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Original Scientific Paper

Photoelectron Spectroscopy of Some trans-2,2'-Disubstituted Stilbenes*

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The He I photoelectron (PE) spectra of stilbene (1), 2,2'-dichlorostilbene (2), 2-amino-2'-chlorostilbene (3), 2,2'-diaminostilbene (4), and 2,2'-dinitrostilbene (5), all in their trans configuration are recorded and discussed. The electronic structure of 1—5 can well be described on the basis of the composite molecule method and simple Hückel molecular orbital (HMO) calculations. Results indicate the importance of substituent effects causing characteristic shifts of low energy electronic band systems in the PE spectra.

INTRODUCTION

Elucidation of substituent effects on electronic structure of conjugated molecules in a general manner is an intriguing problem which has been the subject of numerous investigations. PE spectroscopy and MO calculations, within the validity of Koopmans' theorem provide a powerful tool for such investigations. In the present study we wish to report such results on some trans-2,2'-disubstituted stilbenes, 2—5, which as compared with the expected splitting of low energy π -ionizations caused by the substituents (»conjugative effect«) indicate the overwhelming importance of their characteristic shifts (»inductive effect«). Besides numerous results on the PE spectra of trans and cis-stilbene⁶⁻⁸ so far only one paper reported spectra of some 4-substituted stilbenes.⁹

EXPERIMENTAL

The HeI PE spectra of 1—5 have been recorded on a Vacuum Generators UVG3 spectrometer employing elevated temperatures of the inlet system (100 °C, 110 °C, 140 °C, 200 °C, and 230 °C for 1—5, respectively). Details of the instrument are described in ref. 1. No decomposition of the samples under these conditions was observed. The energy scale was calibrated by admitting small amounts of Xe and/or CH₃J to the sample flow.

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Besides **1**, which was of commercial origin (zone melted) compounds **2–5** were synthesized as described in ref. 2.

Standard HMO calculations for **1–5** have been performed using the same parameter set as in ref. 3, 4 (NH_2 , NO_2) and $h_{\text{Cl}} = 2.0$, $k_{\text{Cl}} = 0.4$ for chlorine.⁵

RESULTS

The HeI PE spectra of **1–5** are reproduced in Figure 1. The numbers above each spectrum correspond to vertical ionization energies of observed band systems which are assigned below according to standard notation. The m_k coefficients of the HMO calculations defining the energy E_k of the molecular orbital by $E_k = \alpha_c + m_k \beta_{\text{CC}}$, $k = 1, 2, \dots, n$ are listed for compounds **1–5** in Table I. Correlation of low energy π -ionizations in **1–5** with the calculated

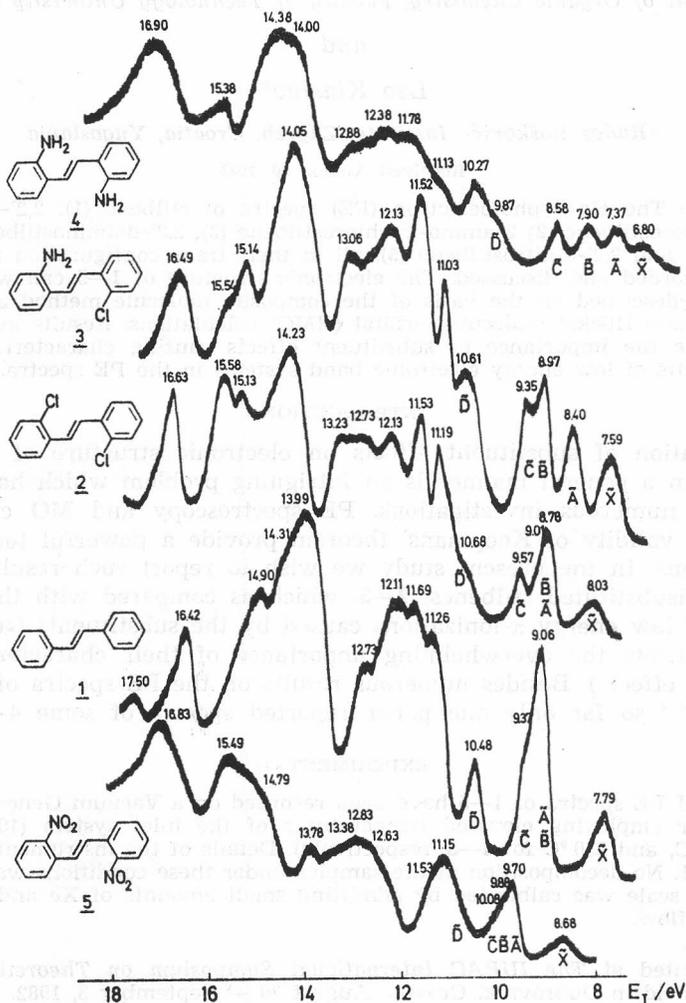


Figure 1. The HeI photoelectron spectra of 2,2'-diaminostilbene (**4**), 2-amino-2'-chlorostilbene (**3**), 2,2'-dichlorostilbene (**2**), stilbene (**1**) and 2,2'-dinitrostilbene (**5**)

π -electron distribution within the corresponding MO's (area of circles are proportional to squared coefficients of atomic orbitals) is given in Figure 2.

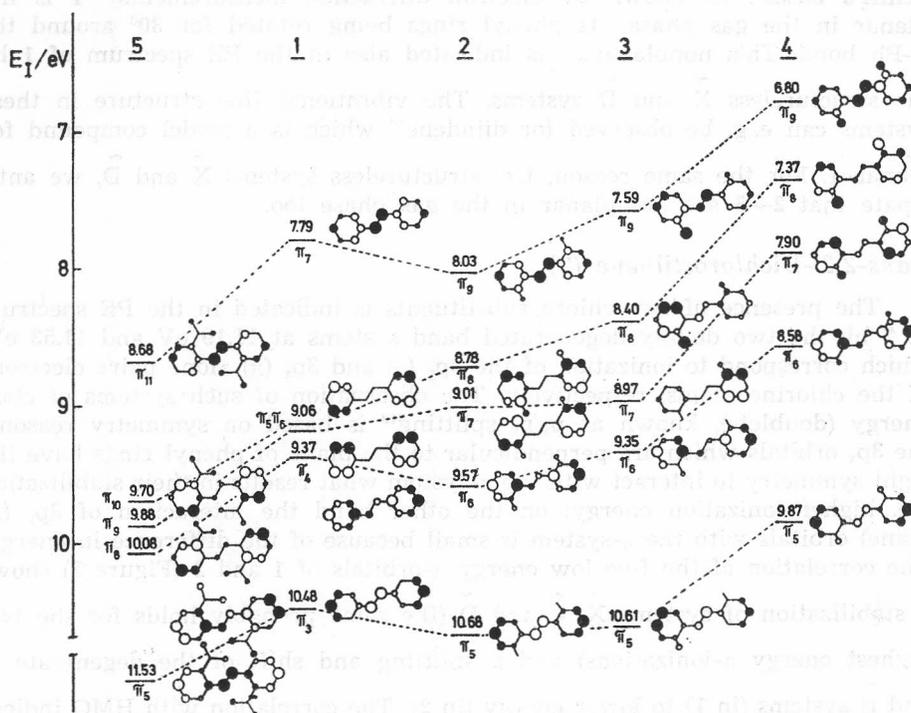


Figure 2. Correlation diagram for π -ionizations of *o,o'*-disubstituted stilbenes 1-5

TABLE I
HMO Results for Compounds 1-5

Compound	m_1	m_2	m_3	m_4	m_5	m_6	m_7	m_8	m_9	m_{10}	m_{11}
1	2.21	2.06	1.50	1.16	1.00	1.00	0.50				
2	2.30	2.23	1.98	1.91	1.50	1.15	0.96	0.96	0.49		
3	2.34	2.24	1.95	1.69	1.50	1.15	0.96	0.82	0.44		
4	2.36	2.27	1.72	1.66	1.50	1.14	0.84	0.79	0.40		
5	4.19	4.19	2.23	2.09	1.51	1.50	1.50	1.17	1.09	1.07	0.56

trans-Stilbene (1)

The PE spectrum of 1, as well as of its isomer *cis*-stilbene has been reported several times⁶⁻⁸ and the assignment of the five lowest energy systems to π -ionizations can be taken as established. The location of π_2 at 12.11 eV and π_1 at 12.73 eV is less certain, and will be proven in near future either through measurement of the Penning ionization spectrum of stilbene¹⁰ or by the »perfluoro effect« in the PE spectrum of perfluoro stilbene. The correlation

of the π -ionizations with HMO coefficients yields a fairly good straight line which practically coincides with those obtained for indene analogs³ and Schiff's bases⁴. As shown by electron diffraction measurements¹¹ **1** is not planar in the gas phase, its phenyl rings being rotated for 30° around the C-Ph bond. This nonplanarity is indicated also in the PE spectrum of **1** by the structureless \tilde{X} and \tilde{D} systems. The vibrational fine structure in these systems can e. g. be observed for diindene¹² which is a model compound for planar **1**. For the same reason, i. e. structureless systems \tilde{X} and \tilde{D} , we anticipate that **2**—**5** are not planar in the gas phase too.

trans-2,2'-Dichlorostilbene (**2**)

The presence of two chloro substituents is indicated in the PE spectrum of **2** by the two doubly degenerated band systems at 11.19 eV and 11.53 eV, which correspond to ionization of the $3p_y$ (σ) and $3p_x$ (π) »lone pair« electrons of the chlorine atoms, respectively. The observation of such systems of close energy (doublets), known as p_x/p_y splitting¹³ is based on symmetry reasons: the $3p_x$ orbitals which are perpendicular to the plane of phenyl rings have the right symmetry to interact with the π -system what results in their stabilization i. e. higher ionization energy; on the other hand the interaction of $3p_y$ (in plane) orbitals with the σ -system is small because of the difference in energy. The correlation of the five low energy π -orbitals of **1** and **2** (Figure 2) shows a stabilization of systems \tilde{X} , \tilde{C} and \tilde{D} (the same probably holds for the two highest energy π -ionizations) and a splitting and shift of the degenerate \tilde{A} and \tilde{B} systems (in **1**) to lower energy (in **2**). The correlation with HMO indices of the five low energy π -ionizations yields practically the same line as for *trans* stilbene.

trans-2-Amino-2'-chlorostilbene (**3**)

In the PE spectrum of **3** we see the separation of the \tilde{A} , \tilde{B} and \tilde{C} systems which was indicated also in **2** and will become complete in **4**. This is well predicted by the respective HMO results. In correlation with **2** the low energy π -ionizations are shifted to lower values (Figure 2) in accordance with the expected effect of an amino group. Again, correlation with the corresponding HMO indices yields the same regression line as for **1** and **2**. The system at 11.03 eV in **3** corresponds to the p_y (in plane) ionization of chlorine and is followed by the system at 11.52 eV arising from the p_x -ionization.

trans-2,2'-Diaminostilbene (**4**) and *trans*-2,2'-Dinitrostilbene (**5**)

The effect of electron donating and electron withdrawing substituents on **1** is illustrated by the spectra of compounds **4** and **5**, respectively. What one readily observes is the strong shift of π -ionizations into opposite direction and a different behaviour respective to conjugative effects. Namely, systems \tilde{A} , \tilde{B} and \tilde{C} come apart in **4**, but nearly coincide in the PE spectrum of **5**. Both is qualitatively predicted by simple HMO calculations (Table I). However,

correlations with HMO indices for 4 and 5 although yielding straight lines with the same slope as for 1–3 have clearly different intercepts caused by corresponding shifts of about 0.5 eV to lower and higher ionization energies, respectively.

DISCUSSION

The characteristic influence which certain substituents or heteroatoms exhibit on the PE spectrum of a »parent« compound has been widely recognized and usually interpreted in terms of »perfluoro«, »aza«, »nitro group«, »methyl-group« and other effects. Hereby the observation was meant that characteristic and structurally defined parts of the »parent« PE spectrum remained practically unchanged in shape, but were shifted to higher or lower ionization energies in the related spectrum. In the present case we have a similar situation, namely that besides the splitting of systems which even within the simple HMO method is well described by conjugative effects, in compounds 4 and 5 with strong electron donating and electron withdrawing groups as substituents, respectively, we observe, in correlation to the parent compound, the overwhelming effects of energy shifting: all systems in 4 are shifted to lower and all in 5 to higher ionization energies. One can define such shift as a characteristic of the substituent. The similar has been shown¹⁴ in the case of monosubstituted benzenes, naphthalenes and anthracenes. However, in the present compounds enlarged twisting caused by the substituents additionally influences the spectra yielding structureless and rather broad systems \tilde{X} and \tilde{D} .

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SAŽETAK

Fotoelektronski spektri nekih trans-2,2'-disupstituiranih stilbena

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Snimljeni su i diskutirani He I fotoelektronski spektri stilbena (1), 2,2'-diklorstilbena (2), 2-amino-2'-klorstilbena (3), 2,2'-diaminostilbena (4) i 2,2'-dinitrostilbena (5), svih u trans konfiguraciji. Elektronska struktura spojeva 1–5 može se dobro opisati na osnovu metode sastavljene molekule i jednostavnim računima Hückelovih molekularnih orbitala. Rezultati ukazuju na značaj efekata supstituenata, koji izazivaju karakteristične pomake nisko energetske elektronske sisteme vrpce u fotoelektronskim spektrima.