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Ab Initio SCF and CI Calculations on the Barrier to Internal Rotation of 1,3-Butadiene

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Ab initio SCF and CI calculations employing a set of gaussian lobe functions have been carried out for the ground and excited states of five geometrical C_4H_6-structures occurring in the course of rotation from *cis*-butadiene to the *trans*-isomer. The rotational potential curves are discussed for the ground and excited states. Particularly the potential curve of the lowest triplet state is considered in this connection thereby substantiating quantitatively the proposed mechanism for induced dimerisation of C_4H_6. Possible assignments of the lowest singlet excited states in *trans*-butadiene are discussed.

Mit einem Satz von Gaußfunktionen wurden *ab initio* SCF und CI Rechnungen für den Grundzustand und angeregte Zustände von fünf C_4H_6-Konformeren, die durch Drehung von *cis*-Butadien in *trans*-Butadien entstehen, durchgeführt. Die Potentialkurve für die innere Rotation von 1,3-Butadien wird für den Grundzustand und die Anregungszustände diskutiert. Besonders wird in diesem Zusammenhang die Potentialkurve des niedrigsten Triplettzustandes betrachtet, da hierbei der vorgeschlagene Mechanismus der induzierten Dimerisierung von Butadien quantitativ bestätigt wurde. Weiterhin werden mögliche Zuordnungen für die niedrigsten Singulettzustände von *trans*-Butadien diskutiert.

Calculs SCF et CI *ab initio* en orbitales gaussiennes pour les états fondamentaux et excités de cinq structures géométriques de C_4H_6 intervenant au cours de la rotation du *cis*-butadiène à l'isomère *trans*. Les courbes de potentiel correspondant à la rotation pour l'état fondamental et les états excités sont l'objet d'une discussion. En particulier on examine la courbe correspondant à l'état triplet le plus bas confirmant ainsi quantitativement le mécanisme proposé pour la dimérisation induite de C_4H_6. Discussion des attributions possibles des états excités singulets les plus bas dans le *trans*-butadiène.

1. Introduction

The nature of the equilibrium existing between the *cis*- and *trans*-isomers of 1,3-butadiene has often been the object of both experimental and theoretical investigations. From a quantitative point of view of greatest interest is the shape of the potential curve for internal rotation of the carbon-carbon double bond in these systems and also the difference in energy between their equilibrium conformations. It has generally been concluded that 1,3-butadiene in the gas phase exists predominantly in the *trans*-form at equilibrium; this conclusion is based on the electron diffraction experiments of Shoemaker and Pauling [1] and Almenningen *et al.* [2], on the infrared and Raman spectroscopic measurements by Sverdlov and Tarasova [3], Marais *et al.* [4] and Reznikova *et al.* [5], and also on the results of the thermodynamical treatment of the problem by Aston *et al.* [6]. Sudgen and Walsh [7] on the other hand have argued that at room temperature a considerable portion of 1,3-butadiene exists in the *cis*-form, on the basis of their observation of relatively low ionization potential at 8.7 eV, which they assigned to the *cis*-compound; recent measurements by Watanabe [8] were unable to confirm this result, however, despite the relatively high resolution attainable with his apparatus.

Until recently theoretical investigations on this general subject have been based exclusively on semiempirical calculations. Previous π-electron calculations by Polansky [9] taking account of nuclear repulsive forces in an indirect manner have found the *trans*-conformer to be more stable than the *cis* by 2.1 kcal/mole; other π-electron calculations by Parr and Mulliken [10] find a value of 2.8 kcal/mole for this difference, again predicting *trans*- to be the favoured conformer. On the other hand approximate calculations by Berry [11] find *cis*-butadiene to be the more stable, by as much as 23 kcal/mole. Differences in the description of the internal rotation potential curve among the aforementioned treatments are even larger.

Calculations of the *ab-initio* variety for *cis*- and *trans*-butadiene have been reported by Buenker and Whitten [12] and Radom and Pople [13], and have found *trans*- to be the more stable in all cases. The former authors have reported energies of isomerization by employing a limited CI-calculation in addition to the SCF treatment (5.0 kcal/mole SCF, 3.9 kcal/mole CI, compared to the experimental value of 2.3 kcal/mole [6]). Radom and Pople have employed a relatively small AO-basis and have considered only the SCF-method in their work but have included several geometrical models for the internal rotation in their study with interesting results; isomerization energy values of 5.7, 2.9 and 2.05 kcal/mole have been reported, with improvements noted as a result of geometrical optimization.

In the present work the results of a series of *ab-initio* SCF and CI calculations using a relatively large basis set will be considered in an attempt to evaluate the effect of the level of treatment employed upon the description of the internal rotation barrier as well as the importance of considering geometrically optimized structures in the course of the isomerization. As a second point the spectra in the ultraviolet region will be studied on the basis of the CI-calculations carried out for the excited states in this work; the main problem is the second strong band system near 7.12 eV, which can be interpreted only with great difficulties. Attention will also be given to the excited states which are important for possible mechanisms for a photochemically induced isomerization of *cis*- and *trans*-butadiene.

2. Calculations

The basis chosen for the present study consists of 130 gaussian lobe functions (40 s and 60 p functions on the carbon atoms and 30 s functions on the hydrogens). These primitive gaussians are grouped in 42 fixed linear combinations (atomic orbitals): one 1s group (4 components), one 2s group (3 components) and one additional s group (3 components with large exponents to simulate the behaviour near the nuclei) on each carbon atom, one 1s group (5 components) on each hydrogen atom and two sets of p groups (p_x, p_y, p_z with 4 and 1 components respectively) on each carbon atom. In contrast to Buenker and Whitten [12] the

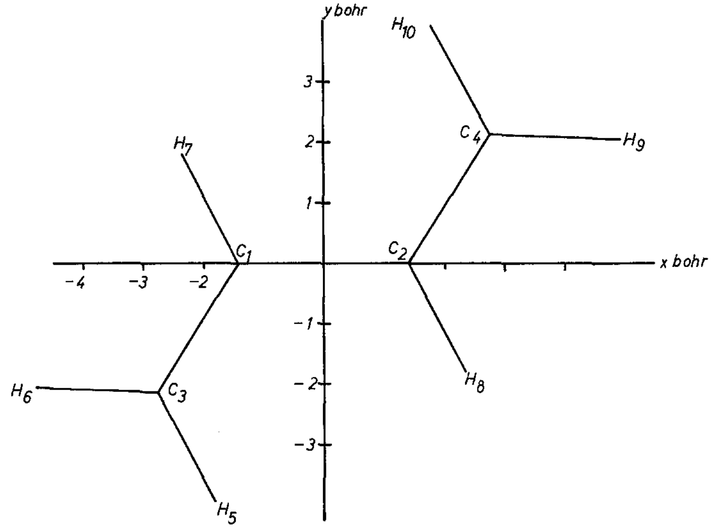

Fig. 1. Geometry of *trans*-butadiene. Coordinates of carbon and hydrogen nuclei (in atomic units) $C_{1,2}$ (±1.401250, 0.0, 0.0), $C_{3,4}$ (±2.755067, ±2.133280, 0.0), $H_{5,10}$ (±1.801435, ±3.941990, 0.0), $H_{6,9}$ (±4.797678, ±2.040533, 0.0), $H_{7,8}$ (±2.354903, ±1.808750, 0.0). The other conformations are obtained by rotating the plane of the nuclei C_1, C_3, H_5, H_6, H_7 about the C_1–C_2 bond

long range components of the carbon *p* group functions are treated as separate functions. Thus the number of group functions (and hence SCF-coefficients) increases from 30 to 42 compared to the former calculation, but the total number of primitive gaussians and the exponents remain unchanged.

The geometry assumed for the *trans*-conformer is that inferred experimentally by Allmenningen *et al.* [2] (see Fig. 1). A rigid model has been assumed in choosing the other nuclear conformations considered, that is, the C=C–C angles are held fixed at 122.4° throughout the rotation about the inner C–C bond. Explicit calculations are then carried out at 45° intervals from 0° (*trans*-butadiene) to 180° (*cis*-butadiene), for five geometries in all [14]. Calculated orbital energies resulting from the present SCF treatment are given in Fig. 2. As is to be expected in all cases the σ MO's of one isomer (a_g, b_u) correlate with σ species of the other (a_1, b_2), despite the fact that for the rotated structures σ and π MO's are allowed to mix (C_2 point group). All $C_1 - C_2$ bonding σ-MO's (a_1 in the *cis*-case) are seen to become less stable upon rotation out of the *cis*-conformation, while all the correspondingly antibonding species show the opposite behaviour. These energy changes, although somewhat different in magnitude for the various MO's due to the individual charge distributions, can easily be understood since the in-phase overlap of the AO's in the *cis*-isomer is greater than in the *trans*-case. An interesting consequence of these various considerations is that bonding π-orbitals in one conformer correlate with antibonding species in the other (a_u with a_2, b_g with b_1); the σ orbitals by contrast maintain a strict separation of $C_1 - C_2$ bonding and antibonding MO's throughout the rotation. The minimum ionization potential calculated for the *trans*-conformer is 8.79 eV according to

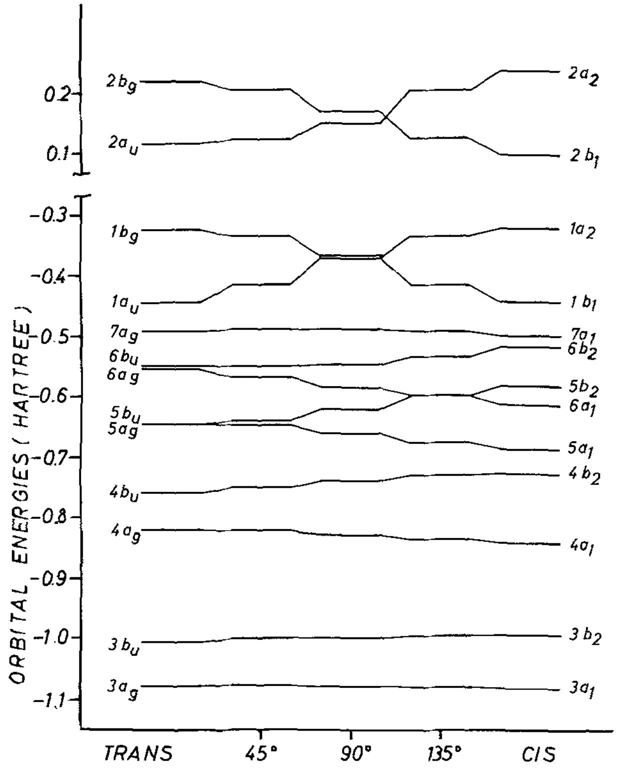

Fig. 2. Correlation and energies of the molecular orbitals of 1,3-butadiene in the five conformations considered

Koopman's theorem in quite good agreement with the experimental value [8, 15, 16] of 9.08 eV. The less flexible basis set calculations [12] obtained a somewhat worse value of 9.78 eV.

On the basis of the aforementioned SCF treatment CI calculations were performed according to a method given by Buenker and Peyerimhoff [17]. In this method all electronic configurations are considered which can be constructed from a certain limited basis of MO's. The present CI-calculations are carried out with three different valence sets (orbitals which are allowed variable occupation in the configurations explicitly considered). First four π MO's, secondly four π and one σ MO and in the third case four π and two σ MO's ($7a_g$, $1a_u$, $1b_g$, $2a_u$, $2b_g$, $7b_u$ in C_{2h} notation) are included in the valence set. In the course of these variations of the valence set only negligible changes in excited state energies could be observed.

3. Potential Curve for Internal Rotation (Ground State)

The SCF total energies and CI ground state energies calculated for the five 1,3-butadiene structures considered are shown in Fig. 3 and Table 1. In general these energies are on the order of 0.1 hartree (roughly 70 kcal/mole) lower than

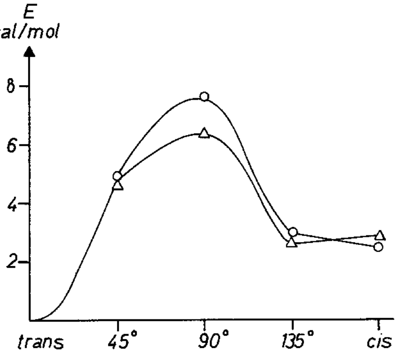

Fig. 3. Ground state potential curve to internal rotation of 1,3-butadiene (○ SCF-, △ CI treatment)

Table 1. Total energies (in hartrees) and scaling factor η of 1,3-butadiene in the five conformations compared with the results of previous calculations

		0° (*trans*)	45°	90°	135°	180° (*cis*)
E_T	This work SCF	−154.8214	−154.8137	−154.8093	−154.8167	−154.8175
	This work CI	−154.8579	−154.8504	−154.8478	−154.8537	−154.8534
	Ref. [12] SCF	−154.7103				−154.7023
	Ref. [12] CI	−154.7723				−154.7660
	Ref. [13] SCF	−153.0166				—
	$\eta = -V/2T$	1.00057	1.00052	1.00050	1.00054	1.00051

the corresponding values obtained with the basis set which does not decompose the 2*p* group functions [12]. In comparison with the work of Radom and Pople employing much smaller basis sets the present total energies are lower by 1.8 hartree (over 1100 kcal/mole). Decomposition of the 2*p* groups is seen to have a salutary effect with respect to satisfaction of the virial theorems; the scaling factors $-V/2T$ are decreased from 1.003 (Ref. [12]) to 1.0006 in the present calculations. Energy lowering effected by scaling of the SCF-functions is thus $6.0 \cdot 10^{-5}$ hartree with the present basis compared with the value of $1.6 \cdot 10^{-3}$ hartree obtained before. Since the energy of isomerization is only $4.0 \cdot 10^{-3}$ hartree [5, 6], such a distinction could be of possible significance in the determination of the potential curve for internal rotation, although it must be pointed out that in both sets of calculations the energy lowering due to scaling is very nearly independent of the conformation.

The present calculated barrier heights and isomerization energies are given in Table 2 for comparison with the result of previous calculations and with experiment. Increasing the flexibility in the 2*p* representation apparently succeeds in allowing a more balanced treatment of the conformers, decreasing the isomerization energy from 5.0 kcal/mole to values within 0.2 of the experimental value of 2.3 kcal/mole [5, 6]. The results of Radom and Pople [13] on the other

Table 2. Isomerization energy $\Delta E_{c/t}$ and barrier height ΔE_B relative to *trans*-butadiene for 1,3-butadiene (in kcal/mole (C=C–C angle for $A = 120°$, for C optimized, for $D = 124.2°$))

	$\Delta E_{c/t}$	ΔE_B
This work SCF	2.5	7.6
This work CI	2.7	6.4
Ref. [12] SCF	5.0	—
Ref. [12] CI	3.9	—
SCF calc., Ref. [13]		
A	5.66	6.71
C	2.05	6.61
D	2.92	6.73
exptl., Ref. [6]	2.3	4.9
exptl., Ref. [5]	1.7 ± 0.5	—

hand suggest that part of this distinction between the present calculation and that of Buenker and Whitten could be caused by the fact that a larger value of the C=C–C angle (122.4°) has been applied than that used in the other case (120° in Ref. [12]). The calculations of Radom and Pople succeed in decreasing the isomerization energy under a rigid rotation model from 5.66 to 2.92 kcal/mole by increasing the value of the C=C–C angle from 120° to 124.2°. But before drawing too many conclusion from these results it is well to consider a third possible influence on the calculated isomerization energy and rotational potential curve in addition to basis set and assumed geometry, namely the effect of configuration interaction.

To consider the latter point a CI treatment has been carried out for the ground (and also excited) states of 1,3-butadiene in the aforementioned five configurations. The energy lowering affected by the CI method is on the order of 0.03–0.04 hartree for each conformation (see Table 1) in the present calculations compared to an analogous lowering of 0.06 hartree using the more restricted basis. This result is quite similar to that observed in connection with calculations for benzene and borazine [18], and can be rationalized as follows: in the larger basis set there are twice as many π type AO's and thus by using a valence set in the CI which includes only four π MO's in each case, the smaller basis set calculations actually allow for a more complete reoptimization of the total charge distribution as a result of the CI. This result has its most significant ramifications in connection with the calculated isomerization energy; thus while the smaller basis set obtains a relatively large change for this quantity upon introduction of CI (5.0 kcal/mole SCF to 3.9 kcal/mole CI) the present calculations find very little variation (Table 2). These results emphasize that effectiveness of CI can depend significantly on the nature of the AO basis set employed.

The influence of the three factors discussed to this point is also apparent in considering the calculated rotational potential curves (Fig. 3). The SCF and CI curves of the present work find, just like the three sets of data of Radom and Pople [13] and the experimental values of Aston *et al.* [6] that the *trans*-conformer is relatively stable with respect to internal rotation. The maximum in total energy occurs in all cases at roughly 90°. The barrier heights relative to the *trans*-conformer vary from 5 to 8 kcal/mole; experimentally Aston [6] estimates this quantity to be 4.9 eV. In the present calculations then it is seen that the CI value is apparently in better agreement with experiment than is the SCF result (see Table 2), a fact which can be understood in terms of the foregoing considerations.

One of the most interesting questions that arises upon examination of the various potential curves is whether the 180° (*cis*) structure corresponds to a minimum or a maximum in potential. The present calculations show different results. From a naive point of view the planar *cis*-conformer should be favored, such as in the SCF curve. On the other hand the rather small spatial distance between the end CH_2 groups could affect the torsion result given by the CI-calculations. The aforementioned semiempirical calculations of Polansky show a shallow maximum for the *cis*-conformer. According to Reznikova [5] this result would also be in accordance with the theoretical interpretation of some experimental infrared absorption bands of 1,3-butadiene, although experiments are not decisive on this point. Furthermore the results of Radom and Pople indicate that the potential surface in this region is critically dependent on the value of the C=C–C angle chosen, with the *cis*-form being relatively favored by increase in this parameter. The present SCF potential curve (carried out with 122.4° for the C=C–C angle) is quite similar to curve *C* of the latter authors (Fig. 1 of Ref. [13]) which corresponds to a larger value of the C=C–C angle (126.4°). Unfortunately not enough points have been obtained to be certain whether the present SCF treatment predicts a minimum or a maximum in energy for the *cis*-form but it is clear that even if it did find a minimum away from this structure it would not be at all as deep as is shown in curve *A* of Radom and Pople (C=C–C angle 120°). In order to obtain some idea of the effect of assuming a different value of the C=C–C angle for the present rigid rotation model it is well to consider another series of calculations [19], which employ the same basis as Buenker and Whitten [12], and in which the C=C–C angle is varied for *cis*-butadiene. The resulting total energies for 120° and 125° of the C=C–C angle differ by only 0.0016 hartree (the 120° value is the lower) or approximately 1.0 kcal/mole. This result is in contrast to the energy of approximately 5 kcal/mole obtained by Radom and Pople [13] for structures having C=C–C angles equal to 120° and 126.4° respectively. The indication is thus that in the environment of the *cis*-conformation the shape of the internal rotation potential curve is much less critically dependent on the value of the C=C–C angle chosen when the relatively large basis of Ref. [12] is employed than for that used by Refs. [13, 20]. Thus for a definite statement whether the *cis*-form corresponds to a potential maximum or minimum more accurate information is needed, both experimentally and theoretically. All calculations do show, however, that the energy is very weakly varying with the CCCC dihedral angle in the region around *cis*-butadiene, so that the total energy variation between 180 and 135° is quite small compared to that from 135 to 90°. The isomerization energy in all four of these treatments lies between 2.0 and 2.9 kcal/mole, in quite good agreement with the experimental value of 2.3 kcal/mole. The barrier height (relative to the *trans*-form) seems to be more dependent on the nature of the treatment varying between 6.4 to 7.6 kcal/mole in the present calculation, in comparison with Aston's value of 4.9 kcal/mole. The calculated shape of the rotational potential curves on the other hand can be said to mesh quite well with the results of Aston [6], based on data derived from the rotational and vibrational spectrum of 1,3-butadiene, the partition function and an assumed variable form for the potential curve in question. The resulting experimental barrier function possesses a steep run in the region of the *trans*-conformer and a flat one near the *cis*-form, in obvious agreement with the calculations under discussion. It is also interesting in this connection that Borrel and Greenwood [21] have explained the strong temperature dependence of the *cis-trans*-stilbene quantum yield in terms of a rotational potential curve which is also quite similar to that calculated for 1,3-butadiene. Of course their predicted potential minimum for 135° could be specific to stilbene because of steric considerations, but in principle this empirical curve closely resembles that evaluated for butadiene.

Finally the reason that all the theoretical treatments have overestimated the barrier height might well be due to the fact that the optimum geometry for the 90° conformation is significantly different from that assumed in a rigid rotation model. The improvement observed upon introduction of CI might result from the fact that the electronic configuration has much less closed shell character for conformations away from the two equilibria so that CI is much more effective for intermediate structures. Together with the experimental uncertainty for the value of the barrier height it is certainly gratifying in light of all these considerations that the theoretical treatments *overestimate* this value since obviously much more is known about the optimum *cis*- and *trans*-structures than for the 90° intermediate.

4. Electronic Spectrum

The CI treatment discussed in the previous section also allows for a description of the valence excited states of 1,3-butadiene in the five conformations considered. The resulting excited state rotational potential curves are given in Fig. 4a, b for singlet and triplet states respectively. Detailed descriptions of the constitutions of the low-lying states will not be given in this paper. In contrast to single excitation π electron calculations many of the low-lying excited states cannot be described by one predominant electron configuration only. In particular the lowest singlet excited state is found to be a mixture of essentially three configurations $(1b_g \rightarrow 2b_g)$, $(1a_u \rightarrow 2a_u)$ and $(1b_g^2 \rightarrow 2a_u^2)$ in the *trans*-case possessing ${}^1A_g$-symmetry, not the ${}^1B_u$ species from a $1b_g \rightarrow 2a_u$ transition predicted by single excitation CI calculations [12]. For the description of the third excited singlet state ($1\,{}^1A_u$ in the *trans*-conformer) which is essentially given by a $7a_g \rightarrow 2a_u$ transition (in the *trans*-case), inclusion of $\sigma \rightarrow \pi$ excitations is alredy necessary.

The distinctions in AO basis set between the present and previous [12] *ab initio* calculations do lead to some significant changes in calculated transition energies, although the energy order is unchanged, at least among the low-lying states. For example, in the present work the $1\,{}^1B_u$ state is found to lie only 1.1 eV above the $2\,{}^1A_g$ (Table 3 and Fig. 4a) and the corresponding ${}^1B_2$ of the *cis*-conformer, only 0.2 eV above the $2\,{}^1A_1$ state, whereas Buenker and Whitten

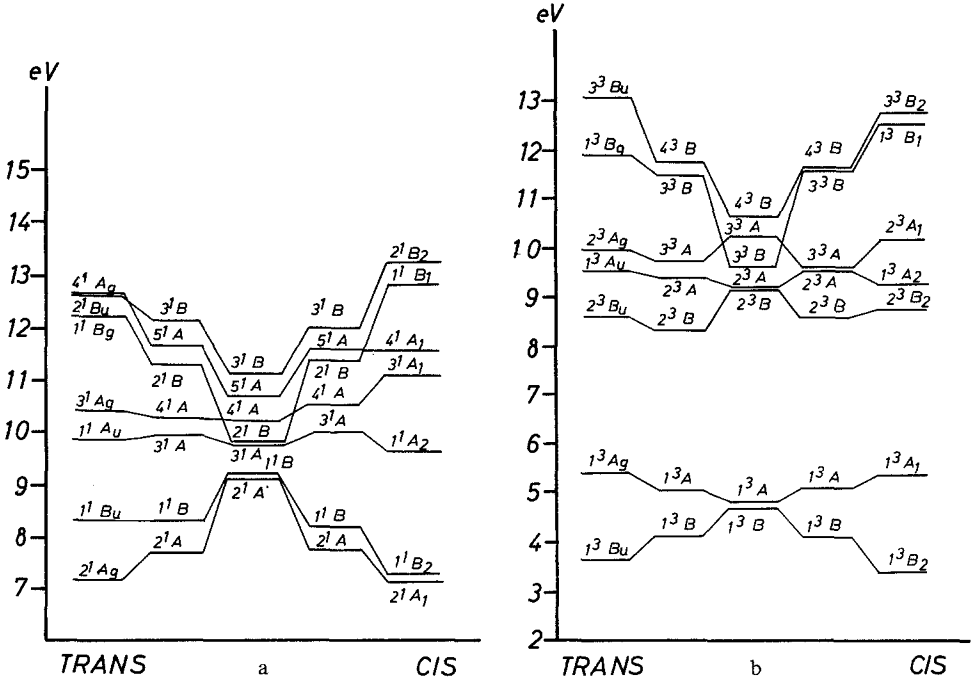

Fig. 4. a Energies of the lowest lying excited singlet states of the various conformers of 1,3-butadiene. b Energies of the lowest lying excited triplet states of the various conformers of 1,3-butadiene

Table 3. Comparison of the singlet excited state energies of *trans*-butadiene with those of Ref. [12] and with experiment and assignment of the states

Excited state energies in eV			Assignment of the states	
This work	Buenker and Whitten [12]	exptl. [15, 22, 23]	This work	Mulliken [23]
—	—	—	1^1A_g	1^1A_g
7.18	7.69	—	2^1A_g	
8.28	10.19	6.07	1^1B_u	1^1B_u
9.82	10.24	7.12	1^1A_u	2^1A_g
10.40	12.91		3^1A_g	
12.20	13.16		1^1B_g	
12.58	15.31		2^1B_u	

[12] found both energy differences in the range of 2.3–2.5 eV. By contrast the present calculations find higher energy splittings between the ${}^1B_u$ and ${}^1B_2$ states on the one hand and the lowest lying $\sigma \rightarrow \pi^*$ states (${}^1A_u$ and ${}^1B_1$) on the other. In general the present CI transition energies are lower than those of the former treatment, reflecting the smaller energy lowering effected by the ground state CI and also the more flexible basis employed. The calculated vertical transition energy to the ${}^1B_u$ excited state of *trans*-butadiene is still over 2.0 eV above the energy of the first known [15, 22, 23] singlet-singlet absorption (6.0 eV). Since a

limited CI treatment based on the ground state MO's at the level discussed herein is expected to be biased toward the representation of the ground state this result seems to be quite consistent with Mulliken's identification of the fully allowed ${}^1A_g \rightarrow {}^1B_u$ transition with the strong 6.07 eV absorption band of the experimental spectrum. In both cases the main configuration of the ${}^1B_u$ state is the $1b_g \rightarrow 2a_u$ excitation.

The identification of the second strong band at 7.12 eV is still questionable. According to Mulliken's interpretation this band may correspond primarily to an unallowed $1\,{}^1A_g \rightarrow 2\,{}^1A_g$ transition or possibly to an (allowed) $1\,{}^1A_1 \rightarrow 2\,{}^1A_1$ transition in the *cis*-conformer or to a Rydberg band of *trans*-butadiene perturbed by the weak $1\,{}^1A_g \rightarrow 2\,{}^1A_g$ transition. The relative high intensity is in conflict with the first interpretation. Furthermore, the spacing of the vibrational levels which is expected to become smaller with increasing excitation also seems to speak against the first assignment, since the 7.12 eV band has a spacing of more than 1500 cm^{-1} whereas it is 1634 cm^{-1} in the ground state and 1450 cm^{-1} in the $1\,{}^1B_u$ state [15, 22, 23]. Finally, the present calculations find the $2\,{}^1A_g$ state even *below* the $1\,{}^1B_u$ state believed to be responsible for the 6.07 eV absorption. All these difficulties could be removed by identifying the 7.12 eV band with the $1\,{}^1A_g \rightarrow 1\,{}^1A_u$ transition; this would explain the position (calc. 1.54 eV above ${}^1B_u$, exp. 1.05 eV), the intensity and also the wavenumber distances of this band because the ${}^1A_u$ state is essentially described by a $7a_g \rightarrow 2a_u$ ($\sigma \rightarrow \pi^*$) single excitation of which both orbitals are antibonding with respect to the C=C double bonds and thus that no decrease in the vibrational wavenumbers must be expected. The location of the transition to the lowest ${}^1A_g$ excited state would then be on the long wave length side of the strong $1\,{}^1A_g \rightarrow 1\,{}^1B_u$ transition, possibly covered by the intensity of the latter. These assignments are shown in Table 3.

At the same time it must be pointed out, however, that in neither CI treatment discussed so far has the possibility of low-lying Rydberg transitions been taken into account since both basis sets lack the appropriate diffuse functions necessary for their description. Since the lowest $\pi \rightarrow \pi^*$ singlet-singlet transition in ethylene has recently been calculated [24, 25] to possess a great deal of diffuse character and also because of Mulliken's conjecture about the 7.12 eV band having some Rydberg character [23] further expansion of the AO basis set seems necessary for the definitive theoretical identification of the lowest lying singlet-singlet transitions

Table 4. Comparison of the triplet excited state energies relative to the singlet ground state energy and the energy difference ($2\,{}^1A_g - 1\,{}^3B_u$) of *trans*-butadiene with the results of Ref. [12] and with experiments

States	Excited state energies this work	Buenker and Whitten [12]	exptl. [26]
$1\,{}^3B_u$	3.66	3.81	3.2
$1\,{}^3A_g$	5.37	5.52	3.9
$2\,{}^3B_u$	8.59	9.04	
$1\,{}^3A_u$	9.83	9.91	
$2\,{}^1A_g - 1\,{}^3B_u$	3.52	3.87	2.8

of *trans*-butadiene. The description of the singlet-triplet species, which have been obtained experimentally by Evans [26], is similar to that of the calculations with the smaller basis and appears to be much less in doubt especially since triplet states are not expected to be diffuse [24, 25]. There seems little doubt that the lowest triplet is ^3B_u followed closely thereafter by a ^3A_g species (Table 4); the present calculations overestimate the experimentally determined transition energies for this system by 0.5 and 1.5 eV respectively.

5. Photochemically Induced Isomerization

The fact that the present calculations apparently allow for a valid description of the triplet states of butadiene, particularly the most stable of these species, encourages one to use these calculations to explain the results of existing photochemical experiments for 1,3-butadiene.

Contrary to the case in ethylene a direct photochemical isomerization does not occur for this system [23]. The calculated potential curves for the singlet excited states are quite consistent with this observation because the low-lying singlet excited states possess relatively high maxima for partially rotated structures. In addition the lowest lying triplet state also exhibits a high barrier to internal rotation. At the same time the calculated results appear to give qualitative confirmation to existing theories of the photochemical dimerization of this system [27].

Hammond [27] has suggested that the photochemically induced dimerization of butadiene involves triplet state intermediates, designated by an asterisk, occuring according to the following three mechanisms.

a) $trans\text{-}C_4H_6^* + trans\text{-}C_4H_6 \rightarrow$ cyclobutane and cyclooctadiene

b) $\left.\begin{matrix} trans\text{-}C_4H_6^* + cis\text{-}C_4H_6 \\ cis\text{-}C_4H_6^* + trans\text{-}C_4H_6 \end{matrix}\right\} \rightarrow$ cyclohexane

c) $cis\text{-}C_4H_6^* + cis\text{-}C_4H_6 \rightarrow ?$

The necessary triplet states are created by sensitizers acting upon an equilibrium mixture of *cis-trans*-butadiene and the yield of energy transfer is observed to be a function of the excitation energy of the sensitizers. Three results of these experiments stand out (see Fig. 5):

I. Sensitizers with energy in excess of 60 kcal/mole yield a fairly constant and high (~ 80%) percentage of cyclobutane and cyclooctadiene;

II. As the energy of the sensitizer is reduced from 60 to 53 kcal/mole the yield of cyclohexane increases almost linearly;

III. Below 53 kcal/mole energy the efficiency of the sensitizers is decreased markedly with the yield of cyclohexane decreasing. In energy region III other mechanisms not involving triplet species are believed to be operative.

The investigation of these results given by Hammond [27] can be verified by the present calculations in terms of the following model. At energies above 60 kcal/mole the ^3B_u state of *trans*-butadiene can be relatively highly populated (region I) and this mechanism a) is quite important, especially since the barrier to internal rotation to the corresponding *cis*-triplet is quite high (23 kcal/mole in

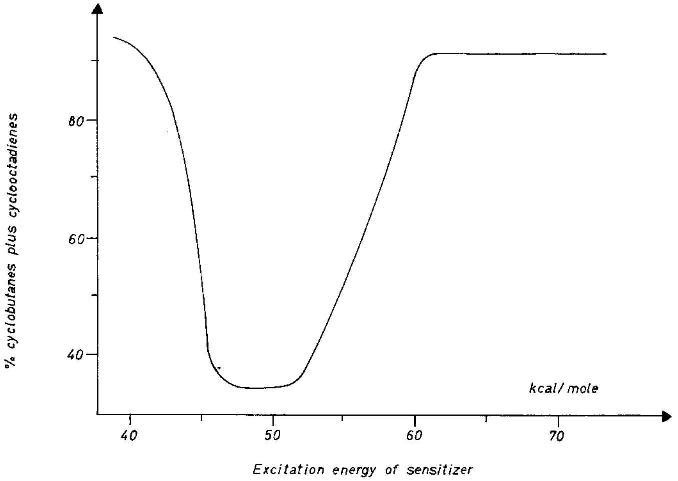

Fig. 5. Photochemical dimerization according to Hammond [27]. The percentage of the cyclobutane plus cyclooctadiene mixture plotted against the excitation energy of sensitizer

Fig. 4 b). In region II the energy of the sensitizers falls below the vertical transition energy of the ^3B_u of the *trans*-conformer, making population of the lowest *cis*-triplet (also via vertical excitation) relatively more likely, hence a regular increase in the yield of cyclohexane formed via mechanism b). In region III the sensitizer energy falls below both the *cis*- and *trans*-vertical transition energies and therefore neither triplet is sufficiently populated to be effective in any of the three dimerization reactions considered.

According to this interpretation the difference in vertical transition energies to the lowest triplets of *cis*- and *trans*-butadiene respectively should be approximately equal to the difference in energy of the two extreme values over which production of cyclohexane is varying regularly, that is, the limiting energies of region II. In fact the calculated difference in these quantities is 6.7 kcal/mole, in very good agreement with the experimentally observed range of 7 kcal/mole for region II. Thus the present CI calculations of the excited state rotational potential curves of 1,3-butadiene not only are consistent with the qualitative observation that this system is not prone to photochemical isomerization but also appear to be in quantitative agreement with data for the photochemically induced dimerization of this compound.

6. Conclusion

The potential curves obtained by the SCF and CI methods in the present work appear to be consistent with a rather wide range of experimental data known for 1,3-butadiene. The use of a basis set with several 2*p* functions (obviously allowing for a better description of the charge distribution), obtains a more realistic and reliable comparison between the different conformers than do calculations employing only the simple 2*p* functions, suggesting of course that improvements in the flexibility of the treatment are worthwhile. On the other hand there is some evidence that the addition of CI to the overall treatment renders the choice of basis somewhat less critical. Existing theoretical treatments seem to be quite definite about the shape of the rotational barrier curve. It rises rather sharply upon rotation out of the *trans*-form until a 90° intermediate is reached, then decreases at a similar rate until the CCCC dihedral angle has a value of above 135°. From there on the energy surface is extremely flat, leaving considerable doubt as to whether the *cis*-conformer corresponds to a potential minimum or a potential maximum; if there is indeed a potential well away from the *cis*-form it is undoubtedly extremely shallow, with a depth of probably less than 0.2 kcal/mole. The barrier height is apparently overestimated in all treatments suggesting that the rigid rotation model is less valid in the region of the 90° rotated structures.

Finally the present calculations again find that the lowest singlet excited state of *trans*-butadiene is a mixture of single and double excitation configurations possessing A_g symmetry. The state responsible for the strong 6.0 eV absorption is most likely the ^1B_u state originally believed. There is good reason to believe that the second strong band at 7.12 eV is a $^1A_g \rightarrow {}^1A_u$ transition and not $^1A_g \rightarrow {}^1A_g$ as assumed previously, if it corresponds to a valence excitation at all. In general there is the possibility that many of the more stable excited singlets of butadiene are of a more diffuse nature than could be obtained with the present basis lacking $3s$ and $3p$ functions. The lowest lying triplet states seem to be well represented with calculated potential curves being quite consistent with known photochemical experimental results. All the low-lying excited states show relatively high barriers to internal rotation, thereby explaining the known inability of this system to achieve isomerization photochemically. In addition the transition energy to the lowest triplet *trans*-butadiene is found to be almost 7.0 kcal/mole higher than the corresponding value for the lowest *cis*-triplet, thereby substantiating Hammond's theory of the mechanism of photochemically induced dimerization of this system.

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20. Alternatively since the aforementioned calculations of Buenker, Peyerimhoff and Hsu employed the experimental (*trans*-conformer) [2] bond distances and bond angles for 1,3-butadiene while the smaller basis set calculations used certain standard values in their place it may be that the value of the C=C–C angle is more sensitive to changes in other geometrical parameters than it is to variations in the CCCC dihedral (torsional) angle. The optimum value of the C=C–C angle for *cis*-butadiene obtained in Ref. [19] is only 121.2° in rather large disagreement with the 126.4° value calculated by Radom and Pople [13].
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