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An MCSCF study of the low-lying states of *trans*-butadiene

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Ab initio MCSCF gradient method is applied to explore the potential surfaces of the low-lying excited states of 1, 3-*trans*-butadiene. The determination of the equilibrium geometries and the force constants shows that there are several local minima for the 1^3B_u (T_1), 2^1A_g (S_1), and 1^1B_u (S_2) states. Since each excited state has a different electronic character, its potential energy surface is complicated with respect to the rotation of C–C double bond and C–C stretching motions. The second 1A_g state is found to have four minima with low symmetry (C_i , C_2 , and C_1). A planar local minimum with C_{2h} symmetry is found on the 1^1B_u surface. The comparable planar minimum was found for the 1^1B_u state of *trans*-hexatriene. This is the first *ab initio* confirmation on the experimental analysis for the planar structure of the state. The present full π space MCSCF calculation gives not only reasonable transition energies but also detailed structures for low-lying states.

I. INTRODUCTION

The dynamics of the excited states of simple polyenes has been the subject of extensive researches both theoretically and experimentally.¹ There have been several controversies even for the state ordering. One concerns the position of the 2^1A_g state, and the other the nature of the 1^1B_u state. Recently for octatetraene and decapentaene, Kohler and his collaborators found a series of the vibronic bands below the one-photon allowed $1^1B_u \leftarrow 1^1A_g$ transition in their one-photon and two-photon excitation spectra and they assigned them to the $2^1A_g \leftarrow 1^1A_g$ transitions.^{2,3} Johnson failed to find the 2^1A_g state in his multiphoton ionization spectrum for butadiene.⁴ Theoretically *ab initio* SCF-CI calculations,⁵ as well as semiempirical calculations,⁶ predicted a relatively low transition energy to the 2^1A_g state. The ordering of the 2^1A_g and 1^1B_u state, however, was difficult to determine, because *ab initio* calculations are known to overestimate the energy of the 1^1B_u state. Experimentally, it is well established that the final state of the lowest allowed transitions of butadiene and other simple polyenes is the valence-type 1^1B_u state. On the other hand, in their *ab initio* SCF-CI calculation, Buenker and Peyerimhoff⁷ showed that the 1^1B_u state is almost purely Rydberg-like, while in other CI and effective Hamiltonian CI⁸ studies, the calculated transition energy was higher by more than 1 eV than the experimental one.

To elucidate the dynamical behavior of simple polyenes in the excited states, the potential energy surfaces and at least the stationary geometrical conformations are needed. Even for butadiene, they are little known. Simple guesses from ethylene or from longer polyenes are assumed in most cases. Recently, Granville *et al.*⁹ attempted to determine the structure of the 1^1B_u state of butadiene to octatetraene by simulating the absorption spectra. Their conclusion is that the 1^1B_u state is planar even in butadiene, in contrast with the 1^1B_{1u} state of ethylene. Until now, no *ab initio* calculations have supported these results. One of the difficulties in dealing with the electronic structures of simple polyenes by *ab initio* SCF-CI method is that a multiconfiguration de-

scription is required even for the ground state. Thanks to the recent progress of the multiconfiguration self-consistent field (MCSCF) method, combined with the analytical evaluation of the first energy derivatives, we were able to optimize the structures of butadiene. In the present work, the full geometry optimization was carried out for the ground, first triplet, first and second excited singlet states of butadiene as well as for the ground and first 1B_u states of hexatriene. We have located several stationary structures; some of them are local minima and others are the transition state-like structures at which all of the first energy derivatives are zero but with some negative force constants. Most of the optimized structures are ones not expected previously. Particularly, we found the stable planar conformation both for the 1^3B_u and 1^1B_u states. This is the first *ab initio* confirmation for the analysis by Granville *et al.* for the structure of the 1^1B_u state.

In the following sections, first the method is described, and then the results of the electronic and geometrical structures are presented. Next the calculated excitation energies are compared with the experimental and previous theoretical values. Finally, the characteristics of the potential energy surfaces and its photochemical implication are discussed.

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 1^1A_g , 1^3B_u , 2^1A_g , and 1^1B_u states at a planar geometry with C_{2h} symmetry. Because the multiconfiguration description is essentially needed for some of the states, we have used the CAS (complete active space)¹⁰ type configurations for each state in the MCSCF procedure, where all possible configurations are generated by occupying four electrons in four π orbitals [20 configuration state functions (CSF) for the singlet states and 15 CSF's for the triplet states]. All geometries are optimized with STO-3G basis set¹¹ using the MCSCF energy gradient technique implemented in a modified version of GAMESS program, which was developed by Dupuis *et al.* in NRCC.¹²

The force constants are evaluated by the numerical differentiation of the energy gradient.

In addition, we reevaluated the energies using the split-valence type MIDI4¹³ and the MIDI4 + diffuse basis sets at all STO-3G optimized geometries. The MIDI4 basis set was augmented with diffuse *sp* functions (exponent $\alpha_s = 0.023$ and $\alpha_p = 0.021$) which were placed at the middle of each of the terminal C = C bonds. When the diffuse orbitals were added to the basis set, the π orbital of a Rydberg character was included in the active orbital space of the MCSCF procedure (50 and 45 CSF's 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 set, if otherwise mentioned. The geometries for some of the states were reoptimized with the MIDI4 + diffuse set.

For hexatriene, the six-electron six-orbital CAS MCSCF calculations (175 CSF's) were carried out to optimize the geometries of the ground and 1^1B_u states.

III. ELECTRONIC STRUCTURES AND GEOMETRIES

The excited states of polyenes are expected to be stabilized by the rotation around the terminal C–C bond, as the excited states of ethylene. Bonacic-Koutecky *et al.*, in their *ab initio* SCF-CI calculation,¹⁴ found the minima on the potential energy curves of the 1^3B_u , 2^1A_g , and 1^1B_u states of butadiene with respect to the twisting of a C–C double bond. Since their calculations and the other previous calculations maintained most of the geometrical parameters fixed in drawing the potential curves for the twisting motion, the most stable structure has never been determined for the excited states of butadiene.

The optimized molecular geometries are illustrated in Figs. 1–4. Table I summarizes the total energies (in hartree) and relative energies (in eV) obtained with the basis sets examined. The electronic structure for each state can be easily seen from the occupation numbers of the active orbitals in the MCSCF wave function, which are given in Table II. To determine whether the optimized geometry is a stable structure or a transition state-like, the force constant matrix has

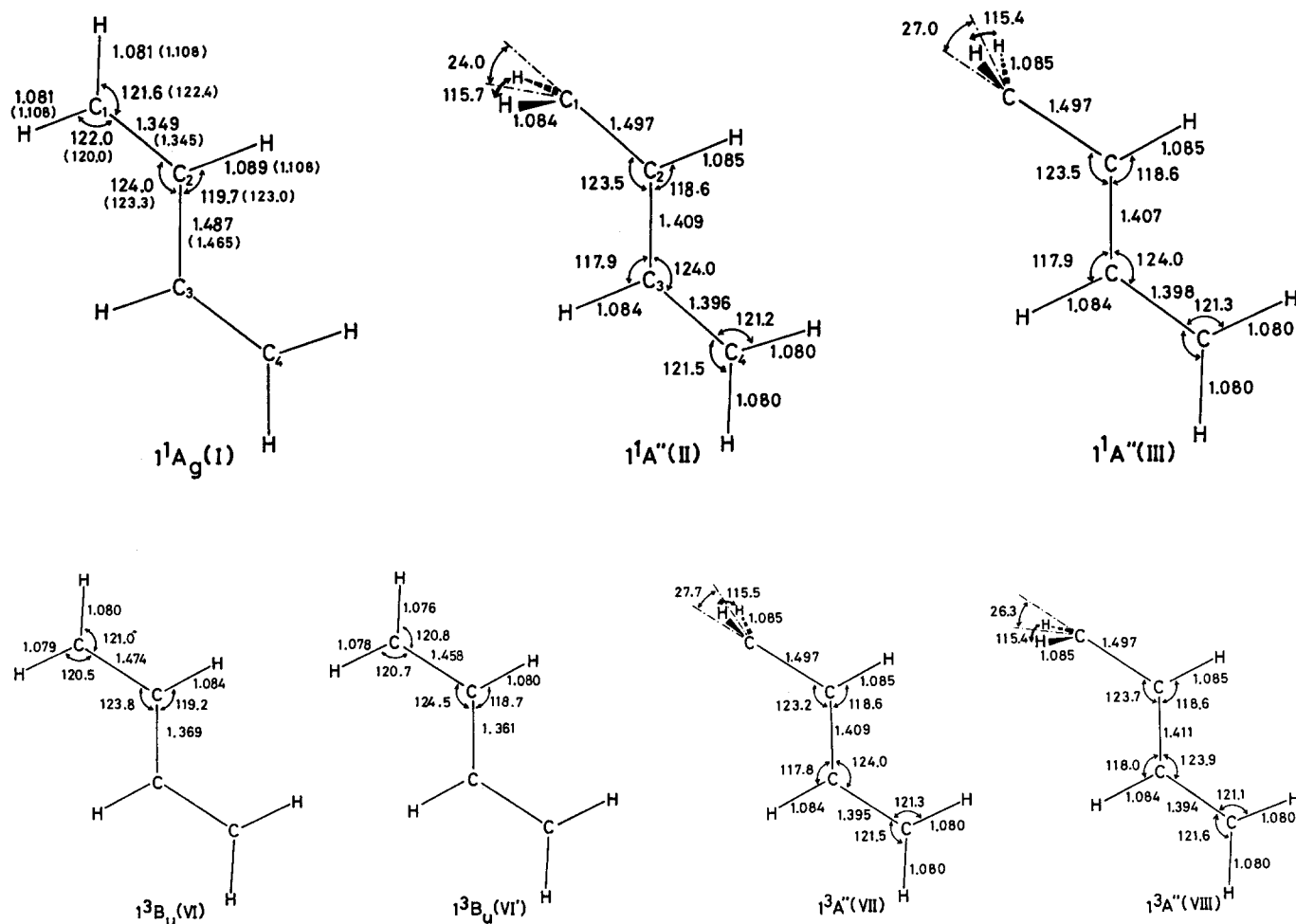


FIG. 1. Optimized geometries of the ground (S_0) and first triplet (T_1) states of *trans*-butadiene. Planar (I) and the transition states (II) and (III) are of the ground state. In the first triplet state (T_1), (VI) and (VI') are the planar conformations with C_{2h} symmetry, optimized with STO-3G and MIDI4, respectively, although (VI) is stationary with two negative force constants. (VII) and (VIII) are twisted geometries with C_s symmetry. In the following figures (1 to 4) the geometrical parameters (angstrom for length and degree for angles) are those optimized with STO-3G, and in the parentheses the experimental values (Ref. 16), if they exist, are given. When the geometry is optimized with the MIDI4 + diffuse set, the numbers are given in the square brackets.

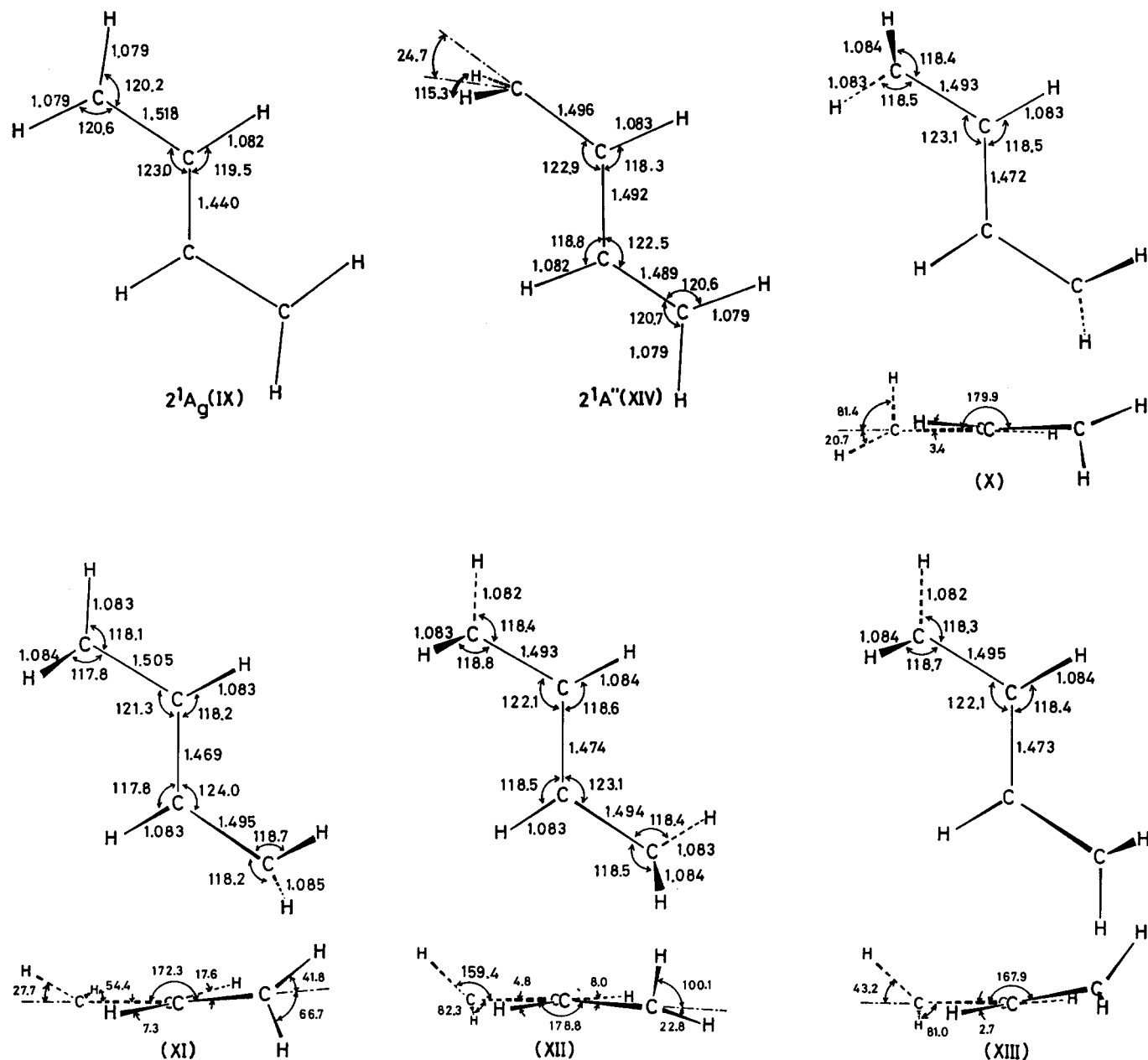


FIG. 2. The geometries at transition state-like and the local minima on the S_1 surface. The structure (IX) and (XIV) have four imaginary frequencies. The structures (X), (XI), (XII), and (XIII) have symmetry C_2 , C_1 , C_1 , and C_2 , respectively. Below each structure, the figure projected on a plane perpendicular to the middle C-C bond is shown.

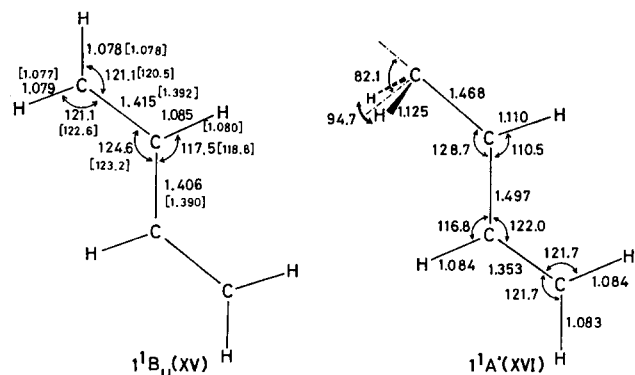


FIG. 3. The optimized geometries of the S_2 state at planar C_{2h} geometry (XV) and 90° twisted geometry (XVI) with C_s symmetry.

been evaluated. The results of vibrational analysis at the stationary points for S_0 , T_1 , and S_1 are given in Table III. One has to keep in mind that the calculated vibrational frequencies with STO-3G basis set generally overestimate by 10%–20%¹⁵ the experimental values¹⁶ shown in parentheses.

A. Ground state S_0 (1^1A_g)

As shown in Figure 1 (I), the calculated bond lengths and bond angles are in good agreement with experimental values.¹⁶ Molecular structures of valence electronic states can be reasonably predicted by the valence MCSCF method with a minimal basis set with accuracy of 0.02 Å and 3° .

We found that there are two geometries of the transition state for the twisting of the terminal C = C bond shown in

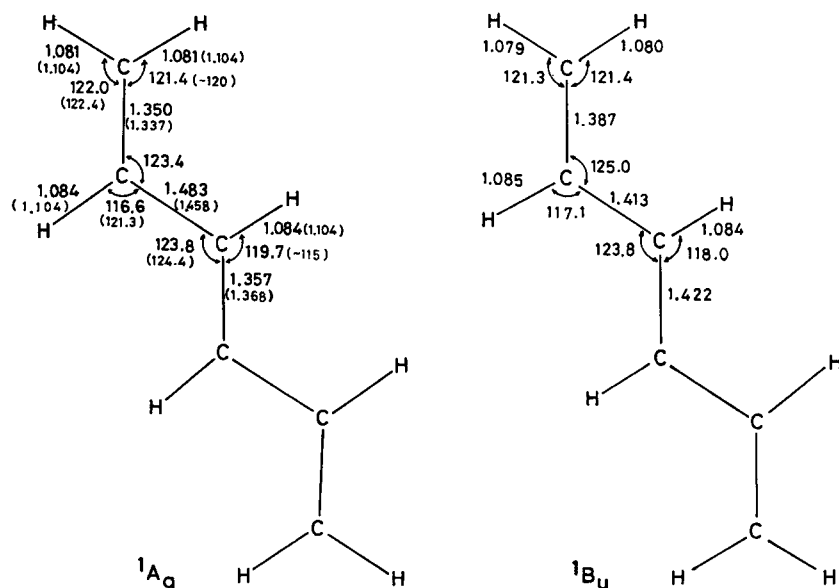


FIG. 4. The optimized geometries of the ground and $1B_u$ states of 1, 3, 5-*trans*-hexatriene.

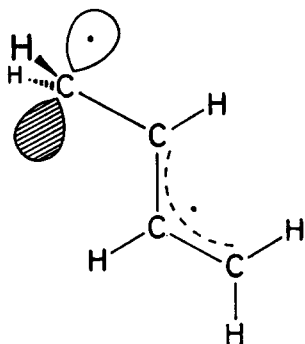
Fig. 1 (II) and (III). The vibrational analysis shows that both geometries have only one imaginary frequency for the torsional mode of C–C bond. Since the stabilization energy by the flapping of CH_2 group is very small (0.06 kcal/mol), the potential energy surface is very flat along the flapping mode of twisted CH_2 group. The angle of this pyramidalization (24° – 27°) does not have a particular meaning on the global surface and might be sensitive to the computational method used. In fact, the flapping angle optimized by Ohmine and Morokuma (who used the SCF method with the 4-31G basis set) is 5° .¹⁷ The other calculated geometrical parameters are very similar to those of Ohmine and Morokuma.

The MCSCF wave function for the two structures of the ground state are calculated as follows:

$$\Psi_{1A_g}(I) = 0.934|\dots 1a_u^2 1b_g^2| - 0.228|\dots 1a_u^1 1b_g^1 2a_u^1 2b_g^1| - 0.210|\dots 1a_u^2 2a_u^2| + \dots, \quad (1)$$

$$\Psi_{1A_g}(II) = 0.920|\dots 1a''^2 13a'^1 3a''^1| + 0.195|\dots 2a''^1 13a'^1 3a''^1 4a''^1| - 0.182|\dots 1a''^1 13a'^1 3a''^2| + \dots. \quad (2)$$

The closed-shell character corresponding to the planar equilibrium geometry turns into the biradical character of the twisted transition state. As clearly shown by the coefficient of the main configuration in Eq. (2), the electronic structure at the transition state can be characterized as “methyl radical + allyl radical”, i.e.,



The geometries II and III are consistent with the preceding picture.

B. T_1 (1^3B_u) state

It is well known that the lowest triplet π – π^* state of butadiene has a minimum structure with a 90° twisted conformation around the C–C double bond similar to the $^3B_{1u}$ state of ethylene. We, however, found two new local-energy-minimum structures (IV and V, which are not shown in the figure) near a planar geometry in addition to the expected twisted structures (VII and VIII). Two minima were found with a nearly planar structure in the MCSCF geometry optimization with STO-3G; in one structure (IV), both terminal CH_2 groups are lying above the molecular plane and, in the other (V), one of the CH_2 is up and the other down. The out-of-plane angles are only about 9° . We have confirmed that these structures are true minima within the STO-3G basis set approximation by evaluating the force constants. Because these near-planar structures (IV and V) in the T_1 surface have not been observed before, a MCSCF geometry optimization with MIDI4 was carried out. Even though as a starting structure the out-of-plane conformation was used, a planar structure was obtained after optimization. The determined geometry is given in Fig. 1 (VI'), while (VI), which is also shown in Fig. 1, is a planar transition-type structure with the STO-3G surface. Although the full force analysis could not be carried out, the stability with respect to the CH_2 out-of-plane mode was clear, since the starting geometry was nonplanar. The C–C bond lengths in Fig. 1 (VI') and the occupation numbers of the active orbitals in Table II are suggestive of the electronic structure. The MCSCF wave function (MIDI4) is

$$\Psi_{1^3B_u}(VI') = 0.904|\dots 1a_u^1 1b_g^1 2a_u^1| - 0.231|\dots 1a_u^1 1b_g^1 2a_u^2| + 0.218|\dots 1a_u^1 1b_g^2 2b_g^1| + 0.200|\dots 1a_u^2 2a_u^1 2b_g^1| + \dots. \quad (3)$$

The middle C–C bond becomes a double bond while the

TABLE I. Total energies (in hartrees) and relative energies (in eV) for the low-lying states of *trans*-butadiene obtained by the MCSCF calculations with three types of basis sets.

States	Geometries	STO-3G	Basis set MIDI4	MIDI4 + diffuse
S_0				
1^1A_g	C_{2h} (I)	-153.1043(0.0)	-154.7165(0.0)	-154.7234(0.0)
$1^1A''$	C_s (II)	-153.0129(2.49)		
$1^1A''$	C_s (III)	-153.0132(2.48)	-154.6253(2.49)	
T_1				
1^3B_u	C_{2h} (I)	-152.9693(3.67)	-154.5926(3.37)	-154.5998(3.36)
1^3B_u	C_{2h} (VI)	-153.0077(2.63)	-154.6209(2.60)	
	C_2 (IV)	-153.0080(2.62)		
	C_i (V)	-153.0081(2.62)	-154.6198(2.63)	-154.6270(2.62)
$1^3A''$	C_s (VII)	-153.0139(2.47)	-154.6261(2.46)	
$1^3A''$	C_s (VIII)	-153.0135(2.45)		
S_1				
2^1A_g	C_{2h} (I)	-152.8267(7.55)	-154.4681(6.67)	-154.4748(6.77)
2^1A_g	C_{2h} (IX)	-152.8959(5.67)	-154.5124(5.55)	
	C_i (X)	-152.9039(5.45)	-154.5174(5.42)	-154.5239(5.43)
	C_1 (XI)	-152.9034(5.48)		
	C_1 (XII)	-152.9035(5.46)		
	C_2 (XIII)	-152.9034(5.47)		
$2^1A''$	C_s (XIV)	-152.9039(5.45)	-154.5095(5.63)	
S_2				
1^1B_u	C_{2h} (I)	-152.6852(11.4)	-154.3920(8.83)	-154.4707(6.88)
1^1B_u	C_{2h} (XV)	-152.7022(10.9)	-154.4062(8.44)	-154.4796(6.63)
$1^1A'$	C_s (XVI)	-152.8477(6.98)	-154.5041(5.78)	

end C-C bonds ($R_{cc} = 1.46 \text{ \AA}$) are similar to a single bond of the middle C-C ($R_{cc} = 1.49 \text{ \AA}$) of the ground state S_0 (I). In other words, the electrons in the π orbital on each terminal CH_2 are not purely biradical, but the conjugation over four π orbitals is important to make this structure (VI') a local minimum.

The most stable structures we have found are the twisted one shown in Fig. 1 (VII) and (VIII); they are only 3.3 kcal/mol more stable than the planar local minimum (VI'). Note that there is very much similarity on the molecular geometries and the electronic structures between the transition states (II and III) of the ground state and the 90° twisted conformations (VII and VIII) of the T_1 state. Furthermore, the vibrational frequencies of twisted T_1 state are very similar to those of the corresponding modes of the ground state as shown in Table III, except for the terminal C-C torsion (ν_{17}) and CH_2 wagging motion (ν_{20}). The twisted T_1 state is also characterized as "methyl radical + allyl radical."

C. S_1 (2^1A_g) state

It is known that the 2^1A_g state should be described with a multiconfiguration wave function because of the large con-

tribution of the doubly excited configurations. Hereafter we call the state originated from 2^1A_g in a planar C_{2h} conformation S_1 although the ordering of 2^1A_g and 1^1B_u states is still controversial. Lasaga *et al.*^{6,18} emphasized the importance of the effect of two-electron excitations in CI calculations in order to calculate the potential energy surface, the vibrational frequencies, and the excitation energy correctly. For this state, the MCSCF gradient technique is essentially needed for optimizing the geometry.

First, two types of restricted optimization were carried out; in one, the molecule is kept in a plane and in the other, a terminal CH_2 is twisted to 90° . These geometries are shown in Fig. 2 (IX) and (XIV). The vibrational analyses at the converged geometries show that both planar (IX, C_{2h}) and twisted (XIV, C_s) geometries have four imaginary frequencies, whose modes are the out-of-plane motions of the terminal CH_2 groups and the terminal C-C torsional modes (Table III). Then considering these results, we obtain the fully optimized geometries which are shown in Fig. 2 (X)-(XIII).

These four geometries are found to be all shallow minima on the S_1 surface. The structures (X)-(XIII) are regarded as the mixed forms of two CH_2 out-of-plane bending (*trans* bent and *cis* bent) and two C-C torsional modes (conrotatory

TABLE II. Occupation numbers of active orbitals.

State and geometry	$1a_u(\pi_1)$	$1b_g(\pi_2)$	$2a_u(\pi_3^*)$	$2b_g(\pi_4^*)$	State and geometry	$2a''(\pi_2)$	$13a'(n)$	$3a''(\pi_3)$	$4a''(\pi_4)$
1^1A_g (I)	1.902	1.835	0.167	0.095	$1^1A''$ (III)	1.839	1.000	1.008	0.154
1^3B_u (VI)	1.828	1.016	1.001	0.155	$1^3A''$ (VII)	1.859	1.000	1.000	0.141
2^1A_g (IX)	1.336	0.962	1.149	0.553	$2^1A'$ (XIV)	1.294	1.000	1.069	0.637
1^1B_u (XV)	1.929	0.965	1.053	0.054	$1^1A'$ (XVI)	1.886	1.994	0.047	0.072

TABLE III. Vibrational frequencies (cm⁻¹) of the low-lying states of *trans*-butadiene. The experimental values¹⁶ are shown in parentheses.

State and geometry	1 ¹ A _g (I)	1 ³ B _u (VI)	2 ¹ A _g (IX)	1 ¹ A'' (II)	1 ³ A'' (VII)	2 ¹ A'' (XIV)	
$\nu_1(a_g)$	3819(3101)	3840	3842	$\nu_1(a')$	3829	3828	3839
$\nu_2(b_u)$	3819(3095)	3840	3842		$\nu_2(a'')$	3781	3773
3768							
$\nu_3(a_g)$	3715(3014)	3713	3724	$\nu_3(a')$	3713	3708	3723
$\nu_4(b_u)$	3712(3030)	3698	3715	$\nu_4(a')$	3693	3677	3704
$\nu_5(a_g)$	3658(3014)	3655	3659	$\nu_5(a')$	3657	3644	3665
$\nu_6(b_u)$	3650(3000)	3651	3657	$\nu_6(a')$	3619	3613	3609
$\nu_7(a_g)$	1895(1643)	1824	2094	$\nu_7(a')$	1755	1765	2074
$\nu_8(b_u)$	1847(1599)	1718	1734	$\nu_8(a')$	1742	1742	1748
$\nu_9(a_g)$	1724(1442)	1733	1713	$\nu_9(a')$	1654	1664	1707
$\nu_{10}(b_u)$	1617(1385)	1536	1503	$\nu_{10}(a')$	1511	1525	1488
$\nu_{11}(b_u)$	1495(1283)	1110	1290	$\nu_{11}(a')$	1412	1419	1452
$\nu_{12}(a_g)$	1486(1279)	1473	1469	$\nu_{12}(a')$	1278	1263	1308
$\nu_{13}(a_g)$	1377(1205)	1347	1315	$\nu_{13}(a')$	1169	1170	1238
$\nu_{14}(b_u)$	1139 (978)	981	1084	$\nu_{14}(a'')$	1138	1141	1107
$\nu_{15}(a_u)^a$	1128(1014)	1043	659 <i>i</i>	$\nu_{15}(a'')^d$	1051	1064	554 <i>i</i>
$\nu_{16}(b_g)^b$	1089 (967)	751	667 <i>i</i>	$\nu_{16}(a')$	1032	1026	1004
$\nu_{17}(a_g)$	999 (890)	1011	961	$\nu_{17}(a'')^e$	942 <i>i</i>	709	532 <i>i</i>
$\nu_{18}(b_g)^c$	899 (910)	355 <i>i</i>	366 <i>i</i>	$\nu_{18}(a')$	679	723	661
$\nu_{19}(a_u)^c$	896 (909)	330 <i>i</i>	301 <i>i</i>	$\nu_{19}(a'')^f$	659	661	280 <i>i</i>
$\nu_{20}(b_g)$	762 (680)	300	15	$\nu_{20}(a'')^g$	623	348	209 <i>i</i>
$\nu_{21}(a_g)$	550 (513)	547	504	$\nu_{21}(a'')$	582	587	79
$\nu_{22}(a_u)$	549 (520)	287	469	$\nu_{22}(a')$	552	534	474
$\nu_{23}(b_u)$	324 (309)	302	277	$\nu_{23}(a')$	303	304	279
$\nu_{24}(a_u)$	150 (170)	253	146	$\nu_{24}(a'')$	213	230	30

^aC₁-C₂, C₂-C₃, C₃-C₄ torsion.^bC₁-C₂, C₃-C₄ torsion.^cH-C₁-H, H-C₄-H out-of-plane bent.^dC₃-C₄ torsion.^eC₁-C₂ torsion.^fH-C₄-H out-of-plane bent.^gH-C₂-H out-of-plane bent.

and disrotatory). Since the energies of four minima are very close to the one of twisted conformation (XIV), the terminal C-C bonds can rotate freely. The wave functions at the planar geometry and 90° twisted conformations are written as follows:

$$\begin{aligned} \Psi_{2^1A_g}(\text{IX}) = & 0.513|\dots 1a_u^2 2a_u^2| - 0.444|\dots 1b_g^2 2a_u^2| \\ & + 0.401|\dots 1a_u^1 1b_g^1 2a_u^1 2b_g^1| \\ & - 0.368|\dots 1a_u^2 2b_g^2| + 0.304|\dots 1a_u^2 1b_g^2| \\ & + 0.254|\dots 1a_u^2 1b_g^1 2b_g^1| + \dots, \end{aligned} \quad (4)$$

$$\begin{aligned} \Psi_{2^1A''}(\text{XIV}) = & 0.667|\dots 1a''^1 13a''^1 3a''^2| \\ & + 0.581|\dots 2a''^2 13a''^1 4a''^1| \\ & - 0.361|\dots 2a''^1 13a''^1 4a''^2| \\ & - 0.221|\dots 2a''^1 13a''^1 3a''^1 4a''^1| + \dots \end{aligned} \quad (5)$$

D. S₂ (1 ¹B_u) state

As in the 1 ¹B_{1u} state of ethylene, the planar conformation in the 1 ¹B_u state (first π-π* excited state) of butadiene has been thought to be unstable with respect to CH₂ twisting. On the other hand, recently, the semiempirical analysis for the observed absorption spectra of butadiene, hexatriene, and octatetraene suggested the planarity of the 1 ¹B_u state for these molecules.⁹ In the following section, we discuss this in more details. In the present geometry optimization, a stable planar conformation (XV in Fig. 3) is found for the first

time in *ab initio* calculations. We have confirmed the stability of (XV) by carrying out a vibrational analysis, which yielded all positive force constants. In this structure (XV), three C-C bond lengths are nearly equal to that of the benzene (1.399 Å).

It is known that an addition of diffuse orbitals to the basis set is necessary to describe the electronic state of 1 ¹B_u correctly. Buenker *et al.*⁷ characterized the first ¹B_u state as a Rydberg-like state dominated by the one-electron excited configuration from highest occupied MO to 3pπ orbital.

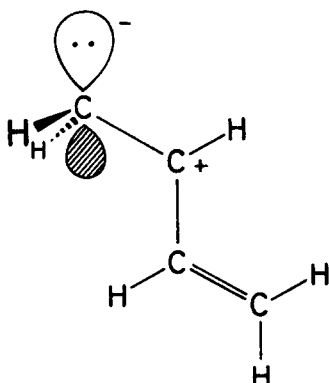
As shown in Table I, the excitation energy of 1 ¹B_u state at planar geometry depends on the basis set used. The relative energy is very high when the minimal basis set is used. Therefore, we have also optimized the geometry using MI-DI4 + diffuse basis set; the parameters of this geometry are given in square brackets of Fig. 3. There is not a large structural change from adding the diffuse orbitals. The MCSCF wave function with diffuse orbitals at the equilibrium geometry is as follows:

$$\begin{aligned} \Psi_{1^1B_u}(\text{XV}) = & 0.840|\dots 1a_u^2 1b_g^1 2a_u^1| \\ & - 0.478|\dots 1a_u^2 1b_g^1 3a_u^1| + \dots, \end{aligned} \quad (6)$$

where both 2a_u and 3a_u are composed of the mixture of valence-like π* and diffuse orbitals. The ratio of the electron distribution of the valence vs diffuse orbitals is roughly 4:6. Although the force analysis is not carried out, the stability of the planar conformation is likely to be correct with the MI-

DI4 + diffuse set, because the inclusion of the diffuse character in the wave function is expected to favor the planar conformation as in the case of the 1^1B_{1u} state of ethylene.

The second minimum structure of the S_2 state is found to be a 90° twisted conformation accompanied with a considerable flapping (about 82°) of the CH_2 group as is given in Fig. 3 (XVI). The electron charge distribution shows that the terminal carbon atom is purely anionic, i.e.,



The twisted S_2 ($1^1A'$) state can be described with almost one configuration, i.e.,

$$\Psi_{1^1B_u}(\text{XVI}) = 0.992|\dots 2a''^2 13a'^2| + \dots \quad (7)$$

and has no Rydberg character.

E. 1, 3, 5 *trans*-Hexatriene

The geometries of the ground and 1^1B_u states of hexatriene were optimized with the STO-3G basis set, and are shown in Fig. 4. The calculated geometrical parameters for the ground state are in reasonable agreement with the experimental ones as in butadiene. Because the double excitations have a large contribution in the ground state wave function

$$\begin{aligned} \Psi_{1^1A_g} = & 0.900|\dots 1a_u^2 1b_g^2 2a_u^2| \\ & - 0.192|\dots 1a_u^2 1b_g^2 2b_g^2| \\ & + 0.182|\dots 1a_u^2 1b_g^1 2a_u^1 2b_g^1 3a_u^1| \\ & - 0.169|\dots 1a_u^1 1b_g^2 2a_u^1 2b_g^1 3b_g^1| + \dots, \end{aligned} \quad (8)$$

the MCSCF method had to be used for the geometry optimization.

As in the case of the 1^1B_u state of butadiene, a planar conformation is found to be stable for the 1^1B_u state of hexatriene. For hexatriene, the force analysis and the MIDI-4 + diffuse calculation could not be carried out.

IV. EXCITATION ENERGIES

The energies of the low-lying excited states relative to the ground state energy are summarized in Table IV with the corresponding experimental and other theoretical values. The present vertical transition energies are evaluated with the MIDI4 + diffuse basis set using the MCSCF method for each state at the ground-state geometry optimized with the STO-3G MCSCF. The theoretical values of the excitation energies to triplet states, 1^3B_u and 1^3A_g , are in good agreement with the experimental results (3.22 and 4.93 eV) obtained by the electron impact and with the previous theoretical calculations.

The UV spectra^{19,25} show two sets of broad bands with peaks at about 5.9 ($\nu_{0-0} = 5.73$) and 7.07 eV. The first strong band has been generally assigned to the 1^1B_u state, and the experimentalists believe that the state has more valence character than Rydberg.

In the present calculations, the vertical excitation energy to 1^1B_u state gives 6.88 eV and the transition energy to a planar local minimum (approximate ν_{0-0}) is 6.63 eV. The theoretical value overestimates the vertical excitation energy to the 1^1B_u state because the important effect of σ correlation is neglected in the present MCSCF wave function. The 2^1B_u state lies 1.2 eV above the 1^1B_u state and both 1^1B_u states have mixed valence-Rydberg character.

A number of recent experiments have attempted to observe the 2^1A_g state in simple polyenes. The 2^1A_g state of octatetraene is claimed to be identified as a two-photon allowed state.² Although the 2^1A_g state (called S_1 in the present paper), of butadiene has not been spectroscopically observed yet, our calculation clearly shows the existence of the doubly excited states close to the 1^1B_u state. Our result is in good agreement with the other theoretical values as shown in Table IV.

V. DISCUSSION ON POTENTIAL ENERGY SURFACES

Figure 5 depicts the energy levels obtained by the

TABLE IV. Transition energies (in eV) to the low-lying states of *trans*-butadiene.

State	Hosteny ^a	Buenker ^b	Lee ^c	Present study	Experiment
1^1A_g	0.0	0.0	0.0	0.0	0.0
1^3B_u	3.45	3.31	3.74	3.36	3.22 ^d
1^3A_g	5.04	4.92	5.49	5.06	4.93 ^d
2^1A_g	6.77	7.02	7.19	6.77	
1^1B_u	7.05	7.67	6.61	6.88	5.76–6.09 ^e
2^1B_u	8.06	6.67	6.93	8.08	7.07 ^f
($\pi-3p\pi$)					

^a CI calculations, Ref. 5.

^b CI calculations, Ref. 7.

^c *Ab initio* effective valence shell Hamiltonian method, Ref. 8.

^d Electron impact experiment, Ref. 23.

^e UV absorption, Ref. 24.

^f The first member of the Rydberg series with the quantum defect $\delta = 0.42$ in Ref. 25.

MCSCF wave functions using the MIDI4 + diffuse basis set at each geometry discussed in Sec. III.

From the information of the vibrational analysis, we can look over the potential energy surfaces of low-lying states. It is noticeable that there is a wide variety of stable molecular conformations in the excited states, especially with respect to the geometrical change of the C–C bond lengths and the torsional angles of the terminal C–C bond.

A. The energy surfaces of S_0 and T_1 states

Let us examine the torsional barrier height of a C–C double bond related to the photo-isomerization. The present calculation gives 57 kcal/mol in the ground state of butadiene, and Bonacic-Koutecky *et al.* calculated it to be 60 kcal/mol.¹⁴

For the T_1 state, the stabilization energy from the vertical (ground state) conformation to the C_{2h} optimized structure (VI) is 17.8 kcal/mol, which includes an important contribution from the change of C–C bond lengths. The energies of S_0 (II) and T_1 (VIII) states are nearly degenerate at the 90° twisted conformation and both geometries are very similar. Although the inclusion of σ^2 – σ^{*2} correlation reverses the state ordering,²⁰ as is now known, one can expect that a radiationless transition would easily occur leading to isomerization around the C–C double bond. This situation is exactly the same as for the biradical state of the twisted eth-

ylene, because a similar energy relationship holds on butadiene when the terminal CH_2 group of ethylene is replaced to the allyl radical ($-\text{CH}-\text{CH}-\text{CH}_2$).

The transition state for the twisting motion, (VI') to (VII) or (VIII), has not been located in the present work. The barrier height is expected to be low enough so that the CH_2 group can rotate with the excess energy in the vertical photoabsorption.

B. The energy surfaces of excited singlet states (S_1 and S_2)

Bonacic-Koutecky *et al.*¹⁴ also calculated the singlet energy surfaces with the CI method by changing the torsional angle by assuming the accompanying change of the terminal C–C bond length. Since they fixed the other internal coordinates at each geometry, the reliability of the potential energy curves obtained for excited singlet states is limited.

In the 2^1A_g (S_1) state, the calculated energy difference between the vertical conformation (I) and four local minima (X, XI, XII, XIII) is as much as 30 kcal/mol. This considerably large stabilization energy is caused by the geometry relaxation with the elongation of C–C double bonds. The stationary states (IX) and (XIV), in which all first derivatives are zero with four negative force constants, lie only 3.1 and 5.0 kcal/mol, respectively, above the minimum structures (X, XI, XII, XIII). Therefore, a nearly free rotation, including the double rotation of two terminal CH_2 's, is expected, if the 2^1A_g state is created vertically from the ground state by two-photon absorption.

Our vibrational analysis indicates that a planar structure of the 1^1B_u state with C_{2h} symmetry is a local minimum on the S_2 surface. This provides the first *ab initio* support for the experimental analysis by Granville *et al.*⁹ By carrying out the Franck–Condon analysis for the strong UV transitions, they concluded that the linear polyenes (butadiene to octatetraene) are nearly planar in their excited 1^1B_u states. Although changes of only two normal frequencies for single and double C–C bonds are taken into account in their analysis, the simulated absorption spectra were in good agreement with the observed ones. Similar analyses, with more sophisticated models and more adjustable parameters, were carried out for the spectrum of butadiene by Hemley *et al.*²¹ and by Dinur *et al.*²² Hemley *et al.* estimated the change of the single bond as $\Delta r_s = -0.060 \text{ \AA}$ and the double bond as $\Delta r_d = 0.077 \text{ \AA}$, while ours are $\Delta r_s = -0.081 [-0.072 \text{ with MIDI4 + diff.}]$ and $\Delta r_d = 0.066 [0.046]$. In the experimental spectra, the 0–0 band in hexatriene becomes more evident than that in butadiene. Therefore, to confirm the argument of Granville *et al.*, the geometry optimization of the 1^1B_u state of hexatriene with the STO-3G MCSCF method was carried out, and the stable structure (Fig. 4) in a plane conformation (C_{2h}) was found. Though the force analysis with the MCSCF method was too time consuming to be carried out, our full geometry optimization is enough to support the analysis of Granville *et al.* They also estimated the change of the single $|\Delta r_s|$ and double $|\Delta r_d|$ bond lengths; $|\Delta r_s| = 0.12 \text{ \AA}$ and $|\Delta r_d| = 0.11 \text{ \AA}$ for hexatriene. Our corresponding Δr_s and Δr_d are -0.070 and $+0.065 \text{ \AA}$, respectively.

As discussed already, the most stable structure on the S_2

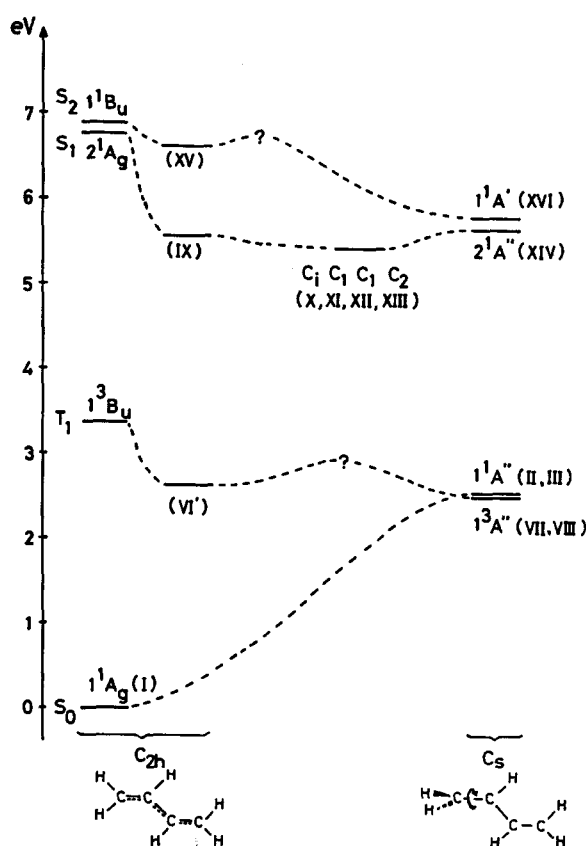


FIG. 5. The energy diagram of the low-lying states of *trans*-butadiene. The levels of the left column are the vertical excitation energies and the next column shows the energy levels at the planar optimized geometry for each state. The levels of the rightmost column are ones optimized with a 90° twisted CH_2 .

surface is the twisted one (XVI); the energy gain from the planar (XV) is 15 kcal/mol. The structure of the transition state from (XV) to (XVI) and the barrier height are one of the future questions to be examined, because of their significance in the singlet mechanism of photoisomerization. As for the singlet mechanism, the role of the 2^1A_g (S_1) state has been controversial. The present calculations cannot definitely determine the ordering of the 2^1A_g and 1^1B_u states at the vertical conformation. In the corresponding relaxed planar geometries (IX and XV), however, the 2^1A_g (S_1) state is much more stable than the 1^1B_u state (S_2). Therefore, it is most likely that the lowest singlet state of *trans*-butadiene in a planar conformation is the 2^1A_g state. Calculations based on larger basis sets and extensive CI may not change this conclusion. Because the potential energy surface of S_1 for the twisting of terminal CH_2 's is nearly flat, once the C–C bond lengths are relaxed, the photo-isomerization may easily take place if the internal conversion from the S_2 state to the S_1 state occurs.

VI. CONCLUDING REMARKS

(1) The 3B_u state, T_1 , of butadiene has a local minimum at (or near) a planar conformation.

(2) The singlet state, S_1 , originated from the 2^1A_g state has a nearly flat potential energy surface for the twisting motion of the terminal CH_2 's.

(3) The singlet state 1^1B_u (S_2) of butadiene has also a local minimum at a planar conformation. This is also true for the 1^1B_u state of hexatriene.

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