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Pentacyclohexyloxyphosphorane

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Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.006 Å
R factor = 0.043
wR factor = 0.108
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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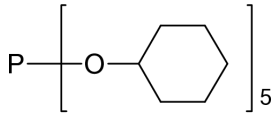
The crystal structure of pentacyclohexyloxyphosphorane, $C_{30}H_{55}O_5P$, has been determined at 180 (2) K. In space group *P*1, there are four independent molecules in the unit cell, each displaying trigonal bipyramidal geometry at the P atom.

Comment

Pentaoxyphosphoranes $(RO)_5P$, where two or three of the O*R* groups are OH, or ionized to O^-, are of interest as potential intermediates in the hydrolysis reactions of phosphodiesters. Their lifetimes and protonation states are of paramount importance in, for example, understanding the mechanisms of action of nuclease enzymes (Perreault & Anslyn, 1997). However, such species are too short-lived for them to be isolated, so that the pK_a values of the OH groups cannot be measured directly.



(I)

A possible solution to this problem lies in the simple linear relationship (Kirby, 1994) between the length of a C—O*X* bond and the pK_a of the acid HO*X*: the stronger the acid, the longer the bond. The sensitivity of this bond length to the pK_a depends on the substituents on C (Kirby, 1994); a good correlation has been established for derivatives of cyclohexanol (Jones *et al.*, 1992), and this correlation can, in principle, be used to estimate pK_a values of compounds HO*X* too unstable to exist as the free acid or anion. For example, the method has been used recently to estimate the pK_a of 2,4-dinitrobenzenesulfenic acid (Green *et al.*, 2000). As a first step, we have prepared the title compound, pentacyclohexyloxyphosphorane $(CyO)_5P$, with the maximum number of cyclohexyl–O*X* bonds.

Experimental

The title compound was prepared using the method of Chang *et al.* (1977). It is liquid at room temperature, melting just above 273 K. The crystal was obtained by slow cooling in a freezer and transferred to the diffractometer with the aid of a microscope equipped with a cold stage.

Crystal data

$C_{30}H_{55}O_5P$	$Z = 4$
$M_r = 526.71$	$D_x = 1.143$ Mg m^{-3}
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 10.0853$ (2) Å	Cell parameters from 37 465 reflections
$b = 10.0892$ (2) Å	$\theta = 1.0$–$25.0°$
$c = 30.1129$ (7) Å	$\mu = 0.12$ mm^{-1}
$\alpha = 88.403$ (2)°	$T = 180$ (2) K
$\beta = 88.589$ (9)°	Block, colourless
$\gamma = 90.0210$ (10)°	0.37 × 0.32 × 0.32 mm
$V = 3061.95$ (11) Å^3	

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.042$
Thin-slice ω and φ scans	$\theta_{max} = 25.0°$
22 250 measured reflections	$h = -11 \rightarrow 9$
13 809 independent reflections	$k = -11 \rightarrow 8$
12 562 reflections with $I > 2\sigma(I)$	$l = -35 \rightarrow 33$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.8978P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.108$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.28$ e Å^{-3}
13 809 reflections	Absolute structure: Flack (1983), 3513 Friedel pairs
1297 parameters	Flack parameter = −0.01 (7)
H-atom parameters constrained	

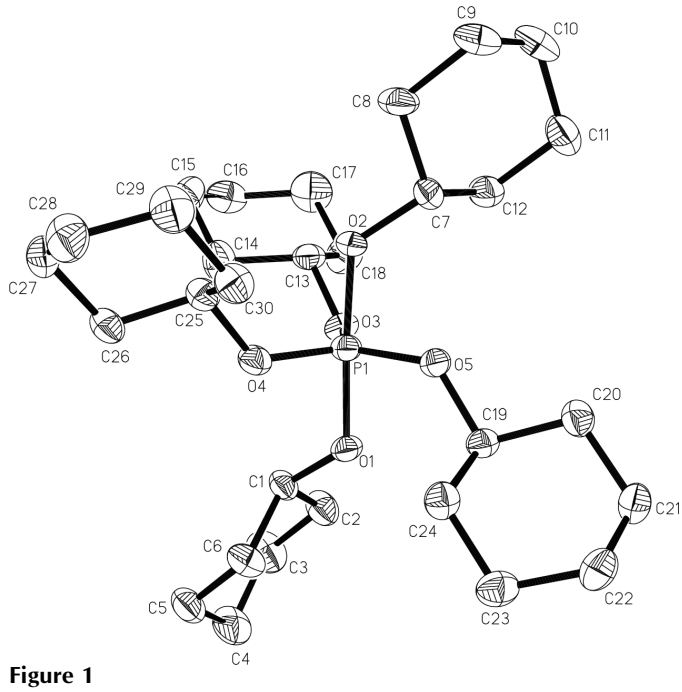


Figure 1
One of the four independent molecules in the asymmetric unit of (I) with displacement ellipsoids at the 50% probability level. In the deposited tables, independent molecules are distinguished by _*n* (*n* = 1–4).

Despite the suspicious cell dimensions (*a* approximately equal to *b*, α approximately equal to β), many strenuous efforts to locate extra symmetry all failed conspicuously. There is a pseudo-*C*-centred monoclinic cell, but R_{int} for this setting is *ca* 0.26. The refinement shows no anomalies: with anisotropic displacement parameters for all non-H atoms, all H atoms placed geometrically, and no constraints on other atoms, there are no unusual bond distances, displacement parameters or correlation coefficients. Furthermore, and perhaps most significantly, the orientation of the cyclohexyl groups in one of the four independent molecules in the asymmetric unit (with atom labels ending in _4) is noticeably different from that observed for the other three molecules. From this we conclude that the space group really is *P*1, as described.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL*97.

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