organic compounds

Coulombic interactions, hydrogen bonding and supramolecular chirality in pyridinium trifluoromethanesulfonate

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The title compound, $C_5H_6N^+ \cdot CF_3SO_3^-$, was serendipitously crystallized in the chiral space group $P4_32_12$. The component entities associate into hydrogen-bonded helical chains, which propagate along the a and b axes of the crystal, with an alternating disposition of the cations and anions along the chain. N—H···O charge-assisted hydrogen bonds, from each pyridinium cation to two adjacent trifluoromethanesulfonate anions and from every anion to two different cations, direct the formation of the supramolecular chiral arrays. The crystal packing exhibits nonconventional C—H···O and C—H···F hydrogen bonds between the components. The observed structure demonstrates induction of supramolecular chirality by a combination of Coulombic attractions and intermolecular hydrogen bonds.

Comment

Pyridinium trifluoromethanesulfonate, (I), is a common commercially available reagent (Aldrich) used in diverse chemical syntheses, in particular as a convenient source for the highly reactive trifluoromethanesulfonate anion. However, the crystal structure of this compound alone has never been reported and the simultaneous incorporation of its two components into crystals of other compounds has been rarely observed (Salmon *et al.*, 2006, 2007; Cambridge Structural Database, Version 5.30, Allen, 2002). Crystals of pure pyridinium trifluoromethanesulfonate were obtained serendipitously. The uniquely interesting features of the resulting structure provided, however, an adequate justification of its more detailed analysis, which relates to our recent efforts on the supramolecular synthesis of chiral architectures from achiral building blocks using hydrogen and halogen bonds (Muniappan *et al.*, 2008; Lipstman *et al.*, 2008; George & Goldberg, 2006; George *et al.*, 2006; Vinodu & Goldberg, 2005). Induction of supramolecular chirality in crystals of achiral salts as well as neutral compounds has received considerable attention in recent years owing to its potential significance for optical resolution and asymmetric synthesis (*e.g.* Tanaka *et al.*, 2006; Perez-Garcia & Amabilino, 2007).
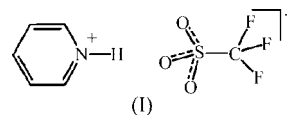
An *ORTEPIII* (Burnett & Johnson, 1996) representation of (I) is shown in Fig. 1. This simple structure is of particular interest because of the variety of intermolecular interactions that operate in it and because it affords the possibility to evaluate their relative contributions to the supramolecular organization. It is evident that Coulombic forces and N—H···O hydrogen bonds play a major role to this end. Firstly, as in simple *AB*-type inorganic salts (*e.g.* halites and sphalerites), optimization of the electrostatic attractions requires an alternating close-packed arrangement of ions bearing opposite charges. Thus, several trifluoromethanesulfonate anions are positioned in the immediate environment of the pyridinium cations, and *vice versa* (Fig. 2). Secondly, the component species in (I) are prone to charge-assisted hydrogen bonding. The cationic species is a rather strong H-atom donor from the acidic NH^+ site. In turn, the O atoms of the negatively charged trifluoromethanesulfonate anion are excellent H-atom acceptors in hydrogen bonding. Excess of the latter leads to the formation of bifurcated hydrogen bonds, where the pyridinium cation interacts simultaneously with the different O-atom sites of two trifluoromethanesulfonate anions (Fig. 2 and Table 1). Concurrently, every trifluoromethanesulfonate anion is thus involved in hydrogen bonding to two neighboring pyridinium ions, leading to the formation of one-dimensional hydrogen-bonded supramolecular arrays, which propagate in the crystal along the a and b axes of the unit cell (Fig. 3). Optimization of the hydrogen bonding (with each ion being involved in two such bonds), along with the need for charge neutrality (see above), imparts 2_1 helicity to the hydrogen-bonded arrays.

The peripheries of the hydrogen-bonded helices described above (see Fig. 3) are lined by the C—H bonds of the aromatic component and by the CF_3 residues of the trifluoromethanesulfonate anions. Thus, atom O4 of the latter, which is not
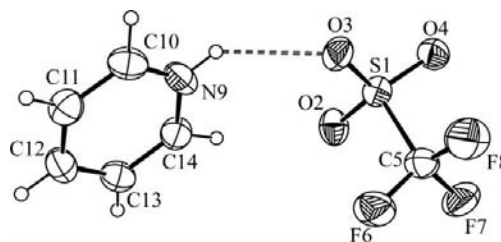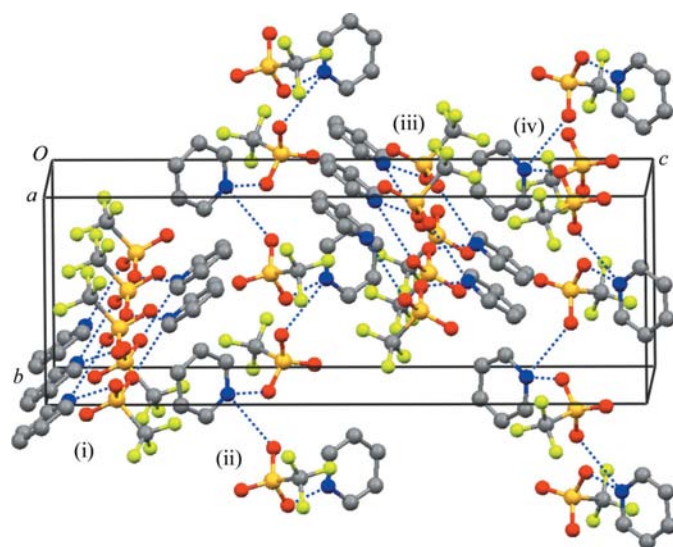

Figure 1
The molecular structure of (I), showing the atom-labeling scheme. The atomic ellipsoids represent displacement parameters at the 50% probability level. One hydrogen bond between the component species of the asymmetric unit is indicated by a double dashed line.

involved in the N—H···O hydrogen bonding, is also turned outward. Correspondingly, side packing of the helical arrays leads to secondary C—H···O and C—H···F interactions in the interface (Table 1). These nonconventional hydrogen bonds are considered to be attractive, the CH groups being electron deficient while the highly electronegative O and F sites are negatively charged (Desiraju & Steiner, 1999). All the corresponding contact distances (Table 1) are either equal to or slightly longer than the respective sums of the van der Waals radii (Bondi, 1964), reflecting the fact that they are very
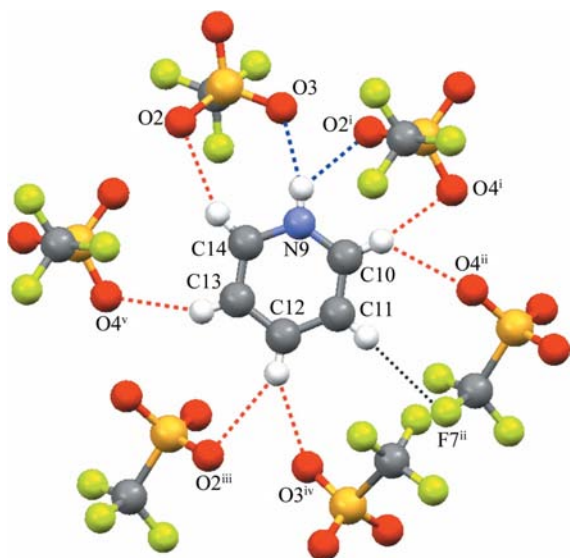
Figure 2
The interactions of a given pyridinium ion with the surrounding species (Table 1) *via* N—H···O hydrogen bonds and C—H···O and C—H···F interactions (all indicated by dashed lines). [Symmetry codes: (i) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + \frac{5}{4}$; (ii) $y + \frac{3}{2}$, $-x + \frac{3}{2}$, $z + \frac{1}{4}$; (iii) $y + \frac{1}{2}$, $-x + \frac{3}{2}$, $z + \frac{1}{4}$; (iv) $-y + 1$, $-x + 2$, $-z + \frac{3}{2}$; (v) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + \frac{5}{4}$.]

Figure 3
The crystal packing of (I), showing the hydrogen-bonded helical chains formed in this structure, with an alternating arrangement of the pyridinium and trifluoromethanesulfonate ions. Chains (i) and (iii) extend along the 2_1^a screw, and chains (ii) and (iv) along the 2_1^b screw axis. The N—H···O hydrogen bonds (Table 1) are indicated by dashed lines. All H atoms have been omitted.

weak interactions. The shortest intermolecular F···F interaction distances observed in (I) are similar to twice the van der Waals radius of the F atom (1.40–1.47 Å; Bondi, 1964) and may represent very weak interactions (Chopra *et al.*, 2006; Tsuzuki *et al.*, 2003).

In summary, this study characterizes for the first time the unique crystal structure of pure pyridinium trifluoromethanesulfonate and the supramolecular chirality it exhibits. The latter is induced by a combination of nondirectional Coulombic interactions and directional hydrogen bonding between the ionic constituents, leading to the formation of supramolecular arrays of unidirectional helical symmetry. Common van der Waals-type cohesive forces (including nonconventional hydrogen bonds, which are the 'bread-and-butter' of the vast majority of organic crystals) operate in the interfaces between neighboring chains. The chirality of the entire crystalline architecture seems to have been induced by that of the individual chain arrays (Tanaka *et al.*, 2006; Muniappan *et al.*, 2008). The observed structure reflects the hierarchical significance of the Coulombic, hydrogen-bonding and van der Waals-type interactions (in that order) with regard to directing the crystallization modes of organic compounds.

Experimental

Pyridinium trifluoromethanesulfonate was obtained commercially (Aldrich). Colorless crystalline plates were obtained by chance when a solution of this compound in a 1:1 dichloromethane–*n*-hexane mixture was left in the open air. The crystals were characterized by large mosaicity (with a mean value of 1.47°) and weak scattering, which dictated collection of the diffraction frames at 0.3° intervals and limited significant diffraction to $2\theta_{max} = 52°$.

Crystal data

$C_5H_6N^+ \cdot CF_3SO_3^-$	$Z = 8$
$M_r = 229.18$	Mo $K\alpha$ radiation
Tetragonal, $P4_32_12$	$\mu = 0.40$ mm^{-1}
$a = 8.5265$ (8) Å	$T = 110$ K
$c = 24.388$ (2) Å	$0.45 \times 0.20 \times 0.10$ mm
$V = 1773.0$ (3) Å^3	

Data collection

Nonius KappaCCD diffractometer	1222 reflections with $I > 2\sigma(I)$
11922 measured reflections	$R_{int} = 0.057$
1752 independent reflections	

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

D—H···A	D—H	H···A	D···A	D—H···A
N9—H9···O3	0.83 (4)	2.24 (5)	2.921 (5)	140 (4)
N9—H9···O2^i	0.83 (4)	2.29 (4)	2.911 (5)	132 (4)
C10—H10···O4^i	0.94 (4)	2.46 (4)	3.330 (5)	153 (3)
C10—H10···O4^{ii}	0.94 (4)	2.61 (4)	3.199 (5)	121 (3)
C11—H11···F7^{ii}	0.88 (4)	2.69 (4)	3.528 (5)	159 (4)
C12—H12···O2^{iii}	0.89 (4)	2.61 (5)	3.389 (5)	147 (4)
C12—H12···O3^{iv}	0.89 (4)	2.59 (4)	3.345 (5)	142 (4)
C13—H13···O4^v	0.88 (4)	2.60 (4)	3.315 (5)	138 (3)
C14—H14···O2	0.95 (4)	2.40 (4)	3.292 (5)	156 (4)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{5}{4}$; (ii) $y + \frac{3}{2}, -x + \frac{3}{2}, z + \frac{1}{4}$; (iii) $y + \frac{1}{2}, -x + \frac{3}{2}, z + \frac{1}{4}$; (iv) $-y + 1, -x + 2, -z + \frac{3}{2}$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{5}{4}$.

Refinement

The atomic coordinates of the H atoms, initially placed in calculated positions, were refined freely, while $U_{iso}(H)$ values were fixed at $1.2U_{eq}(C,N)$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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