# organic compounds

# 2-(2,3,5,6-Tetrafluoro-4-iodoanilino)-ethanol

**Pierangelo Metrangolo,[a] Franck Meyer,[a] Tullio Pilati[b]* and Giuseppe Resnati[a]**

[a]Dipartimento di Chimica, Materiali e Ingegeria Chimica 'G. Natta', Politecnico di Milano, Via Mancinelli 7, I-20131 Milano, Italy, and [b]Istituto di Scienze e Tecnologie Molecolari del CNR, Via Golgi 19, 20133 Milano, Italy

Correspondence e-mail: tullio.pilati@istm.cnr.it

The reaction of 2-aminoethanol and iodopentafluorobenzene in the presence of $K_2CO_3$ gave the title compound, $C_8H_6F_4INO$, in high yield. The structure is characterized by double layers of molecules linked by O—H···O and N—H···O hydrogen bonds, and linear C—I···F [I···F = 3.049 (2) Å] and bent C—I···I [I···I = 3.9388 (7) Å] interactions between pairs of nearly parallel iodotetrafluorophenyl groups. No O···I or N···I halogen bonding is found.

## Related literature

For related literature, see: Metrangolo & Resnati (2001); Metrangolo et al. (2005, 2007).
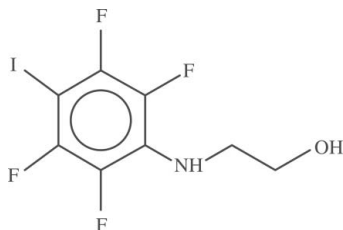


## Experimental

### Crystal data

| | |
|---|---|
| $C_8H_6F_4INO$ | Monoclinic, $C2/c$ |
| $M_r$ = 335.04 | $a$ = 13.327 (2) Å |
| $b$ = 17.663 (3) Å | Mo $K\alpha$ radiation |
| $c$ = 8.3044 (14) Å | $\mu$ = 3.33 mm$^{-1}$ |
| $\beta$ = 96.94 (2)° | $T$ = 158 (2) K |
| $V$ = 1940.5 (6) Å$^3$ | $0.24 \times 0.16 \times 0.08$ mm |
| $Z$ = 8 | |

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 8054 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 1999) | 2924 independent reflections |
| $T_{min}$ = 0.691, $T_{max}$ = 1.000 (expected range = 0.529–0.766) | 2422 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.026 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.036 | 8 restraints |
| $wR(F^2)$ = 0.092 | All H-atom parameters refined |
| $S$ = 1.04 | $\Delta\rho_{max}$ = 1.65 e Å$^{-3}$ |
| 2924 reflections | $\Delta\rho_{min}$ = −0.47 e Å$^{-3}$ |
| 162 parameters | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1N···O1$^i$ | 0.87 (2) | 2.23 (3) | 3.046 (3) | 157 (3) |
| O1—H1O···O1$^{ii}$ | 0.82 (5) | 1.90 (7) | 2.715 (4) | 175 (8) |
| O1—H2O···O1$^{iii}$ | 0.82 (5) | 1.99 (5) | 2.781 (4) | 162 (8) |

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR2002* (Burla et al., 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae et al., 2006); software used to prepare material for publication: *SHELXL97*.

## References

Bruker (1999). *SADABS, SMART and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Metrangolo, P., Neukirch, H., Pilati, T. & Resnati, G. (2005). *Acc. Chem. Res.* **38**, 386–395.

Metrangolo, P. & Resnati, G. (2001). *Chem. Eur. J.* **7**, 2511–2519.

Metrangolo, P., Resnati, G., Pilati, T., Liantonio, R. & Meyer, F. (2007). *J. Polym. Sci. Part A*, **45**, 1–15.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

# supporting information

## 2-(2,3,5,6-Tetrafluoro-4-iodoanilino)ethanol

**Pierangelo Metrangolo, Franck Meyer, Tullio Pilati and Giuseppe Resnati**

### S1. Comment

Supramolecular architectures assembled by halogen bonding (XB) are our long-standing interest (Metrangolo & Resnati, 2001; Metrangolo *et al.*, 2005, 2007). As preliminary work, we need to design and to synthesize molecules showing functional and geometric properties adequate to give the supramolecular structures we wish to obtain. In the present study, we report the structure of 2-(2,3,5,6-tetrafluoro-4-iodo-phenylamino)ethanol, an intermediate in the synthesis of more complex molecules to be used in XB supramolecular engineering and in particular to cover gold surfaces with iodo-tetrafluorobenzene pendants. The molecular structure is shown in Figure 1. Containing alcohol and amino H atoms, the main interactions in this structure are O—H···O and N—H···O hydrogen bonds (HB) rather then O···I or N···I XB. In fact, we find the short distances O1···O1(-$x$,$y$,1/2 - $z$), O1···O1(-$x$,-$y$,1 - $z$) and N1···O1($x$,-$y$,1/2 + $z$) of 2.715 (5), 2.781 (5), 3.046 (4) Å, respectively. These HBs generate one-dimensional sandwich ribbons; the distance between the centroids of a benzene ring and the mean plane through the nearest benzene ring in the sandwich is 3.393 Å. As shown in Figure 2 and 3, parallel one-dimensional ribbons are linked together by I1···I1(-$x$,1 - $y$,2 - $z$) and I1···F3($x$,1 - $y$,1/2 + $x$) interactions, with length of 3.9388 (7) and 3.049 (2) Å, respectively, to form a two-dimensional sandwich layer. These are linked together only by residual forces; no distance below the sum of van der Waals radii is found between atoms in different sandwiches, as shown by the distance between the benzene centroid and the plane of the nearest benzene ring in a second two-dimensional layer, 0.074 Å larger than the intra-sandwich one (see Figure 4).

### S2. Experimental

500 mg (8.2 mmol) of ethanolamine, 1.64 ml (12.3 mmol) of iodopentafluorobenzene and 1.24 g (9.03 mmol) of $K_2CO_3$ were stirred in 15 ml of refluxing THF. After 5 h, water was added and the aqueous phase was extracted three times with dichloromethane. The combined organic phases were washed with saturated aqueous $Na_2S_2O_3$ solution and dried over $Na_2SO_4$. The residue was chromatographied on silica gel (240–400 mesh, eluent dichloromethane) to give the product in 86% yield. 1H NMR (500 MHz, $CDCl_3$): $\delta$ 3.84 (2$H$, t, J = 5.2 Hz, $CH_2$), 3.56 (2$H$, tt, J = 1.4 Hz, J = 5.2 Hz, $CH_2$), 3.06 (2$H$, br s, OH and NH); 19 F NMR (470 MHz, $CDCl_3$): $\delta$ -157.8 (2 F, m, CF—C), -124.3 (2 F, m, CF—CI)

### S3. Refinement

Exchanging the atomic assignments of N1 and O1 worsens the results of the least-squares refinement, thus confirming that the tetrafluoroiodobenzene is bound to the amine group of ethanolamine. The H atoms were located in a difference map. For H of the hydroxyl group two possible positions were found. Both the positions (corresponding to H1O and H2O) are incompatible with a symmetry-equivalent position. In fact, the H1O···H1O(-$x$, $y$, 1/2 - $z$) distance is only 1.08 Å, and the H2O···H2O(-$x$, -$y$, 1 - $z$) distance is 1.24 Å. However, the distances H1O···H2O(-$x$, $y$, 1/2 - $z$) and H1O···H2O(-$x$, -$y$, 1 - $z$) are compatible with hydrogen bonding, being 2.17 and 2.32 Å, respectively. Any rotation of C—O—H around the C—O bond does not remedy the situation. The the hydroxyl group is thus disordered. H atoms were refined with the

following restraints: all the C—H distances are approximately equal, O—H is 0.82 (1) Å, and N—H is freely refined.
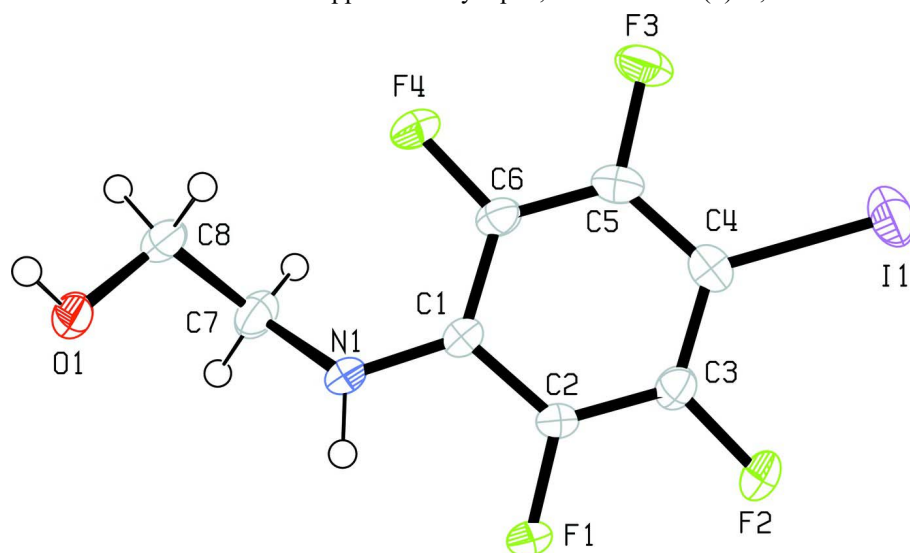


**Figure 1**

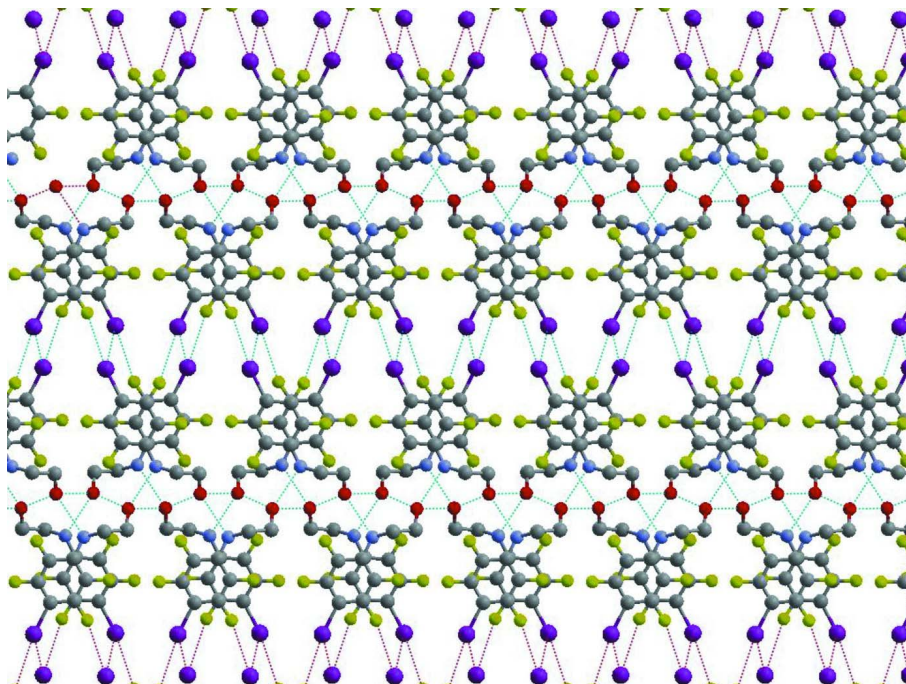Molecular structure with the numbering scheme and ADPs at the 50% probability level.



**Figure 2**

A two-dimensional sandwich (see text) projected along the a* axis, in Mercury ball and stick style. H atoms omitted.
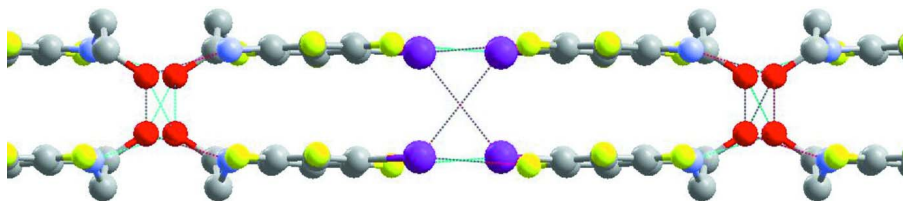
**Figure 3**

The two-dimensional sandwich projected along the *c* axis.
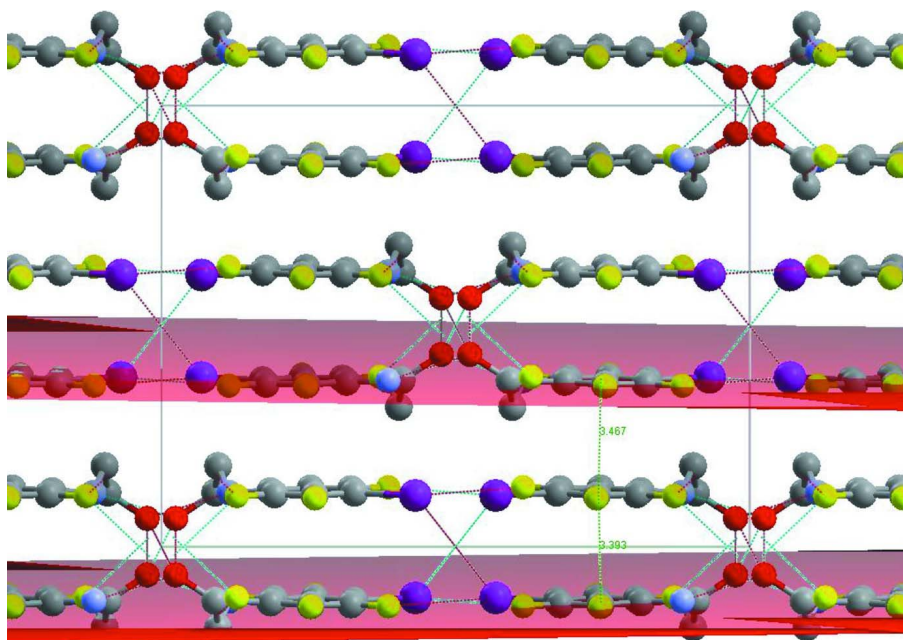


**Figure 4**

The complete packing viewed along the *c* axis with the distances between the centroid of the benzene ring and the planes of the two nearest benzene rings.

**2-(2,3,5,6-Tetrafluoro-4-iodoanilino)ethanol**

*Crystal data*

| | |
|---|---|
| $C_8H_6F_4INO$ | $F(000) = 1264$ |
| $M_r = 335.04$ | $D_x = 2.294$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Melting point = 343–348 K |
| Hall symbol: -C 2yc | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 13.327$ (2) Å | Cell parameters from 2964 reflections |
| $b = 17.663$ (3) Å | $\theta = 3.0–29.1°$ |
| $c = 8.3044$ (14) Å | $\mu = 3.33$ mm$^{-1}$ |
| $\beta = 96.94$ (2)° | $T = 158$ K |
| $V = 1940.5$ (6) Å$^3$ | Irregular table, colourless |
| $Z = 8$ | $0.24 \times 0.16 \times 0.08$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 8054 measured reflections |
| Radiation source: fine-focus sealed tube | 2924 independent reflections |
| Graphite monochromator | 2422 reflections with $I > 2\sigma(I)$ |
| $\omega$ and $\varphi$ scans | $R_{int} = 0.026$ |
| Absorption correction: multi-scan | $\theta_{max} = 31.3°$, $\theta_{min} = 1.9°$ |
| ($SADABS$; Bruker, 1999) | $h = -18 \rightarrow 18$ |
| $T_{min} = 0.691$, $T_{max} = 1.000$ | $k = -16 \rightarrow 25$ |
| | $l = -11 \rightarrow 12$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | Hydrogen site location: difference Fourier map |
| $wR(F^2) = 0.092$ | All H-atom parameters refined |
| $S = 1.04$ | $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 2.2775P]$ |
| 2924 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 162 parameters | $(\Delta/\sigma)_{max} = 0.001$ |
| 8 restraints | $\Delta\rho_{max} = 1.65$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{min} = -0.47$ e Å$^{-3}$ |

*Special details*

**Experimental**. Data collection using an OXFORD low temperature device. Below 158 K the structure possibly shows a phase transition.

**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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| I1 | 0.116120 (18) | 0.431723 (13) | 1.05305 (3) | 0.03962 (10) | |
| F1 | 0.11489 (13) | 0.12833 (11) | 1.03239 (18) | 0.0310 (4) | |
| F2 | 0.10979 (15) | 0.26089 (11) | 1.1821 (2) | 0.0341 (4) | |
| F3 | 0.13483 (15) | 0.38552 (11) | 0.6853 (2) | 0.0375 (4) | |
| F4 | 0.13603 (14) | 0.25397 (11) | 0.53509 (19) | 0.0320 (4) | |
| N1 | 0.12288 (19) | 0.11508 (15) | 0.7067 (3) | 0.0256 (5) | |
| H1N | 0.120 (3) | 0.080 (2) | 0.779 (5) | 0.032 (10)* | |
| O1 | 0.06410 (19) | 0.02423 (13) | 0.3901 (2) | 0.0322 (5) | |
| H1O | 0.026 (5) | 0.027 (5) | 0.306 (6) | 0.048* | 0.50 |
| H2O | 0.022 (5) | 0.020 (5) | 0.454 (8) | 0.048* | 0.50 |
| C1 | 0.12620 (19) | 0.18530 (16) | 0.7785 (3) | 0.0211 (5) | |
| C2 | 0.1188 (2) | 0.19221 (15) | 0.9451 (3) | 0.0220 (5) | |
| C3 | 0.11614 (19) | 0.26044 (18) | 1.0212 (3) | 0.0239 (5) | |
| C4 | 0.1225 (2) | 0.32801 (16) | 0.9396 (4) | 0.0257 (5) | |

| | | | | |
|---|---|---|---|---|
| C5 | 0.1307 (2) | 0.32223 (17) | 0.7744 (4) | 0.0266 (6) |
| C6 | 0.13237 (19) | 0.25369 (15) | 0.6968 (3) | 0.0235 (5) |
| C7 | 0.1830 (2) | 0.0964 (2) | 0.5749 (3) | 0.0300 (6) |
| H7A | 0.216 (3) | 0.0485 (14) | 0.602 (4) | 0.031 (9)* |
| H7B | 0.237 (2) | 0.1319 (17) | 0.573 (4) | 0.032 (9)* |
| C8 | 0.1226 (3) | 0.0915 (2) | 0.4085 (3) | 0.0303 (6) |
| H8A | 0.079 (3) | 0.136 (2) | 0.388 (6) | 0.072 (15)* |
| H8B | 0.161 (2) | 0.090 (2) | 0.319 (3) | 0.029 (9)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| I1 | 0.04639 (16) | 0.02605 (13) | 0.04478 (15) | 0.00436 (8) | −0.00122 (10) | −0.00885 (8) |
| F1 | 0.0507 (11) | 0.0251 (9) | 0.0177 (7) | −0.0040 (7) | 0.0061 (7) | 0.0048 (6) |
| F2 | 0.0505 (10) | 0.0345 (10) | 0.0177 (7) | 0.0006 (8) | 0.0052 (7) | −0.0053 (7) |
| F3 | 0.0486 (11) | 0.0235 (9) | 0.0403 (10) | −0.0035 (8) | 0.0052 (8) | 0.0108 (8) |
| F4 | 0.0446 (10) | 0.0336 (10) | 0.0190 (8) | −0.0037 (8) | 0.0089 (7) | 0.0048 (7) |
| N1 | 0.0371 (13) | 0.0243 (12) | 0.0161 (10) | −0.0009 (10) | 0.0068 (9) | 0.0017 (9) |
| O1 | 0.0516 (14) | 0.0244 (10) | 0.0190 (9) | 0.0051 (10) | −0.0024 (9) | −0.0019 (8) |
| C1 | 0.0215 (11) | 0.0249 (13) | 0.0171 (11) | 0.0001 (10) | 0.0032 (9) | 0.0004 (9) |
| C2 | 0.0263 (12) | 0.0208 (12) | 0.0192 (11) | −0.0011 (10) | 0.0040 (9) | 0.0039 (9) |
| C3 | 0.0248 (13) | 0.0273 (14) | 0.0195 (12) | −0.0018 (10) | 0.0021 (10) | −0.0017 (10) |
| C4 | 0.0229 (12) | 0.0215 (13) | 0.0325 (14) | 0.0001 (10) | 0.0021 (10) | −0.0011 (11) |
| C5 | 0.0243 (12) | 0.0253 (13) | 0.0297 (14) | −0.0023 (11) | 0.0020 (10) | 0.0084 (11) |
| C6 | 0.0240 (12) | 0.0275 (14) | 0.0194 (12) | −0.0035 (11) | 0.0045 (10) | 0.0030 (10) |
| C7 | 0.0345 (15) | 0.0359 (16) | 0.0204 (12) | 0.0057 (13) | 0.0061 (11) | −0.0026 (11) |
| C8 | 0.0408 (16) | 0.0331 (15) | 0.0172 (12) | 0.0021 (13) | 0.0049 (11) | 0.0016 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| I1—C4 | 2.067 (3) | C1—C6 | 1.393 (4) |
| F1—C2 | 1.345 (3) | C1—C2 | 1.404 (4) |
| F2—C3 | 1.349 (3) | C2—C3 | 1.363 (4) |
| F3—C5 | 1.346 (3) | C3—C4 | 1.380 (4) |
| F4—C6 | 1.350 (3) | C4—C5 | 1.392 (4) |
| N1—C1 | 1.375 (4) | C5—C6 | 1.373 (4) |
| N1—C7 | 1.470 (4) | C7—C8 | 1.516 (4) |
| N1—H1N | 0.87 (4) | C7—H7A | 0.97 (2) |
| O1—C8 | 1.419 (4) | C7—H7B | 0.96 (2) |
| O1—H1O | 0.818 (10) | C8—H8A | 0.97 (2) |
| O1—H2O | 0.818 (10) | C8—H8B | 0.96 (2) |
| | | | |
| C1—N1—C7 | 122.3 (2) | F3—C5—C6 | 118.0 (3) |
| C1—N1—H1N | 110 (3) | F3—C5—C4 | 119.6 (3) |
| C7—N1—H1N | 115 (3) | C6—C5—C4 | 122.3 (3) |
| C8—O1—H1O | 108 (6) | F4—C6—C5 | 117.9 (2) |
| C8—O1—H2O | 115 (6) | F4—C6—C1 | 120.0 (2) |
| H1O—O1—H2O | 99 (8) | C5—C6—C1 | 122.0 (2) |

| | | | |
|---|---|---|---|
| N1—C1—C6 | 124.9 (2) | N1—C7—C8 | 114.5 (3) |
| N1—C1—C2 | 120.3 (2) | N1—C7—H7A | 107 (2) |
| C6—C1—C2 | 114.8 (2) | C8—C7—H7A | 110 (2) |
| F1—C2—C3 | 119.1 (2) | N1—C7—H7B | 110 (2) |
| F1—C2—C1 | 118.0 (2) | C8—C7—H7B | 110 (2) |
| C3—C2—C1 | 122.9 (3) | H7A—C7—H7B | 105 (3) |
| F2—C3—C2 | 118.2 (3) | O1—C8—C7 | 111.7 (3) |
| F2—C3—C4 | 119.8 (3) | O1—C8—H8A | 110 (3) |
| C2—C3—C4 | 122.0 (3) | C7—C8—H8A | 110 (3) |
| C3—C4—C5 | 115.9 (3) | O1—C8—H8B | 104 (2) |
| C3—C4—I1 | 122.3 (2) | C7—C8—H8B | 116 (2) |
| C5—C4—I1 | 121.8 (2) | H8A—C8—H8B | 105 (4) |
| | | | |
| C7—N1—C1—C6 | 38.5 (4) | C3—C4—C5—F3 | 178.5 (2) |
| C7—N1—C1—C2 | −144.3 (3) | I1—C4—C5—F3 | 0.1 (4) |
| N1—C1—C2—F1 | 4.1 (4) | C3—C4—C5—C6 | 0.0 (4) |
| C6—C1—C2—F1 | −178.5 (2) | I1—C4—C5—C6 | −178.3 (2) |
| N1—C1—C2—C3 | −176.3 (3) | F3—C5—C6—F4 | −1.3 (4) |
| C6—C1—C2—C3 | 1.1 (4) | C4—C5—C6—F4 | 177.1 (2) |
| F1—C2—C3—F2 | 0.1 (4) | F3—C5—C6—C1 | −178.6 (2) |
| C1—C2—C3—F2 | −179.5 (2) | C4—C5—C6—C1 | −0.1 (4) |
| F1—C2—C3—C4 | 178.3 (2) | N1—C1—C6—F4 | −0.3 (4) |
| C1—C2—C3—C4 | −1.3 (4) | C2—C1—C6—F4 | −177.6 (2) |
| F2—C3—C4—C5 | 178.8 (2) | N1—C1—C6—C5 | 176.9 (3) |
| C2—C3—C4—C5 | 0.7 (4) | C2—C1—C6—C5 | −0.4 (4) |
| F2—C3—C4—I1 | −2.8 (4) | C1—N1—C7—C8 | −106.0 (3) |
| C2—C3—C4—I1 | 179.0 (2) | N1—C7—C8—O1 | −74.4 (4) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N1—H1*N*···O1[i] | 0.87 (2) | 2.23 (3) | 3.046 (3) | 157 (3) |
| O1—H1*O*···O1[ii] | 0.82 (5) | 1.90 (7) | 2.715 (4) | 175 (8) |
| O1—H2*O*···O1[iii] | 0.82 (5) | 1.99 (5) | 2.781 (4) | 162 (8) |

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