(He 1) PHOTOELECTRON SPECTRA OF VINYL- AND (1-DIMETHYLAMINOVINYL)PYRIDINES

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The (He 1) photoelectron spectra of α-, β-, γ-vinyl, α-, β-, and γ-(1-dimethylvinyl)-pyridines, 1-dimethyl- and 1-diethylaminostyrenes were obtained and interpreted within the framework of the molecular orbital perturbation theory. In both pyridine derivative series, there is a regular increase in the ionization energy of the $1a_2$, $\pi_{C=C}$ and n_{en} orbitals and decrease in the ionization energy of the $2b_1$ orbitals in the order $\alpha < \beta < \gamma$ (inversion of orbitals $1a_2$ and $2b_1$ is found for γ-vinylpyridine). The splitting of the energy levels of the heterocycle in dimethylaminovinylpyridines is less than in the corresponding vinyl derivatives, which indicates a weakening of the interaction between the aromatic (or heteroaromatic) ring and the enamine fragment extruding from the ring plane. The ionization energy of the unshared electron pair of the nitrogen atom of the pyridine ring for all the compounds except for α-(1-dimethylaminovinyl)pyridine (which displays an ortho effect) is close to that for pyridine. The photoelectron spectral data are compared with the MO energies calculated by the MINDO/3 method.

The direction of the reactions of arylenamines and hetarylenamines with dienophiles [1, 2] and also the quantum chemical data calculated for these compounds by the MINDO/3 method [2-5] indicate significant isolation of the π-orbitals of the enamine fragment and the noncoplanar aromatic ring. Clarification of the nature of this interaction relative to the site of the substituent in readily available and highly reactive pyridylenamines [2, 6], which hold considerable synthetic interest, required additional studies using photoelectron spectra. The photoelectron spectra of the (1-dimethylaminovinyl)pyridines were interpreted on the base of the spectra of simpler compounds, namely, 1-dimethyl and 1-diethylaminostyrenes and isomeric vinylpyridines which have not yet been described.

The photoelectron spectra of these compounds are shown in Fig. 1a, b and the values for the vertical ionization energies corresponding to the positions of the band maxima as well as some literature data are given in the correlation diagram in Fig. 2. These results are examined in the framework of the Koopmans approximation, i.e., the ionization energies taken with reverse sign are equated to the energies of the corresponding molecular orbitals (MO).

Let us consider the interaction of the pyridine ring and the vinyl group from the viewpoint of the simple theory of MO perturbations, according to which the splitting of the orbital energies are directly proportional to the coefficients of the atomic orbitals (AO) and inversely proportional to the difference in energies of the starting unperturbed levels. Figure 2 shows that the ionization energies of the nitrogen "unshared pair" n-orbital (9.60 eV) and the π-orbitals with $1a_1$ (9.75 eV) and $2b_1$ (10.50 eV) symmetry are very close to the ionization energies of ethylene (10.51 eV). Nevertheless, the n-orbital lying in the ring plane will experience only a weak perturbation due to the ethylenic fragment such that the position of its ionization band in the photoelectron spectra of all the vinylpyridines should hardly be altered. On the basis of the distribution of the coefficients of the $1a_2$ and $2b_1$ AO of pyridine (Fig. 3), we should also expect that the $1a_2$ orbital in γ-vinylpyridine, having a node at the site of attachment of the ethylenic fragment, should also remain unperturbed. On the other hand, the $2b_1$ MO will be mixed efficiently with the $\pi_{C=C}$ MO to form new ($2b_1 - \pi$) and ($2b_1 + \pi$) orbitals with energies higher and lower than the energies of the initial levels.

These conclusions are in good accord with the experimental data and the photoelectron spectra of γ-vinylpyridine (III) differs considerably from the spectra for the α- and β-derivatives (I and II) (Fig. 1a). The interaction between the $2b_1$ and $\pi_{C=C}$ levels in γ-vinylpy-

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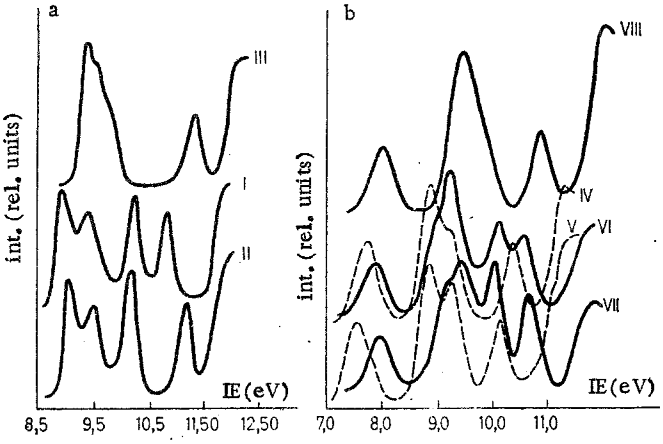

Fig. 1. Photoelectron spectra: vinylpyridines: α- (I), β- (II), γ- (III), b) 1-dimethyl- (IV) and 1-diethylaminostyrenes (V), (1-dimethylaminovinyl)pyridines: α- (VI), β- (VII), and γ- (VIII).

ridine leads to a "shift" in band for the ($2b_1 - \pi_{C=C}$) orbital in its photoelectron spectrum toward the region of the n- and Ia_2 MO (the position of these bands relative to their position in the pyridine spectrum are virtually unchanged) (Fig. 1a and Fig. 2). As a result, the single strong band at 9.37 eV with shoulders at 9.55 and ~9.7 eV correspond to the three orbitals. The second band with maximum at 11.37 eV corresponds to the ($2b_1 + \pi_{C=C}$) ionization orbital. The difference between the ionization energies of the $2b_1$ orbital in pyridine and the ($2b_1 - \pi_{C=C}$) orbital in γ-vinylpyridine (1.13 eV may serve, in a first approximation, as an index of the interaction between the $2b_1$ and $\pi_{C=C}$ MO. We should note that the destabilization of the $2b_1$ MO in styrene is only about 0.8 eV [9].

All the bands corresponding to the ionization of the three π-orbitals (based on the initial $1a_2$, $2b_1$ and $\pi_{C=C}$ MO) and the n-orbital are clearly observed in the photoelectron spectra of α- and β-vinylpyridines (Fig. 1a) in contrast to the γ-derivative. The second bands in the spectra of both these compounds are naturally assigned to the ionization of the n-orbital since their shift relative to the n-band in pyridine is not greater than 0.2 eV (Fig. 2). Since the $2b_1$ orbital has low electron density on the α- and β-carbon atoms of the ring, its mixing with the $\pi_{C=C}$ MO and the corresponding change in energy should be slight. Hence, the third bands in the spectra of α- and β-vinylpyridines may be related to the ionization of the $2b_1$ orbital. The destabilization of this level relative to pyridine is 0.27 and 0.33 eV for the α- and β- derivatives. Thus, the first and fourth bands in the photoelectron spectra of these compounds correlates with the pyridine $1a_2$ MO and $\pi_{C=C}$ MO of the vinyl group. Figure 2 indicates that the destabilization of the $1a_2$ level is 0.85 and 0.78 eV in α- and β-vinylpyridines relative to pyridine, i.e., less that destabilization of the $2b_1$ level in γ-vinylpyridine. This is not surprising since the difference in the energies of the initial $1a_2$ and $\pi_{C=C}$ levels is greater than between the $2b_1$ and $\pi_{C=C}$ levels and in light of the difference in their AO coefficients (Fig. 3). The higher position of the ($2b_1 + \pi_{C=C}$) orbitals of the α- and β-derivatives (I and II) relative to the same orbital of γ-vinylpyridine also indicates a diminution of the interaction of the vinyl group with the π-ring system. If, to a first approximation, we assume that the inductive effect of the pyridine ring on the $\pi_{C=C}$ MO is independent of the site of attachment of the vinyl group, we may conclude on the basis of the position of the fourth band of the photoelectron spectra of the vinylpyridines that the interaction of the π-electrons of the vinyl group and the heterocycle falls off in the sequence γ > β > α.

Before considering the photoelectron spectra of the pyridylenamines, let us consider the spectra of the most simple aliphatic enamines which contain two bands in the low ionization energy region, which are assigned to the ionization of the ($n_{en} - \pi_{C=C}$) and ($n_{en} + \pi_{C=C}$) orbitals [11]. The ab initio calculations for simple enamines [11] and MINDO/3 calculations for conjugated enamines [4] show that the nitrogen unshared pair makes a somewhat larger contribution to the HOMO, while the π-electrons of the double bond make a somewhat larger contribution to the formation of the second MO. Thus, we shall refer to these orbitals as n_{en} and $\pi_{C=C}$ although such terms are rather arbitrary in light of the strong interaction of the initial n and π levels. Since the photoelectron spectrum of dimethylaminoethylene has not been reported in the literature, we estimate its ionization energies (n_{en}) and ($\pi_{C=C}$) from the data for alipha-

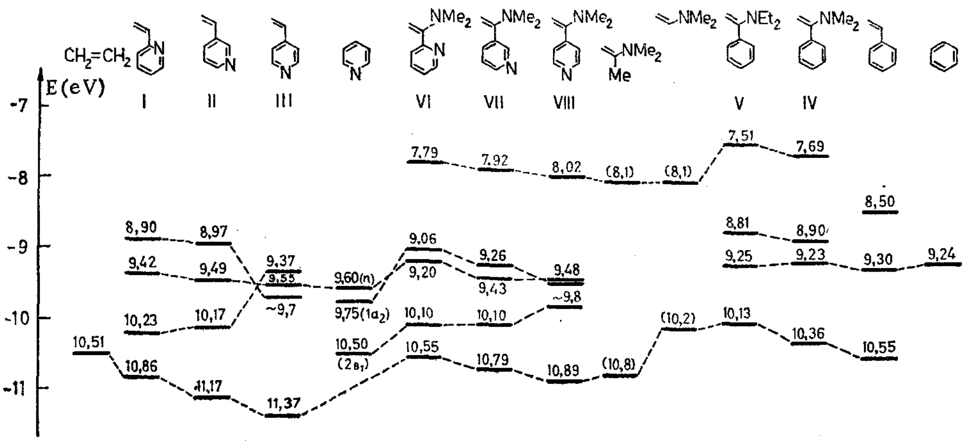

Fig. 2. Correlation diagram of energy levels in the photoelectron spectra of vinylpyridines I-III, arylenamines IV and V, (1-dimethylaminovinyl)pyridines VI-VIII, pyridine [7, 10], styrene, ethylene and benzene [8, 9], dimethylaminoethylene and dimethylaminopropylene (see below).

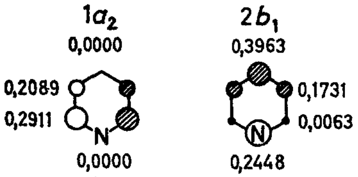

Fig. 3. Distribution of AO coefficients in the pyridine $1a_1$ and $2b_1$ MO according to the Hückel calculation [10].

tic amines. According to Müller et al. [11], the introduction of a methyl group at the β-position of an enamine reduces the (n_{en}) and ($\pi_{C=C}$) ionization energies approximately by the same amount (0.3-0.4 eV), while the introduction of an α-methyl substituent has virtually no effect on the (n_{en}) ionization energy but reduces the ($\pi_{C=C}$) ionization energy by about 0.6 eV (hyperconjugation effect). The energies thereby calculated of the two upper MO of dimethylaminoethylene and its α-methyl derivative are given in Table 2 in parentheses.

The photoelectron spectra of arylenamines IV and V (Fig. 1b) show that the presence of an aromatic ring in the α-position of the enamine leads to a reduction in the ionization energy of both (n_{en}) and ($\pi_{C=C}$) relative to dimethylaminoethylene (Fig. 2). Some reduction in the ionization energies for (n_{en}) and ($\pi_{C=C}$) in going from IV to V is due to the larger +I effect of the ethyl groups relative to the methyl groups. In turn, the interaction of the enamine fragment with the doubly degenerate e_{1g} level of benzene leads to its splitting: the energy of one orbital is increased while the position of the other orbital which has a node at the site of attachment of the enamine fragment is virtually unchanged (Fig. 2). Partially overlapping bands correspond to these levels in the spectrum (Fig. 1b).

In going from phenyl derivatives IV and V to pyridyl-substituted enamines VI-VIII, the qualitative nature of the interaction of the enamine fragment with the aromatic ring is retained (Fig. 1b and Fig. 2). The first and fifth bands in these spectra are related to the ionization of the dimethylamino group nitrogen unshared electron pair (n_{en}) and of the enamine double bond ($\pi_{C=C}$), while the intermediate bands are related to the ionization of the orbitals of the pyridine ring. The nature of their splitting in α-, β-, and γ-(1-dimethylaminovinyl)-pyridines VI-VIII is the same as for the splittings for α-, β-, and γ-vinylpyridines I-III, although the changes in the MO energies themselves relative to pyridine are less for all the isomers. For this reason, the inversion of the $1a_2$ and $2b_1$ levels which occurs in γ-vinylpyridine (III) is not observed in the γ-substituted pyridylenamine VIII. Another difference is that the energies of the $1a_2$, n, and $2b_1$ MO for α-vinylpyridine (I) are virtually the same for the energies of the orbitals with the same symmetry in the β-isomer II, while differences are observed in the α- and β-substituted pyridylenamines VI and VII. The ionization energy of the heterocycle nitrogen unshared electron pair in α-substituted enamine VI is lower while the corresponding ionization energies in the β- and γ-isomers VII and VIII are very similar to each other and do not differ significantly from the ionization energy of the n-band in pyridine (Fig. 2). Since the nitrogen unshared pair lies in the plane of the pyridine ring and, as a consequence of symmetry considerations, cannot efficiently interact with the π-electrons of the enamine fragment, the ortho effect seen in the case of the α-derivative VI is related either to an interaction through space or with a change in molecular geometry due to approximation of the electron-rich dimethylaminovinyl group and the pyridine ring nitrogen unshared pair.

On the whole, the lower splittings of the levels of the aromatic and heteroaromatic ring in aryl- and pyridylenamines IV, V and VI-VIII relative to styrene and vinylpyridines I-III and rather low (n_{en}) ionization energies for IV-VIII relative to dimethylaminoethylene indicate a weakening of the interaction of the aromatic and enamine molecular fragments. These findings indicate that the noncoplanarity of the aromatic and enamine fragments of aryl- and hetarylenamine molecules which was previously demonstrated for solutions of these compounds in nonpolar solvents [3] is retained in the gas phase. On the other hand, the photoelectron spectral data gave the unexpected finding that the capacity of the pyridine ring in the gas phase to conjugate with the vinyl and 1-dimethylaminovinyl groups falls off in the series γ-Py > β-Py > α-Py. The usually observed for electron-withdrawing strength of the pyridine ring (both in pyridylenamines [2] and vinylpyridines [12]) α > γ > β is related to competition of the +M effect of the unsaturated substituent which is greatest for the γ-position and the -I effect of the nitrogen atom which is greatest for the α-position [13] and also with the solvation effect.

In conclusion, let us compare the ionization energies of the phenyl and pyridyl derivative I-V and VI-VIII (Fig. 2) obtained from the photoelectron spectra with the data calculated for these compounds using the MINDO/3 method (Table 1). The good agreement of the calculated and experimentally determined ionization energies of the π-orbitals of styrene and 1-dimethylaminostyrene (IV) (and of dimethylaminoethylene) indicates that this method is entirely applicable for evaluating the interaction of the aromatic ring with the vinyl and 1-dimethylaminovinyl groups. In the latter, the proximity of the dimethylamino group nitrogen unshared electron pair, which, as noted by the authors of the MINDO/3 method, reduces the accuracy of the calculations [14] and leads to a reduction in the calculated ionization energy of the HOMO by only about 0.2 eV (0.06 eV for styrene), while the energy levels of the ring are very well reproduced. Even greater accuracy in the calculation of the energies of these levels is achieved taking account of the noncoplanarity of the aromatic and enamine molecular fragments (the fifth and sixth columns in Table 1). However, the calculations significantly overestimate the energies of the σ-levels as indicated by the absence of the corresponding bands in the photoelectron spectrum of styrene in the vicinity of 10 eV [8]. Less satisfactory correlation is seen for pyridyl derivatives I-III and VI-VIII between the calculated and experimental data not only for pyridylenamines VI-VIII, whose conformation may differ from the conformation of phenyl derivative IV (see note to Table 1), but also for planar vinylpyridines I-III. For both series of compounds, the calculations overestimate the energies of the σ levels and especially of the n levels of the heterocycle and do not reflect the inversion of the $1a_2$ and $2b_1$ levels* in the case of γ-vinylpyridine (III) (Fig. 2 and Table 1). On the other hand, the absolute ionization energies of the HOMO of VI-VIII are very well reproduced by the calculations although the difference is 0.17 eV for the α-derivative VI, which may be related to the already mentioned ortho effect. Thus, comparison of the calculated ionization energies with the experimental values shows that the properties of the enamine fragment related to the aromatic substituent within the framework of the MINDO/3 method are described significantly better than the properties of the pyridine ring.

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*Recent nonempirical calculations for pyridine, α- and γ-vinylpyridines with complete optimization of the molecular geometry reproduce the inversion of the $1a_2$ and $2b_1$ levels in γ-vinylpyridine and the energies of the n-levels but overestimates the ionization energy of the π-levels of the ring by more than 1.5 eV and distort the order of the π- and n-levels [15].

TABLE 1. Energies of the First Four Occupied MO (eV) (with reverse sign) of Styrene, Dimethylethylene and I-IV, VI-VIII Calculated by the MINDO/3 Method[a]

MO No.	Compound									
	styrene	I	II	III	$\mathrm{IV}_{\mathrm{plan}}$	$\mathrm{IV}_{\mathrm{opt}}$	VI	VII	VIII	dimethylaminoethylene
1 (HOMO)	8,56	8,46[b]	8,43[b]	8,43[b]	7,85	7,90	7,97	7,90	9,75	8,03
2	9,28	8,60	8,55	8,79	9,04	9,02	8,52[b]	8,49[b]	8,46[b]	10,85
3	10,01[c]	9,47	9,48	9,15	9,30	9,36	9,04	9,08	9,28	—
4	10,26[c]	10,19[c]	10,09[c]	10,22[c]	9,51[c]	9,84	9,60	9,67	9,43	—

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[a] Styrene and I-III were calculated for the planar conformation, IV was calculated for a planar and optimized conformation with rotation of the phenyl ring relative to the double bond of 55° [3-5], pyridylenamines VI-VIII were calculated in the optimized conformation of IV, dimethylaminoethylene was calculated in the optimized conformation [3]. Values are given for the MO energies for I, II, VI-VIII which are intermediate between those for the s-cis and s-trans conformations of the vinyl group since the difference in the energies of the MO of conformers ≤0.03 eV. [b] The n-orbital of the pyridine ring. [c] The σ-orbitals.

EXPERIMENTAL

The photoelectron spectra of I-VIII were taken on a spectrometer manufactured at the Chemistry Research Institute of Leningrad State University with resolution of at least 200 [16]. Samples of 2- and 4-vinylpyridines obtained from the Swiss firm, Fluka were distilled in vacuum in an argon stream prior to distillation. A sample of 3-vinylpyridine was obtained by the reduction of 3-acetylpyridine by lithium aluminum hydride with subsequent dehydration by P_2O_5 [17]. The synthesis of aryl- and pyridylenamines IV, V and VI-VIII was described in our previous work [1, 2]. The procedure for the quantum chemical calculations [2-4] and some parameters of the compounds studied such as electronic charge, AO coefficients and MO levels were partially published in our previous work [2, 4, 5].

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