554. *Ultra-violet Absorption Spectra of* trans- *and* cis-*Stilbenes and Their Derivatives. Part I.* trans- *and* cis-*Stilbenes.*

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The ultra-violet absorption spectra of solutions of *trans*- and *cis*-stilbene have been measured at room temperature and of *trans*-stilbene at −130°. The results for *trans*-stilbene have been compared with recent semi-theoretical calculations of ν- and *f*-values, which employ LCAO MO methods or the free-electron model or regard the molecule as a system of coupled harmonic oscillators. This comparison reveals that good prediction of ν may be achieved, while predicted *f*-values deviate by amounts up to 100% from the observed figure. Possible explanations are given for the considerable spectral changes in *trans*-stilbene on refrigeration.

Earlier investigations of certain basic derivatives of *trans*-stilbene, some of which are tumour-inhibitory and carcinogenic, revealed a correlation between biological effects and molecular shape, the latter property being reflected in the near-ultra-violet absorption spectra of the compounds considered (Haddow, Harris, Kon, and Roe, *Phil. Trans.*, *A*, 1948, **241**, 147; see also Beale and Roe, *J. Amer. Chem. Soc.*, 1952, **74**, 2302). In order to classify in greater detail the effects of the type and position of substitution on the frequency and intensity of this absorption, a larger series of stilbene derivatives has been examined. For an interpretation of their spectra, an understanding of the mechanism of ultra-violet absorption in *trans-* and *cis*-stilbene is of fundamental importance and our first study is concerned therefore with the experimental results for these two compounds and with a discussion of theoretical predictions and interpretations of the spectroscopic data.

Ultra-violet Absorption in trans-*Stilbene.*—Since the earliest published spectrum of *trans*-stilbene (Baly and Tuck, *J.*, 1908, **93**, 1909) interpretation of its near-ultra-violet absorption bands in terms of the chromophores responsible for absorption has been attempted by a number of investigators. Among these, Stobbe and Ebert (*Ber.*, 1911, **44**, 1289) noted the stronger, lower-frequency absorption in stilbene and tolane compared with diphenylmethane. Ley (*Ber.*, 1917, **50**, 243; 1918, **51**, 1817), who had observed the changes in frequency and extinction which occur with substitution at the stilbene α-carbon atom, attributed the long-wave-length band first (*loc. cit.*, 1917) to the ·C═C· chromophore and later (1918) to a chromophore comprising either the complete molecule or the styrene portion thereof. Arends (*Ber.*, 1931, **64**, 1936), comparing the spectra of stilbene and styrene, assigned the stilbene long-wave-length band at 294 mμ to the Ph·C═C· chromophore which in styrene gives rise to the band at 244 mμ. The 210-mμ stilbene band he attributed to the benzene chromophore, but neglected to assign the band in the 226-mμ region. The measurements by Smakula and Wasserman (*Z. physikal. Chem.*, 1931, **155**, *A*, 353) and Smakula (*ibid.*, 1934, **25**, *B*, 90) indicated the presence of vibrational fine structure in *trans*-stilbene's long-wave-length band, and this, together with Hausser's data (*Z. tech. Physik*, 1934, **15**, 10) on fine-structure frequency differences in the higher diphenylpolyenes (where these differences, of the order of 1500 cm.$^{-1}$, were correlated with the Raman frequency of 1600 cm.$^{-1}$), was regarded as evidence that this band is due to an excitation involving the ethylenic double bond.

Recent Experimental and Theoretical Work.—More recent semi-theoretical investigations of the spectra of stilbene and related polyenes have been concerned with the prediction of band frequencies and intensities (Mulliken and Rieke, *Rept. Progr. Phys.*, 1941, **8**, 231; Bayliss, *J. Chem. Phys.*, 1948, **16**, 287; W. Kuhn, *Helv. Chim. Acta*, 1948, **31**, 1780; H. Kuhn, *J. Chem. Phys.*, 1949, **17**, 1198; Dewar, *J.*, 1952, 3544). It is of interest to compare these values with the experimental data, and since the detail reported in the literature for the spectra of *trans-* and *cis*-stilbene varies considerably, both high- and low-wave-length bands have been re-examined. Our experimental results are shown in the Figure.

The broad high-wave-length band (subsequently called the A-band) in *trans*-stilbene can be further sub-divided into three bands, two with maxima at 307·5 and 295·5 mμ and a third, submerged band at 321 mμ. The low-wave-length band (subsequently called the B-band) is of about half the intensity of A (measured as $f = 4{\cdot}315 \times 10^{-9}\int \varepsilon d\nu$, where ν is in cm.$^{-1}$ and ε is the molar extinction coefficient), but it has a closely similar pattern of structure, with submerged bands at 236 * and 222 mμ * and a maximum at 228·5 mμ. The Table summarises these spectral data. Thus, at 20° the A-band structure in *trans*-stilbene shows frequency separations of ~1340 cm.$^{-1}$ (in ethanol, hexane, glycerol, and Perspex solutions) which become 1480 cm.$^{-1}$ at −130° (in mixed alcohols). The differences between these values may not be significant, since broadening and overlap of vibrational peaks at room temperatures would tend, in any case, to reduce their frequency intervals. In the B-band at 20° the frequency separations are also ~1340 cm.$^{-1}$ (in ethanol, hexane, and glycerol); for technical reasons (see Experimental section) a value at low temperatures could not be obtained. Comparison with the most recently published spectrum of *trans*-stilbene (Calvin and Alter, *J. Chem. Phys.*, 1951, **19**, 765; A-band only) at room temperature in ethanol solution shows agreement for the extinction of the 295·5-mμ maximum; Calvin and Alter's measurements were made at larger wave-length intervals and so revealed a shoulder rather than a maximum at 307·5 mμ. This is also the case in Smakula and Wasserman's curve (*loc. cit.*) where extinction values (corrected for their definition of

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* See note in Table.

extinction coefficient by a factor $1/2{\cdot}3 \times 10^3$) are ~7% lower than those reported here for both A- and B-bands, owing probably to a difference in concentration (or some other experimental detail) rather than to isomerisation, which changes the extinctions of A- and B-bands in opposite directions.

Ultra-violet absorption spectra of trans- *and* cis-*stilbene.*

		A-band		B-band		
Compound	Temp.	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε	Solvent
trans-Stilbene	~20°	(321) *	(~17,600)	(236)	(~11,100)	95% EtOH
		307·5	28,300	228·5	16,400	
		295·5	29,000	(222)	(~14,900)	
trans-Stilbene	~20	(320)	(~16,600)	(236)	(~11,000)	Hexane
		307	27,300	228·5	17,200	
		294	29,100	(222)	(~16,000)	
trans-Stilbene	−130	326·2	25,000	—	—	Mixed alcohols †
		311·2	38,500			
		297·5	22,500			
cis-Stilbene	~20	280	10,450	224	24,400	100% EtOH

* Figures in parentheses denote the estimated maxima of submerged bands.
† Mixture of 80% EtOH, 10% MeOH, and 10% $\text{Pr}^{\text{i}}\text{OH}$.

From these results, it is reasonable to conclude, with Smakula and Hausser and their colleagues, that the vibrational fine structure in the A-band originates in an ethylenic C═C stretching frequency. The results of Coulson and Jacobs (*J.*, 1949, 1983) show that the C═C bond undergoes the largest change in bond-order on excitation of the molecule, and thus the greatest change in amplitude of vibration. As a result the A-band fine structure should show the C═C vibrational frequency more strongly than any other. The similar pattern of fine structure and the same approximate Δν-value in the B-band suggest the same origin for the fine structure also. The detailed characteristics of this band will be discussed in a later publication.

The experimental data may now be compared with recent predicted f- and ν-values for the A-band, and it may be noted that Ley's suggestion (*loc. cit.*, 1918) that this band originates in an electronic transition involving the complete molecule is supported by this recent work. In Mulliken and Rieke's investigations (*loc. cit.*) conventional LCAO MO theory was used and the equation derived for the intensity of an absorption band in terms of oscillator strength f was :

$$f = 1{\cdot}085 \times 10^{11}\nu D \qquad (1)$$

where D is the dipole strength of a transition between two electronic states with orbital wave functions ψ_k and ψ_l. Further :

$$D = GQ^2 \qquad (2)$$

where

$$Q = \int \psi_k(\Sigma_i r_i)\psi_l \mathrm{d}\tau \qquad (3)$$

and G is a numerical factor to allow for degeneracy of levels; r_i is the radius vector of the ith electron referred to real co-ordinate axes fixed in the molecule. These authors showed that *trans*-stilbene's A-band, due to an N–V transition (Mulliken, *J. Chem. Phys.*, 1939, **7**, 14 *et seq.*), should be the strongest of their four calculated transitions and contain the major part of the spectral intensity. Their semi-theoretical f-value for the band is 0·55 (a correction factor * of 0·34 is used for this molecule). The authors compare this figure with their value calculated from the experimental data of Lewis, Magel, and Lipkin (*J. Amer. Chem. Soc.*, 1940, **62**, 2973), and the resulting $f = 0{\cdot}67$ is in good agreement with semi-theoretical computation. These experimental data are obtained, however, at −90° (*iso*octane solution), under which condition the extinction and f-value are reduced below those at room temperature, as shown later in this discussion.

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* Such a factor has been shown recently (Coulson *et al.*, *Proc. Roy. Soc.*, 1951, *A*, **206**, 287, 297) to be necessitated by neglect of configuration interaction in simple MO theory, and when this is included much better agreement between theory and experiment is obtained; *e.g.*, for butadiene, $f_{\text{theor.}} = 0{\cdot}6$, and $f_{\text{calc.}} = 0{\cdot}53$. Configuration interaction is even more important in LCAO predictions for "round-field" molecules such as benzene, coronene, etc., than for "long-field" polyenes, styrene, etc. (Platt, *J. Chem. Phys.* 1950, **18**, 1168).

Bayliss's calculation (*loc. cit.*), on the other hand, assumed for the conjugated polyenes a metallic model in which the π-electrons are " 100% mobile " and subject to a potential-energy field due to the chain of $-CH=$ groups; *i.e.*, the problem was treated as that of an electron gas in a field of uniform potential. This leads to the equation :

$$f \simeq 0{\cdot}134(2N + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where N is the number of double bonds in the molecule. For diphenylbutadiene, Bayliss assumes a contribution of one double bond for the two phenyl groups, and if the same assumption be made for *trans*-stilbene the calculated f-value is 0·67. With the more usual equivalent of 1·5 double bonds for each phenyl group the calculated f-value is 1·21. Frequency calculations, on Bayliss's assumption, depend not only on N but also on X, the overall length of the potential field, and are very sensitive to this value. It is difficult to decide a value for X; *e.g.*, in the diphenylpolyenes, good agreement with experimental ν-values is found if X is assumed to be considerably shorter than the overall length of the molecule, and if the phenyl groups contribute, as before, only one double bond to the conjugated system. Bayliss himself points out the weaknesses of the method, namely, the difficulty of deciding a value for X, and the assumption of a uniform potential field and infinite ionisation energy.

This model has been modified by H. Kuhn (*loc. cit.*) for the case of the polyenes, by placing the π-electrons in a one-dimensional potential field having a sinusoidal periodicity. The maximum wave-length of the long-wave-length system is then given by

$$\lambda_1 = \frac{1{\cdot}23 \times 10^4}{18{\cdot}8\,(2j' + 1)^{-1} + V_0(1 - (2j')^{-1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where j' = number of conjugated double bonds and V_0 = amplitude of the sine-shaped potential along the chain, taken as 2 ev for the polyenes. Thus only one experimentally determined parameter is used and this (V_0) is chosen arbitrarily to be twice the value obtained experimentally for the anhydro-bases of the symmetrical cyanine dyes. Good agreement with experimental λ-values is found and, by using equation (5) with $j' = 1{\cdot}5$ double bonds for phenyl, the calculated λ_1 is 320 mμ for stilbene. Kuhn does not discuss the f-values of the polyenes.

Reasonable values of the right order for both f and λ in polyenes have been obtained by W. Kuhn (*loc. cit.*) who regards such linear molecules as systems of coupled harmonic oscillators in a variable potential field. Energy levels were obtained into which were fitted all the π-electrons of the system. The method was more satisfactory than that of Lewis and Calvin (*Chem. Reviews*, 1939, **25**, 273) who took the lowest level of an imaginary harmonic oscillator as the ground state and the first excited level as a molecularly excited state and so treated the molecule as having but one mobile electron. From Kuhn's calculations, the value for the coupling coefficients is so large that an increase of 10% would lead to free mobility of electrons along the chain, as is assumed in Bayliss's model. The following semi-theoretical expressions are derived :

$$\lambda_1 = \lambda_0/\sqrt{1 - 2\alpha\cos[\pi/(n + 1)]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where λ_1 = wave-length of maximum absorption for the longest-wave-length transition of the polyene, λ_0 = 157 mμ, as for the isolated double bond in ethylene, and n = the number of double bonds in the molecule. The constant α cannot be determined theoretically, but is calculated from the experimental data for the polyene with $n = 14$ and λ_1 = 500 mμ. Then α is found to be 0·461. Again, for the longest-wave-length band :

$$f_1 = 0{\cdot}811 f_0 n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $f_0 = 0{\cdot}22$, for the corresponding ethylene band at 157 mμ. If one assumes with Kuhn (cf. Hausser, *loc. cit.*, 1934) a value of 1·5 double bonds for phenyl, calculation (equation 6) shows that the longest-wave-length band in *trans*-stilbene should occur at 311·5 mμ. When a recent value for λ_0, *i.e.*, 163 mμ (Platt, Klevens, and Price, *J. Chem. Phys.*, 1949, **17**, 466), is used the predicted λ_1 for *trans*-stilbene becomes 319 mμ. Strictly, comparison should be made between calculated and observed values for the 0–0 band of the long-wave-length transition. In fact, Kuhn's parameter α is obtained by the use of the experimental datum $\lambda_1 = 500$ mμ for the polyene with $n = 14$, and this wave-length corresponds with the longest-wave-length vibrational peak in the spectrum (corrected for solvent shift from hexane to benzene from the data of Hausser *et al.*, *Z. physikal. Chem.*, 1935, **29**, *B*, 442), and not with that of the centre of the system. The author is using, therefore, to obtain one parameter, a wave-length very near the O–O line, and in his comparison of calculated λ_1-values [from (6)] with the observed data he has referred, again, to the longest-wave-length vibrational bands in the spectra of a number of substituted polyenes showing fine structure. The O–O line in *trans*-stilbene would be that included in the shoulder at 321 mμ at room temperatures and in the separated band at 326 mμ at −130°. More accurately it will be at some wave-length longer than this if the contribution of low-energy molecular deformations could be eliminated (Mulliken, *J. Chem. Phys.*, 1939, **7**, 372). Since the O–O line should be located between the first absorption peak and the first fluorescence peak in the polyenes and the " tails " of these bands overlap in *trans*-stilbene, the O–O transition is found by inspection to occur at about 330 mμ (data of Hausser *et al.*, *loc. cit.*, 1935, pp. 397, 435). Application of Brodersen and Langseth's analysis * to our data (Fig. 1) confirms this; *i.e.*, when $T_2 = 293°$ K the value for *trans*-stilbene's O–O line is 328 mμ, to be compared with that calculated by Kuhn's theory to be 311·5 or 319 mμ, as shown above. For the oscillator strength f_1, equation (7) gives a value of 0·71 for *trans*-stilbene, or, by using the $f_0 = 0{\cdot}34 \pm 0{\cdot}15$ of Platt *et al.* (*loc. cit.*), $f_1 = 1{\cdot}1 \pm 0{\cdot}5$. This, together with the corrected value of 0·55 of Mulliken and Rieke, and Bayliss's values of 0·67 or 1·21, may be compared with our experimental *f*-value of 0·755 (at 20°, 95% ethanol as solvent; see Experimental section).

The most recent theoretical treatment of the spectra of polyenes is that by Dewar (*loc. cit.*) who uses a first approximation of the LCAO MO method. By assuming that the double and single bonds require different resonance integrals but that all bonds of one type are equivalent, an equation is derived for the maximum wave-length of the first strong series of bands (neglecting fine structure where this exists) :

$$\lambda_0 = D(1 - a^{-2N-2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where a = an empirically determined parameter ($=2^{\frac{1}{8}} \simeq 1{\cdot}09$) and D = a constant, involving a value for the C–C resonance integral. If a $\text{C–C}_{\text{aromatic}}$ resonance integral is taken, then $\lambda_0 = 311$ mμ for stilbene, a value not far from the 320 mμ of H. Kuhn and 311·5 or 319 mμ of W. Kuhn. When D is chosen to give good agreement between theory and experiment for butadiene and involves a $\text{C–C}_{polyene}$ resonance integral, the predicted λ_0 is 256 mμ, in poor agreement with experiment. Thus, it appears possible by three different methods to achieve reasonably good semi-theoretical prediction of the λ-value for *trans*-stilbene, while similarly predicted *f*-values deviate by amounts up to 100% from the observed figure.

The Effect of Low Temperatures on the Spectrum of trans-*Stilbene.*—It is evident from the Figure that considerable changes in the spectrum of *trans*-stilbene are brought about by refrigeration to −130°. Hausser *et al.* (*loc. cit.*, 1935, p. 391), in their extensive investigations of absorption and fluorescence in substituted polyenes, examined this absorption semi-quantitatively in ethanol–ether at −196°, and in agreement with them we find that the A-band, at low temperature, is much more sharply resolved into its three peaks, called here α, β, and γ, the α-peak occurring at longest wave-lengths. Temperature reduction results also in a small red-shift of about 4 mμ and a marked redistribution of intensity among the vibrational bands. Thus (see Figure) at 20° the intensities of the bands

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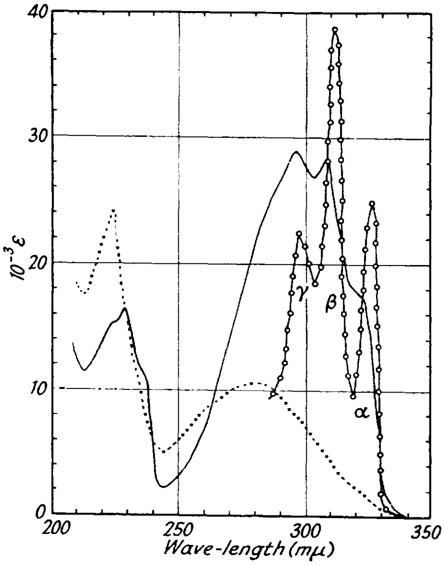
* Brodersen and Langseth (*Kgl. Danske Videnskab. Selsk.*, 1951, **26**, No. 3) have suggested and illustrated the use of changes in absorption with temperature as the basis of a method to localise the O–O line. $\Delta \log \varepsilon$ values are plotted against wave-length or frequency values for the absorption of the pure compound in solution, where $\Delta \log \varepsilon = \log \varepsilon_2 - \log \varepsilon_1$, and ε_2 and ε_1 are molar extinction coefficients taken for the same frequency at temperatures T_2 and T_1, T_2 being greater than T_1. A rise in temperature results in an increased number of thermally excited molecules in the solution, leading to increased absorption at frequencies below that of the O–O transition. This increased absorption corresponds to the maximum at lowest frequencies in the $\Delta \log \varepsilon$ v–ν curve, and the frequency of the following minimum (rather than that where $\Delta \log \varepsilon = 0$, for reasons discussed in the paper) is identified as the O–O transition.

are in the order $\gamma > \beta > \alpha$, while at $-130°$ this becomes $\beta > \alpha \simeq \gamma$. In spite of increased extinction values for the α- and β-bands, the total f-value of the A-system is reduced from 0·755 to ~0·41.

In this connection, Mulliken and Rieke's theoretical consideration (*loc. cit.*) of the effect of temperature on the intensity of an electronic transition is of interest. In equation (3) (p. 2757), the levels k and l are not single each consists of a complicated family of levels, resulting from molecular vibration and rotation and often also electron spin) but, according to these authors, no serious error should be involved if D is defined as the sum total of dipole strengths of all possible transitions from the initial level l to the final level k; the distribution of the molecules among the individual initial states should not affect significantly the total D per molecule for a mass of absorbing molecules, and it was noted that the experimental D should be independent of temperature. It may be observed also, since $f = k\int \varepsilon d\nu$ and $f = k'\nu D$ (where ν is the centre of the band-system), that

$$\int \varepsilon d\nu = k''\nu \qquad (9)$$

since D is constant. Thus, if the band does not shift on reduction of the temperature, the integrated area under the band should remain the same; similarly, a bathochromic shift should accompany a reduction in intensity. As shown above, there is an f-reduction of ~45% in the *trans*-stilbene A-band at $-130°$, accompanying a bathochromic shift of only 4 mμ (385 cm.$^{-1}$).



trans-*Stilbene*, 20° (*in* 95% EtOH), ——
trans-*Stilbene*, −130° (*in mixed alcohols*), -o-o-
cis-*Stilbene*, 20° (*in* 100% EtOH), - - - -

This f-reduction is much larger than predicted for such a small shift, so that other factors, as discussed below, must be of great importance. Mulliken and Rieke have noted that deviations from the sum rule for D would be due principally to the fact that the forms of the electronic wave-functions are not quite independent of nuclear positions. Thus, for molecules no longer assumed fixed in their equilibrium configurations the values of Q and D in eqn. (2) will vary somewhat with internuclear distances. It is well known that perturbations due to solvent molecules affect the ν, f, and fine structure in absorption bands and their changes with temperature (see, for example, Sheppard *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 2923, 2937; 1944, **66**, 380; Coggeshall and Lang, *ibid.*, 1948, **70**, 3283). It is of interest, therefore, briefly to compare with the *trans*-stilbene measurements the available related data on spectral changes with temperature and those resulting from changing solvents, particularly for non-polar solutes. This is a necessary basis for discussion of the different behaviour of the spectra of basic stilbene derivatives on refrigeration in alcohol solutions and should assist understanding of the changes in *trans*-stilbene's A-band.

Changes in such solvent properties as refractive index and dielectric constant would not be expected to affect considerably the transition dipole of a centrally symmetrical, non-polar solute molecule such as *trans*-stilbene, but the increasing viscosity of the alcohol solutions at lower temperature could make a small contribution to the observed *f*-reduction. Sheppard *et al.* (*loc. cit.*, 1944) in their discussion of temperature changes in dye spectra suggest that the reduced Brownian movement consequent upon increased viscosity should reduce the uncertainty or spread in energy levels, and Brodersen and Langseth (*loc. cit.*) have shown that if the normal blurring of these levels follows a statistical distribution the standard deviation is of the order of hundreds of wave numbers (~400 cm.$^{-1}$) for a linear conjugated molecule (diphenylbutadiene) at ordinary temperatures. It will be of interest, therefore, to investigate the effects on the A-band *f*-value (and other properties) of solvents more viscous than the alcohols used hitherto, without refrigeration of the solutions.*

An additional result of the sharpening of location of electronic energy levels by this increased viscosity should be greater resolution of vibrational fine structure in the spectrum. However, the main cause of the observed resolution increase is the well-known progressive elimination of higher-energy vibrational and rotational levels by temperature reduction. The lack of this low-temperature resolution in the spectrum reported by Lewis *et al.* (*loc. cit.*) for *trans*-stilbene could be due to the low viscosity of the solution (in *iso*octane) at −90° as well as to the low degree of refrigeration, for their curve shows some changes in extinction values for the main peaks and shoulder.

More than one factor appears to operate to produce the small bathochromic shift of the A-band on refrigeration. Hausser *et al.* (*loc. cit.*) noted that the frequency of absorption in polyenes was proportional to the temperature, and that the ν-change (bathochromic) increased at room temperature with the refractive index of the solvent, as suggested by Kundt's rule (*Ann. Physik*, 1878, **4**, 34). Thus, some small part of the red shift on refrigeration could be due to the concomitant increase in refractive index of alcohol solutions. Recent theoretical work by Bayliss (*J. Chem. Phys.*, 1950, **18**, 292) concerning spectral changes on passing from vapour to solution supports this, and suggests, in addition, that such a red shift should be proportional, *inter alia*, to the intensity of the band. This had been confirmed by Coggeshall and Pozefsky (*J. Chem. Phys.*, 1951, **19**, 980) for the solvent-induced frequency shifts for cata-condensed aromatics and is supported by observations of frequency changes on refrigeration. Thus, like *trans*-stilbene's A-band, the allowed 240—290-mμ transition in naphthalene, having a small *f*-value (0·10),† shows a small red shift (~10 Å) on refrigeration in alcoholic solutions, while the very weak, forbidden, long-wave-length (290—320 mμ) band system in naphthalene ($f = 0{\cdot}002$) † and the similar system at 260 mμ in benzene ($f = 0{\cdot}002$) † undergo no frequency shift with temperature (Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 334; Clar, *Spectrochim. Acta*, 1950, **4**, 116). Further, similarity between the effect of refrigeration and that due to increase in solvent polarity is apparent when comparing the benzene 260-mμ and naphthalene 240—290-mμ systems: the latter shifts bathochromically on passing from *iso*octane to alcohol solutions, while the former is almost independent of solvent (Coggeshall and Lang, *loc. cit.*). The suggestion has been made by the last authors that dipole–dipole interaction between solute and solvent molecules in their excited states could stabilise the excited electronic levels in some systems and produce a red shift, for example, on passing from non-polar to polar solvents. This, again, may play a part in the spectral changes of *trans*-stilbene at low temperatures. It is conceivable that an increased polarity of the refrigerated solvent (due to increased association, cf. Sheppard *et al.*, *loc. cit.*, 1944) would cause increased polarisation of the solute molecules in their excited states, to which polar structures will make a small but definite contribution which should be negligible in the ground state. If this is so, the low-temperature bathochromic shift should be reduced on using a less polar

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* Preliminary measurements in glycerol at room temperatures show a small reduction in *f*-value, a bathochromic shift (possibly due to the high refractive index of the solvent), and redistribution of intensity among the vibrational bands; cf. p. 2762.

† $f = 0{\cdot}10$ for naphthalene's 240—290-mμ transition is calculated by the authors from the data of Mayneord and Roe (*Proc. Roy. Soc.*, 1935, *A*, **152**, 299). *f*-values for the forbidden systems in naphthalene and benzene are from Klevens and Platt (*J. Chem. Phys.*, 1949, **17**, 470) whose value ($f = 0{\cdot}18$) for the naphthalene 240—290-mμ system is in error, owing to incorrect extinction data.

solvent, and might be noted on changing solvents at room temperatures. In fact, in the *iso*octane solution used by Lewis *et al.* there is no bathochromic shift at −90°, although, as already noted, the higher temperature (compared with our measurements) is probably an important factor, and the effect of further refrigeration in a completely non-polar solvent should be tested. At room temperature we have found small differences (5—15 Å) between the $\lambda_{max.}$ values in ethanol and hexane, so this effect may have some small importance in our experiments. Clearly, it should have greater importance in the low-temperature spectra of basic stilbene derivatives, and this appears to be the case (unpublished work).

Redistribution of intensity within the A-band system of *trans*-stilbene is a striking further consequence of temperature reduction. It has been suggested by Professor M. Kasha * that the torsional-potential curves in the ground and excited states of *trans*-stilbene overlap at room temperature, the potential being a maximum for 90° of twist about the double bond in the ground state, and a minimum in the excited state of the molecule (Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265). On refrigeration, fundamental changes are envisaged in the shapes of these curves, with the production of new minima in the excited torsional potential, causing, according to the Franck–Condon principle, redistribution of intensity among the vibrational transitions. An alternative view, for which we are indebted to Professor J. R. Platt, is that at room temperatures some low-wave-length absorption in the A-band results from coupled higher-energy vibrational transitions due to twist of the phenyl rings about the *single* bonds of the bridge. This absorption would be reduced with reduction in probability of twist on increasing the viscosity of the solvent and on refrigeration, clearly altering the relative extinctions of the α, β, and γ vibrational bands. It corresponds in position with the A-bands of sterically hindered stilbene derivatives, *e.g.*, 2 : 4 : 6-trimethyl- and 2 : 4 : 6 : 2′ : 4′ : 6′-hexamethylstilbene (Haddow *et al.*, *loc. cit.*). Further work at lower wave-lengths and in solvents of varying viscosity and at different temperatures is necessary. The preliminary measurements at room temperatures in glycerol solution show trends in fine structure differences similar to the above, *e.g.*, $\varepsilon_{\beta}/\varepsilon_{\gamma} = 1{\cdot}04$, compared with 0·98 in 95% alcohol.

Ultra-violet Absorption in cis-*Stilbene*.—The spectrum of *cis*-stilbene in ethanol (see Figure) shows, as in the *trans*-isomer, two main absorption regions; fine structure, however, appears to be missing. The A-band, much less intense, arises at lower wave-lengths ($\lambda_{max.}$ 280 mμ; ε 10,450) than in *trans*-stilbene, while the B-band, increased in intensity, occurs in almost the same region ($\lambda_{max.}$ 224 mμ; ε 24,400) as in *trans*-stilbene. Our data are in good agreement with those of Calvin and Alter (*loc. cit.*) who examined the A-band only, and while there is approximate wave-length agreement with Smakula and Wasserman's curve (*loc. cit.*) their ε value is 30% higher for the A-band and 3% lower for the B-band than reported here, suggestive, with the indications of structure in the A-band, of some *cis–trans*-isomerism during their investigation.

From our Figure, an experimental *f*-value of 0·35 may be calculated for *cis*-stilbene's A-band, to be compared with Mulliken and Rieke's semi-theoretical figure of 0·33 (again with a correction factor of 0·34), calculated without allowance for non-planarity. The reduced intensity of this transition results from at least two effects: (i) the molecule is less extended spatially than that of the *trans*-isomer, so that vector addition of the r_i-terms in equation (3) gives a smaller resultant (Mulliken and Rieke, *loc. cit.*; cf. Förster, *Z. Elektrochem.*, 1939, **45**, 548); (ii) steric hindrance to planarity is present, owing to overlap between hydrogen atoms in the phenyl rings, *ortho* to the double bond (Lewis and Calvin, *Chem. Reviews*, *loc. cit.*). The effect of the latter factor on *f*-values has been discussed in connection with sterically hindered *trans*-stilbene derivatives (Beale and Roe, *loc. cit.*).

The absence of fine structure from this A-band, even at −90° (Lewis *et al.*, 1940, *loc. cit.*), has been attributed by these authors to the "loose-bolt effect." Thus, in certain circumstances, the vibrations of low energy of a radical having large mass or low constraint are assumed to couple with the electronic oscillation in such a way that, on excitation,

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* Personal communication. A detailed discussion and other aspects of this problem will be published by this author.

there is an abrupt transition from a state in which an electron cloud is oscillating along a single axis to one in which the electronic energy is obliterated and converted into violent atomic vibrational and rotational energies. This will blur the energy levels corresponding to the chief atomic vibrations of high energy and lead to broadening or obliteration of fine structure in the absorption bands. Further, since the process removes the electronic energy of the excited state almost instantaneously, no fluorescence can occur. Lewis *et al.* found no fluorescence in *cis*-stilbene, even at −90° (*iso*octane solution), and their theory was found also to be adequate to explain their experimental data on the quantum yields for the photochemical interconversion of the isomers. It is possible, however, that a further cause of the obliteration of fine structure in *cis*-stilbene is the lack of planarity in the ground state of the molecule (and probably in the excited state, although in the latter the equilibrium shape will differ from that of the ground state both in angles and in degree of non-planarity). Thus, for this reason also, practically every type of vibrational motion is expected to be excited in absorption, in contrast to the case of the *trans*-isomer with its more symmetrical, planar ground state and its planar or near-planar excited state. Both the loose-bolt effect and the non-planarity of the molecule might be expected to diminish at still lower temperatures, so that refrigeration far below −90° might remove these hindrances to the appearance of fine structure without differentiating between them. The non-planar ground state does not provide a ready explanation of lack of fluorescence in *cis*-stilbene. It is of interest that in the non-planar 2 : 4 : 6-trimethylstilbene (in 95% EtOH) fluorescence is reduced considerably below that of planar *trans*-stilbene.

In agreement with this emphasis on the vibrational consequences of the non-planar ground state, although not proving it, is the fact that *cis*-stilbene's A-band is shifted hypsochromically compared with *trans*-stilbene's. This probably results mainly from electronic differences due to non-coplanarity, however, and so far no theoretical treatment has predicted the amount of this shift.

EXPERIMENTAL

At room temperatures, solutions of the compound in 95% or 100% ethanol or in hexane were examined in matched cells in the Beckman or Uvispek spectrophotometer. In each case cell corrections were applied to each optical-density reading to allow for any imbalance in absorption when both cells were filled with solvent. Readings were taken at 4 or 2 mμ intervals on slopes of the curves, the intervals being reduced to 1 or 0·5 mμ in the regions of maxima, minima, and shoulders. Reliance was placed only on optical density readings in the range 0·1—0·8, resulting in ε values with an estimated accuracy of ±0·5% for *trans*-stilbene in ethanol and ±1% for *cis*-stilbene and for *trans*-stilbene in hexane. f-Values were calculated as before (Beale and Roe, *loc. cit.*, 1952). Note that sublimation of the *trans*-stilbene specimen used before resulted in increases in ε values of <2% and in A-band f-value from 0·745 to 0·755.

Absorption measurements at low temperatures were made by a method already described (Beale and Roe, *J. Sci. Instr.*, 1951, **28**, 109), with the Hilger medium quartz spectrograph and Spekker photometer. Absorption by the mixed alcohol solvent in the 1·6-cm. cells required by this apparatus prevented accurate measurements below ~270 mμ. ε values were corrected for the changes in concentration resulting from contraction of solutions at −130° and are estimated to be accurate to ±3%.

The *trans*-stilbene used (m. p. 124°) was a commercial sample purified by repeated crystallisation from alcohol, followed by sublimation *in vacuo*. For the preparation of *cis*-stilbene the method of Taylor and Crawford (*J.*, 1934, 1140) was used, the oil being purified by repeated fractional distillation *in vacuo*; it had b. p. 134°/10 mm.

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