153. The Ionization Energies of Tetrazinodi(heteroarenes)

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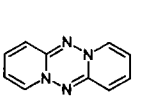
The ionization energies of four [1,2,4,5]tetrazinodi(heteroarenes) of C_{2h} symmetry have been measured by PE spectroscopy. It is found that the first ionization energy is very low (6.2 eV to 6.4 eV) and rather independent of the size and/or topology of the molecules. This is explained, by comparison with the results of a simple MO treatment, as being due to the strong localization of the HOMO (of A_u symmetry) on the [1,2,4,5]tetrazino moiety of the molecules. The PE-spectroscopic data are shown to be in agreement with the UV/VIS- and electrochemical-oxidation data published previously.

Introduction. – Recently, we have reported the synthesis, the electronic spectra [1], and the oxidation potentials [2] of a series of tetrazinodi(heteroarenes). These molecules are of interest as electron donators in charge-transfer complexes and as redox catalysts. In this connection, the ionization energies of these electron donators are important quantities, which now have been determined for four key molecules, using PE spectroscopy.



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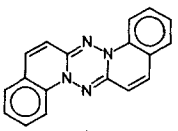

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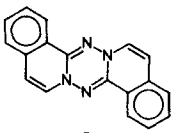

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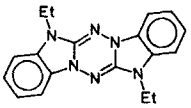

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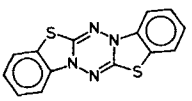

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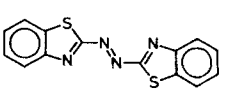

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Experimental Results. – The He(Iα) PE spectra of dipyrido[1,2-*b*:1′,2′-*e*][1,2,4,5]tetrazine (**1**), [1,2,4,5]-tetrazino[1,6-*a*:4,3-*a*′]diquinoline (**2**), [1,2,4,5]tetrazino[1,6-*a*:4,3-*a*′]diisoquinoline (**3**), and of 5,12-diethylbis-(benzimidazolo) [1,2-*b*:1′,2′,-*e*][1,2,4,5]tetrazine (**4**) are shown in *Fig. 1*. The recording temps. were 105° for **1** and 200° for **2**, **3**, and **4**. The ionization energies I_j^m, *i.e.* the positions of the band maxima are collected in the *Table*.

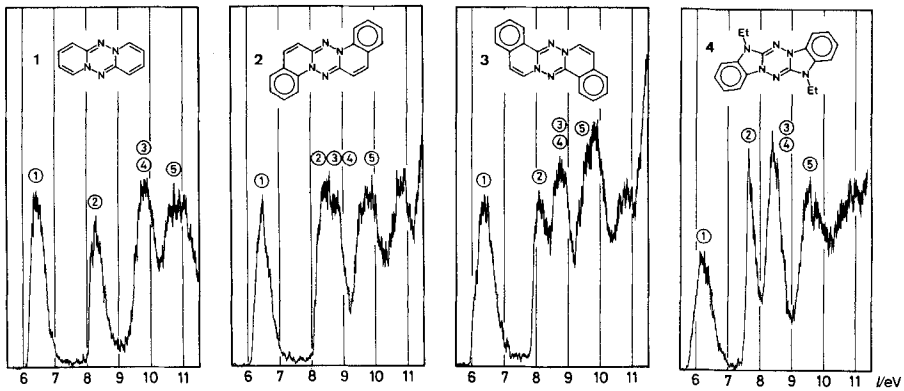

Fig. 1. *He(Iα) PE spectra of the molecules* **1** *to* **4**

Table. *Observed* (I_j^m) *and Calculated* (I_j^{HMO}) *Ionization Energies of the Tetrazinodi(heteroarenes)* **1** *to* **4**. Values in parentheses refer to shoulders. The orbital labels correspond to the assignment based on the HMO-model calculations. The half-wave potentials ($E_{1/2}$) are those for the first and second oxidation step as given in [2].

	1			**2**			**3**			**4**		
	I_j^m/eV	φ_j	I_j^{HMO}/eV	I_j^m/eV	φ_j	I_j^{HMO}/eV	I_j^m/eV	φ_j	I_j^{HMO}/eV	I_j^m/eV	φ_j	I_j^{HMO}/eV
①	6.42[a])	$4a_u$	6.38	6.44[a])	$6a_u$	6.41	6.44[a])	$6a_u$	6.39	6.20	$6a_u$	6.34
②	8.25[a])	$4b_g$	8.14	(8.2_5) 8.4_5[a])	$6b_g$	8.09	8.20[a])	$6b_g$	8.15	7.6_5	$6b_g$	7.96
③	(9.7_5) 9.9[a])	$3a_u$	9.54	(8.6_5)	$5a_u$	8.83	(8.7_5) 8.8_5	$5b_g$	8.70	8.5_0	$5b_g$	8.62
④	(10.0_5)	$3b_g$	9.82	8.8_0	$5b_g$	8.93	(8.9_5)	$5a_u$	8.71	(8.6_5)	$5a_u$	8.75
⑤	(10.6)	$2a_u$	10.83	(9.6)	$4a_u$	9.52	(9.5)	$4a_u$	9.69	(9.5)	$4a_u$	9.35
[2]		$E_{1/2}$/eV			$E_{1/2}$/eV			$E_{1/2}$/eV			$E_{1/2}$/eV	
1. Ox. Step		0.18[b])			0.31[b])			0.21[c])			0.05[b])	
2. Ox. Step		1.47[b])			1.42[b])			(1.22)[c])[d])			1.05[b])	

[a]) Centre of the band or of the band system.
[b]) Solvent: MeCN.
[c]) Solvent: CH_2Cl_2.
[d]) Irreversible oxidation step.

At a temperature of ~ 180°, molecule **5** (Bis(benzothiazolo)[3,2-*b*:3′,2′-*e*][1,2,4,5]-tetrazine) yields a PE spectrum with its first intense maximum at $I_1^m = 9.0$ eV, *i.e.* a position shifted by ~ 2.6 eV towards higher ionization energies than those observed for the first bands in the PE spectra of the molecules **1** to **4**. This spectrum must, therefore, be due to a rearranged (fragmentation) product of **5**, which is quite different from **6**, a known rearrangement product of **5** [1], which yields, at 210° a PE spectrum with maxima at $I_1^m \approx 8.3$ eV (sh), $I_2^m = 8.8_0$ eV, $I_3^m = 9.3$ eV.

Assignment of the PE Spectra. – The X-ray structure analysis of **1** proves that the molecule is flat and of C_{2h} symmetry [1]. One may safely assume that the same is true for the molecules **2** to **4**. Under these conditions, a naive *Hückel* treatment, aided by the usual correlation technique [3], can be expected to provide a sufficiently accurate assignment of the PE spectra.

In a first approximation, one is tempted to use the 'classical' *Streitwieser* parameters [4], *i.e.* $\alpha(\dot{N}) = \alpha + 0.5\beta$ for the N 2p AOs in positions 1 and 4 and $\alpha(\dot{N}) = \alpha + 1.5\beta$ for those in positions 2 and 5 (*cf.* [5]). Using the rough estimates $\alpha = -6.6$ eV and $\beta = -2.7$ eV, derived from the PE-spectroscopic data of unsaturated hydrocarbons [6], yields $\alpha(\dot{N}) = -8.0$ eV and $\alpha(\ddot{N}) = -10.7$ eV. However, the parametrization of the PE spectra of azabenzenes and azanaphthalenes [7] yielded $\alpha(\dot{N}) = -9.9$ eV, corresponding to $\alpha(\dot{N}) = \alpha + 1.2\beta$, notwithstanding the fact that the HMO model used in [7] assumes an *ortho*-transmission coefficient of 0.31. A more reliable check of $\alpha(\dot{N})$ is provided by a comparison of the PE spectra of cycl[3.3.3]azine [8], 1,4,6-triazacycl[3.3.3]azine [9], and of 1,3,4,6,7,9-hexazacycl[3.3.3]azine [10], because of the high symmetry of these molecules. The value $\alpha(\dot{N}) = -9.2$ eV, *i.e.* $\alpha(\dot{N}) = \alpha + 1.0\beta$ lies again below the one derived from the *Streitwieser* parameters [4][5]. As we shall see below, the correlation depicted in *Fig. 2* leads to $\alpha(\dot{N}) \approx -8.8$ eV to -9.6 eV, or $\alpha(\dot{N}) = \alpha + 0.8\beta$ to $\alpha(\dot{N}) = \alpha + 1.1\beta$. We conclude that $\alpha(\dot{N}) = \alpha + 0.75\beta$ is an acceptable compromise between the traditional parameter [4][5] and the somewhat lower ones discussed above, and we have used this value in our calculations.

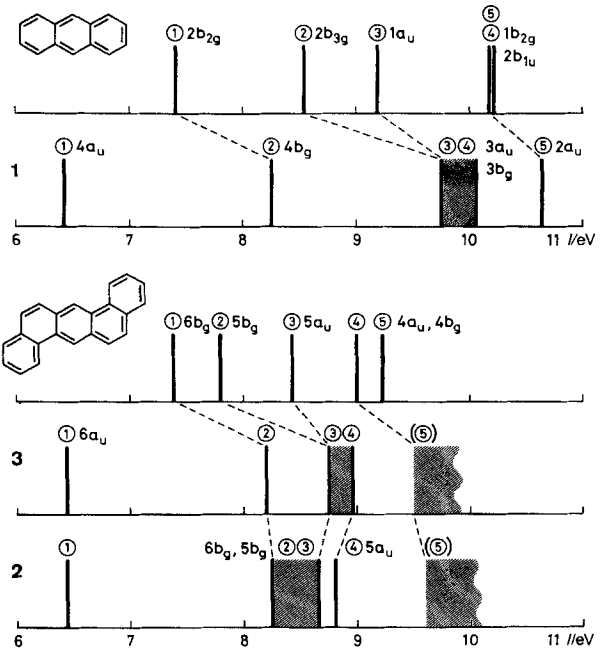

Fig. 2. *Correlation diagrams for the PE spectra of anthracene*↔**1**, *and of dibenz[* a,h*]anthracene*↔**3**↔**2**. The labels refer to C_{2h} (except for anthracene: D_{2h}).

From the PE spectra of aniline [11] and aminonaphthalines [12], *Maier* has derived $\alpha(\ddot{N}H_2) = -10.6$ eV, which corresponds to $\alpha(\ddot{N}H_2) = \alpha + 1.5\beta$, *i.e.* in complete agreement with the original *Streitwieser* approximation [4][5]. A somewhat lower value $\alpha(\ddot{N}H_2) = \alpha + 2\beta$ has been proposed by *Kovač* [13]. An analysis of the correlations presented in *Fig. 2* (using again the HMOs of the hydrocarbons as a basis for first-order perturbation calculations) does not yield a consistent set of $\alpha(\ddot{N})$ values, but suggests that it should lie within the limits $\alpha(\ddot{N}) = \alpha + 1.2\beta$ to $\alpha + 1.8\beta$. In the following, we have used $\alpha(\ddot{N}) = \alpha + 1.5\beta$ for the N centres in positions 2 and 5 of **1**, **2**, and **3**.

For the N centres of the benzimidazole moieties of **4**, the influence of the Et group has to be accounted for. *Maier* has obtained $\alpha(\ddot{N}Me_2) = -8.7$ eV which is 1.9 eV higher than $\alpha(\ddot{N}H_2) = -10.6$ eV. From this, we deduce that $\alpha(\ddot{N}HEt)$ -9.5 to -9.4 eV is reasonable, which suggests that $\alpha(\ddot{N}Et) = \alpha + \beta$ should be used in the calculation for **4**.

Finally, a reduced resonance integral $\beta(C\text{–}N) = 0.8\beta$ has been assumed for the interaction of a N centre with a neighbouring C centre, all other resonance integrals being standard.

Comparing the orbital sequences calculated for **1**, **2**, and **3** with those of anthracene (**7**) and dibenz[*a,h*]anthracene (**8**) suggests that the replacement of four C-atoms by N-atoms will not lead to orbital crossings. Accordingly, the bands of the PE spectra of **7** and **8** [14] can be matched with those of **1**, **2**, and **3** as shown in *Fig. 2*.

Note that the HOMOs of **1**, **2**, and **3** correspond to the LUMOs of **7** and **8**, respectively. Interpreting the ionization energy shifts $I_2^m(\mathbf{1}) - I_1^m(\mathbf{7}) = 0.84$ eV and $I_2^m(\mathbf{2}) - I_1^m(\mathbf{8}) \approx I_2^m(\mathbf{3}) - I_1^m(\mathbf{8}) \approx 0.85$ eV in terms of a perturbation calculation based on the HMOs of **7** and **8** leads to a value $\alpha(\ddot{N}) \approx -8.8$ to -9.6 eV or $\alpha(\ddot{N})\ \alpha+(0.8$ to $1.1)\beta$, in support of the value used in the computations. However, no valid conclusions can be derived with regard to the value of $\alpha(\ddot{N})$, except that $\alpha(\ddot{N}) = \alpha+1.5\beta$ is compatible with the PE-spectroscopic results.

In *Fig. 3* are shown the diagrams of the HOMOs of the molecules **1** to **4**. All four HOMOs are practically non-bonding, all are of A_u symmetry (within C_{2h}) and all are strongly localized on the [1,2,4,5]tetrazine moiety. A direct consequence of the latter property is that expansion of the parent π system of **1** has no significant effect on I_1^m in the case of **2** and **3** and leads only to a small shift of ~ 0.2 eV towards lower energies in the case of **4** (*cf. Table*).

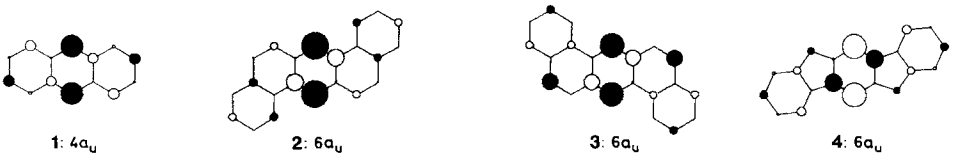

Fig. 3. *Diagrams of the HMOs of* **1** *to* **4**

For an assignment and a rationalization of the observed ionization energies, we use the 20 I_j^m values listed in the *Table* and the corresponding $\varepsilon_j = \alpha+x_j\beta$ values obtained from our HMO model. These yield the regression

$$I_j^{HMO}/\text{eV} = (6.246 \pm 0.078) + (2.934 \pm 0.0090)x_j \qquad (1)$$

with a standard error $s = 0.169$ eV and a correlation coefficient $r = 0.991$. Because regression (*1*) refers to four independent sets of ordered data, the correlation is highly significant [15]. The I_j^{HMO} values obtained from the HMO treatment, *via* (*1*), are given in the *Table*, together with the orbital labels φ_j.

Discussion. – The agreement between I_j^m and I_j^{HMO} (always within the 95% confidence limits of I_j^{HMO}), strongly suggests that the proposed assignment of the bands is reliable, with the possible exception of the sequence of strongly overlapping bands, *e.g.* ③, ④ of **1** and **3**, or ②, ③ of **2**. Our model does not take into account σ orbitals, in particular the lone-pair orbitals n_N of the N atoms in positions 1 and 4 of the tetrazine moiety. However, the n_N^{-1} bands are expected at ionization energies above ~ 9.5 to 10 eV on the basis of previous results observed for [1,2,4,5]tetrazine [7] and of aza compounds [8–10].

The LUMO and the LUMO+1 of the molecules **1** to **4** belong to the irreducible representations A_u and B_g, respectively, according to the results of the HMO calculations. Therefore, the transition LUMO←HOMO is forbidden, whereas the LUMO+1 ←HOMO transition is allowed, in agreement with the UV/VIS-spectroscopic results and the PPP calculations reported in [1]. (For obvious reasons, no relevance can be attached to the corresponding HMO excitation energies.)

The half-wave potentials $E_{1/2}$ for the first and second oxidation step of **1** to **4**, taken from [2], are given in the *Table*. (The solvents used were MeCN for **1**, **2**, and **4**, and CH_2Cl_2 for **3**, which is insoluble in MeCN.) The almost equal and rather low values $E_{1/2} \approx 0.2$ to

0.3 V (*vs.* Ag/AgCl/3.5M KCl) for the first oxidation step of the molecules **1**–**3** reflect the low ionization energies I_1^m, which are the same for **1**, **2**, and **3**, well within the limits of error. On the other hand, the lower half-wave potential $E_{1/2} = 0.05$ V for the first oxidation step of **4** is matched by the lower value $I_1^m = 6.20$ eV.

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