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Bromine and fluorine substituted N-(4-aryl)-benzenesulfonamides: synthesis, crystal structure and Hirshfeld surface analysis

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ABSTRACT

Crystal structures of two N-(4-aryl)-benzenesulfonamides, namely, 4-bromo-N-(4-nitrophenyl)-benzenesulfonamide (1), and 4-fluoro-N-(4-nitrophenyl)-4-benzenesulfonamide (2) were synthesized and their molecular and crystal structures were determined by single crystal X-ray diffraction studies. Both 1 and 2 crystallize in the monoclinic crystal system, in P2₁/n and P2₁/c space groups respectively. The dihedral angle between the benzene rings is quite different in 1 and 2, 32.6(6)° in 1 and 60.4(2)° in 2. Also, the molecules of 1 and 2 show significant differences in the torsional angles defining the conformations of the two benzene rings with respect to the central -C-S(O₂)-N-C-segment. The crystal structures of 1 and 2 exhibit different preferences in their packing modes. In 1, structure directing N-H...O hydrogen bonds and three structure directing C-H...O interactions along with N-O... π and C-Br...O weak interactions consolidate the crystal structure into a three dimensional structure, while, the two dimensional supramolecular architecture in 2 results from a structure directing C-H...O interaction, and also features N-O... π and two π ... π interactions. The N-H...O hydrogen bonds in 2 have no structure directing features.Hirshfeld surface analysis were performed on 1 and 2 to analyse the various intermolecular interactions observed in 1 and 2.

Keywords: Sulfonamides, Crystal Structures, X-ray diffraction, Hirshfeld Surfaces, N-H...O hydrogen bonds, C-H...O interactions, π ... π interactions.

INTRODUCTION

Sulfonamide drugs were the first among the chemotherapeutic agents to be used for the cure and prevention of bacterial infection in human beings [1]. They play a vital role as key constituent in a number of biologically active molecules. Till date, sulfonamides have been known to exhibit a wide variety of biological activities such as antibacterial [2], insecticidal [3], antifungal [4], antihepatitis [5], antiinflamatory [6], antitumor [7], anticancer [8], anti -HIV [9] and antitubercular activities [10]. In recent years extensive research studies have been carried out on the synthesis and evaluation of pharmacological activities of molecules containing sulfonamide moiety for different activities, and have been reported to be important pharmacophores [11].

With these considerations in mind and based on our recent studies on the crystal structures of a few N-(4-substitutedphenyl)-4-arylsulfonamides [12-14], we report herein the synthesis and crystal structures of 4-bromo-N-(4-nitrophenyl)benzenesulfonamide (1), and 4-fluoro-N-(4-nitrophenyl)-4-benzenesulfonamide (2). Further, Hirshfeld surface analysis including d_{norm} surfaces and 2D Fingerprint plots (FP) were performed on 1 and 2 and the results of the analysis are discussed.

MATERIALS AND METHODS

All the reagents were purchased from Spectrochem Pvt. Ltd., India, and were used without further purifications. Melting points of 1 and 2 were determined in open capillary tubes.

Synthesis of 1 and 2

4-Nitroaniline(10 mmol) and excess pyridine were dissolved in dichloromethane (20 ml) and a solution of 4bromobenzenesulfonyl chloride (for 1)/4-fluorobenzenesulfonyl chloride (for 2) (13 mmol) in dichloromethane (20 ml) was added drop wise with vigorous stirring at 273 K (**Scheme 1**). After 1 h, the reaction was quenched by addition of water and the oil thus obtained was washed with dilute HCl. The organic layer separated was evaporated to give the crude product, which was recrystallized from n-hexane-dichloromethane (5:1). 1: Yield: 71%, M. pt. 435 K; 2: Yield: 65%, M. pt. 423 K.



Scheme 1

Preparation of crystals of 1 and 2

Single crystals of both 1 and 2 suitable for single crystal X-ray studies were obtained from slow solvent evaporation technique at room temperature. Compound 1 (50 mg) was dissolved in dichloromethane (15 ml) and to this clear solution n-hexane was addeddropwise till the solution became turbid (about 10 ml of n-hexane was required). The solution was again made clear by adding 2 drops of dichloromethaneand filtered. The solvent was allowed to evaporate at room temperature (27 °C). Colourless prism like crystals of 1 were obtained after 4 days. The colourless prism like crystals of 2 were also obtained from similar procedure after 5 days.

Table 1	Crystal	data	and	structure	refinements	for	1 and	12
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Compound code	1	2		
CCDC No.	1441616	1441617		
Empirical formula	C12H9N2O4SBr	$C_{12}H_9N_2O_4SF$		
Formula weight	357.18	296.27		
Crystal system	monoclinic	monoclinic		
Space group	$P2_1/n$	$P2_1/c$		
a/Å	5.0869(2)	9.9522(4)		
b/Å	12.9864(5)	11.0687(4)		
c/Å	19.8561(7)	11.5526(5)		
β/°	93.7230(10)	97.0900(10)		
Volume/Å ³	1308.94(9)	1262.88(9)		
Z	4	4		
$\rho_{calc}g/cm^3$	1.813	1.558		
μ/mm^{-1}	5.934	2.570		
F(000)	712.0	608.0		
Crystal size/mm ³	0.25×0.19×0.15	0.24×0.17×0.12		
2θ range for data collection/°	11.24 to 128.88	8.96 to 128.72		
Reflections collected	7306	11406		
Independent reflections	2113	2055		
Data/restraints/parameters	2113/1/185	2055/1/185		
Goodness-of-fit on F ²	1.108	1.085		
Einal P indexes $[I > -2\pi]$	$R_1 = 0.0601,$	$R_1 = 0.0489,$		
$\frac{1}{20} (1)$	$wR_2 = 0.1737$	$wR_2 = 0.1420$		
Final R indexes [all data]	$R_1 = 0.0602,$	$R_1 = 0.0498,$		
	$wR_2 = 0.1740$	$wR_2 = 0.1434$		
Largest diff. peak/hole / e Å-3	0.98/-1.42	0.35/-0.50		

X-ray crystallographic study

The X-ray intensity data were collected at a temperature of 296.1(5) K on a Bruker Proteum2 CCD diffractometer equipped with an X-ray generator operating at 45 kV and 10 mA, using Cu-K α radiation of wavelength 1.54178 Å. Data were collected for 24 frames per set with different settings of φ (0° and 90°), keeping the scan width of 0.5°, exposure time of 5 s, the sample-to-detector distance of 45.10 mm, and 2θ value at 46.6°. Image processing and data

reduction were done using SAINT-Plus and XPREP [15]. The structure was solved by direct methods using SHELXS-97 [16]. All the non-hydrogen atoms were revealed in the first-difference Fourier map itself and were refined anisotropically. All the hydrogen atoms were positioned geometrically. In 1 and 2, the C_{arm}-H atoms were positioned geometrically, with C-H = 0.93 Å, and refined using a riding model with $U_{iso}(H) = 1.2 U_{eq}(C)$. The N-H hydrogen atoms in 1 and 2 were located in a difference map and were refined isotropically with the bond length restraint N-H = 0.90(1) Å. To improve considerably the values of R1, wR2, and S(goodness-of-fit), partially obscured reflections (-1 5 1, 0 6 2, 0 1 1, 0 0 2) in 1 and (-2 2 1, 0 5 1) in 2 were omitted from the final refinements. The crystallographic data and refinement parameters for 1 and 2 are summarized in Table 1.All the geometrical calculations for 1 and 2 were carried out using the program *PLATON* [17] within the WinGX suite [18]. The molecular and packing diagrams were generated using the software *MERCURY* [19].

Hirshfeld surface calculations

Hirshfeld surface analyses were carried out and finger print plots were plotted using the software CrystalExplorer 3.0 [20]. The d_{norm} plots were mapped with colour scale in between -0.18 au (blue) and 1.4 au (red). The 2D fingerprint plots [21, 22] were displayed by using the expanded 0.6–2.8 Å view with the d_e and d_i distance scales displayed on the graph axes. When the cif files of 1 and 2 were uploaded into the CrystalExplorer software, all bond lengths to hydrogen were automatically modified to typical standard neutron values i.e., C–H = 1.083 Å and N–H = 1.009 Å.

RESULTS AND DISCUSSION

Single Crystal X-ray diffraction studies Molecular Structures of 1 and 2

The molecular structure of compounds 1 and 2 with thermal ellipsoids drawn at 50% probability is shown in Fig. 1. In both the compounds, all the bond lengths and angles are similar to those observed in the relatedstructures previously reported [12-14], and, hence, are not discussed here. The values of the important torsions defining the confirmations of the central segment and the orientations of the two arylrings with respect to the central segment in compounds 1 and 2 are listed in Table 2.



Fig. 1: Molecular structure of 1 and 2, showing thermal displacement ellipsoids drawn at the 50% probability level

The dihedral angle between the two aryl rings in 1 is $32.6(6)^\circ$, while, in 2, the dihedral angle between the two aryl rings is very high, its value being $60.4(2)^\circ$. This noted difference may be attributed to the large differences in the masses of the atoms occupying the para positions of the sulfonyl benzene rings in 1 and 2, i.e., due to atomic mass of Br (79.9) vs atomic mass of F (19.0) effect. The values of the dihedral angle between the two aryl rings in similarcompounds reported [12-14] fall in the range of 42.0-63.36°. Comparison of the angles describing the orientations of the two rings with the central chain (**Table 2**) indicates that the nature of the halogen atom occupying the para position of the benzene sulfonyl ring has a significant influence on the torsional values, but, has no significant effects on the torsions defining the conformations of the central chain.

Crystal Structures of 1 and 2

The analysis of the nature of hydrogen bonds / intermolecular interactions displayed in the crystal structures of 1 and 2, their preference for forming different packing motifs, and, thereby, their influence on the crystal packing of 1 and 2 is described.

Description	Torsion	1	2
Description	10151011	Angle/°	Angle/°
	C6-C1-S1-O1	-160.9(3)	12.04(19)
	C6-C1-S1-O2	-28.2(4)	143.44(16)
Torsion describing the relative orientation of the sulfonyl benzene ring and the central chain	C2-C1-S1-O1	24.8(4)	-170.51(16)
	C2-C1-S1-O2	157.5(3)	-39.10(19)
	C6-C1-S1-N1	86.0(3)	-99.82(17)
	C2-C1-S1-N1	-88.3(3)	77.63(17)
Tousion describing the relative orientation of the nitrohenzone ring and the control shein	C2-C1-S1-N1 -88.3(3) 77. C8-C7-N1-S1 97.7(4) -5		-53.7(2)
Torsion describing the relative orientation of the introdenzene ring and the central chain	C12-C7-N1-S1	-82.3(4)	128.85(16)
	C7-N1-S1-C1	-64.2(3)	-63.35(17)
Conformations of the central chain	C7-N1-S1-O1	-179.8(3)	-177.98(15)
	C7-N1-S1-O2	51.1(3)	53.83(17)

Table 2. Comparison of various important torsions in 1 and 2

The initial stage of packing of molecules in the crystal structure of 1 involves the formation of strong structure directing hydrogen bonds N1-H1...O2 between the molecules leading to the formation of infinite one dimensional chains having graph set notation C(4) [23] along the crystallographic *a* axis (**Figure 2a**).Further, theseadjacent chains are interlinked by three different C-H...O interactions: C2-H2...O4, C9-H9...O1 and C11-H11...O3, thus, consolidating the crystal packing into a three-dimensional supramolecular architecture. C2-H2...O4 and C9-H9...O1 interactions form chains withfirst level graph set notation of $R_2^{-2}(10)$ [23] (**Figure 2b**). On the other hand, the C11-H11...O3 interactions connect the molecules into dimeric pairs forming $R_2^{-2}(10)$ rings.These two rings form a tape motif as shown in the **Figure 2b**.The three dimensional structure is further stabilized by weak intermolecular contacts N2-O3... π (π system of nitrobenzene ring) and Br1...O3 contacts (**Figure 2c**). The overall crystal packing of 1 is displayed in **Figure 3**, and, the list of various interactionsand their geometries is given in **Table 3**.

The crystal structure of 2 features strong N-H...O hydrogen bonds with a packing preference very different from that observed in 1. The molecules in 2 are connected into dimers via strong N1-H1...O4 hydrogen bonds (**Table 3**, **Figure 4**), thus, forming a $R_2^{(2)}(8)$ ring motif, unlike the C(4) chain motif observed in 1. Thus, the N-H...O hydrogen bonds in 2 have no structure directing characteristics as observed in 1. The $R_2^{(2)}(8)$ dimers in 2 are further interconnected by C6-H6...O4 interactions that connect the dimers into C(11) chains along *c* axis (**Table 3**, **Figure 4**). These C6-H6...O4 interactions are similar to the C2-H2...O4 interactions observed in 1, both forming C(11) chains, and also having structure directing features. However, the interactions in 2 are quite weak compared to those in 1. The $R_2^{(2)}(8)$ rings and the C(11) chains together form ribbon like architecture along *c* axis with second level graph set notation of $R_4^{(4)}(26)$ (**Figure 4**). In addition to these, the crystal structure features N2-O3... π (π system of fluorobenzene ring) and two π ... π interactions (Cg1...Cg1 and Cg2...Cg2: Cg1 and Cg2 are the centroids of nitrobenzene rings respectively) which consolidate the crystal structure into a two dimensional supramolecular architecture (**Figure 5**).





Figure 2. Nature of various hydrogen bonds and intermolecular interactions displayed in 1: a) Strong N-H...O hydrogen bond chains in 1; b) Three C-H...O interactions forming a tape motif; c) weak interactions of the type N-O...π and Br...O



Figure 3. Overall packing of molecules in the crystal structure of 1

 Table 3. Geometric parameters for hydrogen bonds and other intermolecular contacts (Å, °) operating in the crystal structures of 1 and 2.

			1						2		
	D-HA	D-H	HA	DA	D-HA		D-HA	D-H	HA	DA	D-
											НА
<i>a</i> :	N1-H1O2 ⁱ	0.90	2.12	2.956(7)	155	g:	N1-H104 ⁱ	0.89	2.06	2.953(1)	177
b:	C2-H2O4 ⁱⁱ	0.93	2.39	3.137(8)	137	h:	C6-H6O4 ⁱⁱ	0.93	2.60	3.238(3)	127
с:	C11-H11O3 ⁱⁱⁱ	0.93	2.40	3.236(2)	149	i:	N2-O3Cg2 ^{b,}	-	-	3.277(9)	-
d:	C9-H9O1 ^{iv}	0.93	2.50	3.297(1)	144	j:	Cg1Cg1 ^{a, iv}	-	-	3.700(1)	-
<i>e</i> :	C4-Br1O3 ^v	-	-	3.198(7)	-	<i>k</i> :	Cg2Cg2 ^{b, v}	-	-	3.887(2)	-
f٠	N2-O3 Cg ^{a, vi}	-	-	3.450(1)	-						

i: 1+x,y,z; ii: 3/2-x,-1/2+y,1/2-z; iii: -x,1-y,1-z; iv: 3/2-x,1/2+y,1/2-z; v:

1/2+x,3/2-y,-1/2+z;vi: 1-x,1-y,1-z; ^aCg is the centroid of the nitrobenzene ring i: -x,1-y,-z; ii: x,y,-1+z; iii: x,3/2-y,1/2+z; iv: -x,1-y,1-z; v: 1-x,1-y,-z ^aCg1 is the centroid of the nitrobenzene ring

^bCg2 is the centroid of the fluorobenzene ring



Figure 4. N-H...O hydrogen bonds and C-H...O interactions resulting in ribbon like architecture in 2. H-atoms not involved in any hydrogen bonding are omitted for clarity purpose



Figure 5. Weak interactions of the type N-O... π and π ... π displayed in 2

Hirshfeld surface studies

Hirshfeld surface analysis is an effective tool for exploring packing modes and intermolecular interactions in molecular crystals [21-22], as they provide a visual picture of intermolecular interactions and of molecular shapes in a crystalline environment. Surface features characteristic of different types of intermolecular interactions can be identified, and these features can be revealed by colour coding distances from the surface to the nearest atom exterior (d_e plots) or interior (d_i plots) to the surface. This gives a visual picture of different types of interactions present, and also reflect their relative contributions from molecule to molecule. Further, 2D fingerprint plots (FP), in particular the breakdown of FP into specific atom...atom contacts in a crystal, provide a quantitative idea of the types of intermolecular contacts experienced by molecules in the bulk and presents this information in a convenient colour plot. Hirshfeld surfaces comprising d_{norm} surface plots, shape index, curvedness and FP were generated and analysed for the crystals of 1 and 2 in order to explore their packing modes and intermolecular interactions.

The d_{norm} surfaces, curvedness and shape index of molecules 1 and 2 are shown in **Figure 6**, the FP for the overall contacts in 1 and 2 are shown in **Figure 7**, and the percentage contributions of the various intermolecular contacts contributing to the Hirshfeld surfaces of1 and 2 are shown as bar diagrams in **Figure 8**. The dark-red spots on the d_{norm} surface arise as a result of the short interatomic contacts, i.e., strong hydrogen bonds, while the intermolecular interactions appear as light-red spots. The analysis of the d_{norm} surface and FP gives a pictorial conformation (both qualitatively as well as quantitatively) to the nature and geometries of the hydrogen bonds and intermolecular interactions described in the crystal structures of both 1 and 2. Each hydrogen bonds/intermolecular interactions and other contacts in 1 and 2 are designated using alphabets a to k (**Table 3**). The red spots on the d_{norm} surfaces of 1 and 2 (**Figure 6**)(resulting fromvarious short atomic contacts) pictorially confirm the occurrence of various contacts in 1 and 2 as described earlier.Further, $\pi \dots \pi$ interactions in 2 are evident on theHirshfeld surface as large flat regions across the two benzene rings, which is most clearly visible on the curvedness surfaces (**Figure 6**), while, such characteristics are not observed in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvedness surfaces for 1 where $\pi \dots \pi$ interactions are notobserved in the curvednes





contacts in 1 and 2

Further, the pattern of red and blue triangles on the shape index surface of 2 above both the benzene rings areas a result of π ... π interactions j and k. Also, the pattern of alternating red and blue triangles with local 3-fold symmetry indicates offset π ... π stacking interactions in 2.

The quantitative analysis of the intermolecular interactions can be made by comparing the fingerprint plots (FP) of 1 and 2 (**Figure 7**). The full FP of each compound is different in both size and shape, thus indicating that the nature and separation of the various interatomic contacts in 1 and 2 are very different. The two long and sharp spikes occurring in the FP of both 1 and 2 at $d_i+d_e \approx 2.0$ Å are as a result of the strong N-H...O hydrogen bonds *a* and *g* observed in the structures of 1 and 2 respectively, at H...O contact distances of 2.12 and 2.06 Å respectively (**Table 3**). The green points $at_i+d_e \approx 3.6-3.8$ Å, visible on the FP of 2, are characteristic of $\pi...\pi$ stacking interactions, and it is notable that they are almost absent in 1, where these interactions are not observed.

Comparison of the percentage contributions of the various intermolecular contacts (**Figure 8**) contributing to the Hirshfeld surfaces of 1 and 2 shows that the major contribution to the Hirshfeld surfaces is from H...O/O...H contacts, which contributes 34.5% and 40.4% to the overall contacts in 1 and 2 respectively. This fact is quite acceptable as the packing of both 1 and 2 are largely controlled by N-H...O hydrogen bonds and C-H...O intermolecular interactions. Further, it may be noted that, in 2, where π ... π stacking are seen, the contribution from C...C contacts (due to the π ... π stacking) to the Hirshfeld surface is 7.0%, while that in 1, where no π ... π stacking are observed, its contribution is just 0.3%. Thus, the Hirshfeld surfaces and the FP give a qualitative and quantitative pictorial confirmations for the various interactions displayed in the crystal structure of 1 and 2.

Figure 8. Percentage contributions of the various intermolecular contacts contributing to the Hirshfeld surfaces of 1 and 2

CONCLUSION

Crystal structures of two N-(4-aryl)-benzenesulfonamides, namely, 4-bromo-N-(4-nitrophenyl)-benzenesulfonamide (1), and 4-fluoro-N-(4-nitrophenyl)-4-benzenesulfonamide (2) were synthesized and their molecular and crystal structures were determined by single crystal X-ray diffraction studies. The difference in the masses of the halogen atoms occupying the *para* position of the benzene sulfonyl ring showed a significant effect on the dihedral angle between the benzene rings and the torsional angles defining the conformations of the two benzene rings with respect to the central -C-S(O₂)-N-C- segment. The crystal structures of 1 and 2 exhibit different preferences in their packing modes. In 1, structure directing N-H...O hydrogen bonds and three structure directing C-H...O interactions along with N-O... π and C-Br...O weak interactions consolidated the crystal structure directing C-H...O interaction, and, N-O... π &two π ... π interactions. The N-H...O hydrogen bonds in 2 had no structure directing features. Further, the Hirshfeld surfaces and the FP analysis of 1 and 2 gave a qualitative and quantitative pictorial confirmations for the various interactions displayed in the crystal structure of 1 and 2.

SUPPLEMENTARY MATERIALS

CCDC 1441616&1441617 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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