Photoelectron Spectroscopy of Heterocycles. Polypyridines

I. Novak and L. Klasinc *

"Rudjer Bošković" Institute and Faculty of Science, University of Zagreb, Zagreb, Yugoslavia

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The photoelectron (PE) spectra of 2,2′-bipyridine **1**, 2,2′:6′,2″-terpyridine **2**, and 2,2′,2″,2‴-tetrapyridine **3** have been measured using He I radiation. For **1**–**3** standard SCF LCAO MO calculations were also performed. Comparison of PE spectra and these calculations allowed the assignment of π-ionizations and indirectly also the nitrogen lone pair ionizations in **1**–**3**. Factors influencing the conformations of **1**–**3** in the gas phase are also mentioned.

Together with 2,2″-bipyridine **1**, 2,2′:6′,2″-terpyridine **2** and 2,2′,2″,2‴-tetrapyridine **3** are important chelating agents and we therefore studied their electronic structure by means of photoelectron (PE) spectroscopy. The aim of this study was especially to determine the ionization energies of the nitrogen lone pairs in **2** and **3** which in 2,2′-bipyridine are separated by 0.5 eV. 2,2′:6′,2″-terpyridine was a commercial product (Merck m.p. 87–89 °C) while 2,2′,2″,2‴-tetrapyridine was prepared according to the literature [1] and its identity checked mass-spectrometrically and by its melting point (219–220 °C). All PE spectra were recorded on a Vacuum Generators UV-G3 photoelectron spectrometer [2] using He I radiation and employing enhanced temperatures of the inlet system (150 °C and 230 °C for **2** and **3**, respectively). The He I PE spectra of **2** and **3** are shown in Figures 1 and 2. The values on top of the observed systems correspond to vertical ionization energies.

Standard SCF LCAO MO calculations were performed for **1**–**3** assuming standard bond lengths and angles and planar transoid conformations. Parameters for the nitrogen which proved useful to assign the PE spectra of dipyridylethylenes [3] were taken from Reference 4. Planar conformations of **1**–**3** would be favoured by two factors: the hydrogen bonding taking place between the nitrogen lone pair and the hydrogen in ortho position of the neighbouring ring, and by conjugation between the rings as well. On the other hand, non-planarity would be favoured sterically. In the case of 2,2′-bipyridine it was shown that the former effect is stronger and the molecule is planar in the gas phase [5]. We assumed that the same is true for **2** and **3**. The canonical SCF MO energies $\varepsilon_{\pi n}$ (in eV) for **1**–**3** are shown together with experimental energies corresponding to vertical π-ionizations $E_{\mathrm{I}}^{\pi n}$ (in eV) in Table 1. The assignment of the observed low energy ($E_{\mathrm{I}} < 11$ eV) systems in the PE spectra (Figs. 1 and 2) is indicated according to standard notation. However, because of extensive overlap of these systems the assignment, which is based on the validity of Koopmans' theorem, results of SCF MO calculations, band area measurements and conclusions reached for the structurally related 2,2′-bipyridine [5], is somewhat tentative. Besides the π-ionizations in the low energy region ($E_{\mathrm{I}} < 11$ eV) three nitrogen lone pair ionizations in the PE spectrum of **2** and four nitrogen lone pair ionizations in the PE spectrum of **3** are expected. On the basis of the above considerations we assign systems $\tilde{A}$, $\tilde{C}$ and $\tilde{D}$ at 9.01, 9.30 and 9.67 eV,

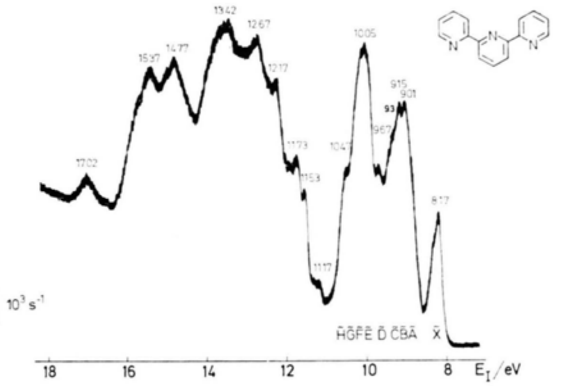

Fig. 1. PE spectrum of 2,2′:6′,2″-tetrapyridine **2**.

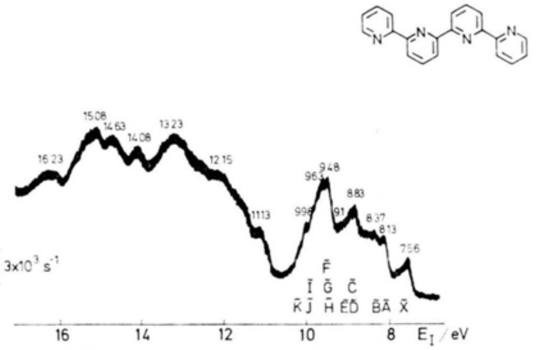

Fig. 2. PE spectrum of 2,2′,2″,2‴-tetrapyridine **3**.

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

Table 1. Canonical SCF MO energies $\varepsilon_{\pi n}$ and energies of corresponding vertical π-ionizations $E_I{}^{\pi n}$ in the PE spectra of 2,2′-bipyridine (**1**), 2,2′:6′,2″-terpyridine (**2**) and 2,2′,2″,2‴-tetrapyridine (**3**).

Compound		Calculated and corresponding PE energies for π-electron levels											
1	$\varepsilon_{\pi n}$/eV	15.02	14.01	11.61	11.36	11.18	9.90						
	$E_I{}^{\pi n}$/eV	—	—	10.48	10.23	9.83	8.60						
2	$\varepsilon_{\pi n}$/eV	15.22	14.61	13.84	11.75	11.53	11.34	11.31	10.46	9.66			
	$E_I{}^{\pi n}$/eV	—	—	—	10.47	10.05	10.05	10.05	9.15	8.17			
3	$\varepsilon_{\pi n}$/eV	15.31	14.92	14.33	13.75	11.86	11.55	11.52	11.33	11.32	10.78	10.07	9.54
	$E_I{}^{\pi n}$/eV	—	—	—	—	9.98	9.63	9.63	9.48	9.48	8.83	8.13	7.56

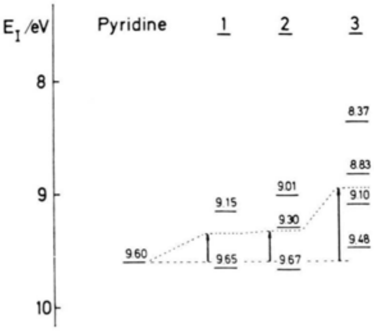

Fig. 3. Energies of lone pair ionizations.

respectively, as the nitrogen lone pair ionizations in **2** and systems $\tilde{B}$, $\tilde{C}$, $\tilde{E}$ and $\tilde{F}$ at 8.37, 8.83, 9.10 and 9.48 eV, respectively, as nitrogen lone pair ionizations in **3**. Thus, similarly as in **1**, degeneracy of the nitrogen lone pairs seems to be removed by "through bond" interaction which can be described for all three compounds by the same interaction parameter $\beta_{NN} \cong 0.25$ eV. Such assignment indicates the existence of an inductive effect associated with the linking of pyridine rings which shifts the center of gravity of the lone pair ionizations to lower energies (0.2, 0.3 and 0.6 eV for **1**–**3**, respectively) as shown in Fig. 3 by the dotted line. However, the high shift found for **3** could be interpreted in another way by its nonplanarity. The planar conformation of **2** is similarly (and even more) favoured by the same arguments which hold for 2,2′-bipyridine. In **3**, if planarity of the two bipyridyl subunits is forced by hydrogen bonding, there remains a free rotation around the central connecting C–C bond. Such rotation would result in appreciable mixing of "lone pair" and π-orbitals of the bipyridyl halves and in lowering the ionization energies of the former.

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