

Deformation Density Study of 2,4-Diphenyl-6a-thiathiophthene

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Abstract

The title compound, 2,4-diphenyl[1,2]dithiolo[1,5-*b*]-[1,2]dithiole-7-*S*^{IV}, C₁₇H₁₂S₃, was studied by X-ray diffraction both at 100 and 300 K. It crystallized in space group $P\bar{1}$, $Z = 2$, $M_r = 312.46$, with lattice parameters $a = 10.192$ (2), $b = 8.466$ (1), $c = 9.720$ (1) Å, $\alpha = 111.91$ (1), $\beta = 74.63$ (1), $\gamma = 101.56$ (1)°, $V = 731$ (2) Å³, at 100 K. The crystal structures are essentially the same at both temperatures. They were studied with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å, $\mu = 4.61$ cm⁻¹) and yielded R indices of 0.034 and 0.037 for 6815 and 2026 reflections at 100 and 300 K respectively. The two fused five-membered rings are planar, with the S–S–S part linear [178.71 (4)°]. The two S–S bond lengths are significantly different [2.2125 (4) and 2.5087 (4) Å]. The X - X deformation density distribution reveals a large positive accumulation at the midpoint of the C–C bond, a somewhat weaker accumulation on the S–C bond, but little accumulation between the S atoms. There is positive residual density around the S atoms both in the plane and perpendicular to the plane.

Introduction

Symmetrical (2,5- or 3,4-) and unsymmetrical (2,4-) dialkyl thiathiophthenes have quite different arrangements of S–S distances (Hordvick, 1971*a,b,c*; Johnson, Llaguno & Paul, 1976; Llaguno & Paul, 1976); most of the symmetrical compounds have two relatively similar S–S distances, whereas the unsymmetrical compounds have significantly different lengths. Earlier theoretical calculations (Gleiter & Hoffman, 1968) predicted the non-equal distance pattern when the 3*d* orbitals of the S atoms were not utilized and the nearly equal distance pattern when 3*d* orbitals were included. The title compound was chosen because there is a large difference between its two S–S lengths. Whether or not such differences arise from a different bonding pattern is the main interest of this study. Thus an X - X deformation density study was performed at 100 K. The merit of this compound for such study is that it contains not only S–S and S–C bonds but also C–C and C–H bonds, and hence can provide a

Table 1. Crystal data of C₁₇H₁₂S₃ at 100 and 300 K

	100 K	300 K
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.111 (1)	10.192 (2)
b (Å)	8.397 (1)	8.466 (1)
c (Å)	9.5779 (6)	9.720 (1)
α (°)	111.179 (6)	111.91 (1)
β (°)	75.679 (6)	74.63 (1)
γ (°)	100.429 (8)	101.56 (1)
θ range (°) for cell parameter determination	12–37	10–17.5
V (Å ³)	731 (2)	746 (2)
D_x (g cm ⁻³)	1.42	1.39
Z	2	2
Crystal size (mm)	0.2 × 0.26 × 0.5	0.2 × 0.3 × 0.5
μ (cm ⁻¹)	4.61	4.61
Radiation	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.7107	0.7107
Transmission range	0.88–0.92	—
θ_{max} (°)	43	30
hkl range	h –18–19 k –15–14 l 0–18	h –14–14 k 0–11 l –12–13
No. of measurements	23 132	4614
No. of unique reflections	7974	4341
R_{int}	0.016	—
No. of observed reflections	6815 (>4 σ), 2651*	2026 (>2 σ)
No. of parameters	229, 181*	230
R	0.034, 0.032*	0.037
wR	0.039, 0.031*	0.023

* High-order refinement [($\sin \theta/\lambda$) > 0.75 Å⁻¹].

quantitative comparison of the well-characterized bonding densities of the C–C and C–H bonds (Wang, Tsai, Liu & Calvert, 1985; Coppens, Dam, Harkema, Feil, Feld, Lehmann, Goddard, Krüger, Hellner, Johansen, Larsen, Koetzle, McMullan, Maslen & Stevens, 1984) with those of the S–S and S–C bonds.

Experimental

The title compound was synthesized according to the literature (Fields, 1955; Klingberg, 1961, 1963). A suitable deep-red crystal was obtained by slow evaporation from a toluene solution. The crystal structure at room temperature was determined previously by photographic methods (Horvdik, Sletten & Sletten, 1969). The crystal data and some details of the experimental conditions are given in Table 1. Low-temperature data were measured on a CAD-4 diffractometer equipped with a liquid N₂ gas-flow set up. A unique set of reflections were measured up to $\theta = 43^\circ$, additional equivalent reflections were collected up to 32° . Seven measurements of ψ from -45 to 45° with a step of 15° were also collected for each reflection up to $\theta = 18^\circ$; beyond 18° only one

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Table 2. Atomic fractional coordinates and equivalent isotropic thermal parameters (\AA^2)

a Full data refinement at 300 K, *b* full data refinement at 100 K, *c* high-order refinement and calculated H atoms at 100 K.

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
S1 <i>a</i>	0.3246 (1)	0.4066 (1)	0.2440 (1)	5.38 (4)
<i>b</i>	0.32934 (3)	0.40609 (3)	0.23883 (3)	1.646 (8)
<i>c</i>	0.32936 (4)	0.40604 (4)	0.23883 (4)	1.634 (7)
S2 <i>a</i>	0.1284 (1)	0.3179 (1)	0.4228 (1)	5.02 (4)
<i>b</i>	0.12971 (3)	0.31706 (3)	0.41969 (3)	1.495 (8)
<i>c</i>	0.12964 (3)	0.31706 (4)	0.41979 (4)	1.490 (7)
S3 <i>a</i>	-0.0453 (1)	0.2428 (1)	0.5870 (1)	6.13 (5)
<i>b</i>	-0.04461 (3)	0.24288 (3)	0.58344 (3)	1.881 (9)
<i>c</i>	-0.04466 (4)	0.24289 (5)	0.58351 (5)	1.852 (9)
C1 <i>a</i>	0.3772 (2)	0.5761 (3)	0.3859 (2)	3.7 (1)
<i>b</i>	0.3802 (1)	0.5758 (1)	0.3844 (1)	1.20 (3)
<i>c</i>	0.3806 (1)	0.5757 (1)	0.3842 (1)	1.23 (3)
C2 <i>a</i>	0.3025 (2)	0.5978 (3)	0.5303 (2)	3.6 (1)
<i>b</i>	0.3047 (1)	0.5989 (1)	0.5306 (1)	1.20 (3)
<i>c</i>	0.3050 (1)	0.5989 (1)	0.5309 (1)	1.25 (3)
C3 <i>a</i>	0.1874 (2)	0.4898 (3)	0.5670 (3)	3.6 (1)
<i>b</i>	0.1888 (1)	0.4894 (1)	0.5661 (1)	1.17 (3)
<i>c</i>	0.1891 (1)	0.4887 (1)	0.5660 (1)	1.24 (3)
C4 <i>a</i>	0.1129 (2)	0.5145 (3)	0.7178 (3)	3.8 (1)
<i>b</i>	0.1126 (1)	0.5147 (1)	0.7187 (1)	1.23 (3)
<i>c</i>	0.1127 (1)	0.5142 (1)	0.7188 (1)	1.28 (3)
C5 <i>a</i>	-0.0007 (3)	0.4035 (3)	0.7370 (3)	4.9 (2)
<i>b</i>	-0.0028 (1)	0.4040 (1)	0.7380 (1)	1.59 (4)
<i>c</i>	-0.0029 (1)	0.4036 (2)	0.7384 (2)	1.63 (4)
C6 <i>a</i>	0.4981 (2)	0.6969 (3)	0.3563 (3)	3.6 (1)
<i>b</i>	0.5014 (1)	0.6984 (1)	0.3563 (1)	1.20 (3)
<i>c</i>	0.5013 (1)	0.6978 (1)	0.3563 (1)	1.25 (2)
C7 <i>a</i>	0.5713 (2)	0.7921 (3)	0.4673 (3)	4.5 (2)
<i>b</i>	0.5721 (1)	0.7965 (1)	0.4732 (1)	1.51 (3)
<i>c</i>	0.5721 (1)	0.7963 (2)	0.4739 (1)	1.55 (3)
C8 <i>a</i>	0.6824 (3)	0.9078 (4)	0.4400 (3)	5.6 (2)
<i>b</i>	0.6823 (1)	0.9151 (1)	0.4483 (1)	1.81 (4)
<i>c</i>	0.6820 (1)	0.9160 (2)	0.4495 (2)	1.85 (4)
C9 <i>a</i>	0.7227 (3)	0.9281 (4)	0.3012 (3)	5.9 (2)
<i>b</i>	0.7244 (1)	0.9371 (1)	0.3068 (1)	1.93 (4)
<i>c</i>	0.7247 (1)	0.9379 (2)	0.3072 (2)	1.95 (4)
C10 <i>a</i>	0.6527 (3)	0.8335 (4)	0.1900 (3)	6.7 (2)
<i>b</i>	0.6574 (1)	0.8380 (1)	0.1891 (1)	2.09 (4)
<i>c</i>	0.6578 (2)	0.8377 (2)	0.1879 (2)	2.15 (4)
C11 <i>a</i>	0.5419 (3)	0.7166 (4)	0.2164 (3)	5.4 (2)
<i>b</i>	0.5472 (1)	0.7188 (1)	0.2134 (1)	1.68 (4)
<i>c</i>	0.5474 (2)	0.7177 (2)	0.2123 (1)	1.76 (3)
C12 <i>a</i>	0.1565 (2)	0.6544 (3)	0.8491 (2)	3.6 (1)
<i>b</i>	0.1552 (1)	0.6555 (1)	0.8524 (1)	1.21 (3)
<i>c</i>	0.1554 (1)	0.6553 (1)	0.8521 (1)	1.27 (2)
C13 <i>a</i>	0.0679 (2)	0.7696 (4)	0.9508 (3)	4.8 (2)
<i>b</i>	0.0622 (1)	0.7696 (1)	0.9551 (1)	1.58 (4)
<i>c</i>	0.0615 (1)	0.7695 (2)	0.9548 (1)	1.61 (3)
C14 <i>a</i>	0.1078 (3)	0.8990 (4)	1.0740 (3)	5.8 (2)
<i>b</i>	0.1016 (1)	0.9007 (1)	1.0803 (1)	1.90 (4)
<i>c</i>	0.1013 (2)	0.9017 (2)	1.0809 (2)	1.93 (4)
C15 <i>a</i>	0.2366 (3)	0.9168 (4)	1.0979 (3)	5.7 (2)
<i>b</i>	0.2339 (1)	0.9210 (1)	1.1044 (1)	1.84 (4)
<i>c</i>	0.2338 (2)	0.9219 (2)	1.1054 (1)	1.91 (4)
C16 <i>a</i>	0.3263 (3)	0.8041 (4)	0.9992 (3)	5.6 (2)
<i>b</i>	0.3274 (1)	0.8087 (1)	1.0036 (1)	1.82 (4)
<i>c</i>	0.3281 (2)	0.8091 (2)	1.0036 (2)	1.90 (4)
C17 <i>a</i>	0.2859 (3)	0.6731 (3)	0.8762 (3)	4.8 (2)
<i>b</i>	0.2884 (1)	0.6762 (1)	0.8791 (1)	1.55 (3)
<i>c</i>	0.2889 (1)	0.6758 (2)	0.8787 (1)	1.61 (3)

additional measurement with $\psi = 15^\circ$ was collected. The standard deviation of the intensity measurement is defined as $\sigma^2(I) = \sigma_c^2(I) + (fI_{ne})^2$, where f is 0 and 0.02 respectively for the 300 and 100 K data, and $\sigma^2(F_o)$ values are calculated accordingly. Normal least-squares refinement was first performed; the final agreement indices are given in Table 1. An additional high-order refinement was carried out on data with $(\sin\theta)/\lambda > 0.75 \text{ \AA}^{-1}$ to obtain all the non-H atom parameters for use in a promolecule model density calculation. The deformation density distributions were all calculated up

to $(\sin\theta/\lambda)_{\max} = 0.75 \text{ \AA}^{-1}$. The H atoms were relocated along the C—H vector to lengthen the C—H distance to 1.085 \AA (Wang, Angermund, Goddard & Krüger, 1987) in order to obtain better C—H bonding density.

Results

Atomic fractional coordinates at both temperatures are given in Table 2.* The *c* parameters in Table 2 were used for the promolecule density calculation to obtain the deformation density distribution. The selected bond lengths are indicated in Fig. 1. It is apparent that the bond lengths at 100 K are 0.01 to 0.02 \AA longer than those at 300 K as a result of lower thermal motion. However, the S2—S3 length at 100 K is slightly shorter and the S1—S2 length at 100 K is somewhat longer than those at 300 K estimated from thermal-motion correction. Thus, the difference between the two S—S lengths is 0.035 (1) \AA greater at 100 K than at 300 K. The dihedral angles of the two phenyl groups with respect to the thiathiophthene plane are 23.55 (3), 53.01 (3) $^\circ$ and 24.40 (8), 54.93 (8) $^\circ$ at 100 and 300 K respectively. The thermal parameters of the non-H atoms at 100 K decreased, on average, to 30% of those at 300 K.

The deformation density for the thiathiophthene plane is shown in Fig. 2. There are apparently positive density accumulations at the midpoints of the C—C, C—H and S—C bonds with peak densities of 0.55, 0.4 and 0.3 $e \text{ \AA}^{-3}$ respectively. The phenyl rings (Fig. 3) show a symmetrical benzene-ring density comparable with those obtained elsewhere (Wang, Angermund,

* Lists of the anisotropic temperature factors of non-H atoms, positional and isotropic thermal parameters of H atoms, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44517 (79 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

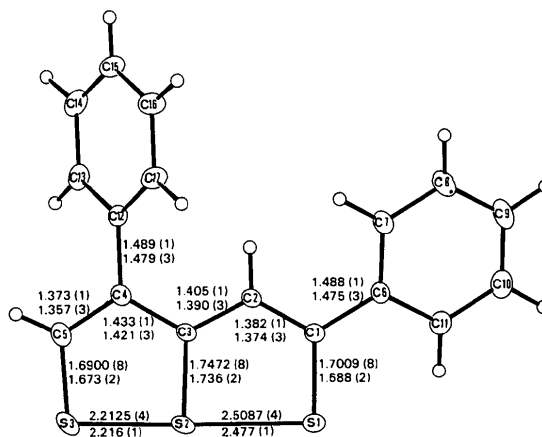


Fig. 1. Molecular structure with selected bond lengths (\AA) and atomic labelling.

Goddard & Krüger, 1987). The density along the S—S bonds is somewhat peculiar; there is obviously depletion of density near the core of the S atoms, but positive density accumulation around the S atoms both in the ring plane and in the plane nearly perpendicular to it (see Figs. 4*a-c*); this is quite similar to the lone-pair electron pattern (Wang, Blessing, Ross & Coppens, 1976). The residual distribution of the central S atom (S2) is definitely different from the other two. This atom (Fig. 4*a*) reveals a unique feature with two peaks about 0.75 Å above and below the plane, and forms a T shape with the S2—C3 bond. In contrast, the terminal S atoms have a more even distribution around the nucleus or an arrangement close to T_d for the two positive peaks and the two bonds (S—C and S—S). There are no close intermolecular contacts between S atoms in the crystal.

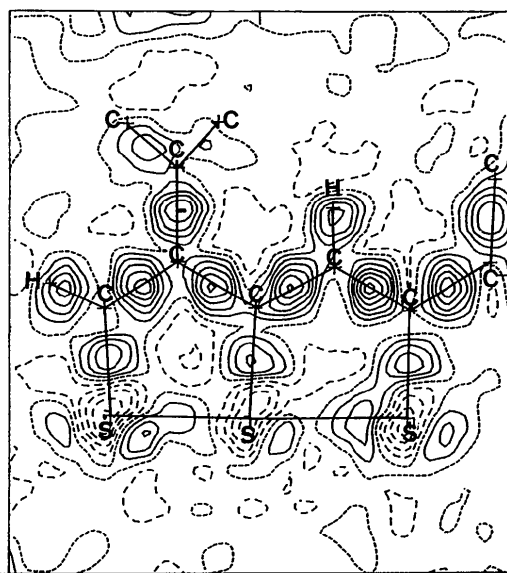


Fig. 2. $X-X$ deformation density map of the thiathiophthene ring plane; contour interval $0.1 e \text{ \AA}^{-3}$, solid lines positive and dashed lines zero and negative contours.

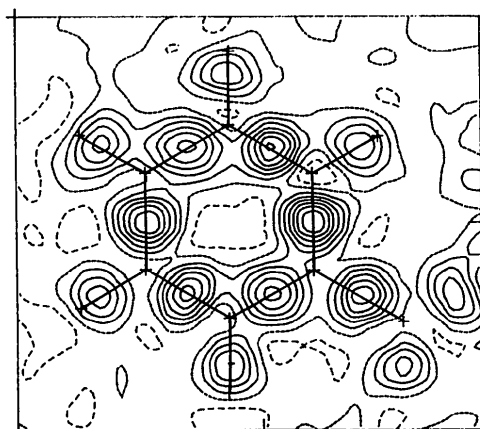
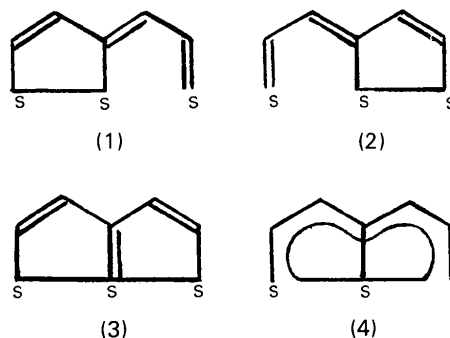


Fig. 3. $X-X$ deformation density map of phenyl ring C6 to C11, contours as in Fig. 2.

Discussion

The nature of the chemical bonding of the thiathiophthene compound (Hordvick, 1971*a,b,c*; Johnson, Llaguno & Paul, 1976; Llaguno & Paul, 1976; Potts, 1984), *i.e.* whether it is a mixture of valence isomers [(1), (2) and (3)] or a delocalized 10- π -electron system (4), has long been the subject of lively discussion.



Earlier extended-Huckel calculations (Gleiter & Hoffman, 1968) indicated the important role of the $3d$ orbitals in relation to the symmetrical or unsymmetrical S—S—S pattern. The title compound shows significant differences not only in S—S lengths, but also

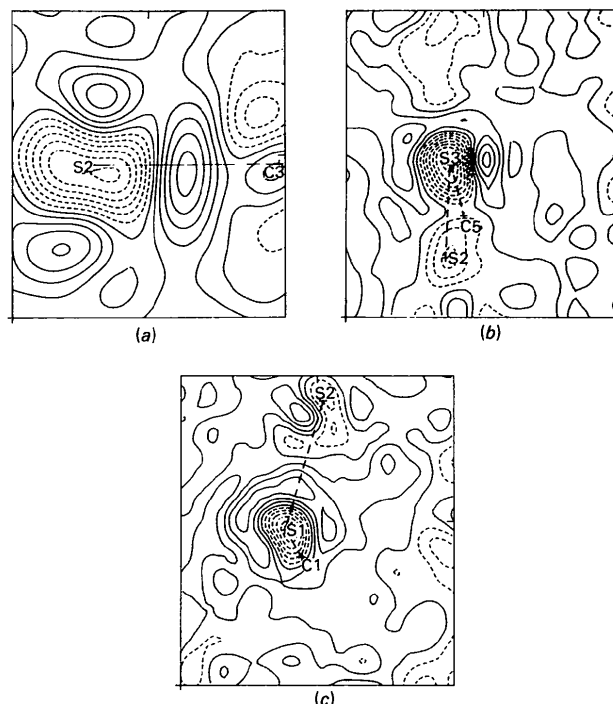


Fig. 4. $X-X$ deformation density map of (a) the plane perpendicular to Fig. 2 and passing through S2 and C3; (b) the plane passing through S3 and two maximum peak density points around it. The shifts of S2 and C5 are -1.40 and 1.37 Å from the plane. (c) same as (b) but through S1; the shifts of S2 and C1 are 0.53 and 1.59 Å from the plane, contours as in Fig. 2.

in C—S lengths; the central C—S bond distance 1.7472 (8) Å is significantly longer than the external ones [1.6900 (8), 1.7009 (8) Å] as has been observed for other thiathiophthene derivatives (Llaguno & Paul, 1976; Llaguno, Mabumi & Paul, 1976) and for cyclic C—S lengths (Wang, Lin & Wei, 1985). Both S—S lengths are longer than typical S—S single bonds, 2.01 to 2.10 Å (Wang, Lin & Wei, 1985; Coppens, Yang, Blessing, Cooper & Larsen, 1977; Chen & Wang, 1984), but significantly shorter than the sum of van der Waals radii. From the distances obtained, the title compound appears to be a mixture of resonance forms (1) and (2), with a minor contribution from form (3). Thus a 10- π -electron system with an electron-rich three-center bond (Gleiter & Hoffman, 1968) is a reasonable bonding scheme for such a compound. The shorter S—S bond correlates with the lower σ -electron density and the higher π -electron density of the terminal S atom (Hordvik & Saethre, 1972). From the deformation density distribution, it is obvious that the electron density accumulations between the bonded atoms are greatest for C—C, C—H and then for C—S; little accumulation is observed between S atoms. This observation is comparable with the order found previously (Dunitz, Schweizer & Seiler, 1983), where all the electron-rich atoms show low or even negative density between the atoms. Figs. 4(a–c) depict the density around S atoms and nearly perpendicular to the thiathiophthene plane. Apparently, around the central S atom there is electron accumulation above and below the plane giving the possibility of π interactions, as around S3 where the shorter S—S bond exists. However, around S1 there are positive but somewhat diffuse residues, which are not as well defined as those around S3 and S2. This finding is consistent with the previously mentioned correlation between π -electron density of the terminal S atoms and the distance between these atoms and the central S atom (Hordvik & Saethre, 1972). Nevertheless, the shape of the deformation density can easily be subject to systematic error; it is hard to draw any definite conclusions at this point.

The differences in deformation density distribution about C—C, C—S and S—S bonds can be rationalized with a recent MO calculation (Kunze & Hall, 1986), which showed that a valence-electron-rich atom tends to have lower deformation density. A study of S...O interactions (Becker, Cohen-Addad, Delley, Hirshfeld & Lehmann, 1986) revealed a similar feature around the S atom. The theoretical deformation density of 1,6-dioxo-6a-thiapentalene gave roughly the same picture in the plane of the two fused five-membered rings and in the perpendicular plane passing through the central S atom. The deformation density shows a negative density along the bond axis but residual density in the lone-pair region, as has been found previously in O—O bond of hydrogen peroxide (Savariault & Lehmann, 1980). From the results of this work and theoretical

studies on similar compounds, we may draw the conclusion that the electronic state of the S atoms certainly involves redistribution of spherical electron density into a hybrid state consisting of σ - and π -electron density with, in this case, the redistribution into π -electron density being more pronounced. Furthermore, the d -orbital contribution of the S atom to the σ -electron density of the linear S—S—S part (Becker *et al.*, 1986; Gleiter & Hoffman, 1968) is not negligible.

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