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(Dicyclohexylphosphino)borane, $BH_3PH(C_6H_{11})_2$, a Precursor to Water-Soluble Phosphine Ligands

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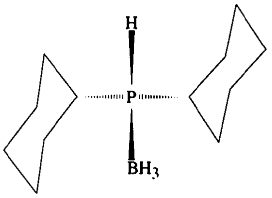
Abstract

(Dicyclohexylphosphino)borane is a precursor in the synthesis of water-soluble phosphines. The boranato group can be removed quantitatively under mild conditions.

Comment

Phosphinoboranes are unique organophosphorus compounds which have recently been applied as useful intermediates in the synthesis of phosphine derivatives such as homochiral mono- and biphosphines (Enders, Berg, Raabe & Runsink, 1996; Brenchley, Fedouloff, Mahon, Malloy & Wills, 1995; McKinstry & Livinghouse, 1994, 1995; Imamoto, 1993). They are typically prepared *via* the reaction of a free phosphine with trihydroborane, although Imamoto *et al.* (Imamoto, Oshiki, Onozawa, Kusumoto & Sato, 1990; Imamoto, Kusumoto, Suzuki & Sato, 1985) have prepared a variety of phosphinoboranes in a one-step synthesis from phosphine oxides, obviating the need to isolate difficult-to-handle primary and secondary phosphine intermediates. Borane-protected phosphines are stable to metallation with lithium reagents and can subsequently be reacted with various electrophiles under mild conditions to yield functionalized phosphinoboranes. Notably, the boranato group acts as both a protecting group and an activating group during the functionalization process; it has been shown to activate hydrogen, methyl and methylene groups adjacent to the P atom to deprotonation by strong bases (Imamoto & Hikosaka, 1994; Gourdel, Ghanimi, Pellon & Le Corre, 1993; Schmidbaur & Weiss, 1981). In the final stage of the synthetic sequence, removal of the boranato group can be achieved quantitatively, and with retention of configuration, by treatment with either a large excess of a nucleophilic amine (Imamoto, 1993) or tetrafluoroboric acid (McKinstry & Livinghouse, 1994, 1995).

The synthesis of (dicyclohexylphosphino)borane, (I), was first described by McKinstry & Livinghouse (1994) as an efficient precursor in the preparation of electron-rich homochiral bisphosphines. Our interest in this compound is based on its widespread use as an intermediate in the synthesis of cationically and anionically functionalized water-soluble phosphines (Mohr, Lynn & Grubbs, 1996).



(I)

Figs. 1 and 2 show drawings of (dicyclohexylphosphino)borane. The geometry around the P atom is approximately tetrahedral (see Table 2) with the angles averaging 109.3 (54)°. The average B—P—*X* angle is 113.6 (8)° while the average H—P—C angle is 102.9 (20)°. The P—B bond distance of 1.919 (3) Å is in good agreement with the values of 1.917 Å (Huffman, Skupinsky & Caulton, 1982) and 1.901 (7) Å (Bryan & Kuczkowski, 1972) reported for Ph_3PBH_3 and Me_3PBH_3, respectively. The average H—B—H angle is 113 (3)° and the average P—B—H angle is 106 (2)°, both of which agree with the corresponding angles of 115 and 103°, respectively, in Ph_3PBH_3 (Huffman *et al.*, 1982). The average C—H distance is 0.92 (5) Å with a range of 0.75 to 0.97 Å. The average U_{eq} for H atoms is 0.088 (22) $Å^2$ with a range from 0.051 to 0.121 $Å^2$.

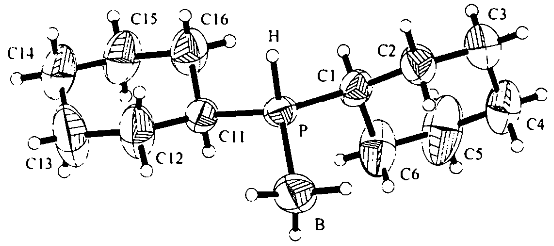


Fig. 1. A labeled diagram of (dicyclohexylphosphino)borane showing 50% probability ellipsoids.

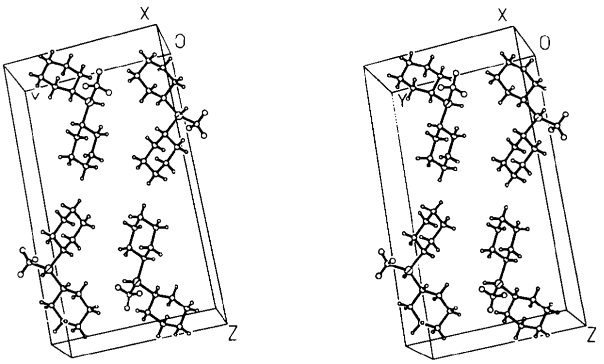


Fig. 2. Stereoview of the packing of (dicyclohexylphosphino)borane showing the unit-cell boundaries and contents.

The e.s.d.'s of the average values reported here are the scatter e.s.d.'s derived from the values being averaged. Both cyclohexyl rings adopt a chair configuration.

Experimental

Dicyclohexylphosphine (19.7 g, 0.99 mol) in tetrahydrofuran (100 ml) was placed into a schlenck tube and purged with argon. The solution was cooled to 273 K and borane tetrahydrofuran (100 ml of a 1.0 molar solution in tetrahydrofuran, 0.1 mol, 1.01 eq.) was added slowly. The colorless solution was stirred for 2 h at 273 K and then allowed to warm to room temperature. Evaporation of the solvent resulted in a crystalline white solid, which was recrystallized from pentane. Yield: 18.9 g (90%).

Crystal data

$C_{12}H_{26}BP$
$M_r = 212.11$
Monoclinic
$P2_1/n$
$a = 5.737\ (2)$ Å
$b = 11.622\ (3)$ Å
$c = 20.827\ (5)$ Å
$\beta = 93.61\ (2)°$
$V = 1385.9\ (7)$ Å^3
$Z = 4$
$D_x = 1.02$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.50–13.25°$
$\mu = 0.17$ mm^{-1}
$T = 293\ (2)$ K
Tabular
0.5 × 0.4 × 0.2 mm
Colorless

Data collection

CAD-4 diffractometer
ω scans
Absorption correction: none
5265 measured reflections
2434 independent reflections
1958 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.022$

$\theta_{\rm max} = 25.0°$
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 13$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: within counting statistics

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.092$
$S = 2.29$
2427 reflections
232 parameters
H atoms refined freely
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.014 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.04052 (7)	0.49664 (4)	0.79167 (2)	0.0416 (2)
B	−0.2353 (5)	0.5815 (3)	0.80924 (15)	0.0727 (8)
C1	0.1316 (3)	0.3934 (2)	0.85394 (8)	0.0478 (5)
C2	0.2102 (5)	0.4550 (2)	0.91613 (10)	0.0634 (6)
C3	0.2812 (5)	0.3717 (3)	0.96978 (13)	0.0865 (9)
C4	0.0909 (6)	0.2855 (3)	0.98041 (12)	0.0822 (8)
C5	0.0137 (9)	0.2239 (3)	0.91922 (14)	0.1048 (12)
C6	−0.0588 (6)	0.3066 (2)	0.86560 (12)	0.0796 (9)
C11	0.0252 (3)	0.4249 (2)	0.71389 (8)	0.0468 (5)
C12	−0.0387 (7)	0.5104 (3)	0.66088 (11)	0.0821 (9)
C13	−0.0542 (10)	0.4537 (5)	0.59531 (14)	0.117 (2)
C14	0.1604 (6)	0.3889 (3)	0.58116 (12)	0.0782 (8)
C15	0.2193 (6)	0.3024 (2)	0.63312 (11)	0.0744 (7)
C16	0.2407 (5)	0.3569 (2)	0.69940 (11)	0.0670 (7)
H	0.219 (3)	0.5598 (14)	0.7908 (7)	0.051 (5)
H*A*	−0.364 (5)	0.525 (2)	0.8042 (13)	0.121 (10)
H*B*	−0.217 (4)	0.6118 (18)	0.8580 (12)	0.093 (7)
H*C*	−0.248 (4)	0.647 (2)	0.7742 (12)	0.109 (9)

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

P—C1	1.819 (2)	C3—C4	1.508 (4)
P—C11	1.819 (2)	C4—C5	1.504 (4)
P—B	1.919 (3)	C5—C6	1.512 (4)
P—H	1.26 (2)	C11—C12	1.513 (3)
B—H*A*	0.99 (3)	C11—C16	1.513 (3)
B—H*B*	1.07 (2)	C12—C13	1.514 (4)
B—H*C*	1.05 (2)	C13—C14	1.489 (4)
C1—C6	1.518 (3)	C14—C15	1.500 (3)
C1—C2	1.523 (3)	C15—C16	1.517 (3)
C2—C3	1.515 (3)		
B—P—H	112.6 (7)	P—B—H*A*	104.7 (15)
B—P—C1	113.97 (13)	P—B—H*B*	108.4 (11)
B—P—C11	114.27 (12)	P—B—H*C*	104.9 (13)
C1—P—C11	109.15 (9)	H*A*—B—H*B*	110.4 (19)
H—P—C1	101.4 (7)	H*A*—B—H*C*	113 (2)
H—P—C11	104.3 (7)	H*B*—B—H*C*	114.7 (18)

The intensities were collected at room temperature and averaged in point group 2/*m*. The variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term $(0.014I)^2$ and the variances of the merged data were obtained by propagation of error plus the addition of another term, $(0.014\langle I\rangle)^2$.

Oscillation photographs revealed the presence of a superstructure requiring a doubling of the *a* axis. The intensities of the additional layer lines observed in these photographs are approximately 0.01% of that for the layer lines corresponding to the substructure. The intensities of the additional layer lines are sufficiently weak that the structure described here is an accurate representation of the molecular geometry of (dicyclohexylphosphino)borane.

The structure was solved by direct methods. The initial solution revealed the position of all the non-H atoms. After one round of least-squares refinement, difference Fourier maps revealed the positions of the H atoms. H-atom parameters were refined without restraints.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1263). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-Bromo-2*H*-3,1-benzoxazine-2,4(1*H*)-dione at 153 K

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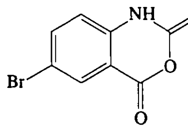
Abstract

The crystal structure of the title compound, $C_8H_4BrNO_3$, was determined at 153 K. The structure was solved by direct methods and refined by least-squares calculations to a final *R* value of 0.056. The molecular geometry is similar to that of the parent non-brominated compound but the crystal packing differs.

Comment

The title compound, (I), crystallizes in space group $Pna2_1$ with one molecule in the asymmetric unit. The molecule is planar (the r.m.s. deviation from the best plane through all the atoms is 0.019 Å, with a maximum deviation of 0.045 Å for O2).



(I)

The distances as well as the angles are generally as expected. The molecular geometry adopted is very similar to that observed in the parent compound without the Br atom (Kashino, Nakashima & Haisa, 1978) but the crystal packing displays some different features. In the non-brominated structure, the packing results from the stacking of dimers held together by hydrogen bonds between N and O2. In the present structure, these dimers

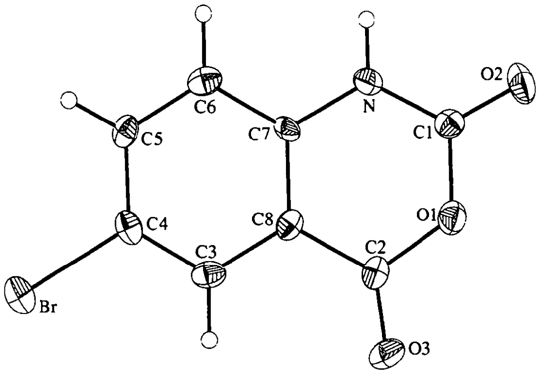


Fig. 1. Molecular structure of the title compound. Non-H atoms are represented by displacement ellipsoids at the 50% probability level. The atomic numbering scheme used in the paper is shown and is equivalent to the one used by Kashino *et al.* (1978) for the non-brominated compound.

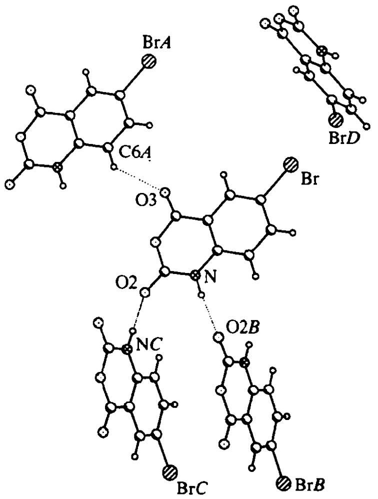


Fig. 2. View of the crystal packing of the title compound. For clarity, only the molecules surrounding the central one are displayed.