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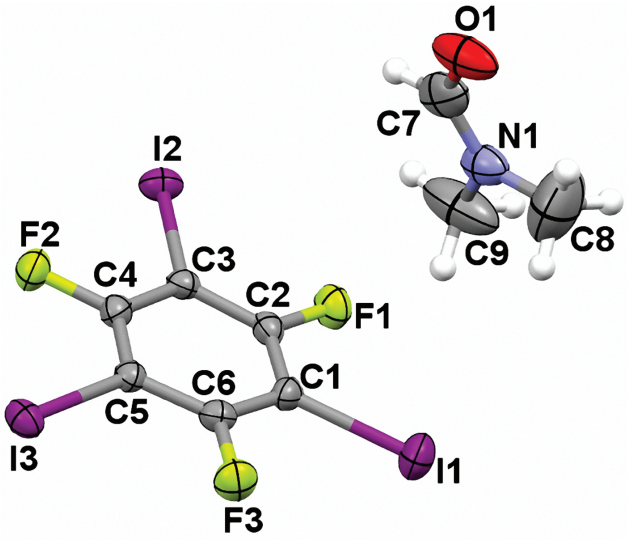
Halogen bonds and π–π interactions in the crystal structure of 1,3,5-trifluoro-2,4,6-triiodobenzene–*N*,*N*-dimethylformamide (1/1), $C_9H_7F_3I_3NO$



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Abstract

$C_9H_7F_3I_3NO$, monoclinic, $P2_1/n$ (no. 14), $a = 7.5581(4)$ Å, $b = 20.9303(11)$ Å, $c = 9.3548(5)$ Å, $\beta = 92.208(5)°$, $V = 1478.78(13)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0336$, $wR_{ref}(F^2) = 0.0610$, $T = 290$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Block, clear, colourless
Size:	0.29 × 0.14 × 0.11 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	6.36 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω-scans
$2\theta_{max}$, completeness:	26.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7946, 2695, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2324
$N(param)_{refined}$:	157
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], OLEX2 [4]

Source of material

The 1,3,5-trifluoro-2,4,6-triiodobenzene and *N*,*N*-dimethylformamide were purchased from Aldrich Chemical Co., and used as received. The 1,3,5-trifluoro-2,4,6-triiodobenzene (51.0 mg, 0.1 mmol) was dissolved in approximately 10 mL of *N*,*N*-dimethylformamide with gentle stirring at 50–60 °C. The undissolved materials were removed by filtration. The filtrate was set aside for crystallization by slow evaporation at room temperature. After a few days, colourless crystals of title compound were obtained.

Experimental details

H atom H7 was placed in at calculated position with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl group were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density, with U_{iso}(H) set to 1.5U_{eq}(C).

Discussion

The crystal packing is a consequence of a delicate balance between many weak non-covalent intermolecular forces. Hence, different types of non-covalent interactions should be considered jointly in crystal structure analysis. These intermolecular interactions include: hydrogen bond [5], halogen bond [6–8], chalcogen bond [9], π···π stacking interaction [10], etc. Evidently, it is important to study the cooperation and competition between the directional or non-directional non-covalent interactions of different nature

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
I1	0.75542(6)	0.54578(2)	0.91796(4)	0.07562(18)
I2	0.62380(5)	0.35271(2)	0.44873(4)	0.05582(15)
I3	0.86979(5)	0.62061(2)	0.30805(4)	0.05378(15)
F1	0.6449(4)	0.41963(16)	0.7510(3)	0.0635(9)
F2	0.7455(4)	0.47525(15)	0.2763(3)	0.0612(9)
F3	0.8575(5)	0.62321(15)	0.6439(4)	0.0643(9)
C1	0.7510(7)	0.5220(3)	0.7017(5)	0.0454(13)
C2	0.6981(7)	0.4625(3)	0.6550(5)	0.0438(13)
C3	0.6973(6)	0.4448(2)	0.5121(6)	0.0414(12)
C4	0.7471(6)	0.4911(3)	0.4161(5)	0.0446(13)
C5	0.7998(6)	0.5512(2)	0.4553(5)	0.0391(12)
C6	0.8026(6)	0.5650(2)	0.6003(6)	0.0431(13)
O1	0.9966(8)	0.2729(3)	0.8581(7)	0.112(2)
N1	0.7267(8)	0.2921(3)	0.9394(7)	0.0774(17)
C7	0.8320(14)	0.2689(4)	0.8478(9)	0.095(3)
H7	0.7820	0.2477	0.7686	0.113*
C8	0.7941(19)	0.3249(7)	1.0568(12)	0.195(6)
H8A	0.7475	0.3676	1.0559	0.292*
H8B	0.9208	0.3265	1.0538	0.292*
H8C	0.7609	0.3035	1.1425	0.292*
C9	0.5371(12)	0.2862(5)	0.9276(13)	0.157(5)
H9A	0.4956	0.2647	1.0106	0.236*
H9B	0.5042	0.2621	0.8435	0.236*
H9C	0.4849	0.3280	0.9209	0.236*

and strength in crystal engineering. In recent years, the key role of the halogen bond in crystal growth and design has been revealed both experimentally and theoretically [6–8]. The π···π stacking interaction is another one of the most important non-covalent driving forces for supramolecular assembly [10]. The structural competition between the C—I···N halogen bond and the π–π stacking interaction was investigated [11]. 1,3,5-Trifluoro-2,4,6-triiodobenzene and *N*,*N*-dimethylformamide are good candidates for the formation of the C—I···O halogen bond and the π···π stacking interaction, allowing to explore the cooperation and competition between the C—I···O halogen bond and the π···π stacking interaction.

All bond lengths and angles in the title crystal structure are in normal ranges. One *N*,*N*-dimethylformamide molecule and two 1,3,5-trifluoro-2,4,6-triiodobenzene molecules are linked by two asymmetric bifurcated halogen bonds with d(I2···O1) = 2.913 Å, d(I3···O1) = 2.923 Å, <(C3—I2···O1) = 176.13° and <(C5—I3···O1) = 170.49°. At the same time, the π···π stacking interactions between two 1,3,5-trifluoro-2,4,6-triiodobenzene molecules are present. All these non covalent bonds cooperate to construct a 2D network. According to the quantum chemical calculations [12, 13], the π···π stacking interaction between two 1,3,5-trifluoro-2,4,6-triiodobenzene molecules is much stronger than the halogen bond with the type of C—I···N, and the C—I···N halogen bond is much stronger than the C—I···O halogen bond.

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