Reactions of Tetrasulphur Tetranitride with Alkynes; 1,4,2,6-Dithiadiazines and 1,3,2-Dithiazoles

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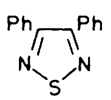
Reaction of S_4N_4 with diphenylacetylene and phenylacetylene gives two new, thermally stable heterocyclic systems, the 1,4,2,6-dithiadiazine (**3**) and the 1,3,2-dithiazolylimine (**7**), respectively, as minor products; these structures, determined by *X*-ray diffraction, correct earlier assignments.

The reaction of tetrasulphur tetranitride, S_4N_4, with diphenylacetylene in boiling toluene for 48 hours was reported to give 3,4-diphenyl-1,2,5-thiadiazole (**1**) (87%) and 5,6-diphenyl-1,3$\lambda^4\delta^2$,2,4-dithiadiazine (**2**) as orange needles, m.p. 79—80.5 °C, in less than 1% yield.[1] The latter structure contains an interesting, novel heterocyclic ring which, if planar, would be an 8π antiaromatic system. However this structure was assigned on meagre evidence and was later precluded (though not withdrawn) by the ^{13}C n.m.r. data which showed that the two phenyl groups were magnetically equivalent.[2]† It seemed to us that, to produce a stable structure which accorded with the ^{13}C n.m.r. data, the two acetylenic carbons must become separated; we had previously observed this type of cleavage in the reaction of dimethyl acetylenedicarboxylate with S_4N_4.[4] We therefore repeated the diphenylacetylene reaction and obtained the thiadiazole (**1**) in high yield together with the minor, highly crystalline, orange product, m.p. 78—80 °C, which was shown by *X*-ray diffraction to be 3,5-diphenyl-1,4,2,6-dithiadiazine (**3**)‡ (Figure 1). The ring is not planar and adopts a boat conformation characteristic of the simpler dithiins. The C=N bond lengths [1.274(4) Å] are short; these and the other bond lengths in the ring show there to be no delocalisation. The molecule has non-crystallographic C_s symmetry with an 'open book' conformation and with the atoms in each of the two halves of the molecule coplanar within 0.1 Å. The dihedral angle between the two halves is 128.6°. The molecules stack one above the other along the *a* direction with an S· · ·S′ separation of 3.95 Å and with a distance of 3.52 Å between the planes of the phenyl rings.



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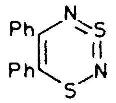

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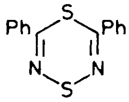

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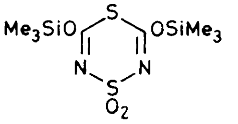

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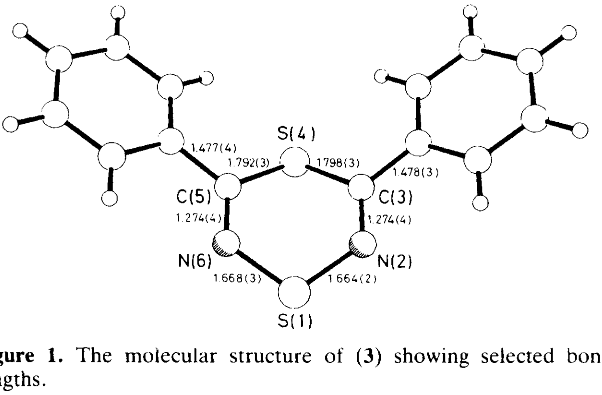

Figure 1. The molecular structure of (**3**) showing selected bond lengths.

The dithiadiazine (**3**) was also produced, though only as a minor by-product (1—2%) in the formation of thiadiazole (**1**), on reaction of S_4N_4 (1 equiv.) with diphenylacetylene (2 equiv.),[2] or with diphenylcyclopropenone, under various other conditions. When the molar ratio of S_4N_4 to the acetylene was changed to 2 : 1 the yield of (**3**) increased to 7%.

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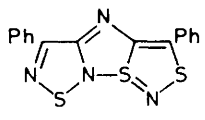
† Koenig and Oakley have very recently described the first authentic derivative of this ring system, benzo-1,3$\lambda^4\delta^2$,2,4-dithiadiazine, which is deep blue.[3]

‡ *Crystal data* (**3**) $C_{14}H_{10}N_2S_2$, triclinic, $a = 3.951(1)$, $b = 12.527(6)$, $c = 12.950(5)$ Å, $\alpha = 77.29(4)$, $\beta = 82.61(3)$, $\gamma = 85.37(3)°$, $U = 619$ Å^3, space group $P\bar{1}$, $Z = 2$, $M = 270.4$, $D_c = 1.46\,g\,cm^{-3}$. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation and using ω-scans. The structure was solved by direct methods and refined anisotropically to $R = 0.039$ for 1444 independent observed reflections [$\theta \leqslant 55°$, $|F_O| > 3\sigma(|F_O|)$].



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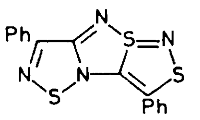

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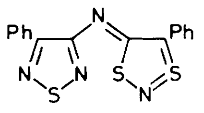

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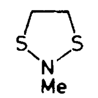

(8)

Dithiadiazine (**3**) was synthesised independently by the reaction of thiobenzamide, sulphur dichloride, and triethylamine in ether; again the yield was low (8%) since the major product, here and in several other reactions designed to give (**3**), was 3,5-diphenyl-1,2,4-thiadiazole, a known product of thiobenzamide oxidation.[5]

Compared with 1,4-dithiins[6] and 1,2,4-dithiazines,[7] the dithiadiazine (**3**) is surprisingly stable thermally. It is unchanged on long boiling in xylene and decomposes only slowly in boiling decalin (190 °C); after 6 hours, 10% has decomposed to give the 1,2,5-thiadiazole (**1**) (and none of the isomeric 1,3,4-thiadiazole). However (**3**) readily gives thiadiazole (**1**) on photolysis (300 nm, light petrol). Whilst 1,4-dithiins[6] and 1,2,4-dithiazines[7] have been widely studied, 1,4,2,6-dithiadiazines are unknown, and only the dioxide (**4**) has been reported.[8]

Tashiro and coworkers[2] also treated S_4N_4 with phenylacetylene in boiling toluene for 6 hours and obtained 3-phenyl-1,2,5-thiadiazole (16%), 3-amino-4-phenyl-1,2,5-thiadiazole (5%), and a deep violet compound (8%), m.p. 178—179 °C, for which they proposed either structure (**5**) or (**6**). Since either of these structures, if near to planar, could be a delocalised 14π aromatic system, we decided to reinvestigate this reaction. We isolated a compound with the same colour and m.p., in similar yield, but found that the yield was increased to 22% in the presence of $AlCl_3$. After many experiments minute crystals of the violet compound were obtained, from chloroform–ethanol, for *X*-ray diffraction analysis.§

The compound has the interesting bicyclic structure (**7**) (Figure 2), similar to (**5**) but with no central N–S bond. The stable, aromatic 1,2,5-thiadiazole is thus unperturbed; the other ring is the first example of an unsaturated 1,3,2-dithiazole.¶ In this the bond lengths do not accord with the covalent structure shown but require delocalisation over S(3)–N–S(1)–C(5). The thiadiazole and dithiazole rings are coplanar with a maximum deviation from the least-squares plane of 0.02 Å [S(9)]. The phenyl rings are rotated in the same sense out of this plane by 27° and 31° for rings A and B respectively. The interannular S· · ·N separation of 2.695 Å is much greater than for a single bond (1.74 Å) but is shorter than the sum of the van der Waals radii (3.35 Å), suggesting a small interaction between the two atoms, as shown by the space filling representation (Figure 2). This may simply result from the planarity of the molecule since the bond angle and lengths at the imine nitrogen are normal.

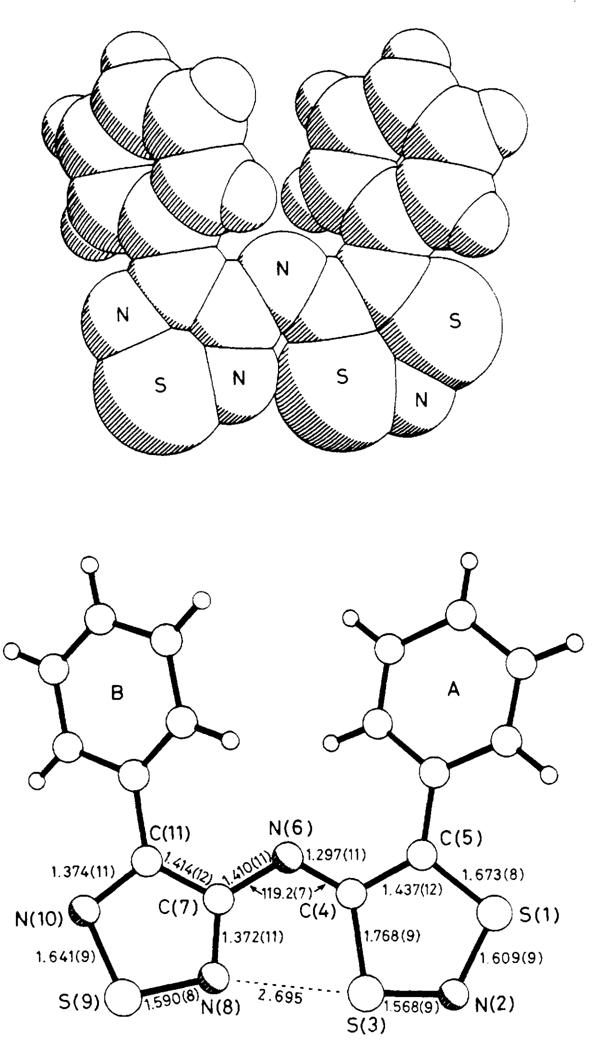

Figure 2. Space-filling and skeletal representations of the molecular structure of (**7**) showing selected bond lengths, angle and contact distance.

Compound (**7**) is surprisingly stable thermally, being decomposed only very slowly in boiling decalin (190 °C). This thermal stability, and the planarity of the molecule, would suggest a possible contribution from the tricyclic 14π structure (**5**). However the *X*-ray results show that such a contribution must be small. Furthermore the compound was completely decolourised by *m*-chloroperbenzoic acid in dichloromethane at room temperature within 2 hours, showing it to be considerably more reactive than the monocyclic 10π S–N aromatic systems recently reported.[4]

Mechanisms for the formation of compounds (**3**) and (**7**) based on cycloaddition, rearrangement, and ring cleavage reactions will be proposed in the full paper.

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§ *Crystal data* (**7**) $C_{16}H_{10}N_4S_3$, monoclinic, a = 18.502(7), b = 11.388(3), c = 7.422(2) Å, β = 96.46(3)°, U = 1554 Å^3, space group Cc, Z = 4, M = 354.5, D_c = 1.52 g cm^{-3}. Data collection, solution, and refinement were the same as for (**3**) giving R = 0.051 for 914 independent observed reflections [$\theta \leqslant 58°$, $|F_O| > 3\sigma(|F_O|)$]. The atomic co-ordinates for these structures are available on request from the Director of 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.

¶ Indeed the only other example of the ring system seems to be the fully saturated compound (**8**).[9]

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References

1 M. Tashiro and S. Mataka, *Heterocycles*, 1976, **4**, 1243.

2 S. Mataka, K. Takahashi, Y. Yamada, and M. Tashiro, *J. Heterocycl. Chem.*, 1979, **16**, 1009.

3 H. Koenig and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1983, 73.

4 S.T.A.K. Daley, D. J. Williams, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1983, preceding communication.

5 J. Liebscher, *Liebigs Ann. Chem.*, 1977, 1005.

6 D. S. Breslow and H. Skolnick, 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Wiley, New York, 1966, vol. 21, pt. 2, p. 1112.

7 J. Nakayama, A. Sakai, A. Tokiyama, and M. Hoshino, *Tetrahedron Lett.*, 1983, **24**, 3729 and references therein.

8 H. W. Roesky and H. Zamankhan, *Z. Naturforsch., Teil B*, 1977, **32**, 1390.

9 H. Mueller and M. Dines, *J. Heterocycl. Chem.*, 1969, **6**, 627.