

## КРАТКИЕ СООБЩЕНИЯ

UDC 541.6:548.737

FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR AND X-RAY CRYSTALLOGRAPHIC STRUCTURE DETERMINATION OF 4-NITRO-BENZENESULFONIC ACID 2,4-BIS-(1-PHENYL-ETHYL)-NAPHTHALEN-1-YL ESTERM. Kayalvizhi<sup>1</sup>, G. Vasuki<sup>1</sup>, A. Veerareddy<sup>2</sup>, B. Sreenivasulureddy<sup>2</sup>,  
A. Veerabhadrrao<sup>3</sup><sup>1</sup>Department of Physics, Kunthavai Naachiar Government Arts College (w) Autonomous, Tamilnadu, India  
E-mail: vasuki.kayal@gmail.com<sup>2</sup>R & D Laboratories, Suven Life Sciences Limited, Hyderabad, Andhra Pradesh, India<sup>3</sup>Department of Chemistry, Pondicherry University, Pondicherry, India

Received November, 13, 2013

Revised — June, 28, 2014

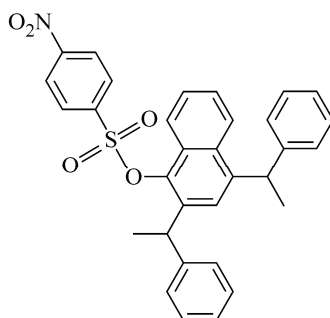
The title compound C<sub>32</sub>H<sub>27</sub>NO<sub>5</sub>S belongs to the monoclinic system, space group *P*2<sub>1</sub>/*c* with *a* = 14.4530(5) Å, *b* = 13.9185(5) Å, *c* = 13.5714(4) Å, α = γ = 90°, β = 87.174(3)°, *V* = 2726.76(16) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.310 g/cm<sup>3</sup>, *F*(000) = 1128, *R* = 0.053 and *wR* = 0.133, *S* = 1.03, *T* = 296 K. In the title compound, the naphthalene unit is planar (r.m.s. deviation = 0.0227 Å). The dihedral angle between the naphthalene unit and nitro-benzenesulfonic acid, 2-phenyl-ethyl and 4-phenyl-ethyl are 49.68(05)°, 82.96(06)°, and 81.94(07)° respectively. The structure is stabilized by intra- and intermolecular C—H...O hydrogen bonds.

**Keywords:** nitro-benzenesulfonic acid, phenyl-ethyl, naphthalene, ester.

Arene sulfonic acids and their derivatives are important materials of industrial chemistry: they serve as a basis to synthesize many pharmaceuticals, plant protecting agents, high-temperature polymers (polysulfones), food additives, dyes, detergents, antioxidants, and extractants. Hydrates, nitro- and hydroxy-substituted derivatives of benzenesulfonic acid are of interest as proton-conducting components of polymeric membranes in fuel cells [1]. Sulfonic acids are interesting and widely used chemical reagents. Their functionality in materials such as sulfonated polystyrene resins is not yet fully understood and depends directly on their acidity, including possible cooperative effects between the acid groups and hydration of the resin matrix. Benzenesulfonic acid (BSA) is a very strong acid (p*K*<sub>a</sub> = -2.8, approximately equal to sulphuric acid), solid at room pressure and temperature and is very soluble in the usual organic solvents [2]. Large amounts of sulfonated aromatic compounds are being produced as building blocks for the synthesis of dyes and detergents and released into the environment as waste during their manufacture and use [3]. Due to the formation of intra- and intermolecular hydrogen bonds and high polarization of the sulfo groups in the presence of water, aromatic sulfonic acids are good model systems for the elucidation of the proton migration pathways in the crystal structures [4].

A chemical diagram of compound **1** is shown in the Scheme. CIF-file containing complete information on the studied structure was deposited with CCDC, deposition number 970590, and is freely available upon request from the following web site: [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Synthesis.** 1-(1-Phenyl-ethoxy)-naphthalene **2** (5.0 g, 0.02 mol) was heated (Neat) to 140—145 °C in a test-tube and maintained for 10 hours. (The reaction was monitored by TLC). After cooling the crude (5.0 g), the crude compound was purified on silica gel column chromatography to get pure 2-(1-phenyl-ethyl)-naphthalen-1-ol **3** (1.15 g, 23.54 %), 4-(1-phenyl-ethyl)-naphthalen-1-ol **4** (1.5 g,



Scheme

30.13 %), 1-naphthol **5** (0.9 g, 18.80 %), and a new product 2,4-bis-(1-phenyl-ethyl)-naphthalen-1-yl **6** (1.2 g, 24.14 %). Compound **6** (1.2 g, 0.0034 mol) was dissolved in DCM (10 ml). 4-Nitro benzene sulfonyl chloride (0.82 g, 1.1 mol) was slowly added using a solid dropping funnel while the mixture was stirred in an ice bath (0–5 °C). TEA (3.0 ml) was added and the mixture was continuously stirred at 0–5 °C for 1 h. After TLC confirmed the absence of the starting material, water (20 ml) was added and stirred at RT for 30 minutes. The layers were separated and the aqueous layer was extracted using DCM (10 ml). The organic layers were combined, dried and concentrated under vacuum to give 4-nitro-benzenesulfonic acid **2**, 4-bis-(1-phenyl-ethyl)-naphthalen-1-yl ester **1** as an off-white solid. The structure of the product was confirmed by its analytical data and finally confirmed by the X-ray crystal structure. Yield: 1.4 g (76 %) MR: 177.5–180.3 °C, IR(KBr): 3105 cm<sup>-1</sup>, 3064 cm<sup>-1</sup>, 2972 cm<sup>-1</sup>, 2933 cm<sup>-1</sup>, 1601 cm<sup>-1</sup>, 1531 cm<sup>-1</sup>, 1377 cm<sup>-1</sup>, 1347 cm<sup>-1</sup>, 1313 cm<sup>-1</sup>, 1186 cm<sup>-1</sup>, 1042 cm<sup>-1</sup>, 837 cm<sup>-1</sup>, 741 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.60–1.63 (m, 6H), 4.63–4.68 (q, 1H), 4.75–4.81 (q, 1H), 7.14–7.23 (m, 7H), 7.24–7.27 (m, 2H), 7.28–7.31 (m, 4H), 7.71–7.73 (d, 1H, *J* = 8.0 Hz), 7.93–7.96 (d, 1H, *J* = 8.4 Hz), 8.14–8.16 (d, 2H, *J* = 8.74 Hz), 8.32–8.34 (d, 2H, *J* = 8.72 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 21.05, 22.61, 38.02, 40.83, 122.83, 124.27, 124.44, 124.52, 126.31, 126.39, 126.45, 127.51, 127.60, 128.02, 128.39, 128.44, 128.64, 129.59, 131.77, 135.65, 141.48, 141.62, 142.41, 144.34, 145.99, 150.91.

**Characterization by spectroscopy. FT-IR.** The FT-IR data for title compound **1** is given in the experimental data. The vibrational bands with the wave numbers of 1531.44 cm<sup>-1</sup> (asymmetric ArNO<sub>2</sub> stretching), 1377.40 cm<sup>-1</sup> (asymmetric SO<sub>2</sub> stretching), and 1186.60 cm<sup>-1</sup> (symmetric SO<sub>2</sub> stretching) were observed.

**<sup>1</sup>H NMR.** The <sup>1</sup>H NMR spectrum of title compound **1** was recorded using CDCl<sub>3</sub> as the solvent and the data was given in the experimental section. The methyl protons were observed as a multiplet at 1.60 ppm and CH moieties were observed as two quartets at 4.63 ppm and 4.75 ppm respectively. The aromatic protons of phenyl and naphthalene moieties are observed as multiplets at 7.14 ppm, 7.24 ppm, 7.27 ppm, and 7.28 ppm, a doublet at 7.71 ppm, and a doublet at 7.93 ppm respectively. The other aromatic protons of the nitro benzene moiety were observed as a doublet at 8.14 ppm and a doublet at 8.32 ppm respectively.

**<sup>13</sup>C NMR.** The <sup>13</sup>C NMR spectrum of title compound **1** was recorded using CDCl<sub>3</sub> as the solvent and the data was given in the experimental section. The methyl carbon atoms were observed at 21.05 ppm and 22.61 ppm respectively and the CH carbon atoms were observed at 38.02 ppm and 40.83 ppm respectively. The phenyl ring moiety carbon atoms were observed at 127.60 ppm, 128.44 ppm, 128.64 ppm, 129.59 ppm, 135.65 ppm, 141.48 ppm, 141.62 ppm, and 142.41 ppm respectively. The naphthalene ring moiety carbon atoms were observed at 122.83 ppm, 124.27 ppm, 124.44 ppm, 124.52 ppm, 126.31 ppm, 126.45 ppm, 127.51 ppm, 128.39 ppm, 131.77 ppm, and 144.34 ppm respectively. The nitro benzene ring moiety carbon atoms were observed at 126.39 ppm, 128.02 ppm, 145.99 ppm, and 150.91 ppm respectively.

**X-ray crystallography.** A colourless crystal of title compound **1** with dimensions 0.35×0.30×0.25 mm was chosen for the data collection. The data were collected with graphite-monochromated MoK<sub>α</sub> radiation (λ = 0.71073 Å). For compound **1** data collection: APEX2 [ 5 ]; cell refinement: APEX2/SAINT [ 5 ]; data reduction: SAINT/XPREP [ 5 ]; molecular graphics: ORTEP-3 [ 6 ] for Win-

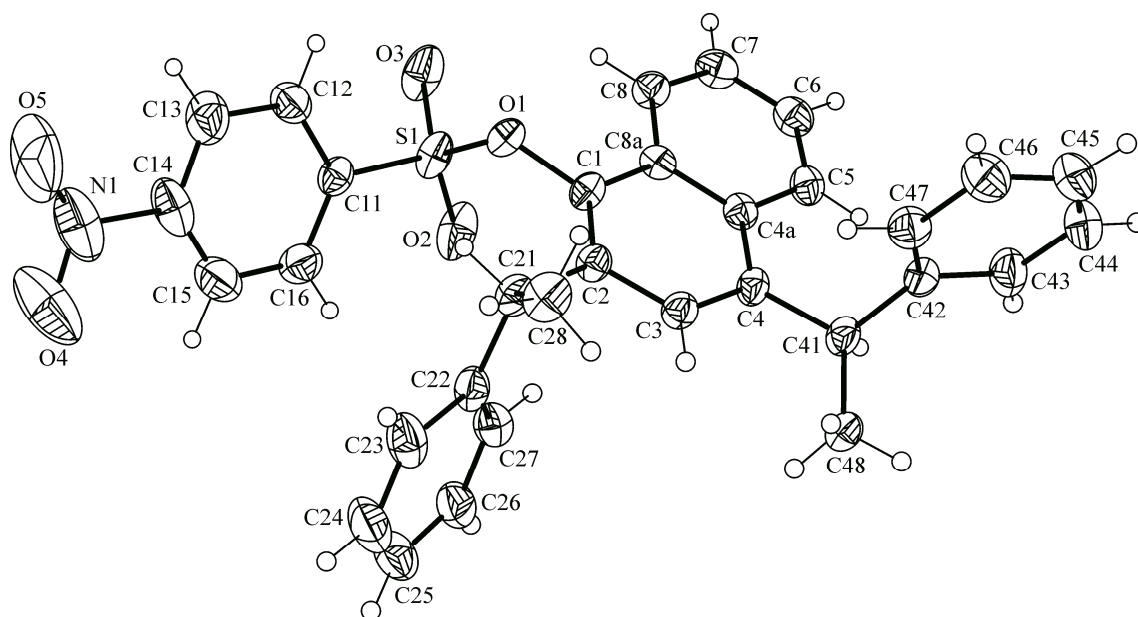


Fig. 1. Molecular structure of the title compound showing atom numbering with displacement ellipsoids drawn at the 30 % probability level

dows; publication software: PLATON [ 8 ]. The structure of compound **1** was solved by direct methods using SHELXS-97 [ 9 ] and refined using SHELXL-97 [ 9 ]. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.93 Å (aromatic), 0.96 Å (methyl), and 0.98 Å (methylene), and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  or  $1.5U_{\text{eq}}$  (parent atom). In the range 4.1—26.0, a total of 15888 reflections were collected, out of which 5321 were independent ( $R_{\text{int}} = 0.054$ ). The maximum and minimum peaks and holes are  $0.20 \text{ e}/\text{Å}^3$  and  $-0.34 \text{ e}/\text{Å}^3$  respectively.  $S = 1.03$  and  $wR = 0.133$ .

**Results and discussion.** The title compound  $\text{C}_{32}\text{H}_{27}\text{NO}_5\text{S}$  crystallized in the monoclinic system, space group  $P2_1/c$  with  $a = 14.4530(5) \text{ Å}$ ,  $b = 13.9185(5) \text{ Å}$ ,  $c = 13.5714(4) \text{ Å}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 87.174(3)^\circ$ ,  $V = 2726.76(16) \text{ Å}^3$ ,  $Z = 4$ ,  $D_c = 1.310 \text{ g/cm}^3$ ,  $F(000) = 1128$ ,  $R = 0.053$  and  $wR = 0.133$ ,  $S = 1.03$ ,  $T = 296 \text{ K}$ . The molecular structure of the title compound  $\text{C}_{32}\text{H}_{27}\text{NO}_5\text{S}$  is displayed in Fig. 1. The dihedral angle between the naphthalene ring system (C1—C8A) and the benzene ring (C11—C16) is  $49.25(07)^\circ$  with the root mean square value of  $0.0227 \text{ Å}$ . The naphthalene ring system (C1—C8A) makes dihedral angles of  $74.80(07)^\circ$  and  $87.43(07)^\circ$  respectively with two phenyl rings (C22—C27) and (C42—C47). The dihedral angle between the two phenyl rings (C22—C27) and (C42—C47) is  $39.61(09)^\circ$  with the rms deviation of  $0.0074 \text{ Å}$ . The nitro-benzene unit, the naphthalene

T a b l e 1

Hydrogen-bond geometry

Type	Donor—H...Acceptor	D—H	H...A	D...A	D—H...A
Intra	C(8)—H(8)...O(1)	0.93	2.51	2.831(3)	101
Intra	C(16)—H(16)...O(2)	0.93	2.58	2.940(3)	104
Intra	C(21)—H(21)...O(1)	0.98	2.43	2.909(3)	110
Inter	C(41)—H(41)...O(3) <sup>i</sup>	0.98	2.58	3.538(3)	165

Symmetry codes: (i)  $1-x, -1/2+y, 1/2-z$ .

unit (C1—C8A), and the two phenyl rings (C22—C27), (C42—C47) are planar. The sum of bond angles around N1 (359.99°) indicates that the N1 atom exhibits  $sp^2$  hybridization. The torsion angle (C23—C22—C21—C28 = 43.42(29)°) indicates that the side chain is in the synclinal position. The torsion angle (C43—C42—C41—C48 = 95.48(26)°) indicates that the side chain is anticlinal looking down the C41—C42 bond. The widening of the exocyclic C4—C41—C48 angle (114.72(19)°) from the normal value of 109° may be due to steric repulsion between H3 at C3 and H48A at C48 (H3...H48A = 2.232 Å). Intermolecular and intramolecular C—H...O hydrogen bonds are present in the crystal structure (Table 1). An intramolecular C—H...O hydrogen bond results in the formation of a seven-membered ring (C1—O1—S1—O3—H8—C8—C8A) and there by producing the S(7) motif.

**Acknowledgments.** The authors thank the DST-FIST X-ray facility at the Department of Chemistry, Pondicherry University, Pondicherry, for the single-crystal X-ray data collection.

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