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Photoelectron Spectra of the *cis*- and *trans*-Isomers of Some Ethylene Derivatives

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The photoelectron spectra of *cis*- and *trans*-stilbenes, fumaric acid, dimethyl maleate, and dimethyl fumarate were measured and interpreted, special attention being paid upon their difference between the corresponding *trans*- and *cis*-isomers. The two characteristics were found for the photoelectron spectra of *cis*- and *trans*-stilbenes: (1) the splitting between the first and fifth bands is smaller for the *cis*-isomer (steric-hindrance effect); (2) the splitting between the second and third bands is larger for the *cis*-isomer (through-space interaction). The difference in the carbonyl n orbital ionization potentials between dimethyl maleate and fumarate was interpreted in terms of through-bond interaction.

The effect of steric configuration upon photoelectron spectra (PES) of organic molecules is an interesting research subject not only from the study of their electronic structures but also from the application of the spectra to the structural determination. So far several studies have been carried out for the PES of *cis*- and *trans*-isomers of some ethylene derivatives. The PES of dichloroethylenes were studied by Jonathan and coworkers$^{1)}$ and also by Lake and Thompson.$^{2)}$ Chadwick and coworkers$^{3)}$ studied the PES of dibromoethylenes. Bock and coworkers studied the PES of dicyanoethylenes,$^{4)}$ dibromo- and dichloroethylenes,$^{5)}$ and dithiomethoxyethylenes.$^{6)}$ In a series of compounds mentioned above, the out-of-plane π orbital vertical ionization potentials, I_v's, of a *cis*-isomer are rather similar to those of the corresponding *trans*-isomer. In *cis*-dihalogenoethylenes or *cis*-dicyanoethylene in-plane orbitals often show I_v's different from those of the corresponding *trans*-isomer because of the difference in the through-bond and through-space interactions$^{7)}$ between these isomers. Wittel and coworkers$^{8)}$ have demonstrated the importance of spin-orbit coupling in the case of iodoethylenes.

We have studied the PES of *cis*- and *trans*-stilbenes, dimethyl maleate, and dimethyl fumarate for the purpose of clarifying experimentally and explaining theoretically the difference in PES between the corresponding *cis*- and *trans*-isomers. The PES of fumaric acid has also been studied for the sake of comparison. Concerning the PES of *cis*- and *trans*-stilbenes, a brief report was published by Maier and Turner$^{9)}$ after our work had been completed. In this paper, we report the more details of the PES of *cis*- and *trans*-stilbenes.

Experimental and Theoretical

cis-Stilbene was purified with the alumina column chromatography, *trans*-stilbene and fumaric acid by recrystallization from ethanol and aqueous ethanol, respectively. Dimethyl maleate was purified by distillation and dimethyl fumarate by sublimation.

The PES of these compounds were measured with the photoelectron spectrometer described previously,$^{10)}$ 584 Å He resonance line being used as the excitation source. The sample inlet and target chamber system was heated to 97 °C for *trans*-stilbene, 46 °C for *cis*-stilbene, 124 °C for fumaric acid and 38 °C for dimethyl fumarate and 47 °C for dimethyl maleate.

The CNDO/2$^{11)}$ calculations of the compounds under consideration were carried out with a FACOM 230—60 computer at the Institute of Physical and Chemical Research. Their structures were properly assumed on the basis of the appropriate structural data given in Refs. 12, 13, and 14.

Results and Discussion

cis- and trans-Stilbenes. The observed PES of *cis*- and *trans*-stilbenes are shown in Fig. 1 and those

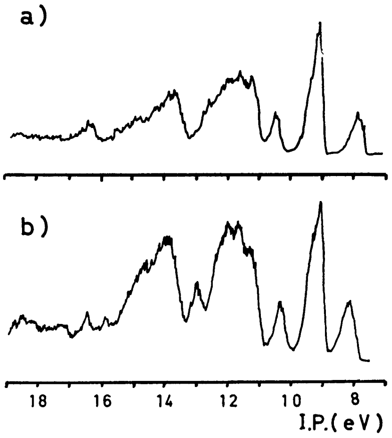

Fig. 1. Photoelectron spectra of (a) *trans*-stilbene and (b) *cis*-stilbene.

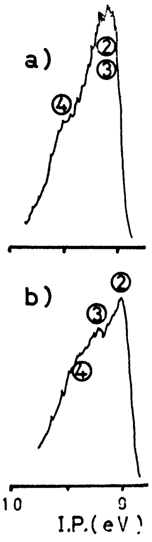

Fig. 2. Expanded photoelectron spectra in the 8.5∼10 eV region: (a) *trans*-stilbene; (b) *cis*-stilbene.

Table 1. Vertical ionization potentials of stilbenes and related compounds in eV

PES band	1	2	3	4	5	6
cis-Stilbene	8.17	8.99	9.22	9.36	10.27	11.3
trans-Stilbene	7.87	9.08	9.08	9.50	10.51	11.3
Benzene[a]	9.23	11.67	12.32	13.97		
Ethylene[b]	10.51	12.85	14.66	15.87		

a) T. Kobayashi and S. Nagakura, *Chem. Lett.*, **1972**, 903. b) Ref. 16.

measured on the expanded energy scale around 9~10 eV are shown in Fig. 2, and the I_v's of these compounds and related ones obtained from the PES are summarized in Table 1.

The stilbenes commonly show three groups of bands in the region of 7.5~11 eV. This is also the region for the benzene $e_{1g}\pi$[15] (9.23 eV) and ethylene $b_{3u}\pi$ (10.51 eV[16]) bands. The stilbenes contain two benzene rings and one ethylene group. So it is quite reasonable to consider that the observed three groups of bands correspond to the five occupied π orbitals constructed mainly from the four benzene $e_{1g}\pi$ orbitals and one ethylenic π orbital.

The experimental orbital energy diagram obtained on the assumption $\varepsilon = -I_v$ (Koopmans' theorem[17]) is shown in Fig. 3.

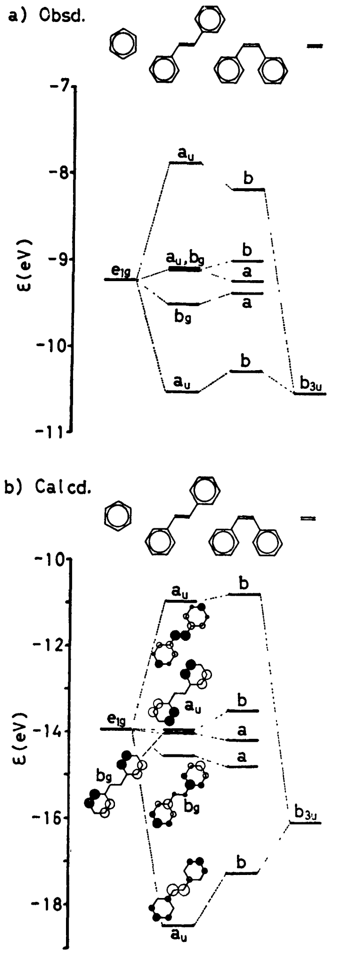

Fig. 3. Observed and calculated π orbital energy diagrams for stilbenes.

The CNDO/2 calculations and also qualitative consideration show that the first and fifth bands of each isomer should be assigned to the ionizations from two π orbitals in which the two benzene rings and the ethylene group interact strongly and, therefore, π electrons delocalize over the entire molecular carbon framework; the higher one corresponding to the highest occupied π orbital of each isomer is antibonding in the nature of the C–C bonds connecting the benzene rings with the ethylene group and the lower one corresponding to the fifth highest occupied π orbital of each isomer is bonding.

According to the CNDO/2 calculations the second and third bands of each isomer should be assigned to the two occupied π orbitals completely localized on the two benzene rings. This is consistent with the fact that the I_v's of both bands are close to that of the first band of benzene corresponding to the ionization from the $e_{1g}\pi$ orbitals.

According to the CNDO/2 calculations the fourth band of each isomer should be assigned to the π orbital almost completely localized on the benzene rings but slightly mixed with the antibonding π orbital of the ethylene group. The fact that the I_v of the band is only slightly greater than that of the first band of benzene, supports this assignment. The slight mixing of the vacant antibonding π orbital of the ethylene group shifts the fourth band to the slightly higher ionization energy side than the second and third bands.

The PES of *cis*- and *trans*-stilbenes are different from each other in the following points:

i) The splitting between the first and fifth bands of *cis*-stilbene (2.10 eV) is smaller than that of *trans*-stilbene (2.64 eV). This can be explained in terms of the fact that in the *cis*-isomer the conjugation between the ethylenic group π orbital and the benzene ring π orbitals decreases because of the twisting of the two benzene rings from the molecular plane caused by the steric hindrance effect between them.[13] This was pointed out also by Maier and Turner.[9]

ii) The second and third bands of *cis*-stilbene split by 0.2 eV but those of *trans*-stilbene are almost degenerate. This fact can be explained as follows. The corresponding π orbitals of *trans*-stilbene are completely localized on the two benzene rings and the I_v's of these orbitals should be equal to each other. On the other hand, in the case of *cis*-stilbene the two benzene rings approach each other so closely that the pπ atomic orbitals at the *ortho* positions can overlap with each other, though slightly. This is a reason why the second and third bands split from each other for the *cis*-isomer. This tendency was qualitatively reproduced by the CNDO/2 calculation (see Fig. 3). Therefore this difference between the *trans*- and *cis*-isomers is due to the so-called through-space interaction[7] at the classically non-bonded position.

Fumaric Acid, Dimethyl Fumarate, and Dimethyl Maleate. The PES of fumaric acid, dimethyl fumarate, and dimethyl maleate are shown in Fig. 4. The PES of dimethyl fumarate and dimethyl maleate measured on the expanded energy scale around 10~12 eV are shown in Fig. 5.

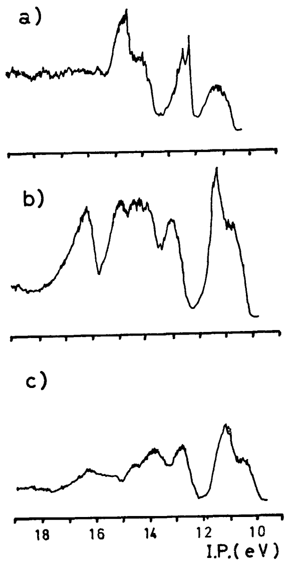

Fig. 4. Photoelectron spectra of (a) fumaric acid, (b) dimethyl fumarate, and (c) dimethyl maleate.

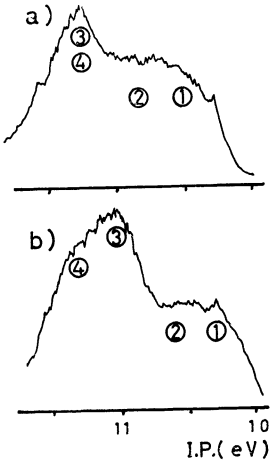

Fig. 5. Expanded photoelectron spectra around 11 eV: (a) dimethyl fumarate; (b) dimethyl maleate.

Table 2. Vertical ionization potentials of fumaric acid, dimethyl fumarate, dimethyl maleate, and related compounds in eV

PES band	1	2	3	4	5
Fumaric acid	10.9	11.1	12.15	12.41	13.9
Dimethyl fumarate	10.5	10.8	11.27	11.27	12.91
Dimethyl maleate	10.3	10.6	11.04	11.3	12.77
Acetic acid[a]	10.87	12.05			
Methyl acetate[a]	10.48	11.16			

a) Ref. 18.

The vertical ionization potentials of these compounds and related ones obtained from their PES are summarized in Table 2.

The correlation diagram for the higher occupied orbitals of these compounds obtained on the assumption $\varepsilon=-I_v$ (Koopmans' theorem[17]) is shown in Fig. 6. The calculated orbital energy diagram given by the CNDO/2 method is also shown in Fig. 6 for the sake of comparison.

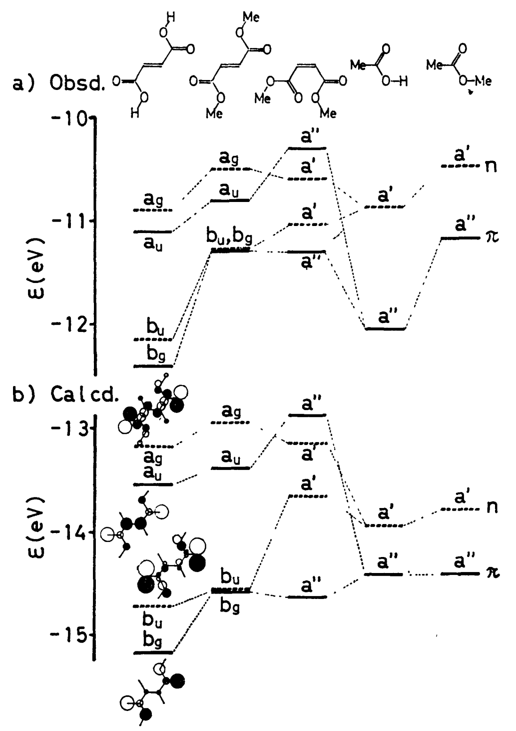

Fig. 6. Observed and calculated orbital energy diagrams for fumaric acid, dimethyl fumarate, and dimethyl maleate.

The PES of fumaric acid has two groups of bands in the region of 10.5~13 eV. This is also the region for the bands of the acetic acid carbonyl n (10.87 eV[18]) and carboxyl π (12.05 eV[18]) orbitals and also for the band of the ethylenic π orbital (10.51 eV[16]). So the observed bands under consideration may correspond to the molecular orbitals constructed by the interaction among the two n orbitals and two π orbitals of the two carboxyl groups and the ethylenic π orbital.

The calculated orbital energy diagram for fumaric acid can explain satisfactorily from the qualitative point of view the observed relative pattern of the first two groups of bands. The calculation suggests that the first group of bands may correspond to $a_g n$ and $a_u \pi$ orbitals and the second group of bands to $b_u n$ and $b_g \pi$ orbitals from the top, respectively.

Sweigart and Turner[18] studied the assignment of the PES of acetic acid and showed that the n band of the acid is quite sharp and the π band is rather broad. According to our CNDO/2 calculation of fumaric acid the fourth highest occupied molecular orbital, $b_g \pi$ orbital, is quite similar to the corresponding π orbital of acetic acid, and the third highest occupied molecular orbital, $b_u n$ orbital, is of the nonbonding nature and is almost completely localized on the two carbonyl groups. So it is reasonable to assign the sharp band at 12.15 eV to the ionization from the third highest occupied $b_u n$ orbital. Accordingly, the remaining fourth band at 12.41 eV may be assigned to the fourth highest occupied $b_g \pi$ orbital.

The first and second bands highly overlap with each other. The CNDO/2 calculation indicates that they are assigned to $a_g n$ and $a_u \pi$ orbitals, respectively.

Here let us turn to dimethyl fumarate and dimethyl maleate. The CNDO/2 calculations predict that the third and fourth highest occupied orbitals are nearly accidentally degenerate for dimethyl fumarate and split from each other for dimethyl maleate. The experimental result shown in Fig. 5 satisfies this prediction. Furthermore, according to the CNDO/2 calculations, the fourth highest occupied orbitals of both compounds are almost completely composed of the carbomethoxyl π orbitals and have almost the same energy. In agreement with this prediction, the observed fourth bands of both compounds show almost the same I_v's; 11.27 eV for dimethyl fumarate and 11.3 eV for dimethyl maleate. Therefore, the fourth bands of both compounds may reasonably be assigned to the fourth highest occupied π orbitals obtained by the CNDO/2 calculations. The fact that the I_v's of these bands are close to the carbomethoxyl π I_v of methyl acetate, 11.16 eV,[18] also supports this assignment.

The third band of dicarbomethoxyethylenes may be assigned to the n orbitals, b_un in dimethyl fumarate and a′n in dimethyl maleate. The b_un I_v of the former is larger than the corresponding a′n I_v of the latter. This difference between both isomers is brought about by through-bond interaction. According to the CNDO/2 calculations, the through-bond interaction between the carbonyl n orbitals is greater for the *cis*-isomer than for the *trans*-isomer.

According to the CNDO/2 calculations the first and second bands of dimethyl fumarate may be assigned to the a_gn and $a_u\pi$ orbitals, respectively, and those of dimethyl maleate to the a″π and a′n orbitals, respectively. The overall qualitative agreement between the pattern of the calculated orbital energy diagram and the observed spectral pattern may support the assignment predicted by the CNDO/2 method for fumaric acid, dimethyl fumarate, and dimethyl maleate.

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