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Hydrogen-bonding in 4-(hydroxymethyl)-imidazolium picrate

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The title compound, $C_4H_7N_2O^+ \cdot C_6H_2N_3O_7{}^-$, crystallizes in space group $P2_1$ with one ion pair in the asymmetric unit. Strong N—H···O and O—H···O hydrogen bonds, together with weak C—H···O contacts between the two components, generate a two-dimensional layered structure containing $R_1^2(6)$, $R_2^1(7)$, $R_3^3(10)$ and $R_5^5(24)$ rings. These layers are further connected by an additional C—H···O interaction, resulting in an extensive three-dimensional hydrogen-bonding network.

Comment

The assembly and construction of two-component molecular crystals with predictable topologies and properties has become one of the main goals of crystal engineers working on the synthesis of purely organic molecular crystals; this has a considerable importance in designing not only new organic solids materials but also solid-state photoreactions (Desiraju, 1995; Koshima *et al.*, 1996). Nowadays it is well known that both strong O—H···O and weak C—H···O hydrogen bonds are useful in crystal design for the preparation of molecular materials with controlled physical properties (Desiraju, 1991; Desiraju & Steiner, 1999). Thus, in discussing the packing modes of molecular crystals, it is important to understand weaker forces, such as C—H···O hydrogen bonding and π–π stacking interactions, which play an important role in controlling the total supramolecular network. In the present paper, we report the crystal structure of the title compound, (I), and the hydrogen-bonding interactions in detail.
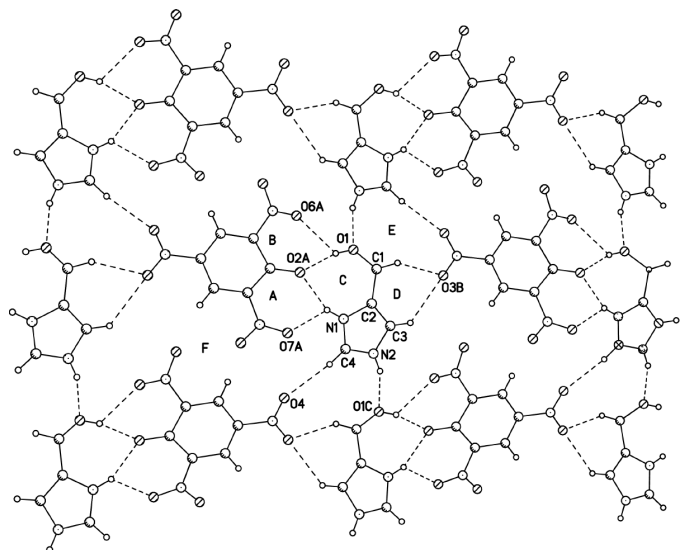

(I)
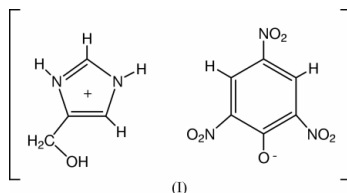
A view of the ion pair of (I) with the atomic numbering scheme is depicted in Fig. 1. Selected bond lengths and angles are listed in Table 1. X-ray analysis of the crystal structure confirmed that the ratio of acid to base is 1:1, and the ions are connected through several kinds of hydrogen bonds, as detailed below, with the transfer of a proton to form the salt. Both cation and anion possess non-planar geometry: for the cation, the out-of plane O1 atom is 1.117 (4) Å from the mean plane of the remaining non-H atoms [the maximum deviation of any fitted atom from the mean plane is 0.007 (4) Å, while the average deviation is 0.003 (2) Å], as also indicated by the torsion angles [122.2 (5)° for C3—C2—C1—O1 and −59.2 (5)° for N1—C2—C1—O1]; for the picrate anion, the three nitro groups form dihedral angles of 10.6 (4), 33.0 (5)
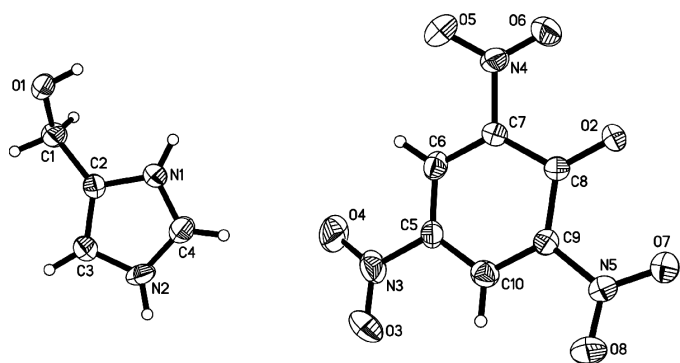
Figure 1
The independent components of compound (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.
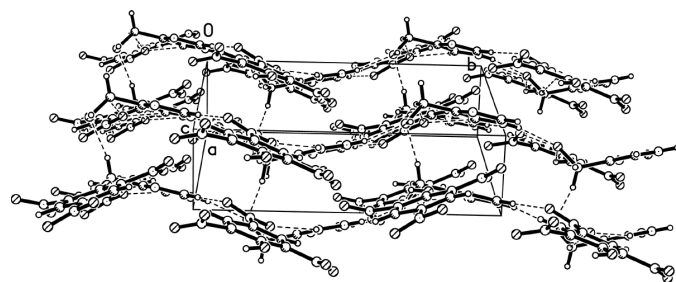

Figure 2
Part of the crystal structure of (I), showing the two-dimensional hydrogen-bonding layer containing $R_1^2(6)$, $R_2^1(7)$, $R_3^3(10)$ and $R_5^5(24)$ motifs.

Figure 3
Three-dimensional packing diagram of (I), showing the intermolecular C1—H1A···O1 interactions between the layers.

Both the C1—H1B and the C3—H3A groups of the 4-hydroxymethylimidazolium cation form weak C1—H1B···O3^{ii} and C3—H3A···O3^{ii} [symmetry code: (ii) $-x$, $y - \frac{1}{2}$, $2 - z$] interactions with the remaining nitro group of the picrate anion, generating an $R_1^2(6)$ motif D. For the remaining C4—H4A and N2—H2B groups of the 4-hydroxymethyl-imidazolium cation, one intramolecular C4—H4A···O4 interaction with the nitro atom of the picrate anion and one intermolecular N2—H2B···O1^{iii} [symmetry code: (iii) $-x$, $y + \frac{1}{2}$, $2 - z$] hydrogen bond with the hydroxy group of the adjacent 4-hydroxymethylimidazolium cation are observed, resulting in an $R_3^3(10)$ graph set E. Thus, the cation and anion components are connected to form a two-dimensional layered structure with the repeating unit F, $R_5^5(24)$, consisting of three cations and two picrate anions (Fig. 2). In addition, these layers are further extended through interlayer C1—H1A···O1^{iv} [symmetry code: (iv) $x + 1$, y, z] weak interactions to form a three-dimensional supramolecular network, as shown in Fig. 3. There is no evidence of any aromatic π–π stacking or C—H···π interactions. Examination of the structure with *PLATON* (Spek, 2003) shows that there are no solvent-accessible voids in the crystal structure of (I).

Experimental

Well shaped cuboidal yellow single crystals of the title compound, (I), suitable for X-ray diffraction analysis, were prepared by spontaneous crystallization from hot water of the individual components (4-hydroxymethylimidazole and picric acid).

Crystal data

$C_4H_7N_2O^+ \cdot C_6H_2N_3O_7^-$	$D_x = 1.696$ Mg m^{-3}
$M_r = 327.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 2351
$a = 3.7925$ (14) Å	reflections
$b = 13.916$ (5) Å	$\theta = 1.7$–25.0°
$c = 12.141$ (4) Å	$\mu = 0.15$ mm^{-1}
$\beta = 90.862$ (5)°	$T = 293$ (2) K
$V = 640.7$ (4) Å^3	Prism, yellow
$Z = 2$	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART 1000	1187 independent reflections
diffractometer	1019 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.022$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*SADABS* (Sheldrick, 1996)	$h = -4 \rightarrow 3$
$T_{min} = 0.957$, $T_{max} = 0.983$	$k = -9 \rightarrow 16$
2660 measured reflections	$l = -14 \rightarrow 13$

and 13.6 (5) with the mean phenol plane [the maximum deviation of any fitted atom from the mean plane is 0.030 (3) Å, while the average deviation is 0.017 (3) Å].

Analysis of the crystal packing of (I) showed that there exist numerous hydrogen bonds, such as strong N—H···O or O—H···O, and weak hydrogen-bonding interactions of the C—H···O type, as listed in Table 2. The atom H1C on the N1 donor of the 4-hydroxymethylimidazolium cation forms two intermolecular N1—H1C···O2^i and N1—H1C···O7^i [symmetry code: (i) $1 - x$, $y - \frac{1}{2}$, $1 - z$] hydrogen bonds with the phenol and one nitro group of the picrate anion, respectively, connecting the cation/anion pair as depicted in Fig. 2. The resulting motif A, in the formalism of graph-set analysis of hydrogen-bond patterns (Etter, 1990; Etter *et al.*, 1990), is characterized as $R_1^2(6)$. Two similar O1—H1···O2^i and O1—H1···O6^i hydrogen bonds are also observed between the hydroxy group of the cation, and the phenol and another nitro group of the picrate anion, also resulting in an $R_1^2(6)$ ring B. Meanwhile, the O1—H1···O2^i and N1—H1C···O2^i interactions involving the phenol group generate an $R_2^1(7)$ motif C.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0716P)^2]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} < 0.001$
1187 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
209 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C4—N2	1.306 (6)	C8—O2	1.252 (5)
C4—N1	1.322 (6)	C9—N5	1.453 (6)
C3—C2	1.350 (6)	N3—O4	1.224 (6)
C3—N2	1.375 (6)	N3—O3	1.228 (6)
C2—N1	1.379 (5)	N4—O6	1.211 (5)
C2—C1	1.494 (6)	N4—O5	1.226 (6)
C1—O1	1.426 (6)	N5—O7	1.217 (4)
C5—N3	1.456 (4)	N5—O8	1.223 (5)
C7—N4	1.470 (6)		
C4—N1—C2	109.1 (4)	O6—N4—O5	123.4 (4)
C4—N2—C3	109.3 (4)	O7—N5—O8	121.4 (4)
O3—N3—O4	123.2 (4)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C4—H4$A\cdots$O4	0.93	2.37	3.294 (5)	172
O1—H1$\cdots$O2^i	0.82	2.00	2.787 (4)	162
O1—H1$\cdots$O6^i	0.82	2.30	2.797 (4)	120
N1—H1$C\cdots$O2^i	0.86	1.95	2.730 (5)	151
N1—H1$C\cdots$O7^i	0.86	2.18	2.796 (4)	129
C3—H3$A\cdots$O3^{ii}	0.93	2.56	3.280 (4)	135
C1—H1$B\cdots$O3^{ii}	0.97	2.55	3.402 (5)	147
N2—H2$B\cdots$O1^{iii}	0.86	1.99	2.811 (5)	160
C1—H1$A\cdots$O1^{iv}	0.97	2.47	3.393 (5)	159

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

All H atoms were found in a difference electron-density map but were then placed in calculated positions (C—H = 0.97 and 0.93 Å for methylene and aromatic H atoms, respectively; N—H and O—H distances are 0.86 and 0.82 Å, respectively), and were included in the final refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C,N)$ for C- or N-bound hydrogen atoms and $1.5U_{eq}(O)$ for O—H. It was impossible to determine the absolute configuration in this case, due to the absence of sufficiently heavy atoms. The Friedel pairs were merged, giving a data/parameter ratio of only 5.7.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

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