Crystal Structure of 6-(4-bromophenyl)-2-((6-methylbenzofuran-3-yl) methyl) imidazo [2, 1-b] [1, 3, 4] thiadiazole ($C_{20}H_{14}BrN_3OS$)

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Abstract **- There are number of reports in the literature on the synthesis and biological activities of the condensed imidazo thiazoles, appeared particularly after the discovery of novel broad spectrum anthelmintic Tetramisole With the hope of evolving a promising drug related to tetramisole, and to prepare various other biologically important compounds, the trend has been shifted to explore the drugs containing bioisosteric thiadiazoles ring in place of thiazole ring of tetramisole.**
Imides thiadiazole nucleus is known for diverse biological properties through innumerable derivatives since the present work involves the synthesis of thiadiazoles, imidazothiadiazole and their derivatives, we have presented a few reports on thiadiazoles and imidazothiadiazole derivatives of biological interest
In the light of above observations following imidazo thiadiazol possessing chloro/bromo substituents have been subjected to X-ray diffraction studies.

Index Terms **- bromophenyl, methylbenzofuran, thiadiazole crystal x-ray study, Molecular Packing and hydrogen bonding.**

I.INTRODUCTION

The required 6-methyl-benzofuran-3-acetic acid [1] has been prepared by the alkali hydrolysis of 7-methyl-4-bromomethylcoumarin, which was synthesized by Pechmann cyclisation of *m*-cresol and 4-bromomethylacetoacetate at 0 - 5 º C. The 4-bromomethylacetoacetate was obtained by the bromination of ethyl acetoacetate in dry ether at 0 - 5 º C. Transformation of 1 to 2 is an illustration of the ring construction of coumarin to benzofuran. It is likely to occur by the formation of the alcohol due to cleavage of lactone. Intramolecular attack of the phenoxide ion followed by tautomeric shift. Acidification of the reaction mixture results in the formation of a colorless high melting solid, which is crystallized from aqueous ethanol. The reaction can be carried out on a multi-gram scale.

II. EXPERIMENTAL

Compound (Fig .1) has been grown by slow evaporation technique using chloroform. Colorless block like single crystals suitable for X-ray diffraction was obtained. The density of the crystal was measured by flotation technique using potassium iodide solution. The measured density agreed with the calculated density for Z = 2.

III.X-RAY DATA COLLECTION

The three-dimensional X-ray intensity data was collected using a crystal of size 0.30 × 0.30 × 0.20 mm mounted on an CAD4 Diffractometer with Cu-K_α radiation (λ = 1.54180Å) with temperature 293(2)K. The intensities of reflections 3247 were collected in the 2θ range 3.03 to 64.94^0. The data was collected using ω and φ scans mode with h,-0<=h<=7, -11<=k<=11, -17<=l<=17.The intensities were collected for Lorentz and polarisation effects. Among the 2936 unique reflections collected, 2554 observed reflections with $I \geq 2\ \sigma$ (I). The space group $P\ \bar{1}$ assigned from the systematic absences. The cell parameters refined using 536 reflections the refined cell parameters are a = 6.2141(17), b = 9.8002(11), c = 14.891(3) Å and $\beta = 97.068(18)^0$, V = 885.7(3) $A^{\circ 3}$. Multi-scan absorption was carried out using SADABS [2]. The calculated absorption coefficient was 4.38 mm^{-1}

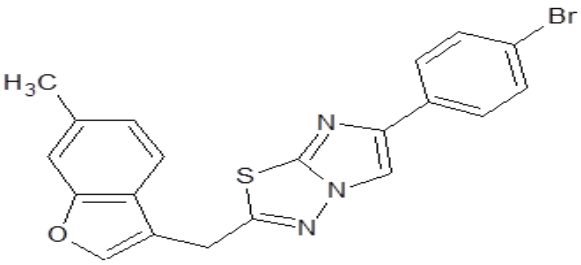

Fig .1

Structure solution and Refinement

The structure was solved by direct methods using SHELXS-97 [3]. The position of all non-hydrogen atoms were revealed in the best E-map. Then refined using the program SHELXL-97 [3] by the full matrix least squares refinement. All non-hydrogen atoms treated isotropically and refined till R-value converged at R (F) = 0.0560, $wR(F^2)$ = 0.1349. The difference Fourier map further revealed all H-atoms. All the hydrogen atoms parameters were included in the final steps of with weight assigned to a structure factor calculation using the scheme $w=1/[\sigma^2(Fo^2)+(0.0732P)^2+0.6587P]$ where $P=(Fo^2+2Fc^2)/3$. The parameters at the end of final refinement were R (F) = 0.0497, $wR(F^2)$ = 0.1290. The minimum and maximum electron densities from difference Fourier map are 0.698 and -0.589 $e.A^{-3}$ respectively.

IV. RESULTS AND DISCUSSIONS

The crystallographic refinement data is given in the Table 1.The bond lengths and bond angles for non-hydrogen atoms are listed in the Table 2 and Table 3. The Table 4. Gives torsion angles involving non-hydrogen atoms. A perspective view of a Ortep plot of the molecule with 50% probability thermal ellipsoids with atomic numbering is shown in Fig. 1. Fig.2 shows packing of molecules [4] with C-H…O Fig .3 shows the single molecule in a unit cell. Contacts and the packing of the molecule in the unit cell [4].. The least square planes and dihedral angles are listed in Table 5. Hydrogen bonding geometry listed in Table 6.

Conformation of the molecule

The molecule exhibits L-shaped conformation. The P-bromo phenyl moiety and the imidazole ring are in one plane whereas the methylene bridged benzofuran moiety is oriented at right angles 81.6°

The number of molecular in the unit cell is 2, the two benzofuran moieties are farther apart and two bromines are anti-two each other.

Bond lengths and angles

The molecule is stabilized strong intermolecular O1-H11B hydrogen bonding (2.881Å) and another association through section S1 and H8 (2.983Å). Two weak C-H associations are also indicated between C4-H13 (2.870Å) or C5-H13 (2.772Å) (Fig .2.(a)). There is C – H…π interactions that links centro symmetrically related molecules (Fig 2.(b)). The L shaped molecules are packed in layers parallel to a-axis

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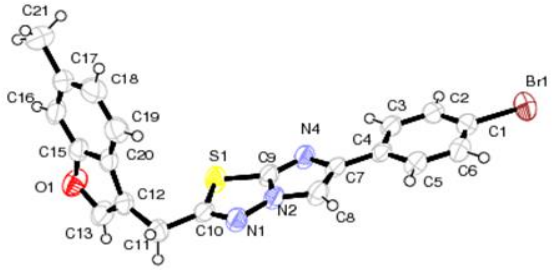

Fig.1 *ORTEP* diagram of the title molecule with 50% probability displacement ellipsoids for non-H atoms.

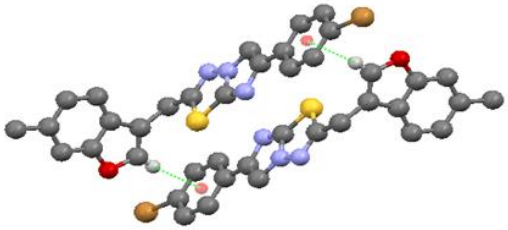

Fig. 2.(a) Packing diagram showing C-H…π Hydrogrn bonding

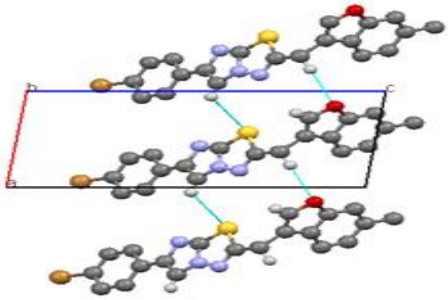

Fig. 2.((b). Packing diagram showing C – H O hydrogen bonding.

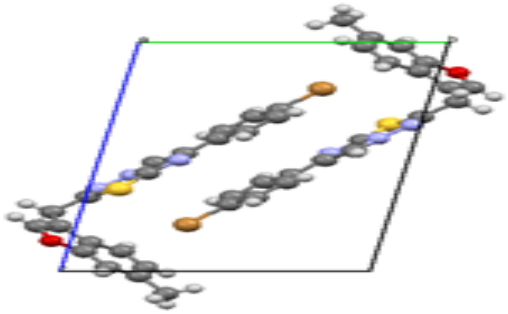

Fig. 3. Packing diagram viewed down b-axis.

Table.1. Crystal data and structure refinement.

DATA	COMPOUND
Empirical formula	C_{20} H_{14} Br N_3 O S
a	6.2141(17) Å
b	9.8002(11) Å
c	14.891(3) Å
β	97.068(18)°
Volume	885.7(3) $Å^3$
Crystal system	Triclinic
Formula weight	424.31
Space group	$P\bar{1}$
F(000)	428
Radiation	Cu-Kα (λ = 1.54180Å)
Z	2
Absorption coefficient	4.381 mm^{-1}
Calculated density	1.591 Mg/m^3
No. Parameters	237
R-obs	0.0497
wR_2 (all)	0.1290
Theta range for data collection	3.03 to 64.94°
h $_{min, max}$; k $_{min, max}$; l $_{min, max}$	0<=h<=7, -11<=k<=11, -17<=l<=17
Max. and min. transmission	0.6541 and 0.5012
Goof(S)	1.123
No. Unique reflections.	2936
Temperature	293(2) K
Largest diff. peak and hole	0.6541 and 0.5012 e $Å^{-3}$

Table 2.List of Bond lengths (Å), esd's given in the parentheses

Atom1-atom2	Angle
C(1)-C(2)	1.371(5)
C(1)-C(6)	1.380(5)
C(1)-Br(1)	1.896(4)
C(2)-C(3)	1.383(5)
C(3)-C(4)	1.395(5)
C(4)-C(5)	1.390(5)
C(4)-C(7)	1.462(5)
C(5)-C(6)	1.384(5)
C(7)-C(8)	1.365(5)
C(7)-N(4)	1.395(4)
C(8)-N(2)	1.368(4)
C(9)-N(4)	1.308(4)
C(9)-N(2)	1.354(4)
C(9)-S(1)	1.729(3)
C(10)-N(1)	1.287(4)
C(10)-C(11)	1.499(5)
C(10)-S(1)	1.752(3)
C(11)-C(12)	1.487(5)
C(12)-C(13)	1.333(5)
C(12)-C(20)	1.451(5)
C(13)-O(1)	1.371(5)
C(15)-C(16)	1.378(5)
C(15)-O(1)	1.381(4)
C(15)-C(20)	1.390(5)
C(16)-C(17)	1.380(6)
C(17)-C(18)	1.384(6)
C(17)-C(21)	1.505(6)
C(18)-C(19)	1.377(6)
C(19)-C(20)	1.382(5)
N(1)-N(2)	1.383(4)

Table 3. List of Bond angles (º), esd's given in the parentheses

Atom1-atom2-atom3	Angle
C(2)-C(1)-C(6)	121.2(3)
C(2)-C(1)-Br(1)	118.7(3)
C(6)-C(1)-Br(1)	120.1(3)
C(1)-C(2)-C(3)	119.2(3)
C(2)-C(3)-C(4)	121.1(3)
C(5)-C(4)-C(3)	118.3(3)
C(5)-C(4)-C(7)	122.1(3)
C(3)-C(4)-C(7)	119.7(3)
C(6)-C(5)-C(4)	120.8(3)
C(1)-C(6)-C(5)	119.4(3)
C(8)-C(7)-N(4)	111.1(3)
C(8)-C(7)-C(4)	128.3(3)
N(4)-C(7)-C(4)	120.6(3)
C(7)-C(8)-N(2)	104.9(3)
N(4)-C(9)-N(2)	112.9(3)
N(4)-C(9)-S(1)	137.9(3)
N(2)-C(9)-S(1)	109.2(2)
N(1)-C(10)-C(11)	123.8(3)
N(1)-C(10)-S(1)	116.7(3)
C(11)-C(10)-S(1)	119.5(3)
C(12)-C(11)-C(10)	113.0(3)
C(13)-C(12)-C(20)	105.7(3)
C(13)-C(12)-C(11)	126.6(3)
C(20)-C(12)-C(11)	127.7(3)
C(12)-C(13)-O(1)	113.2(3)
C(12)-C(13)-H(13)	123.4
O(1)-C(13)-H(13)	123.4
C(16)-C(15)-O(1)	125.7(3)
C(16)-C(15)-C(20)	124.2(4)
O(1)-C(15)-C(20)	110.1(3)
C(15)-C(16)-C(17)	117.0(4)
C(16)-C(17)-C(18)	119.4(4)
C(16)-C(17)-C(21)	119.8(4)
C(18)-C(17)-C(21)	120.8(5)
C(19)-C(18)-C(17)	123.2(4)

C(18)-C(19)-C(20)	118.2(4)
(19)-C(20)-C(15)	118.0(3)
C(19)-C(20)-C(12)	136.3(3)
C(15)-C(20)-C(12)	105.7(3)
C(10)-N(1)-N(2)	108.3(3)
C(9)-N(2)-C(8)	107.4(3)
C(9)-N(2)-N(1)	117.7(3)
C(8)-N(2)-N(1)	134.9(3)
C(9)-N(4)-C(7)	103.6(3)
C(13)-O(1)-C(15)	105.3(3)
C(9)-S(1)-C(10)	88.01(16)

Table 4. List of Torsion angles (º), esd's given in the parentheses

Atom1-atom2-atom3-atom4	Angle
C(6)-C(1)-C(2)-C(3)	-1.4(5)
Br(1)-C(1)-C(2)-C(3)	178.7(3)
C(1)-C(2)-C(3)-C(4)	0.0(5)
C(2)-C(3)-C(4)-C(5)	1.7(5)
C(2)-C(3)-C(4)-C(7)	-177.7(3)
C(3)-C(4)-C(5)-C(6)	-2.1(5)
C(7)-C(4)-C(5)-C(6)	177.3(3)
C(2)-C(1)-C(6)-C(5)	1.0(5)
Br(1)-C(1)-C(6)-C(5)	-179.2(3)
C(4)-C(5)-C(6)-C(1)	0.8(5)
C(5)-C(4)-C(7)-C(8)	2.4(5)
C(3)-C(4)-C(7)-C(8)	-178.2(3)
C(5)-C(4)-C(7)-N(4)	-177.2(3)
C(3)-C(4)-C(7)-N(4)	2.2(4)
N(4)-C(7)-C(8)-N(2)	-0.4(4)
C(4)-C(7)-C(8)-N(2)	179.9(3)
N(1)-C(10)-C(11)-C(12)	153.9(3)
S(1)-C(10)-C(11)-C(12)	-27.8(4)
C(10)-C(11)-C(12)-C(13)	111.8(4)
C(10)-C(11)-C(12)-C(20)	-67.4(4)
C(20)-C(12)-C(13)-O(1)	0.2(4)
C(11)-C(12)-C(13)-O(1)	-179.1(3)
O(1)-C(15)-C(16)-C(17)	179.1(3)
C(20)-C(15)-C(16)-C(17)	-0.4(5)
C(15)-C(16)-C(17)-C(18)	0.3(5)
C(15)-C(16)-C(17)-C(21)	179.7(4)
C(16)-C(17)-C(18)-C(19)	-0.4(6)
C(21)-C(17)-C(18)-C(19)	-179.8(4)
C(17)-C(18)-C(19)-C(20)	0.6(6)
C(18)-C(19)-C(20)-C(15)	-0.7(5)
C(18)-C(19)-C(20)-C(12)	-179.5(4)
C(16)-C(15)-C(20)-C(19)	0.6(5)
O(1)-C(15)-C(20)-C(19)	-178.9(3)
C(16)-C(15)-C(20)-C(12)	179.7(3)
O(1)-C(15)-C(20)-C(12)	0.2(4)
C(13)-C(12)-C(20)-C(19)	178.6(4)
C(11)-C(12)-C(20)-C(19)	-2.1(6)
C(13)-C(12)-C(20)-C(15)	-0.2(4)
C(11)-C(12)-C(20)-C(15)	179.1(3)
C(11)-C(10)-N(1)-N(2)	178.4(3)
S(1)-C(10)-N(1)-N(2)	0.1(4)
N(4)-C(9)-N(2)-C(8)	0.6(4)
S(1)-C(9)-N(2)-C(8)	-178.8(2)
N(4)-C(9)-N(2)-N(1)	-179.9(3)
S(1)-C(9)-N(2)-N(1)	0.6(4)
C(7)-C(8)-N(2)-C(9)	-0.1(4)
C(7)-C(8)-N(2)-N(1)	-179.4(3)
C(10)-N(1)-N(2)-C(9)	-0.5(4)
C(10)-N(1)-N(2)-C(8)	178.8(4)
N(2)-C(9)-N(4)-C(7)	-0.9(4)
S(1)-C(9)-N(4)-C(7)	178.4(3)
C(8)-C(7)-N(4)-C(9)	0.8(4)
C(4)-C(7)-N(4)-C(9)	-179.5(3)
C(12)-C(13)-O(1)-C(15)	0.0(4)
C(16)-C(15)-O(1)-C(13)	-179.6(4)
C(20)-C(15)-O(1)-C(13)	-0.1(4)
N(4)-C(9)-S(1)-C(10)	-179.7(4)
N(2)-C(9)-S(1)-C(10)	-0.4(2)
N(1)-C(10)-S(1)-C(9)	0.2(3)
C(11)-C(10)-S(1)-C(9)	-178.2(3)

Table 5 Dihedral angles formed by LSQ-planes

Plane	Plane	Angle (°)
1	2	81.63(0)

Table.6.Hydrogen bonding geometry.

(D-H…A)	(D-H) Å	(H…A)Å	(D….A) Å	(D-H…A)
C3-H3…N4	0.93(0)	2.520(0)	2.863(0)	102
C8-H8…N1^{i}	0.93(0)	2.972(1)	3.548(1)	121
C8-H8…S1^{ii}	0.93(0)	2.983(1)	3.670(1)	132
C11-H11B…O1^{ii}	0.97(0)	2.581(1)	3.542(1)	171
C16-H16…O1^{iii}	0.93(0)	2.762(1)	3.614(1)	153
C16-H16…π	0.93(0)	2.67(0)	3.692(0)	173

Equivalent positions:

(i) -x+2,-y,-z+1, (ii) x+1,+y,+z (iii) -x,-y,-z+2

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