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Synthesis, Characterization And Crystal Structures of Two N-(Arylsulfonyl)-Arylamides

S. Sreenivasa[1], N. R. Mohan[1], K. E. Manojkumar[1] and P. A. Suchetan[2]*

1. Department of Studies and Research in Chemistry, Tumkur University, Tumkur-572 103, Karnataka, **INDIA**
2. Department of Studies in Chemistry, University College of Science, Tumkur University, Tumkur, Karnataka, **INDIA**

Email: pasuchetan@yahoo.co.in

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ABSTRACT

*Two N-(arylsulfonyl)-arylamides, namely N-(4-methylphenylsulfonyl)-3-methylbenzamide(**1**) and N-(2-methylphenylsulfonyl)-2-chlorobenzamide(**2**), are synthesized by the reaction of the 4-methylbenzene-sulfonamide/2-methylbenzenesulfonamide, 3-methylbenzoic acid / 2-chlorobenzoic acid and phosphorous oxy chloride. The synthesized compounds are characterized by IR, LCMS, ^{1}H-NMR and ^{13}C-NMR studies. The structures are further confirmed by determining their single crystal XRD data. Compound **1** crystallizes in the monoclinic space group $P2_1/c$, with a = 9.895(3) Å, b = 11.022(4) Å, c = 13.639(4) Å, β = 97.78(3)°, V = 1473.8(8) Å^3, Z= 4, R[F^2> 2σ(F^2)] = 0.0810 and wR(F^2) = 0.2383, while compound **2** crystallizes in tetragonal, non-centrosymmetric space group $I4_1cd$, with a = 20.047(1) Å, b = 20.047(1) Å, c = 14.634(1) Å, V = 5881.1(7) Å^3, Z= 16, R[F^2> 2σ(F^2)] = 0.1046 and wR(F^2) = 0.1422. The dihedral angle between the two benzene rings is 89.6(2)° in compound **1**, while that in compound **2** is 60.7(5)°. In the crystal structure of compound **1**, the crystal packing is stabilized by strong N-H…O(Sulfonyl) hydrogen bonds, forming $R_2^2(8)$ rings, and by weak C-H…π interactions, forming C(8) chains. In **2**, the crystal packing is stabilized by strong N-H…O(Carbonyl) hydrogen bonds and weak C-H…O interactions, respectively forming C(4) and zigzag C(7) chains running along [001].*

Keywords: N-(Arylsulfonyl)-arylamides, Non-centrosymmetric, Hydrogen bonds, C-H…O interactions, C-H…πinteractions.

INTRODUCTION

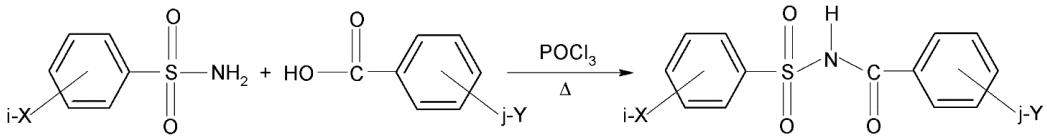
Sulfonamide and amide moieties play a very significant role as a key constituent in a number of biologically active molecules [**1-3**]. In recent years, N-(arylsulfonyl)-arylamides have received much attention as they constitute an important class of drugs for Alzheimer's disease [**4**], antibacterial inhibitors of tRNA synthetases [**5**], antagonists for AngiotensinII [**6**], and Leukotriene D4-receptors [**7**]. Further, N-(arylsulfonyl)-arylamides are known as potent anti-tumor agents against a broad spectrum of human tumor xenografts (colon, lung, breast, ovary, and prostate) in nude mice [**8-10**]. In view of the importance of N-(arylsulfonyl)-arylamides and in continuation of our work on the synthesis and crystal structures of N-

(arylsulfonyl)-arylamides [**11-17**], compounds **1** and **2** were synthesized, characterized and their crystal structures determined.

MATERIALS AND METHODS

All the reagents were purchased from commercial sources and were used without further purification. Melting points were determined in one end open capillary tube on a liquid paraffin bath and were not corrected. IR spectral measurements were carried out on a SHIMADZU-8700 (Japan), FT-IR spectrometer. The resolution was set to 4 cm^{-1} and the scanning range was from 400-4000 cm^{-1}. The spectra were measured in the solid state as pressed KBr pellets (13mm). LCMS and ^{1}H & ^{13}C-NMR spectra were recorded for both the compounds on Agilent Mass spectrometer and Bruker Avance II (300.65 MHz) spectrometer respectively. Chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. Single Crystal X-Ray diffraction studies were carried out in Bruker Smart X2S diffractometer.

Synthesis of compounds 1 and 2



Scheme 1

Compounds **1** and **2** were synthesized by a known procedure reported for the synthesis of their related structures [**18-21**] (**Scheme 1**).

Synthesis of N-(4-methylphenylsulfonyl)-3-methylbenzamide (1): Compound **1** was prepared by refluxing a mixture of 3-methylbenzoic acid, 4-methylbenzenesulfonamide and phosphorous oxy chloride for 3 h on a water bath. The resultant mixture was cooled and poured into ice cold water. The solid obtained was filtered, washed thoroughly with water and then dissolved in sodium bicarbonate solution. The compound was later reprecipitated by acidifying the filtered solution with dilute HCl. It was filtered, dried and recrystallized.

Synthesis of N-(2-methylphenylsulfonyl)-2-chlorobenzamide (2): Compound **2** was prepared by refluxing a mixture of 2-chlorobenzoic acid, 2-methylbenzenesulfonamide and phosphorous oxy chloride for 3 h on a water bath. The resultant mixture was cooled and poured into ice cold water. The solid obtained was filtered, washed thoroughly with water and then dissolved in sodium bicarbonate solution. The compound was later reprecipitated by acidifying the filtered solution with dilute HCl. It was filtered, dried and recrystallized.

Crystal Structure Determination of compounds 1 and 2: Rod like colourless single crystals of compound **1** was obtained from slow evaporation of the solution of the compound in toluene. A single crystal of **1** with dimensions 0.36 x 0.16 x 0.1 mm was chosen for X-ray diffraction study. The data were collected on a Bruker Smart X2S diffractometer equipped with a fine focus, 3 kW sealed X-ray source (graphite monochromated Mo Kα). The crystal to detector distance was fixed at 120 mm with a detector area of 422 x 221 mm^2. Thirty six frames of data were collected at room temperature by the oscillation method. Each exposure of the image plate was set to a period of 300s. Successive frames were scanned in steps of 5^o/min with an oscillation range of 5^o. Image processing and data reduction were done using SAINT-Plus and XPREP [**22**]. All the frames could be indexed using monoclinic $P2_1/c$ lattice. The structure was solved by direct methods using SHELXS-97 [**23**]. All the Q peaks of non-hydrogen atoms

were located in the first Fourier map itself. In the second stage, non-hydrogen atoms were refined anisotropically. The H atom of the NH group was located in a difference map and later restrained to N-H = 0.86 (3) Å. The other H atoms were positioned with idealized geometry using a riding model with C-H = 0.93–0.96 Å. All H atoms were refined with isotropic displacement parameters (set to 1.2 times of the *U*eq of the parent atom). To improve considerably the values of R1, wR2, and GOOF the bad three reflections (11 2 1 11 1 1 11 2 2) were omitted from the refinement and the data was finally refined to $R[F^2> 2\sigma(F^2)]$ = 0.0810 and $wR(F^2)$ = 0.2383. The details of the crystal data of **1** are given in **Table 1**.

Similar to **1**, rod like colourless single crystals of compound **2** was obtained from slow evaporation of the solution of the compound in toluene. A single crystal of **2** with dimensions 0.20 x 0.10 x 0.06 mm was chosen for X-ray diffraction study. The data was collected using the similar procedure as described for **1**. The data was indexed using tetragonal, non-centrosymmetric $I4_1cd$ lattice. The H atoms were positioned with idealized geometry using a riding model with C-H distances of 0.93 Å (C-aromatic) and 0.96 Å (*C*-methyl) and N-H = 0.86 Å. All H atoms were refined with isotropic displacement parameters set at 1.2 *U*eq(C-aromatic, N) and 1.5 *U*eq(*C*-methyl). The U_{ij} components of C1, C3, C4, C5, C8, C9, C10, C11, C12, C14 and N1 were restrained to approximate isotropic behavior. In the absence of significant anomalous dispersion effects, Friedel pairs were merged and the Δf'' term was set to zero. The final refinement was $R[F^2> 2\sigma(F^2)]$ = 0.1046 and $wR(F^2)$ = 0.1422. The details of the crystal data of **2** are given in **Table 1**.

Table 1: The crystallographic data and structure refinements of compounds 1 and 2.

Parameter	*Compound* **1**	*Compound* **2**
Empirical formula	$C_{15}H_{15}NO_3S$	$C_{14}H_{12}ClNO_3S$
Formula weight	289.34	309.76
Temperature/K	299(2)	299(2)
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$	$I4_1cd$
a/Å	9.895(3)	20.047(1)
b/Å	11.022(4)	20.047(1)
c/Å	13.639(4)	14.634(1)
β/°	97.78(3)	90
Volume/Å^3	1473.8(8)	5881.1(7)
Z, Z'	4, 1	16, 1
ρ_{calc}, mg/mm^3	1.290	1.399
Absorption coefficient (cm^{-1})	19.9	0.407
F(000)	1216	2560
Crystal size/mm^3	0.36 × 0.16 × 0.1	0.20 × 0.10 × 0.06
2Θ range for data collection	9.6 to 41.00°	5.74 to 50.06°
Index ranges	$-21 \le h \le 21$, $-14 \le k \le 14$, $-20 \le l \le 20$	$-23 \le h \le 23$, $-23 \le k \le 13$, $-17 \le l \le 9$
Reflections Collected	10158	6065
Independent Reflections	2654	1354
$R[F^2> 2\sigma(F^2)]$	0.1046	0.0810
$wR(F^2)$	0.1422	0.2383

RESULTS AND DISCUSSION

Compounds **1** and **2** were synthesized according to the **Scheme 1** and characterized by LC-MS, IR, ^{1}H & ^{13}C NMR and single crystal X-ray diffraction studies. Spectral data's of **1** and **2** are interpreted in **Table 2** and **3** respectively, and are in agreement with the proposed structure.

Table 2: Physical and Spectral data of compound 1**.**

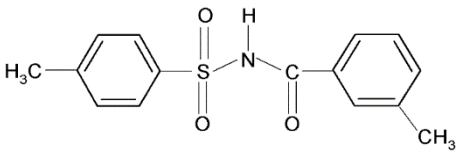
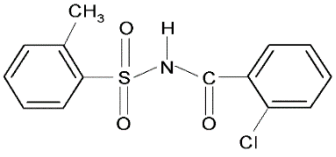
Compound Structure	
Molecular Formula	$C_{15}H_{15}NO_3S$
Colour and Nature	Colourless and Crystalline
LCMS: *m/z*	290.6 (M+ 1)
IR: ν max/cm^{-1}	3443-3329 (very broad strong Ar-H bond), 1726 (Sharp NH stretch) 1645 (C=O broad stretching), S=O: 1276.62 cm^{-1} (Asymmetric), 1167.54 cm^{-1} (Symmetric)
^{1}H NMR ($CDCl_3$ Solvent)	8.01 (s, 1H, NH), 7.84 (d, 1H, Ar-H), 7.74 (d, 2H, Ar-H), 7.72 (s, 1H, Ar-H), 7.45 (d, 1H, Ar-H), 7.41 (d, 2H, Ar-H), 7.36 (t, 1H, Ar-H), 2.31 (s, 6H, $(-CH_3)_2$)
^{13}C NMR ($CDCl_3$ Solvent)	169.2, 138.2, 136.3 (2C), 134.3, 132.4, 130.0 , 129.2 (2), 128.3, 127.9 (2C), 124.1, 19.9, 20.3
MP (K)	394–396

Table 3: Physical and Spectral data of compound 2.

Compound Structure	
Molecular Formula	$C_{14}H_{12}ClNO_3S$
Colour and Nature	Colourless and Crystalline
LCMS: *m/z*	310.8 (M+ 1)
IR: ν max/cm^{-1}	3453-3319 (very broad strong Ar-H bond), 1720 (Sharp NH stretch) 1650 (C=O broad stretching), S=O: 1266.78 cm^{-1} (Asymmetric), 1158.44 cm^{-1} (Symmetric)
^{1}H NMR ($CDCl_3$ solvent)	8.02 (s, 1H, NH), 7.75 (dd, 1H, Ar-H), 7.71 (d, 1H, Ar-H), 7.67-7.63 (m, 2H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.41-7.39 (m, 2H, Ar-H), 7.28 (t, 1H, Ar-H), 2.64 (s, 3H, $-CH_3$)
^{13}C NMR ($CDCl_3$ Solvent)	169.2, 138.1, 136.4, 134.1, 133.2, 131.3 (2C), 130.6, 128.2, 129.1, 127.2, 126.1, 19.6, 21.3
MP (K)	391–395

Crystal Structure Determination : The structure of the molecule 1 with thermal ellipsoids [24] drawn at 30% probability is shown in Fig. 1. In molecule 1, all the bond lengths and angles are consistent with those of our similar compounds previously reported [17, 18]. Selected bond lengths and angles of 1 are listed in Table 4.

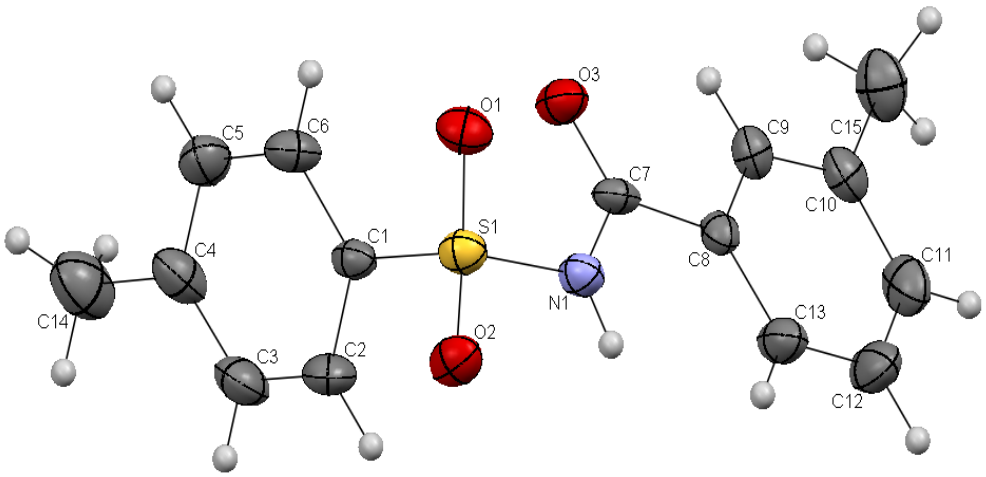


Fig. 1: Molecular structure of the compound 1, showing displacement ellipsoids drawn at the 30% probability level**.**

Table 4. Selected Bond Lengths (Å) and Bond Angles (°) observed in compound 1 (Standard deviations in parentheses)

Parameter	Value	Parameter	Value
C(1)-S(1)	1.759(6)	N(1)-C(7)-C(8)	117.7(5)
S(1)-N(1)	1.644(6)	C(7)-C(8)-C(9)	124.1(5)
N(1)-C(7)	1.385(6)	C(7)-C(8)-C(13)	116.3(5)
C(7)-C(8)	1.488(8)	C(8)-C(7)-O(3)	122.8(5)
C(7)-O(3)	1.207(6)	O(1)-S(1)-N(1)	103.5(3)
S(1)-O(1)	1.431(4)	O(2)-S(1)-N(1)	109.8(2)
S(1)-O(2)	1.416(4)	N(1)-C(7)-O(3)	119.6(6)
C(2)-C(1)-S(1)	118.9(5)	O(1)-S(1)-O(2)	118.5(2)
C(6)-C(1)-S(1)	120.5(4)	C(1)-S(1)-O(1)	109.5(2)
C(1)-S(1)-N(1)	104.7(3)	C(1)-S(1)-O(2)	109.8(3)
S(1)-N(1)-C(7)	122.7(4)		

In **1**, the conformation of the N-C bond in the C-SO_2-NH-C(O) segment has gauche torsions with respect to the SO bonds, and the conformation of the N-H bond is anti to the C=O bond. Further, the conformation of the C=O bond in the C-SO_2-NH-C(O) segment is syn to the *meta*-methyl group in the benzoyl ring. The molecule is twisted at the S atom with the torsional angle of 59.8 (5)° and the dihedral angle between the sulfonyl benzene ring and the -SO_2-NH-C-O segment is 87.0 (2)°. Furthermore, the dihedral angle between the sulfonyl and the benzoyl benzene rings is 89.6 (2)°. In the crystal structure, molecules are linked by strong N1-HN1…O2(Sulfonyl) hydrogen bonds, forming $R_2^2(8)$ rings (**Figure 2**) [Symmetry Code: –x+1, -y, -z+1; H…A = 2.20(3)Å, D…A = 2.973(6)Å, D-H…A = 159(6)°]. The

structure is further stabilized by weak C5-H5…π interactions, forming C(8) chains (**Figure 3**) [Symmetry Code: –x+1, -1/2+y, 1/2-z; H…Cg = 2.80(3)Å, C…Cg = 3.6422(6)Å, C-H…Cg = 151(6)°, Cg is the centroid of the benzoic acid ring].

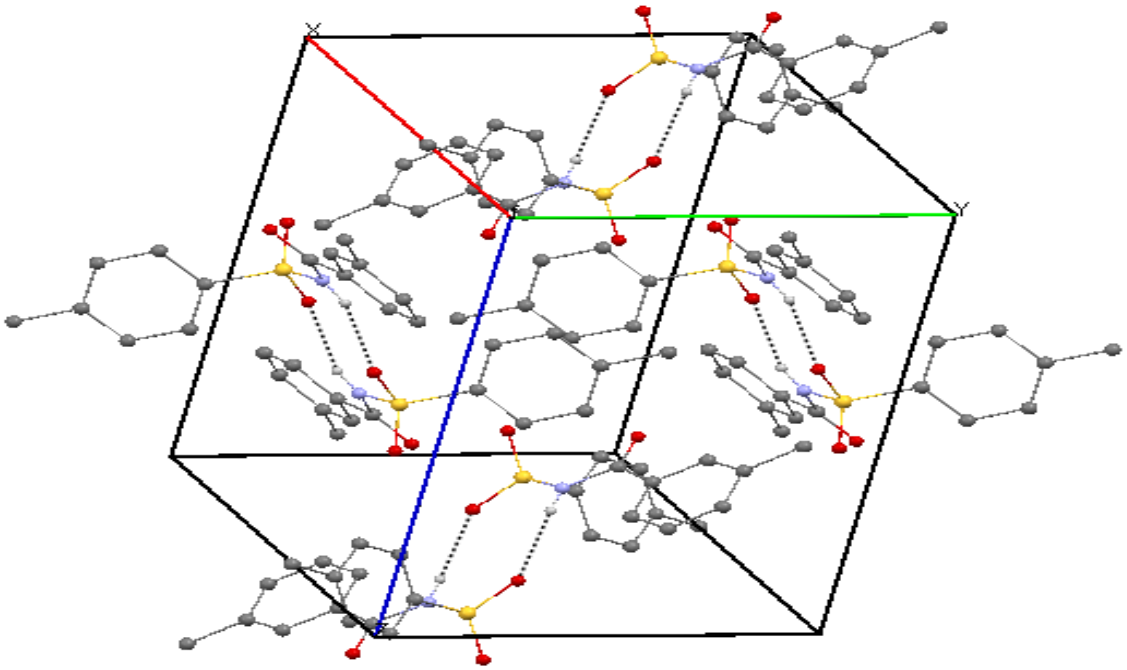


Fig. 2: The packing of molecules 1 in the crystal linked by of N—H···O(S) hydrogen bonds. H-atoms not involved in H-bonding are omitted for clarity purpose.

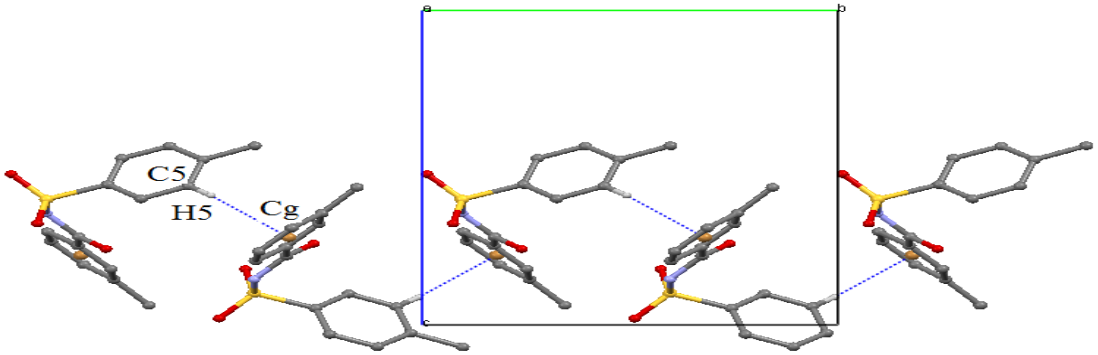


Fig. 3: Formation of C(8) chains due to C-H…π interactions in 1.

The structure of the molecule **2** with thermal ellipsoids [**24**] drawn at 30% probability is shown in **Fig. 4**. In molecule **2**, all the bond lengths and angles are consistent with those of our similar compounds previously reported [**19, 20**]. Selected bond lengths and angles of **2** are listed in **table 5**.

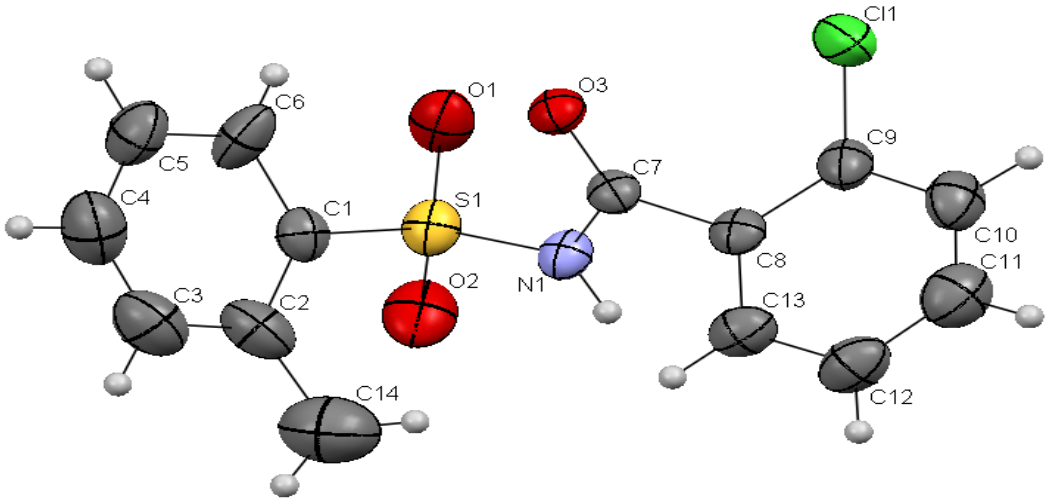


Fig. 4: Molecular structure of the compound 2, showing displacement ellipsoids drawn at the 30% probability level.

Table 5. Selected Bond Lengths (Å) and Bond Angles (°) observed in compound 2 (Standard deviations in parentheses)

Parameter	Value	Parameter	Value
C(1)-S(1)	1.787(1)	N(1)-C(7)-C(8)	114.5(1)
S(1)-N(1)	1.664(1)	C(7)-C(8)-C(9)	120.7(1)
N(1)-C(7)	1.376(1)	C(7)-C(8)-C(13)	120.0(1)
C(7)-C(8)	1.500(2)	C(8)-C(7)-O(3)	124.7(1)
C(7)-O(3)	1.215(1)	O(1)-S(1)-N(1)	104.5(6)
S(1)-O(1)	1.433(8)	O(2)-S(1)-N(1)	108.1(6)
S(1)-O(2)	1.429(9)	N(1)-C(7)-O(3)	120.8(1)
C(2)-C(1)-S(1)	113.4(1)	O(1)-S(1)-O(2)	119.2(7)
C(6)-C(1)-S(1)	123.1(1)	C(1)-S(1)-O(1)	109.4(6)
C(1)-S(1)-N(1)	105.1(6)	C(1)-S(1)-O(2)	109.5(7)
S(1)-N(1)-C(7)	124.3(9)		

In **2**, the conformation of the N-H bond in the C-SO_2-NH-C(O) segment is anti to the C=O bond. Further, the conformation between the C=O bond and the *ortho*-Cl in the benzoyl ring is syn to each other. The molecule is twisted at the S atom with the torsional angle of -64.7 (11)°. The dihedral angle between the sulfonyl benzene ring and the -SO_2-NH-C-O segment is 82.5 (4)°, and that between the sulfonyl and the benzoyl benzene rings is 60.7 (5)°. In the crystal structure, molecules are linked by strong N1-HN1…O3(Carbonyl) hydrogen bonds, forming C(4) chains running along [001] (**Figure 5**) [Symmetry Code: y, -x+1/2, z+1/4; H…A = 2.06(3)Å, D…A = 2.922(12)Å, D-H…A = 179(6)°]. The crystal structure is further stabilized by weak C4-H4…O2(Sulfonyl) interactions, forming zigzag C(7) chains running along [001] (**Figure 6**) [Symmetry Code: x, -y, -1/2+z; H…A = 2.54(3)Å, D…A = 3.3501(3)Å, D-H…A = 146(3)°].

Supplementary Materials: CCDC 985098 & 985099 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.

APPLICATIONS

N-(Arylsulfonyl)-arylamides exhibits various biological activities and studying their molecular and crystal structure might give an insight to the mechanisms of their biological actions.

CONCLUSIONS

Two N-(arylsulfonyl)-arylamides, namely N-(4-methylphenylsulfonyl)-3-methylbenzamide (1) and N-(2-methylphenylsulfonyl)-2-chlorobenzamide (2), were synthesized and well characterized by LC-MS, IR, ^{1}H & ^{13}C NMR and single crystal XRD data's.

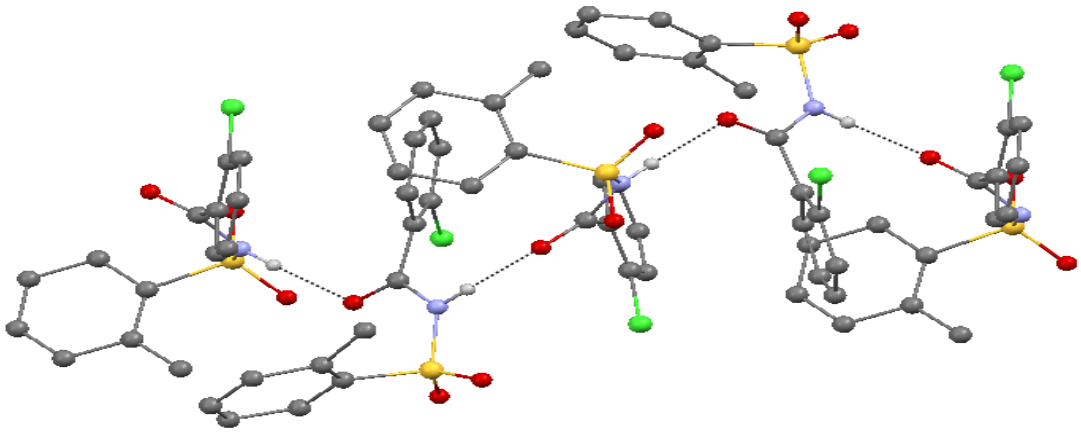


Fig. 5: The packing of molecules 2 in the crystal linked by of N—H···O(C) hydrogen bonds into C(4) chains. H-atoms not involved in H-bonding are omitted for clarity purpose.

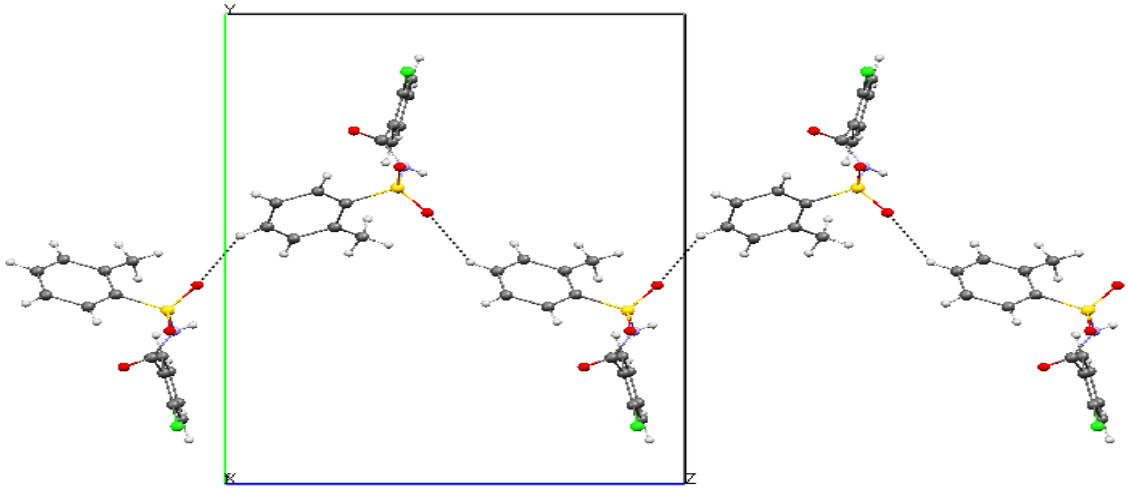


Fig. 6: Formation of zigzag C(7) chains due to C-H…O interactions in 2.

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REFERENCES

[1] N.R. Mohan, S. Sreenivasa, K.E. Manojkumar, T. Madhu Chakrapani Rao, *J. Applicable Chemistry*. **2013**, 2(4), 722-729.
[2] K. E. Manojkumar, Swamy Sreenivasa, Mohan R Nadigar, Tadimety Madhuchakrapani Rao, Tadimety Harikrishna, *J. Applicable Chemistry*. **2013**, 2(4), 730-737.
[3] A. S. Hamad, F. S. Abed, *J. Applicable Chemistry*. **2014**, 3(1), 56-63.
[4] T. Hasegawa, H. Yamamoto, *Bull. Chem. Soc. Jpn*. **2000**, 73, 423-428.
[5] M.G. Banwell, C. F. Crasto, C.J. Easton, A.K. Forrest, T. Karoli, D.R. March, L. Mensah, M.R. Nairn, P.J. O'Hanlon, M.D. Oldham, W. Yue, *Bioorg. Med. Chem. Lett*. **2000**, 10, 2263-6.
[6] L.L. Chang, W.T. Ashton, K.L. Flanagan, T.B. Chen, S.S. O'Malley, G.J. Zingaro. P.K.S. Siegl, S.D. Kivlighn, V.J. Lotti, R.S.L. Chang, W.J. Greenlee, *J. Med. Chem*. **1994**, 37, 4464-4478.
[7] J.H. Musser, A.F. Kreft, R.H.W. Bender, D.M. Kubrak, D. Grimes, R.P. Carlson, J.M. Hand, J. Chang, *J. Med. Chem*. **1990**, 3, 240-245.
[8] A. De Dios, C.S. Grossman, P.A. Hipskind, H.S. Lin, K.L. Lobb, B. Lopez De UraldeGarmendia, J.E. Lopez, M.M. Mader, M.E. Richett, C. Shih, WO Patent 2003/035629, **2003**.
[9] K. L. Lobb, P.A. Hipskind, J.A. Aikins, E. Alvarez, Y. Cheung, E.L. Considine, A. De Dios, G.L. Durst, R. Ferritto, C.S. Grossman, D.D. Giera, B.A. Hollister, Z. Huang, P.W. Iversen, K.L. Law, T. Li, H.-S. Lin, B. Lopez, J.E. Lopez, L.M. Martin Cabrejas, D.J. McCann, V. Molero, J.E. Reilly, M.E. Richett, C. Shih, B. Teicher, J.H. Wikel, W.T. White, M. Mader, *J. Med. Chem*. **2004**,47, 5367–5380.
[10] M. Mader, C. Shih, E. Considine, A. De Dios, C. Grossman, P. Hipskind, H. Lin, K. Lobb, B. Lopez, J. Lopez, L. Cabrejas, M. Richett, W. White, Y. Cheung, Z. Huang, J. Reilly, S. Dinn, *Bioorg. Med. Chem. Lett*. **2005**, 15, 617–620.
[11] B. T. Gowda, S. Foro, P.A. Suchetan, H. Fuess, *Acta Cryst. E*. **2010**, 66, 0794-0795.
[12] P.A. Suchetan, B.T. Gowda, S. Foro, H. Fuess, Acta *Cryst. E*. **2010**, 66, 01040-01041.
[13] P.A. Suchetan, B.T. Gowda, S. Foro, H. Fuess, *Acta Cryst. E*. **2009**, 65, 03156-03157.
[14] B. T. Gowda, S. Foro, P.A. Suchetan, H. Fuess, *Acta Cryst. E*. **2009**, 65, 02750-02751.
[15] P.A. Suchetan, B.T. Gowda, S. Foro, H. Fuess, Acta *Cryst. E*. **2010**, 66, 0766-0767.
[16] S. Sreenivasa, B.S. Palakshamurthy, K.J. Pampa, N.K. Lokanath, P.A. Suchetan, *Acta Cryst. E*. **2014**, 70, o199-o200.
[17] S. Sreenivasa, B.S. Palakshamurthy, S. Madankumar, N.K. Lokanath, P.A. Suchetan, *Acta Cryst. E*. **2014**, 70, o193-o194.
[18] B. T. Gowda, S. Foro, P.A. Suchetan, H. Fuess, *Acta Cryst. E*. **2010**, 66, 0747-0748.
[19] P.A. Suchetan, B.T. Gowda, S. Foro, H. Fuess, *Acta Cryst. E*. **2010**, 66, 01039-01040.
[20] P.A. Suchetan, B.T. Gowda, S. Foro, H. Fuess, *Acta Cryst. E*. **2010**, 66, 01024-01025.
[21] P.A. Suchetan, B.T. Gowda, S. Foro, H. Fuess, *Acta Cryst. E*. **2010**, 66, 01997-01998.
[22] Bruker (2004). APEX2, SAINT-Plus and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
[23] G.M. Sheldrick, *Acta Cryst*. **2008**, A64, 112–122.
[24] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *J. Appl. Cryst*. **2008**, 41, 466–470.