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Crystal structure of 18-crown-6 – 1,4-diiodotetrafluorobenzene – acetonitrile (1/1/2), $C_{22}H_{30}F_4I_2N_2O_6$

Figure 1: Molecular structure of the title complex with displacement ellipsoids draw at the 50% probability level.

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Abstract

$C_{22}H_{30}F_4I_2N_2O_6$, monoclinic, $P2_1/n$ (no. 14), $a = 7.6927(3)$ Å, $b = 12.4813(5)$ Å, $c = 15.0763(5)$ Å, $\beta = 92.862(3)^\circ$, $V = 1445.74(9)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0242$, $wR_{ref}(F^2) = 0.0581$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

18-Crown-6 and 1,4-diiodotetrafluorobenzene for crystallization were purchased from J&K Scientific Ltd., and

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.23 \times 0.18 \times 0.14$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.24 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ϕ and ω
$\theta_{\max}$, completeness:	25.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6533, 2684, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2334
$N(\text{param})_{\text{refined}}$:	165
Programs:	CrysAlis PRO [1], SHELX [2, 3]

used as received. 18-Crown-6 (26.4 mg, 0.1 mmol) and 1,4-diiodotetrafluorobenzene (40.2 mg, 0.1 mmol) were dissolved in approximately 10 mL of acetonitrile with gentle stirring at room temperature. The undissolved materials were removed by filtration. The filtrate was set aside for crystallization by slow evaporation of acetonitrile at room temperature. After about two days, colourless crystals of title complex suitable for single-crystal X-ray diffraction were obtained.

Experimental details

Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. 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 $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{C})$.

Comment

Hydrogen bonds and halogen bonds play key roles in the field of the crystal engineering. Research on hydrogen bonding has long history. In recent years, the study of the halogen bonding has received increasing attention at both the theoretical and experimental levels [4–12]. In two previous studies, Wang investigated in detail the competition between different noncovalent bonds [11, 12]. In the present study, we report the coexistence of halogen bonds and hydrogen bonds in the crystal structure of the title complex (the Figure 1).

The asymmetric unit of the title structure contains a full acetonitrile molecule and two halves of the

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.3682(3)	0.4316(2)	−0.02485(17)	0.0491(6)
C2	0.3547(4)	0.48948(19)	0.05272(17)	0.0476(6)
C3	0.4905(4)	0.5573(2)	0.07586(16)	0.0492(6)
C4	0.7265(4)	0.2383(2)	0.0841(2)	0.0671(8)
H4A	0.7928	0.1940	0.1264	0.081*
H4B	0.7353	0.3121	0.1040	0.081*
C5	0.4733(4)	0.2115(2)	0.1628(2)	0.0651(8)
H5A	0.4731	0.2850	0.1837	0.078*
H5B	0.5390	0.1684	0.2063	0.078*
C6	0.2909(4)	0.1708(2)	0.1520(2)	0.0655(8)
H6A	0.2291	0.1861	0.2050	0.079*
H6B	0.2306	0.2064	0.1022	0.079*
C7	0.1239(4)	0.0136(3)	0.13268(18)	0.0577(8)
H7A	0.0533	0.0473	0.0854	0.069*
H7B	0.0686	0.0256	0.1882	0.069*
C8	0.1383(3)	−0.1033(3)	0.11558(17)	0.0574(7)
H8A	0.2247	−0.1347	0.1568	0.069*
H8B	0.0275	−0.1378	0.1241	0.069*
C9	0.2015(4)	−0.2280(2)	0.0049(2)	0.0658(8)
H9A	0.0877	−0.2615	0.0047	0.079*
H9B	0.2772	−0.2642	0.0487	0.079*
C10	0.8654(4)	0.4174(3)	0.4098(2)	0.0668(8)
H10A	0.9868	0.4286	0.4248	0.100*
H10B	0.8341	0.3454	0.4248	0.100*
H10C	0.7975	0.4669	0.4423	0.100*
C11	0.8325(4)	0.4341(3)	0.3168(2)	0.0602(7)
F1	0.2420(2)	0.36278(13)	−0.05064(11)	0.0653(4)
F2	0.4865(2)	0.61676(13)	0.15008(10)	0.0657(4)
I1	0.13922(2)	0.476008(16)	0.129290(12)	0.05781(11)
N1	0.8053(4)	0.4493(3)	0.2437(2)	0.0973(10)
O1	0.5512(2)	0.20603(15)	0.07992(12)	0.0611(5)
O2	0.2939(2)	0.05886(14)	0.13699(12)	0.0551(5)
O3	0.1873(2)	−0.11909(13)	0.02743(11)	0.0519(4)

1,4-diiodotetrafluorobenzene and the 18-crown-6 molecules, which both reside on inversion centres.

All bond lengths and angles in the title crystal structure are in the normal ranges. One 1,4-diiodotetrafluorobenzene molecule and two acetonitrile molecules are linked by two C—I···N halogen bonds with $d(I1···N1) = 3.182$ Å and $\angle(C2-I1···N1) = 178.35^\circ$. In the crystal structure, besides the C—I···N halogen bonds, C—H···F hydrogen bonds and C—H···O hydrogen bonds are also formed. The H10A atom on the methyl group of the acetonitrile molecule forms a bifurcated hydrogen bond with two oxygen atoms O2 and O3 of the 18-crown-6 molecule; the H10C atom on

the methyl group of the acetonitrile molecule forms a monocoordinate hydrogen bond with the atom O3 of the 18-crown-6 molecule. No C—I···O halogen bond between 1,4-diiodotetrafluorobenzene and 18-crown-6 is found in the crystal structure of the title complex. This is understandable because the C—I···O halogen bond is much weaker than the C—I···N halogen bond [5].

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