with aqueous NaOH. The chloroform layer was combined with the ether extracts and dried. Removal of the solvent gave acetophenone (2.43 g, 20 mmol, 20%) and 1,4-diphenyl-1,4-butanedione (9.06 g, 38 mmol, 76%): mp 145.5–147 °C. The aqueous NaOH solution was acidified with HCl, and a white solid precipitated (0.22 g, 0.70 mmol, 1.4%): mp 122–124 °C. It was identified as diphenacyl sulfone (lit.[7c] mp 121–122 °C).

Reaction of Phenacyl Bromide with Rongalite in the Presence of Molecular Sieves. Phenacyl bromide (1.99 g, 10 mmol) was dissolved in DMF (15 mL) that had been dried over 4A molecular sieves. The solution was stirred with Rongalite (1.54 g, 10 mmol) and 4A molecular sieves (1.0 g) for 24 h. Water (100 mL) was added, and a white solid was removed. The solution was extracted with diethyl ether (4 × 30 mL). Workup as above gave acetophenone (0.216 g, 1.8 mmol, 18%), 1,4-diphenyl-1,4-butanedione (0.89 g, 3.7 mmol, 74%), and diphenacyl sulfone (0.006 g, 0.02 mmol, 0.4%).

Reaction of Phenacyl Chloride or Bromide with Rongalite and Sodium Iodide in the Presence of Molecular Sieves. Phenacyl chloride (1.54 g, 10.0 mmol) or phenacyl bromide (1.99 g, 10 mmol) was dissolved in DMF (15 mL) that had been dried over 4A molecular sieves. This was stirred with Rongalite (1.54 g, 10 mmol), sodium iodide (0.15 g, 1.0 mmol), and 4A molecular sieves (1.0 g) for 24 h in a covered flask. Workup gave acetophenone (0.22 g, 1.8 mmol, 18%), 1,4-diphenyl-1,4-butanedione (0.90 g, 3.8 mmol, 76%), and diphenacyl sulfone (0.01 g, 0.04 mmol, 0.8%).

Reaction of Phenacyl Bromide with Rongalite and Sulfur Dioxide. Phenacyl bromide (1.99 g, 10 mmol) was added to a stirred solution of sulfur dioxide prepared by passing SO_2 into dry DMF (30 mL) for 30 min. Rongalite (3.01 g, 20 mmol) was added, and the solution was stirred for 18 h at room temperature. Workup as above gave diphenacyl sulfone (0.844 g, 2.8 mmol, 56%) and acetophenone (0.36 g, 3.0 mmol, 30%).

Reaction of 4-Phenylphenacyl Bromide with Rongalite. Procedure A. 4-Phenylphenacyl bromide (0.308 g, 1.12 mmol), Rongalite (0.345 g, 2.24 mmol), and potassium bicarbonate (1.1 g, 11 mmol) in DMF–water (11 mL each) gave 4-acetylbiphenyl (0.144 g, 0.734 mmol, 66%): mp 120.4–121.5 °C (heptane) (lit.[51] mp 120.5 °C). The ^{1}H NMR and IR spectra were identical with those previously reported.[52] The material that was insoluble in heptane was 1,4-bis(4-phenylphenyl)-1,4-butanedione (0.043 g, 0.11 mmol, 20%): mp 264–266 °C (benzene) (lit.[53] mp 260–263 °C); IR (KBr) 1680 (s), 1605 (s) cm^{-1}. The ^{1}H NMR spectrum was essentially identical with that reported previously.[29g] **Procedure B.** 4-Phenylphenacyl bromide (0.308 g, 1.12 mmol) and Rongalite (0.345 g, 2.24 mmol) gave 4-acetylbiphenyl (0.081 g, 0.41 mmol, 51%) and 1,4-bis(4-phenylphenyl)-1,4-butanedione (0.063 g, 0.16 mmol, 40%). The latter was identical with the material obtained by the Friedel–Crafts reaction of biphenyl and succinyl dichloride.

Reaction of 4-Phenylphenacyl Bromide with Rongalite and Sulfur Dioxide. 4-Phenylphenacyl bromide (1.42 g, 5 mmol) was added to a stirred solution of sulfur dioxide prepared by passing SO_2 into dry DMF (30 mL) for 30 min. Rongalite (1.54 g, 10 mmol) was added, and the solution was stirred for 18 h at room temperature. Workup as above gave 4-acetylbiphenyl (0.20 g, 20 mmol, 20%), the dione (0.244 g, 1.25 mmol, 25%), and bis(4-phenylphenacyl) sulfone (0.59 g, 1.3 mmol, 52%): mp 208–210 °C; IR (KBr) 1695 (s), 1288 (s), 1140 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.1–7.4 (m, 18 H, Ph), 5.1 (s, 4 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 59.9, 127.3, 127.6, 128.6, 129.0, 129.5, 134.3, 147.4, 148.5, 188.9. Anal. Calcd for $C_{28}H_{22}O_4S$: C, 73.99; H, 4.88. Found: C, 73.84; H, 4.81.

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(52) Sadtler Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, PA; NMR 6582 M, IR 22092.

(53) Private communication from Professor Howard Alper. This value is a correction of that reported in ref 29g.

PE Spectra of Disubstituted 1,2,4,5-Tetrazines[†]

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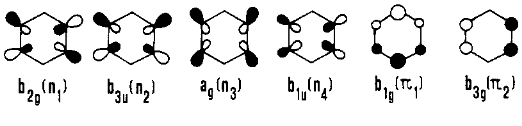
The PE spectra of 21 *s*-tetrazines, disubstituted either with electron-donating groups or with electron-withdrawing groups, have been recorded. Their interpretation is based on the comparison of the spectra using band shapes as a guide and on the results of HAM/3 calculations. The very broad band between 10 and 11 eV is ascribed to the failure of the one-electron picture. In addition electrochemical reduction potentials have been compared with calculated HAM/3 electron affinities. Our investigations reveal that the HOMO of the alkylamino derivatives (except **9**) has π character, in contrast to the *s*-tetrazines with alkyl or electron-withdrawing groups.

Scheme I



In 1,2,4,5-tetrazines (*s*-tetrazines) the lowest unoccupied MO (LUMO), a low-lying π^* MO, strongly determines the properties of these compounds. It is mainly responsible for the deep color ($\pi^* \leftarrow n$),[2,3] the good electron-acceptor properties[4,5] and the high reactivity as a dienophile with inverse electron demand.[6-8] The highest occupied MO's seem to play a less important role. Although the lone pairs

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[†] Dedicated to Professor Hans Bock on the occasion of his 60th birthday.

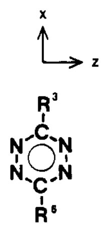
interact considerably with each other,[9] and thus the corresponding energy levels are widely split, the first ionization energy of *s*-tetrazine (**1**) (9.72 eV)[9] is still rather high due to the high electronegativity of nitrogen. Despite this high value, we thought it worthwhile to investigate the possibility of influencing the ionization energy and the level ordering by attaching π-electron-donating groups and electron acceptors to *s*-tetrazine. The method of choice for investigating such effects is the He I photoelectron (PE) spectroscopy.

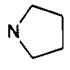
Before discussing the PE spectra we will review briefly the electronic structure of **1**. The four lone pairs on the four nitrogen atoms in **1** interact considerably through-space and through-bond, giving rise to the four linear combinations $b_{2g}(n_1)$, $b_{2u}(n_2)$, $a_g(n_3)$, and $b_{1u}(n_4)$ which are shown schematically in Scheme I. Together with these four lone-pair orbitals MO calculations predict two π-MO's (b_{1g} and b_{3g}) in the outer valence region.

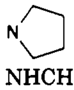
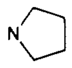
PE spectroscopic investigations on **1**–**3**[9,10] as well as calculations of different degrees of sophistication[9–13] have shown that the first band is due to the ionization from $b_{2g}(n_1)$ using Koopmans' approximation. The corresponding band in the PE spectrum of **1** (9.72 eV) is well separated from five very close lying bands between 12 and 14 eV. Due to the strong overlap of these ionic states, an empirical assignment has been undertaken by comparing the first PE bands of **1** with those of 3,6-dimethyl-*s*-tetrazine (**2**) and 3,6-diphenyl-*s*-tetrazine (**3**),[10] assuming that a methyl and a phenyl group affects the ionic states differently because they arise from lone pairs and π-MO's, respectively. This comparison has led to a consistent assignment of the PE bands of **1**–**3**, which differs somewhat from that derived from nonempirical calculations.[13] As anticipated, a methyl group turned out to be a weaker π donor than a phenyl group. Unfortunately the phenyl groups in **3**, however, give rise to strongly overlapping bands in its PE spectrum and thus a correlation between the higher ionization states **1**–**3** is hampered. We expect to observe much stronger effects with small but typical π donors and acceptors like OCH_3 and $N(CH_3)_2$ groups on one side and CN and CF_3 groups on the other. In this paper we report on the He I photoelectron (PE) spectra of the *s*-tetrazines **1**–**5** and **7**–**22** (Scheme II).

Further information about the HOMO and LUMO of these compounds can be obtained by cyclic voltammetric studies. This paper summarizes the measured half-wave oxidation and reduction potentials $E_{1/2}$ of **1**–**5** and **7**–**16** and correlates the experimental findings with the results of calculations.

Scheme II



	$R^3 = R^6$		$R^3 = R^6$
1	H	**10**	
2	CH_3		
3	C_6H_5		
4	OCH_3	**11**	
5	SCH_3		
6	NH_2	**12**	CO_2CH_3
7	$NHCH_3$	**13**	Cl
8	$N(CH_3)_2$	**14**	F
		15	CN
9		**16**	CF_3

	R^3	R^6
17	$NHCH_3$	OCH_3
18	$N(CH_3)_2$	OCH_3
19		OCH_3
20	$NHCH_3$	SCH_3
21	$N(CH_3)_2$	SCH_3
22		SCH_3

PE Spectra

As representative examples we show in Figure 1 the PE spectra of **4**, **5**, **8**, **13**, **15**, and **16**. The recorded ionization energies of **1**–**5** and **7**–**22** are collected in Table I. A comparison between the ionization energies (see also Figure 2) shows that the spectra can be subdivided into two classes: those that are similar to the PE spectra of **1** and **2**, i.e. one Gaussian-type band is clearly separated from other bands, and those that show two close lying bands in the low energy region. To the first group belong the PE spectra of **14**–**16**, to the second class all the others.

To interpret the spectra, we proceed in two ways: (i) empirically by comparison and by assuming that the strongly electron donating substituents influence the π bands stronger than the σ bands and (ii) by comparing the recorded vertical ionization energies, $I_{v,j}$, with the calculated HAM/3 energies.

We start our discussion with the PE spectrum of **4**. We find two close lying bands in the low energy region. The first feature can be looked at as a result of the strong overlap of a Gaussian-like band and a band with a relatively steep onset. We ascribe the Gaussian-like band to the ejection of electrons from the n_1 orbital, the steep onset to the ionization from π_1. Similarly we assign band 3 to n_2 and the steep band 4 to a π band. A comparison between the first PE bands of **2** and **4** shows that the methoxy group influences the π bands strongly while the n bands remain essentially constant (see Figure 2). This behavior is anticipated from the σ_I and σ_M values of a methoxy substituent.[14]

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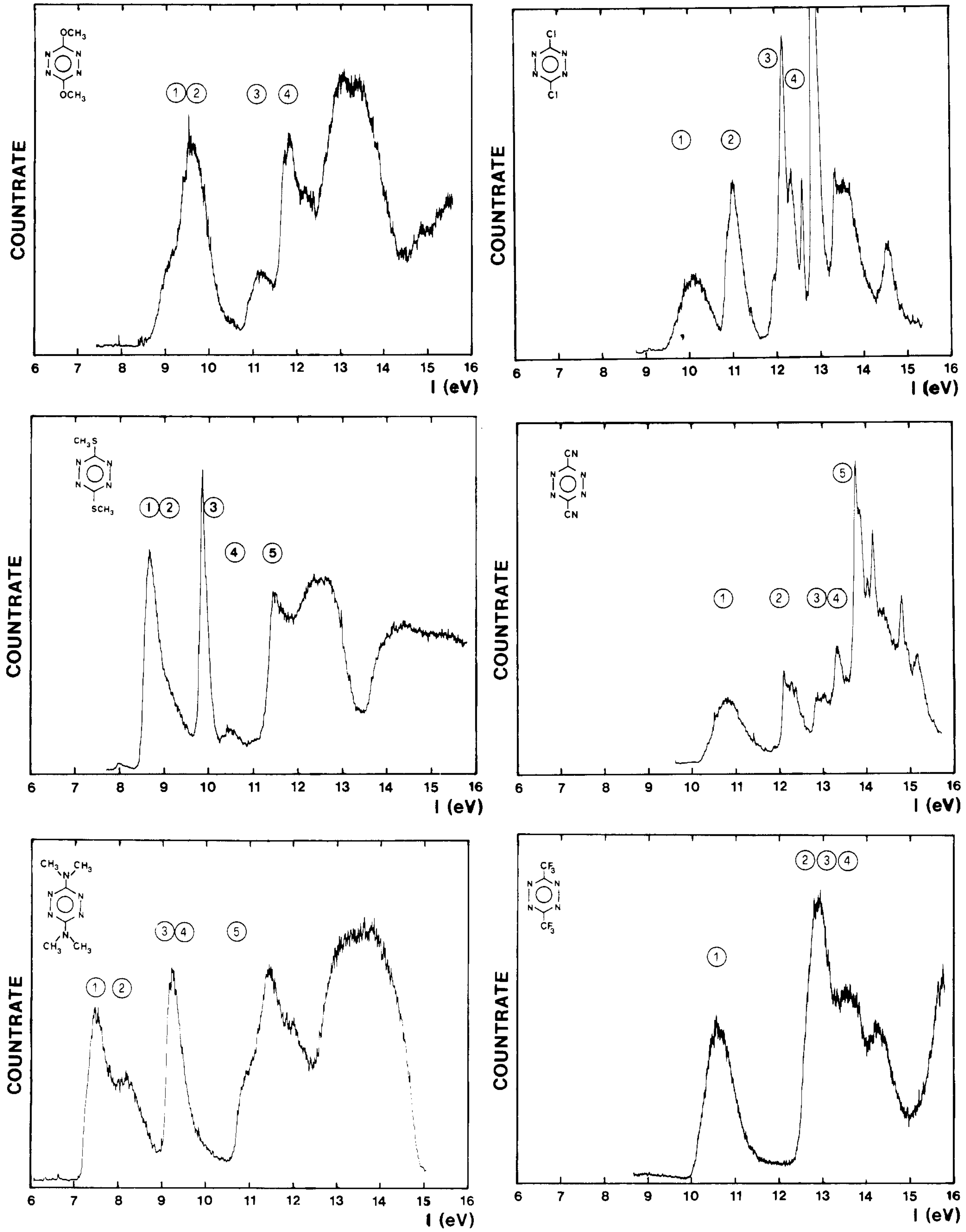

Figure 1. He I PE spectra of 4, 5, 8, 13, 15, and 16.

The comparison of the PE data of 7 and 8 with those of 2 and 4 is shown in Figure 2. This comparison suggests the assignment of two close lying bands in the low energy region followed by another set of two close lying bands. In both cases a π band is close to an n band. In the case of the first two bands this can be seen by looking at the first two PE bands of 8. Here a steep band is followed by a Gaussian-like band. For band 3 and 4 this is less evident, since in all examples investigated they remain closely situated. The fifth band, a shoulder around 11 eV in the

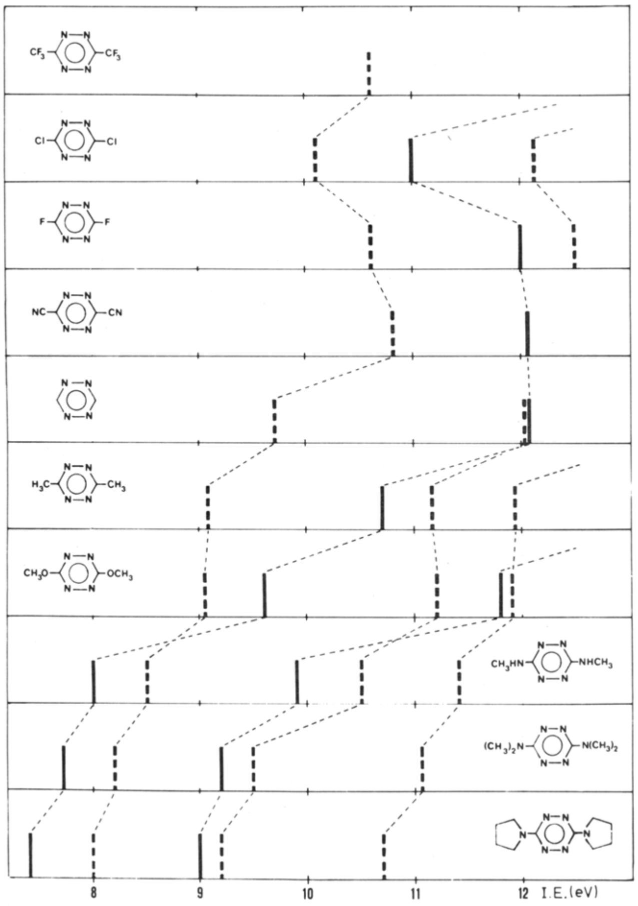

Figure 2. Correlation between the first PE bands of the PE spectra of **1**, **2**, **4**, **7**, **8**, **11**, **13**, **14**, **15**, and **16**. The π bands are marked by full bars, the n bands by broken bars.

PE spectra of **7**, **8**, **9**, **10**, and **11** is assigned to the ionization from the n_3 orbital.

To clarify the assignment of bands 3 and 4 of the PE spectra of **5** and **7–11**, we also investigated the PE spectra of the *s*-tetrazines **17–22** with different substituents at the 3 and 6 positions. As examples, we show in Figure 3 the PE spectra of **17** and **22**. A comparison of the first two bands of the PE spectra of **4** and **17** yields a shift of 0.9 eV for the π_1 band and 0.5 eV for the n_1 band. If we assume a similar shift for bands 3 and 4 in the PE spectrum of **17** with respect to that of **4**, we predict ionization energies of 10.9 eV (π_2) and 10.7 eV (n_2). A similar comparison between the first PE bands of **4** and those of **18** and **19**, respectively, predicts two close lying bands between 10 and 11 eV (see Figure 4).

The PE spectra of **17–19** show in the range between 10 and 11 eV one sharp peak strongly overlapping a broad band (see Figure 3). These results strengthen our assignment of two close lying bands (n_2, π_2) between 10 and 11 eV in the PE spectra of **17–19**. Our assignment is furthermore supported by the correlation of the first four PE bands of **17–19** with the corresponding bands of **7**. The curiously different width and intensity of the two bands in question might be rationalized by assuming that one band is split into several components and thus the one-electron picture breaks down.[15] Such a splitting at such a low energy would be rather interesting. Usually it is encountered at higher energies.[16] Of particular importance could be the quasi-free-internal rotation of the substituents in **4–11** and **17–22**.

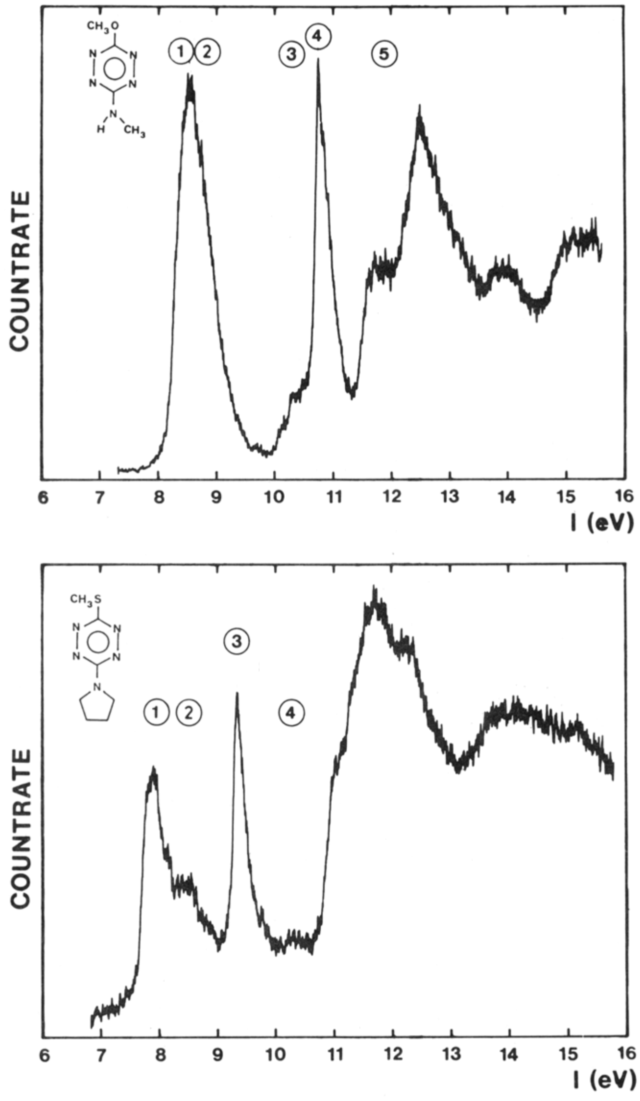

Figure 3. He I PE spectra of **17** and **22**.

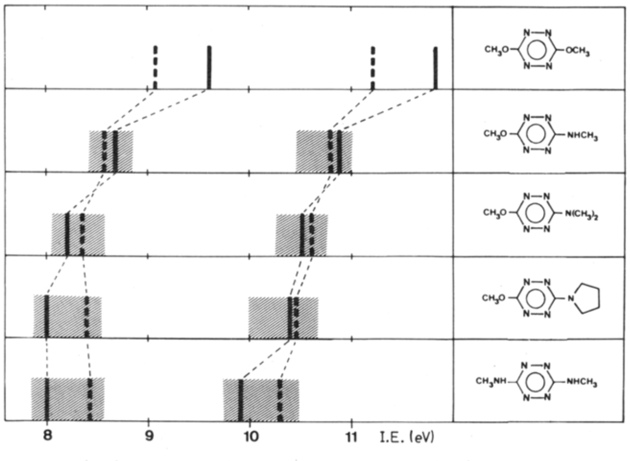

Figure 4. Correlation between the first PE bands of **17–19** with those of **4** and **7**.

Similar arguments as in the preceding paragraph allow us to correlate the PE spectra of **5**, **7**, **8**, and **11** with **20–22**. This comparison leads us to expect two bands (π_2, n_2) between 9 and 10.5 eV for **20–22** if we assign band 4 to the feature at 10.4 eV in the PE spectrum of **5** (see Figure 1).

The comparison of the shape of the first band in the PE spectra of **1** with those in **13–16** shows in all cases the same

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Table I. Comparison between the Measured and Calculated Vertical Ionization Energies, $I_{v,j}$, of 1–5 and 7–22 (Values in eV)

compd	band	$I_{v,j}$	assignment	I(HAM/3)
1	1	9.72	$b_{2g}(n_1)$	9.08
	2 3	12.05	$b_{1g}(\pi_1)$ $b_{3u}(n_2)$	11.89 11.85
	4	12.78	$a_g(n_3)$	12.96
	5	13.36	$b_{1u}(n_4)$	13.10
	6	13.5(?)	$b_{3g}(\pi_2)$	13.42
	7	15.84	$b_{2u}(\pi_3)$	15.50
2	1	9.08	$b_{2g}(n_1)$	8.28
	2	10.72	$b_{1g}(\pi_1)$	10.55
	3	11.15	$b_{3u}(n_2)$	11.08
	4	11.98	$a_g(n_3)$	12.10
	5	≈12.0	$b_{1u}(n_4)$	12.16
	6	12.66	$b_{3g}(\pi_2)$	12.54
	7	13.50	$b_{2u}(\pi_3)$	13.41
3	1 2	8.7	$b_{2g}(n)$ $b_{1g}(\pi)$	
	3 4 5	9.4	$b_{3g}(\pi)$ $a_u(\pi)$ $b_{2u}(\pi)$	
	6	≈9.6	$b_{3u}(n)$	
	7 8	≈11.2	$a_g(n)$ $b_{1g}(\pi)$	
4	1	9.05	$a_g(n_1)$	8.09
	2	9.6	$b_g(\pi_1)$	9.23
	3	11.2	$b_u(n_2)$	10.77
	4	11.8	$a_u(\pi_2)$	11.45
5	1	8.63	$b_g(\pi_1)$	
	2	9.0	$a_g(n_1)$	
	3	9.79	$a_u(\pi_2)$	
	4	10.4	$b_u(n_2)$	
7	1	8.0	$b_g(\pi_1)$	7.62
	2	8.5	$a_g(n_1)$	7.57
	3	9.9	$a_u(\pi_2)$	9.57
	4	10.5	$b_u(n_2)$	10.23
8	1	7.5	$b_{1g}(\pi_1)$	7.40
	2	8.2	$b_{3g}(n_1)$	7.37
	3	9.2	$b_{3u}(\pi_2)$	9.24
	4	9.5	$b_{2u}(n_2)$	10.03
	5	11.05	$b_{1u}(n_3)$	11.04
9	1 2	8.8	n_1 π_1	7.82 8.87
	3	10.2	π_2	10.15
	4	10.6	n_2	10.67
10	1	7.7	$b_{1g}(\pi_1)$	7.27
	2	8.2	$b_{2g}(n_1)$	7.10
	3	9.3	$b_{3g}(\pi_2)$	8.96
	4	9.4	$b_{3u}(n_2)$	9.87
11	1	7.2	$b_{1g}(\pi_1)$	7.10
	2	8.0	$b_{2g}(n_1)$	7.01
	3	9.0	$b_{3g}(\pi_2)$	8.92
	4	9.2	$b_{3u}(n_2)$	9.77
	5	10.7	$a_g(n_3)$	10.88
12	1	9.6	n_1	8.51
	2	11.0	n(O)	10.17 10.33
13	1	10.1	n_1	
	2	11.0	π_1	
	3	12.16	n_2(?)	
14	1	10.6	$b_{2g}(n_1)$	9.89
	2	12.0	$b_{1g}(\pi_1)$	12.07
	3	12.5	$b_{3u}(n_2)$	12.77
	4	13.5	$b_{3g}(\pi_2)$	14.19
15	1	10.80	$b_{2g}(n_1)$	9.55
	2	12.08	$b_{1g}(\pi_1)$	11.66
	3	12.85	$b_{3u}(n_2)$	12.37
	4	13.4	$b_{1u}(\pi_{CN})$	12.61
16	1	10.6	$b_{2g}(n_1)$	9.75
	2 3	12.9	$b_{3u}(n_2)$ $b_{1g}(\pi_1)$	12.57 12.69
	4	13.6	$a_g(n_3)$	13.52
17	1 2	8.55	π_1 n_1	8.30 7.80
	3 4	10.85	π_2 n_2	10.59 10.67
18	1	8.25	π_1	8.13
	2	8.5	n_1	7.66
	3	10.5	π_2	10.34
	4	≈10.6	n_2	10.44
19	1	8.1	π_1	7.96
	2	8.5	n_1	7.47
	3	10.4	π_2	10.12
	4	≈10.6	n_2	10.25
20	1	8.3	π_1	
	2	8.6	n_1	
	3	9.8	π_2	
	4	≈9.9(?)	n_2	
21	1	8.0	π_1	
	2	8.5	n_1	
	3	9.4	π_2	
22	1	7.9	π_1	
	2	8.4	n_1	
	3	9.3	π_2	

feature, namely, a broad Gaussian-like shape that suggests assignment of the first band in all four cases to the same origin, i.e., the ionization from n_1. A comparison between the shape of the first band and the second band in the PE spectra of **13**–**15** suggests assignment of the second band to an ionization from a π MO. These arguments are in line with the observation that the first π band in the PE spectra of **14** and **15** shows about the same ionization energy as in **1**. This result is anticipated from the perfluoro effect[17] in the case of **14** and from the observation that the acceptor properties of π^* of the CN group are nearly cancelled by the π donation.[18]

Our empirical assignment discussed so far for **1**, **2**, **4**, and **7**–**16** is summarized in Figure 2. It is strongly supported by a HAM/3[19] calculation (see Table I). We have chosen this method since it predicts very closely the n and π bands of a number of N-heterocycles.[20] Other semiempirical methods (MINDO/3, MNDO) do not reproduce the level pattern shown in Figure 2. The geometrical parameters adopted for our calculations were those reported in the literature for **1**–**4** and **9**.[21,22] The main difference between the assignment predicted by HAM/3 (see Table I) and that adopted in Figure 2 is the sequence of bands 1 and 2 in **7**–**11**. The adopted assignment (π_1) for the first band is based on the band shape as discussed above. It is furthermore strongly supported by ESR studies of the radical cations.[5] In the case of $\mathbf{1}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, $\mathbf{9}^{\bullet+}$, and $\mathbf{13}^{\bullet+}$, a σ radical is found with the SOMO confined to the four nitrogens. For $\mathbf{8}^{\bullet+}$, $\mathbf{10}^{\bullet+}$, and $\mathbf{11}^{\bullet+}$, however, a π radical is observed

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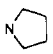
Table II. HAM/3 Electron Affinities (EA) of *s*-Tetrazines 1–16 Together with Half-Wave Reduction and Oxidation Potentials in Acetonitrile

	$R^3 = R^6$	EA/eV	$-E_{1/2}/V^a$	$+E_{1/2}/V^a$
16	CF_3	+2.65	0.45	
15	CN	+2.51	0.31	
14	F	+1.64	0.52	
13	Cl		0.56^b	
12	CO_2CH_3	+2.40	0.79 $(0.83)^c$	
5	SCH_3		1.03^b	
4	OCH_3	+0.82	1.13^b	
3	C_6H_5		1.21^b $(1.24)^c$	
9		+0.79	1.25^b	
2	CH_3	+0.67	1.32^b $(1.36)^c$	
1	H	+0.63	1.16^b $(1.20)^c$	
10		+0.44	1.47^b	0.75^b
8	$N(CH_3)_2$	+0.53	1.55^b	0.71^b
7	$NHCH_3$	+0.34	1.51^b	
6	NH_2	+0.11	*d*	
11		+0.59	1.60^b	0.66^b

[a] $E_{1/2}$ values corrected to ferrocene, $E_{1/2} = 0.0906$ V. [b] Reference 5. [c] Reference 4. [d] The insolubility of **6** prevented the measurement.

with the unpaired electron mainly localized at the amine nitrogens.

Cyclic Voltammetric Measurements

Half-wave reduction potentials of **1**[4,23] and various substituted *s*-tetrazines, mainly 3,6-diaryl derivatives, have been reported.[4] In connection with ESR studies of *s*-tetrazines radical ions, we also carried out cyclic voltammetric measurements of **1–11** and **13**.[5] The $-E_{1/2}$ and $+E_{1/2}$ values obtained, together with additional data of the *s*-tetrazines **12** and **14–16**, are given in Table II. In agreement with published results,[4] the cyclic voltammograms of all *s*-tetrazines studied exhibit a clean reversible process with a wave slope of about 60–70 mV, which indicates a kinetically uncomplicated, diffusion-controlled one-electron reduction to the corresponding radical anions. The $-E_{1/2}$ values of **1**, **2**, **3**, and **12** agree well with published data.[4] The set of half-wave reduction potentials in Table II represents a large experimental sequence of relative LUMO energies in solution. One expects a correlation between experimental half-wave reduction potentials $E_{1/2}$ and calculated electron affinities (EA). The latter ones were calculated by using the HAM/3 procedure.[19] The calculations predict two close lying MO's belonging to the irreducible representations A_u and B_{2u}. In all compounds calculated (see Table II) the LUMO belongs to A_u except for **15**, for which the LUMO is predicted to belong to B_{2u} symmetry. The energy difference between the two lowest unoccupied MO's in **15** is, however, small (0.5 eV). ESR investigations on $\mathbf{15}^{\bullet-}$[24] rule out $^2B_{2u}$ for the ground state of $\mathbf{15}^{\bullet-}$ but favor ^2A_u.[25] The calculated EA (eV) values can be linearly correlated with the recorded $E_{1/2}$ (V) values according to (1).

$$-E_{1/2} = -0.5\text{EA} + 1.6 \qquad (1)$$

Solution-phase $+E_{1/2}$ values can be correlated with vapor-phase first ionization potentials provided the half-wave oxidation potential refers to a reversible one-electron oxidation process. Excellent linear correlations of this kind have been found for various groups of compounds.[26] In our series only the cyclic voltammograms of **8**, **10**, and **11** display a clean reversible one-electron oxidation process. All other *s*-tetrazines show either no oxidation or an irreversible oxidation process (e.g. **7**) under the experimental conditions used. The measured $+E_{1/2}$ values of **8**, **10**, and **11** reflect exactly the order of their first PE ionization potentials (Table II), which correspond to the ejection of electrons from a π HOMO, $b_{1g}(\pi_1)$, of these compounds.

Conclusions

Our studies reveal that the electronic structure of *s*-tetrazine can be strongly influenced by electron-donating substituents. It is shown that the ionization energy of *s*-tetrazine and that of a dialkylamino derivative differs by 2.5 eV. Additionally we also find a change in the symmetry of the HOMO. In **1** and **2** the HOMO is an antibonding linear combination of the four lone pairs on the nitrogen atoms (b_{2g}, n_1). In the alkylamino derivatives, however, the HOMO is a π-MO (b_{1g}, π_1). This change in the symmetry might have consequences in the reactivity toward electrophiles such as metal fragments. In the case of **1–4** we expect "side-on" metal complexes; for **8–11** we anticipate π complexes. The comparison of the bands of **1** with those of **13–16** shows that the inductive effect of the electron-withdrawing group on n_1 is relatively small.

Experimental Section

Materials. Compounds **1**,[27] **2**,[28] **3**,[29] **4**,[30] **5**,[31] **6**,[32] **7**,[5] **8**,[33,34] **9**,[5] **10**,[5] **11**,[5] **12**,[27a] **13**,[35] **14**,[36] **15**,[37] and **21**[33] were obtained as described in the literature. Compound **16** was kindly supplied by Prof. Dr. G. Seitz.

General Procedure for Preparation of 17–20 and 22. To a solution of **4**[30] (711 mg, 5 mmol) or of **5**[31] (871 mg, 5 mmol) in methanol (≈30 mL) was added amine (methylamine, dimethylamine, or pyrrolidine in methanol, 7.5 mmol), and the resulting solution was heated at reflux for approximately 2 min. At this time TLC (methylene chloride) showed the absence of starting material. Then the mixture was evaporated. The crude product was recrystallized or, if necessary, purified by chromatography on silica gel (methylene chloride); yield 75–90%.

3-Methoxy-6-(methylamino)-1,2,4,5-tetrazine (17): red crystals from diethyl ether and petroleum ether, mp 99–100 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz), δ 2.91 (d, $^3J = 5$ Hz, 3 H, NCH_3), 4.04 (s, 3 H, OCH_3), 7.99 (br s, 1 H, NH). Anal. Calcd for $C_4H_7N_5O$: C, 34.04; H, 5.00; N, 49.62. Found: C, 34.05; H, 5.05; N, 49.91.

3-(Dimethylamino)-6-methoxy-1,2,4,5-tetrazine (18): red crystals from methanol, mp 30–31 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz) δ 3.22 (s, 6 H, NCH_3), 4.05 (s, 3 H, OCH_3). Anal. Calcd for $C_5H_9N_5O$: C, 38.70; H, 5.85; N, 45.14. Found: C, 38.41; H, 6.11; N, 45.18.

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(25) Also **16** generates a ^2A_u radical anion on reduction with potassium in dimethoxyethane: $a(N) = 5.25$ (4N), $a(F) = 1.08$ G (6F); $g = 2.0043$.

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3-Methoxy-6-pyrrolidino-1,2,4,5-tetrazine (19): red crystals from diethyl ether and petroleum ether, mp 74–75 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz) δ 2.01 (m, 4 H, CH_2), 3.57 (m, 4 H, NCH_2), 4.05 (s, 3 H, OCH_3). Anal. Calcd for $C_7H_{11}N_5O$: C, 46.40; H, 6.12; N, 38.65. Found: C, 46.48; H, 6.25; N, 38.91.

3-(Methylamino)-6-(methylthio)-1,2,4,5-tetrazine (20): red crystals from methanol, mp 85–86 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz) δ 2.61 (s, 3 H, SCH_3), 2.98 (d, ^3J = 5 Hz, 3 H, NCH_3), 8.30 (br s, 1 H, NH). Anal. Calcd for $C_4H_7N_5S$: C, 30.56; H, 4.49; N, 44.55. Found: C, 30.76; H, 4.55; N, 44.85.

3-(Methylthio)-6-pyrrolidino-1,2,4,5-tetrazine (22): red crystals from diethyl ether and petroleum ether, mp 79–80 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz) δ 2.01 (m, 4 H, CH_2), 2.62 (s, 3 H, SCH_3), 3.59 (m, 4 H, NCH_2). Anal. Calcd for $C_7H_{11}N_5S$: C, 42.62; H, 5.62; N, 35.50. Found: C, 42.61; H, 5.52; N, 35.23.

PE Spectra. The He$^{I\alpha}$ PE spectra were measured on a PS 18 instrument (Perkin-Elmer) and calibrated with reference to the 15.75-eV argon line.

Cyclic Voltammograms. Cyclic voltammetric studies were carried out on deoxygenated acetonitrile[38] solutions containing the *s*-tetrazine sample (0.4–0.8 mM) and tetraethylammonium tetrafluoroborate (0.1 M)[4] at 298 °C. The cyclic voltammograms of these solutions were obtained by using a Bruker Universal Modular Polarograph E 310 attached to an electrochemical cell equipped with a glassy carbon electrode as working electrode, a standard Ag/Ag$^+$ reference electrode, and a platinum counter electrode and were scanned at a current of 0.1–0.5 mA and a sweep rate of about 100 mV s^{-1}. $E_{1/2}$ values are corrected relative to ferrocene, $E_{1/2}$ = 0.0906 V.

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Catalytic Homogeneous Functionalization of Adamantane. Influence of Electronic and Structural Features of the Metalloporphyrin Catalyst on Atom Transfer Selectivity (Oxygenation versus Azidification/Halogenation)

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Upon treatment of the two-phase systems, Mn tetraarylporphyrin, and alkane (organic phase)/Na$^+$X$^-$ (aqueous phase), with iodosylarenes, both alcohols and alkyl azides (or halides), X$^-$ = halide or azide, are formed from the alkane substrates. The Mn porphyrin functions as a catalyst for alkane oxygenation and a phase transfer catalyst for X$^-$. Catalytic functionalization of the exemplary caged alkane, adamantane, by a variety of these two-phase systems as function of the reaction conditions has been examined. The results reported here allow, for the first time, an assessment of the relationship between the electronic and structural features of the metalloporphyrin catalysts and their selectivity with respect to the replacement of unactivated alkane carbon–hydrogen bonds with oxygen versus non-oxygen (halide or azide) functional groups. Of the first-row transition metal metalloporphyrins, only those of manganese are active for both the cleavage of unactivated alkane C–H bonds and replacement of these bonds by halogen or nitrogen-based groups. The oxygen donors that give the highest yields of these non-oxygenated products are the iodosylarenes. Examination of adamantane functionalization by iodosylarenes catalyzed by eight different manganese tetraphenylporphyrin derivatives, whose porphyrin ligands vary widely in electron-donating ability, establishes that the relative tertiary–secondary C–H cleavage selectivities are minimally affected by such electronic effects. In contrast, the selectivity for incorporation of the non-oxygen versus oxygen functions is substantially affected by the electron-donating ability of the catalyst porphyrin rings. The more electron withdrawing the porphyrin ring, and consequently the more anodic the potential of the ligated, S = 2, manganese(III) ion, the lower the selectivity for incorporation of the non-oxygen functions. Functionalization of adamantane catalyzed by the most electron poor manganese porphyrin complex, Mn^{III}(F_{20}TPP)X, is effectively selective for oxygenation. All the metalloporphyrins examined here eventually succumb to deactivation by irreversible oxidative degradation of the organic porphyrin ligand.

Introduction

A number of studies addressing the homogeneous catalytic oxygenation and functionalization of hydrocarbons by metalloporphyrins have been published in recent years. These studies have been stimulated both by attempts to delineate the complex mechanism(s) of hydrocarbon oxidation by cytochrome P-450 and to develop new and practical methods for the selective catalytic oxygenation of organic substrates.[1-4] The catalytic incorporation of oxygen functions, eq 1, and the stoichiometric incorporation of halogen and nitrogen functions, eq 2 into alkanes

$$\mathrm{RH + DO \xrightarrow{Mn^{III}(Por)X} ROH + D} \qquad (1)$$

$$\mathrm{RH + DO + Mn^{III}(Por)X \rightarrow RX + D + Mn^{III}(Por)OH} \qquad (2)$$

RH = alkane; X^- = Br^-, Cl^-, N_3^-, NO_2^-, etc.;
DO= oxygen donor (e.g. iodosylarene)

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