The Ultraviolet Absorption Spectra of Stilbene and Some Related Compounds in the Solid State Measured by the Pressed KCl Disk Technique

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Molecular structures are, needless to say, not rigid. Even the equilibrium or most probable conformation of a compound can vary, depending on, above all, the aggregation state and the temperature. Thus, the equilibrium conformation of a compound determined by the X-ray crystal analysis, for example, is not necessarily maintained in a state other than the crystalline state. A typical example is biphenyl. This compound is planar in the crystalline state, non-planar in the gaseous state, and probably slightly non-planar in solution(1-I).

If the most probable conformation of a compound is appreciably different in various states, the electronic absorption spectra of the compound in the various states must be correspondingly different from each other. The author has shown in a series of papers(1) that the most probable conformations of many conjugated componds in various states, especially in solution, can be inferred with almost complete satisfaction from the electronic absorption spectra. The principle of the inference consists in comparison of the spectrum of a given compound under a given condition with that of a suitable reference compound under a suitable condition, whose conformation is already known, or else, can be presumed reasonably. Since the conformation of the reference compound is determined by the X-ray crystal analysis in most cases, it is frequently necessary to compare the concerned spectrum with the spectrum of the reference compound in the crystalline state.

The spectra of compounds in the crystalline state have been measured so far by various methods and for various purposes. Thus, they have been measured often with single crystals and with polarized light(2). This method is useful particularly for the assignment of absorption bands. Alternatively, they have been measured also with solid films prepared on quartz, silica, or glass plates by sublimation of crystals, by evaporation of thin layers of solutions, or by solidification of melted substances(3). These methods have been used sometimes for the purpose of studying the crystal spectra themselves, and sometimes simply for the reason that the spectra can not be measured in solutions because of the low solubilities of the substances.

In the crystal spectra measured by these

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1) H. Suzuki This Bulletin, (I) 32, 1340, (II) 1350, (III) 1357 (1959), (IV) 33, 109, (V) 379, (VI) 389, (VII) 396, (VIII) 406, (IX) 410, (X) 613, (XI) 619 (1960).

2) See, for example, A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, 23, 1480 (1955).

3) See, for example; J. W. Weigl, ibid., 24, 364 (1956).

methods the effect of the orientation of molecules in crystals reveals itself markedly[4]. This marked orientation effect is, of course, essential to the purpose of assignment of bands. However, this effect makes the spectra measured by these methods unsuitable for direct comparison with the spectra of solutions where molecules are oriented at random.

For this reason, in the foregoing series of papers the spectra measured by the " pressed KCl disk technique " were used as the crystal spectra of the reference compounds. The pressed KCl disk technique is quite analogous to the well-known pressed KBr disk technique developed for infrared spectroscopy, and was applied to electronic absorption spectroscopy first by Dale[4] in 1957. It may be somewhat doubtful whether or not the state of molecules in pressed KCl disks is quite the same as that in the crystals. Thus, there may be a possibility that the state is near to that of solid solutions. It seems, however, to be more probable that micro-crystals are oriented at random in disks. If it is so, it seems reasonable to consider that the spectra measured by this method are most suitable, as the spectra of the compounds in the crystalline state, to be directly compared with the solution spectra.

An additional advantage of this method over the others is that the influence of reflection at the disk surface can approximately be eliminated by using a pressed disk of pure potassium chloride as the reference in measurement of the spectra. In contrast, in spectra measured by the other methods the influence of reflection at the crystal surface, at the surface of the plate, or at the crystal-plate interface is frequently sufficiently great to cause serious distortion of the absorption spectra[5], and consequently it is necessary to correct for this influence of reflection. In addition, the pressed KCl disk technique will be very useful to measure the spectra of compounds of low solubility in usual solvents, and particularly of crystalline molecular complexes, whose spectra are difficult in general to measure by other methods.

It is to be noted here that the difference between the spectrum of a compound in the crystalline state and that in solution may be due partly at least to the effect of intermolecular interactions in crystals, besides the possible difference of the most probable conformation in both the states. In general, molecules in crystals can not be treated simply by a so-called oriented gas model. Forces between molecules in aromatic crystals are small compared with intramolecular forces, but they frequently exert appreciable effects on the electronic states of molecules and consequently affect the electronic absorption spectra. In a spectrum measured with a single crystal and with polarized light, the most important effect of a crystal field appears to reveal itself as a so-called Davydov splitting[6]. It seems to be of interest to notice how the effect of a crystal field manifests itself in the spectrum measured by the pressed KCl disk technique, if the spectrum is the one of micro-crystals oriented at random.

At any rate, in view of the possible usefulness of the pressed KCl disk technique in electronic absorption spectroscopy, it seems to be not only interesting but also desirable to study general characteristic features, if any, of the spectra measured by this technique as compared with the corresponding solution spectra.

The author has measured the spectra of stilbene and its related compounds by this technique, of which the spectra of *trans*-stilbene and tolan were already reported in previous papers (Refs. 1-V and VI), and he has found that some generalizations can be drawn from comparison of the spectra with the corresponding spectra of solutions in *n*-heptane, although their theoretical interpretation has not yet been attained. In the present paper, the results of the measurement are summarized and discussed mainly from a phenomenological standpoint.

Experimental

Materials.—The compounds used in this study were prepared as reported previously[1-V-IX]. Potassium chloride was precipitated from water solution with hydrochloric acid to obtain small particle size and dried at 400~450°C for about 6 hr., according to the procedure described by Hales and Kynaston[7].

Measurements of the Solid State Spectra.—The general procedure of measurements of the solid state spectra by the pressed KCl disk technique is quite analogous to the procedure for *trans*-stilbene and tolan described in the previous papers. Thus, 1 to 10 mg. of the pure organic compound was thoroughly ground in an agate mortar (for about 15~20 min.) with about 200 mg. of the pure potassium chloride. About 10 mg. of the mixture was then ground with about 350 mg. of new potassium chloride. The concentration of the substance in the final mixture, from which a disk was prepared, was adjusted in order that the disk might show suitable absorbances (about 0.8~1.9 at the most intense absorption maximum). For example, in

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[4] J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).

[5] J. W. Weigl, *J. Chem. Phys.*, **24**, 577 (1956).

[6] See, for example, D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, **1955**, 539; D. P. Craig, ibid., **1955**, 2302; D. P. Craig and P. C. Hobbins, ibid., **1955**, 2309.

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

the case of *trans-p*-phenylstilbene, the mixing was carried out as follows; 2.35 mg. of the substance was ground with about 200 mg. of KCl, and about 10 mg. of the first mixture was ground with about 350 mg. of KCl to get the final mixture. II the case of triphenylethylene, 8.35 mg. of the compound was ground with 200 mg. of KCl, 10 mg. of the first mixture was ground with 350 mg. of KCl, and finally 80 mg. of the second mixture was ground with 177 mg. of KCl. As will be described later, the apparent molecular extinction coefficients in the spectra measured by this technique were generally lower than the corresponding values in the solution spectra, and furthermore, were not reproducible. Therefore, the adjustment of the concentrations in the final mixtures was not straightforward and frequently had to be carried out by the method of trial and error.

In most cases except for the cases of *trans*-stilbene and tolan, about 150 mg. (146∼148 mg.) of each final mixture was pressed under vacuum in the usual manner into a transparent disk (pressure: about 12 tons per sq. cm.). The ultraviolet absorption spectrum of the disk was measured with a Cary recording spectrophotometer Model 14 by using a disk prepared of about 150 mg. (146 and 148 mg.) of pure potassium chloride as the reference. The transmission spectrum of one of the reference disks used (weight: 146.25 mg.) is shown in Fig. 1. It is characteristic that the spectrum exhibits a feeble absorption band at near 270.5 mμ. This band was observed similarly in all the spectra of the reference disks used.

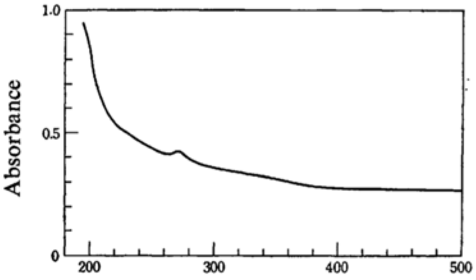

Fig. 1. The transmission spectrum of a reference KCl disk (weight: 146.25 mg.).

Calculations of Thicknesses of Disks, Concentrations, and Molecular Extinction Coefficients.— The radius of a disk is 0.65 cm. Since the weights of the disks used are 146∼148 mg. in most cases, the thicknesses of the disks are calculated to be 0.055∼0.056 cm, when it is assumed that the density of the disks is 1.988. These values of the thicknesses are in fairly good agreement with the rough values obtained by direct measurement. The concentrations of the organic substances in the disks can be calculated easily, on the basis of an assumption that micro-crystals or molecules are evenly dispersed in each mixture. Then, the molecular extinction coefficients (ε) are evaluated in the usual manner as the values of absorbance divided by the thickness of the disk and the molar concentration of the substance in the disk.

Discussion

In the ensuing discussion, the spectra measured by the pressed KCl disk technique are referred to as the solid state spectra. The solution spectra refer to the spectra of solutions in *n*-heptane, except where indicated otherwise.

The newly measured solid state spectra are shown in Figs. 2—6, together with the corresspounding solution spectra reported in previous

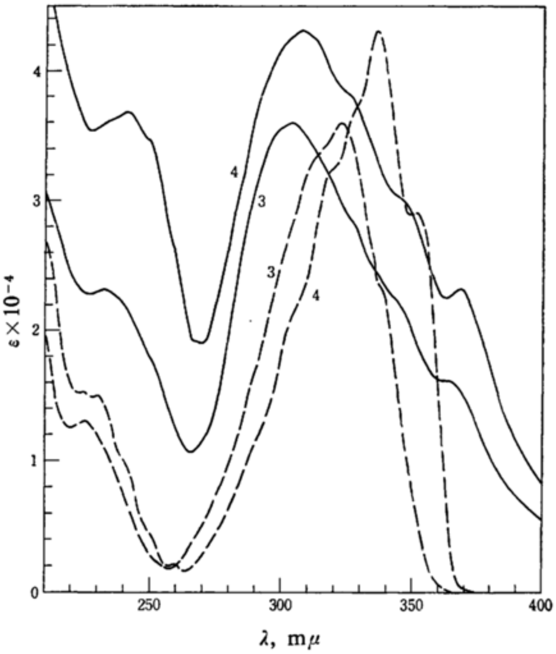

Fig. 2. Ultraviolet absorption spectra: 3, *trans-p*-phenylstilbene; 4, *trans*-1-phenyl-2-(2-fluorenyl)-ethylene.

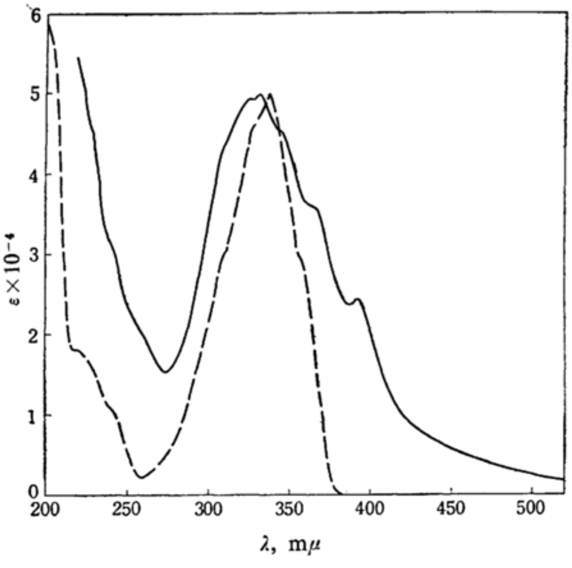

Fig. 3. Ultraviolet absorption spectra: *trans-p, p'*-diphenylstilbene.

papers (Refs. 1-VI—IX). The solid lines represent the solid state spectra and the broken lines the solution spectra. In these figures, the extinction of the most intense maximum of the conjugation band in each solid state spectrum has been arbitrarily set equal to the extinction of the most intense maximum of the conjugation band in the corresponding solution spectrum, because reliable solute extinction values for the solid state spectra could not be obtained. In addition, in Fig. 3 the extinction of the maximum of the conjugation band in the spectrum of *n*-heptane solution has been arbitrarily set equal to that in the spectrum of benzene solution (cf. Ref. 1-IX). It is seen that the solid state spectra resemble considerably the corresponding solution spectra on the whole.

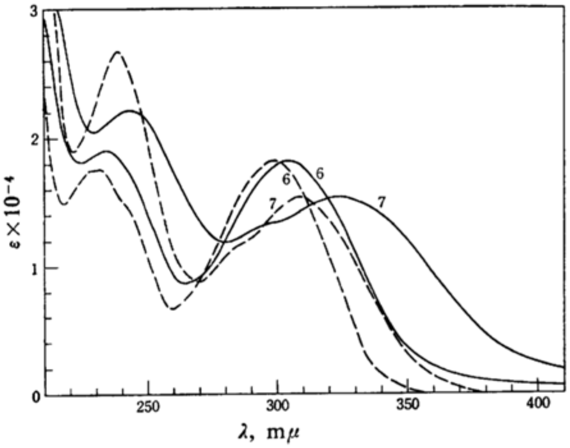

Fig. 4. Ultraviolet absorption spectra: 6, triphenylethylene; 7, tetraphenylethylene.

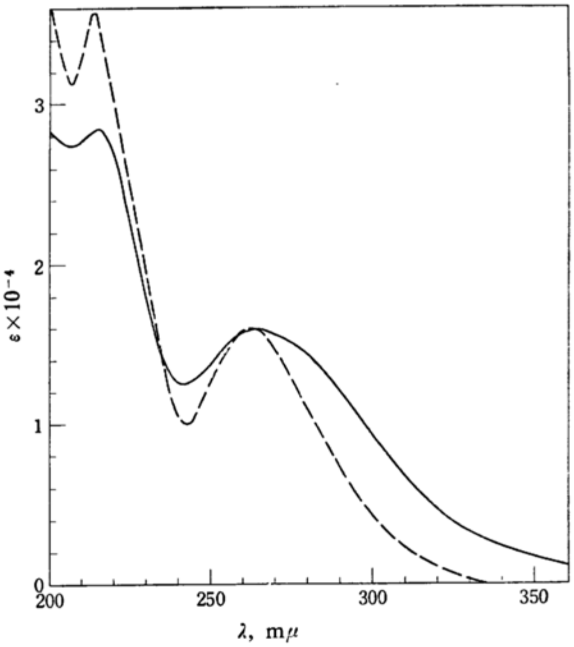

Fig. 5. Ultraviolet absorption spectra: *trans*-1, 2-dimesitylethylene.

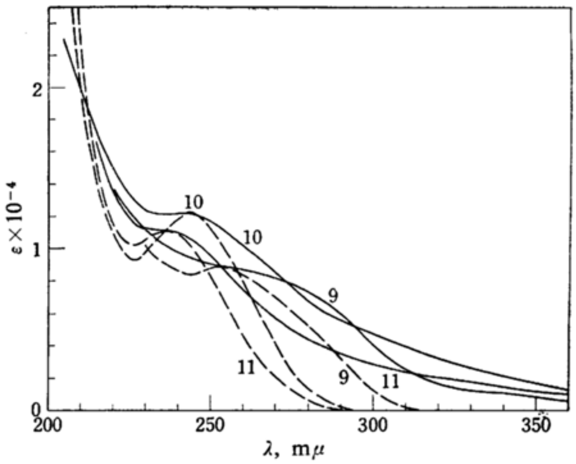

Fig. 6. Ultraviolet absorption spectra: 9, *cis*-α, α'-dimethylstilbene; 10, *trans*-α, α'-dimethylstilbene; 11, *trans*-α, α'-diethylstilbene.

The data of the maxima and the inflections in these spectra as well as in the spectra of *trans*-stilbene and tolan are summarized in Table I. In this table, A refers to the A-band, i. e. the conjugation band due to transitions from the highest occupied orbital to the lowest vacant orbital, and B refers to the B-band, i. e. the band probably due to transitions from the highest occupied orbital to the vacant orbitals localized in the benzene nuclei or from the occupied orbitals localized in the benzene nuclei to the lowest vacant orbital (cf. Ref. 1-V). The symbol △ denotes the most intense maximum of fine structure of the conjugation band in each spectrum. Wavelengths (in mμ) in parentheses denotes inflections, and those in double parentheses denote very indistinct inflections. $\Delta\lambda$ represents the wavelength difference (in mμ) between the band in the solid state spectrum and the probably corresponding band in the solution spectrum. Values of $\Delta\lambda$ in parentheses are values for the cases in which either or both of the bands to be compared are inflections. $\varepsilon_K/\varepsilon_H$ represents the ratio of the apparent value of the molecular extinction coefficient of the band in the solid state spectrum to the value of the corresponding band in the solution spectrum.

Absorption Intensities.—The molecular extinction coefficients in the solid state spectra, calculated by the above mentioned procedure, were not reproducible. Not withstanding, it may be said that they are generally considerably

TABLE I. THE SOLID STATE SPECTRA (BY THE PRESSED KCl DISK TECHNIQUE) AND THE SOLUTION SPECTRA (IN *n*-HEPTANE) OF STILBENE AND RELATED COMPOUNDS

Entry No.	Compound		Solid state spectrum		Solution spectrum		$\Delta\lambda$, mμ	$\varepsilon_K/\varepsilon_H$
			λ_{max}, mμ	$\varepsilon(\varepsilon_K)$	λ_{max}, mμ	$\varepsilon(\varepsilon_H)$		
1	Tolan							
		A	301.6	1920	297.2	27500	4.4	0.070
			292.4	1680	288.5	20800	3.9	0.081
			△ 283.3	2380	△ 279.9	30800	3.4	0.077
			(275.8)	1960	272.7	22400	(3.1)	0.088
			268.0	1760	265.3	20600	2.7	0.085
		B	(239.0)	680	237.2	6930	(1.8)	0.098
					232.2	6520		
			(223.5)	1540	222.0	16500	(1.5)	0.093
			(218.5)	1790	217.2	19000	(1.3)	0.094
2	*trans*-Stilbene							
		A	(327.5)	960	(320.5)	16000	(7.0)	0.060
			(312.5)	1500	306.9	26500	(5.6)	0.057
			(298.5)	1750	△ 294.1	27950	(4.4)	0.063
			△ 287.0	1790	(283)	24500	(4.0)	0.073
			(276)	1610				
		B	(241.5)	1420	(236)	10400	(5.5)	0.137
			233.0	1670	228.5	16200	4.5	0.103
			(225.5)	1640	(222)	15500	(3.5)	0.106
3	*trans*-*p*-Phenylstilbene							
		A	(364.4)	6850				
			((343))	9540	((338))	23200	(5.0)	0.411
			((328))	11880	△ 322.5	36000	(5.5)	0.330
					(311.5)	33200		
			△ 303.6	15240				
		B	232.3	9810	225.5	13100	6.8	0.749
4	*trans*-1-Phenyl-2-(2-fluorenyl)-ethylene							
		A	368.0	5370				
					351.2	29100		
			(345)	6980	△ 335.8	43100	(9.2)	0.162
			(325)	8820	(318.5)	32450	(6.5)	0.272
			(313)	9750				
			△ 307.0	9920	((303.5))	21000	(3.5)	0.472
			((299))	9580				
		B	(249.5)	7970	((237.5))	10900	(12.0)	0.731
			241.0	8470	230.0	15230	11.0	0.556
			(233.5)	8290	223.7	15420	(9.8)	0.538
5	*trans*-*p*, *p'*-Diphenylstilbene							
		A	391.8	12260				
			(366.0)	17980	((357))	29400*	(9.0)	0.612
			(345.2)	22970	△ 337.4	49900*	(7.8)	0.460
			△ 331.6	25130	(327.5)	46200*	(4.1)	0.544
			(324)	24820				
		B	((229))	18640	(220.5)	18200*	(8.5)	1.024
6	Triphenylethylene							
		A	((308))	8090				
			303.8	8180	298.5	18220	5.3	0.449
		B			(242.5)	14570		
			233.9	8550	232.0	17580	1.9	0.486
			((230))	8500	(228)	17540	(2.0)	0.485

TABLE I (continued)

7 Tetraphenylethylene						
A	322.9 (296)	10970 9480	308.7 (285.8)	15300 11700	14.2 (10.2)	0.717 0.810
B	243.3	15940	238.5	26800	4.8	0.595
8 *trans*-1, 2-Dimesitylethylene						
A	264.4	9170	262.7	16000	1.7	0.573
B	215.0	16340	214.0	35700	1.0	0.458
9 *cis*-α, α'-Dimethylstilbene						
A	252.4	570	252.0	8880	0.4	0.064
10 *trans*-α, α'-Dimethylstilbene						
A	(240.6)	2250	243.3	12270	(−2.7)	0.183
11 *trans*-α, α'-Diethylstilbene						
A	(236.9)	2220	236.6	11090	(0.3)	0.200

* Values estimated by taking the value for the maximum of the conjugation band in the spectrum of the *n*-heptane solution to be equal to the value in the spectrum of the benzene solution.

smaller than the values in the corresponding solution spectra. Thus, as is seen in Table I, the values of $\varepsilon_K/\varepsilon_H$ are about 1/3∼2/3 for the compounds of the numbers 3—8, and are only about 1/20∼1/5 for the compounds of the entry numbers 1, 2, 9, 10 and 11.

These depressions of intensities seem to be partly at least intrinsic ones. As is seen in Figs. 2—6, the bands, especially the A-bands, are markedly more broad in the solid state spectra than in the solution spectra. Therefore, it is believed that the intensities of especially the A-bands are actually considerably smaller in the former spectra than in the latter. This presumption is supported also by the fact that in the figures the intensities of the B-bands are apparently much larger in the solid state spectra than in the solution spectra in most cases. If it is assumed that the actual intensities of the B-bands are not markedly different in both spectra, this fact is, of course, considered to indicate the actual depressions of intensities of the A-bands in the solid state spectra.

In addition to the actual or intrinsic depressions, the intensities may be apparently depressed by contribution of other factors. As the factor contributing to the apparent depressions, the following possibilities may be considered. (1) A part of the organic substance weighed in may be lost during grinding and evacuation of the press, as pointed out already by Dale[4]. (2) Mixing may be imperfect in each process of grinding. That is, the substance may be unevenly dispersed in each mixture, and consequently, the actual concentration in the final mixture may be more or less different from the culculated value. (3) The absorption intensities in the solid state spectra may essentially depend on the condition of dispersion of the micro-crystals or the sizes of the micro-crystals, as suggested by the somewhat similar phenomenon observed by Weigl[3] in his study on the absorption spectra of some crystalline cationic dyes. Especially in the cases where the values of $\varepsilon_K/\varepsilon_H$ are extraordinarily small, the contribution of factor 1 may be predominant.

Shapes of Absorption Curves and Wavelengths of Bands.—Although the shape of the absorption curve of the solid state spectrum of a compound varies slightly from disk to disk in some cases, the reproducibility of the wavelength positions of the absorption maxima and the inflections was almost always fairly good.

Comparison of the solid state spectra with the solution spectra seems to suggest that it is convenient to divide the compounds into the following four groups with respect to the shapes of the absorption curves as well as the magnitudes of the wavelength displacements $\Delta\lambda$: (I) entry 1 in Table I, (II) entries 2—5, (III) entries 6 and 7, and (IV) entries 8—11.

Group I.—Tolan. The solid state spectrum it not significantly different from the solution spectrum, except for the bathochromic displacement of the normal magnitude (see below) of each band (cf. Fig. 2 in Ref. 1–VI). *trans*-Azobenzene also belongs to this group, whose spectra will be reported and discussed in a later publication.

Group II.—Redistribution of Intensity among the Vibrational Sub-bands.—*trans*-Stilbene, *trans*-*p*-phenylstilbene, *trans*-1-phenyl-2-(2-fluorenyl)-ethylene, and *trans*-*p*, *p'*-diphenylstilbene. All these compounds are *trans*-stilbene-type compounds which have no substituent at sterically hindering positions and consequently are probably planar. It is a common distinctive feature of the spectra of these compounds that the bands, especially the conjugation bands, exhibit more or less well-resolved fine structures. With these compounds, a marked redistribution of intensity among the vibrational fine structure bands of the conjugation band occurs, that is, the relative intensities of the vibrational bands change markedly, when the state is changed from solution to solid. Thus, the band which appears as the most intense maximum in the solution spectrum, appears as the inflection at a longer wavelength than the most intense maximum in the solid state spectrum. On the other and the band which appears as the inflection at a shorter wavelength than the most intense maximum in the solution spectrum, appears as the most intense maximum in the solid state spectrum.

A typical example is *trans*-stilbene. As described in Ref. 1-V, when the vibrational sub-bands of the conjugation band of this compound are called α, β, γ, δ, ... in the order from longer-wavelength-side, the most intense maximum is the γ-band in the solution spectrum, and is the δ-band in the solid state spectrum. In this connection, it has been known that the temperature affects markedly the relative intensities of the vibrational sub-bands. Thus, in the spectrum of *trans*-stilbene in mixed alcohols at -130°C measured by Beale and Roe[8], the fine structure is much more sharply resolved, the intensities of the α- and the β-bands are much greater, and the intensity of the γ-band is much smaller than in the solution spectrum measured at room temperature. In this low temperature spectrum, the most intense maximum is the β-band. To illustrate the situation, the three spectra of *trans*-stilbene are shown in Fig. 7.

In the present case, both the solution spectra and the solid state spectra are the ones measured at room temperature. Therefore, the fact that the marked redistribution of intensity among the vibrational sub-bands occurs between them may be said to be rather surprising. Further investigation seems to be necessary to interpret satisfactorily this interesting phenomenon.

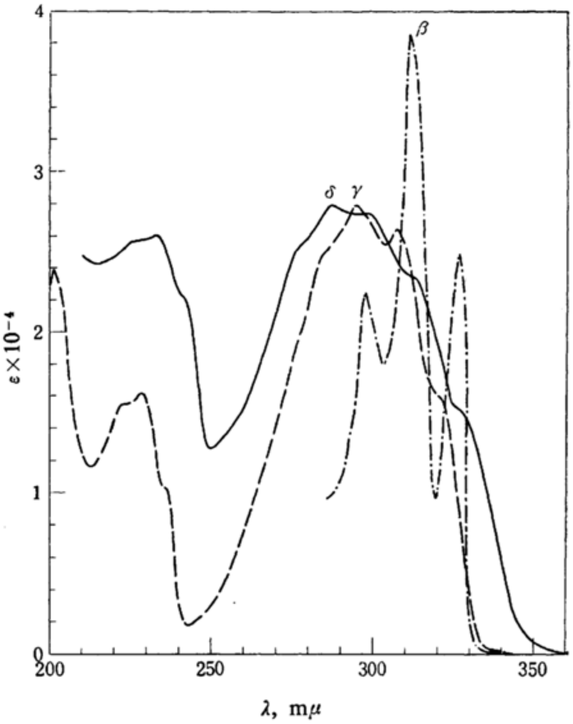

Fig. 7. Ultraviolet absorption spectra of *trans*-stilbene: ——, the solid state spectrum; ----, the solution spectrum; -·-·-, the low temperature spectrum (in mixed alcohols at -130°C, redrawn from Beale and Roe's paper[8]).

Wavelength Shifts of Bands.—In Fig. 8, the values of $\Delta\lambda$ for the compounds belonging to Groups I and II are plotted against the wavelengths λ of the corresponding maxima or inflections in the solution spectra. As mentioned already, $\Delta\lambda$ represents the magnitude of the wavelength shift of the band associated with the change of the state from *n*-heptane solution to solid.

A positive value of $\Delta\lambda$ indicates that the shift is bathochromic. As is seen in Table I, all the shifts, except for that in the case of *trans*-α, α'-dimethylstilbene, are bathochromic. Of course, the individual numerical values of $\Delta\lambda$ may not be decisive because of inevitable uncertainty in determination of the wavelength positions of the absorption maxima and especially of the inflections. Notwithstanding, it may be said that a rough correlation exists between λ and $\Delta\lambda$. Thus, in Fig. 8, almost all the points for the A-bands of all the compounds as well as the B-band of tolan are nearly on a correlation line, which has been drawn as the solid line in the figure. This means that $\Delta\lambda$ for these increases fairly regularly with λ from about 1.5 mμ at 220 mμ to about 5 mμ at 300 mμ, and to about 9.5 mμ

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8) R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 1953, 2755.

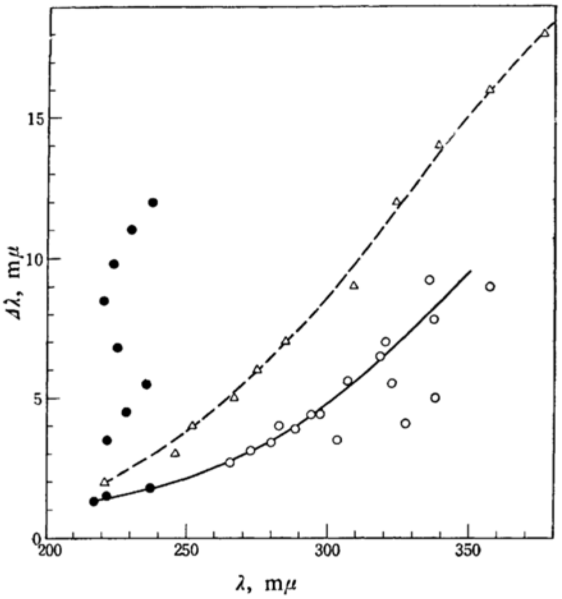

Fig. 8. Correlations between the magnitudes of wavelength shifts of bands (from solution to the solid state) and the wavelengths of the bands in the solution spectra.
○, for the A-bands of tolan and the stilbenes.
●, for the B-bands of tolan and the stilbenes.
△, for the bands of naphthalene and anthracene (according to Dale's data[4]).

at 350 mμ. On the other hand, most of the points for the B-bands, the bands which appear in the region about 220∼250 mμ, are markedly deviating from the correlation line. There appears to be a very rough relation that the longer the conjugated system is, or in other words, the longer the wavelength of the A-band is, the value of $\Delta\lambda$ for the corresponding B-band is the larger.

What is the cause of such bathochromic shifts of bands? This problem is unsettled. If the solid state spectra can be considered to be the spectra of micro-crystals oriented at random directions, the shifts are probably due to the intermolecular interactions in the crystals. Alternatively, if the solid state spectra are to be considered as the spectra of solid solutions, the shifts are probably due to a sort of solvent effect. Furthermore, the shifts may be due to other unknown causes. At any rate, whatever the mechanism of the shifts may be, the fact that there is a regular relation between the magnitudes of the shifts and the wavelengths of the bands is very interesting.

A similar regular relation has been found already by Dale[4] for the spectra of naphthalene and anthracene. According to him, the magnitude of the wavelength shift of a band of these "rigid" molecules due to the change of the state from hexane solution to solid, viz. the "normal red-shift", increases regularly with the wavelength of the band, from about 2 mμ at 220 mμ to about 8 mμ at 300 mμ, and to about 19 mμ at 400 mμ. As discussed in a previous paper (Ref. 1-I), this regular relation appears to hold good regardless of kinds of compounds, of characters of bands, and of intensities of bands. In Fig. 8, the values of the "normal red-shifts" are also plotted against the wavelengths of the bands in the spectra of hexane solutions according to Dale's data. A correlation line for these points is shown as the broken line.

It may be noteworthy that the correlation line obtained in the present work for stilbenes, which is subsequently referred to as the present correlation line, is located considerably lower than Dale's correlation line. That is, it may be said that the *trans*-stilbene-type compounds show the red-shifts of the normal magnitudes in themselves, which are smaller than the magnitudes of the normal red-shifts of naphthalene and anthracene. The latter compounds are, to use Dale's words, the "rigid" compounds which obviously can not assume other conformations in solution thanin the crystal lattice. Therefore, the above mentioned fact may be considered as an evidence indicating that the most probable conformationsof these stilbenes in solution are not significantly different from those in the solid, probably crystalline state, and accordingly, are probably planar.

While the probably planar compounds show the red-shifts of normal magnitudes, some compounds, which are discussed in the succeeding paragraphs as belonging to Groups III and IV, show the shifts of more or less abnormal magnitudes. It may be significant that the latter compounds are evidently non-planar. The conjugation bands of these compounds have no distinct fine structure, in contrast with the foregoing sterically unhindered compounds, and as a matter of fact, the shapes of the solid state spectra of these compounds are apparently not markedly different from those of the solution spectra.

Group III.—Triphenylethylene and tetraphenylethylene. The values of $\Delta\lambda$ for triphenylethylene are very slightly greater, and the values for tetraphenylethylene are much greater than those anticipated from the present correlation line in Fig. 8. The extraordinarily large shifts especially in the case of tetraphenylethylene may be considered to indicate that the most probable conformation of this compound in the solid state is considerably different from that in solution. That is, it may be inferred that the interplanar angles between the phenyl groups and the ethylenic bond are appreciably smaller in the most probable conformation in the solid, probably crystalline state, than in that in solution (cf. Ref. 1-VI).

Group IV.—*trans*-2, 4, 6, 2′, 4′, 6′-Hexamethylstilbene (*trans*-1, 2-dimesitylethylene), *cis*- and *trans*-α, α'-dimethylstilbenes, and *trans*-α, α'-diethylstilbene. The values of $\Delta\lambda$ for these compounds are smaller than anticipated from the present correlation line. Thus, the value for dimesitylethylene is slightly smaller, and the values for α, α'-dialkylstilbenes are much smaller than anticipated from the correlation line. The value for *trans*-α, α'-dimethylstilbene is apparently even negative.

The most probable conformations of these compounds are undoubtedly non-planar, owing to the steric effects of the alkyl substituents (cf. Refs. 1-VII and VIII). Therefore, it seems quite reasonable to correlate the smallness of the shifts with the non-planarity of the molecular structures. It may be presumed that with these non-planar compounds the intermolecular interactions in the crystals (or the interactions of the molecules with potassium chloride) are smaller than in the case of the foregoing planar compounds.

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