

249. *The Electronic Spectra of N-Heteroaromatic Systems. Part V.*
The Rotational Structure of the Vibrationless Band in the $n \rightarrow \pi$
Transition of sym-Tetrazine.*

By S. F. MASON.

The 0-0 band in the absorption spectrum of *sym*-tetrazine, at 5515 Å, has been photographed with a 20-ft. Ebert grating spectrograph. The rotational structure observed shows well-defined *P*, *Q*, and *R* branches, with a slight degradation towards the blue end of the spectrum, and in overall appearance it resembles a parallel band of an oblate symmetric top. The electronic transition moment lies perpendicular to the plane of the molecule, and one or both of the moments of inertia about the twofold axes in the molecular plane decrease on excitation. An analysis of the structure based on the symmetric-top approximation gives an average rotational constant for the ground state agreeing satisfactorily with that calculated from the dimensions of *sym*-tetrazine determined by *X*-ray diffraction.

THE visible absorption spectrum of *sym*-tetrazine (I) in the vapour consists of a series of narrow bands, which were likened to the lines of atomic spectra by Koenigsberger and Vogt,¹ who were the first to examine the absorption quantitatively. The bands comprise the vibrational structure of an absorption due to the transition of an electron from a lone-pair orbital of the nitrogen atoms to a π -orbital of the ring,² and a vibrational analysis has shown³ that there is little change in the size of the molecule on excitation. It appeared probable, therefore, that the moments of inertia of *sym*-tetrazine would not alter greatly during the transition, so that rotational fine structure might be observed with adequate resolution, despite the relatively large size of the molecule, allowing the absorption to be more precisely characterised. The absorption of *sym*-tetrazine in the region of the 0-0

The rotational fine structure of the 0-0 vibrational band in the $n \rightarrow \pi$ electronic absorption spectrum of sym-tetrazine. The positions of the P and the R lines are given relative to the iron arc line at 18,133.583 cm.⁻¹.

<i>J</i>	<i>R_J</i> (cm. ⁻¹)	<i>P_J</i> (cm. ⁻¹)	<i>J</i>	<i>R_J</i> (cm. ⁻¹)	<i>P_J</i> (cm. ⁻¹)	<i>J</i>	<i>R_J</i> (cm. ⁻¹)	<i>P_J</i> (cm. ⁻¹)
5	2.568	-2.327	18	8.689	-7.655	31	14.849	—
6	3.061	—	19	9.327	-8.146	32	15.390	-13.734
7	3.476	-3.212	20	9.597	-8.598	33	15.680	-14.080
8	3.978	-3.732	21	10.022	-8.944	34	16.356	-14.407
9	4.461	-4.039	22	10.601	-9.252	35	16.800	-14.984
10	4.895	-4.443	23	11.181	-9.741	36	17.225	-15.407
11	5.368	-4.789	24	11.547	-10.225	37	17.919	-15.946
12	5.812	-5.251	25	12.049	-10.625	38	18.248	-16.350
13	6.295	-5.628	26	12.455	-10.983	39	18.707	-16.696
14	6.807	-6.047	27	13.073	-11.445	40	—	-17.176
15	7.261	-6.482	28	—	-11.976	41	19.677	-17.600
16	7.685	-6.909	29	13.807	-12.445	42	20.314	-17.908
17	8.207	-7.369	30	14.425	-12.830	43	20.855	-18.215

vibrational band³ at 5515 Å has now been photographed at a resolution of 150,000 with an Ebert grating spectrograph.⁴ A microphotometer tracing of the rotational fine structure found in the 0-0 band is given in Fig. 1, the positions of a number of rotational lines observed being recorded in the Table.

* Part IV, preceding paper.

¹ Koenigsberger and Vogt, *Physikal. Z.*, 1913, **14**, 1269.

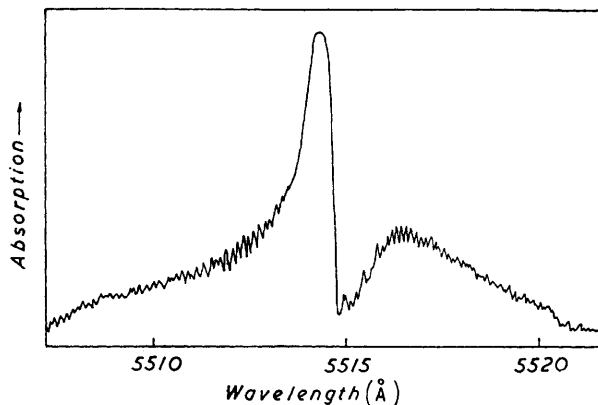
² Part I, *J.*, 1959, 1240.

³ Part IV, preceding paper.

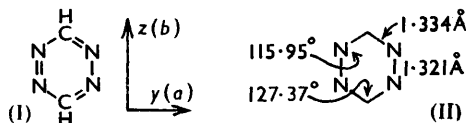
⁴ King, *J. Sci. Instr.*, 1958, **35**, 11.

The rotational structure of the vibrationless band in the visible absorption of *sym*-tetrazine shows well-defined *P*, *Q*, and *R* branches, and indicates that the apparent sharpness of the vibrational bands under lower resolution is due to the particularly prominent central *Q* branch (Fig. 1). A small but distinct degradation of the rotational structure towards the blue region can be observed (Table; Fig. 1), suggesting that the moments of inertia of *sym*-tetrazine are slightly smaller in the excited state than in the ground state. The overall appearance of the rotational-electronic band in the visible absorption of *sym*-tetrazine (Fig. 1) is that of a parallel band of an oblate symmetric top, involving little change in the moments of inertia of the molecule on excitation. For a planar molecule, such a band should consist of simple *P*, *Q*, and *R* branches with almost half of the total intensity of the band in the *Q* branch.⁵

FIG. 1. The rotational structure of the 0—0 band in the visible absorption spectrum of *sym*-tetrazine.



sym-Tetrazine is an asymmetric top, the moments of inertia, I_a , I_b , and I_c , calculated from the bond distances and bond angles (II) determined by *X*-ray diffraction⁶ and an assumed C—H bond distance of 1.0 Å, being 1.200, 1.330, and 2.530×10^{-38} g. cm.², respectively, in the ground state. The asymmetry parameter $\kappa = (2B - A - C)/(A - C) \simeq 0.80$ in the ground state, A , B , and C being the corresponding rotational constants. Thus *sym*-tetrazine is sufficiently similar to an oblate symmetric top for the parallel-type appearance of the rotational-electronic band to show that the visible absorption of the compound is due to an electronic excitation with the transition moment perpendicular to the plane of the molecule.



The assignment of the visible absorption of *sym*-tetrazine to the promotion of an electron from a lone-pair orbital of the nitrogen atoms to a π -orbital of the ring² requires that the transition should be polarised perpendicular to the molecular plane. The highest occupied (ψ_g) of the lone-pair molecular orbitals, which are formed by the overlap and interaction² of the four lone-pair atomic orbitals (ϕ) in *sym*-tetrazine, has the form

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

and the lowest unoccupied π -orbital (ψ_e) is, similarly

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

⁵ Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197.

⁶ Bertinotti, Giacomello, and Liguori, *Acta Cryst.*, 1956, **9**, 510.

where θ is a $2p_x$ atomic orbital. The orbitals, ψ_g and ψ_e , have the symmetries B_{3g} and A_u , respectively, in D_{2h} , axes being taken as in (I), and an electronic transition from ψ_g to ψ_e is allowed ($A_g \rightarrow B_{3u}$), with a transition moment perpendicular to the molecular plane.

A quantitative estimate of the change in the averaged moments of inertia of *sym*-tetrazine during the $n \rightarrow \pi$ transition can be obtained from the observed rotational structure, a symmetric-top approximation being used. The energy levels of an oblate symmetric top ($I_a = I_b$, $\kappa = 1$) are given by

$$E(J,K) = BJ(J+1) + (C-B)K^2 \quad . \quad . \quad . \quad (3)$$

where J and K are quantum numbers associated with the total angular momentum and with its component along the figure axis, respectively, and where $J \geq K$. A slightly asymmetric top has similar energy levels, but all levels with $K > 0$ are split into two components. If the splitting is small, a good approximation to the energy levels is provided by

$$E(J,K) = (A+B)J(J+1)/2 + [C - (A+B)/2]K^2 \quad . \quad . \quad (4)$$

When the symmetric-top approximation to the energy levels is valid for both the ground and excited states, the allowed changes in the rotational quantum numbers for electronic excitations in which the transition moment is parallel to the quasi-symmetry axis [the x or c axis of (I), perpendicular to the molecular plane] are $\Delta J = 0, \pm 1$, and $\Delta K = 0$. For a particular value of K , a sub-band is obtained with P , Q , and R branches, except for $K = 0$: the Q branch is then missing. Each sub-band can be referred to an origin, which is the hypothetical Q line for $J'' = 0$. The frequencies of the sub-band origins, ν_0 , are given by the equation

$$\nu_0 = \nu_{00} + \{[C' - (A' + B')/2] - [C'' - (A'' + B'')/2]\}K^2 \quad . \quad . \quad (5)$$

where the primes refer to the excited state and the seconds to the ground state, and ν_{00} is the frequency of the electronic origin of the band.

The complete parallel rotational-electronic band is formed by the superposition of a number of such sub-bands, corresponding to the various K values which occur at the temperature of observation. If the moments of inertia in the ground and the excited state are the same, the sub-bands of different K values coincide, with $\nu_0 = \nu_{00}$ in each case. The whole of the parallel band then appears with a strong line-like Q branch and P and R branches, like a perpendicular band of a linear molecule, though in contrast to the latter, each line consists of a number of components, $(J+1)$ in the R branch and J in the P branch. The general appearance is retained if the changes in the moments of inertia on excitation are small, but the band structure then becomes degraded.

The rotational-electronic band in the $n \rightarrow \pi$ absorption of *sym*-tetrazine corresponds to the latter case (Fig. 1). A K structure is not evident in the band, though the J structure of the P , Q , and R branches is clear. The average rotational constant $(A+B)/2$ can be obtained for the ground and the excited state from the J structure, by using an approximate treatment based upon the method of combination differences⁷ employed in the analysis of the perpendicular bands of linear molecules. If the term in K^2 of eqn. (4) is neglected, it follows from the definition of P and R branches ($\Delta J = -1$ and $+1$, respectively) that,

$$R(J) - P(J) = 2(A' + B')(J + 1/2) \quad . \quad . \quad . \quad (6)$$

$$R(J-1) - P(J+1) = 2(A'' + B'')(J + 1/2) \quad . \quad . \quad . \quad (7)$$

$$R(J-1) + P(J) = 2\nu_{00} + (A' + B' - A'' - B'')J^2 \quad . \quad . \quad (8)$$

where $R(J)$ and $P(J)$ are the frequencies of the R and the P lines, respectively, with a given J value.

⁷ Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, 1945, p. 390.

The J values of the lines in the P and the R branch of the rotational electronic band in the $n \rightarrow \pi$ absorption of sym-tetrazine have been obtained by means of a Fortrat diagram (Fig. 2), and the combination differences (eqns. 6—8) have been plotted against the derived J values (Figs. 3 and 4). Eqns. (6) and (7) give satisfactorily linear relations (Fig. 3), from which the average rotational constants 0.2215 and 0.2234 cm^{-1} are obtained

FIG. 2. The Fortrat diagram of the relation between the frequencies of the lines in the P and the R branches of the rotational-electronic band of sym-tetrazine and the rotational quantum number, J .

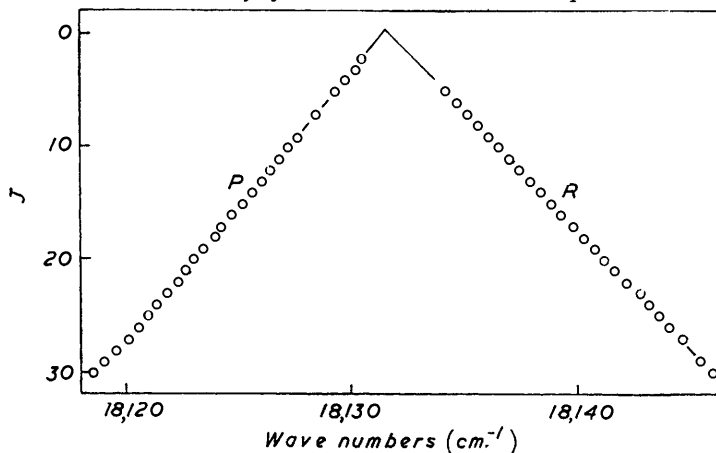


FIG. 3. The relations between the rotational quantum number, J , and the difference in frequency between lines of the R and the P branches (A) with the same J value, and (B) with the quantum numbers $(J - 1)$ and $(J + 1)$, respectively (eqns. 6 and 7).

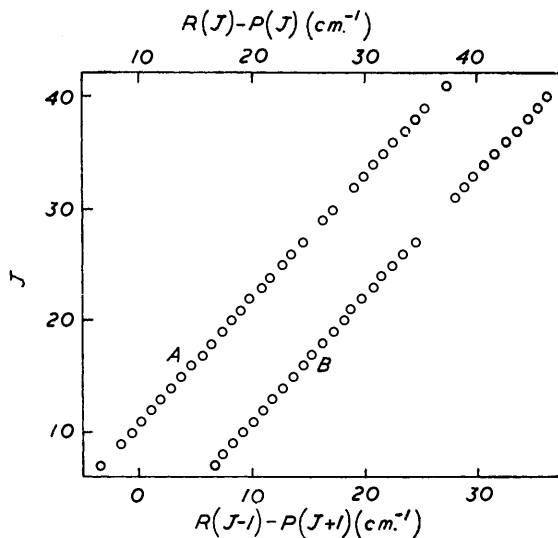
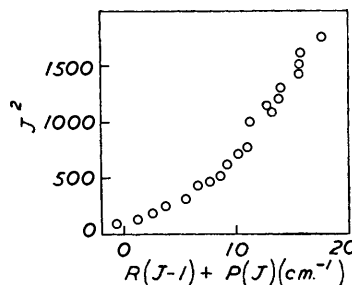


FIG. 4. The relation between the square of the rotational quantum number, J^2 , and the sum of the frequencies of lines in the R and the P branches having the quantum numbers $(J - 1)$ and (J) , respectively (eqn. 8). The origin of the frequency scale is placed arbitrarily at $36,267$ cm^{-1} .



for the ground and the excited state, respectively. The average ground-state rotational constant $(A + B)/2$ calculated from the bond distances and bond angles measured by X-ray diffraction⁶ and an assumed C-H bond distance of 1.0 Å is 0.2219 cm^{-1} , in satisfactory agreement with the spectroscopic value.

Eqn. (8), however, gives a curved plot (Fig. 4), which is due to the approximations employed in the derivation. For J values $<$ about 20, eqn. (8) gives approximately the

same value for the difference between the average rotational constants for the ground and the excited state $(A' + B' - A'' - B'')/2$ as eqns. (6) and (7), but the value falls progressively at higher J values. The larger the J value, the larger are the permitted values of K , and the more important becomes the term in K^2 neglected from eqn. (4). The term enters the expressions for the frequencies of the P and the R lines with the same sign and magnitude (eqn. 4), so that it cancels when the differences of such frequencies are taken (eqns. 6 and 7) but leads to progressive deviations (Fig. 4) when they are summed (eqn. 8).

A notable feature of the present results is the increase in the average rotational constant $(A + B)/2$ of *sym*-tetrazine during the $n \rightarrow \pi$ transition, demonstrating that one or both of the moments of inertia about the axes in the plane of the molecule (I_a and I_b) decrease on excitation. It is improbable that the decrease is due to a non-planar configuration of the molecule in the excited state, since the fall in the delocalisation energy of the six bonding π -electrons would greatly outweigh the stabilisation of the promoted electron in such a configuration. Benzene remains planar in the excited state of the $A_{1g} \rightarrow B_{2u}$, $\pi \rightarrow \pi$ transition⁸ though the excitation energy is more than twice as large as that of the $n \rightarrow \pi$ transition of *sym*-tetrazine.

A planar excited state being assumed, the increase in the average rotational constant $(A + B)/2$ of *sym*-tetrazine is consistent with the increase in the molecular zero-point energy on excitation, which is indicated by the red shift in the 0-0 band when the hydrogen atoms of *sym*-tetrazine are replaced by deuterium.³ The appearance of sequences to the blue side of the vibrationless band also shows that the frequencies of some of the vibrations of *sym*-tetrazine are increased in the excited state.³ The implication that the atoms of *sym*-tetrazine become more tightly bound during the $n \rightarrow \pi$ transition is surprising at first sight, since the excited-state orbital, ψ_e , is more antibonding than the ground-state orbital, ψ_g . The energy of ψ_e lies β_{NN} above that of a $2p$ orbital of nitrogen, the nitrogen-nitrogen resonance integral, β_{NN} , having a value in the region^{2,9} of 2-3 eV, whilst ψ_g is antibonding only to the extent of approximately 0.8 eV relative to an atomic $s-p$ hybrid lone-pair orbital of nitrogen.² Both ψ_g and ψ_e possess two nodal planes perpendicular to the the molecular plane, passing through the 3 and the 6 position and bisecting the N-N bonds, respectively, so that a weakening and a lengthening of the N-N bonds during the $n \rightarrow \pi$ transition might be expected, resulting in an increase in the moment of inertia, I_a .

The CNN bond angle in *sym*-tetrazine⁶ is 115.95° (II), suggesting that the σ bonds of a nitrogen atom have 30.5% and the lone-pair orbital 39.0% of "s" character in the ground state. On the promotion of a lone-pair electron to a π -orbital, the "s" character of the "hole" left behind is shared amongst the remaining σ electrons, notably those of the σ bonds. The increase in the "s" character of the nitrogen σ bond electrons has the consequences that the CNN bond angle should increase and that the effective atomic radius of the nitrogen atoms should decrease on excitation. In the vibrational structure of the $n \rightarrow \pi$ absorption of *sym*-tetrazine the main progression is due to the A_g ring-angle bending mode, showing that the CNN angle changes during the transition.³ An increase in the CNN angle alone does not account for the increased average rotational constant $(A + B)/2$ on excitation, for if the bond lengths of *sym*-tetrazine remain unchanged (II) and all the bond angles become 120° the calculated average rotational constant shows a small fall to the value of 0.2213 cm^{-1} .

If *sym*-tetrazine remains planar in the excited state of the $n \rightarrow \pi$ transition the observed increase in the average rotational constant is probably due to a small decrease in some of the ring-bond lengths, suggesting that the contraction in the covalent radius of the nitrogen atoms owing to the increased "s" character of the σ hybrid bonds on excitation, outweighs the antibonding effect of the promoted electron. The covalent radius of a nitrogen atom may vary considerably with the hybridisation of its σ orbitals.

⁸ Garforth, Ingold, and Poole, *J.*, 1948, 508.

⁹ Paoloni, *Gazzetta*, 1957, **87**, 313.

In azobenzene,¹⁰ where the CNN angle is 120—123°, depending upon the isomeric and crystallographic form of the molecule, the N—N distance is 1.23 Å, compared with 1.321 Å in *sym*-tetrazine.⁹ With the same Coulomb and resonance parameters, the calculated N—N π -bond order is 0.83 in azobenzene¹¹ and 0.66 in *sym*-tetrazine.¹² It is unlikely that the shorter N—N distance in azobenzene is due entirely to the larger N—N bond order. Part of the shortening is probably derived from the 3—6% larger “s” character of the σ bonds in azobenzene, but the relative importance of the two factors cannot be assessed at present.

In the vapour the long-wavelength absorption of the monocyclic azines consists,^{2,13,14,15} in general, of a system of narrow bands, comparable to atomic spectral lines. As in the case of *sym*-tetrazine, the absorption is due to a $n \rightarrow \pi$ transition with a moment perpendicular to the plane of the molecule.² The monocyclic azines either are or resemble oblate symmetric tops, and the $n \rightarrow \pi$ transitions of these compounds should give vibrational bands with a parallel-type rotational structure. If the moments of inertia of the azine do not change greatly during the $n \rightarrow \pi$ excitation the Q lines corresponding to different K values superpose, or nearly so, giving a strong line-like Q branch, as for *sym*-tetrazine (Fig. 1), thus accounting for the narrowness of the long-wavelength absorption bands. One or both of the moments of inertia about the axes in the plane of *sym*-tetrazine decrease slightly during the $n \rightarrow \pi$ transition, and in the other azines, which have $n \rightarrow \pi$ excited states of higher energy, the corresponding moments of inertia probably undergo small increases. The unresolved rotational structure of the narrow vibrational bands in the $n \rightarrow \pi$ absorption of pyrazine degrades¹⁵ towards the red region, in support of this view, but a few weak and broad vibrational bands, degrading towards the blue region, were also observed.¹⁵

EXPERIMENTAL

sym-Tetrazine¹⁶ was examined at the vapour pressure of the solid (about 1 mm.) corresponding to room temperature in an evacuated 10-cm. silica cell. Absorption spectra were photographed in the first order of a 20-ft. Ebert grating spectrograph⁴ with a high-pressure xenon arc as a light source. Iron-arc comparison spectra were superposed immediately before or after each exposure.

The plate dispersion in the absorption region was approximately 0.59 Å/mm. and the resolving power was 150,000, corresponding to a minimum separation between resolvable lines of approximately 0.04 mm. Microphotometer tracings of the plates were taken with a tenfold magnification, and the positions of the rotational lines were measured in both directions from the tracings and from the plates, a travelling microscope reading to 0.01 mm. being used. The wavelengths of the rotational lines were obtained by interpolation from the wavelengths of the iron-arc reference lines, and they were converted into vacuum wavenumbers (Table).

The author is indebted to Dr. G. W. King for the photographs of the spectrum, and to Dr. H. G. Poole for the microphotometer tracings of the plates.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, EXETER.

[Received, September 9th, 1958.]

¹⁰ Lange, Robertson, and Woodward, *Proc. Roy. Soc.*, 1939, *A*, **171**, 398; Hampson and Robertson, *J.*, 1941, 409.

¹¹ Present work.

¹² Liquori and Vaciago, *Ricerca sci.*, 1956, **26**, 181.

¹³ Rush and Sponer, *J. Chem. Phys.*, 1952, **20**, 1847.

¹⁴ Uber, *ibid.*, 1941, **9**, 777.

¹⁵ Ito, Shimada, Kuraishi, and Mizushima, *ibid.*, 1957, **26**, 1508.

¹⁶ Curtius, Darapsky, and Müller, *Ber.*, 1907, **40**, 84.