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Redetermination of the crystal structure of 5,7-dibromoquinolin-8-ol, at 200 K – Analysis of intermolecular forces, $C_9H_5Br_2NO$

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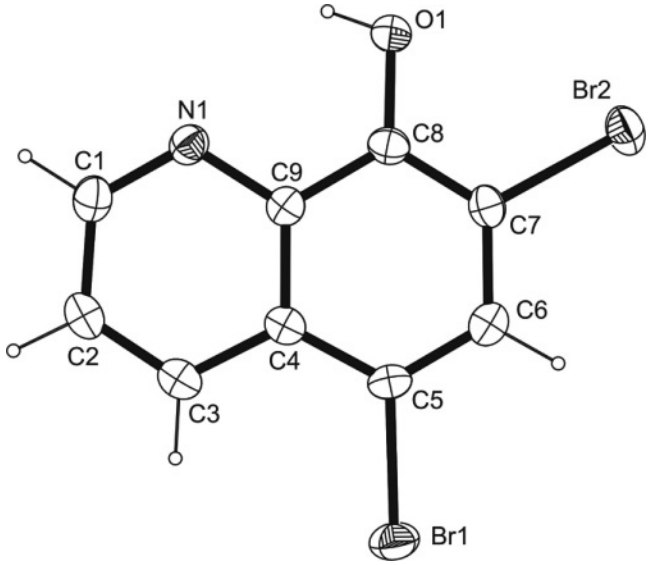

Abstract

$C_9H_5Br_2NO$, monoclinic, *P*2/*c* (no. 13), a = 15.3090(3) Å, b = 3.9828(1) Å, c = 16.1577(4) Å, β = 115.189(1)°, V = 891.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.0219, $wR_{ref}(F^2)$ = 0.0525, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless needles, size 0.08×0.103×0.532 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	90.45 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.68°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8226, 2214
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1863
$N(param)_{refined}$:	119
Programs:	SHELX [8], ORTEP-3 [9], MERCURY [10], PLATON [11]

Source of material

The compound was obtained commercially (Aldrich). Crystals suitable for the Xray study were obtained upon slow evaporation of a solution of the compound in methanol at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atom of the hydroxyl group was allowed to rotate with a fixed angle around the C–O bond to fit the experimental electron density (HFIX 147 in the SHELX program suite [8]), with U_{iso}(H) set to 1.5U_{eq}(O).

Discussion

Chelate ligands play a major role in coordination chemistry due to the enhanced thermodynamic stability of their coordination compounds in relation to similar compounds derived from comparable monodentate ligands. An interesting and versatile donor atom in this aspect is nitrogen as it can be present in various hybridizations and bonded to a large number of other atoms thus allowing fine-tuning of its donor capabilities. The latter allows nitrogen-bearing ligands to act as probes for central atoms of differing Lewis acidities, potentially giving rise to new or rare coordination numbers and patterns. At the beginning of a larger study on this field, 5,7-dibromoquinolin-8-ol was chosen as a starting point as the electronic situation on the aromatic quinoline scaffold itself can be modified easily by changing the substitution pattern. So far, the coordination chemistry of the title compound has not been researched very well, and only few examples of coordination compounds have been elucidated structurally based on diffraction studies on single crystals (e.g. with rhenium [1] and several rare earth elements [2, 3]). The crystal structure of the title compound has been reported earlier, however, without deposition of 3D coordinates [4] or at room temperature lacking discussion of intermolecular forces [5]. Therefore, the crystal structure of the title compound was re-determined at 200 K to close this gap and to allow for comparisons of metrical parameters of the ligand in envisioned coordination compounds. The molecule is essentially planar. The least-squares planes defined by the respective non-hydrogen atoms of each six-membered sub-unit of the quinoline core enclose an angle of 1.88(12)° only. The C–Br bonds are measured at 1.889(2) Å and 1.897(2) Å. In the crystal structure, classical hydrogen bonds of the O–H···N type can be found next to C–H···Br contacts whose range falls by at least 0.1 Å below the sum of van-der-Waals radii of the respective atoms. The O–H···N based contacts connect two molecules to centrosymmetric dimers with the two molecules enclosing an angle of approximately 56.2°. The C–H···Br contacts are supported by the hydrogen atom in *para* position to the nitrogen atom and the bromine atom in *ortho* position to the hydroxyl group. It is pertinent to note that no C–H···O contacts – as could be discussed on the data available for the crystal structure determination at room temperature [5] – are apparent in the present study at low temperature. In total, the molecules are connected to two-fold undulated strands along the crystallographic *c* axis. In terms of graph-set analysis [6,7], the classical hydrogen bonds necessitate a $R^2_2(10)$ graph set descriptor while the C–H···Br contacts are best described by means of a $C^1_1(7)$ descriptor on the same level. The crystal structure is marked by strong π-stacking with the shortest

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intercentroid distance between two centers of gravity measured at only 3.5979(14) Å. The latter interaction is found between the two different six-membered ring systems in neighbouring molecules.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*g*	0.4398	0.7501	0.2793	0.044
H(1A)	4*g*	0.5132	0.3204	0.0933	0.033
H(2)	4*g*	0.3929	0.1701	–0.0487	0.033
H(3)	4*g*	0.2342	0.3300	–0.0881	0.029
H(6)	4*g*	0.0882	0.9288	0.0704	0.028

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}
Br(1)	4*g*	0.06199(2)	0.59880(7)	–0.09706(2)	0.0242(1)	0.0365(2)	0.0272(1)	–0.0019(1)	0.00227(9)	–0.0040(1)
Br(2)	4*g*	0.20042(2)	1.12826(7)	0.25825(2)	0.0400(1)	0.0289(1)	0.0255(1)	0.0091(1)	0.0179(1)	0.0020(1)
O(1)	4*g*	0.3918(1)	0.8691(5)	0.2719(1)	0.0239(8)	0.041(1)	0.0200(8)	0.0049(8)	0.0056(7)	–0.0049(8)
N(1)	4*g*	0.4311(1)	0.5517(5)	0.1404(1)	0.0213(9)	0.026(1)	0.023(1)	0.0015(8)	0.0094(8)	0.0028(8)
C(1)	4*g*	0.4485(2)	0.3839(6)	0.0787(2)	0.027(1)	0.029(1)	0.030(1)	0.003(1)	0.015(1)	0.003(1)
C(2)	4*g*	0.3768(2)	0.2943(6)	–0.0070(2)	0.035(1)	0.026(1)	0.027(1)	0.000(1)	0.018(1)	–0.003(1)
C(3)	4*g*	0.2836(2)	0.3870(6)	–0.0299(2)	0.030(1)	0.022(1)	0.022(1)	–0.004(1)	0.0116(9)	–0.0006(9)
C(4)	4*g*	0.2611(2)	0.5684(6)	0.0336(2)	0.025(1)	0.017(1)	0.020(1)	–0.0034(9)	0.0102(9)	0.0017(8)
C(5)	4*g*	0.1675(2)	0.6824(6)	0.0174(2)	0.020(1)	0.021(1)	0.020(1)	–0.0024(9)	0.0045(8)	0.0028(9)
C(6)	4*g*	0.1513(2)	0.8519(6)	0.0827(2)	0.022(1)	0.020(1)	0.029(1)	0.0004(9)	0.0117(9)	0.0035(9)
C(7)	4*g*	0.2279(2)	0.9122(6)	0.1680(2)	0.027(1)	0.020(1)	0.023(1)	0.0003(9)	0.0147(9)	0.0015(9)
C(8)	4*g*	0.3207(2)	0.8111(6)	0.1888(2)	0.024(1)	0.022(1)	0.019(1)	–0.0016(9)	0.0083(9)	0.0015(9)
C(9)	4*g*	0.3382(2)	0.6412(6)	0.1197(2)	0.022(1)	0.019(1)	0.022(1)	–0.0010(9)	0.0105(8)	0.0031(9)

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References

!: Sigouin, O.; Beauchamp, A. L.: Oxo-rhenium(V) complexes with 8-hydroxyquinoline derivatives. Can. J. Chem. **83** (2005) 460–470.

2: Van Deun, R.; Fias, P.; Nockemann, P.; Schepers, A.; Parac-Vogt, T. N.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K.: Rare-Earth Quinolinates: Infrared-Emitting Molecular Materials with a Rich Structural Chemistry. Inorg. Chem. **43** (2004) 8461–8469.

3. Liu, Y.-C.; Chen, Z.-F.; Song, X.-Y.; Peng, Y.; Qin, Q.-P.; Liang, H.: Synthesis, crystal structure, cytotoxicity and DNA interaction of 5,7-dibromo-8-quinolinato-lanthanides. Eur. J. Med. Chem. **59** (2013) 168–175.

4. Kashino, S.; Haisa, M.: The Crystal and Molecular Structure of 5-Chloro-7-iodo-8-quinolinol, Chinoform. Bull. Chem. Soc. Jpn. **46** (1973) 1094–1098.

5. Stankovic, S.; Ribar, B.; Janic, I.; Lazar, D.; Andreetti, G. D.; Sgarabotto, P.: 5,7-dibromo-8-hydroxyquinoline. Cryst. Struct. Commun. **5** (1976) 645–649.

6. 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. Engl. **34** (1995) 1555–1573.

7. Etter, M. C.; MacDonald, J. C.; Bernstein, J.: Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. **B46** (1990) 256–262.

8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.

9. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.

10. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A.: Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. **41** (2008) 466–470.

11. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.