Qiong Zhong*

Crystal structure of (Z)-2-((adamantan-1-ylimino) methyl)-5-methoxyphenol, C₁₈H₂₃NO₂

<https://doi.org/10.1515/ncrs-2018-0366>

Received September 11, 2018; accepted November 4, 2018;
available online December 5, 2018

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.25 × 0.18 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	29620, 2654, 0.033
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2322
$N(\text{param})_{\text{refined}}$:	192
Programs:	Bruker [1], SHELX [2]

Abstract

C₁₈H₂₃NO₂, monoclinic, $C2/c$ (no. 15), $a = 21.057(3)$ Å, $b = 6.5535(7)$ Å, $c = 24.069(4)$ Å, $\beta = 113.535(3)^\circ$, $V = 2780.9(5)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0607$, $wR_{\text{ref}}(F^2) = 0.1204$, $T = 293(2)$ K.

CCDC no.: 1876999

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of adamantan-1-amine (1 mmol, 151.3 mg) and 2-hydroxy-4-methoxybenzaldehyde (1 mmol, 152.2 mg) in anhydrous ethanol (20 mL) was stirred under reflux conditions (351 K) for 6 h. The solvent was removed under reduced pressure and the solid product was recrystallized from 10 mL of anhydrous tetrahydrofuran. After 3 days, colourless block-shaped crystals suitable for X-ray diffraction determination were obtained.

Experimental details

The coordinates of hydrogen atoms were refined subject to constraints. The U_{iso} values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for methyl H atoms and hydroxyl H atoms, $1.2U_{\text{eq}}$ for the remaining H atoms.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.48892(15)	0.5745(4)	−0.15414(12)	0.0627(7)
H1A	0.5210	0.5154	−0.1171	0.094*
H1B	0.5079	0.5678	−0.1843	0.094*
H1C	0.4460	0.5004	−0.1679	0.094*
C2	0.44971(10)	0.8208(3)	−0.10197(9)	0.0375(5)
C3	0.43941(10)	0.6755(3)	−0.06556(9)	0.0353(5)
H3	0.4510	0.5402	−0.0685	0.042*
C4	0.41146(10)	0.7312(3)	−0.02391(9)	0.0348(5)
C5	0.39548(10)	0.9381(3)	−0.01887(8)	0.0332(4)
C6	0.40751(12)	1.0810(3)	−0.05650(10)	0.0446(5)
H6	0.3975	1.2176	−0.0533	0.053*
C7	0.43369(13)	1.0254(4)	−0.09811(10)	0.0484(6)
H7	0.4406	1.1225	−0.1233	0.058*
C8	0.36995(10)	1.0006(3)	0.02545(9)	0.0368(5)
H8	0.3606	1.1379	0.0285	0.044*
C9	0.33724(10)	0.9264(3)	0.10965(9)	0.0340(5)
C10	0.30631(13)	1.1401(3)	0.10423(11)	0.0483(6)
H10A	0.2667	1.1533	0.0659	0.058*
H10B	0.3405	1.2412	0.1054	0.058*
C11	0.28369(13)	1.1773(3)	0.15664(11)	0.0499(6)
H11	0.2634	1.3138	0.1527	0.060*
C12	0.23055(13)	1.0195(4)	0.15469(13)	0.0578(7)
H12A	0.1904	1.0299	0.1166	0.069*
H12B	0.2157	1.0440	0.1874	0.069*
C13	0.26174(13)	0.8072(4)	0.16096(12)	0.0554(7)
H13	0.2272	0.7054	0.1599	0.066*
C14	0.28354(12)	0.7698(3)	0.10844(11)	0.0472(6)
H14A	0.3027	0.6337	0.1116	0.057*
H14B	0.2434	0.7793	0.0703	0.057*
C15	0.39999(11)	0.9106(4)	0.16992(10)	0.0469(6)
H15A	0.4346	1.0102	0.1710	0.056*
H15B	0.4204	0.7759	0.1739	0.056*

*Corresponding author: Qiong Zhong, Changsha Environmental Protection College, Changsha 410004, Hunan, P.R. China, e-mail: qiongzhong18@126.com

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C16	0.37811(13)	0.9492(4)	0.22262(10)	0.0556(6)
H16	0.4186	0.9388	0.2612	0.067*
C17	0.32438(16)	0.7909(4)	0.22057(12)	0.0643(8)
H17A	0.3442	0.6553	0.2247	0.077*
H17B	0.3105	0.8130	0.2540	0.077*
C18	0.34668(13)	1.1625(4)	0.21624(11)	0.0557(7)
H18A	0.3332	1.1889	0.2497	0.067*
H18B	0.3807	1.2639	0.2173	0.067*
N1	0.35964(9)	0.8718(3)	0.06104(7)	0.0386(4)
O1	0.47684(9)	0.7805(3)	−0.14397(7)	0.0528(4)
O2	0.40018(10)	0.5877(2)	0.01017(7)	0.0520(4)
H2	0.3847	0.6405	0.0331	0.078*

Comment

In recent years, the use of Schiff bases as one of the important synthetic intermediates have attracted increasingly more attention due to their wide applications in the fields of coordination chemistry, biochemistry, pharmacy, nanotechnology, and photochemistry [3–10]. Schiff bases containing an adamantane group are of particular interest because of their biological and medicinal properties [11–13]. In order to search for new adamantane Schiff bases, we have undertaken the synthesis and single crystal structure determination of the title compound (*cf.* the figure).

In the title compound, the rings in the adamantane moiety have normal chair conformations. The bond lengths and angles are within the expected ranges and in good agreement with the structure of the indium(III) chloride complex with the title compound as a ligand [14]. The C=N double bond length is 1.282(3) Å (C8=N4), clearly exhibiting the double-double bond character. The adamantyl and benzene groups are bridged by an imine group, with a C(5)–C(8)–N(1)–C(9) torsion angle of 176.48(17)°.

In the crystal structure, the molecules are linked into infinite dimeric columns by C–H···O hydrogen bonds. An intramolecular O–H···O hydrogen bond forming a S(6) ring motif according to graph-set notation [15] further consolidates the crystal packing. The room-temperature data shows some evidence of keto-(amine)-enol(-imine) tautomerism, which was not modelled further.

Acknowledgements: This work was financial supported by Changsha Enviromental Protection College.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2008).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Pu, X.: The crystal structure of (*E*)-4-chloro-2-(((5-methylpyridin-2-yl)imino)methyl)phenol, C₁₃H₁₁ClN₂O. *Z. Kristallogr. NCS* **233** (2018) 253–254.
4. Başak, K. K.: The crystal structure of (*E*)-4-(3-ethoxy-2-hydroxybenzylideneamino)-benzoic acid, C₁₆H₁₅NO₄. *Z. Kristallogr. NCS* **233** (2018) 157–158.
5. Liu, C.: Crystal structure of (*E*)-2-(anthracen-9-ylmethylene)hydrazine-1-carbothioamide, C₁₆H₁₃N₃S. *Z. Kristallogr. NCS* **233** (2018) 315–316.
6. Tai, X.-S.; Li, P.-F.: The crystal structure (*E*)-4-methyl-*N'*-(2-nitrobenzylidene)benzenesulfonohydrazide, C₁₄H₁₃N₃O₄S. *Z. Kristallogr. NCS* **232** (2017) 1031–1032.
7. Zhai, X.-R.: (*E*)-2-[1-(3-Chloro-4-fluorophenyl)ethylidene]hydrazinecarbothioamide. *Acta Crystallogr. E* **64** (2011) o76.
8. Kukawska-Tarnawska, B.; Les, A.; Dziembowska, T.; Rozwadowski, Z. J.: Tautomeric forms of *N*-(5-nitrosalicylidene)-2-butylamine: experimental and theoretical DFT study. *J. Mol. Struct.* **928** (2009) 25–31.
9. Krygowski, T. M.; Zachara-Horegland, J. E.; Palusiak, M.; Pelloni, S.; Lazzaretti, P.: Relation between π -electron localization/delocalization and H-bond strength in derivatives of *o*-hydroxy-Schiff bases. *J. Org. Chem.* **73** (2008) 2138–2145.
10. Ren, S.; Tokes, Z. A.; Osipke, C.; Zhou, B.; Yen, Y.; Lien, E. J.: Inhibition of tumor cell growth by Schiff bases of hydroxysemicarbazide. *Anticancer Res.* **21** (2001) 3445–3451.
11. Isik, S.; Köysal, K.; Septioğlu, E.; Calı s, U.: 1-[(2-Chloro-3,4-dimethoxybenzylidene)amino]adamantane. *Acta Crystallogr. E* **61** (2005) o1851–o1852.
12. Zhao, G.-L.; Feng, Y.-L.: Crystal structure of (*N*)-(4-chlorobenzylidene)-1-adamantylamine, C₁₇H₂₀ClN, a *Schiff base*. *Z. Kristallogr. NCS* **220** (2005) 197–198.
13. Jin, X.-D.; Xu, C.; Liu, X.-C.; Yin, X.-Y.; Gang, Y.-C.; Yang, Q.; Jin, Y.-H.: Synthesis, characterization, and crystal structure of two zinc(II) complexes with a Schiff base derived from amantadine. *J. Coord. Chem.* **66** (2013) 3970–3978.
14. Jin, X.-D.; Jin, Y.-H.; Zou, Z.-Y.; Cui, Z.-G.; Wang, H.-B.; Kang, P.-L.; Ge, C.-H.; Li, K.: Synthesis, characterization and antibacterial activity of indium(III) complexes with adamantane-ring containing Schiff bases. *J. Coord. Chem.* **64** (2011) 1533–1543.
15. Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L.: Patterns in hydrogen bonding: functionality and graph set analysis in crystals. *Angew. Chem. Int. Ed.* **34** (1995) 1555–1573.