prediction of the conformation from *VAMP* optimizations to serve as a starting model for the structure determination would be an unacceptable approximation.

Concluding remarks

Ropivacaine and bupivacaine crystallize in the same conformation, although their crystallographic packing schemes are quite different. This conformation of the active (protonated) form of both molecules was recognized earlier (Yoo *et al.*, 1975) in related lidocaine derivatives. Molecular-mechanics calculations as implemented in *MacroModel* and *Biograf* can be used to predict these conformations relatively accurately, in contrast to the semi-empirical molecular-orbital calculations.

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Deformation-Density Studies of Thiathiophthenes. I. 2,5-Dimethyl-6a-thiathiophthene

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Abstract

The title compound, 2,5-dimethyl[1,2]dithiolo[1,5-*b*]-[1,2]dithiole-7-S^{IV}, $C_7H_8S_3$, was studied by X-ray diffraction at both 110 and 300 K. Space group *Pnma*, $Z = 4$, $M_r = 188{\cdot}32$, $a = 7{\cdot}956$ (4), $b = 19{\cdot}920$ (7), $c = 5{\cdot}361$ (2) Å, $V = 811{\cdot}4$ (6) Å^3 at 110 K. Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}80$ mm^{-1}), $R = 0{\cdot}036$ and $0{\cdot}032$ for 1527 and 449 reflections at 110 and 300 K respectively. The crystal structures are the same at both temperatures. The

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thiathiophthene is essentially planar with only half of the molecule in the asymmetric unit. The molecular symmetry is close to C_{2v}. The two S—S bond lengths are crystallographically the same [2·3510 (1) Å]. The S—S—S part is linear [177·4 (2)°]. The *X–X* deformation electron-density distribution reveals a large positive accumulation of density at the midpoint of the C—C and C—S bonds, but only a small accumulation in the S—S region. The deformation electron-density distribution, after multipole refinement, shows much clearer features in both the bonding and lone-pair electron regions. The net atomic charge obtained from the multipole refinement is discussed.

Introduction

Thiathiophthenes are planar molecules with two fused heterocyclic five-membered rings and an essentially linear S—S—S part. The symmetrically and unsymmetrically alkyl-substituted thiathiophthenes, which have equal or unequal S—S bond lengths respectively, have aroused particular interest (Johnson, Newton & Paul, 1969; Hordvik, 1971*a*,*b*,*c*; Wei, Paul, Beer & Naylor, 1975; Hordvik & Saethre, 1972; Johnson, Llaguno & Paul, 1976; Wang, Chen & Wu, 1988). In previous extended Hückel calculations (Gleiter & Hoffman, 1968) the relationship between the geometry of compounds with equal and unequal S—S bond lengths and the inclusion of the 3*d* orbitals in the basis function of the S atoms has been discussed. The title compound has exactly equal S—S bond lengths and was chosen for the deformation electron-density study in order to better understand the chemical bonding in such molecules. A similar study was carried out on 2,4-diphenylthiathiophthene (Wang, Chen & Wu, 1988) which contains two unequal S—S bond lengths. A comparison between the two studies may lead to useful information about bonding in such compounds.

Table 1. *Crystal data for* 2,5-*dimethyl*-6*a*-*thiathiophthene*

	300 K	110 K
Space group	*Pnma*	*Pnma*
a (Å)	7·817 (1)	7·596 (4)
b (Å)	20·129 (2)	19·926 (7)
c (Å)	5·370 (1)	5·361 (2)
V (Å^3)	844·4 (2)	811·4 (6)
Cell-parameter determination	25	25
θ range (°) for cell-parameter determination	2·03–12·96	9·82–14·49
Z	4	4
D_x (g cm^{-3})	1·481	1·542
Color	Orange	Orange
Crystal size (mm)	0·2 × 0·2 × 0·15	0·2 × 0·2 × 0·15
Mo $K\alpha$, λ (Å)	0·7107	0·7107
μ (cm^{-1})	7·66	7·971
Transmission coefficient	-	0·86–0·88
$\theta/2\theta$ scan range (°)	$1\cdot6 + 0\cdot7\tan\theta$	$1\cdot4 + 0\cdot7\tan\theta$
$2\theta_{\max}$ (°)	60	76
No. of reflections measured	1265	14318
No. of unique reflections	1265 [$I > 2\cdot5\sigma(I)$, 446]	2246 [$I > 1\cdot5\sigma(I)$, 1539]
Weights	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
R, wR	0·032, 0·022	0·036, 0·022
R, wR ($\sin\theta/\lambda > 0\cdot65$ Å^{-1})	-	0·047, 0·029
$R_{\rm int}$	-	0·024
h,k,l	$0 < h < 10$, $0 < k < 28$ $0 < l < 7$	$-13 < h < 13$, $-34 < k < 34$ $-9 < l < 9$

Experimental

The title compound was synthesized according to the literature method (Dingwall, Mckenzie & Reid, 1968). A suitable crystal was obtained by slow evaporation of an *n*-hexane solution containing 2% methanol. The crystal structure has been determined previously by photographic methods (Bezzi, Mammi & Garbuglio, 1958). The crystal data and some details of the experimental conditions of the present work are given in Table 1. The 110 K data were measured on a CAD-4 diffractometer equipped with a liquid N_2 gas-flow device (Ueng, 1987). The intensity data were measured up to $2\theta = 76°$ for one unique set of reflections (hkl), two equivalent sets ($hk\bar{l}$, $\bar{h}k\bar{l}$) of reflections were measured up to $2\theta = 70°$ and three equivalent sets ($h\bar{k}l$, $\bar{h}kl$, $h\bar{k}\bar{l}$) of reflections were collected up to $2\theta = 60°$. In addition, intensities for various ψ values from -20 to 20° in steps of 10° were collected for reflections up to $2\theta = 60°$. These yielded a total of 14318 measurements, which gave 2246 unique reflections after averaging equivalents. Three standard reflections were monitored every half hour throughout data collection. An absorption correction was applied according to six measured faces. The absorption correction was checked against the experimental ψ curves of three reflections. Normal least-squares refinement based on $F_{\rm obs}$ was performed, the counting statistics weights were applied, and the standard deviation of the averaged intensity was taken as a geometric mean of all the σ's of equivalents. The final agreement indices are given in Table 1, the atomic parameters in rows (*a*) of Table 2. An additional high-order refinement was carried out on data with $(\sin\theta/\lambda) > 0\cdot65$ Å^{-1} in order to obtain all the non-H atom parameters for use in a promolecule model density calculation of the *X–X* deformation-density distribution. The H atoms were relocated along the C—H vector so as to make the C—H bond length 1·08 Å (Wang, Angermund, Goddard & Kruger, 1987). Deformation-density distribution based on multipole refinement (Hansen & Coppens, 1978) was calculated with a multipole expansion of the valence shell up to hexadecapoles for the S atoms, up to octapoles for the C atoms and up to dipoles for the H atoms. Hartree–Fock functions were used for the monopoles. Scattering-factor tables of both core and valence electrons were taken from *International Tables for X-ray Crystallography* (1968, Vol. III). The coefficients of all the multipole terms together with positional and anisotropic thermal parameters were obtained by full-matrix least-squares refinement based on F. Refinement based on F^2 gave similar results but with slightly higher agreement indices. A static multipole deformation-density distribution was also calculated, in which all the thermal parameters were set to zero. All computations were carried out on a local MicroVAXIII computer using mainly *NRCVAX* programs. Refinement of the multipole model was also carried out on the MicroVAX using the program *MOLLY* (Hansen & Coppens, 1978). The deformation-density maps generated from both normal refinement and multipole refinement were produced by a locally developed contour-plotting program (Tsai, 1982).

Results

Atomic parameters at both temperatures are listed in Table 2.* The parameters given in rows (*c*) of Table 2 are those which were used in the promolecule electron-density calculations in order to obtain the experimental deformation-density distribution. Selected bond lengths are given in Fig. 1. The atomic thermal parameters at 110 K decreased, on average, to 30% of those at 300 K. The bond lengths at the two temperatures are not significantly different. The experimental deformation electron density for the thiathiophthene plane is shown in Fig. 2; positive density accumulations are found at the midpoints of the C—H, C—C and S—C bonds. The two side S—C bonds show a greater density than the central bond; the C2—C3 bond displays more density than the C2—C1 bond. These results are in good agreement with the bond lengths given in Fig. 1. The density along the S—S bonds is again very small (Wang, Chen & Wu, 1988; Wang & Liao, 1989); however, there is positive density accumulation around the S atom in the plane perpendicular to the ring shown in Figs. 2(*b*) and 2(*c*). The experimental deformation density map is rather noisy however. An additional set of deformation electron-density distributions based on the multipole expansion of atomic electron density (Hansen & Coppens, 1978) is presented in Fig. 3. The apparent deformation densities in these maps are much more pronounced than those of the experimental maps (Fig. 2), although the features are similar. A progressive addition of monopole, dipole, quadrupole and octapole terms for all the non-H atoms was carried out for the deformation electron-density distribution. For non-H atoms, expansion up to the octapole level is needed to show

Table 2. *Atomic parameters and B_{eq} values* (Å^2) (*e.s.d.'s refer to the last digit printed*)

		x	y	z	B_{eq}
S1	(*a*)	0·4927 (3)	$\frac{3}{4}$	0·2089 (3)	3·52 (8)
	(*b*)	0·47308 (6)	$\frac{3}{4}$	0·21236 (8)	1·093 (15)
	(*c*)	0·47304 (10)	$\frac{3}{4}$	0·21230 (11)	1·085 (21)
	(*d*)	0·47316 (5)	$\frac{3}{4}$	0·21240 (6)	1·045 (21)
S2	(*a*)	0·48992 (21)	0·63321 (5)	0·20066 (21)	4·19 (6)
	(*b*)	0·46984 (5)	0·632043 (14)	0·20362 (6)	1·299 (11)
	(*c*)	0·46991 (7)	0·632040 (19)	0·20354 (9)	1·282 (17)
	(*d*)	0·46997 (4)	0·632040 (10)	0·20364 (5)	1·249 (20)
C1	(*a*)	0·3655 (7)	$\frac{3}{4}$	−0·0553 (10)	2·7 (3)
	(*b*)	0·34680 (22)	$\frac{3}{4}$	−0·0583 (3)	0·90 (6)
	(*c*)	0·3473 (3)	$\frac{3}{4}$	−0·0577 (5)	0·91 (6)
	(*d*)	0·3470 (2)	$\frac{3}{4}$	−0·0576 (4)	0·88 (6)
C2	(*a*)	0·3178 (5)	0·6889 (3)	−0·1575 (7)	3·15 (19)
	(*b*)	0·29730 (16)	0·68822 (6)	−0·16512 (24)	1·04 (4)
	(*c*)	0·29721 (19)	0·68844 (11)	−0·1662 (3)	1·04 (4)
	(*d*)	0·29722 (15)	0·68836 (7)	−0·1658 (2)	1·02 (4)
C3	(*a*)	0·3654 (5)	0·63001 (23)	−0·0574 (7)	3·18 (21)
	(*b*)	0·34649 (16)	0·62860 (6)	−0·05934 (24)	1·08 (4)
	(*c*)	0·34644 (24)	0·62840 (8)	−0·0592 (3)	1·07 (4)
	(*d*)	0·34621 (17)	0·62849 (6)	−0·0599 (3)	1·07 (5)
C4	(*a*)	0·3110 (9)	0·5648 (3)	−0·1660 (13)	4·5 (3)
	(*b*)	0·29201 (20)	0·56236 (6)	−0·1674 (3)	1·48 (5)
	(*c*)	0·2916 (3)	0·56233 (9)	−0·1671 (4)	1·47 (5)
	(*d*)	0·2918 (2)	0·56246 (6)	−0·1671 (3)	1·47 (5)
H2	(*a*)	0·242 (4)	0·6887 (22)	−0·289 (6)	2·5 (8)
	(*b*)	0·2225 (18)	0·6882 (6)	−0·315 (3)	1·6 (3)
	(*c*)	0·2148	0·6882	−0·330	1·6
H4*A*	(*a*)	0·297 (9)	0·567 (4)	−0·329 (13)	13·6 (30)
	(*b*)	0·2490 (21)	0·569 (7)	−0·335 (3)	2·8 (4)
	(*c*)	0·2439	0·5697	−0·355	2·8
H4*B*	(*a*)	0·400 (5)	0·5373 (22)	−0·162 (9)	8·0 (18)
	(*b*)	0·3812 (18)	0·5319 (6)	−0·153 (3)	2·2 (3)
	(*c*)	0·3973	0·5264	−0·150	2·2
H4*C*	(*a*)	0·205 (7)	0·545 (3)	−0·071 (9)	9·2 (17)
	(*b*)	0·1900 (19)	0·5452 (7)	−0·080 (3)	2·1 (3)
	(*c*)	0·1777	0·5431	−0·070	2·1

Notes: (*a*) from full data refinement at 300 K; (*b*) from full data refinement at 110 K; (*c*) from high-angle data ($\sin\theta/\lambda > 0{\cdot}65$ Å^{-1}) refinement at 110 K; (*d*) from multipole refinement at 110 K.

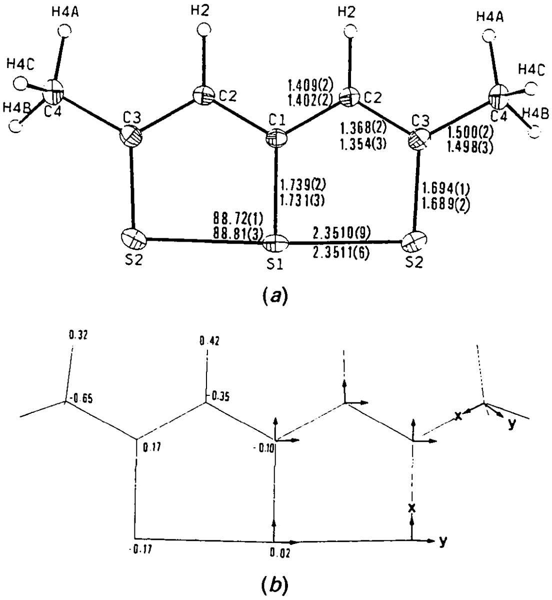

Fig. 1. (*a*) Molecular drawing with thermal ellipsoids (50% probability) at 110 K. Selected bond lengths (Å) and angles (°) at 110 K (top) and 300 K (bottom). (*b*) Choice of local Cartesian axes for the multipole refinements. The numbers near the atoms are the net charges obtained from multipole refinement. The net charge is obtained by subtracting the monopole coefficient from the number of valence electrons in the neutral atom.

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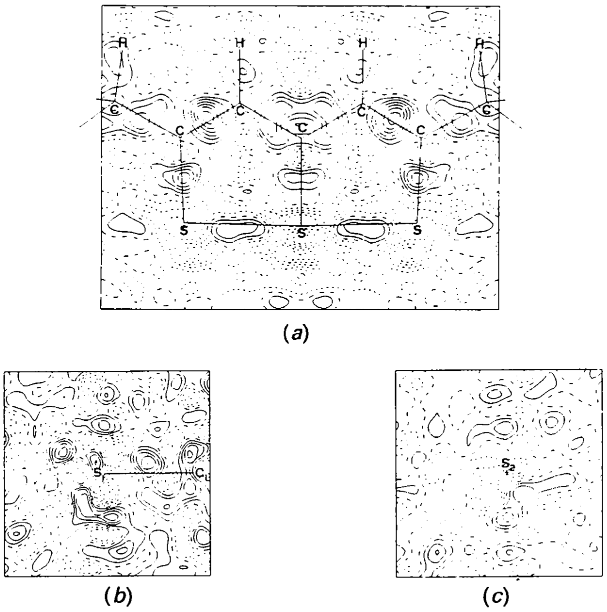
* Lists of anisotropic temperature factors of non-H atoms, multipole coefficients of all atoms and structure factors for both temperatures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53450 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

reasonable bonding features in the deformation density map. However, up to hexadecapole expansion is needed for the S atoms. The agreement indices given in Table 3 show the improvements achieved by including higher expansion terms. In both the experimental and multipole-expansion deformation-density maps, there is very little density accumulation along the S—S bonds in the thiathiophthene plane. However, there is clearly some electron density at 0·6–0·8 Å from the S nucleus in the plane perpendicular to thiathiophthene plane (Figs. 3*b*,*c*). The net atomic charge of each atom in the molecule is given in Fig. 1(*b*) together with the choice of local atomic Cartesian axes used in the multipole refinement.

Discussion

Unlike the diphenyl derivative (Wang, Chen & Wu, 1988; Wang & Liao, 1989), the bond lengths at 110 K are not significantly lengthened from those at 300 K. This indicates that the libration motion of the molecule does not affect the bond length very much if rigid-body motion is assumed. The S—S—S linear part is nearly parallel to the *b* axis, and the largest libration motion is about this direction. Bond-length corrections according to *TLS* (Schomaker & Trueblood, 1968) are not significant based on the standard deviation of bond length. Since the fractional *x* coordinates of the S atoms are very close to *a*/2 at 300 K [see rows (*a*) of Table 2], the intensity data at room temperature appear to have pseudo body-center symmetry (*i.e.* $h + k + l = 2n + 1$ mostly weak). However at 110 K, the *x* coordinates are not as close to $\frac{1}{2}$ as at 300 K and no such pseudo symmetry was found in the 110 K data. The anisotropy of the two atoms in the mirror plane (S1, C1) is apparent, with U_{22} much larger than U_{11} or U_{33}. Such phenomena are consistent at both temperatures.

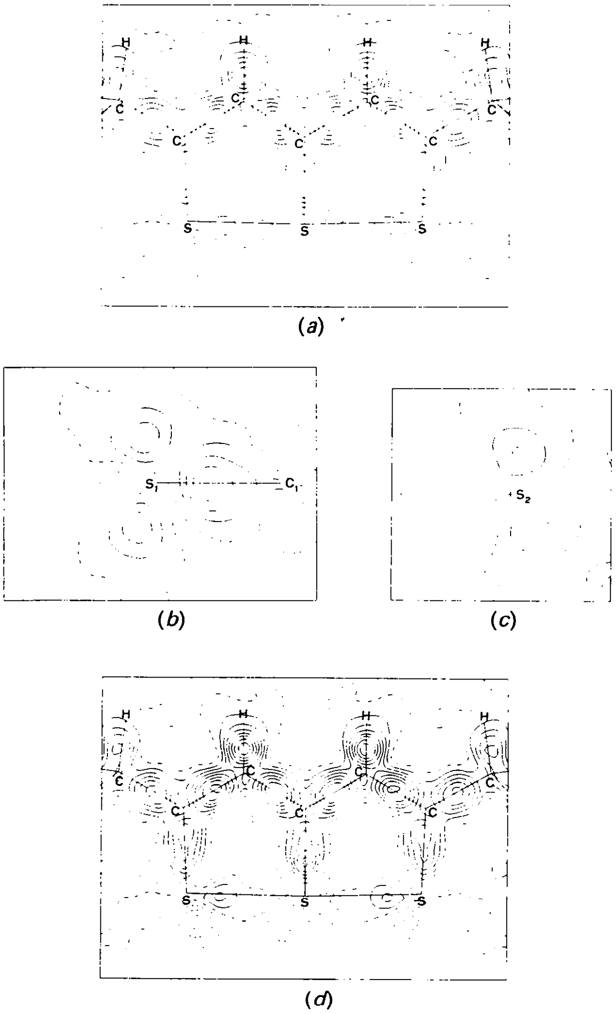
The experimental X–X deformation electron-density distribution shown in Fig. 2 apparently suffers from a high level of noise; however, the well-known features of the C—C bond are still quite



(*a*)

(*b*) (*c*)

Fig. 2. Experimental deformation-density maps (X–$X_{\rm high}$) of 2,5-dimethylthiathiophthene. Contour lines are at 0·1 e Å^{-3} intervals. Lines represent positive (solid), zero (dashed) and negative (dotted) contours. The standard deviation of the map is 0·08 e Å^{-3}. (*a*) Thiathiophthene ring plane; (*b*) plane perpendicular to (*a*), and including C1,S1; (*c*) plane perpendicular to (*a*), and bisecting the C3—S2—S1 angle.



(*a*)

(*b*) (*c*)

(*d*)

Fig. 3. Multipole-model deformation-density maps of the title compound; contour lines as in Fig. 2. (*a*), (*b*) and (*c*) defined as in Fig. 2; (*d*) pseudostatic deformation-density map of the plane in Fig. 2(*a*).

Table 3. *Agreement indices for the least-squares refinements*

	NV[b]	R_1[c]	wR_1[e]	R_2[d]	wR_2[f]	S
Conventional	50	0·048	0·028	0·049	0·038	4·693
Monopole	60	0·043	0·021	0·041	0·027	3·488
Octapole	144	0·035	0·014	0·029	0·017	2·318
Octapole[a]	158	0·034	0·013	0·027	0·016	2·247
Hexadecapole	190	0·034	0·013	0·027	0·015	2·304

Notes: (*a*) up to hexadecapole terms for S atoms only; (*b*) total number of variables; (*c*) $R_1 = \sum|F_o - kF_c|/\sum F_o$; (*d*) $R_2 = \sum|F_o^2 - kF_c^2|/\sum F_o^2$; (*e*) $wR_1 = [\sum w|F_o - kF_c|^2/\sum wF_o^2]^{1/2}$; (*f*) $wR_2 = [\sum w|F_o^2 - kF_c^2|^2/\sum wF_o^4]^{1/2}$.

recognizable. The C—S bonds have somewhat lower density, and the S—S bonds little density accumulation, which is very similar to what was observed previously for 2,4-diphenylthiathiophthene (Wang, Chen & Wu, 1988). Additional multipole deformation-density maps gave a much clearer picture and therefore more meaningful information than the experimental ones. The effect is most pronounced in the plane perpendicular to the molecular ring around the S atoms (Figs. 2 and 3). It is obvious that there is more density located around the terminal S atoms (S2) than the central one (S1). In general, S1 is an electron-deficient center and S2 is an electron-rich center, shown in Fig. 1(*b*) as having positive net atomic charge for S1 but negative for S2. A recent study on 2,5-diaza-1,6-dioxa-6a-thiapentalene (1) (Fabius, Cohen-Addad, Larsen, Lehmann & Becker, 1989) also gives a similar result. It was indicated that the central S atom is in a hypervalent state. Although in our system there are three S atoms instead of one central S atom and two terminal O atoms, the terminal S atoms are still believed to be more negatively charged than the central one, which is quite obvious in Figs. 2 and 3. Compared with compound (1), the terminal S atoms are less electron rich than the terminal O atoms and therefore give less electron density around the S atoms than the O atoms. The relative net charge difference between S2 and S1 is much less than that between O and S in compound (1). As mentioned before (Cohen-Addad, Lehmann, Becker & Davy, 1988) there are significant correlations between the U_{ij}'s and the coefficients of the multipoles during the refinement process. A pseudo-static deformation-density distribution (Fig. 3*d*) is presented in order to show that even with zero vibration of atoms, the deformation feature still appears quite the same. From the deformation-density maps shown here, it seems that the S—S—S σ-electron density lies close to the terminal S atoms, but the π-electron density is evenly distributed between the terminal and central S atoms. The span of terminal π-electron density is rather extensive (from the C3—S2 direction to the bisection direction ∠C3—S2—S1). The C—C, C—H and C—S deformation density distributions are in good agreement with the theoretically calculated map of (1) (Becker, Cohen-Addad, Delley, Hirshfeld & Lehmann, 1986).

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