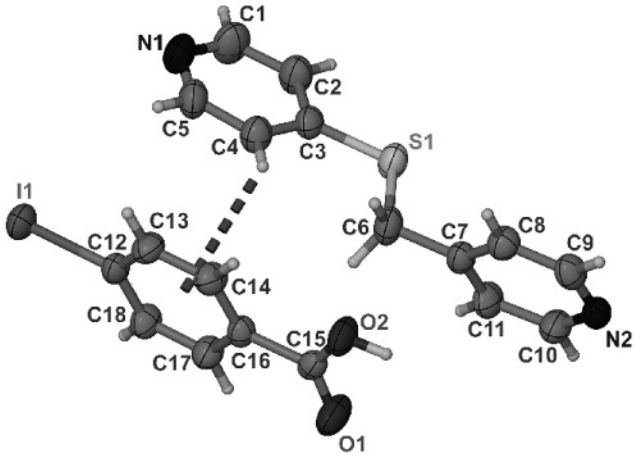
Crystal structure of 4-iodobenzoic acid — 4-((pyridin-4-yl)methylthio)-pyridine (1:1), $C_{18}H_{15}IN_2O_2S$

Hong Qiang*, Shu-Jie Tu and Yong-Li Yang

Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China

Received November 18, 2013, accepted March 17, 2014, available online April 22, 2014, CCDC no. 1267/4075



Abstract

$C_{18}H_{15}IN_2O_2S$, monoclinic, $P2_1/c$ (no. 14), a = 21.078(3) Å, b = 10.537(2) Å, c = 7.938(1) Å, β = 94.46(1)°, V = 1757.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.0344, $wR_{ref}(F^2)$ = 0.0846, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.15×0.20×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.53 cm^{-1}
Diffractometer, scan mode:	Bruker APEXII CCD, φ and ω
$2\theta_{max}$:	55.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17665, 4196
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3145
$N(param)_{refined}$:	221
Programs:	SHELX [7]

Source of material

All reagents and solvents from purchased commercial sources were used without further purification. 4-((pyridin-4-yl)-methylthio)pyridine was synthesized according to a modified procedure already reported [1]. At room temperature, 4-((pyridin-4-yl)methylthio)pyridine (20 mg, 0.1mmol) and 4-iodobenzoic acid (25 mg, 0.1 mmol) were added to a mixed solvent of acetonitrile (2ml) and methanol (3ml) with stirring to afford a clear solution. After 4 h, the solution was filtered and the clear solution was left to slowly evaporate in air to give colourless flaky-like crystals of the title compound suitable for X-ray diffraction (45% yield, based on iodobenzoic acid).

Experimental details

All hydrogen atoms were identified in difference Fourier synthesis. The H atom bonded to the O atom was refined with the O–H distance restrained to 0.9 Å. H atoms bonded to C atoms were positioned geometrically and allowed to ride on their parent atoms, with d(C–H) = 0.93 Å and U_{iso} (H) = 1.2 U_{eq} (C). To get precise intensities for the mass of weak superstructure reflections the exposure time had to be extended, accepting the overexposure of some very strong reflections.

Discussion

Recently, co-crystallization has become a hot topic and has achieved considerable development in the field of crystal engineering [2, 3]. Weak interactions (hydrogen bond, $\pi\cdots\pi$ or C–H$\cdots\pi$ interactions) often dominates co-crystals and hence are important in exploring novel structures in crystal growth and supramolecular assemblies [4-6]. Herein, we reported a new co-crystal structure of 4-iodobenzoic acid and 4-((pyridin-4-yl)-methylthio)pyridine (Figure). X-ray diffraction analysis reveals that the C3–S1–C6–C7 torsion angle of 176.5(3)° in the title structure indicating the conformation of the 4-((pyridin-4-yl)-methylthio)pyridine molecule is a linear type. The dihedral angle between the two pyridine rings is 63.26(2)°, while the 4-iodobenzoic acid molecule links to the N1–C1–C2–C3–C4–C5 ring via a C–H$\cdots\pi$ interaction with H4$\cdots$centroid distance of 3.110(3) Å and C4–H4$\cdots$centroid angle of 131.10(3)°. Finally, a 2D supramolecular aggegration of the title compound is furnished through a set of hydrogen bonds, i.e. O2–H2$\cdots$N2^{i} with the D$\cdots$A distance of 2.644(2) Å and D–H$\cdots$A angle of 175.6(2)°. Symmetry code i: $-x$, $-y$+1, $-z$+1.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.4575	0.7537	0.5489	0.082
H(2A)	4*e*	0.3559	0.7990	0.4526	0.067
H(4A)	4*e*	0.3007	0.4826	0.6781	0.057
H(5A)	4*e*	0.4055	0.4447	0.7608	0.064
H(6B)	4*e*	0.2002	0.4879	0.5396	0.060
H(6A)	4*e*	0.1906	0.5814	0.6905	0.060
H(8A)	4*e*	0.1095	0.4453	0.3480	0.054
H(9A)	4*e*	0.0090	0.4942	0.2359	0.057
H(10A)	4*e*	0.0081	0.8074	0.4939	0.058
H(11A)	4*e*	0.1087	0.7676	0.6146	0.059
H(13A)	4*e*	0.3343	0.2303	0.9465	0.054
H(14A)	4*e*	0.2298	0.2286	0.8400	0.053
H(17A)	4*e*	0.1956	0.5362	1.1142	0.052
H(18A)	4*e*	0.3010	0.5429	1.2133	0.052
H(2)	4*e*	0.079(1)	0.315(4)	0.731(5)	0.07(1)

* Correspondence author (e-mail: qhcnuchem@126.com)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.23856(4)	0.68876(8)	0.4770(1)	0.0355(4)	0.0551(4)	0.0529(5)	0.0015(4)	–0.0032(4)	0.0083(4)
N(1)	4*e*	0.4426(2)	0.5960(3)	0.6656(4)	0.036(2)	0.081(2)	0.065(2)	–0.000(2)	–0.007(1)	0.006(2)
N(2)	4*e*	–0.0011(1)	0.6550(2)	0.3538(3)	0.033(1)	0.056(1)	0.039(2)	–0.002(1)	–0.001(1)	0.003(1)
C(1)	4*e*	0.4256(2)	0.6977(4)	0.5750(5)	0.041(2)	0.083(3)	0.079(3)	–0.014(2)	0.000(2)	0.018(2)
C(2)	4*e*	0.3645(2)	0.7264(3)	0.5171(4)	0.046(2)	0.061(2)	0.059(2)	–0.006(2)	–0.001(2)	0.017(2)
C(3)	4*e*	0.3157(2)	0.6469(3)	0.5550(4)	0.037(2)	0.047(2)	0.038(2)	0.001(1)	–0.004(1)	–0.002(1)
C(4)	4*e*	0.3319(2)	0.5394(3)	0.6492(4)	0.042(2)	0.048(2)	0.051(2)	–0.004(2)	–0.003(2)	0.005(1)
C(5)	4*e*	0.3952(2)	0.5180(3)	0.6995(4)	0.046(2)	0.061(2)	0.051(2)	0.005(2)	–0.009(2)	0.006(2)
C(6)	4*e*	0.1877(2)	0.5733(3)	0.5685(5)	0.036(2)	0.058(2)	0.056(2)	–0.001(1)	–0.007(2)	0.012(2)
C(7)	4*e*	0.1209(2)	0.6011(3)	0.4955(4)	0.033(2)	0.049(2)	0.040(2)	–0.003(1)	–0.001(1)	0.005(1)
C(8)	4*e*	0.0899(2)	0.5196(3)	0.3801(4)	0.041(2)	0.046(2)	0.047(2)	–0.000(1)	0.001(1)	–0.002(1)
C(9)	4*e*	0.0294(2)	0.5498(3)	0.3131(4)	0.045(2)	0.054(2)	0.042(2)	–0.009(2)	–0.003(2)	–0.001(1)
C(10)	4*e*	0.0288(2)	0.7336(3)	0.4645(4)	0.040(2)	0.058(2)	0.046(2)	0.004(2)	0.000(1)	–0.007(1)
C(11)	4*e*	0.0894(2)	0.7103(3)	0.5377(4)	0.041(2)	0.059(2)	0.044(2)	–0.001(2)	–0.008(1)	–0.009(1)
I(1)	4*e*	0.42453(1)	0.39733(2)	1.18445(3)	0.0321(1)	0.0695(2)	0.0522(2)	–0.0009(1)	–0.0045(1)	0.0029(1)
O(1)	4*e*	0.0953(1)	0.4588(2)	0.9518(3)	0.038(1)	0.081(2)	0.072(2)	0.012(1)	–0.009(1)	–0.021(1)
O(2)	4*e*	0.1186(1)	0.3056(2)	0.7773(3)	0.034(1)	0.069(2)	0.060(2)	0.006(1)	–0.011(1)	–0.009(1)
C(12)	4*e*	0.3287(2)	0.3876(3)	1.0897(4)	0.030(2)	0.054(2)	0.038(2)	–0.003(1)	–0.001(1)	0.006(1)
C(13)	4*e*	0.3066(2)	0.2929(3)	0.9787(4)	0.038(2)	0.051(2)	0.046(2)	0.007(1)	0.004(1)	–0.006(1)
C(14)	4*e*	0.2439(1)	0.2913(3)	0.9164(4)	0.041(2)	0.047(2)	0.044(2)	–0.004(1)	0.001(1)	–0.007(1)
C(15)	4*e*	0.1318(1)	0.3842(2)	0.8939(4)	0.032(2)	0.038(1)	0.042(2)	0.000(1)	0.005(1)	0.010(1)
C(16)	4*e*	0.2016(2)	0.3820(2)	0.9658(4)	0.032(2)	0.039(1)	0.038(2)	–0.004(1)	–0.001(1)	0.004(1)
C(17)	4*e*	0.2237(2)	0.4753(3)	1.0788(4)	0.039(2)	0.045(2)	0.047(2)	0.002(1)	0.000(1)	–0.004(1)
C(18)	4*e*	0.2866(1)	0.4789(3)	1.1391(4)	0.039(2)	0.045(2)	0.046(2)	–0.002(1)	–0.004(1)	–0.009(1)

Acknowledgments. This work was supported in part by the Science and Technology program, Beijing Municipal Education Commission.

References

1. Grassetti, D. R., Brokke, M. E., Murray, J. F.: The effect of some sulfur-containing pyridine derivatives on the carbohydrate metabolism of ehrlich ascites tumor. Pyridine Sulfur Compounds and Tumor Metabolism. (1965) 753-756.
2. Aakeröy, C. B.; Forbes, S.; Desper, J.: Using Cocrystals To Systematically Modulate Aqueous Solubility and Melting Behavior of an Anticancer Drug. J. Am. Chem. Soc. **131** (2009) 17048-17049.
3. Bond, A. D.: What is a co-crystal? CrystEngComm. **9** (2007) 833-834.
4. Nath, B.; Baruah, J. B.: Quasi-Isostructural Solvates of Bis(4-hydroxy-3,5-dimethylphenyl)(4-*N*,*N*-dimethylaminophenyl)methane. Cryst. Growth Des. **12** (2012) 6173-6180.
5. Wan, C. Q.; Wang, Z. W.; Wang, G.; Li, A. M.; Jin, Q. H.; Deng, Y. H.; Mak, T. C. W.: Di(4-pyridyl) Sulfoxide as an Angled Building Block for Zigzag-Chain Silver(I) Complexes Stabilized by Supramolecular O=S···π Interactions. Eur. J. Inorg. Chem. (2013) 2591-2600.
6. Wan, C. Q.; Han, J.; Mak, T. C. W.: Intermolecular S···π interactions in crystalline sulfanyl-triazine derivatives. New J. Chem. **33** (2009) 707-712.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.