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1-(4-Methylpiperdinemethyl)-2-(4-bromophenyl)-6-methyl-8-trifluoromethylimidazo-[1,2-*a*][1,8]naphthyridinium picrate

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Key indicators

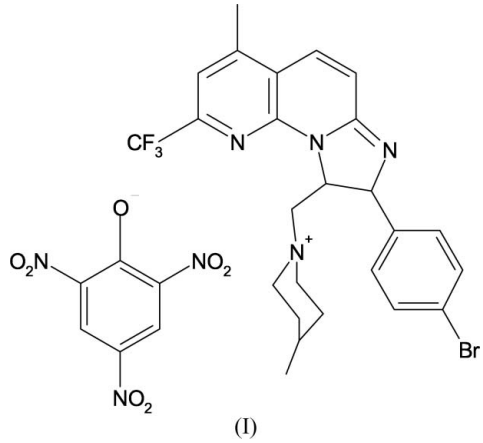
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.081
wR factor = 0.257
Data-to-parameter ratio = 14.9

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

The title molecular complex, $C_{25}H_{25}BrF_3N_4^+\cdot C_6H_2N_3O_7^-$, crystallizes with two pairs of cations and anions in the asymmetric unit. While the orientations of the two cations are nearly parallel to one another, this is not so for the anions. The imidazonaphthyridine moiety is planar and the methylpiperidine group is approximately perpendicular to it and adopts an ideal chair conformation. The planes of the bromophenyl rings deviate from the planes of the imidazonaphthyridine moieties by 30.2 (2) and 22.6 (3)° in the two cations, making a marked difference in the overall conformation of the cations. The N—H···N hydrogen bond forms an intramolecular ring pattern $S(7)$ in both cations. The anions and cations are connected through N—H···O, C—H···O and C—H···F hydrogen bonds.

Comment

Picric acid forms crystalline picrates with various organic molecules, and such picrates are convenient for identification and qualitative analysis of such organic compounds (Takayanagi *et al.*, 1996). The formation of picrates is a common method for the conversion of liquids into stable, tractable solid compounds. Imidazo[1,2-*a*][1,8]napthyridine derivatives were reported to possess potential antibacterial and photophysical activities (Kondo *et al.*, 1990; Vijila *et al.*, 2000). Crystal structures of a large number of picrate salts and picric acid complexes including biological bases have been studied in the past (Smith *et al.*,2004; Goto *et al.*, 2004; Nagata *et al.*,1995). In many cases, the bonding of these electron donor picric acid complexes strongly depends on the nature of the partner. The linkage could involve not only electrostatic attraction but also the formation of molecular complexes (Zaderenko *et al.*, 1997).



(I)

The present molecular complex was prepared to study the possible protonation site in the cation. In addition, our studies

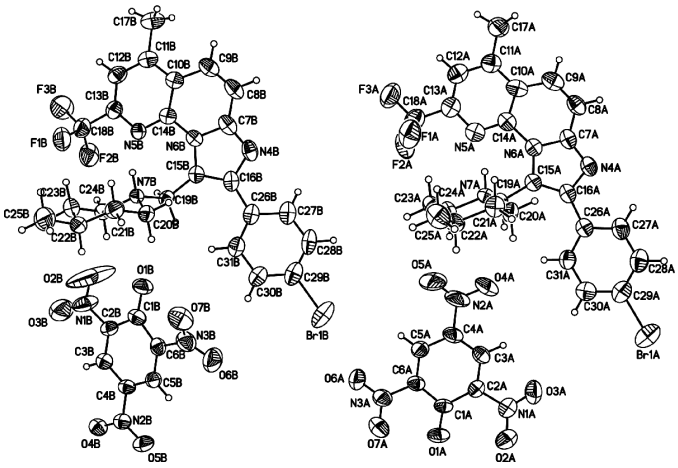


Figure 1
A 50% probability displacement ellipsoid plot of the asymmetric unit of the title complex with the numbering scheme.

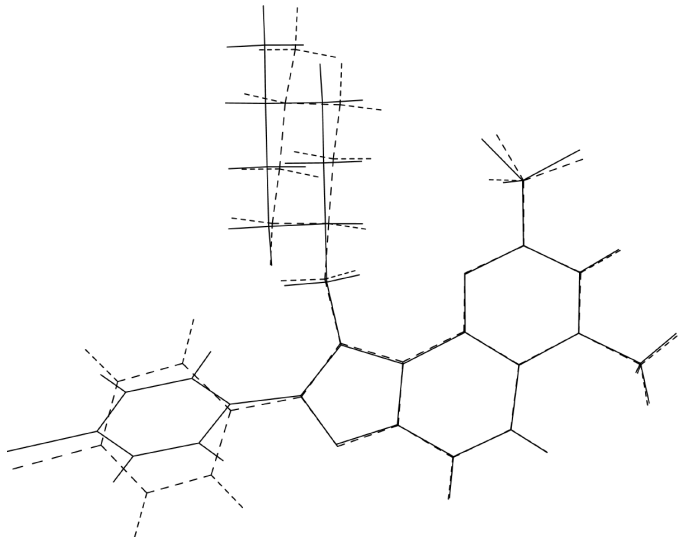


Figure 2
Plot showing the conformational differences between the two cations. The solid lines represent cation *A* and dashed lines are for cation *B*.

focus on the nature and directionality of the specific N—H···O hydrogen bond involving the protonated N atom.

Fig.1 shows a displacement ellipsoid plot of the asymmetric unit of the title complex, (I), with the atom numbering scheme. Selected geometric parameters are given in Table 1. The title molecular complex crystallizes with two pairs of cations and anions in the asymmetric unit. While the orientations of the two cations are nearly parallel to one another, this is not so for the anions. While the dihedral angle between the planes of the naphthyridine moieties is 16.7 (1)°, the angle between the planes of the picrate anions is 35.9 (2)°.

The bond lengths and angles of the picrate anion show characteristic values, with C1—C2 and C1—C6 distances that are longer than regular aromatic values, and C1—O1 distances which show partial double-bond character. These differences are due to the loss of a hydroxy proton at O1, leading to conversion from the neutral to the anionic state. The observed values are comparable to those of many such picrates (Muthamizhchelvan *et al.*, 2005). One of the nitro O atoms, O2*B*, shows high thermal vibration. The twist angles of the three nitro groups from the benzene ring of the picrate ion are 12.6 (5)° [O2—N1—O3], 3.0 (7)° [O4—N2—O5] and 38.3 (7)° [O6—N3—O7] for picrate anion *A*, and 15.0 (9), 37.9 (1) and 34.0 (7)° for anion *B*. An analysis of the tilting nature of the nitro groups in picrate ions shows that the *ortho*-nitro groups, in general, deviate away from the benzene plane, possibly as a result of streric interactions with the phenolic group at C1. However, the *para*-nitro groups lie in the benzene plane. In the present crystal structure, we find that, while picrate ion *A* agrees well with the other structures, in ion *B*, the *para*-nitro group deviates from the plane of the benzene ring. It is found that this deviation facilitates atom O4 in this group taking part in N—H···O hydrogen-bond formation with the cation. Therefore, the tilting of the nitro groups is a consequence of interactions between ions rather than an intramolecular effect.

The C19—N7 bond distances in both the cations are longer than those observed in the related imidazonapthyridine neutral molecules and the values given by Allen *et al.* (1987). Also, the angles around atoms N7 are found to be less than those observed in the related neutral molecules (Sivakumar *et al.*, 1996). These deviations are due to the protonation of atoms N7. The exocyclic angles at C16 are 132.1 (7) and 131.7 (8)°, respectively, in cations *A* and *B*, and are comparable to the reported values of imidazo[1,2-*a*][1,8]napthyridines (Sivakumar *et al.*, 1996). The increase in angle from the ideal value of 120° can be attributed to the steric interaction of the bromophenyl ring with the substituents at C15. The imidazonapthyridine system is almost planar; the dihedral angles between the five-membered ring and the pyridine ring are 1.1 (3) and 2.4 (3) Å, and between the pyridine and methyltrifluoropyridine planes are 1.5 (2) and 3.1 (3)° for cations *A* and *B*, respectively. The planes of the bromophenyl rings deviate from the planes of the imidazonaphthyridine moieties by 30.2 (2) and 22.6 (3)° in cations *A* and *B*, respectively; this makes a marked difference in the overall conformation of the cation, as shown in Fig. 2. The methylpiperidinium group is approximately perpendicular to the imidazonaphthyridine moiety. This is evident from the torsion angles N6—C15—C19—N7 [−77.8 (9)° and −71.3 (9)°] and C16—C15—C19—N7 [104.1 (9)° and 111.7 (9)°] in cations *A* and *B*, respectively. Both the piperidine rings adopt an ideal chair conformation, as expected.

The molecular structure of the imidazonaphthyridine cation has an N—H···N intramolecular hydrogen bond between atoms N7 and N5, forming an intramolecular *S*(7) ring (Bernstein *et al.*, 1995). The positioning and orientation of the two pairs of cations and anions in the asymmetric unit lead to two different intermolecular N—H···O hydrogen bonds between them. The protonated N atom N7*A* forms a strong hydrogen bond with O1*A*, whereas N7*B* forms a weak bond with O4*B*. In addition, the crystal structure is stabilized by C—H···O and C—H···F intra- and intermolecular hydrogen bonds. Interestingly, only the Br1*B*···Br1*B*^{ii} (symmetry code as in Table 2) short contact of 3.679 (1) Å is observed between

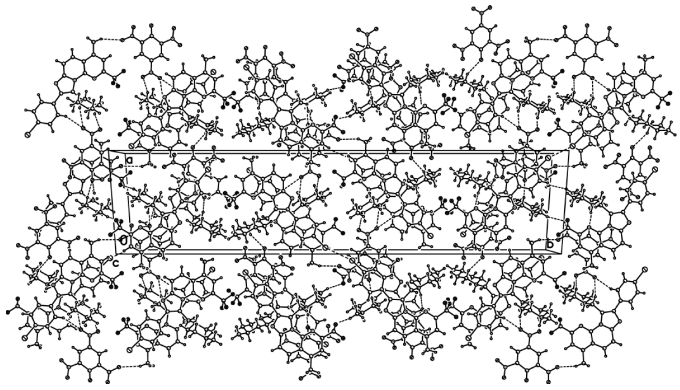


Figure 3
Packing of the structure, viewed down the *c* axis; dashed lines indicate hydrogen bonds.

the centrosymmetrically related cations and the Br atom of cation does not engage in any such interactions. In addition to these, two significant short contacts, O1*A*···N5*A*^{vi} [2.966 (9) Å] and O4*B*···C14*B*^{vi} [2.977 (9) Å; symmetry code: (vi) 1 + *x*, *y*, *z*], are observed in this molecular complex. The expected N—H···O hydrogen bond between the phenolate O atom and the protonated N atom is either weak or missing.

Experimental

Crystals of (I) were prepared from an ethanol solution containing equimolar amounts of picric acid and 1-(4-methylpiperdinemethyl)-2-(4-bromophenyl)-6-methyl-8-trifluromethylimidazo[1,2-*a*][1,8]naphthyridine at room temperature. Yellow prismatic single crystals were obtained by slow evaporation of the ethanol solution.

Crystal data

$C_{25}H_{25}BrF_3N_4^+\cdot C_6H_2N_3O_7^-$
M_r = 746.51
Monoclinic, $P2_1/c$
a = 12.6304 (13) Å
b = 50.875 (7) Å
c = 11.017 (3) Å
β = 112.50 (1)°
V = 6540 (2) Å^3
Z = 8
D_x = 1.516 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 25–45°
μ = 2.38 mm^{-1}
T = 293 (2) K
Prism, yellow
0.4 × 0.3 × 0.28 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.472, T_{max} = 0.514
13 650 measured reflections
13 129 independent reflections
6405 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 75.0°
$h = -5 \rightarrow 15$
$k = -63 \rightarrow 10$
$l = -13 \rightarrow 12$
2 standard reflections
every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.081
$wR(F^2)$ = 0.257
S = 1.04
13 129 reflections
883 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0824P)^2 + 13.6596P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.77 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C1*A*	1.235 (7)	O1*B*—C1*B*	1.230 (7)
C1*A*—C2*A*	1.443 (9)	C1*B*—C6*B*	1.447 (10)
C1*A*—C6*A*	1.453 (9)	C1*B*—C2*B*	1.456 (9)
Br1*A*—C29*A*	1.896 (9)	Br1*B*—C29*B*	1.896 (8)
N4*A*—C7*A*	1.321 (9)	N7*B*—C24*B*	1.495 (7)
N7*A*—C20*A*	1.485 (7)	N7*B*—C20*B*	1.498 (7)
N7*A*—C24*A*	1.488 (7)	N7*B*—C19*B*	1.512 (7)
N7*A*—C19*A*	1.513 (7)		
O1*A*—C1*A*—C2*A*	125.1 (7)	O1*B*—C1*B*—C6*B*	124.8 (7)
O1*A*—C1*A*—C6*A*	123.3 (6)	O1*B*—C1*B*—C2*B*	124.1 (7)
C2*A*—C1*A*—C6*A*	111.5 (5)	C6*B*—C1*B*—C2*B*	111.0 (6)
C20*A*—N7*A*—C24*A*	110.5 (5)	C24*B*—N7*B*—C20*B*	109.7 (5)
C20*A*—N7*A*—C19*A*	111.3 (5)	C24*B*—N7*B*—C19*B*	112.0 (5)
C24*A*—N7*A*—C19*A*	109.6 (4)	C20*B*—N7*B*—C19*B*	112.2 (4)
C24*A*—N7*A*—C20*A*—C21*A*	−56.5 (7)	C24*B*—N7*B*—C20*B*—C21*B*	−56.9 (6)
N7*A*—C20*A*—C21*A*—C22*A*	56.7 (8)	N7*B*—C20*B*—C21*B*—C22*B*	57.2 (7)
C20*A*—C21*A*—C22*A*—C23*A*	−55.4 (8)	C20*B*—C21*B*—C22*B*—C23*B*	−54.0 (8)
C21*A*—C22*A*—C23*A*—C24*A*	55.0 (8)	C21*B*—C22*B*—C23*B*—C24*B*	53.5 (8)
C20*A*—N7*A*—C24*A*—C23*A*	57.1 (7)	C20*B*—N7*B*—C24*B*—C23*B*	57.3 (7)
C22*A*—C23*A*—C24*A*—N7*A*	−57.3 (8)	C22*B*—C23*B*—C24*B*—N7*B*	−56.9 (8)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7*A*—H7*A*···O1*A*^{i}	0.91	1.87	2.730 (6)	156
N7*A*—H7*A*···N5*A*	0.91	2.54	3.083 (8)	119
N7*B*—H7*B*···O4*B*^{i}	0.91	2.18	3.060 (6)	161
N7*B*—H7*B*···N5*B*	0.91	2.51	3.047 (7)	118
C21*A*—H21*A*···O1*A*^{i}	0.97	2.50	3.207 (9)	129
C19*A*—H19*A*···O4*A*	0.97	2.49	3.382 (9)	154
C31*A*—H31*A*···O4*A*	0.93	2.43	3.272 (11)	151
C24*A*—H24*A*···O5*A*	0.97	2.39	3.245 (9)	147
C17*A*—H17*A*···O6*A*^{ii}	0.96	2.51	3.363 (11)	147
C24*B*—H24*C*···O1*B*	0.97	2.36	3.255 (8)	153
C24*B*—H24*C*···O2*B*	0.97	2.58	3.348 (14)	136
C30*B*—H30*B*···O7*B*	0.93	2.62	3.313 (11)	132
C24*A*—H24*B*···F1*A*	0.97	2.63	3.290 (10)	126
C24*B*—H24*D*···F1*B*	0.97	2.70	3.391 (9)	128
C25*A*—H25*A*···F1*A*^{iii}	0.96	2.52	3.283 (9)	136
C28*A*—H28*A*···F1*B*^{iv}	0.93	2.67	3.558 (11)	160
C28*B*—H28*B*···F2*A*^{ii}	0.93	2.77	3.441 (10)	130
C3*B*—H3*B*···F3*B*^{v}	0.93	2.84	3.419 (8)	122

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

All H atoms were positioned geometrically and refined as riding (C—H = 0.93–0.97 Å and N—H = 0.91 Å). For NH, CH and CH_2 groups, U_{iso}(H) values were set equal to 1.2U_{eq}(carrier atom), and for the methyl groups they were set equal to 1.5U_{eq}(carrier atom).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: XCAD4 (Harms & Wocadlo, 1995); 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: *SHELXL97*.

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