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1-Dimethylammoniomethyl-6,8-dimethyl-2-phenyl-1,2-dihydroimidazo[1,2-*a*][1,8]naphthyridine picrate monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.159
Data-to-parameter ratio = 13.5

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

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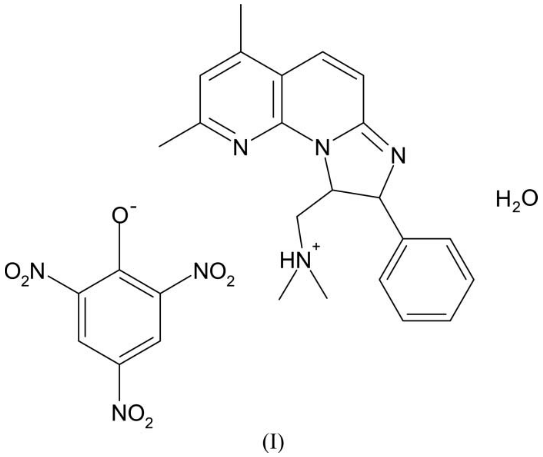
In the title salt, $C_{21}H_{23}N_4^+ \cdot C_6H_2N_3O_7^- \cdot H_2O$, the dimethylammoniomethyl side chain is oriented nearly perpendicular to the imidazonaphthyridine moiety, which is nearly planar. In the crystal structure, intermolecular N—H···O and O—H···O hydrogen bonds link two cations, two anions and two water molecules into clusters, which further interact *via* weak C—H···O hydrogen bonds.

Comment

Picric acid forms crystalline picrates with various organic molecules and such picrates are convenient for the identification and qualitative analysis of the relevant organic compounds (Takayanagi *et al.*, 1996). The formation of picrates is a common method for the conversion of liquids into stable tractable solid compounds and in many cases it yields crystalline solids, which lead to the determination of their molecular structures (Saleh *et al.*, 1997). Imidazo[1,2-*a*]-[1,8]napthyridine derivatives are reported to possess potential antibacterial and photophysical activities (Kondo *et al.*, 1990; Vijila *et al.*, 2000). The crystal structures of a number of imidazonaphthyridine derivatives have been determined in order to understand their structures and conformations (Fun *et al.*, 1996; Sivakumar *et al.*, 1996*a*,*b*). The title imidazonapthyridine picrate complex, (I), was prepared in order to understand the possible protonation site among the different amino positions. In addition, the nature and directionality of the specific N—H···O hydrogen bond involving the protonated N atom is of interest.



(I)

In the picrate anion (Fig. 1), the bond lengths and angles (Table 1) are normal and comparable with those found in the literature (Allen *et al.*, 1987; SethuSankar *et al.*, 2003; Muthamizhchelvan, Saminathan, SethuSankar *et al.*, 2005).

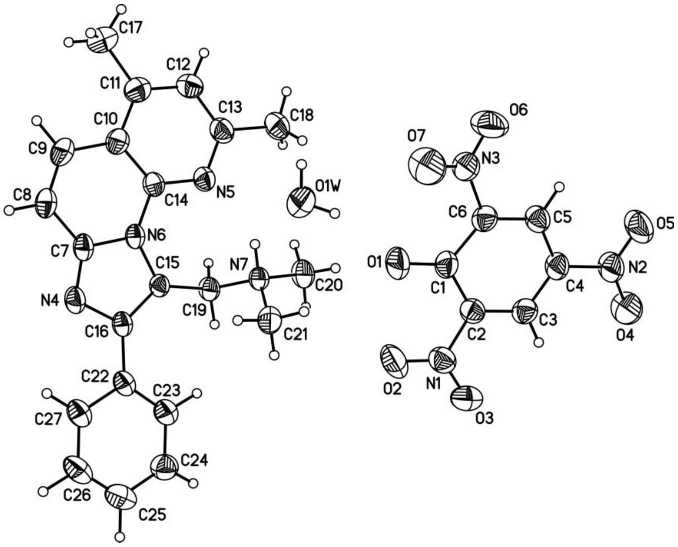


Figure 1
View of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

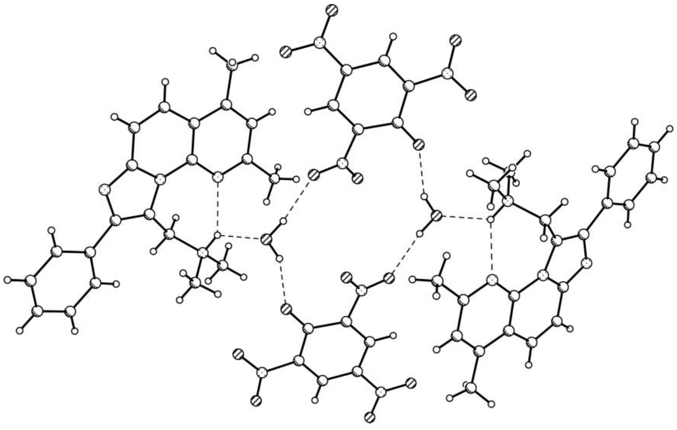


Figure 2
A cluster in (I) formed by intermolecular N—H···O and O—H···O hydrogen bonds (dashed lines).

The twist angles of the three nitro groups attached to the benzene ring at atoms C2, C4 and C6 are 7.74 (2), 2.16 (2) and 25.04 (1)°, respectively. In fact, one *ortho* nitro group (O2—N1—O3) is more coplanar with the benzene ring than that found in other picrates, where both *ortho*-nitro groups have higher twist angles with the benzene ring. This is due to the steric interactions between the neighbouring parallel anions, with a separation distance of 3.366 (3) Å.

In the cation, the C19—N7 bond distance of 1.514 (2) Å is longer than the values reported [1.475 (2), 1.466 (2) and 1.466 (2) Å] for neutral imidazonaphthyridine structures (Sivakumar *et al.*, 1996*b*). The endocyclic angles at C9 [121.1 (2)°] and N6 [121.7 (1)°] are expanded, while at C14 [117.9 (1)°] it is contracted. This effect is probably caused by the fusion of the five-membered ring with the six-membered ring, resulting in angular distortion rather than in bond-length distortion (Allen, 1981). The average C—N—C angle around atom N7 [111.3 (1)°] is slightly less than the reported value of 115.8 (1)° in 1-diethylaminophenyl-2-(4-methoxyphenyl)-6,8-dimethylimidazo[1,2-*a*][1,8]naphthyridine and 113.6 (5)° in 2-(4-bromophenyl-1-diethylaminomethyl-6,8-dimethylimidazo-[1,2-*a*][1,8]naphthyridine (Sivakumar *et al.*, 1996*b*) and is justified by the protonation of this atom, which makes perfect tetrahedral bonding. The imidazonaphthyridine system is almost planar; the dihedral angles formed by the four rings, *viz*. N4/C7/N6/C15/C16, N5/C10–C14, N6/C7–C10/C14 and C22–C27, are in the range 2.85 (6)–4.6 (1)°. The mean plane is found to lie on the crystallographic (210) plane. The torsion angle N6—C15—C19—N7 of 81.6 (2)° describes the orientation of the dimethylaminomethyl side chain as (+)synclinal about C15–C19.

The protonated N7 atom of the cation participates in a bifurcated hydrogen bond (Table 2), *viz*. an intramolecular N—H···N hydrogen bond with atom N5 and an intermolecular N—H···O hydrogen bond with the solvent water molecule. The intramolecular hydrogen bond forms an $S(7)$ ring. The observed intermolecular N7—H7*N*···O1*W* hydrogen bond is weak and peculiar for picrates, where the protonated N atom tries to make strong and more linear N—H···O bonds with the anionic (picrate) molecules (Muthamizhchelvan, Saminathan, Fraanje *et al.*, 2005). The present hydrogen-bonding pattern (Table 2) suggests that two cations, two anions and two solvent water molecules are linked into a cluster (Fig. 2) *via* intermolecular N—H···O and O—H···O hydrogen bonds. The O1*W*—H1*W*···O1 and O1*W*—H2*W*···O6 hydrogen bonds form a cyclic pattern with a graph-set descriptor $R_4^4(16)$ (Bernstein *et al.*, 1995). The crystal packing (Fig. 3) is further stabilized by weak C—H···O hydrogen bonds (Table 2) and van der Waals forces.

Experimental

The title compound was prepared from an ethanol solution containing equimolar amounts of picric acid and 1-dimethylaminomethyl-6,8-dimethyl-2-phenyl-1,2-dihydroimidazo[1,2-*a*][1,8]naphthyridine at room temperature. Yellow prism-shaped single crystals were obtained by slow evaporation of the ethanol solution.

Crystal data

$C_{21}H_{23}N_4^+ \cdot C_6H_2N_3O_7^- \cdot H_2O$
$M_r = 577.56$
Triclinic, $P\overline{1}$
$a = 7.1449$ (8) Å
$b = 12.1932$ (7) Å
$c = 15.790$ (2) Å
$\alpha = 102.435$ (4)°
$\beta = 98.938$ (6)°
$\gamma = 92.123$ (5)°
$V = 1323.5$ (2) Å^3
$Z = 2$
$D_x = 1.449$ Mg m$^{-3$}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15$–50°
$\mu = 0.92$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.50 × 0.40 × 0.35 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.621$, $T_{\max} = 0.725$
6062 measured reflections
5289 independent reflections
4513 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 74.9°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -8 \rightarrow 19$
2 standard reflections every 100 reflections intensity decay: 1%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.159$
$S = 1.10$
5289 reflections
392 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0781P)^2 + 0.5163P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0061 (7)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.233 (2)	N2—C4	1.438 (2)
O2—N1	1.209 (2)	N3—C6	1.456 (3)
O3—N1	1.223 (2)	C1—C2	1.453 (3)
O4—N2	1.221 (3)	C1—C6	1.457 (3)
O5—N2	1.223 (2)	N7—C21	1.486 (3)
O6—N3	1.211 (2)	N7—C20	1.488 (2)
O7—N3	1.205 (2)	N7—C19	1.512 (2)
N1—C2	1.456 (3)		
C16—C15—C19—N7	−109.0 (2)	C15—C16—C22—C23	−5.2 (3)
N6—C15—C19—N7	81.5 (2)	N4—C16—C22—C27	−3.9 (2)
N4—C16—C22—C23	175.25 (17)	C15—C16—C22—C27	175.66 (18)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7*N*···O1*W*	0.95 (3)	2.20 (3)	2.919 (3)	132 (2)
N7—H7*N*···N5	0.95 (3)	2.21 (3)	2.899 (2)	129 (2)
O1*W*—H1*W*···O1	0.87 (4)	1.96 (4)	2.768 (3)	154 (3)
O1*W*—H2*W*···O6^{i}	0.91 (5)	2.06 (5)	2.952 (3)	167 (4)
C25—H25···O5^{ii}	0.93	2.55	3.474 (3)	173
C26—H26···O6^{ii}	0.93	2.54	3.440 (3)	163
C20—H20*C*···O4^{iii}	0.96	2.54	3.416 (3)	152
C21—H21*A*···O1	0.96	2.59	3.489 (3)	156

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x-1, y, z-1$; (iii) $-x+1, -y+2, -z+1$.

All H atoms were located in a difference Fourier map. The C-bound H atoms were refined as riding on their parent atoms, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2–1.5U_{eq}(C), while the N7- and O1*W*-bound H atoms were refined isotropically.

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*; molecular graphics: *ORTEP3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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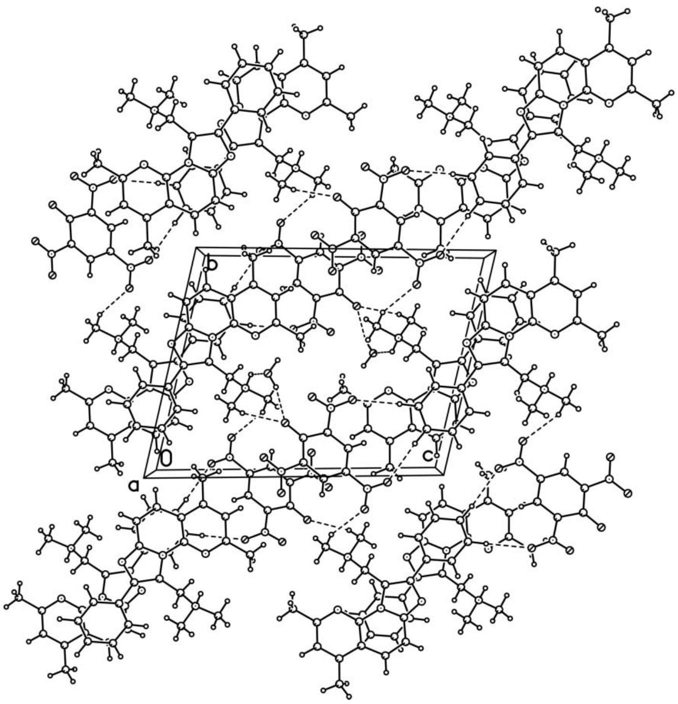

Figure 3
The crystal packing of (I), viewed approximately down the *a* axis. The intermolecular hydrogen bonds are shown as dashed lines.

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