Electronic Absorption Spectra and Geometry of (*E*)-Stilbene and 'Stiff' Stilbenes

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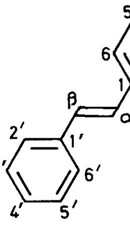
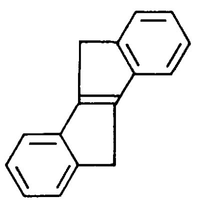
Examination of the electronic absorption spectra of (*E*)-stilbene (**1**), indeno[2,1-*a*]indene (**2**), 5,6,11,12-tetrahydrochrysene (**3**), (*E*)-1,1′-bi-indanylidene (**4**), and (*E*)-1,1′-bitetralinylidene (**5**) in fluid solution at room temperature and in glassy solution at 77 K led to the following conclusions. (a) The torsion angles of the C–Ph bonds in (**1**) deviate from 0° to some extent in the fluid solution and are nearly 0° in the glassy solution. (b) The (*E*)-stilbene skeleton in (**2**)—(**4**) is planar or nearly planar in the fluid as well as in the glassy solution. (c) The torsion angles of the C–Ph bonds in (**5**) substantially deviate from 0° in the fluid solution and become smaller in the glassy solution. However, they still deviate from 0° to a considerable extent. The observed spectral change is explained by the use of the Franck–Condon principle.

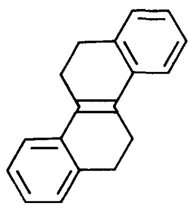
The molecular geometry of (*E*)-stilbene (**1**) has attracted much interest. While in the crystalline state the molecule is nearly planar,[1] in the gas phase the C–Ph bonds are substantially twisted.[2] The geometry in the solution phase is still under discussion, since there is no decisive method to determine the molecular geometry in the solution experimentally. One of us (H. S.) has explained the electronic absorption spectra of the neutral molecules,[3–6] radical ions,[7] and dianions[8] of (**1**) and related compounds on the assumption that the geometry of (**1**) is nearly planar in the solution phase.



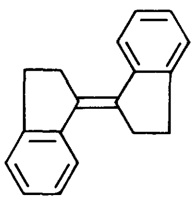
(**1**)



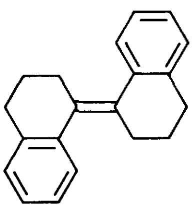
(**2**)



(**3**)



(**4**)



(**5**)

The purpose of the present study is to elucidate the molecular geometry of (**1**) in the solution phase by comparing its electronic absorption spectrum with those of a series of related compounds in which the (*E*)-stilbene skeleton is geometrically fixed by methylene chains: indeno[2,1-*a*]indene (**2**), 5,6,11,12-tetrahydrochrysene (**3**), (*E*)-1,1′-bi-indanylidene (**4**), and (*E*)-1,1′-bitetralinylidene (**5**).

This study is also connected to our interest in the change of molecular geometry upon ionization.[7,8] For the comparison of the molecular geometry of the neutral molecules and the radical ions produced by γ-ray irradiation in glassy solution at 77 K, the spectra of the glassy solution, particularly of the glass of 2-methyltetrahydrofuran (MTHF), in which anion radicals are produced, were examined.

Experimental

Materials.—The following compounds were prepared by the methods described in the literature: (**2**),[9] m.p. 194—199 °C, recrystallized from ethyl acetate and sublimed at 160 °C and 133 Pa, δ_H (90 MHz; $CDCl_3$) 7.0—6.5 (8 H, m), 2.75 (4 H, s); (**3**),[10] m.p. 102—103 °C, recrystallized from methanol; (**4**),[11] m.p. 138—139 °C, recrystallized from methanol; and (**5**),[12] m.p. 142—143 °C, recrystallized from methanol.

Measurements.—The electronic absorption spectra at room temperature were measured on a Shimadzu UV-240 spectrometer and those at 77 K on a Cary 14RI spectrophotometer. The effect of contraction of the solution, caused by lowering the temperature, on the molar absorption coefficient ε was not corrected.

Results and Discussion

The electronic absorption spectra of (**1**)—(**5**) in fluid solution at room temperature and in glassy solution at 77 K are shown in Figure 1 and relevant data are listed in the Table. The main absorption band of each compound at the lowest wavenumber is designated as A and only this band is discussed here.

Character of Main Absorption Band.—According to semi-empirical SCF–MO–CI calculations for the π electronic state of (**1**), band A can be ascribed mainly to a one-electron transition from the HOMO to the LUMO (Figure 2).[6] In the HOMO, bonds α–1 and β–1′ have antibonding character and bond α–β has bonding character. In the LUMO, bonds α–1 and β–1′ have bonding character and bond α–β has antibonding character. If bonds α–1 and/or β–1′ are twisted, the HOMO is stabilized and the LUMO is destabilized. Hence, the energy of transition from HOMO to LUMO increases. As a result, band A shifts to higher wavenumbers when bonds α–1 and/or β–1′ are twisted. When bond α–β is twisted, band A, on the other hand, shifts to lower wavenumbers.

Comparison of Spectra at Room Temperature.—There is no significant difference between the spectra of heptane solution and those of MTHF solution at room temperature except that each band in the latter is located at slightly lower wavenumber than in the former. The red shift is ascribed to an increase in dielectric constant of the solvent.

Band A of (**1**) is located at *ca.* 1.7—0.7 × 10^3 cm^{-1} higher

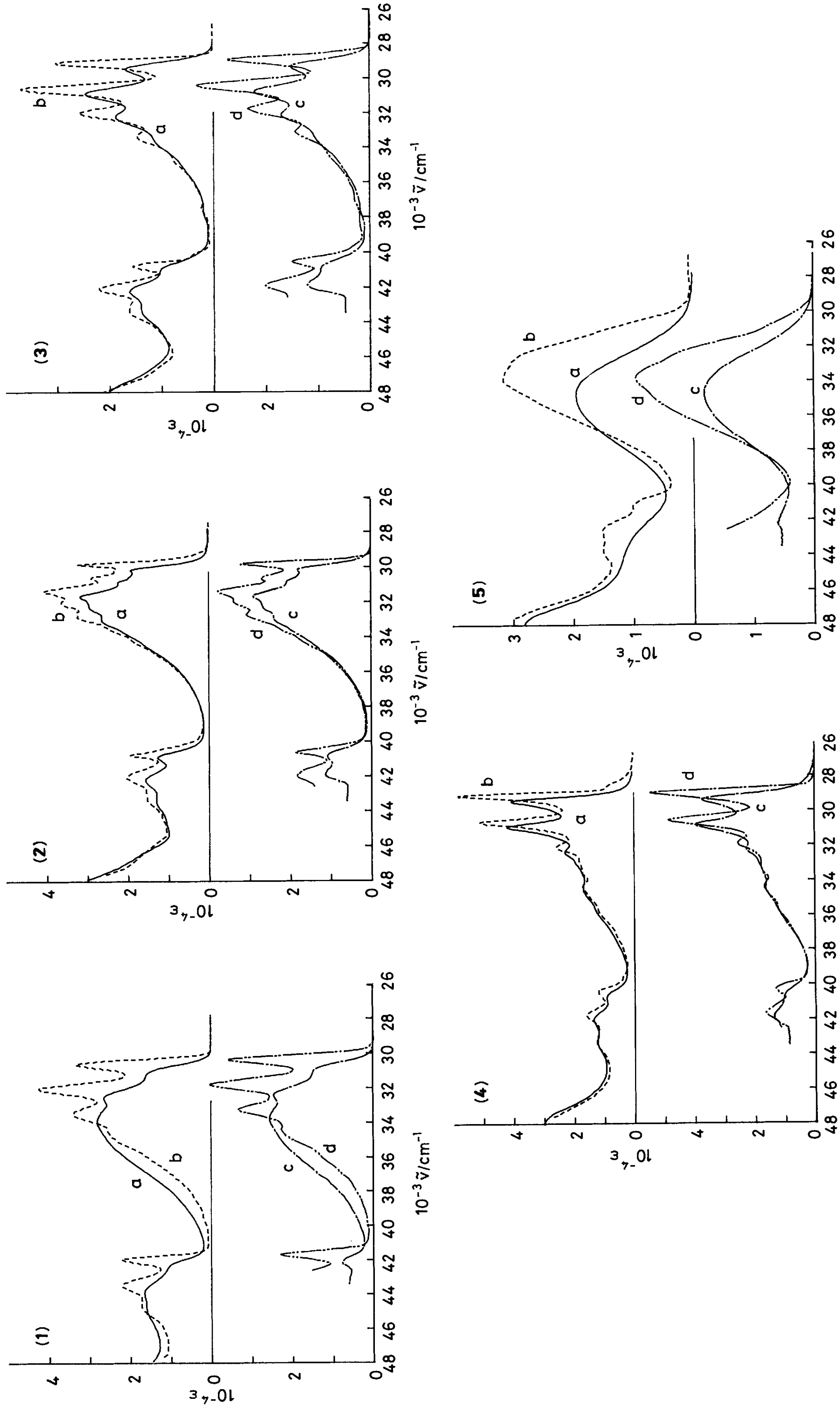


Figure 1. Electronic absorption spectra of (**1**)—(**5**): a, 10^{-5}M in heptane at room temperature; b, 10^{-4}M in 3-methylpentane (3MP) at 77 K; c, 10^{-5}M in 2-methyltetrahydrofuran (MTHF) at room temperature; d, 10^{-4}M in MTHF at 77 K

Table. Sub-band positions of band A of (**1**)—(**5**)

	In hydrocarbons			In MTHF		
Compound	$\tilde{\nu}_f$[a] / 10^3 cm^{-1}	$\tilde{\nu}_g$[b] / 10^3 cm^{-1}	$\tilde{\nu}_f - \tilde{\nu}_g$ / 10^3 cm^{-1}	$\tilde{\nu}_f$[c] / 10^3 cm^{-1}	$\tilde{\nu}_g$[d] / 10^3 cm^{-1}	$\tilde{\nu}_f - \tilde{\nu}_g$ / 10^3 cm^{-1}
(**1**)	31.15	30.61	0.54	31.09	30.37	0.72
	32.57	32.05	0.52	32.41	31.78	0.63
	33.90	33.50	0.40	33.74	33.21	0.53
(**2**)	30.16	29.85	0.31	30.17	29.80	0.37
	30.95	30.62	0.33	30.89	30.62[e]	0.27
	31.67	31.36	0.31	31.68	31.34	0.34
(**3**)	29.48	29.09	0.39	29.34	28.92	0.42
	30.86	30.60	0.26	30.74	30.41	0.33
	32.19	31.95	0.24	32.07	31.75	0.32
(**4**)	29.50	29.14	0.36	29.38	29.00	0.38
	30.96	30.67	0.29	30.82	30.55	0.27
	32.43	32.12	0.31	32.24	31.90	0.34
(**5**)	34.92	33.96	0.96	34.74	33.91	0.83

[a] Absorption maximum in heptane at room temperature. [b] Absorption maximum in 3MP at 77 K. [c] Absorption maximum in MTHF at room temperature. [d] Absorption maximum in MTHF at 77 K. [e] Value at the inflection.

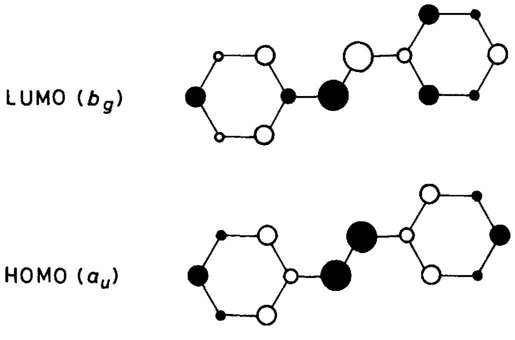


Figure 2. Relevant HMO orbitals of (*E*)-stilbene (**1**)

wavenumber than that of (**2**)—(**4**), and is located at *ca.* 1 × 10^3 cm^{-1} lower wavenumber than that of (**5**). Vibrational structures are observed except for (**5**). Particularly, those of (**3**) and (**4**) are prominent and are quite similar to each other. The vibrational structures are ascribed to the stretching of the central ethylene bond as already pointed out.[5,6,13,14]

Compounds (**2**)—(**4**) are so-called 'stiff' stilbenes,[15—18] in which twisting of the C–Ph bond is severely restricted by the methylene chains. There is no problem in assuming that (**2**) and (**3**), at least, are planar or nearly planar in fluid solution at room temperature as well as in glassy solution at 77 K.

The fact that band A of (**1**) is located at higher wavenumber than that of (**2**)—(**4**) is ascribed partly to the electronic bathochromic effect of alkylene chains of (**2**)—(**4**) and partly to the twisting of the C–Ph bonds of (**1**). The fact that the vibrational structure of (**1**) is less clear than that of (**2**)—(**4**) suggests that the C–Ph bonds of (**1**) are twisted to some extent in the fluid solution, since it has been demonstrated that the twisting of the C–Ph bonds in stilbenes causes blurring of the vibrational structure.[5,6,14]

The fact that band A of (**2**) is located at higher wavenumber (*ca.* 1 × 10^3 cm^{-1}) than that of (**3**) and (**4**) does not mean that the torsion angles of the C–Ph bonds in (**2**) are larger than those in (**3**) and (**4**) but does reflect the general trend that the main absorption band of a compound with a cyclopentadiene moiety is located at higher wavenumber than that of a corresponding compound with a cyclohexa-1,3-diene moiety.[19]

The fact that the position and the vibrational structure of band A of (**4**) is similar to those of (**3**) shows that the geometry of the (*E*)-stilbene skeleton in (**4**) is quite similar to that of (**3**). That is, the (*E*)-stilbene skeleton in (**4**) is nearly planar. The result of the molecular mechanics calculations by Vogel *et al.*,[18] that the torsion angle of the C–Ph bond in (**4**) is 29.0°, is inconsistent with our conclusion.

The facts that band A of (**5**) is located at higher wavenumber than that of (**1**), that it does not exhibit vibrational structure, and that the intensity of band A of (**5**) is considerably lower than that of (**1**) clearly demonstrate that the C–Ph bonds in (**5**) are substantially twisted. This conclusion is consistent with the results of molecular mechanics calculations by Lemmen and Lenoir, that the torsion angle of the C–Ph bonds in (**5**) is 54°.[12]

Comparison of Spectra at Room Temperature with Spectra at 77 K.—For a change from fluid solution at room temperature to glassy solution at 77 K, dramatic changes in spectra are observed. They are summarized as follows.[13,18,20] (1) Vibrational sub-bands become sharp. (2) Each sub-band shifts to lower wavenumber. The magnitude of the red shift increases in the order (**2**) ≈ (**4**) ≈ (**3**) < (**1**) < (**5**) (see Table). (3) Redistribution of intensity among sub-bands occurs especially in (**1**). Sub-bands at lower wavenumbers are intensified. (4) Intervals between sub-bands are increased.

Observation (1), the sharpening of sub-bands, is ascribed to the effects of lowering temperature. In general, lowering the temperature simplifies the population of vibrational and rotational states of the initial state (*i.e.*, the ground electronic state). In other words, the initial state settles down to a state with low quantum number as the temperature is lowered.

Observation (2) is ascribed to the solvent effect, that is, the effect of an increase in the refractive index of the solvent as pointed out by Dyck and McClure[13] and to the change of the conformation. The fact that the red shift of the band for (**1**) and (**5**), in which the C–Ph bonds deviate significantly from 0° in the fluid solution, is much larger than those for (**2**)—(**4**), in which conformational changes are expected to be small, indicates that the decrease in the torsion angles of the C–Ph bonds of (**1**) and (**5**) is large. Probably (**1**) has a nearly planar geometry in the glassy solution.

On the basis of this inference, observations (3) and (4) are explained as follows. With decrease in the torsion angles of the C–Ph bonds, the π bond order of the ethylene bond (*i.e.*, bond α–

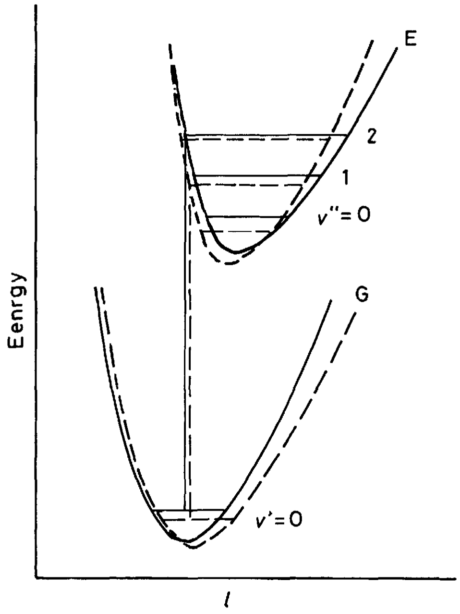


Figure 3. Potential energy curves of the (*E*)-stilbene system as functions of the length of the ethylene bond (l). Solid line and broken line represent potential energy curves in the fluid solution and in the glassy solution, respectively

β) in the ground state decreases and that in the excited state increases. Hence, relationships (1) and (2) are obtained where

$$l_{G,f} < l_{G,g} \quad (1)$$

$$l_{E,f} > l_{E,g} \quad (2)$$

$l_{G,f}$ and $l_{G,g}$ are the equilibrium length of the ethylene bond of the ground-state molecule in the fluid solution and that in the glassy solution, respectively, and $l_{E,f}$ and $l_{E,g}$ are the equilibrium length of the ethylene bond of the excited-state molecule in the fluid solution and that in the glassy solution, respectively. From these relationships, we obtain (3), *i.e.* the difference of the

$$l_{E,f} - l_{G,f} > l_{E,g} - l_{G,g} \quad (3)$$

equilibrium length of the ethylene bond between the excited and the ground state is smaller in the glassy solution than in the fluid solution. In other words, the more planar the geometry, the smaller is the change of the equilibrium length of the ethylene bond associated with the electronic transition.

Therefore, we can draw the potential energy curves as functions of the length of the ethylene bond, l, as shown in Figure 3. The curve of the ground state in the glassy solution is gentler than that in the fluid solution. In contrast, the curve of the excited state in the glassy solution is steeper than that in the fluid solution. The energy of the ground state at the equilibrium bond length is lower and that of the excited state is lower still in the glassy solution than in the fluid solution. Locations of the energy minima of the potential energy curves in the direction of the abscissa obey relations (1) and (2).

This picture gives the following explanation for observations (3) and (4). An observed sub-band is a vibronic transition from $v' = 0$ to v'', where v' is the quantum number for the stretching vibration of the ethylene double bond in the ground electronic state and v'' is that in the excited electronic state. According to the Franck–Condon principle, if the most intense sub-band is 0–$v''_{\max.}$, the value of $v''_{\max.}$ is smaller in the glassy solution than in the fluid solution. That is, with the change from the fluid solution to the glassy solution, the intensities of sub-bands with smaller v'' increase and those with larger v'' decrease due to relation (3) [observation (3)].

The fact that the potential curve of the excited electronic state in the glassy solution is steeper than that in the fluid solution means that the intervals between vibrational levels associated with the electronic excited state in the glassy solution are larger than those in the fluid solution. Hence, intervals between vibrational sub-bands in the glassy solution are larger than those in the fluid solution [observation (4)].

The 0–0 sub-band of (**1**) is an inflection in the fluid solution and appears as a sharp and intense sub-band in the glassy solution. The most intense sub-band of (**1**) changes from 0–2 to 0–1. This feature of the spectra of (**1**) in glassy solution at 77 K is also observed in the spectra of (**1**) in mixed alcohols at 143 K[20] and in stretched poly(vinyl alcohol) sheets at room temperature.[21] Hence, the decrease in the torsion angles of the C–Ph bonds of (**1**) is ascribed partly to lowering the temperature and partly to solidification of the solution.

The relative intensities between the 0–0 and the 0–2 sub-band of (**1**) in the glassy solution depends on the solvent. In 3-methylpentane (3MP), the 0–0 sub-band is weaker than 0–2, and in MTHF the order is reversed. The shape of band A in glassy 3MP solution almost coincides with that of (**3**) in fluid heptane solution.

The most intense sub-bands of (**2**) and (**3**) remain unchanged with the change from the fluid solution to the glassy solution, although the 0–0 sub-bands are intensified. The relative intensities of the 0–0 sub-band to those of higher wavenumber than the most intense sub-band in (**2**) and (**3**) increase. As a result, the shape of band A of (**1**) in the glassy MTHF solution almost coincides with that of (**3**) in the glassy solutions of 3MP and of MTHF.

These facts suggest that the torsion angles of the C–Ph bonds in (**1**) decrease with the change from the fluid solution to the glassy solution and that they are smaller in MTHF glass than in 3MP glass because of the much larger rigidity of MTHF glass.[22]

In the case of (**4**), a new strong shoulder appears at *ca.* 28.6×10^3 cm^{-1} in the glassy 3MP solution. According to Vogel *et al.*, the new shoulder is ascribed to an absorption of an aggregate of (**4**).[18] The increase of intensity of the 0–0 sub-band in (**4**), therefore, may be ascribed partly to the aggregation of (**4**) in the glassy solution.

In the case of (**5**), vibrational structure does not appear even in the glassy solution. The red shift of the absorption maximum associated with the change from the fluid solution to the glassy solution is *ca.* 0.8—1.0×10^3 cm^{-1}, which is substantially larger than the red shifts of the vibrational sub-bands of (**1**)—(**4**). However, the absorption maximum of (**5**) in the glassy solution is still located at much higher wavenumber than that of (**1**)—(**4**). Hence, we conclude that the torsion angles of the C–Ph bonds of (**5**) decrease significantly, but that they still deviate from 0° to a considerable extent in the glassy solution. That is, the geometry of the (*E*)-stilbene skeleton in (**5**) is similar to that of (*E*)-α,β-dimethylstilbene[4,6,23] and it is not regarded as a stiff stilbene.

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