

The Electronic Structure and Spectrum of the Geometric Isomers of 1,4-Diphenyl-1,3-Butadiene

GUNNAR WETTERMARK*, and ROBERT SCHOR**

University of Paris, Institut de Biologie Physico-Chimique, 13, rue Pierre Curie, Paris V,
France

Received June 29, 1967

Using the results of energy calculations to determine the stable conformations, LCAO-SCF-CI semi-empirical computations have been performed on the three geometric isomers of 1,4-diphenyl-1,3-butadiene. The predicted wavelength and intensity changes for the fundamental band, which has been assigned to a ${}^1B \leftarrow {}^1A$ transition, are in agreement with experiment. The second transition has been assigned to be primarily ${}^1G \leftarrow {}^1A$ and the third transition, observed only in the *trans-trans* isomer, ${}^1H \leftarrow {}^1A$.

Zunächst wurden die stabilsten Konformationen der drei Isomeren des 1,4-Diphenyl-1,3-butadiens bestimmt. Für diese Geometrien wurden dann PPP-Rechnungen durchgeführt. Wellenlängen und Intensitäten der Hauptbande stimmen mit den experimentellen Werten sehr gut überein. Die Hauptbande ist vom Typ ${}^1B \leftarrow {}^1A$, die zweite Bande beruht hauptsächlich auf ${}^1G \leftarrow {}^1A$ -Übergängen, der bisher nur beim *trans-trans*-Isomeren beobachteten dritten Bande wird ein ${}^1H \leftarrow {}^1A$ -Übergang zugeordnet.

Des calculs L.C.A.O. S.C.F. C.I. semi-empiriques ont été effectués sur les trois isomères géométriques du 1,4-diphényl-1,3-butadiène, en utilisant les résultats des calculs d'énergie pour déterminer la stabilité des conformations. Les variations de longueur d'onde et d'intensité de la bande fondamentale, attribuée à une transition ${}^1B \leftarrow {}^1A$, sont en accord avec l'expérience. La seconde transition a été attribuée essentiellement à ${}^1G \leftarrow {}^1A$ et la troisième, observée seulement dans l'isomère *trans.trans*, à ${}^1H \leftarrow {}^1A$.

I. Introduction

There is considerable biological and theoretical interest in problems related to the electronic structure and spectrum of aromatic polyenes. The geometric isomers of diphenyl-butadiene may be considered model compounds for the photochemical processes occurring in the carotenes, retinenes, and vitamin A.

The ultraviolet spectrum of 1,4-diphenyl-1,3-butadiene has been reported by a great number of investigators. PINCKARD, WILLE and ZECHMEISTER [1] have made a complete study of the spectra of all the geometric isomers. DALE [2] has extended the measurements on the *trans-trans* isomer to lower wavelengths. The absorption spectra of the three isomers in hexane are shown in Fig. 1. The following features of the spectra are especially noteworthy:

* On leave from the Institute of Physical Chemistry, Uppsala University, Uppsala, Sweden. Financial support from the Swedish National Science Research Council.

** On Sabbatic leave 1966—1967 from the Physics Department and Materials Science Institute, University of Connecticut, Storrs, Connecticut, U.S.A. Financial Support from the University of Connecticut Research Foundation, Storrs, Connecticut, U.S.A.

1. The characteristic wavelength shifts of the fundamental band which occur on *cis-trans* isomerization: *trans-trans* λ_{\max} at 328 m μ , *cis-trans* λ_{\max} at 313 m μ , *cis-cis* λ_{\max} at 299 m μ .

2. The decrease of intensity of the fundamental band in going from *trans-trans* ($f_{\text{exp}} \sim 1.0$) to *cis-trans* ($f_{\text{exp}} \sim 0.7$) and *cis-cis* ($f_{\text{exp}} \sim 0.7$).

3. While the *trans-trans* isomer exhibits well defined vibrational structure in the fundamental band, the other two isomers are characterized by essentially continuous absorption spectra.

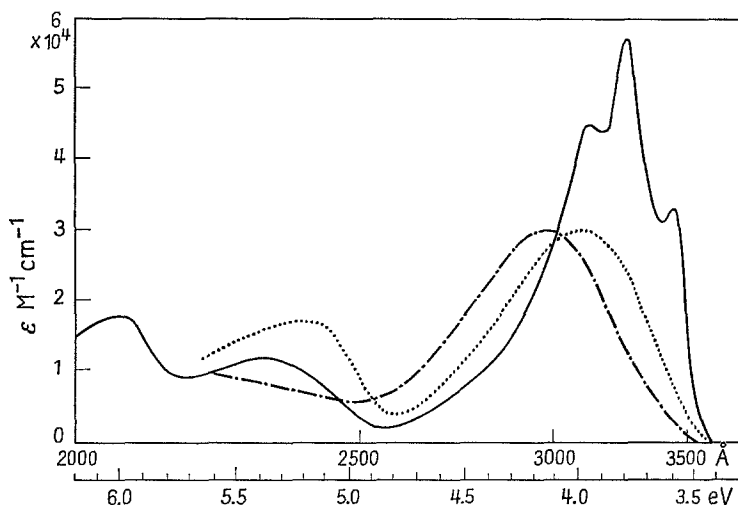


Fig. 1. The ultraviolet absorption spectra of the geometric isomers of 1,4-diphenyl-1,3-butadiene; — *trans-trans* isomer, *cis-trans* isomer; -.-.-.-. *cis-cis* isomer. (The data were obtained from Ref. [1] and [2])

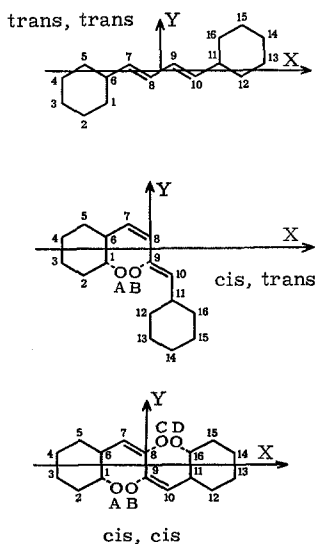


Fig. 2. The planar conformations of the three geometric isomers of 1,4-diphenyl-1,3-butadiene. Top: *trans-trans*; middle: *cis-trans*; bottom: *cis-cis*

Although X-ray diffraction patterns have been obtained for diphenylbutadiene [3], no complete structure determination has been carried out. The planar conformations are shown in Fig. 2. The distances used are: C-C phenyl ring 1.39 Å, C-C ethylenic ("single bond") 1.45 Å, C-C ethylenic ("double bond") 1.33 Å. All valence angles have been assigned a value of 120°.

The present work consists of an attempt using MO theory to explain the characteristics of the fundamental band as well as account for the higher bands of these isomers.

II. Calculations

A) Energy Calculation

For a C-H distance of 1.09 Å and 120° for the CCH angle, an inspection of Fig. 2 shows that there are no short H-H Van der Waals' contacts for the planar *trans-trans* molecule. (For the *trans-trans* isomer, we have considered that the most likely conformation around the 8-9 bond is *trans*). In the case of the *cis-trans* and *cis-cis* isomers, however, there are short H...H contacts (~ 0.5 Å): H_A...H_B for the *cis-trans* isomers, H_A...H_B and H_C...H_D for the *cis-cis* isomers.

In order to relieve the large strain energy of such short Van der Waals' contacts, it is probable that the *cis-trans* and *cis-cis* isomers will distort from the planar conformation. In addition, Pariser-Parr-Pople computations (Section II. B) show that it is not possible to explain the spectral shifts of λ_{\max} for the fundamental absorption band on the basis of a planar geometry for the *cis-trans* and *cis-cis* isomers. In fact, using planar geometries, the predicted shifts are in the wrong direction.

We have therefore investigated the possibility that the molecules deform in order to relieve the strain energy. The steric energy of the *cis-trans* and *cis-cis* isomers can be decomposed into the following contributions: 1. the repulsion energy for pairs of atoms having a smaller distance than the "touching distance"; 2. the energy variation of the π -electrons as a result of rotations around "single bonds"; 3. the bending energy in the plane of the bonds and; 4. the steric energy associated with the stretching of bonds.

On the basis of the work done by other investigators on related compounds [4-8] and of an examination of molecular models, we believe that the most reasonable way to relieve the steric hindrance due to the short hydrogen-hydrogen Van der Waals' contacts is for the molecules to rotate around "single" and/or "double" bonds. In particular, since it is energetically considerably more difficult to rotate around "double" than "single" bonds, we have assumed that only rotations around "single" bonds occur.

For the *cis-trans* isomer, we do not consider rotation around the 10-11 "single" bond since there is no short H_C...H_D contact for this isomer. Such a rotation would involve a loss of resonance energy with no release of strain energy. For the *cis-cis* isomer, on the other hand, the rotation angles around the 6-7 and 10-11 "single" bonds are taken equal by symmetry.

We define (right-handed coordinate system) the rotation angles α and β as follows (s. Fig. 3):

cis-trans isomer: The *xy*-plane contains atoms 8-16 and B. The angle α measures the rotation around link 6-7 and is defined positive when atom A

moves toward positive z values for $\beta = 0$. The angle β measures the rotation around link 8—9 and is defined positive when atom A moves toward negative z values for $\alpha = 0$.

cis-cis isomer: The y -axis contains atoms 8 and 9. The z -axis, passing through the center of the 8—9 bond, is maintained as the two-fold axis. The angles α measure the rotation around links 6—7 and 10—11 and are defined positive when atoms A and D move toward positive z values for $\beta = 0$. The angle β measures the rotation around link 8—9 and is defined positive when atoms A and D move toward negative z values for $\alpha = 0$.

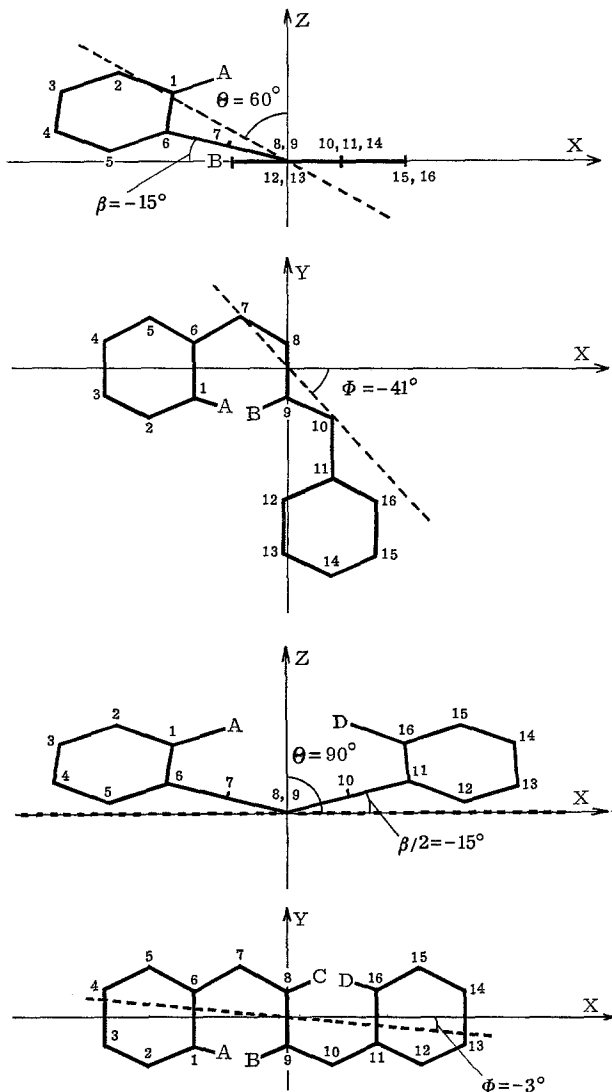


Fig. 3. Projections on the xy - and the xz -plane of the most likely conformations for the *cis-trans* isomer ($\alpha = 40^\circ$, $\beta = -15^\circ$) and for the *cis-cis* isomer ($\alpha = 35^\circ$, $\beta = -30^\circ$). The dashed line shows the predicted polarization of the fundamental absorption band

In order to describe the spatial orientation of the polarization vector M of the absorbed light, we define: $\theta \leq \pi/2$ as the angle between \vec{M} and the z -axis and $-\frac{\pi}{2} \leq \Phi \leq \pi/2$ as the angle between the x -axis and the projection of \vec{M} on the xy -plane. Fig. 3 shows the projections of the predicted conformations for the *cis-trans* and *cis-cis* isomers on the xy - and xz -planes.

The two steric energy factors we consider are:

1. The repulsion energy for pairs of atoms having a distance smaller than the "touching distance" calculated using the Kitaygorodsky formula [9]:

$$E_S = -0.14 \left(\frac{r_0}{r} \right)^6 + 3 \cdot 10^4 \exp \left(-13 \frac{r}{r_0} \right) \text{kcal mole}^{-1} \quad (1)$$

where r is the actual distance and r_0 the touching distance obtained by adding the Van der Waals' atomic radii. The value of r_0 of 2.4 Å for hydrogen has been taken from Pauling's table [10].

2. The resonance energy E_R of the π -electrons has been calculated in the Hückel approximation in which all Coulomb integrals have been set equal to α and all resonance integrals for the planar conformation have been set equal to β_0 . The variation of the energy of the π -electrons, as a result of the rotation around the "single bonds" has been calculated using the relation:

$$\beta_\theta = \beta_{\theta=0} \cos \theta \quad (2)$$

where θ is the twisting angle, i.e., α or β in the present context. The value for β_0 was taken as 18 kcal·mole⁻¹ [11]. The total energy of the electrons can be defined, in this approximation, as:

$$E_T = E_S + E_R. \quad (3)$$

The results of the calculation of E_T as a function of the rotation angles α and β are shown in Fig. 4. Minima are predicted at $\alpha = 40^\circ$, $\beta = -15^\circ$ for the *cis-trans* isomer and at $\alpha = 35^\circ$, $\beta = -30^\circ$ for the *cis-cis* isomer.

B) Pariser-Parr-Pople Calculations

Classical Pariser-Parr-Pople calculations have been performed using atomic orbitals obtained from the usual Slater atomic orbitals by a Löwdin transformation [12]. In the present work, we have used a 16×16 configuration interaction matrix for the singly excited states involving the single particle orbital jumps between the 4 highest occupied energy levels and the 4 lowest virtual orbitals.

The PLATT notation [13] for the molecular states of the isomers of diphenylbutadiene is given in Tab. 1.

Parameters

The diagonal core integrals I_{pp} are given by [14]:

$$I_{pp} = I_p - \sum_A (A | pp) - \sum_{q \neq p} (qq | pp) = U_p - \sum_{q \neq p} (qq | pp) \quad (4)$$

where I_p is the valence state ionization potential of atom p . We have used the value $U_{\text{Carbon}} = -9.5$ eV which gives satisfactory values for the ionization potentials in hydrocarbons. For the off-diagonal core integrals I_{pq} we have

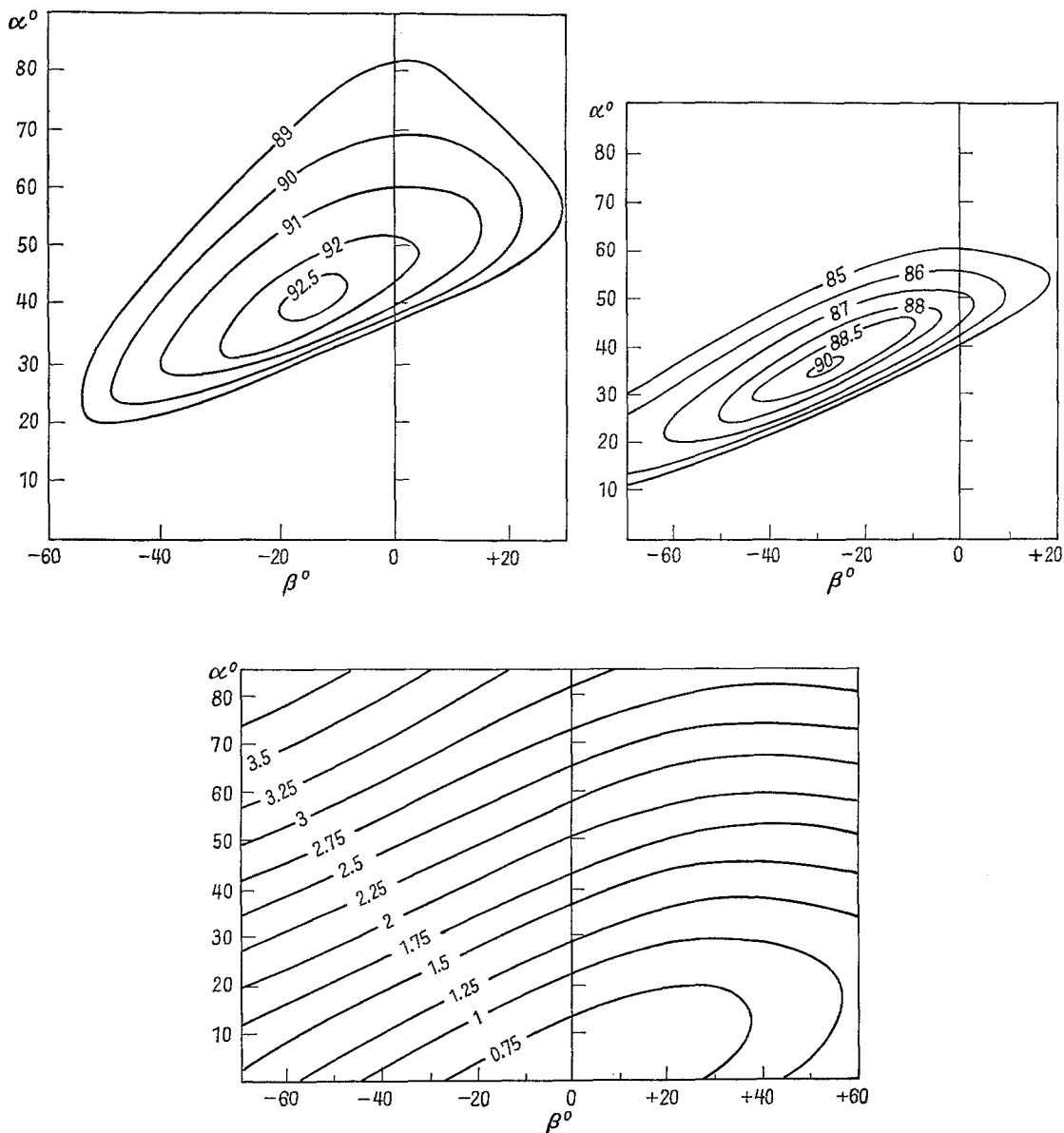


Fig. 4. Energy maps for the *cis-trans* isomer (top left) and for the *cis-cis* isomer (top right). The negative of the energy, $-E_T$, indicated on the contours, is given in kcal · mole⁻¹. The distance in Ångströms (bottom figure) between the "short-contact" hydrogen atoms

Table 1. Ground and singly excited states of 1,4-diphenyl-1,3-butadiene^a

Spin Configurations	Platt Notation		Symmetry C_{2h}	Species C_s
	Configuration	States		
${}^1\Phi_0$	$\nu_2^2\nu_1^2e^2f^2$	1A	A_g	A'
${}^{1,3}\Phi_{8,9'}$	$\nu_2^2\nu_1^2e^2fg$	${}^{1,3}B$	B_u	A'
${}^{1,3}\Phi_{8,11'}$	$\nu_2^2\nu_1^2e^2fw_1$		B_u	A'
${}^{1,3}\Phi_{8,12'}$	$\nu_2^2\nu_1^2e^2fw_2$		A_g	A'
${}^{1,3}\Phi_{7,11'}$	$\nu_2^2\nu_1^2e f^2w_1$		A_g	A'
${}^{1,3}\Phi_{7,12'}$	$\nu_2^2\nu_1^2e f^2w_2$		B_u	A'
${}^{1,3}\Phi_{6,9'}$	$\nu_2^2\nu_1^2e^2f^2g$	${}^{1,3}G$	B_u	A'
${}^{1,3}\Phi_{5,9'}$	$\nu_2^2\nu_1^2e^2f^2g$		A_g	A'
${}^{1,3}\Phi_{6,10'}$	$\nu_2^2\nu_1^2e^2f^2h$		A_g	A'
${}^{1,3}\Phi_{5,10'}$	$\nu_2^2\nu_1^2e^2f^2h$		B_u	A'
${}^{1,3}\Phi_{5,11'}$	$\nu_2^2\nu_1^2e^2f^2w_1$		A_g	A'
${}^{1,3}\Phi_{5,12'}$	$\nu_2^2\nu_1^2e^2f^2w_2$	${}^{1,3}H$	B_u	A'
${}^{1,3}\Phi_{6,11'}$	$\nu_2^2\nu_1^2e^2f^2w_1$		B_u	A'
${}^{1,3}\Phi_{6,12'}$	$\nu_2^2\nu_1^2e^2f^2w_2$		A_g	A'
${}^{1,3}\Phi_{7,9'}$	$\nu_2^2\nu_1^2e f^2g$	${}^{1,3}C$	A_g	A'
${}^{1,3}\Phi_{8,10'}$	$\nu_2^2\nu_1^2e^2fh$		A_g	A'

^a 16 singly excited states have been included in the calculations.

maintained the Pariser-Parr value for benzene but have slightly modified the empirical relationship [15]:

$$I_{pq}^{\text{core}} \propto S \quad (5)$$

for the other distances. This choice of I_{pq} reproduces more accurately the value of the transition energy for the fundamental band of the *trans-trans* isomer:

R (Å)	I_{pq}^{core} (eV)
1.33	-2.50
1.39	-2.39
1.45	-2.28

The cosine variation of the core resonance integral for the π -electrons as a result of rotation around "single bonds" was calculated from Eq. (2).

In the zero-differential-overlap approximation the only non-vanishing Coulomb repulsion integrals are the one-center integrals $(pp|pp)$ and the two-center integrals $(pp|qq)$. The one center integrals $(pp|pp)$ were evaluated using the Pariser relation:

$$(pp|pp) = I_p - A_p \quad (6)$$

where I_p is the ionization potential and A_p the valence state electron affinity of atom p [16]. Following ANNO [17], we have used 11.08 eV for $(pp|pp)$. The two-center Coulomb integrals $(pp|qq)$ were calculated using Roothaan's formula. For

Table 2. *Band assignments for trans stilbene*

Transition	Symmetry	Calculated value $\lambda(\text{m}\mu)$	Observed value $\lambda_{\text{max}}(\text{m}\mu)$
${}^1B \leftarrow {}^1A$	B_u	292	294
${}^1G \leftarrow {}^1A$	B_u	207	223
${}^1H \leftarrow {}^1A$	B_u	199	201

all pairs of atoms p, q which are not nearest neighbors, we have used Slater orbitals with $\zeta_{\text{Carbon}} = 1.625$. For this calculation, the interatomic distances R have been determined from the planar conformations. It has been emphasized that the Coulomb integrals for pairs of bonded atoms affect the results essentially through their difference with the one-center value adopted. The best fit for this difference in carbon compounds requires the use of a reduced value $\zeta_r = 0.830$ for the Slater screening constants of the carbon atoms [18].

The atomic coordinates of the rotated conformations were determined by analytical geometry. The oscillator strengths f and the polarization angles θ, Φ were calculated for the rotated as well as the planar conformations.

The consistency of the parameters used in the present work has been checked by calculations on the isomers of stilbene. The band assignments for *trans* stilbene are given in Tab. 2. The results are satisfactory but differ from those obtained by BEVERIDGE and JAFFÉ [6] who have assigned the bands at 223 $\text{m}\mu$ and 201 $\text{m}\mu$ to ${}^1H \leftarrow {}^1A$ and ${}^1G \leftarrow {}^1A$ transitions respectively. The question of the assignment of these bands has been somewhat controversial. The present assignments are in agreement with those of DALE [2], SUZUKI [19], and other workers. It is interesting to note, however, that the assignments of BEVERIDGE and JAFFÉ could be reproduced by employing the charged sphere approximation instead of the Roothaan formula for the Coulomb repulsion integrals.

III. Results

Pariser-Parr-Pople calculations for the planar conformations of the geometric isomers of 1,4-diphenyl-1,3-butadiene yield the following results for the wavelengths of the fundamental absorption band: *trans-trans* 324 $\text{m}\mu$, *cis-trans* 331 $\text{m}\mu$, and *cis-cis* 330 $\text{m}\mu$. These wavelength shifts are not in agreement with the experimental values: *trans-trans* 328 $\text{m}\mu$, *cis-trans* 313 $\text{m}\mu$, and *cis-cis* 299 $\text{m}\mu$.

The results of the computations for the non-planar conformations using the geometries determined from the energy calculations for the *cis-trans* and *cis-cis* isomers as well as for the planar *trans-trans* isomer are given in Tab. 3. An energy level diagram illustrating the numerotation of the SCF orbitals is given in Fig. 5.

The fundamental band for all the isomers is practically entirely accounted for by the single particle jump $8 - 9'$ between the highest occupied and the lowest unoccupied molecular orbital. The predicted wavelength shift from stilbene of the fundamental band in *trans-trans* 1,4-diphenyl-1,3-butadiene is reasonable on the basis of the increase in size of the conjugated system [20]. Furthermore, a blue shift is predicted for the *cis-cis* and the *cis-trans* isomer as compared to the *trans-trans* species. The calculated oscillator strengths in the *cis-trans* and *cis-cis* isomers are comparable and smaller than that of the *trans-trans* isomer. The predicted

Table 3. Band Assignments in 1,4-diphenyl-1,3-butadiene

Isomer	Transition	Symmetry	Calculated values		Observed values	
			$\lambda(\text{m}\mu)$	f	$\lambda_{\text{max}}(\text{m}\mu)$	f
<i>trans-trans</i> (planar)	${}^1B \leftarrow {}^1A$	B_u	324	1.76	328	1.0
	${}^1G \leftarrow {}^1A$	B_u	212	1.08	232	0.2
	${}^1H \leftarrow {}^1A$	B_u	198	0.70	207	~ 0.2
<i>cis-trans</i> $\alpha = 40^\circ$ $\beta = -15^\circ$	${}^1B \leftarrow {}^1A$	A'	311	1.02	313	0.7
	${}^1G \leftarrow {}^1A$	A'	230	0.41	240	~ 0.4
	${}^1G \leftarrow {}^1A$	A'	215	0.80		
<i>cis-cis</i> $\alpha = 35^\circ$ $\beta = -30^\circ$	${}^1B \leftarrow {}^1A$	B_u	297	1.19	299	0.7
	${}^1C \leftarrow {}^1A$	A_g	234	0.13	≤ 220	~ 0.2
	${}^1G \leftarrow {}^1A$	B_u	209	0.79		
	${}^1G \leftarrow {}^1A$	A_g	209	0.21		

polarization vector for the *trans-trans* isomer is essentially along the long axis of the molecule in accord with our calculations and the calculations of others on *trans* stilbene. For the *cis-cis* isomer $\theta = \pi/2$, and the predicted polarization is also along the long axis of the molecule in the "molecular plane" (i.e., *xy*-plane). A large amount of configuration interaction is necessary in order to account adequately for the higher transitions. Fig. 6 shows a diagram of the effect of configuration interaction for these bands.

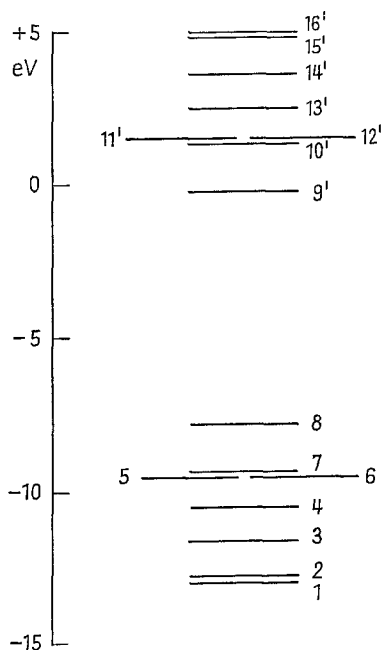


Fig. 5

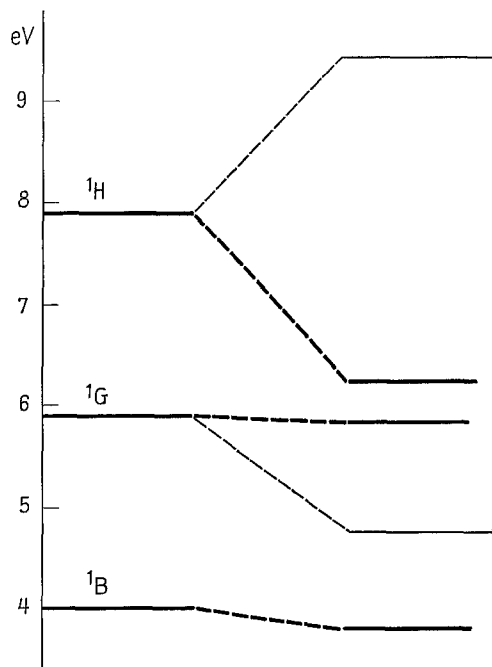


Fig. 6

Fig. 5. Energy level diagram for the SCF orbitals of *trans-trans* 1,4-diphenyl-1,3-butadiene

Fig. 6. Transition energies for *trans-trans* 1,4-diphenyl-1,3-butadiene before and after configuration interaction

The second calculated band has large components of the configuration interaction matrix between degenerate orbitals localized on the phenyl ring and delocalized orbitals.

The highest energy band is described as a transition between degenerate orbitals localized on the phenyl rings.

The band assignments for all the geometric isomers are given in Tab. 3.

IV. Conclusion

From an examination of the results we conclude:

1. On the basis of the conformations derived from energy calculations, a good overall description of the absorption spectra of the geometric isomers of diphenylbutadiene has been obtained.

2. In particular, the predicted wavelength and intensity changes of the fundamental band, assigned to a ${}^1B \leftarrow {}^1A$ transition, are in excellent agreement with experiment.

3. The second transition has been assigned to be primarily ${}^1G \leftarrow {}^1A$, while the third transition, observed only in the *trans-trans* isomer, is ${}^1H \leftarrow {}^1A$.

It is tempting to speculate that the lack of vibrational structure in the fundamental band of the *cis-trans* and the *cis-cis* isomers is associated with the relatively shallow potential energy minima which have been predicted for these isomers in the present work (Fig. 4).

Acknowledgment. It is a pleasure to thank Professors BERNARD and ALBERTE PULLMAN for their interest in this problem and also DRs. DINER and MALRIEU and Mr. GILBERT for stimulating discussions.

Bibliography

1. PINCKARD, J. H., B. WILLE, and L. ZECHMEISTER: J. Amer. Chem. Soc. **70**, 1938 (1948).
2. DALE, J.: Acta chem. Scand. **11**, 971 (1957).
3. DRENTH, W., et E. H. WIEBENGA: Recueil trav. chim. Pays-Bas **72**, 39 (1953).
4. FAVINI, G., u. M. SIMONETTA: Theoret. chim. Acta **1**, 294 (1963).
5. BASU, R.: Theoret. chim. Acta **2**, 215 (1964).
6. BEVERIDGE, D. L., and H. H. JAFFÉ: J. Amer. chem. Soc. **87**, 5340 (1965).
7. LINDNER, P., u. O. MÅRTENSSON: Theoret. chim. Acta **7**, 150 (1967).
8. FAVINI, G., S. TROVATO und A. GAMBA: Theoret. chim. Acta **7**, 305 (1967).
9. KITAYGORODSKY, A. I.: Tetrahedron **14**, 230 (1961).
10. PAULING, L.: The nature of the chemical bond, p. 260. Ithaca: Cornell Univ. Press 1960.
11. PULLMAN, B., and A. PULLMAN: Quantum biochemistry, p. 119. New York, London: Interscience Publishers 1963.
12. LÖWDIN, P. O.: J. chem. Physics **18**, 365 (1950).
13. PLATT, J. R.: Radiation biology, edited by HOLLAENDER, A. New York: McGraw-Hill Book Co., Inc. 1956.
14. PARISER, R., and G. PARR: J. chem. Physics **21**, 767 (1953).
15. MULLIKEN, R. S., C. A. RIEKE, D. ORLOFF, and H. ORLOFF: J. chem. Physics **17**, 1248 (1949).
16. PARISER, R.: J. chem. Physics **21**, 568 (1953).
17. ANNO, T.: J. chem. Physics **29**, 1161 (1958).
18. BERTHOD, H., C. GIESSNER-PRETTRE und A. PULLMAN: Theoret. chim. Acta **5**, 53 (1966).
19. SUZUKI, H.: Bull. chem. Soc. Japan **33**, 381 (1960).
20. JAFFÉ, H. H., and M. ORCHIN: Theory and applications of ultraviolet spectroscopy, p. 229. New York, London: John Wiley and Sons, Inc. 1962.

Dr. G. WETTERMARK
Institute of Physical Chemistry
Uppsala University
Uppsala, Sweden

Dr. R. SCHOR
Physics Department
University of Connecticut
Storrs, Conn. U.S.A. 06268