Oxalic acid–pyridine-4-carbonitrile (1/2)

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In the title compound, $2C_6H_4N_2 \cdot C_2H_2O_4$, the oxalic acid molecule lies about an inversion center. The pyridine ring of the pyridine-4-carbonitrile molecule is almost planar, the largest deviation from the least-squares plane being 0.006 (1) Å; the nitrile N atom deviates from this plane by 0.114 (1) Å. In the crystal, the oxalic acid molecules and the pyridine-4-carbonitrile molecules form stacks. Neighboring molecules within the stacks are related by translation in the a direction, with interplanar distances of 3.183 (1) and 3.331 (2) Å, respectively. Each oxalic acid molecule forms strong O—H⋯N hydrogen bonds with two molecules of pyridine-4-carbonitrile. Besides this, there are also weak C—H⋯O interactions.

Related literature

For the structures and ferroelectric properties of related compounds, see: Fu *et al.* (2011*a*,*b*,*c*); Dai & Chen (2011); Xu *et al.* (2011); Zheng (2011). For standard bond lengths, see: Allen *et al.* (1987).
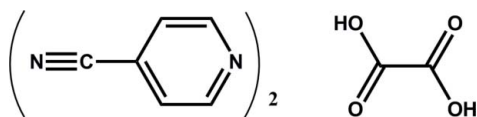
Experimental

Crystal data

$C_6H_4N_2 \cdot 0.5C_2H_2O_4$
$M_r = 149.13$
Triclinic, $P\bar{1}$
$a = 3.6842$ (6) Å
$b = 7.5816$ (5) Å
$c = 12.4511$ (1) Å
$\alpha = 78.258$ (1)°
$\beta = 85.301$ (1)°
$\gamma = 82.547$ (1)°
$V = 337.08$ (6) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 298$ K
$0.10 \times 0.03 \times 0.03$ mm

Data collection

Rigaku SCXmini Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.910$, $T_{max} = 1.000$
3634 measured reflections
1528 independent reflections
1268 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.101$
$S = 1.04$
1528 reflections
103 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯N1	0.82 (1)	1.80 (1)	2.6173 (12)	176 (2)
C4—H4A⋯O1^i	0.93	2.48	3.3640 (13)	160

Symmetry code: (i) $x, y + 1, z$.

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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

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supplementary materials

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Comment

Simple organic salts containing strong intermolecular H-bonds have attracted an attention as materials which display ferroelectric-paraelectric phase transitions (Fu *et al.*, 2011*a*,*b*,*c*). With the purpose of obtaining crystals of organic salts exhibiting ferroelectric phase transitions, various organic compounds have been studied and the series of new materials have been elaborated (Dai & Chen, 2011; Xu *et al.*, 2011; Zheng, 2011). Herewith we present the synthesis and crystal structure of the title molecular complex, pyridine-4-carbonitrile–oxalic acid (2/1).

All bond lengths and angles in the studied structure have expected values (Allen *et al.*, 1987). The dihedral angle between the pyridine ring and the oxalic acid molecule is 10.29 (8)°. The H atoms of oxalic acid are involved in strong intramolecular O—H···N hydrogen bonds (Fig. 1 and Table 1), with the O···N distance of 2.617 (3)Å. The weak intermolecular C—H···O interaction is also presented in this structure, with C4···O1 = 3.364 (2)Å. The crystal packing is further stabilized by the π···π interactions between the pyridine rings of the neighbouring pyridine-4-carbonitrile molecules (Fig. 2).

Experimental

The oxalic acid (10 mmol), pyridine-4-carbonitrile (20 mmol) and ethanol (50 mL) were put into a 100mL flask. The mixture was stirred at 60°C for 2 h, and then the precipitate was filtered off. Colourless crystals suitable for X-ray diffraction were obtained by slow evaporation of the solution.

Refinement

All the H atoms attached to C atoms were placed into the idealized positions and treated as riding with C—H = 0.93 Å and with U_{iso}(H)=1.2U_{eq}(C). The positional parameters of the H atom attached to oxygen were refined freely, and at the last stage of the refinement, they were restrained with the H—O = 0.82 (2)Å and with 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).
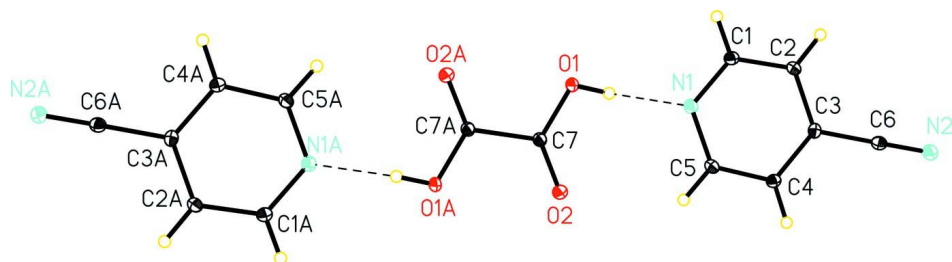
Figure 1

A view of the (2/1) molecular complex with the atomic numbering scheme. The displacement ellipsoids were drawn at the 30% probability level.

Cg is the centroide
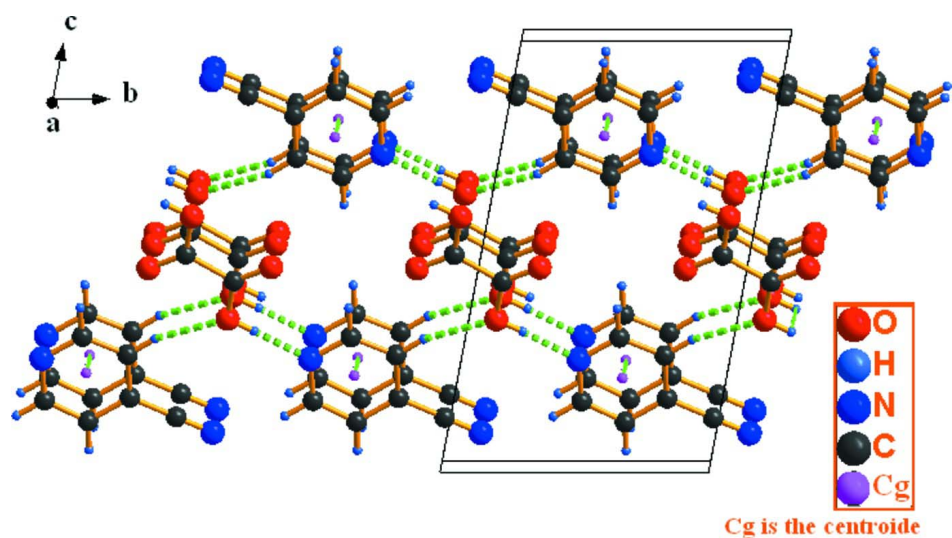
Figure 2

The crystal packing of the title compound viewed along the *a* axis and showing the O—H···N, π···π and C—H···O interactions.

Oxalic acid–pyridine-4-carbonitrile (1/2)

Crystal data

$C_6H_4N_2 \cdot 0.5C_2H_2O_4$	$Z = 2$
$M_r = 149.13$	$F(000) = 154$
Triclinic, $P\overline{1}$	$D_x = 1.469$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 3.6842$ (6) Å	Cell parameters from 1528 reflections
$b = 7.5816$ (5) Å	$\theta = 2.9$–$27.5°$
$c = 12.4511$ (1) Å	$\mu = 0.11$ mm^{-1}
$\alpha = 78.258$ (1)°	$T = 298$ K
$\beta = 85.301$ (1)°	Block, colourless
$\gamma = 82.547$ (1)°	$0.10 \times 0.03 \times 0.03$ mm
$V = 337.08$ (6) Å^3	

Data collection

Rigaku SCXmini Mercury2 diffractometer	Graphite monochromator
Radiation source: fine-focus sealed tube	Detector resolution: 13.6612 pixels mm^{-1}
	ω scans CCD profile fitting

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.910$, $T_{max} = 1.000$
3634 measured reflections
1528 independent reflections
1268 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.9°$
$h = -4\rightarrow4$
$k = -9\rightarrow9$
$l = -16\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.101$
$S = 1.04$
1528 reflections
103 parameters
1 restraint
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.8019 (2)	0.10266 (10)	0.37597 (6)	0.0195 (2)
H1	0.753 (4)	0.2095 (6)	0.3465 (11)	0.029*
O2	1.0250 (2)	0.22804 (10)	0.50208 (6)	0.0196 (2)
N1	0.6137 (3)	0.43796 (12)	0.27800 (8)	0.0157 (2)
N2	0.1419 (3)	1.12502 (13)	0.09513 (8)	0.0207 (2)
C4	0.5310 (3)	0.75440 (15)	0.28546 (9)	0.0147 (3)
H4A	0.5545	0.8461	0.3231	0.018*
C1	0.4759 (3)	0.47781 (15)	0.17793 (9)	0.0158 (3)
H1A	0.4592	0.3835	0.1417	0.019*
C3	0.3848 (3)	0.79346 (14)	0.18234 (9)	0.0141 (3)
C5	0.6404 (3)	0.57355 (15)	0.33014 (9)	0.0152 (3)
H5A	0.7362	0.5455	0.3992	0.018*
C2	0.3578 (3)	0.65365 (14)	0.12654 (9)	0.0150 (3)
H2A	0.2638	0.6777	0.0573	0.018*
C6	0.2532 (3)	0.97886 (14)	0.13355 (9)	0.0161 (3)
C7	0.9557 (3)	0.09891 (14)	0.46785 (8)	0.0140 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0299 (5)	0.0114 (4)	0.0174 (4)	−0.0004 (3)	−0.0102 (4)	−0.0010 (3)
O2	0.0269 (5)	0.0140 (4)	0.0189 (4)	−0.0026 (3)	−0.0066 (3)	−0.0033 (3)
N1	0.0164 (5)	0.0147 (5)	0.0158 (5)	−0.0021 (4)	−0.0022 (4)	−0.0020 (4)
N2	0.0244 (6)	0.0171 (5)	0.0210 (5)	−0.0016 (4)	−0.0067 (4)	−0.0029 (4)
C4	0.0142 (5)	0.0151 (5)	0.0159 (5)	−0.0027 (4)	−0.0002 (4)	−0.0049 (4)
C1	0.0169 (6)	0.0153 (5)	0.0164 (5)	−0.0030 (4)	−0.0017 (4)	−0.0048 (4)
C3	0.0118 (5)	0.0130 (5)	0.0167 (5)	−0.0018 (4)	−0.0004 (4)	−0.0011 (4)
C5	0.0157 (5)	0.0169 (6)	0.0131 (5)	−0.0027 (4)	−0.0025 (4)	−0.0019 (4)
C2	0.0156 (6)	0.0169 (6)	0.0126 (5)	−0.0025 (4)	−0.0023 (4)	−0.0024 (4)
C6	0.0162 (6)	0.0177 (6)	0.0155 (5)	−0.0043 (4)	−0.0014 (4)	−0.0042 (4)
C7	0.0144 (5)	0.0143 (5)	0.0131 (5)	−0.0010 (4)	−0.0012 (4)	−0.0024 (4)

Geometric parameters (Å, º)

O1—C7	1.3113 (12)	C4—H4A	0.9300
O1—H1	0.822 (2)	C1—C2	1.3871 (15)
O2—C7	1.2075 (13)	C1—H1A	0.9300
N1—C5	1.3403 (14)	C3—C2	1.3981 (15)
N1—C1	1.3462 (13)	C3—C6	1.4505 (14)
N2—C6	1.1503 (14)	C5—H5A	0.9300
C4—C5	1.3910 (15)	C2—H2A	0.9300
C4—C3	1.3940 (14)	C7—C7^i	1.557 (2)
C7—O1—H1	107.8 (11)	N1—C5—C4	122.85 (10)
C5—N1—C1	118.83 (9)	N1—C5—H5A	118.6
C5—C4—C3	117.70 (10)	C4—C5—H5A	118.6
C5—C4—H4A	121.1	C1—C2—C3	117.75 (10)
C3—C4—H4A	121.1	C1—C2—H2A	121.1
N1—C1—C2	122.74 (10)	C3—C2—H2A	121.1
N1—C1—H1A	118.6	N2—C6—C3	178.67 (12)
C2—C1—H1A	118.6	O2—C7—O1	126.63 (10)
C4—C3—C2	120.13 (10)	O2—C7—C7^i	121.93 (12)
C4—C3—C6	120.12 (9)	O1—C7—C7^i	111.44 (11)
C2—C3—C6	119.74 (10)		

Symmetry code: (i) −x+2, −y, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82 (1)	1.80 (1)	2.6173 (12)	176 (2)
C4—H4A···O1^{ii}	0.93	2.48	3.3640 (13)	160

Symmetry code: (ii) x, y+1, z.