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Structures of Bis(dialkylthiophosphoryl) Disulfides, $[R_2P(S)]_2S_2$, $R = \text{Me, } ^i\text{Pr}$, and the Question of P—S π Bonding

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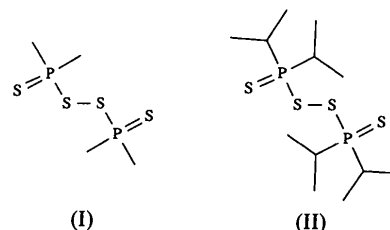
Abstract

The structures of two bis(dialkylthiophosphoryl) disulfides (alkyl = methyl, isopropyl) have been determined. The torsion angles about the disulfide bonds are similar but the geometry with respect to the P—S single bonds is different, the methyl compound tending to be *trans* planar and the isopropyl analog *cis* planar. The *cisoid* geometry is associated with larger S—P—S valence angles. The drive to planarity is interpreted as a π contribution to the P—S single bond.

Comment

It was reported recently (Buranda, Gallacher & Pinkerton, 1991) that, although the torsion angle about the S—S bond in organic disulfides tends to be close to 90° with a significant energy maximum at 0 and 180° , substitution of the organic moieties by thiophosphoryl groups gives rise to a wide variety of torsion angles (values ranging from

93.6 to 180.0°). In previous literature reports on the structures of similar disulfides, $[R_2P(S)]_2S_2$, the S—P—S torsion angles were all close to 180° (*transoid* geometry) and no unusual effects on the geometry at the P atom were noted (Lawton, 1970; Tkachev, Atovmyan & Shchepinov, 1976; Yadav, Bohra, Mehrotra, Rai & Srivastava, 1983). However, when the substituents at the P atom were cyclohexyl groups, a *cisoid* geometry (S—P—S torsion angle $\rightarrow 0^\circ$) was observed for one form, and both *cisoid* and *transoid* geometries for another (Buranda, Gallacher & Pinkerton, 1991). Thus, in the *cisoid* and *transoid* forms, the PS_3 unit has a tendency to planarity. The extremely small S—P—S torsion angle [$20.6(1)$ – $24.7(1)^\circ$] in the *cisoid* form of the cyclohexyl compound leads to an opening of the S—P—S valence angle by about 10° with respect to the *transoid* geometry. This opening of the valence angle is evidence for an important S—S steric interaction as the molecule moves towards planarity. It was suggested that the driving force towards planarity (*cis* or *trans*) is a π interaction between filled p (or π) orbitals on S and empty d orbitals on P. As the only observation of *cisoid* geometry is for the bulky cyclohexyl substituent, we have determined the structures of two other disulfides with smaller alkyl substituents [methyl (I) and isopropyl (II)].



Despite the similarity between the alkyl substituents, these two disulfides fall at the two extremes of the behavior described above. The torsion angles about the disulfide bond are almost identical [(I) $113.6(1)$, (II) $113.47(3)^\circ$]. However, the thiophosphoryl moiety is *transoid* in the methyl compound [S—P—S—S $167.9(1)$, $171.2(1)^\circ$] but *cisoid* in the isopropyl analog [S—P—S—S $17.17(5)$, $16.35(5)^\circ$]. This difference in conformation has an important effect on the geometry at the P atom. As noted above, there is a large difference between the S—P—S valence angles in the *transoid* methyl compound [$103.6(1)$, $103.8(1)^\circ$] compared with those in the *cisoid* isopropyl analog [$115.96(4)$, $115.08(4)^\circ$]. The opening of the valence angle is associated with a lengthening of the P—S bond [(I) $2.100(2)$, $2.095(3)$ Å; (II) $2.1562(8)$, $2.1584(8)$ Å] and a concomitant shortening of the disulfide bond [(I) $2.074(3)$, (II) $2.0247(8)$ Å]. We note that an analogous trisulfide $[Et_2P(S)]_2S_3$ also has a planar *transoid* geometry for both PS_3 moieties (Gallacher & Pinkerton, 1992).

Although it is still not clear why molecules of this type should exist with a *cisoid* or *transoid* geometry, especially

as one modification of the cyclohexyl compound has both conformations in the same molecule, there is clearly a drive to planarity of the PS_3 unit which we ascribe to the π interaction described previously (Buranda, Gallacher & Pinkerton, 1991).

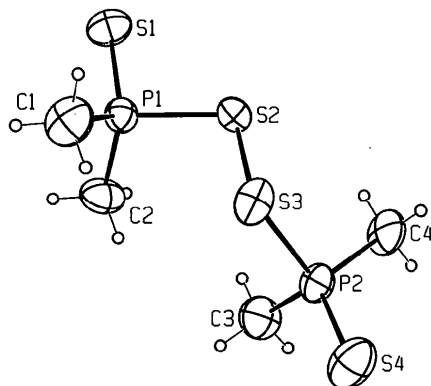


Fig. 1. Bis(dimethylthiophosphoryl) disulfide (I) showing *transoid* geometry. Probability ellipsoids are drawn at 50% and H atoms placed at ideal positions.

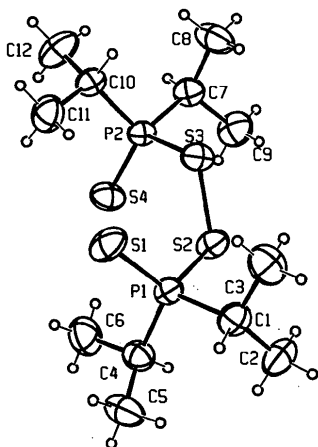


Fig. 2. Bis[di(isopropyl)thiophosphoryl] disulfide (II) showing *cisoid* geometry. Probability ellipsoids are drawn at 50% and H atoms placed at ideal positions.

Experimental

Compound (I)

Crystal data

$\text{C}_4\text{H}_{12}\text{P}_2\text{S}_4$
 $M_r = 250.34$
 Orthorhombic
 $Pna2_1$
 $a = 22.046$ (6) Å
 $b = 6.226$ (1) Å
 $c = 8.480$ (3) Å
 $V = 1164.0$ (9) Å³
 $Z = 4$
 $D_x = 1.43$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 10\text{--}14^\circ$
 $\mu = 1.000$ mm⁻¹
 $T = 294$ K
 Irregular shape
 $0.40 \times 0.36 \times 0.29$ mm
 Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: refined empirical (Walker & Stuart, 1983)
 $T_{\min} = 0.7900$, $T_{\max} = 1.1640$
 1246 measured reflections
 1246 independent reflections

750 observed reflections
 $[I > 3.0\sigma(I)]$
 $\theta_{\max} = 24.98^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 26$
 $l = 0 \rightarrow 7$
 3 standard reflections
 frequency: 50 min
 intensity variation: 2.54%

Refinement

Refinement on F
 Final $R = 0.042$
 $wR = 0.041$
 $S = 1.265$
 750 reflections
 90 parameters
 H atoms riding
 $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$

$(\Delta/\sigma)_{\max} = 0.010$
 $\Delta\rho_{\max} = 0.3604$ e Å⁻³
 $\Delta\rho_{\min} = -0.3156$ e Å⁻³
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) for (I)

The choice of enantiomorph is random as both refine equally well and the bulk sample is racemic. $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	U_{eq}
S1	0.55027 (9)	0.2053 (4)	0.5087 (3)	0.058 (1)
S2	0.42810 (9)	0.3594 (3)	0.6720	0.045 (1)
S3	0.33628 (9)	0.3954 (3)	0.6264 (3)	0.048 (1)
S4	0.2063 (1)	0.3034 (4)	0.7724 (3)	0.066 (2)
P1	0.46323 (9)	0.1781 (3)	0.4843 (3)	0.039 (1)
P2	0.29064 (9)	0.2248 (3)	0.8029 (3)	0.042 (1)
C1	0.4315 (4)	0.289 (1)	0.309 (1)	0.066 (6)
C2	0.4351 (3)	-0.088 (1)	0.499 (1)	0.055 (5)
C3	0.3058 (4)	-0.053 (1)	0.780 (1)	0.059 (6)
C4	0.3246 (4)	0.298 (1)	0.9863 (9)	0.053 (5)

Table 2. Geometric parameters (Å, °) for (I)

S1—P1	1.938 (3)	P1—C1	1.783 (8)
S2—S3	2.073 (3)	P1—C2	1.772 (8)
S2—P1	2.099 (3)	P2—C3	1.773 (8)
S3—P2	2.094 (3)	P2—C4	1.785 (8)
S4—P2	1.941 (3)		
S3—S2—P1	106.1 (1)	C1—P1—C2	106.4 (4)
S2—S3—P2	106.3 (1)	S3—P2—S4	103.7 (1)
S1—P1—S2	103.7 (1)	S3—P2—C3	109.1 (3)
S1—P1—C1	116.4 (3)	S3—P2—C4	107.0 (3)
S1—P1—C2	114.9 (3)	S4—P2—C3	114.3 (3)
S2—P1—C1	106.3 (3)	S4—P2—C4	117.0 (3)
S2—P1—C2	108.7 (3)	C3—P2—C4	105.4 (4)
P1—S2—S3—P2	113.6 (1)	S2—S3—P2—S4	171.2 (1)
S3—S2—P1—S1	167.7 (1)		

Compound (II)

Crystal data

$\text{C}_{12}\text{H}_{28}\text{P}_2\text{S}_4$
 $M_r = 362.56$
 Triclinic

$D_x = 1.26$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å

$P\bar{1}$	Cell parameters from 25 reflections
$a = 7.616 (1) \text{ \AA}$	$\theta = 9-16^\circ$
$b = 11.378 (1) \text{ \AA}$	$\mu = 0.631 \text{ mm}^{-1}$
$c = 12.403 (2) \text{ \AA}$	$T = 294 \text{ K}$
$\alpha = 68.33 (1)^\circ$	Elongated plate
$\beta = 72.61 (1)^\circ$	$0.35 \times 0.20 \times 0.10 \text{ mm}$
$\gamma = 85.53 (1)^\circ$	Colorless
$V = 952.4 (2) \text{ \AA}^3$	
$Z = 2$	
Data collection	
Enraf-Nonius CAD-4 diffractometer	2466 observed reflections
$\theta/2\theta$ scans	$[I > 3.0\sigma(I)]$
Absorption correction: empirical	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.9021, T_{\text{max}} = 0.9995$	$\theta_{\text{max}} = 25.97^\circ$
7482 measured reflections	$h = -9 \rightarrow 9$
3743 independent reflections	$k = -14 \rightarrow 14$
	$l = -15 \rightarrow 15$
	3 standard reflections
	frequency: 50 min
	intensity variation: 3.62%

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.076$
Final $R = 0.025$	$\Delta\rho_{\text{max}} = 0.178 \text{ e \AA}^{-3}$
$wR = 0.032$	$\Delta\rho_{\text{min}} = -0.168 \text{ e \AA}^{-3}$
$S = 1.000$	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
2466 reflections	
163 parameters	
H atoms riding	
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$	

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for (II)

	x	y	z	U_{eq}
S1	-0.46676 (9)	-0.05534 (5)	-0.20811 (5)	0.0516 (3)
S2	-0.20962 (8)	-0.32374 (5)	-0.14043 (4)	0.0412 (2)
S3	-0.05433 (7)	-0.20617 (5)	-0.30360 (4)	0.0434 (2)
S4	-0.29656 (8)	-0.40524 (5)	-0.36624 (5)	0.0519 (3)
P1	-0.42945 (7)	-0.20898 (5)	-0.08292 (4)	0.0354 (2)
P2	-0.08997 (7)	-0.28590 (4)	-0.42920 (4)	0.0351 (2)
C1	-0.3680 (3)	-0.1809 (2)	0.0375 (2)	0.0485 (9)
C2	-0.3438 (3)	-0.3024 (2)	0.1384 (2)	0.062 (1)
C3	-0.1989 (3)	-0.0923 (2)	-0.0156 (2)	0.068 (1)
C4	-0.6227 (3)	-0.3250 (2)	-0.0109 (2)	0.044 (1)
C5	-0.7779 (3)	-0.2851 (2)	0.0772 (2)	0.059 (1)
C6	-0.6895 (3)	-0.3460 (2)	-0.1071 (2)	0.070 (1)
C7	0.1325 (3)	-0.3547 (2)	-0.4733 (2)	0.0440 (9)
C8	0.2950 (3)	-0.2592 (2)	-0.5308 (2)	0.059 (1)
C9	0.1642 (3)	-0.4657 (2)	-0.3665 (2)	0.063 (1)
C10	-0.1027 (3)	-0.1420 (2)	-0.5567 (2)	0.0410 (9)
C11	-0.2816 (3)	-0.0755 (2)	-0.5260 (2)	0.059 (1)
C12	-0.0801 (4)	-0.1729 (2)	-0.6703 (2)	0.067 (1)

Table 4. Geometric parameters ($\text{\AA}, ^\circ$) for (II)

S1—P1	1.9312 (8)	C1—C2	1.527 (3)
S2—S3	2.0249 (8)	C1—C3	1.520 (3)
S2—P1	2.1563 (8)	C4—C5	1.520 (3)
S3—P2	2.1582 (7)	C4—C6	1.527 (3)
S4—P2	1.9350 (8)	C7—C8	1.527 (3)

P1—C1	1.830 (2)	C7—C9	1.522 (3)
P1—C4	1.831 (2)	C10—C11	1.521 (3)
P2—C7	1.827 (2)	C10—C12	1.532 (3)
P2—C10	1.829 (2)		
S3—S2—P1	104.45 (3)	C7—P2—C10	107.7 (1)
S2—S3—P2	103.61 (3)	P1—C1—C2	113.4 (2)
S1—P1—S2	115.94 (4)	P1—C1—C3	110.4 (2)
S1—P1—C1	113.35 (8)	C2—C1—C3	111.7 (2)
S1—P1—C4	115.24 (8)	P1—C4—C5	111.2 (2)
S2—P1—C1	102.62 (8)	P1—C4—C6	110.3 (2)
S2—P1—C4	100.53 (8)	C5—C4—C6	111.4 (2)
C1—P1—C4	107.7 (1)	P2—C7—C8	113.9 (2)
S3—P2—S4	115.09 (3)	P2—C7—C9	111.0 (2)
S3—P2—C7	103.00 (8)	C8—C7—C9	110.6 (2)
S3—P2—C10	100.80 (7)	P2—C10—C11	111.3 (2)
S4—P2—C7	113.55 (8)	P2—C10—C12	110.3 (2)
S4—P2—C10	115.24 (8)	C11—C10—C12	111.1 (2)
P1—S2—S3—P2	-113.48 (3)	S2—S3—P2—S4	16.36 (5)
S3—S2—P1—S1	17.19 (5)		

Data collection: CAD-4 (Enraf-Nonius, 1977). Cell refinement: CAD-4. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: (I) *MULTAN* (Main *et al.*, 1980), (II) *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *BTABLE, PTABLE, CIF IN, MolEN*.

The title compounds were obtained easily from iodine oxidation of the corresponding anions $R_2PS_2^-$ (Maier, 1965) and crystallized from ethanol.

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). For the isopropyl compound, the structure was solved in space group $P1$, using *DIRDIF* (Beurskens, 1984) starting with one P atom at the origin, and then transformed into the correct space group.

We thank the College of Arts and Sciences of the University of Toledo for generous support of the X-ray facility.

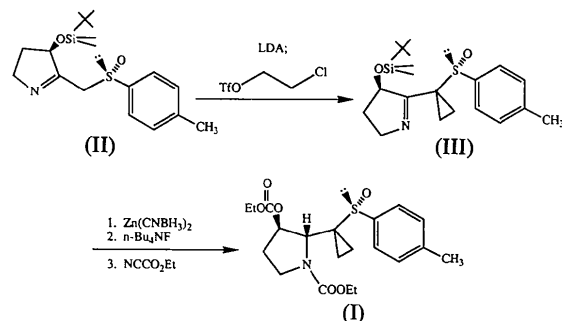
Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55393 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1019]

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was isolated unexpectedly [yield 55%, based on 26% recovery of (II)]. Subsequent stereoselective reduction of (III) with zinc cyanoborohydride followed by desilylation with tetra-*n*-butylammonium fluoride and then ethoxycarbonylation with 3 equivalents of LDA and 2.5 equivalents of ethyl cyanofornate gave the title compound (I); $[\alpha]_D^{22} = +34.4^\circ$ (*c* 0.5, CHCl_3), m.p. 369–374 K (recrystallized from CH_2Cl_2 –hexane).



The C(7)—C(8) bond in the cyclopropyl ring of (I) is shorter [1.48(1) Å] than both the normal distance for cyclopropane (1.51 Å) (Vollhardt, 1987) and the C(6)—C(7) and C(6)—C(8) bonds. In addition, the bond angle S(1)—C(6)—C(2) [123.2(6)°] is substantially larger than the corresponding angle (115°) in cyclopropane.

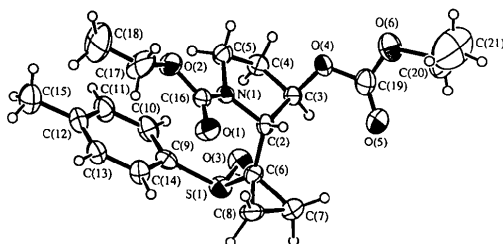


Fig. 1. Molecular configuration and atom-numbering scheme with thermal ellipsoids at the 30% probability level. H atoms are shown as unlabeled circles of arbitrary radius.

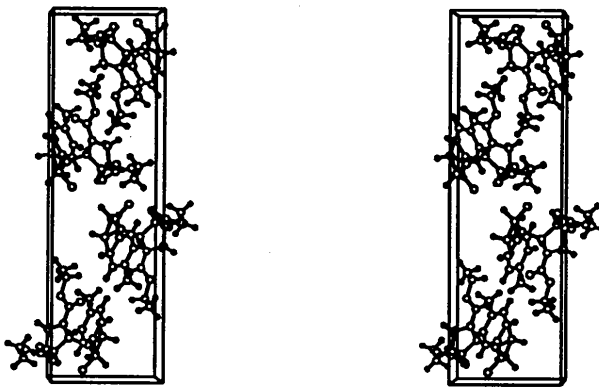


Fig. 2. Stereoscopic illustration of the molecular packing. The origin is at the lower-right-front, *a* is into the plane of the paper, *b* is vertical, and *c* is horizontal.

Acta Cryst. (1992). **C48**, 2088–2090

Ethyl (2*R*,3*R*,*S**R*)-3-(Ethoxycarbonyloxy)-2-[1-(*p*-tolylsulfinyl)cyclopropyl]-1-pyrrolidinecarboxylate

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Abstract

The title compound, derived in four steps beginning with the cyclopropanation reaction of the anion of the α -sulfinyl ketimine (4*R*,*S**S*)-4-(*tert*-butyldimethylsilyloxy)-3,4-dihydro-5-[(*p*-tolylsulfinyl)methyl]-2*H*-pyrrole with 2-chloroethyl trifluoromethanesulfonate, contains a shorter than expected bond [C(7)—C(8) 1.48 (1) Å] and a larger than expected angle [S(1)—C(6)—C(2) 123.2 (6)°] in the cyclopropane framework.

Comment

The title compound (I) was synthesized using α -sulfinyl ketimine chemistry (Hua, Bharathi, Panagadan & Tsujimoto, 1991) as part of our investigations into the asymmetric total synthesis of the anti-tumor agent indicine *N*-oxide (Kovach, Ames, Powis, Moertel, Hahn & Cregan, 1979). When (4*R*,*S**S*)-4-(*tert*-butyldimethylsilyloxy)-3,4-dihydro-5-[(*p*-tolylsulfinyl)methyl]-2*H*-pyrrole (II) was treated with 1.3 equivalents of lithium diisopropylamide (LDA) in THF at 195 K followed by 2-chloroethyl trifluoromethanesulfonate, 5-cyclopropyldihydropyrrole (III)

[†] Fellow of the Alfred P. Sloan Foundation, 1989–1993.