Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.1695 (3)	0.0083 (3)	0.6461 (2)	0.047 (2)
C1*A*	0.1202 (4)	−0.0010 (4)	0.7184 (2)	0.049 (2)
O1	0.1975 (3)	−0.0251 (3)	0.7711 (2)	0.066 (2)
C1*B*	−0.0257 (4)	0.0297 (4)	0.7336 (2)	0.046 (2)
C1*C*	−0.0927 (4)	0.1225 (4)	0.6950 (2)	0.056 (3)
C1*D*	−0.2247 (5)	0.1573 (5)	0.7158 (3)	0.070 (3)
C1*E*	−0.2882 (5)	0.0981 (6)	0.7740 (3)	0.078 (3)
C1*F*	−0.2235 (5)	0.0055 (6)	0.8122 (3)	0.077 (3)
C1*G*	−0.0925 (5)	−0.0274 (5)	0.7927 (2)	0.064 (3)
C2	0.1008 (4)	−0.0165 (4)	0.5786 (2)	0.047 (2)
C2*A*	−0.0250 (4)	−0.0916 (3)	0.5744 (2)	0.041 (2)
C2*B*	−0.0435 (5)	−0.1951 (4)	0.6194 (2)	0.052 (3)
C2*C*	−0.1611 (6)	−0.2655 (4)	0.6127 (2)	0.068 (4)
C2*D*	−0.2600 (5)	−0.2343 (5)	0.5612 (3)	0.068 (3)
C2*E*	−0.2423 (5)	−0.1334 (5)	0.5154 (3)	0.066 (3)
C2*F*	−0.1250 (4)	−0.0625 (4)	0.5220 (2)	0.054 (2)
N3	0.1645 (3)	0.0226 (3)	0.5200 (2)	0.052 (2)
C4	0.2872 (4)	0.0912 (4)	0.5453 (2)	0.060 (2)
C4*A*	0.4062 (5)	0.0685 (5)	0.4908 (3)	0.086 (3)
C4*B*	0.2488 (6)	0.2291 (5)	0.5437 (3)	0.082 (4)
C5	0.3142 (4)	0.0418 (4)	0.6268 (2)	0.057 (2)
C5*A*	0.3729 (5)	0.1389 (6)	0.6802 (3)	0.084 (3)
C5*B*	0.3994 (5)	−0.0771 (5)	0.6281 (3)	0.083 (3)
O1*S*	0.4341 (4)	−0.0760 (4)	0.8687 (2)	0.103 (2)

Table 2. *Geometric parameters* (Å, °)

N1—C1*A*	1.378 (5)	C2*A*—C2*B*	1.387 (5)
N1—C2	1.401 (5)	C2*A*—C2*F*	1.385 (5)
N1—C5	1.498 (5)	C2*B*—C2*C*	1.382 (6)
C1*A*—O1	1.230 (5)	C2*C*—C2*D*	1.372 (6)
C1*A*—C1*B*	1.486 (6)	C2*D*—C2*E*	1.373 (6)
C1*B*—C1*C*	1.380 (6)	C2*E*—C2*F*	1.382 (6)
C1*B*—C1*G*	1.383 (6)	N3—C4	1.478 (5)
C1*C*—C1*D*	1.391 (6)	C4—C4*A*	1.531 (6)
C1*D*—C1*E*	1.366 (7)	C4—C4*B*	1.537 (7)
C1*E*—C1*F*	1.364 (8)	C4—C5	1.569 (6)
C1*F*—C1*G*	1.371 (7)	C5—C5*A*	1.527 (7)
C2—N3	1.286 (5)	C5—C5*B*	1.530 (7)
C2—C2*A*	1.472 (5)		
C1*A*—N1—C2	128.3 (3)	C2*F*—C2*A*—C2	119.8 (3)
C1*A*—N1—C5	124.1 (3)	C2*C*—C2*B*—C2*A*	120.1 (4)
C2—N1—C5	107.5 (3)	C2*D*—C2*C*—C2*B*	120.4 (4)
O1—C1*A*—N1	120.9 (4)	C2*C*—C2*D*—C2*E*	120.2 (5)
O1—C1*A*—C1*B*	119.7 (4)	C2*D*—C2*E*—C2*F*	119.5 (4)
N1—C1*A*—C1*B*	119.2 (3)	C2*E*—C2*F*—C2*A*	121.0 (4)
C1*C*—C1*B*—C1*G*	118.6 (4)	C2—N3—C4	108.0 (3)
C1*C*—C1*B*—C1*A*	121.7 (4)	N3—C4—C4*A*	109.9 (4)
C1*G*—C1*B*—C1*A*	119.3 (4)	N3—C4—C4*B*	106.5 (4)
C1*B*—C1*C*—C1*D*	120.2 (4)	C4*A*—C4—C4*B*	109.2 (4)
C1*E*—C1*D*—C1*C*	119.7 (5)	N3—C4—C5	104.3 (3)
C1*F*—C1*E*—C1*D*	120.8 (5)	C4*A*—C4—C5	113.8 (4)
C1*E*—C1*F*—C1*G*	119.7 (5)	C4*B*—C4—C5	112.8 (4)
C1*F*—C1*G*—C1*B*	121.1 (5)	N1—C5—C5*A*	112.1 (4)
N3—C2—N1	113.7 (3)	N1—C5—C5*B*	107.8 (4)
N3—C2—C2*A*	122.8 (3)	C5*A*—C5—C5*B*	111.3 (4)
N1—C2—C2*A*	123.2 (3)	N1—C5—C4	97.8 (3)
C2*B*—C2*A*—C2*F*	118.6 (4)	C5*A*—C5—C4	113.9 (4)
C2*B*—C2*A*—C2	121.5 (4)	C5*B*—C5—C4	113.0 (4)

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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 71185 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1061]

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Structures of the Bis(diarylthiophosphoryl) Disulfides $[Ph_2P(S)]_2S_2$ and $[(PhO)_2P(S)]_2S_2$ and the Question of P—S π Bonding

ANTHONY C. GALLACHER AND A. ALAN PINKERTON

Department of Chemistry, University of Toledo, Toledo, OH 43606, USA

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Abstract

The structures of bis(diphenylthiophosphoryl) disulfide, $[Ph_2P(S)]_2S_2$, and bis(diphenoxythiophosphoryl) disulfide, $[(PhO)_2P(S)]_2S_2$, are reported. The torsion angles about the disulfide bonds are similar; however, the geometry with respect to the P—S single bonds is different. The S—P—S—S moiety in the phenyl compound tends to *cis* planar, and the phenoxy analog to *trans* 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. Two of the aromatic rings in the phenyl compound are offset cofacial with a separation of 3.89 (1) Å.

Comment

It has been reported (Buranda, Gallacher & Pinkerton, 1991; Gallacher & Pinkerton, 1992; Lawton, 1970; Tkachev, Atovmyan & Shchepinov, 1976; Yadav, Bohra, Mehrotra, Rai & Srivastava, 1983) that substitution of the organic moieties in organic disulfides by thiophosphoryl groups gives rise to a wide variety of S—S torsion angles. The values range from 93.6 to 180.0° compared to values close to 90° for the simple organic disulfides. The S—P—S—S moiety may have either a *cisoid* geometry (S—P—S—S torsion angle tending towards 0°) or a *transoid* geometry (S—P—S—S torsion angle tending towards 180°). Indeed, in the cyclohexyl analogs of the present compounds both geometries are observed in the same molecule. Thus, there is a tendency to planarity for the PS_3 unit in both the *cisoid* and *transoid* forms. The

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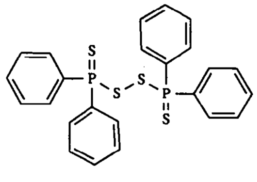
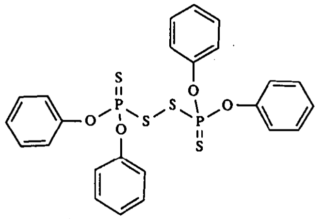
small S—P—S—S torsion angles in the *cisoid* forms lead to an opening of the S—P—S valence angle by about 10° with respect to the *transoid* geometry. The opening of the valence angle results from an S—S steric interaction as the molecule moves towards planarity. The driving force towards planarity (*cis* or *trans*) is attributed to a π interaction between filled *p* (or π) orbitals on sulfur and empty *d* orbitals on phosphorus (Buranda, Gallacher & Pinkerton, 1991). As the only reported structures of these disulfides have either alkyl or alkoxy substituents at phosphorus, we have determined the structures of two other disulfides with phenyl (I) and phenoxy (II) substituents.


(I)


(II)

Molecule (I) has crystallographic twofold symmetry (Fig. 1), but (II) lies in a general position (Fig. 2). Both molecules are composed of two tetrahedral phosphorus units joined by a disulfide bridge. The torsion angles about the disulfide bond are similar [(I) 93.56 (4), (II) 112.03 (7)°] and at the lower end of the expected range. However, the thiophosphoryl moiety is *cisoid* in compound (I) [S1—P—S2—S2′ 31.90 (6)°] but *transoid* in compound (II) [S1—P1—S2—S3 −179.27 (7), S4—P2—S3—S2, −175.98 (7)°]. As predicted above, this difference in conformation is reflected in the geometry at phosphorus. The S—P—S valence angles are 114.44 (4)° for *cisoid* (I), but only 108.39 (7) and 107.92 (8)° for *transoid* (II). The opening of the valence angle is associated with a lengthening of the P—S single bond [(I) 2.139 (1); (II) 2.075 (2), 2.076 (2) Å] and a shortening of the disulfide bond [(I) 2.0271 (9); (II) 2.070 (1) Å]. The shorter P—S bond observed for the *transoid* geometry is in agreement with the π interaction being maximized by a planar S—P—S—S geometry. We note that two of the phenyl groups in (I) are cofacial (dihedral angle < 1°) with an offset (graphite-like) geometry (Fig. 1*a*). At a separation of 3.89 (1) Å (compared to 3.35 Å in graphite) an attractive π-σ electrostatic interaction is to be expected between the two aromatic groups (Hunter & Sanders, 1990). Indeed, this may be the origin of the larger S—P—S—S torsion angle observed for (I) compared to other *cisoid* analogs, mentioned below. From the current data and from the previously reported structures (Buranda, Gallacher & Pinkerton, 1991; Gallacher & Pinkerton, 1992; Lawton, 1970; Tkachev, Atovmyan & Shchepinov, 1976; Yadav, Bohra, Mehrotra, Rai & Srivastava, 1983), we have calculated the following average values for comparison purposes. *Transoid*: S—S—P—S 174 (4)°, S—P—S 105 (2)°, S—S 2.08 (2), P—S 2.09 (2) Å. *Cisoid*: S—S—P—S 22 (6)°, S—P—S 115.3 (6)°, S—S 2.024 (3), P—S 2.153 (7) Å. The S—S distance in the mixed *transoid*/*cisoid* cyclohexyl derivative is intermediate in value [2.063 (1) Å]. Significantly, there is no correlation of the

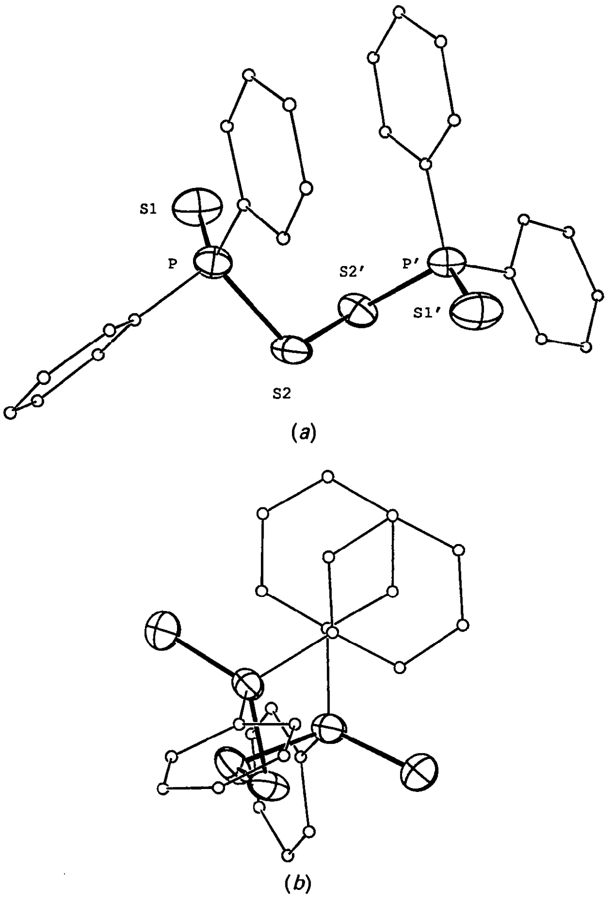


Fig. 1. Bis(diphenylthiophosphoryl) disulfide showing (*a*) *cisoid* geometry, (*b*) interaction of phenyl groups. (50% probability ellipsoids for non-C atoms.)

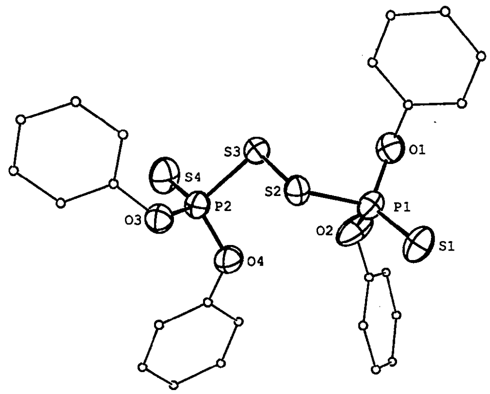


Fig. 2. Bis(diphenoxythiophosphoryl) disulfide showing *transoid* geometry. (50% probability ellipsoids for non-C atoms.)

P=S distance with these geometrical parameters. However, it is correlated with the presence or absence of oxy-substituents [R 1.937 (5), OR 1.904 (5) Å; R = alkyl or aryl].

The consistency of the geometrical correlations in these disulfides provides convincing support for the π interaction proposed previously (Buranda, Gallacher & Pinkerton, 1991), showing it to be maximized when the S—P—S—S moiety is planar.

Experimental

Compound (I)

Crystal data

$C_{24}H_{20}P_2S_4$
M_r = 498.63
Monoclinic
$C2/c$
a = 22.268 (8) Å
b = 9.039 (2) Å
c = 12.361 (5) Å
β = 100.27 (3)°
V = 2448 (2) Å^3
Z = 4

D_x = 1.35 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11-15°
μ = 0.511 mm^{-1}
T = 294 K
Needle
0.31 × 0.10 × 0.08 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.8553, $T_{\max}$ = 0.9976
3184 measured reflections
3095 independent reflections
1585 observed reflections [$I > 3.0\sigma(I)$]

R_{int} = 0.027
$\theta_{\max}$ = 25.98°
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 11$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 50 min
intensity variation: 0.98%

Refinement

Refinement on F
Final R = 0.034
wR = 0.043
S = 1.265
1585 reflections
176 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\max}$ = 0.004
$\Delta\rho_{\max}$ = 0.2236 e Å^{-3}
$\Delta\rho_{\min}$ = −0.2543 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* (I)

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.41247 (4)	0.40076 (8)	0.40759 (6)	0.0579 (2)
S2	0.46183 (3)	0.56934 (7)	0.19141 (6)	0.0428 (2)
P	0.40315 (3)	0.41219 (7)	0.24955 (5)	0.0367 (2)
C1	0.4143 (1)	0.2386 (3)	0.1830 (2)	0.0377 (6)
C2	0.4284 (1)	0.2350 (3)	0.0788 (2)	0.0484 (8)
C3	0.4341 (1)	0.0988 (3)	0.0290 (3)	0.0598 (9)
C4	0.4271 (1)	−0.0292 (3)	0.0835 (3)	0.0647 (9)
C5	0.4133 (2)	−0.0250 (3)	0.1867 (3)	0.067 (1)
C6	0.4069 (1)	0.1094 (3)	0.2370 (2)	0.0528 (8)
C7	0.3314 (1)	0.4892 (3)	0.1805 (2)	0.0431 (7)
C8	0.3082 (1)	0.6109 (4)	0.2291 (3)	0.072 (1)
C9	0.2538 (2)	0.6740 (4)	0.1775 (3)	0.089 (1)
C10	0.2231 (2)	0.6184 (4)	0.0831 (4)	0.082 (1)
C11	0.2443 (1)	0.4989 (4)	0.0353 (3)	0.080 (1)
C12	0.2994 (1)	0.4343 (4)	0.0833 (3)	0.0618 (9)

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

S1—P	1.930 (1)	P—C1	1.809 (3)
S2—S2′	2.0271 (9)	P—C7	1.811 (2)
S2—P	2.139 (1)		
S2′—S2—P	104.16 (4)	S2—P—C1	106.34 (9)
S1—P—S2	114.44 (4)	S2—P—C7	97.32 (9)
S1—P—C1	114.52 (9)	C1—P—C7	107.5 (1)
S1—P—C7	115.1 (1)		
S2′—S2—P—S1	31.90 (6)	S2′—S2—P—C7	153.74 (9)
S2′—S2—P—C1	−95.57 (9)	P—S2—S2′—P′	93.56 (4)

Compound (II)

Crystal data

$C_{24}H_{20}O_4P_2S_4$
M_r = 562.63
Orthorhombic
$P2_12_12_1$
a = 6.618 (1) Å
b = 11.584 (2) Å
c = 34.533 (4) Å
V = 2647 (1) Å^3
Z = 4
D_x = 1.41 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12-14°
μ = 0.491 mm^{-1}
T = 294 K
Plate
0.50 × 0.40 × 0.10 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.9243, $T_{\max}$ = 0.9762
3036 measured reflections
3036 independent reflections

2176 observed reflections [$I > 3.0\sigma(I)$]
$\theta_{\max}$ = 25.97°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 42$
3 standard reflections
frequency: 50 min
intensity variation: 0.99%

Refinement

Refinement on F
Final R = 0.034
wR = 0.043
S = 1.274
2176 reflections
307 parameters
H atoms riding
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\max}$ = 0.013
$\Delta\rho_{\max}$ = 0.2800 e Å^{-3}
$\Delta\rho_{\min}$ = −0.0915 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The differences in the refinements of the two enantiomorphs are small: R = 0.03403 and 0.03433, wR = 0.04307 and 0.04353, S = 1.274 and 1.288. The results from the marginally better refinement are quoted; however, the crystals were chosen from a racemic mixture.

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

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.3790 (2)	1.1861 (1)	0.95189 (4)	0.0640 (4)
S2	0.4926 (2)	0.92319 (9)	0.93016 (3)	0.0446 (3)
S3	0.3916 (2)	0.80382 (9)	0.88998 (3)	0.0455 (3)
S4	0.5492 (2)	0.6850 (1)	0.81147 (4)	0.0658 (4)
P1	0.3080 (2)	1.06342 (9)	0.91801 (3)	0.0434 (3)
P2	0.6322 (2)	0.78518 (9)	0.85192 (3)	0.0439 (3)
O1	0.0808 (4)	1.0162 (2)	0.91926 (8)	0.0485 (8)
O2	0.3197 (6)	1.0791 (2)	0.87300 (7)	0.068 (1)
O3	0.8239 (5)	0.7475 (2)	0.87654 (8)	0.0492 (8)
O4	0.6932 (5)	0.9139 (2)	0.84200 (8)	0.0536 (8)
C1	−0.0081 (7)	0.9803 (3)	0.9544 (1)	0.044 (1)
C2	−0.0148 (7)	0.8650 (3)	0.9623 (1)	0.049 (1)
C3	−0.1116 (7)	0.8292 (4)	0.9954 (1)	0.060 (1)
C4	−0.2020 (8)	0.9079 (4)	1.0194 (1)	0.066 (1)
C5	−0.1944 (9)	1.0242 (4)	1.0107 (1)	0.068 (1)
C6	−0.0969 (7)	1.0615 (4)	0.9778 (1)	0.058 (1)
C7	0.3764 (7)	1.1758 (3)	0.8511 (1)	0.047 (1)
C8	0.2455 (9)	1.2054 (4)	0.8222 (1)	0.062 (1)
C9	0.297 (1)	1.2934 (4)	0.7977 (2)	0.093 (2)
C10	0.469 (1)	1.3501 (5)	0.8030 (2)	0.107 (2)
C11	0.600 (1)	1.3217 (5)	0.8317 (2)	0.109 (2)
C12	0.5537 (9)	1.2309 (5)	0.8563 (2)	0.081 (2)
C13	0.8621 (6)	0.6313 (4)	0.8876 (1)	0.047 (1)
C14	0.7585 (9)	0.5829 (4)	0.9174 (1)	0.074 (2)
C15	0.809 (1)	0.4718 (5)	0.9287 (2)	0.097 (2)
C16	0.9595 (9)	0.4136 (4)	0.9110 (2)	0.086 (2)
C17	1.0653 (9)	0.4646 (4)	0.8819 (2)	0.086 (2)
C18	1.0174 (8)	0.5754 (4)	0.8693 (1)	0.063 (1)
C19	0.8172 (7)	0.9431 (3)	0.8104 (1)	0.049 (1)
C20	0.7465 (8)	1.0247 (4)	0.7853 (1)	0.057 (1)
C21	0.8682 (8)	1.0593 (4)	0.7549 (1)	0.066 (1)
C22	1.0565 (8)	1.0119 (4)	0.7499 (1)	0.073 (2)
C23	1.1255 (8)	0.9302 (5)	0.7755 (1)	0.075 (2)
C24	1.0067 (8)	0.8962 (4)	0.8063 (1)	0.060 (1)

Table 4. *Geometric parameters* (Å, °) *for* (II)

S1—P1	1.900 (2)	P1—O1	1.600 (3)
S2—S3	2.070 (1)	P1—O2	1.567 (3)
S2—P1	2.075 (2)	P2—O3	1.588 (3)
S3—P2	2.076 (2)	P2—O4	1.582 (3)
S4—P2	1.898 (2)		
S3—S2—P1	101.38 (6)	O1—P1—O2	96.5 (2)
S2—S3—P2	104.26 (6)	S3—P2—S4	107.92 (8)
S1—P1—S2	108.39 (7)	S3—P2—O3	107.6 (1)
S1—P1—O1	118.1 (1)	S3—P2—O4	103.6 (1)
S1—P1—O2	120.8 (1)	S4—P2—O3	117.2 (1)
S2—P1—O1	106.3 (1)	S4—P2—O4	119.4 (1)
S2—P1—O2	105.2 (1)	O3—P2—O4	99.9 (2)
P1—S2—S3—P2	112.03 (7)	S2—S3—P2—S4	−175.98 (7)
S3—S2—P1—S1	−179.27 (7)		

The title compounds were obtained from iodine oxidation of the corresponding anions, $Ph_2PS_2^-$, $(PhO)_2PS_2^-$ (Maier, 1965), and crystallized from ethanol. Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). Data collection: CAD-4 (Enraf-Nonius, 1977). Cell refinement: CAD-4. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: direct methods *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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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 71242 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1049]

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18-Crown-6–Bis(methyl 10-camphorsulfonate) (1/2)

Robert Chênevert and René Gagnon

Département de Chimie, Université Laval,
Québec (Qué.), Canada G1K 7P4

Francine Bélanger-Gariépy*

Département de Chimie, Université de Montréal,
CP 6128, Succ. A, Montréal (Qué.), Canada H3C 3J7

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Abstract

The 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) molecule has a regular conformation with approximate D_{3d} symmetry. The guest molecules (methyl 7,7-dimethyl-2-oxobicyclo[2.2.1]heptane-1-methanesulfonate) are coordinated above and below

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