Photoelectron Spectroscopy of Heterocycles. Dipyridylethylenes

I. Novak and L. Klasinc *

"Rudjer Bošković" Institute and * Faculty of Science, University of Zagreb,
Zagreb, Croatia (Yugoslavia)

and J. V. Knop

Rechenzentrum, University of Düsseldorf, Düsseldorf, Germany

(Z. Naturforsch. **32 a**, 886–889 [1977]; received June 15, 1977)

The photoelectron (PE) spectra of 1,2-di-(2-pyridyl)-ethylene **1**, 1-(2-pyridyl)-2-(3-pyridyl)-ethylene **2**, 1-(2-pyridyl)-2-(4-pyridyl)-ethylene **3** and 1,2-di-(4-pyridyl)-ethylene **4** all in their trans conformation have been measured using He I radiation. For **1**–**4** standard SCF LCAO MO calculations were performed changing the angle of twist ϑ of the pyridine rings around their bonds to ethylene conrotatively from 0° to 60°. Comparison of PE spectra and these calculations allowed the assignment of all π-ionizations and indirectly also the nitrogen lone pair ionizations in **1**–**4** but not a determination of their conformation in the gas phase. There is only indication that ϑ in these molecules is rather small ($\vartheta < 30°$).

Introduction

Turner and co-workers[1] have shown that certain band systems in PE spectra of diarylethylenes are rather sensitive to conformational changes i. e. to rotation of the arene ring around its bond to ethylene. An extensive study of PE spectra of stilbenes[2] mono- and disubstituted in different positions by several types of substituents revealed that this is still the case in substituted compounds. Thus, in some cases information about conformation of molecules in the gas phase from PE spectroscopy could be obtained[3–5]. Recent results indicate that this dependency is considerably lost if heteroatoms are members either of the aryl or of the ethylenic double bond[6, 7]. Such compounds are also **1**–**4**. However, our interest in **1**–**4** was not only because of their conformation in the gas phase, but also because of their electronic structure, especially concerning the energy of the nitrogen lone pair electrons in them. Separated by the additional ethylene bridge **1**–**4** are related to the important complex forming bipyridyls, terpyridyls and tetrapyridyls in which considerable interaction of these electrons takes place[8]. On the other hand dipyridylethylenes are also of interest because of their photoreactions[9–12]. In the present work we report the results concerning the conformation and electronic structure of **1**–**4** as obtained from their PE spectra in comparison with semiempirical molecular orbital calculations.

Experimental

Compounds: 1,2-di-(2-pyridyl)-ethylene, **1** m. p. 119.5 °C, 1-(2-pyridyl)-2-(3-pyridyl)-ethylene **2** m. p. 72 °C, 1-(2-pyridyl)-2-(4-pyridyl)-ethylene **3** m. p. 73 °C and 1,2-di-(4-pyridyl)-ethylene **4** m. p. 152.5 to 153 °C were of commercial origin (Dr Raschig GmbH) and recrystallized before use.

Spectra: All PE spectra were recorded on a Vacuum Generators UV-G3 photoelectron spectrometer[13]. Enhanced temperatures of the inlet system (120 °C, 80 °C, 80 °C and 160 °C for **1**–**4**, respectively) were employed as to produce satisfactory spectra. The PE spectra were obtained under low (~35 meV) and high (<20 meV) resolution and were calibrated by admition of small amount of CH_3J to the sample flow. The reported ionization energies are accurate to 0.03 eV.

Calculations: Standard SCF LCAO MO calculations as described in Ref.[14] were performed for **1**–**4** assuming standard bond lengths and angles. Hereby, for **1**–**4** a number of trans conformations determined by changing the angle of twist ϑ of the pyridine rings around their bonds to ethylene conrotatively from 0° to 60° in steps of 15° were assumed. The parametrization for **1**–**4** as suggested in Ref.[14] has proven to be very useful for the calculation of several physicochemical properties of these compounds[14, 15].

Results and Discussion

The He I PE spectra of **1**–**4** are reproduced in Figs. 1–4, respectively. The experimental vertical ionization energies (E_I/eV) are listed at the top of

Reprint requests to Prof. Dr. L. Klasnic, Institute Rudjer Bošković, P. O. Box 1016, *J-41001 Zagreb*, Jugoslawien.

the corresponding band systems. The assignment of individual low energy systems is indicated below, according to standard notation. The canonical SCF MO energies $\varepsilon_n^{\vartheta}$ (in eV) of the ground state of **1** – **4** calculated for different trans conformations defined by the angle of twist ϑ are given in Table 1. In Table 1 are also given these ionization energies E_{π_n} observed in the PE spectra of **1** – **4** which we assign to π-ionizations assuming Koopmans' theorem to be valid. The assignment is based on the correlation of the $\varepsilon_n^{\vartheta}$ values with the low energy ionizations from the PE spectra of each compound taking into account also the shape of the systems and the area below them. Namely, from previous investigations we know that systems corresponding to nitrogen lone pair and π-ionizations in this region $(E_I < 12\,\text{eV})$ have a characteristic shape and that their areas are a good measure of their overlap

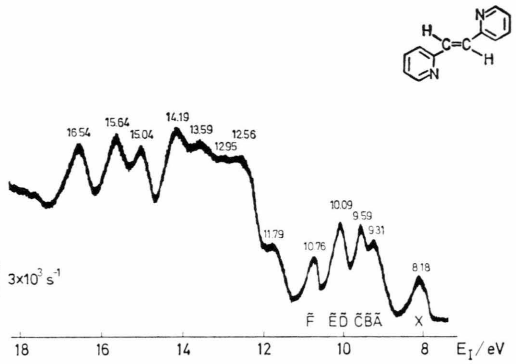

Fig. 1. PE spectrum of 1,2-di-(2-pyridyl)-ethylene **1**.

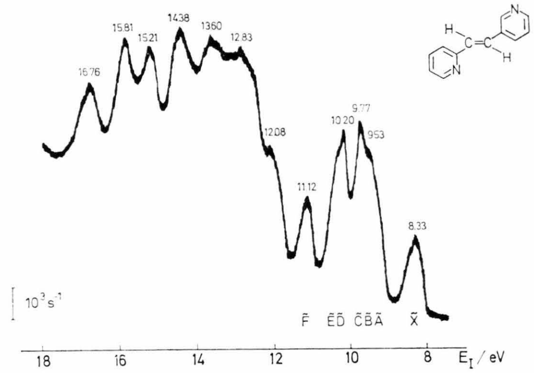

Fig. 2. PE spectrum of 1-(2-pyridyl)-2-(3-pyridyl)-ethylene **2**.

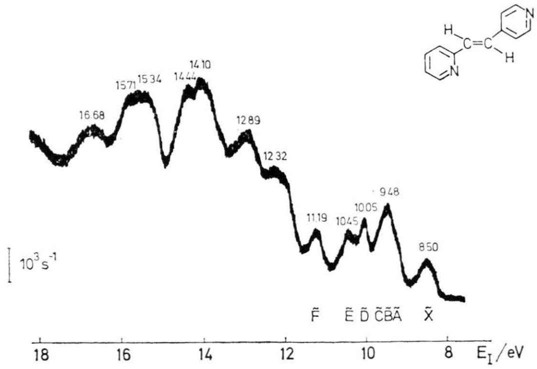

Fig. 3. PE spectrum of 1-(2-pyridyl)-2-(4-pyridyl)-ethylene **3**.

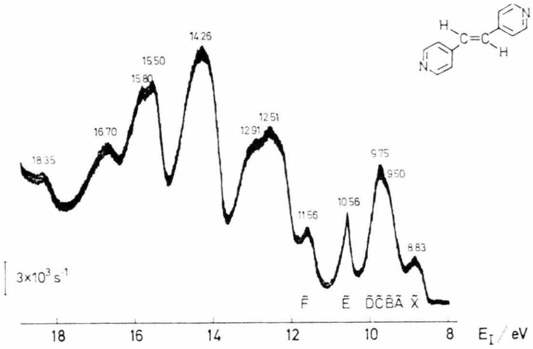

Fig. 4. PE spectrum of 1,2-di-(4-pyridyl)-ethylene **4**.

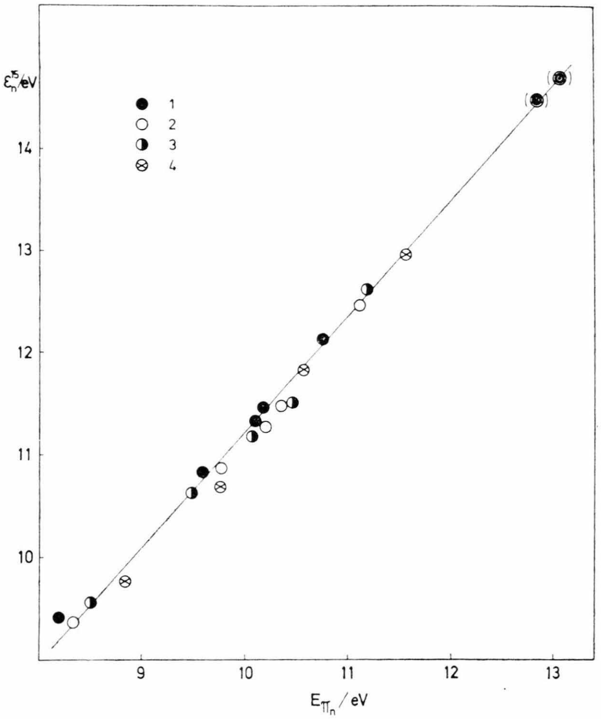

Fig. 5. Correlation of SCF MO energies ε_n^{15} (i. e. calculated for $\vartheta = 15°$) with corresponding π-ionizations of compounds **1**–**4**.

Table 1. Canonical SCF MO Energies $\varepsilon_n{}^{\vartheta}$ (in eV) of the Ground State of **1**, **2**, **3** and **4** for Different Conformations (angle ϑ in degrees) and Corresponding π-ionizations $E_{\pi n}$ (in eV) Observed in Their PE Spectra (Koopmans' Theorem).

Compound	n	$\varepsilon_n{}^0$	$\varepsilon_n{}^{15}$	$\varepsilon_n{}^{30}$	$\varepsilon_n{}^{45}$	$\varepsilon_n{}^{60}$	$E_{\pi n}$
1	7	9.37	9.41	9.54	9.75	10.03	8.18
	6	10.87	10.83	10.79	10.73	10.67	9.59
	5	11.36	11.33	11.33	11.32	11.29	10.09
	4	11.46	11.43	11.42	11.42	11.41	10.16
	3	12.17	12.12	12.02	11.84	11.61	10.76
	2	14.53	14.46	14.44	14.42	14.39	(12.8)
	1	14.79	14.71	14.64	14.54	14.46	(13.1)
2	7	9.28	9.36	9.50	9.73	10.04	8.33
	6	10.87	10.86	10.82	10.76	10.70	9.77
	5	11.27	11.27	11.26	11.24	11.21	10.20
	4	11.48	11.47	11.46	11.46	11.45	10.35
	3	12.50	12.45	12.32	12.10	11.82	11.12
	2	14.53	14.47	14.45	14.43	14.40	(12.8)
	1	14.74	14.68	14.62	14.54	14.47	(13.1)
3	7	9.49	9.56	9.70	9.91	10.20	8.50
	6	10.61	10.62	10.62	10.61	10.61	9.48
	5	11.20	11.18	11.14	11.09	11.03	10.05
	4	11.54	11.51	11.49	11.48	11.47	10.45
	3	12.68	12.63	12.49	12.27	11.97	11.19
	2	14.50	14.44	14.43	14.41	14.39	(12.8)
	1	14.76	14.70	14.64	14.56	14.49	(13.1)
4	7	9.67	9.75	9.89	10.13	10.45	8.83
	6	10.67	10.67	10.67	10.67	10.67	9.75
	5	10.67	10.68	10.67	10.67	10.67	9.75
	4	11.89	11.83	11.76	11.67	11.57	10.56
	3	13.03	12.96	12.81	12.56	12.21	11.56
	2	14.52	14.47	14.46	14.45	14.43	(12.8)
	1	14.69	14.63	14.58	14.52	14.47	(13.0)

(degeneracy)[2, 4, 6, 8]. On the other hand we also have to expect besides two ionizations from nitrogen lone pair electrons (somewhere between 9 – 10 eV) possibly some σ-ionizations starting from about 11 eV of ionizing energy. For each compound the correlation of the five energies which we assigned as π-ionizations (E_{π_7} to E_{π_3}) with the corresponding $\varepsilon_n{}^{\vartheta}$ values is excellent for every angle of ϑ. However, the correlation coefficient which is practically the same for $\vartheta = 0°$, $15°$ and $30°$ ($r > 0.99$) is reduced at higher ϑ values (but being lowest 0.96 for $\vartheta = 60°$ in compound **2**). Such an assignment excludes in the PE spectrum of each compound a band system with a doubled area and a characteristic shape which readily can be attributed to the unsplit (unresolved) nitrogen lone pair ionizations. Thus, they appear at 9.31, 9.53, 9.48 and 9.50 eV as systems $\tilde{\mathrm{A}}$, $\tilde{\mathrm{B}}$ in **1** – **4**, respectively. Now assuming $\vartheta = 15°$ we can try to determine the energy required for the deeper π-ionizations for each compound i. e. E_{π_2} and E_{π_1}. The corresponding least squares regressions gave their energy nearly constant at 12.8 and 13.1 eV, respectively (values in parentheses in Table 1). This is to be expected since the corresponding ionizations in stilbene[2] are 12.11 and 12.73 eV respectively and their energy should be raised in **1** – **4** by the "aza-effect". However, in the PE spectra of **1** – **4** these systems are hidden by the σ-onset. The still unassigned systems in the low energy part of the PE spectra can thus be attributed to σ-ionizations. They appear at 11.79, 12.08, 12.32 and 12.51 eV in **1** – **4**, respectively. The change in their energy correlates well with the change of the lowest energy system $\tilde{\mathrm{X}}$ (8.18, 8.33, 8.50 and 8.83, for **1** – **4**, respectively) indicating the inductive nature of this effect. It is, namely, only partially reproduced within the SCF LCAO MO calculation (Table 1). From a comparison of the PE spectra of stilbene and 2,2′, 3,3′, 4,4′, 5,5′, 6,6′-dekafluorostilbene we have indications that this low energy σ-ionization mainly arises from electrons "located" at the ethylene bridge[2]. The correlation of all π-ionizations E_{π_n} vs. the canonical SCF MO energy $\varepsilon_n{}^{15}$ (i. e. calculated for $\vartheta = 15°$) is given in Fig. 5 ($r = 0.99$, $s = 0.13$).

In conclusion we feel that within the applicability of Koopmans' theorem the electronic structure of **1** – **4** can well be described by the present procedure. There seems also to be no worth mentioning interaction between the nitrogen lone pairs in the PE spectra of **1**–**4**. The conformation of the compounds in the gas phase is less certain, but all results suggest that the angle of twist ϑ is rather small ($0° \leqq \vartheta \leqq 30°$).

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