Conrotatory and Disrotatory Stationary Points for the Electrocyclic Isomerization of Cyclobutene to *cis*-Butadiene

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Abstract: The stereospecificity of the cyclobutene isomerization was explained in the first of the series of papers by Woodward and Hoffmann concerning the conservation of orbital symmetry. The conrotatory and disrotatory reaction pathways are considered here with use of analytic first and second energy derivative methods in the context of ab initio molecular quantum mechanics. Standard double ζ (DZ) and double ζ+d function (DZ+d) basis sets are employed in concert with two-configuration self-consistent-field (TCSCF) and configuration-interaction (CI) wave functions. Both conrotatory and disrotatory stationary points have been characterized via harmonic vibrational analyses. At the level of theory considered, the conrotatory stationary point is a true transition state, while the disrotatory stationary point has two imaginary vibrational frequencies, i.e., it is a maximum with respect to 2 of the 24 internal nuclear degrees of freedom.

The thermolysis of cyclobutene leading to ring opening and butadiene formation or, conversely, the cyclization of butadiene into cyclobutene is the prototypical example of concerted stereospecific reactions which may be understood by the work of Woodward and Hoffmann.[1,2] Whether the methylene groups bonded to the termini of the final diene system will rotate in the same direction—giving rise to the conrotatory process—or in opposite directions—a disrotatory process—is determined by the number of π electrons in the system. According to the Wood-

conrotatory disrotatory

ward–Hoffmann rules, which may be understood on the basis of symmetry considerations and correlation diagrams, a system containing $4n$ π electrons will favor a conrotatory isomerization. Conversely, a system of $(4n + 2)$ π electrons will prefer a disrotatory motion.

Due to its particular simplicity among pericyclic reactions, much theoretical work has been devoted to the cyclobutene/*cis*-butadiene isomerization, as may be seen in several review.[3-8] However, the only ab initio study of both conrotatory and disrotatory processes was carried out by Hsu, Buenker, and Peyerimhoff[9] more than a decade ago. In that study both pathways for cyclobutene isomerization were calculated with a slightly better than minimal basis set. Although very impressive by the theoretical standards of that time, the calculations suffered from several drawbacks: not all the parameters were varied simultaneously along the potential surfaces, leading to an implicit arbitrary choice of coordinate of reaction; the "transition regions" were located by means of a pointwise procedure, without use of any rigorous criterion for the characterization of a transition state; the CI expansions were severely truncated. For all these reasons, the evidence of a "stepwise" mechanism for the allowed conrotatory process where the rotation of the methylene groups would take place abruptly after the bond stretching has to be taken very cautiously.

Subsequently, several semiempirical calculations of the conrotatory transition state were reported, using a rigorous criterion for the location of a transition state by means of gradient techniques[10,11] or other quantitative methods.[12,13] For the disrotatory process, which is photochemically allowed, semiempirical[14] and ab initio[15] studies are now available for excited electronic states. However, the only proposed ground-state disrotatory transition state to date is that of Dewar and Kirschner[11] obtained via the MINDO/3 method. We were somewhat concerned about their predictions since there are two configurations that might be expected to be important for this process, while the MINDO/3 procedure was restricted to a single-configuration model.

The present research makes use of two-configuration self-consistent-field (TCSCF) wave functions, along with analytic gradient and analytic second derivative[16] methods. This paper provides a discussion of both conrotatory and disrotatory processes and, specifically, a tentative characterization of both stationary points on the basis of the predicted harmonic frequencies. Thermochemical data will be discussed at different levels of MCSCF plus configuration-interaction (CI) theory.

Theoretical Approach

As suggested by Woodward and Hoffmann[1,3] and later by Longuet-Higgins and Abrahamson,[2] the stereospecificity of the interconversion of cyclobutene and *cis*-butadiene may be rationalized on the basis of a correlation diagram involving the four π orbitals of butadiene that are transformed smoothly into two π and two σ orbitals of cyclobutene. Indeed, during the standard disrotatory process, a plane of symmetry is maintained (C_s). It appears that the π bonding orbital of cyclobutene correlates with the antibonding orbital ψ_3 of *cis*-butadiene (Figure 1). Fur-

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(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).
(2) See also: H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).
(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970.
(4) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum, New York, 1975, see pp 343-346.
(5) H. E. Zimmerman, "Pericyclic Reactions", Vol. I, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, see pp 53-107.
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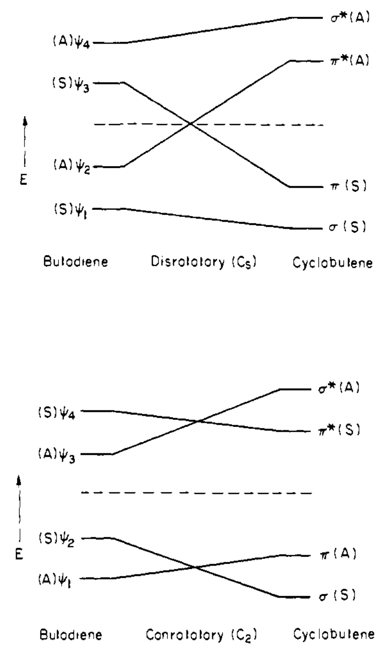

Figure 1. Correlation diagrams for the conrotatory and disrotatory isomerization of cyclobutene to *cis*-butadiene.

thermore, the π^* antibonding orbital correlates with the ψ_2 bonding orbital. This pathway, involving an orbital crossing and therefore presumably a high activation energy, is referred to as symmetry forbidden.

On the other hand, during the conventional conrotatory process, a C_2 axis of symmetry is maintained and the correlation diagram is quite different, giving rise to a symmetry-allowed reaction (Figure 1). The stereospecificity may also be explained by the fact that the proposed conrotatory transition state adopts a Möbius-type configuration,[5] which is aromatic in the case of $4n$ electrons. Conversely, the disrotatory transition state would be of the Hückel type, antiaromatic[4] and therefore higher in energy. This explanation, however, is based exclusively on the energy criterion and upon the existence of both transition states.

From the above arguments, it follows that the conrotatory process may be described correctly with a single-configuration wave function, an internal rearrangement of the orbitals taking place during the reaction. It is equally evident from Figure 1, however, that the description of the disrotatory process requires at least a two-configuration wave function involving the π–π^* orbitals (HOMO–LUMO). This might be more rigorously understood on the basis of the ground-state electron configurations for the two species. Indeed, the ground-state configuration for cyclobutene is (C_{2v})

$$\ldots\ 1a_2^2\,7a_1^2\,5b_2^2\,2b_1^2 \tag{1}$$

the ground-state configuration of *cis*-butadiene being (C_{2v}):

$$\ldots\ 6b_2^2\,7a_1^2\,1b_1^2\,1a_2^2 \tag{2}$$

Clearly, both configurations correlate in the C_2 point group with the common electron configuration

$$\ldots\ 7a^2\,8a^2\,6b^2\,7b^2 \tag{3}$$

allowing a smooth one-configuration description of the conrotatory interconversion.

This adequacy of the single-configuration picture is obviously not the case for the disrotatory process. There the correlation of (1) and (2) in the C_s symmetry group gives:

$$\text{cyclobutene (eq 1)} \xrightarrow{C_s} \ldots\ 5a''^2\,8a'^2\,9a'^2\,6a''^2 \tag{4}$$

$$\text{butadiene (eq 2)} \xrightarrow{C_s} \ldots\ 6a''^2\,7a'^2\,8a'^2\,7a''^2 \tag{5}$$

As Figure 1 suggests, configuration 4, the C_s correlation product from cyclobutene, is the π^{*2} configuration of *cis*-butadiene, namely

$$\ldots\ 6b_2^2\,7a_1^2\,1b_1^2\,2b_1^2 \tag{6}$$

(which results from the HOMO–LUMO double excitation). Similarly, configuration 5, the C_s correlation product from *cis*-butadiene, is the π^{*2} configuration of cyclobutene:

$$\ldots\ 1a_2^2\,7a_1^2\,5b_2^2\,2a_2^2 \tag{7}$$

(also HOMO–LUMO double excitation). This shows clearly that the two-configuration wave function eq 4 + eq 5, which gives us a smooth correlation between both ground states in the disrotatory process, spans also the HOMO–LUMO space as explained by Woodward and Hoffmann.

Although from a symmetry point of view the use of a two-configuration wave function is not mandatory in the case of the conrotatory process, we wish to compare the activation energies for the two reactions. This prompts us to incorporate the HOMO–LUMO excitation in the conrotatory wave function as well, i.e., we add to configuration 3 the configuration

$$\ldots\ 7a^2\,6b^2\,7b^2\,8b^2 \tag{8}$$

As will be shown later, the mixing of configurations 3 and 8 is far from negligible at the conrotatory transition state, strongly supporting the use of a two-configuration wave function. The geometries of the four following species—cyclobutene (I), *cis*-butadiene (II), the stationary point for the conrotatory process (III), and the stationary point for the disrotatory process (IV)—have been optimized by the minimization of analytical gradients in the standard Huzinaga–Dunning double-ζ basis set C(9s 5p/4s 2p) and H(4s/2s).[17] At the stationary points given by eq III and IV, vibrational analyses were carried out with the use of analytic second derivatives method.[16] Whether the stationary point is a transition state (or something more exotic) is determined by the presence (or absence) of only one imaginary vibrational frequency.

The geometries have not been redetermined with a larger basis set due to the magnitude of such a task. However, at the DZ geometries a set of d functions has been added to the carbon atoms (orbital exponent $\alpha = 0.75$) for the prediction of relative energies (barriers, exothermicities) in the framework of configuration interaction including all single and double excitations (CISD), relative to both TCSCF reference configurations.[18,19] The largest CI treatment reported here has been carried out for the conrotatory transition state with the DZ+d basis set and includes in a fully variational manner 196 350 configurations. The CI description was designed to correlate only the valence electrons. That is, the four lowest occupied TCSCF orbitals (atomic carbon 1s-like) were held doubly occupied in all configurations. In addition the four highest virtual orbitals, the core counterparts for a DZ-like basis set, were omitted from the CI.

Geometrical Structures

A. Cyclobutene. The only assumption in the geometry optimization of cyclobutene was the symmetry constraint of the C_{2v} point group. The resulting optimized geometry is seen in Figure 2. The geometrical parameters are listed in Table I where they are also compared to experimental,[20] MINDO/2,[10] and MINDO/3[11] results and other ab initio results.[9] The type of agreement between our theoretical results and experimental values is very typical for the level of theory reported here. The C–C bond lengths are always slightly too large, which is not surprising since the TCSCF method partially incorporates correlation effects. This lengthened bond distance prediction would probably largely disappear with the addition of polarization functions to the basis set. Overall, our results are in better agreement with experiment than MINDO/2 and previous ab initio results. The MINDO/3

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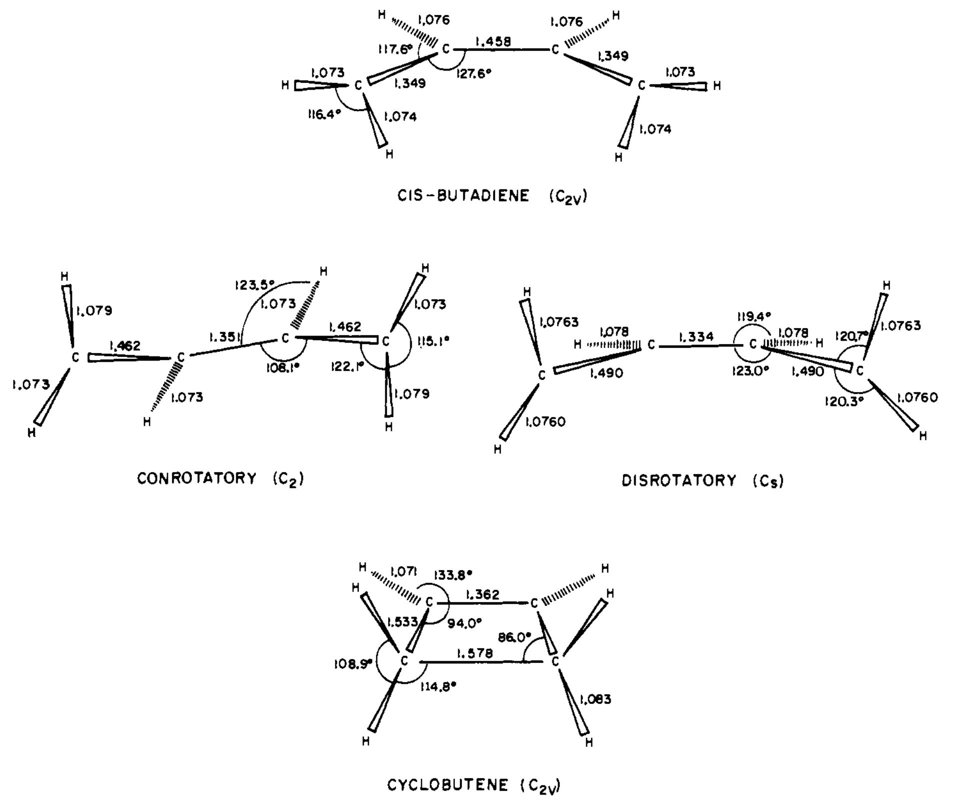

Figure 2. Predicted stationary point geometrical structures for the isomerization of cyclobutene. Bond distances are in angstroms. All structural predictions were made at the DZ TCSCF level of theory.

Table I. Geometrical Description of Cyclobutene[e]

parameter	present research	expt[a]	MINDO/ 2[b]	MINDO/ 3[c]	Hsu[d,f]
		Bond Lengths			
C_1C_2	1.578	1.566	1.51	1.535	1.545
C_1C_3	1.533	1.517	1.48	1.512	1.540
C_3C_4	1.362	1.342	1.33	1.345	1.330
C_1H_1	1.083	1.094	1.21	1.116	1.093*
C_3H_5	1.071	1.083	1.19	1.099	1.086*
		Angles			
$C_1C_3C_4$	94.0	94.2	93.6	93.6	94.0
$C_3C_1C_2$	86.0	85.8	86.4	86.4	86.0
$H_5C_3C_4$	133.8	133.5	135.6	134.7	120*
$H_1C_1H_3$	108.9	109.5	102.1		114*
$H_1C_1C_2$	114.8	114.5	117.6		
α	140.1	135.8	132.6		137

[a] Reference 20. [b] Reference 10. [c] Reference 11. [d] Reference 9. [e] Bond lengths are in Å and angles in deg. α is the angle between C_1C_2 and the bisector of methylene groups. (See ref 9). The numbering of atoms should be apparent from Figure 2. [f] An asterisk indicates fixed values.

Table II. Geometrical Description of Planar *cis*-Butadiene[f]

parameter	present research	MINDO/2[a]	Hsu[b]	4-31G SCF[e]
		Bond Lengths		
C_1C_3	1.349	1.32	1.337	1.323
C_3C_4	1.458	1.46	1.483	1.472
C_1H_1	1.073	1.094[c]	1.093[d]	1.078
C_1H_3	1.074	1.094[c]	1.093[d]	1.079
C_3H_5	1.076	1.094[c]	1.086[d]	1.079
		Angles		
$C_1C_3C_4$	127.6	127.1	120.0	127.1
$C_1C_3H_5$	117.6	118.6	120.0[d]	118.1
$H_1C_1H_3$	116.4	110.8	114.0[d]	115.9

[a] Reference 10. [b] Reference 9. [c] Average value. [d] Assumed value. [e] C. W. Bock, M. Trachtman, and P. George, *J. Mol. Spectrosc.*, 84, 243 (1980). [f] Bond lengths are in Å and angles in deg. The numbering of the different atoms should be apparent from Figure 2.

results show good agreement with experiment, particularly for the two shorter C–C bond lengths.

B. *cis*-Butadiene. We applied here exactly the same level of theory as for cyclobutene. The resulting geometry is seen at the top of Figure 2. The main difference here is that there is no experimental geometry available since the *cis*-butadiene has never been experimentally characterized (see, for example, ref 21). Our fully optimized C_{2v} geometry is compared to the partially optimized MINDO/2[10] and ab initio results[9] and also to a fully optimized 4-31G SCF geometry. Contrary to previous work, we predict a C=C bond length of 1.349 Å, close to the experimental C=C bond length in *trans*-butadiene (1.342 Å).[21] The C–C single bond length turns out as well to be very close to the experimental value in *trans*-butadiene (1.463 Å). We suggest that the present structure may be more realistic than those previously predicted. Of course, all theoretical studies to date of the structure of *cis*-butadiene have assumed planarity, and there is some indirect experimental evidence[22] that the true structure is nonplanar. Theory should now be able to resolve the issue of the nonplanarity of *cis*-butadiene and this might be profitably carried out in the framework of a comprehensive study of the cis–trans isomerization.

C. Transition State for the Conrotatory Process. As stated above the only constraint in the optimization of the transition state for the conrotatory process is that it takes place in the C_2 point group. The C_2 axis in Figure 2 is perpendicular to the plane of the paper and bisects the central C–C axis. This allows the carbon skeleton of the molecule to be puckered, as confirmed by the optimization process. As is well-known,[23] the necessary condition for a stationary point to be a transition state is that it shows a

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(23) J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371 (1968).

Table III. Geometrical Description of the Conrotatory Transition State

parameter	present research	MINDO/2[a]	MINDO/3[b]	MNDO[b]	MNDOC[b]	Hsu[c]
			Bond Lengths			
C_1C_2	2.238		2.058	2.117	2.142	2.23
C_1C_3	1.462	1.36	1.388	1.417	1.421	1.45
C_3C_4	1.351	1.40	1.418	1.406	1.401	1.40
C_1H_1	1.073	1.20				
C_1H_3	1.079	1.20				
C_3H_5	1.073	1.20				
			Angles			
$C_1C_3C_4$	108.1	102.3	102.0	103.1	104.0	
$C_3C_1C_2$	70.8	74.4	75.8	74.5	74.2	
$H_5C_3C_4$	123.5	128.8				
$H_1C_1H_3$	115.1	106.5				
$H_3C_1C_3$	122.1	122.4				
$H_1C_1C_3$	118.1	127.4				
			Dihedral Angles			
$C_1C_2C_3C_4$	16.4	26.3	21.0	22.6	19.4	23
$H_6C_4C_2H_4$	39.1	14.7				
$H_6C_4C_2H_2$	115.3	140.6				
$H_6C_4C_3H_5$	17.1	54.3	49.2	50.8	52.4	49

[a] Reference 10. [b] Reference 11. [c] Reference 9.

single imaginary vibrational frequency and $(3N - 7)$ real frequencies, the imaginary vibration corresponding to the reaction coordinate.[10] This is why we analytically[16] constructed the hessian matrix at the stationary point and diagonalized it in order to obtain a description of the normal modes. Only one imaginary frequency was found, corresponding to the expected reaction coordinate. This motion clearly corresponds to a combined stretching of the central CC bond and the conrotatory rotation of the methylene groups, giving evidence for a progressive and concerted mechanism rather than the stepwise mechanism suggested by Hsu et al.[9]

Table III lists the geometrical parameter values and compares them to MINDO/2,[10] MINDO/3,[11] MNDO,[11b] correlated MNDO,[11b] and previous ab initio[9] results. Important differences may be pointed out, especially concerning the bond lengths and the fact that our transition state (TS) is slightly less puckered than the MINDO/2 and MINDO/3 ones (this is indicated by the dihedral angles in Table III). This last point might conceivably be an effect of the DZ basis set used, since it is known that DZ-like basis sets sometimes give excessive relative stability to structures with high local symmetry.[24] The main difference with respect to the semiempirical results is that our transition state does not resemble the *cis*-butadiene molecule (the product) more than it does cyclobutene. On the contrary, the structure seems, as a whole, quite intermediate between the two isomers and in fact closer to cyclobutene, in agreement with Hammond's postulate[25] for an exothermic reaction. In this respect, the MNDOC (correlated MNDO[11b]) result seems closer to the present ab initio structural predictions.

Interesting to note is the fact that the CI coefficients obtained for the two-configuration SCF wave function are (for the DZ basis set) the following, at the conrotatory transition state: $C_1 = 0.948$ and $C_2 = -0.312$, strongly supporting our choice of a zeroth order wave function including two configurations.

D. Search for a Disrotatory Stationary Point. The only constraint adopted here consisted of maintaining the C_s plane of symmetry during the optimization process. In Figure 2, this is the plane perpendicular to the paper and bisecting the central carbon–carbon bond. A careful search all along the disrotatory hypersurface was carried out. A stationary point, shown in Figure 2 and whose geometrical parameters are listed in Table IV, was eventually located. However, the vibrational analysis, summarized in Table V, showed two imaginary vibrational frequencies. One of these (341i cm^{-1}) corresponded to the expected displacement (disrotatory motion), but the other (379i cm^{-1}), actually the larger in magnitude, demonstrated a symmetry breaking motion. To

Table IV. Geometrical Description of the Disrotatory Stationary Point[a]

	Bond Lengths		
C_1C_2	2.956	C_1H_1	1.076
C_1C_3	1.490	C_1H_3	1.076
C_3C_4	1.334	C_3H_5	1.078
	Angles		
$C_1C_3C_4$	123.0	$H_1C_1H_3$	117.5
$C_3C_1C_2$	57.0	$H_3C_1C_3$	120.7
$H_5C_3C_4$	119.4	$H_1C_1C_3$	120.3
	Dihedral Angles		
$H_6C_4C_2H_4$	64.5	$C_1C_2C_3C_4$	0.0
$H_6C_4C_2H_2$	101.1	$H_6C_4C_3H_5$	0.0

[a] Bond lengths in Å and angles in deg. This structure was predicted at the DZ TCSCF level of theory.

the extent that the search along the hypersurface was exhaustive, this means that there is no transition state for the strictly disrotatory motion, i.e., that restricted to the C_s point group pathways. This finding is in agreement with analogous recent work by Volatron, Anh, and Jean[26] on the ring opening of oxirane. These authors point out that the stationary point for the oxirane disrotatory pathway is a maximum with respect to several coordinates of reaction.

For the particular case of cyclobutene, a nonsynchronous disrotatory pathway was shown in the MINDO/3 method to be more likely on energetic grounds by Dewar and Kirschner.[11] It has of course been shown that when there are two imaginary vibrational frequencies for a stationary point in a given symmetry there exists a lower saddle point in another symmetry.[23] However, we cannot be certain a priori whether that saddle point will simply be the conrotatory one or a second transition state in symmetry C_1 corresponding perhaps to the diradical species proposed in the MINDO/3 study. Indeed these authors do not provide a rigorous vibrational characterization of the nature of the nonsynchronous disrotatory stationary point located. Moreover, it is not apparent that the type of constraint adopted in the MINDO/3 study (preventing one CH_2 group from rotating in the "wrong" direction) is less restrictive than the classic disrotatory approach followed here.

In our opinion the term "disrotatory" is strictly applicable only to structures of C_s symmetry, such as that seen in the center right section of Figure 2. In this sense we predict no disrotatory transition state for the cyclobutene isomerization. A C_1 (no elements of symmetry other than the identity) transition state

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Table V. Predicted Vibrational Frequencies (in cm^{-1}) for Cyclobutene and the Conrotatory and Disrotatory Stationary Points Leading to *cis*-Butadiene (Experimental Cyclobutene Frequencies[32] Are Given in Parentheses)

	cyclobutene				
largest contribution	theory	expt	diff, %	conrotatory transition state	disrotatory stationary point
CH_2 asym str, in phase	A_2 3285	?		A 3416	A' 3417
out of phase	B_1 3304	2952	11.9	B 3416	A" 3416
CH_2 sym str, in phase	A_1 3243	2934	10.5	A 3296	A' 3303
out of phase	B_2 3229	2934	10.1	B 3297	A" 3301
CH str, in phase	A_1 3432	3057	12.3	A 3403	A' 3347
out of phase	B_2 3397	3046	11.5	B 3371	A" 3315
CH_2 scissors, in phase	A_1 1637	1442	13.5	A 1626	A' 1585
out of phase	B_2 1625	1425	14.0	B 1632	A" 1589
CH_2 wag, in phase	A_1 1357	984	?	A 869	A' 416
out of phase	B_2 1389	1208	15.0	B 886	A" 406
CH_2 rock, in phase	A_2 1119	?		A 1011	A' 1123
out of phase	B_1 1185	1074	10.3	B 1110	A' 1060
CH_2 twist, in phase	A_2 1296	1144	13.5	A 637 i	A" 341 i
out of phase	B_1 912	848	7.6	B 653	A" 379 i
CH in-plane bend, in phase	A_1 1206	1182	2.0	A 1215	A' 1337
out of phase	B_2 1437	1290	11.4	B 1505	A" 1530
CH out-of-plane bend, in phase	A_2 896	909	−1.4	A 1130	A' 755
out of phase	B_1 671	638	5.2	B 937	A" 1179
C–C unique str	A_1 1657	1564	5.9	A 1734	A' 1838
terminal C–terminal C str[a]	A_1 958	874	9.6	A 641	A' 207
C–C str, in phase[a]	A_1 1073	1112	?	A 1267	A' 1027
out of phase[a]	B_2 965	1009	−4.4	B 1223	A" 1134
ring deformation	B_2 947	885	7.0	B 764	A" 732
ring puckering	A_2 329	327	0.6	A 422	A" 437

[a] Labeled cyclobutene ring expansion by Lord and Rea.

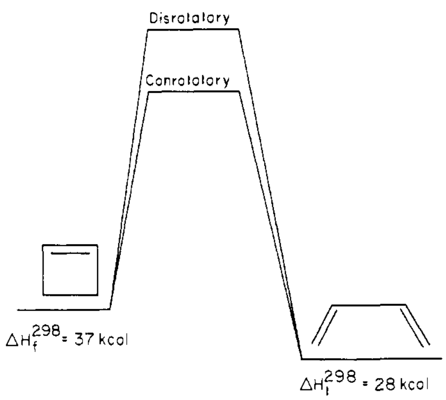

Figure 3. Qualitative sketch of the energetics of the isomerization of cyclobutene (left) to *cis*-butadiene (right).

would be labeled simply "low symmetry" rather than disrotatory.

Energetic Considerations

In Figure 3, we label the various energetic quantities we wish to predict and compare to available experiment data. Since the conrotatory process is the favored one, ΔE_a, the activation energy will be the most interesting quantity to discuss. In Table VI we have reported the results obtained at the TCSCF level with the DZ and DZ+d basis sets. For ΔE_a, those wave functions are augmented by all single and double excitations. The CI calculations are performed by means of the shape-driven graphical unitary group approach.[19] As may be observed, the CISD (DZ) classical barrier falls in best agreement with the experimental activation energy of 32.9 kcal/mol.[27] The DZ+d results remain within the range of the type of agreement that can be expected for such an activation barrier. The TCSCF barrier appears to be relatively insensitive to higher order correlation effects.

ΔE_b has been predicted only at the DZ TCSCF level of theory. As expected, the disrotatory potential barrier is higher than in the conrotatory process. This, however, does not settle the question of the forbidden character of the disrotatory process since there

Table VI. Thermochemical Data for the Cyclobutene-*cis*-Butadiene Isomerization, in kcal/mol (See Text for a Description of Basis Sets and Methods)

	conrotatory ΔE_a	ΔE_b (conrotatory − disrotatory)	ΔE_i (cyclobutene − *cis*-butadiene)
TCSCF DZ	39.4	10.5	−5.0
DZ+d	42.9		
+ CISD DZ	35.8	16.0	−6.2
DZ+d	42.4		
exptl	32.9[a]	≥15[b]	−9.1[c]

[a] Reference 27. [b] Reference 29. [c] References 22 and 28.

may exist a lower-energy transition state. The energy difference between the two isomers (ΔE_i) is in good agreement with experimental data, especially at the CISD (DZ) level. It must be noted, however, that there has to date been no precise experimental characterization of *cis*-butadiene; the experimental estimate of the exothermicity of the reaction comes from the difference between the heat of formation of cyclobutene (37.5 kcal/mol) and *trans*-butadiene (26.3 kcal/mol)[28] and the energy difference between *cis*- and *trans*-butadiene (2.1 kcal/mol).[22] The values predicted here are in closer agreement with experiment than MINDO/3 (16.3 kcal/mol above) and previous ab initio[9] calculations (16.1 kcal/mol above).

There has been considerable discussion of the energy difference between the barriers for conrotatory and disrotatory isomerization of cyclobutene. The early work of Brauman and Golden[29] yielded an estimate of ≥15 kcal/mol for the added stabilization for the allowed (conrotatory) process. Later detailed pyrolysis studies of *cis*-3,4-dimethylcyclobutene by Brauman and Archie[30] confirmed the earlier Brauman–Golden estimate. Buenker and Peyerimhoff's theoretical study[9] yielded 14 kcal for the conrotatory

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(29) J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968); D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(30) J. I. Brauman and W. C. Archie, *J. Am. Chem. Soc.*, **94**, 4262 (1972).

– disrotatory barrier difference while MINDO/3 suggests 16.6 kcal.[31] Table VI shows that the DZ TCSCF prediction for this energy difference is 10.5 kcal, somewhat less than previous estimates, but nevertheless in qualitative agreement. However, close agreement with Brauman's experiments[29,30] is found at the TCSCF + CI level of theory (16.0 kcal).

Vibrational Frequencies

For the reactant cyclobutene molecule, all but two of the ground-state vibrational frequencies have been assigned by Aleksanyan and Garkusha,[32] based in part on earlier research by Lord and Rea.[33] As a general rule, the predicted harmonic vibrational frequencies follow the well-established DZ SCF pattern[34] of being ~10% higher than the observed (anharmonic) fundamentals. Careful examination of Table V shows that a reassignment of several cyclobutene normal modes provides much better agreement between theory and experiment. Thus, for example, the predicted A_1 CH_2 in-phase wag at 1357 cm^{-1} agrees much better with the observed A_1 frequency at 1112 cm^{-1}, labeled ring expansion by Lord and Rea.[33]

Similarly, a rearrangment of the B_1 modes at 1185, 912, and 671 cm^{-1} allows a much closer agreement between theory and experiment than does the assignment of Aleksanyan and Garkusha. And in fact we have in Table V made this change in the experimental assignments, since the distinction between the different modes borders on the arbitrary. For example, the predicted B_1 frequency at 1185 cm^{-1} is assigned CH_2 out-of-plane rock in Table V. In fact this vibrational displacement is roughly 50% CH_2 out-of-phase rock, roughly 25% out-of-phase twist, and roughly 25% CH out-of-plane bend.

In general, there is a reasonably close correspondence between the vibrational frequencies of cyclobutene and those of conrotatory and disrotatory stationary points. Note, for example, that the in-phase CH_2 twisting of cyclobutene becomes the reaction coordinate (637i cm^{-1}) for the conrotatory transition state. Similarly, the out-of-phase CH_2 twisting becomes the disrotatory motion (379i cm^{-1}) for the disrotatory stationary point.

The central carbon–carbon stretching frequencies are of special interest, this being the C=C double bond stretch for cyclobutene. Although one intuitively expects this double bond to be breaking along the reaction coordinate, the central C–C frequency actually increases to 1734 cm^{-1} (conrotatory) and 1838 cm^{-1} (disrotatory) from the cyclobutene value (1657 cm^{-1}). This finding does, however, correlate with the shorter central C–C distance found at the conrotatory and disrotatory stationary points, confirming the notion that all three structures retain a central C=C double bond.

In several respects the predicted vibrational frequencies of Table V indicate that the disrotatory stationary point is a more "open" structure than is cyclobutene. For example, the CH_2 wagging frequencies span an enormous range, from 1357 and 1389 cm^{-1} for cyclobutene to 869 and 886 cm^{-1} for the conrotatory transition state to 416 and 406 cm^{-1} for the disrotatory stationary point. The same trend is seen in the frequency we have labeled terminal–terminal C–C stretching in Table V. For cyclobutene itself, the same frequency was labeled a ring expansion by Lord and Rea.[33] Whatever the designation, the variation in frequency is great, from 958 cm^{-1} for cyclobutene to 641 cm^{-1} for the conrotatory transition state to only 207 cm^{-1} for the more loosely held together disrotatory stationary point. Thus the vibrational frequencies allow a very straightforward differentiation between the three C_4H_6 structures pertinent to the cyclobutene isomerization.

Finally, the predicted zero-point vibrational energies (within the harmonic approximation) of cyclobutene and the conrotatory transition state are 20 275 and 19 412 cm^{-1}, respectively. Thus, in the framework of transition-state theory, the activation energy is predicted to be 2.5 kcal less than the classical barrier height. Hence this 2.5 kcal should be subtracted from each entry in the first column of Table VI. At the one level of theory (DZ TCSCF) for which a completely consistent (all stationary points rigorously optimized) treatment was performed, the predicted activation energy is thus 39.4 - 2.5 = 36.9 kcal, in quite acceptable agreement with experiment,[27] 32.9 kcal.

Concluding Remarks

The present study of the cyclobutene–*cis*-butadiene rearrangement involves a significantly higher level of theory than previous investigations. In addition, both conrotatory and disrotatory stationary points have been precisely characterized via vibrational analyses. The conrotatory structure is a genuine transition state, while the disrotatory stationary point is a maximum with respect to *two* internal nuclear degrees of freedom.

We suspect that the present theoretical predictions are likely to be secure against qualitative revision as the level of theory is advanced. Nevertheless, it would be desirable to carry out further studies with a basis set including d functions and a larger MCSCF procedure. In addition, the disrotatory structure should be pursued to lower symmetry (i.e., no symmetry at all, C_1 point group) to see if a distinct, genuine transition state is found. Finally, the question of the nonplanarity of *cis*-butadiene should be resolvable by theoretical methods, and we hope to pursue this goal in the future.

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Registry No. Cyclobutene, 822-35-5.

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