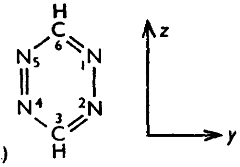
248. *The Electronic Spectra of* N-*Heteroaromatic Systems. Part IV.** *The Vibrational Structure of the* $n \longrightarrow \pi$ *Band of* sym-*Tetrazine.*

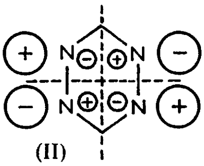
By S. F. Mason.

The vibrational structure of the visible absorption spectrum of *sym*-tetrazine has been measured in the vapour, together with that of the 3 : 6-dideutero-derivative; in *cyclo*hexane at room temperature, together with that of the 3 : 6-dimethyl derivative; and in a 5 : 1-*iso*pentane–methyl*cyclo*hexane glass at 77° K. For the vapour of *sym*-tetrazine the strongest band is the 0–0, which shifts towards the red end of the spectrum in the dideutero-derivative; the observed upper-state progressions are short, indicating the electronic transition, whilst of low oscillator strength, is allowed that by symmetry, and that there is little change in the size of the molecule on excitation, although the molecular zero-point energy increases. The particular vibrations active in the electronic transition suggest that *sym*-tetrazine assumes a more regular hexagonal shape on excitation.

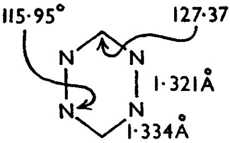
The monocyclic *N*-heteroaromatic compound *sym*-tetrazine (I) has an unusual absorption spectrum in the visible region. Curtius, Darapsky, and Muller remarked upon the sharpness of the absorption and listed qualitatively five main bands.[1] Koenigsberger and and Vogt described [2] the visible absorption of *sym*-tetrazine as " a new kind of molecular spectrum," since, for the first time, bands of molecular origin were observed which appeared to be as sharp as the lines of atomic spectra. These workers measured [2] the positions of some thirty-five absorption bands of *sym*-tetrazine vapour in the visible region, which is about half the number that have been now recorded by use of the relatively low resolution of the Cary spectrophotometer. The vibrational band structure of the visible absorption spectrum of *sym*-tetrazine in *cyclo*hexane at room temperature and in a 5 : 1 *iso*pentane–methyl*cyclo*hexane glass at 77° K has been measured also, and for the purposes of comparison the spectra of 3 : 6-dideuterotetrazine in the vapour and of 3 : 6-dimethyltetrazine in *cyclo*hexane have been recorded. The results obtained are listed in Tables 1—3, and the spectra of *sym*-tetrazine are given in the Figure.



(I)



(II)



(III)

The general features of the visible absorption of *sym*-tetrazine, and of the band of longest wavelength in the spectra of the monocyclic azines generally, suggest [3] that the absorption is due to the transition of a non-bonding electron from a lone-pair orbital of the nitrogen atoms to a π-orbital of the ring. As with most non-polar chromophores, the absorption of *sym*-tetrazine shows a small red shift on change from the vapour to *cyclo*hexane solution (Tables 1 and 2), which is due to the momentary polarisation of the solvent by the transition dipole of the solute,[4] but on change from *cyclo*hexane to aqueous solution the absorption undergoes a considerable blue shift of some 1000 cm.$^{-1}$ (Table 2), a feature which is characteristic of $n \longrightarrow \pi$ transitions.[5,6] In aqueous solution the lone-pair

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* Part III, preceding paper.

[1] Curtius, Darapsky, and Muller, *Ber.*, 1907, **40**, 84.

[2] Koenigsberger and Vogt, *Physikal. Z.*, 1913, **14**, 1269.

[3] Part I, *J.*, 1959, 1240.

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

[5] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.

[6] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.

electrons of *sym*-tetrazine are engaged in hydrogen bonding, and the promotion of such an electron to a π-orbital requires the provision of additional energy to break the hydrogen bonds.

Further, the vibrational fine structure of the visible spectrum of *sym*-tetrazine is entirely lost in aqueous solution, though the main features of the dominant progression observed in the vapour are retained in *cyclo*hexane solution (Fig.). The solvation cage of a solute in the ground state becomes strained when the solute absorbs radiation and

TABLE 1. *The frequencies* (ν) *and the optical densities* (d) *of the bands in the visible absorption spectra of* sym-*tetrazine and deuterated* sym-*tetrazine in the vapour at room temperature.*

Dideuterotetrazine	Tetrazine		
ν (cm.$^{-1}$)	ν (cm.$^{-1}$)	10^3d	Assign.
17320	17320	34	
17390	17410	66	A 1—0
17520	17540	40	
17640	17690	36	
17850	17810	40	
17870	17860	60	
17950	17910	66	
17980	17970	76	
18040	18050	164	
18120	18135	658	0—0
18240	18195	114	D_1
18280	18280	284	
18370	18340	86	
18350	18430	120	
18480	18480	60	
18530	18550	86	
18550	18615	86	
18630	18650	86	
18650	18680	111	
18730	18760	256	
18810	18830	629	0—1 A
18900	18910	447	D_2
18990	18990	276	
19040	19070	194	
19160	19140	177	
19230	19230	137	
19250	19250	149	
19330	19290	131	
19350	19360	111	
19390	19400	131	
19430	19470	208	
19500	19540	377	0—2 A
19590	19620	594	D_3
19640	19690	208	
19690	19780	255	
19730	19850	190	
19800	19910	103	
19920	19940	168	
19950	20010	120	
—	20070	128	
20050	20110	120	
20130	20190	114	
20190	20250	181	0—3 A
20280	20340	409	D_4
20420	20410	114	
—	20460	119	
20480	20490	194	
—	20530	155	
20610	20620	108	
20650	20650	137	
20730	20720	103	
—	20760	111	
20810	20810	100	
—	20900	96	
20880	20950	92	0—4 A
20970	20980	205	D_5
—	21040	100	
21130	21160	114	
—	21200	87	
21170	21230	92	
—	21320	78	
21290	21340	81	
—	21420	76	
21420	21470	66	
—	21510	66	
—	21610	92	
21560	21650	71	0—5 A
21680	21760	76	
—	21880	66	
—	21910	66	

TABLE 2. *The visible absorption spectra of* sym-*tetrazine and* 3 : 6-*dimethyltetrazine in water and in* cyclo*hexane at room temperature. Values in italics refer to shoulders or inflexions.*

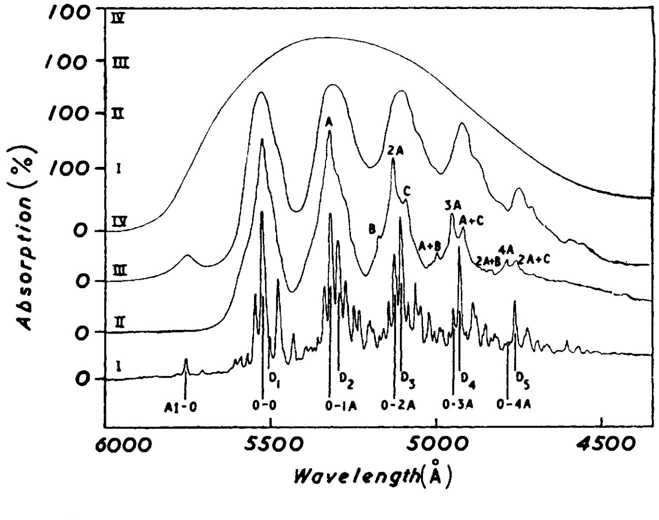
sym-Tetrazine						3 : 6-Dimethyltetrazine			
$\nu_{\text{max.}}$ (cm.$^{-1}$)	$\varepsilon_{\text{max.}}$	$\nu_{\text{max.}}$ (cm.$^{-1}$)	$\varepsilon_{\text{max.}}$	$\nu_{\text{max.}}$ (cm.$^{-1}$)	$\varepsilon_{\text{max.}}$	$\nu_{\text{max.}}$ (cm.$^{-1}$)	$\varepsilon_{\text{max.}}$	$\nu_{\text{max.}}$ (cm.$^{-1}$)	$\varepsilon_{\text{max.}}$
				In *cyclo*hexane					
17160	21·5	*18870*	*262*	*20200*	*250*	16780	69	18660	662
17880	611	19350	625	20810	139	17300	644	19120	524
18020	*112*	*19530*	*300*	*20920*	*109*	17810	832	*19530*	*391*
18560	829	20110	543	21490	55	18300	750	*20040*	*271*
				21620	12				
				In water					
		19600	362			19340	365		

changes in shape and in electron distribution. If the solvation forces are weak dispersion interactions, as in *cyclo*hexane solution, the strain is not large unless the solute undergoes a considerable change in size on excitation, and much of the vibrational structure observed in the spectrum of the vapour should be retained. *sym*-Tetrazine does not undergo any major change in size on excitation in the visible region, since in the vapour the 0–0 vibrational transition gives rise to the most intense absorption band of the whole progression, and the progression itself is short (Table 1; Fig.).

TABLE 3. *The visible absorption spectrum of* sym-*tetrazine in* 5 : 1-iso*pentane–methylhexane at* 77° K. *Values in italics refer to shoulders of inflexions.*

$\nu_{\text{max.}}$ (cm.$^{-1}$)	$\varepsilon_{\text{max.}}$	Assignment	$\nu_{\text{max.}}$ (cm.$^{-1}$)	$\varepsilon_{\text{max.}}$	Assignment
17970	1090	0—0	19760	183	—
18060	*640*	—	19850	230	A + B
18665	1210	A (695 cm.$^{-1}$)	20045	404	3A
18730	*695*	—	20180	337	A + C
18820	*490*	—	20310	171	2B
19175	275	B (1205 cm.$^{-1}$)	20425	167	—
19355	1110	2A	20525	167	2A + B
19430	*503*	—	20730	200	4A
19500	496	C (1530 cm.$^{-1}$)	20860	200	2A + C

The visible absorption spectrum of sym-*tetrazine*: I, *at room temperature in the vapour*; II, *at* 77° K *in a* 5 : 1 iso*pentane–methyl*cyclo*hexane glass*; III, *in* cyclo*hexane*; *and* IV, *in aqueous solution at room temperature. The wavelength scale refers to the spectrum of the vapour,* II *and* III *being shifted* 150 *and* 250 *cm.*$^{-1}$ *to higher frequencies, respectively, and* IV 750 *cm.*$^{-1}$ *to lower frequencies. The frequencies of the bands assigned in* I *and* II *are given in Tables* 1 *and* 3, *respectively.*



On the other hand, if the solvation forces are the stronger hydrogen-bonding and dipole–dipole interactions the solvation cage is subject [4] on the excitation of the solute, not only to packing strain, due to the change in the size of the excited molecule, but also to orientation strain, due to the redistribution of electrons, which changes the dipole moment of the solute, and, in the case of $n \longrightarrow \pi$ transitions, the capacity of the solute to form hydrogen bonds with the solvent. The time required for the electronic excitation of a molecule is very short compared with the relaxation time of the solvent, and the strain of the solvation cage following the excitation of the solute leads to a weakening of vibrational quantisation in the excited state, resulting in a broad absorption band without vibrational fine structure. The $n \longrightarrow \pi$ bands of solutes in aqueous solution are free from vibrational structure also because of hydrogen-bonding in the ground state. The infrared absorption band due to the O–H stretching vibration is greatly broadened on hydrogen-bonding, and the energy of the lone-pair electrons responsible for the bonding must cover a range of values, so that the electronic excitation of such a lone-pair electron to a π-orbital results in a broad and structureless absorption band.

The integrated intensity of the visible absorption of *sym*-tetrazine is small, the oscillator strength of the excitation being [3] 0·0042. The transition is allowed on symmetry grounds, however, as the spectra of *sym*-tetrazine at liquid-nitrogen and room temperatures show (Fig.) the presence of a strong 0–0 vibrational band between the 1–0 and the 0–1 bands. The weakened intensity may be accounted for on other grounds if the absorption is due to a $n \longrightarrow \pi$ transition. The lone-pair and the π-orbitals of *sym*-tetrazine are concentrated in different regions of space, so that transitions between them are improbable,[7] and only the " *s* " component of the *s–p* hybrid lone-pair orbital can contribute to the transition moment of a $n \longrightarrow \pi$ excitation.[8]

The $n \longrightarrow \pi$ band of *sym*-tetrazine lies at a longer wavelength than that of any other monocyclic azine, since on aza-substitution the highest occupied level of pyridine is raised in energy whilst the lowest unoccupied level is stabilised, these effects being most marked in the case of *sym*-tetrazine.[3] The lone-pair atomic orbitals of the nitrogen atoms in *sym*-tetrazine, particularly those of adjacent atoms, overlap one another and interact, giving rise to four lone-pair molecular orbitals, all of which are filled with electrons. The highest occupied lone-pair molecular orbital, ψ_g, is of the form (II), and it is given explicitly by

$$\psi_g = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the ϕ's are lone-pair atomic orbitals of nitrogen. The lowest unoccupied π-orbital of tetrazine, ψ_e, is confined to the nitrogen atoms, having a node through the carbon positions, and it is given by

$$\psi_e = (\theta_2 - \theta_3 + \theta_5 - \theta_6)/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the θ's are $2p_x$ atomic orbitals of nitrogen.

The highest occupied and the lowest unoccupied molecular orbitals of *sym*-tetrazine, ψ_g and ψ_e, are similar in form, having the symmetries B_{3g} and A_u respectively in $\boldsymbol{D}_{2h}$, axes being taken as in (I). The orbitals differ, notably, in that ψ_g has no node in the plane of the molecule, so that an electronic transition from ψ_g to ψ_e is allowed ($A_g \longrightarrow B_{3u}$), with a transition moment perpendicular to the plane of the molecule. ψ_g is antibonding relative to a sp^2 lone pair atomic orbital of nitrogen and ψ_e is antibonding relative to a $2p$ atomic orbital, so that in the $n \longrightarrow \pi$ transition of *sym*-tetrazine there should be little change in the binding and the size of the molecule. There is no great change in the size of *sym*-tetrazine on excitation as the progression of vibrational bands in the spectrum is short and the vibrationless band is the most intense (Fig.). On passing from *sym*-tetrazine to 3 : 6-dideuterotetrazine the 0–0 vibration band in the visible spectrum of the vapour shifts some 15 cm.$^{-1}$ to lower frequencies (Table 1), suggesting that the zero-point energy and the binding of the molecule actually increase slightly on excitation. What appear to be sequences are observed on both the low- and the high-frequency side of the 0–0 band of the spectrum of the vapour (Fig.), indicating that some vibrational modes are increased in frequency and others decreased in the $n \longrightarrow \pi$ excitation of the tetrazine. The vibration responsible for the main progression in the visible spectrum of *sym*-tetrazine falls only from 725 cm.$^{-1}$ in the ground state to 695 cm.$^{-1}$ in the excited state (Tables 1 and 2).

Whilst there is little change in the overall size of the molecule, there should be minor changes in the shape of *sym*-tetrazine on excitation. In the ground state the molecule is not a regular hexagon, the bond lengths and angles determined by *X*-ray diffraction [9] being those of (III). In the excited state of the $n \longrightarrow \pi$ transition the 2—3 and 5—6 bonds of the tetrazine (I) should be weakened and lengthened, as ψ_e is more antibonding

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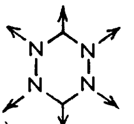
[7] Platt, *J. Chem. Phys.*, 1951, **19**, 101.
[8] Orgel, *J.*, 1955, 121.
[9] Bertinotti, Giacomello, and Liquori, *Acta Cryst.*, 1956, **9**, 510.

than ψ_g. The other bonds of the molecule should remain unaltered in the excited state, since a nodal plane, perpendicular to the molecular plane, passes through the positions 3 and 6 in ψ_e as in ψ_g (II). The CNN bond angle in the ground state [9] is 115·95°, indicating that the lone-pair electrons have some 40% of " *s* " character. In a $n \longrightarrow \pi$ transition the " *s* " character of the " hole " left by the promoted electron is shared by the remaining σ bond electrons of the nitrogen atoms, so that the CNN bond angles of *sym*-tetrazine increase towards 120° in the excited state. Thus the tetrazine should assume a shape near to that of a regular hexagon in the excited state of the $n \longrightarrow \pi$ transition.

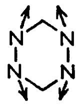
In an electronic transition only the totally symmetric vibrations of a molecule give rise to progressions of bands in the spectrum.[10] The totally symmetric vibrations do not all appear in the spectrum with equal probability, for the nuclear positions and velocities do not change during the electronic jump, and so the equilibrium positions of the nuclei in the ground state are the turning points of the vibrations active in the excited state. Thus the totally symmetric vibrations which transform the ground-state shape (III) into a regular hexagon should appear the most prominently in the band structure of the $n \longrightarrow \pi$ transition.

sym-Tetrazine has four totally symmetric vibrations (symmetry A_g in D_{2h}), the forms of the three ring vibrations being given in (A), (B), and (C). The fourth A_g vibration is the C–H stretching mode, which is not active in the $n \longrightarrow \pi$ transition, for the band structure of the spectrum covers a range of little more than 3000 cm.$^{-1}$, the expected frequency of the mode. Of the A_g ring vibrations, mode (C), and more particularly mode (A), should be strongly active in the excited state of the $n \longrightarrow \pi$ transition, since they are modes appropriate for the transformation of the shape (III) of the ground state into a regular hexagon. At liquid-nitrogen temperatures, where the $n \longrightarrow \pi$ transition takes place from a vibrationless ground state, three main excited-state frequencies appear in the band structure of the spectrum, namely, 695, 1205, and 1520 cm.$^{-1}$ (Fig.; Table 3). These frequencies correspond to the modes (A), (B), and (C), respectively. The main progression in the spectrum is due to the ring angle bending mode (A), and the bands arising from the ring stretching mode (C) are more intense than those produced by the ring breathing mode (B) (Fig.; Table 3). In 1 : 4-dideutero- and 1 : 4-dimethyl-tetrazine the frequency of the vibration mode (A) falls to 690 and 510 cm.$^{-1}$ respectively, indicating that the carbon atom substituents move during this vibration.

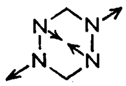
(A)



(B)



(C)



(E)

In the ground state the ring angle bending mode (A) has a frequency of 725 cm.$^{-1}$, as is shown by the position of the 1–0 vibration band in spectra of the vapour and *cyclo*hexane solution at room temperature (Tables 1 and 2). The frequency is consistent with the assignment to the mode (A), as the corresponding vibration has a frequency of 675 cm.$^{-1}$ in *sym*-triazine [11] and of 606 cm.$^{-1}$ in benzene.[12] The ground-state frequencies of the ring breathing and stretching modes, (B) and (C), respectively, are not known, as the Raman spectrum of *sym*-tetrazine, in which the A_g vibrations would be active, could not be determined by the methods available, owing to the absorption of the molecule in the visible region. The ring stretching vibration (C) has frequencies of 1556 and 1596 cm.$^{-1}$ in *sym*-triazine [11] and benzene,[12] respectively, and in both of these molecules the ring breathing mode (B) has the frequency [11,12] of 992 cm.$^{-1}$. The frequency of 1530 cm.$^{-1}$ for the mode (C) in the excited state of the $n \longrightarrow \pi$ transition of *sym*-tetrazine is acceptable, therefore,

[10] Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75.
[11] Lancaster and Colthup, *J. Chem. Phys.*, 1954, **22**, 1149; and private communication.
[12] Herzfeld, Ingold, and Poole, *J.*, 1946, 316.

though the value of 1205 cm.$^{-1}$ for the mode (B) is rather large. Some of the vibrations of *sym*-tetrazine have increased frequencies in the excited state of the $n \longrightarrow \pi$ transition, as is shown by the appearance of sequences on the high-frequency side of the 0–0 band in the spectrum of the vapour (Fig.), and mode (B) may be one of these vibrations.

The simple vibrational structure of the visible absorption spectrum of *sym*-tetrazine at 77° K is complicated at room temperature by a number of progressions in the dominant frequency of 690—700 cm.$^{-1}$, due to the vibration mode (A), which build on the sequences clustering round the band origin. One such progression, marked (D) in the Figure, is notable in that it includes the high-intensity vibrational bands of the shorter wavelength part of the spectrum of the vapour, and that the intensity maximum occurs at the third member, (D_3), in contrast to the main progression in the mode (A) where the intensity maximum is found in the 0–0 band (Fig.). The origin of the progression (D) appears to be the sequence (D_1), which, lying to the blue side of the 0–0 band, is due to a vibration which has a higher frequency in the excited than the ground state. The intensity maximum of the progression (D) indicates that the turning points of the active ground-state vibration correspond most closely to those of a state excited electronically together with one quantum of the same active vibration and two quanta of the mode (A). The active vibration of the sequence (D_1) is probably an in-plane mode, as otherwise the intensity distributions in the progressions (A) and (D) would be similar. For the mode to be appreciably populated in the ground state at room temperature, the vibration must be of low frequency. It cannot be the mode (A) itself, and the only other in-plane ring vibration of *sym*-tetrazine with a frequency less than 1000 cm.$^{-1}$ is the B_{3g} mode (E), which should have a frequency similar to that of (A), as in benzene [12] and *sym*-triazine [11] (A) and (E) are degenerate.

EXPERIMENTAL

Materials.—*sym*-Tetrazine and its 3 : 6-dimethyl and 3 : 6-dicarboxylic acid derivatives were prepared by the methods of Curtius, Darapsky, and Muller.[1,13] Dideuterotetrazine was prepared by the decarboxylation of the dideuterotetrazine-3 : 6-dicarboxylic acid at 150°. No bands due to C–H vibrations were detected in the infrared spectrum of the compound.

Spectra.—These were measured with a Cary recording spectrophotometer. The spectra of the vapour were obtained in an evacuated 10-cm. cell at the vapour pressure of the solid (*ca.* 1 mm.) at room temperature. The spectrum at liquid-nitrogen temperature was measured with a M/2000-solution of *sym*-tetrazine in a glass composed of a 5 : 1-mixture of *iso*pentane and methyl*cyclo*hexane, purified by Potts's method,[14] the low-temperature cell described by Passerini and Ross [15] being used. The measured frequencies were accurate to within 20 cm.$^{-1}$, and the optical densities to within 2—3%.

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[13] Curtius, Darapsky, and Muller, *Ber.*, 1915, **48**, 1614.
[14] Potts, *J. Chem. Phys.*, 1952, **20**, 809.
[15] Passerini and Ross, *J. Sci. Instr.*, 1953, **30**, 274.