

$[(C_6F_5)_2F_2PNCH_3]_2$ , in which the  $C_6F_5$  group makes a dihedral angle of  $23.8^\circ$  with the equatorial plane (Fild, Sheldrick & Stankiewicz, 1975). The librationaly corrected P–C distances of 1.823 (4) and 1.815 (3) Å in  $(C_6F_5)_3PF_2$  are similar to that of 1.817 (4) Å in  $[(C_6F_5)_2F_2PNCH_3]_2$ , but considerably longer than that of 1.728 (11) Å in 2-methyl-5-(tetrafluorophosphoranyl)pyrrole, where the pyrrole  $\pi$  system behaves as a donor. The fact that any residual donor properties of the  $C_6F_5$  group in  $(C_6F_5)_3PF_2$  must be minimal is highlighted by a comparison of the P–F(ax) distance with that in analogous molecules. Electron diffraction studies (Hansen, 1965; Bartell & Hansen, 1965; Yow & Bartell, 1973) on members of the series  $(CH_3)_nPF_{5-n}$  ( $0 \leq n \leq 3$ ) have demonstrated a steady increase in the P–F(eq) and P–F(ax) distances with increasing methyl substitution in these trigonal-bipyramidal molecules, in agreement with the VSEPR model (Gillespie & Nyholm, 1957). Thus the value of the P–F(ax) length varies linearly between 1.577 (5) ( $n=0$ ) and 1.685 (1) Å ( $n=3$ ). In  $(C_6F_5)_3PF_2$  the P–F(ax) distance of 1.638 (2) Å is shorter even than that of 1.643 (3) Å observed in  $(CH_3)_2PF_3$ . It may be inferred, therefore, in accordance with the VSEPR model that the electron density in the P–C bond at P, and thereby the extent of electron donation from the substituent group, is much greater in  $(CH_3)_2PF_3$  than in  $(C_6F_5)_3PF_2$ .

A narrowing of the C–C–C angles in the  $C_6F_5$  groups to  $117.5$  (4) and  $116.4$  (3) $^\circ$ , at the C bonded to P, parallels a similar observation in  $[(C_6F_5)_2F_2PNCH_3]_2$ , where an angle of  $115.6$  (4) $^\circ$  is observed. The mean values of the C–C and C–F distances are 1.377 (2) (librationaly corrected) and 1.333 (3) Å respectively.

The unit cell in the  $yz$  projection is shown in Fig. 2.

This work was carried out within the technology programme of the Bundesministerium für Forschung und Technologie (BRD). The calculations were carried out on the Institute PDP-10 computer with the crystal structure analysis program *SHELX* (Dr G. M. Sheldrick) and programs written by myself. I am indebted to Dr M. Fild for the provision of crystals and to Frau

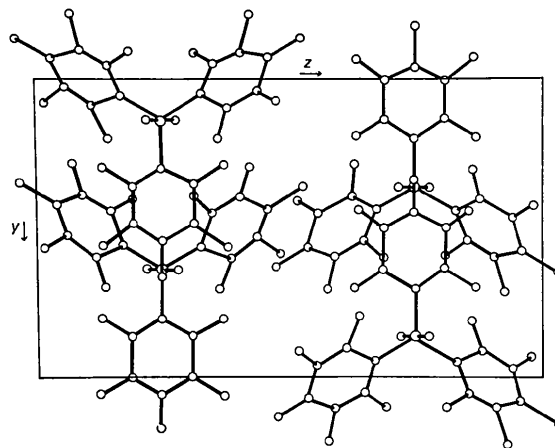


Fig. 2. Projection of the structure perpendicular to [100].

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## The Dimer 2,5-Di-*t*-butyl-3,6-dineopentylthioeno[3,2-*b*]thiophene

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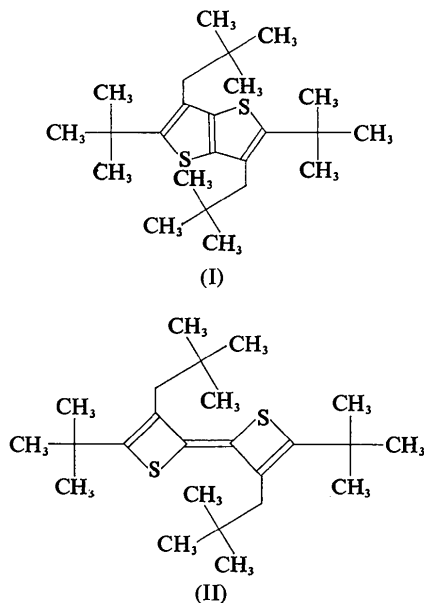
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**Abstract.**  $C_{24}H_{40}S_2$ , monoclinic,  $P2_1/c$ ,  $a=9.640$  (4),  $b=11.938$  (3),  $c=11.796$  (6) Å,  $\beta=117.86$  (4) $^\circ$ ,  $Z=2$ ,  $D_x=1.08$  (1),  $D_c=1.09$  g cm $^{-3}$ , M.W. 392.715,  $R=8.0\%$ . The dimer is planar with the center of inversion mid-way along the internal carbon–carbon bond.

**Introduction.** The dimer was isolated from the reaction of *t*-butyl neopentyl trithione with trimethyl phosphite (D. J. Anderson, unpublished results). The trithione had lost two sulfur atoms and had dimerized, but it was difficult to assign the structure of the product

with the usual spectroscopic methods. In particular, it was not possible to differentiate unambiguously between a thienothiophene with two fused five-membered rings (I) or an alternative bisthienylidene with two four-membered rings (II).



The X-ray data were obtained from a crystal of dimensions 0.28 × 0.28 × 0.25 mm. Unit-cell dimensions were obtained by least-squares refinement of the 2θ angles of 35 reflections measured on a Datex automated General Electric diffractometer. The absence of *h*0*l* reflections for *l* odd and 0*k*0 reflections for *k* odd indicated that the space group is *P*2<sub>1</sub>/*c*.

Intensity data were collected by the θ–2θ scan method with nickel-filtered Cu *K*α radiation (λ = 1.54178 Å). Reflections were collected to a maximum value of 2θ = 135° with a scan rate in 2θ of 2° min<sup>-1</sup>. Three reflections monitored at regular intervals during the data collection showed no significant variation in intensity.

The intensities of 1419 reflections were measured. The intensities of 67 of these were found to be less

Table 2. *Hydrogen atom coordinates*

The values have been multiplied by 10<sup>3</sup>. The hydrogen atoms were not refined.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(14)	276	233	327	H(24)	342	534	283
H(15)	184	150	248	H(25)	387	438	55
H(16)	202	171	413	H(26)	535	532	142
H(17)	-44	416	356	H(27)	572	430	138
H(18)	34	328	445	H(28)	714	396	382
H(19)	141	404	426	H(29)	601	395	458
H(20)	-244	270	162	H(30)	624	520	408
H(21)	-150	166	136	H(31)	434	225	292
H(22)	-126	150	262	H(32)	368	247	149
H(23)	321	437	346	H(33)	529	241	204

than one standard deviation above background and were assigned a value of zero with zero weight throughout the refinement. The data were corrected for Lorentz-polarization effects but not for absorption

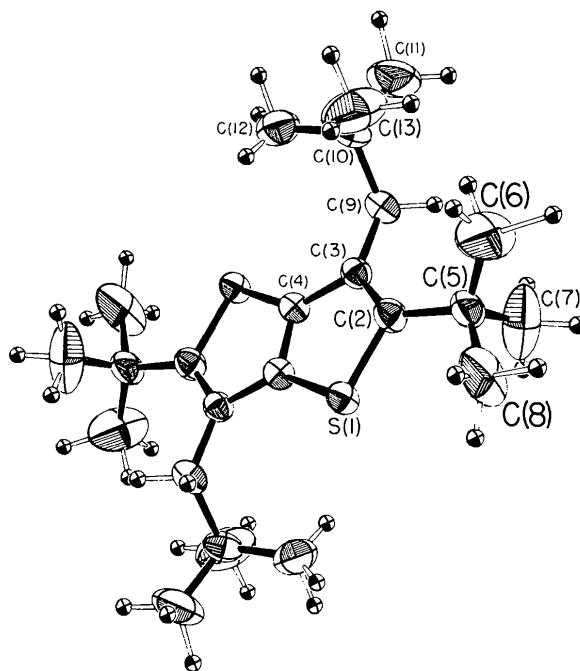


Fig. 1. ORTEP drawing of the sulfur dimer.

Table 1. *Heavier-atom parameters and their standard deviations*

The coordinates have been multiplied by 10<sup>4</sup> and the temperature factors by 10<sup>2</sup>. The temperature factors are in the form  $T = \exp[-2\pi^2(u_{11}a^*h^2 + u_{22}b^*k^2 + u_{33}c^*l^2 + 2u_{12}a^*b^*hk + 2u_{13}a^*c^*hl + 2u_{23}b^*c^*kl)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i> <sub>11</sub>	<i>u</i> <sub>22</sub>	<i>u</i> <sub>33</sub>	<i>u</i> <sub>12</sub>	<i>u</i> <sub>13</sub>	<i>u</i> <sub>23</sub>
S(1)	-1510 (2)	3882 (2)	168 (1)	35 (1)	31 (2)	40 (1)	-3 (1)	13 (1)	6 (1)
C(2)	316 (6)	3686 (7)	1529 (5)	42 (3)	38 (7)	40 (3)	1 (3)	16 (2)	6 (2)
C(3)	1441 (6)	4368 (7)	1529 (4)	38 (3)	32 (6)	37 (2)	5 (3)	16 (2)	4 (2)
C(4)	785 (6)	5072 (6)	409 (4)	37 (3)	21 (6)	36 (2)	1 (3)	16 (2)	0 (2)
C(5)	293 (7)	2841 (9)	2524 (6)	44 (3)	71 (11)	50 (3)	1 (4)	16 (3)	26 (4)
C(6)	1569 (14)	2041 (16)	3031 (12)	112 (9)	110 (24)	208 (11)	63 (11)	97 (8)	124 (12)
C(7)	390 (14)	3557 (14)	3644 (9)	183 (9)	115 (18)	71 (6)	-52 (10)	76 (6)	-13 (7)
C(8)	-1266 (11)	2348 (16)	2068 (9)	80 (6)	164 (26)	103 (7)	-55 (9)	11 (5)	87 (9)
C(9)	3112 (6)	4549 (7)	2594 (5)	41 (3)	36 (7)	38 (3)	2 (3)	10 (2)	1 (2)
C(10)	4527 (7)	4063 (8)	2458 (6)	38 (3)	35 (9)	55 (3)	8 (4)	13 (2)	7 (3)
C(11)	4721 (8)	4608 (11)	1409 (8)	52 (4)	93 (14)	92 (5)	14 (5)	41 (4)	28 (5)
C(12)	5956 (8)	4223 (14)	3708 (7)	47 (4)	188 (21)	67 (5)	26 (7)	-1 (3)	-19 (7)
C(13)	4372 (12)	2845 (16)	2180 (12)	94 (7)	95 (19)	179 (12)	28 (8)	85 (8)	17 (10)

Table 3. Bond distances (Å) and angles (°) and their standard deviations involving the heavier atoms

C(2)—S(1)	1.758 (4)	C(2)—S(1)—C(4')	92.2 (3)		
C(3)—C(2)	1.356 (10)	C(3)—C(2)—S(1)	112.3 (5)	C(3)—C(2)—C(5)	133.0 (4)
C(4)—C(3)	1.439 (8)	C(4)—C(3)—C(2)	110.0 (4)	C(4)—C(3)—C(9)	121.0 (6)
C(4')—C(4)	1.374 (6)	C(4')—C(4)—C(3)	116.0 (6)		
C(4')—S(1)	1.718 (7)	S(1)—C(4')—C(4)	109.4 (4)		
C(5)—C(2)	1.556 (12)	C(5)—C(2)—S(1)	114.4 (4)		
C(6)—C(5)	1.448 (18)	C(6)—C(5)—C(2)	115.5 (9)	C(6)—C(5)—C(7)	108.2 (9)
C(7)—C(5)	1.539 (16)	C(7)—C(5)—C(2)	105.7 (9)	C(7)—C(5)—C(8)	100.3 (9)
C(8)—C(5)	1.462 (14)	C(8)—C(5)—C(2)	110.0 (6)	C(8)—C(5)—C(6)	114.5 (10)
C(9)—C(3)	1.526 (6)	C(9)—C(3)—C(2)	128.4 (6)		
C(10)—C(9)	1.558 (10)	C(10)—C(9)—C(3)	120.0 (5)		
C(11)—C(10)	1.485 (13)	C(11)—C(10)—C(9)	112.3 (7)	C(11)—C(10)—C(12)	110.6 (8)
C(12)—C(10)	1.487 (8)	C(12)—C(10)—C(9)	107.4 (7)	C(12)—C(10)—C(13)	107.2 (9)
C(13)—C(10)	1.482 (21)	C(13)—C(10)—C(9)	112.7 (8)	C(13)—C(10)—C(11)	106.5 (8)

( $\mu = 18 \text{ cm}^{-1}$ ). The data were placed on an absolute scale by Wilson's (1942) method. A Howells, Phillips & Rogers (1950) plot confirmed that the structure is centrosymmetric.

The phases of the 130 reflections with an  $E$  value greater than 1.65 were assigned by Long's (1965) program, which uses a reiterative application of Sayre's (1952) equation. Long's procedure gave a phase assignment with a consistency index of 1.00 which in turn gave an  $E$  map in which all 13 non-hydrogen atoms could be located. Full-matrix least-squares refinement of the coordinates and anisotropic temperature factors using the *CRYM* program (Duchamp, 1964) converged at an  $R$  index of 8.0%. The least-squares routine minimized the quantity  $\sum \omega(F_o^2 - F_c^2)^2$ . The weights  $\omega$  used throughout the refinement of the structure were set equal to  $1/\sigma^2(F_o)^2$  which were derived from counting statistics. The weighted  $R$  index,  $\sum \omega(F_o^2 - F_c^2)^2 / \sum \omega F_o^4$ , was 3.4%, and the goodness of fit,  $[\sum \omega(F_o^2 - F_c^2)^2 / (m - s)]^{1/2}$ , where  $m$  is the number of observations and  $s$  is the number of parameters refined, was 4.3. A difference map revealed all of the hydrogen atoms. The heavier-atom parameters are given in Table 1, and the hydrogen atom coordinates are given in Table 2.\*

**Discussion.** Fig. 1 shows the molecular structure and the numbering system used. Table 3 contains the bond distances and angles with their standard deviations. The average standard deviation in atomic position is 0.009 Å. The least-squares plane through one of the thiophene rings given in Table 4 shows that the aromatic

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30883 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Least-squares plane through the thiophene ring  
Coefficients are direction cosines relative to the crystallographic axes.

Plane through atoms S(1), C(2), C(3), C(4) and C(4'):  
 $-0.5271x + 0.6862y + 0.6895z = 4.093$

Deviations (Å)

S(1)	-0.010	C(4')	0.010
C(2)	0.009	C(5)	0.138
C(3)	-0.004	C(9)	0.162
C(4)	-0.005		

ring is flat within experimental error. The bond lengths and angles in the aromatic ring are in good agreement with those found by Cox, Gillot & Jeffrey (1949) in their classic X-ray structure of the parent unsubstituted thieno[3,2-*b*]thiophene. In particular the length of the central carbon-carbon bond, C(4)—C(4') (1.374 Å), is in good agreement with the value of 1.36 Å found by them.

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