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1*H*-Imidazol-3-ium-4-carboxylate

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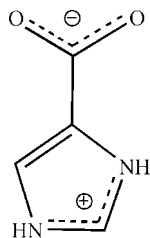
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.029; wR factor = 0.083; data-to-parameter ratio = 7.0.

In the title compound, $\text{C}_4\text{H}_4\text{N}_2\text{O}_2$, both imidazole N atoms are protonated and carboxylate group is deprotonated, resulting in a zwitterion. The molecule is essentially planar, with an r.m.s. deviation of 0.012 (1) Å. In the crystal, $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and $\pi-\pi$ stacking interactions [centroid-centroid distance = 3.674 (2) Å] between the imidazole rings link the molecules into a three-dimensional supramolecular network.

Related literature

For general background to the construction of coordination polymers based on 1*H*-imidazole-4,5-dicarboxylic acid, see: Alkordi, Liu *et al.* (2008); Alkordi, Brant *et al.* (2009); Gu *et al.* (2010); Lu *et al.* (2006); Nouar *et al.* (2009); Wang *et al.* (2010). For related complexes with 1*H*-imidazole-4-carboxylic acid, see: Haggag (2005); Starosta & Leciejewicz (2006); Gryz *et al.* (2007); Yin *et al.* (2009); Shuai *et al.* (2011); Zheng *et al.* (2011). For the synthesis of 1*H*-imidazole-4-carboxylic acid, see: Davis *et al.* (1982).



Experimental

Crystal data

$\text{C}_4\text{H}_4\text{N}_2\text{O}_2$
 $M_r = 112.09$
 Orthorhombic, $Pna2_1$

$a = 10.474$ (6) Å
 $b = 11.676$ (7) Å
 $c = 3.674$ (2) Å

$V = 449.3$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.14$ mm⁻¹
 $T = 298$ K
 $0.25 \times 0.21 \times 0.18$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.967$, $T_{\max} = 0.976$
 2280 measured reflections
 510 independent reflections
 480 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.083$
 $S = 1.10$
 510 reflections
 73 parameters
 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.12$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N2}-\text{H2}\cdots\text{O2}^{\text{i}}$ | 0.86 | 1.82 | 2.648 (2) | 160 |
| $\text{N1}-\text{H1}\cdots\text{O1}^{\text{ii}}$ | 0.86 | 1.91 | 2.736 (2) | 161 |

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LD2040).

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supplementary materials

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1*H*-Imidazol-3-ium-4-carboxylate

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Comment

The organic ligands containing N and O donors, especially the *N*-heterocyclic carboxylates, are ideal candidates for constructing novel metal coordination polymers, because of their versatile coordination modes and potential hydrogen bonding donors and acceptors. Particular attention has been paid to the 1*H*-imidazole-4,5-dicarboxylic acid ligand (H₃IDC), because it can coordinate with metal ions in different coordination fashions to offer a series of complexes with diverse structures and interesting properties (Alkordi, Liu *et al.*, 2008; Alkordi, Brant *et al.*, 2009; Gu *et al.*, 2010; Lu *et al.*, 2006; Nouar *et al.*, 2009; Wang *et al.*, 2010). Recently, an analogue of H₃IDC, 1*H*-imidazole-4-carboxylic acid (H₂IMC), has also been used to prepare new coordination polymers (Haggag, 2005; Starosta & Leciejewicz, 2006; Gryz *et al.*, 2007; Yin *et al.*, 2009; Shuai *et al.*, 2011; Zheng *et al.*, 2011). However, the crystal structure of H₂IMC ligand has not been determined. With this in mind, we attempted to obtain its crystal structure that is reported here.

As illustrated in Fig. 1, the title compound, C₄H₄N₂O₂, crystallizes as a zwitterion in which the imidazole N atom is protonated and the carboxylate group is deprotonated. In the crystal structure, intermolecular N2—H2⁺⋯O2⁻ and N1—H1⁺⋯O1⁻ hydrogen bonds (Table 1) [symmetry code: (i) $-x + 1/2, y - 1/2, z + 1/2$; (ii) $-x, -y + 1, z + 1/2$] between the imidazole N—H groups and carboxylate O atoms link the molecules into a three-dimensional supramolecular network (Fig. 2). Moreover, the crystal structure is further stabilized by π - π stacking interactions between neighbouring imidazole rings [N2—C4—N1—C2—C3 and N2^v—C4^v—N1^v—C2^v—C3^v, symmetry code: (v) $x, y, z + 1$], with centroid⋯centroid distances of 3.674 (2) Å (Fig. 2).

Experimental

The compound was synthesized from 1*H*-imidazole-4,5-dicarboxylic acid according to the method reported in the literature (Davis *et al.*, 1982). Colourless single crystals suitable for X-ray diffraction were prepared by slow evaporation of a solution of the title compound in water at room temperature.

Refinement

All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The zwitter-ionic structure was established from a difference Fourier synthesis. Consequently, all hydrogen atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{N})$. Since this is a light atom structure (does not contain any atoms heavier than Si) and since the data collection was carried out using Mo radiation, it was not possible to unambiguously determine the absolute configuration of this molecule. In the absence of significant anomalous scattering effects Friedel pairs have been merged.

Figures

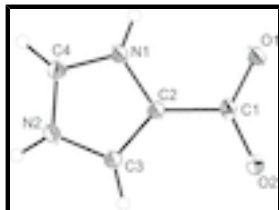


Fig. 1. The structure of the title compound, showing the atom-labelling scheme and displacement ellipsoids drawn at the 30% probability level.

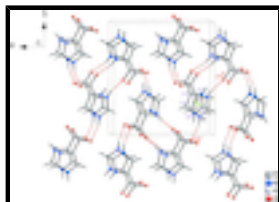


Fig. 2. A view showing part of the three-dimensional supramolecular network linked by N-H...O hydrogen bonds and π - π stacking interactions. Hydrogen bonds and π - π stacking interactions are shown as dashed lines. Symmetry codes: (i) $-x + 1/2, y - 1/2, z + 1/2$; (ii) $-x, -y + 1, z + 1/2$; (v) $x, y, z + 1$.

1H-Imidazol-3-ium-4-carboxylate

Crystal data

$C_4H_4N_2O_2$

$M_r = 112.09$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 10.474 (6) \text{ \AA}$

$b = 11.676 (7) \text{ \AA}$

$c = 3.674 (2) \text{ \AA}$

$V = 449.3 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 232$

$D_x = 1.657 \text{ Mg m}^{-3}$

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

Cell parameters from 1380 reflections

$\theta = 2.6\text{--}27.0^\circ$

$\mu = 0.14 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Block, colourless

$0.25 \times 0.21 \times 0.18 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

phi and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.967, T_{\max} = 0.976$

2280 measured reflections

510 independent reflections

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

$R_{\text{int}} = 0.023$

$\theta_{\max} = 26.0^\circ, \theta_{\min} = 2.6^\circ$

$h = -12 \rightarrow 12$

$k = -14 \rightarrow 12$

$l = -4 \rightarrow 4$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

| | |
|-------------------|--|
| $wR(F^2) = 0.083$ | H-atom parameters constrained |
| $S = 1.10$ | $w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.0406P]$ |
| 510 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 73 parameters | $(\Delta/\sigma)_{\max} < 0.001$ |
| 1 restraint | $\Delta\rho_{\max} = 0.12 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$ |

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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|--------------|------------|----------------------------------|
| C2 | 0.15183 (19) | 0.33109 (16) | 0.6250 (7) | 0.0265 (5) |
| C1 | 0.20900 (19) | 0.44287 (17) | 0.5153 (6) | 0.0268 (5) |
| N2 | 0.10851 (15) | 0.15065 (14) | 0.7501 (6) | 0.0302 (5) |
| H2 | 0.1149 | 0.0774 | 0.7660 | 0.036* |
| C4 | 0.0113 (2) | 0.21278 (18) | 0.8693 (7) | 0.0301 (5) |
| H4 | -0.0610 | 0.1844 | 0.9853 | 0.036* |
| O2 | 0.31910 (13) | 0.43682 (12) | 0.3734 (5) | 0.0361 (5) |
| O1 | 0.14526 (14) | 0.53104 (13) | 0.5736 (6) | 0.0367 (5) |
| N1 | 0.03417 (16) | 0.32279 (14) | 0.7956 (6) | 0.0284 (5) |
| H1 | -0.0158 | 0.3791 | 0.8456 | 0.034* |
| C3 | 0.1970 (2) | 0.22218 (17) | 0.5977 (7) | 0.0280 (5) |
| H3 | 0.2743 | 0.2003 | 0.4940 | 0.034* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|-------------|--------------|-------------|
| C2 | 0.0254 (9) | 0.0223 (10) | 0.0320 (13) | 0.0003 (8) | -0.0016 (10) | 0.0003 (10) |
| C1 | 0.0295 (11) | 0.0190 (9) | 0.0319 (13) | 0.0011 (8) | -0.0047 (9) | 0.0035 (9) |
| N2 | 0.0323 (9) | 0.0181 (8) | 0.0401 (11) | -0.0007 (7) | -0.0033 (9) | 0.0011 (9) |
| C4 | 0.0275 (10) | 0.0271 (10) | 0.0358 (14) | -0.0035 (8) | -0.0004 (9) | 0.0032 (11) |
| O2 | 0.0324 (8) | 0.0235 (7) | 0.0524 (12) | -0.0013 (6) | 0.0078 (8) | 0.0043 (9) |
| O1 | 0.0352 (8) | 0.0203 (7) | 0.0545 (12) | 0.0047 (6) | -0.0018 (8) | 0.0025 (9) |
| N1 | 0.0279 (9) | 0.0203 (8) | 0.0371 (11) | 0.0024 (7) | -0.0016 (9) | -0.0004 (8) |
| C3 | 0.0261 (9) | 0.0222 (10) | 0.0357 (14) | -0.0005 (8) | -0.0022 (10) | 0.0017 (10) |

supplementary materials

Geometric parameters (Å, °)

| | | | |
|-------------|-------------|-------------|-------------|
| C2—C3 | 1.361 (3) | N2—C3 | 1.368 (3) |
| C2—N1 | 1.386 (3) | N2—H2 | 0.8600 |
| C2—C1 | 1.491 (3) | C4—N1 | 1.334 (3) |
| C1—O1 | 1.246 (3) | C4—H4 | 0.9300 |
| C1—O2 | 1.267 (3) | N1—H1 | 0.8600 |
| N2—C4 | 1.324 (3) | C3—H3 | 0.9300 |
| C3—C2—N1 | 106.10 (17) | N2—C4—N1 | 108.81 (19) |
| C3—C2—C1 | 131.2 (2) | N2—C4—H4 | 125.6 |
| N1—C2—C1 | 122.71 (17) | N1—C4—H4 | 125.6 |
| O1—C1—O2 | 127.19 (19) | C4—N1—C2 | 108.57 (17) |
| O1—C1—C2 | 117.49 (18) | C4—N1—H1 | 125.7 |
| O2—C1—C2 | 115.32 (18) | C2—N1—H1 | 125.7 |
| C4—N2—C3 | 108.78 (17) | C2—C3—N2 | 107.74 (19) |
| C4—N2—H2 | 125.6 | C2—C3—H3 | 126.1 |
| C3—N2—H2 | 125.6 | N2—C3—H3 | 126.1 |
| C3—C2—C1—O1 | -180.0 (3) | C3—C2—N1—C4 | 0.5 (3) |
| N1—C2—C1—O1 | -1.9 (3) | C1—C2—N1—C4 | -178.0 (2) |
| C3—C2—C1—O2 | -0.5 (4) | N1—C2—C3—N2 | -0.2 (3) |
| N1—C2—C1—O2 | 177.6 (2) | C1—C2—C3—N2 | 178.1 (2) |
| C3—N2—C4—N1 | 0.4 (3) | C4—N2—C3—C2 | -0.1 (3) |
| N2—C4—N1—C2 | -0.6 (3) | | |

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> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| N2—H2...O2 ⁱ | 0.86 | 1.82 | 2.648 (2) | 160. |
| N1—H1...O1 ⁱⁱ | 0.86 | 1.91 | 2.736 (2) | 161. |

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

Fig. 1

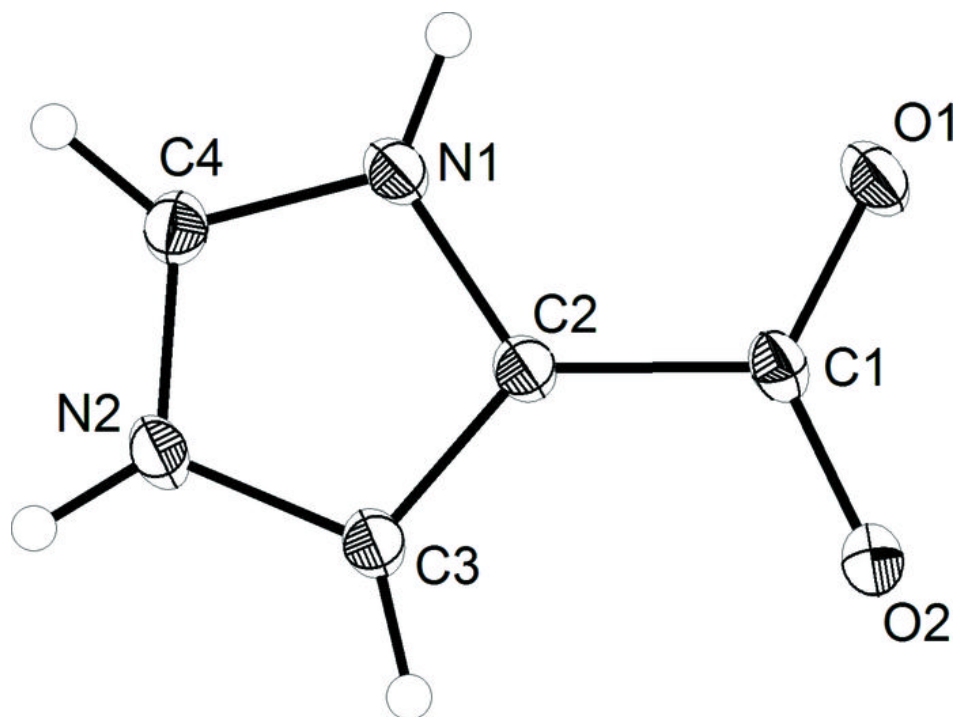


Fig. 2

