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Conformational Analysis of Stilbenes by Photoelectron Spectroscopy

Tsunetoshi KOBAYASHI,* Hiroshi SUZUKI,† and Keiichiro OGAWA†
The Institute of Physical and Chemical Research, Wako, Saitama 351
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
†*Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153*

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Conformations of (*Z*)-stilbene, (*E*)-stilbene, and various methyl-substituted (*E*)-stilbenes were discussed from the standpoint of photoelectron spectroscopy. Photoelectron spectral data of (*Z*)-stilbene and (*E*)-stilbene were found to be perfectly consistent with the results by the gas electron diffraction method concerning the twist angles of the phenyl groups. The twist angles of the phenyl groups in various methyl-substituted (*E*)-stilbenes were estimated using the photoelectron spectral data by the new method presented recently. These estimated values correspond well to those obtained from the standpoint of the electronic absorption spectra.

Steric hindrance and molecular conformation are important subjects in organic chemistry. We have been studying the steric hindrance effect on photoelectron spectra[1)] and the application of photoelectron spectroscopy to conformational analysis[2)] of various types of organic compounds. In this paper we investigate the conformations of some stilbenes from the standpoint of photoelectron spectroscopy.

Conformations of stilbenes have long been and are still attracting great interests from the structural chemical and reaction mechanistic standpoints.[3)] Although (*Z*)-stilbene (ZS) has mostly and reasonably been regarded or concluded to be nonplanar or twisted because of the steric hindrance effect between the two phenyl groups, (*E*)-stilbene (ES) has often been presumed on the basis of the x-ray crystallographic analysis,[4)] or concluded to be essentially planar even in the fluid phases (see, however, Ref. 5, for example). However, according to the recent gas electron diffraction study,[6)] ES is not planar but its two phenyl groups are twisted by 32.2° from the olefinic group plane, and this value is rather close to that of ZS, 43.2°.[7)]

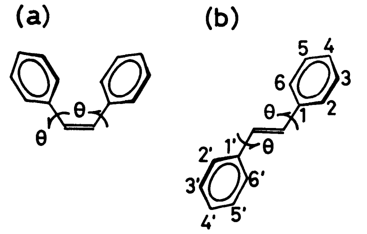

Fig. 1. Twisted conformations of (*Z*)-stilbene (a) and (*E*)-stilbene (b).

In this work, at first we examine if the photoelectron spectral data of ZS and ES are consistent with the gas electron diffraction results[6,7)] concerning the twist angles of the phenyl groups, θ, and then we carry out the conformational analysis of various methyl-substituted ES's. In the conformational analysis we use the new technique developed in our recent paper.[2c)] Concerning the photoelectron spectra of stilbenes, formerly we[1e)] and Maier and Turner[8)] studied both ZS and ES regarding ES as (nearly) planar in the vapors. Dewar and Goodman[9)] reported the ionization energy values of ES by a low-resolution instrument, and Kricka *et al.*[10)] those of ZS without interpretation. Afterwards Hudson *et al.*[11)] treated the photoelectron spectra of ES and diphenylpolyenes regarding these as planar, and McAlduff and Chan[12)] those of ES, (*E*)-4-methylstilbene (E4MS), and other 4-substituted ES's, concluding that these are planar.

Previously one of us (H.S.) developed a method for conformational analysis using electronic absorption spectra on the HMO level and discussed the conformations of various stilbenes in detail.[5,13)] In this paper the conformational analysis by photoelectron spectroscopy is compared with that by this electronic absorption spectroscopic method.

Experimental

Materials. (*E*)-2,2′-Dimethylstilbene (E22′DMS) (mp 81.0—82.0 °C, from hexane), (*E*)-3,3′-dimethylstilbene (E33′DMS) (mp 58.0—58.5 °C, from ethanol), and (*E*)-2,2′,5,5′-tetramethylstilbene (E22′55′TMS) (mp 161.0—162.0 °C, from hexane) were prepared according to the procedure of Mukaiyama *et al.*[14)] (Melting points are uncorrected.) Found for E22′55′TMS: C, 91.31; H, 8.70%; M$^+$, 236. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53%; M, 236. Preparations of (*E*)-4-methylstilbene (E4MS), (*E*)-4,4′-dimethylstilbene (E44′DMS), and (*E*)-2,2′,4,4′,6,6′-hexamethylstilbene (E22′44′66′HMS) were reported previously,[13c)] and ZS was a commercial product of Aldrich Chemical Co.

Measurements. The HeI photoelectron spectra of the methyl-substituted ES's were measured using the photoelectron spectrometer described formerly.[1c)] The sample inlet and target chamber systems were heated and kept at 131 °C for E4MS and E44′DMS, at 115 °C for E22′DMS, at 111 °C for E33′DMS and E22′55′TMS, and at 134 °C for E22′44′66′HMS.

The electronic absorption spectra of ZS, E22′DMS, E33′DMS, and E22′55′TMS in heptane were newly measured on a Hitachi EPS-3T spectrometer.

Computational

The CNDO/S calculations of ZS and ES were carried out with a FACOM 230-75 computer at the Institute of Physical and Chemical Research. All the necessary atomic integrals and parameters were taken from or estimated according to Ref. 15.

The geometrical structural parameters of ES and ZS necessary for the CNDO/S calculations were taken from or properly assumed based on Refs. 6 and 7. Their values are as follows:

The C=C–C bond angles, the C=C and the C–C bond lengths are 129.5°, 1.334 Å, and 1.489 Å for ZS, and 127.0°, 1.332 Å, and 1.483 Å for ES, respectively. The C=C–H bond angles, the C$\overset{\dots}{=}$C and the C–H bond lengths were taken to be 129.4°, 1.398 Å, and 1.095 Å, respectively, commonly both for ZS and ES.

Results and Discussion

(Z)- and (E)-Stilbene. The photoelectron spectra of ZS and ES were formerly studied by us[1e] in detail and also by Maier and Turner.[8] According to these former researches the first and the fifth bands of each compound are the so-called conjugation π bands and correspond to the ionizations from the π molecular orbitals delocalized over the entire molecular carbon frameworks, and the energy difference between these two molecular orbitals is quite sensitive to the change in θ. We use, therefore, the differences between the first and the fifth vertical ionization energies, $\Delta E_{\mathrm{iv}}^{1,5}$, of these compounds to estimate θ from the photoelectron spectra.

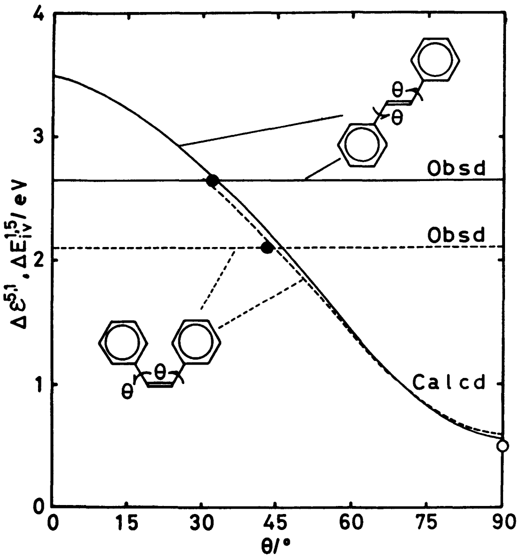

Fig. 2. Twist angle, θ, dependences of calculated energy differences between fifth and first highest occupied π molecular orbitals, $\Delta\varepsilon^{5,1}$, for (*Z*)- and (*E*)-stilbene with observed differences between first and fifth vertical ionization energies, $\Delta E_{\mathrm{iv}}^{1,5}$.
The solid circles denote the gas electron diffraction results combined with the observed $\Delta E_{\mathrm{iv}}^{1,5}$ values and the open one the estimated $\Delta E_{\mathrm{iv}}^{1,5}$ for $\theta = 90°$.

In Fig. 2 are shown the energy differences between the fifth and the first highest occupied π molecular orbitals, $\Delta\varepsilon^{5,1}$, for ZS and ES calculated by the CNDO/S method against θ. In the calculations the twist angles θ of the two phenyl groups of ZS or ES were assumed to be the same as each other. The $\Delta E_{\mathrm{iv}}^{1,5}$ values at the twist angles of 90° for ZS and ES are commonly estimated to be 0.49 eV by using the first and the second ionization energies of ethylbenzene, 8.78 and 9.27 eV,[2c] and the first ones of (*Z*)- and (*E*)-1,2-dimethylethylene, 9.12 eV.[16] The calculated $\Delta\varepsilon^{5,1}$ *vs.* θ curve for ZS or ES passes the point very close to this estimated value at 90°. This fact suggests that the calculated $\Delta\varepsilon^{5,1}$ *vs.* θ curves in Fig. 2 simulate well the real $\Delta E_{\mathrm{iv}}^{1,5}$ *vs.* θ curves for ZS and ES in the large θ region.

At first as a test case we treat ZS which is apparently a heavily sterically hindered compound. If we compare the observed difference between the first and the fifth vertical ionization energies, 2.10 eV, with the $\Delta\varepsilon^{5,1}$ *vs.* θ curve for ZS, we get 45° as the estimation for the θ value of ZS. This estimated value is very close to that observed by the gas electron diffraction method, 43.2°.[7] This satisfactory result and the point that ZS is structurally closely related with ES may guarantee the applicability of the same procedure to ES to estimate θ.

By applying the above procedure to ES we get 33° as θ. This estimated value is again very close to the one determined by the gas electron diffraction method, 32.2°.[6] From this result we can say that the photoelectron spectra of ZS and ES are perfectly consistent with the gas electron diffraction results concerning the twist angles, and that the phenyl groups of ES are considerably twisted in the gas phase from the photoelectron spectral point of view also.

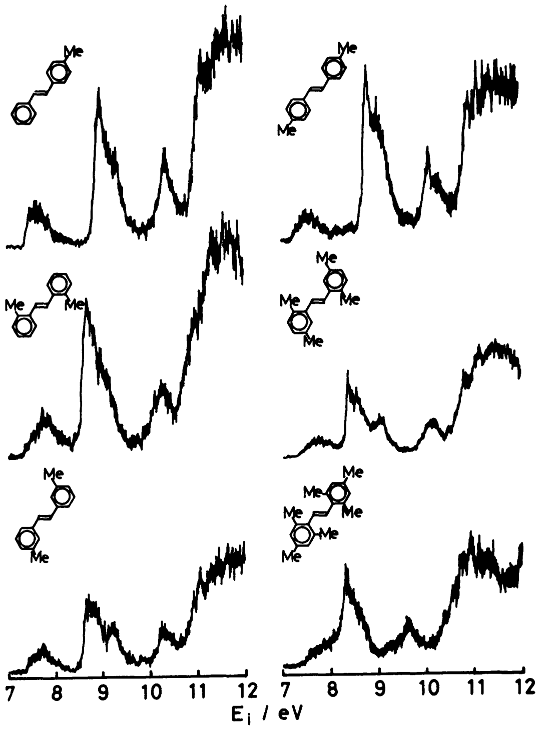

Fig. 3. Photoelectron spectra of methyl-substituted (*E*)-stilbenes.

Methyl-substituted (E)-Stilbenes. Now let us move to the conformational analysis of various methyl-substituted ES's. The photoelectron spectra of various methyl-substituted ES's are shown in Fig. 3. The vertical ionization energies obtained from these spectra are summarized in Table 1.

Judging from the vertical ionization energy values the first five bands of the methyl-substituted ES's are safely correlated with those of ES,[1e] respectively, that is, the first and the fifth bands correspond to the ioniza-

TABLE 1. VERTICAL IONIZATION ENERGIES, E_{Iv}, OF STILBENES

Compound	E_{Iv}/eV					
	Band					
	1	2	3	4	5	6
(*Z*)-Stilbene (ZS)[a]	8.17	8.99	9.22	9.36	10.27	11.3
(*E*)-Stilbene (ES)[a]	7.87	9.08	9.08	9.50	10.51	11.3
(*E*)-4-Methylstilbene (E4MS)	7.63	9.02	9.02	9.33	10.33	11.1
(*E*)-2,2′-Dimethylstilbene (E22′DMS)	7.83	8.72	8.72	9.17	10.27	11.0
(*E*)-3,3′-Dimethylstilbene (E33′DMS)	7.74	8.73	8.73	9.20	10.25	11.1
(*E*)-4,4′-Dimethylstilbene (E44′DMS)	7.54	8.82	8.82	9.0	10.12	11.0
(*E*)-2,2′,5,5′-Tetramethylstilbene (E22′55′TMS)	7.63	8.37	(8.6)	9.02	10.06	10.8
(*E*)-2,2′,4,4′,6,6′-Hexamethylstilbene (E22′44′66′HMS)	7.9	8.29	8.29	8.8	9.61	10.5

a) Ref. 1e.

tions from the π molecular orbitals delocalized over the entire molecular carbon frameworks. The second and the third bands of each compound correspond to the ionizations from the π molecular orbitals formed by the combinations between the two benzene ring e_{1g}(A) type orbitals, and the fourth band to the ionization from the π molecular orbital formed mainly by the out-of-phase type of combination between the two benzene ring e_{1g}(S) type orbitals slightly mixed with the olefinic anti-bonding π orbital. Here the e_{1g}(S) orbital denotes one of the degenerate $e_{1g}\pi$ orbitals of benzene ring and is symmetric against the mirror plane passing the 1- and the 4-position and perpendicular to the benzene ring plane, and the e_{1g}(A) orbital denotes the other e_{1g} orbital orthogonal to the e_{1g}(S) orbital mentioned above.

Now we estimate the θ values of these methyl-substituted ES's using the energy differences between the first and the fifth π bands. We have already seen the fact that the $\Delta\varepsilon^{5,1}$ *vs.* θ curves for ZS and ES pass the points very close to the experimentally estimated point for $\theta=90°$, and the fact that the comparison of the $\Delta\varepsilon^{5,1}$ *vs.* θ curves for ZS and ES with the observed energy differences between the first and the fifth vertical ionization energies give very good estimates for θ in these compounds. Judging from these facts we can safely say that the calculated $\Delta\varepsilon^{5,1}$ *vs.* θ curves simulate very well the real $\Delta E_{\mathrm{Iv}}^{1,5}$ *vs.* θ curves in the case of ZS and ES. Therefore, we use the calculated $\Delta\varepsilon^{5,1}$ *vs.* θ curve for ES as the starting point for the estimation of θ of the methyl-substituted ES's.

In order to estimate the θ values of the methyl-substituted ES's we use the essentially same procedure as developed in our recent paper,[2c)] that is, we correct the $\Delta\varepsilon^{5,1}$ *vs.* θ curve of ES for the methyl-substituent effect by the first order perturbation theory regarding the methyl substitutions as perturbations, and get the estimated $\Delta E_{\mathrm{Iv}}^{1,5}$ *vs.* θ curves for the methyl-substituted ES's. In the perturbation theoretic calculations we use the parameters evaluated in the preceding paper.[2c)] By comparing the estimated $\Delta E_{\mathrm{Iv}}^{1,5}$ *vs.* θ curves for the methyl-substituted ES's with the observed $\Delta E_{\mathrm{Iv}}^{1,5}$ values we can estimate the twist angles. As an example, the estimated $\Delta E_{\mathrm{Iv}}^{1,5}$ *vs.* θ curve for E44′DMS is shown in Fig. 4. By comparing the observed $\Delta E_{\mathrm{Iv}}^{1,5}$ value of this compound with the curve in Fig. 4, we get 36° as θ. The θ values estimated for the various methyl-substituted ES's in this manner are summarized in Table 2 with those by other methods. In the case of E22′DMS the estimated θ values for the three main types of conformers, the (*E*)-2,2′-, (*E*)-6,6′-, and (*E*)-2,6′-dimethyl conformers, were the same. This was also the case for E33′DMS. In the case of E22′55′TMS the estimated θ values for the (*E*)-2,2′,5,5′-, (*E*)-3,3′,6,6′-, and (*E*)-2,3′,5,6′-tetramethyl conformers were 41, 40, and 40°, respectively.

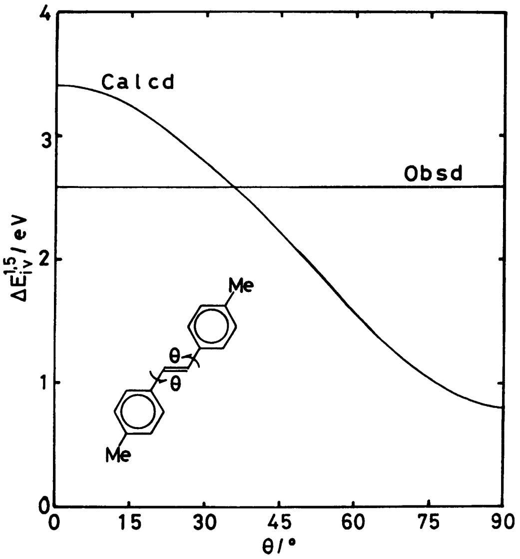

Fig. 4. Estimated θ dependence of $\Delta E_{\mathrm{Iv}}^{5,2}$ for (*E*)-4,4′-dimethylstilbene with observed $\Delta E_{\mathrm{Iv}}^{1,5}$.

The estimated θ value of E4MS, 32°, that of E33′DMS, 37°, and that of E44′DMS, 36°, are very close to that of and the observed one of ES, 33° and 32.2°, as seen in Table 2. This is reasonable because the methyl groups can not cause any steric hindrance in these molecules.

In the case of E22′DMS and E22′55′TMS the estimated θ values are 40 and 40—41°, respectively, and these are slightly larger than that for ES. This suggests the presence of slight steric hindrance by the 2- and 2′-methyl groups. In the case of E22′44′66′HMS, the estimated value is considerably larger than that of E22′DMS or E22′55′TMS, and this is reasonable

Table 2. Twist angles, θ, in stilbenes[a]

Compound	$\theta/°$							
	UPS (gas)		EAS[d] (solution)		ED[f] (gas)	XD[g] (solid)	NDDO[h]	MM[i]
	This work[b]	HMO[c]	I[e]	II[e]				
ZS	45	35	29.4	42.2	43.2±1.3		38	35—40
ES	33	(0)	(0)	(32.2)	32.2±2.1	3.4, 6.9	20	0—15
E4MS	32		(0)	(32.2)				
E22′DMS	40[e]		20.2	37.3				
E33′DMS	37[e]		(0)	(32.2)				
E44′DMS	36		(0)	(32.2)				
E22′55′TMS	40—41[e]		24.4	39.4				
E22′44′66′HMS	60		54.3[j]	59.7				50—55

a) The values in the parentheses are the assumed ones. b) The estimated error range for θ is around ±5° in the case of E22′44′66′HMS and ±4° in the case of the other methyl-substituted ES's. c) The HMO level method, Ref. 8. d) The electronic absorption spectral method on the HMO level, this work except for E22′44′66′HMS. e) See the text. f) The electron diffraction method, Refs. 6 and 7 for ES and ZS, respectively. g) The x-ray diffraction method, Ref. 4d. h) The NDDO method, Ref. 17. i) The molecular mechanics method, Ref. 18. j) Ref. 13c.

because the 2-, 2′-, 6-, and 6′-methyl groups are expected to cause greater steric hindrance than the pair of the 2- and 2′-methyl groups only.

As discussed above the estimated θ values show very reasonable tendency, and this fact supports the validity of the method used here.

Comparison with the Electronic Absorption Spectroscopic and Other Approaches. Formerly one of us (H.S.) developed a method on the HMO level to estimate the twist angles using the energies of the longest-wavelength electronic absorption spectral band maxima and discussed the conformations of various stilbenes in detail.[5,13] We now compare the conformation analytical results obtained by photoelectron spectroscopy with those by electronic absorption spectroscopy.

For this purpose the electronic absorption spectra of ZS, E22′DMS, E33′DMS, and E22′55′TMS were newly measured in heptane and are shown in Fig. 5.

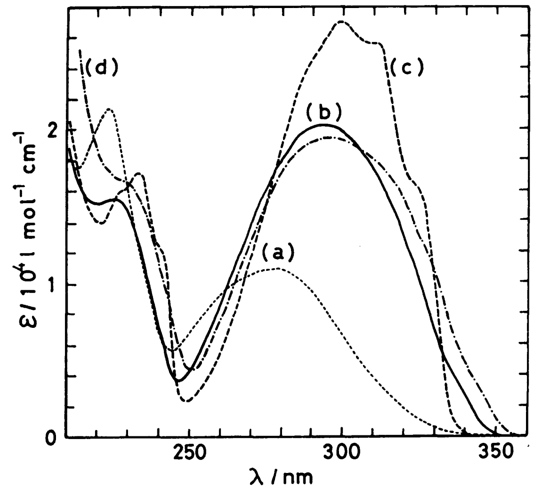

Fig. 5. Electronic absorption spectra of (*Z*)-stilbene (a), (*E*)-2,2′-dimethylstilbene (b), (*E*)-3,3′-dimethylstilbene (c), and (*E*)-2,2′,5,5′-tetramethylstilbene (d) in heptane.

The wavelengths and the molar absorption coefficients at the absorption maxima of the longest-wavelength intense bands of these compounds are as follows: ZS, 278.7 nm, 1.031×10^4 l/mol cm; E22′DMS, 293.6 nm, 2.022×10^4 l/mol cm; E33′DMS, 299.5 nm, 2.699×10^4 l/mol cm; E22′55′TMS, 295.4 nm, 1.945×10^4 l/mol cm.

The spectra of the other stilbenes treated in this study were reported formerly.[5,13c]

The twist angles of the stilbenes estimated by using the energies of the first conjugation bands according to the method described formerly in detail[5,13c] are summarized in Table 2. The electronic bathochromic effects of the methyl substituents located on the benzene nuclei were taken into account by adequately choosing the reference compounds for correlation between the calculated transition energies and the observed ones as described in Ref. 13c. The θ values of the entry I in Table 2 were estimated on the assumption that ES, E4MS, E33′DMS, and E44′DMS are completely planar, and those of the entry II on the assumption that the θ values for these compounds are commonly 32.2°, adopting the gas electron diffraction result for ES.[6]

The θ values estimated from the photoelectron spectral data of these stilbenes are consistent in the tendency with those of the entry I in Table 2 and are almost quantitatively consistent with those of the entry II. These facts support the validities of the both methods which are independent of each other and suggest that the relative conformational situations are similar to each other between the gas and the solution phases.

In Table 2 are also given the θ values calculated by other authors for the sake of comparison. The recent NDDO result[17] seems to be fair as for the θ value of ES. The empirical molecular mechanics type calculation[18] underestimated the θ value for ES though the method is for free molecules.

Electronic Absorption Spectral Band Features. Finally let us examine the band features of the electronic absorption spectra of some stilbenes from the conformational standpoints briefly. Formerly it has been pointed out and discussed in detail[13c,19] that the longest-wavelength absorption band of an apparently sterically hindered stilbene such as E22′44′66′HMS is considerably weaker in intensity than that of a sterically (almost) unhindered one such as ES, E4MS, or E44′DMS, and that the former is almost structureless while the latter shows well-resolved fine structures.

Keeping this point in mind let us see the electronic spectra of E22′DMS and E22′55′TMS shown in Fig. 5. The first bands of these spectra are almost structureless, almost equal to each other in intensity, and considerably weaker in intesity than that of E33′DMS shown in Fig. 5 which is reasonably regarded to be sterically unhindered. These facts mean clearly that the θ values of E22′DMS and E22′55′TMS are almost equal to each other and larger than that of E33′DMS. And this is consistent with the tendency of the θ values for these compounds estimated in this paper.

The longest-wavelength electronic absorption band of E33′DMS is quite similar in intensity and in fine structures to those of ES,[5] E4MS,[13c] and E44′DMS.[13c] These facts mean that E33′DMS is unhindered and support the validity of the mutual closeness of the θ values for these compounds estimated from the photoelectron spectra in this study. However, the fine structures of the longest-wavelength band of E33′DMS are slightly blurred compared to that of ES, E4MS, or E44′DMS, and this point may reflect the fact that the three main conformers, which may be designated as (*E*)-3,3′-, (*E*)-5,5′-, and (*E*)-3,5′-dimethylstilbene and are almost energetically equivalent to one another, are contributing to the ground state of E33′DMS in the fluid phases.

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