Cl_2Dicyd^{2-}			
Cl—C(3)	1.740 (3)	C(2)—C(3)	1.392 (4)
N(1)—C(1)	1.160 (4)	C(3)—C(4)*a*	1.379 (4)
N(2)—C(1)	1.301 (4)	C(4)—H(4)	0.857 (21)
N(2)—C(2)	1.392 (3)		
C(1)—N(2)—C(2)	118.38 (22)	C(3)—C(2)—C(4)	114.96 (24)
N(1)—C(1)—N(2)	174.2 (3)	Cl—C(3)—C(2)	118.92 (21)
N(2)—C(2)—C(3)	119.53 (23)	C(2)—C(3)—C(4)*a*	122.10 (24)
N(2)—C(2)—C(4)	125.51 (25)		
N(2)	0.003 (3)	N(1)	0.305 (6)
C(1)	0.216 (5)		
Cl_4Dicyd^{2-}		C(1)—C(3)	1.426 (6)
Cl(1)—C(1)	1.728 (4)	C(3)—N(1)	1.360 (6)
C(1)—C(2)	1.374 (6)	N(1)—C(4)	1.299 (6)
		C(4)—N(2)	1.167 (7)
Cl(1)—C(1)—C(2)	120.1 (3)	C(2)*a*—C(3)—N(1)	118.9 (4)
C(2)—C(1)—C(3)	122.3 (4)	C(3)—N(1)—C(4)	130.1 (4)
Cl(2)—C(2)—C(3)*a*	115.7 (3)	N(1)—C(4)—N(2)	168.8 (5)
N(1)	0.015 (6)	N(2)	0.290 (16)
C(4)	0.153 (12)		

† Distance from cyanamide atoms to the phenyl ring plane.

All chemicals and solvents were reagent grade or better. Tetraphenylarsonium chloride monohydrate (Strem), phenylenediamine (Aldrich), 2,5-dichloro-1,4-phenylenediamine (Aldrich) and 2,5-dimethyl-1,4-phenylenediamine (Aldrich) were used as received.

A $\theta/2\theta$ scan technique was employed with profile analysis (Grant & Gabe, 1978). The Me_2Dicyd^{2-} salt is easily oxidized and so measurements were carried out on a crystal sealed in a tube. No crystal decay was observed during measurement for any of the compounds of this study. The space groups were determined either by systematic absences or during the analysis.

The structures were solved by direct methods and refined by full-matrix least squares using weights based on counting statistics. H-atom positions were calculated. All the calculations were performed with the *NRCVAX* package (Gabe, Lee, Le Page, Charland & White, 1989). Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV).

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 71067 (108 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1008]

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Structure of a Chiral Bicyclic 1-Hydroxyalkyl Phosphonamide

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Abstract

The crystal structure of a chiral racemic 1-hydroxyalkyl phosphonamide, 1,3-(2,2-dimethylpropyl)-2-[1-hydroxy-3-phenyl-(*E*)-2-propenyl]-2,3,3a,4,5,6,7,-7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 2-oxide, m.p. 455–456 K, has been determined by X-ray diffraction. The title compound consists of a five-membered ring with a tetrahedrally coordinated phosphorus atom. In addition to the two N atoms of the five-membered ring, the phosphorus is bonded to an oxygen and the 1-carbon of a hydroxyalkyl chain. The five-membered ring is *trans* fused to a cyclohexane in the chair conformation. The solid-state structure contains an intermolecular hydrogen-bonded enantiomeric pair.

Comment

We recently reported the preparation and reactions of chiral phosphorous acid diamides (Koeller & Spilling, 1991). Treatment of phosphorous acid diamide (1) with butyllithium in tetrahydrofuran (THF) solution followed by addition of cinnamaldehyde to the resulting anion gave the 1-hydroxy phosphonamides (2) in an 8:1 ratio of diastereoisomers (Koeller & Spilling, 1993). Crystallization from an ethyl acetate/hexane mixture yielded only the major isomer. Evidence for the relative configuration of C(17) was not available by standard spectroscopic methods. Single-crystal X-ray diffraction analysis allowed assignment of the relative configuration of the new chiral centre as *R* resulting from the (*S*,*S*)-diamide.

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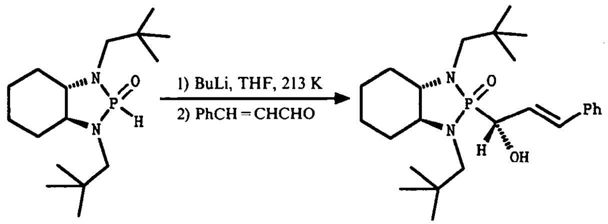

(1) (2)

The bond angles and distances are consistent with the published structures of related bicyclic phosphonamides (Bélanger-Gariépy, Delorme, Hanessian & Brisse, 1986; Bélanger-Gariépy, Bennani, Hanessian & Brisse 1989; Bennani, Bélanger-Gariépy & Hanessian, 1990). The solid-state structure contains an enantiomeric pair with two intermolecular hydrogen bonds in a ten-membered ring (Fig. 2). The hydrogen bonds are formed between the P═O of one enantiomer and the O—H of the other enantiomer. The O(1)···O(2′) distance is 2.66 Å. 1-Hydroxy phosphonates show a similar tendency to form intermolecular hydrogen bonds (Samuel & Weiss, 1969).

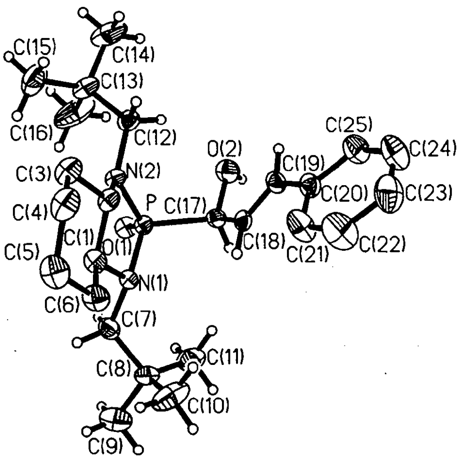

Fig. 1. The molecular structure (*SHELXTL-Plus*; Sheldrick, 1987) of the 1-hydroxy phosphonamide, shown with 25% probability ellipsoids. H atoms are represented as spheres of arbitrary radii. (H atoms of the phenyl and cyclohexyl rings have been omitted for clarity.)

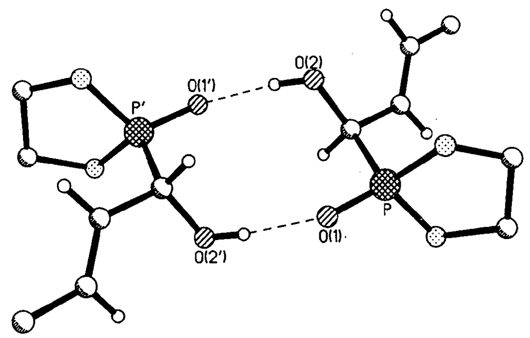

Fig. 2. The enantiomeric pair containing two intermolecular hydrogen bonds in a ten-membered ring (the peripheral atoms have been omitted for clarity).

Experimental

Crystal data

$C_{25}H_{41}N_2O_2P$
$M_r = 432.6$
Monoclinic
$C2/c$
$a = 26.304$ (11) Å
$b = 12.639$ (6) Å
$c = 16.825$ (6) Å
$\beta = 116.68$ (3)°
$V = 4998$ (4) Å^3
$Z = 8$
$D_x = 1.150$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–12.5°
$\mu = 0.132$ mm^{-1}
$T = 298$ K
Irregular
0.5 × 0.4 × 0.3 mm
Colourless

Data collection

Siemens *R3m/V* diffractometer
θ-2θ scans
Absorption correction: none
6456 measured reflections
5983 independent reflections
2340 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 27.5°$
$h = -34 \rightarrow 30$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 21$
4 standard reflections monitored every 50 reflections intensity variation: 3%

Refinement

Refinement on F
Final $R = 0.062$
$wR = 0.065$
$S = 1.15$
2340 reflections
271 parameters
H-atom parameters not refined

$w = [\sigma^2F + 0.0009F^2]^{-1}$
$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 0.54$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
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)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
P	0.3074 (1)	0.1857 (1)	0.9166 (1)	0.042 (1)
O(1)	0.2776 (1)	0.2853 (2)	0.9032 (2)	0.053 (1)
O(2)	0.2436 (1)	0.0984 (3)	0.9830 (2)	0.071 (2)
N(1)	0.3762 (1)	0.1929 (3)	0.9419 (2)	0.041 (2)
N(2)	0.2894 (1)	0.1095 (3)	0.8301 (2)	0.043 (2)
C(1)	0.3863 (2)	0.1339 (4)	0.8747 (3)	0.054 (2)
C(2)	0.3402 (2)	0.0568 (4)	0.8358 (3)	0.050 (2)
C(3)	0.3401 (2)	0.0052 (4)	0.7567 (3)	0.067 (3)
C(4)	0.3971 (2)	−0.0395 (5)	0.7780 (4)	0.078 (3)
C(5)	0.4455 (2)	0.0339 (5)	0.8232 (4)	0.083 (3)
C(6)	0.4433 (2)	0.0891 (4)	0.9004 (3)	0.069 (3)
C(7)	0.4043 (2)	0.2948 (4)	0.9668 (3)	0.060 (2)
C(8)	0.4435 (2)	0.3123 (4)	1.0626 (3)	0.062 (2)
C(9)	0.4717 (3)	0.4153 (5)	1.0688 (5)	0.111 (4)
C(10)	0.4877 (3)	0.2304 (5)	1.0995 (4)	0.123 (4)
C(11)	0.4105 (3)	0.3177 (6)	1.1175 (4)	0.110 (4)
C(12)	0.2348 (2)	0.0544 (4)	0.7929 (3)	0.058 (2)
C(13)	0.1894 (2)	0.0970 (5)	0.7072 (3)	0.066 (3)
C(14)	0.1364 (3)	0.0352 (6)	0.6863 (4)	0.128 (4)
C(15)	0.2050 (3)	0.0841 (6)	0.6321 (4)	0.106 (4)
C(16)	0.1770 (3)	0.2072 (6)	0.7171 (4)	0.146 (4)

C(17)	0.3014 (2)	0.1170 (4)	1.0079 (3)	0.049 (2)
C(18)	0.3355 (2)	0.0193 (4)	1.0336 (3)	0.050 (2)
C(19)	0.3160 (2)	−0.0736 (4)	1.0353 (3)	0.054 (2)
C(20)	0.3495 (2)	−0.1678 (4)	1.0678 (3)	0.057 (3)
C(21)	0.4040 (3)	−0.1770 (5)	1.0814 (4)	0.090 (4)
C(22)	0.4348 (3)	−0.2650 (6)	1.1180 (5)	0.115 (5)
C(23)	0.4115 (4)	−0.3452 (5)	1.1416 (5)	0.104 (5)
C(24)	0.3572 (4)	−0.3377 (6)	1.1269 (5)	0.106 (5)
C(25)	0.3260 (3)	−0.2511 (5)	1.0906 (4)	0.079 (3)

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

P—O(1)	1.446 (3)	P—N(1)	1.664 (4)
P—N(2)	1.628 (4)	P—C(17)	1.833 (6)
O(2)—C(17)	1.404 (6)	N(1)—C(1)	1.473 (7)
N(1)—C(7)	1.450 (6)	N(2)—C(2)	1.458 (6)
N(2)—C(12)	1.459 (6)	C(1)—C(2)	1.460 (6)
C(1)—C(6)	1.475 (7)	C(2)—C(3)	1.480 (8)
C(3)—C(4)	1.489 (8)	C(4)—C(5)	1.481 (8)
C(5)—C(6)	1.499 (10)	C(7)—C(8)	1.490 (6)
C(8)—C(9)	1.479 (9)	C(8)—C(10)	1.469 (8)
C(8)—C(11)	1.526 (10)	C(12)—C(13)	1.500 (6)
C(13)—C(14)	1.496 (9)	C(13)—C(15)	1.502 (10)
C(13)—C(16)	1.457 (9)	C(17)—C(18)	1.472 (7)
C(18)—C(19)	1.286 (7)	C(19)—C(20)	1.435 (7)
C(20)—C(21)	1.350 (10)	C(20)—C(25)	1.360 (9)
C(21)—C(22)	1.351 (10)	C(22)—C(23)	1.333 (13)
C(23)—C(24)	1.340 (14)	C(24)—C(25)	1.338 (9)
O(1)—P—N(1)	116.4 (2)	O(1)—P—N(2)	117.1 (2)
N(1)—P—N(2)	96.2 (2)	O(1)—P—C(17)	107.3 (2)
N(1)—P—C(17)	107.7 (2)	N(2)—P—C(17)	111.6 (2)
P—N(1)—C(1)	109.0 (2)	P—N(1)—C(7)	118.4 (3)
C(1)—N(1)—C(7)	115.4 (4)	P—N(2)—C(2)	108.7 (2)
P—N(2)—C(12)	120.1 (4)	C(2)—N(2)—C(12)	120.5 (4)
N(1)—C(1)—C(2)	106.5 (5)	N(1)—C(1)—C(6)	118.6 (4)
C(2)—C(1)—C(6)	113.9 (4)	N(2)—C(2)—C(1)	106.1 (4)
N(2)—C(2)—C(3)	120.6 (3)	C(1)—C(2)—C(3)	111.4 (5)
C(2)—C(3)—C(4)	110.8 (4)	C(3)—C(4)—C(5)	115.4 (5)
C(4)—C(5)—C(6)	112.2 (6)	C(1)—C(6)—C(5)	110.8 (4)
N(1)—C(7)—C(8)	117.4 (4)	C(7)—C(8)—C(9)	106.8 (5)
C(7)—C(8)—C(10)	112.6 (5)	C(9)—C(8)—C(10)	108.2 (5)
C(7)—C(8)—C(11)	110.9 (4)	C(9)—C(8)—C(11)	108.8 (6)
C(10)—C(8)—C(11)	109.4 (5)	N(2)—C(12)—C(13)	116.5 (4)
C(12)—C(13)—C(14)	107.1 (5)	C(12)—C(13)—C(15)	111.7 (5)
C(14)—C(13)—C(15)	108.9 (5)	C(12)—C(13)—C(16)	110.8 (4)
C(14)—C(13)—C(16)	107.0 (6)	C(15)—C(13)—C(16)	111.1 (6)
P—C(17)—O(2)	108.6 (3)	P—C(17)—C(18)	111.9 (4)
O(2)—C(17)—C(18)	112.6 (4)	C(17)—C(18)—C(19)	125.1 (5)
C(18)—C(19)—C(20)	125.7 (5)	C(19)—C(20)—C(21)	124.0 (6)
C(19)—C(20)—C(25)	118.1 (6)	C(21)—C(20)—C(25)	117.8 (5)
C(20)—C(21)—C(22)	121.5 (7)	C(21)—C(22)—C(23)	120.0 (8)
C(22)—C(23)—C(24)	119.0 (7)	C(23)—C(24)—C(25)	121.7 (8)
C(20)—C(25)—C(24)	119.9 (7)		

Colourless, irregular crystals of appropriate dimensions for X-ray diffraction analysis were obtained by slow diffusion of hexane into an ethyl acetate solution of the compound at 273 K. A set of higher-angle data (2θ) was obtained using the initial orientation matrix. ω scans of several representative reflections indicated acceptable crystal quality. Data reduction, structure solution and refinement were carried out using the *SHELXTL-Plus* (VMS) software package (Sheldrick, 1987). The structure was solved by direct methods and refined successfully in the space group *C*2/*c*. Full-matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o - F_c)^2$. The non-H atoms were refined anisotropically. The H atoms were included in their idealized geometric positions with fixed isotropic displacement parameters.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71084 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1044]

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Structure of Tris(nonafluoroisobutyl)phosphine Oxide

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Abstract

The C—F bond lengths vary depending on the number of attached F atoms. The longest C—F bonds are for the methine C atoms [average 1.370 (1) Å], while the shortest are for the methyl C atoms [average 1.3207 (7) Å]. Intermediate C—F bond lengths are found for the methylene type C atoms [average 1.3482 (8) Å]. The P—C bonds are longer [average 1.915 (1) Å] and the P—O bond is shorter [1.447 (2) Å] than those found in trimethylphosphine oxide [Engelhardt, Raston, Whitaker & White (1986). *Aust. J. Chem.* **39**, 2151-2154]. Even though a perfluoroisobutyl group in the title compound (1) is bulkier than a methyl group, the average C—P—C angle is smaller for (1) [101.63 (5)°] than for the trimethylphosphine oxide (105.9°). These differences can probably be ascribed to the electron-withdrawing effect of the F atoms on the geometry around P.

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