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Crystal structure of 4-bromo-*N'*-(3-bromo-2-hydroxyphenyl)methylidene]benzohydrazide methanol solvate, $C_{15}H_{14}Br_2N_2O_3$

<https://doi.org/10.1515/ncrs-2020-0540>

Received October 18, 2020; accepted November 12, 2020;

published online December 4, 2020

Abstract

$C_{15}H_{14}Br_2N_2O_3$, triclinic, $P\bar{1}$ (no. 2), $a = 7.2748(3)$ Å, $b = 9.0786(4)$ Å, $c = 12.8613(5)$ Å, $\alpha = 99.458(2)^\circ$, $\beta = 100.401(2)^\circ$, $\gamma = 99.499(2)^\circ$, $V = 807.35(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0253$, $wR_{ref}(F^2) = 0.0673$, $T = 150.0$ K.

CCDC no.: 2039205

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

3-Chloro-2-hydroxybenzaldehyde (0.156 g, 1.0 mmol) and 4-bromobenzohydrazide (0.215 g, 1 mmol) were added to a stirring 30 mL methanol solution and refluxed for 12 h. The mixture was filtered and kept undisturbed at room temperature. The colorless square crystals of title compound were afforded after one week.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.12 × 0.12 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.0 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	15,976, 3303, 0.036
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2746
$N(param)_{refined}$:	202
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Experimental details

The structure was solved and refined with the Olex2 program [2] as an interface together with the SHELXT and SHELXL programs [3, 4]. All H atoms were placed in geometrically idealized positions and refined using a riding model, with C-H = 0.98 (methyl), O-H = 0.84 (phenolic hydroxyl), 0.95 Å (aryl), and with $U_{iso}(H) = 1.2 U_{eq}(C)$ for H atoms on methyl, phenolic hydroxyl and aryl.

Comment

The design and synthesis of supramolecular networks of coordination polymers has been one of the academic frontiers in recent years [5, 6]. As a part of our current research interest in exploring the relationship between molecular structure and physicochemical properties of halogenated Schiff-base compounds [7, 8], in this work, we report a new hydrazone.

X-ray diffraction analysis reveals that the asymmetric unit of the structure contains a planar hydrazone molecule and a methanol molecule, as shown in the figure. The five non-hydrogen conjugated atoms [C(=O)N=N=C] constitute the central chromophore and over all exhibit the *E* configuration. The dihedral angles formed between the central plane and the least-squares planes through the flanking hydroxy- and bromo-phenyl rings are 3.49(6)° and 1.95(7)°, respectively. The co-planar geometry between the central chromophore and hydroxyphenyl ring generates an intra-molecular hydroxy-O-H...N hydrogen bond. [O1-H1...N1:

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	0.10184 (4)	0.49086 (3)	0.77333 (2)	0.04662 (10)
Br2	0.34294 (4)	1.34147 (3)	0.03626 (2)	0.05154 (10)
C1	0.1306 (3)	0.7890 (3)	0.51219 (19)	0.0344 (5)
C2	0.2973 (4)	0.7758 (3)	0.5805 (2)	0.0381 (5)
H2B	0.4176	0.8273	0.5733	0.046*
C3AA	0.4688 (5)	0.6853 (4)	0.2888 (3)	0.0709 (10)
H3AA	0.5272	0.6428	0.2307	0.106*
H3AB	0.3538	0.7194	0.2576	0.106*
H3AC	0.4345	0.6070	0.3299	0.106*
C3	0.2883 (4)	0.6879 (3)	0.6589 (2)	0.0397 (6)
H3	0.4016	0.6791	0.7055	0.048*
C4	0.1129 (4)	0.6138 (3)	0.66817 (19)	0.0365 (5)
C5	−0.0543 (4)	0.6275 (3)	0.6030 (2)	0.0385 (5)
H5	−0.1742	0.5770	0.6116	0.046*
C6	−0.0449 (4)	0.7156 (3)	0.52495 (19)	0.0354 (5)
H6	−0.1590	0.7259	0.4800	0.043*
C7	0.1553 (4)	0.8851 (3)	0.42971 (19)	0.0342 (5)
C8	−0.1239 (3)	1.0016 (3)	0.22009 (18)	0.0340 (5)
H8	−0.2486	0.9570	0.2254	0.041*
C9	−0.0972 (4)	1.0896 (3)	0.13783 (19)	0.0343 (5)
C10	0.0854 (3)	1.1611 (3)	0.12888 (19)	0.0355 (5)
C11	0.0982 (4)	1.2425 (3)	0.0477 (2)	0.0377 (5)
C12	−0.0614 (4)	1.2551 (3)	−0.0248 (2)	0.0434 (6)
H12	−0.0481	1.3104	−0.0805	0.052*
C13	−0.2398 (4)	1.1867 (3)	−0.0154 (2)	0.0446 (6)
H13	−0.3503	1.1949	−0.0644	0.054*
C14	−0.2570 (4)	1.1065 (3)	0.0655 (2)	0.0393 (6)
H14	−0.3806	1.0614	0.0723	0.047*
N1	0.0224 (3)	0.9845 (2)	0.28554 (15)	0.0335 (4)
N2	−0.0056 (3)	0.9018 (2)	0.36357 (15)	0.0332 (4)
H2A	−0.1204	0.8620	0.3705	0.040*
O1	0.3128 (3)	0.9463 (2)	0.42131 (15)	0.0433 (4)
O2	0.2476 (2)	1.1526 (2)	0.19744 (14)	0.0404 (4)
H2	0.2191	1.1033	0.2441	0.061*
O3	0.5985 (3)	0.8092 (2)	0.35738 (16)	0.0491 (5)
H3A	0.5388	0.8665	0.3902	0.074*

O1–H1 = 0.840(19) Å, H1⋯N1 = 1.857(2) Å, O1⋯N1 = 2.59(3) Å with an angle at H1 = 144.92(13)°.

As shown in the figure, the oxygen atom (O1) at the carbonyl group accepts a hydrogen bond (H3A–O3) from the methanol molecule [O3–H3A⋯O1: O3–H3A = Distance 0.84 Å, H3A⋯O1 = 1.9808(23) Å, O1⋯O3 = 2.771(3) Å with

angle at H1A = 156.4(2)°]. All geometric parameters are as expected [7–9].

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Fund for Less Developed Regions of the National Natural Science Foundation of China (No. 31760257); Joint Basic Research Program (partial) of Yunnan Local Undergraduate Universities (2017FH001-002); The reserve Academic and Technical Leaders of Yunnan Province (2019HB098).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. BRUKER. *SAINT, APEX2 and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2010, 42, 339–341.
3. Sheldrick G. A short history of SHELX. *Acta Crystallogr.* 2008, A64, 112–122.
4. Sheldrick G. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
5. Guillemin V., Kim D., Eubank J. F., Luebke R., Liu X., Adil K., Lah M. S., Eddaoudi M. A supermolecular building approach for the design and construction of metal-organic frameworks. *Chem. Soc. Rev.* 2014, 43, 6141–6172.
6. Zang X.-S., Wu Q., Chen W., Tan H.-Q., Li Y. G., Wang E. The synthesis and characterization of the 3-D framework of supported Keplerate-type polyoxometalate. *Inorg. Chem. Commun.* 2011, 14, 590–593.
7. Wu Q., Huang M., Li T., Jiao L., Tu Y., Xu X., Ma X., Tian H., Qiao Y. Crystal and electronic structure of poly-halogenated lanthanide Schiff base complex: insights into halogen bond from structural and theoretical analysis. *J. Mol. Struct.* 2021, 1225, 129054.
8. Wu Q., Xiao J.-C., Zhou C., Sun J.-R., Huang M.-F., Xu X., Li T., Tian H. Crystal structure and supramolecular architecture of inorganic ligand-coordinated Salen-type Schiff base complex: insights into halogen bond from theoretical analysis and 3D energy framework calculations. *Crystals* 2020, 10, 334.
9. Lee S., Lo K., Tiekink E. T. Crystal structure of 4-chloro-N'-[(1E)-(3-ethoxy-2-hydroxyphenyl)methylidene]benzohydrazide – a Z' = 3 structure, C₁₆H₁₅ClN₂O₃, Z. Kristallogr. NCS 2019, 234, 1341–1344.