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Photoelectron Spectra of Pteridine and its 4-Methyl and 2,4,6,7-Tetramethyl Derivatives

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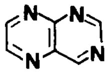
The He(I_α) photoelectron spectra of the three title compounds **1**–**3** have been recorded and analyzed in terms of a simple Hückel-model and of semiempirical calculations. The pK_a value of pteridine (**1**) is predicted to be of the order of −2, with preferred protonation in the pyrimidine ring.

Photoelektronen-Spektren von Pteridin, 4-Methyl- und 2,4,6,7-Tetramethylpteridin

Die He(I_α)-Photoelektronen-Spektren der drei Titel-Verbindungen **1**–**3** wurden aufgenommen und mit Hilfe des Hückel-Modells und semiempirischer Rechnungen interpretiert. Für Pteridin (**1**) wird ein pK_a-Wert von −2 vorausgesagt, mit einer bevorzugten Protonierung im Pyrimidinring.

A number of pteridine (1,3,5,8-tetraazanaphthalene, **1**) derivatives are biologically important, and pteridine chemistry is an area of current and active research[1]. To contribute to the understanding of the electronic structure of the pteridine nucleus, we discuss in this communication the photoelectron (PE) spectra of pteridine (**1**), 4-methylpteridine (**2**), and 2,4,6,7-tetramethylpteridine (**3**).



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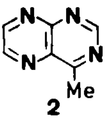

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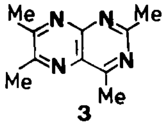

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The PE spectra of **1**–**3** are shown in Fig. 1 and vertical ionization energies estimated from the observed PE band maxima are given in Tables 1 and 2. A tentative correlation of low energy levels for the series is indicated in Fig. 2.

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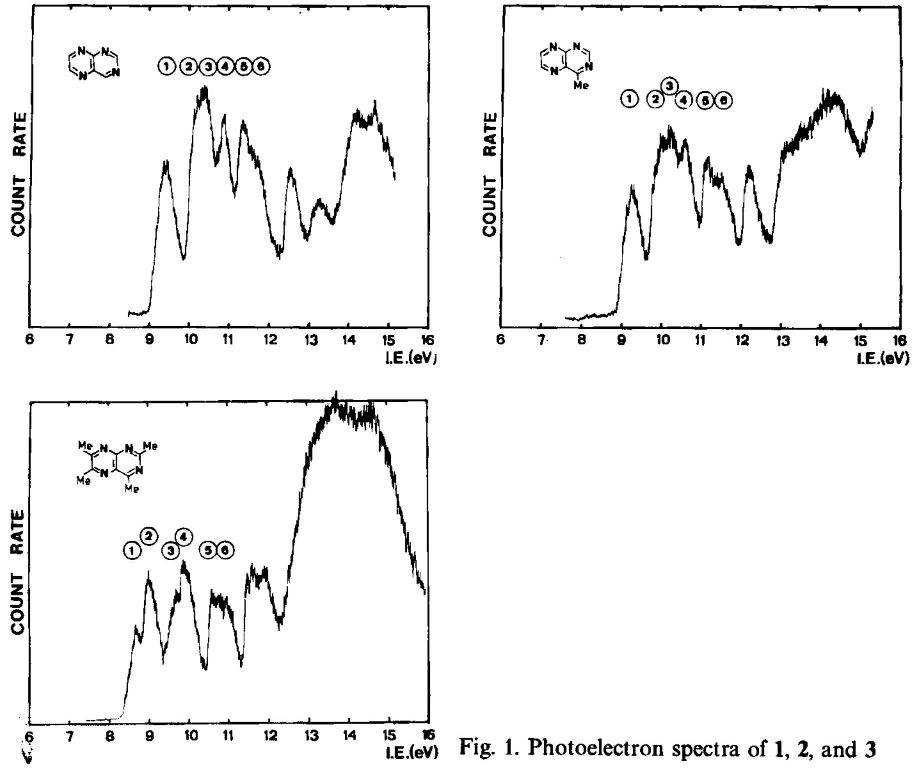

Fig. 1. Photoelectron spectra of **1**, **2**, and **3**

Table 1. Experimental and theoretical ionization energies (eV) for pteridine (**1**)

Band	Experimental $I_{v,j}$	Orbital Assignment	Theoretical $I_{v,j}$ HAM/3	EWMO	HMO
①	9.4	a′(n)	9.02	9.30	9.4
②	10.4	a″(π)	10.19	9.90	10.62
③		a′(n)	9.88	10.25	11.1
④	10.9	a″(π)	10.63	10.78	10.63
⑤	11.4	a′(n)	10.83	11.96	11.7
⑥	(11.8)	a′(n)	11.30	12.02	11.8
⑦	12.6	a″(π)	12.04	12.54	12.44
⑧	13.3	a″(π)	12.58	13.10	12.95

The spectrum of **1** is characterized by a low-energy band with maximum at 9.4 eV, followed by a complex region between 10 and 12 eV with maxima close to 10.4, 10.9, and 11.4 eV. A consideration of the relative integrated intensities indicates the assignment of one, two, one, and two individual transitions, respectively. The assignment of the peak at 10.4 eV to two individual ionization processes is supported by the resolution of two peaks close to 10.0 and 10.2 eV in the spectrum of **2**. The contribution of two transitions to the structure with maximum at 11.4 eV is consistent with the presence of a prominent shoulder at 11.8 eV.

Table 2. Experimental ionization energies (eV) for **1**, **2**, and **3**

Band	Orbital Assignment		$I_{v,j}$	
		1	**2**	**3**
①	a′(n)	9.4	9.3	8.6
②	a″(π)	10.4	10.0	9.0
③	a′(n)		10.2	9.7
④	a″(π)	10.9	10.6	9.9
⑤	a′(n)	11.4	11.2	10.6
⑥	a′(n)	(11.8)	(11.5)	(10.9)

The low-energy band at 9.4 eV has a weak 0-0 component and a broad, Gaussian-like envelope. This suggests the assignment of an ionization process involving the nitrogen n electrons[2]. In the 10–12 eV region the application of band shape criteria is complicated by the strong band overlap, but the relative sharpness of band ④ at 10.9 eV seems to indicate the ejection of a π-electron.

The assignment of the low-energy bands given in the Tables is based on *Koopmans'* approximation: $-\varepsilon_j^{MO} = I_{v,j}$[3]. This assignment is supported by the empirical criteria discussed above, by the substituent shifts outlined in Fig. 2 (to be discussed later), and by the results of three different theoretical procedures: (i) a Hückel-type (HMO) model[2,4,5], (ii) a correlation procedure[6] based on the Energy Weighted Maximum Overlap (EWMO) approximation[7], and (iii) the HAM/3 procedure[8]. The EWMO and the HAM/3 calculation were based on the geometry predicted for pteridine by MNDO/1[9], using computer programs published through QCPE[10].

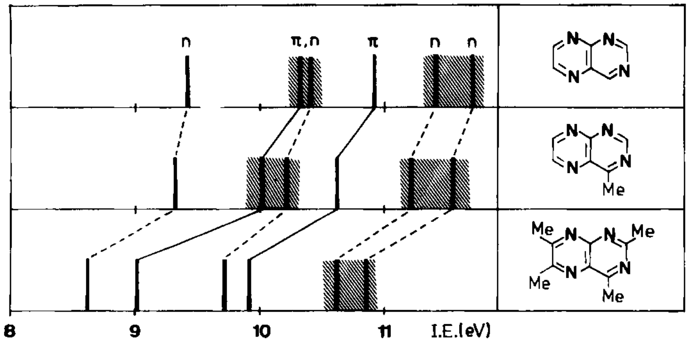

Fig. 2. Correlation of observed photoelectron band maxima for pteridines **1**–**3** with indication of the assignment of π- and n-type levels

The HMO Model

Previous investigations have shown that a reasonably accurate prediction of the position of the π- and n-bands of azabenzenes can be obtained within the framework of simple Hückel-type theory[2,4,5]. Apart from the predictive power, the great advantage of theoretical models at this "pencil and paper" level is that they provide a kind of insight which is not easily obtained by the application of more sophisticated computer-based procedures. For example, a consideration of the effective interaction terms within the HMO model leads directly to the symmetry rule[11]:

> "Two azabenzenes, which are related by 1,4-shifts of the positions of aza-replacement, have essentially similar PE spectra".

General conclusions of this type are not easily derived from the results of, say, ab initio calculations.

In a previous paper[5], the HMO model was applied to the spectrum of 1,4,5,8-tetraazanaphthalene. Now we consider the predictions for pteridine.

π-Bands: The effective π-orbital energies of azabenzenes and azanaphthalenes can be derived by means of simple perturbation theory. According to this approach[2], the energy change $\Delta\varepsilon_j$ of a naphthalene π-orbital $\psi_j = \Sigma_\mu c_{j\mu}\varphi_\mu$ can be estimated by

$$\Delta\varepsilon = -3.30\,[\Sigma_\varrho c_{j,\varrho}^2]\; -1.01[\Sigma_\omega c_{j,\omega}^2]\ (\mathrm{eV})$$

where $c_{j\mu}$ is the coefficient of the j^{th} Hückel orbital at the μ^{th} site, ϱ denotes the positions of aza-replacement, and ω the neighbouring carbon positions. Using this equation, we obtain for the four highest π-levels of pteridine: 10.6, 10.6, 12.4, and 13.0 eV. This suggests the assignment of the PE peaks at 10.4, 10.9, 12.6, and 13.3 eV. Alternatively, the composite band with maximum at 10.4 eV could be assigned to the two near-degenerate π-levels, but application of the band shape criterion lets us prefer the assignment of the sharp peak at 10.9 eV to a π-level. This assignment of the π-bands is consistent with the results of the more sophisticated procedures (Table 1), although the predicted splitting of the first two π-levels is sensitive to the choice of method.

n-Bands: To estimate the energies of the four possible linear combinations of nitrogen sp² "lone pair" orbitals we apply the Hückel-type model previously presented[5]. The basis orbital energy is taken as $A_\mathrm{n} = -11.0$ eV[5]. The effective cross-term for two sp² orbitals in positions μ and ν is estimated from the splitting of the two n-bands of the corresponding μ,ν-diazanaphthalene:

$$B_{\mu,\nu} = -\tfrac{1}{2}\,[I(\mathrm{n}_+) - I(\mathrm{n}_-)]$$

On the basis of the published PE data and assignments for the pertinent diazanaphthalenes[2,6,12], we obtain (eV)

$B_{1,3} = -0.6$ $\qquad$ $B_{3,5} = -0.4$
$B_{1,5} = +0.6$ $\qquad$ $B_{3,8} = -0.2$
$B_{1,8} = +0.5$ $\qquad$ $B_{5,8} = +0.8$

The 4 × 4 secular problem can now be solved, obtaining the solutions (energies in eV):

$\varepsilon_4 = -9.4,\quad \psi_4 = 0.53\,\mathrm{n}_1 - 0.41\,\mathrm{n}_3 + 0.56\,\mathrm{n}_5 + 0.50\,\mathrm{n}_8$
$\varepsilon_3 = -11.1,\quad \psi_3 = 0.29\,\mathrm{n}_1 - 0.72\,\mathrm{n}_3 - 0.31\,\mathrm{n}_5 - 0.55\,\mathrm{n}_8$
$\varepsilon_2 = -11.7,\quad \psi_2 = 0.80\,\mathrm{n}_1 + 0.52\,\mathrm{n}_3 - 0.28\,\mathrm{n}_5 - 0.11\,\mathrm{n}_8$
$\varepsilon_1 = -11.8,\quad \psi_1 = 0.03\,\mathrm{n}_1 + 0.21\,\mathrm{n}_3 + 0.72\,\mathrm{n}_5 + 0.66\,\mathrm{n}_8$

The general shape of the "wave functions" $\psi_1 - \psi_4$ compares quite well with the structure of the n-type orbitals predicted by the more sophisticated procedures, as exemplified by the contour diagrams in Figure 3.

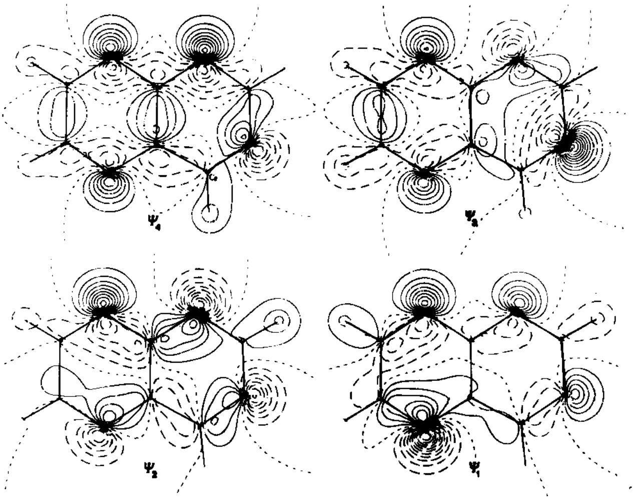

Figure 3. Amplitude contour diagrams of the four nitrogen n-type orbitals of pteridine (**1**) as calculated by MNDO

By subtracting in the PE spectrum of **1** those bands below 14 eV which have been assigned in the previous paragraph to ejection of electrons from one of the four highest occupied π-orbitals, we are left with four bands, namely those close to 9.4, 10.4, 11.4, and 11.8 eV. These bands must be assigned to the four expected n-levels of **1**, in fairly good agreement with the crude HMO estimate, and with the EWMO and HAM/3 results (Table 1).

Concluding Remarks

Our assignment of the π- and n-type PE bands of pteridine indicated in the Tables and Figure 2 is thus supported by a number of experimental and theoretical criteria, but the assignment of the ordering of the five closely spaced levels between 10 and 12 eV is necessarily tentative. Further support for our assignment can be derived from the correlation diagram in Figure 2. Previous experience has shown that, on the average, π-bands are more strongly affected than n-bands by methyl substitution[4,13)]; this seems to support the assignment of band ② (or ③) and band ④ to the two highest occupied π-levels of the pteridine system.

The presence of the so-called non-bonding (n) pairs of electrons at the nitrogen positions enables aza-arenes to act as proton acceptors. However, the proton affinity of pteridine in aqueous solution is masked by fast covalent hydration across the 3,4-bond[14,15)]. The pK_a value of pteridine is unknown, but a value close to 2.6 has been estimated by *Perrin*[14)]. Application of a recently published[16)] structure-reactivity relationship for the pK_a value of aza-arenes suggests that the pK_a

value of pteridine itself is considerably lower than estimated by *Perrin*, namely of the order of −2, with preferred protonation in the pyrimidine ring[17].

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Experimental Part

Compounds **1**−**3** were prepared according to the literature[15,18]. The PE spectra of the pure samples were recorded on a Perkin Elmer PS 18 and on a Leybold Heraeus UPG 200 Spectrometer. For the calibration we used Ar and Xe. A resolution of about 20 meV of the $^2P_{3/2}$ Ar line was obtained. All samples had to be heated between 70 and 100°C.

CAS Registry Numbers
1: 91189 / **2**: 2432215 / **3**: 19899628

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