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29. Photoelectron Spectra of Azabenzenes and Azanaphthalenes: I. Pyridine, Diazines, *s*-Triazine and *s*-Tetrazine¹)

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(8. XI. 71)

Summary. The experimental and theoretical basis of a recently proposed reassignment of the bands in the PE. spectra of pyridine, pyridazine, pyrimidine and pyrazine is discussed in detail. A characteristic feature of the derived orbital sequence is that it takes the 'through-space' and 'through-bond' interaction between the 'lone pair' basis orbitals explicitly into account. A simple parametrization of the orbital energies, based on HMO-type models for the π-orbitals and for the 'lone pair' linear combinations, yields excellent agreement with the observed band positions in the PE. spectra of *s*-triazine and *s*-tetrazine. Our new assignment is compared to those proposed previously.

The interaction between nitrogen or oxygen non-bonding 'lone pair' orbitals has been extensively discussed [2] [3]. In some cases predictions, derived from model MO.-calculations, could be verified by high-resolution photoelectron spectroscopy (*e.g.* [4]). In this connection the diazines II, III, and IV are of special interest, insofar as the recognition of substantial coupling between the non-adjacent nitrogen lone pair orbitals in pyrimidine (III) and pyrazine (IV) leads to a reassignment of the bands in their photoelectron spectra (PE. spectra) [1] [5].

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¹) Part 28 of: 'Applications of Photoelectron Spectroscopy'. Part 27: [1].

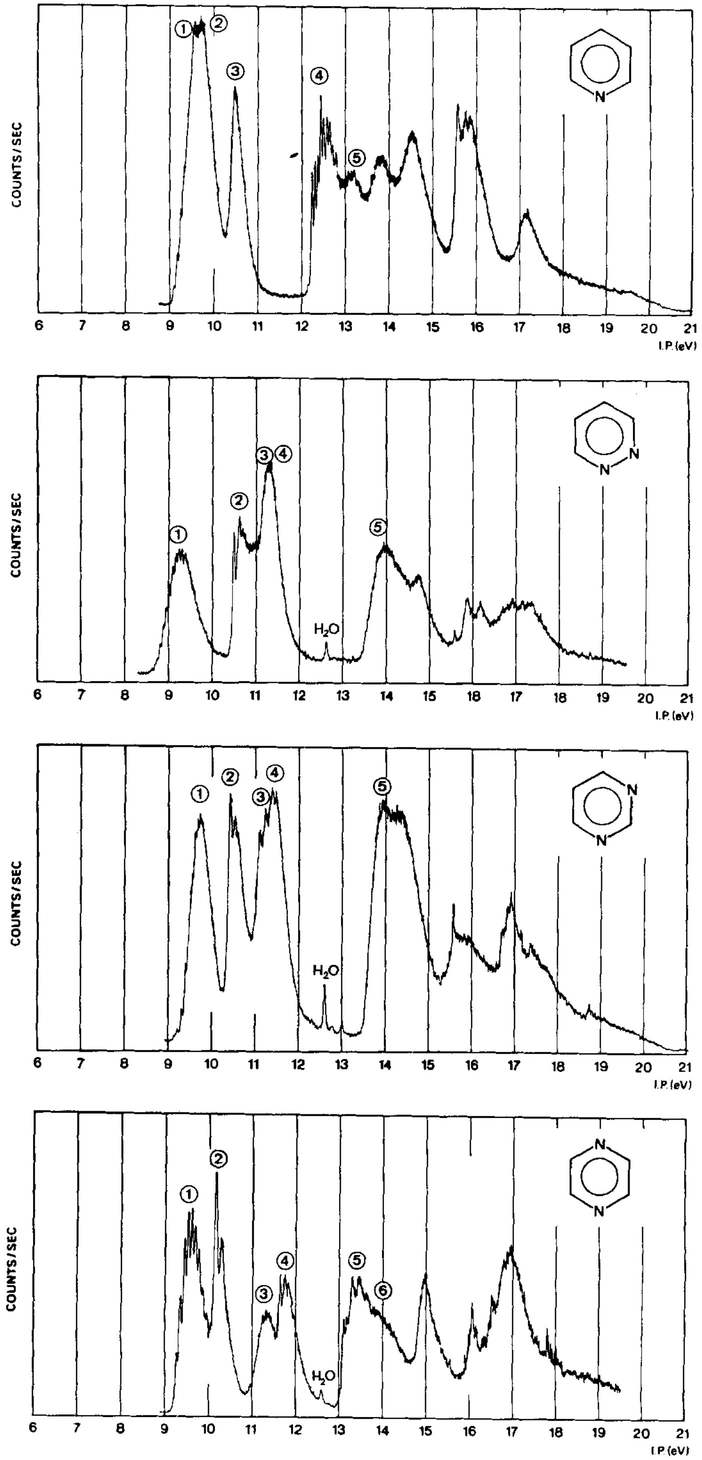
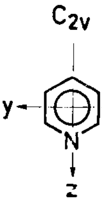
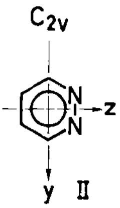


Fig. 1. *PE.-spectra of pyridine (I) and of the three isomeric diazines (II, III, IV)*

In this communication we wish to discuss this previously proposed assignment in some detail and to provide additional support through an analysis of the PE. spectra of *s*-triazine (V) and *s*-tetrazine (VI).



I



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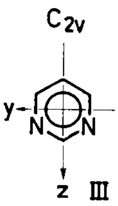

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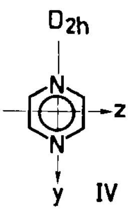

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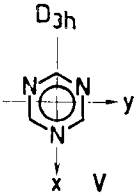
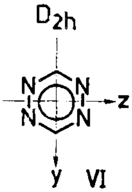


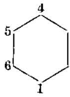
V



VI

The PE. spectra shown in Fig. 1 and 2 have been recorded on a *Perkin-Elmer* PS-15 (I to IV) or PS-16 (V, VI) spectrometer (*Perkin-Elmer Ltd.*, Beaconsfield, England; specifications see: *Turner* [6]). For experimental details see previous communications, *e.g.* [7].

A. Preliminary Remarks. – *π-Orbitals.* In the following we shall be concerned mainly with the two highest occupied π-orbitals of I to VI, which are derived from the degenerate orbital pair $\mathbf{e}_{1g}(\pi, S)$ and $\mathbf{e}_{1g}(\pi, A)$ of benzene, *i.e.* those belonging to the irreducible representation E_{1g} of D_{6h}:



$$\begin{aligned}\mathbf{e}_{1g}(\pi, S) &= (2\,\phi_1 + \phi_2 - \phi_3 - 2\,\phi_4 - \phi_5 + \phi_6)/\sqrt{12}\\ \mathbf{e}_{1g}(\pi, A) &= (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2\end{aligned} \qquad (1)$$

Except in the case of V which has D_{3h} symmetry, replacement of carbon by nitrogen centres removes the degeneracy of $\mathbf{e}_{1g}(\pi, S)$ and $\mathbf{e}_{1g}(\pi, A)$. The resulting orbitals ψ are labelled as usual by the symbol referring to the corresponding irreducible representation of the group (*e.g.* $C_{2v}: \psi \equiv \mathbf{a}_2, \mathbf{b}_1$; $D_{2h}: \psi \equiv \mathbf{b}_{1g}, \mathbf{b}_{2g}$), the coordinate axes being oriented as shown in the formulae I to IV. Furthermore we add the symbol π to classify ψ as a π-orbital, and S or A to indicate from which of the parent $\mathbf{e}_{1g}(\pi)$-orbitals (1) of benzene it has been derived (*e.g.* $\psi(\pi, S) \equiv \mathbf{a}_2(\pi, S)$ in II, $\mathbf{b}_1(\pi, S)$ in III; $\psi(\pi, A) \equiv \mathbf{b}_1(\pi, A)$ in II, $\mathbf{a}_2(\pi, A)$ in III). Note that S and A as used here do *not necessarily* correspond to the symmetric or antisymmetric behaviour of $\psi(\pi, S)$ or $\psi(\pi, A)$ with respect to a mirror plane of the particular molecule but serve only to label the correlation with $\mathbf{e}_{1g}(S)$ and $\mathbf{e}_{1g}(A)$ of benzene.

The third π-orbital derived from the lowest π-orbital $\mathbf{a}_{2u}$ of benzene is uniquely characterized by the symbol π (*e.g.* $\psi(\pi) \equiv \mathbf{b}_1(\pi)$ in II and III).

'Lone pair' orbitals. The basis orbitals are the non-bonding lone pair orbitals $\mathbf{n}_\mu$ of the nitrogen atoms, the positive lobe of $\mathbf{n}_\mu$ pointing radially away from the centre

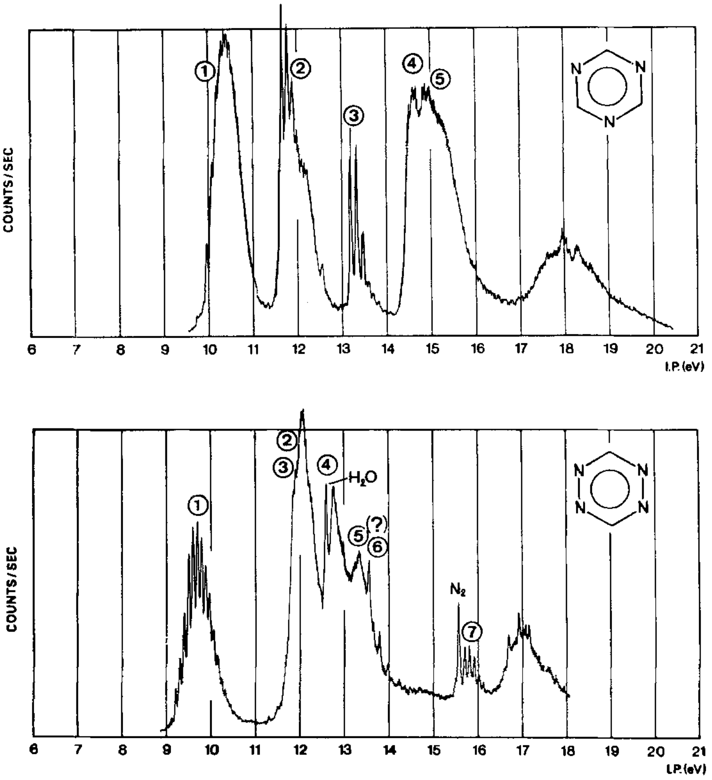


Fig. 2. *PE.-spectra of* s-*triazine* (*V*) *and of* s-*tetrazine* (*VI*)

The spectrum of V shows two small peaks in the ascent of the first band. They arise from ionization of the e″(π)-orbital by the 357-Å-line, which accompanies in small quantities the dominating 584-Å-line of the He discharge.

The irregular intensity distribution in band ⑦ of VI is due to the presence of N_2 and the sharp components on the high energy side of ⑥ to traces of HCN [2]).

of the molecule. If two orbitals $\mathbf{n}_a$, $\mathbf{n}_b$ are present (II, III, IV), we can form the symmetry adapted (degenerate) linear zero-differential-overlap combinations

$$\mathbf{n}_+ = (\mathbf{n}_a + \mathbf{n}_b)/\sqrt{2}\,; \quad \mathbf{n}_- = (\mathbf{n}_a - \mathbf{n}_b)/\sqrt{2}\,. \tag{2}$$

In II and III (C_{2v}) $\mathbf{n}_+$ belongs to A_1 and $\mathbf{n}_-$ to B_2, while in IV (D_{2h}) $\mathbf{n}_+$ belongs to A_g and $\mathbf{n}_-$ to B_{2u}, if the axes are chosen as shown in formulae II to IV.

As a consequence of overlap controlled through space interaction [2] the orbital energies $\varepsilon(\mathbf{n}_+) = \langle \mathbf{n}_+ \mid \mathcal{H} \mid \mathbf{n}_+ \rangle$ and $\varepsilon(\mathbf{n}_-) = \langle \mathbf{n}_- \mid \mathcal{H} \mid \mathbf{n}_- \rangle$ differ from the orbital energies $\alpha(\mathrm{n}) = \langle \mathbf{n}_\mu \mid \mathcal{H} \mid \mathbf{n}_\mu \rangle$ of the basis orbitals:

$$\begin{aligned} \varepsilon(\mathbf{n}_+) &= \alpha(\mathrm{n}) + \langle \mathbf{n}_a \mid \mathcal{H} \mid \mathbf{n}_b \rangle\,, \\ \varepsilon(\mathbf{n}_-) &= \alpha(\mathrm{n}) - \langle \mathbf{n}_a \mid \mathcal{H} \mid \mathbf{n}_b \rangle\,. \end{aligned} \tag{3}$$

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[2]) see p. 269.

(According to the sign convention for $\mathbf{n}_a$ and $\mathbf{n}_b$, as defined above, $\langle \mathbf{n}_a | \mathcal{H} | \mathbf{n}_b \rangle$ is always negative.) In addition $\mathbf{n}_+$ and $\mathbf{n}_-$ interact with bonding and/or antibonding σ-orbitals belonging to the same respective irreducible representation. This 'through bond' interaction leads to mixed 'lone pair' orbitals $\psi(\sigma, \mathbf{n}_\pm)$ which are considerably delocalized over the σ-frame of the molecule. These orbitals are again labelled by the symbol of the corresponding irreducible representation (*e.g.* $\psi \equiv \mathbf{b}_2, \mathbf{a}_1$ in II and III; $\psi = \mathbf{a}_g, \mathbf{b}_{2u}$ in IV) and in brackets, by σ and $\mathbf{n}_+$ or $\mathbf{n}_-$, depending on which of the two linear combinations (2) they contain.

In a first approximation it is useful to identify the delocalized orbitals $\psi(\sigma, \mathbf{n}_+)$ and $\psi(\sigma, \mathbf{n}_-)$ with $\mathbf{n}_+$ and $\mathbf{n}_-$. The orbital energies $\varepsilon(\psi(\sigma, \mathbf{n}_+))$ and $\varepsilon(\psi(\sigma, \mathbf{n}_-))$ derived from the corresponding band positions $I_{v,J}$ in the PE. spectra by applying *Koopmans'* theorem [8], *i.e.* $\varepsilon_J = -I_{v,J}$, can then be described by two parameters:

1) A first-order perturbation $\delta\alpha(\mathrm{n})$ fixes the mean orbital energy

$$\overline{\varepsilon(\mathrm{n})} = [\varepsilon(\psi(\sigma, \mathbf{n}_+)) + \varepsilon(\psi(\sigma, \mathbf{n}_-))]/2 \tag{4}$$

relative to the basis orbital energy $\alpha(\mathrm{n})$:

$$\overline{\varepsilon(\mathrm{n})} = \alpha(\mathrm{n}) + \delta\alpha(\mathrm{n})\ . \tag{5}$$

The quantity $\delta\alpha(\mathrm{n})$ is always negative and in a first approximation proportional to the number of basis orbitals $\mathbf{n}_\mu$.

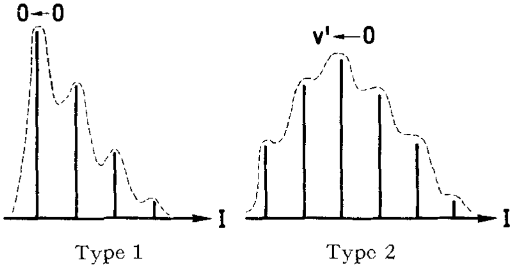
2) An interaction parameter $\varkappa_{\mu\nu}$ defined as

$$\varkappa_{\mu\nu} = [\varepsilon(\psi(\sigma, \mathbf{n}_+)) - \varepsilon(\psi(\sigma, \mathbf{n}_-))]/2\ . \tag{6}$$

If through-space (through-bond) interaction dominates, $\varkappa_{\mu\nu}$ is negative (positive).

In the case of V and VI the parameters $\delta\alpha(\mathrm{n})$ and $\varkappa_{\mu\nu}$ derived from the PE. spectra of I to IV have to be used with the appropriate linear combinations of three or four basis orbitals $\mathbf{n}_\mu$.

Band shapes. In the absence of more precise criteria, such as an analysis of the resolved vibrational fine structure (*e.g.* [9]), the assignment of PE. bands to π- or n-ionization processes has to rely in part on the experimentally observed band shapes, which can be crudely classified into two types:



Type 1: The $0 \leftarrow 0$ vibrational component is the most intense one of the progression, so that the vertical and adiabatic ionization potentials coincide: $I_{a,J} = I_{v,J}$. These strongly unsymmetrical bands are characterized by a steep ascent and slow fall-off.

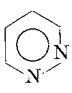
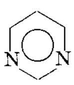
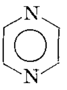
Type 2: A higher vibrational component $v' \leftarrow 0$ is the most intense of the progression, so that $I_{a,J} < I_{v,J}$. Such bands are usually symmetrical, *i.e.* of *Gaussian* or *Lorentzian* shape.

The photoionization process of a molecule M is followed by a relaxation of M^+, in which this radical cation assumes a new equilibrium structure. This change can be specified by the shifts δQ of the origin of the normal coordinates Q of M^+ relative to those of M. A simple harmonic oscillator model [10] which assumes the same force constant and thus the same frequency for the relevant normal mode in M and M^+ predicts that type 1 bands are observed if the δQ associated with the normal mode responsible for the band shape is less than $a_Q\sqrt{2}$. The constant a_Q is the classical amplitude of the zero point vibration of this normal mode.

Photoejection of an electron from an orbital ψ_J leads to small (large) changes in interatomic distances $R_{\mu\nu}$ and/or bond angles ω if the corresponding changes in generalized bond orders $p_{\mu\nu}$ or overlap populations $P_{\mu\nu}$ are small (large). If these changes in internal coordinates $R_{\mu\nu}$ add up to a shift δQ of the origin of the normal coordinate Q, responsible for the vibrational fine-structure, smaller (larger) than $a_Q\sqrt{2}$, we shall observe a PE. band of type 1 (type 2). It is obvious that this criterion has to be used with caution.

There has been a tendency to assume that, since 'lone pair' orbitals are 'non-bonding', ejection from such orbitals should lead to bands of type 1; in the same way ejection from π-orbitals has been assumed to give bands of type 2 as a consequence

Table 1. *Ionization Potentials of Pyridazine (II), Pyrimidine (III) and Pyrazine (IV)*
All values in eV

1	2	3	4	5	6	7		8	
Compound	Band	Orbital	$I_{v,J}$	$I_{a,J}$	$I_{v,J}$[12] a)	$I_{v,J}$[11] a)		$I_{a,J}$[13]	
	①	$\mathbf{b}_2(\sigma,\mathbf{n}_-)$	9.31	8.64	8.90(n)	9.4(π) (n) c)	9.6(π) (π) c)	8.71	($\mathbf{b}_2$)
	②	$\mathbf{a}_2(\pi,S)$	10.61	10.49	10.53(π)	10.6(n) (n)		10.48	($\mathbf{b}_1$)
	③	$\mathbf{b}_1(\pi,A)$	11.3	b)	11.61	11.2(n) (π)		11.1	($\mathbf{a}_2$)
II	④	$\mathbf{a}_1(\sigma,\mathbf{n}_+)$	11.3	b)	–	–		11.1	($\mathbf{a}_1$)
C_{2v}	⑤	$\mathbf{b}_1(\pi)$	13.9	13.45	13.63	13.6(π) (π)		13.5	($\mathbf{b}_1$)
	①	$\mathbf{b}_2(\sigma,\mathbf{n}_-)$	9.73	9.23	9.42(n)	9.7(π) (π)		9.32	($\mathbf{b}_2$)
	②	$\mathbf{b}_1(\pi,S)$	10.41	10.41	10.39(π)	10.4(π) (n)		10.40	($\mathbf{b}_1$)
	③	$\mathbf{a}_1(\sigma,\mathbf{n}_+)$	11.23	11.10	11.06	11.2(n) (n)		11.1	($\mathbf{a}_2$)
III	④	$\mathbf{a}_2(\pi,A)$	11.39	b)	–	11.5(n) (π)		11.3	($\mathbf{a}_1$)
C_{2v}	⑤	$\mathbf{b}_1(\pi)$	13.9	13.51	13.62	13.7(π) (π)		13.6	($\mathbf{b}_1$)
	①	$\mathbf{a}_g(\sigma,\mathbf{n}_+)$	9.63	9.29	9.36(π)	9.7(π) (π)		9.22	($\mathbf{a}_g$)
	②	$\mathbf{b}_{2g}(\pi,A)$	10.18	10.18	10.15(n)	10.3(π) (n)		10.17	($\mathbf{b}_{2g}$)
	③	$\mathbf{b}_{2u}(\sigma,\mathbf{n}_-)$	11.35	11.00	11.14	11.3(n) (n)		10.93	($\mathbf{b}_{3g}$)
IV	④	$\mathbf{b}_{1g}(\pi,S)$	11.77	11.66	11.73	11.8(n) (π)		11.66	($\mathbf{b}_{1g}$)
D_{2h}	⑥	$\mathbf{b}_{3u}(\pi)$	13.9	b)	13.13	13.1(π) (π)		13.1	($\mathbf{b}_{3u}$)

a) The exact nature of these ionization potentials is not defined. See text.
b) Strongly overlapping bands. See Fig. 1.
c) The two columns of bracketed symbols refer to the two differing assignments given in [11].

of the changes in bond orders $p_{\mu\nu}$ and thus in $R_{\mu\nu}$. The reverse, however, is often nearer the truth. Ejection from a *delocalized* 'lone pair' orbital $\psi(\sigma, \mathrm{n})$ may involve quite substantial changes in $R_{\mu\nu}$ because of the changes in σ-bond populations, whereas loss of a π-electron from an 'outer shell' π-orbital induces only minor changes. This is exemplified by a comparison of the first bands in the PE. spectra of ammonia or amines with those of unsaturated hydrocarbons *e.g.* dienes, benzene, etc. [11].

B. Diazines. – Table 1 and the correlation diagram of Fig. 3 summarize our experimental results and the assignment of the first five PE. bands in the interval $I_{v,J} = 9$ to 14 eV. For pyridazine (II) the assignment differs slightly from the one given previously [1] [5], in that bands ③ and ④, corresponding respectively to ejection of an electron from $\mathbf{b}_1(\pi, A)$ and $\mathbf{a}_1(\sigma, \mathbf{n}_+)$, are now assumed to coincide, yielding the intense peak at 11.3 eV.

Our assignment is based on the self-consistency of the following considerations:

1) In the next paper of this series [14] we show that for azabenzenes and azanaphthalenes the π-orbital energies $-I_{v,J}(\text{calc.})$, calculated according to a simple HMO-procedure, correlate closely with the vertical ionization potentials $I_{v,J}$ of the corresponding PE. bands. The regression calculation yields for II, III, and IV:

		$I_{v,J}(\text{exp.})$	$I_{v,J}(\text{calc.})$	
II	$\mathbf{a}_2(\pi, S)$	10,61 eV	10,57 eV	
	$\mathbf{b}_1(\pi, A)$	11,3 eV	11,32 eV	
III	$\mathbf{b}_1(\pi, S)$	10,41 eV	10,57 eV	(7)
	$\mathbf{a}_2(\pi, A)$	11,39 eV	11,32 eV	
IV	$\mathbf{b}_{2g}(\pi, A)$	10,18 eV	10,19 eV	
	$\mathbf{b}_{1g}(\pi, S)$	11,77 eV	11,70 eV	

2) If these bands, which we classify as π-bands, are subtracted from the respective PE. spectra, the remaining bands in the region 9 to 12 eV must be bands corresponding to the ejection of an electron from one of the delocalized 'lone pair' orbitals $\psi(\sigma, \mathbf{n}_+)$ or $\psi(\sigma, \mathbf{n}_-)$. The reason is that the third π-band and the first σ-band (not of 'lone pair' character) both lie at ionization potentials well above 12 eV. These bands, which occur in the PE. spectrum of benzene at 11.5 eV ($\mathbf{e}_{2g}(\sigma)$) and 12.2 eV ($\mathbf{a}_{2u}(\pi)$) [15], show substantial shifts towards higher ionization potentials when carbon centres are replaced by nitrogen.

This is supported by a comparison of the PE. spectra of I and of pyridine-d_5. The band at 12.2 eV has a different vibrational fine structure in the two spectra and must therefore be correlated with the highest σ-(CH)-orbital of I which has been shifted, relative to the $\mathbf{e}_{2g}(\sigma)$ orbital of benzene, by -0.7 eV.

3) As can be seen from the PE. spectra of benzene [11] [15], naphthalene [14] [16], or other hydrocarbons containing larger π-electron systems [16] [17], removal of an electron from one of their two highest occupied π-orbitals leads to PE. bands of type 1. Since the π-electron systems of azabenzenes and azanaphthalenes are not essentially different from those of their isoconjugate parent hydrocarbons [18],

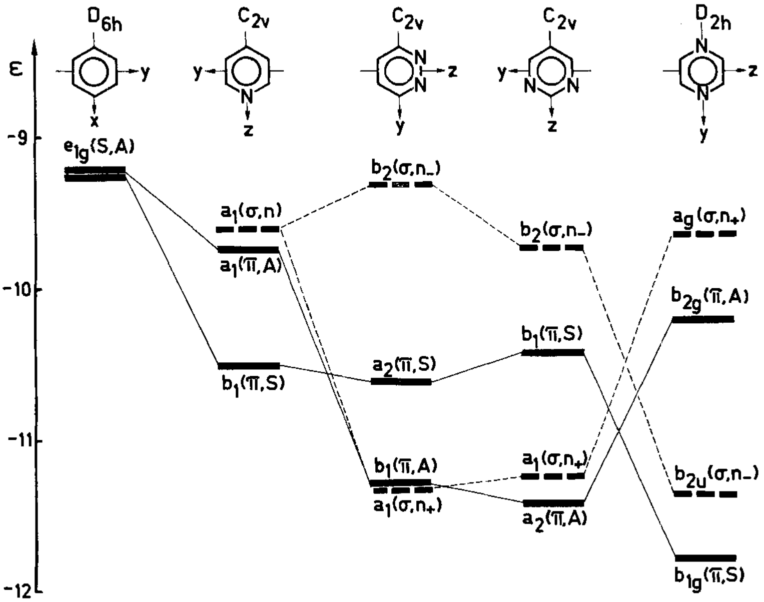


Fig. 3. *Correlation diagram for pyridine (I), pyridazine (II), pyrimidine (III), and pyrazine (IV)*

photoejection of an electron from one of the two highest occupied π-orbitals of azabenzenes or azanaphthalenes must again lead to PE. bands of type 1 or at least to PE. bands in which the first vibrational components ($0 \leftarrow 0$, $1 \leftarrow 0$, $2 \leftarrow 0$) are those of highest intensity. Consequently we assign the label π to the following PE. bands in the region 9 to 12 eV: band ② of II, III, and IV, band ④ of IV. In the PE. spectra of II and III the second π-band overlaps with a n-band as evidenced by the higher integrated intensities (see Fig. 1).

4) As discussed in section A the so-called 'lone-pair' orbitals of aza-derivatives are usually strongly mixed, involving large sections of the C–C- and C–H-σ-frame. In Fig. 4 are shown the plots [19] of those extended *Hückel* orbitals [20] of I, II, III, and IV, to which the basis orbitals $\mathbf{n}_1$ (in I) or the linear combinations (2) $\mathbf{n}_+$, $\mathbf{n}_-$ (II, III, IV) contribute with greatest weight. Removal of an electron from any of these orbitals must lead to significant changes in the structure of the resulting radical cations relative to that of the neutral molecules, because of the strong participation of the C–N and C–C basis σ-orbitals and/or the through-space interaction of the n-orbitals. We therefore except the lone-pair bands to be of type 2. Indeed, this is the case for those identified as such according to the elimination process described in steps 1) and 2), *i.e.* band ① of II, III, IV, band ④ of II and band ③ of III and IV. (Note that the bands labelled ③ and ④ overlap in the spectra of II and III to yield a single peak of double intensity).

5) In many cases the extended *Hückel* treatment (EHT) has proved to be a relatively reliable guide for the interpretation of PE. spectra (*e.g.* [4] [7] [21]): for the diazines the predicted relative sequences of the three highest occupied π-orbitals and the two σ-orbitals with dominating 'lone-pair' character are identical to those derived above

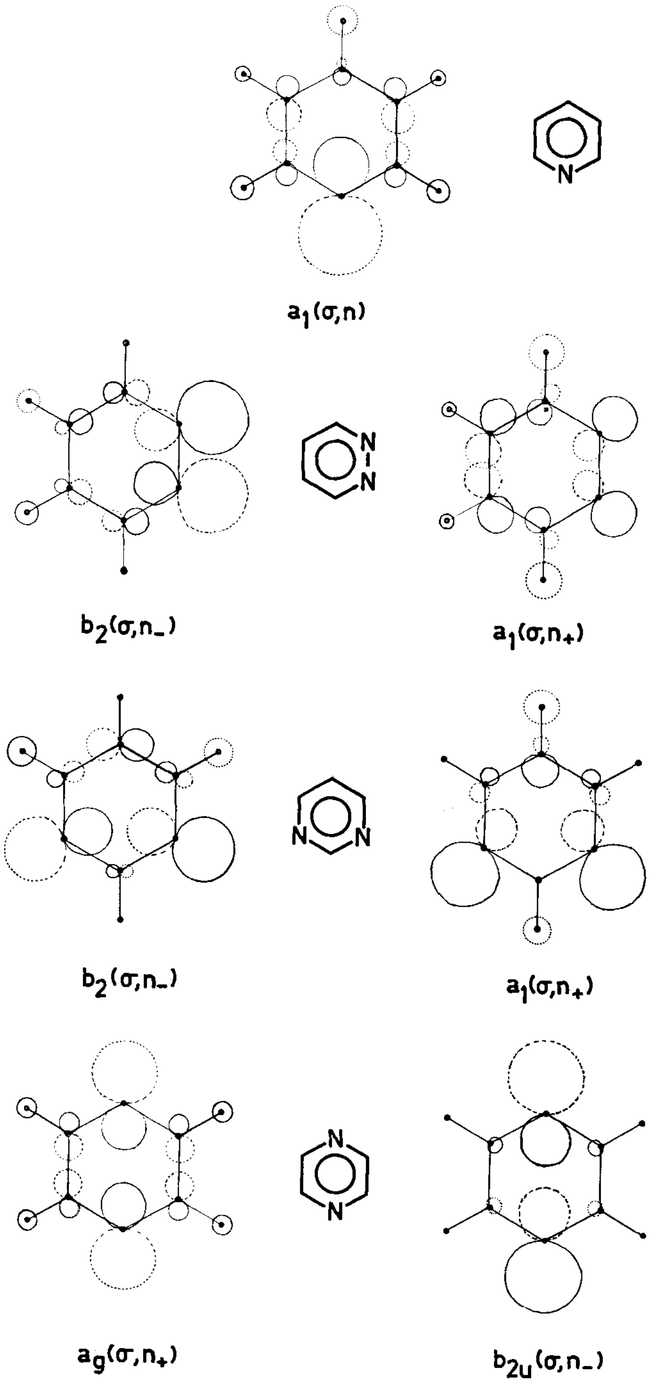


Fig. 4. *Schematic representations of the 'lone pair' orbitals of pyridine (I), pyridazine (II), pyrimidine (III), and pyrazine (IV)*

(see Tab. 2). But, since the theoretical predictions are very sensitive to the assumed geometrical parameters and the choice of the matrix elements H_{ii}, the agreement may be fortuitous.

For comparison we have included in Table 1 results published by other authors.

The data reported by *Dewar & Worley* [12] were obtained with a retarding grid spectrometer [22] and lie therefore between the corresponding adiabatic ($I_{a,J}$) and vertical ($I_{v,J}$) ionization potentials. They should be identical with $I_{a,J} = I_{v,J}$ in the case of type 1 bands. The method is liable to miss the second of two strongly overlapping bands *e.g.* band ④ of II and III. In addition to the data collected in column 6 of Tab. 1 the authors found a second break in their spectra at 9.22 eV for II, 9.64 eV for III, and 9.51 eV for IV, which corresponds more closely to our $I_{v,J}$ values. The assignment given for the first two bands agrees with ours for II and III (sequence (n), (π)) and is the reverse for IV (sequence (π), (n)). But it should be kept in mind that *Dewar & Worley* interpreted their spectra under the implicit assumption that there is no interaction between $\mathbf{n}_a$ and $\mathbf{n}_b$ in III and IV.

The ionization potentials listed in column 7 of Table 1 have been taken from the correlation diagrams given by *Turner, Baker, Baker & Brundle* on page 341 of their book [11]. Comparison with the spectra of III and IV reproduced in the same work indicates that those values refer to vertical rather than to adiabatic ionization processes. Two other assignments have been proposed, both in strong disagreement with ours. The arguments leading to the two assignments have not been discussed (see also [12]).

Recently *Åsbrink, Fridh, Jonsson & Lindholm* [23] have also reinvestigated the PE. spectra of the diazines. The adiabatic ionization potentials $I_{a,J}$ obtained by them are given in column 8 of Table 1. It is gratifying to note that their assignment, based on analysis of the vibrational fine structure of the PE. bands and on the results of extended *Hückel* calculations [20], agrees with ours for the first two bands of III and IV and for the first band of II, the sequence of the next two bands being reversed.

Many theoretical calculations with varying degree of sophistication have been carried out for I, II, III, and IV (*e.g.* references [24] to [27]). In Table 2 we compare some of the results with the observed ionization potentials $I_{v,J}$ and with those derived from an EHT model based on a regular hexagonal framework with $R(\mathrm{CC}) = R(\mathrm{CN}) = 1.4$ Å and $R(\mathrm{CH}) = 1.1$ Å, with standard parameters [20], except for the hydrogen 1*s*-orbitals, for which a *Slater* exponent of 1.3 was used. This model yields an orbital sequence which agrees with our assignment for the first four bands in II, III, and IV. On the other hand it predicts that two of the σ-orbitals should lie above the lowest occupied π-orbitals. Judging from previous experience we believe this to be an artifact of the method.

Column 5 of Table 2 contains the results obtained by *Sundbom* [25] with a *Pariser-Parr-Pople* treatment which includes the lone-pair orbitals n_a, n_b. The major flaw in this calculation is that the parameters were determined by a least-squares routine which fitted the computed orbital energies of I to IV to the ionization potentials given in [11] assuming the assignment shown in column 7 of Table 1 to be correct. This, necessarily, invalidates the predictive value of the model. To account for the lone-pair interaction, the following resonance integrals had to be used: $\beta(\mathit{ortho}) = -0.563$ eV; $\beta(\mathit{meta}) = -0.620$ eV; $\beta(\mathit{para}) = 0.569$ eV.

Another *Pariser-Parr-Pople* treatment including σ-orbitals has been proposed by *Zeiss & Whitehead* [26] (column 7 of Table 2). Only the π-orbital energies which agree with the observed values within ± 1 eV are given.

Finally, *Yonezawa, Kato & Kato* [27] have used a SCF all-valence-electron model. (See column 6 of Table 2). The numerical values of the orbital energies compare favourably with those from other treatments, but they are still not accurate enough to be a safe guide for a band assignment in the absence of other criteria.

Table 2. *Observed vertical Ionization Potentials* $I_{v,J}$ *and calculated Orbital Energies* ε_J *of Pyridazine (II), Pyrimidine (III) and Pyrazine (IV).*

All values are in eV. The correlation lines are based on the assignment proposed in this contribution.

1		2	3	4	5	6	7		
		$I_{v,J}$	Orbital	orbital energies ε_J					
				This work [20]	[25]	[27]	a)	[26] b)	
II	①	9.31	$\mathbf{b}_2(\sigma, \mathbf{n}_-)$	–12.39	– 9.62	–10.24			
	②	10.61	$\mathbf{a}_2(\pi, S)$	–13.34	–10.26	–11.04			
	③	11.3	$\mathbf{b}_1(\pi, A)$	–13.39	–10.34	–11.27			
	④	11.3	$\mathbf{a}_1(\sigma, \mathbf{n}_+)$	–13.48	–11.13	–11.36			
	⑤	13.9	$\mathbf{b}_1(\pi)$	–15.29	–13.59	–13.1(?)			
III	①	9.73	$\mathbf{b}_2(\sigma, \mathbf{n}_-)$	–12.57	– 9.50	–10.62			
	②	10.41	$\mathbf{b}_1(\pi, S)$	–13.09	– 9.92	–10.76	– 9.84	– 9.61	$(\mathbf{b}_1)$
	③	11.23	$\mathbf{a}_1(\sigma, \mathbf{n}_+)$	–13.38	–10.06	–11.03			
	④	11.39	$\mathbf{a}_2(\pi, A)$	–14.00	–11.13	–11.20	–10.82	–11.63	$(\mathbf{a}_2)$
	⑤	13.9	$\mathbf{b}_1(\pi)$	–15.16	–13.15	–13.02	–12.97	–14.09	$(\mathbf{b}_1)$
IV	①	9.63	$\mathbf{a}_g(\sigma, \mathbf{n}_+)$	–12.17	– 9.32	–10.12			
	②	10.18	$\mathbf{b}_{2g}(\pi, A)$	–12.80	–10.10	–10.88	– 9.33	– 8.87	$(\mathbf{b}_{3g})$ d)
	③	11.35	$\mathbf{b}_{2u}(\sigma. \mathbf{n}_-)$	–13.85	–10.30	–11.12			
	④	11.77	$\mathbf{b}_{1g}(\pi, S)$	–14.17	–11.15	–12.48	–11.10	–12.19	$(\mathbf{b}_{2g})$ d)
	⑥	13.9	$\mathbf{b}_{3u}(\pi)$ c)	–15.13	–13.13		–13.05	–14.13	$(\mathbf{b}_{1u})$ d)

a) Parameters according to [28].

b) Parameters according to [29].

c) Assignment based on assumption that the π-orbital ($\mathbf{b}_{3u}$) in IV has the same energy as the corresponding π-orbitals in II and III *i.e.* –13.9 eV.

d) Symmetry label relative to the coordinate system used by *Zeiss & Whitehead* [25]. These labels transform into those given in column 3 as indicated by the correlation lines.

Table 3 summarizes our assignment of the 'lone pair' bands. From the observed vertical ionization potentials $I_{v,J}$ we calculate the mean ionization potentials $\overline{I_n} = -\overline{\varepsilon(n)}$ (see (4) and (5)) which yield, according to (5), $\delta\alpha(n) = 0.7$ to 0.9 eV. The splits ΔI_n are the differences between the $I_{v,J}$, as defined in the legend to Table 3. The negative sign of ΔI_n for IV has been chosen in accordance with the theoretical results [25] [5] [27] and also in view of the sign derived previously for the interaction of the 'lone pairs' in diazabicyclo[2.2.2]octane [4]. Using the definition (6) we obtain the following set of descriptive parameters:

$$\begin{gathered} \delta\alpha(n) = 0.7 \text{ to } 0.9 \text{ eV} \\ \varkappa_{ortho} = -1.00 \text{ eV}; \quad \varkappa_{meta} = -0.75 \text{ eV}; \quad \varkappa_{para} = +0.85 \text{ eV} \end{gathered} \tag{8}$$

The splits ΔI_n given in Table 3 compare favourably with those found previously for the 'lone pair' bands of other diaza compounds. In the case of diazabicyclo[2.2.2]-

Table 3. *Comparison between the difference* $\Delta I_{\mathrm{n}} = I_v(\mathbf{n}_+) - I_v(\mathbf{n}_-)$ *and the calculated value* $\Delta I_{calc.} = \varepsilon(\mathbf{n}_-) - \varepsilon(\mathbf{n}_+)$.
All values in eV

Compound	Band	Orbital	$I_{v,J}$	$\overline{I}_{\mathrm{n}}$	ΔI_{n} (obs.)	ΔI, calc. This work [20]	[25]	[26]
I	①	$\mathbf{a}_1(\sigma,\mathbf{n})$	9.59	9.59	–	–	–	–
II	①	$\mathbf{b}_2(\sigma,\mathbf{n}_-)$	9.31	10.3_1	2.0	1.09	0.79	1.03
	④	$\mathbf{a}_1(\sigma,\mathbf{n}_+)$	11.3					
III	①	$\mathbf{b}_2(\sigma,\mathbf{n}_-)$	9.73	10.4_8	1.5	0.81	0.14	0.58
	③	$\mathbf{a}_1(\sigma,\mathbf{n}_+)$	11.23					
IV	①	$\mathbf{a}_g(\sigma,\mathbf{n}_+)$	9.63	10.4_9	–1.7	–1.68	–1.05	–1.00
	③	$\mathbf{b}_{2u}(\sigma,\mathbf{n}_-)$	11.35					

octane: $\Delta I_{\mathrm{n}} = -2.1$ eV [4] using our sign convention. The value predicted by an EHT calculation is –1.6 eV [2]. For *trans*-azomethane we find $\Delta I_{\mathrm{n}} = -3.3$ eV and for 3,3-dimethyldiazirin $\Delta I_{\mathrm{n}} = 3.6$ eV [4]. In polycyclic systems containing the 1,2-diazacyclobutane moiety one observes $\Delta I_{\mathrm{n}} = 1.6$ eV [1] [30]. These results indicate that the splits $\Delta I_{\mathrm{n}} = 2.0$ eV for II and $\Delta I_{\mathrm{n}} = -1.7$ eV for IV are in line with previous experience.

C. *s*-Triazine. – The PE. spectrum of *s*-triazine (V) is shown in Fig. 2. The relevant data have been collected in Table 4.

The identification of the π-orbitals is again based on the simple HMO model to be described in the following communication [14]:

$$\left.\begin{matrix}\mathbf{e}''(\pi, S)\\ \mathbf{e}''(\pi, A)\end{matrix}\right\} I_{v,2}(\text{exp.}) = 11.67\ \text{eV}; \quad I_{v,2}(\text{calc.}) = 11.84\ \text{eV} \qquad (9)$$

Table 4. *Ionization Potentials of* s-*Triazine (V)*
All values in eV

Band Ⓙ	Orbital	$I_{v,J}$	$I_{a,J}$	$I_{v,J}$[13]	$I_{v,J}$[31]
①	$\mathbf{e}'(\sigma,\mathbf{n}_S)$; $\mathbf{e}'(\sigma,\mathbf{n}_A)$	10.37	9.98	10.01(e′)	10.41 (e′)
②	$\mathbf{e}''(\pi, S)$; $\mathbf{e}''(\pi,A)$	11.67	11.67	11.69(e″)	11.71(e″)
③	$\mathbf{a}_1'(\sigma,\mathbf{n})$	13.21	13 21	13.26($\mathbf{a}_2''$)	13.25($\mathbf{a}_1'$)
④	$\mathbf{a}_2''(\pi)$	14.67	14.51	14.56(e′)	14.65($\mathbf{a}_2''$)
⑤	$\mathbf{e}'(\sigma)$	14.88	[a]	15.00($\mathbf{a}_1'$)	14.85(?)

[a] Onset overlapped by band ④

The shape of band ② in the PE. spectrum of V resembles closely that of the first band in the PE. spectrum of benzene ($I_{v,1} = 9.24$ eV). The characteristic shape is due to a *Jahn-Teller* split, which arises when the photoelectron vacates a degenerate orbital such as $\mathbf{e}_{1g}(\pi)$ of benzene or $\mathbf{e}''(\pi)$ of V.

Consequently, bands ① at 10.37 eV (of double intensity) and ③ at 13.21 eV must correspond to ionization processes where the electron vacates a 'lone pair' orbital. The same conclusion is reached on the basis of the parameter set (8) calibrated on the PE. spectra of I, II, III, and IV. Fig. 5 shows the schematic diagram of the three 'lone pair' orbitals $\mathbf{e}'(\sigma, \mathbf{n}_S)$, $\mathbf{e}'(\sigma, \mathbf{n}_A)$ (degenerate), and $\mathbf{a}_1'(\sigma, \mathbf{n})$ of V (symmetry D_{3h}) [19] as obtained from an EHT calculation. These are the σ-orbitals to which the linear combinations (10) contribute with greatest weight. Assuming again that the

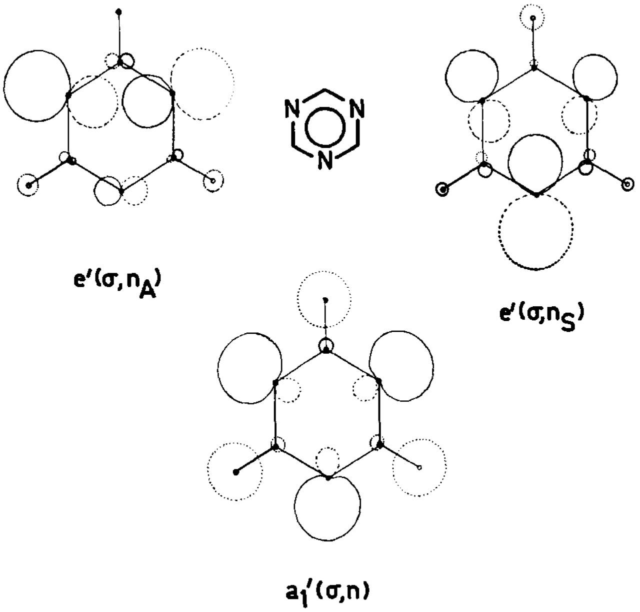


Fig. 5. *Schematic representations of the 'lone pair' orbitals of* s-*triazine* (*V*)

$$E': \begin{cases} \mathbf{n}_S = (2 \cdot \mathbf{n}_1 - \mathbf{n}_3 - \mathbf{n}_5)/\sqrt{6} \\ \mathbf{n}_A = (\mathbf{n}_3 - \mathbf{n}_5)/\sqrt{2} \end{cases} \tag{10}$$
$$A_1': \quad \mathbf{n} = (\mathbf{n}_1 + \mathbf{n}_3 + \mathbf{n}_5)/\sqrt{3}$$

linear combinations (10) are fair representations of $\mathbf{e}'(\sigma, \mathbf{n}_\mathrm{S})$, $\mathbf{e}'(\sigma, \mathbf{n}_\mathrm{A})$, and $\mathbf{a}_1'(\sigma, \mathbf{n})$, we can compute the corresponding orbital energies with the use of the parameters (8):

$$\begin{aligned} \varepsilon(\mathbf{e}'(\sigma, \mathbf{n}_S)) = \varepsilon(\mathbf{e}'(\sigma, \mathbf{n}_A)) &= \alpha(\mathrm{n}) + 2\,\delta\alpha(\mathrm{n}) - \varkappa_{meta} &= -\ 10.52 \text{ eV} \\ \varepsilon(\mathbf{a}_1'(\sigma, \mathbf{n})) &= \alpha(\mathrm{n}) + 2\,\delta\alpha(\mathrm{n}) + 2\,\varkappa_{meta} &= -\ 12.77 \text{ eV} \end{aligned} \tag{11}$$

These results leave no doubt that the bands ① (10.37 eV) and ③ (13.21 eV) of the PE. spectrum of V are indeed the *n*-bands. The double intensity of band ① is due to the degeneracy of the $\mathbf{e}'(\sigma, \mathbf{n}_S)$, $\mathbf{e}'(\sigma, \mathbf{n}_A)$ orbitals (see Fig. 6).

In contrast to what has been observed for the diazines, ejection of an electron from $\mathbf{a}_1'(\sigma, \mathbf{n})$ leads to a band of type 1 rather than that of type 2. The reason is evident from Fig. 5: the $\mathbf{a}_1'(\sigma, \mathbf{n})$ orbital is almost completely localized on the basis orbitals

$\mathbf{n}_1$, $\mathbf{n}_3$, $\mathbf{n}_5$ and does not involve any of the C–N σ-orbitals. Consequently little change in structure is expected to accompany the corresponding ionization process, which should induce only the totally symmetric "breathing" vibration of the ring skeleton ($\Delta\tilde{\nu} = 0.14$ eV or 1100 cm^{-1}).

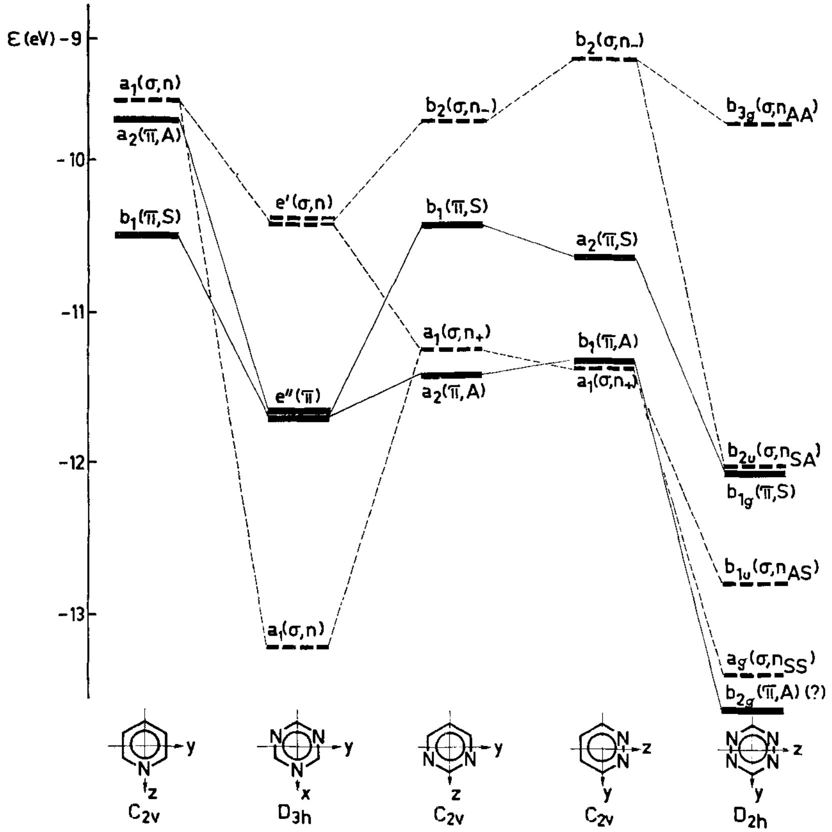


Fig. 6. *Correlation diagram for* s-*triazine* (*V*) *and* s-*tetrazine* (*VI*)

As shown in the last column of Table 4, the assignment derived by *Brundle, Robin & Kuebler* [32] on the basis of the perfluoro effect [31] (*i.e.* comparing the PE. spectra of *s*-triazine and 2,4,6-trifluoro-*s*-triazine) is identical with ours. In particular, band ③ is definitely correlated with the ejection of an electron from the 'lone pair' σ-orbital $\mathbf{a}_1(\sigma, \mathbf{n})$. The interpretation of the PE. spectrum of V given by *Fridh, Åsbrink, Jonsson & Lindholm* [13] agrees with ours as far as bands ① and ② are concerned (see Table 4).

The observed band positions (Table 4) may now be used to check the parameter set (8). The mean ionization potential $\overline{I_n} = (2 \cdot 10.37 + 13.21)/3 = 11.32$ eV yields $\delta\alpha(\mathrm{n}) = 0.86$ eV, *i.e.* within the range given in (8). From the split $\Delta I_n = (13.21 - 10.37) = 2.84$ eV one calculates $\varkappa_{meta} = -0.95$ eV, being 0.2 eV larger than the value obtained before. In Table 5 we compare the observed ionization potentials $I_{v,J}$ with the results of EHT and of two other calculations [25] [26]. The results of the EHT and of *Sundbom's* PPP-model [25] agree with our assignment of the order of n- and π-orbitals, but the numerical values are far off. As in the case of the diazines, the numerical values for the π-orbitals reported by *Zeiss & Whitehead* [26] (*cf.* last column of Table 5) correspond quite well to the experimental values.

Table 5. *Comparison between the ionization potentials $I_{v,J}$ and the calculated orbital energies ε_J of s-Triazine (V).*
All values in eV

Band	$I_{v,J}$	Orbital	orbital energies ε_J This work [20]	[25]	a)	[26] b)
①	10.37	$\mathbf{e}'(\sigma, \mathbf{n}_S)$; $\mathbf{e}'(\sigma, \mathbf{n}_A)$	–12.95	9.97		
②	11.67	$\mathbf{e}''(\pi, S)$; $\mathbf{e}''(\pi, A)$	–14.00	10.08	–10.93	–11.58
③	13.21	$\mathbf{a}_1'(\sigma, \mathbf{n})$	–14.84	11.83		
④	14.67	$a_2''(\pi)$	–15.32	13.48	–13.25	–14.53

a) Parameters according to [28]
b) Parameters according to [29]

D. *s*-Tetrazine. – The PE.-spectrum of *s*-Tetrazine (VI) is shown in Fig. 2 and the relevant data have been collected in Table 6 (see also correlation diagram of Fig. 6).

The HMO model described in [14] gives orbital energies –11.98 eV and –13.49 eV for the two highest occupied π-orbitals $\mathbf{b}_{1g}(\pi, S)$ and $\mathbf{b}_{2g}(\pi, A)$. This identifies band ② ($I_{v,2} = 12.0_5$ eV) and a component of the multiple band ④, ⑤, ⑥ (near 13.5 eV) as π-bands. Both are strongly overlapped by neighbouring 'lone pair'- or σ-bands[2].

Table 6. *Ionization Potentials of* s-*Tetrazine* (*VI*).
Comparison between experimental and calculated results. All values are in eV.

Band Ⓙ	Orbital	$I_{v,J}$	$I_{a,J}$	orbital enegies ε_J This work [20]	[24]
①	$\mathbf{b}_{3g}(\sigma, \mathbf{n}_{AA})$	9.72	9.14	–12.06	9.42
②	$\mathbf{b}_{1g}(\pi, S)$	12.0_5	11.75	–13.63	9.96
③	$\mathbf{b}_{2u}(\sigma, \mathbf{n}_{SA})$	12.0_5		–13.88	–11.26
④	$\mathbf{b}_{1u}(\sigma, \mathbf{n}_{AS})$ b)	12.78	a)	–13.92	–11.42
⑤	$\mathbf{a}_{g}(\sigma, \mathbf{n}_{SS})$ b)	13.36	a)	–14.19	–11.42
⑥	$\mathbf{b}_{2g}(\pi, A)$	~13.5(?)	a)	–14.58	–11.44
⑦	$\mathbf{b}_{3u}(\pi)$	15.84	15.53	–15.54	–14.33

a) Band onset is overlapped by preceeding band.
b) Order based on the correlation diagram of Fig. 8, and differing from the one given in (13) where the two orbitals are almost degenerate within the limits of our perturbation treatment.

Fig. 7 shows the four 'lone pair' orbitals of VI as given by an EHT calculation [20]. These orbitals are again those to which the following symmetry-adapted linear combinations of the basis orbitals $\mathbf{n}_2$, $\mathbf{n}_3$, $\mathbf{n}_5$, $\mathbf{n}_6$ contribute with greatest weight.

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[2] As pointed out by Prof. *E. Lindholm*, the sharp vibrational components on the high energy side of ⑥ are due to traces of HNC.

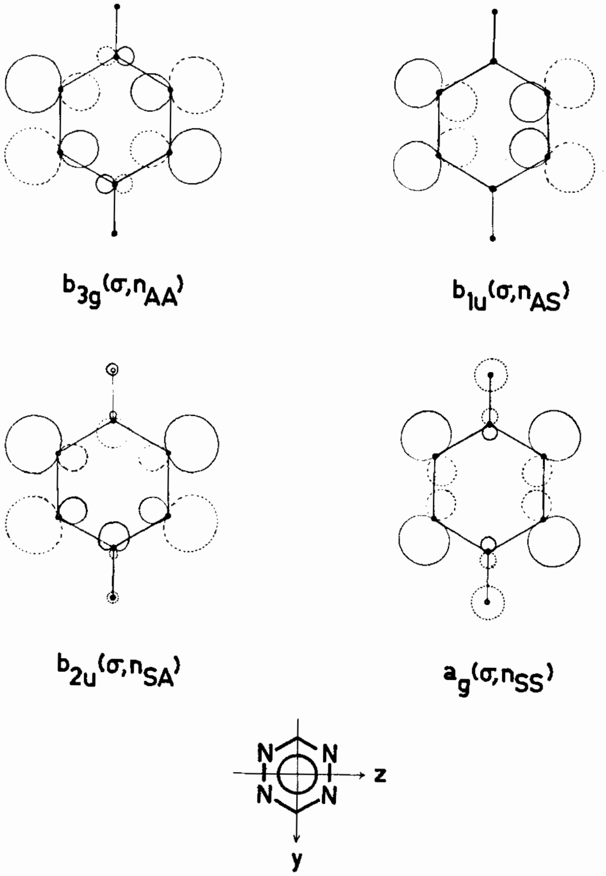

Fig. 7. *Schematic representations of the 'lone pair' orbitals of* s-*tetrazine* (*VI*)

$$\begin{aligned} \mathbf{n}_{SS} &= (\mathbf{n}_2 + \mathbf{n}_3 + \mathbf{n}_5 + \mathbf{n}_6)/2 \\ \mathbf{n}_{SA} &= (\mathbf{n}_2 - \mathbf{n}_3 - \mathbf{n}_5 + \mathbf{n}_6)/2 \\ \mathbf{n}_{AS} &= (\mathbf{n}_2 + \mathbf{n}_3 - \mathbf{n}_5 - \mathbf{n}_6)/2 \\ \mathbf{n}_{AA} &= (\mathbf{n}_2 - \mathbf{n}_3 + \mathbf{n}_5 - \mathbf{n}_6)/2 \end{aligned} \tag{12}$$

The parameters given in (8) with $\delta\alpha(\mathrm{n}) = 0.8$ eV lead to the following orbital energies:

$$\begin{aligned} \varepsilon(\mathbf{b}_{3g}(\sigma, \mathbf{n}_{AA})) &= \alpha(\mathrm{n}) + 3\,\delta\alpha(\mathrm{n}) - \varkappa_{ortho} - \varkappa_{meta} + \varkappa_{para} = -\ 9.39 \text{ eV}, \\ \varepsilon(\mathbf{b}_{2u}(\sigma, \mathbf{n}_{SA})) &= \alpha(\mathrm{n}) + 3\,\delta\alpha(\mathrm{n}) - \varkappa_{ortho} + \varkappa_{meta} - \varkappa_{para} = -\ 12.59 \text{ eV}, \\ \varepsilon(\mathbf{b}_{1u}(\sigma, \mathbf{n}_{AS})) &= \alpha(\mathrm{n}) + 3\,\delta\alpha(\mathrm{n}) + \varkappa_{ortho} - \varkappa_{meta} - \varkappa_{para} = -\ 13.09 \text{ eV}, \\ \varepsilon(\mathbf{a}_{g}(\sigma, \mathbf{n}_{SS}) &= \alpha(\mathrm{n}) + 3\,\delta\alpha(\mathrm{n}) + \varkappa_{ortho} + \varkappa_{meta} + \varkappa_{para} = -\ 12.89 \text{ eV}. \end{aligned} \tag{13}$$

Accordingly, we identify bands ① ($I_{v,1} = 9.72$ eV), ③ ($I_{v,3} = 12.05$ eV), ④ ($I_{v,4} = 12.78$ eV), and ⑤ ($I_{v,5} = 13.36$ eV) as 'lone pair' bands. Without additional information (such as could be derived from the vibrational fine structure of the bands ③, ④, and ⑤) the assignment given in Table 6 is necessarily tentative, especially as all three bands are very close in energy. The double intensity of the second peak in the spectrum is due to the strong overlapping of bands ② and ③.

The last two columns of Table 6 list the orbital energies obtained from an EHT treatment [20] and those derived by *Sundbom* [25] from a PPP-model. Again, the EHT-method predicts the same order as the perturbation treatment with the exception of the orbitals assigned to bands ④ and ⑤, where the order is reversed. The PPP-model predicts an assignment for the bands ①, ②, and ⑦ in agreement with ours but a different sequence is proposed for the remaining bands between ③ and ⑥. As mentioned above, this is due to a different parametrization of the assumed interaction between lone-pair basis orbitals.

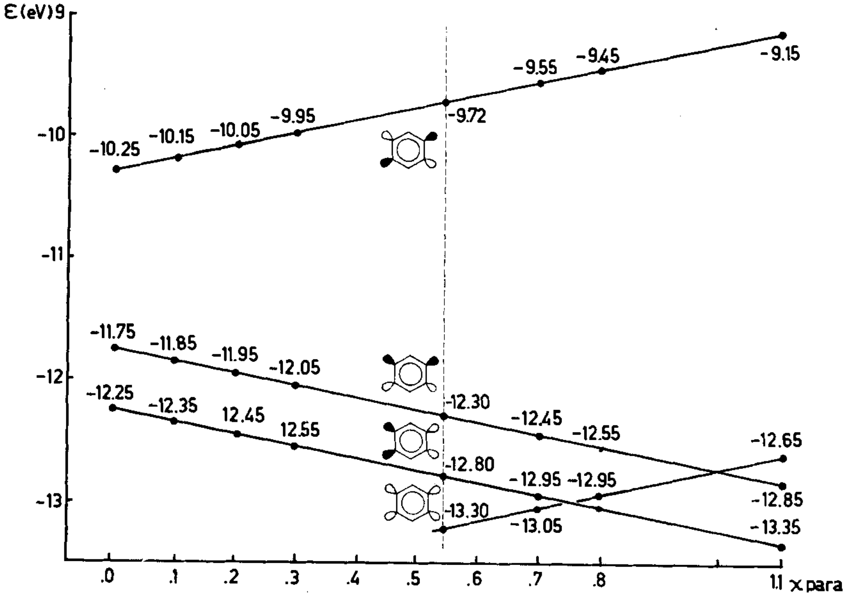

Fig. 8. *The dependence of the calculated lone pair orbital energies of* s-*tetrazine* (*VI*) *on the parameter* $\varkappa_{para}$

Another way to derive the sequence of the four 'lone pair' orbitals in VI is to construct a correlation diagram in which the parameters $\varkappa_{ortho} = -1.0$ eV and $\varkappa_{meta} = -0.75$ eV are kept fixed while $\varkappa_{para}$ is varied from 0 eV (*i.e.* no *para*-interaction) to 1.1 eV (strong through-bond interaction). The diagram so obtained is shown in Fig. 8. In the case of IV the through-bond interaction is due mainly to a mixing of the CC-σ-orbitals with the $\mathbf{n}_+$ combination of the 'lone pair' orbitals. In contrast, only CN-σ-orbitals are involved in VI. Consequently $\varkappa_{para}$ may differ considerably from the value appropriate for IV.

All theoretical calculations predict that the totally antisymmetric 'lone pair' combination $\mathbf{b}_{3g}(\sigma, \mathbf{n}_{AA})$ should be the highest one. Assigning the 'observed' orbital energy $\varepsilon(\mathbf{b}_{3g}(\sigma, \mathbf{n}_{AA})) = -9.72$ eV to this orbital leads to the following sequence for the three remaining 'lone pair' orbitals $\varepsilon(\mathbf{b}_{2u}(\sigma, \mathbf{n}_{SA})) = -12.3$ eV, $\varepsilon(\mathbf{b}_{1u}(\sigma, \mathbf{n}_{AS})) = -12.8$ eV, $\varepsilon(\mathbf{a}_{g}(\sigma, \mathbf{n}_{SS})) = -13.3$ eV and to $\varkappa_{para} = +0.55$ eV. As seen from Fig. 8 the three lower 'lone pair' orbitals $\mathbf{b}_{2u}(\sigma, \mathbf{n}_{SA})$, $\mathbf{b}_{1u}(\sigma, \mathbf{n}_{AS})$, and $\mathbf{a}_{g}(\sigma, \mathbf{n}_{SS})$ are very close in energy so that their order depends critically on the parameter $\varkappa_{para}$.

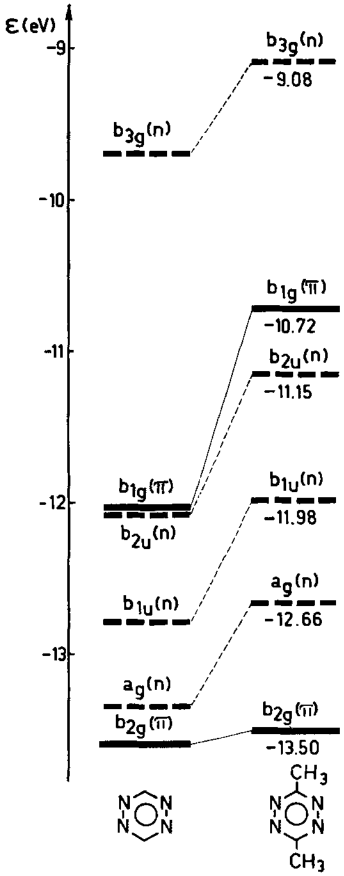

Fig. 9. *Correlation diagram for* s-*tetrazine* (*VI*) *and dimethyl*-s-*tetrazine* (*VII*)

The orbital assignment VI is identical to that of Table 6. The numerical values for the orbital energies for VII correspond to the observed band positions in the PE. spectrum of VII. For the orbital energies of VII, $\varepsilon_J = -I_{v,J}$ (in eV), see legend to Fig. 10.

In Fig. 9 we have correlated the orbitals of *s*-tetrazine with those of 1,4-dimethyl-*s*-tetrazine (VII). The PE. spectrum of VII is reproduced in Fig. 10. Our tentative assignment is based on the assumption that methyl substitution destabilizes π-orbitals to a greater extent than n-orbitals, as has been observed *e.g.* for methyl substituted pyridines [33].

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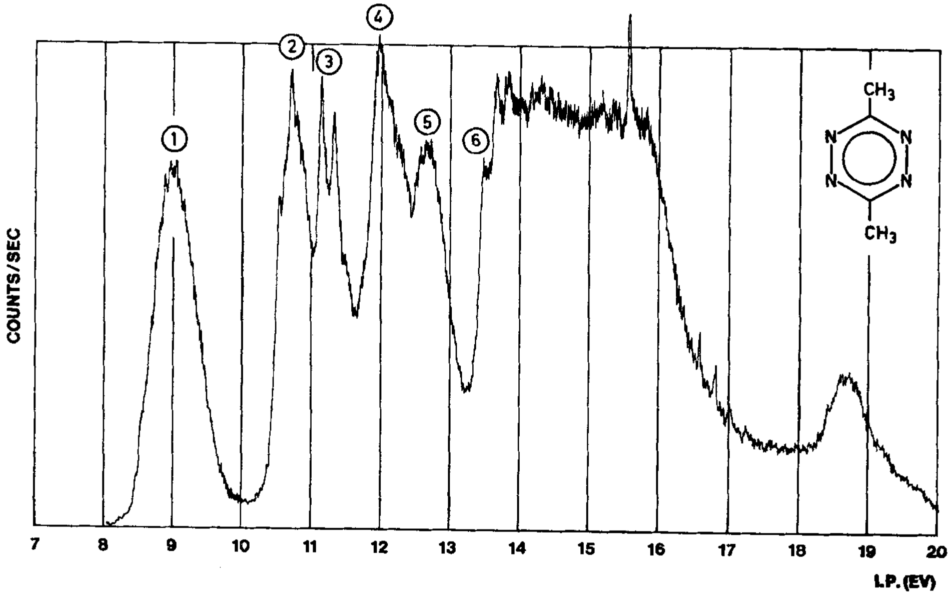

Fig. 10. *PE.-spectrum of dimethyl-*s*-tetrazine* (*VII*)

①: $I_{v,1}$ = 9.08 eV; ②: $I_{v,2}$ = 10.72 eV; ③: $I_{v,3}$ = 11.15 eV; ④: $I_{v,4}$ = 11,98 eV;
⑤: $I_{v,5}$ = 12.66 eV; ⑥: $I_{v,6}$ = 13.50 eV

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30. Photoelectron Spektra of Azabenzenes and Azanaphthalenes: II. A Reinvestigation of Azanaphthalenes by High-Resolution Photoelectron Spectroscopy[1])

by **F. Brogli, E. Heilbronner** and **T. Kobayashi**[2])

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(8. XII. 71)

Summary. The bands with $I_v < 13$ eV in the photoelectron spectra of quinoline (IX), isoquinoline (X), cinnoline (XI), quinazoline (XII), and quinoxaline (XIII) have been reassigned in a way consistent with the assignment proposed for pyridine (II), the diazines (III, IV, V), *s*-triazine

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[1]) Part [29] of: 'Applications of Photoelectron Spectroscopy', Part [28]: [1].

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