

Diisopropylammonium hydrogen difluoride

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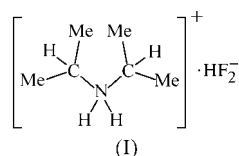
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By the reaction of diisopropylamine with concentrated hydrofluoric acid, the title compound, $C_6H_{16}N^+ \cdot HF_2^-$, was synthesized. The cations and anions are connected *via* hydrogen bonds to form chains along [100]. The interlocked polymeric zigzag chains are hexagonally surrounded by six neighbouring chains. The F^- anion is strongly hydrogen bonded to HF [$F-H$ 0.98 (4), $H \cdots F$ 1.34 (4), $F \cdots F$ 2.3125 (16) Å and $F-H \cdots F$ 174 (3)°]; a better description is that of a non-centred hydrogen difluoride anion.

Comment

Solutions of alkylamines with an excess of hydrogen fluoride have been reported as convenient reagents for selective fluorination reactions (Haufe, 1996). The structure of the



hydrogen difluoride anion (Emsley, 1980) and polyhydrogen fluorides, $H_{n-1}F_n^-$ (e.g. Wiechert *et al.*, 1998), have been intensively studied in recent decades.

The diisopropylammonium cation is well known for stabilizing various anionic systems (Reiß, 1999, and references

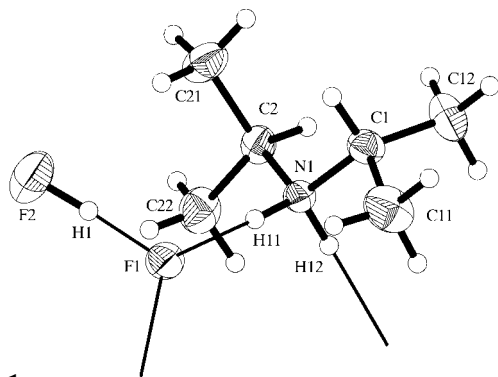


Figure 1

The diisopropylammonium cation and the complex hydrogen difluoride anion connected *via* hydrogen bonds to form chains along [100] (the ellipsoids are drawn at the 50% probability level).

therein). The structures of all diisopropylammonium halogenides (dipHal) known so far have been found to be isostructural but not isotypic. A systematic study of diisopropylammonium halogenides showed that at least dimorphism – a monoclinic and an orthorhombic modification are known – occurs for dipCl and dipBr (Reiß, 2000).

In the course of this investigation, the reaction of diisopropylamine with concentrated hydrofluoric acid yields a compound, (I), that is best described as the salt of the diisopropylammonium cation and the hydrogen difluoride anion. The hydrogen bonding found within the hydrogen difluoride is very similar to that in pyridinium hydrogen difluoride (Boenigk & Mootz, 1988). The H atom of the HF_2^- anion is found in a non-centred position, closer to the F atom not

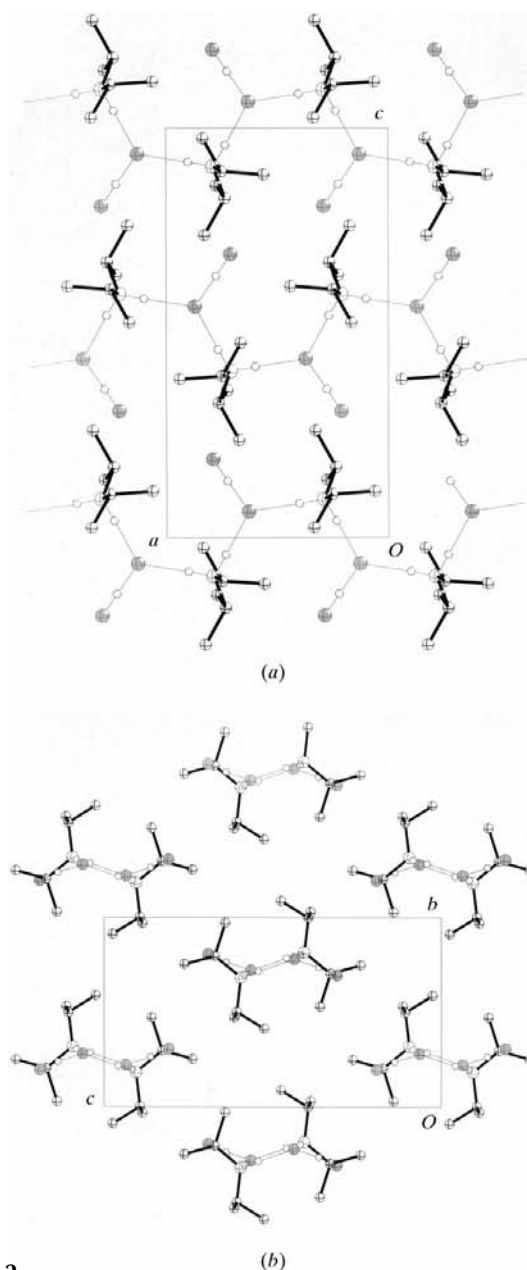


Figure 2

Views of (a) the interlocked hydrogen-bonded zigzag chains viewed towards [100] and (b) the hexagonal closed-rod packing of the hydrogen-bonded chains in the *bc* plane.

involved in further hydrogen bonds (F2), but still donating a strong hydrogen bond to the F atom (F1) accepting two N—H···F hydrogen bonds (Table 2). The donor–acceptor distance within the HF₂[−] anion is, with a value of 2.3125 (16) Å, approximately as short as that found in the pyridinium salt mentioned above. Significant shorter F···F donor–acceptor distances in the range 2.26–2.28 Å are reported for the alkali and ammonium hydrogen difluorides (Emsley, 1980). A new unique finding is the extremely short F···F distance [2.233 (2) Å] reported for L-argininium hydrogen difluoride (Ramos Silva *et al.*, 2000).

All C—C and N—C bond lengths within the diisopropylammonium cations (Table 1) are as expected. Each diisopropylammonium cation donates two hydrogen bonds to HF₂[−] anions and the F1 atom of every HF₂[−] anion accepts two hydrogen bonds from the neighbouring cations. Related to the strong F—H···F hydrogen bond within the complex anion, the hydrogen bonds between the cations and the anions are, as expected, significantly weaker (Table 2). Due to this connectivity, the structure of the title compound consists of hydrogen-bonded interlocked zigzag chains along the [100] direction (Fig. 2*a*). The hydrogen-bonding motif may be classified according to Etter's nomenclature (Etter *et al.*, 1990) as C(4). Each polymeric chain is hexagonally surrounded by six further chains (Fig. 2*b*). Related to the structures of the other known diisopropylammonium halogenides, the title compound is found to be isostructural, with the HF₂[−] anion replacing the single halogen atoms in the corresponding chloride and bromide salts.

Experimental

Diisopropylamine readily reacts with concentrated hydrofluoric acid to give a colourless solution. From this solution, very small thin platelets can be grown within a few weeks at room temperature.

Crystal data

C ₆ H ₁₆ N ⁺ ·HF ₂ [−]	Mo K α radiation
$M_r = 141.21$	650 reflections were selected from the whole data set
Orthorhombic, $P2_12_12_1$	$\theta = 4.7\text{--}24.9^\circ$
$a = 7.726$ (2) Å	$\mu = 0.09$ mm ^{−1}
$b = 8.057$ (3) Å	$T = 293$ (2) K
$c = 14.352$ (6) Å	Platelet, colourless
$V = 893.4$ (6) Å ³	0.20 × 0.05 × 0.01 mm
$Z = 4$	
$D_x = 1.050$ Mg m ^{−3}	

Data collection

Stoe IPDS diffractometer	$R_{\text{int}} = 0.029$
ω scans	$\theta_{\text{max}} = 25.0^\circ$
3729 measured reflections	$h = -8 \rightarrow 8$
1510 independent reflections	$k = -9 \rightarrow 9$
1195 reflections with $I > 2\sigma(I)$	$l = -17 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.10$ e Å ^{−3}
1510 reflections	$\Delta\rho_{\text{min}} = -0.10$ e Å ^{−3}
112 parameters	Extinction correction: <i>SHELXL</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.052 (11)

Table 1

Selected geometric parameters (Å, °).

N1—C1	1.500 (2)	C1—C11	1.510 (3)
N1—C2	1.500 (2)	C2—C22	1.506 (2)
C1—C12	1.501 (3)	C2—C21	1.513 (3)
C1—N1—C2	117.46 (13)		
C2—N1—C1—C12	−62.6 (2)	C1—N1—C2—C22	176.26 (16)
C2—N1—C1—C11	173.42 (16)	C1—N1—C2—C21	−60.9 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H11···F1	0.893 (15)	1.790 (15)	2.6827 (18)	178.0 (17)
N1—H12···F1 ⁱ	0.903 (14)	1.795 (14)	2.6974 (18)	179.0 (15)
F2—H1···F1	0.98 (4)	1.34 (4)	2.3125 (16)	174 (3)

Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.

To stabilize the latest stages of refinement, the N—H distances have been restrained to one refined common value. The atomic coordinates and individual U_{iso} values of all H atoms involved in hydrogen bonds and the H atoms of the C—H groups were refined freely [C—H = 0.93 (2) and 0.94 (2) Å]. The H atoms of the methyl groups were refined riding on their corresponding C atom (C—H = 0.96 Å), allowed to rotate around the C—C bond and with one common U_{iso} value for each group. As the structure has no atoms with significant anomalous scatterers, the resulting Flack (1983) value [−0.1 (8)] in refinement cycles with Friedel pairs was inconclusive as expected; for the final refinement, the Friedel pairs were merged.

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1527). Services for accessing these data are described at the back of the journal.

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