*Journal of Chemical Crystallography, Vol. 35, No. 10, October 2005 (© 2005)*
DOI: 10.1007/s10870-005-4324-8

# Synthesis and crystal structure of 2-acetylnaphthalen-6-yl 4-methylbenzosulfonate

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*Received October 28, 2004; accepted March 18, 2005*

The title compound has been synthesized by the reaction of 1-(6-hydroxy-2- naphthyl)-1-ethanone (**2**) with *p*-toluenesulfonyl chloride. Its structure was determined by single crystal X-ray diffraction. 2-Acetylnaphthalen-6-yl 4-methylbenzosulfonate (**3**) crystallizes in the orthorhombic space group *Pbca* with $a = 12.727(3)$ Å, $b = 14.560(3)$ Å, $c = 17.688(4)$ Å, $V = 3277.8(11)$ Å$^3$, and $Z = 8$. The results demonstrate that the dihedral angle between the benzene ring and the naphthalene ring is 116.5°, and the length (1.417 Å) of single C—O bond of **3** is longer than that of single C—O bond in the relative compounds.

**KEY WORDS:** Synthesis; crystal structure; 2-acetylnaphthalen-6-yl 4-methylbenzosulfonate.

## Introduction

1-(6-Hydroxy-2-naphthyl)-1-ethanone (**2**) is an important intermediate for the preparation of naproxen, an anti-inflammatory drug, and for the synthesis of 2-(1-{6-[(2-[$^{18}$F]fluoroethyl)(methyl)-amino]-2-naphthyl}ethylidene)malononitrile ([$^{18}$F]FDDNP) which is a promising imaging agent in the early diagnosis of Alzheimer's disease.[1–3] We found it was very difficult for the direct amination of **2** in the synthesis of [$^{18}$F]FDDNP, so we tried to activate the hydroxy group of **2** for nucleophilic displacement by transforming it into the tosylate **3** (Scheme 1). Here, we reported its synthesis and the crystal structure.

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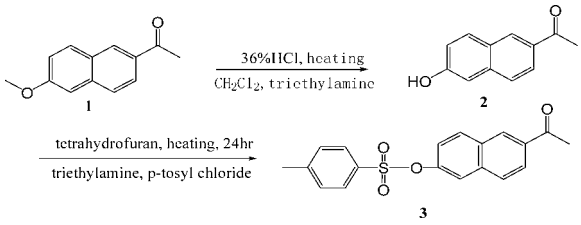
## Experimental

The melting point was determined with XT4A micromelting point apparatus and was uncorrected. Infrared spectra were recorded with a Nicolex FT-IR-400 spectrometer. $^1$H NMR spectra were recorded with RX400 instrument, tetramethylsilane being used as internal standard. Elemental analyses were performed by using the flash EA112 method. MS were recorded with ZAB-HS instrument using the EI method.

### *Synthesis of 1-(6-hydroxy-2-naphthyl)-1-ethanone **2***

A solution of 1.00 g of 1-(6-methoxy-2-naphthyl)-1-ethanone in 2.5 mL of $CH_2Cl_2$ was added to a mixture of 80 mL of HCl ($d = 1.18$) and 15 drops (round 0.75 mL) of triethylamine in a 100 mL three-neck round bottom flask equipped with a reflux condenser and an isobaric dropping




**Scheme 1.**

funnel. The stirred mixture was heated quickly to boil and reflux for 2 h. The hot solution was filtered through a mineral wool plug to remove the oily residue. The solid, after cooling, was filtered out through a glass frit. Then the solid was dissolved in 20 mL of ethyl acetate, washed with brine, dried over with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to give a crude product **2** 0.74 g (79.6%). The solid was dissolved in a base solution, and the diluted HCl was dropped in till white deposit appeared entirely. The solid was filtered out to afford pure product, melted at 172.5–174°C (Ref. 173.5–177°C).[4] All absorption bands in IR data of **2** appeared as expected. 3365 $cm^{-1}$ corresponds to −OH stretching absorption bands, 1660 $cm^{-1}$ corresponds to C=O, and 1630 $cm^{-1}$ corresponds to C=C of naphthalene ring stretching absorption bands. The EI-MS of **2** gave the molecular ion peaks (186, M) and those of the main fragments.

*Synthesis of 2-acetylnaphthalen-6-yl 4-methylbenzosulfonate **3***

0.93 g (5 mmol) of **2**, 1.00 g (5.24 mmol) of *p*-toluenesulfonyl chloride, 10 drops (about 0.5 mL) of triethylamine, and 20 mL of tetrahydrofuran were added into a 50 mL three-neck round bottom flask equipped with a reflux condenser. The resulted mixture was heated to reflux for 24 h. The solution was filtered out to remove the indissoluble substance and the filtrate was evaporated to give 1.23 g (72%) of **3**. Recrystallization from ethyl acetate to give the title compound **3**, melted at 119–120°C. Anal. Calcd. (%) for $C_{19}H_{16}O_4S$: C, 67.04; H, 4.74; S, 9.42. Found (%): C, 67.26; H, 4.87; S, 9.07; $^1H$ NMR ($CD_3COCD_3$, ppm): $\delta = 2.44$ (s, 3H), 2.69 (s, 3H), 7.27 (dd, 1H), 7.46 (t, 2H,), 7.66 (d, 1H), 7.78 (d, 2H), 7.95 (d, 1H), 8.05 (dd, 1H), 8.10 (d, 1H), 8.64 (s, 1H). All sorption bands in IR data of **3** appeared as expected. 1681 $cm^{-1}$ corresponds to C=O, 1594 $cm^{-1}$ corresponds to C=C of naphthalene ring stretching absorption bands, and 1369 $cm^{-1}$ corresponds to O=S=O stretching absorption bands. The EI-MS of **3** gave the molecular ion peaks (340, M) and those of the main fragments.

**Table 1.** Crystallographic Data and Structure Refinement for **3**

| Compound | $CH_3C_6H_4SO_2OC_{10}H_6COCH_3$ |
|---|---|
| CCDC deposit No. | 253163 |
| Chemical formula | $C_{19}H_{16}O_4S$ |
| Formula weight | 340.38 |
| Temperature (K) | 293(2) |
| Crystal size(mm) | 0.81 × 0.41 × 0.11 |
| Crystal system | Orthorhombic |
| Space group | *Pbca* |
| Unit-cell dimensions | |
| *a* (Å) | 12.727(3) |
| *b* (Å) | 14.560(3) |
| *c* (Å) | 17.688(4) |
| Volume ($Å^3$) | 3277.8(11) |
| *Z* | 8 |
| Color/shape | Colorless/platelet |
| Density (calcd.) ($g/cm^3$) | 1.379 |
| Absorption coefficient ($mm^{-1}$) | 0.217 |
| *F*(000) | 1424 |
| Diffractometer/scan | $\omega$ |
| Radiation/wavelength | Mo K$\alpha$ (graphite monochrom.) 0.71073 Å |
| $\theta$ range for data collection (°) | $2.30 \leq \theta \leq 27.44$ |
| Reflections collected | 28209 |
| Independent/observed reflections | 3733 |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.9759 and 0.8438 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 3733/0/217 |
| Goodness of fit on $F^2$ | 0.846 |
| Final *R* indices [$I \geq 2\sigma(I)$] | $R_1 = 0.0402$, $wR_2 = 0.0600$ |
| *R* indices (all data) | $R_1 = 0.1097$, $wR_2 = 0.0660$ |
| Largest diff. Peak and hole (e $Å^{-3}$) | 0.208, −0.229 |

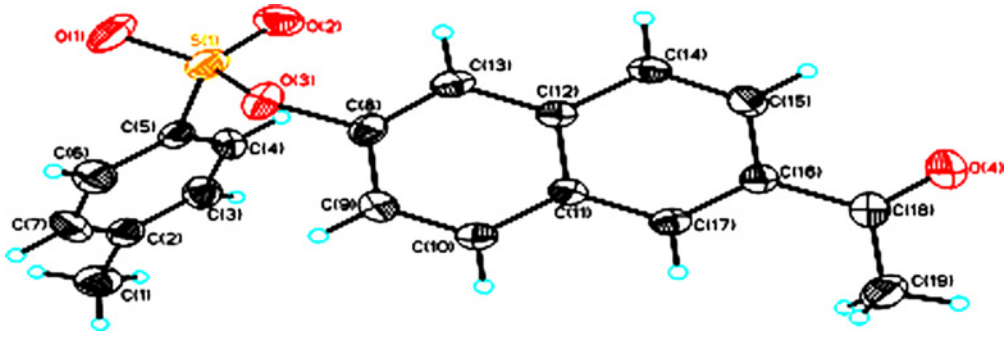



**Fig. 1.** Molecular structure of **3**. Thermal ellipsoids are at the 50% probability level.

*X-ray crystallography*

The colorless single crystal was cultured from a solution of ethyl acetate by slow evaporation at room temperature.

A single crystal of approximate dimensions 0.81 mm × 0.41 mm × 0.11 mm was used. X-ray diffraction data were collected at 293(2) K on a Rigaku Raxis Rapid IP diffractometer, using graphite monochromatized Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 1424 independent reflections were collected in the range of $2.30^\circ \leq \theta \leq 27.44^\circ$ by $\omega$ scan mode. The crystal data, data collection, and refinement parameters for **3** were presented in Table 1.

The structure was solved by direct methods using the program SHELXS-97.[5] Refinements were done by the full-matrix least-squares on $F^2$ using SHELXL-97.[6] Nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located from a difference Fourier map and refined without restraints.

## Results and discussion

The molecular structure of the compound **3** is illustrated in Fig. 1. The molecular packing of the title compound **3** is shown in Fig. 2. The bond lengths and bond angles are listed in Table 2.

In the molecular structure of **3**, acetyl group is a planar with naphthalene ring, and the dihedral angle between the benzene ring and the naphthalene ring is 116.5°.

There are no hydrogen bonds in the crystal of **3**. But three types of short contacts which belong to van der Waals force exist and the crystal of **3** is formed through them. The bond lengths and bond angles of three types of short contacts are listed in Table 3. Three types of short contacts in the crystal of **3** are shown in Fig. 3.

The C—C bond lengths and angles of the naphthalene ring in **3** are in the same range as those found in the relative compounds, such as 3-hydroxy-2-naphthalenecarboxaldehyde.[7] The length (1.417 Å) of single C—O bond of product **3** is longer than that of single C—O bond

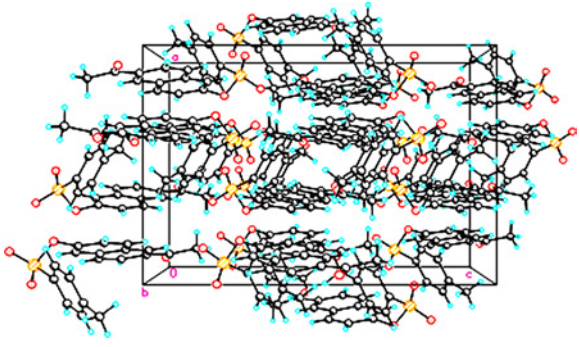


**Fig. 2.** The packing diagram of **3**.

**Table 2.** Bond Lengths (Å) and Angles (°) for **3**

| Bonds | Angles (°) | Bonds | Lengths (Å) |
|---|---|---|---|
| O(2)−S(1)−O(1) | 120.75(10) | S(1)−O(2) | 1.4217(15) |
| O(2)−S(1)−O(3) | 109.11(8) | S(1)−O(1) | 1.4292(14) |
| O(1)−S(1)−O(3) | 102.12(9) | S(1)−O(3) | 1.5983(13) |
| O(2)−S(1)−C(5) | 109.50(10) | S(1)−C(5) | 1.751(2) |
| O(1)−S(1)−C(5) | 109.37(10) | C(1)−C(2) | 1.507(3) |
| O(3)−S(1)−C(5) | 104.65(8) | C(2)−C(3) | 1.368(3) |
| C(3)−C(2)−C(7) | 117.8(2) | C(2)−C(7) | 1.383(3) |
| C(3)−C(2)−C(1) | 122.0(2) | C(3)−C(4) | 1.379(3) |
| C(7)−C(2)−C(1) | 120.3(2) | C(4)−C(5) | 1.378(3) |
| C(2)−C(3)−C(4) | 122.0(2) | C(5)−C(6) | 1.369(3) |
| C(5)−C(4)−C(3) | 119.3(2) | C(6)−C(7) | 1.378(3) |
| C(6)−C(5)−C(4) | 119.7(2) | C(8)−C(13) | 1.348(2) |
| C(6)−C(5)−S(1) | 119.93(17) | C(8)−C(9) | 1.397(2) |
| C(4)−C(5)−S(1) | 120.26(17) | C(8)−O(3) | 1.417(2) |
| C(5)−C(6)−C(7) | 120.1(2) | C(9)−C(10) | 1.361(2) |
| C(6)−C(7)−C(2) | 121.1(2) | C(10)−C(11) | 1.411(2) |
| C(13)−C(8)−C(9) | 122.82(18) | C(11)−C(17) | 1.409(2) |
| C(13)−C(8)−O(3) | 120.23(18) | C(11)−C(12) | 1.419(2) |
| C(9)−C(8)−O(3) | 116.75(18) | C(12)−C(14) | 1.414(3) |
| C(10)−C(9)−C(8) | 119.08(18) | C(12)−C(13) | 1.421(2) |
| C(9)−C(10)−C(11) | 120.92(18) | C(14)−C(15) | 1.356(2) |
| C(17)−C(11)−C(10) | 122.02(18) | C(15)−C(16) | 1.414(2) |
| C(17)−C(11)−C(12) | 118.93(17) | C(16)−C(17) | 1.363(2) |
| C(10)−C(11)−C(12) | 119.03(18) | C(16)−C(18) | 1.496(3) |
| C(14)−C(12)−C(11) | 118.34(18) | C(18)−O(4) | 1.209(2) |
| C(14)−C(12)−C(13) | 122.76(19) | C(18)−C(19) | 1.502(3) |
| C(11)−C(12)−C(13) | 118.88(18) | | |
| C(8)−C(13)−C(12) | 119.23(18) | | |
| C(15)−C(14)−C(12) | 120.95(19) | | |
| C(14)−C(15)−C(16) | 121.22(19) | | |
| C(17)−C(16)−C(15) | 118.67(19) | | |
| C(17)−C(16)−C(18) | 122.67(18) | | |
| C(15)−C(16)−C(18) | 118.63(18) | | |
| C(16)−C(17)−C(11) | 121.87(18) | | |
| O(4)−C(18)−C(16) | 119.9(2) | | |
| O(4)−C(18)−C(19) | 120.6(2) | | |
| C(16)−C(18)−C(19) | 119.47(19) | | |
| C(8)−O(3)−S(1) | 120.76(12) | | |

in the relative compounds, such as 2-hydroxy-1-naphthalenecarboxaldehyde (1.358 Å).[7] This demonstrates the single C−O bond of **3** is

**Table 3.** The Short Contact in the Crystal of **3**

| Bounds | Numbers | Lengths (Å) | Angles (°) |
|---|---|---|---|
| C−H···$\pi$ | 2 | 2.892 | 145.97 |
| C−H···O | 2 | 2.496 | 157.12 |
| C−H···$\pi$ | 2 | 2.871 | 135.46 |

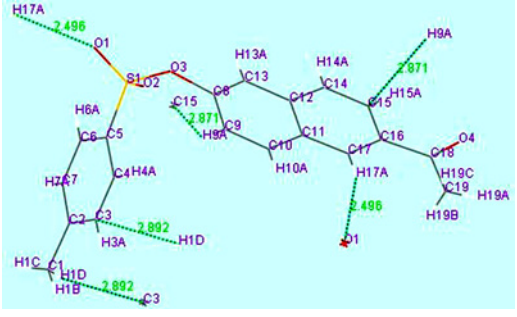



**Fig. 3.** Three types of short contacts in crystal of **3**.

easily ruptured and the amination is easily carried out.

**Supplementary material** CCDC-253163 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, United Kingdom; Direct Line: +44 1223 762910. Tel: +44 1223 336408. Fax: +44 1223 336033; E-mail: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk.

## Acknowledgment

This work was supported by the grant of Beijing Institute of Technology.

## References

1. Agdeppa, E.D.; Kepe, V.; Liu, J.; Flores-Torres, S.; Satyamurthy, N.; Petric, A.; Cole, G.M.; Small, G.W.; Huang, S.-C.; Barrio, J.R. *J. Neurosci*. **2001**, *21,* 189RC, 1–5.
2. Agdeppa, E.D.; Kepe, V.; Petric, A.; Satyamurthy, N.; Liu, J.; Huang, S.-C.; Small, G.W.; Cole, G.M.; Barrio, J.R. *J. Neurosci*. **2003**, *117,* 723–730.
3. Barrio, J.R.; Huang, S.-C.; Cole, G.M.; Satyamurthy, N.; Petric, A.; Phelps, M.E. *J. Labelled Compd. Radiopharm.* **1999**, *42*(Suppl.), S194–S195.
4. Andrej, P.; Tatjana, S.; Barrio, J.R. *J. Monatsh. Chem.* **1998**, *129,* 777–786.
5. Sheldrick, G.M. *Acta Crystallogr.* **1990**, *A46,* 467.
6. Sheldrick, G.M. *SHELXL97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
7. Fernández, G.J.M.; Espinosa-Pérez, G. *J. Chem. Crystallogr*. **1994**, *24,* 151–154.