crystal was cooled to 12 K with a cooling rate of 1 K min^{-1}. During the cooling procedure, several reflections were monitored by φ scan to monitor the crystal quality. The alignment of the crystal was controlled by the *C*8 routine (King & Finger, 1979), based on centring of one reflection in eight equivalent positions. During the cooling of the crystal from room temperature to 12 K, no phase transition was observed.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *Xtal*3.2 (Hall, Flack & Stewart, 1992). Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *ORTEP*II (Johnson, 1971) and *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1034). Services for accessing these data are described at the back of the journal.

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Pyridinium Trifluoroacetate: Spoked Columns of Hydrogen-Bonded Cyclic Dimers

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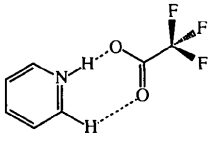
Abstract

The crystal structure of $C_5H_6N^+.C_2F_3O_2^-$ consists of three unique ion pairs. Each unique ion pair packs along a threefold screw axis to generate a distinct spoked column. The three distinct spoked columns are pseudosymmetrically related through a threefold screw axis. Each column comprises an ionic core and non-polar spokes. Columns pack in a manner that maximizes the non-polar interactions between them.

Comment

Evaporation of water from a mixture of pyridine and trifluoroacetic acid results in the crystallization of $C_5H_6N^+.C_2F_3O_2^-$, (I), as clear colourless block-shaped crystals (m.p. = 355 K). Structural characterization of the title compound reveals three rectangular-shaped ion pairs of $C_5H_6N^+.C_2F_3O_2^-$ (identified as N1, N2, N3) within the asymmetric unit cell (Fig. 1). Proton transfer is confirmed by location of the acidic H atoms on the ΔF map and by the increase in the C—N—C bond angle from 116° in the free base to 122.2 (3)° in the title compound.



(I)

Each ion pair contains two hydrogen-bonding interactions: one between the pyridyl N atom and the hydroxyl O atom of the acid (N—H···O); the second between the *ortho*-C atom of pyridinium and the carbonyl O atom of the acid (C—H···O). The graph set that describes this motif of hydrogen bonds is $R_2^2(7)$ (Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995). The consequence of a ring motif of hydrogen bonds is that the dihedral angle between the plane of the pyridine ring and the plane defined by the carboxylate group is small (*i.e.* N1 = 19.5, N2 = 31.5 and N3 = 21.5°).

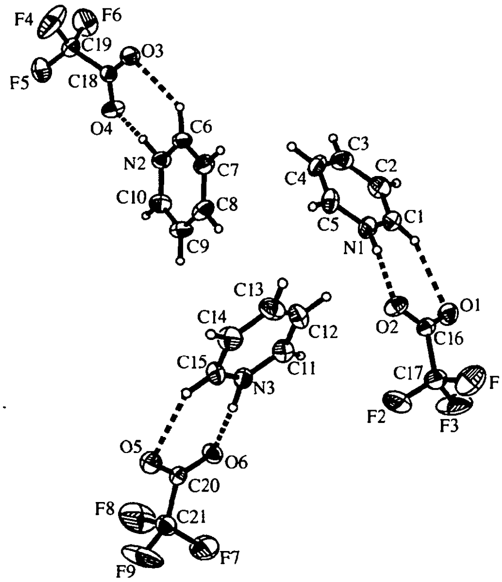


Fig. 1. The structure of pyridinium trifluoroacetate viewed down the z axis showing 50% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines indicate hydrogen bonds. The $R_2^2(7)$ motif of hydrogen bonds in the title compound defines a ring of seven atoms containing two hydrogen-bond donors and two hydrogen-bond acceptors. Each ion pair packs along a threefold screw axis to generate a distinct spoked column.

Each unique ion pair packs along a threefold screw axis to generate a distinct spoked column (Fig. 2). At first glance, the spoked columns generated by each distinct ion pair appear to be symmetry related through either a threefold screw or rotation axis. Threefold symmetry is violated between the spoked columns of N1, N2 and N3, however, by the relative orientation of the pyridinium ring in each distinct ion pair to the *c* axis. The absence of symmetry between spoked columns is illustrated in Fig. 3 (see also Fig. 1). Examination of individual ion pairs from each column relative to the *c* axis reveals that the N2 and N3 ion pairs are approximately related by threefold symmetry. The N1 ion pair, however, deviates from this threefold symmetry due to its rotation (180°) about the axis defined by C1 and C4 of the pyridinium ring. An interesting

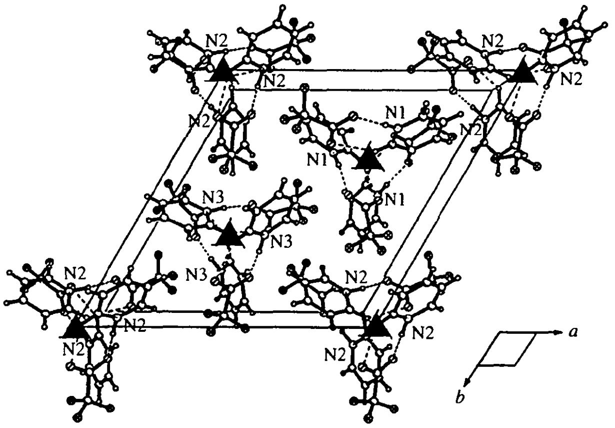


Fig. 2. View down the threefold screw axis illustrating the packing between each unique column (N1, N2, N3). Columns of symmetry related ion pairs (screw triads) are related to each other through a pseudo-threefold screw axis.

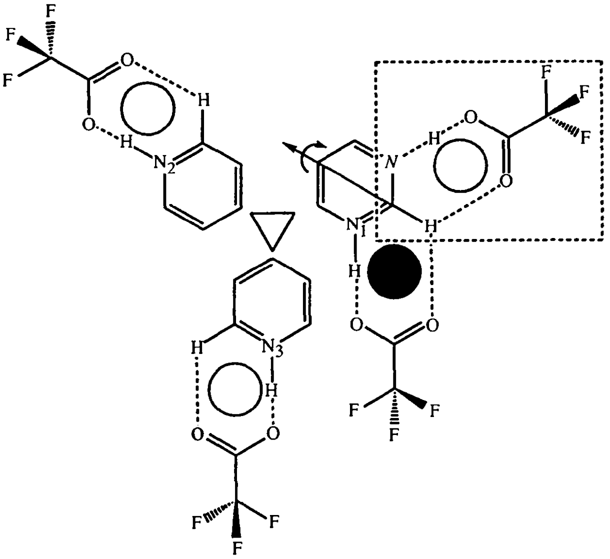


Fig. 3. Schematic representation of the relationship between the three distinct ion pairs. The threefold symmetry is broken by the N1 ion pair, which is rotated 180° about the axis defined by C1 and C4 of the pyridinium ring. Shown in the dashed line box is the orientation that the N1 ion pair would need to adapt for threefold symmetry to be present between the spoked columns. All three ion pairs have concave (empty circle) and convex (filled circle) surfaces due to dihedral angles greater than 0°. The concave surface of the N1 ion pair faces in the opposite direction to that of the N2 and N3 ion pairs.

consequence of this rotation is that the concavity of the N1 ion pair (due to a dihedral angle of greater than 0°) faces in the opposite direction ($-c$) to that of the N2 and N3 ion pairs ($+c$). Nevertheless, the manner in which the ion pairs stack in their individual columns results in three unique spoked columns, which are pseudo-symmetrically related through a threefold screw axis.

The core of each column is ionic, comprising of pyridinium cations and carboxylate anions; the spokes of each column are non-polar, and consist of alternating stacks of trifluoromethyl and aromatic groups. Close contacts between columns occur between the *meta* C—H's of pyridinium on one column and the carbonyl O atoms of trifluoroacetate on an adjacent column [*e.g.* C4—H4···O4 = 3.239 (5) Å]. The predominant interaction between columns, however, is multiple non-polar interactions between the trifluoromethyl groups and the pyridinium rings. No solvent was detected within the crystal lattice and the value for C_k is 69.7%, within the range expected for organic crystals (67–72%). We calculated the packing fraction (C_k) with the program *PLATON* (Spek, 1992). $C_k = V_m/V_c$, where V_m is the volume of the molecules in the unit cell, V_c the total volume of the unit cell. C_k is traditionally calculated using tables of average volume increments.

A search of the Cambridge Structural Database (1994) yields three structures containing trifluoroacetic acid and derivatives of pyridine, $[HNC_5H_{5-n}R_n]^+$, where R represents *para* substituents $(CH_3)_2N$–, CH_3– or NC– on the pyridinium ring (Dega-Szafran *et al.*, 1992). The crystalline solids of these three compounds all contain an $R^2_2(7)$ motif of hydrogen bonds between the acid and base. Proton transfer is observed in all four structures. The length of the N—H···O bond [2.724 (3) Å for $(CH_3)_2N$–, 2.702 (4) Å for CH_3–, 2.681 (4) Å for the title compound and 2.587 (5) Å for NC–] reflects the base strength of the derivative of pyridine. The title compound is unique among these four structures in that it crystallizes in a non-centrosymmetric space group, $P3_2$.

Experimental

The title compound was prepared by mixing pyridine and trifluoroacetic acid in a 1:1 molar ratio in water at 293 K. Crystals were obtained by slow evaporation of the solvent.

Crystal data

$C_5H_6N^+.C_2F_3O_2^-$
$M_r = 193.13$
Trigonal
$P3_2$
$a = 14.493 (2)$ Å
$c = 10.191 (2)$ Å
$V = 1853.8 (5)$ Å^3
$Z = 9$
$D_x = 1.557$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 29 reflections
$\theta = 4.87–25.13°$
$\mu = 0.157$ mm^{-1}
$T = 130 (2)$ K
Clear block
0.62 × 0.52 × 0.30 mm
Colourless

Data collection

Siemens *R3m/V* diffractometer
$\theta–2\theta$ scans
Absorption correction: empirical (*XABS*2; Parkins, Moezzi & Hope, 1995)
$T_{min} = 0.93$, $T_{max} = 0.96$
3010 measured reflections
3010 independent reflections

2870 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.58°$
$h = -18 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 13$
2 standard reflections every 198 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.126$
$S = 1.057$
3006 reflections
372 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*96
Extinction coefficient: 0.0008 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C1	1.330 (5)	C16—O1	1.214 (4)
N1—C5	1.332 (5)	C16—O2	1.258 (4)
C1—C2	1.364 (6)	C16—C17	1.555 (5)
C2—C3	1.384 (6)	C17—F2	1.313 (5)
C3—C4	1.377 (6)	C17—F3	1.319 (5)
C4—C5	1.373 (6)	C17—F1	1.341 (5)
C1—N1—C5	122.0 (3)	O2—C16—C17	113.5 (3)
N1—C1—C2	120.2 (4)	F2—C17—F3	108.7 (4)
C1—C2—C3	119.0 (4)	F2—C17—F1	107.3 (3)
C4—C3—C2	119.7 (4)	F3—C17—F1	105.3 (4)
C5—C4—C3	118.7 (3)	F2—C17—C16	113.8 (3)
N1—C5—C4	120.3 (3)	F3—C17—C16	112.8 (3)
O1—C16—C17	116.1 (3)	F1—C17—C16	108.5 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O2^{i}	0.93 (4)	1.79 (4)	2.681 (4)	160 (4)
N2—H2N···O4	1.03 (6)	1.61 (4)	2.664 (4)	177 (4)
N3—H3N···O6^{i}	1.00 (4)	1.71 (4)	2.698 (4)	176 (4)
C1—H1···O1	0.89 (4)	2.56 (4)	3.214 (5)	132 (4)
C6—H6···O3	1.02 (3)	2.41 (3)	3.212 (4)	135 (4)
C15—H15···O5^{i}	0.93 (4)	2.40 (4)	3.175 (4)	141 (4)

Symmetry code: (i) $-x + y, 2 - x, \frac{1}{3} + z$.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991*a*). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991*b*). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *XCIF* in *SHELXL*96.

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1-Cyano-2-*p*-bromophenylazulene and 2-Azulenylmethyl 2-Anthraquinoate†

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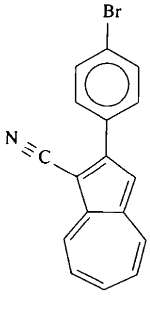
Abstract

The title azulene, $C_{17}H_{10}BrN$, (I), and ester, $C_{26}H_{16}O_4$, (II), are precursors for the preparation of the corresponding 1,8a-dihydroazulenes which are potentially photochromic compounds. In both compounds, the azulene moiety is found to be planar. All aromatic bonds in the azulenes lie in the range 1.369 (7)–1.416 (3) Å and the bridging bond between the seven- and five-membered rings is longer, 1.471 (3) and 1.478 (6) Å in (I) and (II), respectively.

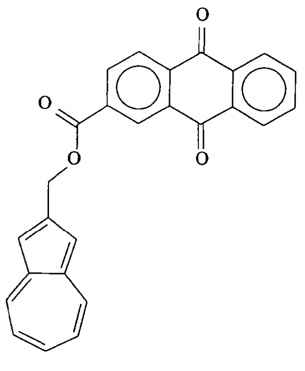
Comment

It is surprising that the crystal structures of only a few azulenes and their derivatives are known: azulene (Robertson, Shearer, Sim & Watson, 1962; Pawley, 1965), 2-aminoazulene (Takaki, Sasada & Nitta, 1959), azulene-*s*-trinitrobenzene complex (Hanson, 1965; Brown & Wallwork, 1965), azulene-1,3-dipropionic acid (Ammon & Sundaralingam, 1966), diazulenium azulene perchlorate (Sly, 1966), 1-(tricyanovinyl)azulene (Chetkina, Zavodnik & Bespalov, 1981), 1-benzoyl-4,6,8-trimethylazulene, 1-trifluoroacetyl-4,6,8-trimethylazulene (Tafeenko, Porshnev, Polyakov, Gerasimov, Cherkashin & Dyumaev, 1983) and bis(isothiocyanatotetrakis(4-methylpyridine)nickel(II) bis(azulene) clathrate (Lipkowski, Gluzinski, Suwinska & Andreetti, 1984).

Our interest in azulenes stems from the potential use of their 1,8a-dihydro derivatives as chemical and physical switches which can utilize a photochemically induced rearrangement (see, for example, Daub *et al.*, 1986, 1989; Daub, Gierisch & Salbeck, 1990; Daub, Fischer, Salbeck & Ulrich, 1990; Achatz, Fischer, Salbeck & Daub, 1991). Both compounds have been synthesized by a procedure outlined by Daub *et al.* (1986).



(I)



(II)

Crystals of (II) were poorly diffracting, leading to the small ratio of observed reflections to the number of refined parameters. An empirical absorption correction, based on azimuthal scans of several reflections, was applied for (I) (*TEXSAN*; Molecular Structure Corporation, 1992). The crystal structures of (I) and (II) (Figs. 1 and 2, respectively) show that the azulene moiety is planar (the out-of-plane displacements are less than 0.004 Å). A comparison of bond lengths and angles in the azulene moieties is given in Table 1. The

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† Alternative name: 2-azulenylmethyl 9,10-dioxo-9,10-dihydroanthracene-2-carboxylic acid.