

## Tetrathiatetraza-azulene; Synthesis and X-Ray Crystal Structure

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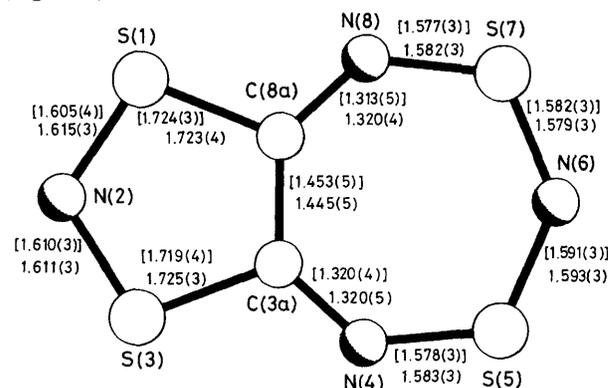
Tetrasulphur tetranitride and phenyl vinyl sulphoxide or sulphone react to give a novel planar delocalised  $14\pi$  electron aromatic system,  $1\lambda^4\delta^2,3,5,7\lambda^4\delta^2$ -tetrathia-2,4,6,8-tetraza-azulene (**4**) in which all the  $S_4N_4$  atoms have been retained; the molecules form parallel overlapping stacks with a minimum interplanar atomic separation of 3.26 Å.

The rich and varied inorganic chemistry of tetrasulphur tetranitride,  $S_4N_4$  (**1**),<sup>1a</sup> has prompted several studies of its reactions with organic substrates as potential sources of sulphur–nitrogen heterocyclic compounds.<sup>2</sup> However, the scope of its cycloaddition reactions has not yet been fully appreciated since the mechanisms of these reactions are so poorly understood. For example,  $S_4N_4$  appears to react quite differently with alkenes and with alkynes; it reacts with electron deficient alkynes<sup>2a</sup> but not with electron deficient alkenes,<sup>2d</sup> and in general it only reacts with alkenes when the double bond is highly strained, as in norbornadiene or *trans*-cyclo-octene.<sup>2d</sup> The alkyne reactions give predominantly 1,2,5-thiadiazoles<sup>2a</sup> together with minor amounts of trithiadiazepines and trithiazepines;<sup>3</sup> the major initial process thus appears to be alkyne cycloaddition across N(2)–N(4). The strained alkenes give cycloadducts in high yield which result exclusively from cycloaddition across S(1)–S(3) and S(5)–S(7).<sup>2e,f</sup> This dichotomy led us to consider the reaction of  $S_4N_4$  with alkenes which are 'acetylene equivalents'.<sup>4</sup> These might give alkene-type products at the alkyne oxidation level, or the initial adducts might rearrange to give alkyne-type products. The latter could provide a direct route to the parent trithiadiazepine (**2**), which is not available from the reaction of  $S_4N_4$  with acetylene itself,<sup>5</sup> but which we have now synthesized independently.<sup>6</sup> We therefore investigated the reaction of  $S_4N_4$  with phenyl vinyl sulphoxide (**3**) which is an effective acetylene equivalent in Diels–Alder<sup>7</sup> and 1,3-dipolar cycloaddition reactions.<sup>8</sup>

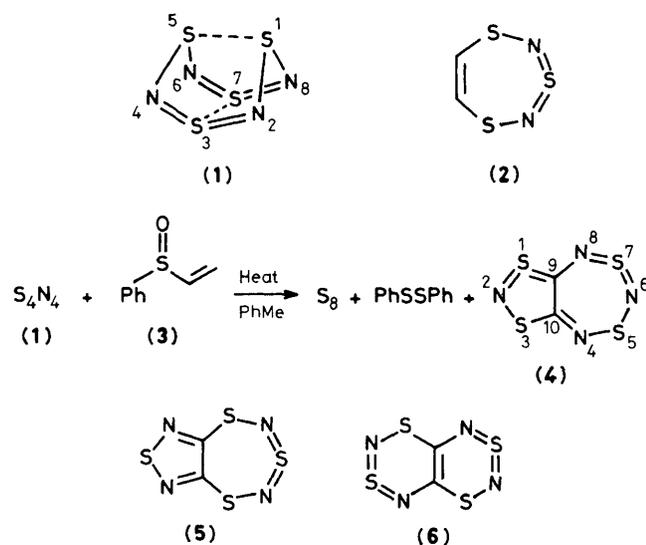
When  $S_4N_4$  (2 equiv.) was heated with the sulphoxide (**3**) (1 equiv.) in toluene for 6 hours, no trithiadiazepine (**2**) was formed; the main products were sulphur, diphenyl disulphide (97%), and a green–black crystalline solid with a metallic lustre, m.p. 142–143 °C (24%),<sup>†</sup> to which the molecular

formula  $C_2N_4S_4$  was assigned from elemental analysis and the mass spectrum. Its <sup>13</sup>C n.m.r. spectrum is a singlet at  $\delta$  161.8; the solution i.r. is very simple with only four absorptions above 600  $cm^{-1}$  at 1488, 895, 885, and 625  $cm^{-1}$ , and the u.v. spectrum has long wavelength maxima at 322 (log  $\epsilon$  3.35) and 492 nm (3.31), suggesting a highly symmetrical and delocalised structure.

Acetylene has thus become incorporated into the  $S_4N_4$  structure but with its hydrogen atoms removed; however  $S_4N_4$  is known to be able to act as a dehydrogenating agent.<sup>5,9</sup> The thermal stability and spectroscopic properties of the new product suggested an aromatic structure in which the alternating arrangement of sulphur and nitrogen atoms of  $S_4N_4$  had been retained; three possible structures are (**4**), (**5**), or (**6**). A single crystal X-ray analysis<sup>‡</sup> showed the product to be  $1\lambda^4\delta^2,3,5,7\lambda^4\delta^2$ -tetrathia-2,4,6,8-tetraza-2a-azulene (**4**) (Figure 1).

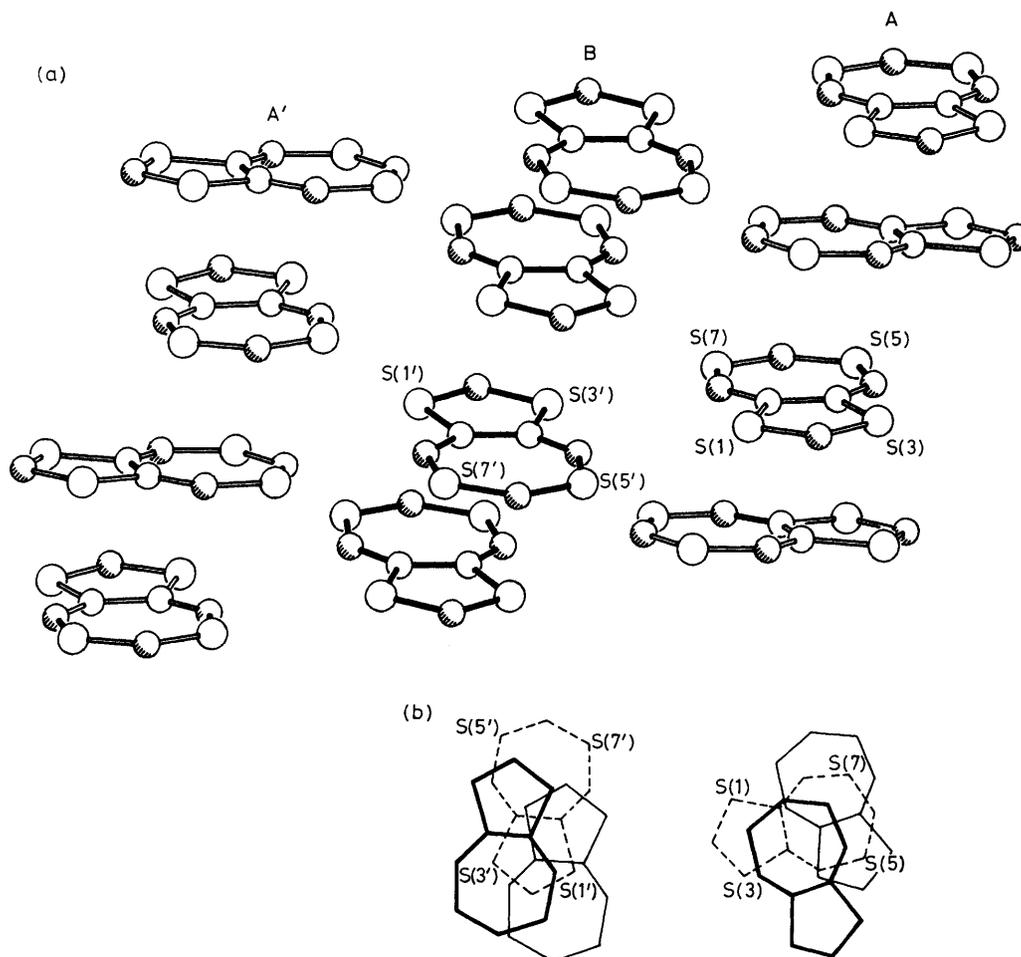


**Figure 1.** The molecular structure of (**4**). Bond lengths (Å) are shown beside the relevant bonds; the values for the second molecule are given in parentheses. A librational analysis indicates that the bond lengths should be increased by approximately 2.5 standard deviations. Bond angles (°): the second value given in each case corresponds to the other independent molecule, N(2)S(1)C(8a) 101.8(2), 101.6(2); S(1)N(2)S(3) 113.8(2), 114.2(2); N(2)S(3)C(3a) 101.6(2), 101.7(2); S(3)C(3a)N(4) 116.7(2), 117.0(3); S(3)C(3a)C(8a) 111.6(3), 111.3(2); N(4)C(3a)C(8a) 131.8(3), 131.7(3); C(3a)N(4)S(5) 132.3(2), 133.1(3); N(4)S(5)N(6) 118.7(2), 118.4(2); S(5)N(6)S(7) 133.6(2), 133.2(2); N(6)S(7)N(8) 118.8(2), 119.1(2); S(7)N(8)C(8a) 131.9(3), 132.8(3); S(1)C(8a)C(3a) 111.2(2), 111.2(3); S(1)C(8a)N(8) 116.0(3), 117.1(2); C(3a)C(8a)N(8) 132.8(3), 131.7(3).



<sup>†</sup> Whilst this product, once isolated, was stable in boiling toluene, it was extensively decomposed under these conditions in the presence of either  $S_4N_4$  or phenyl vinyl sulphoxide.

<sup>‡</sup> *Crystal data:*  $C_2N_4S_4$ ,  $M = 208.29$ , monoclinic, space group  $P2_1/a$ ,  $a = 7.144(1)$ ,  $b = 16.826(2)$ ,  $c = 11.271(2)$  Å,  $\beta = 105.67(1)^\circ$ ,  $U = 1304$  Å<sup>3</sup>,  $Z = 8$  (2 crystallographically independent molecules),  $D_c = 2.13$  g  $cm^{-3}$ ,  $\mu(Cu-K\alpha) = 126$   $cm^{-1}$ . 1431 Independent observed reflections [ $|F_o| > 3\sigma(|F_o|)$ ,  $\theta \leq 50^\circ$ ] were measured on a Nicolet R3m diffractometer with Cu- $K\alpha$  radiation (graphite monochromator) and using  $\omega$ -scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to  $R = 0.033$ ,  $R_w = 0.038$ . Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.<sup>10</sup> The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 2.** (a) The stacking of the molecules of (4) in the crystal. Molecules in stack A are crystallographically independent to those in stack B. The planes of the molecules are parallel to the crystallographic (101) plane. (b) The degree of overlap of molecules in stacks A and B. The uppermost molecule is shown heavy, the next is shown broken, and the next light.

Product (4) contains two crystallographically independent molecules, A and B. Both molecules have approximate  $C_{2v}$  symmetry and all the equivalent bond lengths are, within statistical significance, the same. The S–N bonds are all of similar length, though those of the 5-membered ring are slightly longer than those of the 7. Overall this indicates a completely delocalised  $14\pi$  structure, in accord with MNDO and *ab initio* MO calculations which show a distinct pattern of  $\pi$  energy levels characteristic of an aromatic species.

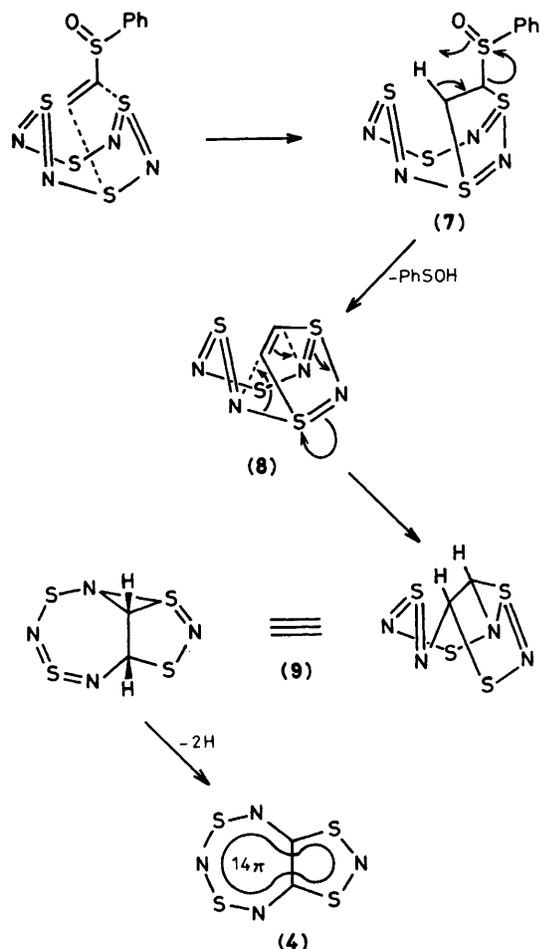
An interesting and novel feature of the structure is the packing of the molecules. They form continuous parallel overlapping stacks (Figure 2a,b), each stack being comprised of one type of molecule only (either all A or all B). Furthermore the mode of stacking for type A molecules is different to that for type B (Figure 2b). Adjacent molecules in type A stacks are rotated by  $\sim 80^\circ$  in plane with respect to each other, whilst those of type B are rotated by  $180^\circ$ . The minimum interplanar atomic separations in the A stacks are 3.26 Å between C(8a) and N(4) and 3.48 Å between C(8a) and N(6); in the B stacks they are 3.46 Å between N(4') and S(1') and 3.50 Å between C(3a') and S(1'). Interestingly, whilst both molecules are essentially planar the atoms in type A have a noticeably larger maximum deviation from their least-squares plane [0.027 Å for N(8)] than those in type B [0.007 Å for S(3')].

Somewhat surprisingly, the electron rich tetrathiatetraazulene (4), like trithiadiazepine (2), does not form charge

transfer complexes with electron acceptors like picric acid or 2,4,7-trinitro-9-fluorenylidene malononitrile.

A possible mechanism for the conversion of  $S_4N_4$  into  $C_2N_4S_4$  (4) is shown (Scheme 1). 1,3-Dipolar cycloaddition of the alkene across S(1)–S(3) to give (7) followed by thermal elimination of phenylsulphenic acid gives the bicyclic structure (8) in which the  $S_4N_4$  cage is opened up and the 5-membered ring of the final product (4) generated. The 7-membered ring of (4) can then be formed by the electrocyclic process shown [arrows in (8)] and the tricyclic species (9) so produced is dehydrogenated with concomitant aromatising valence isomerisation to give (4). The high yield of diphenyl disulphide formed is uncommon for reactions of phenyl vinyl sulphoxide as an acetylene equivalent, and it may be a direct or indirect consequence of the dehydrogenation process. Either benzenesulphenic acid could perform the dehydrogenation to give diphenyl disulphide and water or, as suggested above,  $S_4N_4$  could be the dehydrogenating agent being itself reduced to  $S_4N_4H_4$ <sup>1b</sup> with this hydride then reducing benzenesulphenic acid to the disulphide. However, the presence of other dehydrogenating agents (manganese dioxide, dichlorodicyanobenzoquinone) did not increase the yield of tetrathiatetraza-azulene (4).

We hoped to gain some evidence for the formation of the initial cycloadduct (7) by replacing sulphoxide (3) by phenyl vinyl sulphone, which is expected to undergo a similar initial cycloaddition but not an analogous cycloelimination of



Scheme 1

benzenesulphonic acid. Reaction of this sulphone with S<sub>4</sub>N<sub>4</sub> did not give the desired intermediate however but did give a small amount (4%) of tetrathiatetraaza-azulene (4), so presumably there is some elimination of benzenesulphonic acid, even under these mild conditions, indicating the strong driving force for the formation of compound (4) in which the 12π cage structure of S<sub>4</sub>N<sub>4</sub> has incorporated a C-C π bond to become a planar 14π system.

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