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A pentaerythritol-derived spirodiphosphonate

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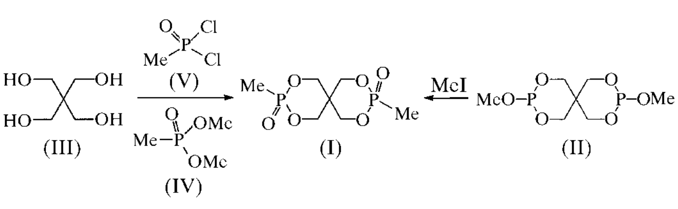
The title spirodiphosphonate, 3,9-dimethyl-2,4,8,10-tetraoxa-3λ^5,9λ^5-diphosphaspiro[5.5]undecane-3,9-dione, $C_7H_{14}O_6P_2$, a polymer additive, has crystallographic symmetry 2. At 100 K, its six-membered rings have chair conformations, with endocyclic torsion-angle magnitudes in the range 51.87 (8)–58.93 (9)°. The P═O distance is 1.4749 (8) Å, while the P—C(methyl) distance is 1.7691 (12) Å.

Comment

Many organophosphorus compounds are commercially available for use as polymer additives. The unique diphosphonate 3,9-dimethyl-2,4,8,10-tetraoxa-3λ^5,9λ^5-diphosphaspiro[5.5]-undecane-3,9-dione, (I) (CAS #3001-98-7), has been claimed to be effective in modifying the stability of resins such as polyolefins, polycarbonates and polycarbonate blends (Granzow, 1981; Hardy *et al.*, 1979; Horn, 1979). We determined the structure of (I) as part of an effort towards the design of even more effective organophosphorus additives.



The synthesis of (I) is reported to proceed by the Arbuzov rearrangement of pentaerythritol dimethyldiphosphite, (II) (Mukmenev & Kamai, 1963; Friedman, 1964), the transesterification of pentaerythritol, (III), with diphenyl methylphosphonate (Honig & Weil, 1977), and the reaction of methylphosphonic dichloride, (V), with pentaerythritol in dimethyl methylphosphonate, (IV) (Kiefer, 1983). The latter procedure gave high purity (I) in good yield, and was our method of choice. The Arbuzov rearrangement of (II) was found to be uncontrollable; heating the reactants above approximately 448 K produced a sudden and violent exotherm resulting in a massive foaming char. The transesterification approach proceeded, with difficulty, to yield (I). An attempt to substitute a more convenient reagent, *i.e.* dimethyl methylphosphonate, for the diphenyl methylphosphonate was not successful.

The molecule lies on a crystallographic twofold axis, as seen in Fig. 1. The two C—C—C angles which lie across the twofold axis are unequal, with C3—C1—C3^i being 4.91 (14)° larger than C2—C1—C2^i [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$], consistent with the steric difference in this conformation between opposite ends of the molecule in the twofold direction. A similar asymmetry exists in two phosphites having similar spiro ring systems, conformations, and approximate twofold symmetry (Heinemann *et al.*, 1994; Barren *et al.*, 1995). The six-membered rings of (I) have the chair conformation, with endocyclic torsion angles having magnitudes within the range 51.87 (8)–58.93 (9)°. While boat (Day *et al.*, 1984) and half-chair (Drew & Rodgers, 1972) conformations have been observed in 2-dioxaphosphorinane rings, the chair conformation seen here is more common (Ul-Haque *et al.*, 1970; Patois *et al.*, 1990; Killean *et al.*, 1971; Browning *et al.*, 1996; Edmundson *et al.*, 1989). The P═O bond has length 1.4749 (8) Å, and is in an axial position of the chair. The P═O bond is more typically in the equatorial position (Ul-Haque *et al.*, 1970; Patois *et al.*, 1990; Killean *et al.*, 1971; Browning *et al.*, 1996; Edmundson *et al.*, 1989). The difference may thus be attributed to the spiro ring system in (I), which is not present in the other 2-dioxaphosphorinanes. The P—C distance in (I), 1.7691 (12) Å, is similar to those in 5-*tert*-butyl-2-methyl-2-oxo-1,3,2-dioxaphosphorinane [1.81 (3) Å] (Ul-Haque *et al.*, 1970) and 2,5,5-trimethyl-1,3,2-dioxaphosphorinan-2-one [1.776 (3) and 1.783 (3) Å; Patois *et al.*, 1990].

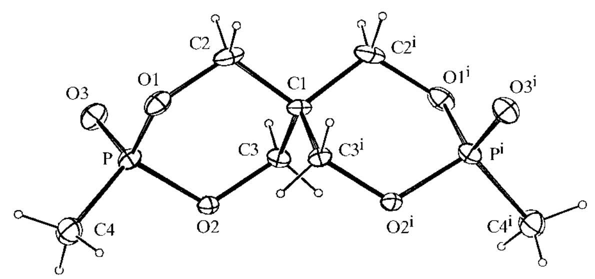


Figure 1
A view of the molecule of (I) with ellipsoids plotted at the 50% probability level [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$].

Experimental

The title compound was prepared by reaction of methylphosphonic dichloride with pentaerythritol in dimethyl methylphosphonate according to the method of Kiefer (1983). Crystals were grown from a methanol solution.

Crystal data

$C_7H_{14}O_6P_2$	D_x = 1.556 Mg m^{-3}
M_r = 256.1	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25 reflections
a = 16.4560 (14) Å	θ = 11.4–18.2°
b = 5.5761 (9) Å	μ = 0.404 mm^{-1}
c = 11.9512 (12) Å	T = 100 K
β = 94.517 (7)°	Fragment, colorless
V = 1093.2 (4) Å^3	0.57 × 0.55 × 0.42 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer (with Oxford Cryosystems Cryostream cooler)	1915 reflections with $I > 3\sigma(I)$
	$R_{\rm int}$ = 0.025
	$\theta_{\rm max}$ = 35°
$\theta/2\theta$ scans	$h = -26 \rightarrow 22$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = -8 \rightarrow 8$
	$l = -19 \rightarrow 16$
$T_{\rm min}$ = 0.83, $T_{\rm max}$ = 0.85	3 standard reflections
6104 measured reflections	frequency: 60 min
2232 independent reflections	intensity decay: 0.5%

Refinement

Refinement on F^2	$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$R(F)$ = 0.031	$(\Delta/\sigma)_{\rm max}$ = 0.008
$wR(F^2)$ = 0.047	$\Delta\rho_{\rm max}$ = 0.64 e Å^{-3}
S = 1.91	$\Delta\rho_{\rm min}$ = −0.57 e Å^{-3}
2137 reflections	Extinction correction: isotropic (Zachariasen, 1963)
98 parameters	
All H-atom parameters refined	Extinction coefficient: 8 (2) × 10^{-7}

Table 1
Selected geometric parameters (Å, °).

P—O1	1.5924 (8)	O1—C2	1.4611 (14)
P—O2	1.5892 (7)	O2—C3	1.4539 (12)
P—O3	1.4749 (8)	C1—C2	1.5315 (13)
P—C4	1.7691 (12)	C1—C3	1.5315 (13)
O1—P—O2	103.25 (4)	C2—C1—C2$^{\rm i}$	107.16 (9)
O3—P—C4	116.09 (6)	C2—C1—C3	109.32 (5)
P—O1—C2	115.67 (6)	C3—C1—C3$^{\rm i}$	112.11 (9)
P—O2—C3	116.57 (6)		
O2—P—O1—C2	51.87 (8)	P—O2—C3—C1	58.50 (9)
O1—P—O2—C3	−52.02 (7)	C3—C1—C2—O1	58.49 (9)
P—O1—C2—C1	−58.93 (9)	C2—C1—C3—O2	−57.95 (10)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

C—H distances fell within the range 0.921 (13)–1.010 (13) Å and $U_{\rm iso}$ values for H atoms were within the range 0.019 (4)–0.047 (5) Å^2.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR* (Burla *et al.*, 1989); program(s) used to refine structure: *LSFM* in *MolEN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *CIFGEN* in *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1533). Services for accessing these data are described at the back of the journal.

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