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Tetrakis(2,3,5,6-tetrafluoro-4-iodophenyloxymethyl)methane bis(pyridine *N*-oxide) monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.038
wR factor = 0.099
Data-to-parameter ratio = 12.8

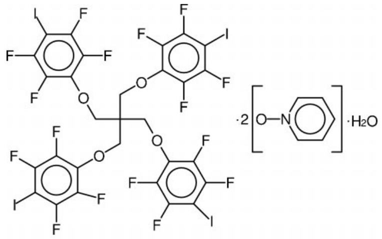
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{29}H_8F_{16}I_4O_4\cdot2C_5H_5NO\cdot H_2O$, is composed of the tetrakis-*p*-iodotetrafluoroether of pentaerythritol, pyridine *N*-oxide and water. It is characterized by the presence of both halogen bonds and hydrogen bonds connecting the three components. The two particularly short I···O halogen bonds (<2.9 Å) involve one pyridine *N*-oxide molecule and water. Consistent with the n-σ^* character of the I···O halogen bond, the shorter the I···O interaction is, the greater the lengthening of the corresponding C—I bond. As is often the case in similar compounds, the C—I···O angles are approximately linear. The structure shows thin hydrocarbon layers alternating with thick perfluorocarbon layers.

Comment

Continuing our studies on halogen bond-driven self-assembly processes involving perfluorocarbon derivatives [see, for example, Liantonio, Metrangolo, Pilati & Resnati, (2003) and Liantonio, Metrangolo, Pilati, Resnati & Stevenazzi (2003), and references therein], we synthesized the adduct of pentaerythritol-tetrakis(2,3,5,6-tetrafluoro-4-iodophenyl)ether (pErPhE) with pyridine *N*-oxide (pyNO).

When pErPhE, a tetradentate halogen bond donor, is reacted with dipyridyl derivatives, which are bidentate halogen bond acceptors, 1:2 adducts are obtained (Caronna *et al.*, 2004) due to the pairing of complementary sites. Pyridine *N*-oxide derivatives are known to act as efficient halogen-bond donors (Messina *et al.*, 2001) and the formation of 1:4 adducts was thus expected on reacting pErPhE with pyNO, a monodentate acceptor. A more complicated self-assembly process was actually observed. Despite the apolar medium used in the crystallization (chloroform/carbon tetrachloride mixture), water (W) was involved in the cocrystal formation and a three-component complex was obtained, in which pErPhE, pyNO and W are present in the ratio 1:2:1. Fig. 1 shows the atom-numbering scheme of the title compound, (I).



(I)

The structure is based on the 'necklace with eight pendants', shown in Fig. 2. The necklace ring is formed by the sequence

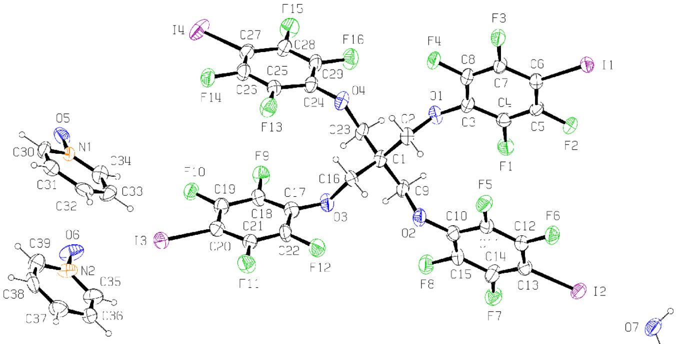


Figure 1
The asymmetric unit of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

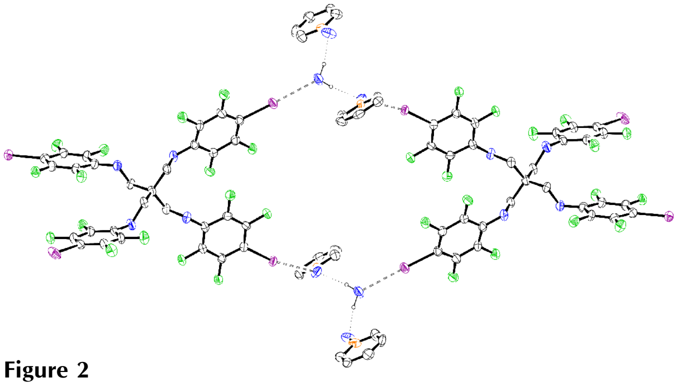


Figure 2
The 'necklace with pendants' which is the basic structure of the title complex. Dashed and dotted lines represent halogen and hydrogen bonds, respectively.

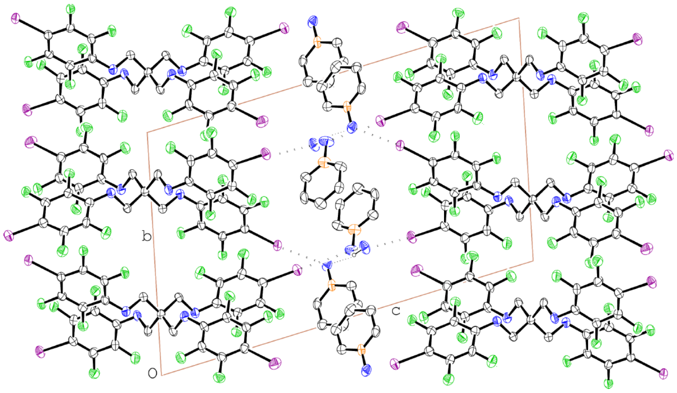


Figure 3
Packing of (I), viewed along the *a* axis.

$\cdots$pyNO5$^{\rm i}\cdots$pErPhE$\cdots$W$^{\rm ii}\cdots$ [symmetry codes: (i) x, y, $z-1$; (ii) $x+1$, y, $z-1$] and their centrosymmetric equivalent. The links are two short, almost linear, halogen bonds, I1$\cdots$O5$^{\rm i}$ and I2$\cdots$O7$^{\rm ii}$, and one O5$\cdots$W hydrogen bond (see Tables 1 and 2). The pyNO6 molecule is not involved in the ring, but it is a pendant of the necklace, attached by the hydrogen bond W$\cdots$O6. The necklaces are linked together by weaker forces such as the long halogen bond I3$\cdots$O6, the C—H$\cdots$F hydrogen bonds shown in Table 2, and dipole–dipole interactions between pairs of antiparallel molecules pyNO5$\cdots$pyNO5$^{\rm v}$ [symmetry code: (v) $-x$, $2-y$, $1-z$] and pyNO6$\cdots$pyNO6$^{\rm vi}$ [symmetry code: (vi) $1-x$, $1-y$, $1-z$]; in these pairs, the distances between the centroids of the two pyridine rings are 3.523 (9) and 3.465 (10) Å, respectively. These interactions are clearly visible in Fig. 3. Table 1 reports the four C—I bond lengths and the corresponding I$\cdots$O halogen bonds, where applicable. Table 2 gives some short hydrogen bonds.

As expected from the *n*-σ* character of the I$\cdots$O interaction, the C—I bond lengthens as I$\cdots$O shortens. The I1$\cdots$O5 halogen bond is very short, but longer than that found in the cocrystal 4,4′-bipyridine-*N*-oxide/1,4-diiodotetrafluorobenzene [2.754 (2) Å; Messina *et al.*, 2001].

As is often the case in structures containing both perfluorocarbon and hydrocarbon residues (Liantonio, Metrangolo, P., Pilati, T. & Resnati, 2003; Metrangolo *et al.*, 2003), segregation occurs between the two types of molecules, as shown in Fig. 4. Thin hydrocarbon layers alternate with thick perfluorocarbon layers.

Experimental

pyNO was purchased from Aldrich. pErPhE was prepared by refluxing a suspension of tetra(hydroxymethyl)methane (pentaerythritol, Aldrich, 5 mmol), iodopentafluorobenzene (Apollo Scientific, 60 mmol) and caesium carbonate (Aldrich, 30 mmol) in benzotrifluoride (Aldrich, 20 ml) for 40 h. After cooling, water was added and the organic products were extracted with diethyl ether. Flash chromatography (toluene–chloroform–*n*-hexane 1:2:13) afforded pErPhE in 42% yield. The title adduct was prepared by dissolving pErPhE (0.05 mmol) and pyNO (0.20 mmol) in chloroform, at room temperature, in a vial. The vial was closed in a cylindrical bottle containing carbon tetrachloride. The volatile solvents were allowed to diffuse at room temperature and, after 3 d, the resulting crystals were filtered off and washed with carbon tetrachloride. Very fragile prisms were obtained (m.p. 387–393 K); IR (KBr; selected bands): 2971, 1632, 1611, 1493, 1471, 1096, 981, 965, 948, 833, 802, 675 cm^{-1}.

Crystal data

$C_{29}H_8F_{16}I_4O_4\cdot 2C_5H_5NO\cdot H_2O$
$M_r = 1440.17$
Triclinic, $P\overline{1}$
$a = 8.034$ (2) Å
$b = 13.412$ (3) Å
$c = 21.624$ (5) Å
$\alpha = 76.25$ (5)°
$\beta = 82.28$ (5)°
$\gamma = 89.73$ (5)°
$V = 2241.9$ (9) Å^3
$Z = 2$
$D_x = 2.133$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2447 reflections
$\theta = 2.8$–22.6°
$\mu = 2.90$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.19 × 0.06 × 0.03 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.744$, $T_{\rm max} = 0.917$
18906 measured reflections
7905 independent reflections
5029 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\rm max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.099$
$S = 0.91$
7905 reflections
619 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.63$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.40$ e Å^{-3}

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Table 1
Halogen-bonding geometry (Å,°).

D—I···A	D—I	I···A	D—I···A
C6—I1···O5^{i}	2.083 (5)	2.849 (5)	169.4 (2)
C13—I2···O7^{ii}	2.078 (6)	2.891 (6)	175.3 (2)
C20—I3···O6	2.070 (6)	3.263 (7)	175.7 (2)
C27—I4	2.059 (6)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7B···O6	0.92 (7)	1.84 (6)	2.753 (7)	170 (6)
O7—H7A···O5^{iii}	0.91 (10)	1.86 (10)	2.741 (7)	161 (8)
C30—H30···F10^{iii}	0.93	2.38	3.227 (7)	152
C38—H38···F6^{iv}	0.93	2.49	3.036 (8)	117

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

Water H atoms were refined with the soft restraint O7—H7A $\simeq$ O7—H7B; their displacement parameters were constrained to be $1.5U_{\rm eq}$(O7). All others H atoms were placed in calculated positions (C—H = 0.93–0.97 Å), with $U_{\rm iso} = 1.2U_{\rm eq}$

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97, *PARST* (Nardelli, 1983) and *GEO* (Pilati, 2004).

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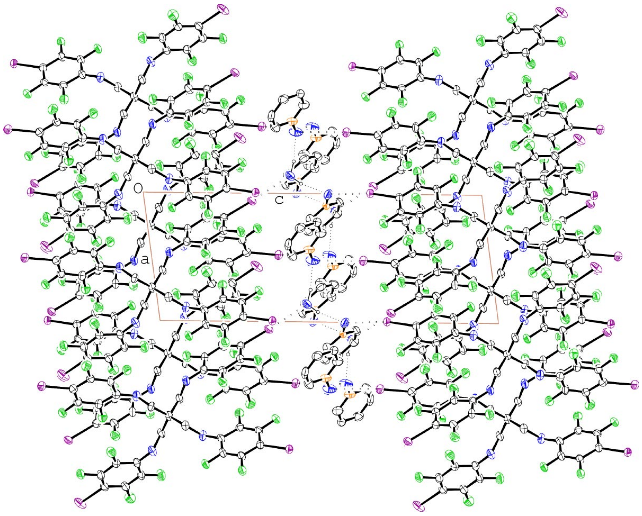

Figure 4
Packing of (I), viewed along the b axis, showing the alternating thin hydrocarbon layers and thick fluorocarbon layers.

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