1,3,5-Trifluoro-2,4,6-triiodobenzene–piperazine (2/1)

Christelle Hajjar, Jeffrey S. Ovens and David L. Bryce*

Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, ON K1N6N5, Canada.
*Correspondence e-mail: dbryce@uottawa.ca

Received 1 September 2021
Accepted 7 October 2021

Edited by R. J. Butcher, Howard University, USA

Keywords: crystal structure; halogen bonding; stoichiometry; co-crystal.

CCDC reference: 2101749

Structural data: full structural data are available from iucrdata.iucr.org

The single-crystal structure of the title compound, C₄H₁₀N₂·2C₆F₃I₃, features a moderately strong halogen bond between one of the three crystallographically distinct iodine atoms and the nitrogen atom. The iodine–nitrogen distance is 2.820 (3) Å, corresponding to 80% of the sum of their van der Waals radii. The C—I···N halogen bond angle is 178.0 (1)°, consistent with the linear interaction of nitrogen via a σ-hole opposite the carbon–iodine covalent bond. The other two iodine atoms do not engage in halogen bonding. Some weak C—H···F and —H···I interactions are also observed. The complete piperazine molecule is generated by symmetry.

Structure description

The halogen bond is a moderately strong and directional non-covalent interaction, which has proven very useful in the field of crystal engineering and for the design of co-crystalline materials. Perfluorinated iodobenzenes are commonly used as halogen-bond donors, in part due to their reliable ability to co-crystallize predictably with a range of electron donors (Cavallo, 2016). The title compound (Fig. 1), which has a 2:1 1,3,5-trifluoro-2,4,6-triiodobenzene:piperazine (1,4-diazacyclohexane) stoichiometry, features a halogen bond between I₁ as the halogen-bond donor and N₁ as the halogen-bond acceptor (Fig. 2). The iodine–nitrogen distance is 2.820 (3) Å, which corresponds to 80% of the sum of their van der Waals radii. This is somewhat shorter than the analogous iodine–nitrogen halogen bonds in co-crystals formed from the same halogen-bond donor with acridine (3.022 Å), 1,10-phenanthroline (3.020 and 3.148 Å), or 2,3,5,6-tetramethylpyrazine (2.991 and 2.993 Å), but comparable to those formed with hexamethylenetetramine (2.864 and 2.879 Å) as the electron donor (Szell et al., 2017). Comparable distances are also noted in an interesting class of halogen-bonded tubular structures...
formed from the self-assembly of 1,4-diiodotetrafluorobenzene and piperazine cyclophanes (Raatikainen, 2009).

The C1—I1·N1 halogen bond angle in the title compound is 178.0 (1)°, consistent with the linear interaction of nitrogen via a σ-hole opposite the carbon–iodine covalent bond. I1 also shows a short contact with C7 of the piperazine molecule of 3.578 (4) Å; this represents approximately 97% of the sum of their van der Waals radii and is likely a structural consequence of the formation of the adjacent halogen bond rather than a structure-directing element in and of itself. Possible weak hydrogen bonds are also observed between H1 and I2, between H7A and F2, between H7AB and I3, between H8A and I2, and between H8AB and I1 (Table 1). Interestingly, no weak hydrogen bonds are observed between H1 and F1, between H7A and F1, between H7AB and F2, between H8A and F1, and between H8AB and F2.

| D—H···A | D—H | H···A | D····A | D—H···A |
|---------|------|-------|--------|----------|
| N1—I1·I2 | 0.86 (2) | 3.12 (2) | 3.978 (3) | 177 (3) |
| C7—I7AB·F2 | 0.98 | 2.40 | 3.299 (4) | 152 |
| C7—I7AB·I3 | 0.98 | 3.23 | 3.990 (3) | 135 |
| C8—I8AB·I1 | 0.98 | 3.26 | 3.879 (3) | 123 |

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

Table 2
Experimental details.

| Crystal data | Chemical formula | $M_r$ |
|--------------|------------------|-------|
| $C_4H_{10}N_2$·2$C_6F_3$I$_3$ | 1105.66 |

| Crystal system, space group | Temperature (K) |
|----------------------------|------------------|
| Triclinic, P $\overline{1}$ | 203 |

| $a$, $b$, $c$ (Å) | $\alpha$, $\beta$, $\gamma$ (°) | $V$ (Å$^3$) |
|------------------|------------------|----------|
| 8.6450 (5), 9.1660 (5), 9.3403 (5) | 67.433 (1), 72.887 (1), 63.062 (1) | 602.75 (6) |

| Radiation type | $\mu$ (mm$^{-1}$) |
|----------------|------------------|
| Mo $K\alpha$ | 0.24 × 0.13 × 0.08 |

| Crystal size (mm) |
|-------------------|
| 0.24 × 0.13 × 0.08 |

| Data collection | Diffractometer |
|-----------------|---------------|
| Bruker APEXII CCD | Multi-scan (SADABS; Krause et al., 2015) |

| Absorption correction | T$_\text{min}$, T$_\text{max}$ |
|-----------------------|------------------|
| Multi-scan (SADABS; Krause et al., 2015) | 0.537, 0.746 |

| No. of measured, independent and observed $|I > 2\sigma(I)|$ reflections | $R$ (I) |
|---------------------------|--------|
| 13748, 3761, 3193 | 0.031 |

| No. of reflections | No. of parameters | No. of restraints |
|--------------------|------------------|------------------|
| 3761 | 139 | 1 |

| H-atom treatment | $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å$^{-3}$) |
|------------------|------------------|
| H atoms treated by a mixture of independent and constrained refinement | 0.56, −0.64 |

Computer programs: APEX3 and SAINT (Bruker, 2010), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), ShelXle (Hubschle et al., 2011) and Mercury (Macrae et al., 2020).

Figure 1
ORTEP plot of the title compound.

Figure 2
Detail of the X-ray crystal structure depicting a halogen bond between iodine and nitrogen, a short contact between iodine and carbon, and a short contact between hydrogen and fluorine. The other two iodine atoms on the aromatic ring do not engage in any halogen bonding or other close contacts.

Figure 3
View along each of the unit cell axes. (a): along the $a$ axis; (b): along the $b$ axis; (c): along the $c$ axis. Hydrogen atoms not shown.
halogen bonds involving I2 and I3 are observed, despite the fact that they are chemically identical to I1. The structure packs in the triclinic $P\overline{1}$ space group and the aromatic molecules lie in layers (Fig. 3). The stoichiometry of the co-crystal is highlighted by noting that pairs of aromatic molecules lying in adjacent layers are connected to each other via halogen bonding to a single common piperazine molecule.

Synthesis and crystallization

1,3,5-Trifluoro-2,4,6-triiodobenzene was purchased from Alfa Aesar and piperazine was purchased from Sigma–Aldrich. In a typical procedure, the title compound was obtained from the slow evaporation of a solution of the halogen-bond donor (0.025 g in 1 ml of chloroform) and a molar excess of halogen-bond acceptor (0.0412 g in 1 ml of ethanol) at room temperature. The two solutions were prepared independently and stirred. After dissolution, the two solutions were mixed, stirred, and covered to allow for slow evaporation and crystal formation.

Refinement

Crystal data, data collection, and structure refinement details are presented in Table 2.

Acknowledgements

We thank members of the Bryce lab for assistance and NSERC for funding.

Funding information

Funding for this research was provided by: Natural Sciences and Engineering Research Council of Canada (grant to David L. Bryce).

References

Bruker (2010). APEX3 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G. & Terraneo, G. (2016). Chem. Rev. 116, 2478–2601.
Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). J. Appl. Cryst. 44, 1281–1284.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platigs, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). J. Appl. Cryst. 53, 226–235.
Raatikainen, K., Huuskonen, J., Lahtinen, M., Metrangolo, P. & Rissanen, K. (2009). Chem. Commun. pp. 2160–2162.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Szell, P. M. J., Gabriel, S. A., Gill, R. D. D., Wan, S. Y. H., Gabidullin, B. & Bryce, D. L. (2017). Acta Cryst. C73, 157–167.
full crystallographic data

_IUCrData_ (2021). _6_, x211044  [https://doi.org/10.1107/S2414314621010440]

1,3,5-Trifluoro-2,4,6-triiodobenzene–piperazine (2/1)

Christelle Hajjar, Jeffrey S. Ovens and David L. Bryce

1,3,5-Trifluoro-2,4,6-triiodobenzene–piperazine (2/1)

Crystal data

| Parameter        | Value                          |
|------------------|--------------------------------|
| Chemical formula | C_{4}H_{10}N_{2}·2C_{6}F_{3}I_{3} |
| Mr               | 1105.66                        |
| System           | Triclinic                      |
| Space group      | _P_ 1                          |
| _a_ (Å)          | 8.6450 (5)                     |
| _b_ (Å)          | 9.1660 (5)                     |
| _c_ (Å)          | 9.3403 (5)                     |
| _α_ (°)          | 67.433 (1)                     |
| _β_ (°)          | 72.887 (1)                     |
| _γ_ (°)          | 63.062 (1)                     |
| _V_ (Å³)         | 602.75 (6)                     |
| _Z_              | 1                              |
| _F_(000)         | 492                            |
| _D_ (Mg m⁻³)     | 3.046                          |
| _λ_ (Å)          | 0.71073                        |
| Radiation        | Mo Kα radiation               |
| _θ_ max (°)      | 30.8                           |
| _θ_ min (°)      | 2.4                            |
| _T_ (K)          | 203                            |
| Shape            | Block, colourless              |
| Size             | 0.24 × 0.13 × 0.08 mm          |

Data collection

| Instrument       | Bruker APEXII CCD      |
|------------------|------------------------|
| Monochromator    | Graphite monochromator |
| Scans            | _ω_ and _π_ hi scans   |
| Absorption       | multi-scan             |
| Software         | SADABS; Krause et al., 2015 |
| _T_ min          | 0.537                  |
| _T_ max          | 0.746                  |
| _R_ int          | 0.031                  |
| _θ_ max          | 30.8°                  |
| _θ_ min          | 2.4°                   |
| _h_ min          | _k_ min               |
| _l_ min          | _l_ max               |

Refinement

| Parameter        | Value                          |
|------------------|--------------------------------|
| Refinement       | on _F^2_                   |
| _R_ [ _F^2_ > 2σ(_F^2_) ] | 0.025                         |
| _w R_ [ _F^2_ ] | 0.048                         |
| _S_              | 1.02                          |
| _R_ int          | 0.031                         |
| Residual density | 0.56 e Å⁻³                  |
| Max. density     | -0.64 e Å⁻³                 |
| Max. restraint    | 0.001                         |

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
Special details

Experimental. Crystallographic data were collected from single crystals mounted on MiTeGen MicroMounts using parabar oil. Data were collected on a Bruker SMART APEXII single-crystal diffractometer equipped with a sealed tube Mo Kα source (λ = 0.71073 Å), a graphite monochromator, and an APEXII CCD detector. Samples were held at low temperature using a dry compressed air cooling system. Raw data collection and processing were performed with the APEX3 software package from Bruker (2010). Initial unit-cell parameters were determined from 36 data frames from select ω scans. Semi-empirical absorption corrections based on equivalent reflections were applied (Blessing, 1995). Systematic absences in the diffraction data-set and unit-cell parameters were consistent with the assigned space group. The initial structural solutions were determined using SHELXT direct methods (Sheldrick, 2015a) and refined with full-matrix least-squares procedures based on F2 using SHELXL and ShelXle (Hübschle et al., 2011; Sheldrick, 2015b). Hydrogen atoms were placed geometrically and refined using a riding model.

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.

Refinement. none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|     | x     | y     | z     | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-----|-------|-------|-------|------|------|------|------|------|------|
| I1  | 0.82683(3) | 0.38276(3) | 0.69997(2) | 0.02587(5) |
| N1  | 1.0231(4)  | 0.1572(3)  | 0.9473(3)  | 0.0297(6)  |
| H1  | 1.079(4)   | 0.212(4)   | 0.952(4)   | 0.036*     |
| C1  | 0.6818(4)  | 0.5589(4)  | 0.5141(3)  | 0.0236(6)  |
| F1  | 0.8619(2)  | 0.3929(2)  | 0.3438(2)  | 0.0350(5)  |
| I2  | 0.70010(3) | 0.60960(3) | 0.02390(2) | 0.03224(6) |
| C2  | 0.7265(4)  | 0.5356(4)  | 0.3663(4)  | 0.0246(6)  |
| F2  | 0.4127(2)  | 0.9155(2)  | 0.1493(2)  | 0.0305(4)  |
| I3  | 0.22867(3) | 1.04531(3) | 0.44595(3) | 0.03033(6) |
| C3  | 0.6376(4)  | 0.6522(4)  | 0.2419(3)  | 0.0226(6)  |
| F3  | 0.4867(2)  | 0.7292(2)  | 0.6764(2)  | 0.0334(4)  |
| C7  | 1.1580(4)  | 0.0068(4)  | 0.8988(4)  | 0.0316(7)  |
| H7A | 1.243223   | 0.060464   | 0.972668   | 0.038*     |
| H7AB| 1.220520   | 0.044203   | 0.794519   | 0.038*     |
| C6  | 0.5381(4)  | 0.7041(4)  | 0.5336(3)  | 0.0235(6)  |
| C5  | 0.4444(4)  | 0.8275(4)  | 0.4131(3)  | 0.0218(6)  |
| C4  | 0.4991(4)  | 0.7972(4)  | 0.2689(3)  | 0.0225(6)  |
| C8  | 0.9301(4)  | 0.1016(4)  | 1.1043(4)  | 0.0315(7)  |
| H8A | 0.841947   | 0.201779   | 1.136757   | 0.038*     |
| H8AB| 1.013321   | 0.034933   | 1.180012   | 0.038*     |

Atomic displacement parameters (Å²)

|     | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-----|------|------|------|------|------|------|
| I1  | 0.02951(11) | 0.02437(10) | 0.02130(10) | −0.00916(8) | −0.00948(8) | −0.00148(8) |
| N1  | 0.0415(17)   | 0.0289(15)   | 0.0227(14)   | −0.0176(13)  | −0.0112(12) | −0.0020(12)  |
| C1  | 0.0253(15)   | 0.0261(16)   | 0.0199(15)   | −0.0109(12)  | −0.0078(12) | −0.0028(12)  |
| F1  | 0.0367(11)   | 0.0271(10)   | 0.0300(11)   | 0.0021(8)    | −0.0089(8)  | −0.0115(8)   |
| I2  | 0.04118(13)  | 0.03267(12)  | 0.02151(11)  | −0.01026(9)  | −0.00498(9) | −0.01114(9) |
|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| C2  | 0.0241 (15) | 0.0223 (15) | 0.0255 (16) | -0.0074 (12) | -0.0017 (12) | -0.0082 (13) |
| F2  | 0.0380 (11) | 0.0267 (10) | 0.0211 (9) | -0.0063 (8) | -0.0141 (8) | -0.0016 (8) |
| I3  | 0.02595 (11) | 0.02909 (11) | 0.02966 (12) | -0.00356 (8) | -0.00403 (8) | -0.01089 (9) |
| C3  | 0.0276 (15) | 0.0227 (15) | 0.0191 (15) | -0.0091 (12) | -0.0049 (12) | -0.0074 (12) |
| F3  | 0.0358 (11) | 0.0399 (11) | 0.0175 (9) | -0.0072 (9) | -0.0039 (8) | -0.0104 (8) |
| C7  | 0.0280 (17) | 0.0381 (19) | 0.0249 (17) | -0.0119 (14) | -0.0076 (13) | -0.0036 (14) |
| C6  | 0.0272 (16) | 0.0287 (16) | 0.0162 (14) | -0.0137 (13) | -0.0017 (11) | -0.0058 (12) |
| C5  | 0.0203 (14) | 0.0207 (14) | 0.0239 (15) | -0.0073 (11) | -0.0039 (11) | -0.0061 (12) |
| C4  | 0.0242 (15) | 0.0221 (15) | 0.0216 (15) | -0.0106 (12) | -0.0103 (12) | 0.0002 (12) |
| C8  | 0.042 (2) | 0.0293 (18) | 0.0219 (16) | -0.0107 (15) | -0.0069 (14) | -0.0092 (14) |

Geometric parameters (Å, °)

| Bond  | Length (Å) | Angle (°) |
|-------|------------|-----------|
| I1—C1 | 2.118 (3)  |           |
| N1—C8 | 1.470 (4)  |           |
| N1—C7 | 1.475 (4)  |           |
| N1—H1 | 0.864 (18) |           |
| C1—C6 | 1.380 (4)  |           |
| C1—C2 | 1.392 (4)  |           |
| F1—C2 | 1.343 (3)  |           |
| I2—C3 | 2.089 (3)  |           |
| C2—C3 | 1.382 (4)  |           |
| F2—C4 | 1.345 (3)  |           |
| C8—N1—C7 | 110.0 (2) |           |
| C8—N1—H1 | 108 (2) |           |
| C7—N1—H1 | 106 (2) |           |
| C6—C1—C2 | 116.5 (3) |           |
| C6—C1—I1 | 121.3 (2) |           |
| C2—C1—I1 | 122.2 (2) |           |
| F1—C2—C3 | 118.5 (3) |           |
| F1—C2—C1 | 118.4 (3) |           |
| C3—C2—C1 | 123.0 (3) |           |
| C4—C3—C2 | 117.1 (3) |           |
| C4—C3—I2 | 120.5 (2) |           |
| C2—C3—I2 | 122.4 (2) |           |
| N1—C7—C8 | 109.0 (3) |           |
| N1—C7—H7A | 109.9 |           |
| C8—C7—H7A | 109.9 |           |
| N1—C7—H7AB | 109.9 |           |
| C8—C7—H7AB | 109.9 |           |

IUCrData (2021). 6, x211044
|     | Bond |  Angle |  Bond | Angle |
|-----|------|--------|------|-------|
| F1—C2—C3—I2 | 2.5 (4) | C2—C3—C4—C5 | −1.6 (5) |
| C1—C2—C3—I2 | −177.3 (2) | I2—C3—C4—C5 | 175.8 (2) |
| C8—N1—C7—C8i | 60.1 (3) | C6—C5—C4—F2 | −179.0 (3) |
| C2—C1—C6—F3 | 177.9 (3) | I3—C5—C4—F2 | 2.4 (4) |
| I1—C1—C6—F3 | −2.6 (4) | C6—C5—C4—C3 | 0.8 (4) |
| C2—C1—C6—C5 | −2.8 (5) | I3—C5—C4—C3 | −177.8 (2) |
| I1—C1—C6—C5 | 176.6 (2) | C7—N1—C8—C7i | −60.3 (4) |

Symmetry code: (i) −x+2, −y, −z+2.

**Hydrogen-bond geometry (Å, °)**

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···I2ii | 0.86 (2) | 3.12 (2) | 3.978 (3) | 177 (3) |
| C7—H7A···F2iii | 0.98 | 2.40 | 3.299 (4) | 152 |
| C7—H7AB···I3iv | 0.98 | 3.23 | 3.990 (3) | 135 |
| C8—H8A···I2v | 0.98 | 3.19 | 4.001 (3) | 141 |
| C8—H8AB···I1i | 0.98 | 3.26 | 3.879 (3) | 123 |

Symmetry codes: (i) −x+2, −y, −z+2; (ii) −x+2, −y, −z+2; (iii) x+1, y−1, z+1; (iv) x+1, y−1, z; (v) x, y, z+1.