Redetermination of the monoclinic crystal structure of *N*-(4-hydroxyphenyl)acetamide as seen by neutrons at 10K, C₈H₉NO₂

Shin Ae Kim^{*,I}, Chang-Hee Lee^I, Tae Hyun Kim^{II} and Jae-Hyeon Ko^{II}

^I Neutron Science Division, Korea Atomic Energy Research Institute, Korea

^{II} Department of Physics, Hallym University, Korea

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Experimental details

Refinement in SHELXL97 involved 182 refined parameters with anisotropic displacement parameters for all atoms including the hydrogen. Unfortunately, only 78% completeness has been achieved for a data set up to a diffraction angle of 106°.

Discussion

In this paper, we report the results of a low temperature neutron single-crystal structural analysis of the monoclinic *N*-(4-hydroxyphenyl)acetamide (acetaminophen) with anisotropic displacement parameters for all atoms including the hydrogen. Acetaminophen molecules (Fig., upper part) form hydrogen-bonded zigzag chains parallel to the *c* axis. These chains are interconnected *via* hydrogen bonds along the *a* axis. Consequently, the molecules form a pleated sheet parallel to the *ac* plane (Fig., lower part; O1–H1 = 1.002(9) Å; H1⋯O2' = 1.687(9) Å; O1⋯O2' = 2.665(6) Å; O1–H1⋯O2' = 163.9(8)°; N–H4 = 1.029(7) Å; H4⋯O1'' = 1.906(7) Å; N⋯O1'' = 2.912(4) Å; N–H4⋯O1'' = 164.8(7)°). The sheets are stacked along the *b* axis. Hydrogen atoms of the methyl group show comparatively large thermal ellipsoids even at 10K because they do not have any hydrogen bonding. For crystallization and structure determination of the orthorhombic poly-morph of acetaminophen, see: Nicols & Frampton (1998) [1]. For charge density analyses of monoclinic polymorph from high-resolution X-ray diffraction, see: Bouhmaida et al. (2009) [2]. For single-crystal neutron & X-ray diffraction of related structures, see: Wilson et al. (1997) [3], Naumov et al. (1998) [4], Oswald et al. (2002) [5].

Abstract

C₈H₉NO₂, monoclinic, *P*2₁/*n* (no. 14), *a* = 7.1250(2) Å, *b* = 9.2200(2) Å, *c* = 11.6000(2) Å, β = 98.130(10)°, *V* = 754.4 Å³, *Z* = 4, *R*_g(*F*) = 0.0641, *wR*_{ref}(*F*²) = 0.1442, *T* = 10 K.

Table 1. Data collection and handling.

Crystal:	colourless rectangular plate, size 3.97×3.2×0.6 mm
Wavelength:	neutron radiation (1.3143 Å)
μ:	3.73 cm ^{−1}
Diffractometer, scan mode:	Neutron Four-Circle Diffractometer, θ/2θ
2θ _{max} :	105.98°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	1423, 1103
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 1097
<i>N</i> (<i>param</i>) _{refined} :	182
Programs:	SHELX [6]

Source of material

The single crystals were grown by means of slow evaporation of acetone (purity 99.5%, Merck) solution in which powder of the title compound (purity 99%, Sigma-Aldrich) was dissolved. Data were collected at 10K on a neutron four-circle diffractometer (FCD) in HANARO, Korea.

* Correspondence author (e-mail: sakim@kaeri.re.kr)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(1)	4e	0.1336(4)	0.1683(4)	1.1290(3)	0.008(2)	0.006(2)	0.008(2)	−0.002(1)	0.004(1)	0.003(1)
C(2)	4e	−0.0390(4)	0.1708(4)	1.0532(3)	0.008(2)	0.009(2)	0.004(2)	−0.000(1)	0.001(1)	0.002(1)
C(3)	4e	−0.0605(5)	0.2659(4)	0.9590(3)	0.007(2)	0.008(2)	0.009(2)	−0.002(1)	0.003(1)	0.005(1)
C(4)	4e	0.0876(4)	0.3585(4)	0.9377(3)	0.006(2)	0.006(2)	0.009(2)	0.001(1)	0.003(1)	0.003(1)
C(5)	4e	0.2590(4)	0.3576(4)	1.0150(3)	0.007(2)	0.006(2)	0.005(2)	−0.001(1)	0.001(1)	0.000(1)
C(6)	4e	0.2804(5)	0.2626(4)	1.1097(3)	0.007(2)	0.008(2)	0.005(2)	−0.001(1)	0.001(1)	0.002(1)
C(7)	4e	0.1789(4)	0.5167(3)	0.7803(3)	0.007(1)	0.005(2)	0.006(2)	−0.001(1)	0.003(1)	−0.001(1)
C(8)	4e	0.0928(5)	0.6050(4)	0.6762(3)	0.011(2)	0.009(2)	0.009(2)	0.000(1)	0.003(1)	0.004(1)
O(1)	4e	0.1638(5)	0.0741(4)	1.2220(4)	0.008(2)	0.009(2)	0.007(2)	0.001(2)	−0.001(1)	0.004(2)
O(2)	4e	0.3536(5)	0.5076(4)	0.8090(4)	0.009(2)	0.012(2)	0.003(2)	−0.001(1)	0.004(1)	0.002(2)
N(1)	4e	0.0519(3)	0.4505(3)	0.8391(2)	0.006(1)	0.007(1)	0.009(1)	0.0014(8)	0.0009(9)	−0.001(1)
H(1)	4e	0.043(1)	0.0325(8)	1.2421(8)	0.022(4)	0.018(4)	0.030(5)	−0.003(3)	0.004(3)	0.011(3)
H(2)	4e	−0.153(1)	0.0980(8)	1.0679(8)	0.029(4)	0.020(4)	0.029(5)	−0.012(3)	0.004(3)	0.002(3)
H(3)	4e	−0.195(1)	0.2675(9)	0.8991(8)	0.017(4)	0.036(4)	0.019(4)	−0.002(3)	−0.001(3)	0.003(3)
H(4)	4e	−0.0884(9)	0.4593(8)	0.8036(7)	0.008(3)	0.026(4)	0.013(4)	0.000(2)	−0.001(2)	0.009(3)
H(5)	4e	0.373(1)	0.4308(9)	1.0021(8)	0.017(3)	0.023(4)	0.030(5)	−0.006(3)	0.001(3)	0.010(3)
H(6)	4e	0.413(1)	0.2634(9)	1.1708(7)	0.016(4)	0.030(4)	0.018(4)	−0.003(3)	−0.006(3)	0.006(3)
H(7)	4e	0.107(2)	0.7197(9)	0.697(1)	0.057(6)	0.013(5)	0.040(6)	−0.001(4)	0.000(4)	−0.001(4)
H(8)	4e	−0.054(1)	0.582(1)	0.651(1)	0.013(4)	0.050(5)	0.044(6)	−0.007(3)	−0.006(3)	0.016(4)
H(9)	4e	0.171(1)	0.586(1)	0.6028(8)	0.047(5)	0.047(5)	0.014(5)	0.020(4)	0.015(4)	0.006(4)

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References

1. Nicols, G.; Frampton, C.S.: Physicochemical Characterization of the Orthorhombic Polymorph of Paracetamol Crystallized from Solution. *J. Pharm. Sci.* **87** (1998) 684-693.
2. Bouhmaida, N.; Bonhomme, F.; Guillot, B.; Jelsch, C.; Ghermani, N. E.: Charge density and electrostatic potential analyses in paracetamol. *Acta Crystallogr.* **B65** (2009) 363-374.
3. Wilson, C. C.; Shankland, N.; Florence, A. J.; Frampton, C. S.: Single-crystal neutron diffraction of bio-active small molecules. *Physica B* **234-236** (1997) 84-86.
4. Naumov, D. Y.; Vasilchenko, M. A.; Howard, A. K.: The Monoclinic Form of Acetaminophen at 150K. *Acta Crystallogr.* **C54** (1998) 653-655.
5. Oswald, I. D. H.; Allan, D. R.; McGregor, P. A.; Motherwell, W. D. S.; Parsons, S.; Pulham, C. R.: The formation of paracetamol (acetaminophen) adducts with hydrogen-bond acceptors. *Acta Crystallogr.* **B58** (2002) 1057-1066.
6. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112-122.