IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Crystal structures of the three heterocyclic compounds: 2-Chloro-3-(4-chloro-phenyl)-3,4-dihydro-benzo[e][1,3,2]oxazaphosphinine 2-sulfide, 2-Chloro-4-(2-hydroxy-benzylamino)-phenol and (1-bromo-2-tosylethane-1,2-diyl)dibenzene

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Abstract:The title compounds, $C_{13}H_{10}Cl_2NOPS$(1a), $C_{13}H_{12}ClNO_2$ (1b) and $C_{21}H_{17}BrO_2S$ (1c), the chlorophenyl ring has atwisted conformation on the C—C bond substituted by the benzene ring and thecarboxylate group. The mean plane of the oxazaphosphinine ring is inclined to the mean plane of the dibenzene ring by 57.07 (9), 58.98 (9) and 60.34 (12)° in (I), (II) and (III),respectively. The benzene rings are inclined to one another by 73.26 (10)° in (I), 65.781)° in (II) and 63.37 (13)° in (III). In the crystals of all two compounds, there are no classical hydrogen bonds present. In compound threeIntra- and Intermolecular C-H…O, O-H…N and N-H…O hydrogen bonds are responsible for the consolidation of the crystal packing of both molecules. In addition to this, weak C-H…π and π…π interactions are also observed. For each compounds, the packing may be described in terms of two weak C-H…O and O-H…N hydrogen bonds, which link the molecules to form one-dimensional (1a, 1c) or three-dimensional (1b) assemblies.

Index Terms: single-crystal X-ray study; oxazaphosphinine, benzylamino, tosylethane, dibenzene; T = 296 K; mean (C–C) = 0.06 A˚; R-factor = 0.0496in I, 0.0511 in II and 0.0420 in III;wR factor = 0.1425 in I, 0.1502 in II and 0.1099 in III; data-to-parameter ratio 25.9.

I. INTRODUCTION

Synthesis of new organic molecules with pharmacological properties is of utmost importance in the process of drug design and discovery [1]. Several derivatives of organic molecules such as pyrrole, pyridine, semicarbazones, thiosemicarbazone, *etc*., possess various biological properties like anti-inflammation, anti-bacterial, anti-fungal, anti-cancer, anti-viral, anti-diabetic and many others biological applications [2,3]. Oxazaphosphinine belongs to a class of organophosphorus

compound well known for its anticancer and immunosuppressant activity [4]. Organophosphorus and their derivatives have developed as an imperative class of bioactive compounds that are structurally appealing and pharmaceutically active candidates [5,6]. Phosphorus derivatives bearing an esterified amino acid group on the phosphorus atom have been found to display useful anti-neoplastic properties. Cyclophosphamide, an oxazaphosphirine derivative, is used in the chemotherapy of several cancer medications [7]. Based on the biological applications, we have synthesized an 2-chloro-3-(*p*-tolyl)-3,4-dihydro-2H-benzo[e][1,3,2]oxazaphosphinine 2-sulfide derivative from 2-((*p*-tolylamino)methyl)phenol and thiophosphoryl chloride in the presence of triethylamine [8].The search for new antibacterial compounds is a challenging task as bacteria are continuously developing resistance to antimicrobial compounds; however, infections due to such bacterial strains are infrequent although potentially fatal [9]. This ongoing problem has resulted in the search for newer, more effective antibacterial compounds [10,11]. Urea, thiourea **3** (X=O or S), and benzo-1,3-oxazine compounds **5** and **6** (Scheme 1) have been shown to possess antibacterial and antifungal properties [12,13]. The benzyl thiourea analogue **3** has been reported to show activity against Gram-positive bacteria [14,15].

II. Experimental

The chemical structure of the compound is shown in Figure 1. The compounds I-III was synthesized using a previously reported procedure [16].

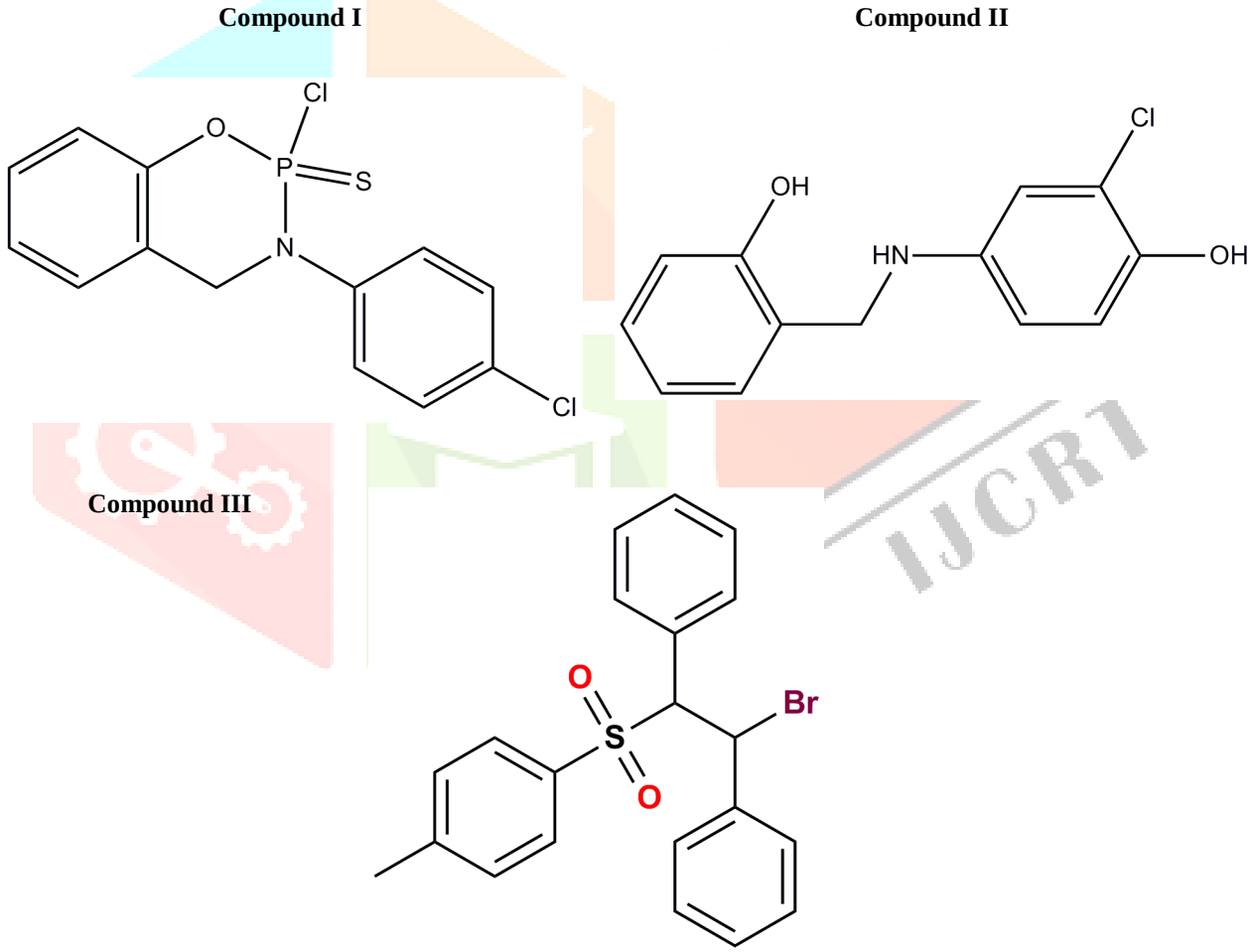

Fig.1. Chemical structure of compounds I, II and III.

III. Data collection

CryAlis Pro (Oxford Diffraction, 2007)[17]; cell refinement: CryAlis Pro; data reduction: CryAlis RED (Oxford Diffraction, 2007); program(s) used to solve structure: SHELXS86 (Sheldrick, 2008)[18]; program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ZORTEPII (Zsolnai, 1997)[19]; software used to prepare material for publication: PARST (Nardelli, 1995)[20].

IV. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Methyl groups were included as idealized rigid groups allowed to rotate but not tip (C—H = 0.98 Å, H—C—H = 109.5°). Other hydrogen atoms were included using a riding model starting from calculated positions (C—$H_{aromatic}$ = 0.95 Å, C—$H_{methylene}$ = 0.98 Å, C— $H_{methine}$ = 1.00 Å). The U_{iso}(H) values were fixed at 1.5°U_{eq} of the parent carbon atoms for methyls and 1.2°U_{eq} for other hydrogens.

V. Structural Commentary

The structure determinations confirm the nature of the products 1a-c. The three molecules, which form a heterocyclic compoundsis shown in Figs.2-4. The title compounds (I) and (II) differ only by the substituent on the benzene ring; 4-chlorophenyl in (I) and o-tolylin(II). Compounds (II) and (III) differ only in that (II) has adibenzene ring while (III) has atosylethane ring. The compounds all crystallize in space group compound I & III Monoclinc (P21/c, C2/c) and compound II Triclinic (P-1)but none of them is isotypic to any other. The bond lengths and angles may be considered normal for these compound types. For instance: the exocyclic angles N-C-C at the ring junctions are appreciably less than 120 and the CH2-CH2-CH2 angles of 1b and 1c are markedly wider than the standard value of 109.5°. The overall form of the molecules, however, differs between 1a and the similar pair 1b/1c.

For 1a, ring C displays a standard planar conformation, with C6 and C7 lying 0.481(2)Å and 0.293(2)Å, respectively, in opposite directions out of the plane defined by C5, C4 and C8. The thiophene ring lies with the sulfur atom on the opposite side of the C4-C11 bond to the sulfide group. The interplanar angle between rings a b is 45.33(4)°.

For 1b and 1c, however the thiophene rings are differentially positioned, with the sulfur atom on the same side of the C4-C12 (1b) or C4-C13 (1c) as the sulfidegroup. The respective S1-N2 distances are 3.676(1)Å and 4.070(1)Å too long to be considered significant interactions and the interplanar angles a/b are 61.40(5)° and 79.67(4)° in the rings c the $(CH2)_n$ moieties are all displaced to the same side of ring b, in the direction opposite to the sulfur atom.

VI. Superamolecular features

In the crystals of compounds (I) and (III), there are no classical hydrogen bonds present.None of the compounds contains a classical hydrogen-bond donor, and so the molecular packing must be interpreted in terms of other 'weak' interactions. The most obvious of these are 'weak' C-H…N hydrogen bonds, mostly involving the nitrogen atom of the nitrile group; however, it is a moot point whether these represent significant interactions or simply the exposed nature of the one-coordinated nitrogen atoms. Each compound displays two such contacts.

For compound I, the two hydrogen bonds (Table 2), one to each of the two nitrogen atoms, combine to form a one dimensional assembly parallel to the a axis (Fig. 6). Both operators involve inversion. Further contacts may be identified: a possible stacking of two rings B, as seen in the Fig.5 [intercentroid distance 3.6516 (6)Å, offset 1.23Å , operator x + 1, y + 1, z + 1]; a C-H contact from H6B to the centroid (Cg) of ring A (H-Cg = 2.90Å , C-HCg = 143, operator x + 3/2, y 1/2, z + 3/ 2); and a possible S contact (Ringer et al., 2007; Daeffler et al., 2012; Motherwell et al., 2018) to ring B [Scentroid 3.5460 (5)Å , same operator x + 3/2, y 1/2, z + 3/2], although this contact is markedly onesided, with S1-C2 at 3.370 (1) Å shorter than the other contact distances.

In the crystal structure of (II), molecules are connected by N-H…O and C-H…O interactions (Table 2) and additional C—Cl [C2—Cl1$Cg1^{i}$ = 3.7693 (1) Å ; 146.35 (1) Å; Cg1 is the centroid of the 4-tert-butylphenyl ring (C3–C8); symmetry code: (i) 1-x, -y, 1-z], forming layers parallel to (100) (Table 2, Fig. 7,8&9). Van der Waals forces between these layers maintain the stability of the molecular packing.

Similarly, for compound III, the two N—H…O and C-H…O hydrogen bonds, both via inversion operators but both involving the same acceptor N2 (Table 2, Fig. 10), lead to a one-dimensional structure parallel to [101]. However, whereas the H1-N2 interaction is quite short, the contact from the methyl borderline case.

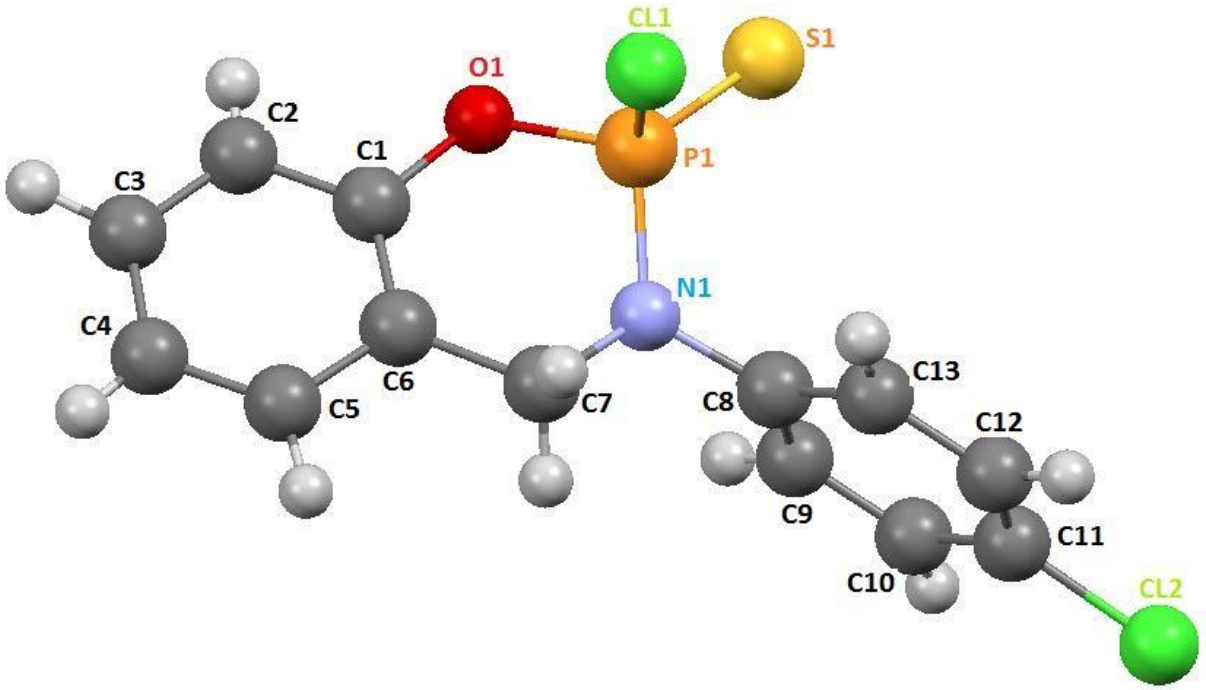

Fig.2. The molecular structure of compound (I), showing the atom labelling. Displacement ellipsoids are drawn at the 30% Probability level.

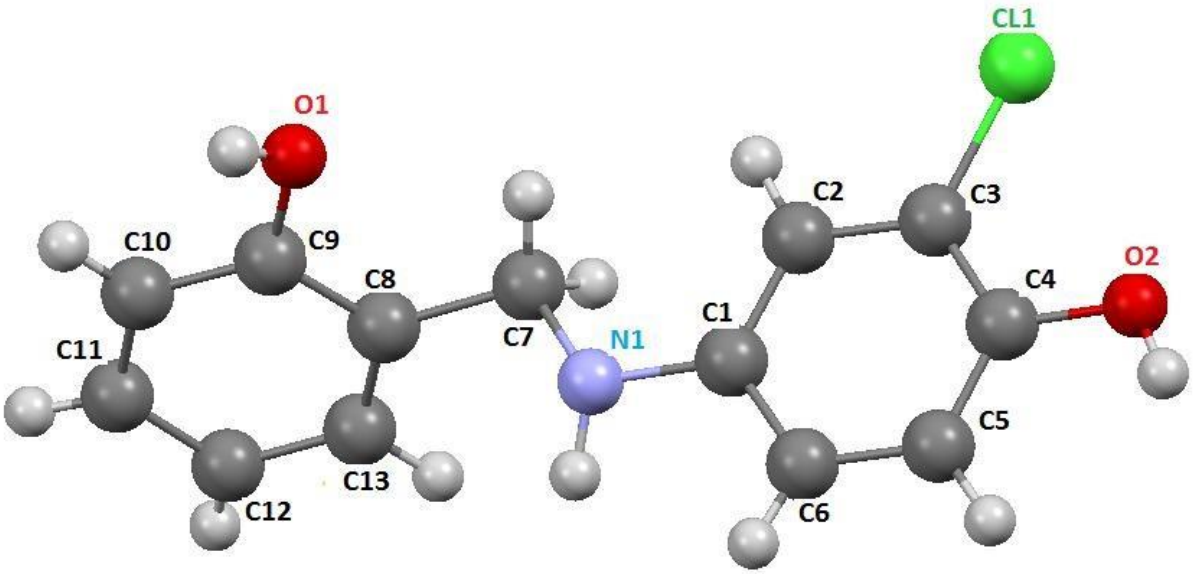

Fig.3.The molecular structure of compound (II), showing the atom labelling. Displacement ellipsoids are drawn at the 30% Probability level.

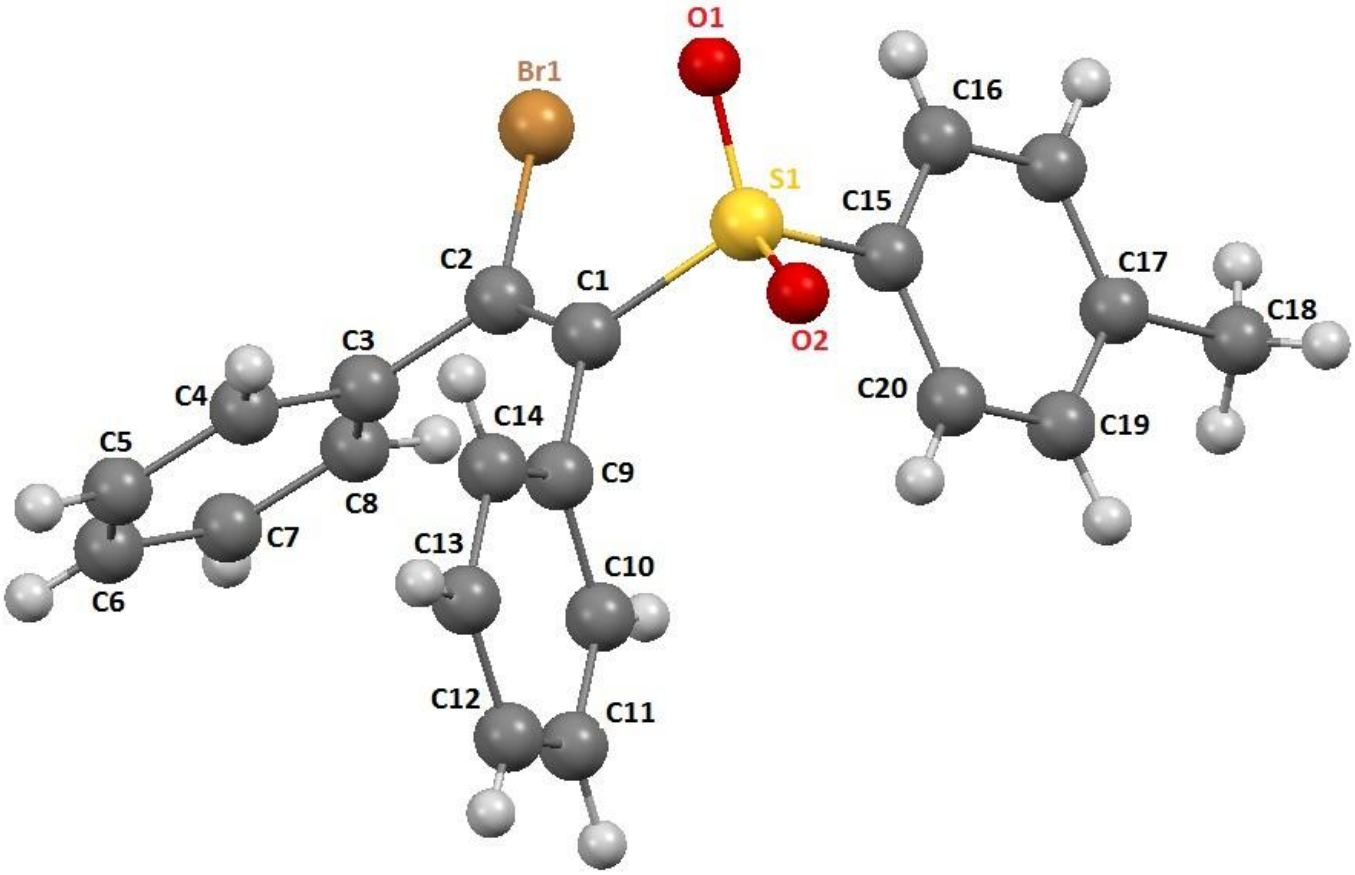

Fig.4.The molecular structure of compound (III), showing the atom labelling. Displacement ellipsoids are drawn at the 30% Probability level.

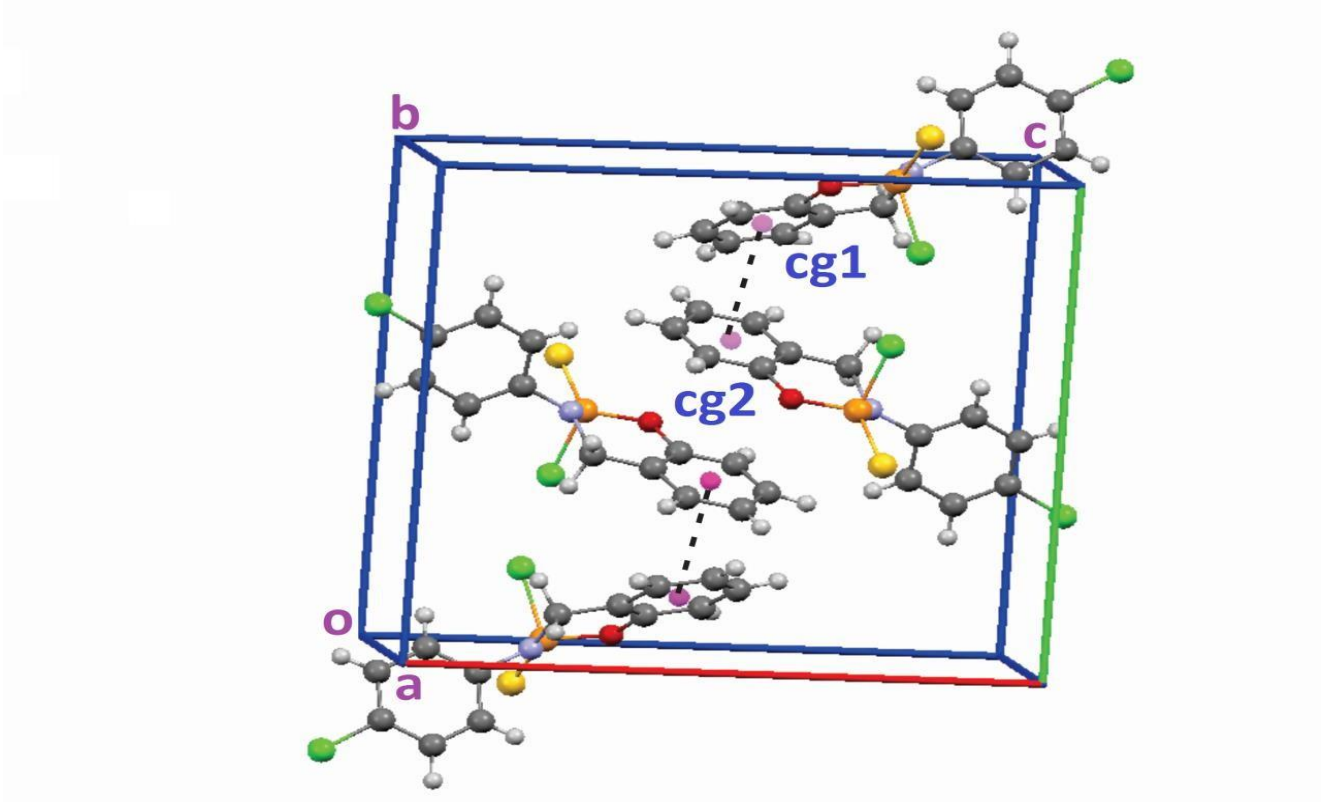

Figure 5A views along the b axis of the crystal packing of compound (I). The dashed cyan lines represent the Cg—Cg centroid distances (see Table 2).

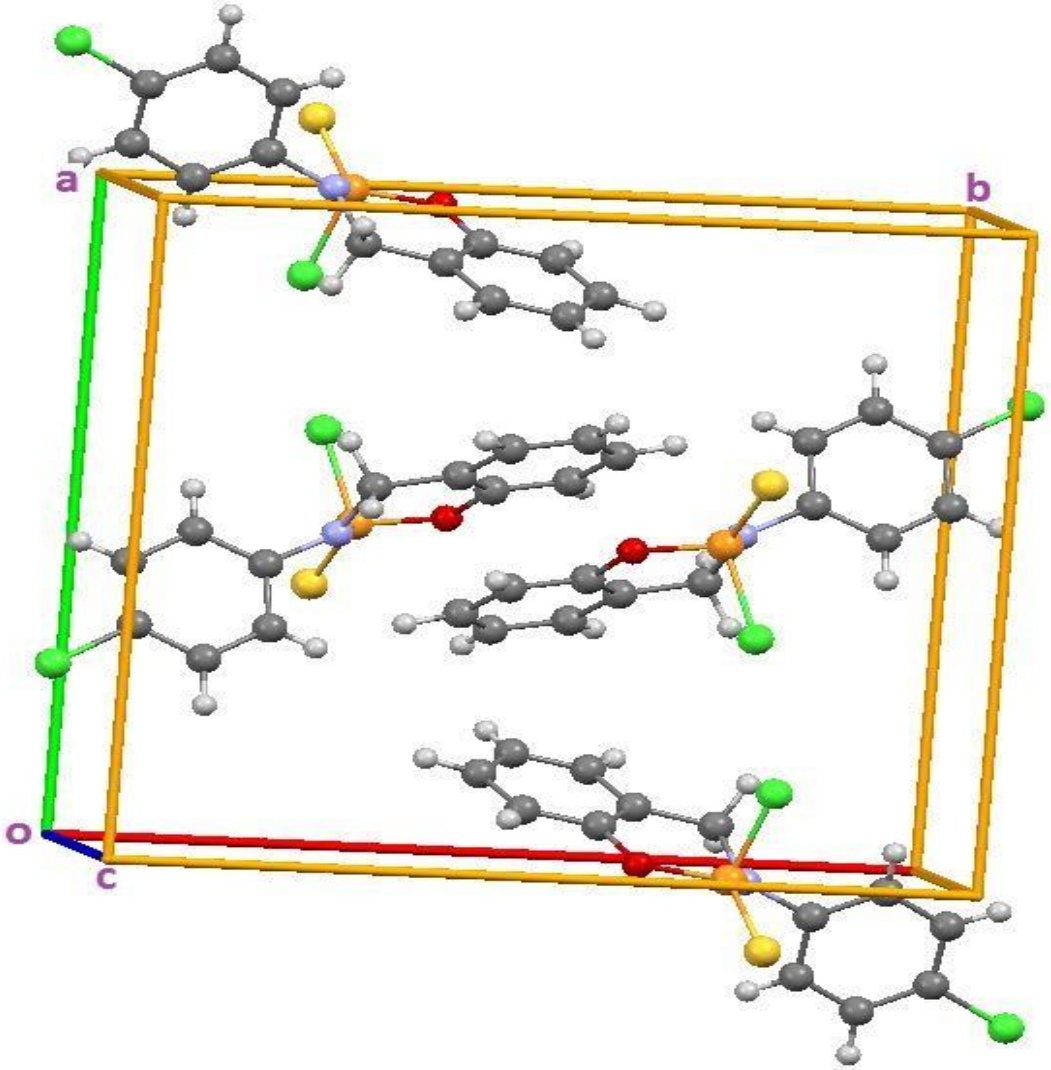

Fig.6. For compound I packing of the molecule in the unit cell, viewed down 'a'-axis

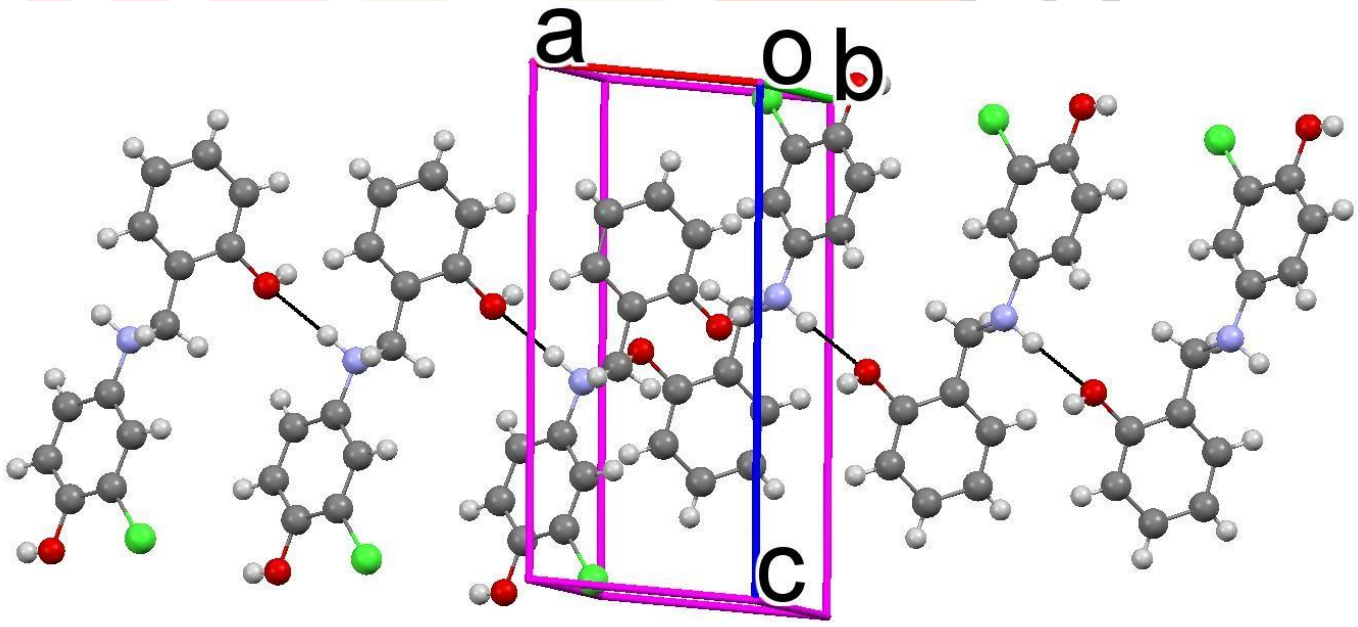

Fig.7 Intermolecular interactions showed compound II normal to the c axis.

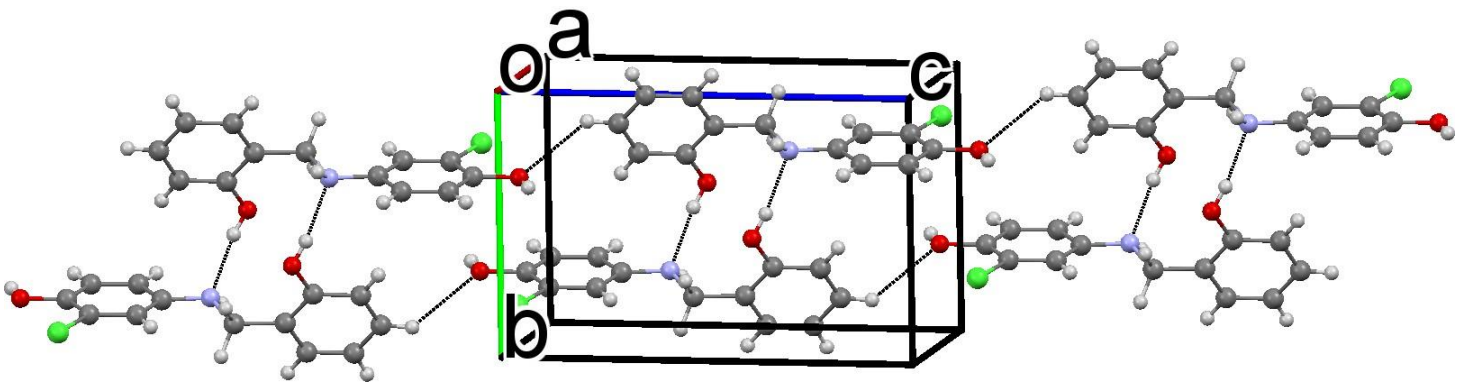

Fig. 8 In Compound II, View of the packing seen along the b-axis direction with O-H…N and C-H…O hydrogen bonds.

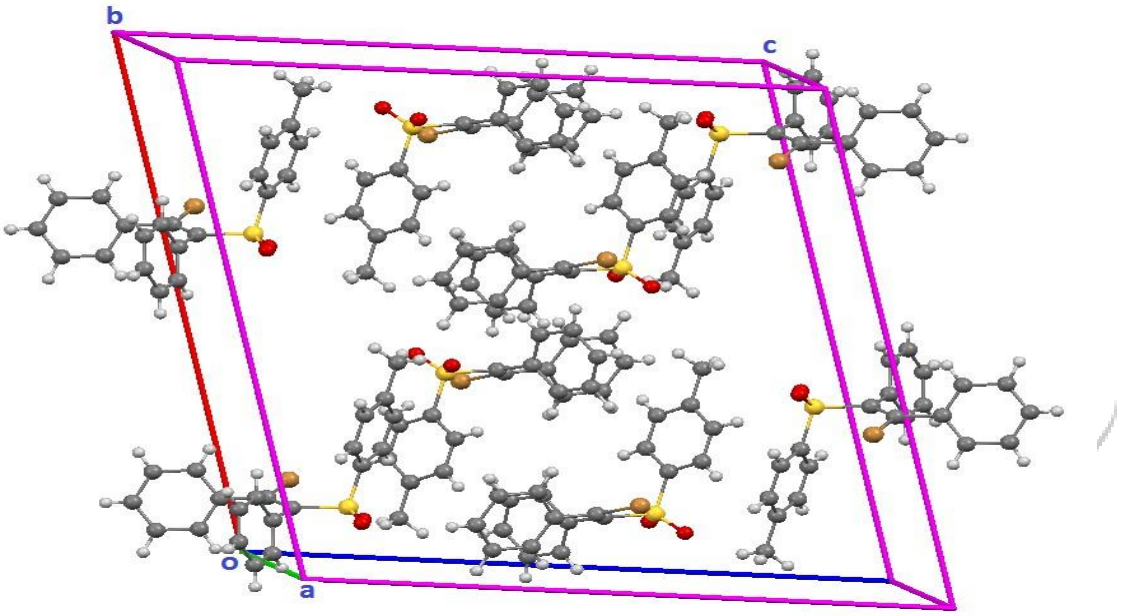

Fig.9. For compound II packing of the molecule in the unit cell, viewed down 'c'-axis

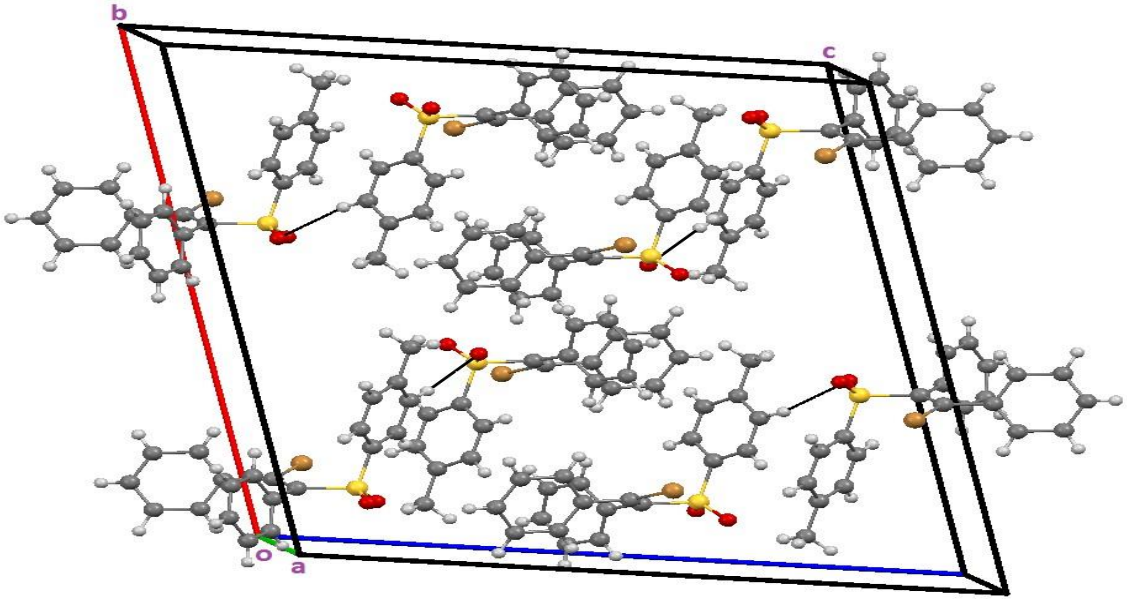

Fig.10. For compound III packing of the molecule in the unit cell, viewed down 'a'-axis

VII. Table: 1

Crystal Data and Details of the Structure Determination

Crystal data	Compound I	Compound II	Compound III
Empirical formula	$C_{13}H_{10}Cl_2NOPS$	$C_{13}H_{12}ClNO_2$	$C_{21}H_{17}BrO_2S$
Formula weight	330.15	249.69	330.15
Temperature	293K	293K	293K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P21/c	P-1	C2/c
Unit cell dimensions	a =15.3449(10) Å α= 90°	a =5.7175 (7) Å α= 91.152(2)°	a =21.561 (9) Å α= 90°
	b = 13.6150(9) Å β= 96.945(1)°	b = 7.8260 (9) Å β= 95.472(2)°	b = 8.505 (4) Å β= 106.04 (9)°
	c = 7.0837(5) Å α= 90°	c = 12.7370 (14) Åα= 91.270(2)°	c = 21.134 (10) Å α= 90°
Volume	1469.07(17) $Å^3$	567.04 (11) $Å^3$	3725 (3) $Å^3$
Z	4	2	8
Density (calculated)	1.4927(2) g/cc	1.4624 (3) g/cc	1.4740 (12) g/cc
Absorption coefficient	6.82 mm^{-1}	0.324mm^{-1}	2.330mm^{-1}
F(000)	672.0	260	1680
Crystal size	0.40 x 0.23 x 0.02 mm^3	0.20 x 0.23 x 0.02 mm^3	0.45 x 0.23 x 0.02 mm^3
Theta range for data collection	1.3 to 28.0°	1.6 to 28.3°	1.3 to 28.6°
Index ranges	-20<=h<=20, -17<=k<=17, -9<=l<=9	-7<=h<=7, -10<=k<=10, -19<=l<=16	-27<=h<=27, -9<=k<=10, -28<=l<=26
Reflections collected	16528	6502	12736
Independent reflections	3442 [R(int) = 0.018]	2561 [R(int) = 0.016]	4273[R(int) = 0.035]
Completeness to theta = 25.00°	100.00%	100.00%	100.00%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9524 and 0.4826	0.9724 and 0.4226	0.9824 and 0.4126
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3442 / 0/ 212	2561 / 0/ 198	4273 / 0/ 277
Goodness-of-fit on F^2	1.05	1.09	1.00
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1425	R1 = 0.0511, wR2 = 0.1502	R1 = 0.0420, wR2 = 0.1099
R indices (all data)	R1 = 0.0869, wR2 = 0.1670	R1 = 0.0769, wR2 = 0.1870	R1 = 0.0669, wR2 = 0.0670
Largest diff. peak and hole	0.59 and -0.36e.$Å^{-3}$	0.47 and -0.38 e.$Å^{-3}$	0.58 and -0.30e.$Å^{-3}$

VIII. Table 2

Hydrogen-bond geometry for Compound I and II(Å ,°).

D-H…A		D-H	H…A	D…A	D-H…A
II	N1-H1…O9^{i}	0.95	2.10	3.028(2)	166
	O9-H9…N1^{ii}	0.83	1.96	2.775(2)	170
	C11-H11…O4^{iii}	0.92	2.59	3.307(3)	140

Symmetry codes: (i) -1+x,y,z
(ii) 1-x,1-y,1-z
(iii) 1+x,y,1+z

IX. ACKNOWLEDGMENT

We are thankful to Dr. J. Haribabu, Faculty of Medicine, University of Atacama, Chile and Dr. Vedavati G. Puranik, Center for Materials Characterization (NCL), CSIR – National Chemical Laboratory, Pune forcrystallographic analysis and discussion.

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