Crystal Structure of Morpholine Hydrofluoride Monohydrate

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Morpholinium fluoride was received during our studies on fluoride derivatives of organic bases. We attempted to use morpholine as a base for trapping of F−. A result quaternary morpholinium fluoride monohydrate has been formed and its crystals have been investigated by X-ray diffraction methods.

Crystal data: C4H9NO·HF·H2O, Mr = 125.145, orthorhombic, P212121, a = 6.0812(6), b = 6.2272(4), c = 16.846(1) Å, V = 637.93(1) Å3, Z = 4, Dc = 1.303 g/cm3, T = 293 K, λ(CuKα) = 1.54178 Å, μ = 1.03 mm−1, F(000) = 272, final R = 0.0305 for 1130 reflections [I > 2σ(I)]. Diffraction data were obtained using KM-4 diffractometer, graphite monochromated CuKα radiation, and ω-2θ scan mode. Two standard reflections 2,−2,4 and 224, recorded every hundred measurements, showed no significant changes of intensity during data collection. The intensities were corrected for Lorentz and polarization factors and empirical absorption correction were introduced. Maximum transmission equals 0.271 and minimum transmission equals 0.175. The structure was solved by direct methods and refined for non-H atoms using anisotropic displacement factors by full-matrix least-squares calculations on F2 with SHELXS-86 [1] and SHELXL-97 [2] programs. H-atom positions were found from Fourier difference map and refined with isotropic displacement factors. The quantity minimized was Σw(ΔF)2 with w = 1/[σ2Fo2 + 0.0589P2 + 0.04P], where P = (Fo2 + 2Fc2)/3. The refinement converged at R = 0.0305 for 1130 data and R = 0.0316 for all 1154 data, by 122 refined parameters. The highest peak and deepest hole on difference map was 0.13 and −0.14, respectively.

Results: Fractional atomic coordinates with their equivalent anisotropic or isotropic displacement parameters are given in Table 1. The bond lengths and bond angles are listed in Table 2. The molecular structure with atom numbering system is shown in Fig. 1.

The structure consists of the morpholinium cation, fluorine anion and water molecule. The morpholine ring accepts the near ideal chair conformation with torsion angles of values between 54.5(2)° and 60.8(2)° and with the asymmetry parameter [3] equal 1.65. The ring is less deformed than in two dimethyl morpholinium bromides [4]. A rich network of hydrogen bonds appears in the crystal, what is shown in Fig. 2 and Table 3. The fluorine ions are linked to two morpholinium nitrogen atoms by two hydrogen bonds of lengths 2.595(2)−2.656(3) Å and to two water molecules by next
hydrogen bonds of lengths 2.711(3)–2.737(3) Å. The infinite columns of hydrogen bonds linking fluorine ions, water molecules and morpholinium N–H groups extend along the bissecting lines between the x and y axes. These columns are situated in the middle and edges (z = 0 and 0.5) of the unit cells. A short contact C2–H...O7 can be also regarded as hydrogen bond linking neighbor to nitrogen C-atom in morpholinium ring with the acceptor oxygen atom of water.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
</tr>
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<tr>
<td>N1</td>
<td>0.1739(4)</td>
<td>0.2931(5)</td>
<td>0.5878(5)</td>
<td>0.0362(3)</td>
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<tr>
<td>C2</td>
<td>0.2851(5)</td>
<td>0.2142(6)</td>
<td>0.6607(6)</td>
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<td>C3</td>
<td>0.3654(6)</td>
<td>0.4036(6)</td>
<td>0.7087(6)</td>
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<tr>
<td>O4</td>
<td>0.1928(4)</td>
<td>0.5469(5)</td>
<td>0.7280(5)</td>
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<tr>
<td>C5</td>
<td>0.0933(6)</td>
<td>0.6275(6)</td>
<td>0.6573(7)</td>
<td>0.0454(4)</td>
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<tr>
<td>C6</td>
<td>–0.0030(6)</td>
<td>0.4478(6)</td>
<td>0.6087(6)</td>
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<tr>
<td>O7</td>
<td>0.1059(5)</td>
<td>0.6636(6)</td>
<td>0.4207(6)</td>
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<tr>
<td>F8</td>
<td>0.0357(4)</td>
<td>0.5088(4)</td>
<td>–0.0044(3)</td>
<td>0.0460(3)</td>
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Table 2. Bond lengths (Å) and angles (°).

<table>
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<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
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<tbody>
<tr>
<td>N(1)–C(2)</td>
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<tr>
<td>C(2)–C(3)</td>
<td>1.511(2)</td>
<td></td>
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<tr>
<td>C(3)–O(4)</td>
<td>1.416(2)</td>
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<tr>
<td>O(4)–C(5)</td>
<td>1.428(2)</td>
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<tr>
<td>C(5)–C(6)</td>
<td>1.505(2)</td>
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<tr>
<td>C(6)–N(1)</td>
<td>1.486(2)</td>
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</tr>
<tr>
<td>N(1)–H(11)</td>
<td>0.99(2)</td>
<td></td>
</tr>
<tr>
<td>N(1)–H(12)</td>
<td>0.97(2)</td>
<td></td>
</tr>
<tr>
<td>Bond</td>
<td>Distance (Å)</td>
<td></td>
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<tr>
<td>----------------------</td>
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<td>C(2)–H(21)</td>
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<td>C(2)–H(22)</td>
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<td>C(3)–H(31)</td>
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<td>C(5)–H(51)</td>
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<td>O(7)–H(71)</td>
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<td>O(7)–H(72)</td>
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<tr>
<td>C(2)–N(1)–C(6)</td>
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<td>O(4)–C(5)–C(6)</td>
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<tr>
<td>C(5)–C(6)–N(1)</td>
<td>109.2(1)</td>
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<tr>
<td>H(11)–N(1)–H(12)</td>
<td>110(1)</td>
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<tr>
<td>H(71)–O(7)–H(72)</td>
<td>98(2)</td>
<td></td>
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**Figure 1.** Molecular structure and atomic numbering showing morpholinium cation. Heavy atoms are drawn as 50% probability ellipsoids and H atoms as circles of arbitrary radii.
Table 3. The geometry of hydrogen bonds.

<table>
<thead>
<tr>
<th>D–H</th>
<th>d(D–H) Å</th>
<th>d(H...F) Å</th>
<th>DHF (°)</th>
<th>d(D...F) Å</th>
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<tbody>
<tr>
<td>N(1)–H(11)</td>
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<td>1.67(3)</td>
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<td>2.656(2)</td>
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<td>N(1)–H(12)</td>
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<td>0.91(3)</td>
<td>1.84(4)</td>
<td>170(2)</td>
<td>2.737(3)</td>
</tr>
</tbody>
</table>

Symmetry codes: i) –x + 1/2, –x + 1, z + 1/2
ii) –x, y – 1/2, –z + 1/2
iii) –x, y + 1/2, –z + 1/2
iv) –x + 1/2, –y + 1, z + 1/2.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK) as deposition No CCDC 142498.

REFERENCES