

Diphenylphosphenium bromide

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Key indicators

Single-crystal X-ray study
 $T = 173\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.041
 wR factor = 0.096
 Data-to-parameter ratio = 15.9

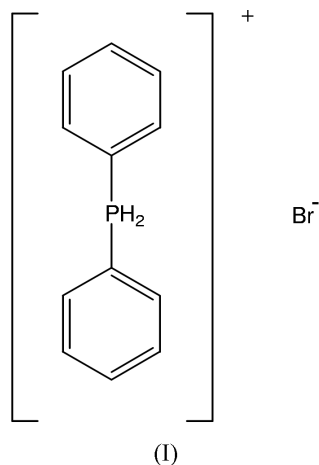
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title compound, $\text{C}_{12}\text{H}_{12}\text{P}^+\cdot\text{Br}^-$, is composed of discrete cations and anions, which are both located on a crystallographic mirror plane. The angle between the two phenyl rings is $69.18(11)^\circ$. The crystal packing is stabilized by $\text{P}-\text{H}\cdots\text{Br}$ hydrogen bonds.

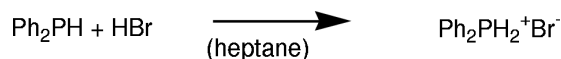
Comment

In contrast to the well established tetraalkyl and tetraaryl phosphonium salts, $\text{R}_4\text{P}^+\cdot\text{X}^-$, only a few phosphonium cations with a $\text{P}-\text{H}$ bond are known. Information regarding the structure and reactivity of these molecules is thus still rather limited. Up to now, only two examples of the type $\text{R}_2\text{PH}_2^+\cdot\text{X}^-$ have been structurally characterized by X-ray crystallography: $\text{R} = \text{Me}$ and $\text{X} = \text{AlCl}_4$ (Aubauer *et al.*, 2000), and $\text{R} = \text{Ph}$ and $\text{X} = \text{GeCl}_3$ (Apostolico *et al.*, 2004). We report here the synthesis and the X-ray crystal structure analysis of the phosphonium bromide, $\text{Ph}_2\text{PH}_2^+\cdot\text{Br}^-$, (I).

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The synthesis of (I) was achieved as indicated below.



A perspective view of (I) is shown in Fig. 1. The structure is composed of discrete $\text{C}_{12}\text{H}_{12}\text{P}^+$ cations and Br^- anions, both located on a mirror plane. Bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 1.6 plus three updates; *MOGUL* Version 1.0; Allen, 2002). The dihedral angle between the two phenyl rings is $69.18(11)^\circ$. The Br^- anions connect the cations *via* short $\text{P}-\text{H}\cdots\text{Br}$ hydrogen bonds into chains running along the crystallographic b axis. Each pair of parallel chains is connected by additional

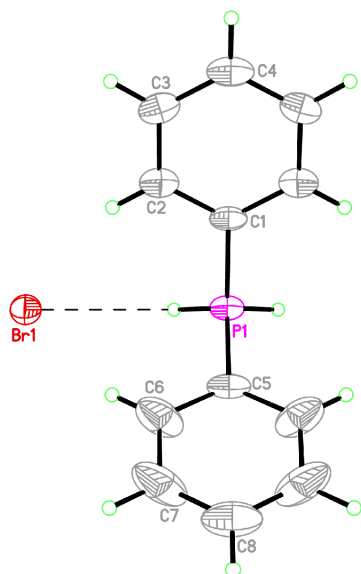


Figure 1
Perspective view of the title compound, showing the atom numbering and displacement ellipsoids at the 50% probability level. P—H···Br hydrogen bonding is shown as dashed lines.

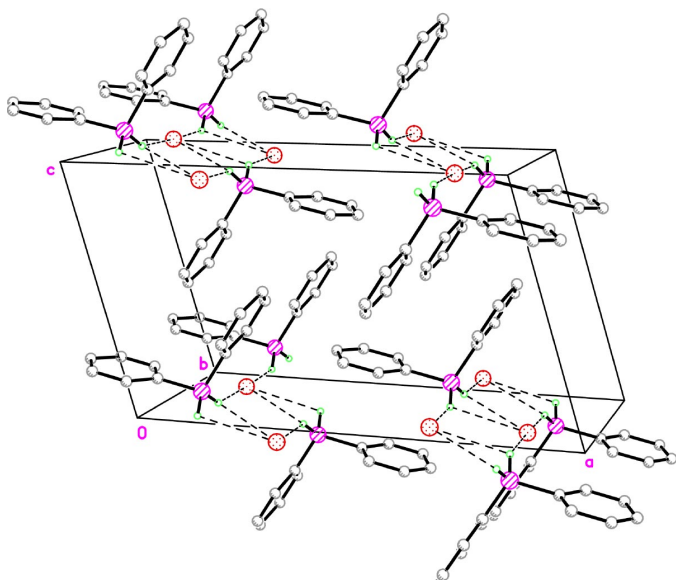


Figure 2
Packing diagram of the title compound, viewed on to the *ac* plane. H atoms bonded to C atoms have been omitted for clarity and P—H···Br hydrogen bonding is shown as dashed lines.

P—H···Br hydrogen bonds. The hydrogen bonds lying parallel to the *b* axis are significantly shorter than those connecting two parallel chains (Table 1). In addition, the P—H···Br angle for the latter of 95.8 (2)° indicates that this should be a very weak interaction.

Experimental

An excess of HBr was added to a mixture of 8.6 mmol Ph₂PH and 3 ml heptane at 77 K. The reaction mixture was warmed up and then stirred for two hours at room temperature. Colourless crystals of (I) were grown by storing this solution at ambient temperature for 2 d.

Crystal data

C₁₂H₁₂P⁺·Br⁻
M_r = 267.10
 Monoclinic, *C*2/*m*
a = 16.778 (2) Å
b = 7.4093 (7) Å
c = 9.8472 (11) Å
 β = 106.097 (9)°
V = 1176.1 (2) Å³
Z = 4

D_x = 1.508 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 8625 reflections
 θ = 3.7–25.7°
 μ = 3.59 mm⁻¹
T = 173 (2) K
 Block, colourless
 0.36 × 0.13 × 0.12 mm

Data collection

Stoe IPDS-II two-circle diffractometer
 ω scans
 Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
 T_{\min} = 0.347, T_{\max} = 0.652
 8687 measured reflections

1222 independent reflections
 1139 reflections with $I > 2\sigma(I)$
 R_{int} = 0.055
 θ_{\max} = 25.8°
 h = -20 → 20
 k = -9 → 9
 l = -12 → 11

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.041
 $wR(F^2)$ = 0.096
 S = 1.08
 1222 reflections
 77 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.2407P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max}$ = 0.001
 $\Delta\rho_{\max}$ = 0.72 e Å⁻³
 $\Delta\rho_{\min}$ = -0.97 e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
P1—H1···Br1	1.19 (4)	2.74 (4)	3.7782 (4)	145 (2)
P1—H1···Br1 ⁱ	1.19 (4)	3.01 (3)	3.3410 (10)	95.8 (18)

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

All H atoms were located in a difference electron-density map and those bonded to C atoms were refined with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model, with C—H = 0.95 Å. The H atom bonded to P was freely refined.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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