The Photoelectron Spectra of 1,3-Diphenyl-2-pyrazolines

M. Klessinger
Organisch-Chemisches Institut der Universität, D-4400 Münster, Germany

D. Srzić, B. Kovač, and L. Klasinc
Rugjer Bošković Institute, Zagreb, Croatia, Yugoslavia

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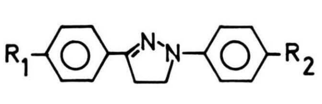
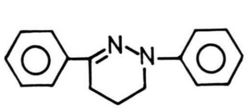
The PE spectra of eight 1,3-diphenyl-2-pyrazolines and a 1,3-diphenyl-tetrahydro-1,2-diazine are reported. The low energy of the first E_i of this class of compounds as well as the effect of electron donor or acceptor substituent in the para positions of any of the phenyl groups are discussed on the basis of a simple MO model.

Introduction

The use of 1,3-diphenyl-2-pyrazolines (**1**) as scintillators and optical whitening agents [1] has initiated detailed investigations of the fluorescence spectra [2] and of the mass spectral behaviour [3] of this class of compounds. The high stability of the molecular ion of **1,** as well as of substituted derivatives of has been attributed to their unusually low ionization energy. In the present study the photoelectron (PE) spectra of **1** and of the derivatives **2**–**8** with substituents in the *para* position of one or both phenyl rings, as well as of 1,3-diphenyl-1,4,5,6-tetrahydro-1,2-diazine (**9**) will be reported and their low ionization energy will be explained on the basis of simple MO arguments.



	R_1	R_2
1	H	H
2	$N(CH_3)_2$	H
3	OCH_3	H
4	H	OCH_3
5	NO_2	H
6	H	NO_2
7	NO_2	OCH_3
8	OCH_3	NO_2



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Results

The PE spectra of **2, 1, 9** and **5** are given (top to bottom) in Fig. 1, those of **3**, **8**, and **6** (top to bottom) in Fig. 2. The values of vertical ionization energies $E_{i,v}$/eV are given on top of the corresponding electronic band systems. The spectra are all very similar insofar as they exhibit one peak at low ionization potential (~ 7 eV) and one group of peaks near 9 eV, which from intensity considerations corresponds at least to four ionization events. At ~ 11 eV ionizations from σ orbitals start. The assumption that all peaks below ~ 11 eV correspond to ionizations from π orbitals is confirmed by the similarity of the PE spectra of **1** and the derivative **9** in which the five-membered pyrazoline is replaced by a six-membered ring. From the PE spectra of pyrazolones [4] the ionization from the σ_N orbital is known to occur at 10.5–11 eV, so that it will be buried by the σ ionizations at ~ 11 eV. Interaction of the lone-pair orbitals of the $-NR_2$ and $-OCH_3$ groups with that of the phenyl ring of appropriate symmetry leads to the observation of two peaks in the corresponding spectra; from work on substituted benzenes [5, 6] the one at lower energy is known to appear at ~ 7.5 and 8.5 eV, respectively, whereas the other is found around 11 eV. Thus in **2,** and in **3, 4, 7,** and **8,** the low energy peak due to this interaction of the lone-pair orbital n_N and n_O of the $N(CH_3)_2$ and OCH_3 substituents, can be identified with the peaks at 7.66 and 8.37 eV in **2** and **3,** respectively. The nitro group is expected to bring

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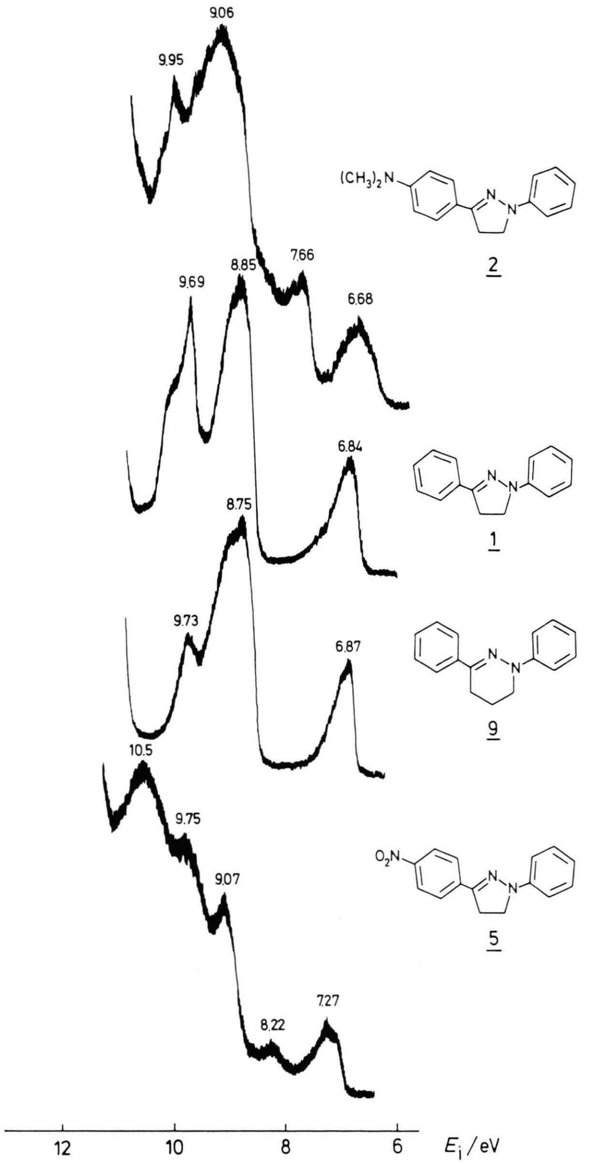

Fig. 1. HeI – PE spectra of compounds **2, 1, 9,** and **5.**

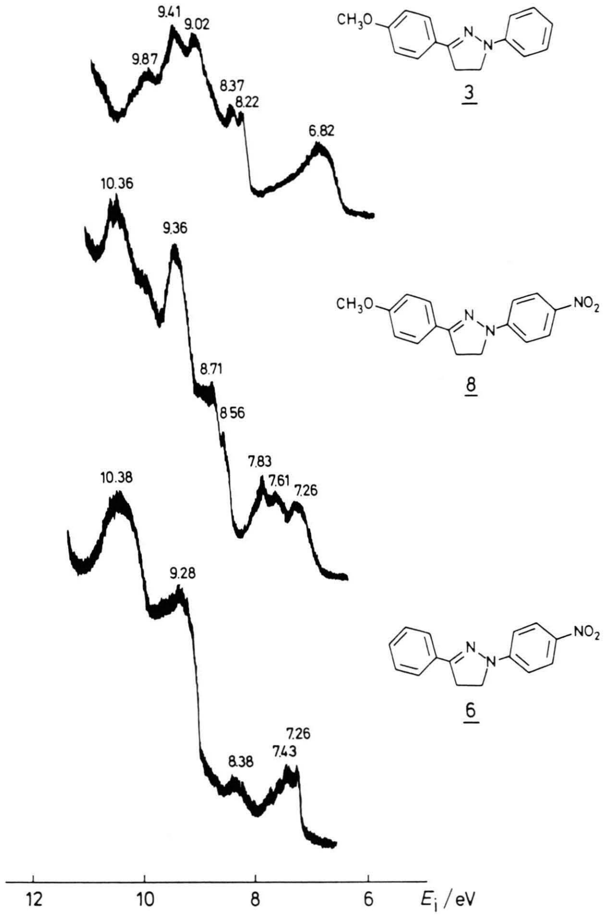

Fig. 2. HeI – PE spectra of compounds **3, 8,** and **6.**

peaks from two orbitals in this region: one corresponding to one of the two possible combinations of the in-plane oxygen lone-pairs, n_{O}, and the other corresponding to the π-electrons located mainly on the oxygen atoms π-orbitals. The peaks at 8.22 and 8.38 eV in **5** and **6,** respectively, correspond to the former of these oxygen lone-pair ionizations, n_{O^+}, of the NO_2 group, whereas the π_{NO_2} are covered by the peaks of benzene π-orbitals. From Fig. 2 it is seen that the main effect of the substituents in the para position of one of the phenyl rings is to shift the first E_i to lower or higher values, depending on whether the substituent is electron releasing (NR_2) or electron attracting (NO_2). This shift is slightly more pronounced for substituents in the 1-phenyl ring than for those in the 3-phenyl ring. In systems with an electron releasing substituent in one of the phenyl rings and an electron attracting substituent in the other one, the effect of the two substituents is nearly additive. Apparently there is no particular push-pull effect, which could be responsible for the low ionization potential of the 1,3-diphenyl-2-pyrazolines.

Discussion

The π system of 1,3-diphenyl-2-pyrazoline can be thought of as being composed of a diaza-group iso-

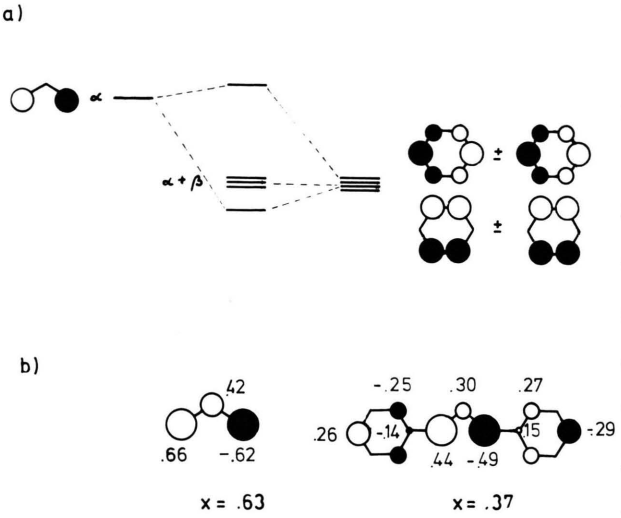

Fig. 3. a) Qualitative correlation diagram for the interaction of the nonbonding allyl π MO with combinations of the degenerate benzene π MOs in 1,3-diphenyl-2-pyrazoline; HMO calculation with $h_{\dot{N}} = 1.0$, $h_{\ddot{N}} = 1.5$ and $k_{NN} = 1.3$ lead to a similar orbital energy diagram with $\varepsilon = \alpha + 0.37\beta$, $\varepsilon = \alpha + \beta$ (triply degenerate) and $\varepsilon = \alpha + 1.36\beta$. b) HOMO of the π system of diaza-allyl and 1,3-diphenyl-2-pyrazoline obtained with parameter values given above.

Table 1. HMO orbital energies of the HMO and observed E_i's of substituted 1,3-diphenyl-2-pyrazolines.

Compound	R_1	R_2	x_{HOMO}*	E_i
1	H	H	0.37	6.84, 8.85, 9.69, 11.53
3	CH_3O	H	0.33	6.82, 8.37, 9.02, 9.41, 9.87
4	H	CH_3O	0.32	6.86, 8.56, 9.11, 10.01
5	NO_2	H	0.43	7.07, 8.22, 9.07, 9.77
6	H	NO_2	0.44	7.26, 8.38, 9.28, 10.38
7	NO_2	OCH_3	0.39	7.06, 7.91, 8.91, 9.56
8	OCH_{3P}	NO_2	0.41	7.26, 7.83, 8.56, 9.36, 10.36

* $\varepsilon_{HOMO} = \alpha + x_{HOMO}\beta$; only the inductive effect of NO_2 was taken into account by using $\alpha_{C-NO_2} = \alpha + \beta$, for CH_3O the parameters $\alpha_O = \alpha + 1.5\beta$ and $\beta_{CO} = 0.8\beta$ were used.

electronic with the allyl anion and phenyl groups attached to each end of this allylic system. In the case of the allyl anion, the symmetry of the problem is such that only one of the four possible combinations of the degenerate benzene (e_{1g}) MOs can interact with the nonbonding allyl MO. Due to this interaction the nonbonding allyl MO will be destabilized and the combination of benzene MO of the appropriate symmetry will be stabilized, as shown in Figure 3. This pattern of one high lying π MO and a group of three degenerate MOs with a fourth one nearby changes only very little if the unsymmetrical nature of the diaza-allyl systems is taken into account. Using the parameters $\alpha_{\dot{N}} = \alpha + \beta$, $\alpha_{\ddot{N}} = \alpha + 1.5\beta$ and $\beta_{NN} = 1.3\beta$ in an HMO calculation, the nonbonding allyl MO ($\varepsilon = \alpha$) is shifted to $\varepsilon = \alpha + 0.63\beta$, but the LCAO coefficients at the terminal centres are still of approximately the same size and of opposite sign (cf. Figure 3b). The interaction with the benzene π MOs destabilizes this orbital by 0.26β, yielding $\varepsilon = \alpha + 0.37\beta$, whereas the stabilization of the bonding combination is 0.36β, yielding $\varepsilon = \alpha + 1.36\beta$. For this particular choice of parameter values three π MOs happen to be degenerate as in the case of the isoelectronic hydrocarbon, so that the orbital energy scheme is exactly as derived from the qualitative considerations (Figure 3a).

The LCAO coefficients of the HOMO at $\varepsilon = \alpha + 0.37\beta$ on the other hand show a considerable mixing between bonding and antibonding MOs (cf. Fig. 3b), as is to be expected from the fact that the amount of the stabilization of the lower and the amount of destabilization of the higher of the two interacting orbitals are not equal. From the LCAO coefficients the effect of substituents on the HOMO orbital energy may be estimated by first order perturbation theory according to

$$\delta\varepsilon_i = c_{\mu i}^2\,\delta\alpha_\mu\,.$$

The fact that $c_{\mu i}^2$ is nearly the same for the para position of the 1-phenyl and of the 3-phenyl group implies similar substituent effects for both positions; electron attracting substituents should stabilize the HOMO and therefore increase the E_i, whereas electron releasing substituents should have the opposite effect. In push-pull systems with an electron attracting substituent at one phenyl group and an electron releasing substituent at the other one, the two effects should be algebraically additive as far as first order perturbation theory is applicable; they should therefore partially compensate, depending on the relative donor and acceptor strengths of the substituents. All these expectations are in good agreement with the experimental data, as can be seen from Table 1, which gives the

HOMO orbital energies together with the E_i values for some of the compounds studied.

The MO considerations also confirm the interpretation of the peaks in the PE spectrum of **1** at 9−10 eV as being due to ionizations from four π MOs mainly localized in the phenyl rings, three of which are nearly degenerate, whereas the fourth one is stabilized by the interaction with the pyrazoline π system.

Conclusion

The results presented here show that the low E_i of 1,3-diphenyl-2-pyrazolines can be interpreted as being due to the allyl-type MO of the pyrazoline π system. The substitution of two carbons in the allyl anion by nitrogens considerably stabilizes the HOMO, which in the hydrocarbon is nonbonding. Delocalization of this MO into the rings at both ends of the system has a destabilizing effect on this MO, thus leading to the low E_i of this class of compounds. MO considerations suggest that the delocalization into polyenic instead of aromatic groups will be more effective, leading to even lower E_i's. Push-pull substitution on the other hand, which leaves the electron distribution in the central allylic part of the π system unchanged to first order, has no such effect and can give even higher E_i's, depending in the relative donator and acceptor strengths of the substituents. This aspect of the electronic structure of pyrazolines is being persued further.

Experimental

Compounds **1−9** have been of high purity, prepared as quoted in [7] (**1−8**) and [8] (**9**).

PE spectra have been measured on a Vacuum Generators UV-G3 spectrometer [9] using He I line for excitation with a resolution of 35 meV FWHM and at the inlet system of the 160, 190, 200, 190, 200, 240, 220, 220, and 140 °C for **1−9,** respectively. The spectra were calibrated by adding small amounts of Xe to the sample flow.

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