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ON THE PHOTOELECTRON SPECTRA OF THE AZANAPHTHALENES

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ABSTRACT

An iterative extended Hückel-level method is applied to the photoelectron spectra of naphthalene, quinoline, isoquinoline and the ten diazanaphthalenes. The thirteen highest molecular orbital energies of each compound are discussed and compared with the experimental spectra in the region 8–16 eV by means of empirical corrections. The identification of π -bands and nitrogen “lone pair” bands is in perfect agreement with the results of Brogli, Heilbronner and Kobayashi¹ and van den Ham and van der Meer².

INTRODUCTION

Almlöf et al.³ have shown that the deviations from Koopmans' theorem⁴ for an aromatic hydrocarbon may be expected to be invariant within a few tenths of an electron volt to replacement of C–H groups by nitrogen atoms. The photoelectron spectra of a series of iso-conjugate aza-aromatics are thus particularly well suited for interpretation by molecular orbital theory. Furthermore, in a comparative study of related compounds one may expect reasonable results from an approximate method. In this paper the Modified Iterative Extended Hückel Method (MIEHM)⁵ is applied to twelve aza-derivatives of naphthalene. For an introduction to the literature on the photoelectron spectra of these compounds see the first two references.

METHOD

The geometries of the azanaphthalenes are estimated from the experimental geometry of naphthalene⁶; the substitution of one or two C–H groups by nitrogen atoms is assumed to affect bond distances and bond angles in the following way:

TABLE I
PARAMETERS USED IN THE MODIFIED ITERATIVE EXTENDED HÜCKEL METHOD CALCULATIONS^a
Energy values in eV

	$W_s(0)$	Q_s	$W_{p\sigma}(0)$	$W_{p\pi}(0)$	Q_p	Slater exp.	γ
<i>"lone pair"</i> levels ^b							
H	-34.349783	2.169478	-	83.89	-	1.000	12.848
C	-82.64	6.460031	-	83.89	5.383609	1.625	10.333
N	-115.58	7.885012	-125.42	-125.42	6.503385	1.950	11.308
levels other than "lone pairs" ^b ; unless otherwise stated the values are as above							
H	-34.349783 \times 10.5/[13.595					0.88	
C				- 83.89 \times 0.79			
N				- 125.42 \times 0.93			

^a Parameters listed in Table 2 of ref. 5.

^b Parameters referred to in a note added in press, ref. 5; the parameters for p π orbitals are chosen to give direct agreement with the π -bands of the azabenzenes.

TABLE 2
CORRECTION TERMS FOR "LONE PAIR" LEVELS

Lettering ^a	Naphthalene level ^a	Naphthalene aza-derivatives								Correction terms		<i>Benzene system^b</i> D_{6h} C_{2v}				
		1	2	1,2	1,3	1,4	2,3	1,5	1,6	1,7	1,8	2,6	2,7	<i>a</i>	<i>b</i> (<i>eV</i>)	
e	9 _{2g} t	n	n-	n-	n+	n+	n+	n-	n-	n+	n-	n+	n+	1.6	- 9.2	3e _{2g} t $\left\{ \begin{array}{l} 11a_1 n \\ 7b_2 n \end{array} \right.$
f	6 _{1g} t	n	n+	n+	n-	n-	n+	n+	n+	n-	n-	n-	n-	1.6	- 9.7	3e _{2g} t $\left\{ \begin{array}{l} 10a_1 n \\ 6b_2 n \end{array} \right.$
g	7 _{3u} t				n-	n-	n-	n-	n-	n-	n-	n-	n-	1.6	- 10.1	3e _{1u} r $\left\{ \begin{array}{l} 10a_1 n \\ 6b_2 n \end{array} \right.$
j	5 _{1g} r				n-											

^a Compare Table 3. ^b Compare Table 4.

Distances	C-C	\rightarrow	(N-) C-C	-1 per cent
		\rightarrow	N-C	-2½ per cent
		\rightarrow	N-N	-3 per cent
Angles	CCC	\rightarrow	(N) CCC	-1 per cent
		\rightarrow	NCC or NCN	+2½ per cent
		\rightarrow	CNC	-2½ per cent
		\rightarrow	NNC	-1 per cent

The tentative distances and angles derived in this way lead to reasonably consistent geometries for the azanaphthalenes.

The MIEHM and the application to the photoelectron spectra of the azabenzenes were discussed in an earlier publication⁵. The method is based on an extended Hückel-level approximation to the Fock matrix⁷, but the atomic orbital energy parameters are chosen in a self-consistent way, including one-center and two-center electron interaction terms in the iterative procedure; the level of sophistication may thus be compared with that of a CNDO method⁸.

Due to shortcomings of the approximate MIEHM technique levels with predominantly nitrogen "lone pair" character ("lone pairs" or "n-levels" for short) and other levels are treated by two separate parametrizations⁵; the parameter values are given in Table 1. Also the empirical corrections necessary to transform the calculated orbital energies into empirical scale are qualitatively different for "lone pair" levels and other levels. The correction terms used for "lone pairs" are of the form

$$\text{I.E.}^{\text{estimated}} = a \mid E^{\text{MO}} \mid + b$$

TABLE 3
CORRECTION TERMS FOR LEVELS OTHER THAN "LONE PAIRS"

Lettering	Naphthalene level ^a		Correction <i>c</i> (eV)
	Symmetry (D_{2h})	Type	
a	1a _u	π	-0.6
b	2b _{1u}	π	-0.3
c	1b _{3g}	π	-0.1
d	1b _{2g}	π	-0.2
e	9a _g	t	+0.7
f	6b _{1g}	t	+1.0
g	7b _{3u}	t	+0.7
h	1b _{1u}	π	-0.5
i	7b _{2u}	r	+0.8
j	5b _{1g}	r	+0.3
k	6b _{3u}	t	+0.6
l	8a _g	r	-0.5
m	6b _{2u}	s	-0.5

^a See Lindholm et al.⁹.

TABLE 4

 π -LEVELS AND n-LEVELS IN THE AZABENZENES

Empirically corrected MIEHM energies are compared with values estimated from ab initio calculations and observed values (eV)

	Level (C_{2v})	Estimated		Observed ^a	
		MIEHM	ab initio ³	Gleiter et al. ¹⁰	Fridh et al. ¹¹
benzene	1a ₁ , 2b ₁	π	9.3	9.1	9.3
	1b ₁	π	12.3	11.8	12.2
pyridine	11a ₁	n	9.5	9.6	9.7
	1a ₂	π	9.6	9.5	9.7
	2b ₁	π	10.6	10.4	10.6
	1b ₁	π	13.1	12.9	13.2
pyridazine	7b ₂	n	9.3	9.3	9.3
	2b ₁	π	10.5	10.5	10.6
	1a ₂	π	11.3	11.2	11.3
	11a ₁	n	11.3	11.5	11.3
	1b ₁	π	13.9	14.0	13.8
pyrimidine	7b ₂	n	9.9	9.6	9.7
	2b ₁	π	10.5	10.4	10.5
	11a ₁	n	11.3	11.2	11.2
	1a ₂	π	11.4	11.6	11.5
	1b ₁	π	13.8	14.1	13.9
pyrazine	11a ₁	n	9.3	9.4	9.4
	1a ₂	π	9.8	10.0	10.2
	10a ₁	n	11.4	11.4	11.7
	2b ₁	π	11.7	11.8	11.7
	1b ₁	π	14.0	13.9	14.0
s-triazine	11a ₁ , 7b ₂	n	10.7	10.4	10.4
	1a ₂ , 2b ₁	π	12.0	12.1	12.1
	1b ₁	π	14.9	15.1	15.6
s-tetrazine	7b ₂	n	9.8	9.6	9.7
	2b ₁	π	12.0	12.3	12.1
	10a ₁	n	12.0	12.6	12.1
	11a ₁	n	12.5	12.8	12.8
	6b ₂	n	13.4	13.3	13.4
	1a ₂	π	13.3	13.7	13.5
	1b ₁	π	15.7	16.1	15.8

^a Quoted from the compilation by Almlöf et al.³.

where a has the value 1.6 and b varies from -9.2 to -10.1 eV, see Table 2. From this table it also appears which naphthalene levels that develop into "lone pairs" in the aza-derivatives. For levels which are not "lone pairs" the correction terms are taken as simple additive constants c

$$\text{I.E.}^{\text{estimated}} = |E^{\text{MO}}| + c$$

with values ranging from -0.6 to $+1.0$ eV, see Table 3. These values are chosen such that agreement with the interpretation of the naphthalene spectrum by Lindholm et al.⁹ is maintained. Although the parameters for π orbitals in Table 1 are adjusted to reproduce directly (i.e. $c = 0$) the measured π -bands of benzene and the azabenzenes (see Table 4), the calculated π -levels for naphthalene and the azanaphthalenes have slightly too high binding energies; the same thing happens to the SPINDO/1-method⁹. This is compensated for by empirical correction terms varying from -0.6 to -0.1 eV.

The results for "lone pair" bands and π -bands of benzene and the azabenzenes are summarized in Table 4, except for the unique inner "lone pair" in *s*-triazine. The agreement with the interpretation by Almlöf et al.³ is very convincing and justifies the application of the present approach to the naphthalene system.

RESULTS

The empirically corrected MIEHM energies are compared with simplified spectra of naphthalene and theaza-derivatives in the region 8–16 eV in Figures 1–3. The results support the identification of the n -bands and the first three π -bands

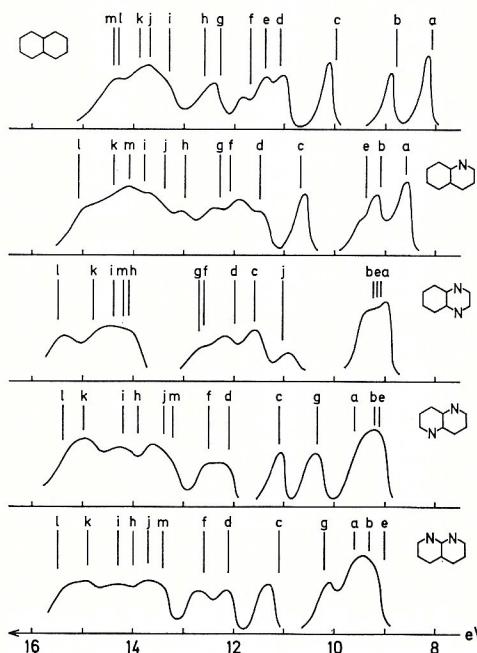


Figure 1. General outline of the spectra of naphthalene, quinoline and 1,4-, 1,5- and 1,8-diazanaphthalenes with indication of empirically corrected MIEHM energies. The curves in this and the following two figures are simplified versions of the spectra published by Brogli et al.¹ and van den Ham and van der Meer².

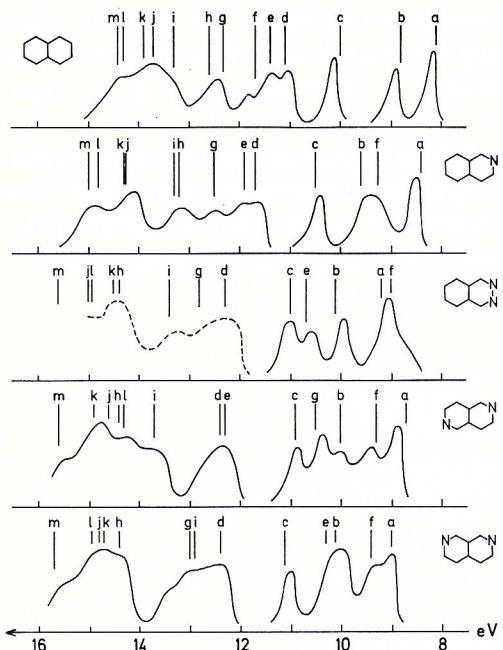


Figure 2. General outline of the spectra of naphthalene, iso-quinoline and 2,3-, 2,6- and 2,7-diaza-naphthalenes with indication of empirically corrected MIEHM energies.

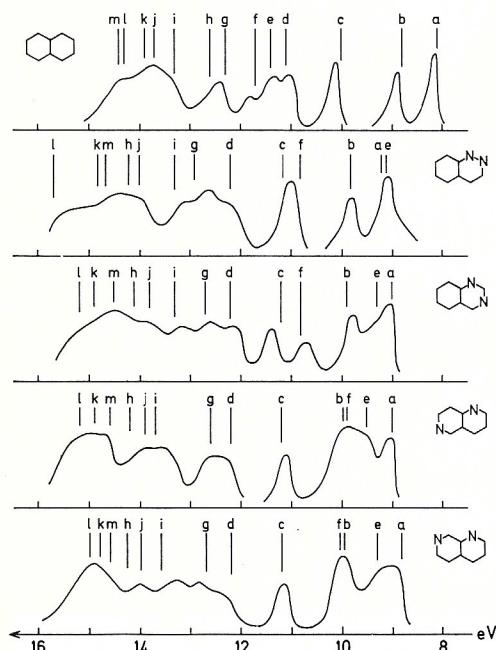


Figure 3. General outline of the spectra of naphthalene and 1,2-, 1,3-, 1,6- and 1,7-diazanaphthalenes with indication of empirically corrected MIEHM energies.

suggested by Brogli et al.¹ and van den Ham and van der Meer². The MIEHM results indicate that ionization from the remaining two π -levels occur close to 11.5 eV and 13 eV in the mono azanaphthalenes and close to 12 eV and 14 eV in the diaza-naphthalenes.

The “lone pair” levels of these compounds are particularly interesting. Orbital amplitudes of the eight highest σ -levels of naphthalene are given in Figure 4, and “lone pair” amplitudes of some aza-naphthalenes are given in Figure 5. The MIEHM yields more recognizable “lone pair” orbitals than an Extended Hückel-level method^{1, 2, 5},

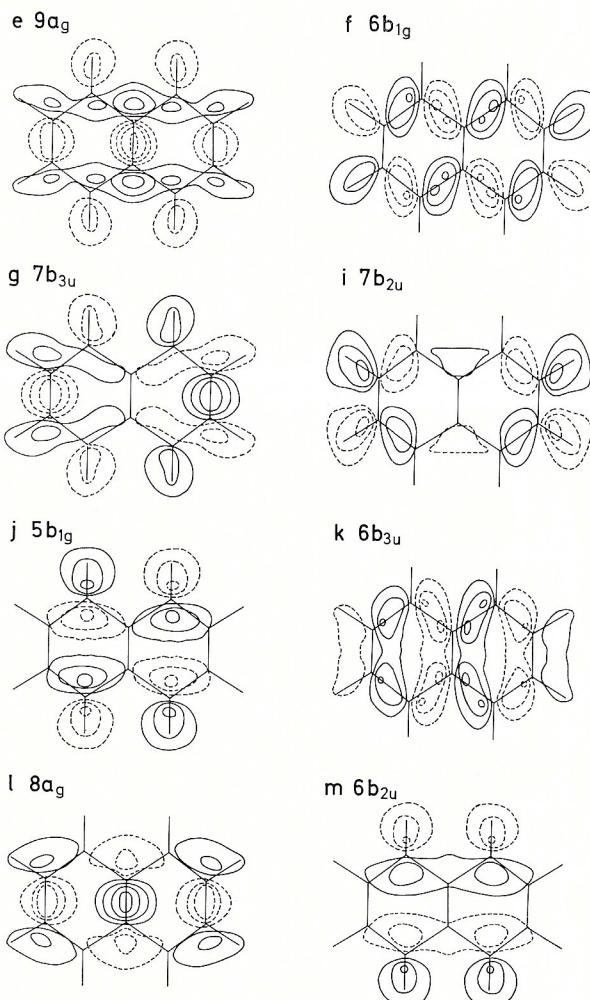


Figure 4. Molecular orbital amplitudes of the eight highest occupied σ -levels of naphthalene, see Table 3. The graphs in this and the following figure show contour lines in the molecular plane for the amplitudes ± 0.05 , ± 0.10 , ± 0.15 and ± 0.20 , solid and dashed lines distinguish between amplitudes of different sign. The graphs are reproduced from approximate plots on a line printer.

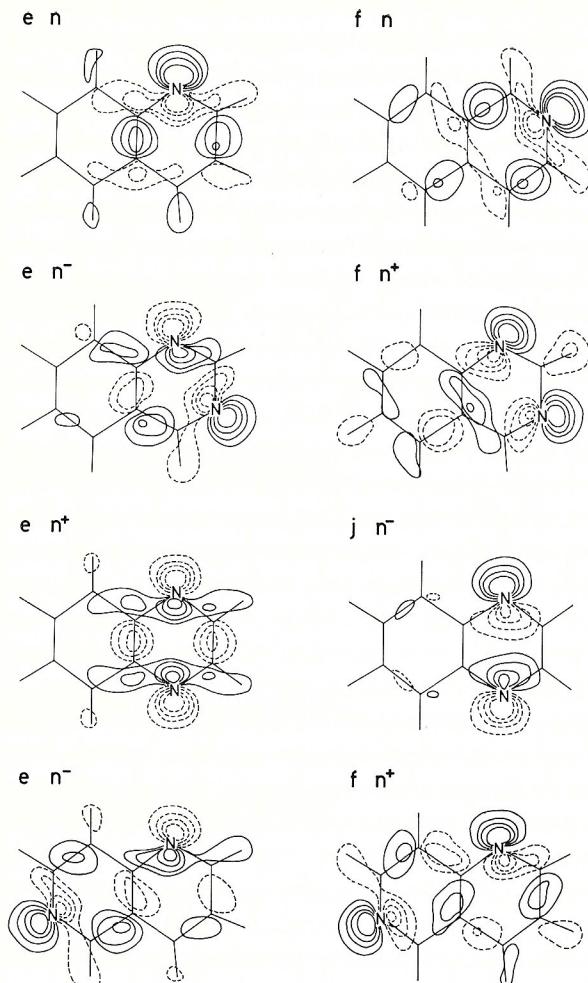


Figure 5. Molecular orbital amplitudes of the "lone pair" levels in quinoline, iso-quinoline and 1,3-, 1,4- and 1,6-diazanaphthalenes. The lettering (e, f, j) indicates the originating naphthalene level in Figure 4.

or the CNDO/2 method², and thus yields a better description of the observed facts. When only one of the constituent rings contains nitrogen atoms the "lone pair" orbitals are almost entirely localized to that ring with adjoining bonds. Six examples are shown in Figure 5. Indeed, the "lone pairs" may be considered as slightly perturbed "lone pairs" of the corresponding azabenzenes. This result supports the conclusions reached by Brogli et al.¹.

The calculated nitrogen "lone pair" orbitals of the azanaphthalenes originate from naphthalene levels as indicated in Table 2. When the aza-derivative possesses

a C_2 axis (i.e. 1,4-, 1,5-, 1,8-, 2,3-, 2,6- and 2,7-diazanaphthalenes) symmetry restrictions must be obeyed, and the two highest naphthalene orbitals of appropriate symmetries develop into symmetrical and antisymmetrical "lone pair" combinations; given a choice between near-degenerate levels of appropriate symmetry for one of the combinations (i.e. $9a_g$ or $6b_{1g}$ for the plus combinations in 1,5- and 2,6-diazanaphthalenes), the orbital with the most suitable form is chosen. In the cases where the aza-compound has no other symmetry than the molecular plane, no symmetry restrictions (apart from σ) apply, and "lone pairs" develop from one or both of the two highest closely spaced σ -levels of naphthalene, $9a_g$ and $6b_{1g}$.

The remaining σ -bands of the azanaphthalenes, i.e. those that are not "lone pairs", occur from about 12 eV and above. The bands are often broad and poorly resolved and an interpretation is difficult to verify. The predicted σ -levels seem, however, to reproduce significant trends. The characteristic large band gaps in 1,4-, 2,6- and 2,7-diazanaphthalenes are thus well reproduced.

Apart from the development of "lone pairs" the calculated shifts of the σ -levels of naphthalene by introduction of nitrogen atoms are influenced by mainly two factors. In the first place, the presence of nitrogen tends to stabilize the levels due to the higher binding energies of the nitrogen atom compared with the carbon atom. In the second place, the removal of hydrogen shifts the levels according to their bonding characteristics. For levels which are C-H bonding in the positions of nitrogen substitution the two effects work in opposite directions.

The $9a_g$, $6b_{1g}$, $7b_{3u}$, $6b_{3u}$ and $8a_g$ levels are predominantly C-C bonding and their positions are governed mainly by the first effect, i.e. they are as a rule shifted towards higher binding energies by nitrogen substitution.

The $7b_{2u}$ and $5b_{1g}$ levels (labeled i and j in the figures) are significantly C-H bonding; the $7b_{2u}$ level is bonding in the β positions and the $5b_{1g}$ level in the α positions. By substitution of nitrogen in the α positions the opposing effects approximately cancel for the $5b_{1g}$ level, while the $7b_{2u}$ level is stabilized according to the first effect. When the nitrogen atoms occupy β positions the picture is reversed. As a result these levels appear in different order for the α -substituted compounds in Figure 1 and the β -substituted ones in Figure 2.

The $6b_{2u}$ level (labeled m) is predominantly C-H bonding but only in α positions. The energy of this level has thus a very characteristic dependence on the substitution pattern; the predicted levels range from 13.2 eV in 1,5-diazanaphthalene to 15.7 eV in 2,7-diazanaphthalene.

CONCLUSIONS

Due to the concordant results of different studies the interpretation of the n-bands and the first π -bands seems well established. So far the complexity of the spectra prevents definite confirmation of the predictions in the 12–16 eV region, such as the reverse orders of the $7b_{2u}$ and $5b_{1g}$ levels for α -substituted and β -substituted

compounds and the characteristic behaviour of the $6b_{2u}$ level; but the predictions reproduce the general structure of the spectra.

Application to the higher aza-derivatives of naphthalene, including biologically important compounds such as pteridine etc., would serve as a further check up on the present approach. Possibly the creation of more n-levels "thins" the compact regions of the spectra and thus simplifies the interpretation.

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