

The Electronic Structure and Spectra of *cis*- and *trans*-Stilbene¹

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Absorption band assignments are proposed for *cis*- and *trans*-stilbene on the basis of semiempirical LCAO-SCF-CI computations. The main transitions responsible for the long wave length absorption on both compounds are the ${}^1B \leftarrow {}^1A$ transition (Platt notation), in accord with previous investigations. The absorption occurring at about 230 $m\mu$ in the spectrum of both *cis*- and *trans*-stilbene is assigned to ${}^1H^+ \leftarrow {}^1A$ and is found to be localized in the phenyl rings. The band observed in *trans*-stilbene at 201 $m\mu$ is assigned to ${}^1G^+ \leftarrow {}^1A$, and an analogous band is predicted for *cis*-stilbene. The geometry of *cis*-stilbene giving the most consistent interpretation at the electronic spectrum is the "propeller-shaped" conformation wherein the phenyl rings are rotated $\sim 30^\circ$ out of plane. The presence of forbidden components in each of the absorption bands of both compounds is discussed.

I. Introduction

The association of electronic transitions in *cis*- and *trans*-stilbene with absorption bands observed in their ultraviolet spectra in solution has been the subject of several investigations in the recent chemical literature,³⁻¹⁰ and considerable controversy has arisen over the assignment of certain absorption bands. Due to the current interest in the chemistry of these compounds, particularly in their photochemical behavior,¹¹ we have attempted a detailed interpretation of their electronic spectra on the basis of transition energies, intensities, and polarizations computed from molecular wave functions obtained by the Pariser-Parr-Pople method.^{12,13} Subsequent articles will deal with *cis*- and *trans*-azobenzene and benzalaniline.

The molecular structure of *trans*-stilbene is known to be planar in the solid state,¹⁴ and a careful study by Suzuki⁷ indicates that it is safe to assume the molecule

to be planar in solution was well. The molecular symmetry group for the *trans* isomer is thus C_{2h} . *cis*-Stilbene is expected to deviate somewhat from a planar conformation in order to relieve steric interaction effects in the *ortho* hydrogens, but a crystal structure investigation has not to our knowledge been reported. A crystal structure of the analogous *cis*-azobenzene is available,¹⁵ and the results indicate that the phenyl rings are rotated approximately 30° out of the plane in a propeller-shaped conformation.

The π -electronic structure of stilbene may be qualitatively described in terms of one-electron molecular orbitals which may be conveniently grouped into two classifications¹⁶: (1) those orbitals having nonvanishing components associated with each atom contributing to the conjugated system, denoted \dots, e, f, g, h, \dots , and (2) those orbitals having nonvanishing components localized in the phenyl rings, denoted v or w . The notations used by various authors to describe the electronic configurations and states of stilbene are summarized in Table I.

Table I. Ground and Lower Excited States of Stilbene Based on One-Electron Molecular Orbitals

Configuration ^a	Platt notation ^b	Spin configurations	Symmetry species		
			C_{2h}	C_{2v}	C_2
$e^2v_2^2v_1^2f^2$	1A	${}^1\Phi_0$	A_g	A_1	A
$e^2v_2^2v_1^2fg$	${}^1B, {}^3B$	${}^1\Phi_{7,8}, {}^3\Phi_{7,8}$	B_u	B_1	B
$e^2v_2^2v_1^2fw_1$	${}^1G, {}^3G$	${}^1\Phi_{7,9}, {}^3\Phi_{7,9}$	A_g	A_1	A
$e^2v_2^2v_1^2fw_2$		${}^1\Phi_{7,10}, {}^3\Phi_{7,10}$	B_u	B_1	B
$e^2v_2^2v_1fg$		${}^1\Phi_{6,8}, {}^3\Phi_{6,8}$	A_g	A_1	A
$e^2v_2v_1^2f^2g$		${}^1\Phi_{6,8}, {}^3\Phi_{6,8}$	B_u	B_1	B
$e^2v_2^2v_1f^2w$		${}^1\Phi_{6,10}, {}^3\Phi_{6,10}$	A_g	A_1	A
$e^2v_2^2v_1f^2w_1$	${}^1H, {}^3H$	${}^1\Phi_{6,9}, {}^3\Phi_{6,9}$	B_u	B_1	B
$e^2v_2v_1^2f^2w_1$		${}^1\Phi_{6,9}, {}^3\Phi_{6,9}$	A_g	A_1	A
$e^2v_2v_1^2f^2w_2$		${}^1\Phi_{6,10}, {}^3\Phi_{6,10}$	B_u	B_1	B
$e^2v_2^2v_1^2fh$	${}^1C, {}^3C$	${}^1\Phi_{7,11}, {}^3\Phi_{7,11}$	A_g	A_1	A
$ev_2^2v_1^2f^2g$		${}^1\Phi_{4,8}, {}^3\Phi_{4,8}$	A_g	A_1	A

^a Reference 16.

The absorption spectrum of *trans*-stilbene in heptane⁷ consists of three distinct absorption bands, often referred to as the A, B, and C bands. The intense A band occurs at 294.1 $m\mu$ (ϵ 27,950) and shows considerable vibrational structure. The B band is centered at 228.5 $m\mu$ (ϵ 17,200) and the C band is observed at 201.5 $m\mu$ (ϵ 23,800).

The assignment of the A band in *trans*-stilbene is well established as ${}^1B \leftarrow {}^1A$.¹⁷ The vibrational structure of this band has been studied by Beale and Roe³

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(14) J. M. Robertson and I. Woodward, *Proc. Roy. Soc. (London)*, A162, 493 (1937).

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(17) R. S. Mulliken, *J. Chem. Phys.*, 7, 14 (1939).

and Suzuki,⁷ who assigned the observed spacings to the central double bond stretching mode. This vibrational assignment was confirmed by the recent investigation of Dyck and McClure¹⁸ on the absorption and emission spectra of *trans*-stilbene in dibenzyl crystal, and in addition they resolved vibrational spacings assigned to a ring deformation mode. Vapor spectra for *trans*-stilbene have been reported by Kanda,¹⁹ and the observed hypsochromic shift of the A band indicates the molecule spends considerable time in a nonplanar conformation in this phase.

The assignment of the B and C bands in *trans*-stilbene has been somewhat controversial. Dale⁴ observed the behavior of the A, B, and C bands in styrene, stilbene, and other molecules containing alternating phenyl rings and ethylenic bridges and assigned the ${}^1G \leftarrow {}^1A$ transitions to the B bands and ${}^1H \leftarrow {}^1A$ to the C bands. Suzuki⁷ arrived at similar assignments on the basis of LCAO-MO computations. Maier, Saupe, and Englert⁵ and later Saupe⁹ interpreted the B band as resulting from a ${}^1G^+ \leftarrow {}^1A$ transition but Saupe found the C band not accounted for in his computation. On the other hand, Jaffé, Yeh, and Gardner⁶ attributed the stationary character of the B band in stilbene, azobenzene, and some azobenzene derivatives to the presence of a ${}^1H \leftarrow {}^1A$ component and suggested the ${}^1G \leftarrow {}^1A$ transitions were actually short wave length components of the A band. Recently Perkampus¹⁰ reported calculations on stilbene in the electron gas model which also indicate the existence of a second component in the A band.

A singlet-triplet transition has been reported for *trans*-stilbene by Dyck and McClure as a diffuse absorption occurring between 431 and 578 μ , with vibrational spacings characteristic of the central double bond stretching mode. From a comparison of the vibrational spacings for the central double bond stretching frequency in the A band absorption and fluorescence, they computed a decrease in central double bond order of 10 to 15% on excitation to the lowest singlet. The observed vibrational structure in the singlet-triplet transition was not sufficiently well defined to compute a significant value for the central double bond order of the lowest triplet; however, the observed spacings suggest a decrease in π bond order of 10 to 30%. This would indicate the central double bond order was considerably higher in the lowest excited singlet and triplet than predicted from simple LCAO-MO computations²⁰⁻²² and presents a higher potential barrier to the *trans-cis* photoisomerization than expected. Dyck and McClure suggested that one of the other low-lying triplet states may be more favorable for the photoisomerization.

The spectrum of *cis*-stilbene in ethanol⁷ shows two distinct absorption bands, one a broad, structureless band centered at 272 μ (ϵ 22,000) and the other centered at 219 μ (ϵ 18,000). *cis*-Stilbene has received considerably less attention than the *trans* isomer from the point of view of band assignments, although the long wave length band is readily associated with the

${}^1B \leftarrow {}^1A$ transition and therefore corresponds to the *trans* A band.

Thus the main problems under consideration in this investigation are: (1) assignment of the short wave length absorption bands observed in both *cis* and *trans* isomers, (2) identification of any additional transitions contributing to absorption in the region of the A bands, (3) determination of the molecular geometry of *cis*-stilbene most consistent with the observed spectrum, and (4) consideration of the central double bond orders of the lower excited states of *trans*-stilbene with respect to the photoisomerization process.

II. Calculations

The methods for computing molecular wave functions accurate enough to use as a guide in the interpretation of the electronic spectra of unsaturated organic molecules have been developed particularly by Pariser and Parr,¹² and Pople.¹³ The computation scheme is based on the π -electron approximation with transition energies and intensities computed from π -electron molecular wave functions obtained from a configuration interaction including all monoexcited configurations. The final-state functions Ψ_m are thus linear combinations of singlet and triplet spin configurations Φ_n

$$\Psi_m = \sum_n A_{mn} \Phi_n \quad (1)$$

The spin configurations are constructed from antisymmetrized products of one-electron molecular spin orbitals ψ_i and $\bar{\psi}_i$. The ground-state configuration for a system of $2n$ electrons is written as

$${}^1\Phi_0 = |\psi_i\bar{\psi}_i \dots \psi_k\bar{\psi}_k \dots \bar{\psi}_n\bar{\psi}_n| \quad (2)$$

and the excited singlet and triplet spin configurations resulting from the promotion of an electron from orbital k to virtual orbital r' are written as

$${}^1\Phi_{k,r'} = \frac{1}{\sqrt{2}} \{ |\psi_i\bar{\psi}_i \dots \psi_k\bar{\psi}_{r'} \dots \psi_n\bar{\psi}_n| - |\psi_i\bar{\psi}_i \dots \bar{\psi}_k\psi_{r'} \dots \psi_n\bar{\psi}_n| \} \quad (3)$$

$${}^3\Phi_{k,r'} = \frac{1}{\sqrt{2}} \{ |\psi_i\bar{\psi}_i \dots \psi_k\bar{\psi}_{r'} \dots \psi_n\bar{\psi}_n| + |\psi_i\bar{\psi}_i \dots \bar{\psi}_k\psi_{r'} \dots \psi_n\bar{\psi}_n| \} \quad (4)$$

The molecular orbitals are taken as linear combinations of $2p\pi$ atomic orbitals χ_p

$$\psi_i = \sum_p C_{ip} \chi_p \quad (5)$$

The precise form of the χ_p is not specified, but they are assumed to be eigenfunctions of the corresponding atomic eigenvalue problem. The C_{ip} are taken as the coefficients of the occupied and virtual orbitals resulting from a closed-shell self-consistent field computation on the ground state of the molecule under consideration.

The energies of the electronic states E_m and the coefficients A_{mn} are the eigenvalues and eigenvectors, respectively, of the secular determinant

$$|H_{mn} - E_m \delta_{mn}| = 0 \quad (6)$$

where

$$H_{mn} = \langle \Phi_m^* | \mathcal{H} | \Phi_n \rangle \quad (7)$$

(18) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(19) Y. Kanda, *Mem. Fac. Sci. Kyushu Univ.*, C1, 189 (1950).

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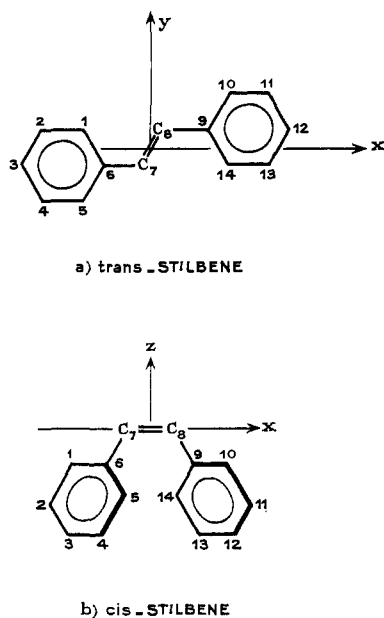


Figure 1. Structural formulas for *cis*- and *trans*-stilbene (hydrogens omitted) showing coordinate axes and numbering systems.

with \mathcal{H}_π the π -electron Hamiltonian operator of the molecular system and δ_{mn} the Kronecker δ . In the evaluation of the elements of eq. 6, differential overlap is strictly neglected. These elements may be reduced to core integrals over atomic orbitals²³

$$\alpha_p^{\text{core}} = \int \chi_p^*(\mu) \mathcal{H}_\pi^{\text{core}}(\mu) \chi_p(\mu) d\tau_\mu \quad (8)$$

$$\beta_{pq}^{\text{core}} = \int \chi_p^*(\mu) \mathcal{H}_\pi^{\text{core}}(\mu) \chi_q(\mu) d\tau_\mu \quad (9)$$

and the electron interaction integrals

$$(pq|st) = \iint \chi_p^*(\mu) \chi_s^*(\nu) \frac{e^2}{r_{\mu\nu}} \chi_q(\mu) \chi_t(\nu) d\tau_\mu d\tau_\nu \quad (10)$$

The diagonal core integrals are expressed as

$$\alpha_p^{\text{core}} = -w_p - \sum_{q \neq p} Z_q (pp|qq) \quad (11)$$

where Z_q is the charge on atom q and w_p is the valence state ionization potential of p . The off-diagonal core resonance integrals β_{pq}^{core} are evaluated in this investigation from a simple overlap proportionality based on the Pariser-Parr value of $\beta_{c=c}^{\text{core}} = -2.39$ e.v. for two parallel $2p\pi$ orbitals at 1.39 Å. For distances other than 1.39 Å., core resonance integrals between two parallel $2p\pi$ orbitals π_p and π_q are evaluated from the formula

$$\beta_{pq}^{\text{core}} = \frac{S_{pq}}{S_{c=c}} \beta_{c=c}^{\text{core}} = -9.55 S_{pq} \quad (12)$$

where S_{pq} is the overlap integral between π_p and π_q evaluated from Slater orbitals.²⁴ When π_p and π_q are not parallel but oriented with their axes at some angle (θ) with respect to one another, the core resonance integrals β_{pq} are evaluated as

$$\beta_{pq}^{\text{core}}(\theta) = \beta_{pq}^{\text{core}} \cos \theta \quad (13)$$

(23) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin Inc., New York, N. Y., 1963.

(24) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949).

where β_{pq}^{core} is defined in eq. 12 and corresponds to the parallel case. The values used for core resonance integrals in this investigation are collected in Table II.

Table II. Core Resonance Integrals

Calculation	Core resonance integrals, e.v.		
	$\beta_{\phi}^{\text{core}}$	β_{78}^{core}	$\beta_{67}^{\text{core}}, \beta_{89}^{\text{core}}$
<i>trans</i> , <i>cis</i> ($\theta = 0^\circ$)	-2.39	-2.69	-2.20
<i>cis</i> ($\theta = 15^\circ$)	-2.39	-2.69	-2.125
<i>cis</i> ($\theta = 30^\circ$)	-2.39	-2.69	-1.905
<i>cis</i> ($\theta = 45^\circ$)	-2.39	-2.69	-1.556

The neglect of differential overlap reduces the electron repulsion integrals required to the one-center ($pp|pp$) and two-center ($pp|qq$) cases. The one-center integrals are evaluated in the Pariser approximation²⁵

$$(pp|pp) = W_p - A_p \quad (14)$$

where A_p is the valence state electron affinity of p . The value employed for ($pp|pp$) in this investigation is 11.08 e.v., following Anno.²⁶ The two-center Coulomb integrals are evaluated in the charged sphere approximation²⁷ for several interatomic distances and an interpolation formula established for intermediate distances. For the case where π_p and π_q are parallel, the interpolation formula

$$(\pi_c \pi_c | \pi_c \pi_c) = 11.03 - 2.934363r + 0.28179r^2 + 0.000996r^3 - 0.000907r^4 \quad (15)$$

was derived and is valid for distances < 10 Å. The parameter r represents interatomic distance in Å. and the value of the integral is given in e.v. When π_p and π_q are not parallel, such as in *cis*-stilbene when the phenyl rings are no longer coplanar, this integral should be resolved into $2p\sigma$ and $2p\pi$ components. However for small deviations from coplanarity the difference is not large, and in the calculations presented here in eq. 15 is used for all carbon-carbon Coulomb integrals.

The bond lengths assumed for the computations are based on the crystal structure investigation of Robertson and Woodward¹⁴ on *trans*-stilbene. The bond lengths for *cis*-stilbene in all conformations considered are assumed to be the same as in the *trans* isomer. All bond angles are taken as 120° . The coordinate systems are defined in Figures 1a and 1b.

III. Results

trans-Stilbene. The transition energies, corresponding oscillator strengths, polarizations, and excited-state wave functions computed for *trans*-stilbene are collected in Table III. The theoretical and observed spectra are compared in Figure 2.

The configuration interaction among the lower excited singlet states of B_u symmetry in *trans*-stilbene is depicted schematically in Figure 3. First-order configuration effects²⁸ are observed in the 1G and 1H states, both doubly degenerate in the one-electron approximation. Each of the degenerate pairs is split into *plus* and *minus* states,²⁹ with electronic transitions

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(27) R. G. Parr, *ibid.*, 20, 1499 (1952).

(28) W. Moffit, *ibid.*, 22, 320 (1954).

(29) R. Pariser, *ibid.*, 24, 250 (1956).

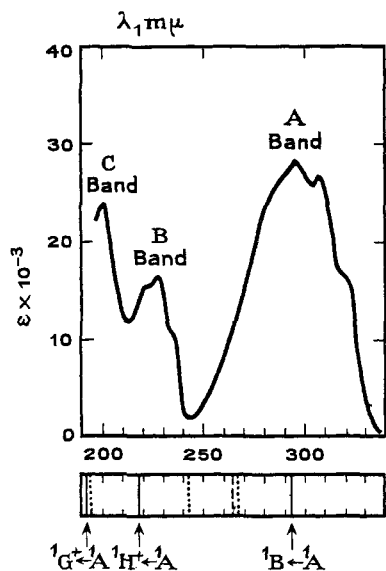


Figure 2. Comparison of calculated transitions and observed spectrum⁷ for *trans*-stilbene. Solid lines indicate allowed B_u transitions, dashed lines indicate forbidden B_u transitions, and dotted lines indicate forbidden A_g transitions. The assignment of the principal allowed component of each absorption band is indicated.

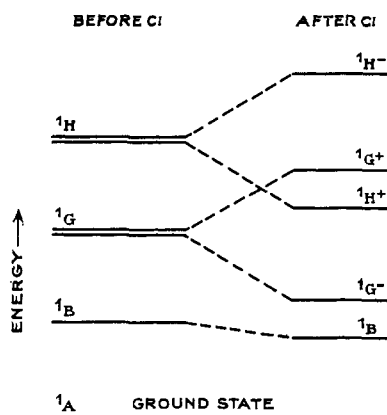


Figure 3. Schematic diagram of configuration interaction among lower singlet B_u states in *trans*-stilbene.

allowed only from the ground state to *plus* excited states of B_u symmetry. The lowest excited singlet state 1B suffers only second-order configuration interaction effects. The relative energies of the B_u excited states, $E({}^1B) < E({}^1G^-) < E({}^1H^+) < E({}^1G^+)$, was observed to be the same for any reasonable choice of core resonance integrals. A similar splitting pattern is observed among the 1G and 1H states of A_g symmetry. The band assignments deduced from the theoretical transition energies for *trans*-stilbene are summarized in Table IV and appear to comprise a satisfactory and consistent interpretation of the electronic spectrum. Essentially new assignments are proposed for the B band and C band and for yet another transition indicated as a low intensity component of the A band.

As mentioned before, the identity of the major component of the A band in *trans*-stilbene is already well established and this investigation concurs in the ${}^1B \leftarrow {}^1A$ assignment. The computed polarization of this transition, parallel to the pseudo-long axis of the molecule, is in accord with experimental observation.¹⁸

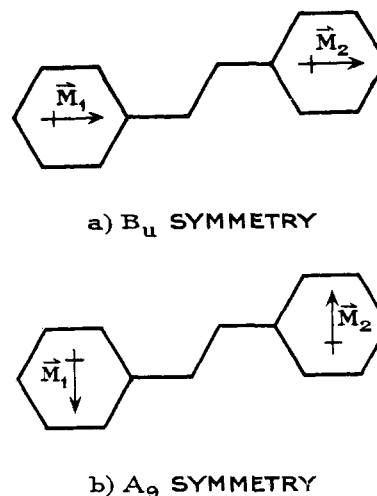


Figure 4. Transition moment vectors for locally excited transitions in *trans*-stilbene arising from benzene ${}^1A_{1g} \rightarrow {}^1E_{1u}$ transitions.

The association of the B band in *trans*-stilbene with the ${}^1H^+ \leftarrow {}^1A$, B_u transition indicates that this absorption is essentially localized in the phenyl rings of the molecule and is mainly of exciton character. This assignment is especially interesting in that this is a case where a *plus* state is of lower energy than the corresponding *minus* state, a situation rarely encountered in aromatic systems to date. The phenomenon arises in the following manner. Consider two excited singlet states ${}^1\Phi_{k,r'}$ and ${}^1\Phi_{l,s'}$ degenerate in the one-electron approximation

$$E = \langle {}^1\Phi_{k,r'} | \mathcal{H} | {}^1\Phi_{k,r'} \rangle = \langle {}^1\Phi_{l,s'} | \mathcal{H} | {}^1\Phi_{l,s'} \rangle \quad (16)$$

First-order configuration interaction gives rise to *plus* and *minus* states, with the energies

$$E^+ = E + \Lambda \quad (17)$$

$$E^- = E - \Lambda \quad (18)$$

where

$$\Lambda = \langle {}^1\Phi_{k,r'} | \mathcal{H} | {}^1\Phi_{l,s'} \rangle \quad (19)$$

Thus the relative energies of the plus and minus states depend on the algebraic sign of the interaction matrix element Λ . It may be shown for locally excited states that this element corresponds to the classical interaction of the transition dipoles associated with the one-electron excitations $k \rightarrow r'$ and $l \rightarrow s'$.^{30,31}

The one-electron excitations giving rise to the 1H states involve v and w orbitals, and these states, being localized in the phenyl rings, are derived from the ${}^1E_{1u}$ states of the benzene molecule. Transitions to the benzene ${}^1E_{1u}$ states have nonvanishing transition dipole moments, and thus to be considered for *trans*-stilbene is the interaction between the transition dipoles \vec{M}_1 and \vec{M}_2 in Figure 4a for B_u states and Figure 4b for A_g states. The classical electrostatic interaction $V(\vec{M}_1, \vec{M}_2)$ between dipoles \vec{M}_1 and \vec{M}_2 is given to a first approximation by the formula³²

(30) J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1952.

(31) H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A235**, 537 (1956).

(32) W. Kaufmann, "Quantum Chemistry," Academic Press Inc., New York, N. Y., 1957.

Table III. Results of Computations on *trans*-Stilbene

State	Symmetry	ΔE , e.v.	f	Polarization ^a		Wt. % of most important spin configurations
				$\cos \alpha$	$\cos \beta$	
¹ B	B _u	4.194	0.571	-0.970	-0.241	87.0 ¹ $\Phi_{7,8}$; 7.0 ¹ $\Phi_{4,11}$
¹ G ⁻	B _u	4.674				31.5 ¹ $\Phi_{7,10}$; 31.5 ¹ $\Phi_{5,8}$; 16.3 ¹ $\Phi_{6,11}$; 16.3 ¹ $\Phi_{4,9}$
¹ G ⁻	A _g	4.679				31.2 ¹ $\Phi_{7,9}$; 31.2 ¹ $\Phi_{6,8}$; 16.4 ¹ $\Phi_{5,11}$; 16.4 ¹ $\Phi_{4,10}$
¹ (C, H) ⁺	A _g	5.114				25.6 ¹ $\Phi_{7,11}$; 25.6 ¹ $\Phi_{4,8}$; 21.4 ¹ $\Phi_{5,9}$; 21.4 ¹ $\Phi_{6,10}$
¹ H ⁺	B _u	5.662	0.558	0.999	0.029	33.5 ¹ $\Phi_{5,10}$; 33.5 ¹ $\Phi_{6,9}$; 8.9 ¹ $\Phi_{7,12}$; 8.9 ¹ $\Phi_{3,8}$
¹ G ⁺	A _g	6.336				44.1 ¹ $\Phi_{7,9}$; 44.1 ¹ $\Phi_{6,8}$; 3.9 ¹ $\Phi_{5,11}$; 3.9 ¹ $\Phi_{4,10}$
¹ C ⁻	A _g	6.426				42.0 ¹ $\Phi_{7,11}$; 42.0 ¹ $\Phi_{4,8}$; 5.5 ¹ $\Phi_{4,12}$; 5.5 ¹ $\Phi_{3,11}$
¹ G ⁺	B _u	6.459	0.831	0.342	0.940	40.5 ¹ $\Phi_{7,10}$; 40.5 ¹ $\Phi_{5,8}$; 3.6 ¹ $\Phi_{6,11}$; 3.6 ¹ $\Phi_{4,9}$
³ B	B _u	2.535				74.2 ³ $\Phi_{7,8}$; 6.3 ³ $\Phi_{4,11}$; 5.48 ³ $\Phi_{3,12}$
³ C ⁺	A _g	3.340				24.7 ³ $\Phi_{7,11}$; 24.7 ³ $\Phi_{4,8}$; 18.7 ³ $\Phi_{5,9}$; 18.7 ³ $\Phi_{6,10}$
³ H ⁺	B _u	3.754				29.2 ³ $\Phi_{5,10}$; 29.2 ³ $\Phi_{6,9}$; 11.7 ³ $\Phi_{7,12}$; 11.7 ³ $\Phi_{3,8}$
³ G ⁺	A _g	4.192				30.5 ³ $\Phi_{7,9}$; 30.5 ³ $\Phi_{6,8}$; 16.4 ³ $\Phi_{5,11}$; 16.4 ³ $\Phi_{4,10}$
³ G ⁺	B _u	4.195				30.8 ³ $\Phi_{7,10}$; 30.8 ³ $\Phi_{5,8}$; 16.6 ³ $\Phi_{6,11}$; 16.6 ³ $\Phi_{4,9}$
³ H ⁺	A _g	4.293				29.0 ³ $\Phi_{5,9}$; 29.0 ³ $\Phi_{6,10}$; 18.4 ³ $\Phi_{7,11}$; 18.4 ³ $\Phi_{4,8}$
³ D	B _u	4.461				20.4 ³ $\Phi_{4,11}$; 19.8 ³ $\Phi_{7,12}$; 19.8 ³ $\Phi_{5,8}$; 16.0 ³ $\Phi_{5,10}$
³ G ⁻	B _u	4.674				31.5 ³ $\Phi_{7,10}$; 31.5 ³ $\Phi_{5,8}$; 16.3 ³ $\Phi_{6,11}$; 16.3 ³ $\Phi_{4,9}$
³ G ⁻	A _g	4.678				31.2 ³ $\Phi_{7,9}$; 31.2 ³ $\Phi_{6,8}$; 16.4 ³ $\Phi_{5,11}$; 16.4 ³ $\Phi_{4,10}$

^a α and β are Euler angles referred to the coordinate system in Figure 1.

Table IV. Summary of Band Assignments in *trans*-Stilbene

Absorption region	Obsd. λ_{\max} ($m\mu$) ^a	Transition	Symmetry	Calcd. λ ($m\mu$)
A band	294	¹ B \leftarrow ¹ A	B _u	296 ^b
		¹ G ⁻ \leftarrow ¹ A	B _u	266
		¹ G ⁻ \leftarrow ¹ A	A _g	265
		¹ (C,H) ⁺ \leftarrow ¹ A	A _g	243
B band	223	¹ H ⁺ \leftarrow ¹ A	B _u	219 ^b
		¹ G ⁺ \leftarrow ¹ A	A _g	196
C band	201	¹ C ⁻ \leftarrow ¹ A	A _g	193
		¹ G ⁺ \leftarrow ¹ A	B _u	192 ^b

^a See ref. 7. ^b Principal allowed component.

$$V(\vec{M}_1, \vec{M}_2) = \frac{x_1x_2 + y_1y_2 - 2z_1z_2}{R_3} \quad (20)$$

where x_i , y_i , and z_i are the vector components of \vec{M}_1 and R is the interorigin distance. The axes of the two coordinate systems and 2 are parallel with the Z axes oriented along the line joining the positive poles of \vec{M}_1 and \vec{M}_2 . Equation 20 is clearly dominated by the negative term when the vectors are oriented as in Figure 4a. Thus the interaction for the B_u case will be attractive and the interaction energy element negative, resulting in $E(^1H^+) < E(^1H^-)$. For the A_g case, the interaction is also attractive but should be less so than the interaction corresponding to the B_u case. $\Delta(B_u) > \Delta(A_g)$ is observed for the ¹H states in the calculations reported herein.

Transitions to both the ¹G⁺ and ¹G⁻ states of B_u symmetry are indicated in the ultraviolet, with ¹G⁺ \leftarrow ¹A being a strongly allowed component of the C band in *trans*-stilbene and ¹G⁻ \leftarrow ¹A a low-intensity short wave length component of the A band. The ¹G \leftarrow ¹A transition is actually forbidden, but is expected to be present since it arises in the same manner as the ¹L_b bands in polynuclear aromatic hydrocarbons, which are observed in those situations where they are not obscured by the more intense ¹L_a bands.

As indicated in Tables III and IV, a number of parity forbidden transitions in *trans*-stilbene have energies corresponding to excitation in the ultraviolet. These would

be expected to have extinction coefficients of 200 or less and would be obscured by the more intense allowed bands.

The partial success and partial failure of the identification of the absorption regions in *trans*-stilbene by Hückel-type computations^{6,7} is readily explained on the basis of the wave functions presented in Table III. Using the Hückel approach, the ¹B \leftarrow ¹A transition was readily established as the major component of the major component of the A band while controversy arose over the other band assignments. The state functions based on configuration interaction indicate the ¹B excited state is well represented by a single spin configuration, which is to say the transition ¹B \leftarrow ¹A may be adequately described as a one-electron excitation from the highest occupied molecular orbital in the ground-state configuration to the lowest unoccupied molecular orbital. The other lower excited states of *trans*-stilbene require a linear combination of spin configurations for their description, and excitations to these states may not be adequately described as one-electron excitations between two specific molecular orbitals. Since only one-electron excitations may be adequately accommodated by the Hückel method, the success of these calculations in describing the ¹B \leftarrow ¹A transition and their failure to properly describe the other excitations is readily understood.

The lowest singlet-triplet transition in *trans*-stilbene is quite well accommodated in the computation. From the state functions obtained we compute a 34% decrease in central double bond order on excitation to the lowest singlet and a 39% decrease on excitation to the

Table V. Central Double Bond Orders of Lower Excited States of *trans*-Stilbene

Configuration	Symmetry	Bond order	
		Singlet	Triplet
B	B _u	0.642	0.625
G ⁻	A _g	0.800	
G ⁻	B _u	0.800	
(C, H) ⁺	A _g	0.821	0.827
H ⁺	B _u	0.860	0.858
G ⁺	A _g		0.868
G ⁺	B _u		0.841

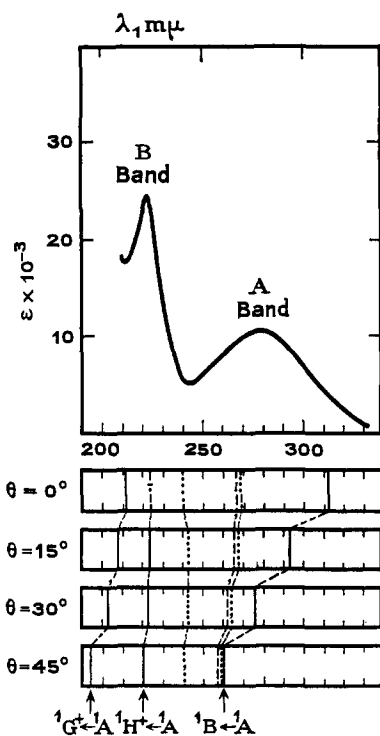


Figure 5. Comparison of observed spectrum of *cis*-stilbene⁷ with electronic transitions computed as a function of θ . Solid lines indicate allowed B transitions, dashed lines indicate forbidden B transitions, and dotted lines indicate forbidden A transitions. The assignment of the principal allowed component of each absorption band is indicated.

lowest triplet. This is slightly lower than the 45% decrease predicted by LCAO-MO methods, but still somewhat higher than the experimentally observed values of Dyck and McClure for the singlet. However from the computed central double bond orders of the lower excited states of *trans*-stilbene, collected in

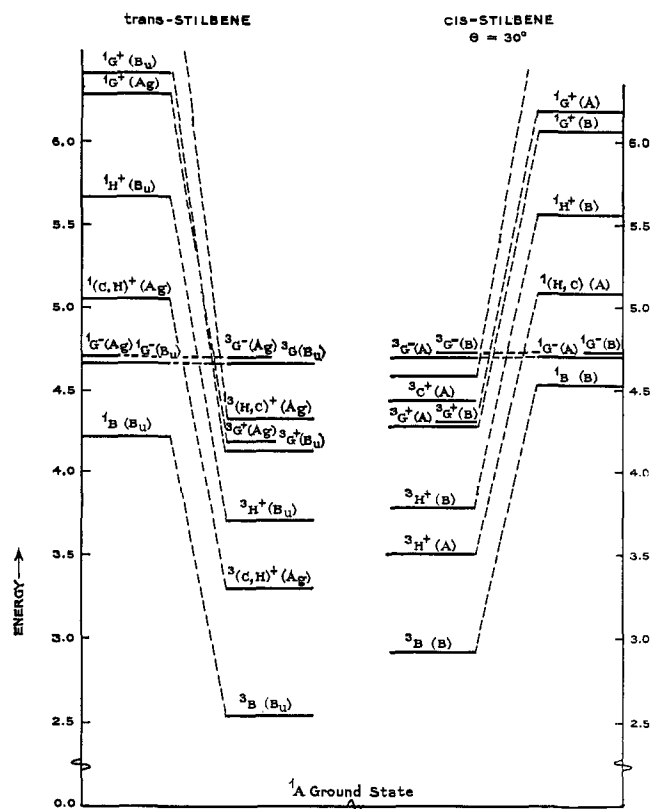


Figure 6. Term level diagrams for *cis*- and *trans*-stilbene.

cis-Stilbene. The interference of the *ortho* hydrogens in *cis*-stilbene causes a deviation from the completely planar conformation favored by the π electrons, and we assume this deviation occurs, as in *cis*-azobenzene, through a rotation of the phenyl rings about the essential single bonds linking the phenyls to the molecular bridge.

Table VI. Results of Computations on *cis*-Stilbene ($\theta = 30^\circ$)

State	Symmetry	$E, \text{e.v.}$	f	Polarization			Wt. % of most important spin configurations
				$\cos \alpha$	$\cos \beta$	$\cos \gamma$	
1B	B	4.594	0.364	-0.995	0.000	0.098	80.2 $^1\Phi_{7,8}$; 9.1 $^1\Phi_{4,11}$
$^1G^-$	A	4.729					28.3 $^1\Phi_{7,9}$; 28.3 $^1\Phi_{6,8}$; 27.9 $^1\Phi_{5,11}$; 17.9 $^1\Phi_{4,10}$
$^1G^-$	B	4.730					28.3 $^1\Phi_{7,10}$; 28.3 $^1\Phi_{5,8}$; 17.9 $^1\Phi_{6,11}$; 17.9 $^1\Phi_{4,9}$
$^1(C, H)^+$	A	5.118	0.035	0.000	1.000	0.000	22.3 $^1\Phi_{7,11}$; 22.3 $^1\Phi_{4,8}$; 23.4 $^1\Phi_{6,10}$; 23.4 $^1\Phi_{5,9}$
$^1H^+$	B	5.514	0.389	0.980	0.000	-0.199	7.90 $^1\Phi_{7,8}$; 33.9 $^1\Phi_{6,9}$; 33.9 $^1\Phi_{5,10}$; 7.78 $^1\Phi_{7,12}$
$^1G^+$	B	6.114	0.723	-0.766	0.000	-0.643	35.4 $^1\Phi_{7,10}$; 35.4 $^1\Phi_{5,8}$; 9.49 $^1\Phi_{6,11}$; 9.49 $^1\Phi_{4,9}$
$^1G^+$	A	6.166	0.279	0.000	-1.000	0.000	39.7 $^1\Phi_{7,9}$; 39.7 $^1\Phi_{6,8}$; 9.24 $^1\Phi_{5,11}$; 9.24 $^1\Phi_{4,10}$
3B	B	2.921					68.7 $^3\Phi_{7,8}$; 7.13 $^3\Phi_{2,12}$; 4.12 $^3\Phi_{4,11}$
$^3H^+$	A	3.501					34.4 $^3\Phi_{6,10}$; 34.4 $^3\Phi_{5,9}$; 10.8 $^3\Phi_{7,11}$; 10.8 $^3\Phi_{4,8}$
$^3H^+$	B	3.666					36.8 $^3\Phi_{6,9}$; 36.8 $^3\Phi_{5,10}$; 7.62 $^3\Phi_{7,12}$; 7.62 $^3\Phi_{3,8}$
$^3G^+$	A	4.279					27.4 $^3\Phi_{7,9}$; 27.4 $^3\Phi_{6,8}$; 18.6 $^3\Phi_{5,11}$; 18.6 $^3\Phi_{4,10}$
$^3G^+$	B	4.280					27.4 $^3\Phi_{7,10}$; 27.4 $^3\Phi_{5,8}$; 18.6 $^3\Phi_{6,11}$; 18.6 $^3\Phi_{4,9}$
$^3C^+$	A	4.417					29.8 $^3\Phi_{7,11}$; 29.8 $^3\Phi_{4,8}$; 14.7 $^3\Phi_{5,9}$; 14.7 $^3\Phi_{6,10}$
$^3C^+$	B	4.584					22.0 $^3\Phi_{7,12}$; 22.0 $^3\Phi_{8,8}$; 26.5 $^3\Phi_{4,11}$; 8.76 $^3\Phi_{6,9}$
$^3G^-$	A	4.729					28.3 $^3\Phi_{7,9}$; 28.3 $^3\Phi_{6,8}$; 17.9 $^3\Phi_{5,11}$; 17.9 $^3\Phi_{4,10}$
$^3G^-$	B	4.730					28.3 $^3\Phi_{7,10}$; 28.3 $^3\Phi_{5,8}$; 17.9 $^3\Phi_{6,11}$; 17.9 $^3\Phi_{4,9}$

Table V, it appears that the central double bond order of any of the other states which might be active in the photoisomerization is considerably higher than the lowest singlet and triplet. On this basis, the 1B and 3B states should still receive primary attention in considerations on the photoisomerization process.

Since the geometry of *cis*-stilbene is not known, calculations were performed first on a planar conformation, then on conformations in which the phenyl rings were rotated out of the molecular plane by 15, 30, and 45° in a "propeller" fashion, maintaining C_2 symmetry. The results of the four computations are presented in

Figure 5 as a function of θ , the angle between the phenyl rings and the xz plane.

The planar C_{2v} conformation, $\theta = 0$, does not give a satisfactory interpretation of the spectrum in solution. Of the nonplanar conformations, both $\theta = 15^\circ$ and $\theta = 30^\circ$ give a reasonable interpretation of the ultraviolet spectrum with essentially the same band assignments. The computed transition energies, oscillator strengths polarizations, and wave functions for $\theta = 30^\circ$ are collected in Table VI.

The main component of the A band in *cis*-stilbene is ${}^1B \leftarrow {}^1A$ and the main component of the B band is ${}^1H^+ \leftarrow {}^1A$, just as in the *trans* isomer. Again the *plus* state falls below the minus state for the 1H states, and an argument analogous to that presented for the *trans* isomer applies. A third band ${}^1G^+ \leftarrow {}^1A$ is indicated just above $200 m\mu$, but the spectrum of *cis*-stilbene has not yet been reported in this region. As in *trans*-stilbene a number of forbidden components appear, with the ${}^1G^- \leftarrow {}^1A$ transition likely to be the most intense. A summary of band assignments proposed for *cis*-stilbene is given in Table VII and term level diagrams indicating the correlation between the states of *trans*-stilbene and the states of *cis*-stilbene are presented in Figure 6.

A study of the spectrum of *cis*-stilbene in dibenzyl crystal¹⁸ indicates the 0-0 band of *cis*-stilbene lies at slightly lower energy than the *trans* isomer in the same phase. In dibenzyl crystal, *cis*-stilbene presumably

Table VII. Summary of Band Assignments for *cis*-Stilbene

Absorption region	Obsd. λ_{\max} ($m\mu$) ^a	Transition	Symmetry	Calcd. λ ($m\mu$)
A band	272	${}^1B \leftarrow {}^1A$	B	270 ^b
		${}^1G^- \leftarrow {}^1A$	A	263
		${}^1G^+ \leftarrow {}^1A$	B	262
		${}^1(H,C) \leftarrow {}^1A$	A	243
B band	219	${}^1H^+ \leftarrow {}^1A$	B	225 ^b
		${}^1G^+ \leftarrow {}^1A$	B	203 ^b
C band ?	...	${}^1G^+ \leftarrow {}^1A$	A	201

^a See ref. 7. ^b Principal allowed component.

would assume a nearly planar conformation. From Figure 5 it may be seen that the ${}^1B \leftarrow {}^1A$ transition energy for *cis*-stilbene at $\theta = 0^\circ$ and $\theta = 15^\circ$ is lower than the ${}^1B \leftarrow {}^1A$ transition energy for *trans*-stilbene and thus, although the calculation is not parametrized to give 0-0 transition energies, the trend is observed in accord with experimental results. For the conformation corresponding to $\theta = 30^\circ$, the energy of the ${}^1B \leftarrow {}^1A$ transition in *cis*-stilbene is greater than in *trans*-stilbene.

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The Vibrational Spectra and Structure of Cyclooctatetraeneiron Tricarbonyl¹

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The infrared ($4000\text{--}110\text{ cm.}^{-1}$) and Raman (up to 1650 cm.^{-1}) spectra of cyclooctatetraeneiron tricarbonyl are reported. The Raman spectra were excited by the rubidium resonance line at 7800 \AA . obtained from a radiofrequency-powered rubidium plasma arc. The spectra indicated a low symmetry (C_2) for the complex, with identical structures in the solid and solution states, and no free rotation between the hydrocarbon ring and the $Fe(CO)_3$ group. The results were also consistent with the presence of some π -electron delocalization in the uncoordinated part of the cyclooctatetraene ring system.

Introduction

Several structures based on a variety of physical and chemical evidence have been postulated for cyclooctatetraeneiron tricarbonyl, $(COT)Fe(CO)_3$.²⁻⁶ The pres-

ence of a single, sharp proton resonance in the nuclear magnetic resonance spectrum and the absence of a strong infrared absorption attributable to an olefinic $C=C$ stretching vibration were widely interpreted as strong evidence for a planar cyclooctatetraene (COT) ring in the complex. Chemical evidence, indicating the absence of free olefinic double bonds, also influenced workers toward this conclusion. Two molecular orbital calculations, based upon a planar configuration of the COT ring claimed to have rationalized the bonding in the complex.^{5,6} Recent X-ray diffraction data, however, clearly established that in the crystalline solid, at least, the $Fe(CO)_3$ group is bonded to the butadiene-like residue in the COT ring.⁷ The structure is shown in Figure 1. The dihedral COT ring lies in two planes, the angle between which is 41° . The $Fe(CO)_3$ group is associated with only one pair of conjugated double bonds, with the remaining

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