

# Nitrosonium complexation by the tetraphosphonate cavitand 5,11,17,23-tetramethyl-6,10:12,16:-18,22:24,4-tetrakis(phenylphosphonato- $\kappa^2O,O'$ )-resorcin(4)arene

Roberta Pinalli and Chiara Massera\*

Received 27 October 2017

Accepted 31 October 2017

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

**Keywords:** crystal structure; tetraphosphonate cavitands; inclusion compounds; nitrosonium ion; C—H $\cdots$ F interactions; C—H $\cdots$  $\pi$  interactions.

**CCDC reference:** 1583086

**Supporting information:** this article has supporting information at journals.iucr.org/e

Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Università di Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy. \*Correspondence e-mail: chiara.massera@unipr.it

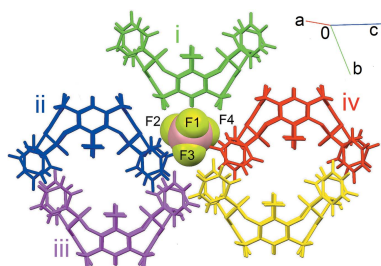
The crystal structure of a new supramolecular complex between the tetraphosphonate cavitand 5,11,17,23-tetramethyl-6,10:12,16:18,22:24,4-tetrakis(phenylphosphonato- $\kappa^2O,O'$ )resorcin(4)arene and the nitrosyl cation  $\text{NO}^+$ , as the  $\text{BF}_4^-$  salt, is reported. The complex, of general formula  $[(\text{C}_{56}\text{H}_{44}\text{P}_4\text{O}_{12})(\text{NO})]\text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$  or  $\text{NO}@\text{Tiiii}[\text{H}, \text{CH}_3, \text{C}_6\text{H}_5] \text{BF}_4 \cdot \text{CH}_2\text{Cl}_2$ , crystallizes in the space group  $P\bar{1}$ . The nitrosyl cation is disordered over two equivalent positions, with occupancies of 0.503 (2) and 0.497 (2), and interacts with two adjacent  $\text{P}=\text{O}$  groups at the upper rim of the cavitand through dipole–charge interactions. In the lattice, the cavitands are connected through a series of C—H $\cdots$  $\pi$  interactions involving the methyl and methylenic H atoms and the aromatic rings of the macrocycle. The structure is further stabilized by the presence of C—H $\cdots$ F interactions between the hydrogen atoms of the cavitands and the F atoms of the tetrafluoridoborate anion. As a result of the disorder, the lattice dichloromethane molecules could not be modelled in terms of atomic sites, and were treated using the *PLATON SQUEEZE* procedure [Spek (2015). *Acta Cryst. C* **71**, 9–18]. The complexation process has also been studied in solution through NMR titrations.

## 1. Chemical context

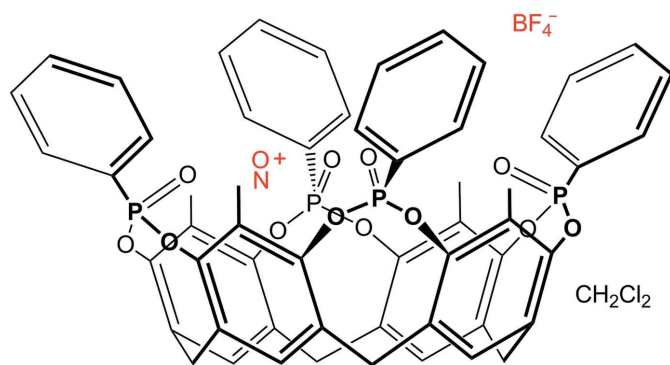
Cavitands (Cram, 1983; Cram & Cram, 1994) are synthetic organic compounds endowed with a rigid, pre-organized cavity that have been used extensively both in solution (Hooley & Rebek, 2009; Pochorowski *et al.*, 2012) and in the solid state (Riboni *et al.*, 2016) as molecular receptors for neutral molecules and cationic species (Pinalli & Dalcanale, 2013). This versatility stems from the possibility of decorating both the upper and the lower rim of the resorcinarene skeleton with desired functionalities.

In our group, we have been particularly interested in tetraphosphonate cavitands of the general formula  $\text{Tiiii}[R, R_1, R_2]$  ( $R$  = lower rim substituents;  $R_1$  = upper rim substituents;  $R_2$  = substituents on the P atom) in which the upper rim of the macrocycle is functionalized with four  $\text{P}=\text{O}$  groups, all pointing inwards towards the cavity (Pinalli & Dalcanale, 2013). In this way, the  $\pi$  basicity of the cavity, useful for C—H $\cdots$  $\pi$  recognition, is enriched with dipolar groups that can act both as hydrogen-bond acceptors and interact with cationic species through cation–dipole interactions.

The nitrosonium ion and its salts have been studied in the past to investigate similarities and differences with the  $\text{O}_2^+$  ion in terms of size, ionization potential, electron affinity, oxida-



tion power *etc* (Mazej *et al.*, 2009). Moreover, the  $\text{NO}^+$  cation can be used as a model for nitrogen oxides in molecular recognition phenomena. Indeed, the formation of stable, host–guest complexes between  $\text{NO}^+$  cations and organic molecular receptors has been studied in solution with resorcinarenes (Botta *et al.*, 2007) or with calixarenes, both in solution (Zyryanov *et al.*, 2002, 2003) and in the solid state (Rathore *et al.*, 2000). In particular, nitrosonium hexachloroantimonate was shown to form an inclusion compound with tetramethoxy- and tetra-*n*-propoxycalix(4)arenes due to the interaction between the positive charge of the guest and the electron-rich aromatic cavity of the host (Rathore *et al.*, 2000). Inspired by this work, we decided to carry out a combined solution and solid-state study of the complexation properties of the rigid tetraphosphonate cavitand 5,11,17,23-tetramethyl-6,10:12,16:18,22:24,4-tetrakis(phenylphosphonato-*O,O'*)resorcin(4)arene (from now on indicated as Tiiii[H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>]) towards  $\text{NOBF}_4$ .



## 2. Studies in solution

Preliminary  $^{31}\text{P}$  and  $^1\text{H}$  NMR studies were performed to probe the complexation properties of the cavitand towards the nitrosonium ion in solution. To this purpose, we synthesized the cavitand Tiiii[C<sub>3</sub>H<sub>7</sub>, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>], functionalized at the lower rim with four –C<sub>3</sub>H<sub>7</sub> alkyl chains to enhance the cavitand solubility. The NMR tube was filled with 0.5 ml of a  $\text{CDCl}_3$  solution containing the cavitand (1 mmol concentration). The  $\text{NOBF}_4$  titrant solution was prepared by dissolving the guest in 0.4 ml (10 mmol) of the above-mentioned cavitand solution to keep the concentration of the host constant during the titration. Portions (0.25 eq., 22.5  $\mu\text{L}$ ) of the titrant were added by syringe to the NMR tube. During the titration, the phosphorous singlet of the cavitand shifted slightly downfield, from 6.01 (signal for the free host) to 7.42 ppm upon addition of an excess (2.5 eq.) of the guest (see Fig. S1 in the *Supporting information*), indicating the presence of cation–dipole interactions between the nitrosonium ion and the phosphonate groups at the upper rim. The broadening of the signal is due to the fast exchange (at the NMR time scale) of the guest inside the cavity.

In Fig. 1, the comparison between the  $^1\text{H}$  spectra recorded after each guest addition is reported. As can be seen, the

protons of the methyl group in the apical position of the cavitand skeleton (purple dot) are shifted up-field, increasing the guest concentration; this means that the presence of the  $\text{NO}^+$  cation in proximity to the cavitand upper rim creates a change in the environment, which results in an overall shielding effect. On the contrary, the signals of the protons at the lower rim, namely the aromatic hydrogens (light-blue dot), the bridging methines (green dot) and the alkyl methylenic groups (red dot), are shifted downfield. This is due to the perturbation created by the  $\text{BF}_4^-$  anion, which is likely positioned among the alkyl feet of the cavitand, as already observed for counter-anions in other crystal structures previously reported (Pinalli *et al.*, 2016). Also in this case, broadening of the signals was observed.

Following these results, solid-state studies were carried out to obtain an insight into the type, number, strength and geometry of the weak interactions taking place in the system.

## 3. Structural commentary

The molecular structure of  $\text{NO@Tiiii}[\text{H}, \text{CH}_3, \text{C}_6\text{H}_5]\text{BF}_4^- \cdot \text{CH}_2\text{Cl}_2$  is reported in Fig. 2. The complex crystallizes in the space group  $P\bar{1}$ , and the asymmetric unit comprises one cavitand, one molecule of  $\text{NOBF}_4$  (with the cation disordered over two equivalent positions) and one disordered molecule of dichloromethane. The  $\text{NO}^+\text{BF}_4^-$  ionic pair is separated, and the nitrosonium ion is located within the macrocycle, not deep inside the cavity, but lying in the mean plane passing through the four phosphonate oxygen atoms O3A, O3B, O3C and O3D (for detailed geometrical parameters, see Table 1). The nitrogen and oxygen atoms of the guest point towards the lower and the upper rims, respectively, and are held in place *via* cation–dipole interactions with two adjacent  $\text{P}=\text{O}$  groups. It is interesting to note that the  $\text{NO}^+$  ion is disordered with 50% probability over two equivalent orientations [N1O1 with occupancy of 0.503 (2) and N2O2 with occupancy of 0.497 (2)], thus forming alternately an interaction with each of the two

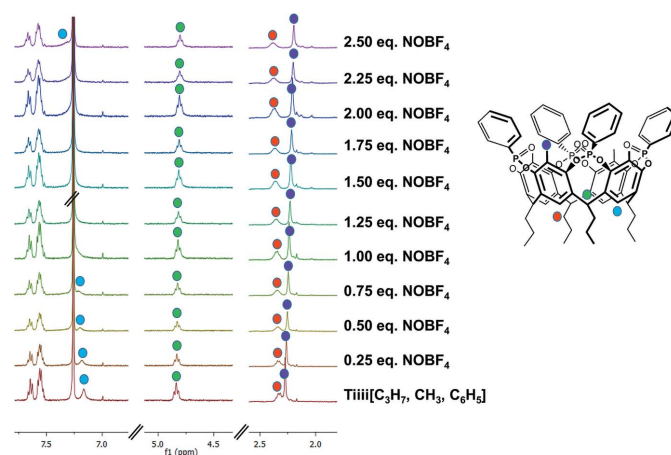


Figure 1

Selected portions of the  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K) spectra recorded during the titration of the cavitand with increasing equivalents of  $\text{NOBF}_4$ .

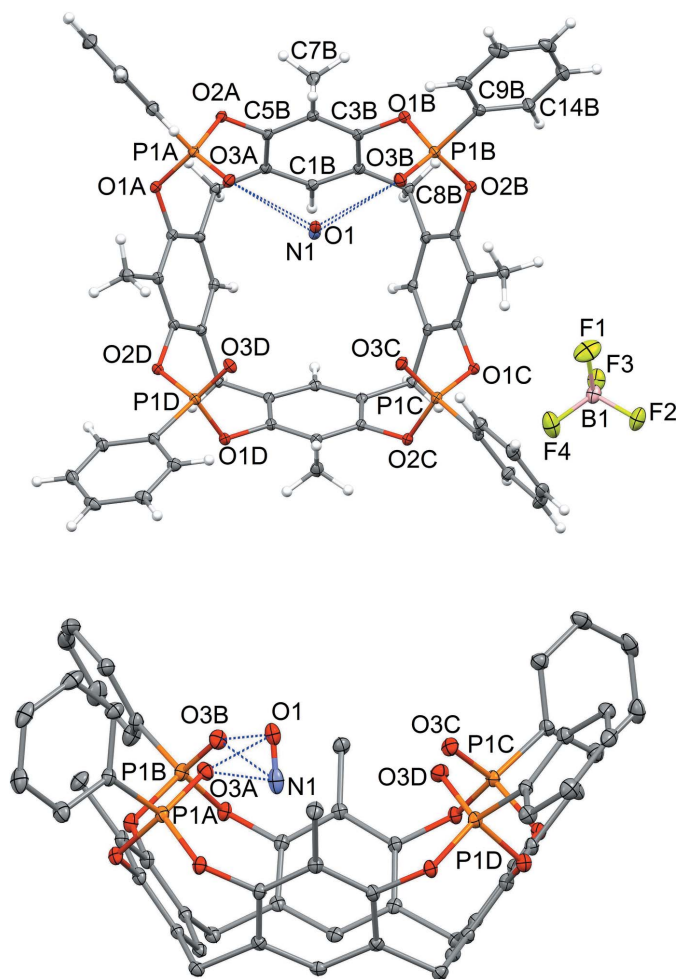
**Table 1**

 Host–guest interactions (Å) in NO@Tiiii[H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>]BF<sub>4</sub>.

O3A...O1	2.621 (5)	O3D...O2	2.604 (4)
O3A...N1	2.661 (6)	O3D...N2	2.650 (4)
O3B...O1	2.609 (3)	O1...PL	0.471 (4)
O3B...N1	2.664 (5)	N1...PL	0.492 (6)
O3C...O2	2.621 (4)	O2...PL	0.466 (4)
O3C...N2	2.625 (7)	N2...PL	0.416 (6)

PL is the mean plane passing through the four phosphonate oxygen atoms, O3A, O3B, O3C and O3D.

opposite P=O groups (Fig. 2; the second orientation is not shown), namely P1A=O3A and P1B=O3B for N1O1 and P1C=O3C and P1D=O3D with N2O2 [O3A...O1, 2.621 (5); O3A...N1, 2.661 (6); O3B...O1, 2.609 (3); O3B...N1, 2.664 (5); O3C...O2, 2.621 (4); O3C...N2, 2.625 (7); O3D...O2, 2.604 (4); O3D...N2, 2.650 (4) Å]. This phenomenon has already been observed in the solid state with


**Figure 2**

Top and side views of the title compound, NO@Tiiii[H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>], with a partial atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level. Only one of the two disordered NO<sup>+</sup> ions is shown. In the side view, the hydrogen atoms and the BF<sub>4</sub><sup>−</sup> counter-ion are not shown for clarity. Cation–dipole interactions are represented as blue dashed lines.

**Table 2**

Hydrogen-bond geometry (Å, °).

Cg1, Cg2 and Cg3 are the centroids of the aromatic rings C9B–C14B, C9D–C14D and C1A–C6A, respectively.

D–H...A	D–H	H...A	D...A	D–H...A
C1B <sup>i</sup> –H1B <sup>i</sup> ...F1	0.95	2.41	3.344 (3)	169
C14B <sup>ii</sup> –H14B <sup>ii</sup> ...F2	0.95	2.57	3.357 (3)	140
C7C <sup>ii</sup> –H7C <sup>ii</sup> ...F2	0.98	2.62	3.484 (2)	147
C8C <sup>i</sup> –H8C <sup>i</sup> ...F2	0.98	2.49	3.379 (3)	150
C1D <sup>i</sup> –H1D <sup>i</sup> ...F2	0.95	2.60	3.439 (2)	147
C11A <sup>iii</sup> –H11A <sup>iii</sup> ...F3	0.95	2.45	3.254 (2)	142
C7C <sup>ii</sup> –H7C <sup>ii</sup> ...F3	0.98	2.64	3.569 (3)	160
C11C–H11C...F4	0.95	2.53	3.447 (3)	162
C1D <sup>i</sup> –H1D <sup>i</sup> ...F4	0.95	2.65	3.509 (3)	150
C14D <sup>iv</sup> –H14D <sup>iv</sup> ...F4	0.95	2.63	3.336 (4)	131
C7D–H7D1...Cg1 <sup>v</sup>	0.98	2.80	3.524 (4)	131
C7B–H7B1...Cg2 <sup>vi</sup>	0.98	2.88	3.530 (4)	124
C8D–H8D2...Cg3 <sup>vii</sup>	0.98	2.87	3.594 (3)	131

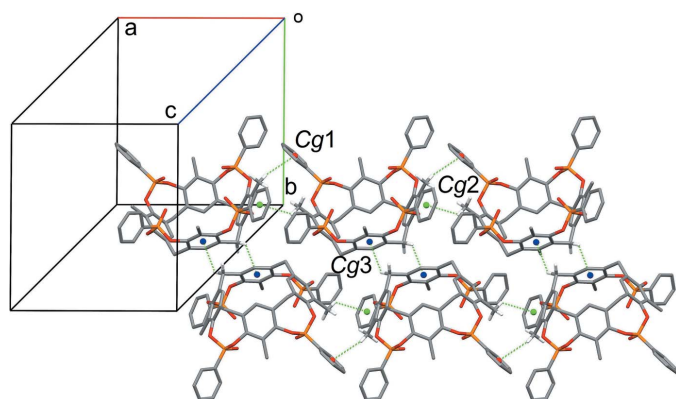
Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $x, y, z - 1$ ; (iv)  $-x, -y + 1, -z + 1$ ; (v)  $x - 1, y, z$ ; (vi)  $x + 1, y, z$ ; (vii)  $-x, -y + 2, -z + 1$ .

phosphonate cavitands hosting methanol and ethanol molecules (Melegari *et al.*, 2008) and confirms that, for these systems, the stability of the host–guest complex is entropic in origin, since the guest can choose from two up to four energetically and geometrically equivalent interaction modes with the host. In this case, the NO<sup>+</sup> cation forms two sets of strong interactions with two adjacent P=O groups, which results in a better stabilizing effect than four weaker interactions with all the phosphonate moieties of the upper rim. The BF<sub>4</sub><sup>−</sup> ion is outside the cavity, forming weak C–H...F interactions with the cavitands (see Section 4 for details).

The dichloromethane solvent molecule is heavily disordered and could not be modelled, but its residual electron density, occupying a void of 312 Å<sup>3</sup> (Spek, 2015) is located in the hydrophobic pockets among the cavitands.

#### 4. Supramolecular features

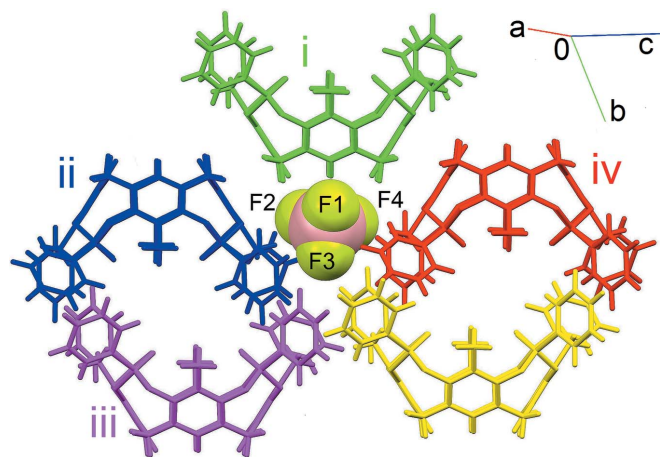
In the lattice, the cavitands form a supramolecular ribbon along the *a*-axis direction through a series of C–H... $\pi$  interactions between the H atoms of the methyl groups at the upper rim and the phenyl rings of the phosphonate moieties. In particular, each cavitand interacts with two adjacent ones acting simultaneously as a donor to two methyl groups and as an acceptor to two aromatic rings (see Table 2 and Fig. 3; the centroids involved are Cg1 and Cg2, represented as red and green spheres, respectively). Moreover, pairs of centrosymmetric cavitands form another set of C–H... $\pi$  interactions involving the methylenic hydrogen atoms at the lower rim and the aromatic walls of the macrocycle (see Table 2 and Fig. 3, Cg3, blue centroids). The structure is further stabilized by the presence of C–H...F interactions between the hydrogen atoms of the cavitands and the fluorine atoms of the tetrafluoridoborate anion. More precisely, each BF<sub>4</sub><sup>−</sup> is surrounded by five cavitands (Fig. 4), with C–H...F distances ranging from 2.408 (2) to 2.653 (2) Å (Table 2).



**Figure 3**  
C–H... $\pi$  interactions (green dashed lines) forming a ribbon along the *a*-axis direction of the unit cell. Centroids Cg1 (C9B–C14B), Cg2 (C9D–C14D) and Cg3 (C1A–C6A) are represented as red, green and blue spheres, respectively.

## 5. Database survey

A search in the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) for structures containing the isolated NO fragment, with no restrictions on the charge or on the type of bond connecting nitrogen and oxygen, yielded 65 species which are, of course, very different in nature. Meaningful comparisons with our complex are only possible with the series of calixarene-based, host–guest complexes already cited in the introduction, namely GOTCAT, GOTDEY, GOTGEB, GOTHAY and GOTHAY01 (Rathore *et al.*, 2000) and with a cationic radical calixarene derivative capable of binding neutral nitric oxide (JAHFOO; Rathore *et al.*, 2004). In particular, in GOTCAT, the NO<sup>+</sup> cation is buried deep inside the cavity, where it interacts with two distal aromatic groups of the calixarene guest. Since the calixarene is in the 1,3-alternate conformation, two sets of co-facial benzene rings are present, and the NO<sup>+</sup> ion is equally distributed between them (see Fig. 5, one pair of rings is shown



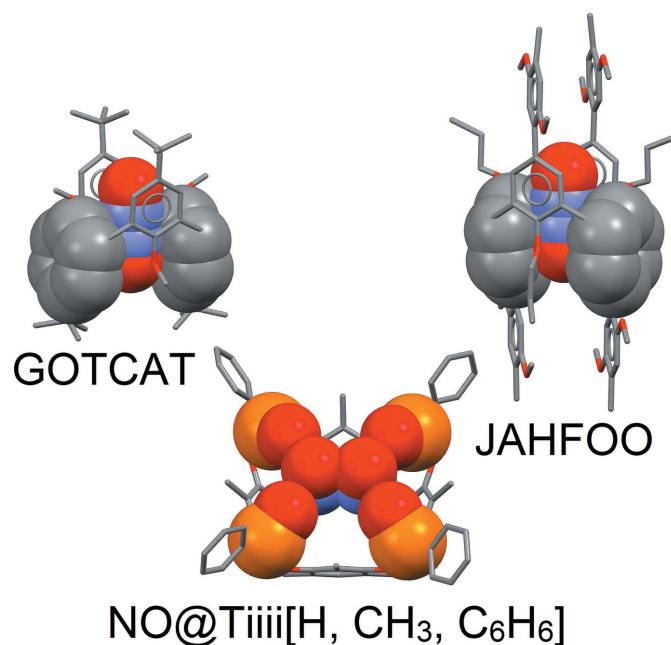
**Figure 4**  
View of the BF<sub>4</sub><sup>−</sup> ion surrounded by the five closest cavitands through C–H...F interactions. [Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) −*x* + 1, −*y* + 1, −*z*; (iii) *x*, *y*, *z* − 1; (iv) −*x*, −*y* + 1, −*z* + 1.]

in space-filling model, the other one in capped-stick mode). The electron-rich pocket formed by the co-facial pair is essential for the complexation, and the NO<sup>+</sup> ion is not bound by a single aromatic ring alone (see, for instance, GOTDEY and GOTGEB). In the case of JAHFOO, the calixarene has been oxidized to carry an overall positive charge on its core, in order to make it a good receptor for an electron rich-guest such as nitric oxide. Nevertheless, the interaction mode is similar to that observed for GOTCAT, with two disordered NO molecules buried between two distinct pairs of distal aromatic rings (Fig. 5). Also, in the title complex the guest is disordered over two equivalent positions, but its interaction with the electron-rich cavity is negligible due to the presence of the dipolar phosphonate groups which ‘hold’ the NO<sup>+</sup> ion at the brim of the upper rim (Fig. 5).

## 6. Synthesis and crystallization

<sup>1</sup>H NMR spectra were obtained using a Bruker AMX-400 (400 MHz) spectrometer. All chemical shifts ( $\delta$ ) were reported in ppm relative to the proton resonances resulting from incomplete deuteration of the NMR solvents. <sup>31</sup>P NMR spectra were obtained using a Bruker AMX-400 (162 MHz) spectrometer. All chemical shifts ( $\delta$ ) were recorded in ppm relative to external 85% H<sub>3</sub>PO<sub>4</sub> at 0.00 ppm. All commercial reagents were ACS reagent grade and used as received. The cavitands Tiiii[H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>] and Tiiii[C<sub>3</sub>H<sub>7</sub>, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>] were prepared following published procedures (Tonezzer *et al.*, 2008; Menozzi *et al.*, 2015).

NO@Tiiii[H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>]BF<sub>4</sub>·CH<sub>2</sub>Cl<sub>2</sub> was obtained by mixing a dichloromethane solution of Tiiii[H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>]



**Figure 5**  
Comparison of the interaction modes of GOTCAT, JAHFOO (side view), and of the title compound, NO@Tiiii[H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>] (top view), highlighting the disorder of the guest over two equivalent positions. The space-filling view is only partial for reasons of clarity.

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	C <sub>56</sub> H <sub>44</sub> P <sub>4</sub> O <sub>12</sub> ·NO <sup>+</sup> ·BF <sub>4</sub> <sup>-</sup> ·CH <sub>2</sub> Cl <sub>2</sub>
<i>M<sub>r</sub></i>	1234.54
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	190
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.856 (1), 14.909 (2), 16.357 (2)
$\alpha$ , $\beta$ , $\gamma$ (°)	63.224 (2), 73.137 (2), 88.093 (2)
<i>V</i> (Å <sup>3</sup> )	2868.2 (6)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.30
Crystal size (mm)	0.16 × 0.13 × 0.10
Data collection	
Diffractometer	Bruker SMART BREEZE CCD area-detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2008)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.812, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	36384, 14109, 9478
<i>R<sub>int</sub></i>	0.033
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.690
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.042, 0.128, 1.00
No. of reflections	14109
No. of parameters	735
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.63, -0.41

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SIR97* (Altomare *et al.*, 1999), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *WinGX* (Farrugia, 2012), *PARST* (Nardelli, 1995) and *publCIF* (Westrip, 2010).

(1 eq.) with a dichloromethane solution of NOBF<sub>4</sub> (1 eq.). The mixture was left to evaporate to yield colourless single crystals of the 1:1 complex that were suitable for X-ray diffraction analysis.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The nitrosonium ion was found to be disordered over two positions, with a refined occupancy ratio of 0.503 (2):0.497 (2). The C-bound H atoms were placed in calculated positions and refined using a riding model: C—H = 0.95–0.98 Å with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C-methyl) and 1.2*U*<sub>eq</sub>(C) for other H atoms.

As a result of severe disorder, the CH<sub>2</sub>Cl<sub>2</sub> solvent could not be sensibly modelled in terms of atomic sites, and was treated using the *PLATON SQUEEZE* procedure (Spek, 2015); the solvent contribution to the diffraction pattern was removed and modified *F*<sub>o</sub><sup>2</sup> written to a new HKL file. The number of electrons corresponding to the solvent molecules were included in the formula, formula weight, calculated density,  $\mu$  and *F*(000).

## Acknowledgements

The Centro Interfacoltà di Misure "G. Casnati" and the "Laboratorio di Strutturistica Mario Nardelli" of the University of Parma are kindly acknowledged for the use of NMR facilities and of the Diffractometer.

## References

- Altomare, A., Burla, M. C., Camalli, M., Casciarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Botta, B., D'Acquarica, I., Delle Monache, G., Nevola, L., Tullo, D., Ugozzoli, F. & Pierini, M. (2007). *J. Am. Chem. Soc.* **129**, 11202–11212.
- Bruker (2008). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cram, D. J. (1983). *Science*, **219**, 1177–1183.
- Cram, D. J. & Cram, J. M. (1994). *Container Molecules and their Guests, Monographs in Supramolecular Chemistry*, edited by J. F. Stoddart, vol. 4. Royal Society of Chemistry, Cambridge, UK.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hooley, R. J. & Rebek, J. Jr (2009). *Chem. Biol.* **16**, 255–264.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Mazej, Z., Ponikvar-Svet, M., Liebman, J. F., Passmore, J. & Jenkins, H. D. B. (2009). *J. Fluor. Chem.* **130**, 788–791.
- Melegari, M., Suman, M., Pirondini, L., Moiani, D., Massera, C., Ugozzoli, F., Kalenius, E., Vainiotalo, P., Mulatier, J.-C., Dutasta, J.-P. & Dalcanale, E. (2008). *Chem. Eur. J.* **14**, 5772–5779.
- Menzio, D., Pinalli, R., Massera, C., Maffei, F. & Dalcanale, E. (2015). *Molecules*, **20**, 4460–4472.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Pinalli, R., Brancatelli, G., Pedrini, A., Menozzi, D., Hernández, D., Ballester, P., Geremia, S. & Dalcanale, E. (2016). *J. Am. Chem. Soc.* **138**, 8569–8580.
- Pinalli, R. & Dalcanale, E. (2013). *Acc. Chem. Res.* **46**, 399–411.
- Pochorowski, I., Ebert, M.-O., Gisselbrecht, J.-P., Boudon, C., Schweizer, W. B. & Diederich, F. (2012). *J. Am. Chem. Soc.* **134**, 14702–14705.
- Rathore, R., Abdelwahed, S. H. & Guzei, I. A. (2004). *J. Am. Chem. Soc.* **126**, 13582–13583.
- Rathore, R., Lindeman, S. V., Rao, K. S. S. P., Sun, D. & Kochi, J. K. (2000). *Angew. Chem. Int. Ed.* **39**, 2123–2127.
- Riboni, N., Trzcinski, J. W., Bianchi, F., Massera, C., Pinalli, R., Sidisky, L., Dalcanale, E. & Careri, M. (2016). *Anal. Chim. Acta*, **905**, 79–84.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2015). *Acta Cryst.* **C71**, 9–18.
- Tonezzer, M., Melegari, M., Maggioni, G., Milan, R., Della Mea, G. & Dalcanale, E. (2008). *Chem. Mater.* **20**, 6535–6542.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Zyryanov, G. V., Kang, Y. & Rudkevich, D. M. (2003). *J. Am. Chem. Soc.* **125**, 2997–3007.
- Zyryanov, G. V., Kang, Y., Stampf, S. P. & Rudkevich, D. M. (2002). *Chem. Commun.* pp. 2792–2793.

## supporting information

*Acta Cryst.* (2017). E73, 1801-1805 [https://doi.org/10.1107/S2056989017015857]

## Nitrosonium complexation by the tetraphosphonate cavitand 5,11,17,23-tetramethyl-6,10:12,16:18,22:24,4-tetrakis(phenylphosphonato- $\kappa^2O,O$ )resorcin(4)arene

**Roberta Pinalli and Chiara Massera**

### Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *APEX2* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *PARST* (Nardelli, 1995) and *publCIF* (Westrip, 2010).

Nitrosonium tetrafluoridoborate-5,11,17,23-tetramethyl-6,10:12,16:18,22:24,4-tetrakis(phenylphosphonato- $\kappa^2O,O$ )resorcin(4)arene-dichloromethane (1/1/1)

### Crystal data

$C_{56}H_{44}P_4O_{12} \cdot NO^+ \cdot BF_4^- \cdot CH_2Cl_2$

$M_r = 1234.54$

Triclinic,  $P\bar{1}$

$a = 13.856$  (1) Å

$b = 14.909$  (2) Å

$c = 16.357$  (2) Å

$\alpha = 63.224$  (2)°

$\beta = 73.137$  (2)°

$\gamma = 88.093$  (2)°

$V = 2868.2$  (6) Å<sup>3</sup>

$Z = 2$

$F(000) = 1268$

$D_x = 1.429$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å

Cell parameters from 250 reflections

$\theta = 1.5$ – $29.4$ °

$\mu = 0.30$  mm<sup>-1</sup>

$T = 190$  K

Prismatic, colourless

$0.16 \times 0.13 \times 0.10$  mm

### Data collection

Bruker SMART BREEZE CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scan

Absorption correction: multi-scan (SADABS; Bruker, 2008)

$T_{\min} = 0.812$ ,  $T_{\max} = 1.000$

36384 measured reflections

14109 independent reflections

9478 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 29.4$ °,  $\theta_{\min} = 1.5$ °

$h = -18 \rightarrow 18$

$k = -20 \rightarrow 20$

$l = -22 \rightarrow 22$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.128$

$S = 1.00$

14109 reflections

735 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map  
 Hydrogen site location: inferred from neighbouring sites  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.63 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

### Special details

**Experimental.** The calculated molar mass, density and absorption coefficient include two disordered dichloromethane molecules per cell which do not appear in the final files because of the refinements carried out with data subjected to SQUEEZE.

**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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.3415 (3)	0.7159 (4)	0.4179 (3)	0.0386 (10)	0.503 (2)
O1	0.3391 (2)	0.6435 (3)	0.4543 (2)	0.0307 (8)	0.503 (2)
N2	0.2020 (3)	0.7031 (4)	0.3846 (3)	0.0426 (11)	0.497 (2)
O2	0.1903 (2)	0.6363 (3)	0.4165 (2)	0.0266 (7)	0.497 (2)
B1	0.2882 (2)	0.2304 (2)	0.12591 (19)	0.0410 (6)	
F1	0.34181 (17)	0.16872 (13)	0.18534 (15)	0.0875 (6)	
F2	0.28773 (14)	0.19718 (12)	0.05981 (11)	0.0638 (4)	
F3	0.33203 (12)	0.32872 (10)	0.08112 (10)	0.0553 (4)	
F4	0.19008 (14)	0.22111 (13)	0.18451 (14)	0.0790 (6)	
P1A	0.35319 (4)	0.75850 (4)	0.63016 (3)	0.02411 (12)	
P1B	0.60883 (4)	0.73524 (4)	0.25305 (4)	0.02623 (12)	
P1C	0.19872 (4)	0.71498 (4)	0.14576 (3)	0.02352 (11)	
P1D	-0.05960 (4)	0.73655 (4)	0.52317 (4)	0.02430 (12)	
O1A	0.26652 (10)	0.82864 (10)	0.64092 (9)	0.0264 (3)	
O2A	0.45495 (10)	0.83412 (10)	0.56545 (9)	0.0256 (3)	
O3A	0.33168 (11)	0.69279 (11)	0.59071 (10)	0.0315 (3)	
O1B	0.64868 (10)	0.81454 (11)	0.27975 (10)	0.0286 (3)	
O2B	0.60145 (10)	0.80000 (11)	0.14780 (9)	0.0275 (3)	
O3B	0.51418 (10)	0.67359 (11)	0.32481 (10)	0.0344 (3)	
O1C	0.29952 (10)	0.78374 (10)	0.06637 (9)	0.0250 (3)	
O2C	0.11212 (10)	0.78858 (10)	0.13782 (9)	0.0260 (3)	
O3C	0.20873 (11)	0.66232 (11)	0.24296 (10)	0.0310 (3)	
O1D	-0.08197 (10)	0.80541 (10)	0.42444 (9)	0.0265 (3)	
O2D	-0.03700 (9)	0.81178 (10)	0.56143 (9)	0.0251 (3)	
O3D	0.02187 (10)	0.67259 (11)	0.51314 (10)	0.0331 (3)	
C1A	0.19513 (14)	0.99115 (14)	0.42444 (13)	0.0239 (4)	
H1A	0.2222	1.0501	0.3648	0.029*	
C2A	0.25267 (14)	0.95390 (14)	0.48748 (13)	0.0233 (4)	
C3A	0.21105 (14)	0.86730 (15)	0.57387 (13)	0.0239 (4)	
C4A	0.11502 (14)	0.81716 (14)	0.60086 (14)	0.0246 (4)	
C5A	0.06242 (14)	0.85866 (14)	0.53393 (13)	0.0235 (4)	

---

C6A	0.09877 (14)	0.94465 (14)	0.44598 (13)	0.0227 (4)
C7A	0.07040 (16)	0.72542 (16)	0.69608 (15)	0.0345 (5)
H7A1	0.1199	0.7067	0.7317	0.052*
H7A2	0.0534	0.6692	0.6853	0.052*
H7A3	0.0088	0.7405	0.7334	0.052*
C8A	0.35871 (14)	1.00412 (15)	0.46023 (14)	0.0253 (4)
H8A1	0.3721	0.9976	0.5188	0.030*
H8A2	0.3630	1.0771	0.4160	0.030*
C9A	0.36897 (14)	0.69707 (15)	0.74569 (14)	0.0265 (4)
C10A	0.35124 (16)	0.59170 (16)	0.79585 (15)	0.0338 (5)
H10A	0.3299	0.5545	0.7686	0.041*
C11A	0.36511 (18)	0.54167 (19)	0.88606 (16)	0.0443 (6)
H11A	0.3528	0.4700	0.9208	0.053*
C12A	0.39638 (18)	0.5952 (2)	0.92518 (16)	0.0463 (6)
H12A	0.4063	0.5604	0.9866	0.056*
C13A	0.41351 (19)	0.6994 (2)	0.87595 (17)	0.0473 (6)
H13A	0.4349	0.7360	0.9037	0.057*
C14A	0.39949 (17)	0.75105 (18)	0.78587 (15)	0.0378 (5)
H14A	0.4108	0.8228	0.7522	0.045*
C1B	0.46749 (14)	0.99163 (14)	0.31262 (13)	0.0244 (4)
H1B	0.4392	1.0488	0.2751	0.029*
C2B	0.53674 (14)	0.94606 (14)	0.26635 (13)	0.0241 (4)
C3B	0.57720 (14)	0.86308 (15)	0.32371 (14)	0.0250 (4)
C4B	0.55347 (14)	0.82460 (15)	0.42299 (14)	0.0263 (4)
C5B	0.48240 (14)	0.87296 (15)	0.46416 (13)	0.0246 (4)
C6B	0.43862 (14)	0.95615 (14)	0.41178 (13)	0.0232 (4)
C7B	0.60064 (17)	0.73656 (17)	0.48175 (15)	0.0365 (5)
H7B1	0.6048	0.7425	0.5379	0.055*
H7B2	0.6690	0.7360	0.4425	0.055*
H7B3	0.5590	0.6735	0.5033	0.055*
C8B	0.56298 (15)	0.98464 (15)	0.15868 (13)	0.0267 (4)
H8B1	0.6338	0.9735	0.1331	0.032*
H8B2	0.5584	1.0583	0.1275	0.032*
C9B	0.71418 (15)	0.66821 (16)	0.23315 (15)	0.0296 (4)
C10B	0.72732 (17)	0.58210 (17)	0.31116 (18)	0.0373 (5)
H10B	0.6810	0.5605	0.3739	0.045*
C11B	0.80909 (18)	0.52802 (18)	0.2962 (2)	0.0459 (6)
H11B	0.8188	0.4697	0.3489	0.055*
C12B	0.87546 (18)	0.5590 (2)	0.2052 (2)	0.0470 (6)
H12B	0.9313	0.5223	0.1955	0.056*
C13B	0.86170 (18)	0.6421 (2)	0.1286 (2)	0.0497 (7)
H13B	0.9075	0.6620	0.0659	0.060*
C14B	0.78131 (17)	0.6980 (2)	0.14123 (17)	0.0434 (6)
H14B	0.7724	0.7560	0.0877	0.052*
C1C	0.40529 (14)	0.97320 (14)	0.11292 (13)	0.0241 (4)
H1C	0.3904	1.0354	0.1140	0.029*
C2C	0.33983 (14)	0.92483 (14)	0.09105 (12)	0.0227 (4)
C3C	0.36369 (14)	0.83356 (14)	0.09052 (13)	0.0232 (4)



---

C4C	0.44987 (14)	0.78914 (15)	0.10945 (13)	0.0246 (4)
C5C	0.51171 (14)	0.84139 (15)	0.13116 (13)	0.0241 (4)
C6C	0.49252 (14)	0.93202 (14)	0.13327 (13)	0.0240 (4)
C7C	0.47466 (16)	0.69088 (16)	0.10745 (16)	0.0317 (5)
H7C1	0.4156	0.6587	0.1053	0.048*
H7C2	0.4923	0.6459	0.1655	0.048*
H7C3	0.5322	0.7041	0.0503	0.048*
C8C	0.24356 (14)	0.96932 (14)	0.07192 (13)	0.0241 (4)
H8C1	0.2544	1.0439	0.0441	0.029*
H8C2	0.2276	0.9529	0.0247	0.029*
C9C	0.16854 (14)	0.63680 (15)	0.09894 (14)	0.0251 (4)
C10C	0.17014 (16)	0.53322 (16)	0.14934 (16)	0.0331 (5)
H10C	0.1867	0.5055	0.2078	0.040*
C11C	0.14744 (17)	0.47044 (18)	0.11403 (19)	0.0418 (6)
H11C	0.1495	0.3996	0.1478	0.050*
C12C	0.12199 (17)	0.5105 (2)	0.0301 (2)	0.0457 (6)
H12C	0.1054	0.4670	0.0067	0.055*
C13C	0.12048 (19)	0.6130 (2)	-0.02015 (19)	0.0462 (6)
H13C	0.1030	0.6400	-0.0781	0.055*
C14C	0.14423 (17)	0.67743 (18)	0.01321 (16)	0.0368 (5)
H14C	0.1439	0.7484	-0.0220	0.044*
C1D	0.13485 (14)	0.97464 (14)	0.22290 (13)	0.0239 (4)
H1D	0.1751	1.0356	0.2027	0.029*
C2D	0.05730 (14)	0.93516 (14)	0.31036 (13)	0.0231 (4)
C3D	-0.00030 (14)	0.84668 (15)	0.33686 (13)	0.0242 (4)
C4D	0.01450 (14)	0.79593 (15)	0.28118 (14)	0.0255 (4)
C5D	0.09407 (14)	0.83894 (14)	0.19564 (13)	0.0232 (4)
C6D	0.15514 (14)	0.92744 (14)	0.16438 (13)	0.0228 (4)
C7D	-0.05138 (17)	0.70142 (17)	0.31159 (16)	0.0365 (5)
H7D1	-0.0530	0.6961	0.2544	0.055*
H7D2	-0.1204	0.7041	0.3481	0.055*
H7D3	-0.0237	0.6424	0.3521	0.055*
C8D	0.03903 (14)	0.98661 (14)	0.37464 (13)	0.0235 (4)
H8D1	0.0594	1.0602	0.3342	0.028*
H8D2	-0.0343	0.9763	0.4101	0.028*
C9D	-0.18126 (14)	0.67358 (15)	0.60172 (14)	0.0258 (4)
C10D	-0.21742 (16)	0.59045 (16)	0.59617 (15)	0.0319 (5)
H10D	-0.1763	0.5680	0.5530	0.038*
C11D	-0.31361 (16)	0.54133 (16)	0.65406 (16)	0.0367 (5)
H11D	-0.3388	0.4852	0.6505	0.044*
C12D	-0.37320 (16)	0.57426 (17)	0.71741 (16)	0.0386 (5)
H12D	-0.4393	0.5406	0.7567	0.046*
C13D	-0.33707 (16)	0.65558 (18)	0.72374 (16)	0.0388 (5)
H13D	-0.3781	0.6770	0.7678	0.047*
C14D	-0.24110 (16)	0.70591 (16)	0.66583 (15)	0.0321 (5)
H14D	-0.2163	0.7620	0.6698	0.039*

---

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.026 (2)	0.068 (3)	0.030 (2)	0.002 (2)	-0.0062 (16)	-0.031 (2)
O1	0.0231 (15)	0.0457 (19)	0.0267 (16)	-0.0007 (14)	-0.0038 (12)	-0.0216 (15)
N2	0.025 (2)	0.084 (4)	0.036 (3)	0.012 (2)	-0.0103 (18)	-0.041 (3)
O2	0.0266 (16)	0.0343 (17)	0.0239 (16)	0.0087 (14)	-0.0083 (12)	-0.0176 (15)
B1	0.0572 (18)	0.0266 (13)	0.0331 (14)	0.0055 (12)	-0.0109 (13)	-0.0106 (11)
F1	0.1356 (18)	0.0472 (10)	0.0887 (13)	0.0254 (11)	-0.0712 (13)	-0.0180 (10)
F2	0.0914 (12)	0.0594 (10)	0.0434 (9)	-0.0021 (9)	-0.0133 (8)	-0.0296 (8)
F3	0.0762 (11)	0.0290 (7)	0.0436 (8)	-0.0007 (7)	-0.0064 (7)	-0.0092 (6)
F4	0.0738 (12)	0.0646 (11)	0.0825 (13)	-0.0121 (9)	0.0162 (10)	-0.0432 (10)
P1A	0.0246 (3)	0.0281 (3)	0.0190 (2)	-0.0001 (2)	-0.0069 (2)	-0.0100 (2)
P1B	0.0213 (2)	0.0333 (3)	0.0237 (3)	0.0047 (2)	-0.0060 (2)	-0.0135 (2)
P1C	0.0246 (3)	0.0281 (3)	0.0211 (2)	0.0035 (2)	-0.0079 (2)	-0.0136 (2)
P1D	0.0200 (2)	0.0283 (3)	0.0246 (3)	0.00258 (19)	-0.0042 (2)	-0.0137 (2)
O1A	0.0255 (7)	0.0335 (8)	0.0207 (7)	0.0036 (6)	-0.0088 (6)	-0.0119 (6)
O2A	0.0254 (7)	0.0322 (7)	0.0175 (6)	-0.0013 (6)	-0.0063 (5)	-0.0100 (6)
O3A	0.0361 (8)	0.0342 (8)	0.0264 (7)	-0.0018 (6)	-0.0103 (6)	-0.0151 (6)
O1B	0.0234 (7)	0.0387 (8)	0.0259 (7)	0.0058 (6)	-0.0076 (6)	-0.0170 (6)
O2B	0.0219 (7)	0.0378 (8)	0.0237 (7)	0.0060 (6)	-0.0073 (6)	-0.0150 (6)
O3B	0.0269 (8)	0.0400 (9)	0.0297 (8)	0.0012 (6)	-0.0030 (6)	-0.0139 (7)
O1C	0.0237 (7)	0.0313 (7)	0.0241 (7)	0.0020 (6)	-0.0074 (5)	-0.0161 (6)
O2C	0.0258 (7)	0.0333 (7)	0.0261 (7)	0.0062 (6)	-0.0090 (6)	-0.0193 (6)
O3C	0.0372 (8)	0.0351 (8)	0.0227 (7)	0.0052 (6)	-0.0116 (6)	-0.0136 (6)
O1D	0.0211 (7)	0.0349 (8)	0.0232 (7)	0.0012 (6)	-0.0036 (5)	-0.0149 (6)
O2D	0.0198 (6)	0.0314 (7)	0.0241 (7)	0.0003 (5)	-0.0042 (5)	-0.0143 (6)
O3D	0.0259 (7)	0.0353 (8)	0.0372 (8)	0.0081 (6)	-0.0053 (6)	-0.0190 (7)
C1A	0.0292 (10)	0.0212 (9)	0.0206 (9)	0.0029 (8)	-0.0048 (8)	-0.0107 (8)
C2A	0.0234 (9)	0.0245 (10)	0.0243 (10)	0.0027 (7)	-0.0053 (8)	-0.0143 (8)
C3A	0.0238 (10)	0.0295 (10)	0.0215 (9)	0.0051 (8)	-0.0089 (8)	-0.0133 (8)
C4A	0.0227 (9)	0.0280 (10)	0.0220 (9)	0.0019 (8)	-0.0044 (8)	-0.0121 (8)
C5A	0.0190 (9)	0.0285 (10)	0.0245 (10)	0.0017 (7)	-0.0038 (7)	-0.0152 (8)
C6A	0.0260 (10)	0.0237 (9)	0.0234 (9)	0.0071 (8)	-0.0084 (8)	-0.0150 (8)
C7A	0.0294 (11)	0.0365 (12)	0.0269 (11)	-0.0024 (9)	-0.0079 (9)	-0.0058 (9)
C8A	0.0268 (10)	0.0260 (10)	0.0242 (10)	-0.0005 (8)	-0.0072 (8)	-0.0127 (8)
C9A	0.0207 (9)	0.0348 (11)	0.0206 (9)	0.0016 (8)	-0.0049 (8)	-0.0107 (8)
C10A	0.0332 (11)	0.0338 (11)	0.0283 (11)	0.0051 (9)	-0.0065 (9)	-0.0112 (9)
C11A	0.0400 (13)	0.0418 (13)	0.0295 (12)	0.0120 (11)	-0.0036 (10)	-0.0030 (10)
C12A	0.0374 (13)	0.0701 (18)	0.0227 (11)	0.0156 (12)	-0.0118 (10)	-0.0132 (12)
C13A	0.0482 (15)	0.0689 (18)	0.0307 (12)	0.0020 (13)	-0.0183 (11)	-0.0237 (13)
C14A	0.0420 (13)	0.0430 (13)	0.0264 (11)	-0.0031 (10)	-0.0121 (10)	-0.0129 (10)
C1B	0.0251 (10)	0.0230 (9)	0.0226 (9)	-0.0024 (7)	-0.0081 (8)	-0.0075 (8)
C2B	0.0227 (9)	0.0259 (10)	0.0211 (9)	-0.0051 (7)	-0.0048 (8)	-0.0092 (8)
C3B	0.0194 (9)	0.0331 (11)	0.0229 (10)	0.0016 (8)	-0.0048 (8)	-0.0142 (8)
C4B	0.0234 (10)	0.0331 (11)	0.0243 (10)	0.0020 (8)	-0.0095 (8)	-0.0134 (9)
C5B	0.0239 (9)	0.0310 (10)	0.0171 (9)	-0.0041 (8)	-0.0050 (7)	-0.0100 (8)
C6B	0.0214 (9)	0.0242 (10)	0.0235 (9)	-0.0032 (7)	-0.0063 (8)	-0.0106 (8)

C7B	0.0389 (12)	0.0436 (13)	0.0253 (11)	0.0145 (10)	-0.0136 (9)	-0.0128 (10)
C8B	0.0277 (10)	0.0282 (10)	0.0194 (9)	-0.0032 (8)	-0.0052 (8)	-0.0079 (8)
C9B	0.0232 (10)	0.0376 (11)	0.0345 (11)	0.0060 (8)	-0.0112 (9)	-0.0207 (10)
C10B	0.0312 (11)	0.0327 (12)	0.0453 (13)	0.0029 (9)	-0.0123 (10)	-0.0155 (10)
C11B	0.0396 (13)	0.0287 (12)	0.0712 (18)	0.0076 (10)	-0.0239 (13)	-0.0206 (12)
C12B	0.0305 (12)	0.0490 (15)	0.081 (2)	0.0129 (11)	-0.0206 (13)	-0.0453 (15)
C13B	0.0350 (13)	0.0731 (19)	0.0529 (16)	0.0167 (13)	-0.0103 (12)	-0.0414 (15)
C14B	0.0358 (13)	0.0615 (16)	0.0351 (12)	0.0169 (11)	-0.0117 (10)	-0.0243 (12)
C1C	0.0290 (10)	0.0238 (9)	0.0155 (9)	0.0007 (8)	-0.0039 (8)	-0.0074 (7)
C2C	0.0221 (9)	0.0264 (10)	0.0136 (8)	0.0009 (7)	-0.0020 (7)	-0.0064 (7)
C3C	0.0231 (9)	0.0285 (10)	0.0174 (9)	-0.0005 (8)	-0.0053 (7)	-0.0104 (8)
C4C	0.0244 (10)	0.0279 (10)	0.0185 (9)	0.0014 (8)	-0.0032 (7)	-0.0102 (8)
C5C	0.0200 (9)	0.0311 (10)	0.0178 (9)	0.0029 (8)	-0.0045 (7)	-0.0091 (8)
C6C	0.0254 (10)	0.0269 (10)	0.0140 (8)	-0.0035 (8)	-0.0029 (7)	-0.0061 (8)
C7C	0.0295 (11)	0.0348 (11)	0.0355 (11)	0.0076 (9)	-0.0103 (9)	-0.0201 (10)
C8C	0.0261 (10)	0.0251 (10)	0.0188 (9)	0.0033 (8)	-0.0062 (8)	-0.0086 (8)
C9C	0.0220 (9)	0.0308 (10)	0.0269 (10)	0.0032 (8)	-0.0063 (8)	-0.0179 (9)
C10C	0.0302 (11)	0.0330 (11)	0.0360 (12)	0.0052 (9)	-0.0082 (9)	-0.0172 (10)
C11C	0.0346 (12)	0.0349 (12)	0.0553 (15)	0.0012 (10)	-0.0030 (11)	-0.0266 (12)
C12C	0.0331 (12)	0.0603 (17)	0.0659 (17)	0.0036 (11)	-0.0112 (12)	-0.0499 (15)
C13C	0.0460 (14)	0.0673 (18)	0.0474 (14)	0.0100 (12)	-0.0237 (12)	-0.0396 (14)
C14C	0.0420 (13)	0.0415 (13)	0.0356 (12)	0.0095 (10)	-0.0180 (10)	-0.0218 (10)
C1D	0.0249 (10)	0.0225 (9)	0.0236 (10)	0.0046 (7)	-0.0092 (8)	-0.0092 (8)
C2D	0.0243 (9)	0.0256 (10)	0.0231 (9)	0.0078 (8)	-0.0102 (8)	-0.0129 (8)
C3D	0.0200 (9)	0.0319 (10)	0.0204 (9)	0.0037 (8)	-0.0050 (7)	-0.0125 (8)
C4D	0.0227 (9)	0.0314 (10)	0.0262 (10)	0.0034 (8)	-0.0081 (8)	-0.0161 (9)
C5D	0.0235 (9)	0.0302 (10)	0.0229 (9)	0.0078 (8)	-0.0093 (8)	-0.0171 (8)
C6D	0.0227 (9)	0.0258 (10)	0.0201 (9)	0.0067 (7)	-0.0089 (7)	-0.0096 (8)
C7D	0.0336 (12)	0.0433 (13)	0.0365 (12)	-0.0068 (10)	-0.0026 (10)	-0.0258 (11)
C8D	0.0250 (10)	0.0243 (9)	0.0232 (9)	0.0067 (8)	-0.0077 (8)	-0.0126 (8)
C9D	0.0212 (9)	0.0282 (10)	0.0238 (10)	0.0027 (8)	-0.0066 (8)	-0.0088 (8)
C10D	0.0305 (11)	0.0316 (11)	0.0324 (11)	0.0034 (9)	-0.0093 (9)	-0.0139 (9)
C11D	0.0326 (12)	0.0286 (11)	0.0417 (13)	-0.0010 (9)	-0.0120 (10)	-0.0095 (10)
C12D	0.0242 (11)	0.0371 (12)	0.0360 (12)	0.0006 (9)	-0.0053 (9)	-0.0035 (10)
C13D	0.0289 (11)	0.0463 (14)	0.0326 (12)	0.0053 (10)	-0.0007 (9)	-0.0165 (11)
C14D	0.0289 (11)	0.0363 (12)	0.0296 (11)	0.0034 (9)	-0.0048 (9)	-0.0163 (9)

*Geometric parameters (Å, °)*

N1—O1	0.966 (5)	C7B—H7B2	0.9800
N2—O2	0.885 (5)	C7B—H7B3	0.9800
B1—F3	1.374 (3)	C8B—C6C	1.524 (3)
B1—F2	1.379 (3)	C8B—H8B1	0.9900
B1—F1	1.382 (3)	C8B—H8B2	0.9900
B1—F4	1.387 (3)	C9B—C14B	1.392 (3)
P1A—O3A	1.4716 (14)	C9B—C10B	1.397 (3)
P1A—O1A	1.5894 (14)	C10B—C11B	1.397 (3)
P1A—O2A	1.5950 (14)	C10B—H10B	0.9500

P1A—C9A	1.768 (2)	C11B—C12B	1.374 (4)
P1B—O3B	1.4688 (15)	C11B—H11B	0.9500
P1B—O2B	1.5825 (14)	C12B—C13B	1.366 (4)
P1B—O1B	1.5943 (15)	C12B—H12B	0.9500
P1B—C9B	1.776 (2)	C13B—C14B	1.392 (3)
P1C—O3C	1.4695 (14)	C13B—H13B	0.9500
P1C—O1C	1.5911 (14)	C14B—H14B	0.9500
P1C—O2C	1.5921 (14)	C1C—C2C	1.391 (3)
P1C—C9C	1.7727 (19)	C1C—C6C	1.396 (3)
P1D—O3D	1.4738 (14)	C1C—H1C	0.9500
P1D—O2D	1.5867 (14)	C2C—C3C	1.393 (3)
P1D—O1D	1.5916 (14)	C2C—C8C	1.521 (3)
P1D—C9D	1.7708 (19)	C3C—C4C	1.392 (3)
O1A—C3A	1.420 (2)	C4C—C5C	1.392 (3)
O2A—C5B	1.418 (2)	C4C—C7C	1.506 (3)
O1B—C3B	1.425 (2)	C5C—C6C	1.382 (3)
O2B—C5C	1.412 (2)	C7C—H7C1	0.9800
O1C—C3C	1.418 (2)	C7C—H7C2	0.9800
O2C—C5D	1.418 (2)	C7C—H7C3	0.9800
O1D—C3D	1.422 (2)	C8C—C6D	1.518 (3)
O2D—C5A	1.418 (2)	C8C—H8C1	0.9900
C1A—C2A	1.392 (3)	C8C—H8C2	0.9900
C1A—C6A	1.399 (3)	C9C—C10C	1.388 (3)
C1A—H1A	0.9500	C9C—C14C	1.394 (3)
C2A—C3A	1.389 (3)	C10C—C11C	1.386 (3)
C2A—C8A	1.520 (3)	C10C—H10C	0.9500
C3A—C4A	1.397 (3)	C11C—C12C	1.377 (4)
C4A—C5A	1.391 (3)	C11C—H11C	0.9500
C4A—C7A	1.502 (3)	C12C—C13C	1.374 (4)
C5A—C6A	1.388 (3)	C12C—H12C	0.9500
C6A—C8D	1.519 (3)	C13C—C14C	1.387 (3)
C7A—H7A1	0.9800	C13C—H13C	0.9500
C7A—H7A2	0.9800	C14C—H14C	0.9500
C7A—H7A3	0.9800	C1D—C6D	1.389 (3)
C8A—C6B	1.521 (3)	C1D—C2D	1.393 (3)
C8A—H8A1	0.9900	C1D—H1D	0.9500
C8A—H8A2	0.9900	C2D—C3D	1.385 (3)
C9A—C14A	1.385 (3)	C2D—C8D	1.522 (3)
C9A—C10A	1.396 (3)	C3D—C4D	1.395 (3)
C10A—C11A	1.391 (3)	C4D—C5D	1.389 (3)
C10A—H10A	0.9500	C4D—C7D	1.502 (3)
C11A—C12A	1.370 (4)	C5D—C6D	1.391 (3)
C11A—H11A	0.9500	C7D—H7D1	0.9800
C12A—C13A	1.380 (4)	C7D—H7D2	0.9800
C12A—H12A	0.9500	C7D—H7D3	0.9800
C13A—C14A	1.391 (3)	C8D—H8D1	0.9900
C13A—H13A	0.9500	C8D—H8D2	0.9900
C14A—H14A	0.9500	C9D—C14D	1.394 (3)

C1B—C6B	1.391 (3)	C9D—C10D	1.402 (3)
C1B—C2B	1.398 (3)	C10D—C11D	1.385 (3)
C1B—H1B	0.9500	C10D—H10D	0.9500
C2B—C3B	1.392 (3)	C11D—C12D	1.390 (3)
C2B—C8B	1.515 (3)	C11D—H11D	0.9500
C3B—C4B	1.392 (3)	C12D—C13D	1.384 (3)
C4B—C5B	1.396 (3)	C12D—H12D	0.9500
C4B—C7B	1.498 (3)	C13D—C14D	1.387 (3)
C5B—C6B	1.391 (3)	C13D—H13D	0.9500
C7B—H7B1	0.9800	C14D—H14D	0.9500
F3—B1—F2	111.3 (2)	H8B1—C8B—H8B2	107.9
F3—B1—F1	109.5 (2)	C14B—C9B—C10B	119.8 (2)
F2—B1—F1	108.9 (2)	C14B—C9B—P1B	121.19 (17)
F3—B1—F4	110.4 (2)	C10B—C9B—P1B	118.96 (16)
F2—B1—F4	110.1 (2)	C11B—C10B—C9B	119.5 (2)
F1—B1—F4	106.6 (2)	C11B—C10B—H10B	120.3
O3A—P1A—O1A	113.25 (8)	C9B—C10B—H10B	120.3
O3A—P1A—O2A	113.39 (8)	C12B—C11B—C10B	120.1 (2)
O1A—P1A—O2A	105.21 (7)	C12B—C11B—H11B	119.9
O3A—P1A—C9A	116.42 (9)	C10B—C11B—H11B	119.9
O1A—P1A—C9A	103.86 (8)	C13B—C12B—C11B	120.5 (2)
O2A—P1A—C9A	103.48 (8)	C13B—C12B—H12B	119.7
O3B—P1B—O2B	114.65 (8)	C11B—C12B—H12B	119.7
O3B—P1B—O1B	112.61 (8)	C12B—C13B—C14B	120.8 (2)
O2B—P1B—O1B	105.36 (8)	C12B—C13B—H13B	119.6
O3B—P1B—C9B	116.20 (10)	C14B—C13B—H13B	119.6
O2B—P1B—C9B	102.10 (9)	C9B—C14B—C13B	119.3 (2)
O1B—P1B—C9B	104.63 (8)	C9B—C14B—H14B	120.3
O3C—P1C—O1C	113.22 (8)	C13B—C14B—H14B	120.3
O3C—P1C—O2C	113.28 (8)	C2C—C1C—C6C	121.17 (18)
O1C—P1C—O2C	105.45 (7)	C2C—C1C—H1C	119.4
O3C—P1C—C9C	116.01 (9)	C6C—C1C—H1C	119.4
O1C—P1C—C9C	103.90 (8)	C1C—C2C—C3C	117.94 (17)
O2C—P1C—C9C	103.83 (8)	C1C—C2C—C8C	120.41 (17)
O3D—P1D—O2D	113.92 (8)	C3C—C2C—C8C	121.62 (17)
O3D—P1D—O1D	112.87 (8)	C4C—C3C—C2C	123.55 (17)
O2D—P1D—O1D	105.77 (7)	C4C—C3C—O1C	117.27 (16)
O3D—P1D—C9D	116.93 (9)	C2C—C3C—O1C	119.14 (16)
O2D—P1D—C9D	103.46 (8)	C5C—C4C—C3C	115.43 (17)
O1D—P1D—C9D	102.56 (8)	C5C—C4C—C7C	121.96 (18)
C3A—O1A—P1A	120.78 (12)	C3C—C4C—C7C	122.60 (18)
C5B—O2A—P1A	118.31 (11)	C6C—C5C—C4C	124.08 (18)
C3B—O1B—P1B	119.32 (12)	C6C—C5C—O2B	118.99 (17)
C5C—O2B—P1B	121.91 (11)	C4C—C5C—O2B	116.88 (17)
C3C—O1C—P1C	120.00 (11)	C5C—C6C—C1C	117.82 (17)
C5D—O2C—P1C	118.16 (11)	C5C—C6C—C8B	121.32 (18)
C3D—O1D—P1D	119.51 (12)	C1C—C6C—C8B	120.85 (17)

C5A—O2D—P1D	121.38 (11)	C4C—C7C—H7C1	109.5
C2A—C1A—C6A	122.21 (17)	C4C—C7C—H7C2	109.5
C2A—C1A—H1A	118.9	H7C1—C7C—H7C2	109.5
C6A—C1A—H1A	118.9	C4C—C7C—H7C3	109.5
C3A—C2A—C1A	117.45 (17)	H7C1—C7C—H7C3	109.5
C3A—C2A—C8A	121.68 (17)	H7C2—C7C—H7C3	109.5
C1A—C2A—C8A	120.82 (17)	C6D—C8C—C2C	110.63 (15)
C2A—C3A—C4A	123.67 (18)	C6D—C8C—H8C1	109.5
C2A—C3A—O1A	118.98 (16)	C2C—C8C—H8C1	109.5
C4A—C3A—O1A	117.30 (16)	C6D—C8C—H8C2	109.5
C5A—C4A—C3A	115.46 (17)	C2C—C8C—H8C2	109.5
C5A—C4A—C7A	121.91 (17)	H8C1—C8C—H8C2	108.1
C3A—C4A—C7A	122.63 (18)	C10C—C9C—C14C	120.11 (19)
C6A—C5A—C4A	124.41 (17)	C10C—C9C—P1C	118.53 (16)
C6A—C5A—O2D	118.99 (17)	C14C—C9C—P1C	121.36 (16)
C4A—C5A—O2D	116.51 (16)	C11C—C10C—C9C	119.7 (2)
C5A—C6A—C1A	116.79 (17)	C11C—C10C—H10C	120.2
C5A—C6A—C8D	122.56 (17)	C9C—C10C—H10C	120.2
C1A—C6A—C8D	120.65 (17)	C12C—C11C—C10C	120.1 (2)
C4A—C7A—H7A1	109.5	C12C—C11C—H11C	119.9
C4A—C7A—H7A2	109.5	C10C—C11C—H11C	119.9
H7A1—C7A—H7A2	109.5	C13C—C12C—C11C	120.4 (2)
C4A—C7A—H7A3	109.5	C13C—C12C—H12C	119.8
H7A1—C7A—H7A3	109.5	C11C—C12C—H12C	119.8
H7A2—C7A—H7A3	109.5	C12C—C13C—C14C	120.5 (2)
C2A—C8A—C6B	111.10 (15)	C12C—C13C—H13C	119.8
C2A—C8A—H8A1	109.4	C14C—C13C—H13C	119.8
C6B—C8A—H8A1	109.4	C13C—C14C—C9C	119.2 (2)
C2A—C8A—H8A2	109.4	C13C—C14C—H14C	120.4
C6B—C8A—H8A2	109.4	C9C—C14C—H14C	120.4
H8A1—C8A—H8A2	108.0	C6D—C1D—C2D	121.92 (18)
C14A—C9A—C10A	120.16 (19)	C6D—C1D—H1D	119.0
C14A—C9A—P1A	121.45 (16)	C2D—C1D—H1D	119.0
C10A—C9A—P1A	118.38 (16)	C3D—C2D—C1D	117.33 (17)
C11A—C10A—C9A	119.4 (2)	C3D—C2D—C8D	121.87 (17)
C11A—C10A—H10A	120.3	C1D—C2D—C8D	120.79 (17)
C9A—C10A—H10A	120.3	C2D—C3D—C4D	124.00 (17)
C12A—C11A—C10A	120.4 (2)	C2D—C3D—O1D	119.04 (16)
C12A—C11A—H11A	119.8	C4D—C3D—O1D	116.93 (17)
C10A—C11A—H11A	119.8	C5D—C4D—C3D	115.41 (17)
C11A—C12A—C13A	120.4 (2)	C5D—C4D—C7D	122.33 (17)
C11A—C12A—H12A	119.8	C3D—C4D—C7D	122.26 (18)
C13A—C12A—H12A	119.8	C4D—C5D—C6D	123.81 (17)
C12A—C13A—C14A	120.2 (2)	C4D—C5D—O2C	116.92 (16)
C12A—C13A—H13A	119.9	C6D—C5D—O2C	119.27 (16)
C14A—C13A—H13A	119.9	C1D—C6D—C5D	117.52 (17)
C9A—C14A—C13A	119.5 (2)	C1D—C6D—C8C	120.72 (17)
C9A—C14A—H14A	120.3	C5D—C6D—C8C	121.72 (17)

C13A—C14A—H14A	120.3	C4D—C7D—H7D1	109.5
C6B—C1B—C2B	122.22 (18)	C4D—C7D—H7D2	109.5
C6B—C1B—H1B	118.9	H7D1—C7D—H7D2	109.5
C2B—C1B—H1B	118.9	C4D—C7D—H7D3	109.5
C3B—C2B—C1B	117.18 (17)	H7D1—C7D—H7D3	109.5
C3B—C2B—C8B	122.31 (18)	H7D2—C7D—H7D3	109.5
C1B—C2B—C8B	120.48 (18)	C6A—C8D—C2D	111.24 (15)
C4B—C3B—C2B	123.83 (18)	C6A—C8D—H8D1	109.4
C4B—C3B—O1B	116.91 (17)	C2D—C8D—H8D1	109.4
C2B—C3B—O1B	119.24 (16)	C6A—C8D—H8D2	109.4
C3B—C4B—C5B	115.61 (18)	C2D—C8D—H8D2	109.4
C3B—C4B—C7B	122.11 (18)	H8D1—C8D—H8D2	108.0
C5B—C4B—C7B	122.28 (18)	C14D—C9D—C10D	120.33 (18)
C6B—C5B—C4B	123.92 (17)	C14D—C9D—P1D	121.92 (16)
C6B—C5B—O2A	119.10 (17)	C10D—C9D—P1D	117.74 (15)
C4B—C5B—O2A	116.97 (17)	C11D—C10D—C9D	119.5 (2)
C5B—C6B—C1B	117.21 (18)	C11D—C10D—H10D	120.3
C5B—C6B—C8A	122.02 (17)	C9D—C10D—H10D	120.3
C1B—C6B—C8A	120.71 (17)	C10D—C11D—C12D	119.9 (2)
C4B—C7B—H7B1	109.5	C10D—C11D—H11D	120.0
C4B—C7B—H7B2	109.5	C12D—C11D—H11D	120.0
H7B1—C7B—H7B2	109.5	C13D—C12D—C11D	120.6 (2)
C4B—C7B—H7B3	109.5	C13D—C12D—H12D	119.7
H7B1—C7B—H7B3	109.5	C11D—C12D—H12D	119.7
H7B2—C7B—H7B3	109.5	C12D—C13D—C14D	120.1 (2)
C2B—C8B—C6C	112.07 (15)	C12D—C13D—H13D	119.9
C2B—C8B—H8B1	109.2	C14D—C13D—H13D	119.9
C6C—C8B—H8B1	109.2	C13D—C14D—C9D	119.5 (2)
C2B—C8B—H8B2	109.2	C13D—C14D—H14D	120.2
C6C—C8B—H8B2	109.2	C9D—C14D—H14D	120.2

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

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the aromatic rings C9B–C14B, C9D–C14D and C1A–C6A, respectively.

<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>
C1B <sup>i</sup> —H1B <sup>i</sup> ...F1	0.95	2.41	3.344 (3)	169
C14B <sup>ii</sup> —H14B <sup>ii</sup> ...F2	0.95	2.57	3.357 (3)	140
C7C <sup>ii</sup> —H7C3 <sup>ii</sup> ...F2	0.98	2.62	3.484 (2)	147
C8C <sup>i</sup> —H8C1 <sup>i</sup> ...F2	0.98	2.49	3.379 (3)	150
C1D <sup>i</sup> —H1D <sup>i</sup> ...F2	0.95	2.60	3.439 (2)	147
C11A <sup>iii</sup> —H11A <sup>iii</sup> ...F3	0.95	2.45	3.254 (2)	142
C7C <sup>ii</sup> —H7C3 <sup>ii</sup> ...F3	0.98	2.64	3.569 (3)	160
C11C—H11C...F4	0.95	2.53	3.447 (3)	162
C1D <sup>i</sup> —H1D <sup>i</sup> ...F4	0.95	2.65	3.509 (3)	150
C14D <sup>iv</sup> —H14D <sup>iv</sup> ...F4	0.95	2.63	3.336 (4)	131
C7D—H7D1... <i>Cg</i> 1 <sup>v</sup>	0.98	2.80	3.524 (4)	131

---

<i>C7B</i> — <i>H7B1</i> ... <i>Cg</i> <sup>2vi</sup>	0.98	2.88	3.530 (4)	124
<i>C8D</i> — <i>H8D2</i> ... <i>Cg</i> <sup>3vii</sup>	0.98	2.87	3.594 (3)	131

---

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $-x+1, -y+1, -z$ ; (iii)  $x, y, z-1$ ; (iv)  $-x, -y+1, -z+1$ ; (v)  $x-1, y, z$ ; (vi)  $x+1, y, z$ ; (vii)  $-x, -y+2, -z+1$ .