245. *The Electronic Spectra of* N-*Heteroaromatic Systems. Part I.** *The* $n \longrightarrow \pi$ *Transitions of Monocyclic Azines.*

By S. F. Mason.

The positions and the intensities of the band in the visible and the ultraviolet spectra of monocyclic azines due to the promotion of an electron from a lone-pair nitrogen orbital to a π-orbital of the ring have been measured for the vapour phase for *cyclo*hexane and aqueous solutions. The frequency of the band is determined primarily by the energy of the benzene-like lowest unoccupied π-orbital of the azine and by ground-state interaction between lone-pair orbitals on different nitrogen atoms. The intensities of the $n \longrightarrow \pi$ bands of the azines increase with the " *s* " character of the lone-pair nitrogen orbitals, but the frequencies of the bands are not greatly affected, owing to orbital-following in the transition.

The ultraviolet and visible absorption of monocyclic azines have been examined by a number of workers,[1-9] who find that these compounds give an absorption band which has no counterpart in the spectrum of benzene. From the relatively low intensity of the band and its shift to higher frequencies with change from non-polar to polar solvents, it has been concluded [10-12] that the band arises from the transmission of a non-bonding electron from a lone-pair orbital of a nitrogen atom to a π-orbital of the ring. The theory of the $n \longrightarrow \pi$ transition in pyridine and the diazines has been discussed,[13] but the $n \longrightarrow \pi$ spectra of the azines as a whole have not been considered in detail. To obtain data for a more comprehensive treatment, the $n \longrightarrow \pi$ transitions of all of the known monocyclic azines have now been examined in the vapour and in *cyclo*hexane and aqueous solutions, the results being recorded in the Table and the Figures.

The $n \longrightarrow \pi$ transitions of the monocyclic azines are weak, possessing oscillator strengths in the range 0·003—0·021 (Table). The transitions are not forbidden by symmetry, however, as strong 0–0 vibrational bands have been identified in the spectra of the vapour of pyridine,[5] pyrimidine,[3] pyrazine,[9] and *sym*-tetrazine.[14] The weakness of the intensity may be ascribed to three main factors. First, the lone-pair and the π-orbitals of an azine are concentrated in different regions of space, and transitions requiring large changes in the position of an electron are improbable.[11] Secondly, only the *s*-component of the *s*–*p* hybrid lone-pair orbital can contribute to the transition moment,[13] since $p_\sigma \longrightarrow p_\pi$ transitions are forbidden. The third factor, the small overlap between π-electron charge distributions [13] of the ground and the excited state, is not of great importance. This factor leads only to a fourfold reduction in the intensity of the $n \longrightarrow \pi$ transition of pyridine,[13] and it is less significant in the case of the polyaza-compounds where the migration of charge from nitrogen to carbon in the transition is smaller, or, as in the case of *sym*-tetrazine, absent.

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* In this series of papers aza-substitution refers to ***replacement*** of a CH-member of a benzene ring by a nitrogen atom; otherwise the term substitution has its usual significance.

[1] Curtius, Darapsky, and Müller, *Ber.*, 1907, **40**, 84.
[2] Koenigsberger and Vogt, *Physikal. Z.*, 1913, **14**, 1269.
[3] Uber, *J. Chem. Phys.*, 1941, **9**, 777.
[4] Halverson and Hirt, *ibid.*, 1951, **19**, 711.
[5] Rush and Sponer, *ibid.*, 1952, **20**, 1847.
[6] Stephenson, *ibid.*, 1954, **22**, 1077.
[7] Hirt, Halverson, and Schmitt, *ibid.*, 1954, **22**, 1148.
[8] Mason, *Chem. Soc. Special Publ.*, 1955, **3**, 139.
[9] Ito, Shimada, Kuraishi, and Mizushima, *J. Chem. Phys.*, 1957, **26**, 1508.
[10] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.
[11] Platt, *J. Chem. Phys.*, 1951, **19**, 101.
[12] McConnell, *ibid.*, 1952, **20**, 700.
[13] Orgel, *J.*, 1955, 121.
[14] Part IV, *J.*, 1959, 1263.

The $n \longrightarrow \pi$ transitions of the azines show a small red shift on change from vapour to *cyclo*hexane solution (Table), which can be ascribed[15] to the momentary polarisation of the hydrocarbon solvent by the transition dipole of the azine solute. On change from *cyclo*hexane to aqueous solution there are considerable blue shifts (Table), and on formation of a cation in acid solution the $n \longrightarrow \pi$ bands of the azines undergo further blue shifts or disappear (Fig. 1). In aqueous solution the lone-pair electrons of the azines are engaged in hydrogen-bonding, and the promotion of such an electron to a π-orbital requires the provision of additional energy to weaken or break the hydrogen bonds. In an azine cation the lone-pair electrons either bind a proton or are held more strongly in their orbital by inductive and electromeric effects originating from a charged centre elsewhere in the molecule. The blue shifts of the $n \longrightarrow \pi$ bands observed on changing from *cyclo*hexane to aqueous solution should provide a measure of the electron-donating capacity of the azines. The shifts vary widely, ranging from 1000 cm.$^{-1}$ for *sym*-tetrazine to 3900 cm.$^{-1}$ for pyridazine, and, in general, the shifts are larger the more basic the azine (Table), apart from the case of 3 : 5 : 6-trimethyl-1 : 2 : 4-triazine which, being an alkyl derivative, is not strictly comparable with the unsubstituted azines.

The frequencies (ν) *and the oscillator strengths* (f) *of the* n $\longrightarrow \pi$ *transitions of the monocyclic azines in the vapour and in* cyclo*hexane and aqueous solution. The red shifts of the band origins* (ν_{0-0}) *in the vapour phase and the band maxima* ($\nu_{\text{max.}}$) *in* cyclo*hexane solution relative to pyridine* ($\Delta\nu_{\text{obs}}$), *and the theoretical red shifts due to the lowering of the energy of the unoccupied* π*-orbitals on aza-substitution* ($\Delta\nu_\pi$) *and to ground state interaction between the lone-pair orbitals* ($\Delta\nu_n$). *The ionisation constants of the azines* (pK_a), *and the blue shift of the band maxima observed on change from* cyclo*hexane to aqueous solution* ($\nu_{H_2O}-\nu_{C_6H_{12}}$). *Values in parentheses refer to tentative assignments.*

Compound	Solvent	ν_{0-0} (cm.$^{-1}$)	$\nu_{\text{max.}}$ (cm.$^{-1}$)	f	$\Delta\nu_{\text{obs.}}$ (cm.$^{-1}$)	$\Delta\nu_\pi$[d] (cm.$^{-1}$)	$\Delta\nu_n$[e] (cm.$^{-1}$)	$\nu_{H_2O} - \nu_{C_6H_{12}}$ (cm.$^{-1}$)	pK_a
Pyridine	Vap.	34,770			0	0	0		5·23
	C_6H_{12}		37,000[c]	0·003[c]					
Pyrimidine	Vap.	31,060	33,790		3710	2300	400		
	C_6H_{12}	30,810	33,500	0·0069	3500			3340	1·30
	H_2O		36,840						
Pyrazine	Vap.	30,870	30,870		3900	4600	−150		
	C_6H_{12}	30,515	30,515	0·0104	6485			2285	0·6
	H_2O		32,800						
Pyridazine	Vap.	(27,390)	30,770		7380	2300	6000		
	C_6H_{12}	(26,790)	29,410	0·0058	7590			3890	2·33[f]
	H_2O		33,330						
sym-Triazine	Vap.	(31,520)	37,000		3150	2300	400		
	C_6H_{12}	(30,900)	36,750	0·0210	250			1700	—
	H_2O		38,450						
3 : 5 : 6-Trimethyl-1 : 2 : 4-triazine	C_6H_{12}		26,000	0·0079	11,000	5750	6250	2600	2·85
	H_2O		28,600						
m-Tetrazine	[a] Vap.	18,135	18,135		16,635	9200	6500		
	C_6H_{12}	17,880	18,560	0·0042	18,440			1040	<0
	H_2O		19,600						
	[b] C_6H_{12}		31,250	0·001[c]	5750	(6900)	(−6500)	1530	
	H_2O		32,780						

[a] First $n \longrightarrow \pi$ band. [b] Second $n \longrightarrow \pi$ band. [c] Derived by the method of ref. 6. [d] Calculated by equation (3) with $\Delta\alpha_N = 0{\cdot}6\beta$, and $\beta = 23{,}000$ cm.$^{-1}$. [e] Calculated by equations (5) and (6). [f] Quoted from Albert and Phillips, *J.*, 1956, 1294. [h] Unstable in aqueous solution.

Relative to that of pyridine the $n \longrightarrow \pi$ transitions of the polyazines are displaced to the red region. The displacements are more dependent upon the positions than the number of aza-substituents, *sym*-triazine showing the smallest and 3 : 5 : 6-trimethyl-1 : 2 : 4-triazine the second largest red shift (Table). If the lone-pair orbitals of the azines are assumed to have approximately the same energy, the frequency displacements should

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[15] Bayliss and McRae, *J. Phys. Chem.*, 1954, **58**, 1002.

be accounted for by the relative energies of the lowest unoccupied π-orbitals of pyridine and the other azines.

Convenient models for the orbital containing the promoted electron in the excited states of the $n \longrightarrow \pi$ transitions of the azines, covering the series as a whole, are the lowest unoccupied π-orbitals of benzene perturbed by aza-substitution. An alternative description of the $n \longrightarrow \pi$ excited state, the pentadienyl radical and a neutral nitrogen atom, whilst informative in the case of pyridine,[13] is inappropriate for the treatment of the polyazines. The lowest unoccupied π-orbitals of benzene are the degenerate pair, ψ_A and ψ_B, the explicit forms of which are given by

$$\psi_A = (2\phi_1 - \phi_2 - \phi_3 - 2\phi_4 - \phi_5 - \phi_6)/(12)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (1)$$

$$\psi_B = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the ϕ's are $2p$ atomic orbitals of carbon. On aza-substitution the degeneracy of ψ_A and ψ_B, in general, is removed, the energy of one orbital being lowered more than that of the other. The forms of the orbitals are qualitatively preserved, however, ψ_B being an exact quantitative representation of the lowest unoccupied level of *sym*-tetrazine (I) and ψ_A giving approximately the form of that of pyrazine (II).

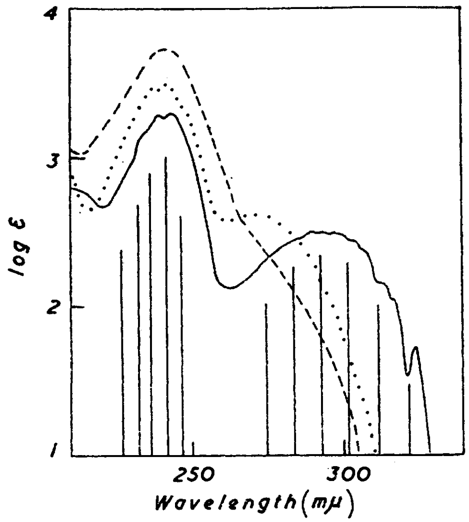


FIG. 1. *The electronic spectrum of pyrimidine:*
———— *in* cyclo*hexane,*
.... *in neutral aqueous solution,*
— — — — *in* 4N-*sulphuric acid (spectrum of cation).*
The vertical lines give one of the main progressions in the spectrum of pyrimidine vapour, the heights of the lines representing relative intensities only.

If the relative energies of the $n \longrightarrow \pi$ transitions of the azines are determined primarily by the relative energies of the lowest unoccupied π-orbital, the red shift of the $n \longrightarrow \pi$ bands relative to that of pyridine are given, by first-order perturbation theory, by

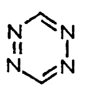
$$\Delta\nu_\pi = \nu_{\text{pyridine}} - \nu_{\text{azine}} = [\textstyle\sum_r C_r{}^2{}_{(\text{azine})} - C_r{}^2{}_{(\text{pyridine})}]\Delta\alpha_N \qquad (3)$$

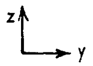
where C_r is the coefficient of a position occupied by a nitrogen in the orbital ψ_A or ψ_B, whichever is lowered the more in energy on aza-substitution, and $\Delta\alpha_N$ is the increment in the Coulomb integral of nitrogen relative to carbon. $\Delta\alpha_N$ being given the empirical value[16] of 0·6β, and β, the carbon–carbon resonance integral, the usual spectroscopic value[17] of 23,000 cm.$^{-1}$, the theoretical red shifts of the $n \longrightarrow \pi$ bands of the azines relative to that of pyridine due to the lowering of the energy of the lowest unoccupied π-orbital are obtained ($\Delta\nu_\pi$). The calculated values ($\Delta\nu_\pi$) do not show good agreement (Table) with the observed red shifts ($\Delta\nu_{\text{obs}}$). The discrepancies are particularly large

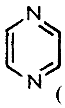
[16] Mason, *J.*, 1958, 674.

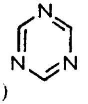
[17] Platt, *J. Chem. Phys.*, 1950, **18**, 1168.

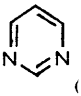
(>5000 cm.$^{-1}$) for the 1 : 2-diaza-compounds, pyridazine, 3 : 5 : 6-trimethyl-1 : 2 : 4-triazine, and *sym*-tetrazine, suggesting that the assumed equality of the energy of the lone-pair orbitals in the azines is untenable. In the 1 : 2-diaza-compounds, lone-pair atomic orbitals are situated on adjacent nitrogen atoms (*e.g.*, III), and these orbitals interact strongly, giving rise to a bonding (*e.g.*, IV) and an antibonding (*e.g.*, V) lone-pair molecular orbital, both of which are filled with electrons. The lowest energy $n \longrightarrow \pi$ transition in these diaza-compounds is from the antibonding lone-pair molecular orbital, which lies at a higher energy than a lone-pair atomic orbital, so that the $n \longrightarrow \pi$ absorption of these compounds is shifted further to the red region.

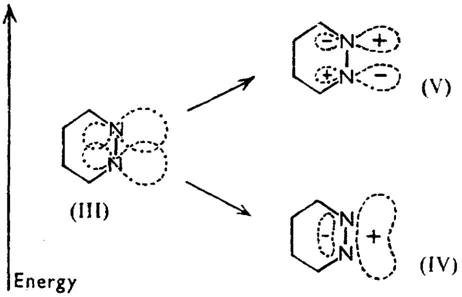

(I)




(II)


(VI)


(VII)



The red shift of the $n \longrightarrow \pi$ transitions of the 1 : 2-diaza-compounds due to ground-state interaction can be calculated approximately from the overlap integral of the adjacent lone-pair atomic orbitals. The axes being taken to be those of (I), and trigonal hybridisation being assumed, the lone-pair atomic orbitals (ϕ_{1p}) have the form

$$\phi_{1p} = \phi_s/\sqrt{3} - \phi_{pz}/\sqrt{6} + \phi_{py}/\sqrt{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The overlap integral (S_{1p}) of two such lone-pair orbitals adjacent to one another as in formulæ (I) and (III) is then given by

$$S_{1p} = S_{2s2s}/3 - S_{2s2p\sigma}(2^{\frac{1}{2}}/3) + S_{2p\sigma2p\sigma}/6 + S_{2p\pi2p\pi}/2 \quad . \quad . \quad . \quad . \quad (5)$$

where $S_{2p\sigma2p\sigma}$ is the σ overlap integral, and $S_{2p\pi2p\pi}$ the π overlap integral of two $2p$ orbitals of nitrogen, and S_{2s2s} and $S_{2s2p\sigma}$ are, respectively, the overlap integrals of two $2s$ orbitals and a $2s$ and a $2p$ orbital of nitrogen. The N–N distance in the 1 : 2-diaza-compounds being taken as that found [18] in an *X*-ray diffraction study of *sym*-tetrazine (1·321 Å), and Slater orbitals being used,[19] it is found that the overlap integral of two adjacent lone-pair orbitals is 0·109. The adjacent lone-pair orbital overlap is about one half that of the π-overlap of the $2px$ orbitals of the ring, and it is itself largely of the π-type, the σ contributions to the overlap cancelling one another. The interaction between the adjacent lone-pair atomic orbitals leads to the formation of two lone-pair molecular orbitals with a difference in energy between them (ΔE) given by [20]

$$\Delta E = AS_{1p}I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where I is the ionisation potential of an electron in a lone-pair atomic orbital on a nitrogen atom and A is a constant which has the value [20] of 1·16 for σ overlap and 1·53 for π overlap. The ionisation potential of pyridine [21] is 9·23 ev, and though this value may represent the potential required to ionise a π-electron, it is unlikely that the ionisation potential of a lone-pair electron would be greatly different. By equation (6) the energy separation between the lone-pair molecular orbitals of the 1 : 2-diaza-compounds is about 12,000 cm.$^{-1}$, so that the energy of the antibonding orbital lies some 6000 cm.$^{-1}$ above that of a

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[18] Bertinotti, Giacomello, and Liquori, *Acta Cryst.*, 1956, **9**, 510.

[19] Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

[20] Mulliken, *ibid.*, 1952, **56**, 295.

[21] Watanabe, *ibid.*, 1957, **26**, 542.

lone-pair atomic orbital. The $n \longrightarrow \pi$ transitions of the 1 : 2-diaza-compounds are displaced about 6000 cm.$^{-1}$ to the red owing to ground-state interaction, therefore, and this effect, together with the lowering of the benzene-like π-orbitals on aza-substitution, accounts for the observed red shifts of the $n \longrightarrow \pi$ bands of the azines relative to that of pyridine to within about 1500 cm.$^{-1}$.

In the 1 : 3- and 1 : 4-diaza-compounds, ground-state interaction between the lone-pair atomic orbitals is much less important. From the nitrogen–nitrogen distances given by structure determinations of pyrazine [22] and *sym*-triazine,[23] it is found, by the use of Slater orbitals,[19] that the overlap integral between two lone-pair atomic orbitals is 0·004 and 0·009 in the 1 : 4- and the 1 : 3-diaza-compounds, respectively. The overlap is entirely of the σ type in the 1 : 4- and of mixed σ and π types in the 1 : 3-diaza-compounds, the resulting energy difference between the bonding and the antibonding lone-pair molecular orbitals being some 300 cm.$^{-1}$ and about 800 cm.$^{-1}$ in the 1 : 4- and the 1 : 3-diaza-compounds, respectively. Such energies are small, but if 1 : 4- and 1 : 3- as well as 1 : 2-ground-state interaction is considered explicitly, the agreement between the calculated $(\Delta\nu_\pi + \Delta\nu_n)$ and the observed $(\Delta\nu_{\text{obs}})$ red shifts of the 0–0 bands of the $n \longrightarrow \pi$ transitions of the polyazines, relative to that of pyridine, is brought to within about 1000 cm.$^{-1}$ (Table), apart from the case of the tentatively-assigned second $n \longrightarrow \pi$ transition of *sym*-tetrazine (see below).

In the polyazines the number of lone-pair molecular orbitals equals the number of aza-substituents, but not all transitions from such orbitals to the lowest unoccupied π-orbital are allowed. *sym*-Tetrazine has four lone-pair molecular orbitals, the one of highest energy (ψ_{I}) having the form

$$\psi_{\text{I}} = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where the ϕ's refer to lone-pair atomic orbitals. ψ_{I} has the symmetry B_{3g} in D_{2h} (taking axes as in formula I), and it differs in form from the lowest unoccupied π-orbital, ψ_{B} (symmetry A_u), only in that it possesses no node in the plane of the molecule. An electronic transition from ψ_{I} to ψ_{B} is allowed, therefore $(A_g \longrightarrow B_{3u})$, with a transition moment perpendicular to the plane of the molecule. There is no migration of charge from nitrogen to carbon in this transition, the promoted electron being confined to a π-orbital covering only the nitrogen atoms. The transition is quasi-atomic $(2s \longrightarrow 2px)$, and there should be no loss of intensity in this transition due to the incomplete overlap of the ground- and excited-state π-electron charge distributions [13]. The remaining three lone-pair molecular orbitals in *sym*-tetrazine have the symmetries, B_{1u}, B_{2u}, and A_g, in descending order of energy, and transitions from them to ψ_{B} are forbidden. An electronic transition from the most bonding of the lone-pair molecular orbitals of *sym*-tetrazine (symmetry A_g) to the unoccupied π-orbital with the form of ψ_{A} (symmetry B_{3u}) is allowed, however, and it may be responsible for the second $n \longrightarrow \pi$ band of *sym*-tetrazine, which appears as a shoulder at 3200 Å upon the first $\pi \longrightarrow \pi$ band at 2520 Å in *cyclo*hexane solution (Table; Fig. 2).

In *sym*-triazine (VI) the highest occupied lone-pair molecular orbitals are a degenerate pair (symmetry E' in D_{3h}), and the unoccupied π-orbitals with the forms of ψ_{A} and ψ_{B} are also degenerate (symmetry E''). First-order configuration interaction leads to four excited states with the symmetries, A_1'', A_2'', and E'', and of these only the transition to the A_2'' state is allowed, with a transition moment perpendicular to the plane of the molecule. Transitions from the bonding lone-pair molecular orbital (symmetry A_1') to the unoccupied π-orbitals are also forbidden. 1 : 2 : 4-Triazine has the lowest symmetry (C_s) of all the monocyclic azines, and all transitions from the lone-pair molecular orbitals (symmetry A') to the unoccupied π-orbitals (symmetry A'') are allowed.

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[22] Wheatley, *Acta Cryst.*, 1957, **10**, 182.

[23] Wheatley, *ibid.*, 1955, **8**, 224; Lancaster and Stoicheff, *Canad. J. Phys.*, 1956, **34**, 1016.

Pyrazine (II) is unique in the azine series in that ground-state interaction increases the frequency of the $n \longrightarrow \pi$ transition, though the increase is small as 1 : 4-interaction is very weak. Transitions from the higher-energy lone-pair molecular orbital (symmetry B_{1u} in D_{2h} with axes as I) to either of the unoccupied π-orbitals with the forms of ψ_A or ψ_B are forbidden. Only a transition from the bonding lone-pair molecular orbital (symmetry A_g) to the lowest unoccupied π-orbital, ψ_A (symmetry B_{3u}), is allowed. In the cases of pyrimidine (VII) and pyridazine (III) the allowed $n \longrightarrow \pi$ transition is from the higher-energy lone-pair molecular (*e.g.*, V) orbital (symmetry B_2 in C_{2v}) to the lowest unoccupied π-orbital which has the form of ψ_B and the symmetry B_2. The calculated red shifts $(\Delta\nu_\pi + \Delta\nu_n)$ of the $n \longrightarrow \pi$ transitions of the polyazines, relative to that of pyridine (Table), refer generally to the allowed transition of lowest frequency, apart from the case of the second $n \longrightarrow \pi$ transition of *sym*-tetrazine.

A subsidiary factor which has influence on the energies and the intensities of the $n \longrightarrow \pi$ transitions of the azines is the percentage " *s* " character of the lone-pair orbitals.

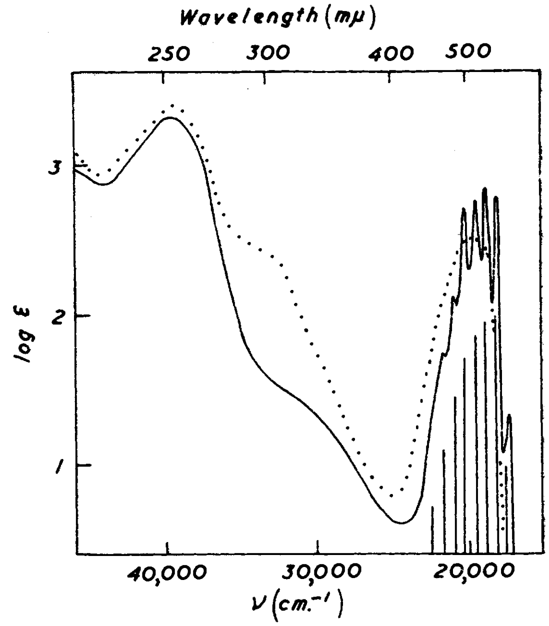

FIG. 2. *The electronic spectrum of* sym-*tetrazine*:

———— *in* cyclo*hexane solution,*

.... *in aqueous solution.*

The vertical lines give the main progression in the visible absorption band of sym-*tetrazine vapour, the heights of the lines representing relative intensities only.*

The CNC and the CNN bond angles of the azines, in the cases where these angles have been determined, suggest that the lone-pair orbitals have somewhat more than trigonal " *s* " character. The CNC angles are 117·5° in pyridine,[24] ~116° in pyrimidine,[25] 115·1° in pyrazine,[22] and 113·2° in *sym*-triazine,[23] whilst in *sym*-tetrazine the CNN angle [18] is 115·95°, indicating that the " *s* " characters of the lone-pair orbitals are 36·8, 38·8, 40·4, 43·6, and 39·0% respectively. Since only the " *s* " component of a *s*–*p* hybrid lone-pair orbital can contribute to the transition moment of a $n \longrightarrow \pi$ absorption, the intensity of the bands should be proportional to the " *s* " character of the lone-pair orbitals. In the series, pyridine, pyrimidine, pyrazine, and *sym*-triazine, the oscillator strength of the $n \longrightarrow \pi$ transition increases with the " *s* " character of the lone-pair orbitals, though the increases are not commensurate with one another (Table). The intensities of the $n \longrightarrow \pi$ bands of the 1 : 2-diaza-compounds are rather low compared with those of the isomeric

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[24] Liquori and Viciago, *Ric. sci.*, 1956, **26**, 1848.

[25] Calculated from unpublished crystallographic data for pyrimidine, kindly supplied by Dr. P. J. Wheatley.

azines, or, in the case of *sym*-tetrazine, relative to the intensity expected from the value of the " *s* " character of the lone-pair orbitals. The low intensity may be due to the strong ground-state interaction in the 1 : 2-diaza-compounds and the spatially forbidden character of $n \longrightarrow \pi$ transitions. In the antibonding lone-pair molecular orbitals (*e.g.*, V) the maxima of the charge distribution are displaced further from the nitrogen nucleus and the π-orbitals than those of the atomic or bonding molecular lone-pair orbitals (*e.g.*, IV), and the displacement may result in a reduced probability of transition.

The percentage " *s* " character of the lone-pair orbitals of the azines may have only a small effect upon the energies of the $n \longrightarrow \pi$ transitions. An electron in a sp^2 orbital of nitrogen has a lower energy than a corresponding p-electron, the ionisation energies of the processes $N(s^2p^3V_3) \longrightarrow N^+(s^2p^2V_2)$ and $N(sp^4V_3) \longrightarrow N^+(sp^3V_2)$ being [26] 13·81 and 14·63 ev, respectively. However, it is probable that orbital-following occurs in the $n \longrightarrow \pi$ transition of an azine, the σ bond orbitals of nitrogen assuming a larger " *s* " character on the promotion of a lone-pair electron to a π-orbital. The stabilisation of the remaining σ electrons due to the increase in their " *s* " character thus partly compensates for that part of the $n \longrightarrow \pi$ transition energy which is required to promote a lone-pair electron from the sp^2 to the p-state. The compensation is likely to be only partial, as the $n \longrightarrow \pi$ transition energies of the azines calculated with neglect of the atomic $sp^2 \longrightarrow p$ promotion term are somewhat low.

In the case of *sym*-tetrazine the $n \longrightarrow \pi$ transition energy can be obtained without the uncertainties arising from the use of perturbation theory and from changes in the Coulomb integral of nitrogen, due to the transfer of charge from nitrogen to carbon in the transition. The lowest unoccupied π-orbital of *sym*-tetrazine is ψ_B (eqn. 2), which lies at an energy of β_{NN} above that of a $2p$ atomic orbital of nitrogen. The highest occupied lone-pair molecular orbital is ψ_I (eqn. 7), which lies at an energy of about 6500 cm.$^{-1}$ above that of an atomic sp^2 hybrid orbital of nitrogen (Table). By giving the nitrogen–nitrogen resonance integral, β_{NN}, the same value as the carbon–carbon resonance integral [17] (23,000 cm.$^{-1}$), and by neglecting the atomic $sp^2 \longrightarrow p$ promotion term, the calculated $n \longrightarrow \pi$ transition energy is found to be 16,500 cm.$^{-1}$ for *sym*-tetrazine, compared with the experimental value of 18,000 cm.$^{-1}$ (Table). The $n \longrightarrow \pi$ transition energies of the other unsubstituted azines, calculated with neglect of the atomic $sp^2 \longrightarrow p$ promotion energy, are similarly 1500—3400 cm.$^{-1}$ lower than the observed values. If the deficits are due to the neglected energy term, orbital-following in a $n \longrightarrow \pi$ transition is likely, since from ionisation data [26] the atomic $sp^2 \longrightarrow p$ promotion energy is 6600 cm.$^{-1}$ for nitrogen.

EXPERIMENTAL

Materials.—Pyrimidine was kindly supplied by Dr. N. Whittaker,[27] 3 : 5 : 6-trimethyl-1 : 2 : 4-triazine by Dr. R. Metze,[28] and *sym*-triazine by Dr. C. Grundmann.[29] *sym*-Tetrazine was prepared by the method of Curtius, Darapsky, and Müller,[1] and the remaining compounds were commercial specimens.

Absorption Spectra.—In the vapour and in *cyclo*hexane the spectra of the monocyclic azines were measured with a Cary recording spectrophotometer; the spectra in aqueous solution were measured, and those in *cyclo*hexane checked, with Hilger Uvispek quartz spectrophotometers.

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