423. *The Electronic Structure of Tetranitrogen Tetrasulphide*, N_4S_4

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The visible and ultraviolet spectrum of N_4S_4 has been measured in a number of solvents at room temperature and at 77°K. The results are rationalised in terms of a molecular orbital scheme in which weak S–S bonding is included. It is shown that structures in which this S–S bond is absent cannot account for the properties of the molecule.

THE nature of the bonding in N_4S_4 is still the subject of controversy,[1–3] although *X*-ray crystallography has definitely established the shape of the molecule [4,5] as a slightly distorted bisphenoid (Fig. 1). The ultraviolet spectrum of N_4S_4 is of particular interest in connection with the general problem of *pπ–dπ* bonding, since the more discussed phosphonitrilic compounds [6–9] absorb only in the far ultraviolet region.[10]

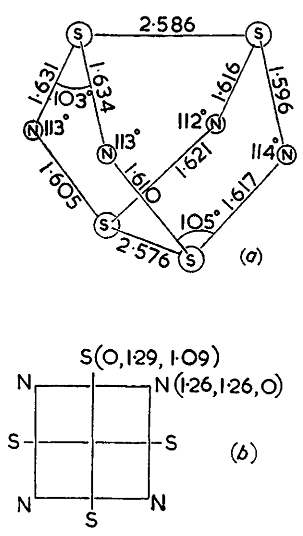

FIG. 1. Geometry of N_4S_4; (*a*) actual, (*b*) idealised. Dihedral angle SNS–NSN = $\cos^{-1}$ 0·5447, angle between S–S and plane NSN = $\cos^{-1}$ 0·03

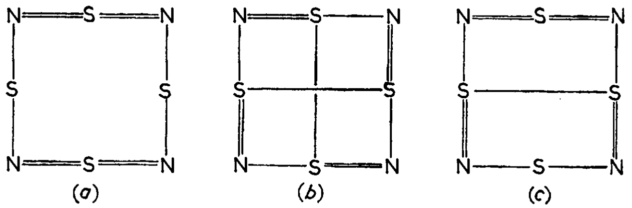

FIG. 2. Valence bond " structures " for N_4S_4

Theories of Bonding.—N_4S_4 is usually described as mesomeric between forms (*a*) of Fig. 2. This is unrealistic, as the two different forms (*a*) differ by more than two one-electron functions, and can interact with another only very weakly. Thus linear polymers $(SN)_x$, probably derived from chain structures of type (*a*), show bond alternation.[11] Both structures (*a*) can, however, mix with structures (*b*), as can the structures (*c*) which we include for completeness as being the only other set of non-polar structures which satisfy the following requirements: all nitrogens are tervalent; all sulphurs are either bi- or quadri-valent; all bonds are between neighbouring atoms. It is possible to demonstrate that while structures (*a*) and (*c*) do not mix with each other or with structures of the same

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[1] (Becke-)Goehring, *Quart. Rev.*, 1956, **10**, 437.
[2] Chapman and Waddington, *Trans. Faraday Soc.*, 1962, **58**, 1679.
[3] Lindqvist, *J. Inorg. Nuclear Chem.*, 1958, **6**, 159.
[4] Clark, *J.*, 1952, 1615.
[5] Sharma and Donohue, *Acta Cryst.*, 1963, **16**, 891.
[6] Craig, *J.*, 1959, 997.
[7] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.
[8] Craig, Heffernan, Mason, and Paddock, *J.*, 1961, 1376.
[9] Craig and Paddock, *J.*, 1962, 1376.
[10] Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.
[11] Chapman, Warn, Fitzgerald, and Yoffe, *Trans. Faraday Soc.*, 1964, **60**, 294.

sort, they can both mix with structures (*b*). This is done by formally regarding the sulphur *p* and *d* orbitals as different " atoms," treating bivalent sulphur as a system in which there is a formal polar bond between S(p) and S(d), and applying the formalism of Craig.[12]

A realistic model of the bonding which does not ignore structures (*a*) entirely, must treat the sulphur *d*, the nitrogen $p\pi$, and the sulphur–sulphur bonding orbital as part of one single resonating system. The problem could in principle be treated by valence bond theory, but the number of possible " structures " is so great as to make this totally unwieldy. We therefore set up the following molecular orbital scheme:

Each nitrogen is in a configuration (lone pair) ^{2} (sp_xp_y hybrid) ^{2} p_z, the local axes being chosen as in Fig. 3*b* (following Craig and Paddock,[9] but right-handed). If the hybrid orbitals are directed along the NS bond, we have a configuration (lone pair)$^2\sigma_+\sigma_-p_z = (0{\cdot}65s - 0{\cdot}76p_y)^2(0{\cdot}76s + 0{\cdot}65p_y)(p_x)(p_z)$ for the nitrogen, where σ_+ is the orbital σ-bonding to the in-phase combination of sulphur atoms, and $\sigma_-(= p_x)$ the orbital bonding to the corresponding out-of-phase combination.

To discuss the sulphur atom of Fig. 3*a*, we ignore the effect of the *d*-orbitals on the σ-bonding. The sulphur is taken as quadrivalent, as in structure (*b*) of Fig. 2. The mixing of structures (*a*) and (*c*) with structure (*b*) in the V.B. description now corresponds to the variation of the parameters of orbitals combining S(d) and N(z), or N(z) and S(p_z), and the sulphur is treated as being (lone pair)$^2\sigma_+\sigma_-$S(z)d, where S(z) is a combination of p_z and s. We do not, at this stage, further specify the *d* orbital.

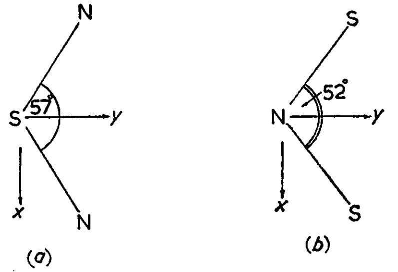

FIG. 3. Local co-ordinate systems (z pointing upwards)

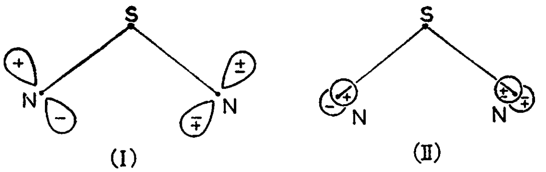

FIG. 4. The two sorts of S–N π-bonding

We regard the σ-electrons, the S lone pairs, and, to a first approximation, the nitrogen lone pair, as not being involved in the π-bonding. In justification of this we note that $S_4(NH)_4$ shows its first absorption band at 46 kK (see below), which is outside the range of our discussion. We also note that the assignment of the σ-bonding to the interaction of (effectively) sp^2-hybridised N with sp^3-hybridised S is consistent with the observed bond angles. The z-axis of each sulphur atom now virtually coincides with (in fact deviates by less than 2° from) the S–S direction.

Choice of sulphur d orbital. We combine the axis-systems of Fig. 3 to obtain Fig. 5. It is immediately apparent that the N(z) orbitals are not parallel to the S(z) orbitals of neighbouring atoms. Since a $p(z)$ orbital transforms like a vector, we can " resolve " it in directions parallel and perpendicular to S(z), thus obtaining the two different sorts of π-bonding I and II of Fig. 4.

The sulphur *d*-orbitals may be classified by their behaviour under the reflection σ_x, which is the only true element (other than the identity) in the C_{2v} pseudo-" site group " of the S atom. Strictly, all of these orbitals should be included in our calculation.[9] For simplicity, we limit the discussion to two such orbitals, labelled d^+ and d^- to represent their behaviour under reflection, and remember that each term involving them is a sum of parts,

[12] Craig, *Proc. Roy. Soc.*, 1950, *A*, **200**, 390.

so that there may be more than one each of d^+, d^- accessible. The classification into I and II is, in a sense, irrelevant, since I, II transform in the same way under the operations of the point group D_{2d} of the idealised molecule, and will always occur with the same relative weighting.

Molecular Orbital Treatment.—LCAO functions spanning irreducible representations of the group D_{2d} are set up as listed in Table 1, following the axis system of Fig. 5. The behaviour of S-atom orbitals under reflection perpendicular to the local x-axis determines their transformation properties, since this is the only element in the site group, other than the identity, which is shared by the molecule. The same is true for the behaviour of N-atom orbitals under rotation round the local y-axis.

Applying a straightforward Hückel-type treatment, we arrive at the energy matrices of Table 2. Resonance integrals with non-nearest neighbours are ignored. The coefficients of the integrals between neighbouring S-atom orbitals are given the same sign as the overlap integral, while those between N and S atom orbitals are given the same sign as the overlap integral between N(z) and S(x) for d^-, or between N(z) and S(z^2) for d^+, S(z). The interaction between S(z), d^+ is set equal to zero. This is equivalent to allowing a certain amount of d–p hybridisation, so as to diagonalise the S(z)–d^+ submatrices. Since we have not chosen our base-functions as eigenfunctions of l_z, our treatment differs from that of Craig *et al.*[8] It would help little to do so, since the highest proper rotation axis is two-fold.

TABLE 1

LCAO's belonging to irreducible representations of D_{2d}

Atom orbital	LCAO	Representation
N(z)	$(z_1 + z_3 + z_5 + z_7)/2$	A_2
	$(z_1 - z_3 + z_5 - z_7)/2$	B_2
	$(z_1 - z_3 - z_5 + z_7)/2$	$E(X + Y)$
	$-(z_1 + z_3 - z_5 - z_7)/2$	$E(X - Y)$
S(d^+)	$(d^+_2 + d^+_4 + d^+_6 + d^+_8)/2$	A_1
	$(d^+_2 - d^+_6)/\sqrt{2}$	$E(X + Y)$
	$(d^+_8 - d^+_4)/\sqrt{2}$	$E(X - Y)$
	$(d^+_2 - d^+_4 + d^+_6 - d^+_8)/2$	B_2
S(d^-)	$(d^-_2 - d^-_4 + d^-_6 - d^-_8)/2$	A_2
	$(d^-_2 - d^-_6)/\sqrt{2}$	$E(X - Y)$
	$(d^-_8 - d^-_4)/\sqrt{2}$	$E(X + Y)$
	$(d^-_8 + d^-_4 + d^-_6 + d^-_8)/2$	B_1
S(z)	Transforms in exactly the same way as S(d^+)	

TABLE 2

Energy matrices of the π and S–$s\sigma$ systems

$$A_1 \quad \begin{array}{c|cc} & \mathrm{S}(z) & d^+ \\ \hline \mathrm{S}(z) & q + \beta[\mathrm{S}(z),\mathrm{S}(z)] & 0 \\ d^+ & 0 & r + \beta(d^+,d^+) \end{array}$$

$$A_2 \quad \begin{array}{c|cc} & \mathrm{N}(z) & d^- \\ \hline \mathrm{N}(z) & p & -2\beta[\mathrm{N}(z),d^-] \\ d^- & & s - \beta[d^-,d^-] \end{array}$$

$$B_1 \quad \begin{array}{cc} d^- & s - \beta(d^-,d^-) \end{array}$$

$$B_2 \quad \begin{array}{c|ccc} & \mathrm{N}(z) & \mathrm{S}(z) & d^+ \\ \hline \mathrm{N}(z) & p & +2\beta[\mathrm{N}(z),\mathrm{S}(z)] & +2\beta[\mathrm{N}(z),d^+] \\ \mathrm{S}(z) & & q + \beta[\mathrm{S}(z),\mathrm{S}(z)] & 0 \\ d^+ & & & r + \beta[d^+,d^+] \end{array}$$

$$E \quad \begin{array}{c|cccc} & \mathrm{N}(z) & \mathrm{S}(z) & d^+ & d^- \\ \hline \mathrm{N}(z) & p & \sqrt{2}\beta[\mathrm{N}(z),\mathrm{S}(z)] & \sqrt{2}\beta[\mathrm{N}(z),d^+] & \sqrt{2}\beta[\mathrm{N}(z),d^-] \\ \mathrm{S}(z) & & q - \beta[\mathrm{S}(z),\mathrm{S}(z)] & 0 & 0 \\ d^+ & & & r - \beta[d^+,d^+] & 0 \\ d^- & & & & s + \beta(d^-,d^-) \end{array}$$

We introduce the following definitions:

$$Q^{+} = \{\beta[\mathrm{N}(z), d^{+}]\}^{2}/\{\mathrm{e}(d^{+}) - \mathrm{e}[\mathrm{N}(z)]\}$$
$$Q^{-} = \{\beta[\mathrm{N}(z), \mathrm{d}^{-}]\}^{2}/\{\mathrm{e}(d^{-}) - \mathrm{e}[\mathrm{N}(z)]\}$$
$$Q_{\sigma} = \{\beta[\mathrm{N}(z), \mathrm{S}(z)]\}^{2}/\{\mathrm{e}[\mathrm{S}(z)] - \mathrm{e}[\mathrm{N}(z) - \beta[\mathrm{S}(z), \mathrm{S}(z)]\}$$
$$Q_{\sigma*} = \{\beta[\mathrm{N}(z), \mathrm{S}(z)]\}^{2}/\{\mathrm{e}[\mathrm{S}(z)] - \mathrm{e}[\mathrm{N}(z)] + \beta[\mathrm{S}(z), \mathrm{S}(z)]\}$$

If we assume that the sequence of one-electron energies ignoring π-bonding is in the order $\mathrm{N}(z) < \mathrm{S{-}S}\sigma < \mathrm{S{-}S}\sigma^{*} < \mathrm{S}(d^{+}), \mathrm{S}(d^{-})$, then we have, to second order, the energy level diagram of Fig. 6. The lowest empty orbital is chosen non-degenerate in view of the work of Chapman and Massey,[13] who found for the $N_4S_4^-$ anion a g value of 2·006, the odd electron interacting equally with all four nitrogen nuclei. (While this is not conclusive evidence for non-degeneracy,[14] the spectrum does not show the line broadening found in degenerate cases.) The N-hyperfine splitting then might arise through the expected π' bonding [6] which gives the π non-bonding S(d) combinations some N(s) character. Two sets of orbitals d^- are shown, so that the assignments of Table 3 may be shown in Fig. 6.

TABLE 3

Visible and ultraviolet spectrum of N_4S_4

Band	$\nu_{\text{max.}}$ (kK)	$\varepsilon_{\text{max.}}$	Assignment *	Comments
I	~24·5	Est.† 250	$B_2^{\,2} \longrightarrow B_1^{\,1}$	Vibronic shoulder
II	~30·6	Est. 1000—2000	$A_1^{\,1} \longrightarrow B_1^{\,1}$ (or $B_2^{\,2} \longrightarrow B_1^{\,1a}$)	Shoulder
III	38·9	19,000	$B_2^{\,2} \longrightarrow E^{2}$	Very broad, $f = 1{\cdot}12$
IV	~49·0	~5500	σ-system?	Shoulder
V	>54·0	>6000	σ-system?	Off scale

* In terms of the one-electron energy levels of Fig. 6. † Est. = estimated.

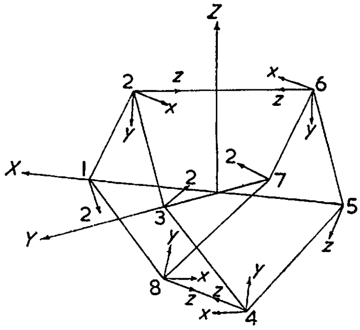

FIG. 5. The numbering of atoms of Table 1. Atoms 1, 3, 5, 7 are N. Atoms 2, 4, 6, 8 are S

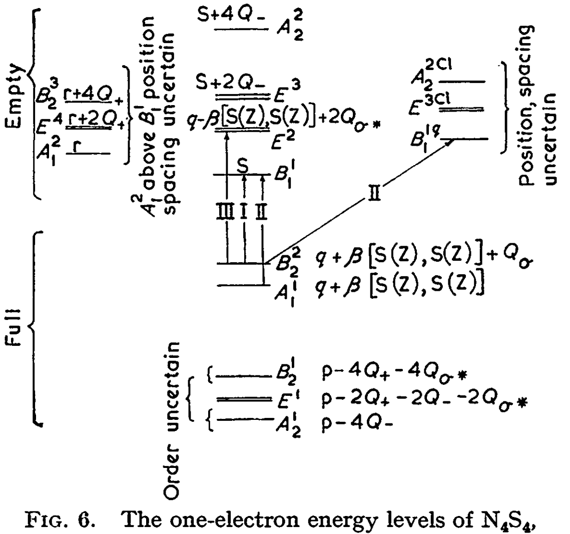

FIG. 6. The one-electron energy levels of N_4S_4, on the present theory, with assignments of the observed transitions

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[13] Chapman and Massey, *Trans. Faraday Soc.*, 1962, **58**, 1291.

[14] McConnell and McLachlan, *J. Chem. Phys.*, 1961, **34**, 1.

EXPERIMENTAL

Solution spectra were measured in a variety of solvents, at ~50, 25, and −196°, with path lengths varying from 1 mm. to 4 cm. Spectra at 25 and *ca.* 50° were measured successively for the same sample on a Unicam S.P. 500 instrument, the solvent blank being maintained at the same temperature as the sample in an electrically thermostated copper holder. Solvents were chosen for their involatility. Room-temperature spectra and spectra at 77°K were measured successively for the same sample on a recording Carey 11 instrument, with a vacuum-jacketed low-temperature cell of a pattern previously described.[15] Spectra in the region 1900—2100 Å were determined on a recording Perkin-Elmer UV 137 instrument.

Solvents were purified by standard methods,[15] preceded in the case of hydrocarbons other than decalin by stirring with concentrated sulphuric acid for 3—4 hr. Decalin, which reacts with concentrated sulphuric acid, was converted to the all-*trans* form [17] before purification, as this made distillation more effective for removing tetralin. The ultraviolet spectra were used as the criterion of purity, both immediately after distillation and immediately before making up solutions. Any solvent containing enough aromatic impurity to be detected in 1 cm. path length in the 2500 Å region, using the Perkin-Elmer instrument, was rejected. Solvents were stored in a refrigerator, in dark glass bottles, over calcium chloride. Solvents for low-temperature measurements, for which it is essential to avoid traces of water, were dried overnight over calcium chloride, and then stored over excess of phosphoric oxide, which was removed immediately before use of the solvent by filtering through glass wool. Special precautions were not taken to keep atmospheric moisture from the solutions. Presumably for this reason, the cold solutions showed irreproducible scattering below 3500 Å, making quantitative intensity measurements at high energies and low temperatures unreliable. It was especially important that the solvents be aromatic-free, since otherwise the vibrationally structured benzenoid absorption at around 2500 Å, being sharper at low temperature, would give spurious structure in precisely the region of maximum absorption of the test substance. Reflection spectra were obtained on a Unicam S.P. 500 instrument, with special reflection attachment, in which the sample is seated on a metal block which can be cooled with liquid nitrogen, sealed off from the atmosphere to prevent frosting.

N_4S_4 prepared by the method of Arnold, Hugill, and Hutson,[18] had m. p. 179° (lit.,[1] 178°) after twice recrystallising from 4 : 1 v/v $CHCl_3$–CCl_4. The substance was pure to chromatography by light petroleum on pentyl acetate paper ($R_F = 0{\cdot}65$), and by dimethylformamide on pentyl acetate paper ($R_F = 0{\cdot}8$).

To study the effect of warming on the spectrum, decalin, several involatile esters, and tetrabromoethane were found suitable, being involatile and dissolving N_4S_4 without reacting. The spectrum was independent of solvent, showing the features of Table 3. The effect of a rise in temperature over part of the range was so small as to be on the limits of instrument reading, but the reproducibility was high enough to show the reality of all the main features. A typical spectrum is shown in Fig. 7, together with the change on heating. Dominating features are the increase in intensity with temperature of the low-energy tails of the bands at 3200 Å and 2500 Å, and the corresponding loss of intensity in these bands on the high-energy side of their origins, a conclusion implicit in the simple theory of the effect,[19] since the integrated intensity of a non-vibronic band is temperature-independent. The upward turn in the plot of $\Delta \log \varepsilon$ against ν at 40,000 cm.$^{-1}$ is genuine, and was used to predict the existence of a band at slightly higher energy before it was directly observed.

For a quantitative study of the effect of raising the temperature on the low-energy tail of the absorption, tetrabromoethane, in which N_4S_4 is appreciably soluble, was chosen. The results are in Fig. 8. The variation of $\log \varepsilon$ with energy is slower than the simple theory requires,[19] but the effect of temperature on the slope of the graph is in closer agreement with theory than could reasonably have been hoped. It follows that the deepening in colour of N_4S_4 on warming can be accounted for entirely by the expected Boltzmann effect on the population of states giving rise to hot bands.

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[15] Passerini and Ross, *J. Sci. Instr.*, 1953, **30**, 274.

[16] A. Weissberger (ed.), " Technique of Organic Chemistry," Vol. VII, 2nd edn., New York, 1955.

[17] Zelinsky and Turowa-Pollak, *Ber.*, 1932, **65**, 1299.

[18] Arnold, Hugill, and Hutson, *J.*, 1936, 1645.

[19] Brodersen and Langseth, *Dansk Mat. Fys. Med.*, 1951, **26**, No. 3.

For low temperatures, methylcyclohexane–pentane (3 : 2 v/v) was used for ultraviolet work, while a mixture, in which N_4S_4 is much more soluble, of equal volumes of n-propyl chloride, isopropyl chloride, n-butyl chloride, and isobutyl chloride was preferred for the visible region. The solvent mixtures, especially the halide solvent mixture, tended to crack on cooling; this tendency could be reduced but not eliminated by gradual cooling. It was therefore shown, in a separate experiment, that the effect of such cracking is to shift the base line (in log units) but not to alter its shape. The spectrum of a cracked solution can thus be fixed by the base line at low energy, where absorption is negligible.

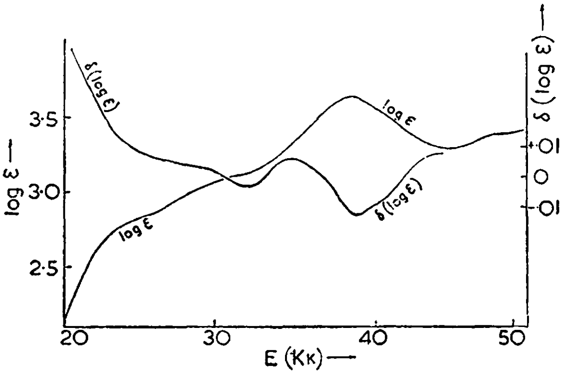

FIG. 7. Absorption spectrum of N_4S_4 in solution at room temperature, and effect of heating [$\delta \log \varepsilon = \log \varepsilon\,(50°) - \log \varepsilon\,(25°)$]

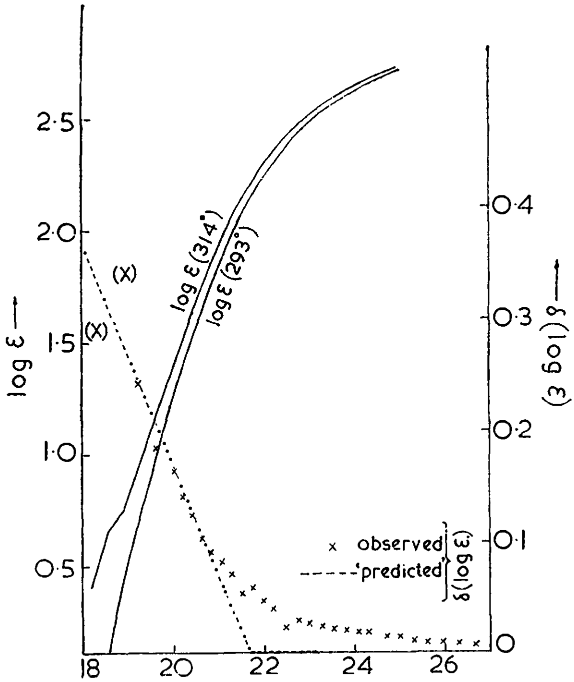

FIG. 8. Comparison of spectra of N_4S_4 in tetrabromoethane at 25° and 41°

The quantitative results of the experiments with alkyl chloride solvent are shown in Fig. 9. In addition to the expected loss of intensity at low temperatures, due to quenching of the hot bands, there is a real loss of intensity in the estimated region of the unresolved lowest energy band. This indicates that the band derives its intensity by a vibronic mechanism, and the size of the effect suggests an activating frequency of some 250 cm.$^{-1}$, which seems reasonable in view of the infrared spectrum.[13] The experiments with hydrocarbon solvent were qualitative rather than quantitative, and yielded only the useful negative information that the spectrum develops neither fine structure nor increased resolution on cooling to 77°K.

The diffuse reflection spectrum of a sample ground cautiously (explosion risk) with NaCl diluent gives no fresh information. The effect of cooling is to cause a loss of intensity in the entire region of measurement, 6000—3500 Å, which is consistent with the vibronic nature of the lowest-energy band.

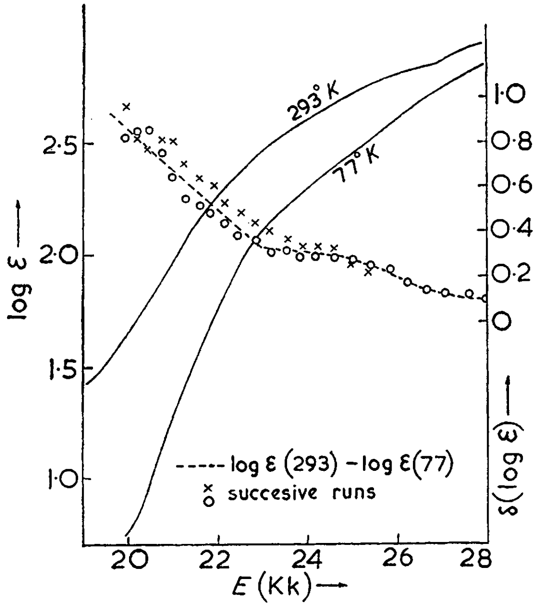

FIG. 9. Comparison of spectra of N_4S_4 in mixed alkyl chloride solvent at 293 and 77°K

The vapour phase spectrum of N_4S_4 was determined at between 80 and 90° on a Hilger medium spectrometer, using a one-metre path length and Ilford R 30 plates, with a hydrogen lamp as source. Under these conditions there was only enough vapour to absorb in the 2500 Å region. No fine structure or other additional information could be obtained.

A sample of $S_4(NH)_4$, donated by Professor M. Becke-Goehring, was twice recrystallised from acetone–methanol. A concentrated solution in acetone [in which $S_4(NH)_4$ is highly soluble] indicated an extinction coefficient less than 2 at wavelengths longer than 3100 Å. There is a shoulder at 43,500 cm.$^{-1}$ (extinction coefficient 2·13 × 10^3) and a peak at 50,500 cm.$^{-1}$ (extinction coefficient 8·9 × 10^3).

DISCUSSION

While thiones show an $n \longrightarrow \pi^*$ transition in the near ultraviolet,[20] we reject such an assignment for the lowest energy transition in N_4S_4 for the following reasons: (i) The transitions in thiones are $n \longrightarrow p\pi^*$, whereas those in N_4S_4 are either $n \longrightarrow \sigma^*(E^2)$, or $n \longrightarrow S(d)$ $(A_1{}^2$ or $B_1{}^2)$. Transitions analogous to these latter should exist also in $S_4(NH)_4$. But $S_4(NH)_4$ does not absorb at all in this region. (ii) Such absorption would be expected only at higher energy than the thione absorption, and would be overlaid by stronger transitions. (iii) The low-energy band of N_4S_4 is vibronic. The excitation of a lone pair is weak because of low spatial overlap, not because of symmetry considerations, and is not increased by vibronic interaction.

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[20] Janssen, *Rec. Trav. chim.*, 1960, **79**, 464.

It follows that the first transition is symmetry-forbidden, and cannot have symmetry E or B_2 in D_{2d}. Possible transitions then are, depending on the order of $S(z)\sigma$ and $N(z)$, and that of d^+, d^-,

$$\begin{array}{lcl} B_2^1 \text{ or } B_2^2 & \longrightarrow & B_1^1 \\ A_2^1 & \longrightarrow & A_1^2 \end{array}$$

But the transitions of electrons from B_2^1 or A_2^1 are of type $\pi \longrightarrow \pi^*$, and there is no obvious reason why they should lie at much lower energy than the corresponding transitions in phosphonitrilic compounds. Indeed, one would expect them to lie at higher energies in N_4S_4, since the π-bonding orbitals [mainly $N(z)$ in character] are stabilised in N_4S_4, as in the phosphonitrilic compounds, while the d orbitals are not stabilised in the same way by adjacent electronegative groups. The first transition is, then, $B_2^2 \longrightarrow B_1^1$.

The very strong ($f = 1{\cdot}12$) band at 38·9 kK is of such a shape as to correspond to a large change in dimensions between the ground state and the excited state. We therefore assign this band as $B_2^2 \longrightarrow E^2$, *i.e.*, essentially S–S $\sigma \longrightarrow \sigma^*$. This band should occur with very high intensity and at lower energy than the corresponding transition in species like S_8 since here the S–S bond is usually long, and the donor level of the transition is raised in energy by π-bonding in the same way as the acceptor level, but to a greater extent. An assignment to a $\pi \longrightarrow \pi^*$ transition would not account for the change in dimensions on excitation.

The weak band around 30·6 kK cannot be $B_2^2 \longrightarrow A_1^2$, for this is symmetry-allowed, and, having a great deal of same-atom $p \longrightarrow d$ character, would presumably be very strong. It follows that it is either $A_1^1 \longrightarrow B_1^1$, or else a transition $B_2^2 \longrightarrow B_1^{1a}$ to the other π-non-bonding d^- level. We cannot distinguish between these possibilities.

Diamagnetism.—$S_4(NH)_4$ has a magnetic susceptibility of -88×10^{-6}/mole,[21] whereas the corresponding figure for N_4S_4 is -102. The predicted effect of the loss of a proton [22] is to cause a paramagnetic shift of $+2{\cdot}9$ units per S atom, whereas the observed shift is $-3{\cdot}5$.

Thus the shift from $S_4(NH)_4$ to N_4S_4 is, after correction for the H atom, $-6{\cdot}4$ units. Of this about half could be assigned to double-bond formation, but the effect of the corrections for electronegativity of neighbours as it affects the S–S bond, and for increased valency, is to produce a paramagnetic shift in the calculated susceptibility.† It follows that there is an appreciable diamagnetic ring current in N_4S_4.

The 8-membered ring, seen along x- or y-axes, becomes a pair of loops of opposed sign. Any ring current is therefore due to H_z. Now H_z belongs to A_2 in D_{2d}, and can thus connect the highest filled and the lowest empty orbital of Fig. 6, which otherwise do not mix. This is the condition for a *paramagnetic* ring current.[8] We infer that because of the large difference in electronegativity of $N(z)$ and $S(d)$ orbitals, this effect is outweighed by the diamagnetic current associated with the mixing of E^1 [mainly $N(z)$] and E^2 [mainly $S(z)$], which are much closer in energy, and may thus give a larger effect.[8]

Conclusions.—The dimensions, spectrum, and diamagnetism of N_4S_4 are in accord with a M.O. scheme related to structures 2(*b*), as is the e.s.r. of the anion $N_4S_4^-$. Rejection of structures 2(*a*) as a basis set is in accord with recent work on $(SN)_x$, which, it has been suggested, shows bond alternation because of the use of such structures.[11] The low-energy bands cannot be explained by the " free-electron " theory of Chapman and Waddington,[2] and the spectroscopic detection of $S(d)$ levels makes it unnecessary to accept Lindqvist's

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† $\chi(SF_6) = -44$ units ($\times 10^{-6}$/mole), $\therefore$ $\chi(S^{VI}) = -6{\cdot}2$. $\chi(SO_2Cl_2) = -54$, $\chi(SO_2) = -24$, $\therefore$, using $\chi(Cl) = 17{\cdot}2$, $\chi(S^{IV}) = -10{\cdot}6 > \chi(S^{II})$. $\chi(S_2Cl_2) = -62{\cdot}2$ (obs.), $-64{\cdot}4$ (calc.), $\therefore$ $\chi(S)$ greater (numerically smaller) in a more electronegative environment. For CS_2, $\chi(\text{obs.}) = -42{\cdot}2$, $\chi(\text{calc.})$ (for $\overline{\mathrm{S{-}C{-}S}}$) $= -36{\cdot}0$. Thus increment for double bond is $-3{\cdot}1$ units. Calculated shift from $H_4N_4S_4$ to N_4S_4 (after correcting for H atoms) is $+2{\cdot}4$ per S atom, and the difference from the observed $-6{\cdot}4$ suggests a real " molecular effect."

[21] (Becke-)Goehring, *Chem. Ber.*, 1947, **80**, 110.

[22] " Tables de Constantes et Donnees Numeriques," Masson (ed.), Vol. 7, Paris, 1957.

highly polar structure.[3] The diamagnetic ring current in the compound is due to mixing with the delocalised system of the orbitals involved in the S–S bond. The striking colour change with temperature is due to the normal effect on hot bands in a region to which the eye is very sensitive.

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