The above experiment was repeated with 2-chlorooctane (0.10 g, 0.67 mmol), potassium *tert*-butoxide (0.167 g, 1.49 mmol), and LiCl (0.34 g, 8.0 mmol) in 10 ml of HMPA. Initially, the chloride had α^{27}D $-28.79°$ (neat, 1 dm); recovered, purified 2-chlorooctane had α^{13}D $-3.89°$ (neat, 1 dm). Racemization had proceeded to more than 86%. (d) To a solution of lithium azide (1.00 g, 20.4 mmol) in 15 ml of HMPA was added 2-octyl trifluoroacetate (0.11 g, 0.486 mmol) in 2 ml of HMPA. The mixture was stirred at 25° for 15 min and then worked up in the manner described above. Gc analysis showed the absence of 2-azidooctane. 2-Octyl trifluoroacetate and a trace of 2-octanol were the only products. (e) 2-Octyl trimethylsilyl ether (0.044 g, 0.22 mmol) and lithium chloride (0.10 g, 2.4 mmol) were stirred at 25° in 10 ml of HMPA for 15 min. Normal work-up afforded a residue which, on gc analysis, showed that only 2–3% of hydrolysis to 2-octanol had occurred. 2-Chlorooctane was absent. (f) A solution of 5.0 mmol of 2 in 30 ml of HMPA was doped with 2.5 g (17 mmol) of 2-butyl trimethylsilyl ether and stirred for 1 hr at 25°. No gas evolution was observed. Addition of water then produced 117 ml (95%) of the theoretical nitrogen evolution.

Structure of Transition States. III. A MINDO/2 Study of the Cyclization of 1,3,5-Hexatriene to 1,3-Cyclohexadiene

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Abstract: The disrotatory closure of 1,3,5-hexatriene to 1,3-cyclohexadiene is investigated using the MINDO/2 molecular orbital method. Minimum energy geometries of reactant and product are in moderately good agreement with the geometries determined by electron diffraction, although the enthalpy of reaction is calculated to be 17.4 kcal larger than the experimental value. The calculated transition state was found to be a C_s symmetry structure resembling a distorted hexatriene. The calculated enthalpy and entropy of activation, relative to hexatriene, are also in moderately good agreement with experiment.

The cyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene is the prototype of thermal, disrotatory, electrocyclic reactions and is thus a textbook example of the application of the Woodward–Hoffmann rules.[2] In addition to its theoretical interest, this type of reaction is of some biochemical significance due to its involvement in the chemistry of vitamins A and D.[3]

Experimentally, the parent reaction has been fairly well characterized; the kinetic parameters have been determined by two independent groups of workers[4,5] and electron diffraction studies have yielded the geometrical parameters of reactant[6] and product.[7] The detailed geometry of the transition state is, as usual, experimentally unavailable.

This experimentally well understood reaction thus appears ideal for a theoretical-computational study on a model potential energy surface; the extent to which the predictions of the model agree with the experimentally known structural, thermodynamic, and kinetic parameters helps to establish the limits of reliability of the model, and if successful in this respect, additional predictions of the model can help clarify our detailed understanding of the reaction. This particular reaction seems well suited for a computational study using the semiempirical MINDO/2 molecular orbital method[8] as the model of the potential energy, since this method works best for unstrained hydrocarbons[8,9] and since it can be applied to a system of this size at only a moderate computational expense. We are unaware of any previous computational study of this reaction.

We reported herein the MINDO/2 calculated geometries of both *cis*- and *trans*-1,3,5-hexatriene, the equilibrium geometry of 1,3-cyclohexadiene, the geometry of the transition state in the thermal cyclization, and the enthalpies and entropies of activation and reaction.

Computational Methods

Given the MINDO/2 potential surface, the problem of the kinetics and thermodynamics of the hexatriene closure was treated by first locating the minima corresponding to the reactant and product geometries and the saddle point corresponding to the transition state. The calculated harmonic force constants of these structures were then used to estimate the vibrational partition functions. These, together with the calculated energies, were then used to obtain the thermodynamic and, using the formalism of transition state theory, kinetic parameters.

Geometries which were believed to be potential

(1) Samuel B. Silbert, Graduate Fellow, 1972–1973.
(2) R. B. Woodward and R. Hoffmann, *Angew Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(3) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961), and references contained therein.
(4) E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Lett.*, 385 (1965).
(5) K. E. Lewis and H. Steiner, *J. Chem. Soc. C*, 3080 (1964).
(6) (a) W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966); (b) M. Traetteberg, *ibid.*, **22**, 2294 (1968).
(7) (a) M. Traetteberg, *Acta Chem. Scand.*, **22**, 2305 (1968); (b) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

(8) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).
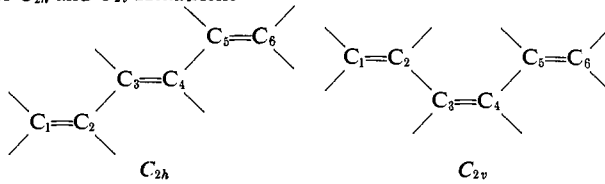(9) (a) J. W. McIver, Jr., and A. Komornicki, *J. Amer. Chem. Soc.*, **94**, 2625 (1972); (b) A. Komornicki and J. W. McIver, Jr., *ibid.*, **95**, 4512 (1973).

energy minima or minima within a given symmetry were obtained using a previously described minimization method.[10] If the desired structure was a saddle point which could not be located by energy minimization methods, it was determined as a stationary point by using the least-squares method of Powell[11] to minimize to zero the sum of the squares (the norm) of the Cartesian components of the potential energy gradient, as previously described.[9] A disadvantage of the latter method is that it requires a relatively accurate initial estimate of the transition state geometry. Previously,[9a] we handled this by varying one geometrical parameter, such as a bond length or angle (the reaction coordinate), in small increments from its reactant value to its product value and minimizing the energy with respect to the remaining degrees of freedom. This uneconomical procedure produces a "reaction path," a path whose passage near or through the transition state depends, among other things, on a successful choice of reaction coordinate. In complicated systems such a choice is not always obvious. Indeed, it is easy to construct two-dimensional examples in which there does not exist a reaction coordinate that produces a continuous path connecting reactants, transition state, and products. Our own recent experience has led us to abandon this procedure in favor of the more reliable and economical method of simply choosing a set of internal coordinates shared between reactant and product (including bond lengths of bonds being broken) and varying them all linearly and simultaneously from their reactant to product values. This method always produces a continuous path connecting the reactant and product geometries. We refer to such paths as linear internal coordinate paths. We have found, in the present case, that the norm of the gradient passes through a secondary minimum (it is zero at the reactant and product equilibrium geometries). The geometry corresponding to this secondary minimum was used as the initial estimate of the transition state geometry in the least-squares procedure which ultimately produced the transition state. Finally, the force constants were calculated for each structure using the finite perturbation method described previously.[9]

Results and Discussion

The calculated geometrical parameters of *trans*-(C_{2h} symmetry) and *cis*- (C_{2v})-1,3,5-hexatriene are given in Table I together with those obtained from the electron diffraction studies of each. A comparison of the MINDO/2 and electron diffraction values shows relatively good overall agreement. Thus, the calculated single C-C bond lengths are within 0.01 Å of the experimental values, and the terminal C=C double bonds in both structures are calculated to be about 0.02 Å shorter than experiment. Both the electron diffraction study and MINDO/2 predict a lengthening of the C_3=C_4 bonds relative to the C_1=C_2 bond lengths, although the calculated effect is less pronounced. The calculated and experimental bond angles are within about 4° of one another with MINDO/2 favoring larger C-C-C angles. A notable discrepancy between the calculated and experimental geometries is the

Table I. Calculated and Experimental Geometrical Parameters of C_{2h} and C_{2v} Hexatriene

Bond, Å	C_{2h} Calcd	C_{2h} Exptl[a,b]	C_{2v} Calcd	C_{2v} Exptl[b]
C_1C_2	1.32	1.337	1.32	1.336
C_2C_3	1.45	1.458	1.45	1.462
C_3C_4	1.33	1.368	1.33	1.362
CH	1.20	1.102	1.21	1.090
Angle, deg				
$C_1C_2C_3$	125	121.7	126	122.1
$C_2C_3C_4$	126	124.4	125	125.9
$C_2C_1H_1$	124		124	124.0
$C_1C_2H_2$	119		121	116.9
$C_4C_3H_3$	119	117.8	120	118.0
Dihedral angle, deg				
$C_2C_3C_4C_5$	180	180.0	0	10.0

[a] Reference 6a. [b] Reference 6b.

failure of MINDO/2 to predict the 10° torsion angle experimentally found for the central double bond in the cis structure. There is, however, some uncertainty in the experimental value.[6b] MINDO/2 C-H bond lengths are consistently about 0.1 Å longer than those found experimentally.[8-10] Finally, it should be noted that by allowing the cis structure to distort to C_2 symmetry by rotation about the C-C single bonds, MINDO/2 gives a structure identical in all other geometrical parameters but 0.7 kcal lower in energy than the planar C_{2v} geometry. The C_{2h} trans structure was found to be the most stable hexatriene, its calculated energy lying 1.5 kcal below that of the C_{2v} cis geometry. This compares favorably with the known experimental value of 1.1 kcal.[12]

Table II shows the MINDO/2 results for some of the calculated geometrical parameters of 1,3-cyclohexadiene in its most stable conformation of C_2 symmetry (resembling a twist boat). A C_s boat structure was also calculated and was found to be unstable under a distortion toward the C_2 structure. Table II also includes the experimental geometrical parameters from two recent independent electron diffraction studies. Here the agreement between the calculated and experimental bond lengths can best be described as moderately good. The calculated C-C bond lengths for both single and double bonds are about 0.02 Å shorter than the experimental values except for the C_1-C_2 bond which is 0.04 Å shorter. The calculated bond angles are all within 5° of the experimental values except for the H-C-H angles which are predicted to be 14° less than electron diffraction values. The tendency to give excessively pinched H-C-H angles seems to be characteristic of MINDO/2.[8-10a]

The MINDO/2 calculated energetics of this reaction are in somewhat better agreement with experiment than the previously reported thermal conrotatory opening of cyclobutene to butadiene[9a] where MINDO/2 incorrectly predicted the reaction to be endothermic by 20.5

(10) (a) J. W. McIver, Jr., and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971); (b) Program OPTMO, Quantum Chemistry Program Exchange, No. 217, University of Indiana, Bloomington, Ind.
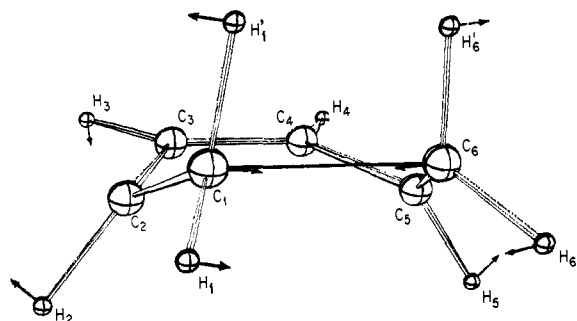(11) M. J. D. Powell, *Comput. J.*, **7**, 303 (1965).

(12) R. B. Turner, B. J. Mallon, M. Tichy, W. von E. Doering, E. R. Roth, and G. Schroder, *J. Amer. Chem. Soc.*, **95**, 8605 (1973).

Figure 1. An ORTEP II plot of the C_s symmetry transition state. The arrows indicate the motion of the atoms along the imaginary frequency direction.

Table II. Calculated and Experimental Geometrical Parameters of 1,3-Cyclohexadiene (C_2 Symmetry)
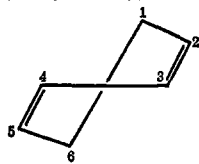
Bond, Å	Calcd	Exptl[a]	Exptl[b]
C_1C_2	1.48	1.523	1.518
C_2C_3	1.33	1.350	1.348
C_3C_4	1.45	1.468	1.464
C_1C_6	1.51	1.534	1.538
CH	1.20	1.082	1.099
Angle, deg			
$C_1C_2C_3$	122	120.1	120.3
$C_2C_3C_4$	120	120.1	120.3
$C_6C_1C_2$	113	110.7	110.9
HCH	100	114.1	
$H_2C_2C_3$	121		118.0
$C_2C_3H_3$	122	122.0	118.0
$C_1C_2H_2$	117	122.0	
Dihedral angle, deg			
$C_2C_3C_4C_5$	12	18.34	17.96
$C_1C_2C_3C_4$	1	0.0	0.0

[a] Reference 7b. [b] Reference 7a.

kcal, an error of about 30 kcal. In the present case MINDO/2 correctly predicts cyclohexadiene to be more stable than the hexatriene although the calculated energy difference of 31.9 kcal is 17.4 kcal larger than the experimental value[13] of 14.5 kcal. On a per C–C bond basis (counting a double bond as the equivalent of two single bonds) this amounts to an error of 2 kcal per bond compared to an error of about 6 kcal per bond for the cyclobutene opening. The smaller error in the present case can be attributed to the lack of strain in the cyclohexadiene system, since MINDO/2 tends to underestimate strain. It would appear, however, that MINDO/2 excessively favors ring formation whether or not the rings are strained.

The search for the transition state on the MINDO/2 surface involved constructing linear internal coordinate paths that were both symmetrical and nonsymmetrical and which included both disrotatory and conrotatory ring closures. The latter were always found to involve a crossing of highest occupied and lowest vacant molecular orbitals, even in the nonsymmetrical cases.

(13) S. W. Benson, H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21 (1970).

This, of course, is commensurate with the Woodward–Hoffmann rules, which predict a disrotatory ring closure for the thermal reaction.[2] Transition state structures of C_2 and C_s symmetry have been suggested by Lewis and Steiner[5] and Marvell and coworkers,[4] respectively. The MINDO/2 calculated transition state is of C_s symmetry and is shown in Figure 1, an ORTEP II[14] plot of this structure. Some of the geometrical parameters are given in Table III. The cal-

Table III. Calculated Geometrical Parameters of Transition State in C_s Symmetry[a]

Bond, Å	Calcd	Angle, deg	Calcd	Dihedral angle, deg	Calcd
C_1C_2	1.36	$C_1C_2C_3$	123	$C_1C_2C_3C_4$	42
C_2C_3	1.42	$C_2C_3C_4$	120	$C_2C_3C_4C_5$	0
C_3C_4	1.35	$C_1C_6C_5$	106		
C_1C_6	2.06	$H_1C_1H_1$	108		
CH	1.21	$C_1C_2H_2$	120		
		$C_2C_3H_3$	118		

[a] Atom numbering refers to Figure 1.

culated structure was verified as a transition state by the criteria[9a,15] that it is a stationary point with a force constant matrix having a single negative eigenvalue with a corresponding eigenvector that is totally symmetric. Moreover, an initial small displacement of the atoms along the vibrational mode of imaginary frequency (illustrated by the arrows in Figure 1) followed by energy minimization helped ensure that there were no other barriers of higher energy lying between the calculated structure and reactants or products.

A comparison of the bond lengths in Tables I–III suggests that the transition state closely resembles a distorted hexatriene. Interestingly, the C_1–C_6 bond length of 2.06 Å is identical with that of the bond being broken in the MINDO/2 transition state for the conrotatory cyclobutene opening.[9a] The calculated barrier height, relative to hexatriene, is 24.6 kcal. This becomes 24.2 kcal when zero-point corrections are included. The experimental activation energy for the closure is 29.6 ± 0.3 kcal,[4,5] so that MINDO/2 appears to have underestimated the barrier height by only 5 kcal. Although the error for the reverse reaction is 12.4 kcal, we find these results encouraging since the error for the activation energy in either direction is less than the error in the enthalpy of reaction.

The entropy of activation was estimated from the calculated vibrational partition functions of hexatriene and the transition state, assuming that the rotational contributions of these species canceled. The result of −6.0 eu (at 421°K) compares favorably with the experimental values of −7.0[4] and −4.8 eu.[5]

(14) C. K. Johnson, "ORTEP: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL 3794 (1965), ORTEP II Oak Ridge National Laboratories, 1971.

(15) J. W. McIver, Jr., and R. E. Stanton, *J. Amer. Chem. Soc.*, **94**, 8618 (1972).