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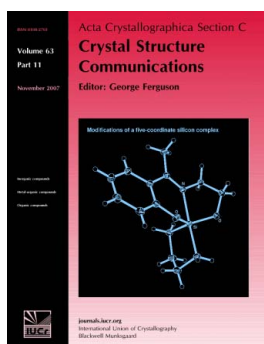
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Acta Cryst. (2015). **C71**, 84–88

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The three-component cocrystal 1,3,5-trifluoro-2,4,6-triiodobenzene–pyridine *N*-oxide–water (1/2/1) built up by halogen bonds, hydrogen bonds and π – π interactions

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Received 16 December 2014

Accepted 22 December 2014

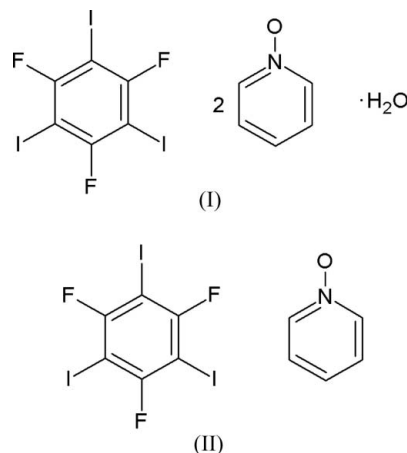
The title three-component cocrystal, $C_6F_3I_3 \cdot 2C_5H_5NO \cdot H_2O$, has been prepared as a strong candidate for multiple $I \cdots O$ interactions. Its crystal structure is compared with its 1:1 close relative, $C_6F_3I_3 \cdot C_5H_5NO$ [Aakeröy *et al.* (2014a). *CrystEngComm*, **16**, 28–31]. The 1,3,5-trifluoro-2,4,6-triiodobenzene and water species both have crystallographic twofold axial symmetry. The main synthon in both structures is the π – π stacking of benzene rings, complemented by a number of $O-H \cdots O$, $C-F \cdots \pi$ and, fundamentally, $C-I \cdots O$ interactions. As expected, the latter are among the strongest and more directional interactions of the sort reported in the literature, confirming that pyridine *N*-oxide is an eager acceptor. On the other hand, the structure presents only two of these contacts per 1,3,5-trifluoro-2,4,6-triiodobenzene molecule instead of the expected three. Possible reasons for this limitation are analyzed.

Keywords: crystal structure; multiple $C-I \cdots O$ interactions; strong pyridine *N*-oxide; acceptor; supramolecular mesogens.

1. Introduction

The halogen bond is a noncovalent interaction that has been known for more than half a century and which has experienced recently an impressive expansion in fields like molecular recognition (Metrangolo *et al.*, 2007; Cavallo *et al.*, 2010), crystal engineering (Metrangolo *et al.*, 2008a) and functional materials (Fourmigué, 2009; Primagi *et al.*, 2013). An interesting example of the application of the halogen bond in advanced materials was the design and realization of supramolecular liquid crystals based on halogen bonds. Both

calamitic and banana-shaped supramolecular mesogens have been prepared and studied (Bruce, 2012). However, discotic supramolecular mesogens based on halogen bonds have not yet been synthesized. It seems that the main limitation for achieving this goal is the low tendency of aromatic compounds bearing several terminal halogen atoms to coordinate three or more halogen-acceptor moieties. This difficulty has been extensively analyzed and discussed (Aakeröy *et al.*, 2014a; Bruce, 2012; Lucassen *et al.*, 2007; Metrangolo *et al.*, 2008a); its origin apparently lies on the way the electronic distribution on the donor sites is modified by the coordination of an acceptor.



A possible way to overcome this limitation is to use the strongest halogen donors having the appropriate geometry (such as 1,3,5-trifluoro-2,4,6-triiodobenzene, denoted hereafter as I_3F_3Bz) and the strongest halogen-bond acceptors.

Following this line of action, Metrangolo and coworkers prepared extended honeycomb structures where all three I atoms of I_3F_3Bz participate in halogen bonds through the combined use of halide anions as tridentate binding acceptors and bulky cations as templates (Metrangolo *et al.*, 2008b). Since then, other structures with I_3F_3Bz triply coordinated to anionic acceptors have been reported (Cauliez *et al.*, 2010; Cavallo *et al.*, 2013; Pfrunder *et al.*, 2012; Triguero *et al.*, 2008). Nevertheless, to the best of our knowledge, there are only two successful cases of triple coordination of neutral acceptors to such a single donor. In the first case, Bruce and co-workers (Roper *et al.*, 2010) succeeded in coordinating three molecules of 4-(dimethylamino)pyridine (DMAP; a base recognized as a strong electron donor in the field of coordination chemistry) to each I_3F_3Bz molecule. In the second case, Aakeröy and co-workers (Aakeröy *et al.*, 2014b) obtained a 1:1 cocrystal of I_3F_3Bz and 1,1'-dibenzyl-2,2'-biimidazole, where each I_3F_3Bz molecule acts as a donor in three different halogen-bond (XB) interactions.

An alternative to these two acceptors could be the use of pyridine *N*-oxide (O-Py), whose superior capacity as an XB acceptor relative to pyridine (Py) has been established (Messina *et al.*, 2001) and interpreted in terms of the high electronic density on the O atom. In a recent report, Aakeröy and co-workers (Aakeröy *et al.*, 2014a) crystallized several cocrystals based on iodo–fluoro aromatics as XB donors and *N*-oxides of different pyridines and bipyridines as XB accep-

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₆ F ₃ I ₃ ·2C ₅ H ₅ NO·H ₂ O
<i>M_r</i>	717.98
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.2226 (12), 19.0094 (18), 7.5203 (5)
β (°)	94.727 (7)
<i>V</i> (Å ³)	2026.3 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.67
Crystal size (mm)	0.60 × 0.16 × 0.09
Data collection	
Diffractometer	Oxford Diffraction Xcalibur CCD (Eos, Gemini) diffractometer
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)
<i>T</i> _{min} , <i>T</i> _{max}	0.408, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	6727, 2358, 1830
<i>R</i> _{int}	0.050
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.680
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.096, 1.06
No. of reflections	2358
No. of parameters	128
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.78, -0.74

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

tors, including one containing I₃F₃Bz and O-Py. They used a 1:1 stoichiometry during the solvent-assisted grinding preparation of their crystals and, indeed, they obtained a cocrystal which showed this same 1:1 stoichiometry. With the aim of enhancing the probability of obtaining a higher number of halogen-acceptor units per acceptor centre, we attempted to use in our synthesis a 1:9 I₃F₃Bz:O-Py molar ratio. Unexpectedly, the compound we obtained, and which we discuss in this report, included water (probably arising from the hydrated O-Py used, see *Experimental*, §2) with an active structural role in the crystal architecture. The crystals we obtained were in fact three-component cocrystals with a 1:2:1 I₃F₃Bz:O-Py·H₂O stoichiometry, namely 1,3,5-trifluoro-2,4,6-triiodobenzene-pyridine *N*-oxide-water (1/2/1), (I), and which, albeit with obvious differences resulting from composition and stoichiometry, present an interaction scheme which strongly resembles that of Aakeröy's 1:1 cocrystals. We thus present herein the crystal structure of (I) which we shall discuss in comparison with Aakeröy's close relative C₆F₃I₃·C₅H₅NO, (II) (see Scheme).

2. Experimental

2.1. Synthesis and crystallization

A tetrahydrofuran (THF) solution of I₃F₃Bz (54.7 mg, 2.5 ml) was added to a THF solution of O-Py (Hyd) (93.2 mg, 1.5 ml). The resulting mixture was allowed to evaporate

slowly, the process being controlled by solvent diffusion in liquid paraffin. After a few days, colourless needles were collected and analyzed. Structure determination proved it to correspond to 1:2:1 I₃F₃Bz:O-Py:H₂O cocrystals. Water very likely came from the hydrated commercial O-Py. In order to establish the actual mixing ratio of the three components, we decided to assess the amount of water in the starting O-Py by measuring the mass loss of a sample of hydrated (hyd) O-Py heated in a glass oven at 343 K until it reached a constant mass. The result indicated a 1.3:1 H₂O:O-Py molar ratio in the starting O-Py (hyd); the masses employed in the crystallization essay corresponded then to a 9.5:7.3:1 H₂O:O-Py:I₃F₃Bz molar ratio.

I₃F₃Bz was synthesized from 1,3,5-triiodobenzene (146 mg), following the procedure reported by Sander (Wenk *et al.*, 2002), with minor variations. Since the crystals obtained this way showed a light-yellow tint instead of the white colour expected, and since it did not correspond to unwashed I₂, we completed the purification *via* column chromatography using hexane as eluent, obtaining 429 mg of needle-like white crystals (76% yield).

2.2. Physicochemical measurements

The IR spectra of (I), I₃F₃Bz and O-Py were recorded as KBr pellets on a Nicolet FT-IR 510P spectrometer, and full spectra are provided as *Supporting information* in Fig. S1. Diagnostic bands (cm⁻¹) for (I): 3381, 3112, 1562, 1463, 1400, 1213, 1166, 1045, 1016, 832, 770, 676, 655, 549, 466; for I₃F₃Bz: 1564, 1406, 1326, 1050, 705, 654; for O-Py: 3404, 3110, 1654, 1607, 1466, 1231, 1175, 1017, 916, 836, 771, 676, 549, 512, 468. Differential scanning calorimetry (DSC) experiments on selected single crystals of (I) were conducted on a Shimadzu DSC-50 apparatus, at a heating rate of 2 K min⁻¹ under an N₂ atmosphere, using aluminium pans. Thermogravimetric analysis (TGA) was performed under similar conditions using a Shimadzu TGA-51H thermobalance. Mass loss was measured on a Sartorius AC 210 P balance for samples heated in a Buchi B-585 oven.

2.3. Refinement

Crystal data, data collection and structure refinement details for (I) are summarized in Table 1. All H atoms were originally found in difference maps but were treated differently in the refinement. The water H atoms was refined with restrained O–H distances [0.85 (1) Å], while pyridine H atoms were repositioned in their expected positions and allowed to ride (C–H = 0.93 Å). All H atoms were assigned *U*_{iso}(H) values of 1.2*U*_{eq}(C,O).

3. Results and discussion

The asymmetric unit of (I) consists of one I₃F₃Bz and one water molecule sitting on two different twofold axes and an O-Py molecule in a general position, resulting in four full 1:2:1 groups in the unit cell (*Z'* = $\frac{1}{2}$, *Z* = 4). As expected, the molecular geometry (Fig. 1) does not depart from expected values

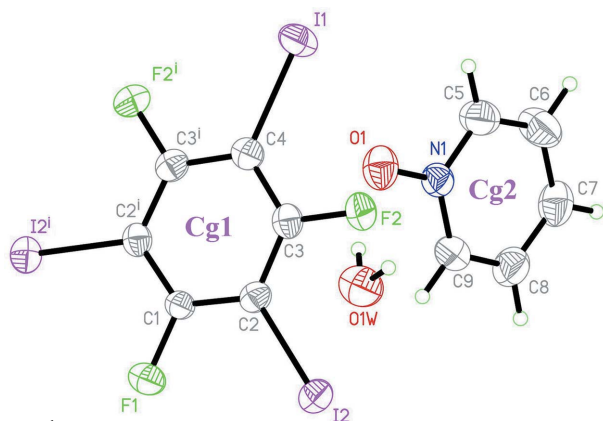


Figure 1
A view of the components of (I), with displacement ellipsoids drawn at the 40% probability level. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$]

and will not be discussed in what follows. The most appealing aspects of the structure are the intermolecular interactions. In order to facilitate the comparison of the current structure, (I), and that of Aakeröy *et al.* (2014*b*), (II), we present a table of the pyridine *N*-oxide π - π contacts (Table 2) and another of the hydrogen-bonding, $C-X \cdots O$ and $C-X \cdots \pi$ interactions (Table 3) common to both structures of interest. The atom labelling for the latter has been taken from the CSD. The most conspicuous synthon is π - π stacking among the I_3F_3Bz molecules, which appears in both structures exactly in the same fashion [Table 2: #1 and #2 for (I); #4 and #5 for (II)]. The columnar arrays they give rise to are absolutely comparable (Fig. 2) and this could be considered the fundamental structural brick from which the packing of both structures is built. Differences arise, however, when the intercolumnar interactions are considered, and this is where the diversity in formulation and stoichiometry begins to appear.

Fig. 3 presents packing views of (I) and (II), drawn along the column direction, where similarities and differences are apparent. Among the similarities, both structures present $C-F \cdots \pi$ and a $C-I \cdots O$ interactions [Table 3: #7 and #8 for (I); #9, #10 and #11 for (II)] which, apart from very minor differences, could be considered identical, and correspond to the ‘framed’ zones in the figure.

However, while these are all the interactions present in (II), giving a full account of the whole connectivity between the stacked columns to form (101) planes (Fig. 3*b*), in the case of (I), these blocks appear ‘split’, with the water molecules acting as ‘wedges’ between them (Fig. 3*a*), and the duplication of the O-Py molecule in the formulation now being apparent. Note the π - π interaction connecting pyridine rings and detailed in Table 2 (entry #3). This new substructure, characteristic of (I) but absent in (II), also provides the packing cohesion of the (010) planes by defining chains parallel to the I_3F_3Bz columns (viewed in projection in the encircled region in Fig. 3*a* and in full in Fig. 4*a*). This should be compared with the equivalent nonconnected region in (II) (encircled region in Figs. 3*b* and 4*b*). Additional evidence for the structural role played by the water molecules comes from the fact that even extremely careful heating experiments aimed at dehydrating individual

Table 2

π - π contacts for (I) and (II).

For ring codes, see Fig. 1. CCD is the centre-to-centre distance (distance between ring centroids); DA is the dihedral angle; SA is the (mean) slippage angle (angle subtended by the intercentroid vector to the plane normal); IPD is the (mean) interplanar distance (distance from one plane to the neighbouring centroid). For details, see Janiak (2000).

	Group1...Group2	CCD (Å)	DA (°)	SA (°)	IPD (Å)
(I)					
#1	Cg1...Cg1 ⁱⁱ	3.828 (2)	0	22.8	3.528 (2)
#2	Cg1...Cg1 ⁱⁱⁱ	3.828 (2)	0	22.8	3.528 (2)
#3	Cg2...Cg2 ^{iv}	3.787 (3)	21	10.5	3.723 (2)
(II)					
#4	Cg1...Cg1 ^v	3.7015 (14)	0	20.7	3.4619 (10)
#5	Cg1...Cg1 ^{vi}	3.8182 (14)	0	24.9	3.4620 (10)

Symmetry codes: for (I), (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 2, y, -z + \frac{1}{2}$; for (II), (v) $-x + 1, -y, -z$; (vi) $-x + 1, -y + 1, -z$.

specimens of these single cocrystals using a DSC-based technique, which proved successful recently (Harvey *et al.*, 2014), in the present case yielded only an opaque (white) material without any single-crystal character. The first process detected by thermogravimetric analysis (TGA; see Fig. S2 in the *Supporting information*), at *ca* 338 K, corresponds to the mass loss expected for the water content of (I) (experimental: 2.2%; expected: 2.5%).

To assess the real strength of the (almost identical) $BzI \cdots O$ -Py interactions in (I) and (II), we carried out searches in the Cambridge Structural Database (Version 5.3, updated to March 2014; Groom & Allen, 2014) for $C-I \cdots O$ contacts with $I \cdots O < 3.25$ Å, under different restrictions, *viz.*

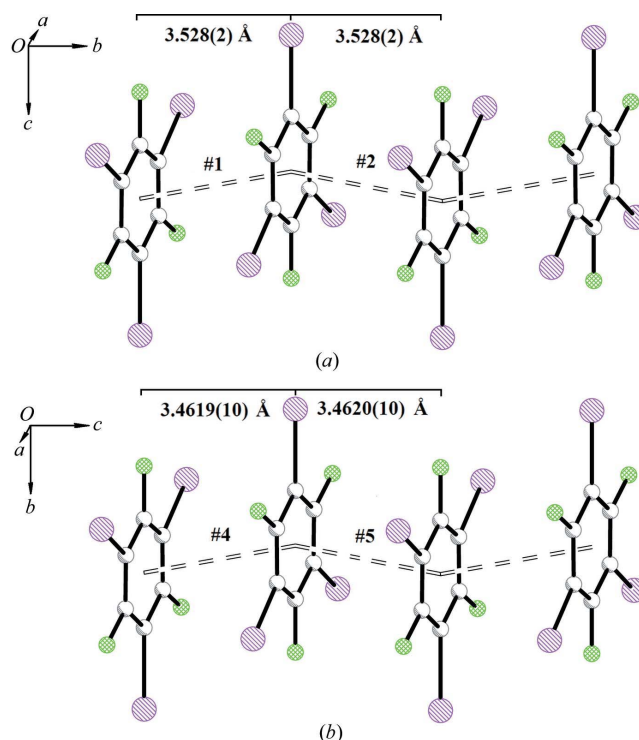
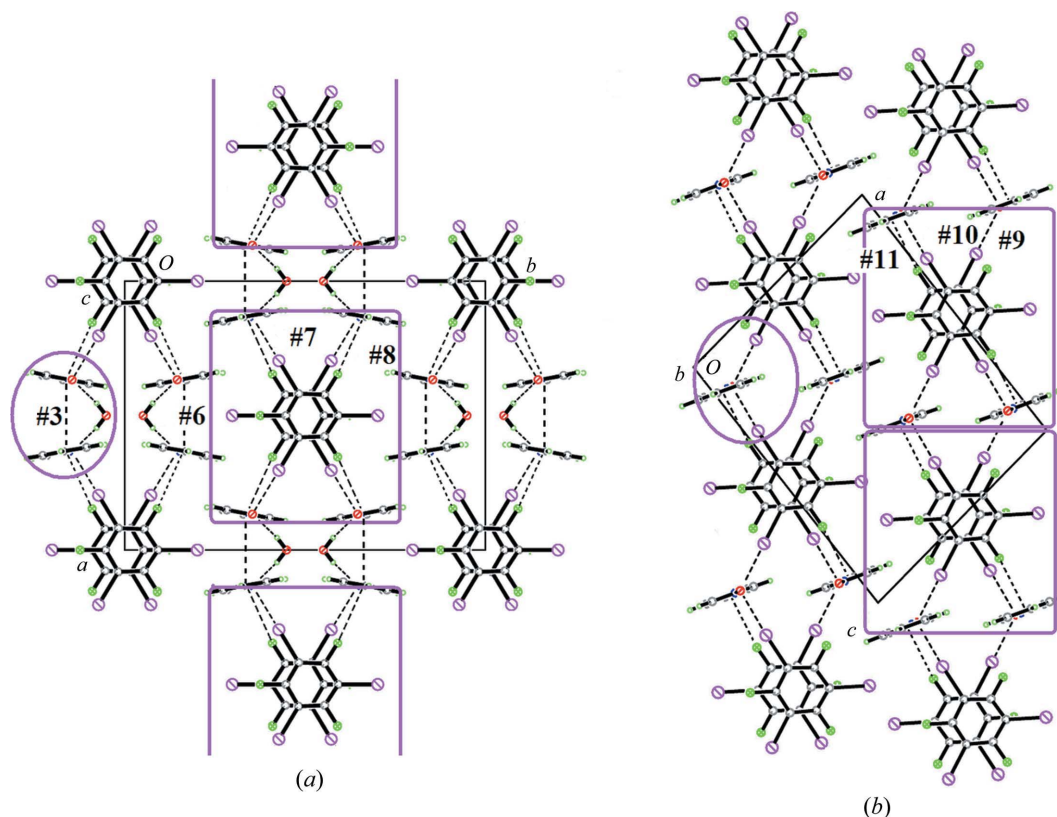


Figure 2

The I_3F_3Bz columnar arrays in (a) (I) and (b) (II). For #*n* interaction codes, see Table 2.

**Figure 3**

Packing views drawn along the column direction, showing the whole interaction scheme for (a) (I) and (b) (II). For #*n* interaction codes, see Tables 2 and 3.

Table 3

Hydrogen-bond or halogen-bond geometry for (I) and (II) (Å, °) (*X* = H, I or F).

For ring codes, see Fig. 1.

	<i>D</i> – <i>X</i> ··· <i>A</i> '	<i>D</i> – <i>X</i>	<i>X</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> – <i>X</i> ··· <i>A</i>
(I)					
#6	O1W–H1W···O1	0.85 (3)	2.00 (4)	2.838 (5)	166 (5)
#7	C2–I2···O1 ^{vii}	2.091 (5)	2.807 (4)	4.898 (6)	179.26 (15)
#8	C3–F2···Cg2	1.341 (6)	3.319 (4)	4.580 (5)	156.5 (3)
(II)					
#9	C21–I21···O11	2.093	2.741	4.832	176.89 (8)
#10	C23–I23···O11 ^{viii}	2.087	2.808	4.895	179.53 (8)
#11	C24–F24···Cg2 ^{vi}	1.34	3.063 (2)	4.313 (3)	154.82 (15)

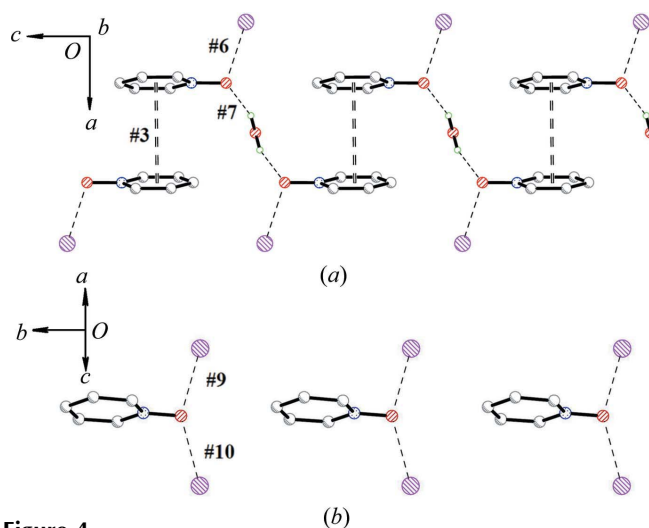
Symmetry codes, for (I): (vii) $x, -y + 1, z - \frac{1}{2}$; for (II): (vi) $-x + 1, -y + 1, -z$; (viii) $x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$.

(a) fully unrestricted and (b) restricting the donor and acceptor to the BzI···O-Py special arrangement, similar to what is present in (I) and (II). The histograms for these searches are presented in the *Supporting information* as Fig. S3, but the main results can be summarized by the number of hits, the distance/angle mean values (Å, °) and the distance/angle span (Å, °), viz. 554, 3.147/151.24 and 0.947/115.01 for search (a), and 14, 2.776/172.01 and 0.142/12.84 for search (b).

It is easily inferable from these results that the BzI···O-Py interaction is stronger and more directional than the average C–I···O interactions and that among the former, those in (I) and (II) lean towards the strong/directional side. Additional analysis (shown in Fig. S4 of the *Supporting information*)

shows this feature is due to the acceptor O-Py unit rather than the donor unit.

To a certain extent, the result of this exercise (in terms of what was originally planned) could be considered negative, as the aim of linking more than two eager XB acceptors, like O-Py, to a single XB donor proved fruitless. The structure obtained, (I), did not show a greater number of *X*···O interactions than was found in the previously reported analogue

**Figure 4**

(a) The [001] O-Py···water column and (b) a view of the corresponding region in (II). For #*n* interaction codes, see Tables 2 and 3.

(II), even if it shared with it the double BzI· · · O-Py linkage. However, the presence of the water molecule, albeit undesirable with respect to our original scope, introduced interesting structural differences which ended up being the basis of the present discussion. These results suggest that the low tendency of those aromatic compounds bearing terminal halogens to make more than two halogen-bond contacts requires more careful synthetic procedures (*e.g.* observing stringent anhydrous conditions) and approaches (*e.g.* use of alkyl-substituted pyridine *N*-oxides), suggesting this as a future line of investigation.

The authors acknowledge ANPCyT (project No. PME 2006-01113) for the purchase of the Oxford Gemini CCD diffractometer, University of Buenos Aires (grant UBACyT 20020100101000) for financial support and Dr Pablo Alborés for his help with the data collection. FDC is a member of the research staff of Conicet.

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supporting information

Acta Cryst. (2015). C71 [doi:10.1107/S205322961402796X]

The three-component cocrystal 1,3,5-trifluoro-2,4,6-triiodobenzene–pyridine *N*-oxide–water (1/2/1) built up by halogen bonds, hydrogen bonds and π – π interactions

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Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

1,3,5-Triiodo-2,4,6-trifluorobenzene–pyridine *N*-oxide–water (1/2/1)

Crystal data

$C_6F_3I_3 \cdot 2C_5H_5NO \cdot H_2O$

$M_r = 717.98$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 14.2226$ (12) Å

$b = 19.0094$ (18) Å

$c = 7.5203$ (5) Å

$\beta = 94.727$ (7)°

$V = 2026.3$ (3) Å³

$Z = 4$

$F(000) = 1328$

$D_x = 2.354$ Mg m⁻³

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

Cell parameters from 2090 reflections

$\theta = 4.3$ – 27.6 °

$\mu = 4.67$ mm⁻¹

$T = 295$ K

Prism, colourless

$0.60 \times 0.16 \times 0.09$ mm

Data collection

Oxford Diffraction Xcalibur CCD (Eos, Gemini) diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 16.1158 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.408$, $T_{\max} = 1.000$

6727 measured reflections

2358 independent reflections

1830 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 28.9$ °, $\theta_{\min} = 3.6$ °

$h = -19 \rightarrow 19$

$k = -24 \rightarrow 25$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.096$

$S = 1.06$

2358 reflections

128 parameters

2 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.044P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.78 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.74 \text{ e } \text{\AA}^{-3}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.5000	0.70155 (3)	0.2500	0.0697 (2)
I2	0.70350 (2)	0.42760 (2)	0.15588 (4)	0.04207 (14)
F1	0.5000	0.3763 (2)	0.2500	0.0550 (11)
F2	0.6537 (2)	0.59032 (16)	0.1621 (4)	0.0510 (7)
O1	0.8668 (3)	0.6459 (2)	0.5808 (5)	0.0560 (10)
N1	0.8666 (3)	0.6535 (2)	0.4053 (5)	0.0413 (9)
C1	0.5000	0.4472 (3)	0.2500	0.0319 (13)
C2	0.5813 (3)	0.4823 (3)	0.2083 (6)	0.0352 (10)
C3	0.5777 (3)	0.5545 (3)	0.2059 (6)	0.0376 (11)
C4	0.5000	0.5925 (4)	0.2500	0.0372 (14)
C5	0.8508 (4)	0.7170 (3)	0.3336 (8)	0.0574 (14)
H5	0.8392	0.7548	0.4069	0.069*
C6	0.8514 (5)	0.7272 (3)	0.1536 (8)	0.0667 (17)
H6	0.8415	0.7719	0.1053	0.080*
C7	0.8670 (4)	0.6707 (4)	0.0442 (7)	0.0594 (15)
H7	0.8675	0.6767	-0.0785	0.071*
C8	0.8815 (4)	0.6060 (4)	0.1197 (8)	0.0597 (15)
H8	0.8916	0.5671	0.0489	0.072*
C9	0.8813 (4)	0.5989 (3)	0.3003 (8)	0.0540 (13)
H9	0.8916	0.5547	0.3514	0.065*
O1W	1.0000	0.5512 (3)	0.7500	0.0665 (16)
H1W	0.9542 (18)	0.5777 (11)	0.713 (9)	0.080*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.1090 (5)	0.0333 (3)	0.0712 (4)	0.000	0.0347 (4)	0.000
I2	0.0413 (2)	0.0472 (2)	0.0380 (2)	0.00513 (14)	0.00465 (14)	-0.00077 (13)
F1	0.056 (2)	0.034 (2)	0.076 (3)	0.000	0.016 (2)	0.000
F2	0.0498 (17)	0.0462 (17)	0.0590 (18)	-0.0109 (14)	0.0165 (14)	0.0014 (14)
O1	0.060 (2)	0.068 (3)	0.0399 (18)	-0.010 (2)	0.0047 (17)	0.0011 (18)
N1	0.041 (2)	0.040 (2)	0.043 (2)	-0.0044 (19)	0.0049 (18)	-0.0011 (18)
C1	0.039 (3)	0.028 (3)	0.028 (3)	0.000	0.002 (3)	0.000
C2	0.036 (2)	0.039 (3)	0.031 (2)	0.004 (2)	0.0018 (18)	-0.0010 (19)
C3	0.040 (3)	0.043 (3)	0.029 (2)	-0.003 (2)	0.0006 (19)	0.0029 (19)
C4	0.045 (4)	0.037 (3)	0.029 (3)	0.000	-0.001 (3)	0.000

C5	0.070 (4)	0.046 (3)	0.057 (3)	0.004 (3)	0.006 (3)	-0.003 (3)
C6	0.097 (5)	0.047 (3)	0.056 (3)	-0.004 (3)	0.001 (3)	0.006 (3)
C7	0.064 (4)	0.074 (4)	0.041 (3)	-0.009 (3)	0.009 (3)	0.002 (3)
C8	0.065 (4)	0.061 (4)	0.056 (3)	-0.007 (3)	0.018 (3)	-0.012 (3)
C9	0.066 (3)	0.040 (3)	0.057 (3)	-0.001 (3)	0.014 (3)	0.003 (3)
O1W	0.080 (4)	0.058 (4)	0.060 (4)	0.000	0.000 (3)	0.000

Geometric parameters (Å, °)

I1—C4	2.072 (7)	C4—C3 ⁱ	1.383 (6)
I2—C2	2.091 (4)	C5—C6	1.368 (8)
F1—C1	1.349 (7)	C5—H5	0.9300
F2—C3	1.341 (5)	C6—C7	1.382 (9)
O1—N1	1.328 (5)	C6—H6	0.9300
N1—C9	1.331 (7)	C7—C8	1.364 (9)
N1—C5	1.332 (7)	C7—H7	0.9300
C1—C2 ⁱ	1.393 (5)	C8—C9	1.365 (8)
C1—C2	1.393 (5)	C8—H8	0.9300
C2—C3	1.374 (7)	C9—H9	0.9300
C3—C4	1.383 (6)	O1W—H1W	0.851 (10)
O1—N1—C9	121.1 (4)	N1—C5—C6	121.0 (6)
O1—N1—C5	119.2 (4)	N1—C5—H5	119.5
C9—N1—C5	119.7 (5)	C6—C5—H5	119.5
F1—C1—C2 ⁱ	118.6 (3)	C5—C6—C7	119.5 (6)
F1—C1—C2	118.6 (3)	C5—C6—H6	120.3
C2 ⁱ —C1—C2	122.7 (6)	C7—C6—H6	120.3
C3—C2—C1	116.8 (4)	C8—C7—C6	118.6 (5)
C3—C2—I2	121.7 (4)	C8—C7—H7	120.7
C1—C2—I2	121.5 (4)	C6—C7—H7	120.7
F2—C3—C2	118.7 (4)	C7—C8—C9	119.4 (6)
F2—C3—C4	118.0 (5)	C7—C8—H8	120.3
C2—C3—C4	123.3 (5)	C9—C8—H8	120.3
C3—C4—C3 ⁱ	117.0 (6)	N1—C9—C8	121.7 (5)
C3—C4—I1	121.5 (3)	N1—C9—H9	119.1
C3 ⁱ —C4—I1	121.5 (3)	C8—C9—H9	119.1

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