Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. V. Stilbene

By Hiroshi SUZUKI

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Previously[1] the present author explained successfully the hypsochromic shifts of the conjugation band observed in the ultraviolet absorption spectra of *cis*-stilbene and of some α-alkyl- and α, α'-dialkylstilbenes as compared with *trans*-stilbene by correlating those with the most probable spatial configurations of the molecules on the basis of the calculations by the simple LCAO molecular orbital method. Thus, he determined by his calculations the relation between the interplaner angle θ (that is, the angle through which the plane of each phenyl group rotates out of the plane of the central essentially double bond) and the electronic transition energy correspondinng to the conjugation band, and clarified the fact that the perfect coplanarity of the molecular configuration is not prerequisite to an occurrence of conjugation and hence not prerequisite to the appearance of the conjugation band and that the conjugation band is progressively shifted toward shorter wavelengths with increasing θ. He showed also that the value of the interplanar angle of a given compound of the type concerned can satisfactorily be computed from the position of the conjugation band and vice versa. Further, he showed that the earlier interpretations[2,3] of these hypsochromic shifts in terms of " partial chromophores " are to be rejected.

The calculations were carried out on the basis of the assumption that the absorption maximum at about 294 mμ in the spectrum of *trans*-stilbene in solution was due to the transition in the planar molecule of *trans*-stilbene. According to the X-ray crystal analysis by Robertson and Woodward[4], *trans*-stilbene in the crystalline state has a nearly planar or probably completely planar configuration. Strictly speaking, however, it seems that there is no evidence to indicate that the most probable configuration of *trans*-stilbene in solution is also planar. The observation by Wiegand and Merkel[5] that the absorption curve of *trans*-stilbene in solution is closely similar to that of 2-phenylindene in which one of the phenyl groups of *trans*-stilbene may be considered to be maintained in the coplanar or nearly coplanar position with the central ethylenic bond by the methylene bridge is somewhat interesting in this connection, but it should not be considered as a proof of the planarity of the whole configuration of *trans*-stilbene in solution. As already discussed in the first part[6] of this series, biphenyl is probably non-planar in solution, while it is known to be planar in the crystalline state. In view of this fact, the spectrum of *trans*-stilbene in solution should not be considered without sufficient consideration to be due to the planar molecule.

In this part of the series, the results of measurements of the spectra of *trans*-stilbene in various solvents and in the crystalline state carried out from these considerations are reported, and these spectra as well as the vapor spectrum of *trans*-stilbene are discussed with special emphasis on the relation of the spectra to the spatial configuration of the molecule.

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[1] H. Suzuki, This Bulletin, **25**, 145 (1952).
[2] R. N. Jones, *J. Am. Chem. Soc.*, **65**, 1818 (1943).
[3] E. A. Braude, *J. Chem. Soc.*, **1949**, 1902.
[4] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (*London*), **A162**, 568 (1937).
[5] C. Wiegand and E. Merkel, *Ann.*, **550**, 175 (1942).
[6] H. Suzuki, This Bulletin, **32**, 1340 (1959).

TABLE I. SOLUTION SPECTRA OF *trans*- AND *cis*-STILBENES

Solvent	A-band		B-band		$\varepsilon_\beta/\varepsilon_\gamma$
	λ_{max}, mμ	ε	λ_{max}, mμ	ε	
trans-Stilbene					
n-Heptane	α (320.5)	16000	(236)	10400	0.949
	β 306.9	26500	△228.5	16200	
	γ △294.1	27950	(222)	15500	
	δ (283)	24500			
Ethanol (95%)	α 321.0	16980	236	11150	0.977
	β 307.3	27200	△228.8	16400	
	γ △294.5	27850	222.5	15370	
	δ (284)	25200			
Methanol	α 319.5	17380	236.1	11200	0.975
	β 306.8	27350	△228.3	16500	
	γ △294.0	28050	(222)	15500	
	δ (283)	24150			
Chloroform	α (323.5)	16400			0.989
	β 309.9	27150			
	γ △297.9	27450			
	δ (286.5)	23200			
Carbon tetrachloride	α (324.5)	15500			0.988
	β 311.8	24750			
	γ △299.4	25050			
	δ (290)	22100			
Benzene	α (324.5)	15400			1.010
	β △311.2	25600			
	γ 298.8	25340			
	δ (289)	21700			
Mixed alcohols[7] (−130°C)	α 326.2	25000			1.711
	β 311.2	38500			
	γ 297.5	22500			
cis-Stilbene					
Ethanol (100%)[7]	280	10450	224	24400	

Wavelengths in parentheses denote inflections.
Symbol △ denotes the most intense maximum of the fine structure.

Further, on the basis of the results, the relation between the spectrum and the spatial configuration of *cis*-stilbene is discussed by application of the usual method.

Spectra of *trans*-Stilbene in Various States

Solution Spectra of *trans*-Stilbene.—Data of the spectra of *trans*-stilbene in various solvents measured at room temperature are given in Table I, in which data of the spectrum of *trans*-stilbene at low temperature as well as those of *cis*-stilbene measured by Beale and Roe[7] are also included for comparison. The notation of the absorption bands is according to Beale and Roe. The A-bands are considered to be the conjugation bands. In addition to the bands shown in Table I, the spectrum of *trans*-stilbene in *n*-heptane exhibits a band at about 201.5 mμ (ε=23900), and that in ethanol at about 201.0 mμ (ε=23800). These are termed the C–bands.

The absorption curves of the spectra of the *n*-heptane solution and of the benzene solution of *trans*-stilbene are shown in Fig. 1 as the representatives of the solution spectra of *trans*-stilbene. In Fig. 1 the curve of the spectrum of *cis*-stilbene is also shown for comparison. The spectra of *trans*-stilbene in the other solvents resemble that in *n*-heptane on the whole, although especially the A-α-band in the spectrum in carbon tetrachloride as well as in chloroform is somewhat more diffuse than in the spectra in *n*-heptane and in alcohols.

It is notable that th A-band has a fine structure. The somewhat similar pattern of fine structure is seen also in the B-band. Beale and Roe[7] have concluded that the fine structure originates in the stretching frequency of the ethylenic bond. On the

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[7] R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 1953, 2755.

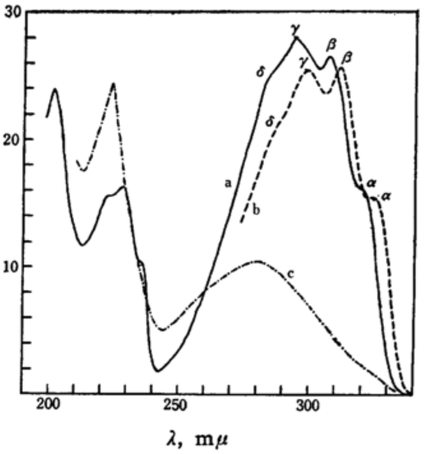

Fig. 1. Solution spectra of *trans*- and *cis*-stilbenes (cf. Table I).

a ——, *trans*-stilbene in *n*-heptane.
b ----, *trans*-stilbene in benzene.
c -·-·, *cis*-stilbene in ethanol.

other hand, in sharp contrast to *trans*-stilbene, *cis*-stilbene as well as α- and α, α'-substituted stilbenes which will be treated in a later part of this series shows no fine structure. These compounds are considered to be non-planar as will be shown later. Accordingly it would be expected that an appearance of fine structure might be related to the planarity of the molecular configuration or to its rigidity as the hypotheses proposed by Wiegand and Merkel[8] and by Kortüm and Dreesen[9]. However, such a relation has not yet been established.

In comparison with *n*-heptane, methanol exerts almost no, or a very small, hypsochromic effect, and ethanol exerts a small bathochromic effect. The magnitude of the bathochromic shift is considerably greater in chloroform, and is extraordinarily great in carbon tetrachloride as well as in benzene.

The great bathochromic effect of benzene may be especially noteworthy. According to Bayliss[10], a magnitude of wavelength displacement of a band of a nonpolar molecule by a nonpolar solvent is related to the refractivity of the solvent. The refractivity of benzene is slightly greater than that of *n*-heptane. However, it seems that the great bathochromic effect of benzene relative to *n*-heptane can not be attributed wholly to the difference of refractivity alone.

In this connection, it may be noted that the distribution of intensity among the vibrational bands of the A-band varies considerably with the solvent. The ratio of the intensity of the β-band to that of the γ-band for each solvent is listed in the last column of Table I. It is seen that the ratio increases in the order *n*-heptane < ethanol ≈ methanol < chloroform ≈ carbon tetrachloride < benzene. It may be noteworthy that while in solvents other than benzene the γ-band is the most intense maximum of the A-band, in benzene the β-band is the most intense maximum.

These facts appear to suggest the presence of a special interaction between the π-orbitals (or π-electrons) of the solute molecule and those of benzene. This problem will be discussed in somewhat greater detail in a later part of this series.

Solution Spectra of Some *p*-Substituted *trans*-Stilbenes. —The special solvent effect of benzene is seen also in the spectra of some *p*-substituted *trans*-stilbenes. The results of measurements of the spectra of *p*-methoxy-*trans*-stilbene and of *p*-nitro-*trans*-stilbene in *n*-heptane as well as in benzene are shown in Table II and Figs. 2 and 3. These spectra, especially those in *n*-heptane, bear a certain similarity in shape to that of *trans*-stilbene, showing similar patterns of fine structure. The magnitudes of the bathochromic displacements of the bands associated with the change of solvent from *n*-heptane to benzene are considerably

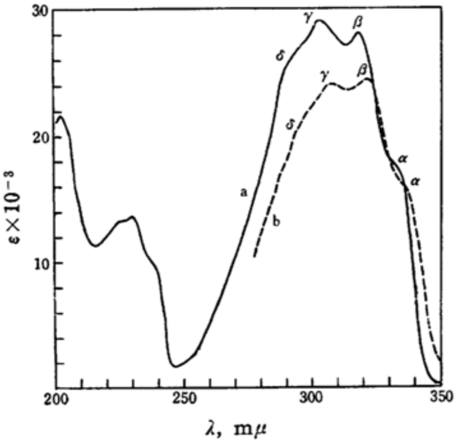

Fig. 2. Solution spectra of *p*-methoxy-*trans*-stilbene (cf. Table II).

a ——, in *n*-heptane.
b ----, in benzene.

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[8] (a) C. Wiegand and E. Merkel, *Ann.*, **557**, 242 (1947). (b) E. Merkel and C. Wiegand, *Naturwissenschaften*, **34**, 122 (1947). (c) E. Merkel and C. Wiegand, *Z. Naturforsch.*, **3b**, 93 (1948).

[9] G. Kortüm and G. Dreesen, *Chem. Ber.*, **84**, 182 (1951).

[10] N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

TABLE II. SOLUTION SPECTRA OF *p*-SUBSTITUTED *trans*-STILBENES

Solvent	A-band			B-band	
		$\lambda_{\max}$, mμ	ε	$\lambda_{\max}$, mμ	ε
p-Methoxy-trans-stilbene					
n-Heptane	α	(332.5)	17700	(238)	9830
	β	317.8	28100	△230.0	13600
	γ	△302.7	28950	(225)	13250
	δ	(291)	25800		
Benzene	α	(337)	15700		
	β	△322.0	24500		
	γ	307.7	24100		
	δ	(295.5)	21000		
p-Nitro-trans-stilbene					
n-Heptane	α	(363)	14200	262.0	7860
	β	△345.0	23820	△240.0	11760
	γ	332.0	23420	△233.7	11760
	δ	(318)	17850	(215)	13770
Benzene	(β)	△350.5	17420		

Wavelengths in parentheses denote inflections.
Symbol △ denotes the most intense maximum of the fine structure.

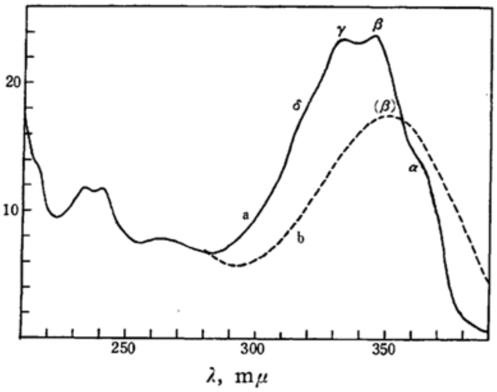

Fig. 3. Solution spectra of *p*-nitro-*trans*-stilbene (cf. Table II).
a ——, in *n*-heptane.
b ----, in benzene.

great (about 5 mμ) also with these compounds. Furthermore, in the spectra of *p*-methoxy-*trans*-stilbene a marked redistribution of intensity between the β-band and the γ-band occurs, quite similarly to the one observed in the spectra of *trans*-stilbene. It is also noteworthy that the fine structure of the A-band of *p*-nitro-*trans*-stilbene disappears almost completely in the spectrum in benzene.

Crystal Spectra of *trans*-Stilbene. — The spectrum of *trans*-stilbene in the crystalline state was measured by the pressed KCl-disk technique. The values of the molecular extinction coefficients were not reproducible and were considerably smaller than th corresponding values in the solution spectra. Thus, the former values varied from about 1/3 to about 1/30 of the latter ones from disk to disk. This fact may be considered to indicate the dependence of the extinction values on the condition of dispersion of the micro-crystals or the sizes of the micro-crystals, in view of the somewhat similar phenomenon observed by Weigl[11] in his study on the absorption spectra of some crystalline cationic dyes. In addition, this lowering of the extinction values may be partly due to the possible loss of the organic substance during grinding and evacuation of the press, as stated by Dale[12]. In spite of this, the reproducibility of the positions of the absorption maxima and inflections was almost completely satisfactory except for the α-band of the A-band. As representatives the results of measurements on the two disks of different thicknesses made from the same mixture (cf. *Experimental*) are shown in Table III and Fig. 4.

The crystal spectra differ considerably in the shape of the absorption curve from the solution spectra. In the crystal spectra the most intense maximum in the fine structure of the A-band is the δ-band, neither the γ-band as in the spectra in *n*-heptane etc., nor the β-band as in the spectrum in benzene. In this connection it may be of interest that in the solution spectrum measured by Beale and Roe[7] at low temperature (−130°C) the β-band is the most intense one, the fine structure being much more sharply resolved.

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[11] J. W. Weigl, ibid., **24**, 364 (1956).
[12] J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).

TABLE III. CRYSTAL SPECTRA OF *trans*-STILBENE MEASURED BY THE KCl-DISK TECHNIQUE

Disk*	A-band		B-band	
	λ_{max}, mμ	A	λ_{max}, mμ	A
(*a*)	α (327.5)	0.276	(241.5)	0.407
	β (312.5)	0.430	△233.0	0.478
	γ (298.5)	0.502	(225.5)	0.470
	δ △287.0	0.511		
	ε (276)	0.460		
(*b*)	α (332)	0.090	242	0.195
	β (313)	0.182	△233.5	0.216
	γ (298.5)	0.245	(225.5)	0.190
	δ △286	0.273		
	ε (276)	0.254		

* See *Experimental*.
Symbol A represents the absorbance.
Wavelengths in parentheses denote inflections.
Symbol △ denotes most intense maximum of fine structure.

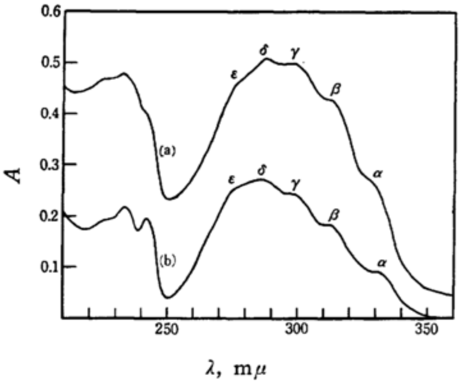

Fig. 4. Crystal spectra of *trans*-stilbene measured by the KCl-disk technique (cf. Table III).

The bands in the crystal spectrum are at longer wavelengths than the corresponding ones in the spectrum in *n*-heptane. The magnitude of the bathochromic shift is about 4.5 mμ for the γ-band and about 5.5 or 6 mμ for the β-band. These values probably corresponding to the "normal red-shift"[12] of the conjugation band are considerably smaller than those (about 8 mμ for the γ-band and about 9 mμ for the β-band) anticipated from the regular relation between the magnitude of the shift and the position of the band determined by Dale[12] for rigid molecules. This fact may be considered to indicate that the most probable spatial configuration of *trans*-stilbene in solution does not significantly differ from the one in the crystalline state and hence is planar or nearly planer.

Therefore, in order to infer the most probable spatial configurations of *cis*-stilbene and some related compounds of stilbene in solution by application of our method, the spectrum of *trans*-stilbene in *n*-heptane is taken as the spectrum of the planar reference compound, and the spectra of the *n*-heptane solutions are compared in principle as far as the data are available. In cases of absence of the data of the spectrum of the *n*-heptane solution, the data of the ethanol solution are used. As already mentioned, the spectra of *cis*-stilbene and the stilbene derivatives with substituents at the α- and α′-positions or at the ortho positions treated in this series all exhibit the structureless conjugation bands in contrast to that of *trans*-stilbene. Therefore, the question arises which maximum of fine structure of the conjugation band in the spectrum of *trans*-stilbene should be taken as the reference for the comparison. In the present treatment the γ-band at 294.1 mμ is tentatively chosen as the reference. This band is not only the most intense maximum of fine structure of the conjugation band in the spectrum of the *n*-heptane solution but also probably the central one.

Besides the above mentioned spectra by the pressed KCl-disk technique, the author attempted to measure the crystal spectrum of *trans*-stilbene also on thin films prepared on quartz plates by sublimation of crystals as well as by evaporation of a thin layer of solution, but these attempts were unsuccessful. Thus, the absorption curves obtained were very diffuse and indicated only indistinctly the presence of a band or bands at near 295∼335 mμ. This failure of revelation of the conjugation band is probably due to the effect of the orientation of the molecules in the crystals as discussed by Dale[12] in the case of biphenyl.

Pesteil⁽¹³⁾ measured the spectrum of *trans*-stilbene on thin crystal plates with polarized light and found a feeble band with two principal maxima at 367 and 387 mμ in addition to the stronger bands below 360 mμ. Jaffé and others⁽¹⁴⁾ have stated that it appears reasonable to assume this feeble band to be the singlet-triplet absorption. Brodin and others⁽¹⁵⁾ measured the spectrum of crystalline *trans*-stilbene at 20°K and found many vibrational frequencies.

Vapor Spectrum of *trans*-Stilbene.—According to Kanda⁽¹⁶⁾, the vapor spectrum of *trans*-stilbene prossesses a discontinuous band with nine maxima at the region from 284.4 to 265.6 mμ, of which the most intense maxima are at 284.4 and 283.4 mμ, and a discontinuous band with ten maxima at the region from 244.3 to 233.5 mμ, of which the most intense maximum is at 240.5 mμ. The former band may be considered to be the conjugation band, viz. the A-band, and the latter the B-band. It is noteworthy that the conjugation band in the vapor spectrum is at considerably shorter wavelengths than the corresponding one in the solution spectra as well as the crystal spectrum. This fact probably indicates that the most likely configuration of *trans*-stilbene in the vapor state deviates considerably from the coplanarity, analogously to biphenyl⁽⁶⁾.

Calculation

The relation between the spatial configurations and the electronic absorption spectra of stilbenes can be determined by the following calculations. The procedures of the calculations are the same in principle as the ones described previously⁽¹⁾. The description is given here in a somewhat more refined form as the basis for the treatments not only in the present part but also in the succeeding parts of this series.

Determination of the Parameters for the Resonance Integrals as Functions of the Bond Length and the Interplanar Angle.—The $\pi-\pi$ resonance integral for the central ethylenic bond, namely the $\alpha-\alpha'$ bond, is denoted by $\eta\beta$, and the one for the $\alpha-1$ bond as well as the $\alpha'-1'$ bond by $\rho\beta$. (Symbols α and γ in the previous paper were replaced by ρ and η, respectively). Symbol β represents the $\pi-\pi$ resonance integral for the C–C bond in the benzene ring, and η and ρ are parameters by which allowances are made for changes of the resonance integrals associated with changes of the bond length and the interplanar angle.

The length of the $\alpha-\alpha'$ bond in *trans*-stilbene was estimated at 1.33±0.04 Å by Robertson and Woodward⁽⁴⁾. The length of the C=C bond in ethylene was recently found to be 1.337 Å⁽¹⁷⁾, and the length of the "double" bonds in butadiene to be 1.337±0.005 Å⁽¹⁸⁾. Therefore, it may be presumed that the length of the ethylenic "double" bond does not significantly vary with the extent of conjugation. Hence the round value of 1.34 Å is taken as the length of the $\alpha-\alpha'$ bond in *trans*-stilbene as well as the related compounds throughout the present treatment. Consequently, the value of the parameter η is estimated at 1.080 from Mulliken's Tables⁽¹⁹⁾ on the basis of the approximate proportionality of the $\pi-\pi$ resonance integral for C–C bond to the $\pi-\pi$ overlap integral.

The parameter ρ can be expressed approximately by the following equation, quite analogously to Eq. 1 in the first part⁽⁶⁾ of this series;

$$\rho=S(R,\ 0^\circ)\cos\theta/S(1.39,\ 0^\circ) \qquad (1)$$

where $S(1.39, 0^\circ)$ represents the $\pi-\pi$ overlap integral for the C–C bond in the benzene ring and $S(R,\ 0^\circ)$ represents the one in the case where the bond length is R and the interplanar angle is 0°.

According to the result of the X-ray crystal analysis of *trans*-stilbene by Robertson and Woodward⁽⁴⁾, two molecules contribute to the asymmetric unit of the crystal, and these molecules have different appearances in the electron density maps. Thus, the length of the "single" bonds joining the phenyl groups to the ethylenic carbon atoms, namely the $\alpha-1$ and $\alpha'-1'$ bonds, and the interplanar angle were estimated at 1.44±0.02 Å and 3°, respectively, for one molecule and at 1.45±0.02 Å and 10°, respectively, for the other. Robertson and Woodward have, however, concluded that the apparent differences are due to the relative orientation of the

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13) (a) P. Pesteil, *Compt. rend.*, **233**, 377 (1951). (b) Idem., ibid., **233**, 924 (1951).

14) H. H. Jaffé, Si-Jung Yeh and R. W. Gardner, *J. Molecular Spectroscopy*, **2**, 120 (1958).

15) M. S. Brodin, O. S. Pakhomova and A. F. Prikhot'ko, *Optika i Spektroskopiya*, **5**, 123 (1958); *Chem. Abstr.*, **53**, 48 (1959).

16) Y. Kanda, *Mem. Faculty Sci., Kyushu Univ. Ser. C, Chem.*, **1**, 189 (1950).

17) (a) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **27**, 1414 (1957). (b) H. C. Allen and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2673 (1958). (c) J. M. Dowling and B. P. Stoicheff, *Bull. Am. Phys. Soc.*, **II3**, 373 (1958).

18) A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

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

molecules and not to any appreciable differences in their shape or dimensions, and that the molecules are nearly planar and may be exactly planar within the limits of experimental error.

Therefore, the values of θ (the interplanar angle) and of R (the length of the $\alpha-1$ bond) may safely be assumed in the present treatment to be 0° and 1.445 Å, respectively, in the configuration of *trans*-stilbene in the crystalline state and hence in the most probable configuration of the molecule in solution. Accordingly, the relation between θ and R is assumed as follows, quite analogously to Eq. 4 in Part I[6].

$$\{S(R,\ 0^\circ)-S(1.54,\ 0^\circ)\}/\{S(1.445,\ 0^\circ)-S(1.54,\ 0^\circ)\}=\cos\theta \qquad (2)$$

Then, from Eqs. 1 & 2 and Eq. 3 in Part I, one obtains

$$\rho=\cos\theta\times0.77108+\cos^2\theta\times(1.54-1.445)\times1.4458 \qquad (3)$$

which is quite analogous to Eq. 7 in Part I. Accordingly, the value of ρ is computed to be 0.9084 when θ is 0° and R is 1.445 Å. It is evident that the value of ρ becomes smaller with increasing θ and that it is 0 when θ is 90°.

Solution of the Secular Equation for the Determination of the Molecular Orbitals.— By solving the secular equation for the determination of the molecular orbitals as linear combinations of $2p\pi$ atomic orbitals, one can obtain the values of energies of the molecular orbitals corresponding to the value of the parameter ρ. Consequently, the values of the extra-resonance energy (subsequently referred to as *R.E.*), of the coefficients of the $2p\pi$ atomic orbitals in the molecular orbital functions, and of the quantities such as the π-bond orders corresponding to the molecular configuration prescribed by the value of ρ can also be obtained by the usual procedures.

The stilbene-type conjugated system can be considered as belonging to the symmetry group D_2 in the present treatment. Then, the highest occupied π-orbital (π_1) belongs to the representation B_1, and coincides with the φ_1 orbital in benzene when ρ is 0. On the other hand, the lowest vacant π-orbital (π_1*) belongs to B_3, and coincides with the φ_2 orbital in benzene when ρ is 0. (The notation for orbitals in benzene is according to Sklar[20].) Transitions from orbitals belonging to B_1 to those belonging to B_3 are allowed by absorption of light polarized along the direction of the long axis of the molecule. Accordingly, the energy difference between the lowest vacant orbital π_1* and the highest occupied orbital π_1 (referred to as ΔE_A) is considered to be the transition energy corresponding to the conjugation band (viz. the A-band). The value of ΔE_A (in $-\beta$) is, of course, twice the absolute value of the enegy (in $-\beta$) of one of the two orbitals.

In addition to the ten orbitals belonging to B_1 and B_3, whose energies vary with ρ (cf. Fig. 2 in Ref. 1), there are two sets of doubly degenerate orbitals belonging to A_1 and B_2, whose energies do not vary with ρ. These orbitals may be considered as ones localized in the benzene rings. Thus, one (φ) of the two orbitals belonging to either A_1 or B_2 has the energy of $+\beta$ and corresponds to the φ_{-1} orbital in benzene, while the other orbital (φ*) has the energy of $-\beta$ and corresponds to the φ_{-2} orbital in benzene. Transitions from the π_1 orbital (B_1) to the φ* orbital belonging to B_2 or from the φ orbital belonging to A_1 to the π_1* orbital (B_3) are allowed by absorption of light polarized along the direction of the short-axis of the molecule. These transitions may be considered as corresponding to the B-band, as suggested by Dale[21]. The value of the corresponding transition energy $\Delta E_B(-\beta)$ can evidently be expressed as $1+\Delta E_A(-\beta)/2$.

Transitions between the orbitals belonging to A_1 and those belonging to B_2 are allowed by absorption of light polarized along the direction of the long-axis of the molecule, and correspond probably to the C-band at about 200 mμ.

The results of the calculations are summarized in Table IV. In this table, $\Delta E_A(-\beta)$ and *R.E.*$(-\beta)$ are values obtained by ignoring the $\pi-\pi$ overlap integral, and $\Delta E_A(-\gamma)$ and *R.E.*$(-\gamma)$ are values obtained by taking the overlap integral into account, assuming the value of the overlap integral for the C–C bond in benzene as 0.25. The symbols $p_{\alpha-\alpha'}$ and $p_{\alpha-1}$ represent the π-bond orders of the $\alpha-\alpha'$ bond and of the $\alpha-1$ as well as the $\alpha'-1'$ bond, respectively.

It is evident that the values of ΔE_A and hence of ΔE_B increase with decreasing ρ and agree with the values for benzene when ρ is 0. This means that A-band as well as the B-bond is gradually shifted toward shorter wavelengths as the value

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[20] A. L. Sklar, ibid., 7, 984 (1939).

[21] J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957).

TABLE IV

ρ	1.1	1.0	0.9	0.8	0.7	0.6
$\Delta E_{\mathrm{A}}(-\beta)$	0.9920	1.0680	1.1492	1.2352	1.3262	1.4216
$\Delta E_{\mathrm{A}}(-\gamma)$	1.0075	1.0874	1.1734	1.2654	1.3637	1.4679
$R.E.(-\beta)$	1.0252	0.8500	0.6904	0.5464	0.4190	0.3084
$R.E.(-\gamma)$	0.3532	0.2922	0.2368	0.1870	0.1432	0.1048
$p_{\alpha-\alpha'}$		(0.829)	0.858	0.8865	0.912	0.934
$p_{\alpha-1}$		(0.423)	0.381	0.340	0.298	0.255

ρ	0.5	0.4	0.3	0.2	0.1	0
$\Delta E_{\mathrm{A}}(-\beta)$	1.5212	1.6246	1.7306	1.8376	1.9398	2
$\Delta E_{\mathrm{A}}(-\gamma)$	1.5783	1.6945	1.8156	1.9400	2.0610	2.1333
$R.E.(-\beta)$	0.2140	0.1372	0.0772	0.0342	0.0084	0
$R.E.(-\gamma)$	0.0726	0.0466	0.0262	0.0118	0.0028	0
$p_{\alpha-\alpha'}$	0.954	(0.9705)				1
$p_{\alpha-1}$	0.213	(0.170)	(0.1275)	(0.085)	(0.0425)	0

The values of the π-bond orders in parentheses were obtained by either interpolation or extrapolation.

TABLE V

Stilbene	λ_{A} mμ	ν_{A} cm^{-1}	ΔE_{A} $-\beta$	ρ	$\theta°$	R Å	$R.E.$ $-\beta$	$p_{\alpha-1}$	$p_{\alpha-\alpha'}$
trans-	294.1	34002	1.1423	0.9084	0	1.445	0.704	0.384	0.8555
cis-	280	35714	1.247	0.787	28	1.456	0.530	0.333	0.890

ρ decreases and therefore as the value of θ increases, and that these bands will coincide with those of benzene when ρ is 0 and therefore when θ is 90°.

It appears that there is no simple quantitative relation between ρ and ΔE_{A}, or between ΔE_{A} and $R.E.$ On the other hand, $R.E.(-\beta)$ is almost completely proportional to ρ^2 and can approximately be expressed as $0.8473\times\rho^2$. In addition, $p_{\alpha-1}$ is roughly proportional to ρ and can roughly be expressed as $0.425\times\rho$.

Correlation of the Calculated Transition Energy with the Observed Position of the Conjugation Band.—The value of ρ when θ is 0° and R is 1.445 Å is 0.9084, and the corresponding value of ΔE_{A} is $1.1423(-\beta)$, which is subsequently referred to as ΔE_{L}. The value of the wave number corresponding to ΔE_{L}, namely ν_{L}, is assumed to be 34002 cm^{-1} (294.1 mμ) which is the wave number of the A-γ-band in the spectrum of *trans*-stilbene in *n*-heptane, on the basis of the considerations mentioned already.

On the other hand, the value of ΔE_{A} when ρ is 0, namely ΔE_{S}, is $2(-\beta)$, and the corresponding value of the wave number, namely ν_{S}, is assumed to be 48000 cm^{-1} (208.3 mμ), the center of gravity of singlets of benzene, as usual.

Then, the value of ΔE_{A} $(-\beta)$ for a given compound of the stilbene-type is obtained from the observed position (ν_{A} in wave number) of the conjugation band by Eq. 8 in the first part[6] of this series. Consequently, the corresponding value of the parameter ρ and then the values of θ, $R.E.$, p, etc. can be obtained in turn.

Spectrum of *cis*-Stilbene

The solution spectrum of *cis*-stilbene (cf. Table I and Fig. 1 and also Refs. 1 and 7) differs considerably from that of the *trans*-isomer. The conjugation band (A-band) in the former is structureless in contrast to the one in the latter, and at a considerably shorter wavelength and of lower intensity than the one in the latter. This hypsochromic shift of the band is explained as being due to the non-planarity of the most probable configuration of *cis*-stilbene. The B-band of *cis*-stilbene is also structureless and at a shorter wavelength than the corresponding band of the *trans*-isomer, while the former is more intense than the latter.

Application of Calculation and Discussion

Data of the spectrum of the *n*-heptane solution of *cis*-stilbene are not available. Hence, the position of the conjugation band (280 mμ) in the spectrum of the ethanol solution is used as the basis of calculation for *cis*-stilbene, since the solvent effect of ethanol on the position of the band is considered not to differ significantly from that of *n*-heptane on the analogy of the observation in the case of *trans*-stilbene. The results of application of the calculations to *cis*- and *trans*-stilbenes are shown in Table V.

The value of about 28° for the interplanar angles in *cis*-stilbene is in fairly good agreement with the value of about 25° estimated from the scale model[1].

At these values of the interplanar angles the steric repulsion between the two phenyl groups may be almost completely relieved. The difference between the stabilities of the isomers may be considered as the sum of the difference of extra-resonance (stabilization) energy and the difference of steric repulsion (destabilization) energy. If it is assumed that the difference of steric repulsion energy is small in the most probable configurations of the two isomers, the difference of stability is ascribed mainly to the difference of extra-resonance energy. When the value of $-\beta$ is tentatively assumed as 20 kcal./mol., the extra-resonance energy in *trans*-stilbene is evaluated as 14.07 kcal./mol. and that in the *cis*-isomer as 10.60 kcal./mol. The former value agrees fairly well with the value of 15 kcal./mol.[22] estimated from the heat of formation as well as the value of 12.5 kcal./mol.[23] estimated from the heat of hydrogenation[24], although the estimations of resonance energy, in general, do not seem to be entirely free from ambiguity. The difference between the extra-resonance energies of the two isomers is evaluated as about 3.5 kcal./mol. This value is also in satisfactory agreement with the experimental value of the energy difference between the isomers, 3 kcal./mol., estimated from the equilibrium of the thermal isomerization by Kistiakowsky and Smith[25] and by Taylor and Murray[26].

With a view to explaining the fact that the conjugation band of *cis*-stilbene is at a shorter wavelength and is of lower intensity than the corresponding one of the *trans*-isomer, Braude and other[27] have stated as follows: "Assuming that the wavelength shift of 150 Å from *trans*- to *cis*-stilbene is wholly due to steric hindrance, the differential de-stabilization amounts to about 6 kcal./mol., a value remarkably close to the resonance energy of *trans*-stilbene". That is, it seems that they have attempted to correlate the shift with the resonance energy or/and the steric repulsion energy. However, as already mentioned, there is no direct relation between the resonance energy and the electronic transition energy. And further, as mentioned in the earlier parts[6,28] of this series, there is also no direct relation between the steric repulsion energy and the transition energy. It seems evident that Braude and other's attempt was unsuccessful.

The values of $\Delta E_{\mathrm{B}}(-\beta)$ for *trans*- and *cis*-stilbenes are estimated at 1.571 and 1.624, respectively. From these values the B-bands of these compounds are expected to be at 41001 cm^{-1} (243.9 mμ) and 41864 cm^{-1} (238.9 mμ), respectively, by application of the relation between ΔE and ν postulated above originally for the A-band. Considering the approximation used, it may be said that the agreement between these expected positions and the observed positions of the B-bands is nearly perfect.

Experimental

Measurements of Spectra. — All the spectra were measured with a Cary recording spectrophotometer Model 14 M-50.

The crystal spectra of *trans*-stilbene were measured by the pressed KCl-disk technique described by Dale[12]. The potassium chloride used had been precipitated from water solution with hydrochloric acid to obtain small particle size and dried at 400 to 450°C for about 6 hr., according to Hales and Kynaston[29]. As an example of the procedures of the preparation of the mixtures, that for the disks on which the spectra shown in Fig. 4 as well as Table III were measured will be described below. About 3.5 mg. of pure *trans*-stilbene was thoroughly ground in an agate mortar with about 200 mg. of potassium chloride. About 10.5 mg. of the mixture was then ground with about 350 mg. of potassium chloride, and pressed under vacuum in the usual manner into transparent disks (a radius, 0.65 cm.). The disk (a) weighed 140.4 mg. (the thickness, about 0.532 mm.), and the disk (b) weighed 111.1 mg. (the thickness, about 0.421 mm.).

Preparations of *p*-Substituted *trans*-Stilbenes.— *p*-Methoxy-*trans*-stilbene was prepared by the

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[22] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

[23] M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4016 (1957).

[24] G. W. Wheland, "Resonance in Organic Chemistry", John Wiley & Sons, Inc., New York (1955), p. 80.

[25] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934).

[26] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, **1938**, 2078.

[27] W. Klyne (Ed.), "Progress in Stereochemistry", Vol. 1, Butterworths Scientific Publications, London (1954), p. 131, (E. A. Braude and E. S. Waight).

[28] H. Suzuki, This Bulletin, **32**, 1350 (1959).

[29] J. L. Hales and W. Kynaston, *Analyst*, **79**, 702 (1954).

Meerwein reaction[30] after the procedure of the preparation of *p*-methoxycarbonyl-*trans*-stilbene described by Fuson and Cooke[31]. The diazonium salt of *p*-anisidine was prepared by adding dropwise a solution of 27 g. of sodium nitrite in 45 ml. of water to a mixture of 150 ml. of 25% hydrochloric acid, 46.2 g. of *p*-anisidine, and 150 g. of ice. Throughout this experiment the reaction mixture was well stirred. An ice bath was placed around the reaction flask and 91.8 g. of crystalline sodium acetate was added. A solution of 55.5 g. of cinnamic acid in 450 ml. of acetone was added and the ice bath was removed. Five minutes later a solution of 20.3 g. of cupric chloride in 45 ml. of water was added dropwise and the mixture was stirred for about two hours at room temperature. After removal of a large amount of acetone, the residue was extracted with benzene. The benzene solution was washed in turn with a dilute solution of sodium carbonate, with dilute hydrochloric acid, and with water, and then dried on calcium chloride. After removal of the solvent, about 33 g. of a dark brown solid product was obtained. Treatment of the crude product with activated charcoal and repeated recrystallization from ethanol gave 23 g. of white crystals of *p*-methoxy-*trans*-stilbene, m.p. 136.8~137.5°C; yield, 29.2%.

p-Nitro-*trans*-stilbene was prepared from *p*-nitroaniline by the Meerwein reaction, quite analogously to the synthesis of the methoxy-analogue mentioned above. The purified product, yellow crystals, melted at 156~157°C; yield, about 15%.

Summary

(1) The quantitative relations between the degree of deviation from the coplanarity of the molecular configuration and the ultraviolet absorption spectrum as well as the quantities such as the extra-resonance energy and the π-bond orders have been determined for the stilbene-type compounds by calculations based on the simple LCAO molecular orbital method.

(2) The ultraviolet absorption spectra of *trans*-stilbene in the crystalline state, in the solution state, and in the vapor state have been discussed in reference to the spatial configurations of the molecule in the various states. The conjugation band in the vapor spectrum is at considerably shorter wavelengths than that in the solution spectra as well as the crystal spectra, a fact which has been considered as probably indicating that the most likely configuration of the molecule in the vapor state deviates considerably from coplanarity. The magnitude of the red-shift of the conjugation band in the crystal spectra measured by the pressed KCl-disk technique relative to the band in the spectrum of the *n*-heptane solution has been found to be smaller than the value anticipated for the rigid molecule. From this fact it has been inferred that the most probable configuration of *trans*-stilbene in solution does not significantly differ from the one in the crystalline state and is planar or nearly planar.

(3) On the basis of the above inference, the calculations have been applied to *cis*- and *trans*-stilbenes, and the interplanar angles in the most probable configuration of *cis*-stilbene have been estimated at about 28° from the position of the conjugation band, in fairly good agreement with the value estimated from the scale model. The results of the calculations have been discussed.

(4) In addition, the solvent effects of various solvents on the spectra of *trans*-stilbene and its *p*-methoxy- and *p*-nitro-derivatives have been discussed with special reference to the effect of benzene which has been found to cause a large bathochromic displacement of the conjugation band and a remarkable redistribution of intensity among the vibrational bands of the conjugation band of each compound.

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Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo

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[30] H. Meerwein, E. Buchner and K. van Emster, *J. prakt. Chem.*, **152**, 237 (1939); *Chem. Abstr.*, **33**, 6261. See also: F. Bergmann et al., *J. Org. Chem.*, **6**, 134 (1941); **9**, 408, 415 (1944); **12**, 57 (1947).

[31] R. C. Fuson and H. G. Cooke, Jr., *J. Am. Chem. Soc.*, **62**, 1180 (1940).