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Zwitterionic 4-carboxy-2-(pyridinium-2-yl)-1*H*-imidazole-5-carboxylate

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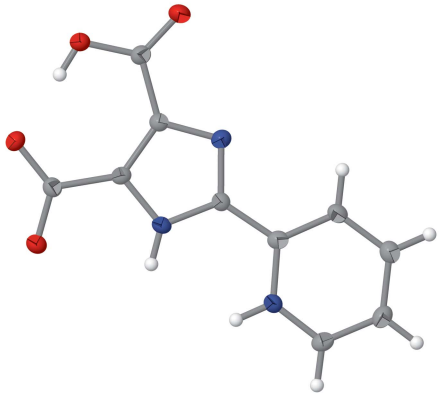
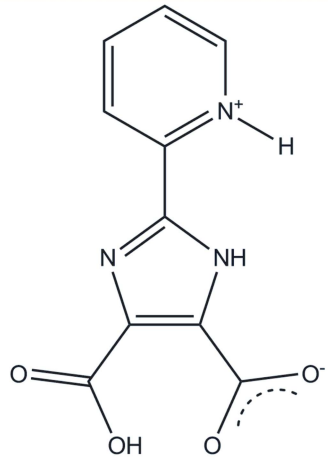
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{10}H_7N_3O_4$, is zwitterionic, with one carboxyl group deprotonated and the pyridyl group protonated. The pyridine ring is close to coplanar with the imidazole ring, making a dihedral angle of 2.79 (8)°, this conformation being maintained by the presence of an intramolecular O—H···O hydrogen bond. In the crystal, two sets of N—H···O hydrogen bonds link the molecules through three conjoined cyclic hydrogen-bonding interactions, with two $R_2^1(7)$ and one $R_2^2(10)$ motifs, forming centrosymmetric cyclic dimers. These are linked through C—H···O hydrogen bonds, giving a supramolecular chain structure extending along the *b*-axis direction.

3D view



Chemical scheme



Structure description

In recent years, interest in carboxylic acid compounds having both pyridine and imidazole ring systems has increased due to their versatility in the assembly of compounds having novel structures. At the same time, their coordination chemistry has become an expanding field of study because of the potential applications in crystal engineering (Zheng *et al.*, 2012; Li *et al.*, 2010, 2013). Because of its structural features, the title compound may be a suitable bridging ligand for the construction of coordination polymers with interesting architectures. The synthesis of this acid has been reported previously (Li *et al.*, 2012, 2014; Wang, Wang *et al.*, 2014; Xin *et al.*, 2013), but its crystal structure has not. Only the crystal structures of its coordination polymers have been described previously (Wang, Yu *et al.*, 2014; Yu *et al.*, 2013).

The title compound is f zwitterionic in the solid state, with one carboxyl group (defined by O1/C1/O2) deprotonated and the pyridyl atom N3 protonated (Fig. 1). The pyridine ring is close to coplanar with the imidazole ring, making a dihedral angle of 2.79 (8)°. The O1/C1/O2 and the O4/C4/O4 carboxyl groups are also essentially coplanar with the imidazole ring, making dihedral angles of 4.265 (14) and 3.48 (9)°, respectively. This

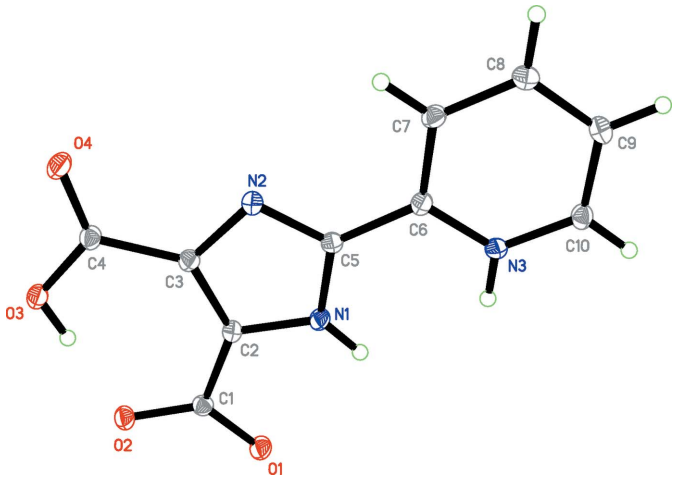


Figure 1
Molecular configuration and atom-numbering scheme, with displacement ellipsoids drawn at the 50% level.

conformation is maintained by the presence of an intramolecular O3—H3···O2 hydrogen bond (Table 1).

In the crystal, two sets of N—H···O hydrogen bonds (N1—H1···O1^{i} and N3—H3*A*···O1^{i}) link two molecules through three conjoined cyclic hydrogen-bonding interactions, with two $R_2^1(6)$ and one $R_2^2(10)$ motifs, forming centrosymmetric cyclic dimers (Fig. 2). These dimers are linked through C—H···O hydrogen bonds, forming a supramolecular chain structure extending along the *b*-axis direction. Present also in the structure are very weak interactions between pyridine and imidazole rings [minimum ring-centroid separation = 3.9510 (7) Å].

Synthesis and crystallization

The title compound was prepared by the literature method (Elagab & Alt, 2016; Zheng *et al.*, 2012). *o*-Phenylenediamine (0.05 mol) was mixed with picolinic acid (0.05 mol) and the mixture was poured into 50 ml of preheated (373 K) polyphosphoric acid. The mixture was stirred and heated at 448 K for 3–5 h after which the reaction mixture was then poured into ice-cold water and allowed to stand overnight. The precipitate was removed by filtration and washed several times with dilute sodium hydrogen carbonate solution and finally with water. The reaction product 2-(2-pyridyl)benzimidazole was then air dried. To 0.04 mol of this product in 55 ml of water was added 70 ml of concentrated H_2SO_4 and $K_2Cr_2O_7$ (37 g). The resulting mixture was allowed to react at 363 K for 15 min and then poured into ice–water. The white precipitate formed was filtered and washed with water to give the crude product in 55% yield. Crystals suitable for X-ray analysis were obtained after recrystallization from an aqueous solution of the title compound.

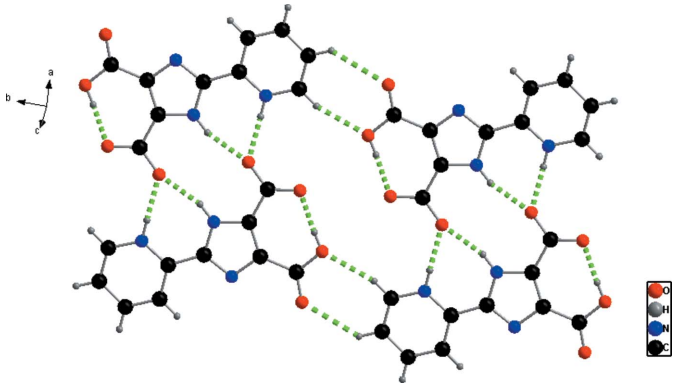


Figure 2
A view of the intermolecular associations showing the centrosymmetric hydrogen-bonded dimers and the inter-dimer C—H···O extensions along *b*. Hydrogen bonds are shown as dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.82	1.70	2.517 (2)	176
N1—H1···O1^{i}	0.86	1.92	2.743 (2)	159
N3—H3*A*···O1^{i}	0.86	1.81	2.656 (2)	169
C10—H10···O3^{ii}	0.93	2.25	3.153 (3)	163
C9—H9···O4^{ii}	0.93	2.52	3.239 (3)	134

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_7N_3O_4$
M_r	233.19
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	113
a, *b*, *c* (Å)	11.701 (2), 10.947 (2), 7.4253 (15)
β (°)	107.68 (3)
V (Å^3)	906.2 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.14
Crystal size (mm)	0.24 × 0.19 × 0.12
Data collection	
Diffractometer	Rigaku Pilatus 200K CCD detector
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.971, 0.989
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8958, 1589, 1460
R_{int}	0.041
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.124, 1.00
No. of reflections	1589
No. of parameters	155
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.28

Computer programs: *CrystalClear* (Rigaku, 2008), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161641 [https://doi.org/10.1107/S2414314616016412]

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4-Carboxy-2-(pyridinium-2-yl)-1*H*-imidazole-5-carboxylate

Crystal data

$C_{10}H_7N_3O_4$
M_r = 233.19
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.701 (2) Å
b = 10.947 (2) Å
c = 7.4253 (15) Å
β = 107.68 (3)°
V = 906.2 (3) Å^3
Z = 4
$F(000)$ = 480
D_x = 1.709 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2533 reflections
θ = 1.8–27.9°
μ = 0.14 mm^{-1}
T = 113 K
Prism, yellow
0.24 × 0.19 × 0.12 mm

Data collection

Rigaku Pilatus 200K CCD detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
profile data from ω–scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.971, T_{max} = 0.989
8958 measured reflections
1589 independent reflections
1460 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.0°, θ_{min} = 1.8°
h = −13→13
k = −13→13
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.124
S = 1.00
1589 reflections
155 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
$w = 1/[\sigma^2(F_o^2) + (0.080P)^2 + 0.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.04791 (13)	0.34830 (13)	−0.0067 (2)	0.0248 (4)
O2	0.99988 (13)	0.15468 (13)	0.0351 (2)	0.0235 (4)
O3	0.82521 (13)	0.04871 (13)	0.0987 (2)	0.0248 (4)
H3	0.8827	0.0852	0.0831	0.037*
O4	0.65300 (13)	0.09509 (14)	0.1472 (2)	0.0298 (4)
N1	0.85670 (15)	0.43688 (16)	0.0864 (2)	0.0186 (4)
H1	0.9034	0.4932	0.0687	0.022*
N2	0.70101 (15)	0.34866 (15)	0.1471 (2)	0.0191 (4)
N3	0.76016 (15)	0.67597 (16)	0.1238 (2)	0.0190 (4)
H3A	0.8277	0.6683	0.1013	0.023*
C1	0.98184 (17)	0.26779 (18)	0.0321 (3)	0.0189 (5)
C2	0.87398 (17)	0.31449 (18)	0.0776 (3)	0.0182 (5)
C3	0.77614 (18)	0.26033 (18)	0.1155 (3)	0.0184 (5)
C4	0.74573 (18)	0.12859 (19)	0.1211 (3)	0.0207 (5)
C5	0.75262 (17)	0.45424 (18)	0.1280 (3)	0.0179 (5)
C6	0.70164 (18)	0.57337 (19)	0.1471 (3)	0.0188 (5)
C7	0.59330 (18)	0.5860 (2)	0.1861 (3)	0.0210 (5)
H7	0.5524	0.5172	0.2066	0.025*
C8	0.54629 (19)	0.7017 (2)	0.1945 (3)	0.0224 (5)
H8	0.4731	0.7105	0.2179	0.027*
C9	0.60908 (19)	0.80397 (19)	0.1676 (3)	0.0226 (5)
H9	0.5783	0.8818	0.1721	0.027*
C10	0.71828 (18)	0.78862 (19)	0.1340 (3)	0.0212 (5)
H10	0.7624	0.8564	0.1187	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0232 (8)	0.0207 (8)	0.0344 (9)	−0.0012 (6)	0.0146 (7)	0.0020 (6)
O2	0.0239 (8)	0.0166 (8)	0.0324 (9)	0.0019 (6)	0.0120 (7)	0.0003 (6)
O3	0.0235 (8)	0.0172 (8)	0.0372 (9)	−0.0009 (6)	0.0142 (7)	0.0012 (6)
O4	0.0268 (9)	0.0203 (8)	0.0476 (10)	−0.0047 (6)	0.0193 (8)	−0.0016 (7)
N1	0.0189 (9)	0.0168 (9)	0.0221 (9)	−0.0018 (6)	0.0092 (7)	0.0018 (7)
N2	0.0208 (9)	0.0164 (9)	0.0203 (9)	−0.0003 (7)	0.0062 (7)	−0.0001 (7)
N3	0.0164 (8)	0.0186 (9)	0.0227 (9)	−0.0003 (7)	0.0071 (7)	0.0009 (7)
C1	0.0181 (10)	0.0199 (11)	0.0191 (10)	0.0003 (8)	0.0063 (8)	0.0008 (8)
C2	0.0199 (11)	0.0151 (10)	0.0195 (10)	−0.0008 (8)	0.0061 (8)	0.0006 (8)
C3	0.0184 (10)	0.0173 (11)	0.0201 (10)	−0.0007 (8)	0.0069 (8)	0.0003 (8)
C4	0.0225 (11)	0.0174 (11)	0.0231 (11)	−0.0008 (8)	0.0083 (9)	−0.0019 (8)
C5	0.0169 (10)	0.0178 (10)	0.0196 (10)	−0.0001 (8)	0.0065 (8)	0.0003 (8)

C6	0.0199 (10)	0.0175 (10)	0.0180 (10)	−0.0018 (8)	0.0044 (8)	0.0003 (8)
C7	0.0197 (10)	0.0208 (11)	0.0244 (11)	−0.0031 (8)	0.0096 (9)	−0.0015 (8)
C8	0.0204 (10)	0.0256 (11)	0.0218 (11)	0.0008 (8)	0.0071 (9)	0.0001 (9)
C9	0.0268 (11)	0.0195 (11)	0.0219 (11)	0.0040 (9)	0.0079 (9)	−0.0006 (9)
C10	0.0243 (11)	0.0171 (11)	0.0209 (11)	−0.0002 (8)	0.0050 (9)	0.0019 (8)

Geometric parameters (Å, º)

O1—C1	1.262 (2)	C1—C2	1.492 (3)
O2—C1	1.255 (2)	C2—C3	1.392 (3)
O3—C4	1.323 (2)	C3—C4	1.489 (3)
O3—H3	0.8200	C5—C6	1.459 (3)
O4—C4	1.215 (2)	C6—C7	1.390 (3)
N1—C5	1.358 (3)	C7—C8	1.390 (3)
N1—C2	1.359 (3)	C7—H7	0.9300
N1—H1	0.8600	C8—C9	1.386 (3)
N2—C5	1.331 (3)	C8—H8	0.9300
N2—C3	1.374 (3)	C9—C10	1.384 (3)
N3—C10	1.338 (3)	C9—H9	0.9300
N3—C6	1.354 (3)	C10—H10	0.9300
N3—H3A	0.8600		
C4—O3—H3	109.5	O3—C4—C3	116.96 (17)
C5—N1—C2	107.80 (16)	N2—C5—N1	111.72 (17)
C5—N1—H1	126.1	N2—C5—C6	123.61 (18)
C2—N1—H1	126.1	N1—C5—C6	124.67 (18)
C5—N2—C3	104.95 (17)	N3—C6—C7	118.21 (18)
C10—N3—C6	123.33 (18)	N3—C6—C5	119.45 (18)
C10—N3—H3A	118.3	C7—C6—C5	122.33 (18)
C6—N3—H3A	118.3	C8—C7—C6	119.88 (19)
O2—C1—O1	125.55 (18)	C8—C7—H7	120.1
O2—C1—C2	118.90 (18)	C6—C7—H7	120.1
O1—C1—C2	115.55 (18)	C9—C8—C7	119.69 (19)
N1—C2—C3	105.46 (17)	C9—C8—H8	120.2
N1—C2—C1	119.79 (17)	C7—C8—H8	120.2
C3—C2—C1	134.74 (19)	C10—C9—C8	119.10 (19)
N2—C3—C2	110.07 (18)	C10—C9—H9	120.4
N2—C3—C4	120.39 (17)	C8—C9—H9	120.4
C2—C3—C4	129.53 (18)	N3—C10—C9	119.75 (19)
O4—C4—O3	121.09 (19)	N3—C10—H10	120.1
O4—C4—C3	121.95 (18)	C9—C10—H10	120.1
C5—N1—C2—C3	0.0 (2)	C3—N2—C5—N1	−0.2 (2)
C5—N1—C2—C1	179.48 (17)	C3—N2—C5—C6	179.00 (18)
O2—C1—C2—N1	176.02 (18)	C2—N1—C5—N2	0.1 (2)
O1—C1—C2—N1	−4.0 (3)	C2—N1—C5—C6	−179.07 (18)
O2—C1—C2—C3	−4.7 (3)	C10—N3—C6—C7	−0.9 (3)
O1—C1—C2—C3	175.2 (2)	C10—N3—C6—C5	178.23 (17)

C5—N2—C3—C2	0.2 (2)	N2—C5—C6—N3	−179.50 (18)
C5—N2—C3—C4	−178.71 (17)	N1—C5—C6—N3	−0.4 (3)
N1—C2—C3—N2	−0.1 (2)	N2—C5—C6—C7	−0.4 (3)
C1—C2—C3—N2	−179.5 (2)	N1—C5—C6—C7	178.63 (19)
N1—C2—C3—C4	178.62 (19)	N3—C6—C7—C8	2.0 (3)
C1—C2—C3—C4	−0.7 (4)	C5—C6—C7—C8	−177.13 (18)
N2—C3—C4—O4	2.5 (3)	C6—C7—C8—C9	−1.3 (3)
C2—C3—C4—O4	−176.2 (2)	C7—C8—C9—C10	−0.4 (3)
N2—C3—C4—O3	−176.70 (17)	C6—N3—C10—C9	−0.9 (3)
C2—C3—C4—O3	4.7 (3)	C8—C9—C10—N3	1.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.82	1.70	2.517 (2)	176
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C10—H10···O3^{ii}	0.93	2.25	3.153 (3)	163
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