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SYNTHESIS, CRYSTAL STRUCTURE, HIRSHFELD SURFACE ANALYSIS, DFT STUDIES of 4-(METHOXYCARBONYL)BIPHENYL-4-YL 5-BROMO THIOPHENE-2-CABOXYLATE

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1.1 Abstract:

The title compound $C_{19}H_{13}BrO_4S$ is a liquid crystal molecule. The dihedral angle between S1 to C5 ring and C7 to C12 ring is 55.61(2) and C7 to C12 ring and C13 to C18 ring is 3.19(2)°. The torsional angle of S1-C1-C5-O2, C10-C9-C12-C13 and C9-C12-C13-C14 are -178.43(14)°, 177.53(19)° and 179.30(18)°. Crystal is further influenced by C-H···π and π···π stacking. Hirshfeld surface analysis indicates electron density distribution around the molecule and interaction among different atoms in title compound. In the title compound maximum interaction are contributed by C···H/H···C (33.9%), H···H/ H···H (19.4%), O···H/H···O (15.4%) and Br···H/H··· Br (12.1%). The Density functional theory studies quantify HOMO and LUMO energy gaps. Hence stability, chemical reactivity, nucleophilic, electrophilic nature and molecular electrostatic potential surface of the title compound have been determined.

1.2 Introduction

Methyl 4-hydroxybiphenyl-4-carboxylate (MHBC) exhibit unique physicochemical property, due to the presence of biphenyl ring moiety in the molecular structure and found to exhibit various applications in organic semiconductors and liquid crystal displays (LCDs). The derivatives of MHBC shows mesomorphic properties, exhibit both solid and liquid emitted characteristics of organic molecules. Which is applicable in the liquid crystal displays in electronic devices [1]. Liquid crystals are essentials in many applications as they have

capacity to manipulate the light effectively. These materials often used in automative and construction industries, with strong durability and resistance towards environmental degradation. Further the chemical architecture of MHBC shows good conductive properties [2-4]. 5-bromo thiophene-2-carboxylic acid (BTPC) is five membered rings with four carbon atoms and sulphur atom. The BTPC can be synthesised in different ways, many researchers have synthesised BTPC using Suzuki cross-coupling reaction, here molecular fragments were joined with the help of palladium catalyst. This technique helped in the generation of many derivatives by coupling BTPC with different aryl functional groups [5]. Another way is by bromination and carboxylation of thiophene derivatives [6]. The BTPC has good thermal stability, and found active in various chemical reactions taking place under heat. The bromine and carboxylic acid functional groups contributes more reactivity than thiophene derivatives. Crystallographic studies shown that the compound exhibit interesting supramolecular structure with good electronic characteristics of BTPC. It presents nonlinear optical properties which is used to design electronic materials [7]. The electronic interaction of thiophene ring and the groups attached to it, helps to synthesis materials for the solar cell [8,9]. The BTPC is also used in the fabrication of organic photovoltaics. The unique optical property and ability to form conductive polymer, when it is subjected to electrochemical process leads to the synthesis of variety of different molecules for solar cells [10,11]. The ability of BTPC in transport of charges further increases the efficiency of the solar cell device [12]. The BTPC is a versatile compound with wide variety of applications in material science, chemistry due to its thermal stability, potential roles in electronic applications. The ongoing research on these derivatives plays a crucial role in future innovations in the materials science.

The title compound consists of biphenyl molecule connected to thiophene ring, which shows very good electronic properties. The presence of methoxy carbonyl group increases solubility in organic solvents. The title compound finds significant application in the field of organic electronics [13,14]. The organic semiconductors synthesised using these moieties, gained a importance in the fabrication of organic light emitting diodes (OLEDs) and organic solar cells (OSCs) [15,16]. The thiophene ring supports charge transportation and increases the efficiency of the device. The structural feature of the biphenyl and thiophene ring of title compound supports electron conjugation and delocalization, which are key factors for efficient light emission and energy conversion. The polymer with thiophene units shows very good conductivity and flexibility. This leads to the innovation of new materials and lightweight materials suitable for various

application in textile and nanotechnology. Introduction of different functional group by electrophilic aromatic substitution or by different reactions can modify the physical and chemical properties, which can be used in developing high-performance materials used in different fields [17].

The biphenyl and thiophene ring exhibits good properties such as solubility, reactivity and electronic behaviour find its applications in organic electronics, polymer science. The current researchers find significance advances in the field of material science and play key role in the upcoming technological advances. In view of the above, researcher was very much interested to study crystal structure, Hirshfeld surface analysis, DFT studies of the title compound.

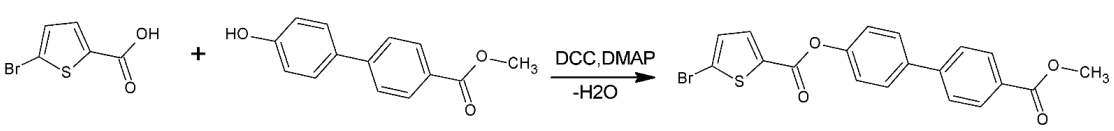
1.3. MATERIALS AND METHODS/EXPERIMENTAL

1.3.1 Synthesis and crystallisation

5-bromotetrahydrothiophene-2carboxylicacid, (Sigma-Aldrich,98%), methyl4'-hydroxy bi phenyl-4-carboxylate(Sigma-Aldrich,98%)),4-Dimethylaminopyridine(DMAP), (SpectrochemPurity-99%), Di cyclohexyl carbodiimide (DCC) (Spectrochem, Purity-99%), chloroform (Molychem, Purity-99.8%), acetic acid (Sigma-Aldrich, 98%), sodium sulphate (Sigma-Aldrich, 98%). All reactants used without any further purification.

1.3.1.2. Synthesis of 4'-(methoxycarbonyl)bipenyl-4-yl 5-bromothiophene-2-carboxylate

The mixture of 5-bromotetrahydrothiophene-2carboxylicacid (1eq) and methyl4'-hydroxybiphenyl-4-carboxylate is subjected to reaction in presence treated with dry chloroform in presence of dicyclohexylcarbodiimide (1.2 eq) (DCC) and catalysis dimethyl aminopyrimidine (DMAP) at room temperature for about 7 hours. Once the reaction is completed, the mixture is mixed with water and extracted in to chloroform. The chloroform is then washed with water (10ml), dilute acetic acid and dried over sodium sulphate to get final product. Final product obtained is crystalized at room temperature to obtain good quality single crystals. The molecular formula of the compound is $C_{19}H_{13}BrO_4S$. The molecular weight of the final product is 417.26.



Scheme 1.1 Reaction scheme for the molecule 4'-(methoxycarbonyl)bipenyl-4-yl 5-bromothiophene-2-carboxylate

1.3.2. Data collection and structure refinement details

The single crystal of title compound is of size 0.24 × 0.20 × 0.18 mm^3 were recognised through polarizing microscope and selected through paratone-N oil. The crystal is placed on goniometer to get single crystal diffraction. The diffraction data were collected by Bruker SMART APEX II CCD diffractometer (MoKα radiation). The scan width is set for Δω = 0.5° and crystal is mounted at a distance of 40mm. The refinement and reduction of data were carried out with the help of SAINT [18]. The crystal structure was solved and refined using SHELXS97[19] and *WinGX* suite [20,21]. Using the MERCURY 3.0 package, *ORTEP* and Packing figures were generated [22]. The *Gaussian 09* program was used to extract DFT data. Absorption and emission spectra were recorded in the wave length region 230 nm to 850 nm using the instrument SR-6 UV-Vis Spectrometer and RF-6000 spectrofluorophotometer.

1.4 RESULTS AND DISCUSSION

The title compound is subjected to X-ray crystallographic studies and the obtained crystallographic data and refinement data is tabulated in the **Table 1.1**. The hydrogen bonds and weak C-H···π and π···π interactions are presented in the **Table 1.2**. The title compound is crystalized in orthorhombic system, *Pna*21 space group associated with the lattice parameter *a* = 5.9011 (1) Å, *b* = 7.1952 (2) Å, *c* = 39.1810 (9) Å and *V* = 1663.61 (7) $Å^3$.

Table 1.1 Crystallographic data, experimental details of the Compound

Compound	MBBTC
Chemical formula	$C_{19}H_{13}BrO_4S$
Mr	417.26
Crystal system, space group	Orthorhombic, *Pna*21
Temperature (K)	296
a, b, c (Å)	5.9011 (1) 7.1952 (2)),39.1810 (9)
α, β, γ	90, 90, 90
V (Å)	1663.61 (7)
Z	4
Radiation type	Mo Kα
μ(mm^{-1})	2.62
Crystal size (mm)	0.24 × 0.20 × 0.18 mm^3
Data collection	
Diffractometer	Bruker SMART APEXII CCD
No. of measured independent and observed [I > 2 σ(I)] reflections	24503, 4094, 3953
Rint	0.040

$(\sin \Theta/\lambda)_{max}$ (Å^{-1})	0.669
(Reciprocal lattice vector)	
Refinement	
R[$F^2 > 2\ \sigma$ (F2)], wR(F^2), S	0.026, 0.069, 0.98
No. of reflections	
Data/restraints/parameters	4094/1/227
Limiting indices	$-7 \le h \le 7$, $-9 \le k \le 9$, $-52 \le l \le 51$
Largest diff. peak and hole	0.69 and -0.48
ρ_{max}, ρ_{min} (Å^{-3})	
Theta range for data collection	2.1 ° to 28.4°
Max. and min. transmission	T_{min} = 0.539, T_{max} = 0.624

1.4.1 Crystal Structures

1.4.1.1 Structural commentary of title compound

The crystal structure of the title compound is shown in **Figure 1.1.** The dihedral angle between S1 to C5 ring and C7 to C12 ring is 55.61(2) and C7 to C12 ring and C13 to C18 ring is 3.19(2)°. The torsional angle of S1-C1-C5-O2, C10-C9-C12-C13 and C9-C12-C13-C14 are -178.43(14)°, 177.53(19)° and 179.30(18)°. The molecular packing is further stabilized by C-H···π interactions. They are C3—H3···Cg1^{i} , C8—H8···Cg2^{ii} , C11—H11···Cg2^{iii}, ^{C}14—H14···Cg3^{iv} , C17—H17···Cg3^{iii} with symmetry codes (i) −x+1/2, −y, z+1; (ii) −x−1/2, y, z+1/2; (iii) −x+1/2, y+1, z+1/2. Which are as shown in **Figure 1.2.** The molecular arrangement is further stabilized by C14—H14···O4 intra molecular interaction. In addition to these, their exist a halogen···Oxygen contact called Bromine···Oxygen(2.948 Å) interaction between the molecules which connects the molecules along [001] direction infinity as shown in Figure 1.3.

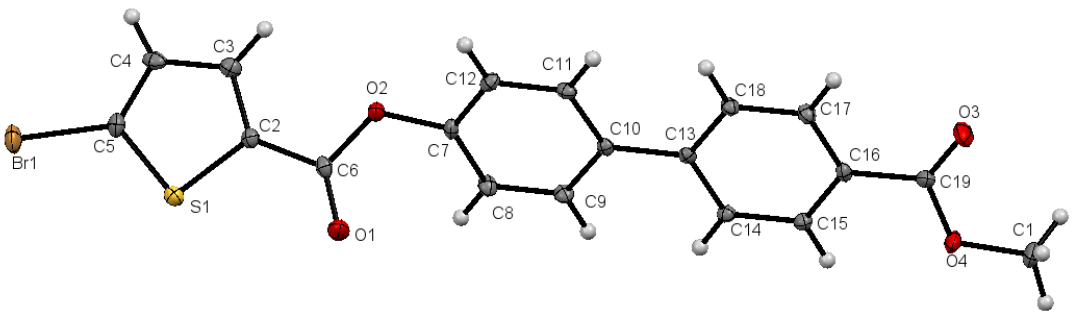


Figure 1.1 *ORTEP* diagram of the title compound drawn with 50% probability ellipsoids.

The bond angle between *Donor*—Hydrogen···*Acceptor* is 98 º is considered and listed in the **Table 1.2.**

Table 1.2 Hydrogen-bond exhibited by title compound , in (Å, º).

D—H···A	*D—H*	*H···A*	*D···A*	*D—H···A*
C3—H3···Cg1^{i}	0.93	2.84	3.505 (2)	129
C8—H8···Cg2^{ii}	0.93	2.81	3.488 (2)	131
C11—H11···Cg2^{iii}	0.93	2.78	3.465 (2)	131
C14—H14···Cg3^{iv}	0.93	2.81	3.463 (2)	128
C17—H17···Cg3^{iii}	0.93	2.89	3.542 (2)	129
C14—H14···O4	0.93	2.44	3.747 (2)	98

Symmetry codes: (i) −x+1/2, −y, z+1; (ii) −x−1/2, y, z+1/2; (iii) −x+1/2, y+1, z+1/2.

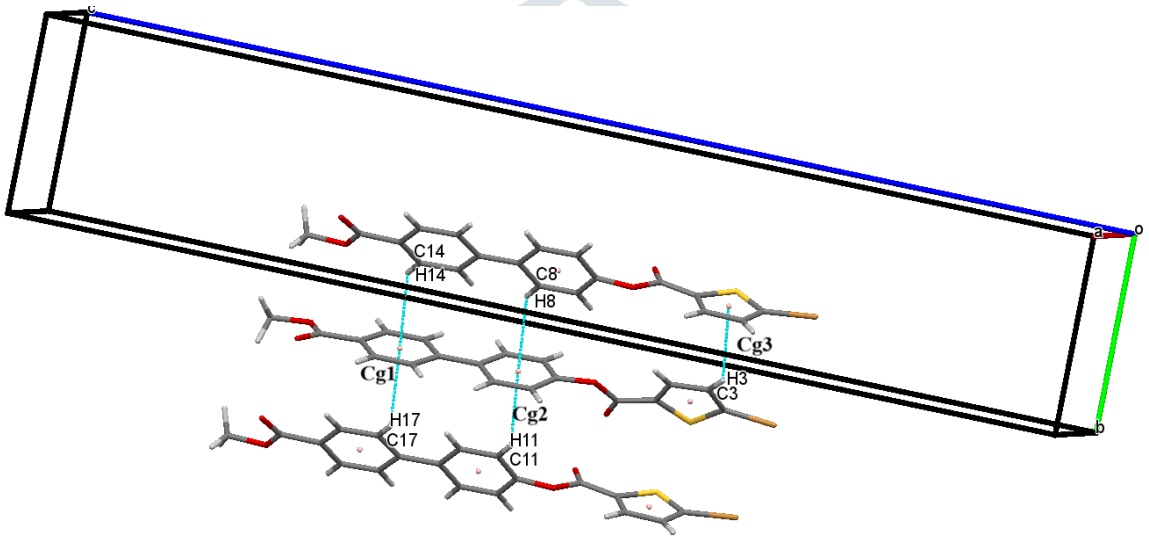


Figure 1.2 The crystal packing of the title compound exhibiting C-H …π. interaction forming *S (4)* chain

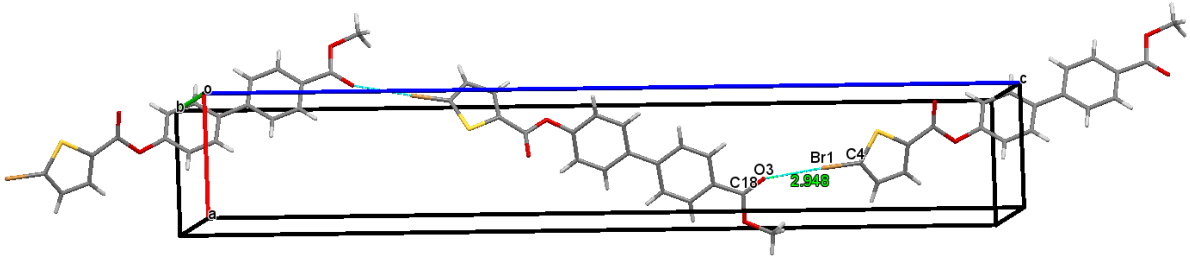


Figure 1.3 The crystal packing of the title compound exhibiting Br1 ··· O3 interaction

In addition to the above details, the selected bond lengths, bond angles and torsion angles are listed in **Tables 1.3-1.4**.

Table 1.3 The selected bond lengths (Å) of the title compound.

Atom-Atom	Bond length	Atom-Atom	Bond length
S1—C4	1.715 (3)	C7—C8	1.381 (4)
S1—C1	1.724 (4)	C6—C7	1.392 (4)
O1—C5	1.205 (4)	C8—C9	1.411 (4)
O2—C5	1.369 (4)	C9—C10	1.403 (4)
O2—C6	1.398 (4)	C9—C12	1.484 (5)
O3—C18	1.212 (4)	C10—C11	1.393 (4)
O4—C18	1.345 (4)	C12—C17	1.405 (4)
O4—C19	1.450 (4)	C12—C13	1.415 (4)
C1—C2	1.375 (4)	C13—C14	1.392 (4)
C1—C5	1.462 (5)	C14—C15	1.393 (4)
C2—C3	1.390 (5)	C15—C16	1.399 (4)
C4—Br1	1.872 (4)	C15—C18	1.483 (5)
C6—C11	1.379 (5)	C16—C17	1.391 (5)

Table 1.4 The selected bond angles (°) of the title compound

Atom-Atom-Atom	Bond angle	Atom-Atom-Atom	Bond angle
C4—S1—C1	90.45 (17)	C10—C9—C8	117.2 (3)
C5—O2—C6	118.9 (3)	C10—C9—C12	121.5 (3)
C18—O4—C19	115.1 (3)	C8—C9—C12	121.3 (3)
C2—C1—C5	128.7 (3)	C11—C10—C9	121.6 (3)
C2—C1—S1	112.1 (3)	C6—C11—C10	119.4 (3)
C5—C1—S1	119.2 (2)	C17—C12—C13	117.1 (3)
C1—C2—C3	112.4 (3)	C17—C12—C9	121.5 (3)
C4—C3—C2	112.7 (3)	C13—C12—C9	121.3 (3)
C3—C4—S1	112.4 (3)	C14—C13—C12	121.3 (3)
C3—C4—Br1	126.8 (3)	C13—C14—C15	120.5 (3)
S1—C4—Br1	120.6 (2)	C14—C15—C16	119.1 (3)

O1—C5—O2	124.1 (3)	C14—C15—C18	122.7 (3)
O1—C5—C1	126.1 (3)	C16—C15—C18	118.2 (3)
O2—C5—C1	109.7 (3)	C17—C16—C15	120.4 (3)
C11—C6—C7	120.9 (3)	C16—C17—C12	121.6 (3)
C11—C6—O2	116.3 (3)	O3—C18—O4	123.8 (3)
C7—C6—O2	122.5 (3)	O3—C18—C15	124.1 (3)
C8—C7—C6	119.3 (3)	O4—C18—C15	112.1 (3)
C7—C8—C9	121.6 (3)		

Table 1.5 Torsional angle for the title compound

Atom-Atom-Atom-Atom	Bond angle	Atom-Atom-Atom-Atom	Bond angle
C4—S1—C1—C2	0.71 (18)	C7—C6—C11—C10	1.4 (3)
C4—S1—C1—C5	179.41 (17)	O2—C6—C11—C10	−173.03 (18)
C5—C1—C2—C3	−179.3 (2)	C9—C10—C11—C6	−0.8 (3)
S1—C1—C2—C3	−0.7 (2)	C10—C9—C12—C17	−2.9 (3)
C1—C2—C3—C4	0.3 (3)	C8—C9—C12—C17	176.7 (2)
C2—C3—C4—S1	0.2 (2)	C10—C9—C12—C13	177.53 (19)
C2—C3—C4—Br1	177.28 (16)	C8—C9—C12—C13	−2.9 (3)
C1—S1—C4—C3	−0.53 (18)	C17—C12—C13—C14	−0.3 (3)
C1—S1—C4—Br1	−177.80 (13)	C9—C12—C13—C14	179.30 (18)
C6—O2—C5—O1	1.0 (3)	C12—C13—C14—C15	0.2 (3)
C6—O2—C5—C1	−176.90 (17)	C13—C14—C15—C16	−0.3 (3)
C2—C1—C5—O1	−177.9 (2)	C13—C14—C15—C18	178.21 (19)
S1—C1—C5—O1	3.7 (3)	C14—C15—C16—C17	0.6 (3)
C2—C1—C5—O2	0.0 (3)	C18—C15—C16—C17	−178.0 (2)
C7—C8—C9—C12	−179.58 (19)	C14—C15—C18—O4	−6.1 (3)
C8—C9—C10—C11	0.1 (3)	C16—C15—C18—O4	172.40 (19)
C12—C9—C10—C11	179.67 (18)	C7—C6—C11—C10	1.4 (3)
C4—S1—C1—C2	0.71 (18)		

1.4.2. Hirshfeld surface analysis

The Hirshfeld surface analysis for the title compound was generated using CIF file as an input for in *Crystal Explorer 17.5*[23]. The basis set B3LYP\631-G(d,p) is used to determine various molecular interactions. The

normalized contact distance d_{norm} mapped over the surface of compound is shown in **Figure 1.4.** The different colours on Hirshfeld surface indicates various molecular interactions of title compound**.** The red colour indicates smaller contacts; blue colour indicates longer contacts and neither small nor long contacts are indicated by white colour. These contacts are called Van der-Waals contacts [24].

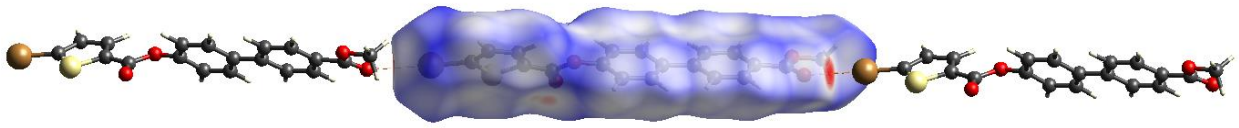


Figure 1.4 The halogen oxygen interaction through HF surface, dashed lines showing the Br1···O3 interactions

The 2-D fingerprint plots of title compound determine the major contributions of the crystal structure are given by C···H/H···C (33.9%), H···H (19.4%), O···H/H···O (15.4%) and Br···H/H··· Br (12.1%) shown in **Figure 1.5**. The red colour sites on the Hirshfeld surface indicates electronegative sites. The oxygen atom(O3) of the molecule is electronegative in nature and hence it acts as nucleophile (electron-pair donor) and bromine atom (Br1) of the molecule acts like electrophile (electron-pair acceptor). Here oxygen acts like a Lewis base (electron donor) and bromine acts like Lewis's acid (electron acceptor). The interaction between oxygen and bromine is non-covalent halogen bond (O···**Br**—**C**).

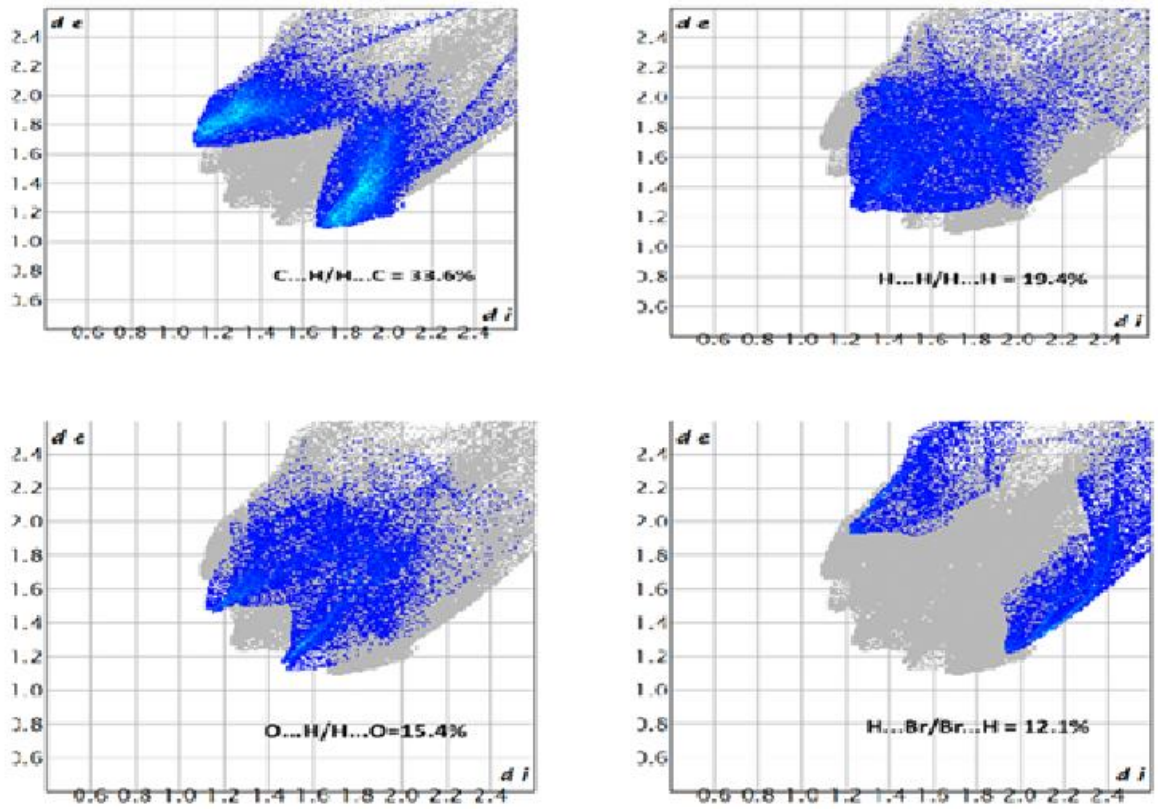


Figure 1.5 The two-dimensional fingerprint plots for the title compound , showing Full interactions, and delineated into C···H/H···C, H···H, O···H/H···O and H···Br/Br···H interactions.

1.4.2.1 ENERGY FRAME WORK CALCULATIONS

Interaction energy frame work is analysis was carried out for the compound **(IV)** using the basis set B3LYP /6-31G(d.p) for the molecule with in radius 3.83.8 Å. The E_{ele}, E_{dis}, *and* E_{tot} energy is calculated with the help of **Table 5.6** and **5.7.** The net interaction energies of the title compound are E_{ele} = -47 kJ mol^{-1}, E_{pol} = -12.4 kJ mol^{-1}, E_{dis} = -213.3 kJ mol^{-1} , E_{rep} = 137.3 kJ mol^{-1} and total energy E_{tot} of -159.8 kJ mol^{-1}. The major contribution to the crystal energy frame work comes from dispersion energy. These energy frame work called electrostatic, dispersion and total energy are shown in the **Figure 1.6**. The cylindrical radii are comparative to stability of the corresponding energies with a cutoff value of 5 kJ mol^{-1}with unit cell 1x1x1.

Table 1.6 The details of Interaction energies of title compound

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	x, y, z	5.90	B3LYP/6-31G(d,p)	-13.9	-3.4	-43.9	29.4	-37.3
1	x+1/2, -y, z	4.56	B3LYP/6-31G(d,p)	-16.4	-4.3	-73.1	56.5	-49.3
0	-x+1/2, y, z+1/2	19.61	B3LYP/6-31G(d,p)	-5.5	-1.9	-7.7	0.0	-14.0
0	-x, -y, z+1/2	20.01	B3LYP/6-31G(d,p)	-0.7	-0.1	-2.9	0.0	-3.3

1	x+1/2, -y, z	4.74	B3LYP/6-31G(d,p)	-13.1	-2.4	-77.1	51.4	-51.0
2	-x+1/2, y, z+1/2	20.24	B3LYP/6-31G(d,p)	2.1	-0.2	-5.1	0.0	-2.3
0	-x, -y, z+1/2	20.05	B3LYP/6-31G(d,p)	0.5	-0.1	-3.5	0.0	-2.6

Table 1.7 The details of K values adopted for the energy calculation of **title compound**

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

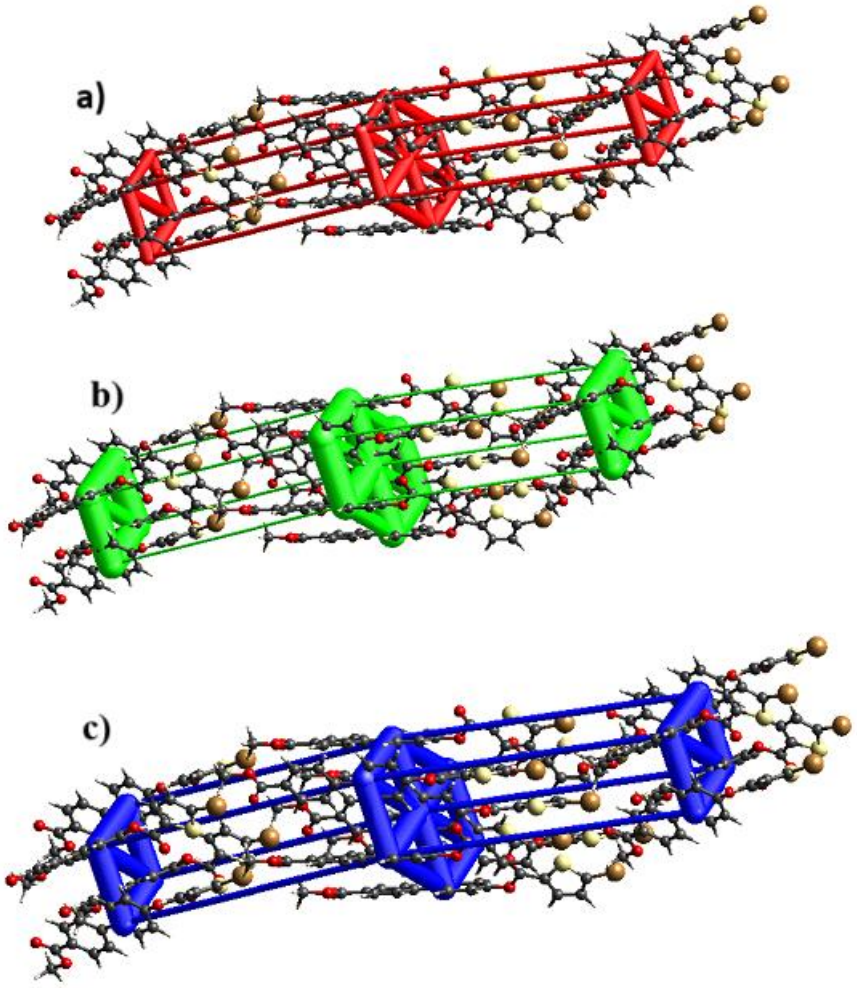


Figure 1.6 Interaction energy framework of title compound , viewed along the a-axis [100]. (a) Coulomb potential force, (b) dispersion force and (c) total energy diagrams. The cylindrical radii are proportional to the relative strength of the respective energies and is a set for 5kJ per mole.

1.5 DENSITY FUNCTION THEORY (DFT) STUDIES

The crystal information file (CIF) of title compound made into .gjf type as input file using mercury software and fed into Gauss View 6.0 [25] and the structure is further optimized using Gaussian 09 [26] which works on Berny algorithm with respect to direct inversion in repeating subspace (GEDIIS) until required points are obtained. This depends on rms displacement, maximum displacement component, rms force and force component. The molecular structure, stability, physical and chemical properties of the compound is studied with the help of DFT.

The molecular structure of the title compound is optimized with the basis set DFT/B3LYP/6-311+G(d,p) shown in **Figure 1.7.** The molecular orbital of HOMO and LUMO are generated for the title compound **.** The energy gap between HOMO and LUMO are found to be 4.3312 eV (**Figure 1.8**). The various reactivity descriptors are tabulated in the **Table 1.8**

Table.1.8 The energy values of reactivity descriptors of compounds **(IV)**

Compound	**(IV)**
E_homo (eV)	-6.6311
E_lumo (eV)	-2.2999
Energy gap =(E_lumo)-(E_homo) (eV)	4.3312
Ionisation Energy(I) (eV)	6.6311
Electron Affinity(A)(eV)	2.2999
Electronegativity(χ)(eV)	4.4655
Chemical Hardness(η)(eV)	2.1656
Chemical Softness(S) $(eV)^{-1}$	0.231
Chemical Potential(μ) (eV)	-4.4655
Electrophilicity Index(ω) (eV)	4.604

The comprehensive reactivity of the title compound is described by global reactivity descriptors. The Physical, chemical and electronic properties of the molecule are decided by the global reactivity descriptors. The ability to accept the electron or to donate the electrons are decided by HOMO and LUMO. The molecules show less stability and high reactivity for smaller energy gap and vice versa. A less electrophile molecule has electrophilicity index ω less than 1 eV and A strong electrophile molecule have electrophilicity index ω greater than 1 eV. A moderate electrophile molecule is having the electrophilicity index ω between 1 eV and 3 eV. The electrophilicity index of title compound shows strong electrophilicity.

The molecular electrostatic potential surface (MEPS) is generated by associating electrostatic potential on entire electron density with the help of Gauss View 06. MEPS structure is shown in **Figure 1.9**. The red and blue colour indicates negative and positive regions respectively.

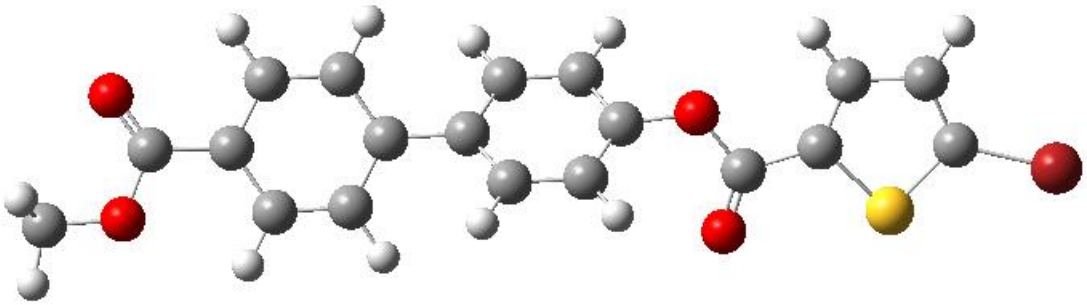


Figure 1.7 The optimised electronic molecular structure of title compound

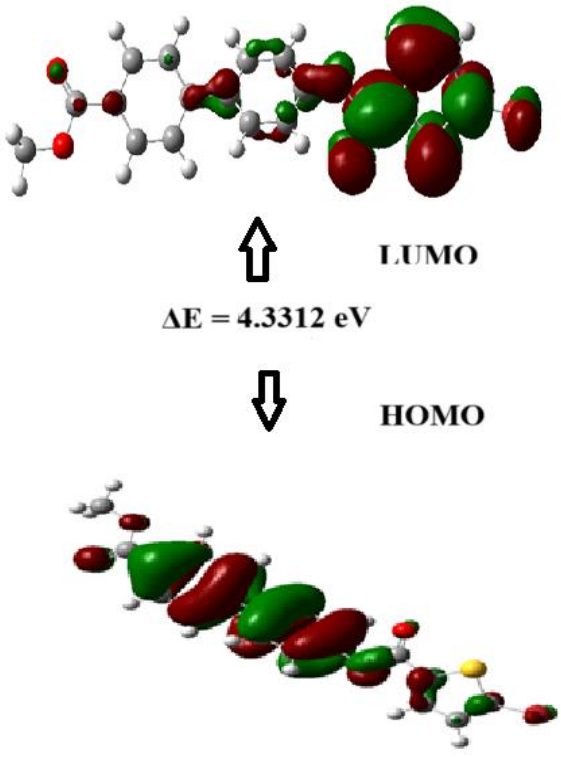


Figure 1.8 The HOMO and LUMO orbitals of title Compound with energy band gap.

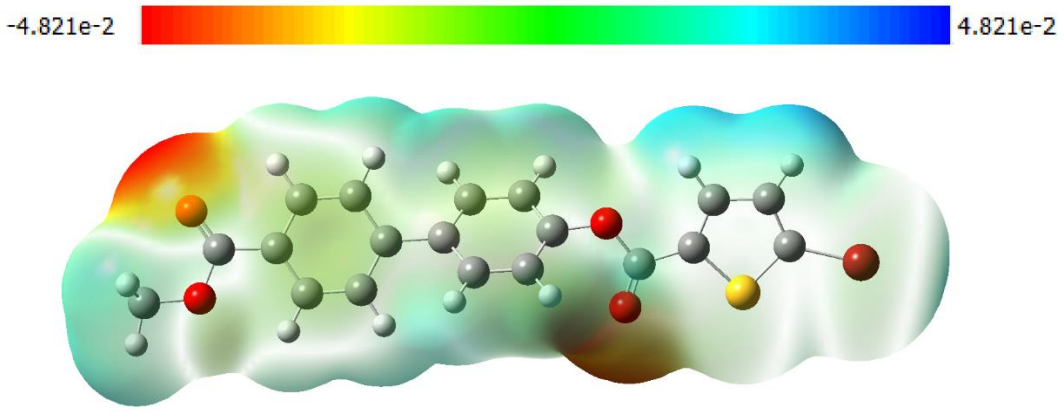


Figure 1.9 Molecular electrostatic potential surface of molecule **.**

1.6 Conclusion

In the synthesised molecule 4-(Methoxycarbonyl)biphenyl-4-yl 5-bromo thiophene-2-caboxylate, the molecular arrangement is stabilized by a weak C14—H14···O4 intra molecular interaction and halogen···Oxygen contact called Bromine···Oxygen (2.948 Å) interaction between the molecules which connects the molecules along [001]. Crystal is further influenced by C-H···π and π···π stacking. Hirshfeld surface analysis indicates electron density distribution around the molecule and interaction among different atoms in title compound. In the title compound maximum interaction are contributed by C···H/H···C (33.9%), H···H/ H···H (19.4%), O···H/H···O (15.4%) and Br···H/H··· Br (12.1%). The energy frame works visualizes the spatial arrangement of intermolecular interactions. Dominant interactions such as C-H···π and π···π among different atoms appear as thicker tubes indicating energy frame work directions, revealing crystals anisotropy. The Density functional theory studies quantify HOMO and LUMO energy gaps. Hence stability, chemical reactivity, nucleophilic, electrophilic nature and molecular electrostatic potential surface of the title compound have been determined.

1.7 References

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