[11] *D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle*, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London 1970.

[12] *M. J. S. Dewar & S. D. Worley*, J. chem. Physics *51*, 263 (1969).

[13] *C. Fridh, L. Åsbrink, B. O. Jonsson & E. Lindholm*, Int. J. Mass Spectrom. Ion Physics, in print; private communication from Prof. *E. Lindholm*.

[14] *F. Brogli, E. Heilbronner & T. Kobayashi*, Helv. *55*, 274 (1972).

[15] *L. Åsbrink, O. Edqvist, E. Lindholm & L. E. Selin*, Chem. Physics Letters *5*, 192 (1970).

[16] *J. H. D. Eland & C. J. Danby*, Z. Naturforschg. *23a*, 355 (1968); *J. H. D. Eland*, Intern. J. Mass Spectrom. Ion Physics *2*, 471 (1969).

[17] *E. Heilbronner, E. Gleiter, H. Hopf, V. Hornung & A. de Meijere*, Helv. *54*, 783 (1971).

[18] *A. Streitwieser & J. I. Braumann*: 'Supplement Tables of Molecular Orbital Calculations', Pergamon Press, Oxford 1965; *E. Heilbronner & H. Bock*: 'Das HMO-Modell und seine Anwendung', Verlag Chemie, Weinheim 1970.

[19] *R. Seeger*, to be published.

[20] *R. Hoffmann & N. Lipscomb*, J. chem. Physics *36*, 2179, 3489 (1962); *ibid. 37*, 2872 (1962); *R. Hoffmann*, *ibid. 39*, 1397 (1963); Tetrahedron *22*, 539 (1966).

[21] *R. Hoffmann, E. Heilbronner & R. Gleiter*, J. Amer. chem. Soc. *92*, 706 (1970).

[22] *M. J. S. Dewar & S. D. Worley*, J. chem. Physics *50*, 654 (1969).

[23] *L. Åsbrink, C. Fridh, B. O. Jonsson & E. Lindholm*, Int. J. Mass Spectrom. Ion Physics, in print; private communication from Prof. *E. Lindholm*.

[24] *E. Clementi*, J. chem. Physics *46*, 4731, 4737 (1967); *M. J. S. Dewar & A. J. Harget*, Proc. Roy. Soc. *A 315*, 457 (1970); *J. Del Bene & H. H. Jaffe*, J. chem. Physics *48*, 1807 (1968); *J. D. Petke*, J. *L. Whitten & J. A. Ryan*, J. chem. Physics *48*, 953 (1968).

[25] *M. Sundbom*, to be published; private communication from Dr. *M. Sundbom*.

[26] *G. D. Zeiss & M. A. Whitehead*, J. chem. Soc. (A) *1971*, 1727.

[27] *T. Yonezawa, H. Kato & H. Kato*, Theor. chim. Acta *13*, 125 (1969).

[28] *J. Hinze & H. H. Jaffe*, J. chem. Physics *84*, 540 (1961).

[29] *J. Thorhallson, C. Fisk & S. Fraga*, Theor. chim. Acta *12*, 80 (1968).

[30] *R. Boschi, F. Brogli, W. Eberbach, E. Haselbach, E. Heilbronner & V. Hornung*, unpublished results.

[31] *C. R. Brundle, M. B. Robin, N. A. Kuebler & H. Basch*, to be published; private communication from Dr. *M. B. Robin*.

[32] *C. R. Brundle, M. B. Robin & N. A. Kuebler*, to be published; private communication from Dr. *M. B. Robin*.

[33] *E. Heilbronner*, V. *Hornung, F. H. Pinkerton & S. F. Thames*, Helv. *55*, 289 (1972).

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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])

Physikalisch-Chemisches Institut der Universität Basel

(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].

[2]) Present address: The Institute for Solid State Physics, The University of Tokyo.

(VI), and 1,2,4,5-tetrazine (VII). The bands corresponding to the ejection of an electron from a π-orbital have been identified by a regression calculation based on a HMO perturbation treatment. It has been found that the combined through-space and through-bond interaction of the lone pairs in III, IV, V and in their corresponding benzologues XI, XII, XIII are the same within experimental error ($\pm$ 0.2 eV). Our assignment is also supported by an empirical correlation of the $pK_{a,1}$-values and the mean lone-pair ionization potentials of the azaderivatives I to XIII.

In the preceeding communication of this series [1] we have proposed an assignment for the photoelectron spectra (PE. spectra) of pyridine (II), pyridazine (III), pyrimidine (IV), pyrazine (V), *s*-triazine (VI), and *s*-tetrazine (VII) (see also [2]), which differs from assignments given previously [3] [4] [5]. An important feature of the new assignment is that it takes account of the large through-bond interaction [6] between nitrogen lone-pair orbitals in 1,3 and/or 1,4 position, which had been neglected in previous assignments (*e.g.* [4] [5]).


I


II

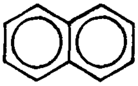

III

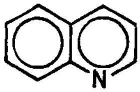

IV

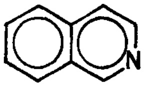

V

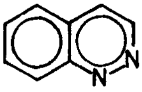

VI

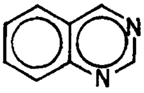

VII

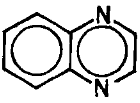

VIII


IX


X


XI


XII


XIII

The concept of competitive through-space and through-bond interaction between non-conjugated basis orbitals, introduced by *Hoffmann, Imamura & Hehre* [7] on the basis of extended *Hückel* calculations, has beeen applied by *Adam* [8] to the diazabenzenes III, IV, and V. His conclusions concerning the orbital energy gap,

$$\Delta\varepsilon(\mathrm{n}) = \varepsilon(\psi(\sigma, \mathbf{n}_-)) - \varepsilon(\psi(\sigma, \mathbf{n}_+)) \qquad (1)$$

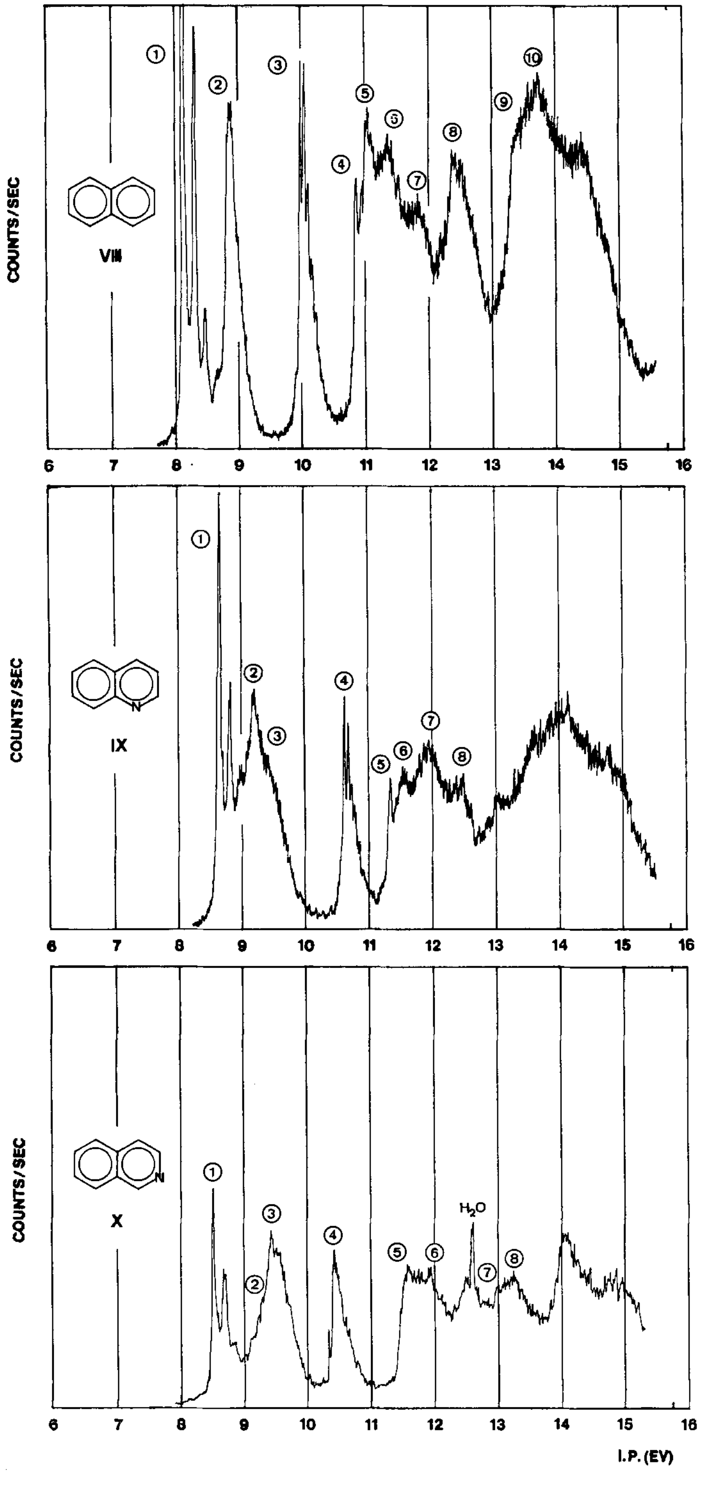


Fig. 1. *Photoelectron-spectra of naphthalene (VIII), quinoline (IX), isoquinoline (X), cinnoline (XI), quinazoline (XII), and quinoxaline (XIII)*

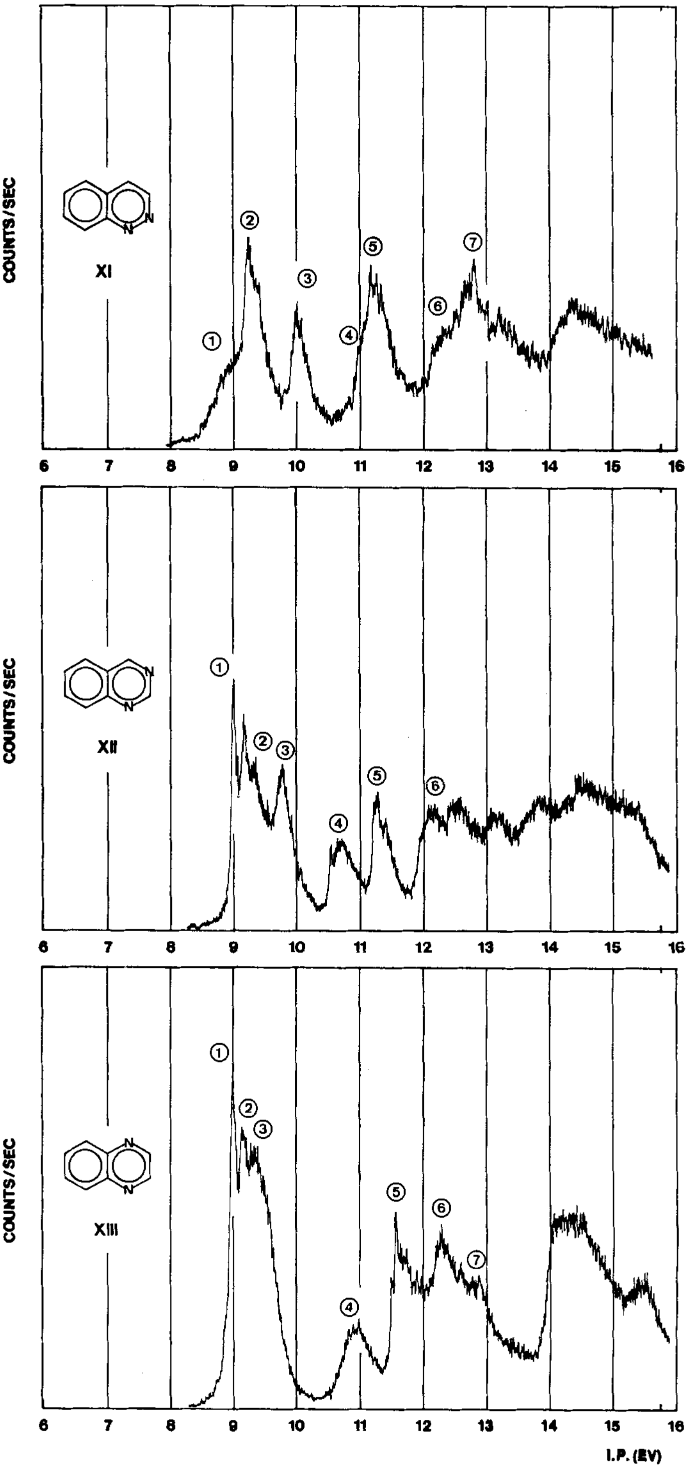


Fig. 1. *Photoelectron-spectra of naphthalene (VIII), quinoline (IX), isoquinoline (X), cinnoline (XI), quinazoline (XII), and quinoxaline (XIII)*

where $\varepsilon(\psi(\sigma, \mathbf{n}_-))$ and $\varepsilon(\psi(\sigma, \mathbf{n}_+))$ are the energies of those orbitals $\psi(\sigma, \mathbf{n}_-)$ and $\psi(\sigma, \mathbf{n}_+)$ to which the linear combinations

$$\begin{aligned} \mathbf{n}_- &= \frac{1}{\sqrt{2}} (\mathbf{n}_a - \mathbf{n}_b) \\ \mathbf{n}_+ &= \frac{1}{\sqrt{2}} (\mathbf{n}_a + \mathbf{n}_b) \end{aligned} \qquad (2)$$

contribute most ($\mathbf{n}_a$, $\mathbf{n}_b$ = basis lone pair orbitals), were supported by the results of SCF-MO calculations [9] due to *Sundbom* [10]. However, no conclusive experimental results concerning the magnitude of the postulated through-bond interactions were known at the time.

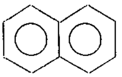
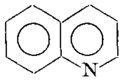
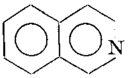
The first direct experimental proof for the existence of large through-bond interactions has been provided by the PE. spectroscopic investigation of 1,4-diazabicyclo[2.2.2]octane [11] and other systems containing semi-localized, little or non-overlapping basis orbitals (*e.g.* [12]). From these results it was obvious that through-bond interaction between the lone-pair orbitals $\mathbf{n}_a$, $\mathbf{n}_b$ must be substantial in aza-derivatives such as IV, V, VI, VII, XI, XII, and XIII.

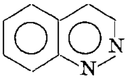
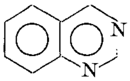
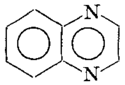
We show here that an analysis of the PE. spectra of quinoline (IX), isoquinoline (X), cinnoline (XI), quinazoline (XII), and quinoxaline (XIII) confirms our previous assignment for I to VII [1], thus yielding additional support for the concept of through-bond interaction of lone-pair orbitals.

Experimental Results. – Fig. 1 and Table 1 summarize our experimental results. The PE. bands have been numbered Ⓙ = ①, ②, ③... according to increasing (vertical) ionization potentials $I_{v,J}$. No correlation between bands of different spectra carrying the same number Ⓙ is implied. The values of $I_{v,J}$ given in Table 1 refer to the band maxima (≈ vertical ionization). Overlapping bands yield $I_{v,J}$-values that are affected with wider confidence limits.

Table 1. *Ionization potentials of naphthalene (VIII), quinoline (IX), isoquinoline (X), cinnoline (XI), quinazoline (XII), and quinoxaline (XIII)*

All values are in eV. This work: ionization potentials refer to the band maxima (vertical ionization potentials); values in italics are adiabatic ionization potentials (0←0 transition); values in parentheses refer to shoulders.

	VIII:			IX:			X:		
PE.- band	This work	[3]	[4]	This work	[3]	[4]	This work	[3]	[4]
①	*8.15*	8.12	8.11	*8.62*	8.67	8.62	*8.50*	8.53	8.54
②	8.88	8.90	8.79	9.16	9.00	9. 07	(9.3 (?))	9.16	9.24
③	*10.10*	10.00	9.96	(9.2–9.3)			9.41		
④	*10.86*	10.85	10.90	*10.58*	10.63	10.64	10.40	10.32	10.50
⑤	11.00			11.30	11.37	11.42	11.56	11.43	11.60
⑥	11.35			11.5			(11.9)		
⑦	(11.8)			11.9			12.5		12.54
⑧	12.36		12.26	(12.4)			13.2		13.26
⑨	(13.3)		13.22						
⑩	13.7								

	XI:		XII:		VIII:	
PE.-band	This work	[4]	This work	[4]	This work	[4]
①	(8.8)	8.51	*9.00*	9.02	*9.01*	8.99
②	9.20	9.03	(9.3)			
					9.3–9.4	
③	9.99	9.75	9.77	9.74		
④	(11.0)	10.83	10.62	10.72	10.90	10.72
⑤	11.14		11.26	11.26	11.57	11.58
⑥	(12.3)	12.04	(12.1)	12.0	12.29	12.32
⑦	~12.7	12.46			(12.9(?))	

Additional references: Position of band ①: VIII, 8.12 eV [14], 8.15 eV [15]; IX, 8.62 eV [15]; X, 8.55 eV [15], 8.30 eV [16]; XI, 8.95 eV [15]; XIII, 9.02 eV [15].

The spectra were recorded on a modified PS-16-photoelectron spectrometer of *Perkin-Elmer Ltd.* (Beaconsfield, England) based on the specifications of *Turner* [13]. For experimental details see previous papers of this series.

For comparison ionization potentials given by *Eland & Danby* [3] and by *Dewar & Worley* [4] are included in Table 1. The former are adiabatic ($I_{a,J}$) referring to 0←0 transitions or band onsets in the high resolution PE. spectra of VIII, IX and X. The latter were obtained with a retarding potential grid-type spectrometer [17]. They are therefore either adiabatic values $I_{a,J}$ (if the 0←0 transition is the strongest band component) or values between $I_{a,J}$ and $I_{v,J}$ (if the band has a *Lorentz*ian or *Gauss*ian shape). It should be noted that the method is liable to miss bands if they are overlapped by others.

π-Bands. We first identify the π-bands in the PE. spectra of IX to XIII by using a simple first-order perturbation treatment based on the standard HMO-model of VIII. For the sake of generality we also discuss the monocyclic aza-derivatives II to VII.

The reference HMOs of the parent hydrocarbons I and VIII are [18]:

$$
\begin{aligned}
\text{I:}\quad & \mathbf{e}_{1g}(\mathrm{S}) = (2\,\boldsymbol{\phi}_1 + \boldsymbol{\phi}_2 - \boldsymbol{\phi}_3 - 2\,\boldsymbol{\phi}_4 - \boldsymbol{\phi}_5 + \boldsymbol{\phi}_6)/\sqrt{12}\\
& \mathbf{e}_{1g}(\mathrm{A}) = (\boldsymbol{\phi}_2 + \boldsymbol{\phi}_3 - \boldsymbol{\phi}_5 - \boldsymbol{\phi}_6)/2;\\
\text{VIII:}\quad & \mathbf{a}_u = 0.425\,(\boldsymbol{\phi}_1 - \boldsymbol{\phi}_4 + \boldsymbol{\phi}_5 - \boldsymbol{\phi}_8) + 0.263\,(\boldsymbol{\phi}_2 - \boldsymbol{\phi}_3 + \boldsymbol{\phi}_6 - \boldsymbol{\phi}_7)\\
& \mathbf{b}_{1u} = 0.408\,(\boldsymbol{\phi}_2 + \boldsymbol{\phi}_3 + \boldsymbol{\phi}_5 + \boldsymbol{\phi}_7 - \boldsymbol{\phi}_9 - \boldsymbol{\phi}_{10})\\
& \mathbf{b}_{2g} = 0.400\,(\boldsymbol{\phi}_1 - \boldsymbol{\phi}_4 - \boldsymbol{\phi}_5 + \boldsymbol{\phi}_8) + 0.174\,(\boldsymbol{\phi}_2 - \boldsymbol{\phi}_3 - \boldsymbol{\phi}_6 + \boldsymbol{\phi}_7) +\\
& \quad 0.347\,(\boldsymbol{\phi}_9 - \boldsymbol{\phi}_{10})\,.
\end{aligned}
\tag{13}
$$

The associated orbital energies are: $\varepsilon(\mathbf{e}_{1g}(S)) = \varepsilon(\mathbf{e}_{1g}(A)) = \alpha + \beta$; $\varepsilon(\mathbf{a}_u) = \alpha + 0.618\,\beta$; $\varepsilon(\mathbf{b}_{1u}) = \alpha + \beta$; $\varepsilon(\mathbf{b}_{2g}) = \alpha + 1.618\,\beta$. The symbols A and S designate the symmetric or antisymmetric behaviour of the HMOs on reflection through the plane $\sigma(xz)$ of I.

Let $\mathcal{H}$ be the HMO-Hamiltonian of the unperturbed systems I or VIII. Replacement at position ϱ of a carbon- by a nitrogen-centre changes $\mathcal{H}$ into $\mathcal{H}' = \mathcal{H} + \mathbf{h}$ where $\mathbf{h}$ is defined by the following list of matrix elements:

$$
\begin{aligned}
\langle \boldsymbol{\phi}_\mu \mid \mathbf{h} \mid \boldsymbol{\phi}_\nu \rangle &= 0, \quad \text{except}\\
\langle \boldsymbol{\phi}_\varrho \mid \mathbf{h} \mid \boldsymbol{\phi}_\varrho \rangle &= \delta\alpha_{\mathrm{N}}\\
\langle \boldsymbol{\phi}_\omega \mid \mathbf{h} \mid \boldsymbol{\phi}_\omega \rangle &= \mathfrak{m} \cdot \delta\alpha_{\mathrm{N}}
\end{aligned}
\tag{4}
$$

The indices ω refer to the positions ortho to ϱ, and $\mathfrak{m}$ is an as yet unspecified factor $(0 < \mathfrak{m} < 1)$.

According to first-order perturbation theory the energy change of an orbital $\psi_J = \Sigma_\mu c_{J\mu} \phi_\mu$ is given by

$$\delta\varepsilon_J = (\Sigma_\varrho c_{J\varrho}^2)\, \delta\alpha_{\mathrm{N}} + (\Sigma_\omega c_{J\omega}^2)\, \mathfrak{m} \cdot \delta\alpha_{\mathrm{N}} . \tag{5}$$

The corresponding shift of the PE. band associated with the ejection of an electron from orbital ψ_J is defined as [(A) = aza-derivative, (P) = parent hydrocarbon]:

$$\delta I_{v,J} = I_{v,K}(\mathrm{A}) - I_{v,J}(\mathrm{P}) \tag{6}$$

if band Ⓚ in the PE. spectrum of (A) is correlated with band Ⓙ in that of (P).

Assuming the validity of *Koopmans*'s theorem [19], *i.e.*

$$I_{v,J} = -\,\varepsilon(\psi_J) , \tag{7}$$

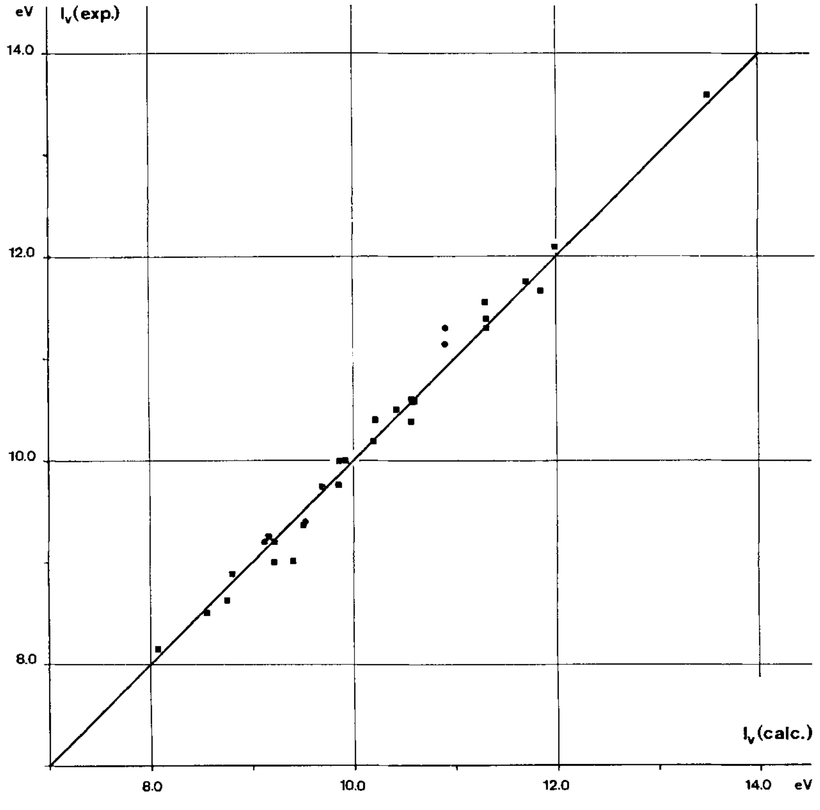
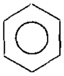
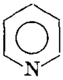
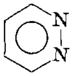
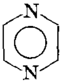
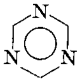
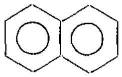
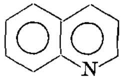
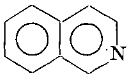
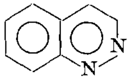
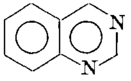
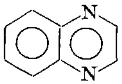


Fig. 2. *Linear correlation between the observed* (I_v(exp.)) *and calculated* (I_v(calc.)) *vertical ionization potentials of the PE.-bands of aza-derivatives of benzene* (*I*) *and naphthalene* (*VIII*) *corresponding to the ejection of an electron from π-orbitals*

The $I_{v,J}$(calc.) values have been obtained from $I_{v,J}$(calc.) $= I_0 + \delta I'_{v,J}$ ($I_0 = 9.24$ eV for $\mathbf{e}_{1g}$ of *I*; $I_0 = 8.15$ eV for $\mathbf{a}_u$, $I_0 = 8.88$ eV for $\mathbf{b}_{1u}$ and $I_0 = 10.00$ eV for $\mathbf{b}_{2g}$ of VIII) with $\delta I'_{v,J}$ according to (10). Points ● refer to bands which have been omitted from the regression calculation leading to the parameters given in (10) (see text).

Table 2. *Regressional analysis of the positions of the π-bands*

Independent variables $X_{J,1}$ and $X_{J,2}$ according to (9). To avoid confusion, the column 'Par. Orb.' contains the designation of the *parent orbital* in I or VIII. $I_{v,J}$ and $I'_{v,J}$ in eV.

Compound	Par. Orb.	$X_{J,1}$	$X_{J,2}$	$I_{v,J}$(exp.)	$I'_{v,J}$(calc.)
I 	$e_{1g}(S)$	0.000	0.000	9.24	9.16
	$e_{1g}(A)$				
II 	$e_{1g}(A)$	0.000	0.500	9.73	9.68
	$e_{1g}(S)$	0.333	0.167	10.50	10.43
III 	$e_{1g}(S)$	0.167	0.833	10.61	10.57
	$e_{1g}(A)$	0.500	0.500	11.3	11.32
IV 	$e_{1g}(S)$	0.167	0.833	10.41	10.57
	$e_{1g}(A)$	0.500	0.500	11.39	11.32
V 	$e_{1g}(A)$	0.000	1.000	10.18	10.19
	$e_{1g}(S)$	0.667	0.333	11.77	11.70
VI 	$e_{1g}(S)$ $e_{1g}(A)$ }	0.500	1.000	11.67	11.84
VII 	$e_{1g}(S)$	0.333	1.667	12.10	11.98
	$e_{1g}(A)$	1.000	1.000	13.59	13.49
VIII 	a_u	0.000	0.000	8.15	8.07
	b_{1u}	0.000	0.000	8.88	8.80
	b_{2g}	0.000	0.000	10.00	9.92
IX 	a_u	0.181	0.069	8.62	8.74
	b_{1u}	0.000	0.333	(9.20)	9.14
	b_{2g}	0.160	0.151	10.58	10.60
X 	a_u	0.069	0.250	8.50	8.56
	b_{1u}	0.167	0.167	(9.40)	9.52
	b_{2g}	0.030	0.190	10.40	10.22
XI 	a_u	0.250	0.319	9.20	9.22
	b_{1u}	0.167	0.500	9.99	9.85
	b_{2g}	0.190	0.341	(11.14)	10.90
XII 	a_u	0.250	0.319	9.00	9.22
	b_{1u}	0.167	0.500	9.77	9.86
	b_{2g}	0.190	0.341	(11.3)	10.90
XIII 	a_u	0.361	0.138	9.01	9.40
	b_{1u}	0.000	0.666	9.35	9.49
	b_{2g}	0.320	0.301	11.57	11.29

we are led to the regression problem defined by

$$\delta I'_{v,J} = a - X_{J,1}\,\delta\alpha_{\mathrm{N}} - X_{J,2}\,\mathfrak{m}\,\delta\alpha_{\mathrm{N}} \tag{8}$$

where the dependent variable $\delta I'_{v,J}$ corresponds to the experimental shifts (6) and where the independent variables are

$$X_{J,1} = \Sigma_{\varrho}\, c^2_{J\varrho},\; X_{J,2} = \Sigma_{\omega}\, c^2_{J\omega}\,. \tag{9}$$

The constant a of (8) has to be included for statistical reasons.

The values of the independent variables $X_{J,1}$ and $X_{J,2}$ are given in Table 2, columns 3 and 4.

For the least-squares analysis based on (8) we have neglected the experimentally uncertain values $I_{v,J}$(exp.) (in brackets in Table 2) corresponding to $\mathbf{b}_{1u}$ of IX and X and to $\mathbf{b}_{2g}$ of XI and XII. The results of the regression calculation (confidence level = 90 percent, degrees of freedom = 23, *Student*'s **t** = 1.71) is:

$$\begin{aligned} \delta I'_{v,J} &= (-\,0.0786 + 3.2947\,X_{J,1} + 1.0299\,X_{J,2})\ \mathrm{eV},\\ a &= -\,0.0786 \pm 0.0810\ \mathrm{eV},\\ \delta\alpha_{\mathrm{N}} &= -\,3.2947 \pm 0.2203\ \mathrm{eV},\\ \mathfrak{m}\,\delta\alpha_{\mathrm{N}} &= -\,1.0299 \pm 0.1330\ \mathrm{eV}. \end{aligned} \tag{10}$$

Note that the confidence limits of a include $a = 0$, so that the parametrization (10) does not differ significantly from one depending simply on two scaling factors $\delta\alpha_{\mathrm{N}} = -\,3.3$ eV and $\mathfrak{m} = 0.31$. The latter indicates that a perturbation $\delta\alpha_{\mathrm{N}}$ in position ϱ induces a perturbation of $\sim\delta\alpha_{\mathrm{N}}/3$ at position ω *ortho* to ϱ, in agreement with the accepted rule of thumb for HMO calculations. The ionization potentials $I'_{v,J}$ calculated from (6) and (10) are given in Table 2. As shown in Fig. 2 they agree closely with the experimental values and provide therefore a convincing identification of the π-bands in the PE. spectra of the aza-compounds IX to XIII.

n-Bands. The highest σ-orbitals of naphthalene (VIII) have orbital energies of about -11 eV and below. Replacement of one or two carbon centres by nitrogen tends to shift these σ-orbitals towards even lower orbital energies, due to the higher electronegativity of the nitrogen core. Previous experience [11] [20] indicates that in the case of the aza-naphthalenes this shift is about -0.6 eV per nitrogen atom, so that the onset of the σ-band system in the PE. spectra of IX and X is expected to occur near 11.5 eV, and in those of XI, XII, and XIII near 12.0 eV.

To identify the 'lone-pair' bands (n-bands) in the PE. spectra of IX to XIII, we now subtract those bands in the regions IP. < 11.0 eV (VIII), IP. < 11.5 eV (IX, X) and IP. < 12.0 eV (XI, XII, XIII), which have been assigned in the previous section to ejection from one of the three highest occupied π-orbitals. This leaves us, in the region of interest, with

0 bands in the case of VIII,
1 band in the case of IX and X,
2 bands in the case of XI, XII and XIII.

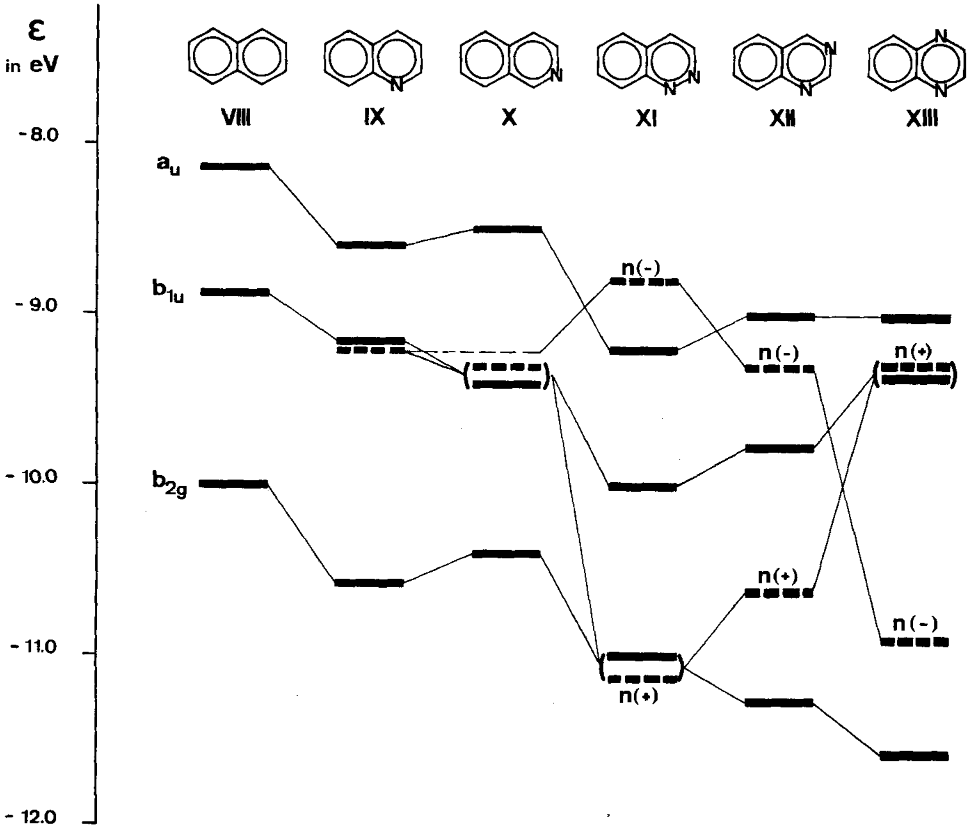


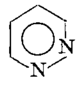
Fig. 3. *Orbital correlation diagram for naphthalene (VIII), quinoline (IX), isoquinoline (X), cinnoline (XI), quinazoline (XII) and quinoxaline (XIII)*
Solid lines = π-orbitals, broken lines = lone pair orbitals

These must be due to photoejection from those σ-type orbitals $\psi(\sigma, \mathbf{n})$ to which the lone-pair orbital $\mathbf{n}$ (in the case of IX and X) or the linear combinations $\mathbf{n}_+$, $\mathbf{n}_-$ (2) (in the case of XI, XII, XIII) contribute most. Applying *Koopmans* theorem (7), we obtain

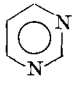
IX: $\varepsilon(\psi(\sigma, \mathbf{n})) = -9.2$ to -9.3 eV;
X: $\varepsilon(\psi(\sigma, \mathbf{n})) = -9.3$ to -9.4 eV;
XI: $\varepsilon(\psi(\sigma, \mathbf{n}_-)) = -8.8$ eV; $\varepsilon(\psi(\sigma, \mathbf{n}_+)) = -11.0$ to -11.1 eV;
XII: $\varepsilon(\psi(\sigma, \mathbf{n}_-)) = -9.3$ eV; $\varepsilon(\psi(\sigma, \mathbf{n}_+)) = -10.6$ eV;
XIII: $\varepsilon(\psi(\sigma, \mathbf{n}_+)) = -9.3$ to -9.4 eV; $\varepsilon(\psi(\sigma, \mathbf{n}_-)) = -10.9$ eV.

The correlation diagram shown in Fig. 3, summarizes the proposed band assignment.

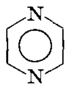
Discussion of the Results. – From considerations of through-space and through-bond interactions between lone-pair orbitals [6] [7] [8] [10], the splits $\Delta I_n = \Delta\varepsilon(n)$ (1) should be almost the same for corresponding pairs of compounds: III, XI; IV, XII and V, XIII. This is indeed what is observed:



III: 2.0 eV

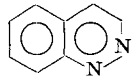


IV: 1.5 eV

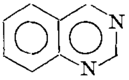


V: –1.7 eV

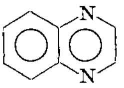
(11)



XI: 2.2 to 2.3 eV



XII: 1.3 eV



XIII: –1.6 to –1.5 eV

The sign of ΔI_n cannot be determined experimentally and has been assigned from theoretical calculations (Extended *Hückel* model [1] [21]; modified *Pariser-Parr-Pople* model [22]; SCF all-valence-electron model [23])all of which yield the same result.

The close agreement of corresponding ΔI_{n} values (11) suggests that lone-pair orbitals, such as $\mathbf{n}_a$ and $\mathbf{n}_b$, are 'short sighted' *i.e.* that their through-bond coupling proceeds only *via* the σ-orbitals in the ring containing the nitrogen centres. One might therefore expect that the orbitals $\psi(\sigma, \mathbf{n}_+)$ and $\psi(\sigma, \mathbf{n}_-)$ of III, IV, and V (see Fig. 4 of [1]) should have recognizable counterparts among the molecular orbitals of XI, XII, and XIII, since the latter should exhibit little participation from semi-localized bond-orbitals of the other ring. No such similarity is found when the molecular orbitals of XI, XII and XIII are calculated according to the extended *Hückel* procedure [21]. This method gives considerable contributions from *all* semi-localized 'lone pair' orbitals $\psi(\sigma, \mathbf{n}_+)$ and $\psi(\sigma, \mathbf{n}_-)$, which are, indeed, quite difficult to identify among the set of σ-molecular orbitals. We believe that this is an artifact of the extended *Hückel* method, which tends to yield CC- and CH-σ-orbitals at too high energies relative to π and/or lone-pair orbitals in larger systems, and hence to overemphasize mixing of such σ-orbitals with the semi-localized orbitals such as $\mathbf{n}_+$ and $\mathbf{n}_-$. This may be why the calculated splits ΔI_n are in somewhat better agreement with the observed ones for III, IV, and V than for XI, XII, and XIII [12]:

	ΔI_n(obs.)	ΔI_n(calc.) [21]		ΔI_n(obs.)	ΔI_n(calc.) [21]
III	2.0 eV	0.99 eV	XI	2.2 to 2.3 eV	0.52 eV
IV	1.5 eV	0.81 eV	XII	1.3 eV	0.69 eV
V	−1.7 eV	−1.68 eV	XIII	−1.5 to −1.6 eV	−1.37 eV

(12)

The mean ionization potentials of the lone-pair bands

$$\overline{I_v(n)} = \frac{1}{m} \Sigma I_{v,j}(n) , \tag{13}$$

(where the summation has to be carried out over the m bands correlated with the delocalized lone-pair molecular orbitals) confirm our hypothesis that these orbitals must be similar in the benzene and naphthalene derivatives.

According to (7) we identify $-\overline{I_v(n)}$ in a first approximation with the energy A_n of the m lone-pair basis orbitals $\mathbf{n}_\mu$ in the molecule. The values $A_n = -9.6$ eV in II, $A_n = -9.2$ eV in IX and $A_n = -9.4$ eV in X show how little the energy is affected by enlargement of the σ-frame in IX and X relative to II, and will be taken as reference values. For the benzene derivatives with $m > 1$ we find: $m = 2$: III $A_n = -10.3$ eV; IV, V $A_n = -10.5$ eV; $m = 3$: VI $A_n = -11.3$ eV; $m = 4$: VII $A_n = -12.0$ eV. If we define the stabilizing influence of one basis n-orbital on another by

$$\delta A_n = \frac{1}{m-1}\left(A_n(\text{derivative}) - A_n(\text{pyridine})\right) \tag{14}$$

we find:

derivative:	III	IV	V	VI	VII
δA_n:	-0.7	-0.9	-0.9	-0.8_5	-0.8 eV.

(15)

From the energies of the basis orbitals in the diazanaphthalenes ($m = 2$), namely XI, XII: $A_n = -9.9_5$ eV and XIII: $A_n = -10.1_5$ eV, we obtain the following shift parameters:

derivative:	XI	XII	XIII
δA_n:	-0.6_5	-0.6_5	-0.9_5 eV.

(16)

(For XI and XII the reference value is the average of -9.2 eV and -9.4 eV observed for IX and X and for XIII the value -9.2 eV of IX.) The similarity of the δA_n values in (16) and (15) points again to the similarity between the delocalized lone pair orbitals $\psi(\sigma, \mathbf{n}_+)$ and $\psi(\sigma, \mathbf{n}_-)$ in the diazabenzenes and their corresponding benzologues.

Finally we wish to show that an empirical correlation between lone-pair ionization potentials and proton affinities of azabenzenes and azanaphthalenes is in agreement with the proposed assignment.

It is not at all obvious that there should be a simple relationship between the lone-pair orbital energies $\varepsilon(\psi(\sigma, \mathbf{n}))$ and the basisities of aza-derivatives. But an empirical comparison of $pK_{a,1}$ (for mono-protonation) with the mean ionization potential (13), rewritten as

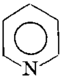
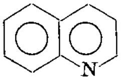
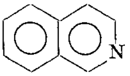
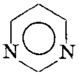
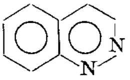
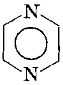
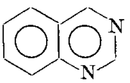
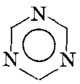
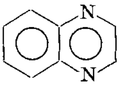
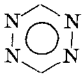
$$\overline{I_v(n)} = \frac{-1}{m} \sum_{J=1}^{m} \varepsilon(\psi_J(\sigma, \mathbf{n})) \tag{17}$$

does yield a crude but significant correlation, as shown in Table 3 and Fig. 4. In (17) m is the number of nitrogen centres in the aza derivative, *i.e.* the number of basis orbitals $\mathbf{n}_\mu$. The orbitals $\psi_J(\sigma, \mathbf{n})$ are again those to which the $\mathbf{n}_\mu$ contribute with greatest weight.

The use of $I_v(n)$, rather than of the lowest lone-pair ionization potential $I_{v,m}(n)$, is suggested by an argument similar to one proposed by *Dewar* [28] in another context. Let $\mathbf{n}_1 \ldots \mathbf{n}_\mu \ldots \mathbf{n}_m$ be a set of (symmetry-equivalent) lone-pair basis orbitals with degenerate orbital energies $\varepsilon(\mathbf{n}_1) = \ldots \varepsilon(\mathbf{n}_\mu) = \ldots \varepsilon(\mathbf{n}_m) = A_n$. We simulate the combined through-space and through-bond interaction between these orbitals by matrix elements $\lambda_{\mu\nu} = \langle \mathbf{n}_\mu | \mathbf{h} | \mathbf{n}_\nu) \rangle$ which depend on the relative position of $\mathbf{n}_\mu$ and $\mathbf{n}_\nu$. The corresponding secular determinant yields the orbital energies $\varepsilon(\varphi_J(\mathrm{n}))$ for the delocalized lone-pair orbitals $\varphi_J(n)$ with $J = 1, \ldots m$. According to a rule of linear algebra

$$\sum_{J=1}^{m} \varepsilon(\varphi_J(n)) = \sum_{\mu=1}^{m} \varepsilon(\mathbf{n}_\mu) = mA_n \tag{18}$$

Table 3. *Correlation between* $pK_{a,1}$ *and mean ionization potential* $\overline{I_v(n)}$ (in eV)

Compound	$pK_{a,1}$	ref.	$\overline{I_v(n)}$[a]	Compound	$pK_{a,1}$	ref.	$\overline{I_v(n)}$
II: 	5.27	[24]	9.6	IX: 	4.93	[26]	~9.2
III: 	2.24	[25]	10.3	X: 	5.44	[26]	~9.3
IV: 	1.23	[25]	10.5	XI: 	2.27	[25]	10.0
V: 	0.51	[25]	10.5	XII: 	1.5	[27]	10.0
VI: 	(0.0 to –0.5[b])		11.3	VIII: 	0.56	[26]	10.1
VII: 	<0 (–1.5 ?)[c]		12.0				

[a] Ref. [1].

[b] From $pK_{a,1}$ (2,4,6-trimethyl-*s*-triazine) = 2.9, taking into account the effect of the methyl groups (see text).

[c] Extrapolated value.

If the linear combinations $\varphi_J(n)$ are identified with $\psi_J(\sigma, \mathbf{n})$, *Koopmans*'s theorem (1) leads to:

$$\overline{I_v(n)} = \frac{-1}{m} \sum_{J=1}^{m} \varepsilon(\varphi_J(n)) = -A_n \tag{19}$$

This result is independent of m, the number of basis orbitals $\mathbf{n}_\mu$. According to (18) and (19), protonation of one of the lone pairs will yield a change in total lone-pair orbital energy of

$$\sum_{I=1}^{m-1} \varepsilon(\varphi'_I(n)) - \sum_{J=1}^{m} \varepsilon(\varphi_J(n)) = A_n = -\overline{I_v(\mathrm{n})} \tag{20}$$

where $\varphi'(\mathrm{n})$ are the delocalized lone-pair orbitals in the mono-protonated species. The neglect of perturbations of the type $\delta A_{n_\mu} = \langle \mathbf{n}_\mu | \mathbf{h} | \mathbf{n}_\mu \rangle$ (which would formally account for inductive effects and for part of the through-bond interaction) is definitely an oversimplification, even in a qualitative treatment. If the energy changes due to formation of a new NH-bond, to solvation effects, and to polarization of the π-system on protonation are roughly constant for all our azaderivatives then (20) implies that $pK_{a,1}$ (for monoprotonation) should correlate with $\overline{I_v(n)}$.

The dissociation constants in Table 3 have been taken from the compilation by *Perrin* [25]. The $pK_{a,1}$ value for triazine (VI) has been extrapolated from that of 2,4,6-trimethyltriazine ($pK_{a,1} = 2.9$) using an empirical parameter of $\Delta pK_{a,1} = 1.4$ to 1.8 for each of the two methyl groups in *ortho*-position to the protonated nitrogen atom. This parameter has been deduced from the known $pK_{a,1}$ values of the diazines and their methyl-derivatives [24]. The extrapolated $pK_{a,1}$ value of tetrazine VII may be seriously in error.

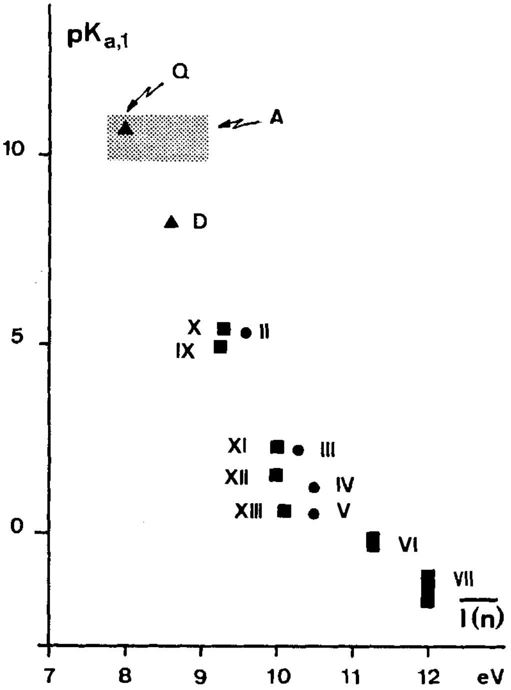


Fig. 4. *Correlation between* $pK_{a,1}$ *–values and mean ionization potentials* $\overline{I_v(n)}$ see (17)) *of aliphatic amines* (*A*), *quinuclidine* (*Q*), *1,4-diazabicyclo*[*2.2.2*]*octane* (*D*), *pyridine* (*II*), *pyridazine* (*III*), *pyrimidine* (*IV*), *pyrazine* (*V*), s-*triazine* (*VI*), *1,2,4,5-tetrazine* (*VII*), *quinoline* (*IX*), *isoquinoline* (*X*), *cinnoline* (*XI*), *quinazoline* (*XII*) *and quinoxaline* (*XIII*)

The correlation shown in Fig. 4 confirms our assignment of the PE. bands corresponding to the lone-pair orbitals $\psi(\sigma, \mathbf{n})$ in the aza-derivatives of I and VIII. In particular, the identification of the band associated with the highest occupied orbital, $\psi(\sigma, \mathbf{n}_-)$ in III, IV and $\psi(\sigma, \mathbf{n}_+)$ in V, on which all authors seem to agree ([1] and references therein), restricts the region within which the band associated with the second lone-pair orbital, $\psi(\sigma, \mathbf{n}_+)$ in III, IV and $\psi(\sigma, \mathbf{n}_-)$ in *V*, can occur. This disposes of the extreme hypotheses that the split ΔI_n should be almost zero or of the order of 5 eV.

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BIBLIOGRAPHY

[1] *R. Gleiter, E. Heilbronner & V. Hornung,* Helv. *55* 255 (1972)

[2] *R. Gleiter, E. Heilbronner & V. Hornung,* Angew. Chem. *82,* 878 (1970); Angew. Chem. Int. Ed. *9,* 901 (1970).

[3] *J. H. D. Eland & C. J. Danby,* Z. Naturforsch. *23a,* 355 (1968).

[4] *M. J. S. Dewar & S. D. Worley,* J. chem. Physics *51,* 263 (1969).

[5] *D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle,* 'Molecular Photoelectron Spectroscopy', *Wiley-Interscience,* London 1970.

[6] *R. Hoffmann,* Accounts chem. Res. *4,* 1 (1971).

[7] *R. Hoffmann, A. Imamura & W. J. Hehre,* J. Amer. chem. Soc. *90,* 1499 (1968); *W. Adam, A. Grimison & R. Hoffmann, ibid. 91,* 2590 (1969).

[8] *W. Adam,* 'The Jerusalem Symposia on Quantum Chemistry and Biochemistry', Volume II, p. 118, Israel Academy of Sciences and Humanities, Jerusalem 1970.

[9] *I. Fischer-Hjalmars & M. Sundbom,* Acta Chem. scand. *22,* 607 (1968).

[10] *M. Sundbom,* op. cit. [8], p. 56.

[11] *P. Bischof, J. A. Hashmall, E. Heilbronner & V. Hornung,* Tetrahedron Letters, *1969,* 4025; *E. Heilbronner & K. A. Muszkat, J.* Amer. chem. Soc. *92,* 3818 (1970).

[12] *R. Hoffmann, E. Heilbronner & R. Gleiter,* J. Amer. chem. Soc. *92,* 706 (1970); *D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner & V. Hornung,* Angew. Chem. *83,* 405 (1971).

[13] *D. W. Turner,* Proc. Roy. Soc. A *307,* 15 (1968).

[14] *K. Watanabe,* J. chem. Physics *26,* 542 (1957): *K. Watanabe, T. Nakayama & J. Mottl,* J. quant. Spectry. Radiative Transfer *2,* 369 (1963).

[15] *J. A. Yencha & M. A. El-Sayed,* J. chem. Physics *48,* 3469 (1968).

[16] *F. J. Vilesov,* Dokl. Akad. Nauk SSSR *132,* 632 (1960), cited. from *W. J. Wedenejew, L. W. Gurwitsch, W. H. Kondratjew. W. A. Medwedew & E. L. Frankewitsch,* 'Energien chemischer Bindungen, Ionisationspotentiale und Elektronenaffinitäten', VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1971.

[17] *M. J. S. Dewar & S. D. Worley,* J. chem. Physics *50,* 654 (1969).

[18] *C. A. Coulson & A. Streitwieser Jr.,* 'Dictionary of π-Electron Calculations', Pergamon Press, Oxford 1965.

[19] *T. Koopmans,* Physica *1,* 104 (1934).

[20] *E. Haselbach & E. Heilbronner,* Helv. *53,* 684 (1970).

[21] *A. D. Jordan, I. G. Ross, R. Hoffmann, J. R. Swenson & R. Gleiter,* J. chem. Phys. Letters, in print.

[22] *M. Sundbom,* to be published, private communication.

[23] *T. Yonezawa, H. Kato & H. Kato,* Theor. chim. Acta *13,* 125 (1969).

[24] *J. M. Essery & K. Schofield,* J. chem. Soc. 1961, 3939.

[25] *D. D. Perrin,* 'Dissociation Constants of Organic Bases in Aqueons Solution', *Butterworths,* London 1965.

[26] *A. Albert & J. N. Philips,* J. chem. Soc. *1956,* 1294.

[27] *A. Albert, W. L. F. Amarego & E. Spinner,* J. Chem. Soc. *1961,* 2689.

[28] *M. J. S. Dewar,* 'The Molecular Orbital Theory of Organic Chemistry', McGraw-Hill Book Company, New York 1969.