



ISSN 0975-413X  
CODEN (USA): PCHHAX

Der Pharma Chemica, 2018, 10(01): 115-121  
(<http://www.derpharmachemica.com/archive.html>)

## Crystal Structure and Hirshfeld Surface Investigation of 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde

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### ABSTRACT

In present study, the compound 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde was synthesized by propargylation of 3,4-dihydroxybenzaldehyde and characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, elemental and X-ray analysis. The compound crystallizes in the P-1 space group of the monoclinic crystal system with unit cell parameters of  $a = 4.5901(6) \text{ \AA}$ ,  $b = 17.835(2) \text{ \AA}$ ,  $c = 13.346(2) \text{ \AA}$ ,  $\beta = 91.612(13)^\circ$ ,  $V = 1092.1(4) \text{ \AA}^3$ ,  $D_x = 1.303 \text{ Mg m}^{-3}$  and  $Z = 4$ . The molecules are arranged in zig-zag manner and crystal packing is stabilized by C13A(sp)—H13A...O1B, C13B(sp)—H13B...O1A and C12B(sp)—H12B...O1B intermolecular interactions. These interactions generate various hydrogen bond patterns e.g. C(11), R<sup>2</sup><sub>2</sub>(20) and R<sup>4</sup><sub>6</sub>(47). The Hirshfeld surfaces and the associated 2-D fingerprint plots analysis were performed for visualizing, exploring and quantifying intermolecular interactions in the crystal lattice of the compound.

**Keywords:** X-ray analysis, Hydrogen-bond patterns, Hirshfeld surfaces, 2-D fingerprint plots, Benzaldehyde

### INTRODUCTION

The carbonyl group is a significant functional group of several biologically relevant molecules such as proteins, carbohydrates, hormones and some vitamins [1]. Benzaldehyde is the simplest representative of the aromatic organic compound containing carbonyl group, occurring naturally as the glycoside amygdalin [2]. Benzaldehyde and its derivatives are versatile starting materials in many organic syntheses. Especially the nucleophilicity of the carbonyl (formyl) group as well as its potential use for Wittig, McMurry and Claisen-Schmidt type reactions next to further functionalizations of the aromatic core foster this role [3]. It is used chiefly in the manufacture of dyes, organic compounds and to some extent in perfumes and flavouring agents [2].

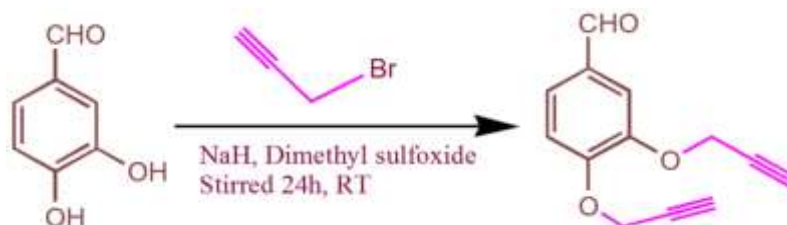
3,4-Dihydroxybenzaldehyde is the simplest derivative of above mentioned nucleus. 3,4-Dihydroxybenzaldehyde derived from *Prunus mume* seed inhibits oxidative stress and enhances estradiol secretion in human ovarian granulosa tumor cells [4]. It is used for lower the blood pressure and as well as a fungistatic substance to inhibit fungal growth [5,6]. The field of crystal engineering is a sub discipline of chemistry, which deals the crystal structures and construction of crystalline materials from molecules or ions using non-covalent interactions [7]. Hydrogen bonding has been widely used to operate aggregation of molecules because of their strength and directionality tends to favor the formation of crystals. Unfortunately, a literature survey revealed that little work had been done in terms of crystal structure study of 3,4-dihydroxybenzaldehyde nucleus [8-10], however this nucleus has tendency to form the crystals. Moreover, we also found few examples which are dealing the crystallographic study of other dihydroxybenzaldehyde derivatives [3,11-14]. In this contest, we are reporting here the crystal structure and Hirshfeld surface studies of new 3,4-dihydroxybenzaldehyde derivative (Scheme 1). 3-D Hirshfeld surface diagram and decomposed 2-D fingerprint plots have been used for visualizing, exploring and quantifying intermolecular interactions in the crystal of this compound. To the best of our knowledge, no report is available for the crystallographic and Hirshfeld surface studies of 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde.

### MATERIALS AND METHODS

All the chemicals and solvents were used without further purification of analytical grade and available commercially. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on JEOL-NMR 400 MHz and 100 MHz spectrometer with Tetramethylsilane (TMS) as the internal reference. The chemical shifts were expressed in  $\delta$  (ppm) downfield from TMS. An elemental analysis was performed on a Perkin-Elmer Model 240B automatic analyzer.

### Synthesis of 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde

NaH (0.20 g, 8.33 mmol) was added into anhydrous dimethyl sulfoxide (5 ml) in small portions under nitrogen with stirring. The solution was cooled up to 0°C and anhydrous dimethyl sulfoxide (5 ml) containing 3,4-dihydroxybenzaldehyde (0.50 g, 3.62 mmol) was added drop wise. Then, the reaction mixture was stirred at room temperature for 30 min. Propargyl bromide (0.81 ml, 9.05 mmol) was added drop wise to the reaction mixture. The mixture was stirred further for 24 h at room temperature. The completion of the reaction was monitored by TLC. After completion, the reaction mixture was poured onto ice water and neutralized by 1 M HCl solution. The separated solid was filtered and washed with water and dried. The compound was crystallized by slow evaporation method from solution of methanol and hexane (8:2) at room temperature to get suitable crystals for X-ray diffraction study. Yield: 0.55 g (71%); M.P: 100-102°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, ppm), δ=9.87 (s, 1H, -CHO), 7.58 (d, *J*=2.32 Hz, 1H, Ar-H), 7.53 (dd, *J*=8.24, 1.84 Hz, 1H, Ar-H), 7.18 (d, *J*=8.24 Hz, 1H, Ar-H), 4.87-4.83 (m, 4H, 2 × -OCH<sub>2</sub>), 2.58-2.55 (m, 2H, 2 × -C≡CH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz, ppm), δ=190.77 (-CHO); 152.55; 147.79; 130.79; 126.81; 113.19; 112.32; 77.74 (-C≡CH); 76.29 (-C≡CH); 56.81 (-OCH<sub>2</sub>); 56.51 (-OCH<sub>2</sub>); Elemental analysis for C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>: Calculated: C 72.89, H 4.71, O 22.40; Found: C 79.91, H 4.70, O 22.39.



Scheme 1: Synthetic procedure of 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde

### X-ray data collection and structure solving procedures

The structure of the title compound was determined by X-ray crystallographic analysis. A good quality single crystal of compound was obtained by the slow evaporation of its solution in methanol-hexane. The selected crystal was mounted on glass fiber and used for data collection. The crystallographic data were collected at 293 K by the X-ray scan technique on an Oxford Diffraction Xcalibur four-circle diffractometer using graphite mono-chromatized Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å). The data were corrected for Lorentz-polarization as well as for absorption effects [15]. The structure was solved by direct method using the program SHELXS-97 [16] and refined by full-matrix least-squares technique on  $F^2$  by SHELXL97 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were positioned geometrically and refined as riding atoms for C—H=0.930 Å (CH), C—H=0.970 Å (CH<sub>2</sub>) with  $U_{iso}(H)=1.2U_{eq}(C)$ . All demonstrated interactions were performed by PLATON program [17]. The program ORTEP-III [18] and Mercury [19] were used in the preparation of the figures. A summary of the crystal data, data collection and structure refinement are given in Table 1, and hydrogen bonding interactions are summarized in Table 2.

Table 1: Crystal data, data collection and structure refinement details

Crystal data			
CCDC No.	942945	$\alpha$ (°)	90
Molecular formula	C <sub>13</sub> H <sub>10</sub> O <sub>3</sub>	$\beta$ (°)	91.612n (13)
Molecular weight	214.21	$\gamma$ (°)	90
Crystal system	Monoclinic	Z	4
Space group	<i>P</i> -1	<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.303
Temperature (K)	293	<i>F</i> (000)	448
<i>a</i> (Å)	4.5901 (6)	$\mu$ (mm <sup>-1</sup> )	0.09
<i>b</i> (Å)	17.835 (2)	Radiation $\lambda$ (Å)	Mo <i>K</i> $\alpha$ (0.71073)
<i>c</i> (Å)	13.346 (2)	Crystal dimensions (mm)	0.37 × 0.35 × 0.34
<i>V</i> (Å <sup>3</sup> )	1092.1 (4)		
Data collection			
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.890/1.000	<i>l</i>	-17→12
$\theta$ <sub>max</sub> (°)	29.3	Measured reflections	8009
$\theta$ <sub>min</sub> (°)	3.3	Independent reflections	3863
<i>h</i>	-5 → 6	Reflections with <i>I</i> >2 $\sigma$ ( <i>I</i> )	2533
<i>k</i>	-22 → 22	<i>R</i> <sub>int</sub>	0.052
Refinement			
Refinement on	$F^2$	Number of reflections	3863
$R[F^2 > 2\sigma(F^2)]$	0.079	Number of parameters	289
<i>wR</i> ( $F^2$ )	0.221	( $\Delta/\sigma$ ) <sub>max</sub>	0.001
<i>S</i>	1.05	$\Delta\rho_{min}, \Delta\rho_{max}$ (eÅ <sup>-3</sup> )	-0.22, 0.28

Table 2: Hydrogen bond distances (Å) and angles (°)

D—H...A	d(H...A)	d(D...A)	<(DHA)	Symmetry operations
C13A—H13A...O1B	2.291	3.193 (4)	163.29	-1-x,1-y,1-z
C13B—H13B...O1A	2.304	3.204 (4)	162.81	-1-x,-y,1-z
C12B—H12B...O1B	2.718	3.512 (5)	143.89	-1-x,1-y,2-z

### Hirshfeld surface calculations

3-D Hirshfeld surfaces and their associated 2-D fingerprint plots were calculated using Crystal Explorer 3.1 program [20] in order to visualize and analyze the intermolecular interactions. All bond lengths to hydrogen atoms were automatically normalized to typical standard neutron values (C–H=1.083 Å), while the CIF file of title compound was read into the Crystal Explorer program for calculations. In this study, the Hirshfeld surfaces were generated using a standard surface resolution. The 3-D  $d_{\text{norm}}$  (Normalized contact distance) surfaces and 2-D fingerprint plots are used for decoding and quantifying intermolecular interactions in the crystal lattices. The  $d_{\text{norm}}$  based on  $d_e$  (the distance from a point on the surface to the nearest atom outside the surface),  $d_i$  (The distance from a point on the surface to the nearest atom inside the surface) and van der Waals radii, enables the identification of the regions of particular intermolecular interactions. The 3-D  $d_{\text{norm}}$  surfaces of title compound are mapped over fixed color scales of -0.353 (red) to 1.098 Å (blue), shape index mapped in the color range of -1.00 to 1.00 Å and curvedness in the range of -4.0 to 4.0 Å. The negative or positive value of  $d_{\text{norm}}$  is showing shorter or longer intermolecular contacts than van der Waals separations, respectively. The  $d_{\text{norm}}$  parameter displayed surfaces with a red-white-blue color scheme, where deeper red spots highlighted shorter contacts, white areas represented contacts around the van der Waals separation and blue regions were devoid of any close contacts. The fingerprint plots are 2-D representations of Hirshfeld surfaces, and are displayed by using the standard ranges 0.909 to 2.349 Å with the  $d_e$  and  $d_i$  distance scales.

## RESULTS AND DISCUSSION

### Description of the crystal structure

X-ray crystallographic analysis was applied to determine an exact structural geometry of molecules in a single crystal including bond distances, bond angles and orientation of atoms and groups. The 3-D structure of title compound 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde was established by present study in the solid state. The compound crystallizes in the monoclinic crystal system with the space group  $P-1$  and having unit cell parameters of  $a=4.5901(6)$  Å,  $b=17.835(2)$  Å,  $c=13.346(2)$  Å,  $\beta=91.612(13)^\circ$ ,  $V=1092.1(4)$  Å<sup>3</sup>,  $D_x=1.303$  Mg/m<sup>3</sup> and  $Z=4$ . The asymmetric unit (an Ortep view) of the crystal lattice contains two molecules as shown in Figure 1 with 50% probability level of thermal ellipsoids. The structural parameters are summarized in Table 3 corresponding to each molecule of the asymmetric unit. The crystal structure of compound is stabilized by C13A(sp)—H13A...O1B, C13B(sp)—H13B...O1A and C12B(sp)—H12B...O1B intermolecular hydrogen bonding. The C13(sp)—H13...O1 (denoted with  $a$ ) hydrogen bonds are exhibited into chain C(11) pattern while C12(sp)—H12...O1 (denoted with  $b$ ) forming Centro symmetric dimer and generating ring  $R^2_2(20)$  pattern as shown in Figure 2. These H-bonds ( $a$ ,  $b$ ) are corroborated into a complex ring  $R^4_6(47)$  pattern. The hydrogen bonds help to arrange the molecules into zig-zag structure along the  $c$  axis (Figure 3) and the molecules appear to be chain structure when viewed along the  $a$  axis (Figure 4). The survey of the crystal geometry at a molecular level reveals that the usual geometrical parameters for bond lengths and angles are within expected ranges with small deviations [21]. The aldehyde group and meta-propyne moiety in the both molecules are approximately lie in the plane of the phenyl ring whereas para-propyne moiety is out of plane and twisted by  $66.23(3)^\circ$  and  $63.74(2)^\circ$  from its mean plane for molecule A and B, respectively. Thus, the spectral and X-ray crystallographic results are consistent with the structure of title compound.

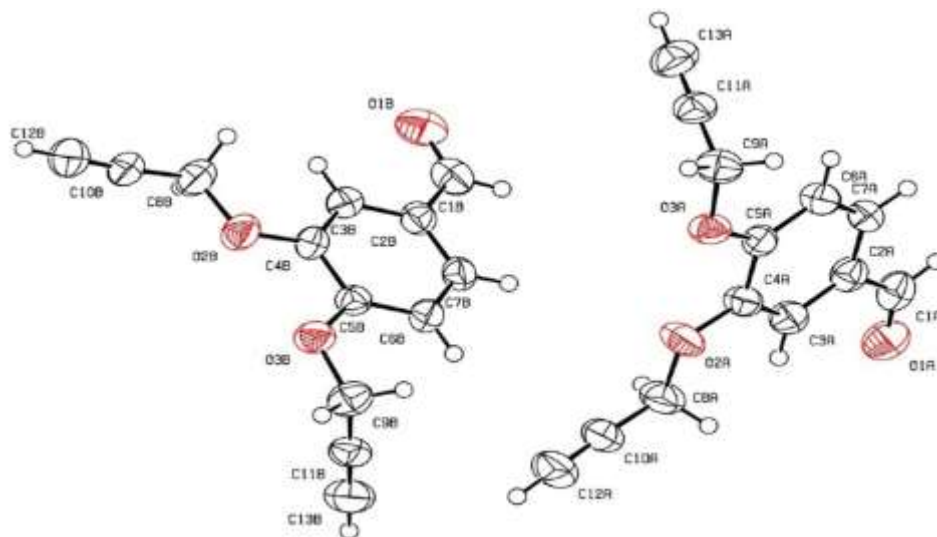


Figure 1: Ortep view of the molecule with thermal ellipsoids drawn at 50% probability level

Table 3: Bonds geometry (Å, °)

Geometrical Parameters	Molecules	
	A	B
<b>Bond lengths (Å)</b>		
C1—C2	1.474 (4)	1.476 (4)
C2—C3	1.397 (4)	1.393 (4)
C3—C4	1.377 (4)	1.382 (4)
C4—C5	1.412 (3)	1.410 (4)
C5—C6	1.376 (4)	1.387 (4)
C6—C7	1.393 (4)	1.394 (4)
C7—C2	1.382 (3)	1.380 (4)
C8—C10	1.466 (4)	1.473 (5)
C10—C12	1.176 (4)	1.181 (5)

C9—C11	1.452 (4)	1.460 (4)
C11—C13	1.190 (5)	1.171 (4)
C1—O1	1.212 (3)	1.208 (4)
C4—O2	1.372 (3)	1.373 (3)
C5—O3	1.373 (3)	1.360 (3)
C8—O2	1.408 (3)	1.408 (4)
C9—O3	1.430 (3)	1.433 (3)
<b>Bond angles (°)</b>		
C2—C3—C4	120.3 (2)	120.4 (3)
C3—C4—C5	118.8 (2)	119.3 (3)
C4—C5—C6	120.8 (2)	120.2 (2)
C5—C6—C7	119.9 (2)	119.6 (3)
C6—C7—C2	119.7 (2)	120.3 (3)
C7—C2—C3	120.5 (2)	120.1 (2)
C9—C11—C13	177.6 (3)	177.9 (3)
C8—C10—C12	175.1 (3)	175.3 (4)
C2—C1—O1	125.2 (3)	124.8 (3)
C3—C4—O2	125.5 (2)	125.5 (3)
C5—C4—O2	115.6 (2)	115.2 (2)
C4—C5—O3	113.6 (2)	114.2 (2)
C6—C5—O3	125.7 (2)	125.6 (2)
C4—O2—C8	116.2 (2)	116.2 (2)
C5—O3—C9	117.4 (2)	118.0 (2)
O2—C8—C10	108.6 (2)	108.7 (2)
O3—C9—C11	112.4 (2)	112.5 (2)
<b>Torsion angles (°)</b>		
O1—C1—C2—C7	-179.0 (3)	178.9 (3)
O1—C1—C2—C3	1.6 (5)	0.1 (5)
C3—C4—O2—C8	-4.5 (4)	4.1 (4)
C5—C4—O2—C8	176.1 (2)	-175.7 (2)
C4—O2—C8—C10	174.1 (2)	-174.0 (2)
O2—C8—C10—C12	-177 (5)	167 (5)
C4—C5—O3—C9	-176.1 (2)	175.9 (2)
C6—C5—O3—C9	3.0 (4)	-3.4 (4)
C5—O3—C9—C11	70.4 (3)	-69.6 (3)
O3—C9—C11—C13	162 (8)	-142 (9)

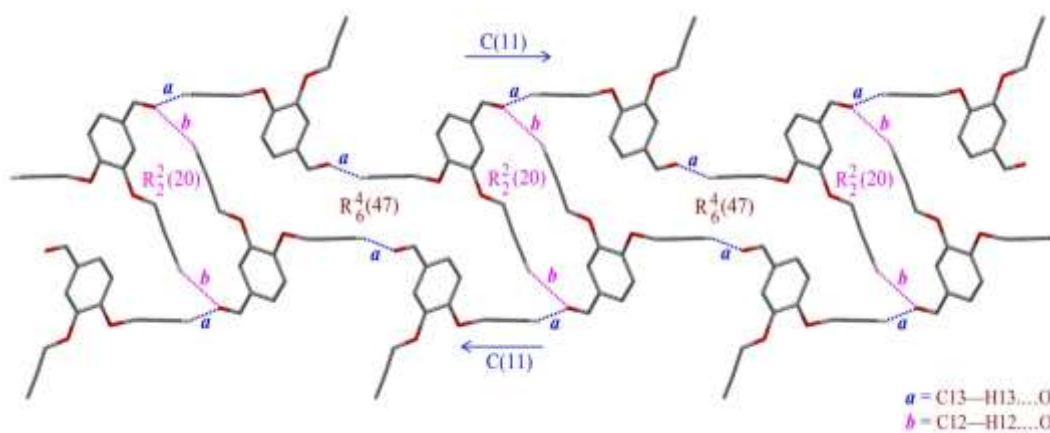


Figure 2: Hydrogen bonding patterns in 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde (non-significant hydrogen atoms are omitted for the reasons of clarity)

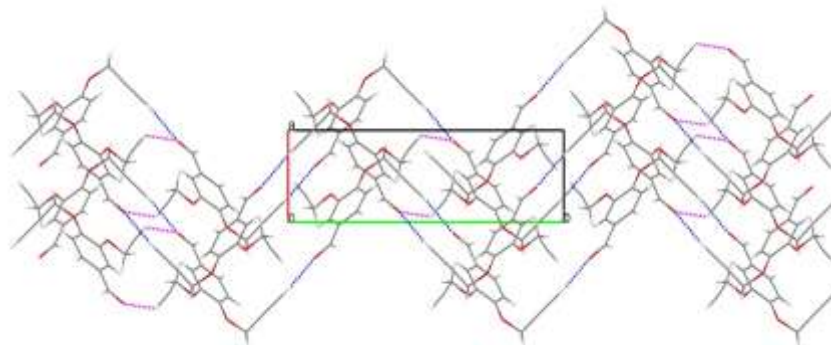


Figure 3: The zig-zag arrangement of molecules within layers of crystal packing viewed along the *c* axis. Dashed lines indicate C(sp)—H...O intermolecular interactions

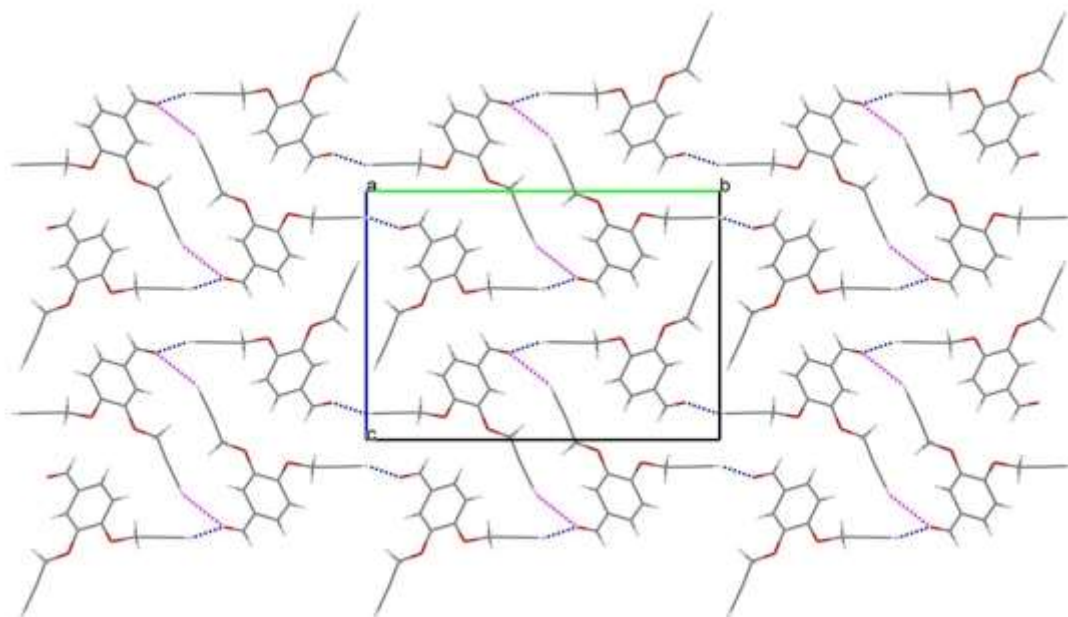


Figure 4: The arrangement of molecules within layers of crystal packing along *a* axis

#### Hirshfeld surface analysis

In order to examine the strength of intermolecular contacts and to further estimate their importance for the stability of crystal lattice, Hirshfeld surface analysis has been conducted. 3-D Hirshfeld surfaces and their 2-D fingerprint plots have been used to quantify the intermolecular interactions in molecules. A comprehensive study of Hirshfeld surfaces, associated 2-D fingerprint plots and the percentage contributions of close intermolecular contacts were carried out in the title compound with the Crystal Explorer 3.1 program. It confirms the occurrence of the intermolecular interactions revealed by PLATON program and given in Table 2. This analysis revealed that the intermolecular C...H/H...C, O...H/H...O and H...H contacts have a major contributor in the crystal packing of compound. The Hirshfeld  $d_{norm}$  surfaces, shape index, and curvedness of compound are shown in Figures 5-7, respectively. Hirshfeld surfaces facilitate a method of visualizing intermolecular interactions, short or long contacts by color-coding, and the color intensity indicating the relative strength of the interactions. The two larger red regions on the  $d_{norm}$  surfaces of each molecule correspond to dominant interactions between C(sp)—H...O, which represent the closest intermolecular interactions in these molecules. The large extent of area and white color on the surface indicates C...H/H...C contacts and other visible spots are because of H...H contacts. The complementary regions are visualized in the 2-D fingerprint plots, highlighting separately the O...H/H...O, C...H/H...C, and H...H intermolecular contacts with their percentage of contributions (Figure 8). The conspicuous presence of strong C(sp)—H...O hydrogen bonds are marked by the occurrence of long spikes with the contribution of O...H/H...O contacts to the total Hirshfeld surface of 21.5% and 21.6% for molecules A and B, respectively. A quite high contribution of C...H/H...C contacts to the total Hirshfeld surfaces is common in both molecules and indicated by the “wing” in the 2-D fingerprint plots. The H...H contacts, which are reflected in the middle of scattered points in the 2D fingerprint plots, have 30.6% and 30.8% contribution to the total Hirshfeld surfaces for molecules A and B, respectively. Apart from those mentioned above, the presence of C...O/O...C and C...C interactions contribute 7.3% and 4.6% for molecule A and 7.2% and 4.4% for molecule B, respectively.

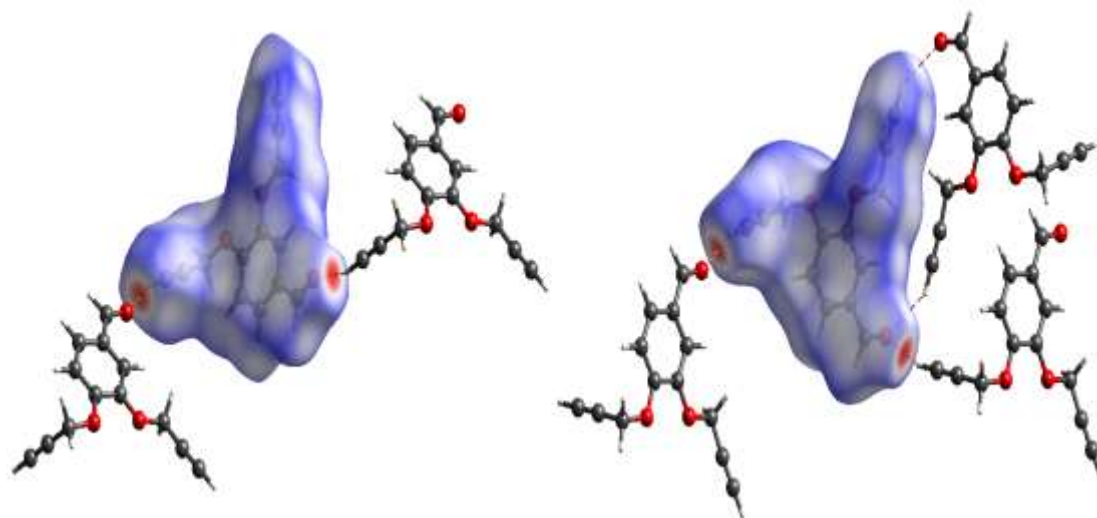


Figure 5: Hirshfeld  $d_{norm}$  surfaces of 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde [left (molecule A), right (molecule B)]: Neighbouring molecules are associated with close contacts

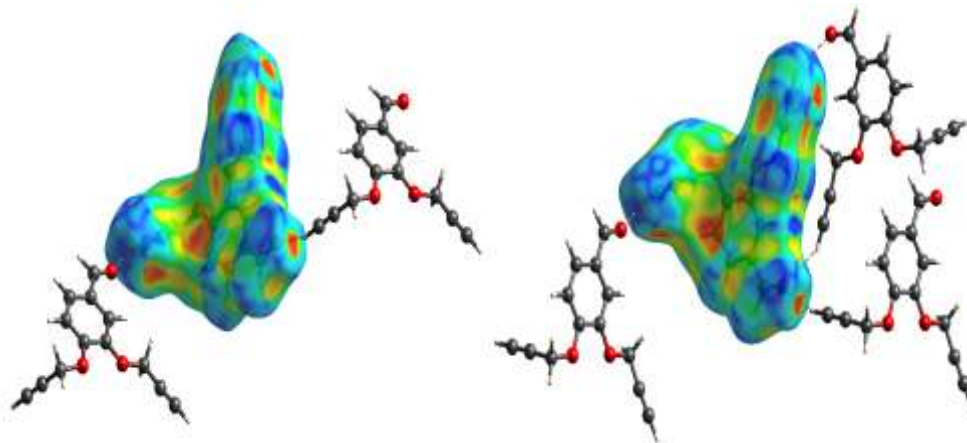


Figure 6: Shape-index [left (molecule A), right (molecule B)]: Neighbouring molecules are associated with close contacts

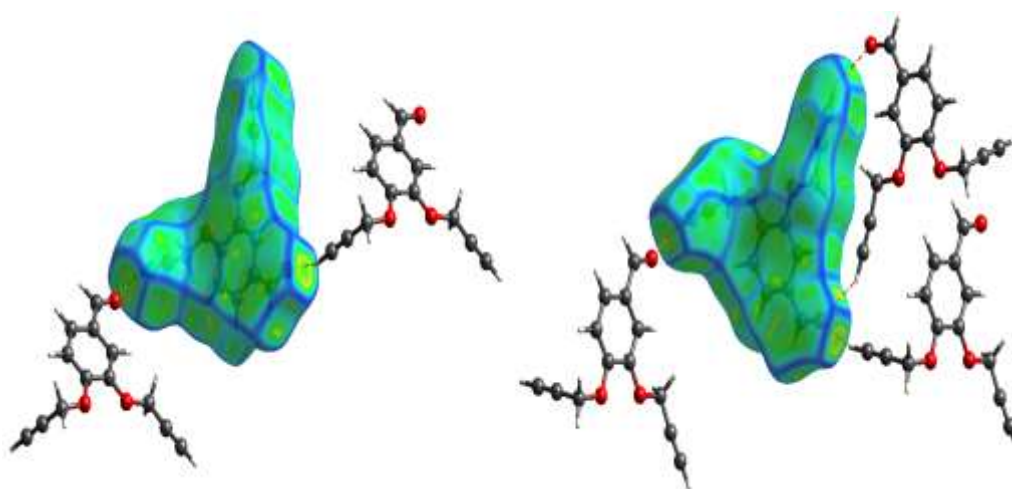


Figure 7: Curvedness [left (molecule A), right (molecule B)]: Neighbouring molecules are associated with close contacts

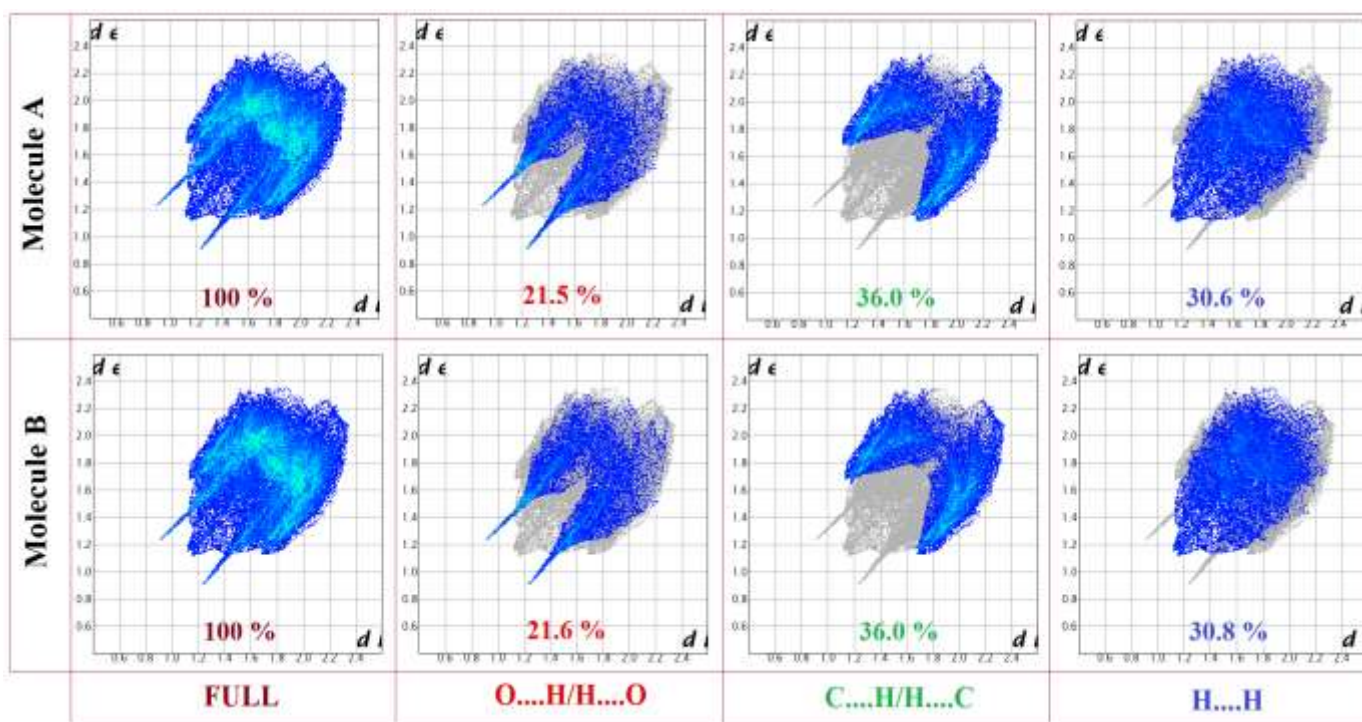


Figure 8: 2-D fingerprint plots: full (left) and resolved into O...H/H...O, C...H/H...C and H...H contacts showing the percentage contribution to the total Hirshfeld surface area of the molecules

## CONCLUSIONS

The crystal structure and Hirshfeld surface investigation of 3,4-bis(prop-2-yn-1-yloxy)benzaldehyde are reporting for the first time to the scientific communication. The compound was synthesized and characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, elemental and X-ray crystallographic analysis. The compound crystallizes in the monoclinic crystal lattice with *P*-1 space group. The crystal lattice of the compound contains two molecules in an asymmetric unit and four molecules in a unit cell. The crystal packing of the compound is stabilized by strong C13A(sp)—H13A....O1B, C13B(sp)—H13B....O1A and C12B(sp)—H12B....O1B intermolecular hydrogen bonding. These hydrogen bondings are helpful to arrange the molecules in zig-zag manner with various H-bond patterns e.g. C(11), R<sup>2</sup><sub>2</sub>(20) and R<sup>4</sup><sub>6</sub>(47). The analyses of 3-D Hirshfeld surfaces and 2-D fingerprint plots revealed that the O....H, C....H and H....H interactions play an important role toward the stabilization of compound. This analysis is also revealed that C....H contacts comprise the majority of interactions.

## ACKNOWLEDGEMENT

Priyanka Singh is thankful to Department of Chemistry, St. Andrews College, Gorakhpur 273001, Uttar Pradesh, India for providing necessary research facilities. Authors are highly thankful to Department of Chemistry, Banaras Hindu University, Varanasi-221005, UP, India for providing <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and single crystal X-ray diffraction facilities.

## SUPPLEMENTARY DATA

CCDC No. 942945 for compound contains the supplementary crystallographic data that can be obtained free of charge at <http://www.ccdc.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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