Through-bond Effects in Pyrazino[2,3-*b*]pyrazine. Photoelectron Spectroscopy and Model Calculations

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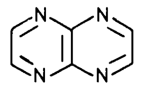
The He$^{I\alpha}$ photoelectron spectra of the title compound and four methyl derivatives are measured and analysed in terms of simple Hückel-type arguments and the results of semiempirical EWMO and HAM/3 calculations. The presence of strong through-bond interaction leading to a highly destabilized totally symmetric nitrogen 'non-bonding' orbital is confirmed.

The photoelectron (p.e.) and electronic absorption data for aza-aromatic compounds with two or more nitrogens are consistent only with the assumption of significant through-bond coupling of the 'non-bonding' (*n*) orbitals.[1–9] A particularly large through-bond effect has been predicted for pyrazino[2,3-*b*]pyrazine (1), leading to a highly destabilized *n* combination of a_g symmetry and a low-energy forbidden n–π^* transition in this compound.[9–11] In order to investigate the *n* orbital structure of this interesting heterocycle, we have recorded the p.e. spectra of (1) and its methyl derivatives (2)—(5).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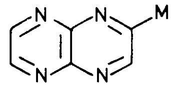
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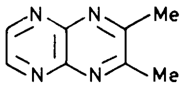
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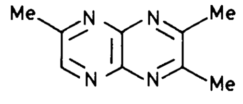
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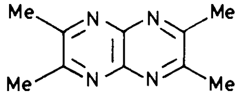
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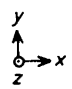

Experimental

Compounds (1)—(5) were synthesized according to directions in the literature.[11] The He$^{I\alpha}$ p.e. spectra were measured at room temperature on a PS 18 instrument (Perkin-Elmer) and calibrated with reference to the 15.75 eV argon line.

P.e. Spectra.—The spectra of (1) and (2) are shown in Figure 1 and vertical ionization energies estimated from the observed p.e. band maxima are given in Tables 1 and 2. The spectrum of (1) is characterized by two well resolved peaks close to 9 and 10 eV, followed by a complex region at *ca.* 11 eV and further maxima close to 12 and 13 eV. A consideration of the relative integrated intensities indicates the assignment of one, one, three, one, and two individual transitions, respectively. The assignment of the compact structure at *ca.* 11 eV to three individual ionization processes is supported by the clear resolution of three peaks in this region in the spectrum of (2) (Figure 1).

The bands in the low-energy region are characterized by markedly different shapes. Band [1] has a weak 0–0 component and a relatively broad, gaussian-like envelope; in contrast, bands [2] and [3] are characterized by intense and sharp 0–0 peaks. In view of the accumulated p.e. spectroscopic evidence,[5,7,8] this strongly suggests the assignment of band [1] to an ionization process involving the nitrogen *n* electrons, and of bands [2] and [3] to ejections of π electrons.

The correlation of band maxima within the series (1)—(5) is indicated in Figure 2. Previous investigations have shown that, as a rule, π bands are more strongly affected than *n* bands by methyl substitution.[7,12–14] In the case of (1), it is evident that band [2] and [3], corresponding to the two highest occupied π orbitals, are shifted differently, indicating different amplitudes on the substituted carbon centres in these orbitals and thereby providing an additional criterion for the orbital assignment of these levels.

Table 1. Experimental and theoretical ionization energies (eV) for (1)

Band	Experimental $I_{v,J}$	Orbital assignment	Theoretical $I_{v,J}$ HMO	EWMO	HAM/3
[1]	9.2	$9a_g(n)$	9.1	9.09	8.84
[2]	9.87	$2b_{1u}(\pi)$	9.82	9.59	10.04
[3]	10.53	$1a_u(\pi)$	10.74	10.96	10.69
[4]	(10.8)	$7b_{3u}(n)$	11.3	10.80	10.08
[5]	11.0	$5b_{1g}(n)$	11.7	11.71	10.94
[6]	11.7	$6b_{2u}(n)$	11.9	11.90	11.41
[7]	12.6	$1b_{3g}(\pi)$	12.40	12.60	12.21
[8]	12.7	$1b_{2g}(\pi)$	12.51	12.97	12.36

Table 2. Experimental ionization energies (eV) for (1)—(5)

Band	Orbital assignment (1)	$I_{v,J}$ (1)	(2)	(3)	(4)	(5)
[1]	$9a_g(n)$	9.2	9.0	8.9	8.7	(8.6)
[2]	$2b_{1u}(\pi)$	9.87	9.54	9.26	9.0	8.8
[3]	$1a_u(\pi)$	10.53	10.32	10.1	10.1	9.86
[4]	$7b_{3u}(n)$	(10.8)	10.6	10.3		
[5]	$5b_{1g}(n)$	11.0	10.8	10.6	10.3	10.2
[6]	$6b_{2u}(n)$	11.7	11.5	11.3	11.1	11.0
[7]	$1b_{3g}(\pi)$	12.6	12.4	(12.1)	(11.7)	(11.5)
[8]	$1b_{2g}(\pi)$	12.7	(12.6)	12.4	12.0	11.7

The assignment of the low-energy bands given in the Tables is based on Koopmans' approximation ($-\varepsilon_J^{MO} = I_{v,J}$).[15] This assignment is supported by the empirical criteria discussed above and by the results of three different theoretical procedures: (i) a Hückel-type (HMO) model,[5,7] (ii) a correlation procedure[6] based on the Energy Weighted Maximum Overlap (EWMO) approximation,[16] and (iii) the HAM/3 procedure.[17]

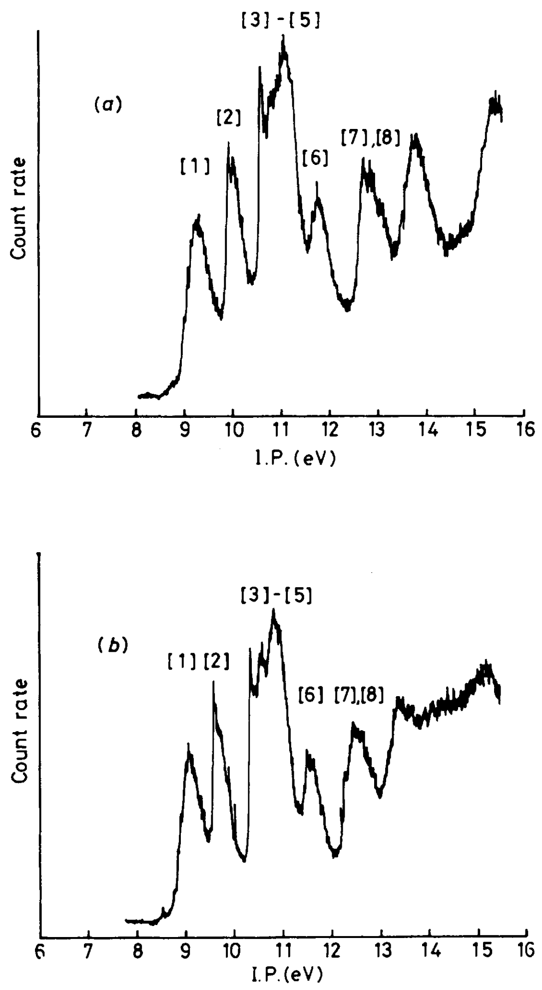

Figure 1. He$^{I\alpha}$ gas-phase p.e. spectra of (a) (**1**) and (b) its 2-methyl derivative (**2**)

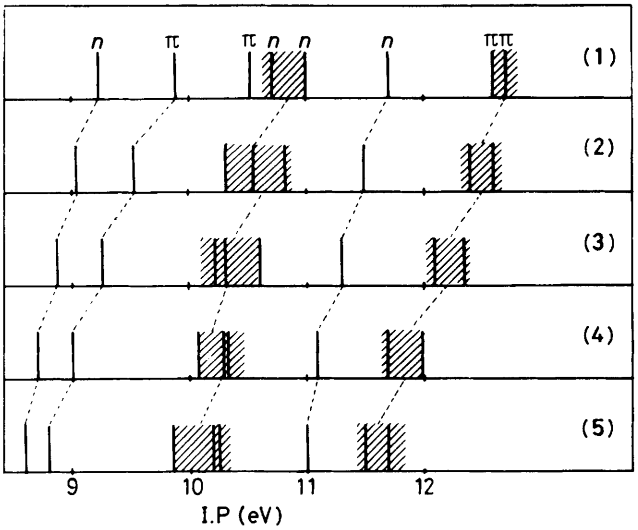

Figure 2. Correlation of observed p.e. band maxima for the series (**1**)—(**5**) with indication of the assignment of π- and *n*-type levels

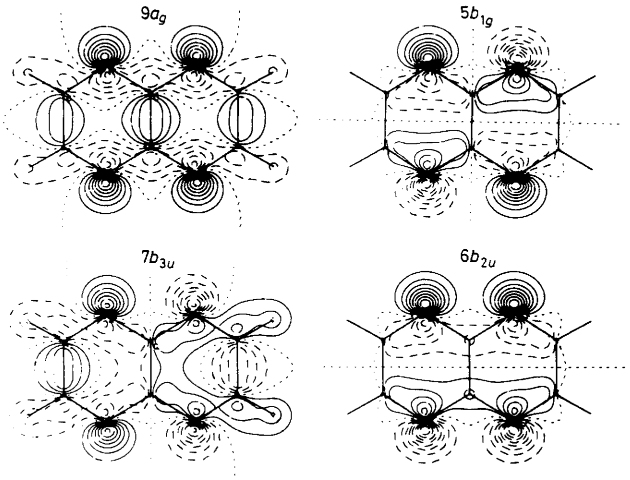

Figure 3. Amplitude contour diagrams of the four nitrogen *n*-type orbitals of (**1**) as calculated by HAM/3

The EWMO and the HAM/3 calculations were based on the geometry predicted by MNDO/1,[18] using computer programs published through QCPE.[19]

HMO Model.—π *Bands.* The effective π orbital energies of aza-benzenes and aza-naphthalenes can be derived by means of simple perturbation theory.[5] According to this approach, the energy change $\Delta\varepsilon_J$ of a naphthalene π orbital $\Psi_J = \Sigma_\mu c_{J\mu}\varphi_\mu$ can be estimated by $\Delta\varepsilon_J = -3.30[\sum_\rho c^2{}_{J\rho}] - 1.01[\sum_\omega c^2{}_{J\omega}]$ (eV) where $c_{J\mu}$ is the coefficient of the *J*th Hückel orbital[20] at the μth site, ρ denotes the positions of aza-replacement, and ω the neighbouring carbon positions. Using this equation, we obtain for the four highest occupied π levels of (**1**): $\varepsilon(2b_{1u}) = -9.82$, $\varepsilon(1a_u) = -10.74$, $\varepsilon(1b_{3g}) = -12.40$, and $\varepsilon(1b_{2g}) = -12.54$ eV. These results suggest the assignment of bands [2], [3], [7], and [8] to π levels, as indicated in Table 1. This assignment is consistent with application of the band-shape criterion (see above) and with the relative shifts of the bands on methyl substitution (Figure 2); the relatively small shift of band [3] can be explained by the localization of the $1a_u(\pi)$ orbital in the α positions.[20] Relative to naphthalene,[5] the ordering of the two highest π levels of (**1**) is reversed. This is consistent with the results of the more sophisticated procedures (Table 1) and is supported by correlation with the p.e. data for related species such as 1,4-, 1,5-, and 1,8-diazanaphthalene.[5,6,8]

n Bands. The structure of the nitrogen *n* orbitals of aza-aromatic compounds is much more complicated than that of the π orbitals. As indicated in the Introduction, these orbitals depend strongly on through-bond coupling *via* C–C and C–H σ orbitals, leading to delocalized wave functions (*e.g.* Figure 3). Furthermore, these orbitals are associated with comparatively large deviations from Koopmans' approximation, leading to poor correlation between calculated orbital energies and observed ionization energies.[21] In spite of these difficulties, previous experience has shown that a surprisingly accurate prediction of the position of the *n* bands of the azabenzenes can be obtained within the framework of simple HMO-type theory.[5,7] Here we extend this procedure to the aza-naphthalene (**1**).

The effective cross term for two nitrogen sp^2 'lone pairs' in positions μ and ν is estimated from the splitting of the two n bands of the corresponding μ,ν-diazanaphthalene: $B_{\mu.\nu} = -\frac{1}{2}[I(n_+) - I(n_-)]$. On the basis of the published p.e. data and assignments for 1,4-, 1,5-, and 1,8-diazanaphthalene,[5–8] we obtain $B_{1.4} = +0.8$, $B_{1.5} = +0.6$, and $B_{1.8} = +0.5$ eV. The effective basis orbital energy for a nitrogen 'lone pair' hybrid orbital in (**1**) can be estimated by a consideration of the increments of the 'centres of gravity,' $\overline{I(n)}$, for related mono-, di-, and tri-azanaphthalenes. Adopting the value $A_n = -11.0$ eV the 4 × 4 secular problem can be solved, the 'wave functions' are completely determined by symmetry:

$$\begin{aligned}
\psi(a_g) &= \tfrac{1}{2}(n_1 + n_4 + n_5 + n_8), \varepsilon = -\ \ 9.1\ \text{eV} \\
\psi(b_{3u}) &= \tfrac{1}{2}(n_1 + n_4 - n_5 - n_8), \varepsilon = -11.3\ \text{eV} \\
\psi(b_{1g}) &= \tfrac{1}{2}(n_1 - n_4 + n_5 - n_8), \varepsilon = -11.7\ \text{eV} \\
\psi(b_{2u}) &= \tfrac{1}{2}(n_1 - n_4 - n_5 + n_8), \varepsilon = -11.9\ \text{eV}
\end{aligned}$$

By subtracting in the p.e. spectrum of (**1**) those bands in the region below 13 eV which have been assigned in the previous section to ejection of electrons from one of the four highest occupied π orbitals we are left with four bands, namely [1] and [4]—[6] close to 9.2, 10.8, 11.0, and 11.7 eV. These bands must be assigned to the four expected n levels of (**1**), in pleasing consistency with the HMO estimate. The predicted ordering of the four n levels is supported by the EWMO and HAM/3 results (Table 1).

Discussion

The assignment indicated in Table 1 is supported by intensity, band shape, and substituent-shift criteria, and by the calculated results. One minor discrepancy concerns the spacing of the close lying $1a_u(\pi)$ and $7b_{3u}(n)$ levels which is sensitive to the choice of calculational procedure. The assignment of the closely spaced levels at *ca.* 11 eV is necessarily tentative, although the shape of band [3] close to 10.5 eV strongly suggests the assignment of a π level [*i.e.*, $1a_u(\pi)$].

Our analysis of the p.e. data confirms the presence of a highly destabilized n level of a_g symmetry. It is well predicted by the simple HMO treatment which predicts a destabilization of $B_{1.4} + B_{1.5} + B_{1.8} = 1.9$ eV relative to the 'centre of gravity' of the n levels. The contour diagrams in Figure 3 of the n orbitals calculated by HAM/3 clearly indicate the large contributions of C–C σ character, evidencing the importance of through-bond coupling. The shape of these orbitals is strongly reminiscent of that of the originating naphthalene orbitals.[6]

Acknowledgements

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