Reversal in the Sequence of the Two Highest Occupied Molecular Orbitals in the Series Pyrazine, 2,6-Dimethylpyrazine, and Tetramethylpyrazine

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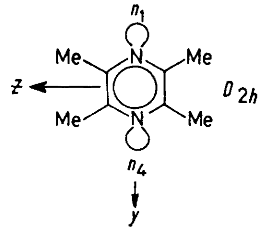
Summary Comparison between the photoelectron spectra of pyrazine (**1**), 2,6-dimethylpyrazine (**2**), and tetramethylpyrazine (**3**) indicates that in (**3**) the HOMO is $\pi(b_{2g})$ while in (**1**) and (**2**) it is n_+, suggesting a different behaviour towards electrophilic attack on (**3**) compared with (**1**) and (**2**).

REPORTS on reactions between carbenes and nonphenolic six-membered aza-heterocycles are sparse.[1] Ring enlargement to a seven-membered ring has not yet been reported. The reactions known so far indicate that the first step is the attack of the carbene on an N-atom and not on the π-system. This can be rationalized by assuming that in the six-membered aza-heterocycles the HOMO is the lone pair or a lone pair combination. Photoelectron (PE) spectroscopic measurements have confirmed this assumption[2] and also have demonstrated that in methyl substituted pyridines[2a] the π-orbital is the HOMO. In pyrazine (**1**) a potential precurser for the synthesis of diazacycloheptatriene via carbene attack, the gap between $n_+(a_g)$ and $\pi(b_{2g})$ is 0·55 eV;[2b] in 2,6-dimethylpyrazine (**2**) it is reduced to 0·08 eV[2c] owing to the effect of the methyl groups. If



$$n_+(a_g) = \frac{1}{\sqrt{2}}(n_1 + n_4)$$

$$n_-(b_{2u}) = \frac{1}{\sqrt{2}}(n_1 - n_4)$$

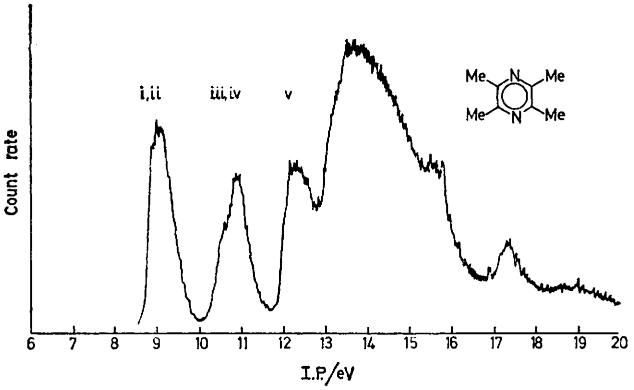


FIGURE 1. PE spectrum of tetramethylpyrazine (**3**).

TABLE

Observed vertical ionization potentials $I_{V,J}$ and calculated orbital energies ϵ_J of tetramethylpyrazine (**3**). All values are in eV.

Band	Assignment	$I_{V,J}$	$-\epsilon_J$ (calc.)
i	$b_{2g}(\pi,A)^a$	8·6	7·9
ii	$a_g(\sigma,n+)$	8·9	8·8
iii	$b_{2u}(\sigma,n-)$	10·40	10·4
iv	$b_{1g}(\pi,S)^a$	10·72	11·2

[a] A and S refer to the symmetry behaviour of the orbital with respect to the xy plane.

four methyl groups have twice the effect of two, in tetramethylpyrazine (**3**) the π (b_{2g}) orbital should be above n_+ (a_g) and thus a reaction between (**3**) and carbene might give the desired ring enlargement. We have therefore measured the PE-spectrum of tetramethylpyrazine[3] (Figure 1 and Table.†) In Figure 2 the PE data of (**1**), (**2**), and (**3**) are correlated using Koopmans' theorem.[4] In Figure 1 there are two peaks below 12 eV which we show later are due to two ionization processes (bands i—iv in Figure 1).

Our assignment (see Table) of bands (i) and (ii) is based on the band shape, perturbation theory,[5] and semiempirical calculations.[6] While in (**2**) the onset of the first band is of roughly similar appearance to that in (**1**), in (**3**), however, the onset of the first band shows a steep ascent as does band (ii) in (**1**).[8] This supports perturbation arguments which predict 8·5 eV for $\pi(b_{2g})$ and 8·8 eV for n_+ (a_g). The additivity of the effect of the methyl groups which is observed in alkenes,[9,2a] alkynes,[10] and conjugated systems[2a] is fully supported by extended Hückel calculations.‡ The results are summarized in the Table.

With regard to the split of π and n_+, we assume that the superposition of an intense (*e.g.* $2 \leftarrow 0$) transition of the π-band and an intense transition of the n_+ band (*e.g.* $3 \leftarrow 0$) coincide in the peak at 8·81 eV. This leads us to take 8·6 as the vertical ionization potential ($I_{\mathrm{v},J}$) for π (b_{2g}) and 8·9 eV that for the $n_+(a_g)$ band. Bands (iii) and (iv) we assign by analogy with (**1**) and (**2**) to the symmetry-adapted linear combination n_- (b_{2u}) and to the π (b_{1g}) orbital. This interpretation is in accord with arguments from perturbation theory and EH-calculations‡ which predict that both orbitals (b_{2u} and b_{1g}) should be shifted almost by the same amount.

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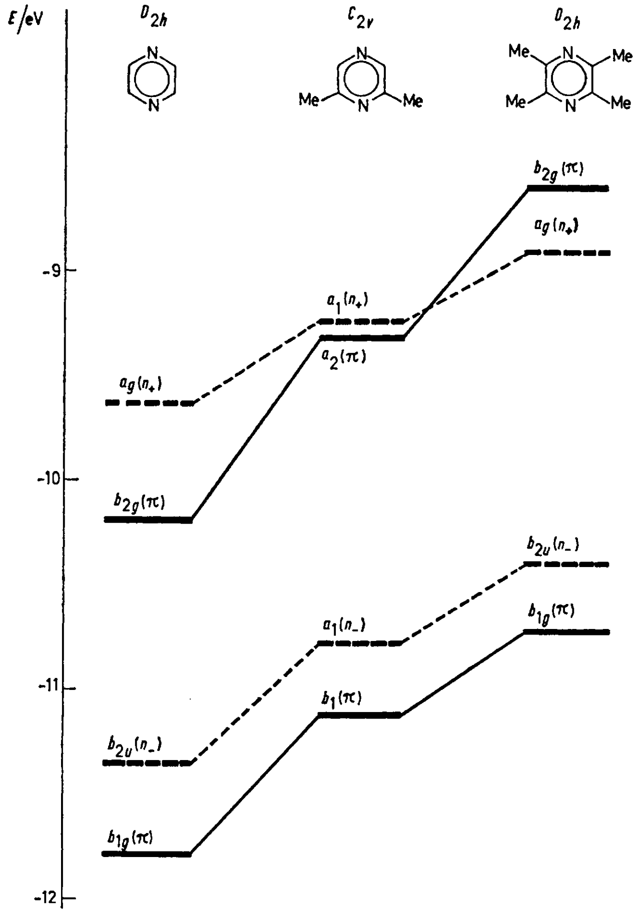

FIGURE 2. Correlation diagram between the measured vertical ionization potentials of pyrazine (**1**), 2,6-dimethylpyrazine (**2**), and tetramethylpyrazine (**3**).

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† PE-spectra have been recorded on a Perkin-Elmer PS 18 photoelectron spectrometer.

‡ According to our experience the extended Hückel method with parameters proposed by Hoffmann[6] underestimates the inductive effect of methyl groups. Therefore Spanget-Larsens[7] modified iterative extended Hückel method (MIEHM) was applied, which reproduces the PE-spectra of azabenzenes,[7a] azanaphthalenes,[7b] and their alkylderivatives[7c] very well.

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