

B. Kovač and L. Klasinc

Rugjer Bošković Institute, Zagreb, Croatia, Yugoslavia
and

B. Stanovnik and M. Tišler

Department of Chemistry, University of Ljubljana, 61001 Ljubljana, Yugoslavia

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The HeI photoelectron (PE) spectra of indole (1), benzimidazole (2), indazole (3), 3-chloroindazole (4), imidazo[1,2-*b*]pyridazine (5), 6-chloroimidazo[1,2-*b*]pyridazine (6), 2-phenylimidazo[1,2-*b*]pyridazine (7), 2-phenyl-6-chloroimidazo[1,2-*b*]pyridazine (8), tetrazolo[1,2-*a*]pyridine (9) and 8-cyanotetrazolo[1,5-*a*]pyridine (10) have been recorded. The spectra of 2-10 are of special interest for studying lone pair interactions. The assignment of the PE spectra submitted here, conjointly with the electronic structure of the studied compounds is discussed on the basis of molecular orbital calculations.

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Introduction.

Perturbation of the π -electron system arising from the substitution of carbon atom(s) by the more electro-negative nitrogen atom(s) in cata-condensed hydrocarbons has long been studied (2,3). In addition, such substitution creates compounds with lone pair electrons and there is still much attention being paid to the nature, "shape", "direction", and interactions of lone pairs in molecules (4,5). Both of these effects are considered here, as photoelectron (PE) spectra of 1-10 seem to allow insight into the changes of electronic structure induced by the aforementioned perturbations.

Some of the compounds, namely 1 (6), 2 (7) and 3 (7) have already been recorded and assigned. Here they are taken in consideration not only because of a better resolution of the corresponding PE spectra, but because they represent the key compounds in discussion of the electronic structure of 4-10.

Results and Discussion.

The π -electron structure of 1 was established from its PE spectrum, molecular orbital (MO) calculations and especially by the "perfluoro effect" (8) in 4,5,6,7-tetrafluoro indole (6). This knowledge gives a basis for the discussion of π -electron systems observed in the spectra of 2-10. Inspecting the PE spectrum of 1 *vs.* those of compounds with two nitrogen atoms (Figures 1 and 2) one notices the increase of the first π -ionization energy from 7.91 eV in 1 to 8.45 eV, 8.35 eV and 8.41 eV in 2, 3 and 4, respectively. This concedes with the so-called "aza-effect" (9) in hydrocarbon substitution. In addition, the introduction of the second nitrogen atom in 1 causes a substantial splitting between π_3 and the close lying π_4 and π_5 ionizations in 2, whereas in 3 and 4 the splitting

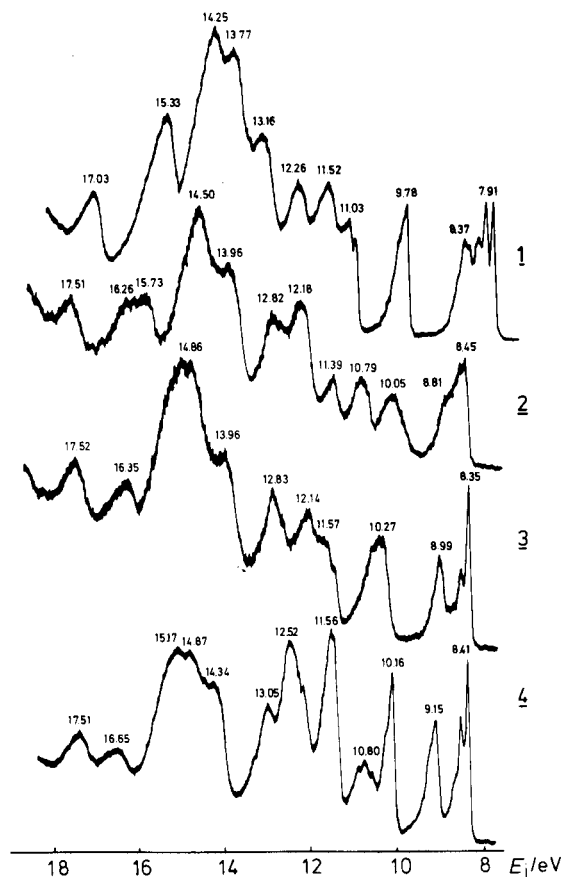


Figure 1. The HeI PE Spectra of Indole (1), Benzimidazole (2), Indazole (3) and 3-Chloroindazole (4).

between the lowest two π -ionizations becomes more prominent and the energy gap to the next π -ionization smaller.

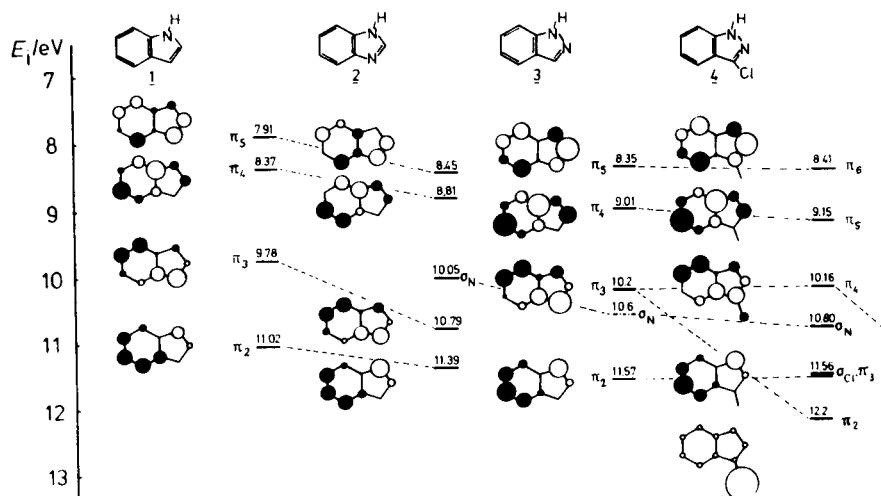


Figure 2. Orbital Correlation Diagram for Indole (**1**), Benzimidazole (**2**), Indazole (**3**) and 3-Chloroindazole (**4**) Based on Quantum Chemical Calculations (Levels Corresponding to Unresolved Systems in PE Spectra are Indicated by Dashed-Lines).

Table I

Comparison of HMO Energies in β Units (Upper Row) with PPP Canonical SCF MO Energies in eV (Lower Row) for **2-10**

Compound No.	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6	ϵ_7	ϵ_8	ϵ_9	
2	2.46	1.77	1.44	0.87	0.65					
	15.61	12.82	12.24	9.94	9.58					
3	2.33	1.74	1.35	0.88	0.73					
	15.29	13.22	11.21	10.39	9.25					
4	2.40	2.07	1.74	1.26	0.88	0.72				
	16.11	15.12	12.97	11.29	10.31	9.36				
5	2.47	1.59	1.44	0.96	0.62					
	16.64	13.48	12.66	10.81	9.58					
6	2.48	2.11	1.53	1.44	0.93	0.62				
	16.71	15.99	13.21	12.37	10.58	9.48				
8	2.51	2.14	2.06	1.56	1.48	1.18	1.0	0.74	0.59	$\theta = 0^\circ$
	16.71	15.95	13.39	12.71	12.37	11.12	10.13	9.95	8.67	
8	2.49	2.13	2.05	1.55	1.47	1.17	1.0	0.76	0.6	$\theta = 30^\circ$
	16.75	16.01	13.31	12.76	12.41	11.02	10.12	9.98	8.82	
9	2.45	1.6	1.42	1.09	0.6					
	17.03	13.64	13.04	11.47	10.08					
10	2.48	1.85	1.51	1.18	1.06	0.6				
	17.18	14.36	13.73	12.58	11.58	10.11				

Such a behaviour is nicely predicted by both MO calculations (Table I) and, in fact, they were the main support for the assignment of systems at 10.05 eV in **2** and 10.6 eV and 10.80 eV in **3** and **4**, respectively, to the σ_N lone pair ionizations. These systems reveal a characteristic broad shape which suggests significant mixing with the skeletal σ -type orbitals, *i.e.*, a rather bonding character of the ejected electron. This characteristic shape and their position might help in the assignment of

σ_N 's in the PE spectra of the rest of compounds. In **3**, the σ_N is overlapped by the π_3 -system. This overlapping is removed by chloro substitution in **4** (Figures 1 and 2). In the σ_N system in **4** a ring vibration of 1130 cm^{-1} is revealed, thus supporting the assumption of the lone pair delocalization.

The area of the peak at 11.56 eV in the PE spectrum of **4** (Figure 1) evidently corresponds to two overlapping systems: to the in-plane chlorine lone pair, σ_{Cl} , and to

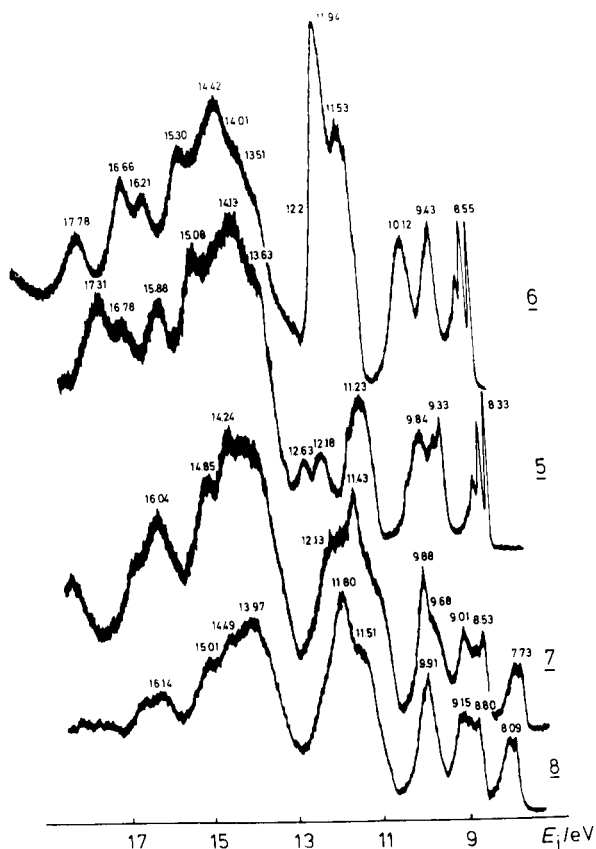


Figure 3. The HeI PE Spectra of 6-Chloroimidazo[1,2-*b*]pyridazine (**6**), Imidazo[1,2-*b*]pyridazine (**5**), 2-Phenylimidazo[1,2-*b*]pyridazine (**7**) and 2-Phenyl-6-chloroimidazo[1,2-*b*]pyridazine (**8**).

the π_3 system which, because of the zero orbital coefficient at the position of substitution, is expected to be at the same energy as π_2 in **3**. The same argument holds for π_4 and π_5 in **3** and **4**, respectively.

The PE spectrum of **4** is especially interesting for the observation of possible interaction of the nitrogen σ_N and in-plane chlorine σ_{Cl} lone pairs. The stabilization of σ_N in **4** relative to **3** (10.80 eV vs. 10.6 eV, respectively) and the location of σ_{Cl} at 11.56 eV in **4** as compared to σ_{Cl} in chlorobenzene, 2-, 3- and 4-chloropyridine (11.31 eV, 11.48 eV, 11.79 eV and 11.71 eV, respectively) (10) indicate a negligible nitrogen-chlorine lone pair mixing in **4**. This may imply either that **4** and consequently **3**, are in the gas phase predominantly 2H-tautomers (7) under the assigned conditions at high temperature, thus reducing possibility for through space interaction, or that nitrogen and chlorine lone pair mixing could be disregarded because of the energy gap between them.

In the heterocycles with the bridgehead nitrogen, the general feature of aza-effect is evident if one compares the energy of the first π -systems in indolizine, imidazo[1,2-*a*]pyridine (11) and in **5**, amounting 7.24 eV, 8.19 eV and 8.33 eV, respectively. In **5-8** attention is paid to the two nitrogen lone pair interaction and complications arising from chloro and/or phenyl substitution (see Figures 3 and 4). As the two nitrogen lone pairs are far apart and not conveniently aligned to interact through space, only through bond interaction can be proposed yielding two linear combinations.

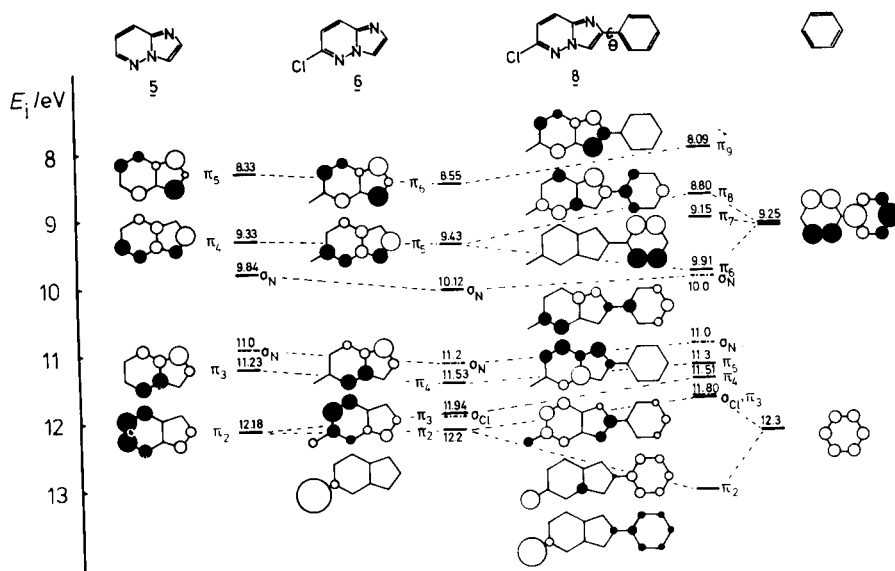


Figure 4. Orbital Correlation Diagram for Imidazo[1,2-*b*]pyridazine (**5**), 6-Chloroimidazo[1,2-*b*]pyridazine (**6**), 2-Phenyl-6-chloroimidazo[1,2-*b*]pyridazine (**8**) and Benzene Based on Quantum Chemical Calculations (Levels Corresponding to Unresolved Systems in PE Spectra are Indicated by Dashed-Lines).

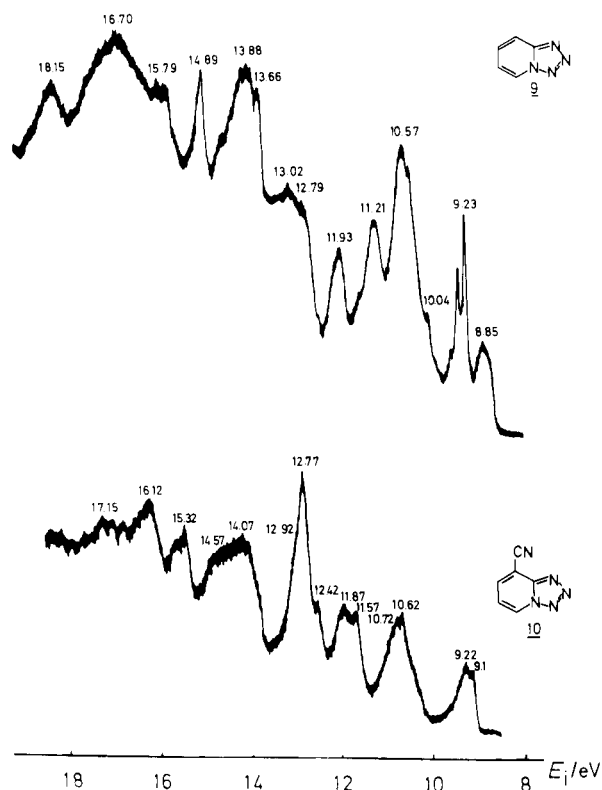


Figure 5. The HeI Spectra of Tetrazolo[1,5-a]pyridine (**9**) and 8-cyanotetrazolo[1,5-a]pyridine (**10**).

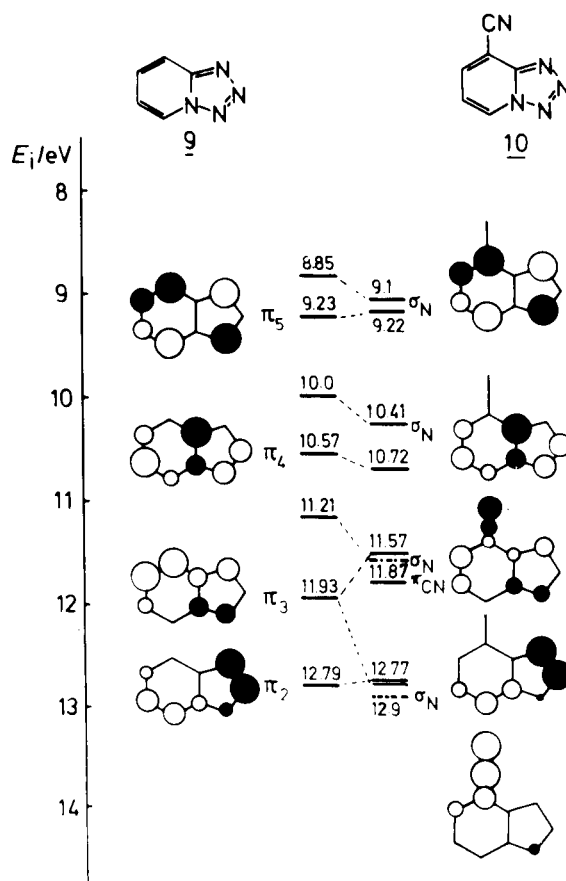


Figure 6. Orbital Correlation Diagram for Tetrazolo[1,5-a]pyridine (**9**) and 8-Cyanotetrazolo[1,5-a]pyridine (**10**) Based on Quantum Chemical Calculations (Levels Corresponding to Unresolved Systems in PE Spectra are Indicated by Dashed-Lines).

nitrogen atoms in para-position (12-15) one might expect a splitting of ~ 1.0 eV. The MO calculations for **5** predict two well separated lowest π -ionizations and a substantial energy gap to the next two ionizations which should be also widely spaced (Table I). Taking this for granted enables one to assign the systems at 8.33 eV, 9.33 eV, 11.23 eV and 12.18 eV to π -ionizations and consequently the systems at 9.84 eV and 11.0 eV (in the later case the area indicates the presence of two overlapped systems) to σ_N -ionizations. Similarly, the lower energy linear combination is found at 10.12 eV in **6**.

The chloro substitution induces the nitrogen lone pair to emerge from the two close lying systems in **5**, as already observed in **4**. The assignment of the remaining π - and lone pair ionizations is not straightforward, as there is extensive overlap of the corresponding systems between 11-13 eV. The prominent system at 11.94 eV is supposed to correspond to σ_{Cl} on the basis of its characteristic shape and by comparison with the PE spectrum of **5**. The π_4 ionization in **6** is expected not to differ much in energy from π_3 in **5** because of the zero orbital coefficient at the position of substitution and is assigned to the system at 11.53 eV. At about the same energy (~ 11.2 eV), as indicated by the possible nitrogen

lone pair splitting (~ 1.0 eV) and the doubled area, the system corresponding to the higher energy linear combination should appear. Finally, since in the π_2 system at 12.18 eV in **5** the orbital coefficient at the position of substitution is substantial according to both PPP and HMO calculations, one expects interaction with the out-of-plane chlorine lone pair. The two π -ionizations are tentatively assigned to the systems at about 11.9 eV (doubled area) and 12.2 eV resulting from such a mixing. According to the orbital correlation diagram based on the MO calculations one finds that the higher energy system should be mainly of chlorine lone pair character.

However, PPP calculations give, as a rule (16,17), too high an energy for such systems, in this particular case 15.99 eV. Substitution of a phenyl group into position 2 yielding e.g. **7** and **8**, results in strong interactions of the close lying π -electron systems of **5** with those of benzene. With the aid of correlation schemes in Figure 4, which do not differ significantly for $\theta = 0^\circ$ and $\theta = 30^\circ$ (Table I), the electronic structure of **7** and **8** might be deduced,

bearing in mind all the possibilities for mixing, so that assignment becomes an intrincating problem.

The PE spectra and assigned electronic structures of related compounds **9** and **10** are shown in Figures 5 and 6. These compounds are especially interesting because of the vicinal position of three nitrogen lone pairs and their through space interaction.

Designation of the π -electron systems is based on the PPP and HMO calculations (Table I), and the complete assignments on the qualitative features of the shapes of systems. Thus, as indicated in Figures 5 and 6, for both compounds the first system in the PE spectrum is assigned to a nitrogen lone pair combination orbital. The remaining two nitrogen lone pair linear combinations are supposed to be at 10.0 eV and 11.21 eV in **9** and at 10.4 eV and 11.57 eV in **10**. This gives an interaction parameter of $\beta = 0.85$ eV for the three vicinal nitrogen lone pairs in agreement with values derived for similar cases of nitrogen lone pair interaction (14,18). The distinct system at 9.23 eV in **9** is assigned to the lowest energy π_5 -ionization as indicated by its shape and ring vibration of 1400 cm^{-1} . In **10** this system coalesces nearly with the lowest energy lone pair combination at 9.1 eV and loses its distinctiveness. The only prominent electron system in **10** is the one at 12.77 eV which can be assigned to the π -bonding orbital located mainly at the CN group. The remaining π_{CN} in-plane orbital might be hidden at about 11.6 eV. The intensity inversion of bonding/nonbonding electron systems is somewhat unusual, as reverse is to be expected, i.e., the nonbonding one should be sharper and more intense. However, a similar feature has been observed in benzonitriles (19,20).

EXPERIMENTAL

Compounds.

The starting compounds, not available commercially, were prepared according to the procedure described in the literature: 3-chloroindazole (**4**) (21), imidazo[1,2-*b*]pyridazine (**5**) (22), 6-chloroimidazo[1,2-*b*]pyridazine (**6**) (23), 2-phenylimidazo[1,2-*b*]pyridazine (**7**) (24), 2-phenyl-6-chloroimidazo[1,2-*b*]pyridazine (**8**) (25), tetrazolo[1,2-*a*]pyridine (**9**) (26) and 8-cyanotetrazolo[1,2-*a*]pyridine (**10**) (27).

PE Spectra.

All spectra have been recorded on a Vacuum Generator UV-G3 photoelectron spectrometer (28). Enhanced temperatures of the inlet system (80, 140, 110, 150, 140, 120, 140, 200, 150, and 160° for **1-10**, respectively) were employed for producing satisfactory spectra. The PE spectra were obtained under low (~ 35 meV FWHM) and for some systems under high (~ 15 meV) resolution and were calibrated by admitting small amounts of an Ar/Xe mixture to the sample flow. Reported ionization energies are accurate to 0.03 eV.

Molecular Orbital Calculations.

SCF LCAO MO calculations within the framework of the PPP method, assuming standard bond lengths and angles, as well as

HMO calculations, were performed for compounds **2-10**. The parameters used in the PPP method were: $\alpha_{\text{C}} = 11.16$ eV, $\gamma_{\text{CC}} = 11.08$ eV, $\beta_{\text{C-C}} = -2.39$ eV, $\alpha_{\text{N}} = 14.43$ eV, $\gamma_{\text{NN}} = 11.19$ eV, $\beta_{\text{C-N}} = -2.58$ eV, $\alpha_{\text{N}} = 24.00$ eV, $\gamma_{\text{NN}} = 12.83$ eV, $\beta_{\text{C-N}} = -2.30$ eV, $\beta_{\text{N-N}} = -2.50$ eV, $\alpha_{\text{Cl}} = 28.67$ eV, $\gamma_{\text{Cl-Cl}} = 13.58$ eV, $\beta_{\text{C-Cl}} = -1.85$ eV, for atoms in cyano group: $\alpha_{\text{C}} = 11.19$ eV, $\gamma_{\text{CC}} = 11.09$ eV, $\alpha_{\text{N}} = 14.18$ eV, $\gamma_{\text{NN}} = 12.52$ eV, $\beta_{\text{C-C}} = -3.5$ eV, whereas the heteroatom parameters in HMO method were: $h_{\text{N}} = 1.50$, $h_{\text{N}} = 0.5$, $k_{\text{C-N}} = 0.75$, $k_{\text{N-N}} = 0.87$, $h_{\text{Cl}} = 2.0$, $k_{\text{C-Cl}} = 0.4$.

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