

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

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Diazoalkanes react with tetrasulphur tetranitride to give red crystalline, 1,3,4,δ²,5,2,4-trithiadiazines [(3), (7), (8)], representatives of a new ring system with a nearly planar S₃N₂ unit; the parent compound (3) was independently synthesised from methanebis(sulphenyl chloride) (11) and sulphur bis(trimethylsilyl)diimide (12).

The reactions of tetrasulphur tetranitride, S₄N₄, with aryl-diazoalkanes are mostly complex and low yielding,¹ though diphenyldiazomethane gave the bis(diphenylmethylene) tetra-azatrithiadene (1) in 45% yield, in ether at room temperature.² We were interested in the reaction of S₄N₄ with diazomethane as a potential route to the trithiazepine (2)³ which could be formed by the introduction of a methylene group into the S₄N₄ ring and loss of an HNS fragment.

However, when diazomethane (4 equiv.) was passed into a solution of S₄N₄ (1 equiv.) in hot dichloromethane the trithiazepine (2) was not formed, but chromatography gave 1,3,4,δ²,5,2,4-trithiadiazine (3) as a stable red crystalline solid, m.p. 43–45 °C (40%). The formation of six-membered rings in the reaction of S₄N₄ with organic substrates is rare, and this ring system is new. The structure of the trithiadiazine (3) was based on analytical and spectral data,† most characteristic being the u.v. [λ_{max}(cyclohexane) 255 (log ε 3.58), 286 (3.46), and 435 nm (2.93)] and i.r. spectra [ν_{max} 1080 cm⁻¹ (N=S=N)], and was confirmed by X-ray diffraction.‡

The structure of trithiadiazine (3) (Figure 1) is closely related to those of tetrasulphur dinitride (4),⁴ which is also red, and 6,7-dihydrotrithiazepine (5).⁵ 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

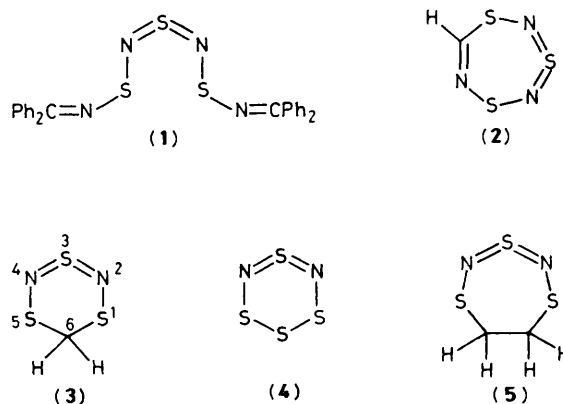
the dihydrotrithiazepine (5) the two methylene groups are symmetrically placed above and below the S₃N₂ plane and are rapidly inverting in solution at room temperature (¹H n.m.r. singlet at δ 3.71). The methylene protons of (3) give a similar sharp singlet, at δ 4.18, with no line broadening down to –80 °C. The equivalent bond lengths and angles of the S₃N₂ 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 S₄N₄ followed by displacement of the diazo nitrogen by transannular sulphur to give the intermediate (6); the required loss of N₂S 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 S₄N₄ in boiling dichloromethane nor did they give any trithiadiazines in boiling toluene or chlorobenzene.

Monoaryl diazomethanes and S₄N₄ (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 S₄N₄ 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.

† 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 S₄N₄ into one mole of trithiadiazine; much S₄N₄ was often recovered and percentage yields were substantially higher.

‡ *Crystal data*: (3) CH₂N₂S₃, monoclinic, *a* = 5.889(2), *b* = 7.765(2), *c* = 10.796(4) Å, β = 99.92(2)°, *U* = 486.3 Å³, space group *P*₂₁/*n*, *Z* = 4, *M* = 138.2, *D*_c = 1.90 g cm⁻³, μ(Cu-Kα) = 125 cm⁻¹. (7c) C₈H₈N₂OS₃, monoclinic, *a* = 10.949(6), *b* = 8.048(3), *c* = 13.184(9) Å, β = 113.54(4)°, *U* = 1065 Å³, space group *P*₂₁/*c*, *Z* = 4, *M* = 244.3, *D*_c = 1.53 g cm⁻³, μ(Cu-Kα) = 61.7 cm⁻¹. (9) CH₂N₂OS₃, monoclinic, *a* = 6.222(3), *b* = 10.074(3), *c* = 8.756(5) Å, β = 108.22(5)°, *U* = 521.3 Å³, space group *P*₂₁/*a*, *Z* = 4, *M* = 154.2, *D*_c = 1.97 g cm⁻³, μ(Cu-Kα) = 119 cm⁻¹. Data for all three structures were measured with a Nicolet R3m diffractometer using graphite monochromated Cu-Kα radiation and ω-scans. All were solved by direct methods and refined anisotropically, using in the case of (3) and (9) absorption-corrected 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*_o| > 3σ(|*F*_o|), θ ≤ 58° for (3) and (7c), θ ≤ 50° 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 Δ*F* maps and refined isotropically. The positions of the hydrogen atoms in (9) were idealised (C–H 0.96 Å), assigned isotropic thermal parameters, *U*(H) = 1.2*U*_{eq}(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 Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



§ 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 derivative (7c) the most stable of the three.

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

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