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Crystal structure of 6,6'-((1*E*,1'*E*)-(propane-1,3-diylbis(azaneylylidene))bis(methaneylylidene))bis(3-bromophenol), C₃₄H₃₂Br₄N₄O₄

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.20 × 0.15 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	4.96 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	29,950, 6738, 0.070
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5825
$N(\text{param})_{\text{refined}}$:	419
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

All chemicals were also commercially available and used without further purification. The title compound was synthesized with the following procedure. Place 4-bromosalicylaldehyde (0.402 g, 2.0 mmol) in 20 mL methanol and stir at room temperature until all solids are dissolved. Then 0.10 mL (0.5 mmol) of 1,3-diaminopropane was added to the aforementioned solution. The resulting solution was stirred and refluxed at 80 °C for 3 h, then naturally cooled and filtered. The filtrate was allowed to stand at room temperature for 1 week to obtain the yellow title compound.

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 = 0.99 (methylene), O–H = 0.84 (phenolic hydroxyl), 0.95 Å (aryl), and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for H atoms on methylene, phenolic hydroxyl and aryl.

Comment

Halogen atoms that are involved in non-covalent interactions are recognized as one of the important factors in

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Abstract

C₃₄H₃₂Br₄N₄O₄, $M_r = 880.27$, monoclinic, C2 (no. 5), $a = 10.6239(7)$ Å, $b = 10.8034(9)$ Å, $c = 28.959(3)$ Å, $\beta = 99.611(2)^\circ$, $V = 3277.1(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0391$, $wR_{\text{ref}}(F^2) = 0.0922$, $T = 150.0$ K.

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The molecular structure is shown in the Figure (two crystallographic independent molecules are present). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	−0.37092 (8)	0.50690 (8)	−0.20586 (3)	0.0525 (2)
Br2	0.91591 (7)	0.57498 (8)	0.20119 (3)	0.0459 (2)
Br3	1.15696 (8)	0.46970 (9)	0.29334 (3)	0.0579 (2)
Br4	0.26346 (7)	0.45187 (8)	0.70738 (3)	0.0475 (2)
O1	−0.0269 (6)	0.6379 (5)	−0.0647 (2)	0.0492 (14)
H1	0.024411	0.694388	−0.054271	0.074*
O2	0.6002 (5)	0.6620 (5)	0.0472 (2)	0.0463 (13)
H2	0.520902	0.667321	0.038585	0.069*
O3	0.9590 (6)	0.3525 (5)	0.4395 (2)	0.0507 (14)
H3A	0.912001	0.300057	0.449674	0.076*
O4	0.4378 (6)	0.3493 (5)	0.55512 (19)	0.0474 (13)
H4	0.504253	0.325569	0.545604	0.071*
N1	0.0692 (6)	0.8622 (6)	−0.0596 (2)	0.0399 (14)
N2	0.3869 (6)	0.7806 (6)	0.0486 (2)	0.0403 (15)
N3	0.8579 (7)	0.1350 (6)	0.4462 (2)	0.0451 (15)
N4	0.6445 (6)	0.2243 (6)	0.5571 (3)	0.0444 (16)
C1	−0.0813 (7)	0.7904 (7)	−0.1256 (3)	0.0370 (16)
C2	−0.0947 (8)	0.6729 (8)	−0.1060 (3)	0.0416 (18)
C3	−0.1818 (7)	0.5868 (8)	−0.1306 (3)	0.0459 (18)
H3	−0.191656	0.506782	−0.118098	0.055*
C4	−0.2525 (7)	0.6214 (7)	−0.1735 (3)	0.0435 (18)
C5	−0.2391 (8)	0.7362 (8)	−0.1926 (3)	0.0464 (19)
H5	−0.288180	0.757817	−0.221986	0.056*
C6	−0.1546 (7)	0.8187 (7)	−0.1690 (3)	0.0434 (18)
H6	−0.145257	0.897629	−0.182516	0.052*
C7	0.0042 (8)	0.8829 (7)	−0.1001 (3)	0.0423 (18)
H7	0.011716	0.961285	−0.114280	0.051*
C8	0.1458 (7)	0.9633 (8)	−0.0363 (3)	0.0445 (17)
H8A	0.100111	1.001130	−0.012683	0.053*
H8B	0.156501	1.027604	−0.059644	0.053*
C9	0.2752 (7)	0.9202 (7)	−0.0125 (3)	0.0410 (18)
H9A	0.325334	0.992140	0.001506	0.049*
H9B	0.321420	0.882652	−0.036034	0.049*
C10	0.2631 (8)	0.8254 (8)	0.0256 (3)	0.048 (2)
H10A	0.217810	0.863697	0.049237	0.058*
H10B	0.211338	0.754516	0.011540	0.058*
C11	0.4285 (8)	0.7961 (7)	0.0934 (3)	0.0428 (18)
H11	0.377202	0.842785	0.110930	0.051*
C12	0.5451 (7)	0.7475 (7)	0.1172 (3)	0.0403 (18)
C13	0.6278 (7)	0.6789 (7)	0.0922 (3)	0.0388 (17)
C14	0.7421 (7)	0.6303 (7)	0.1183 (3)	0.0382 (16)
H14	0.801087	0.586809	0.102973	0.046*
C15	0.7662 (7)	0.6467 (7)	0.1655 (3)	0.0391 (17)
C16	0.6875 (8)	0.7137 (8)	0.1907 (3)	0.0431 (18)
H16	0.709113	0.724517	0.223618	0.052*
C17	0.5789 (8)	0.7625 (7)	0.1661 (3)	0.0443 (19)
H17	0.523830	0.808376	0.182349	0.053*
C18	0.9819 (7)	0.3164 (7)	0.3969 (3)	0.0406 (18)
C19	0.9403 (8)	0.2006 (8)	0.3781 (3)	0.0409 (18)
C20	0.9650 (8)	0.1681 (8)	0.3339 (3)	0.048 (2)
H20	0.937524	0.089855	0.321077	0.058*
C21	1.0288 (8)	0.2477 (8)	0.3085 (3)	0.049 (2)
H21	1.045342	0.225604	0.278288	0.059*
C22	1.0675 (7)	0.3599 (9)	0.3283 (3)	0.048 (2)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C23	1.0441 (7)	0.3985 (8)	0.3714 (3)	0.0444 (18)
H23	1.069612	0.478264	0.383258	0.053*
C24	0.8776 (7)	0.1129 (7)	0.4045 (3)	0.0409 (18)
H24	0.850091	0.036038	0.390392	0.049*
C25	0.8028 (8)	0.0360 (7)	0.4712 (3)	0.0464 (19)
H25A	0.870907	−0.001655	0.494483	0.056*
H25B	0.767771	−0.029232	0.448690	0.056*
C26	0.6959 (7)	0.0843 (8)	0.4965 (3)	0.0426 (17)
H26A	0.628478	0.123458	0.473424	0.051*
H26B	0.657201	0.013821	0.510936	0.051*
C27	0.7462 (8)	0.1767 (8)	0.5338 (3)	0.047 (2)
H27A	0.812414	0.137032	0.557223	0.057*
H27B	0.786537	0.246339	0.519462	0.057*
C28	0.6522 (8)	0.2135 (7)	0.6013 (3)	0.0425 (18)
H28	0.723219	0.171124	0.618527	0.051*
C29	0.5557 (8)	0.2638 (7)	0.6262 (3)	0.0396 (17)
C30	0.4512 (7)	0.3327 (7)	0.6015 (3)	0.0409 (17)
C31	0.3632 (7)	0.3848 (7)	0.6258 (3)	0.0433 (18)
H31	0.292295	0.429475	0.609582	0.052*
C32	0.3790 (7)	0.3714 (7)	0.6739 (3)	0.0410 (17)
C33	0.4779 (8)	0.3052 (8)	0.6984 (3)	0.0463 (19)
H33	0.486936	0.297279	0.731465	0.056*
C34	0.5643 (8)	0.2501 (8)	0.6743 (3)	0.0448 (19)
H34	0.631400	0.201538	0.691025	0.054*

the construction of crystal frameworks [5, 6]. As a part of our current research interest in exploring the relationship between supermolecular structure and physicochemical properties of halogenated Schiff-base compounds [7–9], in this work, we report a salen-type compound.

X-ray diffraction analysis reveals that the asymmetric unit of title compound contains a self-assembled supramolecular dimer, which is build up by two crystallographic independent salen molecules. As shown in the figure, two bromo-phenyl rings on both sides of each salen molecule exhibit a twisted stereochemistry, the dihedral angles between bromo-phenyl rings are 79.9 and 79.1°, respectively. It is noteworthy that, in the title compound halogen bonds (XB) play an important role in the formation of the supramolecular dimers in the title structure; and the geometry can be classified in to type II XB contact [Br2⋯Br3 = 3.5625(11) Å, θ1 = 164.626(242)° and θ2 = 103.650(258)°].

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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. 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.
6. Yi J., Junbai L. Molecular assembly of Schiff base interactions: construction and application. *Chem. Rev.* 2015, 115, 1597–1621.
7. Lin S., Wu Q., Tan H., Wang E. A new organic-inorganic hybrid based on Mn-salen and decavanadate. *J. Coord. Chem.* 2011, 64, 3661–3669.
8. Li Y., Wu Q., Lecren L., Clérac R. Synthesis, structure and magnetism of new polynuclear transition metal aggregates assembled with Schiff-base ligand and anionic *N*-donor ligands. *J. Mol. Struct.* 2008, 890, 339–345.
9. Xiao J., Zhou C., Huang M., Tan H., Wu Q. Crystal structure of aqua-azido- κ^1N -(6,6'-((propane-1,3-diylbis(azanylylidene))bis(methanylylidene))bis(3-bromophenolato)- κ^4N,N',O,O' iron(III), $C_{17}H_{16}Br_2FeN_5O_3$, *Z. Kristallogr. NCS* 2020, 235, 903–904.