

4-Acetylpyridine–fumaric acid (2/1)

Kan Xu,^a Bing-Yu Zhang,^b Jing-Jing Nie^b and Duan-Jun Xu^{b*}^aDepartment of Orthopaedics, Second Affiliated Hospital, School of Medicine, Zhejiang University, People's Republic of China, and ^bDepartment of Chemistry, Zhejiang University, People's Republic of China
Correspondence e-mail: xudj@mail.hz.zj.cn

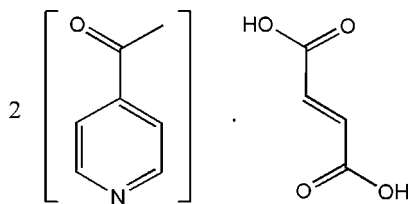
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.040; wR factor = 0.143; data-to-parameter ratio = 12.8.

In the crystal structure of the title cocrystal, $2\text{C}_7\text{H}_7\text{NO} \cdot \text{C}_4\text{H}_4\text{O}_4$, the complete fumaric acid molecule is generated by a crystallographic inversion centre. The two components of the cocrystal are linked by an $\text{O}-\text{H} \cdots \text{N}$ hydrogen bond.

Related literature

For biological and medicinal applications of 4-acetylpyridine and fumaric acid, see: Fidler *et al.* (2003); Thomas *et al.* (2007). For molecular complexes of neutral pyridine derivatives and neutral fumaric acid, see: Bowes *et al.* (2003); Aakeroy *et al.* (2002, 2006, 2007); Haynes *et al.* (2006); Bu *et al.* (2007). For literature on C–O bond distances in fumaric acid, see: Liu *et al.* (2003). For metal complexes of 4-acetylpyridine, see: Steffen & Palenik (1977); Pang *et al.* (1994). For a 4-acetylpyridinium salt, see: Kochel (2005).



Experimental

Crystal data

$2\text{C}_7\text{H}_7\text{NO} \cdot \text{C}_4\text{H}_4\text{O}_4$
 $M_r = 358.34$
 Triclinic, $P\bar{1}$
 $a = 3.9062$ (5) Å
 $b = 8.6809$ (13) Å
 $c = 13.0909$ (18) Å
 $\alpha = 87.925$ (4)°
 $\beta = 89.941$ (3)°

$\gamma = 83.141$ (4)°
 $V = 440.44$ (11) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 294$ K
 $0.30 \times 0.11 \times 0.08$ mm

Data collection

Rigaku R-AXIS RAPID IP
 diffractometer
 Absorption correction: none
 3600 measured reflections

1589 independent reflections
 798 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.143$
 $S = 1.18$
 1589 reflections
 124 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O3}-\text{H3A} \cdots \text{N1}$	0.98 (4)	1.64 (4)	2.599 (3)	166 (4)

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2588).

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supplementary materials

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4-Acetylpyridine-fumaric acid (2/1)

K. Xu, B.-Y. Zhang, J.-J. Nie and D.-J. Xu

Comment

The fumaric acid and acetylpyridine have been widely used in the biological and medicine fields (Thomas *et al.* 2007; Fidler *et al.* 2003). In the medicine composition the carboxyl group of the fumaric acid is usually deprotonated while the pyridine derivatives are protonated. But some crystal structure determinations showed the neutral pyridine derivatives and fumaric acid in the crystal structures, *i.e.* the pyridine derivatives are not protonated while the fumaric acid is also not deprotonated in these crystal structures (Bowes *et al.* 2003; Aakeroy *et al.*, 2002, 2006, 2007; Haynes *et al.* 2006; Bu *et al.* 2007). Herein we report the crystal structure of the new compound containing pyridine derivative and fumaric acid components.

The crystal structure of the title compound consists of fumaric acid and 4-acetylpyridine molecules (Fig. 1). The planar fumaric acid molecule is centrosymmetric with the mid-point of the C=C double bond located at an inversion center. The C8—O2 bond distance of 1.204 (3) Å is much shorter than the C8—O3 bond distance of 1.297 (3) Å, it suggests that the carboxyl group is not deprotonated in the crystal structure (Liu *et al.* 2003).

The acetylpyridine molecule is not protonated in the crystal structure, which contrasts with that found in the crystal structure of the 4-acetylpyridinium chloride (Kochel, 2005). The geometry data of the acetylpyridine is consistent with those found in metal complexes of acetylpyridine (Steffen & Palenik, 1977; Pang *et al.*, 1994). The planar acetylpyridine molecule is twisted to the fumaric acid with a dihedral angle of 25.97 (11)° in the crystal structure.

The intermolecular classic O—H···N hydrogen bonding and weak C—H···O hydrogen bonding help to stabilize the crystal structure (Table 1).

Experimental

Reagents and solvent were used as purchased without further purification. 4-Acetylpyridine (2 mmol) and fumaric acid (1 mmol) were dissolved in water–ethanol (6 ml, 1:5) at room temperature. The single crystals were obtained from the solution after 3 d.

Refinement

The carboxyl H atom was located in a difference Fourier map and refined isotropically. Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and the torsion angle was refined to fit the electron density, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Other H atoms were placed in calculated positions with C—H = 0.93 Å and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

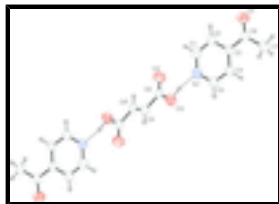


Fig. 1. The molecular structure of the title compound with 40% probability displacement (arbitrary spheres for H atoms). Dashed lines indicate hydrogen bonding.

4-Acetylpyridine–fumaric acid (2/1)

Crystal data

$2C_7H_7NO \cdot C_4H_4O_4$

$M_r = 358.34$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 3.9062$ (5) Å

$b = 8.6809$ (13) Å

$c = 13.0909$ (18) Å

$\alpha = 87.925$ (4)°

$\beta = 89.941$ (3)°

$\gamma = 83.141$ (4)°

$V = 440.44$ (11) Å³

$Z = 1$

$F_{000} = 188$

$D_x = 1.351$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2308 reflections

$\theta = 3.2$ – 24.6 °

$\mu = 0.10$ mm⁻¹

$T = 294$ K

Needle, colourless

$0.30 \times 0.11 \times 0.08$ mm

Data collection

Rigaku R-Axis RAPID IP
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294$ K

ω scans

Absorption correction: none

3600 measured reflections

1589 independent reflections

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

$R_{int} = 0.030$

$\theta_{max} = 25.2$ °

$\theta_{min} = 3.1$ °

$h = -4 \rightarrow 4$

$k = -10 \rightarrow 10$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.143$

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.048P]$$

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

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

$S = 1.18$ $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
 1589 reflections $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
 124 parameters Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.032 (8)
 Secondary atom site location: difference Fourier map

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	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.4491 (6)	0.4588 (3)	0.69775 (18)	0.0630 (7)
O1	0.8832 (6)	0.7499 (3)	0.98158 (16)	0.0900 (8)
O2	0.1660 (6)	0.1037 (2)	0.67034 (15)	0.0775 (7)
O3	0.2584 (6)	0.2870 (3)	0.55473 (16)	0.0764 (7)
C1	0.5832 (8)	0.4178 (4)	0.7899 (2)	0.0733 (9)
H1	0.6122	0.3130	0.8097	0.088*
C2	0.6807 (7)	0.5230 (3)	0.8573 (2)	0.0651 (9)
H2	0.7765	0.4894	0.9204	0.078*
C3	0.6342 (6)	0.6786 (3)	0.82954 (19)	0.0494 (7)
C4	0.4891 (6)	0.7228 (3)	0.73526 (19)	0.0546 (7)
H4	0.4508	0.8270	0.7145	0.065*
C5	0.4019 (7)	0.6088 (4)	0.6724 (2)	0.0612 (8)
H5	0.3048	0.6391	0.6089	0.073*
C6	0.7453 (7)	0.7954 (3)	0.9018 (2)	0.0562 (8)
C7	0.6902 (7)	0.9624 (3)	0.8712 (2)	0.0653 (9)
H7A	0.7914	1.0212	0.9215	0.098*
H7B	0.4474	0.9961	0.8664	0.098*
H7C	0.7961	0.9784	0.8061	0.098*
C8	0.1658 (7)	0.1535 (3)	0.5833 (2)	0.0539 (7)
C9	0.0643 (7)	0.0651 (3)	0.4951 (2)	0.0561 (8)
H9	0.0951	0.1057	0.4295	0.067*
H3A	0.335 (9)	0.337 (5)	0.615 (3)	0.131 (14)*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0771 (16)	0.0500 (17)	0.0641 (16)	-0.0142 (12)	-0.0009 (13)	-0.0083 (13)
O1	0.1244 (18)	0.0731 (17)	0.0703 (14)	-0.0004 (13)	-0.0407 (14)	-0.0077 (12)
O2	0.1167 (18)	0.0640 (15)	0.0548 (13)	-0.0234 (12)	-0.0138 (12)	0.0004 (11)
O3	0.1198 (18)	0.0541 (15)	0.0607 (13)	-0.0313 (13)	-0.0048 (12)	-0.0076 (11)
C1	0.096 (2)	0.046 (2)	0.077 (2)	-0.0096 (17)	-0.0064 (19)	0.0019 (17)
C2	0.082 (2)	0.052 (2)	0.0610 (19)	-0.0053 (15)	-0.0123 (16)	0.0030 (15)
C3	0.0523 (15)	0.0448 (18)	0.0513 (16)	-0.0058 (12)	-0.0004 (13)	-0.0030 (13)
C4	0.0682 (17)	0.0451 (17)	0.0512 (16)	-0.0100 (13)	-0.0046 (14)	-0.0014 (13)
C5	0.0704 (18)	0.057 (2)	0.0566 (18)	-0.0100 (15)	-0.0086 (15)	-0.0024 (15)
C6	0.0577 (16)	0.057 (2)	0.0541 (18)	-0.0048 (13)	-0.0047 (14)	-0.0051 (14)
C7	0.0738 (19)	0.054 (2)	0.070 (2)	-0.0163 (15)	-0.0083 (16)	-0.0077 (16)
C8	0.0604 (16)	0.0446 (18)	0.0567 (18)	-0.0048 (13)	-0.0084 (14)	-0.0063 (14)
C9	0.0680 (17)	0.0469 (18)	0.0534 (16)	-0.0063 (13)	-0.0072 (14)	-0.0016 (14)

Geometric parameters (\AA , $^\circ$)

N1—C5	1.323 (4)	C3—C6	1.512 (4)
N1—C1	1.335 (4)	C4—C5	1.383 (4)
O1—C6	1.207 (3)	C4—H4	0.9300
O2—C8	1.204 (3)	C5—H5	0.9300
O3—C8	1.297 (3)	C6—C7	1.481 (4)
O3—H3A	0.97 (4)	C7—H7A	0.9600
C1—C2	1.378 (4)	C7—H7B	0.9600
C1—H1	0.9300	C7—H7C	0.9600
C2—C3	1.377 (4)	C8—C9	1.488 (4)
C2—H2	0.9300	C9—C9 ⁱ	1.293 (5)
C3—C4	1.381 (3)	C9—H9	0.9300
C5—N1—C1	117.3 (3)	C4—C5—H5	118.2
C8—O3—H3A	108 (2)	O1—C6—C7	121.8 (3)
N1—C1—C2	123.2 (3)	O1—C6—C3	119.3 (3)
N1—C1—H1	118.4	C7—C6—C3	118.9 (2)
C2—C1—H1	118.4	C6—C7—H7A	109.5
C3—C2—C1	118.9 (3)	C6—C7—H7B	109.5
C3—C2—H2	120.5	H7A—C7—H7B	109.5
C1—C2—H2	120.5	C6—C7—H7C	109.5
C2—C3—C4	118.4 (2)	H7A—C7—H7C	109.5
C2—C3—C6	119.6 (2)	H7B—C7—H7C	109.5
C4—C3—C6	122.0 (3)	O2—C8—O3	124.8 (3)
C3—C4—C5	118.6 (3)	O2—C8—C9	123.1 (3)
C3—C4—H4	120.7	O3—C8—C9	112.2 (3)
C5—C4—H4	120.7	C9 ⁱ —C9—C8	123.6 (3)
N1—C5—C4	123.5 (3)	C9 ⁱ —C9—H9	118.2
N1—C5—H5	118.2	C8—C9—H9	118.2

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

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>
O3—H3A···N1	0.98 (4)	1.64 (4)	2.599 (3)	166 (4)
C4—H4···O2 ⁱⁱ	0.93	2.57	3.471 (3)	164
C7—H7C···O2 ⁱⁱⁱ	0.96	2.58	3.489 (3)	158

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

Fig. 1

