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1*H*-Pyrazol-2-ium hydrogen oxalate

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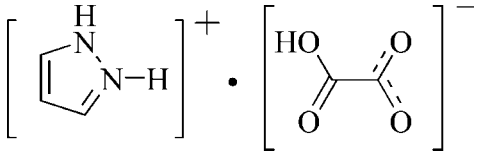
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.095; wR factor = 0.285; data-to-parameter ratio = 15.1.

In the title compound, $C_3H_5N_2^+\cdot C_2HO_4^-$, the anions form centrosymmetric dimers through cyclic O—H···O hydrogen-bonding associations [graph set $R_2^2(10)$]. These dimers are then linked through a cyclic $R_4^2(10)$ N—H···O hydrogen-bonding association involving two cations and the carboxyl O-atom acceptors of separate anions, giving chain structures extending across the (111) plane.

Related literature

For general background to ferroelectric organic frameworks, see: Fu *et al.* (2009); Ye *et al.* (2006); Zhang *et al.* (2008, 2010). For graph-set analysis, see: Etter *et al.* (1990).



Experimental

Crystal data

$C_3H_5N_2^+\cdot C_2HO_4^-$
M_r = 158.12
Triclinic, $P\overline{1}$
a = 3.7286 (7) Å
b = 9.836 (2) Å
c = 10.487 (2) Å
α = 117.35 (3)°
β = 97.01 (3)°
γ = 93.65 (3)°
V = 335.92 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 293 K
0.26 × 0.22 × 0.14 mm

Data collection

Rigaku SCXmini CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.965, T_{max} = 0.993
3484 measured reflections
1527 independent reflections
702 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.095
$wR(F^2)$ = 0.285
S = 1.07
1527 reflections
101 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.86	1.86	2.709 (5)	170
N2—H2A···O1^{ii}	0.86	1.92	2.715 (5)	153
O4—H4···O3^{iii}	0.82	1.95	2.679 (5)	147

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

This work was supported by Southeast University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2209).

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supplementary materials

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1*H*-Pyrazol-2-ium hydrogen oxalate

Chun-Hua Yu and Run-Qiang Zhu

Comment

As a contribution to a search for new ferroelectric materials (Fu *et al.*, 2009; Ye *et al.*, 2006; Zhang *et al.*, 2008, 2010), we have synthesized the title salt, $C_3H_5N_2^+$. $C_2HO_4^-$ from a 1:1 stoichiometric reaction of pyrazole with oxalic acid and the structure is reported here.

In the structure of the title compound (Fig.1) the molecules are organized in a one-dimensional chain structure involving both inter-anionic and cation–anion hydrogen-bonding associations (Table 1). The anions form centrosymmetric dimers through cyclic O—H···O hydrogen-bonding associations [graph set $R^2_2(10)$ (Etter *et al.*, 1990)]. These dimers are then linked through a cyclic $R^2_4(10)$ N—H···O hydrogen-bonding association involving two cations and the carboxyl O-atom acceptors of separate anions, giving one-dimensional chain structures extending across the (111) plane (Fig. 2).

Experimental

A mixture of pyrazole (0.68 g, 10 mmol) and oxalic acid (0.95 g, 10 mmol) in water was stirred for several days at ambient temperature. Colourless crystal plates of the title compound suitable for X-ray analysis were obtained.

Refinement

Hydrogen atom positions were calculated and allowed to ride on their parent atoms with aromatic C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å, and with U_{iso}(H) = 1.2U_{eq}(C or N) and U_{iso}(H) = 1.5U_{eq}(O).

Computing details

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalClear* (Rigaku, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

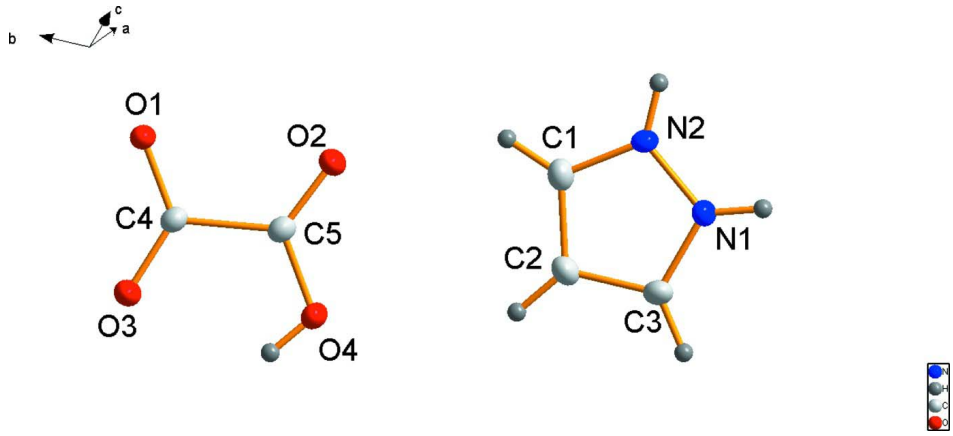

Figure 1

The molecular structure and atom-numbering scheme for the title compound, with the displacement ellipsoids drawn at the 30% probability level.

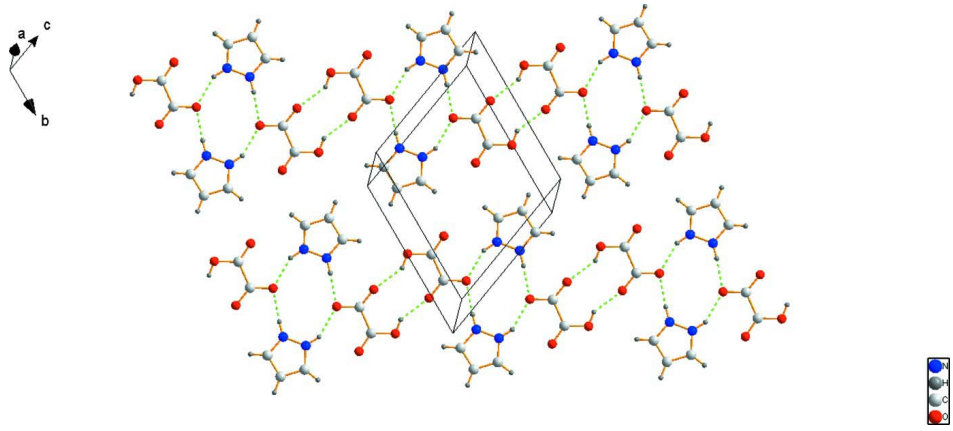

Figure 2

The packing of the title compound in the unit cell viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

1*H*-Pyrazol-2-ium hydrogen oxalate

Crystal data

$C_3H_5N_2^+·C_2HO_4^-$
M_r = 158.12
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 3.7286 (7) Å
b = 9.836 (2) Å
c = 10.487 (2) Å
α = 117.35 (3)°
β = 97.01 (3)°
γ = 93.65 (3)°
V = 335.92 (14) Å^3
Z = 2
F(000) = 164
D_x = 1.563 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1527 reflections
θ = 2.4–27.5°
μ = 0.14 mm^{-1}
T = 293 K
Sheet, colourless
0.26 × 0.22 × 0.14 mm

Data collection

Rigaku SCXmini CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
CCD_Profile_fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.965, T_{max} = 0.993

3484 measured reflections
1527 independent reflections
702 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 27.5°, θ_{min} = 3.9°
h = −4→4
k = −12→12
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.095
$wR(F^2)$ = 0.285
S = 1.07
1527 reflections
101 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
$w = 1/[\sigma^2(F_o^2) + (0.1349P)^2 + 0.0952P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	1.0872 (11)	0.0136 (5)	0.3057 (4)	0.0416 (11)
H1A	1.1595	−0.0585	0.3230	0.050*
N2	1.1523 (11)	0.1643 (5)	0.3992 (4)	0.0412 (11)
H2A	1.2729	0.2054	0.4865	0.049*
C1	0.9992 (15)	0.2395 (6)	0.3352 (6)	0.0493 (15)
H1	1.0047	0.3461	0.3773	0.059*
C2	0.8307 (15)	0.1355 (7)	0.1967 (6)	0.0505 (15)
H2	0.7020	0.1567	0.1277	0.061*
C3	0.8931 (15)	−0.0076 (7)	0.1818 (6)	0.0477 (14)
H3	0.8131	−0.1021	0.0993	0.057*
O1	0.3997 (10)	0.8001 (4)	0.3600 (3)	0.0475 (10)
O2	0.6353 (11)	0.5351 (4)	0.3418 (4)	0.0577 (12)
O3	0.0807 (11)	0.6588 (4)	0.1355 (4)	0.0581 (11)
O4	0.3270 (11)	0.4012 (4)	0.1179 (4)	0.0554 (11)
H4	0.1905	0.4187	0.0612	0.083*
C4	0.2907 (14)	0.6762 (6)	0.2446 (5)	0.0402 (13)
C5	0.4374 (14)	0.5304 (6)	0.2400 (5)	0.0425 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.049 (3)	0.033 (2)	0.041 (2)	0.0045 (19)	−0.0029 (19)	0.019 (2)
N2	0.048 (3)	0.034 (2)	0.031 (2)	0.005 (2)	−0.0023 (19)	0.0087 (19)
C1	0.053 (3)	0.045 (3)	0.056 (4)	0.011 (3)	0.006 (3)	0.029 (3)
C2	0.053 (4)	0.052 (4)	0.048 (3)	0.010 (3)	−0.002 (3)	0.027 (3)
C3	0.047 (3)	0.042 (3)	0.041 (3)	0.004 (2)	−0.006 (2)	0.011 (3)
O1	0.062 (2)	0.033 (2)	0.037 (2)	0.0087 (17)	−0.0074 (17)	0.0110 (18)
O2	0.076 (3)	0.043 (2)	0.045 (2)	0.0122 (19)	−0.0127 (19)	0.018 (2)
O3	0.077 (3)	0.042 (2)	0.044 (2)	0.0123 (19)	−0.0126 (19)	0.0155 (19)
O4	0.075 (3)	0.032 (2)	0.045 (2)	0.0098 (19)	−0.0082 (19)	0.0113 (19)
C4	0.047 (3)	0.032 (3)	0.035 (3)	0.005 (2)	0.005 (2)	0.011 (2)
C5	0.050 (3)	0.033 (3)	0.039 (3)	0.003 (2)	0.004 (3)	0.013 (3)

Geometric parameters (Å, º)

N1—C3	1.325 (6)	C2—H2	0.9300
N1—N2	1.333 (5)	C3—H3	0.9300
N1—H1A	0.8601	O1—C4	1.256 (6)
N2—C1	1.319 (6)	O2—C5	1.202 (6)
N2—H2A	0.8600	O3—C4	1.239 (6)
C1—C2	1.372 (7)	O4—C5	1.317 (6)
C1—H1	0.9300	O4—H4	0.8200
C2—C3	1.380 (8)	C4—C5	1.549 (7)
C3—N1—N2	109.3 (4)	C3—C2—H2	127.4
C3—N1—H1A	125.3	N1—C3—C2	108.0 (5)
N2—N1—H1A	125.4	N1—C3—H3	126.0
C1—N2—N1	108.4 (4)	C2—C3—H3	126.0
C1—N2—H2A	125.8	C5—O4—H4	109.5
N1—N2—H2A	125.8	O3—C4—O1	127.0 (5)
N2—C1—C2	109.1 (5)	O3—C4—C5	117.3 (4)
N2—C1—H1	125.4	O1—C4—C5	115.7 (4)
C2—C1—H1	125.4	O2—C5—O4	122.4 (5)
C1—C2—C3	105.2 (5)	O2—C5—C4	122.1 (5)
C1—C2—H2	127.4	O4—C5—C4	115.4 (4)
C3—N1—N2—C1	0.1 (6)	O3—C4—C5—O2	−178.2 (5)
N1—N2—C1—C2	0.0 (6)	O1—C4—C5—O2	1.9 (8)
N2—C1—C2—C3	0.0 (6)	O3—C4—C5—O4	1.0 (7)
N2—N1—C3—C2	−0.1 (6)	O1—C4—C5—O4	−178.9 (4)
C1—C2—C3—N1	0.1 (6)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{i}	0.86	1.86	2.709 (5)	170

N2—H2*A*···O1^{ii}	0.86	1.92	2.715 (5)	153
O4—H4···O3^{iii}	0.82	1.95	2.679 (5)	147

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