A Novel Trithiadiazapentalene Derivative with Exocyclic C–N Double Bonds

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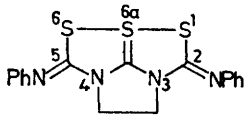
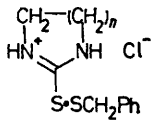
Summary The structure of 3,4-ethano-2,3,4,5-tetrahydro-2,5-bisphenylimino-1,6,6a,S^{IV}-trithia-3,4-diazapentalene (I) has been confirmed by *X*-ray crystallography.

THE structure (I), assigned[1] to the yellow product obtained by treatment of the isothiouronium salt (II; $n = 1$) with aqueous sodium hydrogen carbonate and phenyl isothiocyanate, has been confirmed by *X*-ray crystallography.

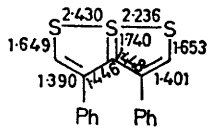
Crystal data: $C_{17}H_{14}N_4S_3$, $M = 365{\cdot}5$, triclinic, $a = 8{\cdot}184(2)$, $b = 19{\cdot}458(4)$, $c = 12{\cdot}040(3)$ Å, $\alpha = 109{\cdot}68(4)$, $\beta = 72{\cdot}85(5)$, and $\gamma = 107{\cdot}66(4)°$, $V = 1680$ Å^3, $Z = 4$, $D_c = 1{\cdot}445$ g cm^{-3}. There are no systematic absences. Space group $P\bar{1}$ (confirmed by the results of the analysis). The



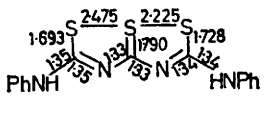
(I)



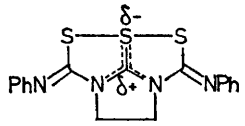
(II)



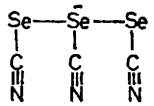
(III)



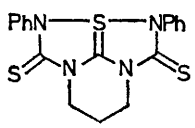
(IV)



(V)



(VI)

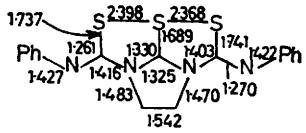


(VII)

structure was solved by a combination of symbolic addition and heavy-atom methods and has been refined to an R-factor of 0·058 on 3693 non-zero reflections collected on a Picker FACS-1 diffractometer (Cu-K_α).

The bond-lengths in the essentially planar central portions of the two crystallographically-independent molecules are shown in the Figure. The agreement in dimensions between the two molecules is quite close. The S–S lengths lie in the range typical of 6a-thiathiophthens,[2] but the C–S distances are significantly different from those normally found in thiathiophthens, *e.g.* compound (III),[3] and related systems, such as the 3,4-diaza compound (IV).[4] In (I), the central C–S bonds [1·689(5) and 1·697(5)] are shorter than the outer ones [1·737(5), 1·741(6), 1·732(6), and 1·735(5) Å].

The phenyl groups in compound (I) are twisted out of the main plane of the molecule by varying amounts (37—76°). Inspection of all the C–N bond lengths suggests that the molecule should be represented as in structure (V), with the exocyclic C–N links as pure double bonds,[5] and with relatively little π-overlap between C(2) and N(3), and N(4) and C(5). Viewed in this light, the new structure may be related to the electron-rich three-centre system found in the triselenocyanate anion (VI).[6]



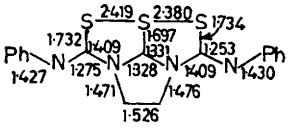


FIGURE. Bond lengths (Å) in the two independent molecules of (I).

Treatment of the isothiouronium salt (II; $n = 2$) with sodium hydrogen carbonate and phenyl isothiocyanate yields a colourless product, which, from its n.m.r. and i.r. spectra, is formulated as the tricyclic dithione (VII), a derivative of 2,3,4,5-tetrahydro-6a-thia-1,3,4,6-tetra-azapentalene.

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