Five organometallic structures have been reported with this phosphite triester as a coordinated ligand,* and their average P—O, O—C and C—C(apex) bond lengths are 1.62 (2), 1.46 (3) and 1.53 (2) Å, the scatter e.s.d.'s being given in parentheses. In comparison, the P—O bond length in the phosphate, 1.583 Å, is significantly shorter than in the average phosphite; the other two bond lengths are indistinguishable between the phosphite and phosphate. The O—P—O angle is notably contracted from that of O═P—O, 104.2 *vs* 114.3°. Comparison can also be made with the inorganic phosphates, of which the most complete analysis is reported by Murray-Rust, Bürgi & Dunitz (1975), to investigate distortions from T_d symmetry. The average P—O for PO_4^{3-} is 1.534 Å from their study, and the shortened P═O and lengthened P—O bond lengths are in remarkably good agreement with their results.

Finally, the distortion at C4, as reflected in the large range of C—C4—C5 angles, clearly indicates that C5 is displaced from an ideally symmetric position. The shortest intramolecular H···H contacts are H31···H61 2.28, H52···H12 2.37, H22···H62 2.48, H51···H11 2.50 and H51···H32 2.51 Å. The only intermolecular H···H contact below 2.7 Å is H22···H51′ (2.65 Å). Thus, the major repulsive interactions are intramolecular, and the tight H31···H61 contact is relieved by an increase in the C3—C4—C5 angle.

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* The five structures are: $[Re_2C_{44}H_{70}O_6P_6]$ and $[Re_2C_{44}H_{71}O_6P_6][BF_4]$ (Green, Huffman & Caulton, 1982), $[FeAs_2C_{20}H_{30}O_6P][BF_4]$ (Newlands & Mackay, 1986), $[UC_{24}H_{32}O_3P]$ and $[CeC_{24}H_{32}O_3P]$ (Brennen, Stults, Anderson & Zalkin, 1988). $[Ru_4C_{44}H_{47}O_{15}P_3]$ (Bruce, Nicholson, Patrick & White, 1983) has also been reported, but the ligand is disordered and has not been included in our survey averages.

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Bis(diethylthiophosphoryl) Trisulfide

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Abstract. $C_8H_{20}P_2S_5$, $M_r = 338.52$, monoclinic, $P2_1/c$, $a = 11.998$ (3), $b = 12.678$ (4), $c = 12.181$ (6) Å, $\beta = 115.96$ (3)°, $V = 1666$ (2) Å^3, $Z = 4$, $D_x = 1.35$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 8.3$ cm^{-1}, $F(000) = 712$, $T = 294(1)$ K, $R = 0.044$ for 1350 unique observed reflections of 3600 total data. This is the first bis(dialkylthiophosphoryl) trisulfide to be structurally characterized. The thiophosphoryl groups are in a *trans* conformation and the geometry about the S—S bonds is similar to that expected for sulfuranes.

Introduction. There is long standing interest in the chemistry of organophosphorus sulfides because of their applications as pesticides (Fest & Schmidt, 1982), motor oil additives (Molyneux, 1967) and in the vulcanization of rubber (McCleverty, Kowalski, Bailey, Mulvaney & O'Cleirigh, 1983). Recent studies have described the characterization of dialkylthiophosphoryl sulfides in solution and in condensed phases by use of NMR spectroscopy (Chu & Potrzebowski, 1990; Komber, Grossmann & Kretschmer, 1988; Neels, Grimmer, Meisel, Wolf &

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Table 1. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s*

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $8\pi^2/3$ × trace (orthogonalized U tensor).

	x	y	z	B (Å^2)
S1	0.4379 (2)	−0.0726 (2)	0.8047 (2)	4.62 (5)
S2	0.5765 (1)	0.0551 (2)	0.6741 (1)	4.23 (4)
S3	0.7014 (1)	0.1755 (2)	0.7024 (1)	4.72 (4)
S4	0.8747 (1)	0.1086 (2)	0.7737 (1)	4.14 (4)
S5	1.0744 (1)	0.0052 (2)	0.7003 (2)	4.61 (5)
P1	0.5552 (1)	0.0425 (1)	0.8371 (1)	3.25 (4)
P2	0.9098 (1)	0.0659 (1)	0.6241 (1)	3.22 (4)
C1	0.5075 (5)	0.1701 (5)	0.8656 (5)	4.9 (2)
C2	0.3772 (6)	0.1995 (6)	0.7770 (7)	6.8 (2)
C3	0.7088 (5)	0.0226 (5)	0.9604 (5)	4.4 (2)
C4	0.7674 (5)	−0.0811 (5)	0.9599 (6)	6.3 (2)
C5	0.7851 (5)	−0.0181 (5)	0.5292 (5)	4.3 (2)
C6	0.7865 (6)	−0.1269 (5)	0.5830 (6)	6.4 (2)
C7	0.8925 (5)	0.1843 (5)	0.5357 (5)	4.4 (2)
C8	0.9876 (6)	0.2676 (6)	0.5983 (6)	6.5 (2)

Table 2. *Bond distances* (Å), *angles* (°) *and selected torsion angles* (°)

S1—P1	1.944 (2)	P1—C3	1.814 (5)
S2—S3	2.060 (3)	P2—C5	1.788 (5)
S2—P1	2.116 (3)	P2—C7	1.806 (6)
S3—S4	2.052 (2)	C1—C2	1.507 (8)
S4—P2	2.112 (3)	C3—C4	1.492 (9)
S5—P2	1.937 (2)	C5—C6	1.524 (9)
P1—C1	1.799 (7)	C7—C8	1.495 (8)
S3—S2—P1	106.1 (1)	S4—P2—C5	106.5 (2)
S2—S3—S4	107.0 (1)	S4—P2—C7	106.7 (2)
S3—S4—P2	106.77 (9)	S5—P2—C5	117.5 (2)
S1—P1—S2	103.8 (1)	S5—P2—C7	116.3 (2)
S1—P1—C1	116.8 (2)	C5—P2—C7	105.3 (2)
S1—P1—C3	116.5 (2)	P1—C1—C2	113.7 (4)
S2—P1—C1	107.0 (2)	P1—C3—C4	115.4 (4)
S2—P1—C3	106.9 (2)	P2—C5—C6	114.4 (3)
C1—P1—C3	105.0 (3)	P2—C7—C8	114.8 (4)
S4—P2—S5	103.62 (9)		
P1—S2—S3—S4	90.41 (0.11)	S2—S3—S4—P2	89.17 (0.12)
S3—S2—P1—S1	−179.54 (0.10)	S3—S4—P2—S5	179.55 (0.11)

Jancke, 1987). Our interests lie in the structure and bonding of disulfides of formula $[R_2P(S)]_2S_2$ where R = alkyl, alkoxy, aryl or aryloxy. We have recently reported structural evidence for a low *trans* barrier to rotation about the disulfide bond in contrast to that found for dialkyl disulfides, and evidence for a π contribution to the P—S single bond (Buranda, Gallacher & Pinkerton, 1991; Gallacher, 1989).

It has been previously observed that the synthesis of the disulfide $[Et_2P(S)]_2S_2$ often gives rise to a significant quantity of the trisulfide $[Et_2P(S)]_2S_3$ as well (Maier, 1965). While preparing samples of the disulfide for X-ray analysis, we also obtained X-ray quality crystals of the trisulfide from ethanol solution and have thus determined its structure.

Experimental. The title compound was obtained as a secondary product in the synthesis of $[Et_2P(S)]_2S_2$ from iodine oxidation of $Et_2PS_2.Na$ (Maier, 1965). Crystals were obtained from slow evaporation of an ethanol solution.

Colorless elongated plate, 0.55 × 0.30 × 0.15 mm, mounted on a glass fiber, Enraf–Nonius CAD-4 diffractometer, graphite monochromator, ω–2θ-scan technique, ω-scan width = $(0.7 + \tan\theta)°$, ω-scan time 1–7° min^{-1}, backgrounds obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974), unit-cell constants from the setting angles of 25 reflections in the range $9 < \theta < 12°$, empirical absorption correction (from 0.946 to 0.999 on I), maximum $2\theta = 52.0°$, $0 < h < 14$, $0 < k < 15$, $-14 < l < 13$, three intensity check reflections monitored every 50 min, anisotropic decay correction (from 0.967 to 1.146 on I), reflection averaging $R_{\text{int}} = 3.9\%$, 3600 total reflections measured, 3434 unique, solution by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refinement by full-matrix least squares using 1350 reflections with $F_o^2 > 3.0\sigma(F_o^2)$, function minimized was $\sum w(|F_o| - |F_c|)^2$, weight w was defined as $4F_o^2/\sigma^2(F_o^2)$, hydrogen atoms refined as riding atoms, 156 refined parameters, $R = 0.044$, $wR = 0.049$, $S = 1.14$, largest shift = 0.03σ, highest peak in final difference map 0.30 (8), lowest peak −0.15 (8) e Å^{-3}. Scattering factors for neutral atoms and the values for $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); computer programs *SDP* (Frenz, 1978). Final atomic coordinates are reported in Table 1, bond lengths and angles in Table 2.* Figure prepared by *ORTEP*II (Johnson, 1976).

Discussion. The molecule (Fig. 1) consists of two tetrahedral dialkyldithiophosphoryl units bridged by a sulfur atom (S3). As shown in Table 2, the tetrahedral units are distorted. The smallest valence angle is S—P=S (103.7° average) as observed for

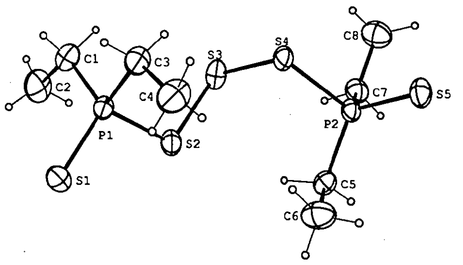

Fig. 1. Bis(diethylthiophosphoryl) trisulfide, 30% probability ellipsoids, ideal hydrogen-atom positions.

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* Tables of calculated hydrogen positional parameters, anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54594 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0349]

analogous disulfides with a *trans* S—S—P=S geometry (Buranda, Gallacher & Pinkerton, 1991; Gallacher, 1989; Lawton, 1970; Tkachev, Atovmyan & Shchepinov, 1976; Yadav, Bohra, Mehrotra, Rai & Srivastava, 1983). The S=P—C angle (116.8° average) is larger than the S—P—C angle (106.8° average) for steric reasons (S=P is shorter than S—P). The S=P distance (1.941 Å average) is comparable to that of alkyl-substituted disulfides but longer than that observed for the alkoxy analogs. The S—P distances (2.114 Å average) follow the same trend. The S—S distances (2.056 Å average) are as expected for normal single bonds (Meyer, 1976; Muller & Diemann, 1987) and the valence angles at sulfur are all close to tetrahedral values (106.6° average).

Analysis of the torsion angles of the S=P—S—S—S—P=S skeleton shows that each end of the molecule has a planar *trans* geometry (S=P—S—S = 179.6° average). Although this may be construed as a simple steric effect, from our studies of disulfide analogs we believe there is also an electronic driving force to obtain planarity of this unit (Buranda, Gallacher & Pinkerton, 1991; Gallacher, 1989). The geometry about the S—S bonds is more in keeping with simple sulfuranes with torsion angles close to 90° (Meyer, 1976; Muller & Diemann, 1987). The conformation of the P—S—S—S—P unit is similar to that of the *trans* S_5^- ion (Meyer, 1976; Muller & Diemann, 1987).

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Structures of Methyl 7-Phenyldibenz[*a,j*]anthracene-14-carboxylate and Methyl 7-Phenylbenzo[1,2-*h*:5,4-*h'*]diquinoline-14-carboxylate: Twisted Aromatic Spacers Containing Bay-Region Esters

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Abstract. $C_{30}H_{20}O_2$, (1), $M_r = 412.49$, triclinic, $P1$ (C_i^1), $a = 11.301$ (7), $b = 12.069$ (3), $c = 9.777$ (2) Å, $\alpha = 96.12$ (2), $\beta = 111.59$ (4), $\gamma = 114.68$ (3)°, $V = 1072$ (2) Å^3, $Z = 2$, $D_x = 1.278$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.73$ cm^{-1}, $F(000) = 432$, $T = 299$ K, final $R = 0.065$ for 1231 observed reflections. $C_{28}H_{18}N_2O_2$, (2), $M_r = 414.46$, monoclinic, $I2/a$ (C_{2h}^6), $a = 20.039$ (10), $b =$

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