

Three-dimensional supramolecular architecture in imidazolium hydrogen 2,3,5,6-tetrafluoroterephthalate

Li-Li Yu, Mei-Ling Cheng, Qi Liu,* Zhi-Hui Zhang and Qun Chen

Key Laboratory of Fine Petrochemical Technology, School of Chemistry and Chemical Engineering, Jiangsu Polytechnic University, Changzhou 213164, Jiangsu, People's Republic of China

Correspondence e-mail: liuqi62@163.com

Received 30 December 2009

Accepted 2 February 2010

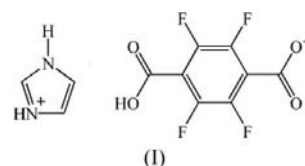
Online 6 March 2010

The asymmetric unit of the title salt formed between 2,3,5,6-tetrafluoroterephthalic acid (H_2tfdc) and imidazolium (ImH), $C_3H_5N_2^+ \cdot C_8HF_4O_4^-$, contains one $Htfdc^-$ anion and one ImH_2^+ cation, joined by a classical $N-H \cdots O$ hydrogen bond. The acid and base subunits are further linked by $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds into infinite two-dimensional layers with $R_6^5(32)$ hydrogen-bond motifs. The resulting (4,4) network layers interpenetrate to produce an interlocked three-dimensional structure. The final three-dimensional supramolecular architecture is further stabilized by the linkages of two $C-H \cdots O$ interactions.

Comment

Hydrogen bonding has long been considered important in biological systems and molecular recognition (Philp & Stoddart, 1996). Nowadays, the application of intermolecular hydrogen bonds is a well known and efficient tool to design and synthesize supramolecular assemblies (Prior & Rosseinsky, 2000; Beatty, 2003; Bhogala *et al.*, 2005). Classical hydrogen bonds (such as $O-H \cdots O$, $O-H \cdots N$, *etc.*) have proved to be ideal tools to rationalize and systematize the relationship between molecular and supramolecular structures (Desiraju & Steiner, 1999; Steiner & Desiraju, 1998; Mascal *et al.*, 2000). For example, many organic crystalline materials, composed of N-donor compounds such as imidazole (ImH), benzimidazole, pyridine and 4,4'-bipyridinium, and aromatic multicarboxylic acids, such as benzene-1,4-dicarboxylic acid, benzene-1,3,5-tricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid and benzene-1,2,3,4,5,6-hexacarboxylic acid, have been documented. Although coordination compounds synthesized with halogen-substituted aromatic multicarboxylic acids have been reported (Wang *et al.*, 2007; Roques *et al.*, 2007; Liu *et al.*, 2008; Sergio *et al.*, 2008; Chen *et al.*, 2008, 2006; Li *et al.*, 2008; Eddaoudi *et al.*, 2002), to the best of our knowledge studies of their supramolecular interactions have been less well explored

(Luo & Palmore, 2002; Lan *et al.*, 2008; He *et al.*, 2009). Recently, we have obtained two complexes with 2,3,5,6-tetrafluoroterephthalic acid (H_2tfdc) under mild solution synthetic conditions (Zhu *et al.*, 2008, 2009). To further the development of such interesting hydrogen-bonded supramolecular systems and as a continuation of our research in this area, we deliberately chose H_2tfdc to react with the excellent N-donor compound ImH , and isolated the the first organic crystalline product containing the $Htfdc^-$ anion. The title salt, (I), was an unexpected product of an attempt to form an extended structure incorporating Cd^{2+} cations.



Compound (I) crystallizes in the orthorhombic space group $Pna2_1$. The asymmetric unit contains one $Htfdc^-$ anion and one ImH_2^+ cation, linked by an $N-H \cdots O$ hydrogen bond between the protonated amine and the deprotonated carboxylate group (Fig. 1). Proton transfer from H_2tfdc to ImH was unequivocally established from difference map plots. The compound is thus shown to be an organic proton-transfer binary salt, in which the acidic H atom of one carboxyl group is transferred to an imidazole N atom while the other carboxyl group remains as the acid. The carboxyl and carboxylate groups are distinctly twisted away from the arene ring, with dihedral angles of $49.1(1)^\circ$ and $51.5(1)^\circ$, respectively, notably larger than the corresponding values in 4-methylimidazolium hydrogen terephthalate [$5.7(1)^\circ$ and $21.9(1)^\circ$, respectively; Meng *et al.*, 2008]. The plane of the aromatic ring of the $Htfdc^-$ anion is inclined at $40.9(1)^\circ$ to that of the ImH_2^+ cation, which is much smaller than the analogous angle in 4-methylimidazolium hydrogen terephthalate [$60.6(1)^\circ$; Meng

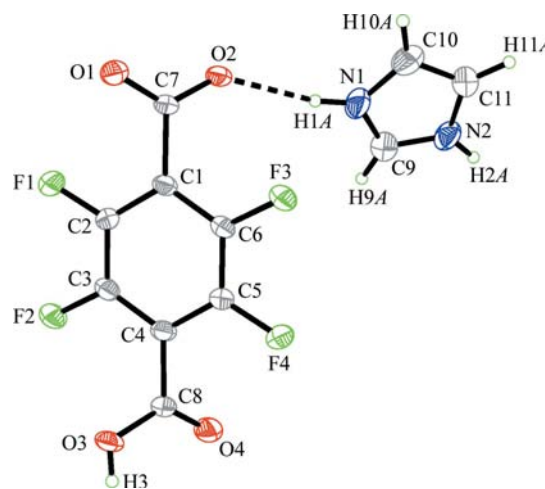


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The interion hydrogen bond is shown as a dashed line.

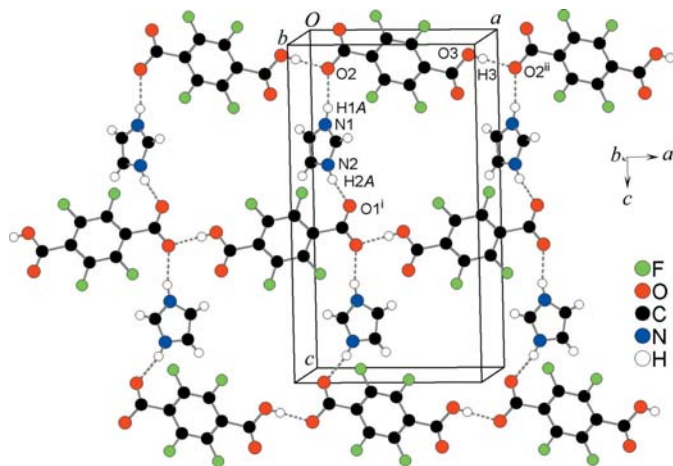


Figure 2

Part of the crystal structure of (I), showing the formation of the two-dimensional layer network with (4,4) topology running parallel to the (011) plane. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x + 1, y, z$.]

et al., 2008]. These differences may be due to the influence of the steric hindrance of the adjacent fluoro substituents.

The carboxyl and carboxylate C—O bond lengths in (I) [C7—O1 = 1.233 (3) Å, C7—O2 = 1.260 (2) Å, C8—O3 = 1.307 (3) Å and C8—O4 = 1.201 (3) Å] agree well with those tabulated by Allen *et al.* (1995) for a carboxyl [1.305 (20) and 1.226 (20) Å] and/or a carboxylate group [1.255 (10) Å] attached to an arene ring. The bond distances and angles in the ImH₂⁺ cation are also indicative of its protonation compared with analogous compounds.

In the extended structure of (I) (Fig. 2), linear tapes of Htfbdc[−] anions are generated along the *a* axis through O3—H3···O2ⁱⁱ hydrogen bonds [symmetry code: (ii) $x + 1, y, z$] (Table 1). The distance between the two carboxyl O atoms in the hydrogen bond is slightly shorter than those seen in other carboxylic acid compounds, such as terephthalic acid (2.620 Å; Domenicano *et al.*, 1990) and bis(2,4'-bipyridin-1'-ium) 2,5-dicarboxybenzene-1,4-carboxylate benzene-1,2,4,5-tetracarboxylic acid (2.607 Å; Cui *et al.*, 2005), indicating the strength of the interactions in (I). The linear tapes are very similar to the one-dimensional chains formed by the hydrogen terephthalate anions in 4-methylimidazolium hydrogen terephthalate (Meng *et al.*, 2008).

Adjacent anion chains are linked together by ImH₂⁺ cations via N1—H1A···O2 and N2—H2A···O1ⁱ hydrogen bonds [symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$], forming two-dimensional layers containing R₆^s(32) hydrogen-bond motifs (Fig. 2) [for the definition of graph-set notation, see Bernstein *et al.* (1995)]. The network thus formed is topologically equivalent to a (4,4) network (Batten & Robson, 1998). These layers lie parallel to the (011) plane, but there are also symmetry-related layers running parallel to (011). The two sets of layers interpenetrate through the cavities within each layer, with an angle between the layers of 45.1° (Fig. 3), to produce an interlocked three-dimensional structure.

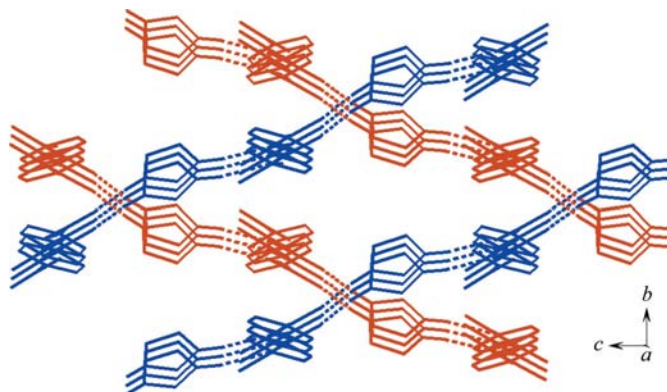


Figure 3

A view of the interpenetrating (4,4) networks in the structure of (I). Four such networks are shown. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif and all F atoms have been omitted.

The ImH₂⁺ cations linked to opposite sides of the same Htfbdc[−] anion chain are almost perpendicular to one another [dihedral angle = 82.0 (1)°], while the dihedral angle between the Htfbdc[−] rings of different chains is 23.5 (1)°. This pattern is somewhat different from what is seen in the two-dimensional layers formed by similar strong O—H···O and N—H···O hydrogen bonds with an R₆^s(32) ring pattern in 4-methylimidazolium hydrogen terephthalate (Meng *et al.*, 2008), in which the Htfbdc[−] anions of adjacent chains are parallel to each other and all 4-methylimidazolium cations are oriented in the same direction, so that the resulting (4,4) network layers are also parallel to each other.

Compound (I) extends further to its final three-dimensional network through weak intermolecular C9—H9A···O4ⁱⁱⁱ and C11—H11A···O1^{iv} interactions (Table 1) [symmetry codes: (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (iv) $-x, -y + 1, z + \frac{1}{2}$]. The H···A lengths of these hydrogen bonds are in the range 2.30–2.60 Å, comparable with those found in protein complexes (Jiang & Lai, 2002).

This work demonstrates the first example of a fluorinated terephthalic acid as a good participant in organic salt formation with an N-donor compound. Compound (I) is linked by O—H···O and N—H···O hydrogen bonds into (4,4) network layers, which interpenetrate to produce an interlocked three-dimensional structure. Additional studies are warranted in order to provide further insight into the potential of these molecules to form engineered structures in salts or co-crystals.

Experimental

All reagents and solvents employed were commercially available and used as supplied without further purification. For the preparation of (I), solid Cd(OH)₂ (0.0365 g, 0.25 mmol), which was found to be necessary for the crystallization of the product, was added to an ethanol–water (1:1 *v/v*) solution (5 ml) of H₂tfdcb (0.0595 g, 0.25 mmol) and ImH (0.0170 g, 0.25 mmol). After stirring for 1 h, the reaction mixture was filtered and left to stand at ambient temperature. Colourless block-shaped crystals of (I) suitable for X-ray diffraction were obtained after slow evaporation of the filtrate over a

period of one week [yield 67%, 0.0513 g (based on ImH)]. Analysis calculated for $C_{11}H_6F_4N_2O_4$: C 43.15, H 1.98, N 9.15%; found: C 43.17, H 1.20, N 9.13%. IR (KBr pellet, ν , cm^{-1}): 3169 (s), 2992 (w), 2856 (w), 1721 (w), 1626 (m), 1590 (m), 1474 (s), 1366 (m), 1307 (s), 1213 (m), 1178 (w), 1055 (m), 991 (s), 768 (m), 707(s), 631 (m), 508 (m), 488 (s).

Crystal data

$C_3H_5N_2^+ \cdot C_8HF_4O_4^-$	$V = 1222.5 (7) \text{ \AA}^3$
$M_r = 306.18$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 9.716 (3) \text{ \AA}$	$\mu = 0.17 \text{ mm}^{-1}$
$b = 7.229 (3) \text{ \AA}$	$T = 296 \text{ K}$
$c = 17.406 (6) \text{ \AA}$	$0.30 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Bruker SMART APEX CCD diffractometer	9957 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	1457 independent reflections
$T_{\min} = 0.952$, $T_{\max} = 0.968$	1330 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	1 restraint
$wR(F^2) = 0.074$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
1457 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
191 parameters	

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O2$	0.86	2.03	2.870 (3)	164
$N2-H2 \cdots O1^i$	0.86	1.89	2.732 (3)	168
$O3-H3 \cdots O2^{ii}$	0.82	1.72	2.5425 (19)	177
$C9-H9A \cdots O4^{iii}$	0.93	2.36	3.041 (3)	130
$C11-H11A \cdots O1^{iv}$	0.93	2.55	3.283 (3)	136

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

All C-bound H atoms were positioned theoretically and treated as riding atoms, with $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. N- and O-bound H atoms were initially located in difference maps, then refined with tight $N-H$ and $O-H$ distance restraints of 0.860 (1) and 0.820 (1) \AA , respectively, and finally refined as riding, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(N)$ or $1.5U_{\text{eq}}(O)$. Friedel pairs were collected but were merged before the final refinement and the absolute structure was chosen arbitrarily.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The authors thank the National Natural Science Foundation of China (grant Nos. 20671045 and 20971060) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3234). Services for accessing these data are described at the back of the journal.

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