

Structure of a 3-Aminothiathiophthen: X-ray Analysis of 3-Amino-2-methylthio-5-phenyl-6a-thiathiophthen {3-Amino-2-methylthio-5-phenyl[1,2]dithiolo[1,5-*b*][1,2]dithiole-7- S^{IV} }

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The molecular structure of the title compound (II) has been determined by single-crystal X-ray diffraction methods. Crystals are monoclinic, with $a = 14.103(3)$, $b = 8.313(4)$, $c = 11.353(7)$ Å, and $\beta = 102^\circ 10'(2')$, $Z = 4$, space group $P2_1/c$. The structure was solved by a combination of the symbolic-addition, and Patterson and Fourier methods and refined to R 0.090 on 1 696 non-zero reflections measured by diffractometer. The molecule is almost planar with the S(1)–S(6a)–S(6) atoms nearly collinear; S(1)–S(6a) and S(6a)–S(6) are 2.375(4) and 2.266(4) Å. A comparison of these lengths with those found in 3-benzoyl-5-*p*-bromophenyl-2-methylthio-6a-thiathiophthen (III) indicates that the conjugative effect of the 3-amino-group has caused a significant shortening of the S(1)–S(6a) length in (II) as compared to that in (III).

THE discovery by X-ray analysis of the structure of 2,5-dimethyl-6a-thiathiophthen (I)^{1,2} has served as a focus for numerous studies regarding the influence of the position and type of various substituents on the lengths of the two S–S bonds in the 6a-thiathiophthen {[1,2]dithiolo[1,5-*b*][1,2]dithiole-7- S^{IV} } nucleus. However, there has been no X-ray study of an amino-6a-thiathiophthen. 2-Amino-derivatives have been syn-

thesized³⁻⁵ and have been found to be anomalously acidic by spectroscopic and chemical methods. The synthesis of a 3-amino-derivative (II) has been reported and the compound was found to be basic,⁶ thus supporting previous results⁷ that the 3-position, at which attack by electrophiles occurs, is relatively electron-rich. The spectra of the 3-amino-6a-thiathiophthens are unusual in that they have an absorption at 560 nm in contrast to the usual maximum at *ca.* 500 nm for the 6a-thiathiophthens. We now report the determination

¹ S. Bezzi, M. Mammi, and C. Garbuglio, *Nature*, 1958, **182**, 247.

² F. Leung and S. C. Nyburg, *Chem. Comm.*, 1969, 137.

³ H. Behringer and R. Wiedenmann, *Tetrahedron Letters*, 1965, 3705.

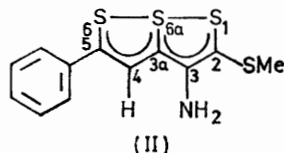
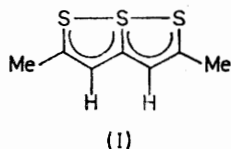
⁴ E. Klingsberg, *J. Org. Chem.*, 1966, **31**, 3489.

⁵ Y. Mollier, F. Terrier, R. Pinel, and N. Lozac'h, *Bull. Soc. chim. France*, 1967, 2074; A. Rouessac and J. Vialle, *ibid.*, 1968, 2054.

⁶ A. J. Barnett, R. J. S. Beer, B. V. Karaoghlanian, E. C. Llaguno, and I. C. Paul, *J.C.S. Chem. Comm.*, 1972, 836.

⁷ R. J. S. Beer, D. Cartwright, R. J. Gait, and D. Harris, *J. Chem. Soc. (C)*, 1971, 963; G. Duguay, D. H. Reid, K. O. Wade, and R. G. Webster, *J. Chem. Soc. (C)*, 1971, 2829; D. T. Clark and D. Kilcast, *Tetrahedron*, 1971, **27**, 4367.

of the crystal structure of (II). A preliminary report has appeared.⁶



EXPERIMENTAL

Crystals of (II) are intensely coloured dark red prisms which appear opaque and black where they are developed to any thickness. The sample (*ca.* 0.3 × 0.3 × 0.4 mm) used for data collection was mounted along the *c* axis. Unit-cell dimensions were determined by a least-squares fit to the angular settings for 10 reflections carefully centred on a four-angle diffractometer.

Crystal Data.—C₁₂H₁₁NS₄, *M* = 297.4. Monoclinic, *a* = 14.103(3), *b* = 8.313(4), *c* = 11.353(7) Å, and β = 102° 10'(2'), *U* = 1 301.7 × 10⁻²⁴ cm³, *D_m* = 1.52 g cm⁻³, *Z* = 4, *D_c* = 1.52 g cm⁻³, *F*(000) = 616. Space group *P*2₁/*c* from systematic absences: *h*0*l* when *l* = 2*n* + 1, 0*h*0, when *h* = 2*n* + 1 Cu-*K*_α radiation, λ = 1.54178 Å; μ(Cu-*K*_α) = 62.2 cm⁻¹.

Intensity data were collected on a computer-controlled four-circle Picker FACS I diffractometer. Reflections in the 2θ sphere from 0–130° were scanned at a rate of 1° min⁻¹ in 2θ, with basewidth 2° for each scan. A 10 s stationary background count was made at each limit of the scan. Attenuators were inserted whenever the counting rate was >1 × 10⁴ counts s⁻¹. A dispersion factor was applied to account for α₁–α₂ splitting. There was no evidence for crystal decomposition during data collection. Of 2 529 intensities measured, 1 696 were considered above background at the 2σ level based on counting statistics.

The solution of the structure was first attempted with the symbolic-addition procedure using the FAME–SYMPL–MAGIC⁸ series of programs. A set of eight starting reflections all with *E* > 2.4 provided the signs for 498 out of 500 reflections with normalized structure amplitudes, *E* > 1.07. The *E* maps calculated from the three sign combinations with the smallest number of contradictions in sign determination all showed three collinear peaks at *y* = 0 which could be attributed to the three adjacent sulphur atoms in the thiathiothiophene nucleus. These special positions for the sulphur atoms each generated a pseudo-two-fold symmetry in the unit cell. The *x* and *z* coordinates of the three sulphur atoms were then determined from a Patterson map. The positions of the three sulphur atoms thus found were adjusted by two cycles of least-squares refinement and then used to phase the reflections for a Fourier map. The fourth sulphur atom was found from this map. The pseudosymmetry was destroyed on a

second Fourier calculation based on the four sulphur atoms, and the positions of all the other non-hydrogen atoms were revealed. The atomic co-ordinates and isotropic thermal parameters were refined by full-matrix least-squares methods⁹ which minimized the function Σ*w*||*F*_o|| – ||*F*_c||². Refinements, including anisotropic thermal parameters for the non-hydrogen atoms and with unit weights for all reflections, gave *R* 0.098. A difference electron-density map calculated at this stage provided positions for all the hydrogen atoms. The parameters of the hydrogen atoms were held constant in all subsequent refinements. Examination of the intensity data at this point revealed six low-order reflections whose calculated values suggested that they suffered from extinction or absorption errors. Least-squares refinement with the data having these six reflections removed, gave the final positional and thermal parameters

TABLE I

Final co-ordinates of (II) in fractions of cell edges, with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	0.3289(2)	–0.0128(3)	0.6647(2)
S(6)	0.6653(2)	–0.0007(3)	0.7647(2)
S(6a)	0.5011(2)	–0.0092(2)	0.7165(2)
S(7)	0.2150(2)	0.2112(3)	0.4806(3)
C(2)	0.3243(6)	0.1381(9)	0.5607(7)
C(3)	0.4108(6)	0.2029(9)	0.5458(7)
C(3a)	0.4995(6)	0.1475(8)	0.6121(7)
C(4)	0.5899(6)	0.2085(9)	0.6010(7)
C(5)	0.6753(6)	0.1536(9)	0.6662(7)
C(8)	0.1250(8)	0.0874(15)	0.5267(13)
N(9)	0.4081(5)	0.3354(8)	0.4656(6)
C(10)	0.7722(6)	0.2134(10)	0.6620(8)
C(11)	0.8530(8)	0.1609(15)	0.7407(12)
C(12)	0.9445(9)	0.2148(17)	0.7396(14)
C(13)	0.9565(9)	0.3293(13)	0.6537(14)
C(14)	0.8767(8)	0.3864(13)	0.5777(11)
C(15)	0.7859(7)	0.3300(12)	0.5793(9)
H(4)	0.592	0.306	0.535
H(8A)	0.051	0.127	0.487
H(8B)	0.137	–0.047	0.521
H(8C)	0.133	0.098	0.637
H(9A)	0.360	0.333	0.392
H(9B)	0.480	0.367	0.447
H(11)	0.843	0.071	0.815
H(12)	1.008	0.168	0.808
H(13)	1.032	0.374	0.645
H(14)	0.886	0.478	0.508
H(15)	0.722	0.384	0.517

The hydrogen atom co-ordinates were not varied in the least squares refinement. They were numbered according to the non-hydrogen atoms to which they are attached.

for the non-hydrogen atoms listed in Tables 1 and 2. The final *R* on all 1 696 non-zero reflections was 0.090, and on all data, including unobserved reflections, 0.106. The weighted factor *R*_w, [Σ*w*||*F*_o|| – ||*F*_c||²/Σ*w*||*F*_o||²]^{1/2} on 1 696 reflections was 0.104. Calculated values for unobserved reflections revealed no anomalous values. An unusual feature of the difference map used to locate the hydrogen atoms was the presence of two large peaks (*ca.* 1 eÅ⁻³) situated between each pair of sulphur atoms in the S–S–S group. There were also two smaller peaks (*ca.* 0.3 eÅ⁻³) lying 1 Å from the two terminal sulphur atoms on the extension of the S–S–S line. We consider that these peaks

⁸ E. B. Fleischer, A. L. Stone, and R. B. K. Dewar, FAME–MAGIC–LINK–SYMPL, University of Chicago, 1968.

⁹ W. R. Busing, K. O. Martin, and H. A. Levy, 1962, ORFLS, Report ORNL TM 305, Oak Ridge National Laboratory, Tennessee.

are more likely to arise from systematic errors in the data or some uncorrected thermal motion rather than to be due to specific bonding effects.

The scattering-factor curves for the non-hydrogen atoms were taken from ref. 10, those for hydrogen atoms from

TABLE 2

Final anisotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	100(2)	142(4)	105(2)	-19(2)	40(2)	9(2)
S(6)	101(2)	142(4)	89(2)	16(2)	14(2)	37(2)
S(6a)	103(2)	103(3)	73(2)	6(2)	31(1)	16(2)
S(7)	72(2)	175(4)	155(3)	-2(2)	20(2)	1(3)
C(2)	70(5)	123(12)	101(8)	-9(7)	30(5)	-25(8)
C(3)	85(6)	101(11)	72(7)	-4(7)	25(5)	-10(8)
C(3a)	71(5)	93(11)	75(7)	4(6)	18(5)	-3(7)
C(4)	76(6)	94(11)	81(7)	5(7)	14(5)	6(8)
C(5)	76(6)	107(12)	79(7)	11(7)	9(5)	-8(8)
C(8)	82(8)	267(24)	287(21)	21(12)	72(10)	51(19)
N(9)	79(5)	138(11)	84(6)	-2(6)	7(4)	31(7)
C(10)	78(6)	117(13)	103(9)	16(7)	16(6)	-10(9)
C(11)	78(8)	287(25)	208(17)	-6(11)	-32(9)	97(17)
C(12)	82(8)	298(28)	271(22)	10(13)	-28(11)	84(21)
C(13)	89(9)	168(19)	262(20)	-14(11)	14(11)	-47(16)
C(14)	69(7)	218(20)	190(14)	4(10)	25(8)	38(14)
C(15)	81(7)	192(18)	135(11)	16(9)	27(7)	35(12)

The anisotropic thermal parameters are expressed as: $\exp - [\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. $B(0) = 3.0 \text{ \AA}^2$ for all hydrogen atoms where the isotropic thermal parameter is expressed as $\exp - [B_0 \sin^2 \theta / \lambda^2]$. This was not varied during refinement.

ref. 11. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21406 (3 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Table 3 lists the bond lengths and bond angles. Figure 1 is a view of the molecule showing the dimensions together with the numbering used for this study.

The general features of the structure of the thiathiophthen nucleus of (II) agree with the results of

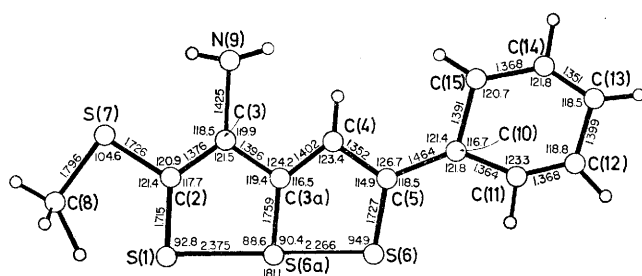


FIGURE 1 The molecule of (II), showing the atom numbering system used in the analysis

previous X-ray studies on thiathiophthens. The central sulphur atom has a nearly linear configuration with S(1)-S(6a)-S(6) $178.9(1)^\circ$, and the central C-S bond length [$1.759(8) \text{ \AA}$] significantly longer than the two

external C-S bond distances [$1.727(8)$ and $1.715(8) \text{ \AA}$]. The C-C bond lengths (Table 3) suggest an aromatic structure, in that their values lie between those for a double (1.334 \AA) and a single (1.544 \AA) C-C bond.¹² The length of the C(2)-S(7) bond [$1.726(9) \text{ \AA}$], linking the methylthio-group to the thiathiophthen system, is nearly equal to those of the two external C-S distances in the ring system but is significantly shorter than the

TABLE 3

Bond lengths (\AA) and angles (deg.) for (II), with estimated standard deviations in parentheses

(a) Distances			
S(1)-S(6a)	2.375(4)	S(7)-C(2)	1.726(9)
S(6)-S(6a)	2.266(4)	S(7)-C(8)	1.796(12)
S(1)-C(2)	1.715(8)	C(10)-C(5)	1.464(12)
S(6)-C(5)	1.727(8)	C(10)-C(11)	1.364(15)
S(6a)-C(3a)	1.759(8)	C(11)-C(12)	1.368(17)
C(2)-C(3)	1.376(12)	C(12)-C(13)	1.399(20)
C(3)-C(3a)	1.396(12)	C(13)-C(14)	1.351(17)
C(3)-N(9)	1.425(10)	C(14)-C(15)	1.368(15)
C(3a)-C(4)	1.402(12)	C(15)-C(10)	1.391(13)
C(4)-C(5)	1.352(12)		

C-H bond lengths are in the range 1.10 – 1.24 \AA . The two N-H bonds are 0.96 and 1.11 \AA .

(b) Bond angles			
S(6a)-S(1)-C(2)	92.8(3)	C(3)-C(3a)-C(4)	124.2(6)
S(6a)-S(6)-C(5)	94.9(3)	C(3a)-C(4)-C(5)	123.4(8)
S(1)-S(6a)-S(6)	178.9(1)	C(4)-C(5)-C(10)	126.7(6)
S(1)-S(6a)-C(3a)	88.6(3)	C(4)-C(5)-S(6)	114.9(6)
S(6)-S(6a)-C(3a)	90.4(3)	S(6)-C(5)-C(10)	118.5(4)
C(2)-S(7)-C(8)	104.6(5)	C(5)-C(10)-C(11)	121.8(9)
S(1)-C(2)-C(3)	117.7(6)	C(5)-C(10)-C(15)	121.4(8)
S(1)-C(2)-S(7)	121.4(5)	C(11)-C(10)-C(15)	116.7(10)
C(3)-C(2)-S(7)	120.9(5)	C(10)-C(11)-C(12)	123.3(12)
C(2)-C(3)-C(3a)	121.5(7)	C(11)-C(12)-C(13)	118.8(8)
C(2)-C(3)-N(9)	118.5(5)	C(12)-C(13)-C(14)	118.5(9)
C(3a)-C(3)-N(9)	119.9(4)	C(13)-C(14)-C(15)	121.8(11)
S(6a)-C(3a)-C(3)	119.4(3)	C(14)-C(15)-C(10)	120.8(8)
S(6a)-C(3a)-C(4)	116.5(6)		

The three S-C-H angles range from 109 – 115° ; the two C-N-H angles 114 and 117° ; C-C-H angles are in the range 118 – 120° . The three H-C-H angles are 98 , 114 , and 106° , and H-N-H is 110° .

C(8)-S(7) bond involving the methyl group [$1.796(12) \text{ \AA}$]. The latter value approaches that given by Pauling for a single C-S bond (1.812 \AA).¹² The C(3)-N(9) bond distance [$1.425(10) \text{ \AA}$] is intermediate between that of a pure C=N double bond (1.287 \AA) and a pure C-N single bond (1.472 \AA).¹² The C-C bond lengths in the phenyl group (Table 3) are also within the range normally found for aromatic C-C bonds.

The two S-S bond lengths are significantly unequal [$2.266(4)$ and $2.375(4) \text{ \AA}$] the longer being in the ring having the amino-substituent. In the crystal of 3-benzoyl-5-*p*-bromophenyl-2-methylthio-6a-thiathiophthen (III) where there were two crystallographically independent molecules, the S-S bonds were also unequal, with the 'short' lengths being $2.168(8)$ and

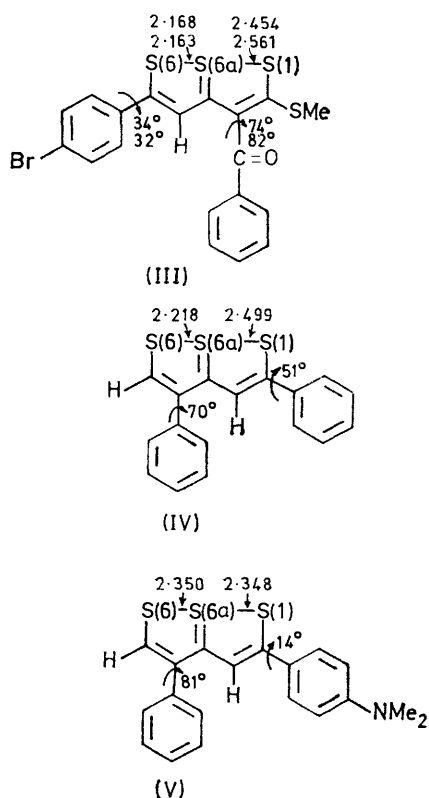
¹⁰ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

¹¹ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

¹² L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960, pp. 221–228.

* For details see Notice to Authors No. 7 in *J.C.S. Perkin, II* 1975, Index issue.

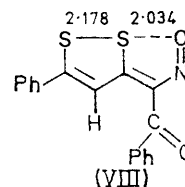
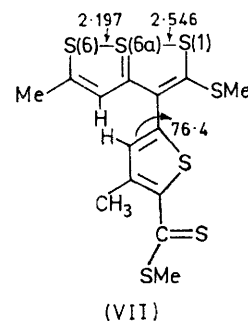
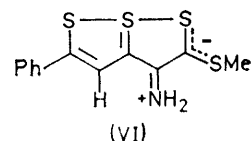
2.163(8) Å, while the 'long' lengths, on the side of methylthio-group, were 2.454(8) and 2.561(8) Å.¹³ The shortening of the S-S bond in a ring with a 2-*p*-dimethyl-anilino-substituent was noted¹⁴ between the structures



of (IV) and (V) where the substitution of the *p*-dimethyl-anilino-group for the 2-phenyl group has made the two S-S bonds nearly equal; the short S-S bond length of 2.218(3) Å in (IV) increased to 2.350(1) Å in (V), while the long bond length of 2.499(3) Å decreased to 2.348(1) Å.^{14,15} The molecular dimensions of the *p*-dimethyl-anilino-ring in (V) support a polar form with extensive conjugation between the 2-*p*-dimethyl-anilino substituent and the thiathiophthen system.¹⁴

Apparently the electron-donating conjugative effect of the amino-substituent in (II) has caused a shortening of the long S-S bond relative to that in (III). As the 3-benzoyl-group was rotated out of the plane of the thiathiophthen ring by 74 and 82° in the two crystallographically independent molecules of (III) in the crystal,¹³ there should be no conjugative effect due to the 3-substituent in (III). Insofar as the hydrogen atoms have been located in the analysis of (II), the positions of the two amino-hydrogen atoms suggest that the amino-group has an orientation which would allow conjugation with the thiathiophthen nucleus. The

lengths of the C(2)-S(7) and C(3)-N(9) bonds suggest that a structure of the type (VI) may be important in describing the molecular structure of (II). This type of conjugation may be responsible for the unusual u.v. spectra (λ 560 nm) of the 3-amino-6a-thiathiophthens⁶ compared to these for other 6a-thiathiophthens (λ 500 nm). The increase in the wavelength for the 3-amino-derivatives may be due to the ability of the amino-group to conjugate with the thiathiophthen nucleus. The differences in the absorption maxima between (II), 560 nm, and 3-amino-2,5-diphenyl-6-thiathiophthen (550 nm)⁶ may also be due to the additional participation of the 2-methylthio-group in conjugation in the molecule of (II). In (II), the 5-phenyl-group is twisted out of the plane of the thiathiophthen nucleus by only 5.7°. In (III), the *p*-bromophenyl-group was twisted out of the plane of the thiathiophthen ring by 34 and 32° in the two independent molecules. The substituent constants (σ) for the amino- and methylthio-groups (see *e.g.* ref. 16) suggest that these groups should have opposite effects on the electron density in the thiathiophthen ring, the amino-having an overall electron-releasing effect, while the methylthio-group is electron-withdrawing. The competing effect of these two groups and, in particular, the



strong influence of the methylthio-group is presumably responsible for the S(1)-S(6a) being longer than the S(6)-S(6a) bond.

¹³ S. M. Johnson, M. G. Newton, and I. C. Paul, *J. Chem. Soc. (B)*, 1969, 986.

¹⁴ A. Hordvik and L. J. Saethre, *Acta Chem. Scand.*, 1970, **24**, 2261; 1972, **26**, 3114.

¹⁵ A. Hordvik, E. Sletten, and J. Sletten, *Acta Chem. Scand.*, 1966, **20**, 2001; 1969, **23**, 1852.

¹⁶ J. D. Roberts and M. C. Caserio, 'Basic Principles of Organic Chemistry,' Benjamin, New York, 1965, pp. 954-62.

Some further evidence for the effect of a 2-methylthio-group on the S-S bond lengths is provided by the results for the molecule (VII), where the S-S distances are 2.197(6) and 2.546(6) Å, with the long bond on the side of the methylthio-group.¹⁷ In (VII), the plane of the 3-thiophen substituent is twisted by 76.4° from that of the thiathiophthen nucleus, so conjugation with this group is not possible. Chemical studies¹⁸ on the competing influences of various groups for interaction with sulphur along the axis of an S-S bond also indicate that there is a weak S...S interaction when there is an exocyclic methylthio-group. The CS·SMe group can be replaced by a nitroso-group, which appears to be the only neutral oxygen-containing group which can form an S...O interaction comparable in strength to an S...S interaction.^{18,19} For example, X-ray studies on

increase in bonding between S(1) and S(6a). Similar trends among the S(7)-C(2), C(2)-S(1), and S(1)-S(6a) bonds can be discerned in the two independent molecules of (III) although the large values for the standard deviations rule out a very definite statement.

While the prediction of S-S lengths from substituent patterns would still qualify as a rather dangerous occupation, certain trends do seem to be emerging. At least, when the substituents are neither strongly electron-releasing nor -withdrawing (e.g. methyl and phenyl), similar 2,5-disubstitution leads to equal or nearly equal S-S lengths,^{1,2,21,22} whereas similar 3,4-disubstitution leads to substantial differences in these lengths.^{23,24} So far there are no examples of dissimilar 2,5- or 3,4-disubstitution. 2-Mono-substitution and 2,4-disubstitution by phenyl or methyl groups lead to significantly

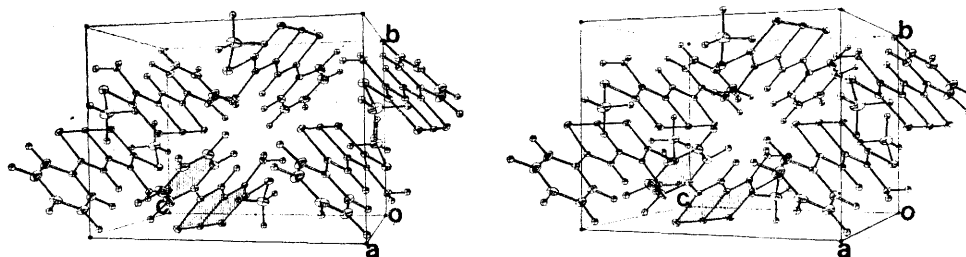


FIGURE 2 Stereoview of the contents of a unit cell looking down the *a* axis

the molecule of (VIII) revealed S-S and S...O distances of 2.178(2) and 2.034(5) Å.¹⁹ While S...S and S...O lengths are not directly comparable, the marked increase in the S-S bond in (VIII) over the normal single-bond value²⁰ implies a strong contact. Applying simply the difference in the covalent single-bond radii given by Pauling¹² for sulphur and oxygen would suggest that the S...O length in (VIII) is comparable to an S...S length of 2.41 Å. If one assumes a direct bond length-bond strength relationship, it would be reasonable for the nitroso group to replace the -CS·SCH₃ group. There is, therefore, both chemical and structural evidence that the presence of a 2-methylthio group causes a relatively weak S(1)...S(6a) interaction.

Another point of contrast between the molecules of (II) and (VII) is in the length of the exocyclic C-S(Me) bond, which in (II) is 1.726(9), and in (VII) 1.773(16) Å; the C(2)-S(1) lengths in the two molecules are 1.715(8) and 1.675(15) Å. It is tempting to speculate that the apparently greater exocyclic double-bond character in the C(2)-S(7) bond in (II), as compared to (VII), is reflected in some relative decrease in double-bond character in the S(1)-C(2) bond and a consequent

unequal lengths with the 'long' S-S bond being in the ring with the 2-substituent,^{15,25,26} although we have seen an example where replacing the phenyl group by an electron-releasing group gives rise to almost equal S-S lengths.^{14,15}

The situation becomes more complex in trisubstituted thiathiophthens. The present results show significant differences in lengths in a trisubstituted derivative when a 3-amino-group in (II), replaces a 3-benzoyl group in (III), while in three different trisubstituted derivatives, (II), (III), and (VII), there is a long S(1)-S(6a) bond when there is a methylthio-group in the 2-position.^{13,17} Clearly, both the position and electronic nature of the substituents affect the S-S lengths and some further examples will be necessary, before the entire picture is clarified. Recent CNDO/2 calculations²⁷ indicate that a 2-methyl or 2-phenyl derivative, if significantly twisted out of the plane of the thiathiophthen nucleus, has a lengthening effect on the S(1)-S(6a) bond, whereas a 3-methyl group has a shortening effect on this bond and a 3-phenyl group has only a very slight shortening effect. Application of this result to the 3-amino- and

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¹⁸ R. J. S. Beer and R. J. Gait, *Chem. Comm.*, 1970, 328.

¹⁹ P. L. Johnson and I. C. Paul, *J. Amer. Chem. Soc.*, 1969, **91**, 781; P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc. (B)*, 1971, 946.

²⁰ A. Hordvik, *Acta Chem. Scand.*, 1966, **20**, 1885.

²¹ A. Hordvik, *Acta Chem. Scand.*, 1968, **22**, 2397; 1971, **25**, 1583.

²² A. Hordvik and L. Milje, *J.C.S. Chem. Comm.*, 1972, 182; *Acta Chem. Scand.*, 1973, **27**, 510.

²³ P. L. Johnson and I. C. Paul, *Chem. Comm.*, 1969, 1014; P. L. Johnson, E. C. Llaguno, and I. C. Paul, following paper.

²⁴ E. C. Llaguno and I. C. Paul, unpublished data.

²⁵ S. Bezzi, *Gazzetta*, 1962, **92**, 859.

²⁶ A. Hordvik and K. Julshamn, *Acta Chem. Scand.*, 1969, **23**, 3611; 1971, **25**, 1835.

²⁷ L. K. Hansen, A. Hordvik, and L. J. Saethre, *J.C.S. Chem. Comm.*, 1972, 222.

3-benzoyl-derivatives (II) and (III) would suggest that the S(6a)–S(6) bond in (III) should be subject to some lengthening effect due to the 32–34° twist of the *p*-bromophenyl groups. While such an effect may operate in (III), it is clearly overwhelmed by other influences.

Calculation of a best plane through the eight atoms comprising the thiathiophthen nucleus, the nitrogen atom, and the two non-hydrogen atoms of the methylthio-group indicates deviations in the range –0.036 to 0.026 Å. However, the best plane through all the non-hydrogen atoms of the molecule shows deviations of –0.195 to 0.087 Å (Table 4); the phenyl group is twisted from the thiathiophthen system by 5.7°.

TABLE 4

Details of best planes, with deviations (Å) of relevant atoms from the planes, in square brackets

Plane (A)

S(1), S(6), S(6a), S(7), C(2)–(5), C(3a)

[S(1) –0.002, S(6) –0.005, S(6a) 0.006, S(7) –0.005, C(2) 0.022, C(3) 0.019, C(3a) 0.008, C(4) 0.006, C(5) –0.008, C(8) 0.053, N(9) –0.050, C(10) –0.044, C(11) –0.197, C(15) 0.041]

Plane (B)

C(10)–(15)

[S(6) 0.118, C(4) –0.124, C(5) –0.005, C(10) 0.006, C(11) –0.010, C(12) –0.006, C(13) 0.018, C(14) –0.011, C(15) –0.001]

Plane (C)

S(1), S(6), S(6a), S(7), C(2)–(5), C(3a), C(8), C(10), N(9)

[S(1) –0.008, S(6) –0.002, S(6a) 0.004, S(7) –0.001, C(2) 0.025, C(3) 0.029, C(3a) 0.017, C(4) 0.021, C(5) 0.006, C(8) 0.048, N(9) –0.032, C(10) –0.024, C(11) –0.179, C(12) –0.218, C(13) –0.091, C(14) 0.018, C(15) 0.069]

Plane (D)

S(1), S(6), S(6a), S(7), C(2)–(5), C(3a), C(8), N(9), C(10)–(15)

[S(1) –0.013, S(6) 0.007, S(6a) 0.006, S(7) –0.005, C(2) 0.023, C(3) 0.032, C(3a) 0.022, C(4) 0.030, C(5) 0.018, C(8) 0.038, N(9) –0.027, C(10) –0.008, C(11) –0.161, C(12) –0.195, C(13) –0.066, C(14) 0.042, C(15) 0.087]

	A	B	C	D
χ^2 *	33.5	4.09	99.1	572.1
P †	<0.01	~0.10	<0.01	<0.01

* Atoms weighted as $1/\sigma^2$ where σ is from the least-square results. † The probability that the deviations from the best planes describe a normal distribution.

Figure 2 is a stereoview of the molecular packing of (II) as viewed down the *a* axis. The molecules are elongated along the *a* axis with the plane of each molecule inclined significantly from the *b* and *c* axes. While molecules related by centres of symmetry are required to be parallel, the molecules related by screw axes and by glide planes are almost mutually perpendicular. The result of this packing is the development of apparent narrow channels in the direction of the *a* axis of the cell. While the use of the term 'channel' provides a convenient description for the packing, there is no implication that the crystals have

the potential to trap molecules in these channels. An example of such a channel can be seen through the centre of the cell in Figure 2.

Table 5 lists all intermolecular contacts between non-

TABLE 5

Intermolecular contacts <4.0 Å

C(8) ... C(13 ^I)	3.64	S(7) ... C(10 ^{IV})	3.90
C(14) ... C(11 ^{II})	3.79	S(7) ... C(11 ^{IV})	3.97
S(6) ... C(15 ^{III})	3.89	C(5) ... C(3 ^{IV})	3.85
S(6a) ... N(9 ^{III})	3.66	C(5) ... C(2 ^{IV})	3.54
S(1) ... N(9 ^{III})	3.67	C(4) ... C(3a ^{IV})	3.86
S(6) ... S(7 ^{IV})	3.96	C(4) ... C(3 ^{IV})	3.80
S(6) ... C(3 ^{IV})	3.85	C(4) ... C(2 ^{IV})	3.75
S(6) ... C(2 ^{IV})	3.90	C(3a) ... C(3 ^{IV})	3.78
S(6) ... N(9 ^{IV})	3.81	C(2) ... C(10 ^{IV})	3.92
S(6a) ... C(4 ^{IV})	3.93	C(8) ... C(10 ^{IV})	3.78
S(6a) ... C(3a ^{IV})	3.90	C(8) ... C(15 ^{IV})	3.96
S(6a) ... C(3 ^{IV})	3.82	C(8) ... C(12 ^{IV})	3.89
S(6a) ... N(9 ^{IV})	3.79	C(8) ... C(11 ^{IV})	3.74
S(1) ... C(5 ^{IV})	3.92	S(7) ... C(15 ^{IV})	3.87
S(1) ... C(4 ^{IV})	3.81	S(7) ... C(14 ^{IV})	3.60
S(1) ... C(15 ^{IV})	3.92	N(9) ... C(15 ^{IV})	3.86
S(7) ... C(5 ^{IV})	3.93	C(14) ... C(12 ^{IV})	3.99

Roman numeral superscripts refer to atoms at the following equivalent positions relative to the reference molecule at *x, y, z*:

I	$-1 + x, y, z$	IV	$1 - x, -y, 1 - z$
II	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	V	$1 - x, 1 - y, 1 - z$
III	$x, \frac{1}{2} - y, \frac{1}{2} + z$	VI	$2 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$

hydrogen atoms <4.0 Å. There are no distances shorter than the sums of the appropriate van der Waals radii.²⁸ The environment of the S(1)–S(6a)–S(6) group consists mainly of nitrogen atoms and the carbon atoms of the thiathiophthen ring in neighbouring molecules. There is an absence of close S ... S intermolecular interactions such as those found in crystals of (III) where a contact of 3.63 Å exists between sulphur atoms belonging to molecules unrelated by symmetry.¹³ Furthermore, there appears to be no evidence for the type of interaction found in the crystals of 2,5-diphenylthiathiophthen, where there is a close contact of 3.25 Å between the terminal sulphur atom of one molecule and the plane of the thiathiophthen system of a symmetry-related molecule.²¹ Since this distance was comparable to the close contact of 3.28 Å between a chlorine atom and a benzene ring in the 1 : 1 charge-transfer complex of benzene and chlorine,²⁹ it has been suggested¹⁴ that a charge transfer could be taking place from the π -system of the thiathiophthen nucleus in one molecule towards the sulphur atom of the symmetry-related molecule. This would alter the electronegativity of the sulphur atom involved in the close contact and could have an effect upon the lengths of the two S–S bonds in the molecule.

The structural results on (II) provide no obvious explanation for the anomalously long wavelength absorption at 560 nm which is apparently typical of 3-amino-6a-thiathiophthens.⁶ The general structural features of the molecule do not seem unusual when

²⁸ Ref. 12, pp. 257–264.

²⁹ O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, 1959, **13**, 1781.

compared with those of other thiathiophthens. The present results do, however, indicate that conjugation of the 3-amino-group with the thiathiophthen nucleus is a possible factor which has not previously been demonstrated.

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