

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55998 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1035]

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Acta Cryst. (1993). **C49**, 1199–1201

Structure of a Chiral Monocyclic Phosphonamide

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(Received 24 August 1992; accepted 9 December 1992)

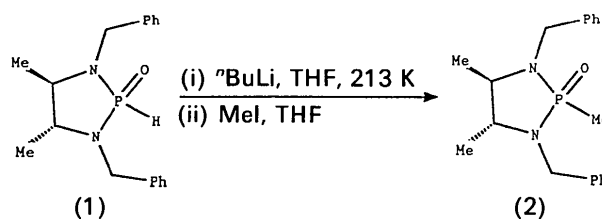
Abstract

The crystal structure of a chiral racemic monocyclic phosphonamide, 1,3-dibenzyl-2,4,5-trimethyl-2,3,4,5-tetrahydro-1*H*-1,3,2-diazaphosphole 2-oxide, $C_{19}H_{25}N_2OP$, m.p. 412.6–414 K, has been determined by X-ray diffraction. The title molecule consists of a five-membered ring with a tetrahedrally coordinated P^V atom and *trans* methyl substituents at C atoms. In addition to two N atoms of the five-membered ring, the P atom is bonded to an O atom and a methyl.

Comment

We recently reported the synthesis of chiral phosphonamides by the alkylation of phosphorous acid diamides (Koeller & Spilling, 1991). Treatment of phosphorous acid diamide (1) with *n*-butyllithium in THF solution followed by alkylation of the resulting

anion with methyl iodide gave the monocyclic phosphonamide (2).



Recently, several publications have described the use of chiral phosphonamides as auxiliaries in asymmetric reactions. Related phosphonamides have shown useful diastereofacial biases upon further reaction of the organic chain. Alkylation of the α anions of bicyclic phosphonamides proceeds with high diastereoselectivity (Hanessian, Delorme, Beaudoin & Leblanc, 1984; Hanessian & Bennani, 1990; Hanessian, Bennani & Delorme, 1990). The stereoselectivity and rate of the carbanion accelerated Claisen rearrangement (CACR) of 2-allyloxy-allyl phosphonamides (Denmark, Stadler, Dorow & Kim, 1991) was shown to be dependent on the nature of the phosphonamide. The crystal structures of four bicyclic phosphonamides have been reported (Bélanger-Gariépy, Delorme, Hanessian & Brisse, 1986; Bélanger-Gariépy, Bennani, Hanessian & Brisse, 1989; Bennani, Bélanger-Gariépy & Hanessian, 1990). The most striking contrast between the monocyclic compound (2) and the bicyclic compounds is the environment of the N atoms. The N atoms in the monocyclic compound (2) are close to planar, as indicated by the sum of the three N-atom bond angles (ΣN). $\Sigma N(1) = 358.9$ (2°) and $\Sigma N(2) = 355.4$ (2°) for compound (2), whereas in the bicyclic compounds the N atoms, are approximately midway between tetrahedral ($\Sigma N = 328.5^\circ$) and planar ($\Sigma N = 360^\circ$) geometry, as indicated by $\Sigma N(1) = 344.3$ and $\Sigma N(2) = 345.5^\circ$ (Bennani *et al.*, 1990).

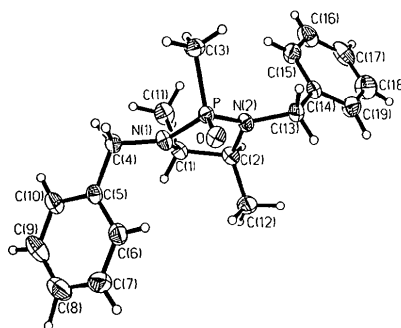


Fig. 1. Thermal ellipsoid plot (*SHELXTL-Plus*; Sheldrick, 1991) of the monocyclic phosphonamide. Ellipsoids are scaled to enclose 50% probability, H atoms are represented as spheres of arbitrary radii.

Experimental

Crystal data

C₁₉H₂₅N₂OPM_r = 328.4

Triclinic

P1

a = 9.098 (4) Å

b = 9.798 (5) Å

c = 10.815 (5) Å

α = 92.73 (4)°

β = 105.81 (3)°

γ = 92.00 (4)°

V = 925.5 (7) Å³

Z = 2

D_x = 1.178 Mg m⁻³

Data collection

Siemens R3m/V diffractometer

θ-2θ scans

Absorption correction:
none

5736 measured reflections

5418 independent reflections

3305 observed reflections

[F > 4.0σ(F)]

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 10–13°

μ = 0.149 mm⁻¹

T = 298 K

Rectangular

0.4 × 0.4 × 0.2 mm

Colourless

Crystal source: crystalliza-
tion from diethyl etherR_{int} = 0.0129θ_{max} = 30°

h = 0 → 12

k = -13 → 13

l = -15 → 14

3 standard reflections

monitored every 50
reflections

Refinement

Final R = 0.0562

wR = 0.0628

S = 1.33

3305 reflections

308 parameters

All H-atom parameters re-
finedw = 1/[σ²(F) + 0.0009F²](Δ/σ)_{max} = 0.043Δρ_{max} = 0.48 e Å⁻³Δρ_{min} = -0.27 e Å⁻³Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 2. Geometric parameters (Å, °)

P—O	1.472 (2)	P—N(1)	1.636 (2)
P—N(2)	1.648 (2)	P—C(3)	1.787 (3)
N(1)—C(1)	1.469 (3)	N(1)—C(4)	1.454 (4)
N(2)—C(2)	1.466 (3)	N(2)—C(13)	1.458 (4)
C(1)—C(2)	1.538 (4)	C(1)—C(11)	1.522 (5)
C(2)—C(12)	1.516 (4)	C(4)—C(5)	1.502 (4)
C(5)—C(6)	1.377 (4)	C(5)—C(10)	1.369 (5)
C(6)—C(7)	1.382 (5)	C(7)—C(8)	1.346 (8)
C(8)—C(9)	1.343 (6)	C(9)—C(10)	1.385 (5)
C(13)—C(14)	1.510 (3)	C(14)—C(15)	1.371 (4)
C(14)—C(19)	1.366 (4)	C(15)—C(16)	1.383 (4)
C(16)—C(17)	1.362 (7)	C(17)—C(18)	1.358 (6)
C(18)—C(19)	1.374 (5)		
O—P—N(1)	116.3 (1)	O—P—N(2)	119.6 (1)
N(1)—P—N(2)	93.1 (1)	O—P—C(3)	108.8 (1)
N(1)—P—C(3)	110.3 (2)	N(2)—P—C(3)	107.8 (1)
P—N(1)—C(1)	114.4 (2)	P—N(1)—C(4)	124.5 (2)
C(1)—N(1)—C(4)	120.0 (2)	P—N(2)—C(2)	113.4 (2)
P—N(2)—C(13)	122.5 (1)	C(2)—N(2)—C(13)	119.5 (2)
N(1)—C(1)—C(2)	104.2 (2)	N(1)—C(1)—C(11)	113.1 (2)
C(2)—C(1)—C(11)	112.5 (2)	N(2)—C(2)—C(1)	103.5 (2)
N(2)—C(2)—C(12)	113.1 (2)	C(1)—C(2)—C(12)	113.4 (2)
N(1)—C(4)—C(5)	113.1 (2)	C(4)—C(5)—C(6)	121.3 (3)
C(4)—C(5)—C(10)	121.7 (3)	C(6)—C(5)—C(10)	117.1 (3)
C(5)—C(6)—C(7)	120.5 (4)	C(6)—C(7)—C(8)	121.2 (4)
C(7)—C(8)—C(9)	119.5 (4)	C(8)—C(9)—C(10)	120.2 (4)
C(5)—C(10)—C(9)	121.6 (3)	N(2)—C(13)—C(14)	112.1 (2)
C(13)—C(14)—C(15)	121.3 (3)	C(14)—C(14)—C(19)	120.2 (2)
C(15)—C(14)—C(19)	118.5 (3)	C(14)—C(15)—C(16)	120.6 (3)
C(15)—C(16)—C(19)	120.0 (4)	C(16)—C(17)—C(18)	119.4 (3)
C(17)—C(18)—C(19)	120.6 (4)	C(14)—C(19)—C(18)	120.7 (3)

Data reduction, structure solution and refinement were carried out using *SHELXTL-Plus* (Sheldrick, 1991). The structure was solved by direct methods and refined successfully in the space group *P1*. Full-matrix least-squares refinement was carried out by minimizing $w(F_o - F_c)^2$. The non-H atoms were refined anisotropically whereas H atoms were refined isotropically to convergence.

We thank the Donors of the Petroleum Research Fund administered by the American Chemical Society, and the University of Missouri-St Louis Weldon Spring Fund for financial support.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U _{eq}
P	0.2599 (1)	0.9059 (1)	0.4006 (1)	0.040 (1)
O	0.2970 (2)	1.0126 (2)	0.5064 (2)	0.052 (1)
N(1)	0.2611 (2)	0.9555 (2)	0.2585 (2)	0.050 (1)
N(2)	0.0840 (2)	0.8385 (2)	0.3484 (2)	0.045 (1)
C(1)	0.1257 (3)	0.9078 (3)	0.1542 (2)	0.050 (1)
C(2)	0.0001 (3)	0.8842 (3)	0.2226 (2)	0.049 (1)
C(3)	0.3855 (3)	0.7693 (3)	0.4444 (4)	0.061 (1)
C(4)	0.3935 (3)	1.0178 (3)	0.2283 (3)	0.052 (1)
C(5)	0.3618 (3)	1.1517 (3)	0.1666 (2)	0.048 (1)
C(6)	0.2902 (3)	1.2523 (3)	0.2179 (3)	0.068 (1)
C(7)	0.2624 (5)	1.3752 (3)	0.1602 (5)	0.092 (2)
C(8)	0.3042 (5)	1.3997 (4)	0.0528 (5)	0.093 (2)
C(9)	0.3730 (5)	1.3026 (4)	0.0002 (4)	0.092 (2)
C(10)	0.4022 (4)	1.1790 (3)	0.0570 (3)	0.070 (1)
C(11)	0.1515 (5)	0.7800 (3)	0.0789 (3)	0.071 (1)
C(12)	-0.0896 (4)	1.0099 (3)	0.2325 (3)	0.066 (1)
C(13)	-0.0006 (3)	0.7876 (3)	0.4349 (3)	0.048 (1)
C(14)	-0.0946 (3)	0.6576 (2)	0.3803 (2)	0.047 (1)
C(15)	-0.0325 (4)	0.5499 (3)	0.3303 (3)	0.067 (1)
C(16)	-0.1202 (5)	0.4318 (3)	0.2802 (3)	0.082 (2)
C(17)	-0.2701 (5)	0.4216 (4)	0.2797 (3)	0.090 (2)
C(18)	-0.3310 (4)	0.5269 (4)	0.3318 (4)	0.095 (2)
C(19)	-0.2449 (3)	0.6454 (3)	0.3796 (3)	0.069 (1)

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 55912 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1036]

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Acta Cryst. (1993). **C49**, 1201–1203

Structure of *endo*-(5*R,6*R**,10*R**,11*S**)-10-(*tert*-Butyldimethylsiloxy)-5,6,10,11-tetrahydro-5-hydroxy-4,11-dimethoxy-7,7,9-trimethyl-6,10-methano-(7*H*)-benzocyclononene-8-carbaldehyde**

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(Received 20 August 1992; accepted 7 December 1992)

Abstract

The seven-membered ring adopts a chair-like conformation with an axial hydroxy group and an equatorial methoxy group; the cyclohexene ring is in a half-chair conformation. There is an intermolecular hydrogen bond between O(2) of the aldehyde group and O(4) of the hydroxy group of the neighboring molecule at $\frac{1}{2} + x, -\frac{1}{2} - y, z$ [O(2)···O(4) 2.788 (4) Å].

Comment

The structure determination of the title compound was undertaken to confirm the tricyclic skeleton and the conformation of the side chains. An X-ray analysis was required for the determination of the seven-membered ring conformation. The compound was obtained by Lewis-acid-promoted seven-membered ring cyclization reaction between C(9) and C(13). Details of the synthetic work will be published elsewhere (Morihiro, Seto, Furukawa, Horiguchi & Kuwajima, 1993).

The seven-membered ring adopts a chair-like conformation (Fig. 1), while NMR spectra of a structurally related compound that we have synthesized suggested a boat-like seven-membered ring. The cyclohexene ring is in a half-chair conformation with a twisted C=C double bond. The largest torsion angle, C(10)—C(11)—C(12)—C(18), is 11.1 (5)°. A search of the January 1992 version of the Cambridge Structural Database (Allen, Kennard

& Taylor, 1983) revealed no structure determinations for bicyclo[4.3.1]dec-7-ene fragments.

The arrangement of the molecules in the unit cell is presented in Fig. 2. O(2) of the aldehyde group is hydrogen bonded to O(4) of the hydroxy group in the neighboring molecule at $\frac{1}{2} + x, -\frac{1}{2} - y, z$ [O(2)···O(4) 2.788 (4) Å].

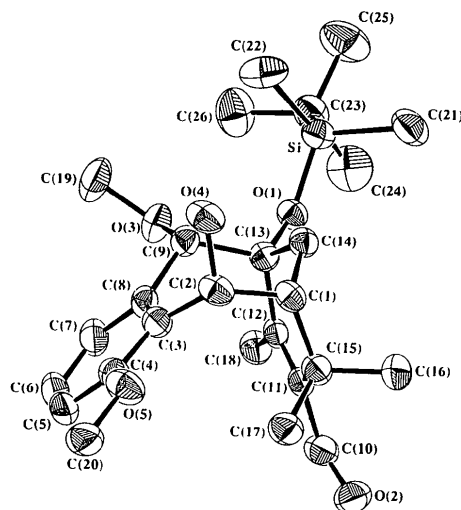


Fig. 1. A perspective view of the molecule (30% probability ellipsoids) with the numbering scheme, excluding H atoms.

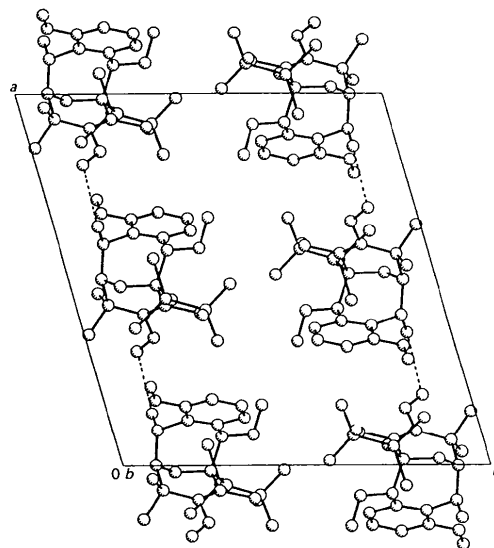


Fig. 2. Crystal structure viewed along the *b* axis. Hydrogen bonds are represented as dashed lines.

Experimental

Crystal data

C₂₆H₄₀O₅Si
M_r = 460.69

Cu Kα radiation
λ = 1.541840 Å