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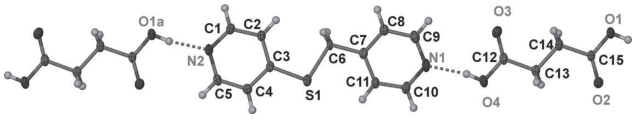
Crystal structure of succinic acid — 4-((pyridin-4-ylmethyl)sulfanylpyridine (1/1), $C_{15}H_{16}N_2O_4S$



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Abstract

$C_{15}H_{16}N_2O_4S$, triclinic, $P\bar{1}$ (no. 2), $a = 7.3024(6)$ Å, $b = 10.7115(7)$ Å, $c = 11.2743(6)$ Å, $\alpha = 109.491(5)°$, $\beta = 100.496(5)°$, $\gamma = 107.860(5)°$, $V = 750.44(9)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0691$, $wR_{ref}(F^2) = 0.2136$, $T = 296$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents obtained from commercial sources were used without further purification. 4-((pyridin-4-ylmethyl)sulfanyl)pyridine was synthesized according to a modified procedure in literature [1]. A mixture of 4-mercaptopyridine (0.56 g, 0.005 mol), 4-(chloromethyl)pyridine hydrochloride (0.82 g, 0.005 mol) and sodium hydroxide (0.6 g, 0.015 mol) were dissolved in methanol (20 mL), the solution was refluxed for 4 h. The methanol was removed under vacuum, the product was extracted with CH_2Cl_2, and then the sovent removed under vacuum. The raw product was further purified by column chromatography on silica gel using CH_2Cl_2/ethyl acetate/methyl alcohol (10:7:5) as eluent. The final product was obtained as yellow powder 0.60 mg (59% yield). 4-((Pyridin-4-ylmethyl)sulfanyl)pyridine (0.20 g, 0.001 mol) and succinic acid (0.12 g, 0.001 mol) were dissolved in acetonitrile (2 mL) and methanol (3 mL). After 4 h, the solution was filtered, the filtrate was left to stand in air for one week to yield yellow block-like crystals of the title complex 0.14 mg (45% yield).

Table 1: Data collection and handling.

Crystal:	Colorless, Block, size 0.30×0.40×0.44 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.36 cm^{-1}
Diffractometer, scan mode:	Bruker Apex II Area Dector, ω scan
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10790, 2947
$N(param)_{refined}$:	199
Programs:	SHELX [8], Diamond [9]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{iso}
H(1B)	2*i*	0.0801	−0.1402	−0.4381	0.109
H(4B)	2*i*	0.3500	0.0738	0.2726	0.117
H(1A)	2*i*	1.0421	0.8725	1.3110	0.069
H(2A)	2*i*	0.8983	0.7118	1.0912	0.063
H(4A)	2*i*	0.7357	0.3949	1.2138	0.065
H(5A)	2*i*	0.8903	0.5647	1.4271	0.067
H(6A)	2*i*	0.6506	0.5621	0.8799	0.047
H(6B)	2*i*	0.8586	0.5477	0.8796	0.047
H(8A)	2*i*	0.7279	0.5291	0.6442	0.075
H(9A)	2*i*	0.5859	0.3719	0.4249	0.082
H(10A)	2*i*	0.3444	0.0553	0.5142	0.079
H(11A)	2*i*	0.4790	0.2009	0.7348	0.072
H(13A)	2*i*	0.2891	−0.1254	−0.0391	0.060
H(13B)	2*i*	0.0739	−0.1245	−0.0427	0.060
H(14A)	2*i*	0.1358	0.0502	−0.1280	0.062
H(14B)	2*i*	0.3515	0.0504	−0.1237	0.062

Experimental details

The U_{iso} values of the hydrogen atoms of carboxyl groups were set to $1.5U_{eq}$(C) and the U_{iso} values of all other hydrogen atons were set to $1.2U_{eq}$(C, N).

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Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	2*i*	0.6824(2)	0.3960(1)	0.9679(1)	0.0963(9)	0.0464(6)	0.0283(6)	0.0163(5)	0.0087(5)	0.0071(4)
N(1)	2*i*	0.4520(5)	0.1980(4)	0.4477(3)	0.073(2)	0.063(2)	0.024(2)	0.015(2)	0.012(2)	0.010(2)
N(2)	2*i*	0.9786(5)	0.7361(3)	1.3892(3)	0.069(2)	0.048(2)	0.026(2)	0.016(2)	0.009(1)	0.011(1)
O(1)	2*i*	0.1284(4)	−0.0738(3)	−0.3638(2)	0.124(2)	0.047(2)	0.025(2)	0.015(2)	0.012(2)	0.011(1)
O(2)	2*i*	0.0612(5)	−0.2531(3)	−0.3013(3)	0.134(3)	0.040(2)	0.037(2)	0.014(2)	0.008(2)	0.012(1)
O(3)	2*i*	0.3669(5)	0.1803(3)	0.1315(3)	0.145(3)	0.044(2)	0.036(2)	0.007(2)	0.018(2)	0.007(1)
O(4)	2*i*	0.3002(5)	0.0059(3)	0.1993(3)	0.128(3)	0.058(2)	0.025(2)	0.015(2)	0.012(2)	0.015(1)
C(1)	2*i*	0.9795(6)	0.7748(4)	1.2907(4)	0.086(3)	0.037(2)	0.030(2)	0.015(2)	0.008(2)	0.006(2)
C(2)	2*i*	0.8928(6)	0.6790(4)	1.1577(4)	0.077(3)	0.043(2)	0.029(2)	0.018(2)	0.012(2)	0.012(2)
C(3)	2*i*	0.7981(5)	0.5339(4)	1.1268(3)	0.050(2)	0.038(2)	0.026(2)	0.014(2)	0.007(2)	0.006(2)
C(4)	2*i*	0.7977(6)	0.4918(4)	1.2308(4)	0.075(3)	0.042(2)	0.035(2)	0.013(2)	0.012(2)	0.016(2)
C(5)	2*i*	0.8894(6)	0.5943(4)	1.3584(4)	0.077(3)	0.056(2)	0.028(2)	0.019(2)	0.015(2)	0.018(2)
C(6)	2*i*	0.7154(5)	0.4943(4)	0.8619(3)	0.053(2)	0.045(2)	0.014(2)	0.022(2)	0.006(1)	0.006(1)
C(7)	2*i*	0.6190(5)	0.3841(4)	0.7170(3)	0.049(2)	0.043(2)	0.029(2)	0.016(2)	0.011(2)	0.008(2)
C(8)	2*i*	0.6498(6)	0.4326(4)	0.6206(4)	0.085(3)	0.047(2)	0.033(2)	0.006(2)	0.010(2)	0.014(2)
C(9)	2*i*	0.5640(6)	0.3369(5)	0.4885(4)	0.092(3)	0.065(3)	0.036(2)	0.014(2)	0.020(2)	0.021(2)
C(10)	2*i*	0.4234(6)	0.1523(4)	0.5406(4)	0.086(3)	0.049(2)	0.029(2)	0.003(2)	0.010(2)	0.005(2)
C(11)	2*i*	0.5031(6)	0.2395(4)	0.6737(4)	0.086(3)	0.048(2)	0.026(2)	0.005(2)	0.014(2)	0.011(2)
C(12)	2*i*	0.3020(5)	0.0547(4)	0.1077(3)	0.059(2)	0.054(3)	0.027(2)	0.014(2)	0.009(2)	0.011(2)
C(13)	2*i*	0.2124(6)	−0.0651(4)	−0.0303(3)	0.064(2)	0.044(2)	0.030(2)	0.013(2)	0.011(2)	0.010(2)
C(14)	2*i*	0.2130(6)	−0.0098(4)	−0.1371(3)	0.070(2)	0.046(2)	0.025(2)	0.017(2)	0.011(2)	0.008(2)
C(15)	2*i*	0.1263(5)	−0.1261(4)	−0.2748(3)	0.065(2)	0.043(2)	0.023(2)	0.015(2)	0.006(2)	0.009(2)

Discussion

Co-crystals, or multicomponent molecular crystals, are crystalline materials comprising at least two different molecular components. They belong to an interdisciplinary field of research that deals with the understanding of non-covalent interactions [2–4]. Interactions between carboxylic acids and pyridyl derivates are extensively used to develop supramolecular assemblies [5–8]. In the asymmetry unit of the title structure, there are one 4-((pyridin-4-ylmethyl)sulfanyl)pyridine and one succinic acid (Figure). Along the *c* axis, 4-((pyridin-4-ylmethyl)sulfanyl)pyridine and succinic acid molecules are connected through O–H···N(py) (D···A 2.616(3)/2.633(2) Å, D—H···A 166/170°) hydrogen bonds (Figure). The dihedral angle of two pyridyl rings is 7.98(5)°. The C(12)—C(13)—C(14)—C(15) torsion angle of succinic acid is 179.6(3), and the C3—S1—C6—C7 angle equals 180.0(2)°. Consequently, a well-defined chain along the *c* axis is formed. Further structural analysis reveals that, the formed parallel chains are interconnected through π···π interactions (centroid···centroid distance = 3.971(3) Å, 4.011(2) Å) to form a layer-like structure.

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References

1. Grassetti, D. R.; Brokke, M. E.; Murray Jr, J. F.: The effect of some sulfur-containing pyridine derivatives on the carbohydrate metabolism of ehrlich ascites tumor. J. Med. Chem. **8** (1965) 753–756.
2. Aakery, C. B.; Seddon, K. R.: The hydrogen bond and crystal engineering. Chem. Soc. Rev. **22** (1993) 397–407.
3. Kole, G. K.; Tan, G. K.; Vittal, J. J.: Crystal engineering studies on the salts of *trans*-4,4′-stilbenedicarboxylic acid in the context of solid state [2 + 2] cycloaddition reaction. CrystEngComm. **13** (2011) 3138–3145.
4. Srirambhatla, V. K.; Kraft, A.; Watt, S.; Powell, A. V.: Crystal design approaches for the synthesis of paracetamol co-crystals. Cryst. Growth Des. **12** (2012) 4870–4879.
5. Chatterjee, S.; Pedireddi, V. R.; Rao, C. N. R.: Unexpected isomerization of maleic acid to fumaric acid on co-crystallization with 4,4′-bipyridine. Tetrahedron Lett. **39** (1998) 2843–2846.
6. Edwards, S. H.; Kahwa, I. A.; Mague, J. T.: Ethylenedi ammonium phthalate. Acta crystallogr. **E57** (2000) o20–o21.
7. Almarsson, O.; Zaworotko, M. J.: Crystal engineering of the composition of pharmaceutical phases. Do pharmaceutical co-crystals represent a new path to improved medicines? Chem. Commun. **17** (2004) 1889–1896.
8. Oliveira, M. A.; Peterson. M. L.; Klein, D.: Continuously substituted solid solutions of organic co-crystals. Cryst. Growth Des. **8** (2008) 4487–4493.
9. Sheldrick, G. M.: SHELXTL 5.1 for Windows NT, Structure Determination Software Programs, Bruker Analytical X-ray Systems, Madison, WI, 2014.
10. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2i. Crystal Impact, Bonn, Germany 2012.