Orderings of π and σ Ionization Potentials in Carbocyclic and Heterocyclic Aromatic Compounds

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Orderings of π and σ ionization potentials in carbocyclic and heterocyclic aromatic compounds

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Data on calculated orbital energies and experimentally measured ionization potentials of carbocyclic and heterocyclic aromatic compounds are compared and contrasted. The ordering or orbital energies and ionization potentials do not always seem to parallel one another, probably owing to either electron correla tion effects, or to deviations from Koopman's theorem. The effects on photoelectron spectra of using different light sources and analysers are discussed in relation to their bearing on the orbital orderings of aromatic compounds. The high resolution He 584 Å photoelectron spectrum of pyridine is shown to be open to two interpretations regarding the ordering of the ionization potentials of the π orbitals and the 'nitrogen lone pair' (n). One of the interpretations involves the three lowest pyridine ionization potentials being π (9.2 eV), π (9.5 eV) and n (10.5 eV) whilst the other has the first three ionization potentials being the order π, n, π. The photoelectron spectra of substituted pyridines and diazines are discussed in the light of the two possible explanations for the pyridine spectrum.

1. INTRODUCTION

The energetic ordering of the orbitals in organic compounds containing multicentre π orbitals has been the cause of much discussion in the past two or three years. The object of this paper is to collect together as much as possible of the relevant evidence, and to discuss it in relation to the high resolution photoelectron spectra of a number of such compounds.

2. EXPERIMENTAL

The procedures adopted for obtaining photoelectron spectra were as described in previous papers (Turner 1968; Baker, May & Turner 1968; Baker, Brundle & Turner 1968). Most of the compounds examined were obtained from commercial sources. 4-Chloropyridine was generated from its hydrochloride with sodium hydroxide immediately before it was required for examination in the spectrometer. One batch of 2-chlorofuran was prepared from 2-furoic acid according to the method of Hill & Jackson (1888), and another batch by the direct chlorination of furan at −40 °C, followed by fractional distillation of the resultant mixture of chlorofurans. The results obtained on the different batches were identical.

3. RESULTS AND DISCUSSION

The lowest π ionization potential in aromatic compounds

Combination of the six carbon $2p_z$ atomic orbitals of benzene produces six π molecular orbitals. However two orbital pairs are degenerate and consequently only four π orbital levels result, as indicated in figure 1. The highest occupied level in the molecular ground state is e_{1g} consisting of degenerate π_3 and π_2 components with the nodal properties shown. The orbital a_{2u} was once commonly supposed to be the second highest level in the molecular ground state (see, for example, El-Sayed, Kasha & Tanaka 1961; Al-Joboury & Turner 1964), but this

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supposition has now been questioned on the grounds of *ab initio* and other types of molecular orbital calculations (see, for example, Schulman & Moskowitz 1965). Molecular orbital calculations on pyridine, the diazines, and furan have also pointed to the lowest π orbital energy of these molecules being below some of the σ orbital energies (table 1).

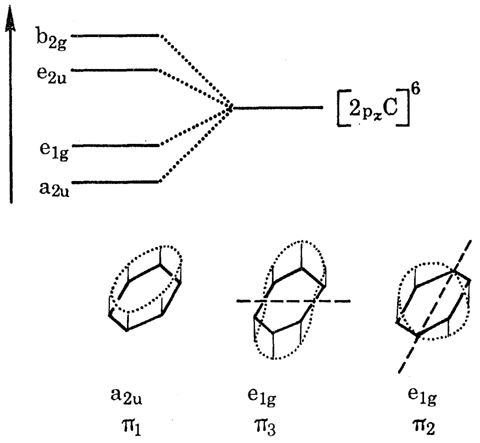

FIGURE 1. π-molecular orbitals in benzene.

TABLE 1. MOLECULAR ORBITAL CALCULATIONS ON SOME AROMATIC COMPOUNDS

compound	orbital energies/eV	reference and method
benzene	7.8($\pi 1e_{1g}^4$); 10.2($\sigma 3e_{2g}^4$); 12.2($\sigma 1b_{2u}^2$); 12.3($\pi 1a_{2u}^2$); 13.0($\sigma 3e_{1u}^4$); 15.3($\sigma 2b_{1u}^2$); 15.5($\sigma 3a_{1g}^2$); 19.4($\sigma 2e_{2g}^2$); 24.2($\sigma 2e_{1u}^4$); 26.9($\sigma 2a_{1g}^2$)	Schulman & Moskowitz (1965); s.c.f.m.o. Gaussian
	9.4($\pi 1e_{1g}^4$); 9.8($\sigma 3e_{2g}^4$); 13.0($\sigma 3e_{1u}^4$); 13.8($\sigma 1b_{2u}^2$); 14.3($\sigma 2b_{1u}^2$); 15.2($\pi 1a_{2u}^2$); 19.6($\sigma 3a_{1g}^2$); 20.1($\sigma 2e_{2g}^4$); 24.8($\sigma 2e_{1u}^4$); 31.2($\sigma 2a_{1g}^2$)	Clarke & Ragle (1967); semiempirical s.c.f.m.o.
pyridine	12.2($\pi 1a_2$); 12.5($\pi 2b_1$); 12.7($n 11a_1$); 15.8($\sigma 7b_2$); 16.9($\pi 1b$); 17.4($\sigma 10a_1$); 18.2($\sigma 6b_2$); 19.1($\sigma 9a_1$); 19.8($\sigma 5b_2$); 21.2($\sigma 8a_1$)	Clementi (1967*a*); s.c.f.m.o. Gaussian
	9.4(n); 10.9(σ); 11.4(π); 12.4(π); 13.4(σ); 15.5(σ); 16.9(σ); 19.4(σ); 20.1(π)	Emsley (1968); c.n.d.o. s.c.f.m.o.
pyrazine	11.9($n 11a_1$); 12.2($\pi 1a_2$); 13.4($\pi 2b_1$); 14.5($n 10a_1$); 16.7($\sigma 7b_2$); 17.7($\pi 1b_1$); 18.7($\sigma 6b_2$); 19.6($\sigma 9a_1$)	Clementi (1967*b*); s.c.f.m.o. Gaussian
	10.8(π); 11.7(n); 12.3(π); 13.8(n)	Del Bené & Jaffé (1968); c.n.d.o. s.c.f.m.o.
pyrimidine	11.0(π); 11.8(n); 12.1(π); 12.9(n)	Del Bené & Jaffé (1968); c.n.d.o. s.c.f.m.o.
pyridazine	11.0(π); 11.1(n); 11.9(π); 12.9(n)	Del Bené & Jaffé (1968); c.n.d.o. s.c.f.m.o.
furan	10.1(π); 12.1(π); 12.2(σ); 12.5(σ); 12.9(σ); 14.1(σ); 19.6(π); 21.6(σ)	Clark (1968); s.c.f.m.o.

We have therefore examined the molecules included in table 1 by high resolution photoelectron spectroscopy to throw more light on the π, σ ordering problem. In table 2 are collected together some experimental data on the ionization potentials of benzene, furan, pyridine, and the diazines obtained in the past from techniques other than photoelectron spectroscopy.

El-Sayed *et al.* (1961) interpreted the pyridine Rydberg series limits of 9.266 eV, *ca.* 10.3 eV, and *ca.* 11.56 eV as representing ionization potentials of, respectively, the outermost π orbital (symmetry species a_2), the 'nitrogen lone pair' (species a_1) and the second π orbital. This assignment conflicted with one proposed previously by Omura, Baba & Higasi (1956) on the basis of their electron impact first ionization potentials of substituted pyridine derivatives (see table 2). These workers believed a nitrogen 'lone pair' electron to have the lowest ionization potential. A second electron impact study of substituted pyridines (Basila & Clancy 1963), however, seemed to indicate that the first ionization potential related in every case to a π electron. Frequencies of charge-transfer bands in the ultraviolet spectra of pyridine derivatives (Krishna & Chowdhury 1963) also substantiated the assignment of El-Sayed *et al.* (1961) for the lowest ionization potential.

Photoionization efficiency measurements of first ionization potentials of pyridine and the diazines have generally confirmed the values obtained from Rydberg series limits. A paper reporting the results of the most recent measurements of this type (Yencha & El-Sayed 1968) contained a discussion of the new data found in relation to some of the previous evidence concerning the ordering of the n and π ionization potentials.

TABLE 2. PREVIOUS EXPERIMENTAL IONIZATION POTENTIALS OF SOME AROMATIC COMPOUNDS

compound	ionization potentials/eV	references
benzene	9.25, 11.48, 16.84† 9.25, 11.5‡ 9.25 (10.3) (10.9), 11.5†	Price & Walsh (1947); El-Sayed *et al.* (1961); Wilkinson (1956); Dibeler & Reese (1964); Momigny *et al.* (1968)
pyridine	9.266, 10.3 (11.56)†	El-Sayed *et al.* (1961)
pyrazine	9.29† 9.29‡	Parkin & Innes (1965); Yencha & El-Sayed (1968)
pyridazine	8.71‡	Yencha & El-Sayed (1968)
pyrimidine	9.35‡	Yencha & El-Sayed (1968)
furan	8.89†‡	Watanabe *et al.* (1958)

Values in parentheses are not confirmed by photoelectron spectroscopy.
† Rydberg limits.
‡ Photoionization efficiency.

The Rydberg series limits for benzene are recorded in table 2. Breaks at 9.25 and 11.50 eV corresponding to the first two Rydberg limits have also been observed in the photoionization efficiency curves reported by Dibeler & Reese (1964) and by Momigny, Goffart & D'Or (1968). In addition to the breaks at 9.25 and 11.5 eV reported by Dibeler & Reese (1964), there is also evident some possibly autoionizing structure near 10.5 eV, and Momigny *et al.* (1968) have noted that there appear to be overall increases in ion yield at 10.35 and 10.85 eV, and have suggested that these are indicative of two previously unsuspected σ orbital ionization potentials. Early low resolution helium 584 Å photoelectron spectra of benzene (Al-Joboury & Turner 1964; Baker *et al.* 1968*b*) confirmed the existence of states of the $C_6H_6^+$ ion at 9.25 and 11.50 eV, but showed no intermediate states. Higher resolution studies (Baker *et al.* 1968*a*) likewise did not detect electrons ejected from any orbitals having i.p. between 9.25 and 11.50 eV, and showed that any such orbitals would be undetected only if their ionization cross sections were less than 0.5% of those of the observed levels.

Photoelectron experiments on benzene with argon resonance lamps, however, have shown (Baker *et al.* 1968*a*; Natalis, Collin & Momigny 1968) that some electrons are released with energies intermediate between those of electrons ejected from the 9.25 and 11.50 eV levels by the impact of argon resonance radiation (1068 and 1047 Å), but Baker *et al.* (1968) have suggested that they are merely due to impurity (nitrogen and hydrogen) lines in the argon lamp causing ionization from the orbital with i.p. 9.25 eV. That all the extra features are explicable in these terms is strongly suggested by the fine structure on the 'extra' bands since in each case it is very similar to that seen in the 9.25 eV i.p. band ($\pi 1e_{1g}$) in the He 584 Å spectrum. Ionization from σ orbitals should of course result in the appearance of photoelectron spectral bands quite different in form.

In view of the results of molecular orbital calculations (table 1) showing deep occupied π levels in carbocyclic and heterocyclic aromatic compounds, it was considered (Baker *et al.* 1968*a*) that the existence of structured or sharp bands near 17 eV in the photoelectron spectra of benzene, pyridine, and furan derivatives (figure 2) might relate to the lowest π level in every case. Studies on the shifts of the 11.5 and 16.8 eV benzene bands incurred by the presence of substituent groupings in the ring (table 3) suggested that the 11.5 eV band corresponded to the lowest π level, but were not conclusive. E. Lindholm (personal communication 1968), however, has recently found that the quantum defect (0.45) associated with the benzene Rydberg series converging at 16.83 eV is inconsistent with the orbital concerned being (q.d. calculated for $3a_{1g}(\sigma) = 0.46$) and thus there is little reason to doubt that the i.p. of an electron in the lowest π orbital of aromatic compounds is near 11.5 eV as originally suggested. The apparent disagreement between this conclusion and the results of m.o. calculations can be rationalized in terms of either large deviations from the Koopmans's theorem basis (Newton 1968) involving appreciable electron correlation effects (cf. Clementi 1967*c*; McKoy & Sinanaglii 1964).

π *and 'lone pair' ionization potentials in azines*

The ionization potentials of pyridine measured from photoelectron band onsets or $0 \leftarrow 0$ vibrational components can be found from figure 2. It can be seen from the spectrum that there is no evidence for an i.p. at *ca.* 11.56 eV, and this suggests that the Rydberg series supposedly converging to this value cannot be genuine. Expansion of the first band of the photoelectron spectrum reveals a complex fine structure (figure 3), but it is possible to pick out peaks spaced at regular 0.07 eV intervals, corresponding perhaps to the excitation of the ring breathing vibration, ν_5, with frequency 560 cm^{-1} in the $C_5H_5N^+$ electronic ground state. The frequency of ν_5 in the molecular ground state is 992 cm^{-1}. The doublet character of the first band of the pyridine spectrum shown up in the expansion must mean that there are two orbitals with very close ionization energies. The next band (i.p. 10.5 eV) is the narrowest in the spectrum, suggesting therefore that the nitrogen lone pair orbital is involved. The 10.5 eV band has a larger energy spread than those associated with bands corresponding to ionization of for example halogen lone pairs, but this could indicate that the nitrogen lone pair electrons are delocalized to a significant extent throughout the pyridine molecule, in accord with m.o. calculations (del Bené & Jaffé 1968) using the c.n.d.o. method (Pople & Segal 1965). Assigning the 10.5 eV band to 'nitrogen lone pair' would then make the two upper pyridine π levels (corresponding to the two degenerate e_{1g} benzene π levels) the ones with i.p values of *ca.* 9.3 eV and *ca.* 9.6 eV. An alternative interpretation of the photoelectron spectrum cannot be completely ruled out however. This alternative involves the first three ionization potentials being π (9.3 eV), n (9.6 eV), and π (10.5 eV), and it requires the substitution of a nitrogen atom into the benzene nucleus to cause an increase of about 1.2 eV (from 9.25 to 10.5 eV) in the i.p. of the B_1 type e_{1g} orbital (π_3). The two possible interpretations of the pyridine spectrum are shown schematically in figure 4.

Portions of the He 584 Å photoelectron spectra of several substituted pyridines are shown in figure 5 (spectra marked M are those obtained by using only a magnetic field deflexion analyser of lower resolving power than the electrostatic analyser used to obtain the other spectra shown in this paper). The contrasting effect of α, β, and γ substitution on the upper pyridine orbitals are revealed by these spectra. α and β substituents seem to cause an increase in the separation of the top two occupied levels, but affect the i.p of third orbital only marginally. γ substituents,

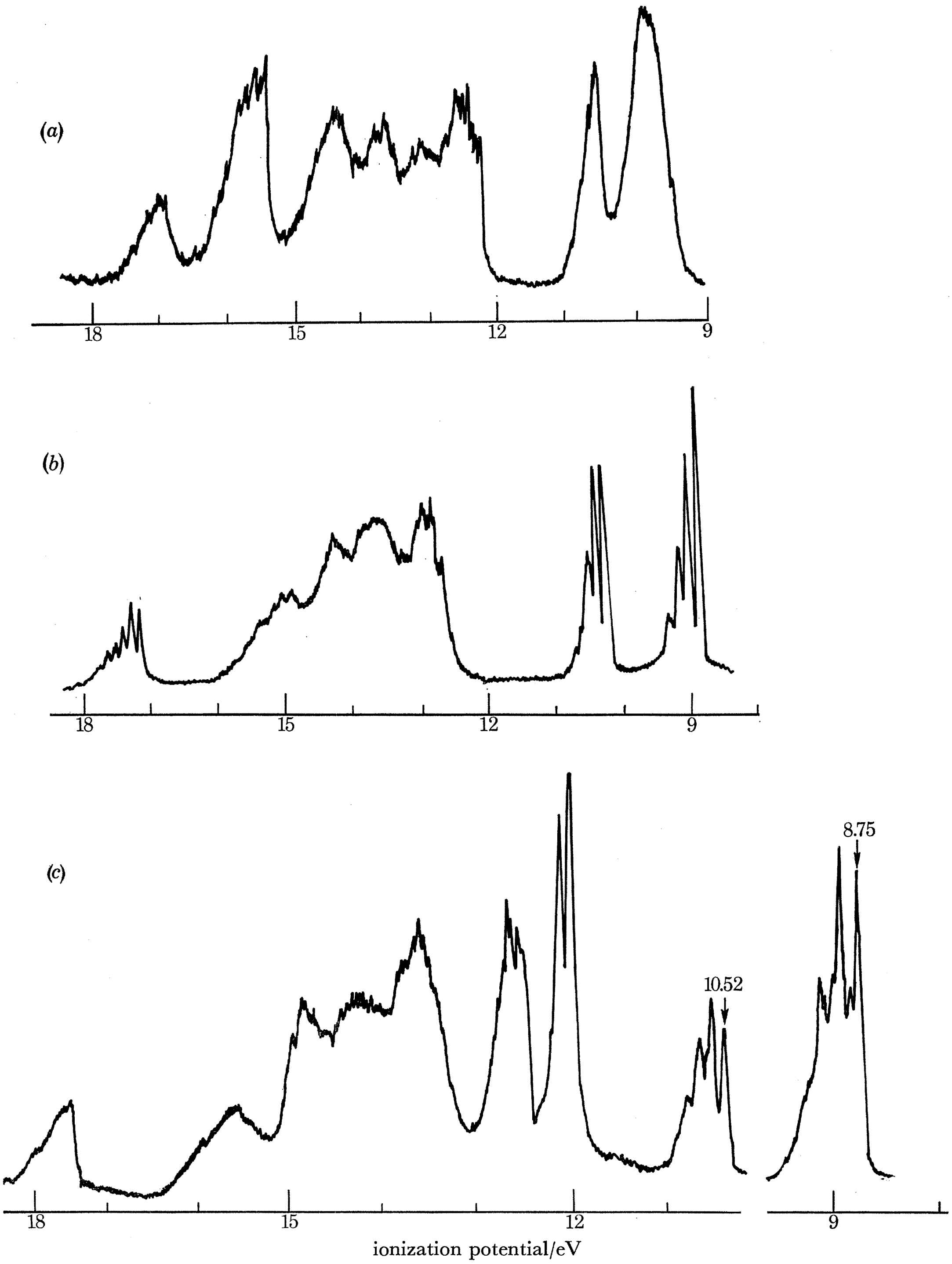

FIGURE 2. He 584 Å photoelectron spectra of (*a*) pyridine, (*b*) furan, (*c*) 2-chlorofuran.

Table 3. Effects of substituents on the 11.5 eV and 16.8 eV ionization potentials of benzene

compound	C_6H_6	C_6H_5I	C_6H_5Br	C_6H_5Cl	C_6H_5F	$C_6H_5CF_3$	$C_6H_5CH_3$	p-$CF_3C_6H_4CF_3$
i.p.	11.5	11.3	11.8	12.2	11.8	11.9	11.2	12.4
	16.8	16.4	16.8	16.9	17.3	18.1	16.4	18.6

The values given are derived from $0 \leftarrow 0$ vibrational components of bands, or from band onsets, and thus are approximately 'adiabatic'.

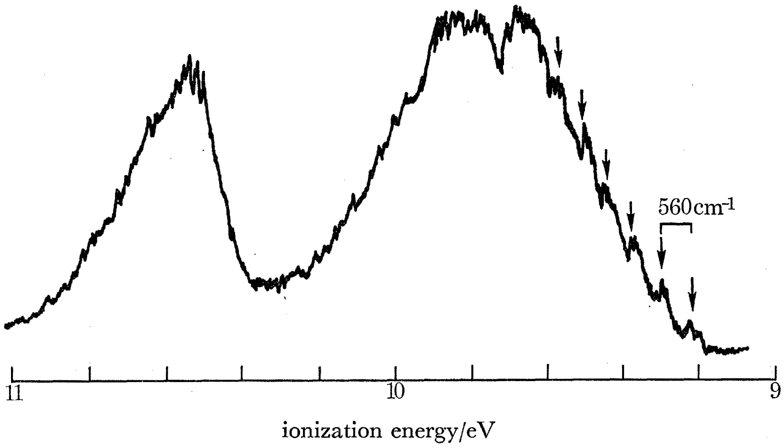

Figure 3. Low i.p. bands of pyridine photoelectron spectrum shown to an expanded energy range.

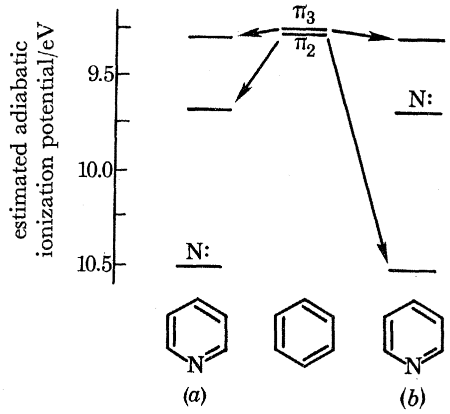

Figure 4. Two possible interpretations of the photoelectron spectrum of pyridine.

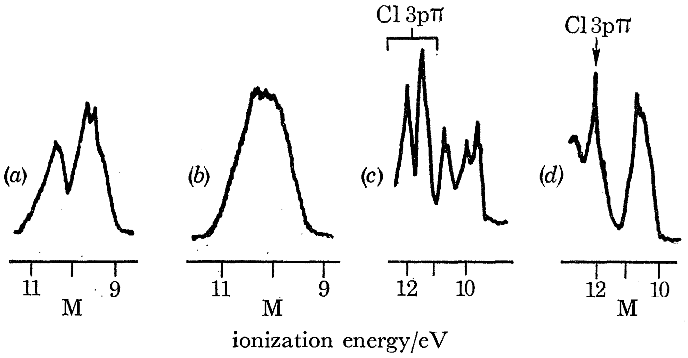

Figure 5. Parts of the He 584 Å photoelectron spectra of (*a*) α-methylpyridine, (*b*) γ-methylpyridine, (*c*) α-chloropyridine, (*d*) γ-chloropyridine.

on the other hand, seem to decrease the third orbital i.p. markedly, and also to increase the i.p. of the highest filled orbitals since only one broad band below 11 eV is apparent in the photoelectron spectra of γ-chloro and γ-methyl pyridines, whereas there are three bands in pyridine.

If the 10.5 eV level of pyridine does relate to an essentially non-bonding nitrogen orbital (see figure 4*a*), its i.p. would appear to depend strongly on the nature of the γ substituent. This is somewhat reminiscent of the effects noted previously for para substituted chlorobenzenes, where the i.p. of the 'chlorine lone pair' electrons has been found to vary considerably as the para substituent is changed (Baker *et al.* 1968*b*). This merging on γ substitution of the two bands of lowest i.p. is, however, also explicable in terms of the second interpretation (figure 7*b*) for the pyridine spectrum. The assumption then would be that the B_1 π orbital i.p. was increased in pyridine with respect to benzene owing to the replacement of a C—H group by a nitrogen atom, but was lowered again by the presence of electron releasing substituents in the γ position of the ring which is the position at which the B_1 orbital has an electron density maximum.

The photoelectron spectra of the diazines pyridazine (1,2), pyrimidine (1,3), and pyrazine (1,4) are shown in figure 6. Each of the diazine molecules has two orbitals approximating to 'nitrogen lone pair'. The simplest picture of these two 'nitrogen' orbitals ψ_a and ψ_b in diazines is that they are derived from positive and negative combinations of two hybrid orbitals:

$$\psi_a = \text{hy } N_1 + \text{hy } N_2, \tag{i}$$

$$\psi_b = \text{hy } N_1 - \text{hy } N_2. \tag{ii}$$

The π orbitals in diazines can be supposed to have the same forms as those in benzene: thus the highest filled π orbital of pyrazine has a nodal surface passing through both nitrogen atoms. In view of this, the corresponding ionization potentials in benzene, pyridine, and pyrazine ought to be very similar. The first ionization potentials for the three molecules are 9.25, 9.26 and 9.29 eV respectively, and this close agreement provides good evidence that the first i.p. relates to a π orbital throughout. In each case, also, the ring breathing vibration appears to be excited on ionization. This is indicated in the pyrazine photoelectron spectrum by the long series of peaks constituting the first band and separated by 615 ± 50 cm^{-1}. Yencha & El-Sayed's (1968) photoionization efficiency curves for pyrazine show a vibrational fine structure associated with the lowest ionization threshold of pyrazine, but the frequency they measure, 726 cm^{-1}, is a little higher than our value.

The second highest filled π orbital of pyrazine has its maximum electron density in the vicinity of the nitrogen atoms. Since the energy separation of the two highest π levels of benzene effected by para substituents has been found to be roughly the sum of the separations produced by either substituent alone (Baker *et al.* 1968*b*), the separation of the corresponding two orbitals in pyrazine might be expected to approximate to double the separation in pyridine. The π_3/π_2 separation in pyridine has been deduced to be either *ca.* 0.4 eV (figure 4*a*) or *ca.* 1.2 eV (figure 4*b*) and as the adiabatic π_2 i.p. for pyrazine is *ca.* 9.29 eV it would be predicted that the π_3 i.p. was either *ca.* 10.1 or 11.7 eV. This could correspond to either the second (figure 7*a*) or the fourth band (figure 7*b*) in the photoelectron spectrum of pyrazine. The vibrational structure on the second band is certainly in keeping with it characterizing the second π ionization potential, since it shows that a vibration with frequency 1015 ± 50 cm^{-1} has been excited on ionization. The orbital type is indicated as being virtually non-bonding, and thus this vibration is probably again ν_4, the symmetrical 'ring-breathing' which has the value 1015 cm^{-1} in the molecule.

Assignment of the first two photoelectron bands of pyrazine to the upper levels makes the two n ionization potentials about 11.2 and 11.6 eV. By analogy with these arguments, the spectra of pyrimidine and pyridazine could be interpreted in terms of two π ionizations causing the first two bands and two n ionizations producing the next two bands. This is shown schematically in figure 7*a*. Yencha & El-Sayed (1968), have, however, pointed out that it would be a little surprising to find a lowest π i.p. for pyridazine which was lower than that for pyrazine, and on this account have assigned the first pyridazine i.p. to an n orbital. Such an assignment based upon the interpretations of figure 4*b* for pyridine would require one to postulate a 'crossing over' the lowest π and n ionization potentials on going from pyridine to pyridazine. This is again illustrated in figure 7.

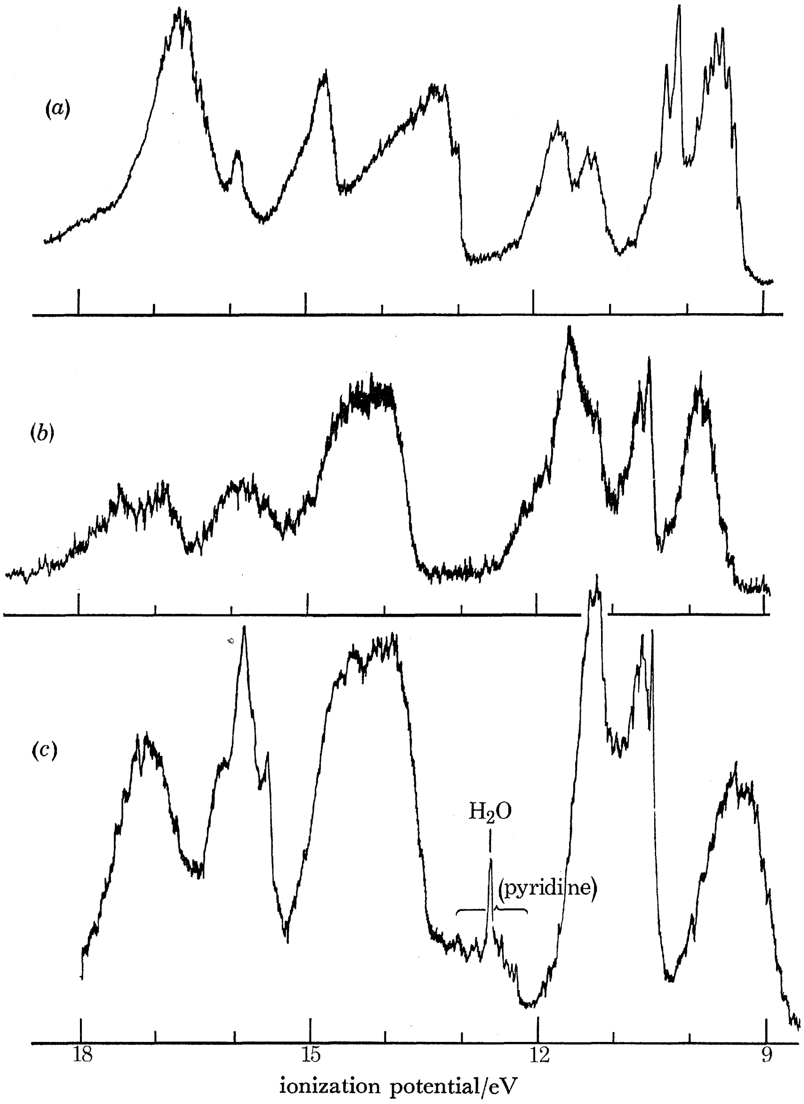

FIGURE 6. He 584 Å photoelectron spectra of (*a*) pyrazine, (*b*) pyrimidine, (*c*) pyridazine.

The i.p. orderings of both figures 7*a* and *b* are at variance with Clementi's (1967*a*, *b*, *c*) and with del Bené & Jaffé's (1968) calculated orbital energy orderings, which are also in disagreement with each other. However both Clementi and del Bené & Jaffé agree that the simple assumption about the n orbitals being positive and negative combinations of hybrid orbitals is inadequate.

The reason del Bené & Jaffé give for dismissing the simple concept is that it leads one to predict a separation of the two n orbitals in diazines which is largest in the case of 1,2 diazine (i.e. pyridazine) and this is not indicated by their calculations (table 1).

The photoelectron results, however, suggest that such an effect many be present. It is also difficult to reconcile the photoelectron results for pyrazine with Clementi's results showing the upper nitrogen 'lone pair' to be the highest occupied orbital in this molecule, and the more non-bonding of the two nitrogen 'lone pairs'.

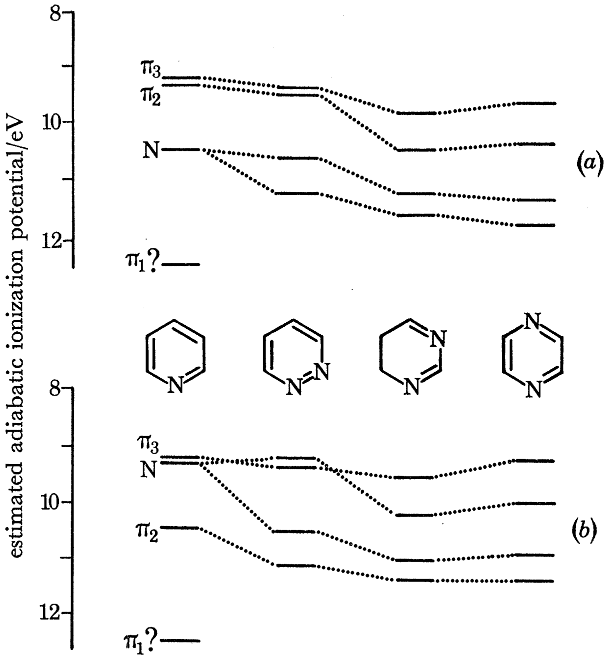

FIGURE 7. Two possible interpretations of the photoelectron spectra of diazines.

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Note added in proof (May 1970). Since this paper was originally compiled, further evidence has come to light which strongly suggests that the ordering of the first three ionization potentials of pyridine are in the order π, n, π as discussed in the text. See Baker *et al.* (1970), Dewar & Worley (1969) and Heilbronner *et al.* (1968).

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