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A New Method for Conformational Analysis by Photoelectron Spectroscopy with Application to Alkyl-substituted Styrenes

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A new method for molecular conformational analysis using photoelectron spectral data was developed and applied to alkyl-substituted styrenes as an example. The dihedral angle between the phenyl ring and the olefinic group planes, θ, in each molecule is evaluated by comparing the observed difference between the first and the third vertical ionization energies, $\Delta E_{\mathrm{iv}}^{1,3}$, with the empirically estimated $\Delta E_{\mathrm{iv}}^{1,3}$ *vs.* θ curve, the alkyl substituent effect being taken into account by the first order perturbation theory. The new method gives reasonable results consistent qualitatively with those given by other former methods.

As a part of our program to investigate the steric hindrance effect on molecular photoelectron spectra and the application of photoelectron spectroscopy to molecular conformational analysis,1) in this paper a new method for conformational analysis by photoelectron spectroscopy is presented and applied to some β-alkylstyrenes and related compounds as an example.

The simplest method for molecular conformational analysis by photoelectron spectroscopy is at present that by Maier and Turner.2) They estimated empirically the dihedral angles in molecules by the composite molecule type consideration on the HMO level taking into account the interaction between two group orbitals only, that is, in their method the conjugative interaction of these two group orbitals with other group orbitals are completely neglected throughout the calculations. The new method presented in this paper is devised to be applicable even to the cases where this type of interaction is not negligible.

The relations between the molecular conformations and photoelectron spectra of some styrenes have formerly been studied by us1c) and Maier and Turner.2b) During the course of our photochemical study of β-alkylstyrenes3) it was found that the accurate conformational data of these molecules useful for the interpretation of photochemistry are still completely lacking. This is the reason why alkylstyrenes are revisited here.

Experimental

Measurements. The photoelectron spectra were recorded with the He I resonance line as the excitation source in the same way as described formerly.1c)

Materials. *cis*-β-Methylstyrene4) and *cis*-β-ethylstyrene4) were obtained by hydrogenation of 1-phenylpropyne and 1-phenylbutyne, respectively, on Pd/C in ethyl alcohol and purified by column chromatography. *trans*-β-Methylstyrene4) and *trans*-β-ethylstyrene4) were prepared by dehydration of the alcohols obtained through the reaction of acetaldehyde and benzaldehyde, respectively, with the appropriate Grignard reagents. A mixture of *cis*- and *trans*-β-*t*-butylstyrene was synthesized according to Ref. 5 and the *cis*- and *trans*-isomer were isolated by column chromatography. The purities of the samples were checked by gas chromatography and their molecular structures were identified by NMR spectroscopy. These styrenes were distilled under reduced pressure just before use.

Computational

The CNDO/S6) calculations of styrene, *s-trans*-butadiene, and naphthalene 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. 6.

The structural parameters of *s-trans*-butadiene and naphthalene were taken from Ref. 7 and those of styrene were assumed as follows:

The C=C and the C–H bond lengths of the phenyl group were assumed to be 1.397 Å and 1.084 Å, respectively, on the basis of the data for benzene.7) The C=C, the C–H bond lengths of the vinyl group, and the C–C bond length between the phenyl and the vinyl groups were assumed to be 1.337 Å, 1.08 Å, and 1.483 Å, respectively, by consulting the data for *s-trans*-butadiene.7) All the C–C–C and the C–C–H bond angles were assumed to be 120°.

Results and Discussion

Photoelectron Spectra. The photoelectron spectra of *cis*- and *trans*-β-methyl-, ethyl-, and *t*-butylstyrene measured in this study are shown in Figs. 1, 2, and 3. The vertical ionization energies of the lower energy bands of these compounds obtained from the spectra are summarized in Table 1 with those of the related compounds.

The first three bands of β-methyl-, β-ethylstyrenes, or *trans*-β-*t*-butylstyrene are well separated from one another, their vertical ionization energies being rather close to those of styrene, and are safely correlated with the first three bands of styrene,1c) from the top respectively. The first and the third bands of styrene,1c) respectively, correspond to the ionizations from the two molecular orbitals approximately expressed as the anti-bonding and the bonding types of combinations of the benzene ring $e_{1g}(S)$-like group orbital with the vinyl group occupied π orbital. Here $e_{1g}(S)$ denotes one of the doubly degenerate e_{1g} π orbitals of benzene, and is symmetrical with respect to the mirror plane passing the 1- and the 4-position and perpendicular to the benzene ring. On the other hand, the second

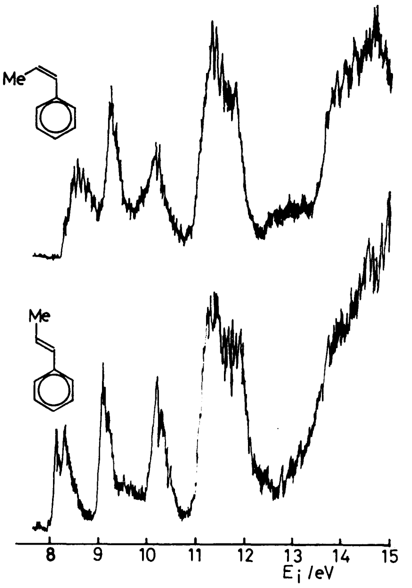

Fig. 1. Photoelectron spectra of *cis*-β-methylstyrene and *trans*-β-methylstyrene.

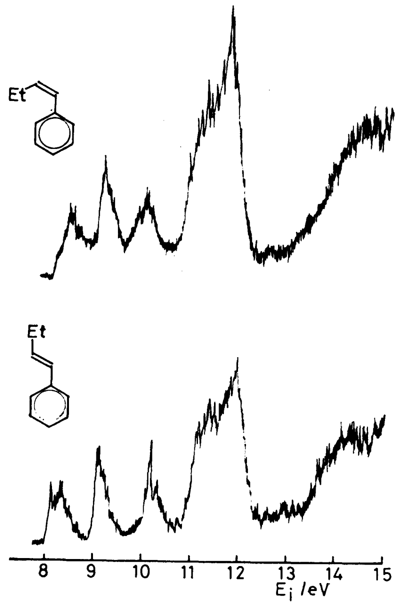

Fig. 2. Photoelectron spectra of *cis*-β-ethylstyrene and *trans*-β-ethylstyrene.

band corresponds to the ionization from the orbital composed almost completely of the benzene ring e_{1g}(A)-like orbital. Here e_{1g}(A) denotes the other e_{1g} orbital of benzene which is antisymmetrical with respect to the mirror plane mentioned above. The ionization energies of and the splitting between the first and the third bands of styrene are, therefore, quite sensitive to the dihedral angle, θ, between the vinyl group and the benzene ring planes, while the second ionization energy is almost indifferent to the change in θ because of its completely localized nature on the benzene ring as visualized in Fig. 4 of Ref. 1c.

In the case of *cis*-β-*t*-butylstyrene the second and the third bands are evidently highly overlapping with each other, and it is quite natural to consider that this has been caused by the heavy steric hindrance effect of the bulky *t*-butyl group. But one should be careful in the point that the electronic effect of *t*-butyl group is also contributing to the lower ionization energy shift of the third band of *cis*-β-*t*-butylstyrene when compared to styrene. Similar care is more or less important for the other bands and for the other alkyl-substituted styrenes also.

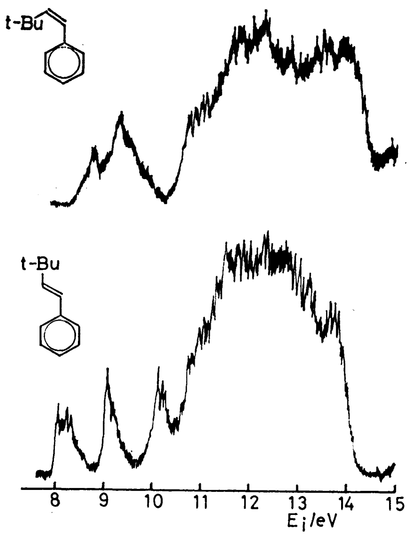

Fig. 3. Photoelectron spectra of *cis*-β-*t*-butylstyrene and *trans*-β-*t*-butylstyrene.

Table 1. Vertical ionization energies, E_{iv}, of styrenes and related compounds

Compound	E_{iv}/eV Band 1	2	3	4
Styrene[a]	8.49	9.27	10.55	11.52
2-Methylstyrene[a]	8.53	8.99	10.37	11.22
3-Methylstyrene[a]	8.37	8.98	10.34	11.27
4-Methylstyrene[a]	8.20	9.11	10.24	11.29
α-Methylstyrene[a]	8.52	9.18	10.12	11.26
cis-β-Methylstyrene	8.48	9.18	10.26	11.30
trans-β-Methylstyrene	8.34	9.09	10.25	11.46
cis-β-Ethylstyrene	8.54	9.16	10.02	11.24
trans-β-Ethylstyrene	8.30	9.09	10.19	11.37
cis-β-*t*-Butylstyrene	8.85	9.27	9.5[c]	10.91
trans-β-*t*-Butylstyrene	8.18	9.05	10.10	11.02
2,4-Dimethylstyrene[a]	8.22	8.80	10.11	11.06
2,6-Dimethylstyrene[a]	8.48	8.62	10.04	11.04
Propylene[b]	9.744			
Ethylbenzene[a]	8.78	9.27		

a) Ref. 1c. b) Ref. 8. c) This value is the approximate one because of the heavy overlapping between the second and the third bands of *cis*-β-*t*-butylstyrene.

In the following we use the observed differences between the first and the third vertical ionization energies of alkyl-substituted styrenes, $\Delta E_{\mathrm{iv}}^{1,3}$, for the estimation of the dihedral angles, taking into account the electronic effect of the alkyl groups.

Conformational Analysis by Photoelectron Spectroscopy. The calculational steps of the new method for conformational analysis by photoelectron spectroscopy are described in the following.

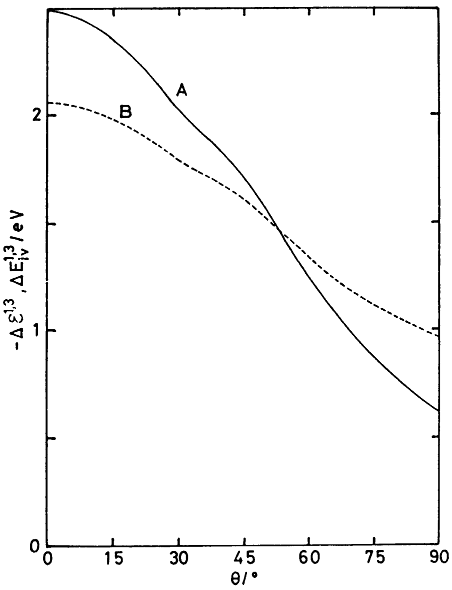

Fig. 4. Twist angle, θ, dependence of calculated orbital energy difference between the highest and the third highest occupied π orbitals for styrene, $\Delta\varepsilon^{1,3}$, (curve A) and that of difference between the first and the third vertical ionization energies of styrene, $\Delta E_{iv}^{1,3}$, estimated using curve A and formula (1) (curve B).

At first SCFMO calculations including all valence electrons are carried out for various twist angles of the parent compound. In this study we carried out CNDO/S[6)] calculations of styrene itself for the twist angle from 0° to 90° at the intervals of 15°.

The calculated energy difference between the highest and the third highest occupied π orbitals of styrene, $\Delta\varepsilon^{1,3}$, is plotted against θ. Thus we get the $\Delta\varepsilon(\theta)^{1,3}$ *vs.* θ curve (curve A in Fig. 4).

In most cases this type of curve deviates more or less from the corresponding $\Delta E_{iv}(\theta)^{1,3}$ *vs.* θ curve. To estimate the realistic $\Delta E_{iv}(\theta)^{1,3}$ *vs.* θ curve, in this paper we transform curve A in Fig. 4 by the following simple formula:

$$\Delta E_{iv}(\theta)^{1,3} = a\Delta\varepsilon(\theta)^{1,3} + b \tag{1}$$

Here a and b are constants and are evaluated by using the experimental $\Delta E_{iv}^{1,3}$ of styrene as $\Delta E_{iv}(0°)^{1,3}$ and the difference between the first ionization energies of propene[8)] and ethylbenzene[1c)] as $\Delta E_{iv}(90°)^{1,3}$. Styrene itself is planar in the ground state according to the Raman spectral study.[9)] The a and b values thus evaluated are -0.586 and 0.603 eV, respectively. Now we get curve B in Fig. 4.

The $\Delta E_{iv}(\theta)^{1,3}$ *vs.* θ curve obtained above takes into account effectively the effect of the interactions of the two molecular orbitals under consideration with other orbitals. This curve B is expected to simulate rather well the real $\Delta E_{iv}(\theta)^{1,3}$ *vs.* θ curve, especially in the small θ region because styrene, which is known to be planar in the ground state as mentioned before, was used as the reference compound for $\theta=0°$.

By the way, the following equation can simulate well curve B in Fig. 4 if we adopt the same $\Delta E_{iv}(0°)^{1,3}$ and $\Delta E_{iv}(90°)^{1,3}$ values as in the case of formula (1):

$$\Delta E_{iv}(\theta)^{1,3} = \sqrt{\{\Delta E_{iv}(90°)^{1,3}\}^2 + [\{\Delta E_{iv}(0°)^{1,3}\}^2 - \{\Delta E_{iv}(90°)^{1,3}\}^2]\cos^2\theta} \tag{2}$$

This equation can easily be derived by the composite molecule type consideration on the HMO level taking into account the interaction between two group orbitals only. This means that in the case of styrene the two-orbital model is not bad approximation.

Returning to the main story, for the conformational analysis of alkyl-substituted styrenes, we must correct curve B by taking into account the alkyl substituent electronic effect. This effect on the ionization energies can be estimated by the following formula according to the first order perturbation theory:[10,11)]

$$-\Delta E_{ivj} = g\{\sum_{\alpha} C_{j\alpha}^2 + m\sum_{\beta} C_{j\beta}^2\} + h \tag{3}$$

Here ΔE_{ivj} denotes the j-th vertical ionization energy change caused by alkyl substitution, C_{jk} the pπ atomic orbital coefficient of the atom k in the j-th molecular orbital, being calculated by the CNDO/S method in this study, α the alkyl-substituted carbon atom(s) and β the carbon atom(s) adjacent to the atom α. The parameter m is a kind of damping factor and is put equal to 1/3 by consulting the result in Ref. 10. Though the g and h values for methyl and t-butyl groups have already been given in Ref. 11, we reevaluated these parameter values by the least square method using the recent ionization energy data with those for ethyl group.

The compounds and the vertical ionization energy data used for the evaluation of g and h are as follows:

For methyl group, the first ionization energies of ethylene,[8)] its methyl,[8)] *cis*- and *trans*-1,2-dimethyl derivatives,[8)] *s-trans*-butadiene,[12)] its 1-methyl[12)] and 1,4-dimethyl derivatives,[12)] benzene,[13)] toluene,[1d)] and *m*-xylene.[1d)]

For ethyl group, the first ionization energies of ethylene,[8)] its ethyl derivative,[8)] *s-trans*-butadiene,[12)] its 4-ethyl derivative,[12)] benzene,[13)] ethylbenzene,[1c)] and the first three ionization energies of naphthalene, 8.15, 8.88, 10.00 eV,[10)] those of 1-ethylnaphthalene, 7.91, 8.72, 9.68 eV, and those of 2-ethylnaphthalene, 7.94, 8.63, 9.83 eV.

For *t*-butyl group, the first ionization energies of ethylene,[8)] its *t*-butyl derivative,[8)] propylene,[8)] its *cis*- and *trans*-*t*-butyl derivatives,[8)] three isomers of di-*t*-butylethylenes,[8)] benzene,[13)] and the first two ionization energies of *t*-butylbenzene.[11)]

The g and h values with the mean square errors, and the mean square error for ΔE_{ivj} thus obtained are for methyl group, $1.04^0 \pm 0.04^2$ eV, $-0.00^7 \pm 0.03^1$ eV, $\pm 0.06^4$ eV; for ethyl group, $1.30^0 \pm 0.03^1$ eV, $0.00^3 \pm 0.00^8$ eV, $\pm 0.02^3$ eV; for *t*-butyl group, $1.33^8 \pm 0.04^6$ eV, $0.00^2 \pm 0.03^5$ eV, $\pm 0.08^4$ eV, respectively.

Thus we can estimate the $\Delta E_{iv}(\theta)^{1,3}$ *vs.* θ curve for each alkyl-substituted styrene by correcting curve B in Fig. 4 for alkyl substituent effect by applying formula (3) to the highest and the third highest occupied π orbitals of styrene. For example, we get the curve shown in Fig. 5 in the case of 2-methylstyrene.

Now it is quite easy to estimate the twist angle θ. By comparing the observed $\Delta E_{iv}^{1,3}$ value of 2-methylstyrene, for example, with the curve shown in Fig. 5

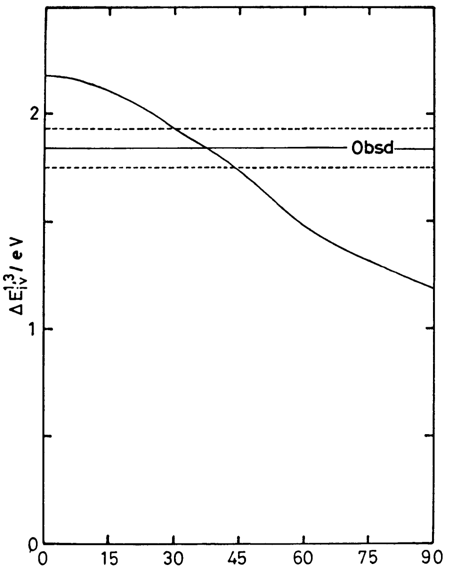

Fig. 5. Estimated twist angle, θ, dependence of difference between the first and the third vertical ionization energies of 2-methylstyrene, $\Delta E^{1,3}_{iv}$ with observed $\Delta E^{1,3}_{iv}$. Broken lines denote the mean square error.

Table 2. Dihedral angles, θ, in styrenes

Compound	θ/°			
	UPS		UVS	
	This work	M.-T.[a)]	S.[b)]	B.-S.[c)]
2-Methylstyrene	$38\pm^{7}_{8}$	22	31	28
3-Methylstyrene	$18\pm^{9}_{18}$			
4-Methylstyrene	$11\pm^{12}_{11}$		(0)[d)]	
α-Methylstyrene	29±6	38	33	
cis-β-Methylstyrene	22±6		35.2	
trans-β-Methylstyrene	$12\pm^{7}_{12}$	(0)	(0)	
cis-β-Ethylstyrene	$38\pm^{1}_{2}$			
trans-β-Ethylstyrene	12±4			
cis-β-t-Butylstyrene	72[e)]			
trans-β-t-Butylstyrene	$8\pm^{14}_{8}$			
2,4-Dimethylstyrene	41±8		30.7	
2,6-Dimethylstyrene	$68\pm^{12}_{10}$	55	54	

a) Ref. 2b. b) Ref. 14. c) Ref. 15. d) The values in the parentheses are the assumed ones. e) This value is the approximate one. See footnote c) for Table 1.

the twist angle θ of 2-methylstyrene is estimated to be $38°\pm^{7°}_{8°}$. The error limits for θ were approximately estimated from the mean square error for ΔE_{ivj} multiplied by $\sqrt{2}$. The dihedral angles of the other molecules were also estimated in the same way and are summarized in Table 2.

In the case of 3-methyl-, 4-methyl-, *trans-β*-methyl-, and *trans-β-t*-butylstyrene, the error ranges for θ include 0° as shown in Table 2, and in the case of *trans-β*-ethylstyrene the lower error limit is not so far from 0°. These results are reasonable because *trans-β*-alkyl substitution can not be considered to cause any steric hindrance effect upon the benzene ring parts in these cases. These reasonable results support the validity of the method developed here.

The θ value for *cis-β*-ethylstyrene given in Table 2 is slightly larger than that for *cis-β*-methylstyrene, and that for *cis-β-t*-butylstyrene is far larger than that for *cis-β*-ethylstyrene. These tendencies are also reasonable.

Suzuki[14)] estimated the twist angles of some styrenes from the UV absorption band energies in solution by the HMO level consideration. Braude and Sondheimer[15)] estimated the angles from the UV absorption spectral intensities on the assumption of $\varepsilon/\varepsilon_0=\cos^2\theta$ where ε and ε_0 are the molar absorptivity of the conjugation band of the alkylstyrene in question and that of the corresponding planar reference system, respectively. Maier and Turner[2b)] estimated the twist angles for 2-methyl-, α-methyl-, and 2,6-dimethylstyrene by the two-orbital model consideration on the HMO level mentioned before. The twist angles of some styrenes estimated by these authors are also summarized in Table 2. The general tendency of the calculated twist angles in this paper seems to correspond roughly to those by the other methods mentioned above.

To our regret there are at present no accurate data on the conformations for these alkyl-substituted styrenes as yet. The θ values predicted here may be useful as guiding data until accurate conformational data become available.

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