X-Ray Crystal Structure of Benzo[1,2-*c*; 3,4-*c*′; 5,6-*c*″]tris[1,2]dithiole-1,4,7-trithione: a Sulphur Analogue of Coronene

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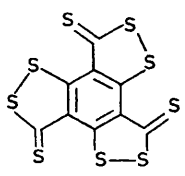
Summary The sulphocarbon benzo[1,2-*c*; 3,4-*c*′; 5,6-*c*″] tris[1,2]dithiole-1,4,7-trithione has a coronene-like structure in the crystalline state with S–S bond lengths in the range 2·420 (8)—2·433 (8) Å.



(I)

THE sulphocarbon (I) has been synthesized by two methods.[1,2] The structural formula of (I) suggests that there may be delocalized σ-bonding in the linear three-sulphur sequences analogous to that in the three-sulphur sequence

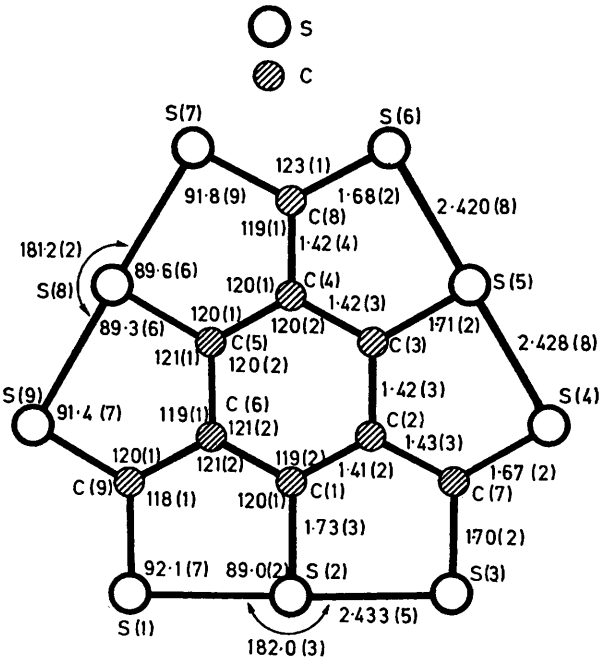


FIGURE. Bond lengths (Å) and bond angles (°) in S_9C_9.

of 6a-thiathiophthen.[3] However, attempts to find experimental evidence for this assumption have failed.[2]

The molecular structure of (I) has now been studied by *X*-ray crystallographic methods, and the bond lengths and angles from this study are given in the Figure. The molecule is almost exactly planar and lies on a crystallographic two-fold axis passing through S(2), C(1), C(4), and C(8).

The six fused disulphide rings of (I) are equal within experimental error, *cf.* Figure, and the symmetry of the molecule is approximately D_{3h}. Furthermore, compound (I) has a 24π-electron system and may therefore be described as a sulphur analogue of coronene.[4,5] The C–C bonds in the central ring of (I) as well as those in the central ring of coronene[4,5] are found to be somewhat longer than the aromatic C–C bond, 1·397 Å, in benzene.

The S–S distances in (I) indicate that there is delocalized bonding in the linear three-sulphur sequences of the molecule. However, the S–S distances in (I) of 2·43 Å are longer than those of 2·36 Å in 6a-thiathiophthen.[3]

In crystals of (I) there are a series of intermolecular sulphur-sulphur contacts in the range 3·47—3·70 Å. The distance between the planes of adjacent molecules is 3·47 Å.

The crystals of C_9S_9 are brown-red, monoclinic, space group $I2/c$ with unit cell dimensions $a = 7{\cdot}485(4)$, $b = 10{\cdot}096(6)$, $c = 15{\cdot}792(5)$ Å, $\beta = 90{\cdot}87(4)°$ $Z = 4$, $D_c = 2{\cdot}21$ g cm^{-3}, $D_m = 2{\cdot}2$ g cm^{-3}.

Using Mo–K_α radiation, 437 out of 900 independent reflections in the range $0 < \theta < 23°$, for which $I \geqslant 2\sigma(I)$ were accepted as observed. The structure was solved by the heavy atom (S) method and refined by full-matrix least-squares. With anisotropic temperature coefficients for sulphur and isotropic for carbon the final R is 0·086.

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