Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

3-Carboxy-2-(2,6-dimethylphenylamino)-pyridinium trifluoroacetate

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Received 20 December 2006
Accepted 18 January 2007

Key indicators

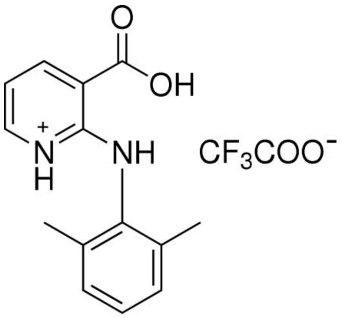
Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.002 Å
Disorder in solvent or counterion
R factor = 0.046
wR factor = 0.132
Data-to-parameter ratio = 15.2

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

In the title compound, $C_{14}H_{15}N_2O_2^+\cdot C_2F_3O_2^-$, the two aromatic rings of the cation are almost perpendicular to each other. The cations and anions are connected through hydrogen bonds into a one-dimensional network. There is an intramolecular N—H···O hydrogen bond between the secondary amine group and the carboxylic acid group.

Comment

During our attempt to synthesize 2-(2,6-dimethylphenylamino)nicotinic acid (Ting *et al.*, 1990), we obtained the title organic salt, (I), by accidentally adding trifluoroacetic acid to the desired product during the workup procedure.



(I)

The asymmetric unit of (I) consists of one trifluoroacetate anion and one 3-carboxy-2-(2,6-dimethylphenylamino)pyridinium cation (Fig. 1). The two aromatic rings of the cation are twisted relative to each other, with a dihedral angle of 75.68 (5)°. A similar conformation was adopted by 2-(2-isopropylanilino)pyridine-3-carboxylic acid in its crystal structure (Long *et al.*, 2006).

The carboxylic acid group of the cation is in a *syn* conformation. It is intramolecularly hydrogen bonded *via* its carbonyl O atom to the secondary amino group bridging the two aromatic rings, generating an $S(6)$ motif (Etter, 1990). The anion accepts two hydrogen bonds from two cations, linking to them *via* the pyridinium N—H group and the carboxylic acid group (Table 1). These hydrogen bonds assemble the ions into a one-dimensional network parallel to the [110] direction (Fig. 2).

Experimental

2-Chloronicotinic acid (3.5 g, 20 mmol), 2,6-dimethylaniline (2.5 g, 20 mmol), p-toluenesulfonic acid (0.5 g, 3 mmol) and triethylamine (3 ml) were added to a mixture of water (20 ml) and dimethylformamide (8 ml) in a round-bottomed flask. The resulting mixture

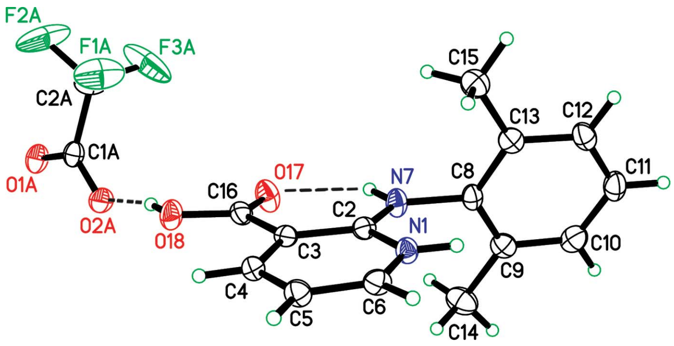


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms). The minor disorder component of the trifluoromethyl group is not shown.

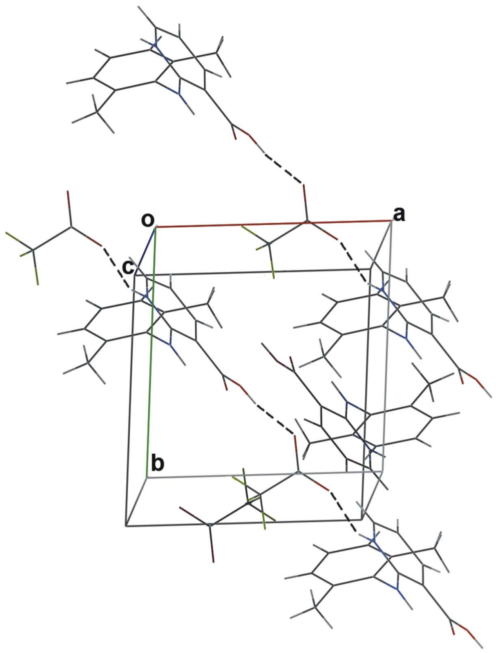


Figure 2
A packing diagram for (I), showing the hydrogen-bonded chains. Hydrogen bonds are shown as dashed lines. The minor disorder component of the trifluoromethyl group is not shown.

was refluxed overnight. After the reaction, the solvents were removed under high vacuum, and then water (25 ml) and ethyl acetate (25 ml) were added to the residue. The crude product was recovered from the organic layer (2.4 g, 45%). During the process of purification, trifluoroacetic acid was accidentally added to the crude product. The title compound, (I), was recovered as colourless blocks from a solution in methanol.

Crystal data

$C_{14}H_{15}N_2O_2^+ \cdot C_2F_3O_2^-$
$M_r = 356.30$
Triclinic, $P\overline{1}$
$a = 8.1899\ (2)$ Å
$b = 8.7140\ (2)$ Å
$c = 11.4579\ (3)$ Å
$\alpha = 91.0513\ (11)^\circ$
$\beta = 102.6354\ (11)^\circ$
$\gamma = 92.0117\ (12)^\circ$
$V = 797.13\ (3)$ Å^3
$Z = 2$
$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 90.0\ (2)$ K
Block, colourless
$0.32 \times 0.13 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.960$, $T_{\max} = 0.987$
7239 measured reflections
3662 independent reflections
2628 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.132$
$S = 1.04$
3662 reflections
241 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.2811P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.016 (5)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1$A^{\rm i}$	0.88	1.91	2.6623 (17)	143
N7—H7$\cdots$O17	0.88	2.00	2.6741 (17)	132
O18—H18$\cdots$O2A	0.84	1.72	2.5447 (16)	167

Symmetry code: (i) $x - 1, y - 1, z$.

The CF_3 group of the trifluoromethanesulfonate anion is disordered over two orientations, with refined occupancy factors of 0.909 (5) and 0.091 (5). Since the occupancy factor of the minor component is small, it was given isotropic displacement parameters and its geometry was restrained to conform to that of the major component, so that both are essentially tetrahedral. H atoms were found in a difference Fourier map, but for calculations they were placed in idealized positions, with C—H distances of 0.98 (CH_3) and 0.95 Å ($C_{\rm ar}$), N—H distances of 0.88 Å and O—H distances of 0.84 Å. $U_{\rm iso}$(H) values were set to either $1.5U_{\rm eq}$(parent) for methyl H and O-bound H, or $1.2U_{\rm eq}$(C,N) for the remaining atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* and local procedures.

TL and SL thank the NSF for financial support (grant No. DMR-0449633).

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