

Imidazolium fumarate

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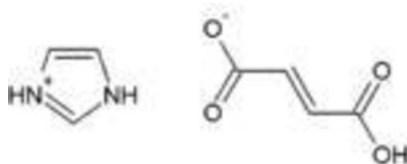
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.051; wR factor = 0.149; data-to-parameter ratio = 16.3.

In the title compound, $\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{C}_4\text{H}_3\text{O}_4^-$, the dihedral angle between the imidazolium ring and the plane formed by the fumarate anion is $80.98(6)^\circ$. In the crystal structure, intermolecular $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds form extended chains along $[100]$ and $[01\bar{1}]$, creating a two-dimensional network.

Related literature

For background information on the anti-pyretic and anti-inflammatory biological activity of imidazole derivatives, see: Tudek *et al.* (1992); Puig-Parellada *et al.* (1973). For fumaric acid, see: Bednowitz & Post (1966) and for imidazole, see: McMullan *et al.* (1979). For hydrogen-bond motifs, see: Etter (1990).



Experimental

Crystal data

$\text{C}_3\text{H}_5\text{N}_2^+ \cdot \text{C}_4\text{H}_3\text{O}_4^-$
 $M_r = 184.15$
Triclinic, $P\bar{1}$
 $a = 7.4794(4)$ Å
 $b = 7.7522(3)$ Å
 $c = 8.4231(4)$ Å
 $\alpha = 69.695(3)^\circ$
 $\beta = 81.415(2)^\circ$

$\gamma = 66.193(2)^\circ$
 $V = 419.04(3)$ Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 294$ K
 $0.12 \times 0.02 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
7824 measured reflections
1922 independent reflections
1443 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.087$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.149$
 $S = 1.07$
1922 reflections
118 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1} \cdots \text{O4}^{\text{i}}$	0.82	1.75	2.5699 (16)	173
$\text{N2}-\text{H8} \cdots \text{O3}^{\text{ii}}$	0.86	1.82	2.6600 (18)	166
$\text{N1}-\text{H9} \cdots \text{O4}^{\text{iii}}$	0.86	1.94	2.7969 (16)	172

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

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PARST95* (Nardelli, 1995).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2920).

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supporting information

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S1. Comment

This work is part of a series of studies on the structural behavior of imidazole derivatives. Imidazole molecule is a heterocyclic compound which is present in important biological building blocks such as histidine, histamine, guanine (Tudek *et al.*, 1992). The analgesic, anti-inflammatory and anti pyretic properties of imidazole have been reported (Puig-Parellada *et al.*, 1973). In search of systems that form cyclic motifs linked by intermolecular hydrogen bonds, our research group focused its attention on the structural properties of molecular complex formed by fumaric acid (FUM) and imidazole (IM) moieties (I). The general crystallographic behavior of fumaric acid (Bednowitz & Post, 1966) and the imidazole free molecules (McMullan, *et al.*, 1979) may be used as reference systems in order to compare to the title imidazolium salt. A displacement ellipsoid plot of (I) with the atomic numbering scheme is shown in Figure 1. The free molecule of fumaric acid as well as other organic acids, are characterized by forming dimers in their structures. In the formation of the title adduct (I), dimers of fumaric acid decompose, to gain new and stronger hydrogen bonds and a more stable structure with imidazole moiety (see Table 1), (Nardelli, 1995). The C4–O4 bond length changes from 1.290 (5) in free fumaric acid molecule (Bednowitz & Post, 1966) to 1.2664 (17) Å in (I). The title structure shows a dihedral angle of 80.98 (6)° between the imidazole ring and the plane formed by FUM molecule. The other bond lengths and bond angles of (I) are in good agreement with the standard values and correspond to those observed in the free molecules. The transference of the proton from one of the carboxylic acid groups of FUM molecule to the basic N-atom of the IM molecule is carried out. This proton transfer allows the formation of new interactions in the FUM-IM adduct. The title adduct is characterized by the formation of hydrogen-bond interactions between O—H···O and N—H···O. One of the strongest hydrogen bond O—H···O interaction is responsible for crystal growth in [100] direction. Indeed, in a first substructure, atom O4 in the molecule at (*x*, *y*, *z*) acts as hydrogen bond donor to carboxyl O1ⁱ atom in the molecule at (*x* + 1, *y*, *z*). The propagation of this interaction forms a C(7) (Etter, 1990) chain running along [100] direction (Fig. 2). In a second substructure, atom N2ⁱⁱ in the molecule at (−*x* + 1, −*y* + 1, −*z*) acts as hydrogen bond donor to the atom O3 in the molecule at (*x*, *y*, *z*). While the atom N1ⁱ in the molecule at (−*x* + 1, −*y*, −*z* + 1) acts as hydrogen bond donor to carboxy O4 atom in the molecule at (*x*, *y*, *z*). These interactions form C(8) chains which are running parallel to the [01−1] direction (Fig.3). All of these interactions in [100], and [01−1] directions define the overall two dimensional network.

S2. Experimental

The synthesis of the title adduct (I) was carried out by slow evaporation of equimolar quantities of fumaric acid (0.739 g, 637 mmol) and imidazole (0.433 g,) in 100 ml of aqueous solution of methyl alcohol at 2%. After 3 days, colourless prisms of poor quality, with a melting point greater than 424 K, were formed. Crystalline sample decomposes at temperatures greater than this value. The initial reagents were purchased from Aldrich Chemical Co., and were used as received.

S3. Refinement

All H-atoms were located from difference maps and were positioned geometrically and refined using a riding model with (C—H= 0.93, N—H= 0.86 and O—H= 0.82 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.2–1.5 times U_{eq} of the parent atom).

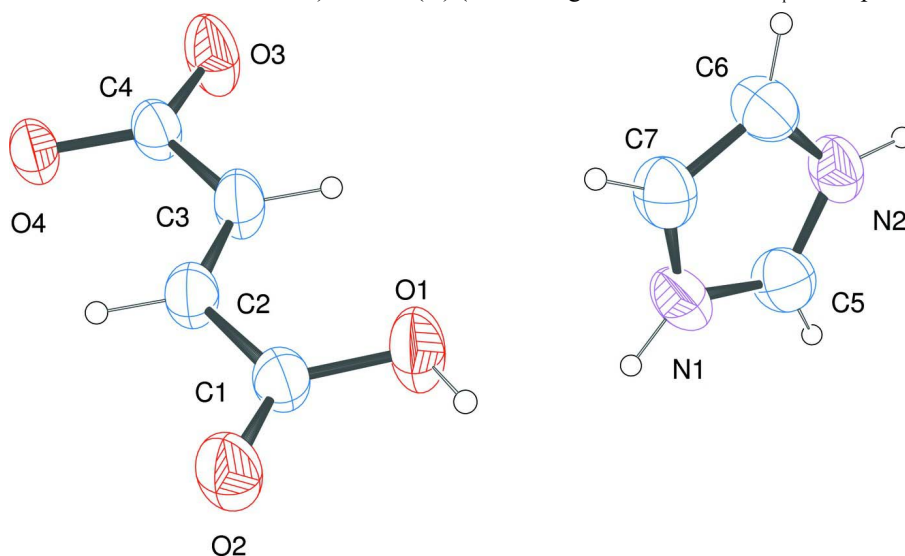


Figure 1

An *ORTEP-3* (Farrugia, 1997) perspective drawing of (I), with the atomic labelling scheme for non-H atoms, which are represented by displacement ellipsoids drawn at the 50% probability level and, for the sake of clarity, H atoms are shown as spheres of arbitrary radius.

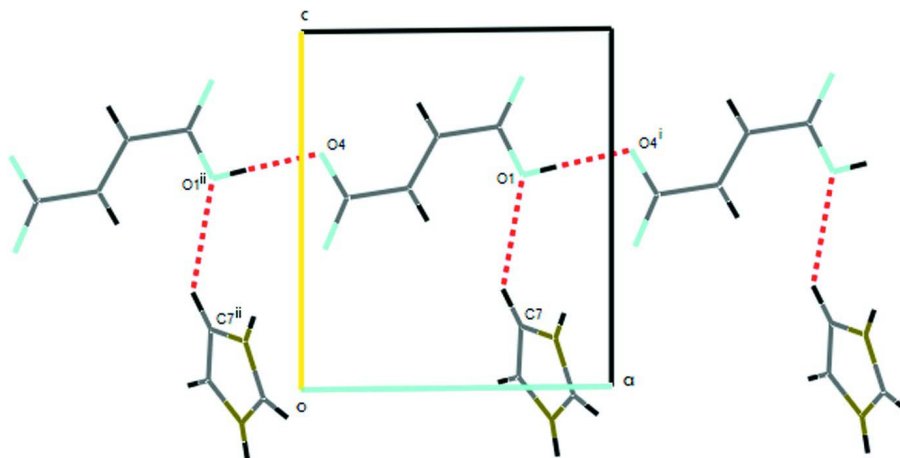


Figure 2

Part of the crystal structure of (I), showing the formation of C(7) chains running along [100] direction. Symmetry code: (i) $x + 1, y, z$; (ii) $x - 1, y, z$

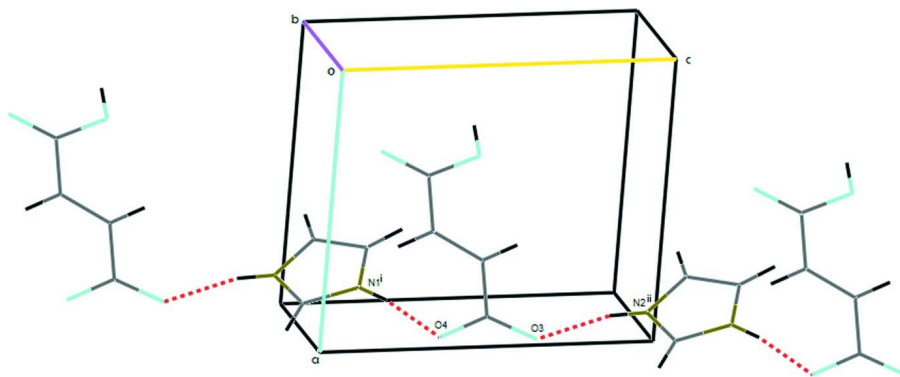


Figure 3

Part of the crystal structure of (I), showing the formation of C(8) chains running along [01-1]. Symmetry code: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z$

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Crystal data

$C_3H_5N_2^+ \cdot C_4H_3O_4^-$

$M_r = 184.15$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.4794\ (4)\ \text{\AA}$

$b = 7.7522\ (3)\ \text{\AA}$

$c = 8.4231\ (4)\ \text{\AA}$

$\alpha = 69.695\ (3)^\circ$

$\beta = 81.415\ (2)^\circ$

$\gamma = 66.193\ (2)^\circ$

$V = 419.04\ (3)\ \text{\AA}^3$

$Z = 2$

$F(000) = 192$

$D_x = 1.460\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4127 reflections

$\theta = 2.6\text{--}27.5^\circ$

$\mu = 0.12\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Prism, colourless

$0.12 \times 0.02 \times 0.02\ \text{mm}$

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

CCD rotation images, thick slices scans

7824 measured reflections

1922 independent reflections

1443 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.087$

$\theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 2.6^\circ$

$h = -9 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.149$

$S = 1.07$

1922 reflections

118 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0832P)^2 + 0.0432P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.31\ \text{e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.29\ \text{e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O4	0.06367 (15)	0.14005 (15)	0.66024 (12)	0.0409 (3)
O2	0.71272 (18)	0.03156 (19)	0.86710 (14)	0.0507 (4)
O1	0.71448 (18)	0.2024 (2)	0.59326 (14)	0.0592 (4)
H1	0.8224	0.1913	0.6157	0.089*
O3	0.0768 (2)	0.3167 (2)	0.39170 (14)	0.0587 (4)
N1	0.8197 (2)	0.25796 (19)	0.13620 (16)	0.0466 (4)
H9	0.8473	0.1397	0.2063	0.056*
N2	0.8081 (2)	0.4960 (2)	-0.09082 (16)	0.0443 (4)
H8	0.8267	0.5605	-0.1937	0.053*
C2	0.4385 (2)	0.1246 (2)	0.70462 (18)	0.0380 (4)
H2	0.3770	0.0624	0.7974	0.046*
C4	0.1475 (2)	0.2259 (2)	0.53479 (17)	0.0365 (4)
C1	0.6358 (2)	0.1144 (2)	0.72978 (18)	0.0373 (4)
C3	0.3458 (2)	0.2155 (2)	0.56046 (18)	0.0415 (4)
H3	0.4073	0.2778	0.4678	0.050*
C5	0.8781 (3)	0.3027 (2)	-0.0231 (2)	0.0475 (4)
H5	0.9560	0.2119	-0.0781	0.057*
C6	0.7006 (3)	0.5786 (2)	0.0293 (2)	0.0493 (4)
H6	0.6342	0.7135	0.0147	0.059*
C7	0.7089 (3)	0.4285 (3)	0.1717 (2)	0.0485 (4)
H7	0.6500	0.4391	0.2751	0.058*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O4	0.0376 (6)	0.0512 (6)	0.0305 (6)	-0.0243 (5)	-0.0008 (4)	0.0002 (5)
O2	0.0456 (7)	0.0681 (8)	0.0344 (6)	-0.0282 (6)	-0.0079 (5)	-0.0006 (5)
O1	0.0435 (7)	0.0886 (9)	0.0388 (7)	-0.0404 (7)	-0.0064 (5)	0.0083 (6)
O3	0.0548 (8)	0.0869 (9)	0.0302 (6)	-0.0419 (7)	-0.0100 (5)	0.0079 (6)
N1	0.0564 (9)	0.0408 (7)	0.0368 (7)	-0.0217 (7)	-0.0059 (6)	0.0006 (5)
N2	0.0499 (8)	0.0517 (8)	0.0288 (6)	-0.0259 (7)	-0.0019 (6)	-0.0012 (5)
C2	0.0358 (8)	0.0450 (8)	0.0334 (7)	-0.0207 (7)	0.0019 (6)	-0.0072 (6)
C4	0.0369 (8)	0.0428 (7)	0.0278 (7)	-0.0196 (6)	-0.0013 (6)	-0.0033 (6)
C1	0.0354 (8)	0.0427 (7)	0.0317 (7)	-0.0180 (6)	-0.0013 (6)	-0.0051 (6)
C3	0.0380 (8)	0.0550 (9)	0.0317 (7)	-0.0264 (7)	0.0010 (6)	-0.0042 (6)
C5	0.0506 (10)	0.0498 (9)	0.0401 (9)	-0.0181 (8)	-0.0011 (7)	-0.0127 (7)

C6	0.0584 (11)	0.0412 (8)	0.0431 (9)	-0.0182 (8)	-0.0011 (8)	-0.0079 (7)
C7	0.0554 (10)	0.0546 (9)	0.0341 (8)	-0.0233 (8)	0.0028 (7)	-0.0109 (7)

Geometric parameters (Å, °)

O4—C4	1.2664 (17)	N2—H8	0.8600
O2—C1	1.2109 (18)	C2—C3	1.310 (2)
O1—C1	1.3084 (17)	C2—C1	1.489 (2)
O1—H1	0.8200	C2—H2	0.9300
O3—C4	1.2363 (17)	C4—C3	1.497 (2)
N1—C5	1.317 (2)	C3—H3	0.9300
N1—C7	1.356 (2)	C5—H5	0.9300
N1—H9	0.8600	C6—C7	1.339 (2)
N2—C5	1.307 (2)	C6—H6	0.9300
N2—C6	1.368 (2)	C7—H7	0.9300
C1—O1—H1	109.5	O2—C1—C2	121.36 (13)
C5—N1—C7	109.00 (14)	O1—C1—C2	114.43 (12)
C5—N1—H9	125.5	C2—C3—C4	124.42 (14)
C7—N1—H9	125.5	C2—C3—H3	117.8
C5—N2—C6	108.60 (13)	C4—C3—H3	117.8
C5—N2—H8	125.7	N2—C5—N1	108.58 (15)
C6—N2—H8	125.7	N2—C5—H5	125.7
C3—C2—C1	124.31 (14)	N1—C5—H5	125.7
C3—C2—H2	117.8	C7—C6—N2	107.01 (15)
C1—C2—H2	117.8	C7—C6—H6	126.5
O3—C4—O4	124.23 (14)	N2—C6—H6	126.5
O3—C4—C3	117.70 (13)	C6—C7—N1	106.81 (15)
O4—C4—C3	118.06 (12)	C6—C7—H7	126.6
O2—C1—O1	124.20 (13)	N1—C7—H7	126.6
C3—C2—C1—O2	178.47 (16)	C6—N2—C5—N1	-0.09 (19)
C3—C2—C1—O1	-1.1 (2)	C7—N1—C5—N2	-0.12 (19)
C1—C2—C3—C4	179.96 (13)	C5—N2—C6—C7	0.27 (19)
O3—C4—C3—C2	-179.96 (16)	N2—C6—C7—N1	-0.33 (19)
O4—C4—C3—C2	-0.5 (2)	C5—N1—C7—C6	0.3 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O4 ⁱ	0.82	1.75	2.5699 (16)	173
N2—H8...O3 ⁱⁱ	0.86	1.82	2.6600 (18)	166
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