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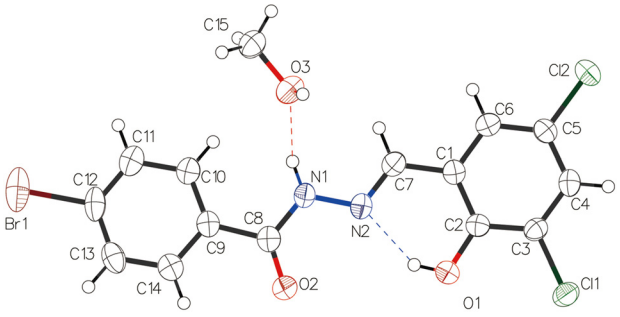
Crystal structure of 4-bromo-*N*′-[3,5-dichloro-2-hydroxyphenyl)methylidene]benzohydrazide methanol solvate, $C_{15}H_{13}BrCl_2N_2O_3$



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Abstract

$C_{15}H_{13}BrCl_2N_2O_3$, monoclinic, $P2_1/c$ (no. 14), a = 7.4135(4) Å, b = 13.3008(8) Å, c = 16.9956(7) Å, β = 104.445(2)°, V = 1622.88(15) Å^3, Z = 4, $R_{gt}(F)$ = 0.0380, $wR_{ref}(F^2)$ = 0.1031, T = 150(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.22 × 0.18 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.88 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}:	35,252, 3323, 0.079
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2507
$N(param)_{refined}$:	211
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

Source of material

3,5-Dichloro-2-hydroxybenzaldehyde (0.191 g, 1.0 mmol) and 4-bromobenzohydrazide (0.215 g, 1 mmol) were added to a stirring methanol solution (30 mL) and refluxed for 12 h. The mixture was filtered and kept undisturbed at room temperature. The colorless block crystals of the title compound were afforded after one week.

Experimental details

The structure was solved 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 (methylene), O–H = 0.84 (phenolic hydroxyl), 0.95 Å (aryl), and with U_{iso}(H) = 1.2 U_{eq}(C) for H atoms at methylene, phenolic hydroxyl and aryl.

Comment

The design and synthesis of supramolecular network 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 complexes [7, 8], in this work, we report a new polyhalogenated hydrazone.

X-ray diffraction analysis reveals that the asymmetric unit contains a planar hydrazone molecule and a methanol molecule. The bond lengths and angles are within the normal ranges [9–11]. As shown in the figure, the five non-hydrogen conjugated atoms [C(=O)N–N=C] constitute the central

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

Atom	*x*	*Y*	*z*	U_{iso}*/U_{eq}
Br1	0.77904 (5)	0.89354 (4)	0.86277 (2)	0.06807 (19)
Cl1	−0.30365 (12)	1.21652 (6)	0.15479 (5)	0.0425 (2)
Cl2	−0.31253 (11)	0.82843 (7)	0.06522 (5)	0.0405 (2)
O1	−0.0590 (3)	1.14818 (17)	0.30602 (13)	0.0383 (5)
H1	0.013028	1.126379	0.347185	0.057*
O2	0.2746 (3)	1.13505 (17)	0.52458 (14)	0.0412 (5)
N1	0.2114 (3)	0.9750 (2)	0.48045 (15)	0.0346 (6)
H1A	0.222483	0.911708	0.491089	0.042*
N2	0.1088 (3)	1.0089 (2)	0.40587 (15)	0.0330 (6)
C1	−0.0668 (4)	0.9713 (2)	0.27191 (18)	0.0320 (7)
C2	−0.1169 (4)	1.0723 (2)	0.25351 (18)	0.0314 (6)
C3	−0.2326 (4)	1.0941 (2)	0.17724 (19)	0.0323 (7)
C4	−0.2941 (4)	1.0196 (3)	0.11974 (19)	0.0351 (7)
H4	−0.372302	1.035418	0.069396	0.042*
C5	−0.2375 (4)	0.9215 (2)	0.13830 (18)	0.0335 (7)
C6	−0.1270 (4)	0.8960 (2)	0.21329 (19)	0.0337 (7)
H6	−0.092324	0.829392	0.225124	0.040*
C7	0.0437 (4)	0.9419 (3)	0.35212 (19)	0.0349 (7)
H7	0.067092	0.874231	0.364316	0.042*
C8	0.2943 (4)	1.0443 (3)	0.53643 (18)	0.0334 (7)
C9	0.4132 (4)	1.0026 (2)	0.61413 (18)	0.0329 (7)
C10	0.4721 (4)	0.9035 (3)	0.6241 (2)	0.0375 (7)
H10	0.437814	0.858494	0.581098	0.045*
C11	0.5817 (5)	0.8715 (3)	0.6980 (2)	0.0440 (8)
H11	0.620426	0.804838	0.705011	0.053*
C12	0.6332 (4)	0.9389 (3)	0.76121 (19)	0.0428 (9)
C13	0.5810 (4)	1.0386 (3)	0.7525 (2)	0.0419 (8)
H13	0.619785	1.083717	0.795125	0.050*
C14	0.4691 (4)	1.0698 (3)	0.67851 (19)	0.0371 (7)
H14	0.430849	1.136471	0.671743	0.045*
O3	0.0830 (3)	0.78089 (19)	0.50528 (15)	0.0450 (6)
H3	−0.026018	0.790540	0.505585	0.067*
C15	0.1463 (5)	0.6902 (3)	0.5470 (2)	0.0449 (8)
H15A	0.069000	0.635516	0.521558	0.067*
H15B	0.139873	0.695964	0.602578	0.067*
H15C	0.272756	0.677860	0.545226	0.067*

chromophore. The dihedral angles formed between the central plane and the least-squares planes through the flanking dichloro-hydroxy- and bromo-phenyl rings are 8.951(14)° and 12.881(17)°, respectively. The co-planar geometry between the central chromophore and dichloro-hydroxyphenyl ring generates an intramolecular hydroxy–O–H···N hydrogen bond. [O1–H1···N2: O1–H1 = 0.84 Å, H1···N2 = 1.88 Å, O1···N2 = 2.610(4) Å with angle at H1 = 143.6°].

In contrast to reported analogues containing additional water [12–14], a methanol molecule co-crystallised in the unit cell. As shown in the figure, the oxygen atom (O3) at the methanol molecule accepts a hydrogen bond (H1A–O3) from the hydrazine group [N1–H1A···O3: N1–H1A = distance 0.86 Å, H1A···O3 = 2.07 Å, N1···O3 = 2.820(4) Å with angle at H1A = 145°].

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