Crystal and Molecular Structure of Bis(diphenylmethylene)trisulphur Tetranitride

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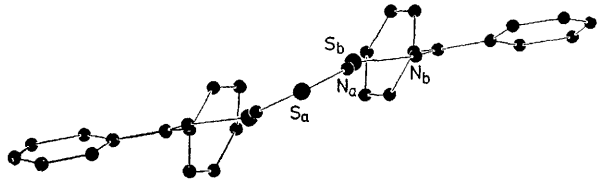
Summary In crystalline form $Ph_2CNSNSNSNCPh_2$ exists as a chain structure with the central five members of the sulphur–nitrogen chain coplanar.

FLUCK[1] has reported the preparation of bis(diphenylmethylene)trisulphur tetranitride from S_4N_4 and diphenyldiazomethane. As in the reaction of S_4N_4 with triphenylphosphine, a sulphur atom is lost and a product containing the S_3N_4 fragment is formed. However, the reaction with triphenylphosphine produces a six-membered sulphur–nitrogen ring, five members of which are planar,[2] whereas an open chain compound results from the reaction with diphenyldiazomethane. In view of the unexpected partial planarity of the ring compound we have determined the structure of the open chain compound to determine whether the chain is flat or puckered.

Crystal data: $Ph_2CNSNSNSNCPh_2$, M 456, orthorhombic, $a = 12{\cdot}590(4)$, $b = 26{\cdot}020(9)$, $c = 7{\cdot}286(2)$ Å, $U = 2386{\cdot}8$ Å^3, $D_m = 1{\cdot}28$, $Z = 4$, $D_c = 1{\cdot}26$ g cm^{-3}, space group *Pcan*. Intensities were recorded on a Picker diffractometer using Cu radiation. Of the 1709 reflections measured, 1107



FIGURE

were classed as observed $[(|F_o|/\sigma|F_o|) > 1{\cdot}5]$. The structure was refined by least-squares to an R value of 7·4%, ignoring hydrogens and using anisotropic temperature factors for the 17 independent atoms.

The structure (Figure) shows the central sulphur atom of the molecule lying on an axis of two-fold symmetry. The angle at this sulphur atom is 123·8(7)° compared with the 100° angle usually found. The central five members of the sulphur–nitrogen chain are planar to within 0·04 Å. The remaining nitrogens are 0·49 Å from that plane. This partial planarity of the sulphur–nitrogen chain is unexpected considering the possible further delocalization of the π bonding that would result from full planarity.

The sulphur–nitrogen bond lengths are: S_a–N_a = 1·549(8), N_a–S_b = 1·656(9), and S_b–N_b = 1·685(8) Å compared with the sulphur–nitrogen double-bond length of 1·55 Å and the single-bond length of 1·76 Å.

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[1] E. Fluck, *Z. anorg. Chem.*, 1961, **312**, 195.
[2] E. M. Holt and S. L. Holt, *Chem. Comm.*, 1970, 1704.