

STERIC HINDRANCE IN BUTADIENE AND ETHYLENE

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(Received in the UK 16 March 1970; Accepted for publication 31 March 1970)

Abstract—The structure of ethylene, *trans*- and *cis*-butadiene was determined theoretically, based on self consistent steric analysis. The calculated structures agree with the known experimental data. The energy path of the *cis*-*trans* isomerization of butadiene was calculated both for the ground state and the first excited state. The influence of the steric hindrance on the π -electronic spectrum was investigated on the basis of the β -variable SCF LCAO CI method.

INTRODUCTION

THERE are several theoretical methods for calculating the ground state structure of molecules.* In this work we report the results of application^{1,2} to ethylene and *cis*- and *trans*-butadiene. The self consistent steric analysis method is basically an extension of the Longuet-Higgins and Salem method³ to molecules with steric effects and of the conformation analysis of Coulson and Haigh⁴⁻⁵ to molecules with a large deformation. As regards the Longuet-Higgins and Salem method, we replaced their formula for the resonance integral between next neighbours β_{ij} by formula (1) and their dependence of the bond length R_{ij} on the mobile bond order p_{ij} by formula (2):

$$\beta_{ij}(R_{ij}, \theta_{ij}) = \beta_{ij}(R_{ij}, 0) \cos \theta_{ij} = \beta_0 \exp [-x(R_{ij} - 1.397)] \cos \theta_{ij} \quad (1)$$

$$R_{ij} = a - bp_{ij}(\theta_{ij}) \cos \theta_{ij} + \frac{b}{2x\beta(R_{ij}, 0)} \frac{\partial W}{\partial R_{ij}} \quad (2)$$

where W is the interaction energy between all non-bonded atoms except the second neighbours (like $\overset{\curvearrowright}{\text{C}}-\text{C}-\overset{\curvearrowleft}{\text{H}}$), θ_{ij} is the twisting angle of the bond $i-j$, and $\beta_0 = -1.403$ eV, $a = 1.517$ Å, $b = 0.18$ Å, $x = 4.1/\text{Å}$ in the case of hydrocarbons.¹ The contribution to W from interacting H...H and C...H pairs was taken in accordance with the Bartell approximation⁶ and from the C...C pairs in accordance with Dashevsky and Kitajgorodsky.⁷ The out-of-plane deformations z_i 's and the changes of the valence angles, α_i 's (Fig 1-2) were calculated with a modified Coulson and Haigh

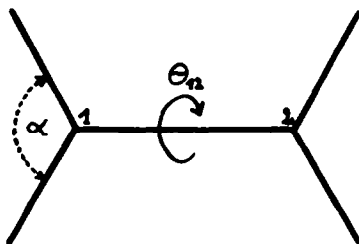


FIG 1. Definition of deformation coordinates in ethylene.

* See ref. 1 for a review of these methods.

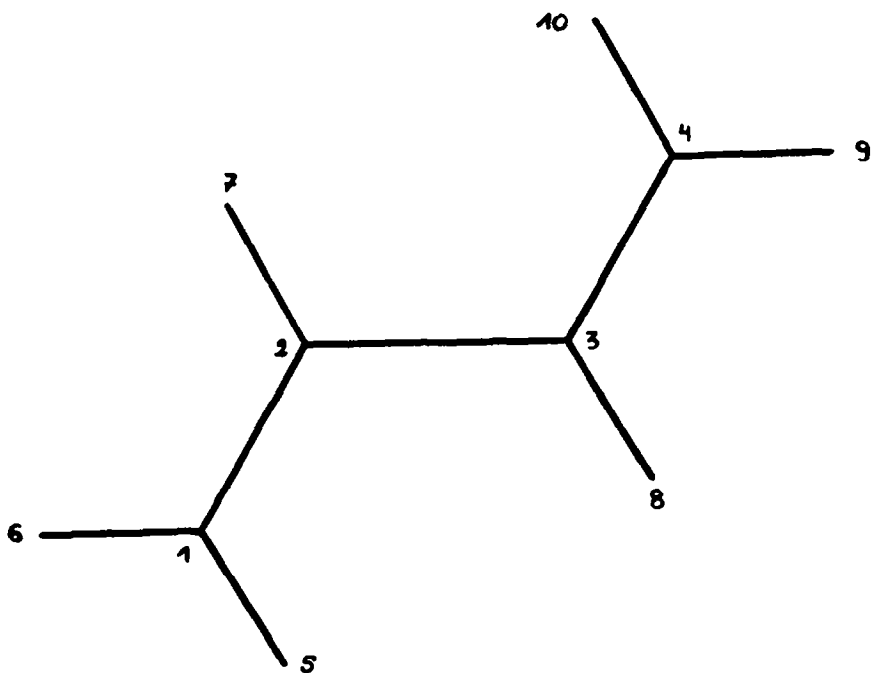
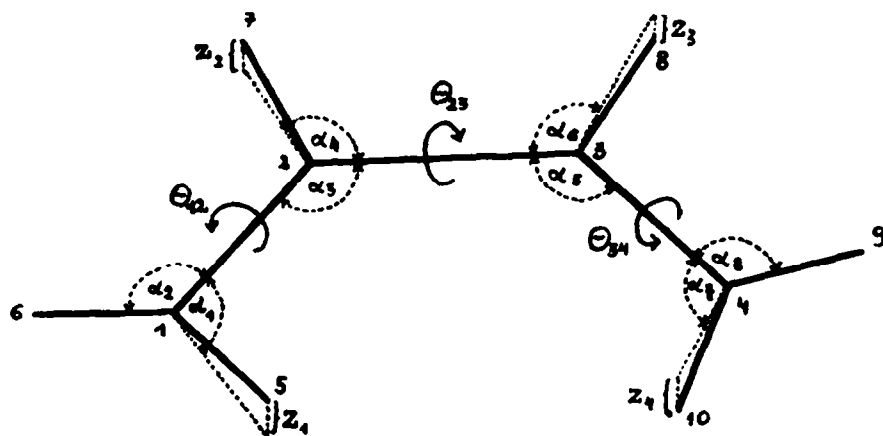


FIG 2. Definition of deformation coordinates and numbering of atoms in butadiene.

method.¹ The calculations were performed iteratively until a self consistency of Eqs (1) and (2) was obtained. All the empirical parameters in this treatment have been estimated from some properties of biphenyl and from the bond lengths in ethylene, benzene and graphite.

Ethylene

The large number of papers concerned with ethylene, have been partly reviewed by Kaldor and Shavitt⁸ who carried out SCF LCAO-type calculations for ethylene, its

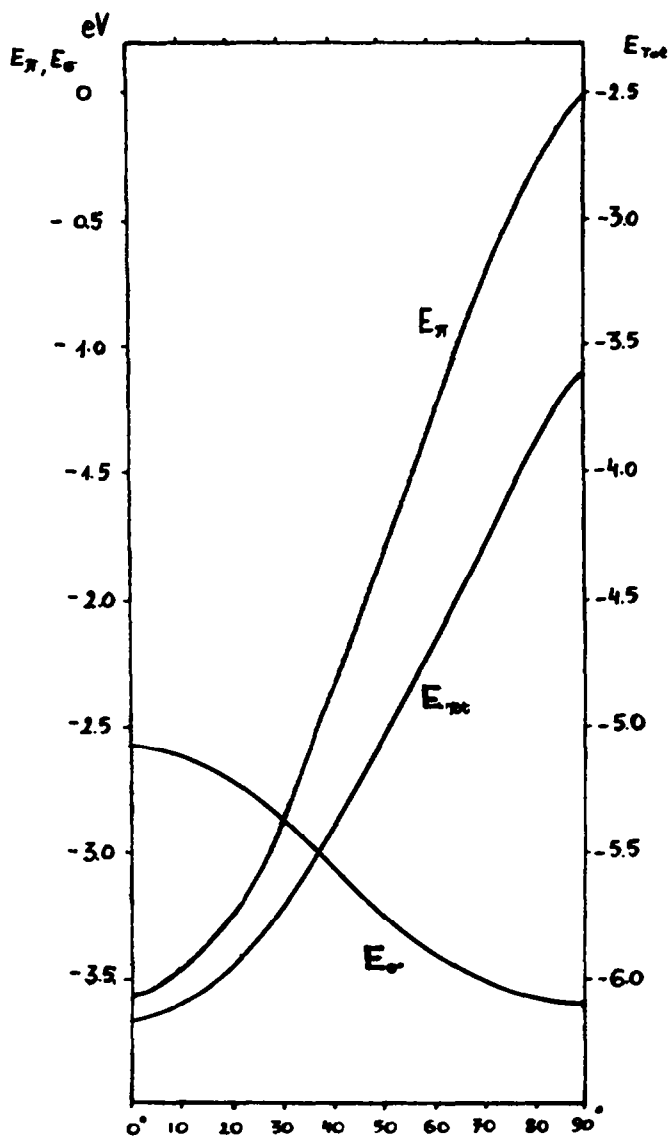


FIG 3. Dependence of the total (E_{Tot}), π -electronic (E_π) and σ -electronic (E_σ) energy on the twisting angle θ_{12} in ethylene.

cation and anion and for several values of the twisting angle θ_{12} . Many older references can be also found in Ohno's review.⁹

We consider the present calculations for ethylene as further proof of utility of the self consistent steric method.

In Fig 3, we give the calculated dependence of the total energy E_{tot} , the π -bonding energy E_{π} and the σ -electronic energy E_{σ} on the rotation angle θ_{12} . The barrier of 2.53 eV, is in good agreement with the experimental value, 2.67 eV, known from isomerization of di-deutero-ethylene.¹⁰ The extended Hückel method¹¹ and the *ab initio* SCF LCAO CI method⁸ result in too high barriers, equal to 3.49 eV and 3.61 eV respectively.

Considering the equilibrium values, we obtained $R_{12} = 1.337 \text{ \AA}$ (assumed for parametrization) and $\angle \text{HCH} = 119^{\circ} 35'$. The experimental data are¹² 1.337 \AA , 117.3° . Our result agrees with others obtained: Jacob *et al.*¹³ obtained $\angle \text{HCH} = 115^{\circ}$ using a mechanical model, from SCF-type calculations¹⁴ one obtains $R_{12} = 1.333 \text{ \AA}$; the EHT method¹¹ yields 1.47 \AA and 125° , the FSGO method¹⁴⁻¹⁵— 1.351 \AA and $118^{\circ} 42'$.

Butadiene

The thermodynamic equilibrium of the two isomers was studied by Aston *et al.*¹⁶ and more recently by Miyarawy and Pitzer.¹⁷ The Raman and IR spectra were analyzed by Marias *et al.*¹⁸ and Cole *et al.*¹⁹ The electron diffraction method was applied to *trans*-butadiene²⁰ and recently again and with a higher precision by Haugen, Traetteberg²¹ and Kuchitsu *et al.*²² The mean amplitude of vibration has been discussed.²³

The dependence of the transition energy on the twisting angle θ_{23} (Fig 2) was discussed by Charney.²⁴ He applied the Hückel method to this problem, varying β_{ij} on R_{ij} . A detailed theoretical analysis of the electronic structure of butadiene was given by Parr and Mulliken in 1950, based on the SCF LCAO MO method.²⁵

Closely related to the present work is that of Fischer-Hjalmars²⁶ who analyzed the dependence of the total energy on the twisting of the central bond, based on the familiar PPP approximation of the SCF LCAO MO method. All important van der Waals (vdW) interactions were included in these calculations, for several sets of potentials. However, she kept all valence angles and all bond lengths constant, keeping thus constant also the σ -bonding energy. As will be shown, the contribution of the neglected terms is rather significant.

Energy path of cis-trans isomerization

In Fig 4 we depict the calculated dependence of the total ground state and excited state energies on the twisting angle of the central bond, θ_{23} . In these calculations we have optimized the geometry of the molecule for any fixed value of θ_{23} . It follows from Fig 4 that the *trans*-form is more stable in the ground state by 1.73 kcal/mole and that the *trans*-to-*cis* barrier amounts to 5.15 kcal/mole. Experimentally it is known²⁷ that the *trans*-form is more stable, that the difference of energies is of the order of 2 kcal/mole and that the barrier is equal to 4.9 kcal/mole. Thus the agreement with experiment is most gratifying.

Parr and Mulliken obtained for the difference of energies of the two forms 2.8 kcal/mole. Fischer-Hjalmars²⁶ considered two types of vdW potentials. Assuming

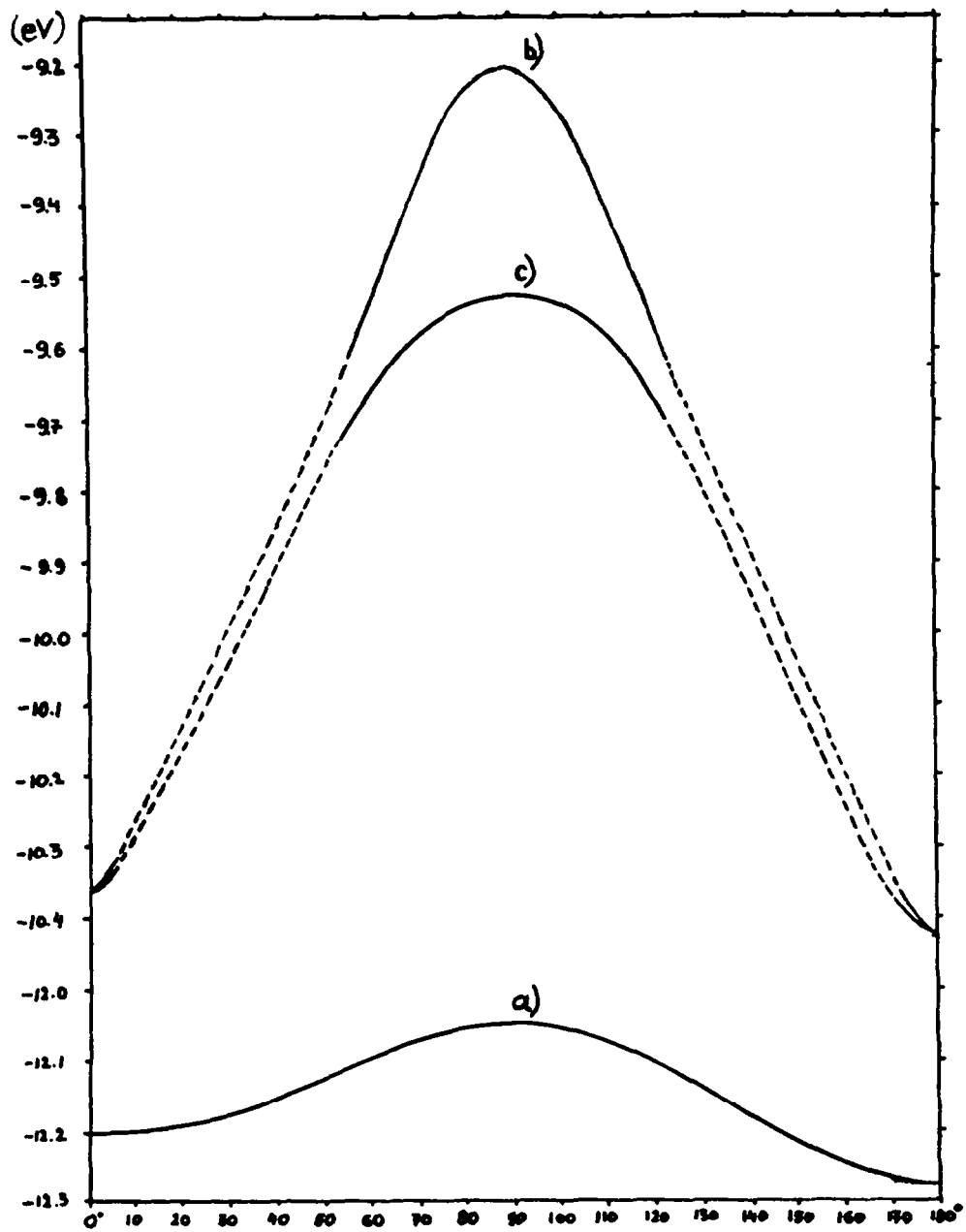


FIG 4. Dependence of the total energy on the twisting angle of the central bond in butadiene: (a) for the ground state, (b) for the symmetrical conformation of the first excited state, (c) for the non-symmetrical conformation of the first excited state.

Bartell's potentials she obtained 8.1 kcal/mole for the difference of energies and 10.0 kcal/mole for the barrier. Using Haigh's potentials, on the other hand, she obtained 5.9 kcal/mole and 10.3 kcal/mole accordingly. This way or the other, these values are much too high. As both in her and in our calculations very similar vdW potentials were used, the rôle of the structural rearrangement must be significant.

Fig 4 shows the energy path for the first excited state. As a self consistent Hückel method was the basis for this treatment, the energies should be interpreted as a center of gravity of the V_1 and T_1 states. However, bond orders in the V_1 and T_1 states usually do not differ much. On the other hand, as our eigenfunction is orthogonal to the ground state function only for the triplet state, we attribute the path to the triplet state.

We see that the barrier is now definitely larger. Note, however, that there is a very remarkable behaviour of butadiene for twisting angles close to 90° . There is no doubt that a nonsymmetric conformation of the excited state is definitely more stable than the symmetric one. This interesting property will be discussed in more detail in the next section.

Conformation of the ground state and the excited state

It follows from our calculations that both forms of butadiene are planar in the ground state. This result is expected for the *trans* form but is certainly not trivial for the *cis* one. The results of our calculations are given in Table 1, and compared with

TABLE 1. THE STRUCTURE OF *cis*- AND *trans*-BUTADIENE

Structural parameter	<i>trans</i> -Butadiene		<i>cis</i> -Butadiene
	Experimental ^a	Calculated	Calculated
R _{CH}	1.094	1.1 as.	1.1 as.
R ₁₂	1.344	1.346	1.348
R ₂₃	1.467	1.469	1.474
R ₁₄	3.695	3.672	2.997
R ₃₆	3.456	3.453	3.481
R ₃₅	2.692	2.685	2.783
R ₁₈	2.709	2.718	3.449
R ₁₉	4.577	4.569	4.094
R _{1,10}	4.031	4.025	2.755
R ₆₇	2.422	2.430	2.399
R ₅₇	3.081	3.100	3.102
R ₇₈	3.151	3.197	2.495
R ₆₈	3.798	3.814	4.325
R ₅₈	2.469	2.483	3.864
R ₆₉	5.536	5.540	5.188
R ₅₉	4.724	4.734	3.823
R _{5,10}	4.610	4.620	2.128
∠123	122° 50'	121°	124° 24'
∠215	119° 31'	120° 51'	122° 17'
∠216	119° 31'	119° 53'	119° 13'
∠127	119° 31'	119° 09'	117° 55'
∠327	117° 40'	119° 51'	117° 41'
θ ₂₃	0°	0°	0°

^a Kuchitsu, Fukuyama and Morino's data, as cited in ref 23

the most recent experimental data for the *trans* form.²¹⁻²² The agreement with experiment is in general very good. For both bond lengths the deviations are smaller than 0.002 Å. For other distances the deviations are usually smaller than 0.01 Å except for R_{78} , where $\Delta R_{78} = 0.046$ Å and for R_{14} , where $\Delta R_{14} = 0.023$ Å. However, a revision of the experimental data is expected in this respect; in the case of the mean amplitude of vibration along the 3-7 distance (which influences the R_{78} distance directly) a serious discrepancy was found between the results of the spectroscopical and diffractive estimates.²⁸

Changes of geometry during the cis-trans isomerization

In Fig 5 we show the calculated dependence of the bond lengths on the twisting angle of the central bond of butadiene, both for the ground state (R_{ij} 's) and the first

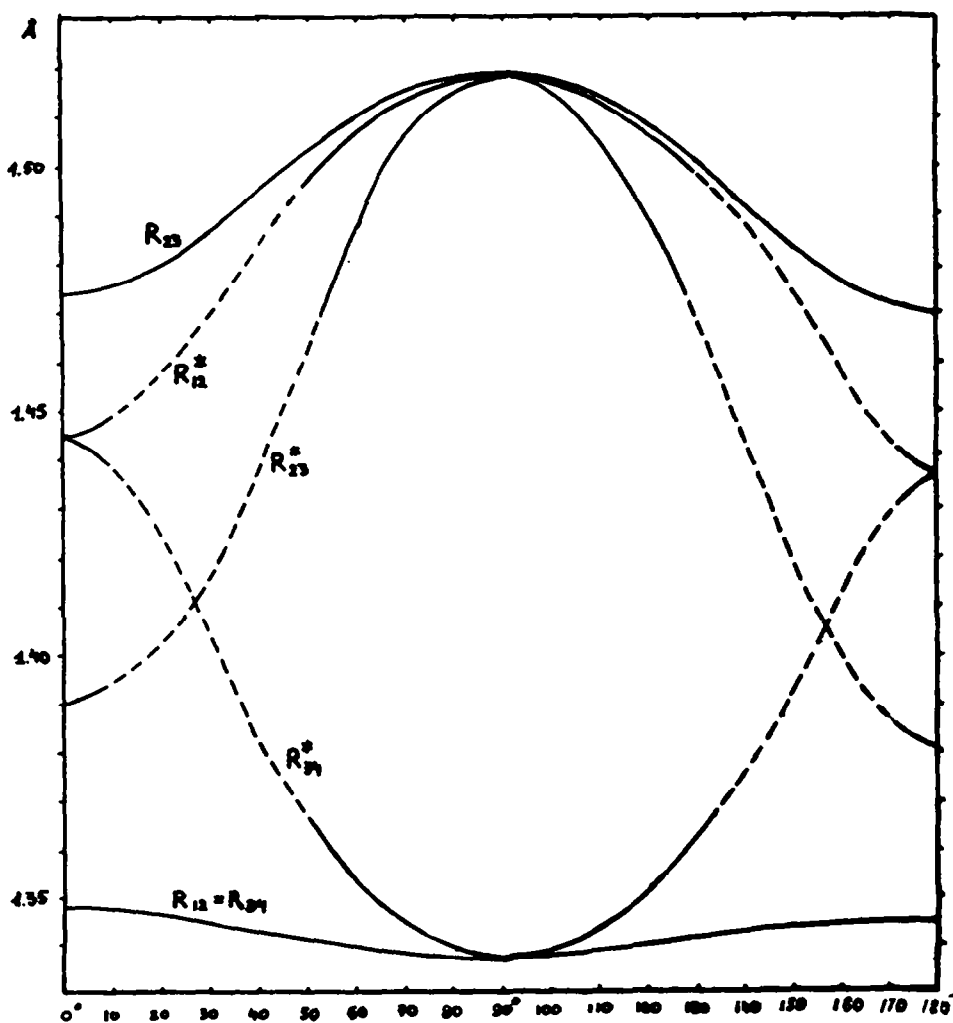


FIG 5. Dependence of the bond lengths in butadiene on the twisting angle of the central bond : R_{12} , R_{23} and R_{34} refer to the ground state and R_{12}^* , R_{23}^* , R_{34}^* to the first excited state.

excited state (R_{ij}^* 's). There is a strong dependence of R_{23} on θ_{23} and a variation of R_{12} and R_{34} .

The results for the first excited (triplet) state, show that in the case of $\theta_{23} = 90^\circ$, the Jahn-Teller effect is active, causing a complete localization of the excitation on one of the bonds: $R_{12}^* = 1.517 \text{ \AA}$ and $R_{34}^* = 1.337 \text{ \AA}$, or *vice versa*. The barrier between the two equivalent localizations is rather high, about 8 kcal/mole (Fig 4). Therefore, the static Jahn-Teller effect seems to dominate, the barrier being too high for a dynamical coupling.

The localization of the excitation takes place continuously. Even for a twisting of $5-10^\circ$ there is already a difference of the external bond lengths of the order of 0.01 \AA .

Other properties of trans-butadiene

In Fig 6 we show the dependence of the π -electronic orbital energies on θ_{23} in β_0 units. The figure corresponds to the ground state conformation.

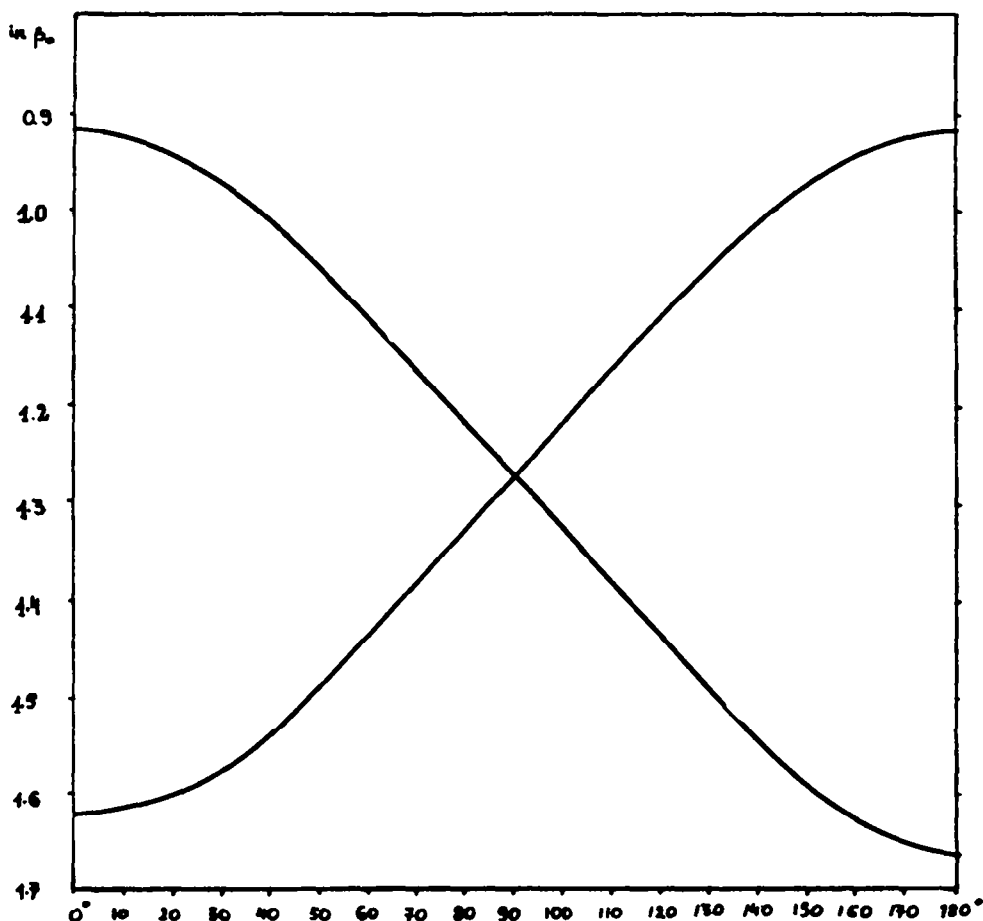


FIG 6. Dependence of orbital energies in butadiene on the twisting angle of the central bond, calculated for the ground state conformation.

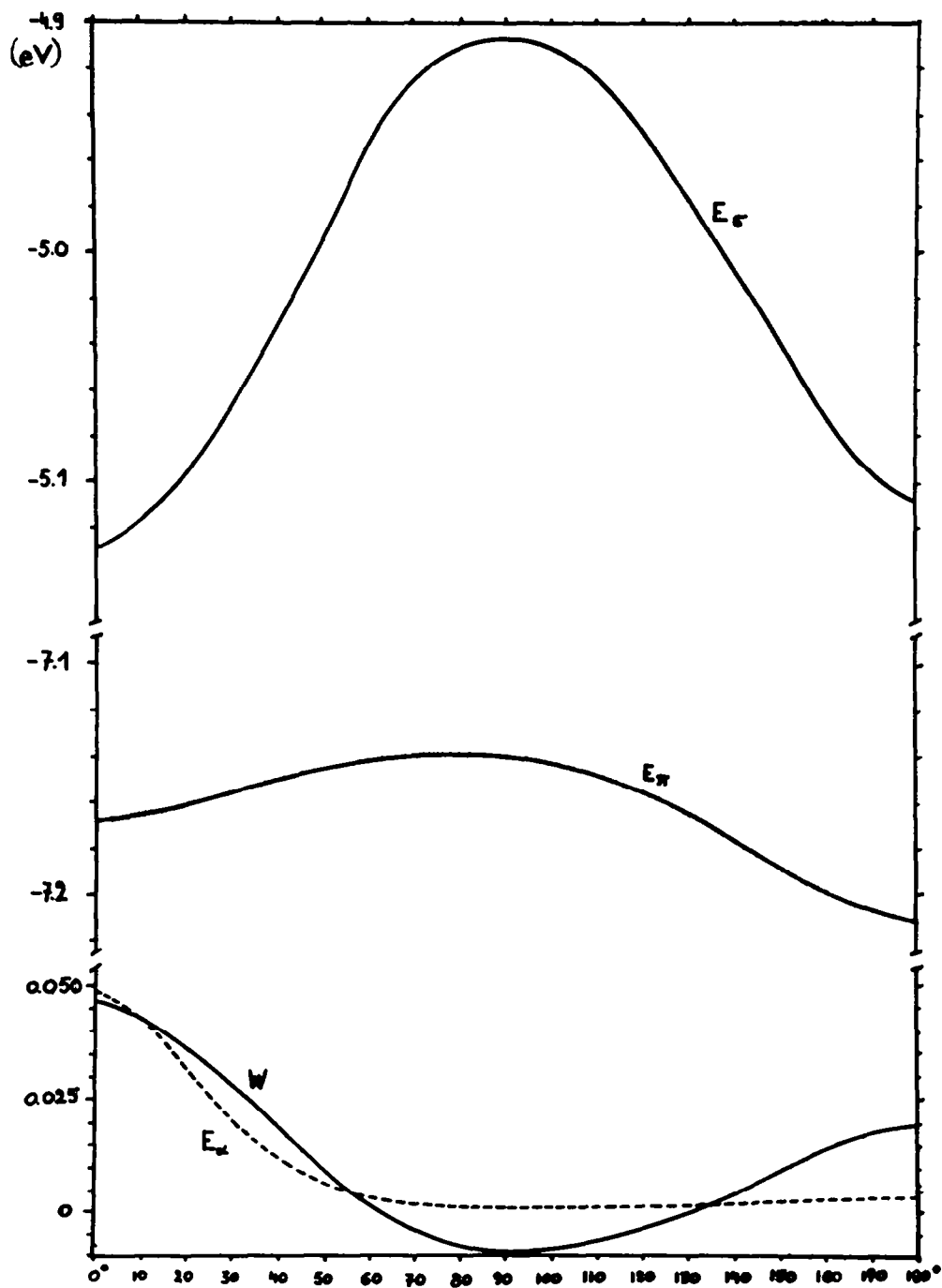


FIG 7. Dependence of various contributions to the total energy of butadiene on the twisting angle of the central bond.

Gołębiewski and Nowakowski²⁹ have found a linear correlation between the observed values of several physical and chemical properties of alternant hydrocarbons and the calculated ones with the self consistent Hückel method. Using their correlation formulae, we could estimate the $N \rightarrow V_1$ and charge-transfer bands, and also the ionization potential. We have compared the results for butadiene with the experimental and with the calculations of Gołębiewski and Nowakowski in Table 2.

TABLE 2. SOME PHYSICAL PROPERTIES OF *trans*-BUTADIENE ACCORDING TO GOŁĘBIEWSKI AND NOWAKOWSKI'S CORRELATION LINES

Property	Experimental	Self consistent Hückel method	
		With steric effects	Without steric effects ²⁹
$N-V_1$ (kK)	46.1	46.07	45.72
CT to TCE ^a (kK)	23.6	23.87	23.68
CT to TNB ^b (kK)	32.8	32.74	32.56
IP (eV)	9.07	9.02	8.99

^a TCE = tetracyanoethylene

^b TNB = 1,3,5-trinitrobenzene

Electronic spectrum of butadiene according to the SCF CI method

The experimental value of the $N \rightarrow V_1$ transition is 5.71 eV = 46.1 kK.³⁰⁻³¹ According to older experiments $\Delta E(N \rightarrow V_1) = 5.92$ eV.

Owing to the many publications concerning the spectrum of butadiene,³²⁻⁴⁶ only the most recent are considered. Nishimoto³⁵ applied a modified PPP method, including an upper-lower correlation of π -electrons. He obtained $\Delta E = 5.49$ eV for the *trans*-form and 5.22 eV for the *cis* one. Yamaguchi, Nakajima and Kunii³⁴ also applied the PPP method, varying the resonance integral on the bond length and relating the bond lengths to the bond orders. Assuming two different sets of parameters they obtained 5.62 eV (1.01) and 5.85 eV (1.03), with the oscillator strengths given in brackets. Adams and Miller,³⁷ using a SCF LCAO CI method based on orthogonalized atomic orbitals, obtained the value 5.48 eV (1.054). In order to complete our work on the steric hindrance we calculated the UV spectrum with a version of the SCF LCAO CI method, described elsewhere.⁴⁷ The method resembles that used by Yamaguchi *et al.* All singly excited configurations were included. The geometrical structure was that which followed from the conformation analysis. The results are given in Table 3. We see from the Table that the agreement with experiment is good for the $N \rightarrow V_1$ transition providing the Mataga-Nishimoto formula is used for interelectronic interaction. It is known, however, that the Mataga-Nishimoto formula yields too low values for the triplet states and that the Ohno formula is much better in this respect. As can be seen from the Table, the agreement with experiment is in the latter case much better although for the $N \rightarrow V_1$ case this is not so.

Acknowledgement—The author is indebted to Dr. Gołębiewski, Krakow, for stimulating discussions and critical comments.

TABLE 3. CALCULATED SPECTRUM OF *trans*- AND *cis*-BUTADIENE (in eV)

<i>trans</i> -Butadiene				<i>cis</i> -Butadiene			
M.N.'s formula		Ohno's formula		M.N.'s formula		Ohno's formula	
S → S	S → T	S → S	S → T	S → S	S → T	S → S	S → T
5.87 (0.941)	1.70	5.60 (1.003)	2.71	5.69 (0.499)	1.70	5.23 (0.432)	2.72
6.86 (0)	2.88	7.35 (0)	3.86	6.77 (0)	2.90	7.51 (0)	3.88
8.27 (0)	6.86	7.64 (0)	7.64	8.51 (0.839)	6.77	7.75 (0.776)	7.51
9.57 (0.409)	7.54	9.29 (0.144)	8.54	9.38 (0.017)	7.42	9.09 (0.007)	8.36

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