Crystal and Molecular Structure of Benzylidenimine Tetrasulphide

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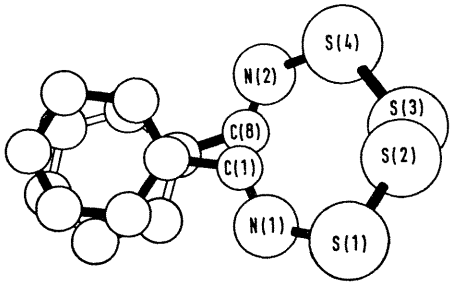
Summary The crystal and molecular structure of the title compound has been established; it shows alternating S–S bond lengths and a short N–S bond.

THE reaction of benzylamine with tetrasulphur tetranitride,[1,2] of elemental sulphur with benzylamine in the presence of lead oxide,[3,4] of either sulphur monochloride[4,5] or trisulphur dichloride with benzylamine[5] and the decomposition of either benzylamine disulphide[4] or *N*-benzylheptasulphurimide[6] all lead to the same stable yellow solid which has, however, been assigned five different structures. In the two most recent cases[2,5] the same physical data, namely n.m.r. and i.r. spectra, led to different structural assignments. Under these circumstances an *X*-ray structural determination seemed appropriate.

The compound ($C_{14}H_{12}N_2S_4$) used in this study was obtained by the procedure described by Schenck[1] and was recrystallized from methanol to give yellow needle-shaped crystals, m.p. 100·5—102°. The lattice parameters derived from least-squares refinement of 2θ values for 15 well-centred reflections on the Syntex P1 automatic diffractometer are $a = 13{\cdot}85(1)$, $b = 19{\cdot}72(2)$, $c = 5{\cdot}981(5)$ Å and $\beta = 101{\cdot}33(5)°$ with the needle axis along c and has space group $P2_1/a$, $Z = 4$, $D_m = 1{\cdot}404$ g/cm^3 and $D_c = 1{\cdot}395$ g/cm^3. hkn Data with $n = 0$—5, were recorded with Cu-K_α radiation using an integrating Weissenberg camera while shl data, $s = 0$—4, were recorded with an integrating precession camera using Mo-K_α radiation. The reflections were measured with a Joyce Loebl microdensitometer and yielded 2550 symmetry-independent reflections of which 1038 were intense enough to measure. A trial structure was derived using the sign determining procedure incorporated in the computer program XRAY 67. The signs of 207 reflections with large E_H values were determined initially and from the subsequently prepared Fourier synthesis the positions of the four sulphur atoms could be discerned.

The rest of the structure was gradually determined utilizing difference electron density synthesis and configurations derived from the structural study of benzylidenimine trisulphide.[7] The structure was refined by a full-matrix least-squares program to conventional R value of 0·075.



FIGURE

The structure contains a tetrameric sulphide chain with the molecule folding back upon itself in such a way that the two phenyl groups are nearly superimposed when projected down the a axis. The planes of the phenyl rings deviate by about 9·2° from coplanarity with the closest approach being the C(1)–C(8) separation of 3·23 Å. The atoms of the S_4 chain form a spiral nearly showing a non-crystallographic 3_1 axis extending over the four sulphurs which intersects the normals to the phenyl groups at 60° and 62°. The central S–S bond is 2·088(4) Å; the terminal S–S bonds at 2·026(3) and 2·031(3) Å, though insignificantly different from each other, are substantially shorter than S(2)–S(3). These compare with the sulphur–sulphur bond lengths[8,9] in S_8 of 2·048(2) Å. A similar alteration in sulphur–sulphur bond lengths in another organo tetrasulphide has been recently described.[10] The S–S–S bond angles are both within 1σ of 106·3° and the N–S–S angles are both within 2σ of 111·0°.

The two unique N–S bond lengths at 1·690(6) Å and 1·685(6) Å, which do not differ significantly, are well below the N–S single bond length of 1·76 Å found in sulphamic acid[11] suggesting[12] an N–S bond order of about 1·4. The mean ring C–C bond length is 1·37 Å, with individual bonds ranging from 1·32 to 1·42 Å. Ten out of twelve of these bonds lie within 3σ of the mean and all lie within 4σ of this value.

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[1] R. Schenck, *Annalen*, 1896, **290**, 171.
[2] Y. Sasaki and F. P. Olsen, *Canad. J. Chem.*, 1971, **49**, 271.
[3] T. G. Levi, *Gazzetta*, 1931, **61**, 294.
[4] Y. Sasaki and F. P. Olsen, *Canad. J. Chem.*, 1971, **49**, 283.
[5] J. S. Pond, Ph.D. Thesis, University of Minnesota, Minneapolis, Minnesota, 1964.
[6] B. A. Olsen and F. P. Olsen, *Inorg. Chem.*, 1969, **8**, 1736.
[7] J. Barrick, C. Calvo, and F. Olsen, to be published.
[8] G. A. Slack, *Phys. Rev.*, 1965, **139A**, 511.
[9] A. Sugawara, *J. Appl. Chem.*, 1965, **36**, 2375.
[10] J. S. Ricci, jun., and I. Bernal, *Chem. Comm.*, 1969, 1453.
[11] R. L. Sass, *Acta Cryst.*, 1960, **13**, 320.
[12] D. Chapman and T. C. Waddington, *Trans. Faraday Soc.*, 1962, **58**. 1679.

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