

# Crystal structure of $(\pm)$ -[*trans*-cyclohexane-1,2-diylbis(azanediyl)]diphosphonium dibromide dichloromethane disolvate

Aurora Rodríguez Álvarez, Hugo Tlahuext and Jean-Michel Grévy\*

Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Av. Universidad No. 1001, Col. Chamilpa, CP 62209, Cuernavaca Mor., Mexico. \*Correspondence e-mail: jeanmichelg@gmail.com

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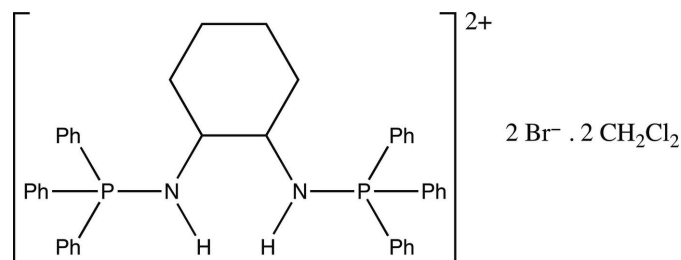
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The cation of the title solvated salt,  $C_{42}H_{42}N_2P_2^{2+} \cdot 2Br^- \cdot 2CH_2Cl_2$ , lies on a crystallographic twofold rotation axis. The 1,2-diaminocyclohexane fragment has a chair conformation with two N atoms in a *transoid* conformation [N—C—C—N = 163.4 (2)°]. In the crystal, the cations are linked to the anions by N—H...Br and C—H...Br hydrogen bonds, forming a chain structure along the *c* axis. The dichloromethane molecule takes part in the hydrogen-bond network through C—H... $\pi$  and C—H...Br interactions.

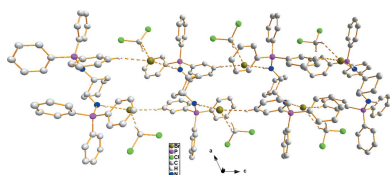
## 1. Chemical context

Quaternary phosphonium salts are very attractive compounds possessing widespread applications in synthetic organic chemistry and have played various important roles as stoichiometric reagents, phase-transfer reagents, reactive intermediates, ionic liquids, building blocks for supramolecular assemblies and catalysts (Werner, 2009). In particular, *P,P*-triaryl-*P*-aminophosphonium salts bearing a primary amino group are isolable intermediates in the Horner & Oediger (1959) synthesis of iminophosphoranes. The title phosphonium compound was used to synthesize new chiral iminophosphorane complexes in view of its catalytic application for organic transformations including olefin-CO copolymerization (Tardif *et al.*, 1998) and enantioselective copper-catalysed cyclopropanation (Reetz & Bohres, 1998), but its crystal structure had not been determined.

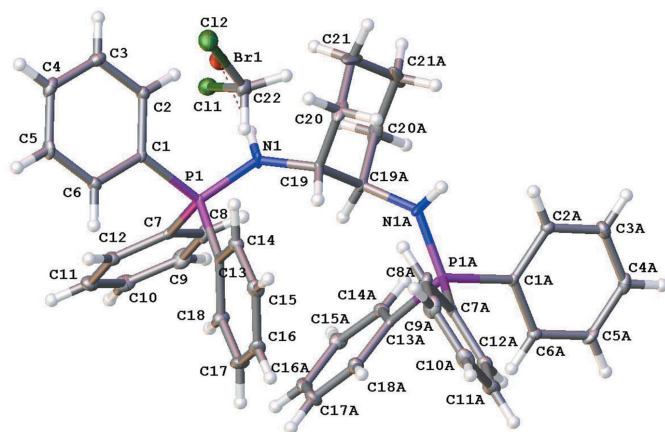


## 2. Structural commentary

The cation is situated on a crystallographic twofold rotation axis (Fig. 1). The 1,2-diaminocyclohexane fragment has a chair conformation with N atoms in a *transoid* conformation [N1—C19—C19<sup>i</sup>—N1<sup>i</sup> = 163.4 (2)°; symmetry code: (i)  $-x + 1, y, -z + \frac{3}{2}$ ]. The phosphorus atom has a tetrahedral geometry; the C—P—C angles are in the range 108.61 (12)–108.89 (12)° and



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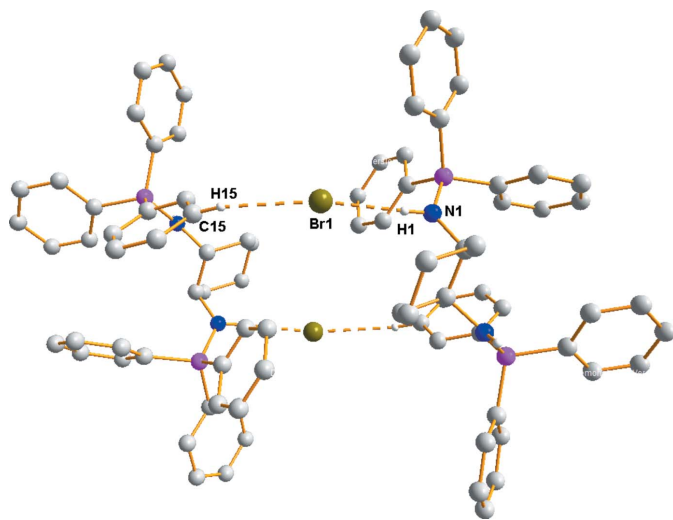


**Figure 1**  
The molecular structure of the title compound, showing the atom-labelling scheme. Atoms with the suffix A are at the symmetry position  $(-x + 1, y, -z + \frac{3}{2})$ .

the N–P–C angles in the range 109.47 (12)–111.00 (12)°. The N–P distance is 1.623 (2) Å.

### 3. Supramolecular features

The Br anion is an acceptor of four hydrogen bonds, three of which are donated by phenyl and amine groups of the *trans*-1,2-diamino(*N,N'*-ditriphenylphosphonio)cyclohexane molecule and the last is donated by the solvent dichloromethane molecule (Table 1). In the hydrogen-bond pattern, the graph-set motif  $R_4^2(22)$  involving atoms  $(-C19-N1-H1 \cdots Br1 \cdots H5-C5-C6-C1-P1-N1-C19)_2$  can be distinguished (Fig. 2). The  $R_4^2(22)$  pattern generates a supramolecular chain running along the *c* axis. The dichloromethane molecule is also linked to the chain *via* C–H  $\cdots \pi$  and C–H  $\cdots Br$  interactions (Fig. 3 and Table 1).



**Figure 2**  
A cation dimer of the title compound formed by N–H  $\cdots$  Br and C–H  $\cdots$  Br hydrogen bonds (dashed lines) with a centrosymmetric  $R_4^2(22)$  motif.

**Table 1**  
Hydrogen-bond geometry (Å, °).

*C*<sub>g</sub> is the centroid of the C7–C12 ring.

<i>D</i> –H $\cdots$ <i>A</i>	<i>D</i> –H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> –H $\cdots$ <i>A</i>
N1–H1 $\cdots$ Br1	0.86 (3)	2.43 (3)	3.285 (2)	172 (3)
C6–H6 $\cdots$ Br1 <sup>i</sup>	0.93	2.80	3.670 (3)	157
C15–H15 $\cdots$ Br1 <sup>ii</sup>	0.93	2.84	3.718 (3)	158
C22–H22A $\cdots$ Br1 <sup>ii</sup>	0.97	2.80	3.562 (3)	136
C22–H22B $\cdots$ C <sub>g</sub> <sup>ii</sup>	0.97	2.54	3.479	163

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

### 4. Database survey

A search of the Cambridge Structural Database (Version 5.37; Groom & Allen, 2014) revealed the existence of 33 deposited phosphonium structures of general formula  $[R_3PNHR']^+$ , where *R* and *R'* are either aryl or alkyl groups. Amongst those, only two structures are polycationic: MELCIQ (Alajarín *et al.*, 2006) is tricationic with a tricyclic structure and trifluoroacetate counter-ions, and WERROB (Demange *et al.*, 2006) is dicationic and contains bromide counter-ions. All the remaining structures are monocationic and only four of them contain a bromide counter-ion: ECUJOC (Boubekour *et al.*, 2006), NEPZUF (Martínez de León *et al.*, 2013), ZOFYAU and ZOFYEU (Imrie *et al.*, 1995). For all the reported compounds, the P–N bond distances assume a partial double-bond character with values falling within the narrow range of 1.60–1.66 Å, regardless of the counter-ion and substituents on both N and P. The N–P distance of the title compound [1.623 (2) Å] agrees with these values. In addition, the P–N–C angle in the present compound [126.9 (2)°] indicates a planar *sp*<sup>2</sup> geometry for the N atom, and falls within the range of 120–133° reported for all related phosphonium structures.

### 5. Synthesis and crystallization

Under an N<sub>2</sub> atmosphere, a solution of 3.07 g of Br<sub>2</sub> in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise under stirring at 273 K, to a solution of Ph<sub>3</sub>P (5.04 g, 19.24 mmol) in 100 ml of the same solvent. After four h of stirring at room temperature and the formation of white precipitate, a mixture of half an equivalent of (*±*)-*trans*-1,2-diaminocyclohexane (1.09 g, 9.62 mmol) and one equivalent of triethylamine (2.68 ml, 19.24 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> was added dropwise under stirring at 273 K. The suspension was left under continuous stirring for 12 h at room temperature. Then the reactant was extracted twice with 25 ml of distilled water, and the organic phase was dried over MgSO<sub>4</sub>. All volatiles were eliminated under vacuum, and the resulting light-yellow solid was stirred with Et<sub>2</sub>O overnight. After filtration, 6.0 g of the title compound was obtained as a white powder (yield 93%, m.p. 563 K). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a dichloromethane solution at room temperature.

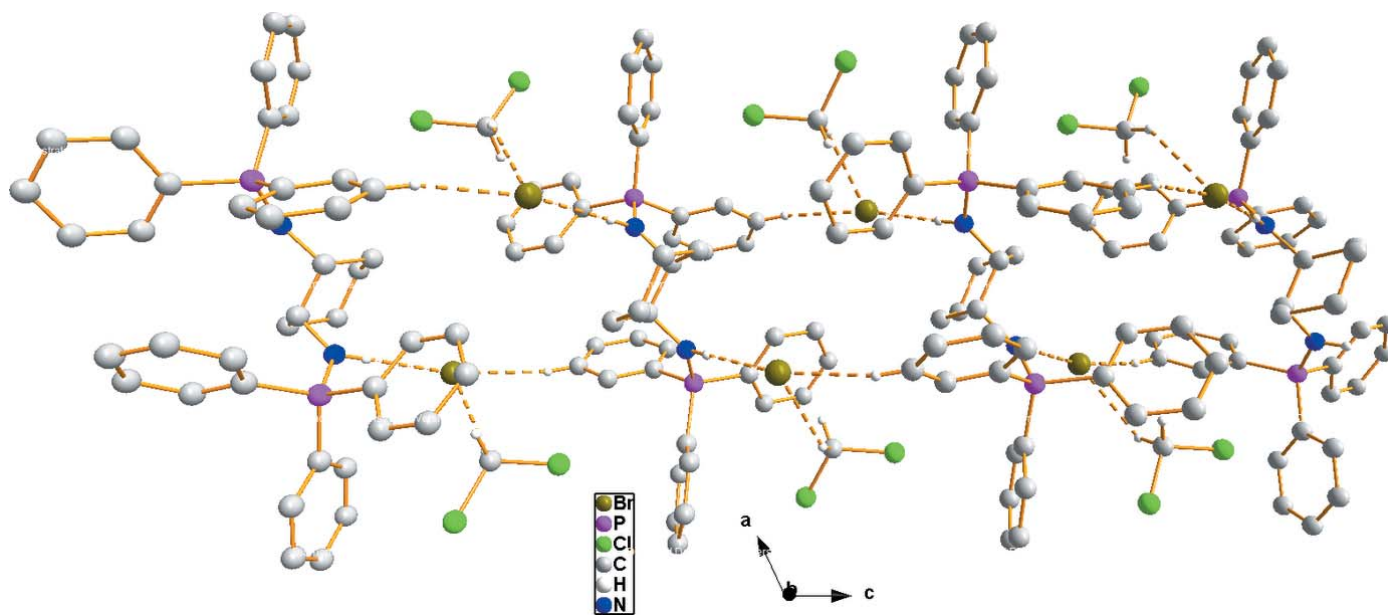


Figure 3

A view of the supramolecular chain, generated by the N—H···Br and C—H···Br interactions, running along the *c* axis. The solvent dichloromethane molecule also makes C—H··· $\pi$  and C—H···Br interactions to the chain. The N—H···Br and C—H···Br hydrogen bonds are indicated by dashed lines. Hydrogen atoms not involved in the hydrogen bonds are omitted for clarity.

Table 2  
Experimental details.

Crystal data	
Chemical formula	$C_{42}H_{42}N_2P_2^{2+} \cdot 2Br^- \cdot 2CH_2Cl_2$
$M_r$	966.39
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
$a, b, c$ (Å)	17.1911 (2), 14.9027 (2), 18.4492 (2)
$\beta$ (°)	114.2547 (15)
$V$ (Å <sup>3</sup> )	4309.34 (10)
$Z$	4
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	5.63
Crystal size (mm)	0.17 × 0.12 × 0.09
Data collection	
Diffractometer	Agilent SuperNova Dual Source diffractometer with an EosS2 detector
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)
$T_{min}, T_{max}$	0.145, 0.602
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	16763, 4256, 4203
$R_{int}$	0.021
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.619
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.098, 1.04
No. of reflections	4256
No. of parameters	248
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	1.54, -1.50

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound H atom was located in a difference Fourier map and its coordinates were refined with a distance restraint of N—H = 0.86 (1) Å with  $U_{iso}(H) = 1.2U_{eq}(N)$ . Other H atoms were positioned geometrically (C—H = 0.93 or 0.97 Å) and constrained using the riding-model approximation with  $U_{iso}(H) = 1.2U_{eq}(C)$ .

## Acknowledgements

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## supporting information

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## Crystal structure of $(\pm)$ -[*trans*-cyclohexane-1,2-diylbis(azanediyl)]diphosphonium dibromide dichloromethane disolvate

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### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

### $(\pm)$ -[*trans*-Cyclohexane-1,2-diylbis(azanediyl)]diphosphonium dibromide dichloromethane disolvate

#### Crystal data

$C_{42}H_{42}N_2P_2^{2+} \cdot 2Br^- \cdot 2CH_2Cl_2$

$M_r = 966.39$

Monoclinic, *C2/c*

$a = 17.1911(2) \text{ \AA}$

$b = 14.9027(2) \text{ \AA}$

$c = 18.4492(2) \text{ \AA}$

$\beta = 114.2547(15)^\circ$

$V = 4309.34(10) \text{ \AA}^3$

$Z = 4$

$F(000) = 1968$

$D_x = 1.490 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation,  $\lambda = 1.54184 \text{ \AA}$

Cell parameters from 13228 reflections

$\theta = 2.6\text{--}72.5^\circ$

$\mu = 5.63 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Plate, colourless

$0.17 \times 0.12 \times 0.09 \text{ mm}$

#### Data collection

Agilent SuperNova Dual Source  
diffractometer with an EosS2 detector

Radiation source: sealed X-ray tube, SuperNova  
(Cu) X-ray Source

Mirror monochromator

Detector resolution:  $8.0769 \text{ pixels mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan  
(*CrysAlis PRO*; Agilent, 2014)

$T_{\min} = 0.145$ ,  $T_{\max} = 0.602$

16763 measured reflections

4256 independent reflections

4203 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 72.7^\circ$ ,  $\theta_{\min} = 4.1^\circ$

$h = -20 \rightarrow 21$

$k = -18 \rightarrow 18$

$l = -22 \rightarrow 22$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.098$

$S = 1.04$

4256 reflections

248 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 29.4173P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.54 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.50 \text{ e \AA}^{-3}$

Extinction correction: SHELXL2014  
 (Sheldrick, 2015),  
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.00026 (3)

### Special details

**Experimental.** MS (FAB<sup>+</sup>) 716 m/z (M-Br)<sup>+</sup> 12%; <sup>31</sup>P NMR (CDCl<sub>3</sub>, 80 MHz, 20°C) 37.05 p.p.m.; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 20°C):  $\delta$  = 0.909-0.859 (m, 2H, CH<sub>2</sub>), 1.349-1.493 (m, 2H, CH<sub>2</sub>), 1.525-1.493 (m, 2H, CH<sub>2</sub>), 1.928-1.902 (m, 2H, CH<sub>2</sub>), 3.626-3.615 (m, 2H, CH-N), 7.918-7.864 (m, 12H, o-C<sub>6</sub>H<sub>5</sub>), 7.677-7.635 (m, 12H, m-C<sub>6</sub>H<sub>5</sub>), 7.553-7.505 (m, 6H, p-C<sub>6</sub>H<sub>5</sub>),  $\delta$  8.59 (s, 2H, NH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 20°C): 24.34 (s, 2C, CH<sub>2</sub>), 36.10 (s, 2C, CH<sub>2</sub>), 57.949 (dd, <sup>2</sup>J<sub>CP</sub> = 2.9 Hz, <sup>3</sup>J<sub>CP</sub> = 10.3 Hz, 2C, CH-N), 121.372 (d, <sup>1</sup>J<sub>CP</sub> = 102.5 Hz, 6 *Cipso*, C<sub>6</sub>H<sub>5</sub>), 129.599 (d, <sup>3</sup>J<sub>CP</sub> = 13.2 Hz, 12 *Cmeta*, C<sub>6</sub>H<sub>5</sub>), 134.307 (d, <sup>4</sup>J<sub>CP</sub> = 2.9 Hz, 6 *Cpara*, C<sub>6</sub>H<sub>5</sub>), 134.505 (d, <sup>2</sup>J<sub>CP</sub> = 7.9 Hz, 12 *Corto*, C<sub>6</sub>H<sub>5</sub>).

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
Br1	0.64866 (2)	0.38834 (2)	0.63298 (2)	0.02162 (12)
P1	0.67384 (4)	0.61073 (4)	0.77021 (4)	0.00659 (15)
Cl1	0.80208 (4)	0.46666 (4)	1.00873 (4)	0.01662 (16)
Cl2	0.88621 (4)	0.41641 (5)	1.17643 (4)	0.02132 (17)
N1	0.61012 (14)	0.52543 (15)	0.75374 (13)	0.0112 (4)
H1	0.619 (2)	0.4854 (17)	0.7247 (17)	0.013*
C1	0.78312 (15)	0.57703 (17)	0.82238 (14)	0.0077 (5)
C2	0.80581 (16)	0.48708 (17)	0.82314 (15)	0.0107 (5)
H2	0.7643	0.4441	0.7977	0.013*
C3	0.89130 (17)	0.46215 (19)	0.86238 (16)	0.0146 (5)
H3	0.9068	0.4022	0.8639	0.017*
C4	0.95309 (17)	0.5265 (2)	0.89913 (16)	0.0151 (5)
H4	1.0100	0.5096	0.9248	0.018*
C5	0.93061 (17)	0.61616 (19)	0.89792 (16)	0.0143 (5)
H5	0.9726	0.6590	0.9224	0.017*
C6	0.84553 (16)	0.64224 (18)	0.86028 (15)	0.0105 (5)
H6	0.8303	0.7021	0.8602	0.013*
C7	0.66066 (16)	0.66197 (17)	0.67754 (15)	0.0097 (5)
C8	0.58964 (17)	0.6405 (2)	0.60814 (16)	0.0154 (5)
H8	0.5494	0.5999	0.6100	0.018*
C9	0.57900 (18)	0.6797 (2)	0.53601 (16)	0.0190 (6)
H9	0.5317	0.6655	0.4898	0.023*
C10	0.63935 (19)	0.7401 (2)	0.53352 (16)	0.0178 (6)
H10	0.6326	0.7659	0.4854	0.021*
C11	0.71012 (18)	0.76242 (19)	0.60279 (17)	0.0158 (6)
H11	0.7501	0.8031	0.6007	0.019*
C12	0.72098 (17)	0.72393 (18)	0.67497 (16)	0.0123 (5)
H12	0.7679	0.7391	0.7212	0.015*
C13	0.64931 (15)	0.69184 (17)	0.82921 (15)	0.0084 (5)

C14	0.66580 (16)	0.67095 (18)	0.90835 (15)	0.0115 (5)
H14	0.6924	0.6172	0.9305	0.014*
C15	0.64235 (18)	0.73048 (19)	0.95346 (16)	0.0143 (5)
H15	0.6519	0.7162	1.0055	0.017*
C16	0.60443 (17)	0.81180 (18)	0.92062 (16)	0.0148 (5)
H16	0.5890	0.8519	0.9510	0.018*
C17	0.58951 (18)	0.83340 (19)	0.84306 (17)	0.0163 (6)
H17	0.5647	0.8882	0.8218	0.020*
C18	0.61150 (17)	0.77332 (18)	0.79696 (16)	0.0134 (5)
H18	0.6009	0.7876	0.7447	0.016*
C19	0.54401 (15)	0.51184 (17)	0.78478 (14)	0.0089 (5)
H19	0.5465	0.5627	0.8194	0.011*
C20	0.55975 (19)	0.4261 (2)	0.83400 (18)	0.0231 (7)
H20A	0.6181	0.4261	0.8739	0.028*
H20B	0.5222	0.4253	0.8614	0.028*
C21	0.5447 (2)	0.3415 (2)	0.7836 (3)	0.0352 (9)
H21A	0.5515	0.2891	0.8168	0.042*
H21B	0.5868	0.3382	0.7612	0.042*
C22	0.79291 (18)	0.4616 (2)	1.10118 (17)	0.0178 (6)
H22A	0.7831	0.5215	1.1164	0.021*
H22B	0.7443	0.4247	1.0955	0.021*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02498 (19)	0.01596 (17)	0.0295 (2)	-0.00524 (11)	0.01685 (14)	-0.00967 (12)
P1	0.0049 (3)	0.0080 (3)	0.0064 (3)	-0.0004 (2)	0.0019 (2)	-0.0009 (2)
Cl1	0.0175 (3)	0.0173 (3)	0.0136 (3)	0.0011 (2)	0.0049 (2)	0.0002 (2)
Cl2	0.0207 (3)	0.0256 (4)	0.0166 (3)	0.0007 (3)	0.0065 (3)	0.0065 (3)
N1	0.0089 (10)	0.0127 (11)	0.0148 (11)	-0.0054 (8)	0.0075 (9)	-0.0065 (9)
C1	0.0056 (11)	0.0111 (12)	0.0059 (11)	0.0000 (9)	0.0018 (9)	0.0011 (9)
C2	0.0104 (12)	0.0108 (12)	0.0103 (12)	-0.0009 (10)	0.0038 (10)	-0.0004 (9)
C3	0.0146 (13)	0.0147 (13)	0.0142 (13)	0.0049 (10)	0.0058 (11)	0.0021 (10)
C4	0.0094 (12)	0.0252 (15)	0.0102 (12)	0.0029 (11)	0.0036 (10)	0.0026 (11)
C5	0.0087 (12)	0.0212 (14)	0.0106 (12)	-0.0057 (10)	0.0014 (10)	-0.0026 (10)
C6	0.0111 (12)	0.0101 (12)	0.0095 (11)	-0.0016 (10)	0.0033 (10)	-0.0013 (9)
C7	0.0111 (12)	0.0117 (12)	0.0071 (11)	0.0043 (10)	0.0046 (10)	0.0010 (9)
C8	0.0086 (12)	0.0236 (14)	0.0127 (13)	-0.0004 (11)	0.0032 (10)	0.0002 (11)
C9	0.0149 (13)	0.0284 (16)	0.0094 (12)	0.0038 (12)	0.0006 (11)	0.0017 (11)
C10	0.0229 (15)	0.0201 (14)	0.0100 (12)	0.0072 (11)	0.0064 (11)	0.0052 (11)
C11	0.0198 (14)	0.0129 (13)	0.0160 (13)	0.0015 (11)	0.0087 (11)	0.0031 (10)
C12	0.0132 (12)	0.0114 (12)	0.0111 (12)	0.0011 (10)	0.0037 (10)	0.0007 (10)
C13	0.0063 (11)	0.0092 (11)	0.0103 (11)	-0.0017 (9)	0.0038 (9)	-0.0027 (9)
C14	0.0122 (12)	0.0108 (12)	0.0096 (12)	-0.0003 (10)	0.0024 (10)	0.0000 (10)
C15	0.0173 (13)	0.0165 (13)	0.0089 (12)	-0.0029 (11)	0.0051 (10)	-0.0027 (10)
C16	0.0161 (13)	0.0132 (13)	0.0162 (13)	-0.0019 (10)	0.0078 (11)	-0.0073 (10)
C17	0.0193 (14)	0.0101 (12)	0.0200 (14)	0.0037 (10)	0.0084 (11)	0.0001 (11)
C18	0.0152 (13)	0.0138 (13)	0.0119 (12)	0.0028 (10)	0.0062 (10)	0.0028 (10)

C19	0.0068 (12)	0.0125 (12)	0.0085 (11)	-0.0028 (9)	0.0042 (10)	-0.0022 (9)
C20	0.0123 (13)	0.0358 (18)	0.0209 (14)	0.0096 (12)	0.0067 (11)	0.0199 (13)
C21	0.043 (2)	0.0136 (15)	0.070 (3)	0.0149 (14)	0.043 (2)	0.0217 (16)
C22	0.0172 (14)	0.0196 (14)	0.0205 (14)	0.0039 (11)	0.0118 (12)	0.0039 (11)

*Geometric parameters (Å, °)*

P1—C13	1.789 (3)	C11—C10	1.395 (4)
P1—N1	1.623 (2)	C12—H12	0.9300
P1—C7	1.800 (3)	C12—C11	1.390 (4)
P1—C1	1.795 (2)	C12—C7	1.404 (4)
C11—C22	1.778 (3)	C13—C14	1.403 (4)
C12—C22	1.767 (3)	C13—C18	1.390 (4)
N1—H1	0.856 (10)	C14—H14	0.9300
N1—C19	1.482 (3)	C14—C15	1.385 (4)
C2—H2	0.9300	C15—H15	0.9300
C2—C1	1.395 (4)	C16—H16	0.9300
C3—H3	0.9300	C16—C17	1.384 (4)
C3—C2	1.396 (4)	C16—C15	1.392 (4)
C4—H4	0.9300	C17—H17	0.9300
C4—C3	1.385 (4)	C18—H18	0.9300
C5—H5	0.9300	C18—C17	1.390 (4)
C5—C4	1.388 (4)	C19—C19 <sup>i</sup>	1.530 (5)
C5—C6	1.392 (4)	C19—H19	0.9800
C6—H6	0.9300	C19—C20	1.526 (4)
C6—C1	1.403 (3)	C20—H20A	0.9700
C8—H8	0.9300	C20—H20B	0.9700
C8—C7	1.396 (4)	C21—C21 <sup>i</sup>	1.527 (8)
C8—C9	1.395 (4)	C21—H21A	0.9700
C9—H9	0.9300	C21—H21B	0.9700
C10—H10	0.9300	C21—C20	1.524 (5)
C10—C9	1.389 (4)	C22—H22A	0.9700
C11—H11	0.9300	C22—H22B	0.9700
C13—P1—C7	108.80 (12)	C7—C12—H12	120.2
C13—P1—C1	108.61 (12)	C14—C13—P1	119.1 (2)
N1—P1—C13	109.47 (12)	C18—C13—P1	121.0 (2)
N1—P1—C7	110.03 (12)	C18—C13—C14	119.9 (2)
N1—P1—C1	111.00 (12)	C13—C14—H14	120.0
C1—P1—C7	108.89 (12)	C15—C14—C13	119.9 (2)
P1—N1—H1	113 (2)	C15—C14—H14	120.0
C19—N1—P1	126.91 (18)	C14—C15—C16	119.7 (2)
C19—N1—H1	121 (2)	C14—C15—H15	120.1
C6—C1—P1	119.42 (19)	C16—C15—H15	120.1
C2—C1—P1	120.07 (19)	C17—C16—H16	119.8
C2—C1—C6	120.5 (2)	C17—C16—C15	120.5 (2)
C3—C2—H2	120.3	C15—C16—H16	119.8
C1—C2—C3	119.5 (2)	C16—C17—C18	120.1 (3)



C1—C2—H2	120.3	C16—C17—H17	120.0
C4—C3—H3	119.9	C18—C17—H17	120.0
C4—C3—C2	120.1 (3)	C13—C18—H18	120.1
C2—C3—H3	119.9	C17—C18—C13	119.8 (2)
C5—C4—H4	119.8	C17—C18—H18	120.1
C3—C4—C5	120.4 (2)	N1—C19—C19 <sup>i</sup>	109.1 (2)
C3—C4—H4	119.8	N1—C19—H19	108.1
C6—C5—H5	119.8	N1—C19—C20	111.6 (2)
C4—C5—H5	119.8	C19 <sup>i</sup> —C19—H19	108.1
C4—C5—C6	120.3 (2)	C20—C19—C19 <sup>i</sup>	111.81 (18)
C5—C6—H6	120.4	C20—C19—H19	108.1
C5—C6—C1	119.1 (2)	C19—C20—H20A	109.1
C1—C6—H6	120.4	C19—C20—H20B	109.1
C12—C7—P1	120.3 (2)	C21—C20—C19	112.6 (3)
C8—C7—P1	119.7 (2)	C21—C20—H20A	109.1
C8—C7—C12	120.0 (2)	C21—C20—H20B	109.1
C7—C8—H8	120.0	H20A—C20—H20B	107.8
C9—C8—H8	120.0	C21 <sup>i</sup> —C21—H21A	109.5
C9—C8—C7	120.1 (3)	C21 <sup>i</sup> —C21—H21B	109.5
C8—C9—H9	120.1	H21A—C21—H21B	108.0
C10—C9—C8	119.8 (3)	C20—C21—C21 <sup>i</sup>	110.9 (2)
C10—C9—H9	120.1	C20—C21—H21A	109.5
C11—C10—H10	119.8	C20—C21—H21B	109.5
C9—C10—C11	120.4 (3)	C11—C22—H22A	109.4
C9—C10—H10	119.8	C11—C22—H22B	109.4
C12—C11—H11	119.9	C12—C22—C11	111.12 (15)
C12—C11—C10	120.2 (3)	C12—C22—H22A	109.4
C10—C11—H11	119.9	C12—C22—H22B	109.4
C11—C12—H12	120.2	H22A—C22—H22B	108.0
C11—C12—C7	119.6 (2)		
P1—C13—C14—C15	-176.0 (2)	C7—P1—C13—C18	10.7 (2)
P1—C13—C18—C17	177.0 (2)	C7—P1—N1—C19	-122.4 (2)
P1—N1—C19—C19 <sup>i</sup>	115.00 (18)	C7—P1—C1—C6	75.4 (2)
P1—N1—C19—C20	-121.0 (2)	C7—P1—C1—C2	-102.7 (2)
N1—P1—C13—C14	68.0 (2)	C7—C12—C11—C10	0.5 (4)
N1—P1—C13—C18	-109.6 (2)	C7—C8—C9—C10	0.1 (4)
N1—P1—C7—C12	-166.0 (2)	C9—C8—C7—P1	-179.9 (2)
N1—P1—C7—C8	14.6 (3)	C9—C8—C7—C12	0.7 (4)
N1—P1—C1—C6	-163.30 (19)	C11—C12—C7—P1	179.6 (2)
N1—P1—C1—C2	18.5 (2)	C11—C12—C7—C8	-1.0 (4)
N1—C19—C20—C21	-69.6 (3)	C11—C10—C9—C8	-0.6 (4)
C1—P1—C13—C14	-53.3 (2)	C12—C11—C10—C9	0.3 (4)
C1—P1—C13—C18	129.0 (2)	C13—P1—N1—C19	-2.9 (3)
C1—P1—N1—C19	117.0 (2)	C13—P1—C7—C12	74.1 (2)
C1—P1—C7—C12	-44.1 (2)	C13—P1—C7—C8	-105.4 (2)
C1—P1—C7—C8	136.4 (2)	C13—P1—C1—C6	-42.9 (2)
C3—C2—C1—P1	178.5 (2)	C13—P1—C1—C2	138.9 (2)

C3—C2—C1—C6	0.4 (4)	C13—C14—C15—C16	-1.6 (4)
C4—C5—C6—C1	-1.2 (4)	C13—C18—C17—C16	-0.6 (4)
C4—C3—C2—C1	-1.0 (4)	C14—C13—C18—C17	-0.6 (4)
C5—C6—C1—P1	-177.4 (2)	C15—C16—C17—C18	0.7 (4)
C5—C6—C1—C2	0.7 (4)	C17—C16—C15—C14	0.4 (4)
C5—C4—C3—C2	0.6 (4)	C18—C13—C14—C15	1.7 (4)
C6—C5—C4—C3	0.5 (4)	C19 <sup>i</sup> —C19—C20—C21	52.9 (3)
C7—P1—C13—C14	-171.7 (2)	C21 <sup>i</sup> —C21—C20—C19	-55.1 (4)

Symmetry code: (i)  $-x+1, y, -z+3/2$ .

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

*Cg* is the centroid of the C7–C12 ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ Br1	0.86 (3)	2.43 (3)	3.285 (2)	172 (3)
C6—H6 $\cdots$ Br1 <sup>ii</sup>	0.93	2.80	3.670 (3)	157
C15—H15 $\cdots$ Br1 <sup>iii</sup>	0.93	2.84	3.718 (3)	158
C22—H22 <i>A</i> $\cdots$ Br1 <sup>iii</sup>	0.97	2.80	3.562 (3)	136
C22—H22 <i>B</i> $\cdots$ <i>Cg</i> <sup>iii</sup>	0.97	2.54	3.479	163

Symmetry codes: (ii)  $-x+3/2, y+1/2, -z+3/2$ ; (iii)  $x, -y+1, z+1/2$ .