foregone accurate ab initio methods and have used the semiempirical MINDO/2[9] molecular orbital method which allows the rapid calculation of geometries and force constants.[10] Although caution is still needed when comparing energies of **1** with those of reactants or products, we would expect the relative energies to be of at least qualitative accuracy when forms of the monocyclic structure **1** are compared with one another. Our approach has the advantage of allowing the computation of fully optimized structures and to identify them as transition states or intermediates, and also to obtain the energy and entropy of activation.[11] The latter is estimated from the partition function, which is obtained in turn from the calculated force constants.

Previous computational studies on the C_6H_{10} system have largely focused on only two of the proposed structures, the chair and boat suggested in the Cope rearrangement. These investigations, ranging in complexity from valence force fields[12] and Hückel theory to the more elaborate self-consistent field molecular orbital methods[14] were directed at an understanding of the difference in stability between these two structures. Since most investigations have implicitly assumed that the Cope rearrangement proceeds in a concerted fashion, without the presence of intermediates, the calculated structures were never explicitly characterized as intermediates or transition states. We are unaware of any computational studies on the inversion and cleavage of bicyclo[2.2.0]hexane.

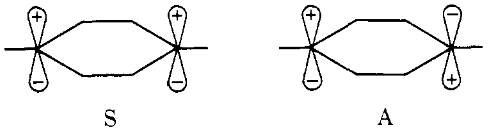
The purpose of this work is to identify the significant features of the C_6H_{10} potential energy surface and to interpret these features in terms of some of the possible rearrangements within this system. In particular, only those reactions involving [3,3] sigmatropic shifts, double methylene twists of 1,5-hexadiene, and its closure to bicyclo[2.2.0]hexane will be considered. The computation of the structures, energies, and vibrational frequencies, together with a knowledge of the symmetry of the vibrational modes, enables us[11b,c] to unify the chemistry implied by the C_6H_{10} potential surface. This is done by locating and characterizing 16 stationary structures on this surface. Our results indicate that the classical chair and boat can be classified as *metastable intermediates* in the Cope rearrangement. This is in contrast to most previous assumptions. Doering et al., however, have pointed out that an intermediate with negligible activation energy is also consistent with the experimental results.[4a] Structures which act as transition states in the cleavage and isomerization of bicyclo[2.2.0]hexane have also been found along with the two transition states for the Cope rearrangement. In the following section the computational methodology is outlined. The computed results for each structure are presented in the Results while the Discussion describes the mechanistic implications of these results.

Computational Methods

The MINDO/2 method, as developed by Dewar and coworkers,[9] shows some promise as a useful model of potential energy for the study of chemical structure and reactivity. Like other semiempirical molecular orbital methods, the power of MINDO/2 lies in its computational economy and its interpretability. Equilibrium geometries and transition states for systems the size of C_6H_{10} (and even larger) can be located and characterized at only a moderate computational expense, and the results of these computations can be discussed in terms of such familiar concepts as orbital symmetry, etc. The MINDO/2 method in particular was specifically designed, via its parameters, as a vehicle for studying molecular structure and energy. Finally, and perhaps most significantly, extensive use of this method is fairly clearly establishing the limits of its reliability and accuracy, thus leading to further refinements for overcoming MINDO/2's difficulties.[15]

MINDO/2 works best for hydrocarbons where calculated geometries are in reasonable accord with experiment and in many cases the relative energies as well. MINDO/2 fails in predicting relative energies between ring compounds and their open-chain analogues: the rings are found to be excessively stable. This problem is most serious for strained rings. We find in the C_6H_{10} system reported here, for example, that MINDO/2 predicts bicyclo[2.2.0]hexane to be 42 kcal more stable than 1,5-hexadiene. Experimentally, it is known to be about 10 kcal *less* stable.[16] Within a given ring system such as **1**, however, we cautiously expect the calculated relative stabilities of various conformers to have a somewhat closer correspondence to experimental reality. This was found to be true in the cyclohexane system (which resembles **1** in some ways), where the calculated energies were always within 5 kcal of the experimental energies.[11b]

An important distinction between **1** and cyclohexane lies in the diradicaloid character of the former. In simple molecular orbital theory this manifests itself in the presence of a high-lying doubly occupied and a low-lying vacant orbital mainly involving symmetric (S) and antisymmetric (A) combinations of atomic orbitals of the two radical sites, as illustrated in **2** (the symmetry element here being a C_2 axis perpendicular to the ring). Aside from the question of the sense of which the orbitals are designated by their symmetry, it is not always obvious which of them will be occupied in the ground-state molecular orbital wave function at any particular geometry. In a Hückel theory this question is settled by the aufbau: by first determining the orbital energies and then populating them in ascending order. In an SCF theory such as MINDO/2, there may very well be two (or more) solutions to the SCF equations which will differ in the symmetry of the highest occupied orbitals and both of these solutions may satisfy the aufbau in that there will be no vacant orbitals lying below occupied orbitals. Thus there may be two MINDO/2 potential energy surfaces in the diradical region, each with its own set of optimum geometries corresponding to the various conformers of **1**. In order to determine which surface is lower in energy for any given configuration of the nuclei, it is necessary to compute both. This computational problem is treated here by populating



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the highest occupied orbital by its symmetry (or approximate symmetry) rather than by its energy.

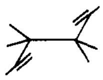
The optimization procedures for determining the various geometries have been previously described.[10] Briefly, they involve locating structures which are stationary points (points of zero gradient) on the potential energy surface. A variable metric method[10b] was used to find geometries which were believed to be minima, or minima within a given symmetry, whereas a least-squares method applied to the norm of the gradient was used to locate structures believed to be saddle points.[10a] Starting geometries for the least-squares method were determined by the linear internal coordinate path method recently described.[11c] Further characterization of the stationary points as minimum energy geometries (equilibrium geometries and intermediates) or saddle points (transition states) requires computation of the force constants: energy minima require that all eigenvalues of the force constant matrix be positive, whereas transition states require that there be one and only one negative eigenvalue.[11a] As described previously, the symmetry species of the eigenvector of the force constant matrix in Cartesian coordinates corresponding to the single negative eigenvalue provides an important tool for determining the reactions for which a given structure can serve as transition state.[17] The force constants were computed by the finite difference technique described in the first paper in this series.[10] Aside from our use of Cartesian coordinates, this technique is essentially identical with the "Force Method" of Pulay.[18]

Results

We report herein 16 stationary points on the MINDO/2 potential surfaces for this C_6H_{10} system. Five of these correspond to various conformations of 1,5-hexadiene, and another to the equilibrium geometry of bicyclo[2.2.0]hexane. Ten more, labeled by their symmetry, correspond to various forms of **1**. Three of these (of D_{2h}, D_2, and C_{2h} symmetry) were found in both high- and low-energy forms corresponding to the two solutions of the SCF equations. In order to save journal space, the Cartesian coordinates of each structure appear in tables in the microfilm supplement. The more interesting structural features along with other computational results are summarized below.

1,5-Hexadiene. Of the many conceivable stable conformers of 1,5-hexadiene arising from rotations about the three C-C single bonds, it is difficult to estimate which would be the most stable and by how much. We are also unaware of any experimental structural work on this molecule.

The four lowest energy conformers calculated are given below. The most stable calculated conformer is **3**, with the 1234 and 2345 dihedral angles of 103 and 69°, respectively. The structure **3** has C_2 symmetry with the C_2 axis perpendicular to the plane of the paper. Other than the dihedral angles about the C-C single bonds, the geometrical parameters of all the conformers were found to be virtually identical with one another. The C(1)-C(2) double bond lengths were found to be 1.32 Å, while the C(2)-C(3) and C(3)-C(4) single bond lengths are 1.48 and 1.51 Å, respectively. The energies of **4**, **5**, and **6** relative to the most stable conformer **3** are 0.5, 2.3, and 2.5 kcal, respectively. An examination of the force constants revealed that among the four structures only **3** was a true energy minimum, the others being unstable with respect to torsional motion about one or more of the C-C single bonds. The energies of all the optimized 1,5-hexadiene structures were within 3 kcal of one another. The structure resembling **3** was chosen as the reference compound in this study.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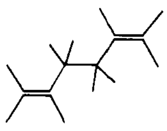
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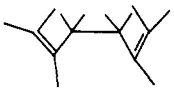
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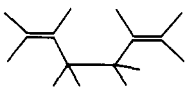
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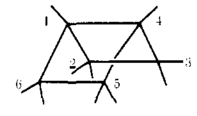
Bicyclo[2.2.0]hexane. A recent electron diffraction study[19] indicates that like cyclobutane itself, the two rings in this compound are puckered. The puckering angle here is only 11.5°, compared to 35° in cyclobutane. MINDO/2 predicts both compounds to have planar rings. However, an examination of the calculated force constants indicates a very low (calculated 142 cm^{-1}) vibrational frequency corresponding to the ring puckering mode. The remaining geometrical parameters are typical of those predicted by MINDO/2. Thus, the CH bond lengths are too long by about 0.1 Å. The calculated C-C bond lengths ($R_{12} = R_{23} = 1.51$ Å, $R_{14} = 1.52$ Å, as numbered in **7**) are a few hundredths of an angstrom shorter than experiment (1.557, 1.542, and 1.577 Å, respectively, with an experimental error of about 0.02 Å), although the correct ordering of these values is obtained. The HCH bond angles (101°) fairly well reproduce the experimental values (105°). The C(3)-C(4)-C(5) bond angle (119° calculated, 113.5 ± 1.1° experimental) is found to be several degrees too large. The overall agreement between the calculated and experimental geometry can be described as reasonable. However, as mentioned earlier, this is not the case with the calculated energy: the energy of this molecule, relative to 1,5-hexadiene, is a pathological example of MINDO/2's tendency to underestimate strain.



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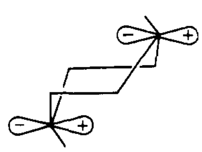
Monocyclic Structures. Goldstein and Benzon,[8] in their elegant analysis of the first-order kinetics of the sigmatropic shifts of 1,5-hexadiene-d_4, have suggested five symmetrical forms of **1** as possible intermediates or transition states. We have investigated four of these: C_{2h} chair, C_{2v} boat, D_2 twist-boat, and D_{2h} (or C_{2h}) plane named in analogy to cyclohexane. In addition, two different structures of C_s symmetry, one involved in the Cope rearrangement and one in the cleavage of bicyclo[2.2.0]hexane, and a C_2 structure (for the Cope rearrangement) were found. The results for each structure are discussed below.



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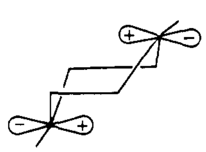

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C_{2h} Chair. Two chair-like structures were located by minimizing the energy in C_{2h} symmetry. The low energy (20.2 kcal above 1,5-hexadiene) structure **8** is characterized by a highest occupied orbital that is antisymmetric under a C_2 rotation, whereas the high energy (52 kcal above hexadiene) structure **9** has a highest occupied orbital that is symmetric under C_2, as illustrated. There are a number of geometrical differences between the two structures. The C(1)-C(6) bond lengths are 1.61 Å for the low-energy structure **8** and only 1.50 Å for the high-energy form **9**. In both cases, the methine CH bonds lie out of the plane of the allyl carbons, in contrast to the MINDO/2 results reported by Dewar and co-workers on this structure.[14] In **8**, the CH bond points toward the center of the C_6 ring having an angle of 156° with the plane of the allyl carbons, whereas in **9** these CH bonds point away from the ring with an angle of 164°. The results of force constant calculations on these structures indicate that the low-energy structure is an energy minimum and must therefore be regarded as an in-

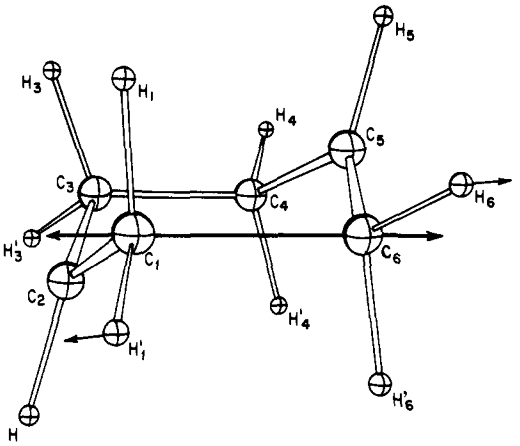


Figure 1. ORTEP drawing of the C_2 transition state for Cope rearrangement through "chair" intermediate. The arrows indicate relative displacements of the atoms along the transition vector.

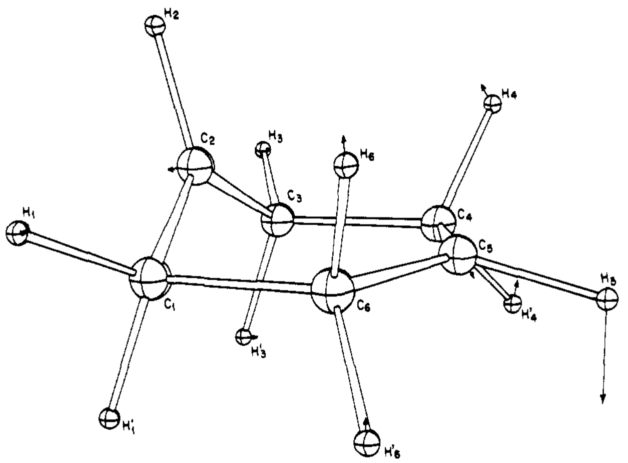


Figure 2. ORTEP drawing of the C_s transition state connecting the "chair" intermediate and bicyclo[2.2.0]hexane. The arrows indicate relative displacements of the atoms along the transition vector.

termediate rather than a transition state. Experimental work by Dewar and co-workers on phenyl-substituted hexadienes does suggest the presence of intermediates in these substituted systems.[20] The force constant matrix of the high-energy structure had two negative eigenvalues with corresponding eigenvectors of B_u symmetry. Because of these two negative eigenvalues, this structure is neither an intermediate nor a transition state. An interesting implication of this result will be mentioned in the next section.

C_2 Transition State. The revelation that the low-energy C_{2h} chair structure **8** was an intermediate led us to search for the transition state connecting this structure and 1,5-hexadiene. The result of this search is the C_2 structure shown in Figure 1, an ORTEP[21] plot of the calculated geometry. The geometry of this species lies intermediate between that of the C_{2h} structure **8** and 1,5-hexadiene. Thus, from Table I we see that the C(1)-C(6) and the C(2)-C(3) bond lengths have lengthened from 1.61 and 1.42 Å in C_{2h} (**8**) to 1.91 and 1.47 Å in the C_2 transition state, whereas the C(1)-C(2) and C(3)-C(4) bonds have shrunk from 1.42 and 1.61 Å in C_{2h} (**8**) to 1.36 and 1.54 Å in the transition state. The other geometrical parameters of C_2 are nearly identical with those corresponding in C_{2h} (**8**).

The energy of this transition state lies 22.4 kcal above 1,5-hexadiene and thus only 2.2 kcal above the C_{2h} chair **8**, indicating that the chair intermediate lies in a rather shallow well. When the calculated zero point corrections are included, the depth of this well shrinks to 2.0 kcal.

Table I. Calculated Geometrical Parameters of C_{2h}, Low-Energy, and C_2 Structures

Bond, Å	C_{2h}	C_2
C(1)-C(2)	1.42	1.36
C(2)-C(3)	1.42	1.47
C(3)-C(4)	1.61	1.54
C(1)-H(1)	1.22	1.21
C(2)-H(2)	1.20	1.20
C(3)-H(3)	1.22	1.22
C(1)-C(6)	1.61	1.91
Angle, deg		
C(1)-C(2)-C(3)	119.4	121.1
C(2)-C(3)-C(4)	107.5	109.0
H(1)-C(1)-H(1)'	102.2	106.3
H(2)-C(2)-C(3)	117.5	116.5
H(3)-C(3)-H(3)'	102.2	101.0
Dihedral angle, deg		
C(1)-C(2)-C(3)-C(4)	57.2	61.7
C(2)-C(3)-C(4)-C(5)	50.1	49.0
Angle with plane, deg[a]		
C(1)-C(2)-C(3)-H(2)	156.5	160.3

[a] (A-B-C-D) refers to the angle between the plane defined by atoms A, B, C, and the B-D bond.

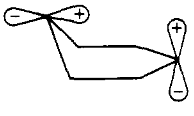
The force constant matrix of the C_2 structure possessed a single negative eigenvalue. The transition vector[17] is illustrated by the arrows in Figure 1. This vector can be seen to be totally symmetric as is required by symmetry if C_2 is to be a transition state for the C_{2h} hexadiene conversion.[17b] That this structure indeed serves as a transition state connecting 1,5-hexadiene and **8** was verified by displacing the atoms slightly along the transition vector and performing a geometry optimization. The resulting structure was either hexadiene or **8**, depending on the direction of the initial displacement.

The highest occupied orbital of this structure, like that of the low-energy C_{2h} intermediate **8**, was found to be antisymmetric under C_2.

C_s Transition State. The C_s structure shown in Figure 2 was found to be the transition state connecting the C_{2h} chair intermediate **8** and bicyclo[2.2.0]hexane. It lies 33.8 kcal above 1,5-hexadiene. As was the case in the C_2 transition state, the geometry of this structure, measured by the bond lengths, lies intermediate between C_{2h} (**8**) and bicyclohexane. Geometrical parameters are given in Table II.

The identification of this structure as a transition state again resulted from the fact that its force constant matrix possessed a single negative eigenvalue. The arrows in Figure 2 illustrate the transition vector. Displacement of the atoms along this vector, followed by geometry optimization resulted in C_{2h} (**8**) or bicyclohexane, depending on the direction of the initial displacement.

Although the highest occupied orbital cannot be characterized by its symmetry, analysis of the coefficients of this orbital shows that it is of the form illustrated in **10** below, which is consistent with a "low-energy" assignment of this structure.



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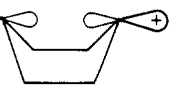
C_{2v} Boat. Like the chair intermediates, the C_{2v} boat structure **11** was obtained by minimizing the energy in C_{2v} sym-

Table II. Calculated Geometrical Parameters of the C_s Transition State

Bond, Å	Calcd	Angle, deg	Calcd
C(1)-C(2)	1.45	C(1)-C(2)-C(3)	134.5
C(3)-C(4)	1.53	C(2)-C(3)-C(4)	110.4
C(4)-C(5)	1.44	C(3)-C(4)-C(5)	100.1
C(1)-H(1)	1.23	C(4)-C(5)-C(6)	121.8
C(2)-H(2)	1.21	H(1)-C(1)-H(1)′	99.8
C(4)-H(4)	1.22	H(2)-C(2)-C(1)	112.4
C(5)-H(5)	1.20	H(4)-C(4)-H(4)′	102.1
		H(5)-C(5)-C(6)	119.1
Dihedral angle, deg		Angle with plane, deg	
C(2)-C(1)-C(3)-C(4)	178.6	C(1)-C(2)-C(3)-H(2)	15.4
C(5)-C(6)-C(4)-C(3)	105.8	C(6)-C(5)-C(4)-H(5)	1.7
C(1)-C(2)-C(3)-C(4)	1.5		
C(2)-C(3)-C(4)-C(5)	27.8		

metry. The highest occupied orbital of this species is antisymmetric under the C_2 rotation. Attempts to optimize the C_{2v} structure with the highest occupied orbital restricted to be symmetric under C_2 led, in all cases, to the collapse of the initial structure to bicyclo[2.2.0]hexane. We thus label the C_{2v} structure (**11**) which lies 29.9 kcal above 1,5-hexadiene as the



11

"high-energy" C_{2v} and bicyclohexane, which lies 42 kcal below hexadiene, as the low-energy C_{2v}. The calculated geometry of **11** resembles in many ways that of the low-energy C_{2h} chair **8**. Thus the CH bonds involving the methine hydrogens point into the C_6 ring and have an angle of 151° with the plane of the allyl carbons. Similarly, the C-C bond lengths (R_{16} = 1.64 Å, R_{12} = 1.42 Å) also resemble those of **8**. An examination of the force constant matrix for **11** revealed that it too was an energy minimum and is thus designated an intermediate rather than a transition state in the Cope rearrangement.

C_s' Transition State. The structure shown in Figure 3, which we label C_s', is the MINDO/2 transition state connecting the C_{2v} boat intermediate **11** and 1,5-hexadiene. Its energy lies 30.3 kcal above hexadiene and is thus only 0.4 kcal above **11**, indicating that the boat intermediate lies in a very shallow well. Although the energy of this structure lies very close to that of C_{2v} (**11**), the C-C bond lengths are close to the mean of those of C_{2v} and 1,5-hexadiene. Thus the C(1)-C(2) bond length is 1.38 Å in C_s', midway between 1.42 (C_{2v}) and 1.32 Å (1,5-hexadiene). Similarly the C(2)-C(3) bond length of 1.45 Å lies halfway between 1.42 (C_{2v}) and 1.48 Å (1,5-hexadiene), as does the C(3)-C(4) bond (1.58 Å in C_s', 1.64 Å in C_{2v}, and 1.51 Å in hexadiene). The geometrical parameters of C_{2v} and C_s' are summarized in Table III.

As with all structures labeled as transition states in this paper, the force constant matrix of C_s' was found to have a single negative eigenvalue. The transition vector in this case is totally symmetric. The arrows in Figure 3 correspond to a displacement along this transition vector.

The highest occupied orbital is antisymmetric under reflection in the mirror plane. We thus label C_s' as a "high-energy" structure.

D_2 Transition State. Both "low energy" (40 kcal above hexadiene) and "high energy" (50 kcal) D_2 transition states

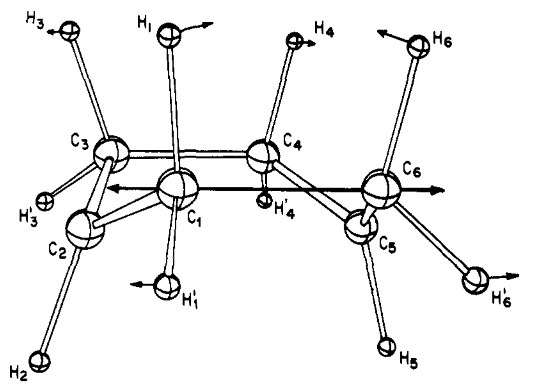
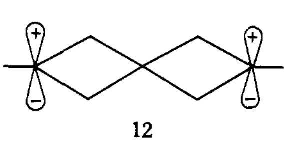


Figure 3. ORTEP drawing of the C_s' transition state for the Cope rearrangement through the "boat" intermediate. The arrows indicate relative displacements of the atoms along the transition vector.

Table III. Calculated Geometrical Parameters of the C_{2v} and C_s', High-Energy Transition State

Bond, Å	C_{2v}	C_s'
C(1)-C(2)	1.42	1.38
C(2)-C(3)	1.42	1.45
C(3)-C(4)	1.64	1.58
C(1)-H(1)	1.22	1.21
C(2)-H(2)	1.21	1.21
C(3)-H(3)	1.22	1.22
C(1)-C(6)		1.79
Angle, deg		
C(1)-C(2)-C(3)	119.4	120.2
C(2)-C(3)-C(4)	111.2	111.9
H(1)-C(1)-H(1)′	102.4	105.2
H(2)-C(2)-C(3)	116.3	115.8
H(3)-C(3)-H(3)′	102.4	101.2
Dihedral angle, deg		
C(1)-C(2)-C(3)-C(4)	48.5	51.4
C(2)-C(3)-C(4)-C(5)	0.0	0.0
Angle with plane, deg		
C(1)-C(2)-C(3)-H(2)	151.4	153.5

were found. The symmetry of the highest occupied orbitals of these two structures are illustrated below (**12** and **13**, respectively). The geometries of these structures are nearly identical.



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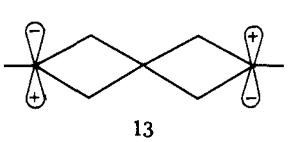


13

Thus the C(1)-C(2) and C(1)-C(6) bond lengths of 1.44 and 1.52 Å, respectively, are the same in both structures and the bond angles are within a few degrees of one another. The geometrical parameters of the low-energy D_2 structure are given in Table IV.

Both structures can act as transition states; both have force constant matrices possessing a single negative eigenvalue. The corresponding transition vectors are of different symmetries, however. The transition vector of the low-energy structure **12** is symmetric under a C_2 rotation about the axis perpendicular to the plane of the paper (illustrated in Figure 4), whereas the high-energy structure **13** is antisymmetric under this operation. The reactions for which these structures can serve as transition states can be determined by the use of symmetry rules, as will be discussed later.

Planar Structures. Goldstein and Benzon[8] have suggested

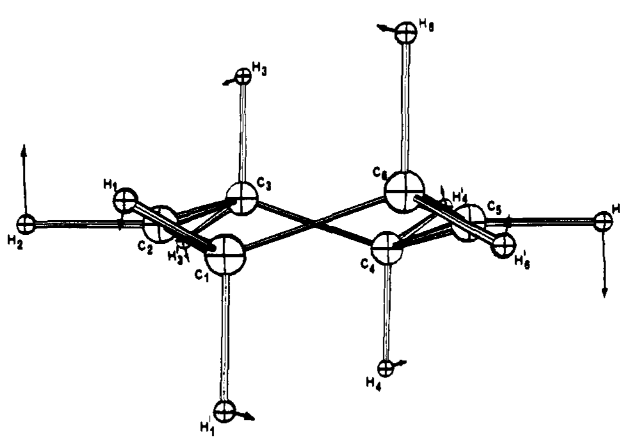


Figure 4. ORTEP drawing of the low-energy D_2 transition state. The arrows indicate relative displacements of the atoms along the transition vector.

Table IV. Calculated Geometrical Parameters of the Low-Energy D_2 Transition State

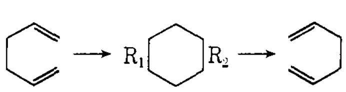
Bond, Å	Calcd	Angle, deg	Calcd
C(1)-C(2)	1.44	C(1)-C(2)-C(3)	125.5
C(2)-C(3)	1.44	C(2)-C(3)-C(4)	112.3
C(3)-C(4)	1.52	H(1)-C(1)-H(1)′	99.5
C(1)-H(1)	1.22	H(2)-C(2)-C(3)	117.2
C(2)-H(2)	1.21		
Angle with plane, deg		Dihedral angle, deg	
C(1)-C(2)-C(3)-H(2)	0.0	C(1)-C(2)-C(3)-C(4)	19.9
		C(2)-C(3)-C(4)-C(5)	36.7

that a structure of C_{2h} symmetry with the carbon atoms coplanar might act as a transition state in the Cope rearrangement. Energy minimization of several structures of this type led in all cases to a D_{2h} geometry. Both low- and high-energy forms were found with the highest occupied orbitals of the S and A symmetries, respectively, illustrated in **2.** The low-energy structure lies 42 kcal above hexadiene, whereas the high-energy structure is 57 kcal above hexadiene. As was the case with the D_2 structures, the geometries of these species are very similar. Neither structure is a transition state since the force constant matrix of each possessed three negative eigenvalues. The corresponding eigenvectors of each are of B_{1g}, B_{2u}, and A_u symmetries. The bond lengths of the two D_{2h} and the two D_2 structures are very similar (C(1)-C(6) = 1.52 Å, C(1)-C(2) = 1.44 Å in all).

Discussion

The main task of this section is to assemble the computed results into a qualitative picture of a small portion of the potential energy surface of the C_6H_{10} system and to discuss the mechanistic consequences of this surface. Before doing this, however, some preliminary discussion of the characteristics of the individual structures and their implications is appropriate.

Previous calculations of the Cope rearrangement have implicitly assumed that the C_{2h} chair and C_{2v} boat structures obtained by minimizing the energy in each symmetry are transition states rather than the intermediates we have found them to be. It has been argued on the basis of force constants that these structures should be intermediates.[22] Thus, if one assumes (1) that the bond lengths R_1 and R_2 depicted in **14**



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below are the only important degrees of freedom in the Cope rearrangement, (2) that they are equal in the intermediate structure, and (3) that this intermediate structure is an energy minimum within the appropriate symmetry (e.g., C_{2h} or C_{2v}), then the symmetric stretching force constant $K + K'$

$$K = \frac{d^2E}{dR_1{}^2} = \frac{d^2E}{dR_2{}^2}, \; K' = \frac{d^2E}{dR_1 dR_2}$$

must be positive. Only in the unlikely event that $|K'| > |K|$ (unlikely since K' should be small due to the 2.5 Å separating these bonds) will the antisymmetric force constant be negative so that the symmetrical structure is probably a minimum rather than a transition state. From this reasoning we might conclude that, contrary to our results, all such energy minimized structures (e.g., D_2 twist-boat) are intermediates rather than transition states. As can be seen from Figure 4, the failure of the argument is due to the failure of the first assumption (the latter two are rigorous requirements of symmetry for the structure to be a transition state), so that such naive arguments must be used with great caution.

There is a nearly universal tendency among chemists to visualize a chemical reaction in terms of a reaction path: a continuous line in configuration space representing the transformation of a reactant geometry into one which represents the product. One cannot uniquely specify such a path without also specifying the types of coordinates used,[23] so that the detailed path is rather arbitrary. Certain points along the path are well defined, however. These are the stationary points corresponding to the reactant and product equilibrium geometries and the transition state (the lowest energy barrier) lying between the reactant and product. In complex systems, such as C_6H_{10}, having many reactants, products, and conceivable transformations among them, one is concerned with questions of mechanism and knowledge of the energetically favorable reaction paths. The determination of these reaction paths gives us a picture of the energy surface from which we can make some mechanistic predictions. In the present case a trivial example of such reaction paths is illustrated in Figure 5 for the Cope rearrangements through the chair and boat intermediates. The calculated relative energies in kilocalories are given alongside the arrows. Although such reaction profile diagrams as Figure 5 clearly illustrate the presence of the C_{2h} and C_{2v} structures as intermediates, they tend to mask the fact that the two Cope rearrangements are quite distinct reactions: the rearrangement through the chair structure involves a conrotatory twisting of adjacent methylenes, whereas the boat reaction involves a disrotatory twist. In considering several rearrangements, the situation is considerably simplified by the presence of two MINDO/2 energy surfaces and the existence of a rather high degree of symmetry. The former allows us to characterize reactions as being thermally allowed or forbidden in the Woodward-Hoffman sense, while the latter allows us to rigorously characterize the reaction paths by using symmetry rules which permit or exclude certain structures as transition states for a given reaction.

The monocyclic structures described in the previous section were characterized as "high energy" or "low energy" depending upon the symmetry of the highest occupied molecular orbital of each. If one were to construct an orbital correlation diagram connecting a "high-energy" structure with its "low-energy" counterpart of the same symmetry, one would always encounter a crossing of highest occupied and lowest vacant molecular orbitals, and hence also of the MINDO/2 energy curves. The transformation can thus be characterized as thermally forbidden by the Woodward-Hoffmann rules.[24]

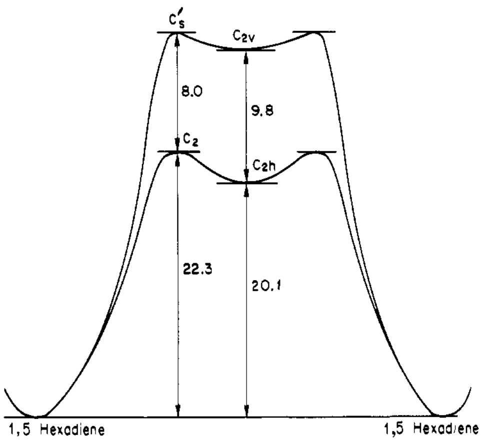


Figure 5. Reaction profile diagram comparing the relative energies along the reaction paths for the "chair" and "boat" Cope rearrangements.

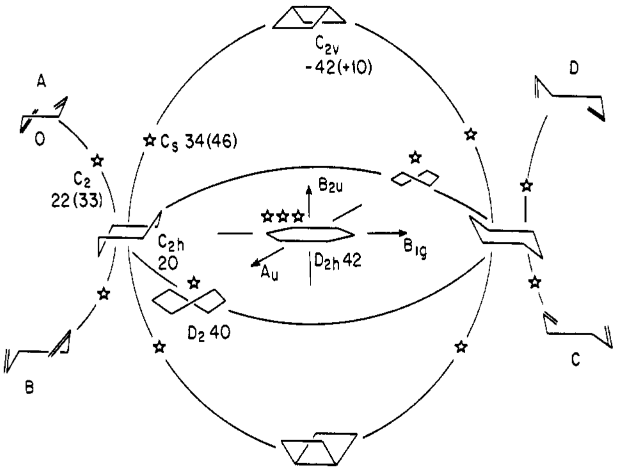


Figure 6. Illustration at the "low-energy" MINDO/2 potential surface. Tie lines indicate reaction paths. Structures shown without a star are minimum energy geometries. A single star indicates the presence of a transition state. Structures with two or three stars have force constant matrices with two or three negative eigenvalues, respectively.

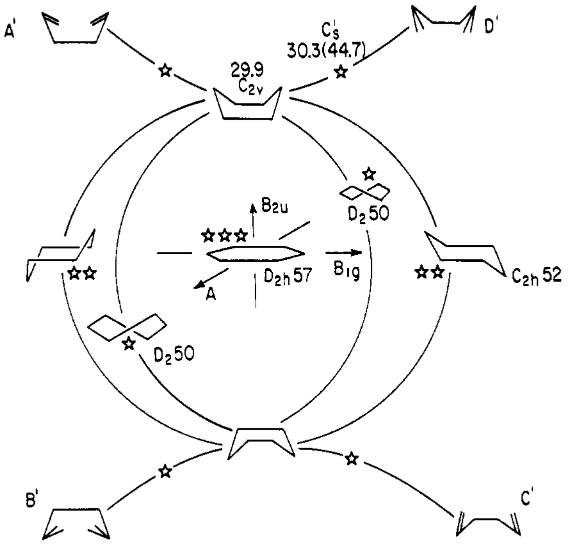


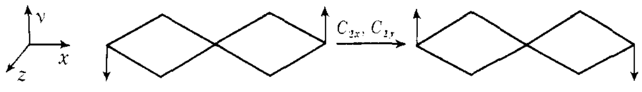
Figure 7. Illustration at the "high-energy" MINDO/2 potential surface. Tie lines indicate reaction paths. Structures shown without a star are minimum energy geometries. A single star indicates the presence of a transition state. Structures with two or three stars have force constant matrices with two or three negative eigenvalues, respectively.

Hoffmann[25] has noted this tendency of certain biradicaloid geometries to favor a given orbital occupancy and has accounted for it in a conceptually simple way by analyzing the relative importance of "through-space" and "through-bond" interactions coupling the atomic orbitals of the radical sites. Dewar and co-workers have labeled two such structures as LUMOmers of one another.[26] One can also construct molecular orbital correlation diagrams connecting two "high-energy" structures or two "low-energy" structures and will find no crossing of occupied and vacant orbitals. These are referred to as HOMOmers. Transformations between HOMOmers are "allowed", while those between LUMOmers are "forbidden" in the Woodward-Hoffmann sense.

From the above discussion it is convenient to distinguish between a "low-energy" and a "high-energy" MINDO/2 potential surface with any two points on one of these surfaces being HOMOmeric and two points, one from each surface, being LUMOmeric. It is important to recognize that this situation does not exist in the Born-Oppenheimer reality, but is rather an artifact of the use of closed-shell molecular orbital theory. The exact wave function or even a simple configuration-interaction wave function would give only a single potential surface with both "high-energy" and "low-energy" geometries of the same symmetry corresponding to two different stationary points on this surface. Cases in which the two geometries are very similar, such as the D_2 or D_{2h} structures, would probably correspond to a single stationary point on the exact surface.

The low- and high-energy surfaces are illustrated in Figures 6 and 7, respectively. The figures are drawn using the symmetry of this system as follows. The "origin" of each figure is taken to be the planar D_{2h} structure with the numbering of the atoms the same in each. The three Cartesian axes are labeled B_{1g}, B_{2u}, and A_u, corresponding to the symmetry species of the distortions of D_{2h} into the C_{2h}, C_{2v}, and D_2 structures, respectively, on each surface. It turns out in the present case that these are also the symmetry species of the three normal modes of the imaginary frequency calculated for both the high- and low-energy D_{2h} structures. The three asterisks adjacent to the D_{2h} structures denote the presence of these three modes of imaginary frequency. Similarly, a single asterisk denotes a structure with a single mode of imaginary frequency and two asterisks indicate a structure with two normal modes of imaginary frequency. The structures drawn without asterisks are energy minima: all vibrational frequencies are real. The low-energy C_2 and C_s transition states are not drawn in Figure 6, but their presence is indicated by a single asterisk. The high-energy C_s' transition state is similarly indicated in Figure 7. The numbers adjacent to the structures are the calculated MINDO/2 energies in kilocalories relative to 1,5-hexadiene. Experimental energies, similarly adjusted to hexadiene, are given in parentheses (they are obtained from enthalpies of reaction and activation).

The curved tie lines connecting various structures represent reaction paths: they connect energy minima with transition states. It is the determination of these tie lines that allow us to make mechanistic deductions. They can be located computationally by distorting each transition state along its transition vector and performing an energy minimization. The possible reactions for which a given structure can serve as transition state can also be deduced by utilizing the known symmetry species of the transition vector.[17] For example, the D_2 structure could conceivably serve as a transition state for the inversion of C_{2v}, C_{2h}, both, or neither. To determine whether or not D_2 can serve as transition state for the C_{2h} chair we first attach arrows to the atoms of D_2 such that sliding the atoms along the arrows results in the chair configuration as shown in **15,** and then apply the symmetry operations of D_2 to the arrows,



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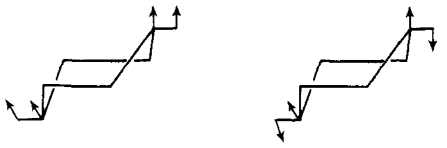
leaving the atoms unchanged. As shown, the operations C_{2x} and C_{2y} convert reactant into product, whereas E and C_{2z} leave the reactant unchanged. According to symmetry rules,[17] the transition vector must belong to the B_1 representation if D_2 is to serve as transition state for the chair inversion. For the C_{2v} inversion, similar reasoning leads us to conclude that the transition vector must be of B_2 symmetry. The calculated results show that the low-energy D_2 structure has a transition vector of B_1 symmetry, whereas the high-energy structure has a transition vector of B_2 symmetry. Thus we draw the tie lines from D_2 to the C_{2h} structure in Figure 6 and to C_{2v} in Figure 7. One can carry this procedure a step further to deduce the relative energies of the barriers in the rearrangements among A, B, C, and D on the low-energy surface and A′, B′, C′, and D′ on the high-energy surface. Thus the D_2 structures can be tested as transition states for each of these sets of rearrangements. The results are that the low-energy D_2 structure *can* serve as the transition state for both A $\rightleftarrows$ D *and* B $\rightleftarrows$ C, and our calculations confirm this. From the discussion of theorem IV of ref 17 we know that if a single structure such as D_2 can serve, albeit accidentally, as transition state for two (or more) reactions A $\rightleftarrows$ D and B $\rightleftarrows$ C, and if there are no other intervening barriers of the same energy, then there must exist *lower energy* transition states of different symmetry than D_2 for A $\rightleftarrows$ B and C $\rightleftarrows$ D or A $\rightleftarrows$ C and B $\rightleftarrows$ D. Here, this lower energy barrier turns out to be the C_2 structure in Figure 6. In general, given the transition vectors (if they exist) for any of the symmetrical monocyclic structures, the nature of the tie lines can be deduced from the diagrams in Table II of ref 17b. Thus the high-energy D_2 structure is simpler than the low-energy D_2 since the corresponding diagram follows rigorously from theorem IV and not the *accidental* sharing of the D_2 transition state between two reactions.

The tie lines connecting the high-energy C_{2h} chair deserve special attention because this structure possesses two vibrational modes of imaginary frequency, both of B_u symmetry. They are schematically illustrated in **16** below. Since this structure has two imaginary frequency modes it cannot be a transition state. If, however, it were to have a single imaginary frequency mode of B_u symmetry, then it could act as the transition state for the inversion of the high-energy C_{2v} boat and the tie lines have been drawn accordingly. The existence of the second B_u imaginary mode implies that there will exist two equivalent lower energy barriers of C_s symmetry on either side of each C_{2h} structure. Although we have not located these C_s barriers, their existence as enantiomers implies that the tie lines connecting each of them with the C_{2v} boat structures will form asymmetric reaction paths, the dynamics of which have been recently investigated by Wolfe and co-workers.[27] Here the C_{2h} structure corresponds to their chiral point. Note that the existence of this situation follows from the calculated properties of the C_{2h} structure alone.



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In discussing the mechanistic implications of the tie lines in Figures 6 and 7, it should first be noted that the four 1,5-hexadiene structures labeled A, B, C, and D on the low-energy surface convert into one another through conrotatory twisting of the methylenes, whereas the structures A′, B′, C′, and D′ interconvert via disrotatory methylene twists.[15,17b] The unprimed structures are related to their primed counterparts by the rotation of a single methylene and as mentioned earlier, the conversion of any unprimed structure into a primed structure is thermally forbidden by the Woodward-Hoffmann rules.[24b]

On the high-energy surface, the Cope rearrangements A′ $\rightleftarrows$ D′ and B′ $\rightleftarrows$ C′ proceed through the expected C_{2v} boat intermediates, whereas the Cope rearrangements A′ $\rightleftarrows$ B′ and mechanism as the double bond isomerizations A $\rightleftarrows$ C and B $\rightleftarrows$ D and can rearrange either via the C_s transition state and bicyclo[2.2.0]hexane as an intermediate or more directly through the D_2 transition state. Although the former pathway is energetically more favorable, equilibration with the bicyclohexane could conceivably render the kinetic parameters of the latter direct pathway measurable. The MINDO/2 energies are not of sufficient accuracy to confirm this, however. We note also that both the inversion and cleavage of bicyclo[2.2.0]hexane appear to *proceed via the same* C_{2h} chair intermediate. This is commensurate with the results of Goldstein and Benzon,[6a] but does not support the suggestion that the inversion of the bicyclohexane proceeds through a twist-boat structure.[7,28]

On the high-energy surface, the Cope rearrangements A′ $\rightleftarrows$ D′ and B′ $\rightleftarrows$ C′ proceed though the expected C_{2v} boat intermediates, whereas the Cope rearrangements A′ $\rightleftarrows$ B′ and C′ $\rightleftarrows$ D′ share the mechanisms of the double bond isomerizations A′ $\rightleftarrows$ C′ and B′ $\rightleftarrows$ D′ via the inversion of the C_{2v} boat. This could take place by either the D_2 or a C_{2h} like structure. However, the similarity of the high- and low-energy D_2 structures indicates that rather than invert, the C_{2v} boat would cross into the low-energy system, thus favoring LUMOmeric rearrangements over the HOMOmeric A′ $\rightleftarrows$ C′.

As mentioned earlier, the calculated energies are in rather poor agreement with experimental enthalpies. Thus the calculated enthalpy of activation for the Cope rearrangement via the C_2 transition state is 22.3 kcal compared to 33.5 kcal observed experimentally,[4] whereas the calculated enthalpy of activation of 30.3 kcal for the C_s' boat Cope rearrangement is also lower than the experimental 44.6 kcal.[5] However, within the monocyclic system the calculated difference in energy between the C_s' and C_2 structures of 8 kcal compares favorably with the 12 kcal experimental difference.[5] The entropies of activation were also calculated for these two Cope rearrangements (ignoring the internal rotation contribution to the partition functions). The activation entropy for the Cope rearrangement via C_2 was found to be −4.0 eu compared to the experimental −13.8 eu[5] and the calculated value for the rearrangement via C_s' is −3.8 eu compared to the experimental −3 ± 3.6 eu.[5] Thus, we conclude that the calculated results are of at least qualitative accuracy and that calculations such as these can be useful in understanding complex mechanisms.

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Supplementary Material Available: Tables of Cartesian coordinates of each structure (11 pages). Ordering information is given on any current masthead page.

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The Cyclobutene/Butadiene Anion Radical Electrocyclic Reaction

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Abstract: The generalized cyclobutene anion radical/butadiene anion radical electrocyclic reaction has been explored experimentally and theoretically. Its preferred stereochemical course is conrotation. Simple theoretical methods are discussed for treating radical electrocyclic reactions, but SCF reaction path calculations are also described. The HOMO method, alone among the theoretical approaches evaluated, is found to be unsatisfactory.

The stereochemistry of an electrocyclic reaction of a free radical was first discussed in 1965.[1] Applying the now familiar concept of HOMO,[1,2] the allyl/cyclopropyl radical interconversion was predicted to occur conrotatorily. Shortly thereafter an orbital correlation diagram analysis of the same transformation was presented.[3] Neither rotatory pathway was found "allowed" but conrotation was again predicted on the basis of estimated relative energies of the two cyclopropyl radical excited states with which the respective dis- and conrotatory cyclizations of the allyl radical "intend" to correlate. Reaction path calculations of the extended Hückel type also envision conrotation,[1] but MINDO[4] and an ab initio[5] calculation generate the contrary disrotatory prediction. No definitive experimental results are available for this or other uncharged radical systems. Study of the stereochemistry of electrocyclic reactions of anion radicals has been more fruitful, however, and in one case in particular, the generalized cyclobutene/butadiene anion radical system, the results are clear and instructive.[6,7] These are now reported in full.

Theoretical Section

The butadiene anion radical HOMO is symmetric, eliciting a HOMO prediction of disrotation. Orbital correlation diagrams for the cyclobutene/butadiene anion radical reaction (Scheme I) do not find the decision quite so straightforward. As in the cyclopropyl/allyl radical case, neither reaction mode is allowed. A variety of quantitative treatments, however, select the conrotatory mode as favored, in contradiction to HOMO's prediction. One such treatment amounts to a quantitative extension of the orbital correlation diagram approach. With reference to Scheme I, the intended product of the disrotatory cleavage of the cyclobutene anion radical is what will be designated the 212 excited state of the butadiene anion radical. In this notation the ground state is 221, the successive numbers representing electron populations of the diene π MO's as they increase in energy from left to right. The intended correlation for the conrotatory path is with the 2201 excited state. The Hückel energies of these states are 2.618 and 2.858 β, respectively. The conrotatory route is thus favored by 0.240 β. This kind of treatment, incidentally, finds the two cyclopropyl radical pathways degenerate.[8]

A second means of ordering the energies of the dis- and conrotatory transition states relies on the Zimmerman concept according to which conrotatory transition states are likened to cyclic Möbius systems and disrotatory ones to systems of Hückel topology.[9] The HMO energies of the Möbius and Hückel topologues of the cyclobutadiene anion radical are 4.24 and 4.00 β, respectively. The difference, 0.24 β, is exactly the same as derived via the quantitative orbital correlation diagram approach and, again, conrotation is foreseen. The Hückel/Möbius comparison can also be made using INDO energies. The Möbius state is calculated by assigning one nearest

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