ISSN 1063-7745, Crystallography Reports, 2020, Vol. 65, No. 7, pp. 1106–1110. © Pleiades Publishing, Inc., 2020.

STRUCTURE OF ORGANIC COMPOUNDS

Molecular Structure and Supramolecular Architecture of (*E*)-2-Bromo-6-[(2,4,6-Tribromophenylimino)methyl]-4-Chlorophenol

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Received April 22, 2019; revised October 4, 2019; accepted October 7, 2019

Abstract—In this study, the molecular structure and supramolecular architecture of a new compound have been studied in depth using single crystal X-ray diffraction (XRD) technique. Crystallographic results show that the compound exists in phenol-imine form that is twisted with the dihedral angle of 51.77° between the aromatic rings of the molecule. Various types of non-covalent interactions (C···O, C–H···O, Br···Br, C–H···Cl, π···π, O···Br, and Br···π) take part effectively in the construction of 3D network in the compound. The C···O and C–H···O interactions have the role of forming the 1D structure along the direction [010] with the support of π···π and π···Br interactions. The 2D structure of the compound is reached by the inter-connection of 1D chains in the (101) plane through the C–H···Cl interactions. The 3D supramolecular structure of the compound is completed by the non-covalent Br···Br and Br···O interactions responsible for the connection of 2D sheets.

DOI: 10.1134/S1063774520070093

INTRODUCTION

Salicylidenanilines continue to be the intense research subject in scientific and industrial fields due to a number of useful properties (antimicrobial, antifungal, antitumor and cytotoxic activites, catalysts, DNA cleavage, optical switch, ophthalmic glasses, dyes, polymers and so on.) that are known to be associated with their interesting molecular geometries [1–8] as well as their crystal packings as in the photochromic and thermochromic phenomena [9, 10]. From the perspective of molecular geometry, these compounds have two tautomeric forms in both solid state and solvent media as phenol-imine and keto-amine forms [11–13]. Previous studies reveal that there are two other possible molecular geometries of these compounds named Zwitter ionic and resonance hybrid structures [14, 15]. In this study, a new salicylidenaniline derivative, (*E*)-2-bromo-6-[(2,4,6-tribromophenylimino)methyl]-4-chlorophenol, has been synthesized. The molecular structure and supramolecular architecture of the compound have been investigated in detail by using X-ray diffraction technique (XRD).

EXPERIMENTAL METHODS

Synthesis

The solution of 3-bromo-5-chloro-2-hydroxybenzaldehyde (0.15 g; 0.64 mmol) and ethanol (20 mL) was added to solution of 2,4,6-tribromoaniline (0.165 g; 0.64 mmol) and ethanol (20 mL). After the mixture was refluxed by stirring for 1 h, the yellow solid was filtered, washed and dried. The single crystals of (*E*)-2-bromo-6-[(2,4,6-tribromophenylimino)methyl]-4-chlorophenol for X-ray diffraction were obtained by slow evaporation of the acetonitrile (yield: 25%, m.p.= 82–83°C).

Crystallographic Studies

The crystal structure of the compound has been solved by direct methods using SHELXT-2014/4 [16]. All non-hydrogen atoms have been refined anisotropically by full matrix least-squares methods using SHELXL-2018/3 [17]. All H atoms have been located geometrically and refined by a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H_{OH}) = 1.5U_{eq}(C)$. WinGX (Version 2018.3) [18], ORTEP-3 [19], and MERCURY [20] softwares have been used in obtaining the figures and other materials related to the

Table 1. Unit cell information and refinement details of the title compound

Formula	$C_{13}H_6Br_4ClNO$
Formula weight	547.24
Temperature (K)	298
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	4
a, Å	14.729(5)
b, Å	7.841(5)
c, Å	15.381(5)
α, °	90
β, °	118.289(5)
γ, °	90
V, Å^3	1564.2(12)
Radiation type	MoK_α
μ, mm^{-1}	10.46
θ_{max}, θ_{min}	28.4, 3.00
h, k, l	$-19 < h < 19$, $-10 < k < 10$, $-20 < l < 19$
$R[F^2 > 2\sigma(F^2)]$	0.080
$wR(F^2)$	0.133
S	1.210
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.34, −0.95

molecular structures. Experimental conditions and other details are given in Table 1 and crystallographic information file (CCDC 1903738).

RESULTS AND DISCUSSION

Investigation of Molecular and Crystal Structure

The molecular structure of the compound obtained from XRD analysis is given in Fig. 1. Significant bond lengths characterizing the tautomeric structure are C–O, C–N and aromatic bond lengths. The C1–O1, C7–N1, and C6–C7 bond lengths in molecule are 1.343(11), 1.274(12), and 1.456(11) Å. These values suggest a single bond character for the C–O and C6–C7 bonds and double bond character for the C–N bond. The bond lengths of (C1/C6) ring (Table 2), which are other characteristic bond distances for tautomeric conversion, correspond to those of an aromatic compound in a phenol-imine form and agree well with previously reported values [21–23]. In addition, the final refinement parameters have the best values for the case of the tautomeric proton (H1) located on phenolic oxygen atom (O1). Therefore, it can be proposed that the compound exists in phenol-imine form in solid state.

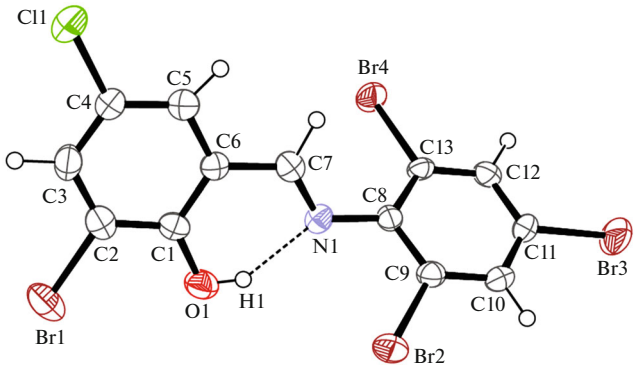

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Hydrogen atoms are represented with small spheres of arbitrary radii.

The compound has intra-molecular O–H···N hydrogen bonds which can be characterized by the distance of 2.606 Å between the nitrogen and the oxygen atoms. The dihedral angle between the two aromatic rings is 51.77° and the molecule is significantly deviated from the planarity. While the C1/C6 ring is planar with the effect of intramolecular hydrogen bonding, the steric effect of bromine atoms in *ortho* positions (respect to the imino group) causes C8/C13 ring to twist significantly. The geometric details of all non-covalent interactions are given in Table 3.

The halogen···halogen contacts (C–X1···X2–C) are generally classified in two groups: Type I contacts correspond to the interactions where the atoms are arranged in *cis* and *trans* geometries. Type II contacts contain the interactions defined by a single geometry of L-shape [24]. The crystallographic studies show the presence of mutual C–Br···Br–C interactions in the compound. The Br1···Br2 distance is 3.617 Å, and θ1 and θ2 angles are 159.84° and 130.17°, respectively. Based on these values, the intermolecular C12–Br1···Br2^i–C14^i interaction in the compound can be described as a Type II interaction with an L-geometry. Molecules are held together by the electrostatic interaction between the positive region (σ hole) of Br2 atom and the electron density in the lateral negative region of the Br1 atom in neighboring molecule [25–27].

There are various non-covalent interactions (C···O, C–H···O, Br···Br, C–H···Cl, π···π, O···Br, and Br···Cg; Cg: centroids of C1–C6 or C8–C13 rings) taking part in the construction of 3D network in the compound. The roles of these interactions in the formation of 3D structure can be explained as follows: Three adjacent molecules are connected to each other by C7···O1^i (i: $1/2 - x$, $1/2 + y$, $1/2 - z$), C7^{ii}···O1 (ii: $-1/2 - x$, $-1/2 + y$, $1/2 - z$) and C7–H7···O1^i (i: $1/2 - x$, $1/2 + y$, $1/2 - z$), C7^{ii}–H7^{ii}···O1 (ii: $-1/2 - x$, $-1/2 + y$, $1/2 - z$) interactions between the aromatic carbon, hydrogen and oxygen atoms. Thus, 1D chain is formed, propagating along the direction [010]. The

Table 2. Selected experimental bond lengths (Å) for the compound

Experimental (XRD)	
N1–C7	1.274(9)
O1–C1	1.343(9)
C6–C7	1.456(10)
C1–C2	1.407(10)
C2–C3	1.367(11)
C3–C4	1.378(11)
C4–C5	1.380(11)
C5–C6	1.385(10)
C6–C1	1.410(10)
N1–C8	1.407(9)
C2–Br1	1.896(8)
C4–Cl1	1.736(8)
C9–Br2	1.891(7)
C11–Br3	1.900(7)
C13–Br4	1.890(7)

chain structure is also supported by Cg···Br and Cg···Cg interactions (Fig. 2, Table 3).

These chains are inter-connected to each other through the C–H···Cl1^{iii} (iii: $1-x$, $1-y$, $-z$) interactions. Thus, a 2D supramolecular sheet is formed in (101) plane, including $R_2^2(8)$ rings (Fig. 3). The 2D sheet structure of the title compound topologically corresponds to a (6, 3) or (6^3) network in which each node is three-connected, taking the shape of brick wall [28].

It should be noted here that the Br2 atom plays an important role in the construction of a 3D structure by participating in O···Br and Br···Br contacts with the adjacent molecules. Br···Br contacts are connected to each other to form eighteen-membered rings (Fig. 4).

CONCLUSIONS

On the basis of the X-ray results, the title compound has phenol-imine form, adopting a *trans* configuration with respect to the imino group. The dihedral angle (51.77°) between the aromatic rings of the molecule show a significantly twisted molecule. There are various types of non-covalent interactions (C···O, C–H···O, Br···Br C–H···Cl, Cg···Cg, O···Br and Br···Cg, Table 3) taking part effectively in the construction of a 3D network in the compound. In the crystal packing, the C···O and C–H···O interactions have the role of forming the 1D structure with the support of π···π and Cg···Br interactions along the direction [010]. The 2D structure of the compound is achieved by the inter-connection of 1D chains in the (101) plane through the C–H···Cl interactions. The

Table 3. The geometry of non-covalent interactions in the title compound

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	θ(D–H···A)	Symmetry
O1–H1···N1	0.82	1.885	2.606(8)	146	—
C7–H7···O1^{i}	0.930	2.671	3.106	104.63	$1/2-x$, $1/2+y$, $1/2-z$
C7 ^{ii}–H7^{ii}···O1	0.930	2.671	3.106	104.63	$1/2-x$, $-1/2+y$, $1/2-z$
C3–H3^{iii} ··· Cl	0.930	2.930	3.847	168.17	$1-x$, $1-y$, $-z$
C3–H3···Cl^{iii}	0.930	2.930	3.847	168.17	$1-x$, $1-y$, $-z$
C–X···X–C	*d*(X···X)	θ1(C–X1···X2)	θ2(X1···X2–C)		
C2–Br1···Br2^{iv}–C9^{iv}	3.617	130.17	159.84		$-x$, $1-y$, $-z$
C9–Br2···Br1^{iv}–C2^{iv}	3.617	130.17	159.84		$-x$, $1-y$, $-z$
C7···O1^{i}	3.106	112.68	124.24		$1/2-x$, $1/2+y$, $1/2-z$
C7^{ii}···O1	3.106	112.68	124.24		$1/2-x$, $-1/2+y$, $1/2-z$
C1–O1···Br4 ^{v}–C13^{v}	3.229	150.68	153.24		$-1/2+x$, $1/2-y$, $-1/2+z$
CgI···CgJ	*d*(CgI···CgJ)	α	β	*d*(Cg···J)	
Cg1–Cg2^{i}	3.619(5)	4.5(4)	17.9		$1/2-x$, $1/2+y$, $1/2-z$
Cg2–Cg1^{ii}	3.619(5)	4.5(4)	13.4		$1/2-x$, $-1/2+y$, $1/2-z$
C–X···Cg		*d*(X–Cg)	θ(C–X···Cg)		
C2–Br1···Cg2^{ii}		3.675(4)	87.7(2)		$1/2-x$, $-1/2+y$, $1/2-z$
C9–Br2···Cg1^{i}		3.714(4)	86.9(2)		$1/2-x$, $1/2+y$, $1/2-z$

Cg1: Centroid of the ring defined by the atoms C1 to C6; Cg2: centroid of C8–C13 ring.

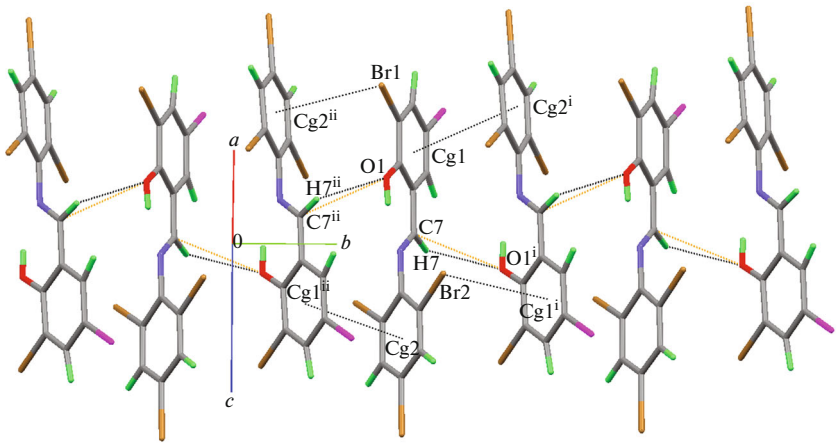

Fig. 2. One dimensional polymeric chain formed by C···O and C–H···O type interactions in the crystal packing of the compound through the *b* axis.

3D supramolecular structure of the compound is completed by the non-covalent Br···Br and Br···O interactions responsible for the connection of 2D sheets.

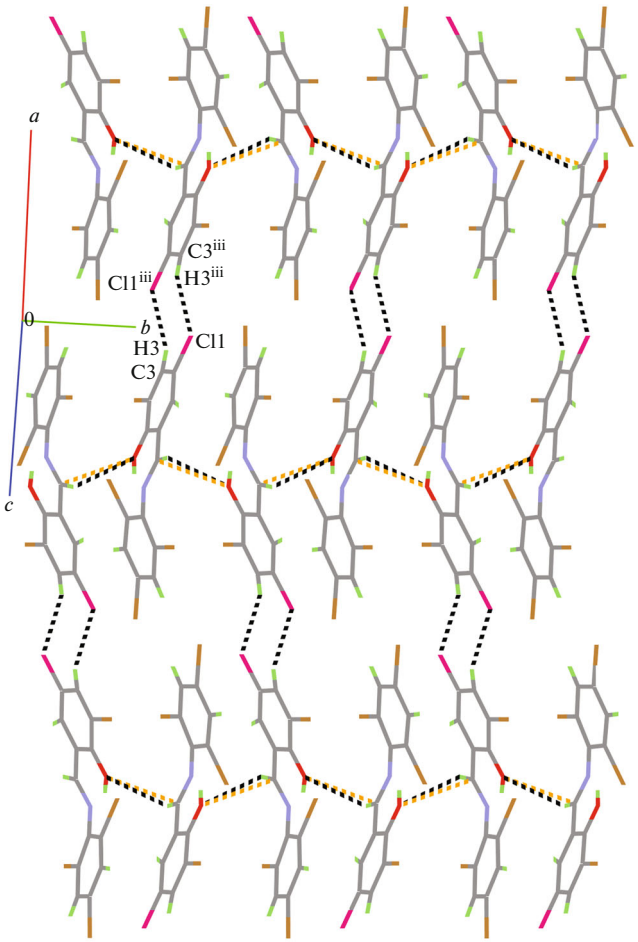

Fig. 3. The 1D chain structure in Fig. 2 extends to a 2D structure through the C–H···Cl interactions.

ACKNOWLEDGMENTS

This work was supported by Sinop University Scientific Research Coordination Unit. Project no. FEF-1901-13-07. The authors acknowledge to Scientific and Technological Research Application and Research Center, Sinop Univer-

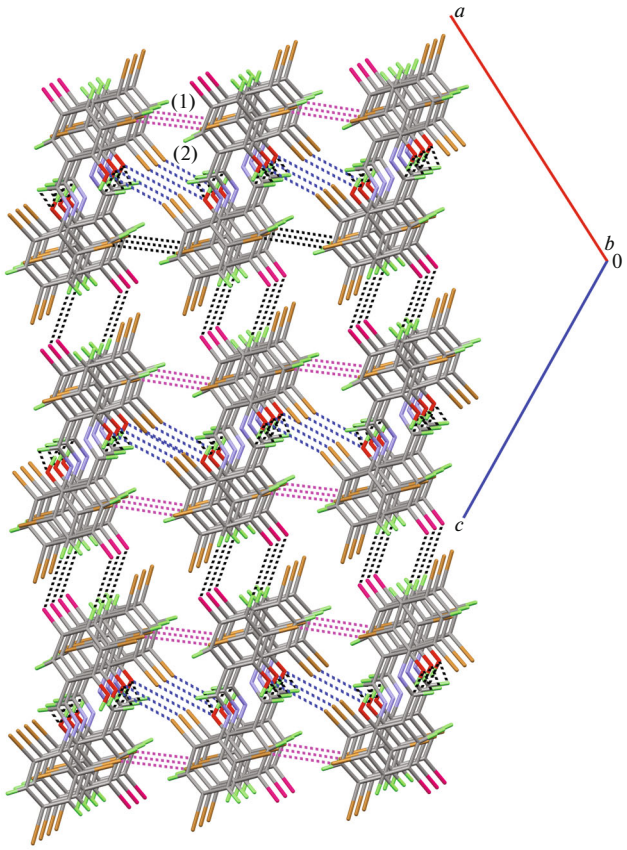

Fig. 4. The 3D supramolecular architecture of the compound, which is formed by the connection of 2D layers in (101) with the Br···Br (1) and Br···O (2).

sity, Turkey, for the use of the Bruker D8 QUEST diffractometer.

SUPPLEMENTARY MATERIALS

Relevant crystal data, experimental conditions and final refinement parameters can be obtained from Cambridge Structural Database CCDC: 1903738 for the compound. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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