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Diethyl [(2*RS*,5*RS*)-5-isopropyl-2,3,3-trimethylpyrrolidin-2-yl]phosphonate

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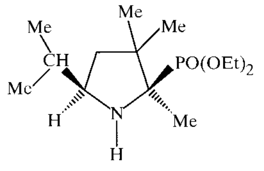
The *cis* or *trans* conformation of the title compound ($C_{14}H_{30}NO_3P$) is difficult to predict because of its dependancy on experimental conditions. X-ray analysis shows a *trans* stereochemistry of the methyl and isopropyl groups in α positions with respect to the N atom.

Comment

Nitroxide radicals are becoming an increasingly important aspect of chemical applications due to the enormous need of materials enjoying new or improved physical and chemical properties. After being used in ESR as spin probes (Zhdanov, 1992; Keana, 1984; Berliner, 1976), they have also been applied as contrast-enhancing agents for magnetic resonance imaging (Kuppusamy *et al.*, 1995). Recently, stable nitroxide radicals found a successful application in the field of Living Free Radical Polymerization (Hawker, 1997; Grimaldi *et al.*, 1997). The concept of using stable free radicals, such as pyrrolidine derived from β-phosphorylated nitroxides, has been extensively developed in our laboratory. These nitroxides are prepared by oxidation of the corresponding α-phosphorylated pyrrolidines (Roubaud *et al.*, 1994, 1996). However, mixtures of *cis* and *trans* isomers were obtained by using this method. Recently, we have reported the cyclization of β-allenic aminophosphonates into α-phosphorylated pyrrolines (Amedjkouh *et al.*, 1997). Its reduction with $NaBH_4$ leads only to the *cis* isomer, thus a series of (2,3,5-alkylpyrrolidin-2-yl)diethylphosphonates was prepared. In the present paper, we report the structure of diethyl [(2*RS*,5*RS*)-5-isopropyl-2,3,3-trimethylpyrrolidin-2-yl]phosphonate, (I).



(I)

As a precursor for a new serie of pyrrolidinyl nitroxides, the title compound was obtained using our new procedure. The crystallographic conformation of the pyrrolidinyl ring is $^3T_4$ [the puckering parameters (Cremer & Pople, 1975) are: q = 0.374 (3) Å and φ = 85.1 (5)°] as it is usually observed for this kind of molecules. The methyl and isopropyl moities borne by C_5 and C_6, respectively, are in *trans* positions. The diethoxyphosphoryl group occupies the axial position on C_5 [the angle between the bond C—P and the normal of the ring mean plane is 14.3 (2)°]. The crystal packing is assumed by N1—H30···O3(3/2−*x*, *y*-1/2, 3/2-*z*) hydrogen bond with H30···O3 2.30 (3) Å and N1—H30···O3(3/2 −*x*, *y*-1/2, 3/2-*z*) 152 (3)°, and usual van der Waals interactions of which the shortest distance is C14···H10(C8)(*x*-1/2, 1/2-*y*, *z*-1/2) 3.09 (19) Å.

Experimental

(5-Isopropyl-2,3,3-trimethylpyrrolidin-2-yl)diethylphosphonate was synthesized by reduction of the corresponding pyrroline (Amedjkouh *et al.*, 1997, 2000) with sodium borohydride. Suitable colorless prisms for X-ray analysis were grown in pentane solution in the fridge or at room temperature by slow evaporation.

Crystal data

$C_{14}H_{30}NO_3P$
$M_r = 291.37$
Monoclinic, $P2_1/n$
a = 9.552 (3) Å
b = 11.853 (7) Å
c = 15.615 (4) Å
β = 96.47 (2)°
V = 1757 (2) Å^3
$Z = 4$
D_x = 1.10 Mg m^{-3}

D_m = 1.11 (2) Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–16°
μ = 0.162 mm^{-1}
T = 294 K
Prism, colorless
0.50 × 0.40 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3018 measured reflections
2744 independent reflections
1861 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.030$

$\theta_{\rm max}$ = 24.70°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 17$
2 standard reflections
frequency: 60 min
intensity decay: −9.64%

Refinement

Refinement on F
$R = 0.049$
R = missing
$wR = 0.069$
$S = 1.167$
1861 reflections
173 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0025F_o^4]$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.20 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P—O1	1.579 (2)	C2—C9	1.529 (4)
P—O2	1.578 (3)	C3—C4	1.528 (4)
P—O3	1.463 (2)	C3—C10	1.537 (5)
P—C2	1.827 (3)	C4—C5	1.515 (4)
O1—C1	1.442 (5)	C5—C12	1.528 (4)
O2—C7	1.469 (5)	C7—C8	1.441 (6)
N—C2	1.484 (4)	C3—C11	1.533 (5)
N—C5	1.474 (4)	C12—C13	1.521 (5)
C1—C6	1.490 (6)	C12—C14	1.529 (5)
C2—C3	1.566 (5)		
O1—P—O2	101.7 (1)	N—C2—C9	110.3 (2)
O1—P—O3	115.4 (1)	C3—C2—C9	115.8 (3)
O1—P—C2	103.0 (1)	N—C5—C4	104.6 (2)
O2—P—O3	112.4 (1)	N—C5—C12	111.6 (3)
O2—P—C2	106.2 (1)	C4—C5—C12	114.3 (3)
O3—P—C2	116.5 (1)	C5—C4—C3	105.4 (3)
P—O1—C1	121.4 (2)	C2—C3—C4	100.9 (2)
P—O2—C7	121.1 (2)	C2—C3—C10	114.7 (3)
C2—N—C5	110.5 (2)	C2—C3—C11	110.2 (3)
O1—C1—C6	108.5 (4)	C4—C3—C10	112.8 (3)
O2—C7—C8	110.1 (4)	C4—C3—C11	109.2 (3)
P—C2—N	103.3 (2)	C10—C3—C11	108.8 (3)
P—C2—C3	114.1 (2)	C5—C12—C13	111.2 (3)
P—C2—C9	108.2 (2)	C5—C12—C14	110.8 (3)
N—C2—C3	104.4 (2)	C13—C12—C14	111.2 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H30···O3^{i}	0.85 (4)	2.30 (3)	3.078 (4)	152 (3)

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

All the H atoms were theoretically located except for the H_{30} atom borne by the N atom, which was refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *BEGIN SDP* (Frenz, 1985); program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980); program(s) used to refine structure: *LSFM SDP* (Frenz, 1985); software used to prepare material for publication: *CIF VAX MolEN* (Fair, 1990).

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