2-Aminopyrimidin-1-ium trichloroacetate

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The 2-aminopyrimidin-1-ium trichloroacetate ion-pairs in the title compound, $C_4H_6N_3^+ \cdot C_2Cl_3O_2^-$, are held together by two N—H$\cdots$O hydrogen bonds [$N_{amino}\cdots O$ = 2.733 (5); $N_{pyrimidinium}\cdots O$ = 2.783 (6) Å], and adjacent ion-pairs are linked into a linear helical chain by a third and substantially weaker N—H$\cdots$O hydrogen bond [$N\cdots O$ = 3.026 (3) Å]. The calculated structure of the ion-pair geometry, optimized at the *PM*3 level, shows good agreement with the experimental results.

Comment

A number of carboxylic acids have been crystallographically documented as secondary-ammonium carboxylates; these compounds generally adopt dimeric hydrogen-bonded motifs (Ng *et al.*, 2001). In the title 2-aminopyrimidin-1-ium carboxylate, the amino group forms a hydrogen bond with an O atom of the carboxylate group, whose second O atom is involved in hydrogen bonding with the protonated N atom of the aromatic cation (Fig. 1). The ion-pairs are linked by a third, substantially weaker, hydrogen bond to furnish a helical chain that runs parallel to the *b* axis of the monoclinic cell (Fig. 2).
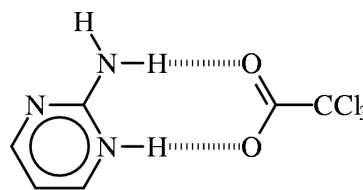
(I)

The calculated structure of the ion-pair that has been optimized at the *PM*3 level (Table 1) shows good agreement with the solid-state structure in the hydrogen-bonding interaction. However, the calculated structure has a delocalized carboxylate —COO$^-$ group, whereas the geometry of this group in the experimental structure is indicative of at least partial localization of single and double carbon–oxygen bonds.

Experimental

The organic salt was the crystalline compound that resulted from the reaction of europium perchlorate (0.45 g, 1 mmol), 2-amino-pyrimidine (0.20 g, 2 mmol) and trichloroacetic acid (0.33 g, 2 mmol). 2-Aminopyrimidine dissolved in a small volume of ethanol was added to europium perchlorate dissolved in water to afford a precipitate. Trichloroacetic acid, dissolved in water, was then added to dissolve the precipitate; the clear solution was filtered and then set aside. Colorless crystals of the title compound separated from the solution after several days.
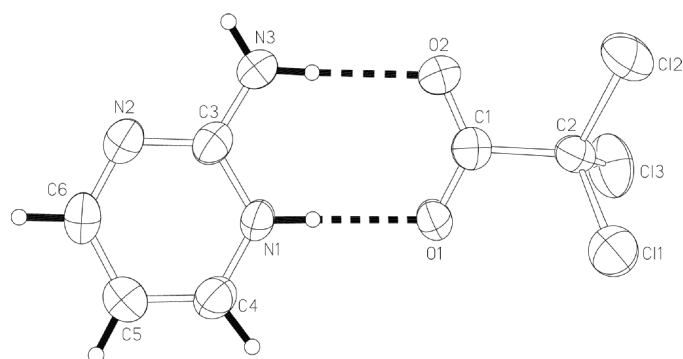
Figure 1
*ORTEP*II (Johnson, 1976) plot of the hydrogen-bonded ion-pair. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.
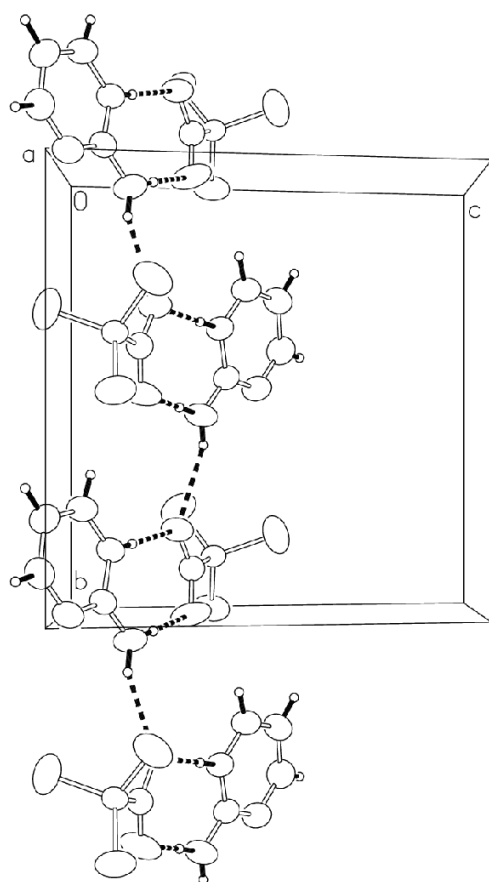

Figure 2
*ORTEP*II (Johnson, 1976) plot, showing the ion-pairs linked by a weak N···O hydrogen bond [N3···O1^i = 3.026 (6) Å; N3—H···O^i = 137 (5)°; symmetry code (i): $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$] into a helical chain along the *b* axis.

Crystal data

$C_4H_6N_3^+ \cdot C_2Cl_3O_2^-$
$M_r = 258.49$
Monoclinic, $P2_1/c$
$a = 8.468$ (2) Å
$b = 11.297$ (2) Å
$c = 10.957$ (2) Å
$\beta = 102.314$ (3)°
$V = 1024.1$ (3) Å^3
$Z = 4$

$D_x = 1.677$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1504
reflections
$\theta = 2.5$–24.8°
$\mu = 0.87$ mm^{-1}
$T = 298$ (2) K
Block, colorless
$0.40 \times 0.30 \times 0.10$ mm

Data collection

Siemens CCD area-detector
diffractometer
ω scans
Absorption correction: none
5155 measured reflections
1748 independent reflections

1081 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 24.8°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 12$
$l = -10 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.181$
$S = 1.04$
1748 reflections
139 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0924P)^2 + 0.867P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 1
Comparison of experimental and geometry-optimized bond dimensions (Å,°).

	X-ray structure	Geometry-optimized structure
Cl1—C2	1.772 (5)	1.757
Cl2—C2	1.753 (5)	1.754
Cl3—C2	1.760 (5)	1.760
O1—C1	1.250 (6)	1.263
O2—C1	1.227 (6)	1.253
N1—C3	1.362 (6)	1.404
N1—C4	1.344 (6)	1.382
N2—C3	1.338 (6)	1.402
N2—C6	1.321 (7)	1.328
N3—C3	1.315 (7)	1.351
C1—C2	1.563 (7)	1.531
C4—C5	1.360 (7)	1.374
C5—C6	1.387 (8)	1.418
N1···O1	2.733 (5)	2.704
N3···O2	2.783 (6)	2.721
C4—N1—C3	120.9 (4)	118.5
C6—N2—C3	116.7 (4)	119.0
O1—C1—O2	128.8 (5)	121.1
O1—C1—C2	114.7 (4)	118.6
O2—C1—C2	116.4 (5)	120.3
C1—C2—Cl1	111.1 (3)	111.0
C1—C2—Cl2	112.8 (3)	113.5
C1—C2—Cl3	108.2 (3)	109.4
Cl1—C2—Cl2	106.6 (3)	107.8
Cl1—C2—Cl3	108.0 (3)	108.1
Cl2—C2—Cl3	110.1 (3)	107.9
N1—C3—N2	121.5 (5)	121.1
N1—C3—N3	118.5 (5)	120.2
N2—C3—N3	119.9 (5)	118.8
N1—C4—C5	119.3 (5)	120.7
C4—C5—C6	116.8 (5)	119.1
N2—C6—C5	124.6 (5)	121.7
N1—H···O1	177 (5)	180
N2—H···O2	166 (5)	168

The nitrogen-bound H-atoms were located and refined, subject to N—H = 0.85±0.01 Å; the aromatic H atoms were positioned geometrically and were allowed to ride on their parent C-atoms, with $U(H) = 1.2U_{eq}(C)$. A residual peak of 1 e Å^{-3} was found at 1.1 Å from the Cl3 atom.

For the geometry-optimization calculations, the initial structure was taken from the X-ray results. It was optimized in its lowest energy state (singlet spin state), using the semi-empirical quantum chemical *PM*3 Hamiltonian in *HYPERCHEM* (Hypercube, Inc., 2001). The unrestricted Hartree–Fock method was employed in the optimization.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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