## 1,3,5,2,4-Trithiadiazines; a New Ring System

## Robin M. Bannister, Ray Jones, Charles W. Rees, and David J. Williams

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

Diazoalkanes react with tetrasulphur tetranitride to give red crystalline,  $1,3\lambda^4\delta^2,5,2,4$ - trithiadiazines [(3), (7), (8)], representatives of a new ring system with a nearly planar  $S_3N_2$  unit; the parent compound (3) was independently synthesised from methanebis(sulphenyl chloride) (11) and sulphur bis(trimethylsilyl)diimide (12).

The reactions of tetrasulphur tetranitride,  $S_4N_4$ , with aryldiazoalkanes are mostly complex and low yielding,<sup>1</sup> though diphenyldiazomethane gave the bis(diphenylmethylene) tetra-azatrithiadiene (1) in 45% yield, in ether at room temperature.<sup>2</sup> We were interested in the reaction of  $S_4N_4$  with diazomethane as a potential route to the trithiatriazepine (2)<sup>3</sup> which could be formed by the introduction of a methylene group into the  $S_4N_4$  ring and loss of an HNS fragment.

However, when diazomethane (4 equiv.) was passed into a solution of  $S_4N_4$  (1 equiv.) in hot dichloromethane the trithiatriazepine (2) was not formed, but chromatography gave 1,3 $\lambda^4\delta^2$ ,5,2,4- trithiadiazine (3) as a stable red crystalline solid, m.p. 43—45 °C (40%). The formation of six-membered rings in the reaction of  $S_4N_4$  with organic substrates is rare, and this ring system is new. The structure of the trithiadiazine (3) was based on analytical and spectral data,<sup>†</sup> most characteristic being the u.v. [ $\lambda_{max}$ (cyclohexane) 255 (log  $\varepsilon$  3.58), 286 (3.46), and 435 nm (2.93)] and i.r. spectra [ $v_{max}$  1080 cm<sup>-1</sup> (N=S=N)], and was confirmed by X-ray diffraction.<sup>‡</sup>

The structure of trithiadiazine (3) (Figure 1) is closely related to those of tetrasulphur dinitride (4),<sup>4</sup> which is also red, and 6,7-dihydrotrithiadiazepine (5).<sup>5</sup> All three compounds have a nearly planar S-N=S=N-S unit. In both (3) and (4) the ring has a slightly puckered 'envelope' conformation, the dihedral angles between the S(1)N(2)N(4)S(5) plane and the S(1)C(6)S(5) and N(2)S(3)N(4) planes in (3) being 48 and 4°, respectively; the equivalent values in (4) are 56 and 5°. In

 $\ddagger$  Crystal data: (3) CH<sub>2</sub>N<sub>2</sub>S<sub>3</sub>, monoclinic, a = 5.889(2), b = 7.765(2),c = 10.796(4) Å,  $\beta = 99.92(2)^\circ$ , U = 486.3 Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 4, M = 138.2, D_c = 1.90 \text{ g cm}^{-3}, \mu(\text{Cu}-K_{\alpha}) = 125 \text{ cm}^{-1}.$  (7c)  $C_8H_8N_2OS_3$ , monoclinic, a = 10.949(6), b = 8.048(3), c = 13.184(9)Å,  $\beta = 113.54(4)^{\circ}$ , U = 1065 Å<sup>3</sup>, space group  $P2_1/c$ , Z = 4, M = 244.3,  $D_c = 1.53 \text{ g cm}^{-3}, \mu(\text{Cu-}K_{\alpha}) = 61.7 \text{ cm}^{-1}.$  (9) CH<sub>2</sub>N<sub>2</sub>OS<sub>3</sub>, monoclinic,  $a = 6.222(3), b = 10.074(3), c = 8.756(5) \text{ Å}, \beta = 108.22(5)^\circ, U = 100.22(5)^\circ$ 521.3 Å<sup>3</sup>, space group  $P2_1/a$ , Z = 4, M = 154.2,  $D_c = 1.97 \text{ g cm}^{-3}$ ,  $\mu(Cu-K_{\alpha}) = 119 \text{ cm}^{-1}$ . Data for all three structures were measured with a Nicolet R3m diffractometer using graphite monochromated Cu-K<sub>a</sub> radiation and  $\omega$ -scans. All were solved by direct methods and refined anisotropically, using in the case of (3) and (9) absorptioncorrected data, to give for (3) R = 0.036,  $R_w = 0.036$  for 593 independent observed reflections, for (7c) R = 0.042,  $R_w = 0.047$  for 1290 independent observed reflections, and for (9) R = 0.064,  $R_w =$ 0.055 for 388 independent observed reflections  $[|F_0| > 3\sigma(|F_0|), \theta \leq$ 58° for (3) and (7c),  $\theta \le 50^\circ$  for (9)]. With the exception of the methyl group in (7c) which was refined as a rigid body, all the hydrogen atoms in (3) and (7c) were located from  $\Delta F$  maps and refined isotropically. The positions of the hydrogen atoms in (9) were idealised (C-H 0.96Å), assigned isotropic thermal parameters,  $U(H) = 1.2U_{cq}(C)$ , and allowed to ride on their parent carbon atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Cystallographic Data Centre. See Notice to Authors, Issue No. 1.

the dihydrotrithiadiazepine (5) the two methylene groups are symmetrically placed above and below the  $S_3N_2$  plane and are rapidly inverting in solution at room temperature (<sup>1</sup>H n.m.r. singlet at  $\delta$  3.71). The methylene protons of (3) give a similar sharp singlet, at  $\delta$  4.18, with no line broadening down to -80 °C. The equivalent bond lengths and angles of the  $S_3N_2$ unit in (3), (4), and (5), are all similar, though the bond lengths in (4) are slightly greater than those in (5), and the angles in (5) are enlarged to accommodate the extra ring member.

The trithiadiazine (3) could be formed via nucleophilic attack by diazomethane at sulphur in  $S_4N_4$  followed by displacement of the diazo nitrogen by transannular sulphur to give the intermediate (6); the required loss of  $N_2S$  from this might be effected by further reaction with diazomethane. The yield of trithiadiazine (3) increased with the quantity of diazomethane, up to a four-fold excess. Diazoalkanes with electron-withdrawing substituents, such as ethyl diazoacetate, diethyl diazomalonate, and benzoylphenyldiazomethane, did not react with  $S_4N_4$  in boiling dichloromethane nor did they give any trithiadiazines in boiling toluene or chlorobenzene.

Monoaryl diazomethanes and  $S_4N_4$  (4:1) in boiling dichloromethane reacted similarly to give 6-aryltrithiadiazines (7a), m.p. 82—84 °C (40%), (7b), m.p. 78—79 °C (20%), and (7c), m.p. 93—95 °C (25%), as red crystalline solids which were less stable than the parent compound (3) or its 6,6-disubstituted derivatives.§ The latter were made similarly from  $S_4N_4$  and 2-diazopropane, diphenyldiazomethane, and 1,2-diphenyldiazoethane which gave compounds (8a), m.p. 29 °C (50%), (8b), m.p. 125—128 °C (6%),¶ and (8c), m.p.



§ This instability could be associated with the reactivity of the 6-hydrogen atom, since the *p*-nitrophenyl derivative (7b) was the least stable and the *p*-methoxyphenyl derivate (7c) the most stable of the three.

¶ The major product in this particular reaction was the tetraazatrithiadiene (1) (65%).

<sup>&</sup>lt;sup>†</sup> All new compounds gave satisfactory spectroscopic and analytical data, except for elemental analysis of the somewhat unstable *p*-nitrophenyl compound (**7b**). The yields reported are based on the conversion of one mole of  $S_4N_4$  into one mole of trithiadiazine; much  $S_4N_4$  was often recovered and percentage yields were substantially higher.





105—106 °C (45%), respectively, as red crystalline solids which were stable indefinitely at 4 °C. Compounds (7) and (8) had analytical and spectroscopic properties consistent with the trithiadiazine structure, and this was confirmed for (7c) by X-ray diffraction (Figure 2).‡ The p-methoxyphenyl group is equatorial and virtually orthogonal (88°) to the trithiadiazine ring, thus minimising steric interaction between the ortho hydrogen on C(12) and the ring sulphur atoms S(1) and S(5). The heterocyclic ring again adopts a slightly puckered 'envelope' conformation with dihedral angles of 49 and 4° [cf. (3) and (4)]. The ring bond lengths do not differ significantly from those of the parent compound (3).

The trithiadiazine (3) was inert towards iodomethane in boiling dichloromethane but was rapidly decomposed by u.v. irradiation (254 and 350 nm), and by triphenylphosphine. With *m*-chloroperbenzoic acid (1 equiv.) in dichloromethane the red colour faded immediately and the mono-oxide (9), m.p. 96-97 °C (50%) was formed; the same oxide was produced (43%), and more easily purified, with dinitrogen tetraoxide (1 equiv.) in dichloromethane. Structure (9), in which divalent sulphur has been oxidised in preference to sulphur diimide sulphur, was based on the strong i.r. absorption at 1075 cm<sup>-1</sup> (N=S=N intact) and the pair of geminally coupled proton signals at  $\delta$  2.72 and 5.33 in the <sup>1</sup>H n.m.r. spectrum (unsymmetrical methylene). The structure was unambiguously established by X-ray diffraction (Figure 3),‡ which showed the S-O bond to be 'equatorial,' and the ring to have the same 'envelope' conformation with dihedral angles of 57 and 3°, analogous to those for (3), (4), and (7c).

The parent trithiadiazine structure (3) was also confirmed by an independent, rational, synthesis based on our earlier preparation<sup>5</sup> of dihydrotrithiadiazepine (5) from ethane-1,2bis(sulphenyl chloride) and sulphur bis(trimethylsilyl)diimide (12). The pentathiepane (10), the natural product lenthionine,<sup>6</sup> was prepared from di-iodomethane and disodium



Figure 1. The molecular structure of (3). Bond lengths (Å): S(1)-N(2)1.671(3), N(2)-S(3) 1.549(3), S(3)-N(4) 1.560(3), N(4)-S(5)1.668(3), S(5)-C(6) 1.796(4), C(6)-S(1) 1.798(4); bond angles (°): C(6)S(1)N(2) 104.8(2), S(1)N(2)S(3) 125.6(2), N(2)S(3)N(4)120.8(2), S(3)N(4)S(5) 125.7(2), N(4)S(5)C(6) 104.5(2), S(5)C(6)S(1)116.8(2).



Figure 2. The molecular structure of (7c). Selected bond lengths (Å): S(1)–N(2) 1.667(3), N(2)–S(3) 1.539(3), S(3)–N(4) 1.553(4), N(4)–S(5) 1.679(4), S(5)–C(6) 1.810(3), C(6)–S(1) 1.806(4); bond angles (°): C(6)S(1)N(2) 105.1(2), S(1)N(2)S(3) 126.4(3), N(2)S(3)N(4) 120.8(2), S(3)N(4)S(5) 125.2(2), N(4)S(5)C(6) 104.6(2), S(5)C(6)S(1) 115.3(2).



Figure 3. The molecular structure of (9). Ring bond lengths (Å): S(1)-N(2) 1.675(10), N(2)-S(3) 1.552(9), S(3)-N(4) 1.538(10), N(4)-S(5) 1.658(10), S(5)-C(6) 1.804(11), C(6)-S(1) 1.836(11); bond angles (°): C(6)S(1)N(2) 99.2(5), S(1)N(2)S(3) 129.1(6), N(2)S(3)N(4) 118.7(5), S(3)N(4)S(5) 124.5(6), N(4)S(5)C(6) 105.6(5), S(5)C(6)S(1) 112.3(6).

disulphide in a two-phase aqueous dichloromethane mixture, and then cleaved with chlorine in tetrachloromethane at 0 °C to give methanebis(sulphenyl chloride) (11). This, with sulphur diimide (12) at high dilution, gave the trithiadiazine (3) identical with that from the  $S_4N_4$ -diazomethane reaction.

<sup>||</sup> The main structural changes on conversion of the trithiadiazine (3) into its oxide (9) are contraction of the ring angles at carbon and at the oxidised sulphur from 117 to  $112^{\circ}$  and from 105 to  $99^{\circ}$ , respectively, and expansion of the ring angle at the adjacent nitrogen, N(2), from 126 to  $129^{\circ}$ . In compounds (3), (4), (7c), and (9) the puckering of the ring produces a chair-like conformation.

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## References

- 1 'Gmelin Handbook of Inorganic Chemistry,' 8th edn., 'Sulfur-Nitrogen Compounds, part 2,' Springer-Verlag, Berlin, 1985, p. 209.
- 2 E. Fluck, Z. Anorg. Chem., 1961, 312, 195; E. M. Holt, S. L. Holt, and K. J. Watson, J. Chem. Soc., Dalton Trans., 1974, 1357.
- 3 J. L. Morris and C. W. Rees, *Chem. Soc. Rev.*, 1986, 15, 1.
  4 T. Chivers, P. W. Codding, W. G. Laidlaw, S. W. Liblong, R. T.
- 4 1. Univers, P. W. Codding, W. G. Laidlaw, S. W. Liblong, R. T Oakley, and M. Trsic, J. Am. Chem. Soc., 1983, 105, 1186.
- 5 J. L. Morris and C. W. Rees, J. Chem. Soc., Perkin Trans. 1, 1987, 211; R. Jones, J. L. Morris, A. W. Potts, C. W. Rees, D. J. Rigg, H. S. Rzepa, and D. J. Williams, J. Chem. Soc., Chem. Commun., 1985, 398.
- 6 K. Morita and S. Kobayashi, *Chem. Pharm. Bull.*, 1967, 15, 988;
  I. W. J. Still and G. W. Kutney, *Tetrahedron Lett.*, 1981, 22, 1939.