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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C)$ = 0.002 Å
R factor = 0.042
wR factor = 0.116
Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

N—H⁺...Cl⁻ and C—H...O interactions in 6-fluoro-3-(4-piperidinio)benz[d]isoxazole chloride

Supramolecular assembly of the title compound, C₁₂H₁₄Cl·FN₂O, is primarily governed by N—H⁺...Cl⁻ and C—H...O interactions, and a putative C—H...F interaction. The piperidine ring assumes a chair conformation, with the substituted benzisoxazole ring in an equatorial position.

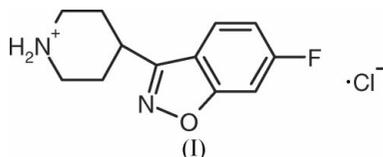
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Comment

Non-conventional intermolecular interactions, as compared with the ubiquitous N—H...O, O—H...O, O—H...N and N—H...N hydrogen bonds, have received considerable attention in recent times because of their importance in molecular recognition for structure-aided drug discovery, supramolecular assembly and the design of advanced materials (Desiraju, 2002). They are generally observed in molecules where such types of hydrogen bonding are not feasible. A plethora of non-conventional interactions, namely C—H...O, X—H...Halogen(Ha), X—H... π , X—Ha... π , π - π and several others, have been recognized and characterized in many different molecular systems (Desiraju & Steiner, 1999). Atomic scale characterization of organic molecules, viable for such types of interactions, is currently a convenient approach to understanding the roles of these interactions in shaping molecular structure, function and assembly. As a part of our continuing interest in non-conventional intermolecular interactions, in this report we discuss the structure and assembly of the title compound, (I), which is an intermediate for the synthesis of the antipsychotic drug risperidone (Kennis & Vandenberg, 1986; Jottier *et al.*, 1992; Umbricht & Kane, 1995).



The bond distances and angles in (I) are in general agreement with those in related crystal structures reported previously (Jottier *et al.*, 1992; Peeters *et al.*, 1993). The maximum out-of-plane deviation from the least-square plane of the fluorobenzisoxazole ring is 0.07 (1) Å for atom C4. Fig. 1 illustrates the structure. The piperidine ring assumes a chair conformation. The Cremer & Pople (1975) puckering parameters (q_2 , q_3 , φ_2 and θ_2) and the total puckering amplitude (Q) are 0.025 (2) Å, -0.572 (2) Å, 8(4)°, 177.5 (2)° and 0.573 (2) Å, respectively. The internal torsion angles of the piperidine ring are indicated in Fig. 1. The asymmetry parameter (Duax *et al.*, 1976) $\Delta C_s(2)$ about the approximate mirror plane passing through N2 and C4 is 0.6°, thus indicating

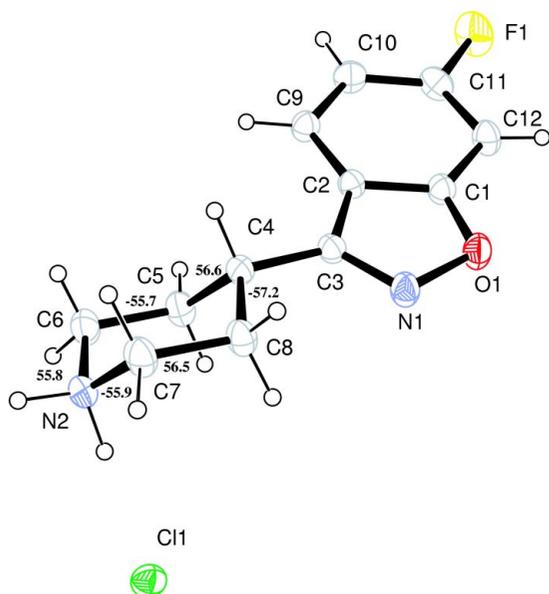


Figure 1
ORTEP-3 (Farrugia, 1997) plot of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level, and H atoms are shown as small circles of arbitrary radii. The values of the torsion angles of the piperidine ring in the chair form are shown.

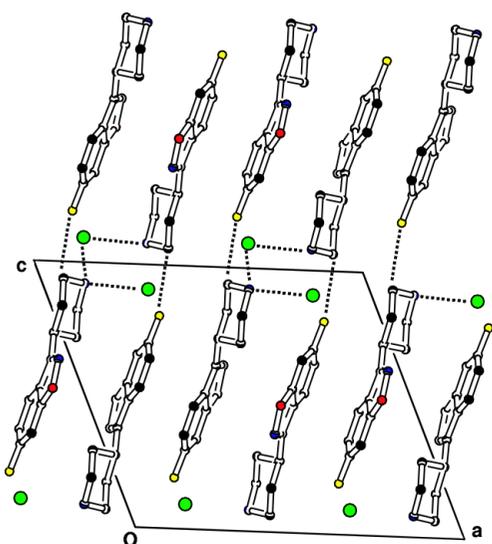


Figure 2
Packing diagram of (I), viewed along the *b* axis, illustrating intermolecular interactions (dashed lines). H atoms have been omitted.

a marginal deviation from the ideal chair conformation. The attached benzisoxazole ring is in an equatorial position. The torsion angle N1–C3–C4–C5 is $-117.4(2)^\circ$.

In the crystal structure, shown in Figs. 2 and 3, the intermolecular association is mainly determined by $X\text{--}H\cdots H_a$ and $C\text{--}H\cdots O$ interactions. The $X\text{--}H\cdots H_a$ interactions play a predominant role in the crystal packing. The ammonium and chloride ions are interconnected by strong $\text{NH}^+\cdots\text{Cl}^-$ interactions. The interactions are formed by N2–H2A \cdots Cl1 and N2–H2B \cdots Cl1 hydrogen bonds (Table 1). The C9–H9 \cdots O1 hydrogen bond links the aromatic ring to the isoxazole ring of a molecule translated along the *b* axis (Fig. 3). Another weak $C\text{--}H\cdots F$ contact (Desiraju, 2002) was also observed in the

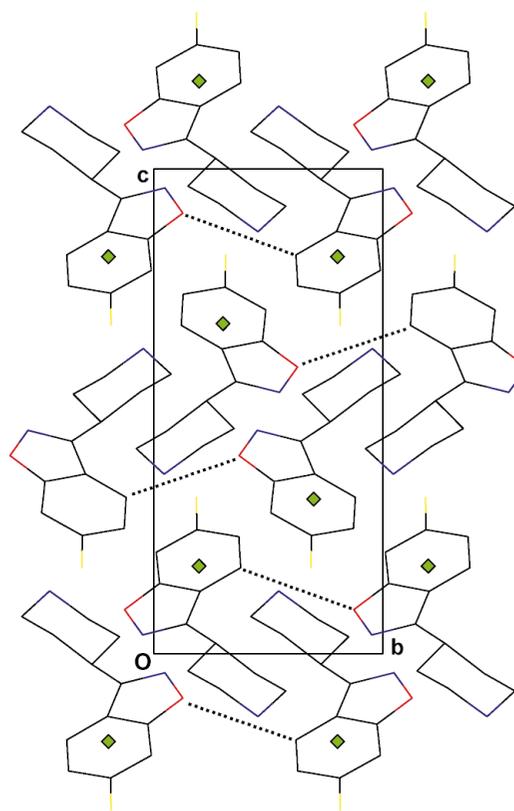


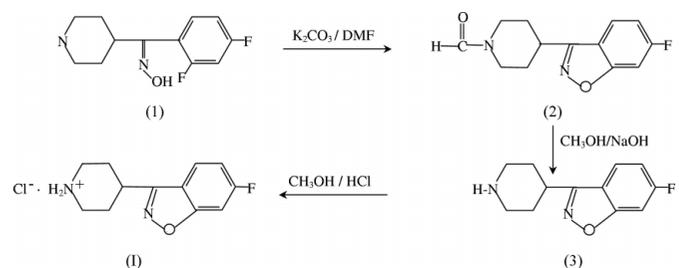
Figure 3
Crystal packing view along the *a* axis, showing $C\text{--}H\cdots O$ interactions (dashed lines). H atoms have been omitted. Color key: C black or gray, N blue, O red, F yellow and Cl green.

crystal structure. The putative C7–H7A \cdots F1 contact links the piperidine ring to the benzisoxazole ring.

In summary, non-conventional interactions, $\text{N}\text{--}\text{H}^+\cdots\text{Cl}^-$, $C\text{--}H\cdots O$ and possibly $C\text{--}H\cdots F$, govern the packing mode in (I), illustrating the propensity of formation of such interactions in molecular structures in which conventional hydrogen bonds are not viable.

Experimental

Oxime (1) was treated with K_2CO_3 (0.57 g, 4.13 mmol) in dimethylformamide (10 ml) at room temperature and stirred for 6 h. The product, (2), was hydrolysed using $\text{CH}_3\text{OH}/\text{NaOH}$ at reflux temperature to obtain (3), which was then converted to the hydrochloride salt (I). The overall yield of (I) was 70% and it chars at 560 K. The compound was recrystallized from ethanol.



Crystal data

C₁₂H₁₄FN₂O⁺·Cl⁻
M_r = 256.70
 Monoclinic, *P*2₁/*c*
a = 13.020 (6) Å
b = 6.608 (3) Å
c = 15.119 (7) Å
 β = 113.109 (7)°
V = 1196.4 (9) Å³
Z = 4

D_x = 1.425 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 998 reflections
 θ = 7–55°
 μ = 0.32 mm⁻¹
T = 293 (2) K
 Plate, colorless
 0.5 × 0.2 × 0.08 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
T_{min} = 0.971, *T_{max}* = 0.984
 13 392 measured reflections

2854 independent reflections
 2554 reflections with *I* > 2σ(*I*)
R_{int} = 0.018
 θ_{\max} = 28.0°
h = -16 → 17
k = -8 → 8
l = -19 → 19

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.116
S = 1.10
 2854 reflections
 210 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.2204P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$

Table 1
 Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2A···Cl1	0.96 (3)	2.15 (3)	3.106 (2)	178 (2)
N2—H2B···Cl1 ⁱ	0.96 (3)	2.17 (2)	3.113 (2)	166 (2)
C7—H7A···F1 ⁱⁱ	1.00 (2)	2.38 (2)	3.119 (2)	130 (2)
C9—H9···O1 ⁱⁱⁱ	0.93 (2)	2.69 (2)	3.475 (2)	142 (2)

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

H atoms were located in a difference electron-density map and all were refined isotropically [*C*—H = 0.88 (2)–1.03 (2) Å].

Data collection: SMART (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: WinGX (Farrugia, 1999) and PARST (Nardelli, 1995).

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