Prior to the availability of the abundant gas-phase electron-transfer equilibria data,[6] electron affinities were often obtained[1,2,11] from available $E_{1/2}$ values via eq 6 and the assumption that $\Delta\Delta G_{\text{sol}}°$ is constant, particularly in dipolar aprotic solvents like DMF. The results in Figures 5 and 6 show that for some groups of compounds this assumption breaks down and can lead to relative errors of 10 kcal/mol or more. Now that EA data are available, it is appropriate to concentrate on the solvation energies of the ions and their relative magnitudes and build up an extensive data bank. The availability of abundant data will lead to a much needed improved understanding of ion solvation of diverse systems. Very desirable in this quest are extensive modern determinations of reduction potentials and their temperature dependence under standardized conditions. Fortunately some such work is being done.[29]

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A Theoretical Study of the Potential Energy Surface of Butadiene in the Excited States

Mutsumi Aoyagi† **and Yoshihiro Osamura***

Contribution from the Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464, Japan, and Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku, Yokohama 223, Japan. *Received March 22, 1988*

Abstract: The molecular structures and the potential energy surfaces of the low-lying states of 1,3-butadiene are examined by using the ab initio MCSCF method. The equilibrium structures of *cis*-butadiene in the excited states are very similar to those of *trans*-butadiene. While single $\pi \rightarrow \pi^*$ excitation leads to the twisting of one C–C double bond, the doubly excited $\pi \rightarrow \pi^*$ state has a very flat potential energy surface for the torsion of all C–C bonds. The contribution of this $\pi \rightarrow \pi^*$ excited state to cis–trans isomerization and ring closure reactions is discussed.

I. Introduction

The study of the excited states of olefins is a subject of great importance in understanding spectroscopic data as well as mechanisms of photochemical reactions.[1] The electronically excited states of molecules which contain π electrons play an important role in the reactions induced by photons, such as photoisomerization, photodecomposition, or cycloaddition reactions.[2] Although the Woodward–Hoffmann rule[3] gives a beautiful explanation for the stereoselectivity of electrocyclic reactions, there is not enough evidence to support this rule in the case of reactions in the excited state. One of the reasons that few of the experimental results support this rule is that the chemistry occurring in the excited states is very complicated and often varies depending on the reaction conditions. Another important reason is that several excited states are generated upon irradiation.

The excited states of π-electron systems are especially complex in that the different states have different electronic character. Such differences may be influenced by the strong effect of substituents, which may lead to reaction along different potential surfaces. This feature can be even seen in ethylene which has only one double bond. Ethylene has a twisted equilibrium structure in the lowest triplet and two low-lying excited singlet states, and the energies of these states are very close to each other.[4] It is known that the lowest excited singlet state has ionic character and the triplet and ground states have biradical nature at the twisted geometry. Given these considerations, the cycloaddition of two ethylene molecules in the excited state does not seem to be a concerted reaction. It is obvious that the Woodward–Hoffmann rule does not apply to the case of a reaction via biradical or excited states.

There are more low-lying excited states when the ethylenic units are conjugated. In a previous paper,[5] we have studied the potential energy surfaces of *trans*-butadiene in the low-lying states. While the ground state of butadiene maintains the planality due to π electron delocalization, the molecular structures in the excited states are no longer planar. The previous calculation[5] shows that the equilibrium structures are very different in each electronic state. It is even more interesting that there exists a doubly excited singlet state which arises from the coupling of two triplet states of each ethylene unit.[6]

Another interesting aspect lies in the possibility of butadiene undergoing an electrocyclic reaction.[3] Although *trans*-butadiene is thermally stable, less stable *cis*-butadiene can undergo electrocyclization to cyclobutene. In this respect, a cis–trans isomerization process should also be considered in the course of thermal or photochemical reactions. It is known that the barrier height from *trans*-butadiene to *cis*-butadiene is 5 kcal/mol in the ground state.[7] In the excited states, however, isomerization can occur at two different positions, namely, the terminal C–C bond or center C–C bond.

In order to explore the electronic states which play an important role in the photochemical reactions of species containing two double bonds, we have conducted a theoretical study of the potential energy surfaces of the low-lying states of *cis*-butadiene as well as the trans form. One might expect to find a relationship between geometrical relaxation in the excited states of *cis*-butadiene and isomerization or ring closure reaction paths, even though *cis*-butadiene is less stable in the ground state. We will elaborate on these considerations in conjunction with our results in the last part of this paper.

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* Address correspondence to this author at Keio University.

† Present address: Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

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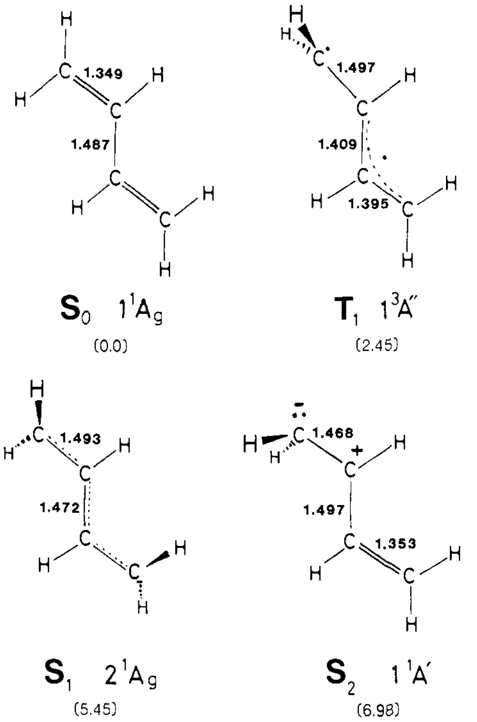

Figure 1. The equilibrium structures of *trans*-butadiene in the ground and excited states optimized by using the MCSCF method with the STO-3G basis set. The values in parentheses show the energies (eV) relative to the ground state.

II. Theoretical Procedure

The states studied in the present paper are the ground (S_0), lowest triplet (T_1), and two low-lying excited singlet (S_1 and S_2) states; they correspond to the 1^1A_1, 1^3B_2, 2^1A_1, and 1^1B_2 states, for a planar geometry with C_{2v} symmetry. We have used the CAS (Complete Active Space) type configurations for each state in the MCSCF procedure, where all possible configurations are generated by occupying four electrons in four π orbitals. The MCSCF wave function consists of 20 configuration state functions (CSF's) for the singlet state and 15 CSF's for the triplet state of C_1 symmetry. All geometries are optimized with the STO-3G basis set,[8] using the MCSCF energy gradient technique implemented in a modified version of the GAMESS program, which was developed by M. Dupuis et al.[9] The harmonic frequencies and the normal coordinates are obtained by the conventional GF matrix methods, where the force constant matrix is evaluated by numerical differentiation of the energy gradient.

In order to obtain more reliable information about the potential surface, we have carried out MCSCF calculations at all STO-3G optimized geometries, by using both the split-valence MIDI4[10] basis set and MIDI4 augmented with diffuse sp functions. The diffuse orbitals were placed at the midpoint of each of the terminal C–C bonds, so that a Rydberg character was included in the active space of the MCSCF procedure. The exponents for the diffuse s and p functions were chosen to be 0.023 and 0.021, respectively. When the diffuse orbitals were added to the basis set, the number of CSF's were 50 and 45 for the singlet and triplet states, respectively. Hereafter, the numbers cited in the text and in the figures are those evaluated with the MIDI4 + diffuse basis set at the geometries optimized with the STO-3G basis set, unless otherwise mentioned.

III. Electronic Structures and Geometries

A. Summary of the Molecular Structures of *trans*-Butadiene. Before discussing the results of *cis*-butadiene, we summarize the electronic character and molecular structures of *trans*-butadiene obtained in the previous calculation.[5] There are four low-lying electronic states, i.e., ground state (1^1A_g), $\pi \rightarrow \pi^*$ singlet and triplet states ($1^{1,3}B_u$), and $\pi \rightarrow \pi^*$ singlet (2^1A_g) state which has the character of double excitation. As shown in Figure 1, each electronic state has a different molecular structure which reflects the differences in electronic character. Both triplet ($1^3A''$) and singlet ($1^1A'$) states come from the B_u state of *trans*-butadiene which can be described with the singly excited electron configuration, with promotion from π(HOMO) to π^*(LUMO). In these states, the equilibrium structure is characterized by the twisting of the terminal CH_2 group. It should be noted that the triplet state has a biradical nature, but the corresponding singlet state is strongly ionic. Such ionic character relates to the sudden polarization effect in the excited state of ethylene.[11] The energetically lowest excited singlet state (S_1) at the equilibrium structure is calculated to be the doubly excited state which comes from the 2^1A_g state of *trans*-butadiene. This state has a very flat potential for rotation about the three C–C bonds. It is also found that there are four local minima, which arise from a combination of CH_2 bending and twisting motions.

Table I. Total Energies (in Hartrees) and Relative Energies (in eV) for the Low-Lying States of *cis*-Butadiene Obtained by the MCSCF Calculations

			basis set	
	states	geometries	STO-3G	MIDI4 + diffuse
S_0	1^1A_1	C_{2v}(I)	−153.1016 (0.0)	−154.7191 (0.0)
	$1^1A''$	C_s(II)	−153.0127 (2.42)	−154.6252 (2.56)
	$1^1A''$	C_s(III)	−153.0124 (2.43)	
T_1	1^3B_2	C_{2v}(I)	−152.9685 (3.62)	−154.6024 (3.18)
	1^3B_2	C_{2v}(IV)	−153.0067 (2.58)	−154.6297 (2.43)
	$1^3A''$	C_s(V)	−153.0134 (2.40)	−154.6261 (2.53)
	$1^3A''$	C_s(VI)	−153.0130 (2.41)	
S_1	2^1A_1	C_{2v}(I)	−152.8247 (7.54)	−154.4740 (6.67)
	2^1A_1	C_{2v}(VII)	−152.8949 (5.62)	−154.5201 (5.42)
		C_s(VIII)	−152.9035 (5.39)	−154.5261 (5.25)
		C_2(IX)	−152.9031 (5.40)	
	$2^1A''$	C_s(X)	−152.8966 (5.58)	−154.5098 (5.69)
S_2	1^1B_2	C_{2v}(I)	−152.6963 (11.03)	−154.4693 (6.80)
	1^1B_2	C_{2v}(XI)	−152.7153 (10.51)	−154.4801 (6.50)
	$1^1A'$	C_s(XII)	−152.8513 (6.81)	−154.5010 (5.93)

B. Excitation Energies. Table I summarizes the total energies and the relative energies for the low-lying electronic states of *cis*-butadiene calculated with various basis sets at the ground-state geometry(I) and the equilibrium geometries optimized by the MCSCF method with the STO-3G basis set. The vertical excitation energies from the ground state to the T_1, S_1, and S_2 states of *cis*-butadiene are a little smaller than those of *trans*-butadiene, because *cis*-butadiene is less stable than the trans conformer in the ground state. The general features of the potential energy surface seem to be very similar for both isomers.

C. Ground State $S_0(1^1A_1)$. Figure 2 shows the optimized geometries at the C_{2v} and C_s symmetry of *cis*-butadiene in the ground state. The vibrational frequencies at the optimized geometries are shown in Table II. The present MCSCF calculation indicates that the ground state of planar *cis*-butadiene, having C_{2v}(I) symmetry, seems to be an energy minimum, although the frequency for the rotational mode about the central C–C bond is very small (80 cm^{-1}). The SCF-CI calculation by Schaefer et al.[12] gives an imaginary frequency for this mode, and the twisted conformation is a local minimum in the ground state. Since this frequency is, however, very small, one cannot reach a definite conclusion as to whether the planar geometry of *cis*-butadiene is located at the saddle point or at the local minimum.[13] The barrier

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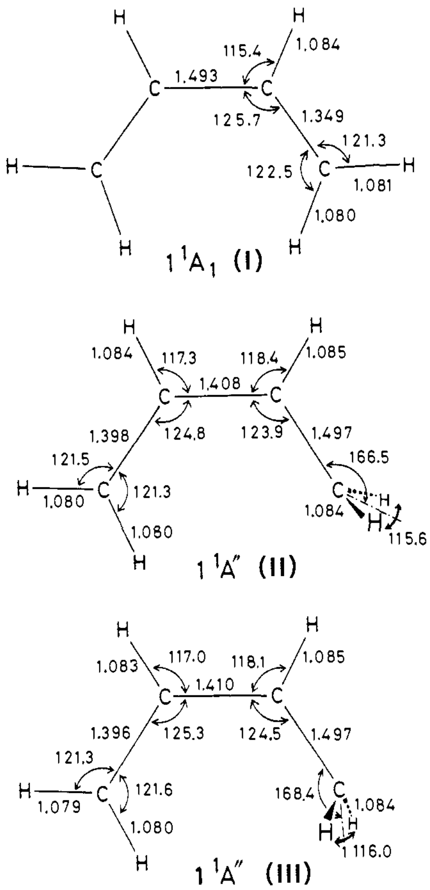

Figure 2. Optimized geometries of the ground state (S_0) of *cis*-butadiene. (I) is the equilibrium structure with C_{2v} symmetry. (II) and (III) are twisted geometries with C_s symmetry, which correspond to the saddle points for the terminal C–C torsion.

Table II. Vibrational Frequencies (cm^{-1}) of the Gound and the First Excited Singlet States of *cis*-Butadiene

state geometry	1^1A_1 (I)	2^1A_1 (VII)		$1^1A''$ (II)	$2^1A''$ (X)
$\nu_1(a_1)$	3824	3850	$\nu_1(a')$	3830	3841
$\nu_2(a_1)$	3720	3728	$\nu_2(a')$	3714	3724
$\nu_3(a_1)$	3664	3671	$\nu_3(a')$	3686	3690
$\nu_4(a_1)$	1862	2085	$\nu_4(a')$	3658	3661
$\nu_5(a_1)$	1707	1728	$\nu_5(a')$	3618	3606
$\nu_6(a_1)$	1525	1448	$\nu_6(a')$	1766	2066
$\nu_7(a_1)$	1195	1129	$\nu_7(a')$	1742	1748
$\nu_8(a_1)$	989	959	$\nu_8(a')$	1647	1720
$\nu_9(a_1)$	325	284	$\nu_9(a')$	1589	1607
$\nu_{10}(b_2)$	3821	3846	$\nu_{10}(a')$	1322	1432
$\nu_{11}(b_2)$	3712	3706	$\nu_{11}(a')$	1247	1268
$\nu_{12}(b_2)$	3660	3662	$\nu_{12}(a')$	1153	1142
$\nu_{13}(b_2)$	1891	1756	$\nu_{13}(a')$	1047	998
$\nu_{14}(b_2)$	1681	1609	$\nu_{14}(a')$	719	736
$\nu_{15}(b_2)$	1477	1305	$\nu_{15}(a')$	582	570
$\nu_{16}(b_2)$	1258	1149	$\nu_{16}(a')$	270	244
$\nu_{17}(b_2)$	629	580	$\nu_{17}(a'')$	3780	3765
$\nu_{18}(a_2)$	1106	417	$\nu_{18}(a'')$	1144	1108
$\nu_{19}(a_2)$	894	114	$\nu_{19}(a'')$	1036	568i[c]
$\nu_{20}(a_2)$	755	664i[a]	$\nu_{20}(a'')$	656	530i[d]
$\nu_{21}(a_2)$	80	339i[b]	$\nu_{21}(a'')$	612	282i[e]
$\nu_{22}(b_1)$	1108	317	$\nu_{22}(a'')$	507	184i[f]
$\nu_{23}(b_1)$	902	663i[a]	$\nu_{23}(a'')$	305	142
$\nu_{24}(b_1)$	521	360i[b]	$\nu_{24}(a'')$	940i[c]	44

[a] Out-of-plane bending of two terminal CH_2's. [b] Two terminal C–C torsions. [c] Terminal C–C torsion. [d] Out-of-plane bending of a terminal CH_2. [e] Out-of-plane bending of two central CH's. [f] Central C–C torsion.

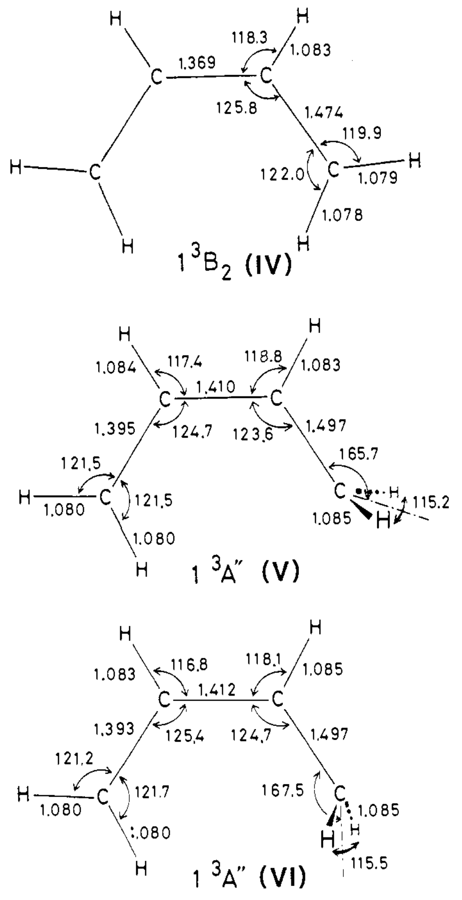

Figure 3. Optimized geometries of the first triplet state (T_1). The planar geometry (IV) at C_{2v} symmetry is not an equilibrium structure. Twisted geometries (V) and (VI) are the energy minima on the T_1 surface.

height of cis–trans isomerization in ground-state butadiene is calculated to be 4.8 kcal/mol, and this value is in good agreement with the other theoretical values (6.1 kcal/mol)[14] and the experimental value[7] (5.0 kcal/mol).

D. $T_1(1^3B_2)$ State. The optimized geometries of the lowest triplet state of *cis*-butadiene are shown in Figure 3. The excitation from the second π orbital to π^*(LUMO) causes an elongation of the terminal C–C bonds. The planar geometry having C_{2v}(IV) symmetry is not an equilibrium structure. The energy minimum results from the torsion of the terminal CH_2 group. The stabilization energy from the optimized planar geometry(IV) to the equilibrium twisted structure (V or VI) is very small (2.3 kcal/mol) because the terminal C–C bond is nearly a single bond in the T_1 state. Here we note that the energy of the equilibrium structure (V, VI) of the T_1 state is very close to that (II, III) of the transition state for the rotation of the terminal C–C double bond in the ground state. Furthermore, both T_1 and S_0 states at the twisted geometry have a biradical nature and can be described as "methyl radical + allyl radical", as we mentioned in the case of *trans*-butadiene.

E. $S_1(2^1A_1)$ State. The lowest excited singlet state of a polyene is known to involve a large contribution of the doubly excited configurations. This 2^1A_1 state has to be described with multiconfigurational wave function, just as in the case of *trans*-butadiene. The wave functions at the planar (VII) and 90° twisted (X) geometries are given as follows:

$$\Psi(2^1A_1) = 0.215[...1a_2^2 1b_1^2] + 0.400[...1a_2^2 1b_1^1 2b_1^1] + 0.499[...1a_2^1 1b_1^2 2a_2^1] - 0.412[...1a_2^1 1b_1^1 2a_2^1 2b_1^1] - 0.524[...1a_2^2 2a_2^2]$$

$$\Psi(2^1A'') = 0.680[...2a''^1 3a''^2 13a'^1] - 0.613[...2a''^2 4a''^1 13a'^1] + 0.269[...3a''^2 a''^1 13a'^1] - 0.300[...2a''^1 4a''^2 13a'^1]$$

From the vibrational analysis (see Table II), we find that neither

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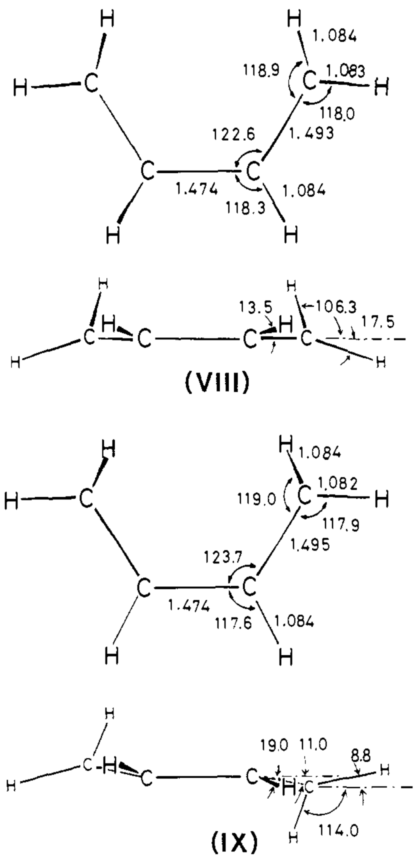

Figure 4. Optimized geometries of the first singlet excited state (S_1). The structures (VIII) and (IX) have C_s and C_2 symmetry, respectively, and they correspond to the energy minima on the S_1 surface. The figure projected on a plane perpendicular to the middle C–C bond is illustrated below each structure.

the planar nor the twisted structure is calculated to be an energy minimum, but the equilibrium geometries have low symmetry. We found that there are two local minima (VIII and IX) which are illustrated in Figure 4. Since all three C–C bonds are elongated, it would be expected that both the terminal C–C bonds and the central C–C bond easily rotate. The energy difference is, in fact, very small among the planar, the single twisted, and the equilibrium geometries. This suggests that cis–trans isomerization would easily occur via the 2^1A_g and/or 2^1A_1 state of butadiene.

F. S_2 (1^1B_2) State. Although the state symmetry of S_2 is the same as that of the lowest triplet state of butadiene, the electronic character in the two states is very different. In contrast to the biradical nature of the triplet state, the 1^1B_2 state is originally a Rydberg state in the vertical excitation. The calculation with inclusion of diffuse functions shows that the excitation energy from the ground state to the 1^1B_2 state of *cis*-butadiene or 1^1B_u state of *trans*-butadiene is very close to the 2^1A_1 or 2^1A_g state. Extensive calculations of vertical excited state for *trans*-butadiene and hexatriene shows that the energy of the 1^1B_u state is slightly lower than that of the 2^1A_g state.[15] Although we might have to assign 1^1B_2 state to be S_1, given the energy ordering, we denote this state as S_2 in consideration of the fact that the lowest excited singlet state of longer polyene is the doubly excited (2^1A_g type) state[16] and that the energy lowering by geometry relaxation from the vertical excited state is less in the 1^1B_2 state than in the 2^1A_1 state. As shown in Figure 5, the terminal CH_2 group is 90° twisted and is sp^3 hybridized at the equilibrium structure (XII). While the planar structure (XI) is located at a very shallow energy minimum,

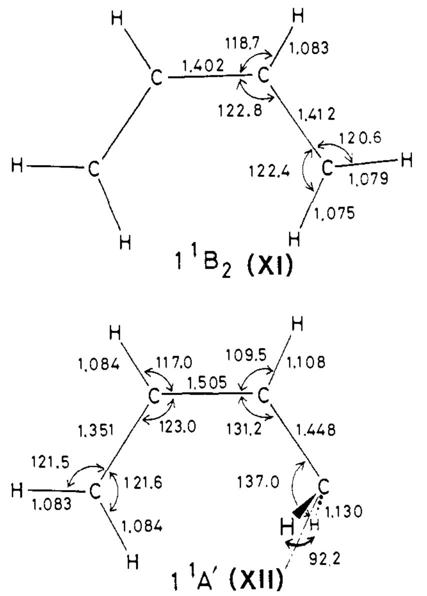

Figure 5. Optimized geometries of the second singlet excited state (S_2): planar C_{2v} symmetry structure (XI) and twisted geometry (XII) with C_s symmetry.

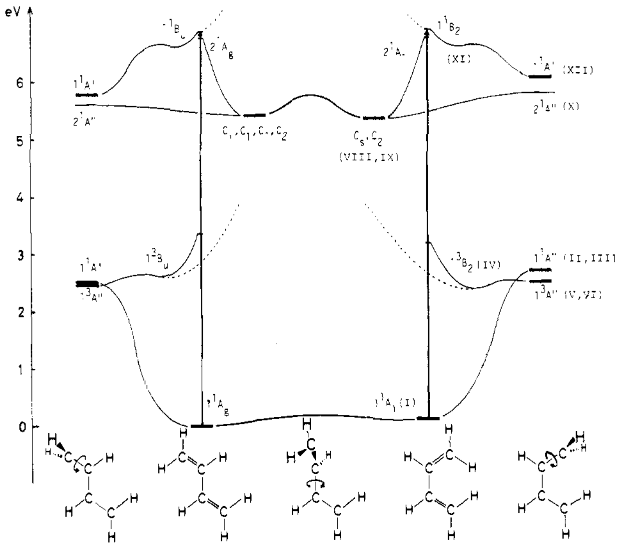

Figure 6. Energy diagram for the low-lying states of *trans*- and *cis*-butadiene. The energy levels for the terminal C–C bond twisted geometries are shown in the left column. The second column corresponds to the energy levels obtained for the C_{2h} optimized geometries and the vertical excitation energies of the trans form. The middle column shows the energy levels for the central C–C bond twisted geometries. The forth and fifth columns for the cis form correspond to the second and first columns for the trans form, respectively.

rotation of the terminal C–C bond causes stabilization and leads to an ionic structure.

IV. Potential Energy Surfaces

The present results for *cis*-butadiene show that its molecular and electronic structures resemble those of *trans*-butadiene, except for the number of local minima of the doubly excited state, S_1. Figure 6 illustrates the main features of the potential energy surfaces of butadiene for low-lying states. The most important variables involve terminal C–C bond torsion and central C–C bond rotation. Since the molecular structures in the excited states are very flexible and many geometrical distortions are involved, one should remember that all the coordinates are not necessary to be identical in the horizontal axis of the Figure 6.

A. Central C–C Bond Rotation. The cis–trans isomerization process has been studied theoretically by many authors[14] in the

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ground state. The energy difference between cis and trans forms is calculated to be 2.8 kcal/mol in the present study. The energy barrier is obtained to be 4.8 kcal/mol, and this transition state is located at the 97° twisted conformation about the central C–C bond.

The analysis of the vibrational frequencies of the ground state for *cis*-butadiene indicates that the frequency for the rotational mode about the central C–C bond is very small. Several authors[14] have proposed that the gauche form is the real energy minimum. However it is not essential to use the gauche form at the cis side in Figure 6 because the potential energy surface for the central C–C torsion is very flat between gauche and cis structures.

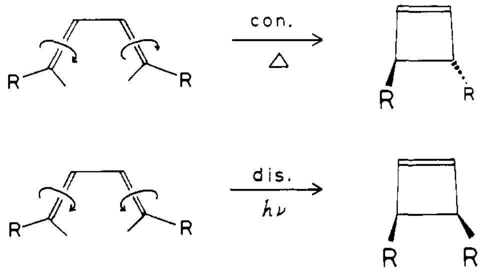
The next question concerns the potential energy surface in the excited states. Since the highest occupied molecular orbital (HOMO) has a node on the central C–C bond and the LUMO does not have a node there, the excitation from HOMO to LUMO will hinder the rotation of the central C–C bond. The increase in the double bond nature of the central C–C bond can be seen in the optimized structures at the planar geometries in the T_1 and S_2 states (IV and XI). The energies of the singly excited states ($^{1,3}B_2$, $^{1,3}B_u$) increase substantially upon twisting of the central C–C bond as is shown by the dotted lines in Figure 6. On the other hand, the S_1 state, which has a nature of double excitation, shows a completely different potential energy surface. Since the equilibrium structures for this state demonstrate that all C–C bonds are very long, the potential energy surface of the rotation is expected to be very flat about both central and terminal C–C bonds.

B. Terminal C–C Bond Rotation. The T_1 and S_2 ($^{1,3}B_2$ and $^{1,3}B_u$) states have a minimum at a geometry in which one terminal C–C bond is twisted by 90° (V, VI, and XII). This situation is similar to the case of the excited state of ethylene.

In the S_1 state originating to 2^1A_g or 2^1A_1 state, the energy difference between terminal C–C bond twisted conformation and equilibrium structures is found to be very small (5.0 kcal/mol for trans and 4.3 kcal/mol for cis). Moreover, the barrier height to the rotation of the central C–C bond is calculated to be 5.4 kcal/mol from the trans side and 4.8 kcal/mol from the cis side in the S_1 state. These results strongly suggest that the rotation of all C–C bonds can occur when the molecule is excited in the 2^1A_g state. Such evidence is experimentally observed[16] for the 2^1A_g state of *all-trans*-octatetraene. The 2^1A_g state may be generated by the internal conversion from the 1^1B_u state in which the electronic transition from the ground state is allowed.

C. Comment on the Ring Closure Path. The potential energy surfaces presented in this study reveal important aspects of the excited states. There are two kinds of isomerization processes. Upon rotation of the terminal C–C bond, all low-lying excited states (T_1, S_1, and S_2) give a more stable structure, unlike the ground state. The cis–trans isomerization of the central C–C bond is facile in the doubly excited state (S_1) as well as in the ground state. Given these facts, one may speculate on the reaction profile of the photochemical reaction of butadiene which has been rationalized by the Woodward–Hoffmann rule.

The formation of *cis*-butadiene should be considered to lead to ring closure to cyclobutene, since *cis*-butadiene is a thermally unstable species. The Woodward–Hoffmann rule predicts that the reaction proceeds in conrotatory in the ground state and that the disrotatory path is favorable in the excited state. While the conrotatory path is thermally favorable, Schaefer et al.[17] have shown that the transition state of the disrotatory path also exists for the thermal process. The ab initio SCF-CI calculation by Morihasi and Kikuchi[18] shows that the disrotatory ring-closure path gives an endothermic potential surface in the S_2 state, with no barrier.



When the reaction goes through the excited state, *trans*-butadiene is thought to be excited. Since the excited state, 1^1B_u, relaxes to the structure which has a twisted geometry of the terminal C–C bond, the S_2 state seems to be a nonreactive state for the ring closure. The fact that the rotation of the central C–C bond is prohibited in the S_2 state also denies the course of the reaction via *cis*-butadiene. On the other hand, the S_1 state has a very flat potential energy surface for C–C bond rotation. Since the energy separation between the S_1 and S_2 state is small, the internal conversion to the S_1 state should be possible, giving the cis form. The equilibrium structures shown in Figure 4 would be reasonable intermediates of the ring closure to cyclobutene because these structures involve torsion and bending of the terminal CH_2 groups.

One would expect that the stereospecificity predicted by the Woodward–Hoffmann rule no longer holds if the reaction proceeds via a doubly excited state, although experimental evidence is not sufficient. Our conclusion is in accord with the result of the recent photochemical study of cyclobutenes by Clark and Leigh,[19] which suggests that photochemical ring opening is not stereospecific. The present calculations suggest that further studies on the photochemical reaction would show that the S_2 state has ionic character and this state is strongly affected by substituents or solvents, while the S_1 state has "loose" C–C bonds and gives nonstereospecific reaction.

V. Concluding Remarks

The potential energy surfaces of butadiene in the ground and low-lying excited states give important indication regarding isomerization processes of the C–C bonds. The cis–trans isomerization of the central C–C bond is facile in the doubly excited singlet state S_1 (2^1A_g or 2^1A_1) as well as in the ground state. The excited states, S_2 and T_1, caused by the single electron excitation from HOMO to LUMO have an equilibrium structure in which the terminal C–C bond is 90° twisted. The electronic character at this geometry corresponds to that of twisted ethylene. The S_1 state is expected to play an important role in the photochemical reaction. This is a doubly excited singlet state of butadiene which has a very flat potential surface for the torsions of three C–C bonds. This state is the energetically lowest of the excited singlet states at relaxed geometries.

Acknowledgment. We are grateful to Professors S. Iwata and I. Ohmine for their valuable discussions. We are also grateful to Dr. Andrea Dorigo for his valuable suggestions and for improving the English in this manuscript. Numerical calculations were carried out at IMS Computer Center and Nagoya University Computer Center. The present research is supported in part by the Grant-in-Aid from the Ministry of Education.

Registry No. 1,3-Butadiene, 106-99-0.

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