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Original Scientific Paper

## Photoelectron Spectroscopy of Heterocycles. 1-(2-Furyl)-2-arylethenes\*

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HeI photoelectron spectra of 2-ethenylfuran (1), cis-2-(2-phenylethenyl)-furan (2), trans-2-(2- $\alpha$ -naphthylethenyl)-furan (3), cis-2-(2-phenylethenyl)-5-methylfuran (4) and trans-2-(2- $\alpha$ -naphthylethenyl)-5-methylfuran (5) were recorded. Their assignment is attempted by comparison with the electronic structure reported for molecules which can be regarded as constituent fragments of the title compounds.

### INTRODUCTION

The compounds formed from ethene by substituting the hydrogen atoms with aryl or heterocyclic groups have an interesting electronic structure. It arises, on the one hand, from the possibility of electron transfer between the substituents via the ethene bridge and, on the other hand, from the existence of different conformations and isomers in which only the position of the ring heteroatom is varied. Their photoelectron (PE) spectra can provide some insight into the preferred conformations of these compounds in the gas phase while their electronic structure can be rationalized by combining the electronic structures of their constituent fragments. Several investigations have been reported so far dealing with the PE spectra of aryl substituted ethenes, most of them concerning the trans derivatives of stilbene.<sup>1-7</sup> The electronic structure of these compounds was investigated both with the aid of semiempirical calculations and by the composite molecule approach which proved to be more useful. However, conformations in the gas phase have not been determined accurately although Maier and Turner<sup>8</sup> have shown that certain systems in the PE spectra of stilbene are rather sensitive to conformational changes. By correlating the ionization energies ( $E_i$ ) measured in the spectra with calculated MO energies it was possible to conclude that there are no large deviations from planarity.  $\alpha$ -Methyl substituted trans-styrylpyridines constitute an ex-

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ception with significant deviations from planarity<sup>2</sup> caused by steric hindrance of the methyl group. A study of the electronic structure of related compounds — the thienylarylethenes<sup>6</sup> has recently been reported.

#### EXPERIMENTAL

The HeI PE spectra of compounds 1—5 shown in Figures 1 and 2 were recorded on a Vacuum Generators UV G3 instrument<sup>9</sup> at low resolution ( $\approx 30$  meV) and at elevated temperature (up to 80 °C) of the inlet system. The values indicated above the systems in the spectra correspond to vertical ionization energies  $E_i$ , expressed in eV. The spectra were calibrated by addition of small amounts of xenon and argon to the sample flow. The sample compounds were prepared and purified according to the procedure reported in the literature.<sup>10</sup>

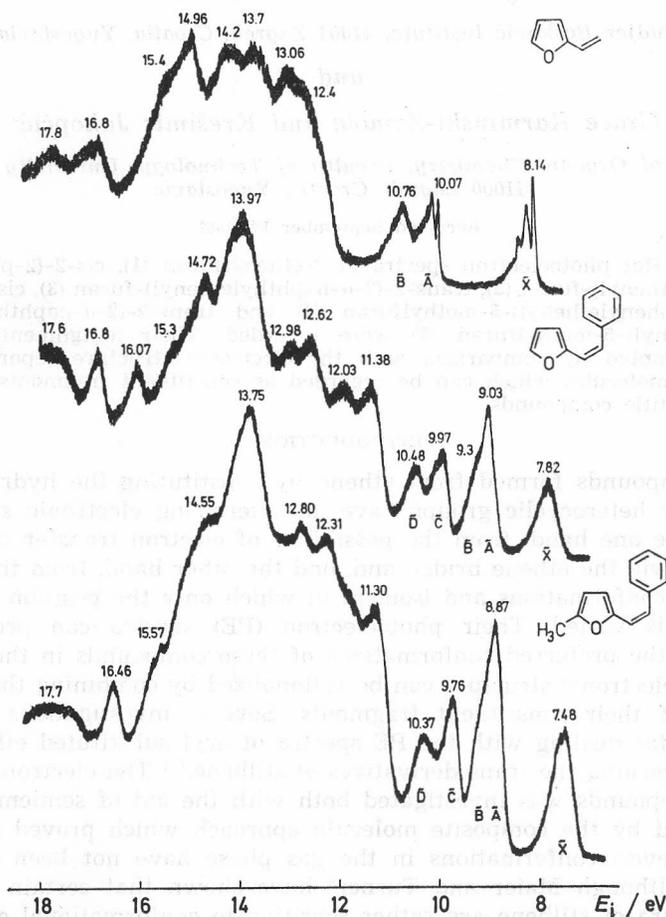


Figure 1. HeI photoelectron spectra of compounds 1, 2, and 4.

#### RESULTS AND DISCUSSION

A comparison of the PE spectra shown in Figures 1 and 2 reveals that the methyl derivatives 4 and 5 possess essentially the same spectra as their

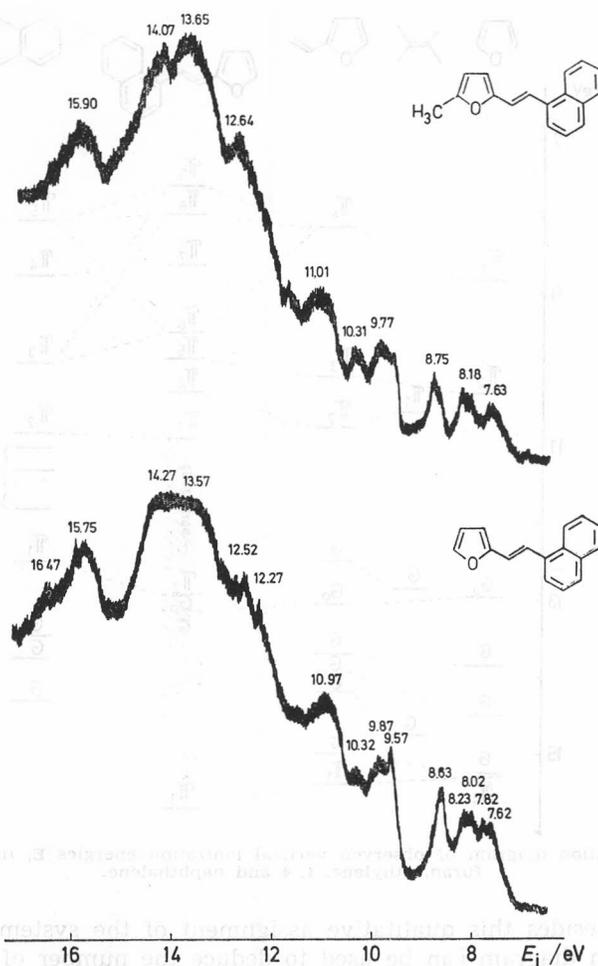


Figure 2. HeI photoelectron spectra of compounds 3 and 5.

parent compounds 2 and 3, respectively. Only slight inductive shifts of some systems towards lower  $E_i$  values can be observed. The identity of spectra implies very similar electronic structures so that no distinction between a methyl derivative and its parent compound will be made in the subsequent discussion.

The PE spectrum of 1 can be assigned by comparison with the molecular fragments furan and ethene, which can be thought of as building blocks for this molecule. The energy levels and assignments for furan and ethene were taken from their PE spectra.<sup>11,12</sup> The correlation diagram in Figure 3 allows the assignment of the PE spectrum to be made. The systems at 8.14, 10.07, 10.76 and 15.4 eV correspond to ionization from  $\pi_4$ ,  $\pi_3$ ,  $\pi_2$ , and  $\pi_1$  orbitals, respectively. Since the microwave spectroscopic study<sup>13</sup> of 1 in the gas phase showed the molecule to be planar ( $C_s$  point group), the  $\pi$ -orbitals belong to  $a''$  symmetry species. The rest of the systems can be attributed to  $\sigma$ -ionizations

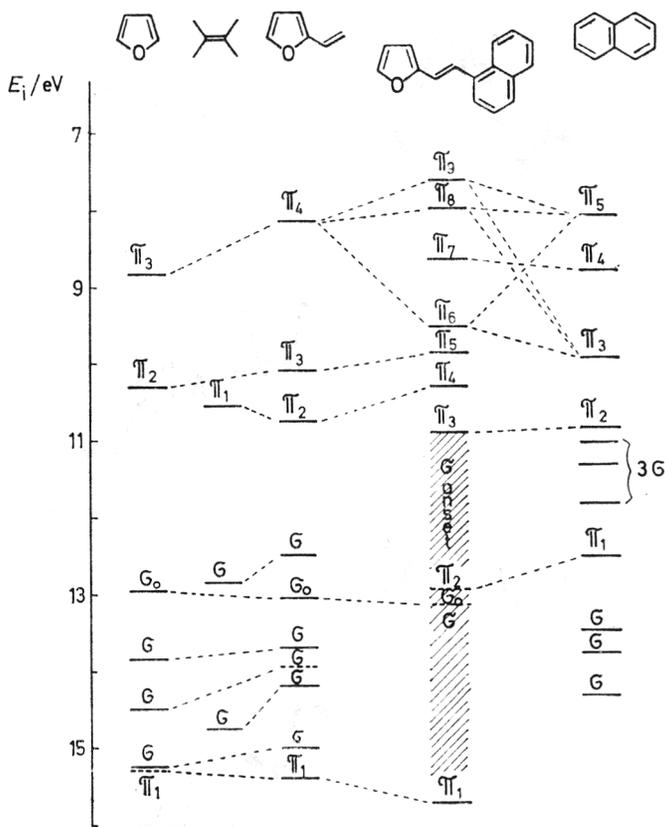


Figure 3. Correlation diagram of observed vertical ionization energies  $E_i$  (in electronvolts) of furan, ethylene, 1, 4 and naphthalene.

( $a'$  species). Besides this qualitative assignment of the systems up to 18 eV, the correlation diagram can be used to deduce the number of ionizations occurring in the region of the PE spectrum where electronic systems overlap each other, e. g. between 12.4 and 15.4 eV. From Figure 3 it can be seen that seven systems altogether could be expected in this region. In favourable cases such as this, even the composition of particular MO's could be predicted from the correlation diagrams. The  $\pi_4$ ,  $\pi_3$ , and  $\pi_1$  orbitals of **1** are probably localized on the ring atoms, while the  $\pi_2$  orbital corresponds essentially to the ethene  $\pi$ -orbital. Vibrational fine structures can be observed in systems at 8.14 and 10.07 eV with wave numbers of 1290 and 810  $\text{cm}^{-1}$ , respectively. The observed progressions probably correspond to ring stretching with a molecular ground state wave number<sup>14</sup> of 1329  $\text{cm}^{-1}$  and ring CH in-plane bending. The proposed modes support the assignment of  $\tilde{X}$  and  $\tilde{A}$  systems to ionizations from ring localized orbitals.

The PE spectra of **2** and **4** (Figure 1) can also be assigned by the composite molecule approach. However, one can use either furan and styrene fragments or **1** and benzene, both correlations giving the same assignment (Figure 4.) On the basis of these correlations, the systems at 7.82, 9.03, 9.3, 9.97, 10.48, 12.62

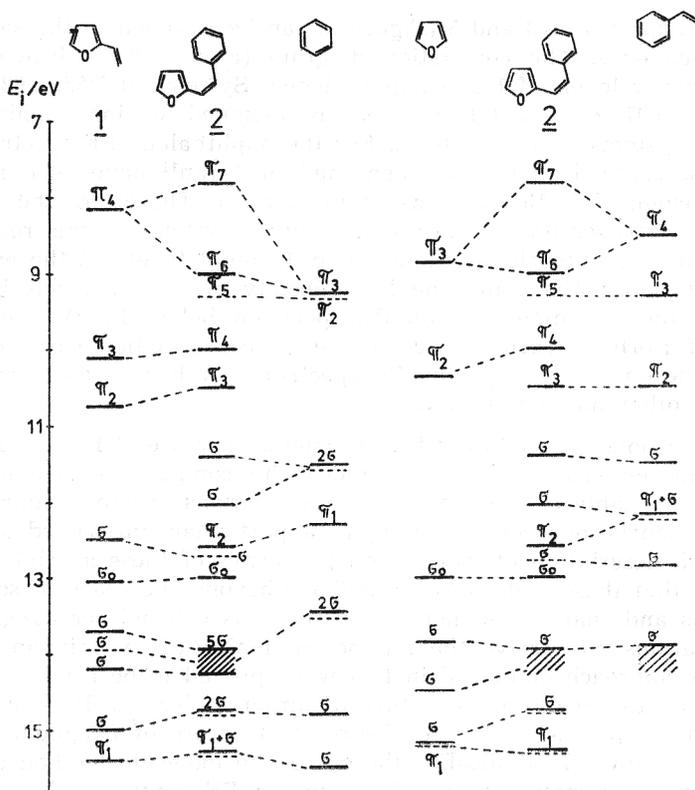


Figure 4. Comparison of correlation diagrams for 2.

and 15.3 eV can be attributed to  $\pi_7$ — $\pi_1$  ionizations, respectively, while the other systems correspond to  $\sigma$ -orbital ionizations. The assignments for benzene and styrene were taken from the literature.<sup>15,16</sup> Since all the valence ionizations in benzene have been assigned, the correlation with benzene and 1 allows the assignment of the PE spectrum of 2. This correlation is also useful in the analysis of those regions of the spectrum where several systems overlap so that the numbers of ionizations expected in this region cannot be deduced at all on intensity grounds. The MO properties can be described in qualitative terms on the basis of the diagram in Figure 4. The  $\pi_7$ ,  $\pi_4$  and  $\pi_1$  orbitals are probably localized mainly on the furan ring while the  $\pi_6$ ,  $\pi_5$  and  $\pi_2$  orbitals should greatly resemble in character the benzene  $\pi$  orbitals. The remaining  $\pi_3$  orbital probably has a significant ethene character. The proposed MO description is, of course, only tentative but since no large  $\pi$  energy shifts are observed when 2 is composed of 1 and benzene, the conjugative interactions between fragments seem to be small, thus justifying our MO description. On the other hand, small conjugative interactions can also be expected because of the nonplanarity of this molecule. Although the conformation of 2 in the gas phase has not been determined, steric hindrance might be reduced by twisting the bulky phenyl group out of the ethenylfuran plane. Some results obtained by analysis of the UV spectra in solution tend to suggest that this might be the case.<sup>17</sup>

The PE spectra of **3** and **5** (Figure 2) can be assigned in the same way as the previous ones. The correlation diagram (Figure 3) is drawn from the assigned energy levels of **1** and naphthalene.<sup>18</sup> Systems at 7.62, 8.02, 8.63, 9.57, 9.87, 10.32, 10.97, ~ 13 and 15.5 eV can be assigned to nine  $\pi$ -ionizations; the rest of the systems to  $\sigma$ -ionizations. For the naphthalene PE spectrum no calculations as sophisticated as for benzene<sup>19</sup> or furan<sup>11</sup> have been reported so that the region  $E_i > 13$  eV remains unassigned. Therefore, the number of ionizations corresponding to several unresolved systems in this region cannot be established on intensity grounds alone. Incompleteness of the energy level pattern for naphthalene and the high density of energy levels in **5** makes ambiguous the assignment of its PE spectrum below 13 eV. However, the ordering of  $\pi$  orbitals seems to be reliable. No conformational predictions for **5** can be made on the basis of the PE spectrum nor has its conformation been studied by other methods so far.

In conclusion, the studies of the electronic structure of **1**–**5** by PE spectroscopy, using empirical arguments under the composite molecule approach permit (i) a reliable assignment of all  $\pi$  ionizations, (ii) the deduction of the number of ionizations corresponding to a particular unresolved system, and (iii) a rough description of localization properties of these  $\pi$  orbitals. In view of the fact that these molecules are still far beyond the reach of sophisticated calculations and that the semiempirical methods can neither assign correctly all  $\pi$ -ionizations nor derive the number of ionizations within an unresolved system, the approach employed in this work proved to be a very good option for analyzing the electronic structure of larger molecules. It is implicitly assumed in this approach that the electronic structure of fragment compounds is precisely known. If applicable, the composite molecule method can help in the assignment of many more systems in the PE spectra of large molecules than just those preceding the  $\sigma$ -onset.

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### SAŽETAK

#### Fotoelektronska spektroskopija heterocikličkih spojeva. 1-(2-furil)-2-arileteni

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Snimljeni su HeI fotoelektronski spektri 2-etenilfurana (1), cis-2-(2-feniletetil)-furana (2), trans-2-(2 $\alpha$ -naftiletetil)-furana (3), cis-2-(2-feniletetil)-5-metilfurana (4) i trans-2-(2- $\alpha$ -naftiletetil)-5-metilfurana (5). Asigniranje spektara izvršeno je usporedbom s poznatim elektronskim strukturama molekula koje predstavljaju konstitucijske fragmente navedenih spojeva.