

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

**(Furfurylamino)triphenylphosphonium bromide**Carla Martínez de León,<sup>a</sup> Hugo Tlahuext,<sup>a</sup> Angelina Flores-Parra,<sup>b</sup> Angélica María Duarte-Hernández<sup>b</sup> and Jean-Michel Grévy<sup>a\*</sup><sup>a</sup>Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos. Av. Universidad 1001 Col., Chamilpa, CP 62100, Cuernavaca Mor., Mexico, and<sup>b</sup>Departamento de Química, Cinvestav México, 07000 Mexico DF, Mexico  
Correspondence e-mail: jeanmichelg@gmail.com

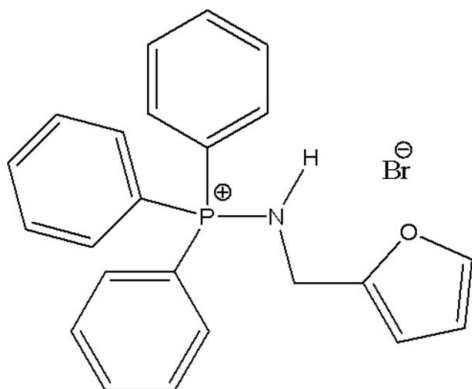
Received 30 November 2012; accepted 13 December 2012

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.129; data-to-parameter ratio = 14.9.

In the title salt,  $\text{C}_{23}\text{H}_{21}\text{NOP}^+\cdot\text{Br}^-$ , the dihedral angles between the phenyl rings are 70.41 (18), 73.6 (2) and 80.85 (19)°. In the crystal, neighboring molecules are linked through an  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bond and four weak  $\text{C}-\text{H}\cdots\text{Br}$  contacts, forming a three-dimensional network.

**Related literature**

For (amino)phosphonium bromides derived from primary amines, see: Cao *et al.* (2010); Boubekeur *et al.* (2006); Dyer *et al.* (2011); Horner & Oediger (1959). For  $\text{C}-\text{H}\cdots\text{X}$  hydrogen bonds, see: Jeffrey (1997); Zhang *et al.* (2003). For graph-set motifs, see: Bernstein, *et al.* (1995).

**Experimental***Crystal data*

$\text{C}_{23}\text{H}_{21}\text{NOP}^+\cdot\text{Br}^-$   
 $M_r = 438.29$   
 Triclinic,  $P\bar{1}$   
 $a = 9.5190$  (19) Å  
 $b = 9.812$  (2) Å

$c = 12.726$  (3) Å  
 $\alpha = 110.30$  (3)°  
 $\beta = 104.89$  (3)°  
 $\gamma = 96.81$  (3)°  
 $V = 1048.7$  (4) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.05$  mm<sup>-1</sup>

$T = 293$  K  
 $0.20 \times 0.17 \times 0.13$  mm

*Data collection*

Siemens P4 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.685$ ,  $T_{\max} = 0.777$

11498 measured reflections  
 3673 independent reflections  
 3213 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.129$   
 $S = 1.02$   
 3673 reflections  
 247 parameters  
 1 restraint

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.32$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.46$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                                 | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1A}\cdots\text{Br1}$               | 0.81 (3)     | 2.49 (3)           | 3.293 (3)   | 170 (4)              |
| $\text{C8}-\text{H8}\cdots\text{Br1}^{\text{i}}$     | 0.93         | 2.98               | 3.835 (4)   | 153                  |
| $\text{C15}-\text{H15}\cdots\text{Br1}^{\text{ii}}$  | 0.93         | 3.00               | 3.728 (4)   | 137                  |
| $\text{C21}-\text{H21}\cdots\text{Br1}^{\text{iii}}$ | 0.93         | 2.94               | 3.829 (6)   | 161                  |
| $\text{C23}-\text{H23}\cdots\text{Br1}^{\text{iv}}$  | 0.93         | 2.97               | 3.782 (4)   | 147                  |

Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $x, y+1, z$ ; (iv)  $-x, -y+1, -z$ .

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: SAINT-Plus NT (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: PLATON (Spek, 2009), publCIF (Westrip, 2010) and DIAMOND (Brandenburg, 2006).

This work was supported by the Consejo Nacional de Ciencia y Tecnología (proyecto No. 134528, CB 2009-01)

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5227).

**References**

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Boubekeur, L., Ulmer, S., Ricard, L., Mézailles, N. & Le Floch, P. (2006). *Organometallics*, **25**, 315–317.  
 Brandenburg, K. (2006). *DIAMOND*. Crystal Impact, Bonn, Germany.  
 Bruker (2001). *SAINTE-Plus NT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Cao, T. P. A., Payet, E., Auffrant, A., Le Goff, X. F. & Le Floch, P. (2010). *Organometallics*, **29**, 3991–3996.  
 Dyer, H., Picot, A., Vendier, L., Auffrant, A., Le Floch, P. & Sabo-Etienne, S. (2011). *Organometallics*, **30**, 1478–1486.  
 Horner, L. & Oediger, H. (1959). *Liebigs Ann. Chem.* **627**, 142–162.  
 Jeffrey, G. A. (1997). *An Introduction to Hydrogen Bonding*, ch. 5. New York: Oxford University Press Inc.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Siemens (1994). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.  
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.  
 Zhang, F., Lerner, H.-W. & Bolte, M. (2003). *Acta Cryst.* **E59**, o1181–o1182.

## supporting information

*Acta Cryst.* (2013). E69, o118 [https://doi.org/10.1107/S1600536812050805]

**(Furfurylamino)triphenylphosphonium bromide**

**Carla Martínez de León, Hugo Tlahuext, Angelina Flores-Parra, Angélica María Duarte-Hernández and Jean-Michel Grévy**

**S1. Comment**

Aminophosphonium salts are important species because of their reactivity and their role as intermediates in numerous organophosphorus reactions. For instance, aminophosphonium derived from primary amine are key intermediates in the preparation of iminophosphoranes through the Horner-Oediger reaction (Horner & Oediger, 1959). Apart from their use in the aza-Wittig reaction, this class of compounds became very important ligands during the past few years due to their good activity in various catalytic processes when coordinated to transition metals (Dyer *et al.*, 2011). Here we report the structure of the (furfurylamino) triphenylphosphonium bromide obtained as an intermediate during the synthesis of the corresponding iminophosphorane.

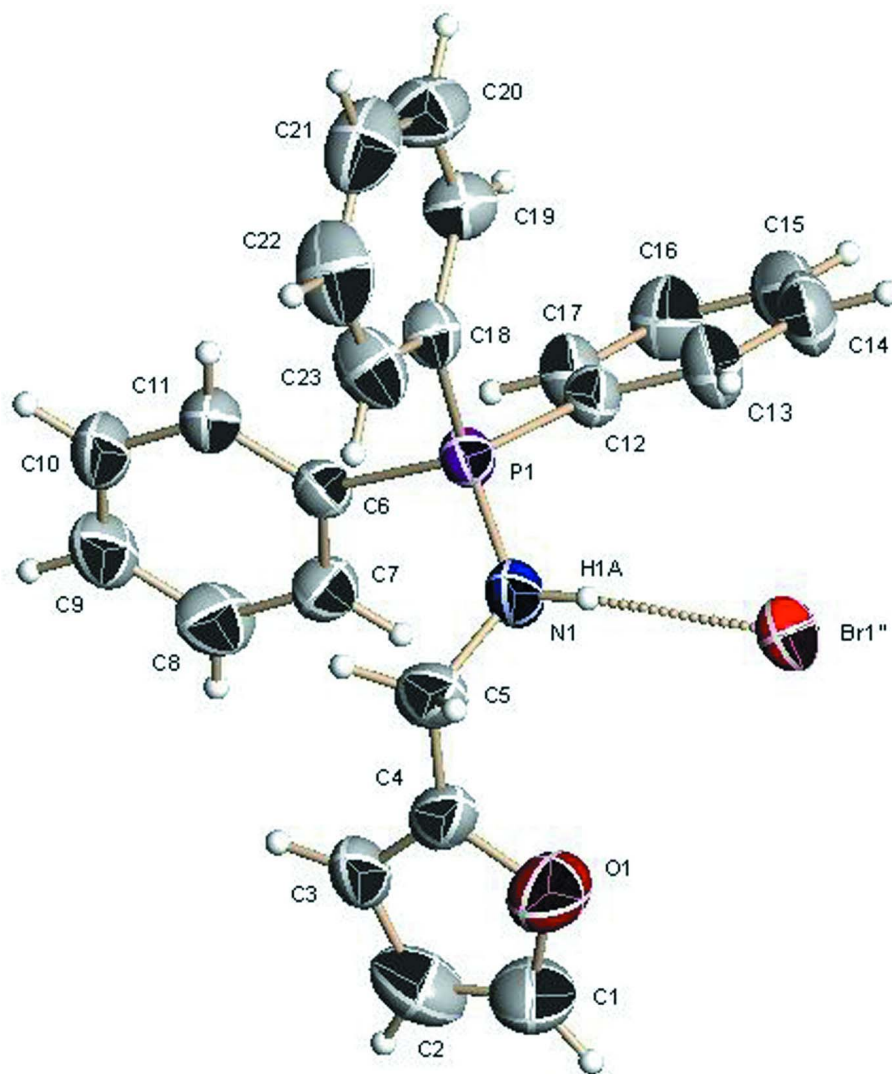
In the crystal structure, neighboring molecules are linked through an N—H $\cdots$ Br hydrogen bond and four weak C—H $\cdots$ Br contacts (Jeffrey, 1997; Zhang, *et al.*, 2003; Table 1), forming a three-dimensional network. In the hydrogen-bond pattern, the C—H $\cdots$ Br contacts form corrugated sheets. These sheets are composed of  $R^2_4(12)$ ,  $R^2_4(18)$ ,  $R^2_4(22)$  and  $R^2_4(24)$  graph set motifs (Bernstein, *et al.* 1995; Fig. 2). Neighboring sheets are further linked by N—H $\cdots$ Br hydrogen bonds, generating the three-dimensional network.

**S2. Experimental**

A mixture of 630 mg of DABCO (5.65 mmol) and 1 ml of furfurylamine (11.31 mmol) in 10 ml of dry benzene was added dropwise through canula between 0 and 5 °C to a stirred suspension of Ph<sub>3</sub>PBr<sub>2</sub> (11.31 mmol) in 20 ml of dry benzene. After 3 h of stirring at ambient temperature, 10 ml of distilled water were added to the medium and the compound extracted with 20 ml of methylene chloride. The organic phase was further washed with 10 ml of water, dried over MgSO<sub>4</sub> and all volatiles were eliminated under vacuum. The off white powder obtained was suspended in Et<sub>2</sub>O and left under stirring overnight. After filtration of the suspension, the solid was crystallized from hot THF giving 4.05 g (81%) of colorless crystals of the title compound, which were suitable for X-ray crystal structure analysis and fully characterized by standard analytical methods. <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>) 30.03 p.p.m.; m. p. 420 K.

**S3. Refinement**

H atoms were positioned geometrically and constrained using the riding-model approximation [C—H<sub>aryl</sub> = 0.93 Å,  $U_{\text{iso}}(\text{H}_{\text{aryl}}) = 1.2 U_{\text{eq}}(\text{C})$ ; C—H<sub>methylene</sub> = 0.97 Å,  $U_{\text{iso}}(\text{H}_{\text{methylene}}) = 1.2 U_{\text{eq}}(\text{C})$ ]. The hydrogen atom bonded to N1 was located in a difference Fourier map. Its coordinates were refined with a distance restraint N—H = 0.86 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$ .



**Figure 1**

The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radius.

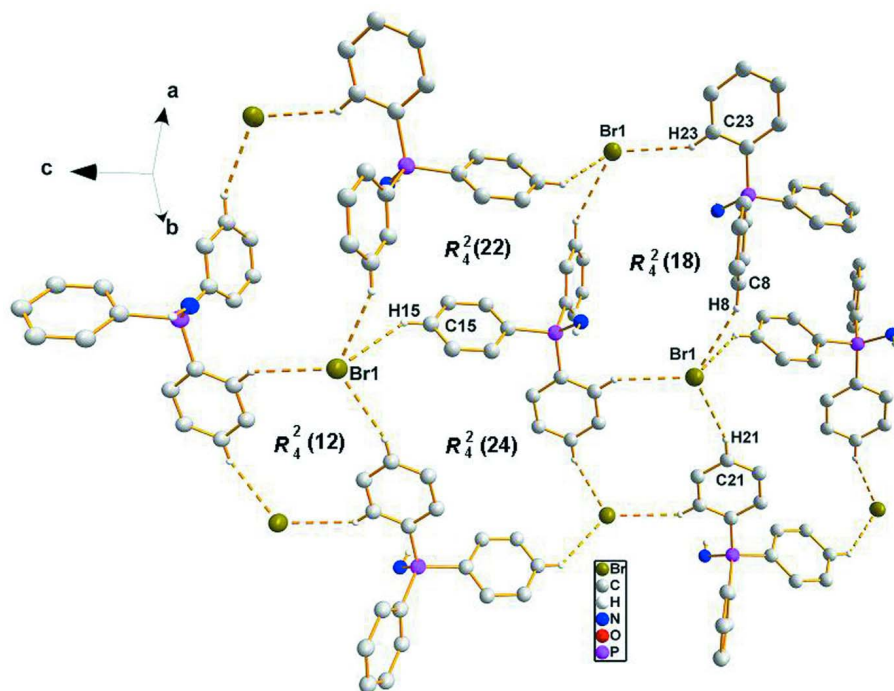


Figure 2

A view of the C—H···Br interactions (dashed lines), showing the  $R_4^2(12)$ ,  $R_4^2(18)$ ,  $R_4^2(22)$  and  $R_4^2(24)$  graph set motifs. The furfuryl group and hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

### (Furfurylamino)triphenylphosphonium bromide

#### Crystal data

$C_{23}H_{21}NOP^+Br^-$

$M_r = 438.29$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 9.5190(19)\ \text{\AA}$

$b = 9.812(2)\ \text{\AA}$

$c = 12.726(3)\ \text{\AA}$

$\alpha = 110.30(3)^\circ$

$\beta = 104.89(3)^\circ$

$\gamma = 96.81(3)^\circ$

$V = 1048.7(4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 448$

$D_x = 1.388\ \text{Mg m}^{-3}$

Melting point: 420 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3600 reflections

$\theta = 4.2\text{--}30^\circ$

$\mu = 2.05\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Plate, colourless

$0.20 \times 0.17 \times 0.13\ \text{mm}$

#### Data collection

Siemens P4  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution:  $8.3\ \text{pixels mm}^{-1}$

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.685$ ,  $T_{\max} = 0.777$

11498 measured reflections

3673 independent reflections

3213 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 4.2^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 15$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.129$   
 $S = 1.02$   
 3673 reflections  
 247 parameters  
 1 restraint  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.001P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

*Special details*

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|     | <i>x</i>     | <i>y</i>    | <i>z</i>    | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|-------------|----------------------------------|
| Br1 | -0.09719 (3) | 0.34393 (3) | 0.15232 (3) | 0.05548 (17)                     |
| C1  | 0.3290 (6)   | 0.1167 (5)  | 0.0155 (5)  | 0.0990 (16)                      |
| H1  | 0.3038       | 0.0160      | 0.0015      | 0.119*                           |
| C2  | 0.4595 (5)   | 0.1890 (6)  | 0.0228 (4)  | 0.0888 (13)                      |
| H2  | 0.5425       | 0.1495      | 0.0163      | 0.107*                           |
| C3  | 0.4491 (4)   | 0.3371 (4)  | 0.0425 (3)  | 0.0671 (9)                       |
| H3  | 0.5230       | 0.4131      | 0.0485      | 0.081*                           |
| C4  | 0.3156 (4)   | 0.3483 (3)  | 0.0509 (3)  | 0.0562 (8)                       |
| C5  | 0.2489 (4)   | 0.4800 (4)  | 0.0737 (3)  | 0.0582 (8)                       |
| H5A | 0.3108       | 0.5592      | 0.0654      | 0.070*                           |
| H5B | 0.1508       | 0.4539      | 0.0157      | 0.070*                           |
| C6  | 0.4994 (3)   | 0.7451 (3)  | 0.2917 (2)  | 0.0435 (6)                       |
| C7  | 0.5865 (4)   | 0.6410 (3)  | 0.2895 (3)  | 0.0564 (7)                       |
| H7  | 0.5496       | 0.5515      | 0.2936      | 0.068*                           |
| C8  | 0.7281 (4)   | 0.6699 (4)  | 0.2812 (4)  | 0.0693 (9)                       |
| H8  | 0.7861       | 0.5996      | 0.2788      | 0.083*                           |
| C9  | 0.7826 (4)   | 0.8027 (4)  | 0.2765 (3)  | 0.0690 (10)                      |
| H9  | 0.8779       | 0.8225      | 0.2711      | 0.083*                           |
| C10 | 0.6976 (4)   | 0.9062 (4)  | 0.2797 (3)  | 0.0651 (9)                       |
| H10 | 0.7360       | 0.9963      | 0.2771      | 0.078*                           |
| C11 | 0.5550 (4)   | 0.8782 (3)  | 0.2867 (3)  | 0.0523 (7)                       |
| H11 | 0.4973       | 0.9485      | 0.2880      | 0.063*                           |
| C12 | 0.3181 (3)   | 0.6870 (3)  | 0.4351 (3)  | 0.0447 (6)                       |
| C13 | 0.1854 (4)   | 0.6505 (4)  | 0.4558 (3)  | 0.0623 (8)                       |

|     |             |             |             |             |
|-----|-------------|-------------|-------------|-------------|
| H13 | 0.0946      | 0.6267      | 0.3965      | 0.075*      |
| C14 | 0.1884 (4)  | 0.6497 (4)  | 0.5642 (3)  | 0.0690 (9)  |
| H14 | 0.0992      | 0.6258      | 0.5781      | 0.083*      |
| C15 | 0.3221 (4)  | 0.6841 (4)  | 0.6525 (3)  | 0.0638 (9)  |
| H15 | 0.3228      | 0.6832      | 0.7255      | 0.077*      |
| C16 | 0.4526 (4)  | 0.7190 (4)  | 0.6332 (3)  | 0.0659 (9)  |
| H16 | 0.5427      | 0.7420      | 0.6930      | 0.079*      |
| C17 | 0.4520 (4)  | 0.7205 (4)  | 0.5243 (3)  | 0.0545 (7)  |
| H17 | 0.5418      | 0.7440      | 0.5113      | 0.065*      |
| C18 | 0.2227 (3)  | 0.8445 (3)  | 0.2856 (2)  | 0.0443 (6)  |
| C19 | 0.2166 (4)  | 0.9579 (4)  | 0.3855 (3)  | 0.0545 (7)  |
| H19 | 0.2557      | 0.9558      | 0.4597      | 0.065*      |
| C20 | 0.1531 (4)  | 1.0735 (4)  | 0.3751 (4)  | 0.0727 (10) |
| H20 | 0.1491      | 1.1490      | 0.4423      | 0.087*      |
| C21 | 0.0956 (4)  | 1.0780 (5)  | 0.2661 (5)  | 0.0790 (12) |
| H21 | 0.0534      | 1.1565      | 0.2591      | 0.095*      |
| C22 | 0.1011 (5)  | 0.9652 (6)  | 0.1673 (4)  | 0.0837 (12) |
| H22 | 0.0630      | 0.9685      | 0.0935      | 0.100*      |
| C23 | 0.1620 (4)  | 0.8474 (4)  | 0.1758 (3)  | 0.0660 (9)  |
| H23 | 0.1621      | 0.7703      | 0.1080      | 0.079*      |
| H1A | 0.157 (3)   | 0.490 (4)   | 0.193 (4)   | 0.079*      |
| N1  | 0.2354 (3)  | 0.5341 (3)  | 0.1936 (2)  | 0.0576 (7)  |
| O1  | 0.2369 (3)  | 0.2133 (3)  | 0.0317 (3)  | 0.0935 (9)  |
| P1  | 0.31407 (8) | 0.69765 (8) | 0.29668 (6) | 0.0415 (2)  |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Br1 | 0.0476 (2)  | 0.0683 (2)  | 0.0579 (2)  | 0.01512 (15) | 0.02311 (15) | 0.02845 (17) |
| C1  | 0.118 (4)   | 0.070 (2)   | 0.147 (4)   | 0.049 (3)    | 0.080 (4)    | 0.049 (3)    |
| C2  | 0.078 (3)   | 0.106 (3)   | 0.085 (3)   | 0.041 (3)    | 0.038 (2)    | 0.026 (2)    |
| C3  | 0.058 (2)   | 0.064 (2)   | 0.068 (2)   | -0.0066 (16) | 0.0343 (16)  | 0.0094 (16)  |
| C4  | 0.071 (2)   | 0.0468 (15) | 0.0448 (16) | 0.0052 (14)  | 0.0174 (14)  | 0.0147 (13)  |
| C5  | 0.071 (2)   | 0.0541 (17) | 0.0449 (16) | 0.0118 (15)  | 0.0177 (14)  | 0.0151 (13)  |
| C6  | 0.0419 (14) | 0.0445 (14) | 0.0417 (14) | 0.0072 (11)  | 0.0166 (11)  | 0.0128 (11)  |
| C7  | 0.0508 (17) | 0.0490 (15) | 0.072 (2)   | 0.0138 (13)  | 0.0261 (14)  | 0.0223 (14)  |
| C8  | 0.0502 (18) | 0.069 (2)   | 0.088 (2)   | 0.0212 (16)  | 0.0285 (17)  | 0.0226 (19)  |
| C9  | 0.0449 (17) | 0.075 (2)   | 0.075 (2)   | -0.0001 (16) | 0.0280 (16)  | 0.0140 (18)  |
| C10 | 0.058 (2)   | 0.0620 (19) | 0.070 (2)   | -0.0046 (15) | 0.0287 (17)  | 0.0207 (17)  |
| C11 | 0.0536 (17) | 0.0487 (15) | 0.0551 (17) | 0.0071 (13)  | 0.0227 (14)  | 0.0187 (13)  |
| C12 | 0.0485 (16) | 0.0439 (14) | 0.0486 (15) | 0.0119 (11)  | 0.0203 (12)  | 0.0223 (12)  |
| C13 | 0.0513 (18) | 0.085 (2)   | 0.0552 (18) | 0.0065 (16)  | 0.0207 (14)  | 0.0328 (17)  |
| C14 | 0.069 (2)   | 0.082 (2)   | 0.071 (2)   | 0.0107 (18)  | 0.0389 (18)  | 0.0381 (19)  |
| C15 | 0.084 (2)   | 0.0650 (19) | 0.0555 (18) | 0.0161 (17)  | 0.0283 (17)  | 0.0353 (16)  |
| C16 | 0.064 (2)   | 0.079 (2)   | 0.058 (2)   | 0.0146 (17)  | 0.0115 (16)  | 0.0368 (18)  |
| C17 | 0.0498 (17) | 0.0644 (18) | 0.0545 (17) | 0.0096 (14)  | 0.0173 (13)  | 0.0303 (15)  |
| C18 | 0.0375 (14) | 0.0532 (15) | 0.0461 (15) | 0.0113 (12)  | 0.0138 (11)  | 0.0234 (13)  |
| C19 | 0.0508 (17) | 0.0547 (16) | 0.0538 (17) | 0.0143 (13)  | 0.0115 (13)  | 0.0196 (14)  |

|     |             |             |             |              |             |             |
|-----|-------------|-------------|-------------|--------------|-------------|-------------|
| C20 | 0.061 (2)   | 0.0589 (19) | 0.092 (3)   | 0.0228 (16)  | 0.0202 (19) | 0.0232 (19) |
| C21 | 0.058 (2)   | 0.080 (2)   | 0.117 (4)   | 0.0233 (19)  | 0.022 (2)   | 0.063 (3)   |
| C22 | 0.074 (3)   | 0.121 (3)   | 0.086 (3)   | 0.034 (2)    | 0.023 (2)   | 0.075 (3)   |
| C23 | 0.064 (2)   | 0.092 (2)   | 0.0545 (19) | 0.0258 (18)  | 0.0226 (16) | 0.0379 (18) |
| N1  | 0.0556 (16) | 0.0542 (14) | 0.0539 (15) | -0.0049 (12) | 0.0266 (12) | 0.0099 (12) |
| O1  | 0.0757 (18) | 0.0658 (15) | 0.141 (3)   | 0.0168 (13)  | 0.0499 (18) | 0.0326 (17) |
| P1  | 0.0393 (4)  | 0.0451 (4)  | 0.0424 (4)  | 0.0081 (3)   | 0.0177 (3)  | 0.0171 (3)  |

*Geometric parameters (Å, °)*

|          |           |             |            |
|----------|-----------|-------------|------------|
| Br1—H1A  | 2.49 (2)  | C12—C13     | 1.387 (4)  |
| C1—C2    | 1.319 (7) | C12—P1      | 1.791 (3)  |
| C1—O1    | 1.365 (5) | C13—C14     | 1.376 (5)  |
| C1—H1    | 0.9300    | C13—H13     | 0.9300     |
| C2—C3    | 1.407 (6) | C14—C15     | 1.377 (6)  |
| C2—H2    | 0.9300    | C14—H14     | 0.9300     |
| C3—C4    | 1.317 (5) | C15—C16     | 1.354 (5)  |
| C3—H3    | 0.9300    | C15—H15     | 0.9300     |
| C4—O1    | 1.350 (4) | C16—C17     | 1.390 (5)  |
| C4—C5    | 1.479 (5) | C16—H16     | 0.9300     |
| C5—N1    | 1.477 (4) | C17—H17     | 0.9300     |
| C5—H5A   | 0.9700    | C18—C23     | 1.380 (4)  |
| C5—H5B   | 0.9700    | C18—C19     | 1.389 (4)  |
| C6—C11   | 1.379 (4) | C18—P1      | 1.796 (3)  |
| C6—C7    | 1.387 (4) | C19—C20     | 1.377 (5)  |
| C6—P1    | 1.794 (3) | C19—H19     | 0.9300     |
| C7—C8    | 1.383 (5) | C20—C21     | 1.372 (6)  |
| C7—H7    | 0.9300    | C20—H20     | 0.9300     |
| C8—C9    | 1.371 (6) | C21—C22     | 1.375 (7)  |
| C8—H8    | 0.9300    | C21—H21     | 0.9300     |
| C9—C10   | 1.368 (6) | C22—C23     | 1.378 (6)  |
| C9—H9    | 0.9300    | C22—H22     | 0.9300     |
| C10—C11  | 1.384 (5) | C23—H23     | 0.9300     |
| C10—H10  | 0.9300    | N1—P1       | 1.614 (3)  |
| C11—H11  | 0.9300    | N1—H1A      | 0.817 (19) |
| C12—C17  | 1.386 (4) |             |            |
| C2—C1—O1 | 109.1 (4) | C12—C13—H13 | 120.1      |
| C2—C1—H1 | 125.4     | C13—C14—C15 | 120.7 (3)  |
| O1—C1—H1 | 125.4     | C13—C14—H14 | 119.7      |
| C1—C2—C3 | 106.9 (4) | C15—C14—H14 | 119.7      |
| C1—C2—H2 | 126.5     | C16—C15—C14 | 120.2 (3)  |
| C3—C2—H2 | 126.5     | C16—C15—H15 | 119.9      |
| C4—C3—C2 | 107.4 (3) | C14—C15—H15 | 119.9      |
| C4—C3—H3 | 126.3     | C15—C16—C17 | 120.1 (3)  |
| C2—C3—H3 | 126.3     | C15—C16—H16 | 120.0      |
| C3—C4—O1 | 109.4 (3) | C17—C16—H16 | 120.0      |
| C3—C4—C5 | 129.4 (3) | C12—C17—C16 | 120.3 (3)  |

|                 |            |                 |             |
|-----------------|------------|-----------------|-------------|
| O1—C4—C5        | 121.2 (3)  | C12—C17—H17     | 119.9       |
| N1—C5—C4        | 111.2 (3)  | C16—C17—H17     | 119.9       |
| N1—C5—H5A       | 109.4      | C23—C18—C19     | 119.3 (3)   |
| C4—C5—H5A       | 109.4      | C23—C18—P1      | 119.2 (2)   |
| N1—C5—H5B       | 109.4      | C19—C18—P1      | 121.4 (2)   |
| C4—C5—H5B       | 109.4      | C20—C19—C18     | 120.2 (3)   |
| H5A—C5—H5B      | 108.0      | C20—C19—H19     | 119.9       |
| C11—C6—C7       | 119.8 (3)  | C18—C19—H19     | 119.9       |
| C11—C6—P1       | 122.2 (2)  | C21—C20—C19     | 120.4 (4)   |
| C7—C6—P1        | 117.9 (2)  | C21—C20—H20     | 119.8       |
| C8—C7—C6        | 120.2 (3)  | C19—C20—H20     | 119.8       |
| C8—C7—H7        | 119.9      | C20—C21—C22     | 119.3 (4)   |
| C6—C7—H7        | 119.9      | C20—C21—H21     | 120.4       |
| C9—C8—C7        | 119.6 (3)  | C22—C21—H21     | 120.4       |
| C9—C8—H8        | 120.2      | C21—C22—C23     | 121.2 (4)   |
| C7—C8—H8        | 120.2      | C21—C22—H22     | 119.4       |
| C10—C9—C8       | 120.4 (3)  | C23—C22—H22     | 119.4       |
| C10—C9—H9       | 119.8      | C22—C23—C18     | 119.5 (4)   |
| C8—C9—H9        | 119.8      | C22—C23—H23     | 120.2       |
| C9—C10—C11      | 120.6 (3)  | C18—C23—H23     | 120.2       |
| C9—C10—H10      | 119.7      | C5—N1—P1        | 125.8 (2)   |
| C11—C10—H10     | 119.7      | C5—N1—H1A       | 110 (3)     |
| C6—C11—C10      | 119.4 (3)  | P1—N1—H1A       | 119 (3)     |
| C6—C11—H11      | 120.3      | C4—O1—C1        | 107.1 (3)   |
| C10—C11—H11     | 120.3      | N1—P1—C12       | 107.89 (14) |
| C17—C12—C13     | 119.0 (3)  | N1—P1—C6        | 107.03 (14) |
| C17—C12—P1      | 121.1 (2)  | C12—P1—C6       | 111.12 (14) |
| C13—C12—P1      | 119.9 (2)  | N1—P1—C18       | 115.68 (15) |
| C14—C13—C12     | 119.8 (3)  | C12—P1—C18      | 106.98 (13) |
| C14—C13—H13     | 120.1      | C6—P1—C18       | 108.18 (13) |
| O1—C1—C2—C3     | -1.0 (6)   | C19—C18—C23—C22 | 2.2 (5)     |
| C1—C2—C3—C4     | 2.6 (5)    | P1—C18—C23—C22  | -175.4 (3)  |
| C2—C3—C4—O1     | -3.1 (5)   | C4—C5—N1—P1     | 119.5 (3)   |
| C2—C3—C4—C5     | 178.7 (4)  | C3—C4—O1—C1     | 2.5 (5)     |
| C3—C4—C5—N1     | -108.5 (4) | C5—C4—O1—C1     | -179.1 (4)  |
| O1—C4—C5—N1     | 73.5 (4)   | C2—C1—O1—C4     | -0.8 (6)    |
| C11—C6—C7—C8    | -0.6 (5)   | C5—N1—P1—C12    | -160.2 (3)  |
| P1—C6—C7—C8     | 177.6 (3)  | C5—N1—P1—C6     | -40.5 (3)   |
| C6—C7—C8—C9     | 0.7 (6)    | C5—N1—P1—C18    | 80.1 (3)    |
| C7—C8—C9—C10    | -0.2 (6)   | C17—C12—P1—N1   | 120.1 (3)   |
| C8—C9—C10—C11   | -0.5 (6)   | C13—C12—P1—N1   | -62.5 (3)   |
| C7—C6—C11—C10   | -0.1 (5)   | C17—C12—P1—C6   | 3.1 (3)     |
| P1—C6—C11—C10   | -178.2 (2) | C13—C12—P1—C6   | -179.5 (2)  |
| C9—C10—C11—C6   | 0.7 (5)    | C17—C12—P1—C18  | -114.8 (3)  |
| C17—C12—C13—C14 | 0.7 (5)    | C13—C12—P1—C18  | 62.6 (3)    |
| P1—C12—C13—C14  | -176.7 (3) | C11—C6—P1—N1    | 128.4 (3)   |
| C12—C13—C14—C15 | -0.4 (6)   | C7—C6—P1—N1     | -49.7 (3)   |



|                 |           |                |            |
|-----------------|-----------|----------------|------------|
| C13—C14—C15—C16 | 0.0 (6)   | C11—C6—P1—C12  | -114.0 (3) |
| C14—C15—C16—C17 | 0.1 (6)   | C7—C6—P1—C12   | 67.8 (3)   |
| C13—C12—C17—C16 | -0.7 (5)  | C11—C6—P1—C18  | 3.2 (3)    |
| P1—C12—C17—C16  | 176.7 (3) | C7—C6—P1—C18   | -175.0 (2) |
| C15—C16—C17—C12 | 0.3 (5)   | C23—C18—P1—N1  | -39.4 (3)  |
| C23—C18—C19—C20 | -1.2 (5)  | C19—C18—P1—N1  | 143.0 (3)  |
| P1—C18—C19—C20  | 176.4 (3) | C23—C18—P1—C12 | -159.6 (3) |
| C18—C19—C20—C21 | -0.2 (6)  | C19—C18—P1—C12 | 22.8 (3)   |
| C19—C20—C21—C22 | 0.5 (7)   | C23—C18—P1—C6  | 80.6 (3)   |
| C20—C21—C22—C23 | 0.6 (7)   | C19—C18—P1—C6  | -97.0 (3)  |
| C21—C22—C23—C18 | -2.0 (6)  |                |            |

*Hydrogen-bond geometry (Å, °)*

| <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—H1A $\cdots$ Br1                 | 0.81 (3)    | 2.49 (3)            | 3.293 (3)                  | 170 (4)                       |
| C8—H8 $\cdots$ Br1 <sup>i</sup>     | 0.93        | 2.98                | 3.835 (4)                  | 153                           |
| C15—H15 $\cdots$ Br1 <sup>ii</sup>  | 0.93        | 3.00                | 3.728 (4)                  | 137                           |
| C21—H21 $\cdots$ Br1 <sup>iii</sup> | 0.93        | 2.94                | 3.829 (6)                  | 161                           |
| C23—H23 $\cdots$ Br1 <sup>iv</sup>  | 0.93        | 2.97                | 3.782 (4)                  | 147                           |

Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $-x, -y+1, -z+1$ ; (iii)  $x, y+1, z$ ; (iv)  $-x, -y+1, -z$ .