between the two pairs of chains C(2)–C(19), C(20)–C(37) and C(38)–C(54), C(56)–C(73). The phenyl rings show deviations from planarity: r.m.s.d.'s 0.0255 [C(6)–C(11)], 0.0069 [C(24)–C(29)], 0.0168 [C(42)–C(47) and 0.0074 Å [C(60)–C(65)].

The steric hindrance induced by the presence of two *tert*-butyl moieties in *ortho* positions to each phenolic OH group prevents the formation of strong intermolecular hydrogen bonds. However, two weak intermolecular interactions between phenolic OH and ester O═C groups [O(3)···O(11)(x, $1-y$, $z+\frac{1}{2}$) 3.14 (1) and O(6)···O(8)(x, $1-y$, $z-\frac{1}{2}$) 3.17 (1) Å] are responsible for the formation of layers parallel to the *ab* plane. No hydrogen bond is formed between different layers.

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Structure of an Organic Phosphate: $O{=}P(OCH_2)_3CCH_2CH_3$

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Abstract. 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane 1-oxide, $C_6H_{11}O_4P$, $M_r = 178.13$, orthorhombic, *Pbca*, $a = 11.356\,(1)$, $b = 11.771\,(1)$, $c = 12.290\,(1)$ Å, $V = 1642.8\,(2)$ Å^3, $Z = 8$, $D_x = 1.440$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 2.91$ cm^{-1}, $F(000) = 752$, $T \simeq 295$ K, goodness of fit = 1.76, $R = 0.047$, $wR = 0.059$ for 802 reflections with $I > 3\sigma(I)$. The P═O bond length is 1.454 Å, and the average P—O, O—C and C—C bond lengths are 1.583, 1.468 and 1.541 Å (all corrected for librational motion). The average O═P—O and O—P—O angles are 114.3 and 104.2°.

Introduction. Phosphines and phosphites are commonly employed as ligands in organometallic synthesis, and a number of organometallic–phosphite complexes have been prepared with use of the ligand 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_2CH_3$. It is easily oxidized to the phosphate in air. The phosphite and the phosphate triesters have, nominally, C_{3v} symmetry. Since no report on the structure has appeared, we report herein on a precise determination of the metrical details of this $O{=}P(OR)_3$ structure.

Experimental. Single clear colorless crystals from a cold solution of toluene/hexane. Specimen, 0.12 × 0.20 × 0.32 mm, mounted on a glass fiber with epoxy. Space group *Pbca*, No. 61 (systematic absences: $0kl$, k odd, $h0l$, l odd, and $hk0$, h odd). Diffractometry: Enraf–Nonius CAD-4 automated diffractometer, 295 K, Mo $K\alpha$ radiation with graphite monochromator, $\lambda = 0.7107$ Å. Cell constants and orientation matrix by least-squares refinement of the setting angles of 22 reflections, determined at $\pm\theta$, in the range $19.9 < \theta < 25{\cdot}1°$. Intensity data with ω–2θ scans at 2.0° min^{-1} (in θ), ω-scan width = $(0.60 + 0.347\tan\theta)°$, maximum $2\theta = 60°$, ($\pm h$, $-k$, $\pm l$, in the range h 0–15, k 0–16, l 0–17). Three check reflections every 120 min, average variation approximately 4.6%; no decay correction employed. A total of 6455 intensities were collected, and reduced to F_o's. Structure derivation: *MITHRIL* (Gilmore, 1983). Refinement: full-matrix least squares on F, weight $w = 4F_o^2/\sigma^2(F_o^2)$, analytic scattering factors with f' and f'' components of anomalous dispersion (*International Tables for X-ray Crystallography*, 1974, Vol. IV, Table 2.2B) included in the calculations of all non-H atoms.

The H atoms were generated at idealized calculated positions by assuming a C—H bond length of 0.95 Å and the appropriate sp^3 geometry. On the methyl group, they were idealized by least-

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squares refinement of the coordinates derived from a difference Fourier map. All H atoms were then included in the calculations with fixed isotropic U values of 1.2 times the value of U of the attached atom, and constrained to 'ride' on the attached atom.

The refinement of the coordinates and isotropic U values for all non-H atoms was continued to convergence. At that stage the data were corrected for absorption by use of an empirical scheme based on the absorption surface method of Walker & Stuart (1983). The maximum and minimum correction factors applied to F_o were 1.1233 and 0.5702. After averaging over *mmm* symmetry (R from merging on $F = 0.078$), there were 2546 averaged observations, 802 with $I > 3\sigma(I)$, which were used in the subsequent cycles of refinement. Included in the refinement was a parameter for the correction of secondary extinction with an isotropic coefficient (Stout & Jensen, 1989); the final value was 1.35 (5) × 10^{-6}. In the final cycle, 101 parameters were refined using the 802 observations with $I > 3\sigma(I)$, and the maximum and average shift/e.s.d. ratios were less than 0.01. As a result, the final goodness of fit was 1.76, $R = 0.047$ and $wR = 0.059$. An analysis of wR in terms of F_o, $\sin\theta/\lambda$ and various combinations of h, k, l indicated no unusual trends. Maximum and minimum heights in the final difference Fourier map were at a density of 0.32 (5) and −0.21 (5) e Å^{-3}. Enraf–Nonius *SDP* (1985) and *ORTEP* (Johnson, 1965) were used in this analysis.

Discussion. The coordinates and U_{eq} values of the non-H atoms are given in Table 1, and selected bond lengths and angles in Table 2,* including the averaged values of chemically equivalent groups. Included in Table 2 are corrected values of the bond lengths and angles, as derived from a rigid-body analysis of the U_{ij} values by *THMB* (Trueblood, 1978). The agreement between the observed and calculated U_{ij} values is very good, as indicated by the relatively low $R = 0.060$, derived from the sum of weighted residuals on U_{ij}. The librational eigenvalues in the inertial frame are $L_i = 4.07$, 4.84 and 8.18°, and $T_i = 0.21$, 0.23 and 0.25 Å, corresponding to normal mode frequencies in the 25–50 cm^{-1} range. Fig. 1 shows a perspective view of the molecule with atomic labelling scheme.

Table 1. *Atom coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

U_{eq} is $(1/3)\sum_{i=1}^{3} r_i^2$, where r_i are the root-mean-square amplitudes of the anisotropic Gaussian displacement parameters.

	x	y	z	U_{eq}
O	−173 (3)	1652 (3)	3340 (3)	96
P	453 (1)	2342 (1)	2558 (1)	65
O1	−358 (3)	3042 (3)	1783 (2)	74
O2	1273 (3)	1663 (2)	1771 (3)	76
O3	1291 (3)	3249 (3)	3083 (2)	83
C1	274 (4)	3767 (4)	1014 (4)	62
C2	1905 (4)	2361 (4)	983 (3)	67
C3	1919 (4)	3947 (4)	2295 (4)	74
C4	1602 (3)	3615 (3)	1144 (4)	53
C5	2215 (4)	4356 (4)	266 (4)	80
C6	3507 (5)	4263 (5)	180 (5)	106

Table 2. *Selected bond lengths* (Å) *and angles* (°) (*averages over chemically equivalent groups*)

	Uncorrected	Average (σ_1,σ_2)*	Corrected	Average
O—P	1.445 (4)		1.454	
P—O1	1.560 (3)		1.579	
P—O2	1.562 (3)	1.563 (2,3)	1.582	1.583
P—O3	1.570 (4)		1.588	
C1—O1	1.462 (5)		1.471	
C2—O2	1.459 (5)	1.459 (4,2)	1.468	1.468
C3—O3	1.456 (6)		1.466	
C4—C1	1.527 (6)		1.546	
C4—C2	1.528 (6)	1.522 (4,6)	1.546	1.541
C4—C3	1.511 (6)		1.531	
C4—C5	1.552 (6)		1.562	
C5—C6	1.475 (7)		1.492	
O—P—O1	114.3 (2)			
O—P—O2	114.7 (2)	114.3 (1,3)		
O—P—O3	114.0 (2)			
O1—P—O2	104.1 (2)			
O1—P—O3	104.4 (2)	104.2 (1,1)		
O2—P—O3	104.0 (2)			
P—O1—C1	114.4 (3)			
P—O2—C2	114.6 (2)	114.4 (2,1)		
P—O3—C3	114.1 (3)			
O1—C1—C4	110.4 (3)			
O2—C2—C4	110.3 (3)	110.5 (2,1)		
O3—C3—C4	111.0 (4)			
C1—C4—C2	108.8 (3)			
C1—C4—C3	107.7 (3)	108.3 (2,2)		
C2—C4—C3	108.5 (3)			
C1—C4—C5	107.8 (3)			
C2—C4—C5	110.6 (3)			
C3—C4—C5	113.4 (4)			
C4—C5—C6	117.1 (4)			

* Weighted average = $(\sum_i x_i/\sigma_i^2)/(\sum_i 1/\sigma_i^2)$, $\sigma_1 = (\sum_i \sigma_i^2/6)^{1/2}$ and $\sigma_2 = [\sum_i (x_i - \bar{x})^2/6]^{1/2}$.

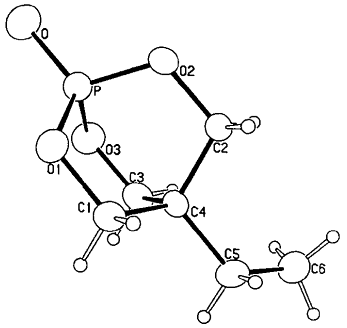

Fig. 1. Perspective view of the molecule showing the atom-labelling scheme for the non-H atoms. Atoms are represented by Gaussian ellipsoids at the 20% probability level.

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* Lists of fractional coordinates for H atoms, anisotropic Gaussian displacement parameters for non-H atoms, least-squares-planes information, torsion angles and structure-factor amplitudes, and a stereoview of the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54641 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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, β = 115.96 (3)°, V = 1666 (2) Å^3, Z = 4, D_x = 1.35 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 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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