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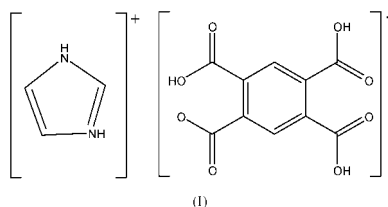
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.058
 wR factor = 0.156
Data-to-parameter ratio = 9.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Imidazolium trihydrogen-1,2,4,5-benzene-
tetracarboxylate

The crystal of the title compound, imidazolium trihydrogen-1,2,4,5-benzenetetracarboxylate, $\text{C}_3\text{H}_5\text{N}_2^+\cdot\text{C}_{10}\text{H}_5\text{O}_8^-$, is built of imidazolium cations and trihydrogen-1,2,4,5-benzenetetracarboxylate anions. The anions use two of their 'active' H atoms to generate hydrogen bonds linking to the neighbouring anions, thus creating a two-dimensional hydrogen-bonding network parallel to the bc plane of the crystal. The third oxygen-bound H atom of the anion is involved in an intramolecular hydrogen bond, which closes the six-membered pseudo-ring. The imidazolium cations are linked to the anionic hydrogen-bonded network through $\text{N}-\text{H}\cdots\text{O}$ bonds which target two of the O atoms of the carboxyl groups of the anions as acceptors. The mean plane of the imidazolium cation is almost orthogonal to the mean plane of the benzene ring of benzenetetracarboxylate, with a dihedral angle of $89.7(1)^\circ$.

Comment

Intermolecular interactions, such as hydrogen bonds and aromatic $\pi\cdots\pi$ stacking interactions, play a dominant role in molecular recognition in nature, and in designing molecular aggregates (Juan *et al.*, 2002). Of particular interest are compounds, such as 1,2,4,5-benzenetetracarboxylate anions, which can act not only as a hydrogen-bond acceptor but also as a hydrogen bond-donor, depending on the numbers of deprotonated carboxyl groups. 1,2,4,5-Benzenetetracarboxylic acid in its supramolecular adducts is most frequently encountered in the forms with either two or four deprotonated carboxyl groups. Thus, complexes $2[(2,2'\text{-bipyridyl})\text{H}]^+\cdots[\text{C}_6\text{H}_2(\text{COO})_4\text{H}_2]^{2-}\cdots[\text{C}_6\text{H}_2(\text{COOH})_4]$ (Mrvos-Sermek *et al.*, 1996), $2[(4,4'\text{-bipyridyl})\text{H}]^+\cdots\text{C}_{10}\text{H}_4\text{O}_8^{2-}$ (Lough *et al.*, 2000), $2\text{C}_6\text{H}_{13}\text{N}_4^+\cdots\text{C}_{10}\text{H}_4\text{O}_8^{2-}$ (Lough *et al.*, 2000) and $2\text{CH}_6\text{N}_3^+\cdots\text{C}_{10}\text{H}_4\text{O}_8^{2-}$ (Sun *et al.*, 2002) contain the doubly deprotonated dianionic form, whereas the structures of $\text{C}_{24}\text{H}_{42}\text{N}_6^{4+}\cdots\text{C}_{10}\text{H}_2\text{O}_8^{4-}\cdots 6\text{H}_2\text{O}$ (Zhu *et al.*, 2002) and $4[\text{C}(\text{NH}_2)_3]^+\cdots[\text{C}_{10}\text{H}_2(\text{COO})_4]^{4-}\cdots 4\text{H}_2\text{O}\cdots\text{H}_2\text{O}_2$ (Adams & Ramdas, 1978) involve totally deprotonated tetraanions. Herein we report a rare case of a mono-deprotonated 1,2,4,5-benzenetetracarboxylate salt with an imidazolium cation.

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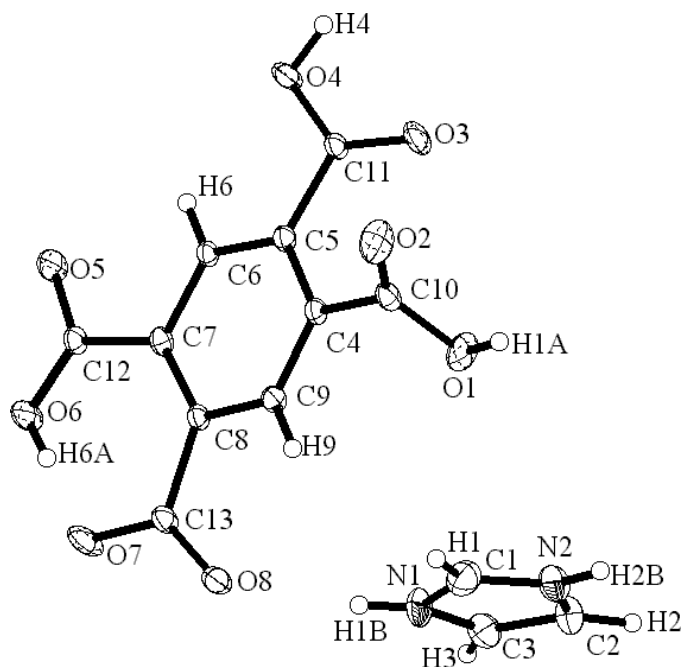


Figure 1
The cation and anion in the structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.

The asymmetric unit of the triclinic cell of the title compound, (I), includes one monoprotonated imidazolium cation, $C_3H_5N_2^+$, and one mono-deprotonated benzenetetracarboxylic acid, $C_{10}H_5O_8^-$ (Fig. 1). The mean plane of the cation is almost orthogonal to the mean plane of the anion, with a dihedral angle of $89.7(1)^\circ$.

As may be expected, three carboxyl groups of the anion, *viz.* those with atoms C10, C11, and C12, show considerable differences in the C—O bond lengths; bonds involving protonated O atoms are 0.06–0.10 Å longer than the others. The C13, O7, O8 group represents an ionized carboxylate with almost equal C13—O7 and C13—O8 bonds (see Table 1).

There is only one intramolecular O—H...O hydrogen bond in the anion (O6—H6A...O7). Two other oxygen-bound H atoms of the anion and two nitrogen-bound H atoms of the cation give rise to four symmetry-independent intermolecular (or, to put it more accurately, ‘interionic’) hydrogen bonds (Table 2), which link the cations and anions of the structure into infinite layers parallel to the *bc* plane of the crystal (Fig. 2).

Experimental

A mixture of pyromellitic dianhydride (0.109 g, 0.5 mmol), imidazole (0.034 g, 0.5 mmol) and H_2O (10 ml, 567.7 mmol), in the mole ratio of *ca.* 1:1:1135, was sealed in a 35 ml stainless-steel reactor with a teflon liner, and was heated at 433 K for 72 h. After cooling, the mixture was filtered and colorless single crystals were obtained by slow evaporation of the filtrate at room temperature.

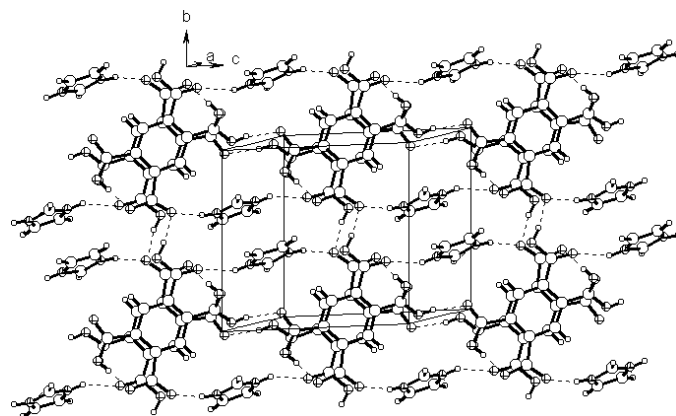


Figure 2
Packing diagram, viewed down $[301]$, showing the hydrogen-bond system in the crystal of the title compound.

Crystal data

$C_3H_5N_2^+ \cdot C_{10}H_5O_8^-$
 $M_r = 322.23$
Triclinic, $P\bar{1}$
 $a = 7.6045(12)$ Å
 $b = 9.6885(15)$ Å
 $c = 9.7991(16)$ Å
 $\alpha = 88.804(2)^\circ$
 $\beta = 69.069(2)^\circ$
 $\gamma = 72.853(2)^\circ$
 $V = 641.46(18)$ Å³

$Z = 2$
 $D_x = 1.668$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 49 reflections
 $\theta = 2.2$ – 25.1°
 $\mu = 0.14$ mm⁻¹
 $T = 293(2)$ K
Column, colorless
 $0.38 \times 0.32 \times 0.26$ mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.948$, $T_{\max} = 0.964$
3343 measured reflections
2238 independent reflections
1790 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = -9 \rightarrow 4$
 $k = -11 \rightarrow 10$
 $l = -11 \rightarrow 11$
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.156$
 $S = 1.07$
2238 reflections
249 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.5307P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.32$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C10	1.304 (3)	O8—C13	1.241 (3)
O2—C10	1.197 (3)	C1—N1	1.324 (5)
O3—C11	1.197 (3)	C1—N2	1.296 (4)
O4—C11	1.302 (3)	C2—N2	1.355 (5)
O5—C12	1.216 (3)	C2—C3	1.333 (5)
O6—C12	1.284 (3)	C3—N1	1.361 (5)
O7—C13	1.254 (3)		
C9—C4—C10	118.3 (2)	O2—C10—O1	124.6 (2)
C6—C5—C4	119.4 (2)	O3—C11—O4	123.0 (2)
C6—C7—C8	117.6 (2)	O5—C12—O6	121.0 (2)
C9—C8—C7	118.7 (2)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1A \cdots O5 ⁱ	0.93 (6)	1.72 (6)	2.648 (3)	174 (6)
O6—H6A \cdots O7	1.11 (5)	1.29 (5)	2.392 (3)	177 (4)
N1—H1B \cdots O8	0.90 (4)	2.00 (4)	2.878 (4)	166 (4)
N2—H2B \cdots O3 ⁱⁱ	0.86 (4)	2.00 (4)	2.774 (3)	149 (3)
O4—H4 \cdots O8 ⁱⁱⁱ	0.89 (4)	1.72 (4)	2.599 (3)	170 (4)

Symmetry codes: (i) $x, y, 1 + z$; (ii) $1 - x, 2 - y, 2 - z$; (iii) $x, 1 + y, z$.

All H atoms were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. The N—H bond lengths are equal to 0.86 (4) and 0.90 (4) Å and the C—H bond lengths range from 0.92 to 0.96 Å. The O—H bond lengths are between 0.89 and 1.11 Å. Atom H6A, participating in the intramolecular hydrogen bond, refined to a position 1.11 (5) Å from O6 and 1.29 (5) Å from O7. Taking into account this difference in the O—H distances, as well as the distribution of C—O bond lengths in the carboxyl groups (see *Comment*), we concluded that C12, O5, O6 is, in fact, a protonated carboxylic group, whereas the C13, O7, O8 group represents a deprotonated carboxylate.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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