X-Ray Structure of Diphenylcyclopropenethione

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Summary The structure of diphenylcyclopropenethione has been determined from three-dimensional *X*-ray diffraction data and average values of bond distances and angles from the two crystallographically independent molecules have been computed.

IN view of structural studies involving cyclopropene[1] and its derivatives[2] including cyclopropenium salts[3] we report preliminary details of the molecular structure of diphenylcyclopropenethione (I) determined by *X*-ray diffraction.

Small, lemon-yellow crystals of (I) were obtained from benzene–n-heptane. The crystals rapidly turn orange-red in the air, but this decomposition appeared to be limited to the surface. The crystals are monoclinic, space-group $P2_1/n$: $a = 14{\cdot}171(7)$, $b = 10{\cdot}082(5)$, $c = 17{\cdot}409(9)$ Å, $\beta = 101{\cdot}92°$, $U = 2433{\cdot}7$ Å^3; D_m 1·19 g/cm^3; D_c 1·21 g/cm^3 for $Z = 8$. Thus, there are two crystallographically independent molecules per asymmetric unit.

Intensity data were collected on a Picker FACS-I diffractometer using graphite-monochromatized Cu-K_α radiation and a θ–2θ scanning procedure; a total of 2021 independent data was collected with $2\theta \leqslant 90°$. The crystal showed no appreciable decomposition in the *X*-ray beam. The data were corrected for Lorentz and polarization effects.

The structure was solved by a combination of direct methods[4] and Fourier techniques. The initial *E* map clearly revealed one complete molecule and fragments of the second. The missing atoms were located by a subsequent Fourier synthesis. Full-matrix least-squares refinement of the 32 non-hydrogen atoms with isotropic thermal parameters followed by additional refinement with anisotropic thermal parameters for both sulphur atoms resulted in $R^1 = 0{\cdot}10$ and $R^2 = 0{\cdot}118$. The 20 hydrogen atoms were located (calculated co-ordinates) and two final cycles of refinement gave $R^1 = 0{\cdot}089$ and $R^2 = 0{\cdot}102$ for 1465 data with $F_0^2 \leqslant 2\sigma(F_0^2)$. The Figure summarizes the observed average bond distances and angles.

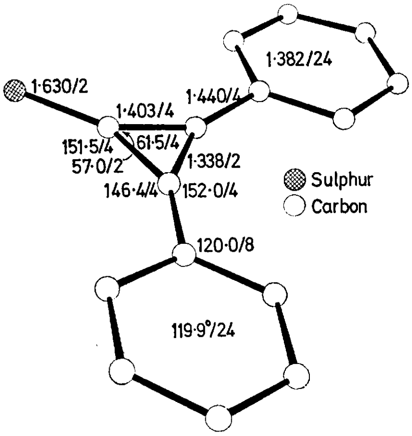
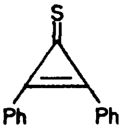


FIGURE. *Perspective view of the diphenylcyclopropenethione molecule with the observed average distances and angles. The notation, distance/N, is the average distance of N apparently equivalent distances for the two independent molecules. Similar notation is used for the various angles. The standard deviations of the average distances or angles are* <0·01 Å *and* 0·3° *respectively.*

The phenyl rings and the fragments (II) and (III) are all planar within experimental error. However, the phenyl rings are twisted out of the plane of the cyclopropenyl ring by an average of 4°. Apparently this small amount of twisting accompanied by an increase in the exocyclic angle

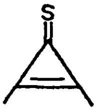
(Figure) to 152° is sufficient to satisfy the steric requirements of the phenyl *ortho*-hydrogen atoms.

The cyclopropenyl–phenyl bond length (1·44 Å) agrees well with similar bonding in triphenylcyclopropenium perchlorate[3] (average 1·436 Å) and is considerably shorter than the accepted $C(sp^2)$–$C(sp^2)$ bond length (1·48 Å). In addition, the cyclopropenyl C–C 'single' bond (1·403 Å) is *ca.* 0·1 Å shorter than that found for cyclopropene[1] or perchlorocyclopropene.[2] In contrast, the double bond length (1·338 Å) is in good agreement with that found for ethylene (1·332 Å).[5] The structure is not well defined as an aromatic 2π electron zwitterionic structure (IV), which would result in equivalent bond lengths, as has been demonstrated for the cyclopropenium ion.[3]

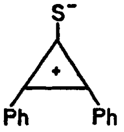


(I)

(II)



(III)



(IV)

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