H-atom positions could be found from difference Fourier maps, but refinement resulted in slightly deformed arrangements. Thus, for final refinement, H atoms were set at calculated positions and included as riding atoms in refinement.

Data collection: *CAD*-4 *EXPRESS* (Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*-92 (Keller, 1992). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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8-(4-Methylphenoxy)-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*][1,3,2]dioxaphosphocine 8-Sulfide

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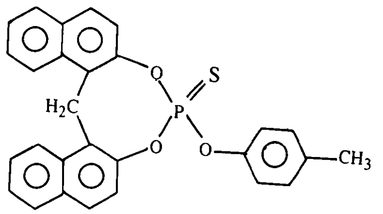
Abstract

The eight-membered dioxaphosphocine ring in $C_{28}H_{21}O_3PS$ adopts a distorted boat conformation with the phosphoryl S atom axial and the phenoxy group equatorial. The phenyl ring takes a perpendicular orientation with respect to the two naphthalene ring systems; the dihedral angle between the naphthalene planes is 64.78 (7)°. The structure is stabilized by van der Waals interactions.

Comment

The crystal structures and conformations of organophosphorus compounds have become the subject of intense study due to their involvement in many biological processes (Corbridge, 1977; Emsley & Hall, 1976; Sankara Reddy & Devendranath Reddy, 1995). The proven toxic effects of phosphoric acid esters on pests and their possible application as lubricant additives prompted the synthesis of a new class of organophosphorus heterocyclic esters (1,3,2-dioxaphosphocine derivatives) (Reddy, 1988). To our knowledge, there have been few reports of structural studies of eight-membered heterocyclic organophosphorus compounds, which prompted us to undertake the crystal structure determination of 1,3,2-dioxaphosphocin derivatives (Mani Naidu, 1990). The present work on the title compound, (I), forms part of our studies of the structure and conformation of 1,3,2-dioxaphosphocine derivatives. A perspective view of the molecule with the atomic numbering scheme is shown in Fig. 1.



(I)

The bond lengths and angles in this structure have normal values. The P=S bond length of 1.894 (1) Å agrees well with the reported value of 1.894 (1) Å for 6-(4-chlorophenoxy)dibenzo[*d*,*f*][1,3,2]dioxaphosphocine 6-sulfide (Sivakumar, Subramanian, Natarajan, Krishnaiah & Ramamurthy, 1989). The dioxaphosphocine ring adopts a distorted boat conformation. Atoms O(1), C(1), C(12) and C(21) are puckered to the same side of the least-squares plane through the atoms P, O(2), C(10) and C(11) with varying magnitudes. The deviations are 0.896 (2) [O(1)], 0.436 (3) [C(1)], 1.102 (3) [C(12)] and 1.081 (3) Å [C(21)]. The conformation of the dioxaphosphocine ring has been found in all the naphtho-substituted structures reported so far. For example, a similar conformation was observed for 8-(2,3-dimethylphenyl)-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*][1,3,2]dioxaphosphocine 8-oxide (Reddy, 1988). The substitution of sulfur for the phosphoryl oxygen does not appear to have any effect on the molecular conformation. This dioxaphophocine ring with naphtho fusion was not found in any of the canonical conformations described by Evans & Boeyens (1988) for eight-membered ring systems. The sulfur substituent is axial and the phenoxy group is equatorial.

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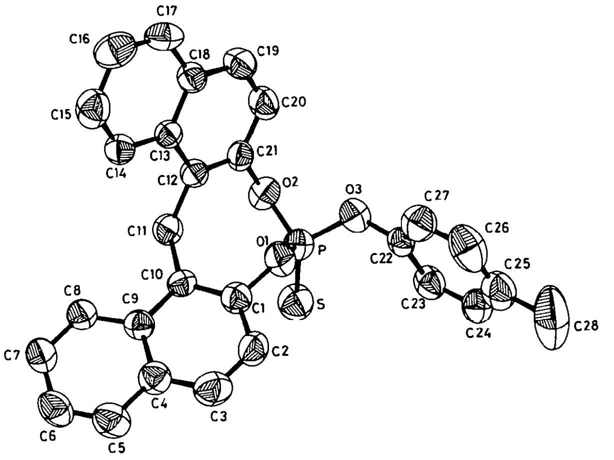

Fig. 1. View of the molecule drawn using *ORTEP*II (Johnson, 1976) with 50% probability ellipsoids.

The C_{sp^2}—C_{sp^2} bond distances in the two naphthalene ring systems vary from 1.346 (4) to 1.435 (4) Å with an average value of 1.393 (4) Å. Both groups are planar with a dihedral angle of 64.78 (7)° between them. One of the naphthalene groups [C(12)–C(21)] is found to be parallel to the *ac* plane. The phenyl ring is also planar and is almost perpendicular to the two naphthalene planes; the dihedral angles between the plane of the phenyl ring and the naphthalene planes are 86.25 (7) and 80.81 (8)°. This feature of the molecule is found in naphtho-fused dioxaphosphocine structures (Mani Naidu, 1990). There are no unusual short contacts between the molecules and the crystal structure is stabilized by van der Waals interactions.

Experimental

0.01 mol of bis(2-hydroxy-1-naphthyl)methane in 30 ml of dry benzene and 0.02 mol of triethylamine in 20 ml of benzene were stirred together at room temperature, and 0.01 mol of 4-methylphosphothioic dichloride in 30 ml of dry benzene was added dropwise over a period of 30 min. The reaction mixture was refluxed with stirring for 10 h. The progress of the crystallization was monitored by thin-layer chromatography. The solid triethylamine hydrochloride salt was removed by filtration. The filtrate was concentrated in a rotary evaporator and the residue, after washing with water, was recrystallized from 1-butanol.

Crystal data

$C_{28}H_{21}O_3PS$
$M_r = 468.51$
Monoclinic
$P2_1/c$
$a = 9.803\ (2)$ Å
$b = 10.467\ (3)$ Å
$c = 23.386\ (4)$ Å
$\beta = 95.69\ (1)^\circ$
$V = 2387.8\ (9)$ Å^3
$Z = 4$
$D_x = 1.30$ Mg m^{-3}
$D_m = 1.32$ Mg m^{-3}
D_m measured by flotation in KI

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 15$–25°
$\mu = 0.22$ mm^{-1}
$T = 298$ K
Needle
0.40 × 0.28 × 0.20 mm
Colourless

Data collection

Nicolet *P3F* diffractometer
ω scans
Absorption correction: analytical
$T_{\min} = 0.917$, $T_{\max} = 0.968$
4209 measured reflections
4209 independent reflections
2268 observed reflections $[I > 3\sigma(I)]$

$\theta_{\max} = 25^\circ$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -27 \rightarrow 27$
3 standard reflections monitored every 100 reflections
intensity decay: <2%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.051$
$S = 1.35$
2268 reflections
298 parameters
$w = 1/[\sigma^2(F_o) + 0.0045F_o^2]$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ 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 displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.4099 (1)	0.2115 (1)	0.1483 (1)	6.47 (3)
P	0.2184 (1)	0.1823 (1)	0.1383 (1)	4.53 (2)
O(1)	0.1604 (2)	0.1063 (2)	0.0829 (1)	4.28 (5)
O(2)	0.1326 (2)	0.3102 (2)	0.1382 (1)	4.94 (6)
O(3)	0.1503 (2)	0.1046 (2)	0.1858 (1)	5.19 (6)
C(1)	0.2109 (3)	0.1149 (3)	0.0284 (1)	4.06 (8)
C(2)	0.2776 (4)	0.0063 (3)	0.0104 (1)	5.13 (10)
C(3)	0.3269 (4)	0.0062 (3)	−0.0415 (1)	5.83 (11)
C(4)	0.3086 (3)	0.1125 (3)	−0.0779 (1)	4.70 (10)
C(5)	0.3594 (4)	0.1130 (4)	−0.1326 (2)	6.13 (13)
C(6)	0.3415 (4)	0.2153 (4)	−0.1679 (1)	6.61 (12)
C(7)	0.2750 (3)	0.3226 (4)	−0.1503 (1)	5.66 (11)
C(8)	0.2240 (3)	0.3268 (3)	−0.0981 (1)	4.46 (8)
C(9)	0.2391 (3)	0.2213 (3)	−0.0599 (1)	3.82 (8)
C(10)	0.1889 (3)	0.2225 (3)	−0.0043 (1)	3.48 (7)
C(11)	0.1247 (3)	0.3407 (3)	0.0187 (1)	3.96 (8)
C(12)	−0.0049 (3)	0.3263 (3)	0.0485 (1)	3.66 (11)
C(13)	−0.1384 (3)	0.3299 (3)	0.0173 (1)	3.64 (11)
C(14)	−0.1580 (3)	0.3318 (3)	−0.0432 (1)	4.30 (8)
C(15)	−0.2856 (4)	0.3400 (3)	−0.0711 (1)	5.36 (10)
C(16)	−0.4002 (4)	0.3467 (4)	−0.0405 (2)	6.23 (11)
C(17)	−0.3862 (3)	0.3437 (4)	0.0175 (2)	5.54 (11)
C(18)	−0.2556 (3)	0.3336 (3)	0.0487 (1)	4.18 (8)
C(19)	−0.2376 (3)	0.3280 (3)	0.1093 (1)	5.00 (10)
C(20)	−0.1123 (3)	0.3178 (3)	0.1382 (1)	4.81 (9)
C(21)	0.0018 (3)	0.3180 (3)	0.1068 (1)	4.07 (8)
C(22)	0.1731 (3)	−0.0274 (3)	0.1960 (1)	4.28 (9)
C(23)	0.2945 (3)	−0.0703 (3)	0.2222 (1)	4.81 (10)
C(24)	0.3094 (4)	−0.1992 (4)	0.2342 (1)	5.70 (11)
C(25)	0.2076 (5)	−0.2848 (4)	0.2212 (1)	5.90 (12)
C(26)	0.0888 (5)	−0.2380 (4)	0.1950 (2)	6.82 (14)
C(27)	0.0677 (4)	−0.1111 (4)	0.1819 (1)	5.80 (12)
C(28)	0.2278 (7)	−0.4236 (5)	0.2341 (2)	11.7 (3)

Table 2. *Selected geometric parameters (Å, °)*

S—P	1.894 (1)	P—O(2)	1.581 (2)
P—O(1)	1.578 (2)	O(1)—C(1)	1.415 (4)
P—O(3)	1.577 (2)	O(2)—C(21)	1.415 (3)
O(3)—C(22)	1.416 (4)	C(1)—C(2)	1.397 (5)
C(1)—C(10)	1.366 (4)	C(10)—C(11)	1.511 (4)
C(11)—C(12)	1.516 (4)	C(12)—C(21)	1.361 (3)
S—P—O(3)	118.7 (1)	S—P—O(2)	112.6 (1)
O(2)—P—O(3)	100.1 (1)	P—O(2)—C(21)	120.3 (2)
O(1)—P—O(3)	100.1 (1)	S—P—O(1)	117.1 (1)
O(1)—P—O(2)	106.1 (1)	O(1)—C(1)—C(10)	120.4 (2)
P—O(3)—C(22)	123.4 (2)	C(2)—C(1)—C(10)	123.7 (2)
P—O(1)—C(1)	125.3 (2)	O(1)—C(1)—C(2)	115.8 (2)
C(1)—C(10)—C(9)	116.8 (3)	C(9)—C(10)—C(11)	121.5 (2)
C(1)—C(10)—C(11)	121.6 (2)	C(10)—C(11)—C(12)	118.7 (3)
C(11)—C(12)—C(21)	120.5 (3)	C(11)—C(12)—C(13)	121.8 (2)
C(13)—C(12)—C(21)	117.5 (3)	C(12)—C(21)—C(20)	124.4 (3)
O(2)—C(21)—C(20)	117.3 (2)	O(2)—C(21)—C(12)	118.3 (3)
O(3)—C(22)—C(27)	118.7 (3)	O(3)—C(22)—C(23)	121.0 (3)
P—O(1)—C(1)—C(10)	−71.4 (3)		
O(1)—C(1)—C(10)—C(11)	6.9 (4)		
C(1)—C(10)—C(11)—C(12)	−48.3 (4)		
C(10)—C(11)—C(12)—C(21)	96.1 (3)		
C(11)—C(12)—C(21)—O(2)	−6.3 (4)		
C(12)—C(21)—O(2)—P	−73.9 (3)		
C(21)—O(2)—P—O(1)	21.7 (2)		
O(2)—P—O(1)—C(1)	91.3 (2)		

Preliminary cell parameters were determined from Weissenberg photographs and the accurate cell parameters from diffractometer data. The intensities were corrected for Lorentz–polarization and absorption factors, but a secondary-extinction correction was not applied. The structure was solved by the heavy-atom method using *SHELXS*86 (Sheldrick, 1985) and refined on F by the full-matrix least-squares method using *SHELX*76 (Sheldrick, 1976). The H-atom positions were located from a difference Fourier map. The positional and anisotropic displacement parameters of the non-H atoms were refined. The isotropic displacement parameters of the H atoms were set equal to the equivalent isotropic displacement parameters of the attached C atoms. The positional and isotropic displacement parameters of H atoms were not refined. Geometric calculations were performed with *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1558–1563

1-*O*-Benzyl-*β*-L-arabinopyranose, 1-*O*-Benzyl-3,4-*O*-isopropylidene-*β*-L-arabinopyranose and 1-*O*-Benzyl-2-*O*-benzoyl-3,4-*O*-isopropylidene-*β*-L-arabinopyranose

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Abstract

The sugar ring of 1-*O*-benzyl-*β*-L-arabinopyranose ($C_{12}H_{16}O_5$), (I), adopts the $^4C_1$ chair conformation. In 1-*O*-benzyl-3,4-*O*-isopropylidene-*β*-L-arabinopyranose ($C_{15}H_{20}O_5$), (II), and 1-*O*-benzyl-2-*O*-benzoyl-3,4-*O*-isopropylidene-*β*-L-arabinopyranose ($C_{22}H_{24}O_6$), (III), the pyranosyl rings have chair $^4C_1$ conformations slightly distorted towards $^0H_1$ conformations. In both (II) and (III), the five-membered isopropylidene ring adopts a slightly distorted envelope conformation. The methylene C atoms of the benzyl group are slightly displaced out of the plane of the phenyl ring in all three crystal structures. All three hydroxy groups in (I) participate in hydrogen bonds, each as donor and acceptor simultaneously, forming a two-dimensional hydrogen-bond network. In (II), molecules linked by hydrogen bonds form polymeric chains along the b axis.

Comment

It is well known that carbohydrates diluted in alcohols in the presence of mineral acid yield acetals. The chemical combination of carbohydrates and benzyl alcohol forms one type of widely explored sugar derivatives, but only a few crystal structures of the 1-*O*-benzyl simple sugars derivatives are known, and none of these is of arabinose (Allen *et al.*, 1991).

The molecular structures and atomic numbering of compounds (I), (II) and (III) are illustrated in Figs. 1,