

## 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<sup>1</sup> 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.<sup>2</sup>

No exact structural data have been reported for "isothiathiophthens",<sup>3-5</sup> 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<sup>1</sup> = R<sup>3</sup> (or R<sup>4</sup>) = Ar, R<sup>2</sup> = R<sup>4</sup> (or R<sup>3</sup>) = H] have maxima in their electronic absorption spectra at *ca.* 490, 340, and 265 nm,<sup>3,6</sup> resembling 6a-thiathiophthens.<sup>7</sup> The iso-compounds are thermally stable;<sup>5</sup> they are converted<sup>3,5</sup> into dithiolylidene ketones by

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

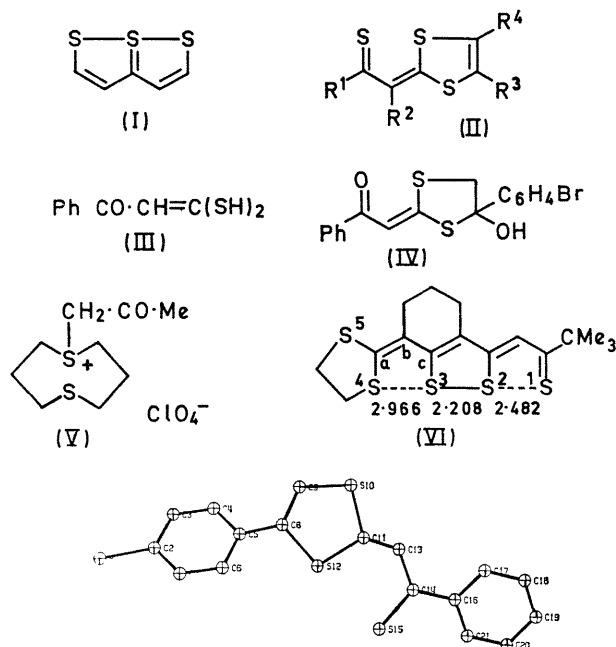


FIGURE. Stereoscopic view of a single molecule along the *b* axis.

We now report structural data for the isothiathiophthen (II; R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = *p*-Br·C<sub>6</sub>H<sub>4</sub>) prepared in the following way. *p*-Bromophenacyl bromide was condensed<sup>9</sup> 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<sub>max</sub> 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<sub>17</sub>H<sub>11</sub>S<sub>3</sub>Br, *M* = 391.4, triclinic, *a* = 17.775 (3), *b* = 7.190 (2), *c* = 6.474 (1) Å, α = 90°55(1)',

β = 110°1(1)', γ = 89°6(1)', *V* = 777.3 × 10<sup>-24</sup> cm<sup>3</sup>, ρ<sub>m</sub> = 1.60 g cm<sup>-3</sup>, *Z* = 2, ρ<sub>c</sub> = 1.672 g cm<sup>-3</sup>. Space group *P*1̄. A total of 1144 non-zero independent reflexions with 2θ < 90°, was measured on an automatic diffractometer with Cu-K<sub>α</sub> 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<sup>4</sup> 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),<sup>10</sup> 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.<sup>1b,11</sup> The transannular S...S distance in 1-acetonyl-1-thionia-5-thiacyclo-octane perchlorate (V) is 3.13 Å,<sup>12</sup> 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).<sup>13</sup> 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.

(Received, November 28th, 1969; Com. 1811.)

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