Photoelectron Spectroscopy of Heterocycles

1-(Diazinyl)-2-(Pyridyl)-ethenes (Triazastilbenes)

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The photoelectron (PE) spectra of 1-(4-pyrimidyl)-2-(3-pyridyl)-ethene **1**, 1-(2-pyrimidyl)-2-(3-pyridyl)-ethene **2**, 1-(4-pyridazinyl)-2-(3-pyridyl)-ethene **3**, 1-(3-pyridazinyl)-2-(3-pyridyl)-ethene **4** and 1-(2-pyrazinyl)-2-(3-pyridyl)-ethene **5** all in their trans conformations have been recorded using HeI radiation. Comparisons with the PE spectra of styrylpyridines, dipyridylethenes and diazabenzenes allowed the assignment of all ionization energies, E_{i}, corresponding to π- and nitrogen lone pair ionizations in the region of $E_{\mathrm{i}} < 12$ eV. The variations in PE spectra of five isomeric triazastilbenes studied are due to different nitrogen atom positions in the diazinyl ring.

Introduction

This work is an extension of our earlier study [1] of aza-analogues of stilbene. When nitrogen replaces carbon in one or both benzene rings of stilbene, several changes can be observed. Thus, nitrogen in ortho-position decreases the dihedral angle between two ring planes in comparison to stilbene, by relieving steric hindrance. The π-ionization energies of the nitrogen containing compounds increase when compared to stilbene. The increase depends on the number of nitrogens and is the manifestation of the "aza-effect". The positions of nitrogen atoms in isomeric molecules determine the appearance of both electron (E) and photoelectron (PE) spectra. However, a large number of conformers can influence the E and PE spectra and contribute to loss of resolution. The PE spectra of styrylpyridines [2] and dipyridylethenes [1, 3] had been reported so far, as well as the E spectra of styryldiazines [4] and dipyridylethenes [5].

Experimental

The PE spectra of **1**–**5** have been recorded with a Vacuum Generators UV-G3 instrument [6]. The sample compounds have been prepared according to [7]. Elevated temperatures of the inlet system (120 °C, 140 °C, 160 °C, 160 °C and 120 °C for **1**–**5**, respectively) were employed in order to get satisfactory spectra. The regions of $E_{\mathrm{i}} < 12$ eV in the HeI PE spectra of **1**–**5** are shown in Figure 1. Experimental vertical E_{i} values of the first eight systems are indicated above the peaks with an accuracy of ± 0.05 eV.

Results and Discussion

It has been shown recently that Koopmans' theorem is inapplicable for the assignment of the PE spectra of diazines [8]. The existence of low lying virtual orbitals lead to nonuniform many-body effects causing shifts of lone pair E_{i}'s relative to those of π-electrons. The few lowest E_{i}'s in diazines can nevertheless still be described in the familiar one-particle ionization picture. In spite of the breakdown of Koopmans's theorem even for the lowest E_{i}'s of diazines, CNDO/2 calculations were performed for **1**–**5** (assuming planar geometry throughout, i.e. C_s point group) since these molecules are still out of reach of the sophisticated von Niessen approach. One readily observes (Table 1) that CNDO/2 results put an extra σ-MO in the region where (in comparison with dipyridylethenes [1, 3] and stilbazoles [2]) only three σ-type nitrogen lone pair ionizations are to be expected. Furthermore, CNDO/2 calculations of **1**–**5** predict the highest occupied π- and lone pair MO's to be nearly degenerate, in disagreement with the PE

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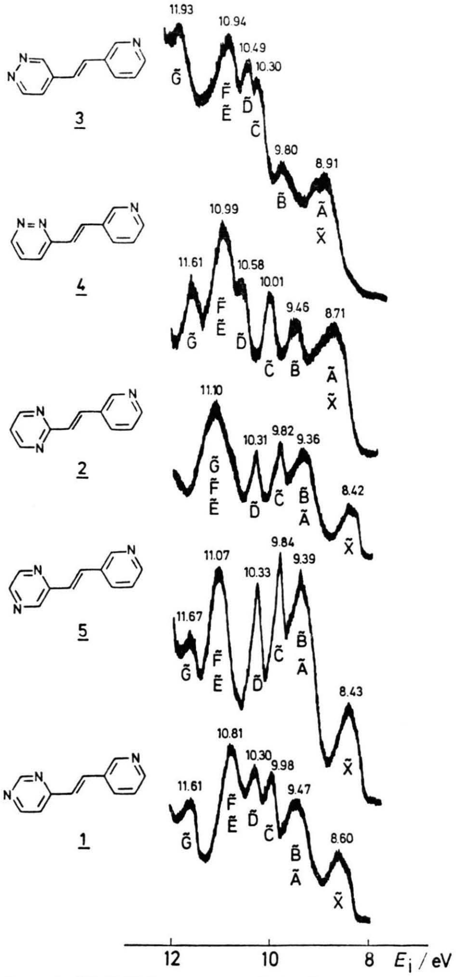

Fig. 1. HeI PE spectra of **1**–**5**.

Table 1. Comparison of energies and corresponding symmetries of canonical SCF-molecular orbitals (CNDO/2) of the ground states of **1**–**5** (ε_i/eV) with the values and assignment of vertical ionization energies (E_i/eV) from their PE spectra.

Compound	CNDO/2 Energy (ε_i/eV)	Orbitals Symmetry	Electronic band systems Energy (E_i/eV)	Assignment
1	10.16	a′	8.60	π
	10.31	a″(π)	9.47	n_-
	10.76	a′	9.47	n
	11.79	a′	9.98	π
	12.20	a′	10.30	π
	12.68	a″(π)	10.81	n_+
	12.71	a″(π)	10.81	π
	13.14	a″(π)	11.61	π
2	10.24	a″(π)	8.42	π
	10.32	a′	9.36	n_-
	10.61	a′	9.36	n
	11.62	a′	9.82	π
	12.37	a′	10.31	π
	12.67	a″(π)	11.10	n_+
	12.86	a″(π)	11.10	π
	13.02	a″(π)	11.10	π
3	10.30	a″(π)	8.91	π
	10.54	a′	8.91	n_-
	10.73	a′	9.80	n
	11.93	a′	10.30	π
	12.20	a′	10.49	π
	12.73	a″(π)	10.94	n_+
	12.78	a″(π)	10.94	π
	13.23	a″(π)	11.93	π
4	10.19	a″(π)	8.71	π
	10.42	a′	8.71	n_-
	10.78	a′	9.46	n
	11.62	a′	10.01	π
	12.50	a′	10.58	π
	12.67	a″(π)	10.99	n_+
	12.97	a″(π)	10.99	π
	13.07	a″(π)	11.61	π
5	9.97	a′	8.43	π
	10.14	a″(π)	9.39	n_+
	10.69	a′	9.39	n
	11.96	a′	9.84	π
	12.66	a″(π)	10.33	π
	12.84	a″(π)	11.07	n_-
	13.13	a″(π)	11.07	π
	13.15	a′	11.67	π

spectra of **1**, **2** and **5**. In view of the known deficiencies of the CNDO/2 method and the breakdown of Koopmans' theorem applied to diazines [8], another approach to assign the PE spectra of **1**–**5** was attempted.

A MO correlation diagram was constructed (Fig. 2) for the composite molecules **1**–**5** starting with vertical E_i's ($E_i < 12$ eV) from the assigned PE spectra of their parts: pyridine, diazines and ethene. The assignment for pyridine and diazines was taken from [8]. Such a qualitative approach has doubtful validity. Namely, by simply correlating the E_i's and the assignments of diazine and pyridine fragments (in which manybody effects have been explicitly included and where Koopmans' theorem was proved useless) in order to get qualitative orbital energy patterns for the composite molecules **1**–**5**, no account has been taken of many-body corrections which might appear in the latter. Therefore, if many-body effects in **1**–**5** play as an important a role as in diazines, then E_i shifts of up to 1 eV can be expected and our assignment will be erroneous. However, a successful assignment can be achieved in this way, either by fortuitous cancellation of errors or because of uniform many-body effects in the ionization energy region studied. In the case of **1**–**5** this

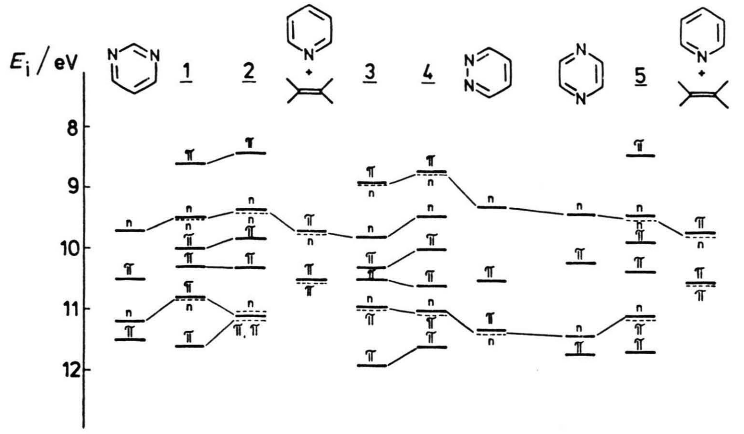

Fig. 2. MO correlation diagram for composite molecules **1**—**5** and their parts-pyri dine, ethene and the diazines-on the basis of PE spectra.

approach offers a more consistent interpretation of their PE spectra than CNDO/2 calculations do. Nevertheless, the assignment proposed should be regarded as tentative.

The systems $\tilde{A}$, $\tilde{B}$ and $\tilde{E}$ in the PE spectra of **1** – **5** are assigned to nitrogen lone pair ionizations and the rest of the systems with $E_i < 12$ eV to π-ionizations by a comparison with the results on dipyridylethenes [1, 3] (Fig. 2 and Table 1). Nitrogen lone pair orbitals in diazine rings interact strongly, yielding n_+ (in-phase) and n_- (out-of-phase) combinations, while the nitrogen lone pair in the pyridine ring remains unaffected by such interactions. This conclusion is suggested by the electronic structures of dipyridylethenes [1, 3] where the lone pair E_i's are nearly degenerate and close to the pyridine value. The E_i's of $\tilde{B}$ systems remain in the interval 9.6 ± 0.2 eV close to the lone pair ionization energy of pyridine at 9.7 eV [8] and can thus be attributed to the lone pair ionization of nitrogen from the pyridine ring. The n_+/n_- orbital energy splittings (1.34 eV, 1.74 eV, 2.03 eV, 2.28 eV and 1.68 eV for **1** – **5**, respectively) remain within ±0.3 eV close to the corresponding values in diazines, thus favouring the present assignment. The ionization when compared to those of **1**, **2** and **5**. This can be explained by a stronger n_+/n_- splitting in pyrid-energies of the $\tilde{A}$ systems in **3** and **4** are decreased azinyl derivatives due to interactions of neighbouring nitrogens. The resulting quasidegeneracy of the highest π- and lone pair orbitals of **3** and **4** is reflected in the electron spectra of triazastilbenes [9] where n-π* transitions were observed for pyridazinyl derivatives only.

The "aza-effect" (cf. Introduction) can also be observed in the PE spectra of **1** – **5** because all the π-ionization energies increase when compared to the corresponding ones in dipyridylethenes. The magnitude of the shift can be rationalized by different localisation characteristics of the particular orbital being ionized. Thus, for instance, all the π-ionization energies of **2** are up to 0.9 eV higher than the corresponding ones of 1-(2-pyridyl)-2-(3-pyridyl)-ethene. The continuous increase of the π-ionization energies in the sequence stilbene → stilbazole → dipyridylethene → triazastilbene further substantiates our assignment. Lone pair E_i's ($E_i < 9$ eV) in **3** and **4** possibly indicate their electron-donor potentials as chelating agents.

In conclusion, the electronic structures of triazastilbenes **1** – **5** differ significantly from those of styrylpyridines and dipyridylethenes. While in the last two groups of molecules Koopmans' theorem can be successfully applied to the assignment of the PE spectra this is no longer the case for triazastilbenes. The tentative assignments of the PE spectra of the composite molecules **1** – **5** can be obtained by comparison with the spectra of the molecular parts (pyridine, diazines). Also, variations of the nitrogen atom positions influence the orbital energy patterns more profoundly than in the case of styrylpyridines and dipyridylethenes.

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