The Molecular Structure of an Isothiathiophthen

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Summary *X*-Ray crystallographic data for an isothiathiophthen support its formulation as a 1,3-dithiol-2-ylidene thioketone rather than as a bicyclic system analogous to 6a-thiathiophthen.

X-RAY crystallographic studies[1] have shown that the 6a-thiathiophthen system (I) is essentially planar, with the three sulphur atoms arranged almost linearly. The sum of the two S–S distances in each compound studied is nearly constant (*ca.* 4·7 Å) but, subject to this condition, the individual S–S distances show considerable variation, depending presumably on the substitution pattern. Nevertheless, 6a-thiathiophthens can be regarded as bicyclic systems, admittedly of a special type, with a particularly interesting bonding situation at the central sulphur atom.[2]

No exact structural data have been reported for "isothiathiophthens",[3–5] the 1,3-dithiole analogues (II) of 6a-thiathiophthens, and the nature of the bonding in the iso-compounds is unknown.

Certain similarities in spectra and in chemical behaviour between the two series may be noted. Thus, isothiathiophthens with aryl substituents [II; $R^1 = R^3$ (or R^4) = Ar, $R^2 = R^4$ (or R^3) = H] have maxima in their electronic absorption spectra at *ca.* 490, 340, and 265 nm,[3,6] resembling 6a-thiathiophthens.[7] The iso-compounds are thermally stable;[5] they are converted[3,5] into dithiolylidene ketones by

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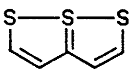
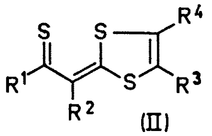
methods familiar in the 6a-thiathiophthen series, and with triethyloxonium fluoroborate they give *S*-ethyl derivatives,[3] as do 6a-thiathiophthens. Nitrosation of the diphenylisothiathiophthen [II; $R^1 = R^3$ (or R^4) = Ph, $R^2 = R^4$ (or R^3) = H] gives the nitroso-derivative of the corresponding 1,3-dithiolylidene ketone,[6] exactly paralleling the behaviour of 2,5-diphenyl-6a-thiathiophthen.[8]



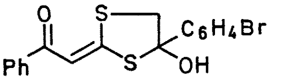
(I)



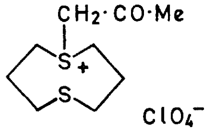
(II)

$\mathrm{Ph\ CO{\cdot}CH{=}C(SH)_2}$

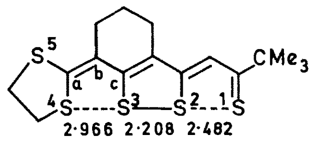
(III)



(IV)



(V)



(VI)

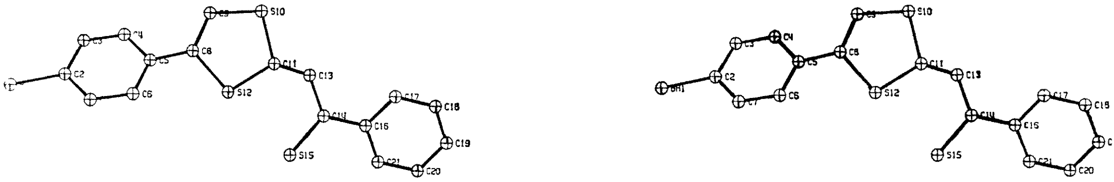


FIGURE. *Stereoscopic view of a single molecule along the* b *axis.*

We now report structural data for the isothiathiophthen (II; R^1 = Ph, $R^2 = R^3$ = H, R^4 = *p*-Br·C_6H_4) prepared in the following way. *p*-Bromophenacyl bromide was condensed[9] with the *gem*-dithiol (III), derived from acetophenone, to give the cyclic hemi-thioacetal (IV or geometrical isomer) and this product was converted directly, by the action of phosphorus pentasulphide in benzene, into the isothiathiophthen (dark purple needles from benzene, m.p. 200—203°), λ_{max} 265, 343, and 490 nm (ϵ 24,880, 12,740, and 30,550).

The crystals are very fine needles elongated along the *b* axis. *Crystal data*: $C_{17}H_{11}S_3Br$, $M = 391{\cdot}4$, triclinic, $a = 17{\cdot}775$ (3), $b = 7{\cdot}190$ (2), $c = 6{\cdot}474$ (1) Å, $\alpha = 90°55(1)'$, $\beta = 110°1(1)'$, $\gamma = 89°6(1)'$, $V = 777{\cdot}3 \times 10^{-24}$ cm^3, $\rho_m = 1{\cdot}60$ g cm^{-3}, $Z = 2$, $\rho_c = 1{\cdot}672$ g cm^{-3}. Space group $P\bar{1}$. A total of 1144 non-zero independent reflexions with $2\theta < 90°$, was measured on an automatic diffractometer with Cu-K_α radiation. While the shape and size of the crystal were not ideal for very accurate data, the structure, incorporating anisotropic temperature factors, has been refined to a conventional *R*-factor of 0·11 on the observed data. A view of the molecular structure is shown in the Figure. The e.s.d. for C–S and C–C lengths are 0·025 and 0·035 Å, respectively, while angles are ±2°.

From the Figure, it can be seen that the *p*-bromophenyl group occupies the position corresponding to R^4 in structure (II). The central group of eight atoms is approximately planar (maximum deviation 0·08 Å), with the phenyl ring and the *p*-bromophenyl ring making angles of 26° and 29° with this plane, respectively. The exocyclic S · · · S distance is 2·91 (1) Å which, although much less than twice the van der Waals radius of sulphur (3·70 Å),[10] is considerably longer than any S · · · S distance found in a thiathiophthen; the longest such distance is 2·56 Å in one of the molecules of 5-*p*-bromophenyl-3-benzoyl-2-methylthio-6a-thiathiophthen.[1b,11] The transannular S · · · S distance in 1-acetonyl-1-thionia-5-thiacyclo-octane perchlorate (V) is 3·13 Å,[12] although in this molecule, one of the sulphur atoms probably bears a substantial positive charge, while a S(3) · · · S(4) distance of 2·966 Å was reported in (VI).[13] The long S · · · S distance in (VI) is achieved by increasing the angles, *a*, *b*, and *c* from 120° to 127·1, 125·5, and 122·5°, respectively, whereas the corresponding angles in the isothiathiophthen are 131, 127, and 119°.

The C(11)–C(13), C(13)–C(14), and C(14)–S(15) lengths (Figure) are 1·26, 1·42, and 1·72 Å, respectively. These dimensions, and the S–S distance of 2·91 Å, are more in accord with a structure of type (II) than with a bicyclic structure analogous to structure (I) for 6a-thiathiophthen.

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