Benzo[1,2-*c*;3,4-*c*′;5,6-*c*″]tris[1,2]dithiole-1,4,7-trithione

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The title compound has been synthesised in crystalline form by two methods.

THE synthesis of 1,2-benzodithiole-3-thione from *o*-chlorobenzyl chloride and sulphur–dimethylformamide[1] suggested use of the readily available[2] polyhalogenomesitylene (1; R = Br) to prepare the novel tetracyclic system (2).

The halogeno-compound (1; R = Br) was treated with a little more than the calculated amount of sulphur in boiling dimethylformamide, a large volume of solvent being used to minimise intermolecular reactions and to allow for the insolubility of intermediates. Pale coloured solids containing halogen were obtained. It was then thought that a more soluble starting material should be tried and the halogeno-compound was therefore converted into two triamines (1; R = NMe_2 or piperidino). The first of these, as a 2% solution in boiling dimethylformamide, gave after 40 h reaction with sulphur, an amorphous infusible red solid, whose carbon and sulphur contents were close to those calculated for $(CS)_n$, the yield on this basis being 55%. While halogen was absent, small but definite amounts of hydrogen and nitrogen were present, however, and mass spectrometry indicated that the product contained both the desired substance, C_9S_9, molecular weight 396, and a nitrogen compound ($C_{10}H_3NS_8$), molecular weight 393, formed by reaction of methylamine with one of the dithiolethione rings, presumably having the structure (3) or the isomer with one 3-imino-1,2-benzodithiole ring.[1] The microanalytical results suggested that 30—40% of nitrogen compound was present.†

The mixed reaction product was insoluble in common solvents, but it dissolved in boiling quinoline to give

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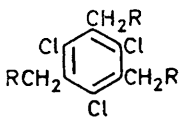
† The infusibility and insolubility of the product greatly hindered analytical and spectroscopic studies; the mass spectrometer was operated at the upper limit of its temperature range before a detectable signal was obtained.

[1] J. P. Brown and M. Thompson, preceding paper.

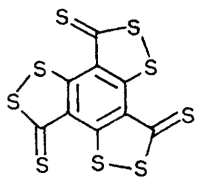
[2] S. D. Ross, E. R. Coburn, M. Markarian, and M. Schwarz, *J. Org. Chem.*, 1960, **25**, 2102.

$<0{\cdot}1\%$ solutions. (Equilibrium was slowly attained and there was evidence of decomposition on prolonged heating.) Microcrystalline material separated on cooling.

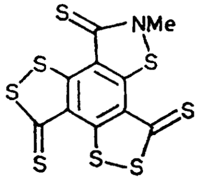
The nitrogen compound was more soluble than the compound C_9S_9. 2-Alkylaminobenzisothiazoline-3-thiones are converted by hydrogen sulphide into 1,2-benzodithiole-3-thione,[3] but passage of hydrogen sulphide through a boiling solution of our mixed product in quinoline did not noticeably increase the content of C_9S_9. However, repetition of the original preparation with continuous passage of hydrogen sulphide through the reaction mixture gave after 14 h a product (50%) which contained substantially less of compound (3) and which was already microcrystalline. On fractional crystallisation of this material from quinoline we obtained a sample of almost pure C_9S_9. When the final crystallisation liquors were cooled very slowly[*] a visibly crystalline product was obtained as long crimson needles.



(1)



(2)



(3)

Attempts at more fundamental changes of the conditions of the preparation, so as to prevent completely the formation of compound (3), failed. Mass spectrometry of the original products from the bromo-compound (1; R = Br) showed that traces of both compound (2) and the nitrogen compound (3) were present. This indicated that use of dimethylformamide as solvent must be avoided. Use of an excess of sulphur, or of quinoline, as solvent for the reaction with the halogeno-compound (I; R = Br) gave, in fact, crude products in which compound (2) could be detected by mass spectrometry, and the peak at 393 was absent. However, insufficient compound (2) was present to permit isolation. Use of quinoline as a solvent with the amine (I; R = NMe_2) also gave compound (2) only in trace amounts, confirming earlier indication[4] that dimethylformamide has its own part in thiation reactions, as well as serving as a source of dimethylamine. More surprisingly, preparation of the amine (I; R = NEt_2) and reaction in diethylformamide also failed to give isolable C_9S_9, an amorphous black product being obtained. Use of the thiol (I; R = SH) in quinoline or in an excess of sulphur also failed. Finally, an attempt was made to apply to the problem Becke and Hagen's synthesis of dithiobenzoic acid from benzyl chloride,[5] using sulphur and sodium methoxide in methanol. It was conceivable that a halogen atom *ortho* to the new dithiocarboxylic group might also be attacked by polysulphide, and subsequent cyclisation might then give the dithiolethione ring. The bromo-compound (1; R = Br) was therefore subjected to this reaction and, after treatment of the crude product with boiling dimethyl sulphoxide, the undissolved red material was extracted with boiling quinoline to give a low yield (*ca.* 2%) of compound (2). However this contained traces of nitrogenous impurities, presumably derived from the action of quinoline on active halogen compound in the crude product.

The structural formula (2) suggests that 'bond–no bond resonance' leading to equivalence of the nine sulphur atoms is possible. Professor N. Lozac'h suggested to us that, if so, the compound might undergo replacement of three nominal thiocarbonyl groups by carbonyl groups on treatment with concentrated sulphuric acid, as do 6a-thiathiophthens.[6] In fact, compound (2) reacts with hot sulphuric acid with evolution of sulphur dioxide. The amorphous product so obtained had an unexpectedly low carbon content and attempts to crystallise it have failed. Mass spectrometry indicated that only a small amount of a compound of molecular weight 348 might be present. 1,2-Benzodithiole-3-thione was recovered largely unchanged under the same conditions, but a small increase in temperature led to a sudden blackening and evolution of sulphur dioxide, with *ca.* 50% conversion into an amorphous solid of low carbon content. Hence, this reaction cannot be used diagnostically.

The infusibility of compound (2) led us to consider the possibility that it was polymeric, but the crystallinity, the fact that the solubility of the crude product in boiling quinoline, though low, is complete, and the absence of lines in the mass spectrum from m/e 400 to at least 600, support the monomeric structure.

EXPERIMENTAL

Mass spectra were recorded on an A.E.I. MS 12 spectrometer.

1,3,5-*Trichloro*-2,4,6-*tris(dialkylamino)benzenes* (1; R = NMe_2, NEt_2, *or piperidino*).—1,3,5-Tris(bromomethyl)-2,4,6-trichlorobenzene (5 g) and diethylamine (10 ml) were heated in boiling ethanol (100 ml) for 2 h. The solvent was evaporated off and water (100 ml) was added. The *tris(diethylamino)-compound* (4·4 g), m.p. 44—45°

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[*] Suggestion of Professor A. Hordvik, who is examining the structure by X-ray crystallography.

[3] E. W. McClelland, L. A. Warren, and J. H. Jackson, *J. Chem. Soc.*, 1929, 1582.

[4] J. P. Brown, *J. Chem. Soc.* (*C*), 1968, 1077.

[5] F. Becke and H. Hagen, *Chem.-Ztg.*, 1969, **83**, 474.

[6] M. Stavaux, and N. Lozac'h, *Bull. Soc. chim. France*, **1967**, 2082; F. Arndt, R. Schwarz, C. Martius, and E. Aron, *Rev. Fac. Sci. Istanbul*, 1948, **A13**, 57.

formed prisms, m.p. 44—45° (from ethanol) (Found: C, 57·6; H, 8·1; N, 9·5. $C_{21}H_{36}Cl_3N_3$ requires C, 57·7; H, 8·2; N, 9·5%). The *dimethylamino*- [m.p. 75° (Found: C, 50·5; H, 6·7; H, 11·9. $C_{15}H_{24}Cl_3N_3$ requires C, 51·0; H, 6·8; N, 11·9%)] and *piperidino*- [m.p. 116—118° (Found: C, 60·2; H, 8·0; N, 9·0. $C_{24}H_{36}Cl_3N_3$ requires C, 60·9; H, 7·6; N, 8·9%)] *analogues* were similarly made.

1,3,5-*Trichloro*-2,4,5-*tris*(*mercaptomethyl*)*benzene* (1; R = SH).—The bromo-compound (1; R = Br) and thiourea (3 g) were heated in boiling methanol (100 ml). 2N-Sodium hydroxide (50 ml) was added and the solution was boiled for 15 min. The mixture was filtered and then acidified to liberate the *tris*(*mercaptomethyl*) *compound* (3·2 g), m.p. 153—154°. Recrystallisation from ethanol gave pale yellow needles, m.p. 154—155° (Found: C, 34·0; H, 2·9. $C_9H_9Cl_3S_3$ requires C, 33·8; H, 2·8%).

Benzo[1,2-c;3,4-c′;5,6-c″]*tris*[1,2]*dithiole*-1,4,7-*trithione* (2).—A mixture of the triamine (1; R = NMe_2) (1·3 g), sulphur (0·6 g), and dimethylformamide (78 ml) was saturated with hydrogen sulphide and passage of the gas was continued while the liquid was boiled and stirred for 14 h. A red microcrystalline solid (0·73 g) was filtered off (Found: C, 27·4; H, 0·0; N, 0·7; S, 72·8. C_9S_9 requires C, 27·3; S, 72·7%). The product (100 mg) was heated for 5 min with boiling quinoline (100 ml). The undissolved material (71 mg) was filtered off and treated with fresh boiling quinoline (100 ml). The material (38 mg) still undissolved was treated with a third portion of boiling quinoline and the mixture was filtered at the boil to remove a residue (2 mg) which was discarded. Slow cooling of the filtrate (from 225 to 140° during 6 h) gave *compound* (2) (9 mg) as slender crimson needles (infusible, blackening above 300°) (Found: C, 27·6; H, 0·0; N, 0·0%).

Compound (2) was also obtained when the bromo-compound (1; R = Br) (2 g) was heated with sulphur (3 g) and sodium methoxide (3·5 g) in boiling methanol (100 ml) for 120 h. The insoluble material (3·4 g) was filtered off, moistened with methanol, and boiled with water (60 ml) to leave a residue (1·94 g), a portion (0·5 g) of which was boiled with dimethyl sulphoxide (50 ml) for 10 min. The insoluble red powder (0·18 g) so obtained was treated with boiling quinoline (100 ml) and the mixture was filtered hot. From the filtrate, compound (2) (8 mg) separated as squat orange micro-prisms (Found: C, 29·2; H, 0·0; N, 0·4%).

The mass spectra of the samples from the two routes indicated the presence of the nitrogen compound (3) in the original product from the first route (and in much diminished quantity in the purified sample: the method does not permit exact quantitative findings), and its complete absence in the sample from the second route. The latter sample, however, did contain a little impurity, which was detectable from the i.r. spectrum, and the microanalysis indicates that nitrogenous material may be present; the apparent high carbon content may reflect carbonisation during isolation.

In the following attempts to prepare compound (2) by prolonged heating with elemental sulphur it was in no case obtained as the main component of a crystalline fraction, but it was in all cases detectable by mass spectrometry: (a) halogeno-compound (1; R = Br) in boiling dimethylformamide; (b) amine (1; R = piperidino) in boiling dimethylformamide; (c) amine (1; R = NMe_2) in quinoline; (d) halogeno-compound (1; R = Br) in boiling quinoline; (e) halogeno-compound (1; R = Br) and an excess of sulphur at 220°. Compound (3) was also detectable in the first three cases. The thiol (1; R = SH), in either quinoline or an excess of sulphur at 220—240°, and the amine (1; R = NEt_2) in diethylformamide, gave amorphous products from which no crystalline material could be isolated in boiling quinoline and which were not examined in the mass spectrometer.

Mass spectra of samples of the purified compound (2) showed the molecular ion at m/e 396 with an isotope pattern from 396 to 401 consistent with C_9S_9. The largest peak in the spectrum corresponded to C_8S_7 (loss of CS_2) and the other major peaks corresponded to C_5S_2, C_7S_2, C_6S_2, C_7S_5, and C_3S_2. When substantial amounts of the nitrogen compound (3) were present, in addition to its molecular ion at m/e 393, a peak corresponding to C_9S_8, presumably arising from loss of NCH_3, was also seen.

The i.r. spectrum of the insoluble and deep coloured compound (2) (in KBr disc) showed considerable scatter and contained relatively few bands ($\nu_{max.}$ 1480, 1175, and 958 cm^{-1}).

Reaction of Compound (2) *with Sulphuric Acid*.—Compound (2) (50 mg) was dissolved in hot concentrated sulphuric acid (3 ml) at 200° and kept at this temperature for 5 min. Sulphur dioxide was evolved. A little sulphur (1·5 mg) was filtered from the cooled mixture and washed with sulphuric acid (1 ml). The filtrate was diluted with water (8 ml). An orange-yellow solid (38 mg) (Found: C, 20·4; H, 0·0%) was filtered off. Further dilution gave gelatinous material (9·5 mg).

Under the same conditions, 1,2-benzodithiole-3-thione (100 mg) was recovered unchanged (72%), but on raising the temperature to 210°, sudden blackening and evolution of sulphur dioxide was observed and after recovery of unchanged thione (30%), an orange-yellow, chloroform-insoluble, amorphous solid (50 mg) (Found: C, 36·6; H, 2·6; S, 28·1%) was obtained.

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