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One-step synthesis of 6-acetamido-3-(*N*-(2-(dimethylamino) ethyl) sulfamoyl) naphthalene-1-yl 7-acetamido-4-hydroxynaphthalene-2-sulfonate and its characterization with 1D and 2D NMR techniques

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A one-step method was reported for the synthesis of 6-acetamido-3-(*N*-(2-(dimethylamino) ethyl) sulfamoyl) naphthalene-1-yl 7-acetamido-4-hydroxynaphthalene-2-sulfonate by treating 7-acetamido-4-hydroxy-2-naphthalenesulfonyl chloride with equal moles of *N, N*-dimethylethylenediamine in acetonitrile in the presence of K_2CO_3. The chemical structure of the obtained compounds was characterized by MS, FTIR, ^{1}H NMR, ^{13}C NMR, gCOSY, TOCSY, gHSQC, and gHMBC. The chemical shift differences of ^{1}H and ^{13}C being δ 0.04 and 0.2, respectively, were unambiguously differentiated. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: NMR; ^{1} H NMR; ^{13}C NMR; 2D NMR; synthesis

Introduction

Owing to the distinct features of fabric and dyestuff, for any given fabric, only limited types of dyestuffs are applicable.[1] If one dye can be used to color all types of fabrics, both the dyeing process and effluent treatment can be simplified. As the residual dye bath may be reused, the amount of dyeing effluent can be reduced as well. Apparently, all of these will lower the dyeing costs and provide environmental advantages. However, the proof of concept of universal dye is in its infancy, and the development of novel universal dyes is high desirable.[2–5] Herein, we design a new universal dye precursor, 6-acetamido-3-(*N*-(2-(dimethylamino) ethyl) sulfamoyl) naphthalene-1-yl 7-acetamido-4-hydroxynaphthalene-2-sulfonate (**III**) (Scheme 1); the structure of which has several characteristics. (i) A naphthalene sulfonamide moiety is included, which is thought to be beneficial for the improvement of sublimation fastness of dye on fabrics.[6] (ii) Two naphthalene rings are presented, which may increase the substantivity of dye to fibers.[7] (iii) A tertiary amine group is incorporated, which means this structure has the potential to be used as the precursor for cationic dyes.[8]

Conventionally, **III** can be synthesized by two steps: the condensation of 7-acetamido-4-hydroxy-2-naphthalenesulfonyl chloride (**II**) with *N,N*-dimethylethylene-diamine[9] and followed by the esterfication of hydroxyl group using excessive sulfonyl chloride (**II**) in high boiling point solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and 1-methyl-2-pyrrolidone in the presence of a base, for instance, triethylamine and pyridine.[10–12] In this study, a one-step approach was applied to synthesize **III** by the condensation of sulfonyl chloride (**II**) with equal moles of *N,N*-dimethylethylenediamine in acetonitrile in the presence of K_2CO_3, and the structure of **III** was unambiguously confirmed by ^{1}H and ^{13}C NMR.

Experimental

Materials and apparatus

All chemical reagents were the commercial products of analytical grade. The mass spectra were obtained on an HP 1100 System of HPLC/MSD or HP6890 Series GC System/5973 Mass Select Detector (Hewlett Packard Ltd. Co., Palo Alto, CA, USA). The IR spectra (the sample was made into KBr wafer) were recorded with an FTIR 430 infrared spectrophotometer (JASCO Ltd. Co., Tokyo, Japan). Varian INOVA 400 MHz NMR spectrometer (Varian, Palo Alto, CA, USA) was used for the characterization of sulfonate **III** in deuterated dimethyl sulfoxide (~0.1 mol in concentration). The TMS (δ 0.00) was used as chemical shift reference. ^{1}H NMR spectrum was operated at 399.715 MHz with 10 000 Hz spectral width, flip angle 30°, and recycle time 7 s, and determined at 40 °C. ^{13}C NMR spectrum was performed at 100.518 MHz and 40 °C with Waltz proton decoupling, flip angle 30°, spectral width 22 000 Hz, recycle time 6.2 s, and accumulation 1600 times. The gCOSY and TOCSY experiments were run at 5911 Hz spectral width, zero filling to 4096 × 4096 data matrix, relaxation delay 1 s, and acquisition time 0.167 s. The gHSQC and gHMBC were recorded at spectral widths of 4650 Hz for ^{1}H and 21894 Hz for ^{13}C, zero filling to 2048 × 4096 data matrix, relaxation delay 1 s, and 32 repetitions. A sinbell window function was used prior to Fourier transformation.

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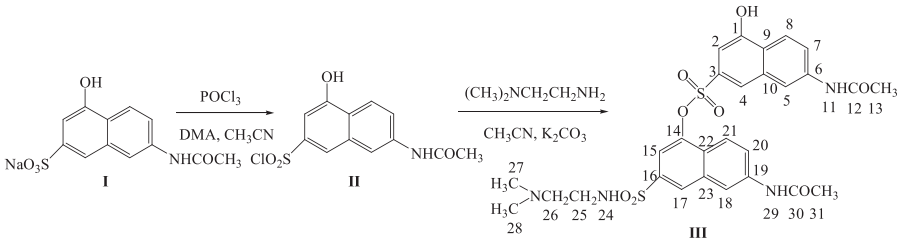


Scheme 1. Synthesis route for 6-acetamido-3-(*N*-(2-(dimethylamino) ethyl) sulfamoyl) naphthalene-1-yl 7-acetamido-4-hydroxynaphthalene-2-sulfonate (**III**).

Synthesis of III

Scheme 1 illustrates the synthesis route for **III**.

Synthesis of N,N-dimethylethylenediamine

N,N-Dimethylethylenediamine was synthesized using ethanol amine in accordance with references,[13] as illustrated in Scheme 2. Boiling point: 97–102 °C. GS/MS: *m/z* (relative intensity) 58 (100%), 42(25%), 30(23%), 88(M^+, 6%); relative purity: 89. 2%.

*Synthesis of sulfonyl chloride (**II**)*

To the mixture of 5.4 g **I**, 6.6 ml *N,N*-dimethylacetamide, and 28 ml acetonitrile, 4.9 ml phosphorus oxychloride was added. The resulting mixture was stirred at 55–60 °C for 4 h and poured into cold water. **II** was collected by filtration with a yield of 92%. TLC: R_f = 0.86 (EtOAc/HOAc/EtOH, 4 : 1 : 3). The structure of **II** was confirmed by the comparison of its IR spectrum with standard IR spectrum of **I**. The main absorption bands of **I** appear at 3480 cm^{-1} (–SO_2–OH), 3387 cm^{-1} (–NH–), and 1672 cm^{-1} (–CO). The main absorption peaks of **II** (cm^{-1}) are present at 3383 cm^{-1} (–NH–), 1677 cm^{-1} (–CO), 1358 cm^{-1} (–SO), and 1167 cm^{-1} (–SO).

*Synthesis of **III***

A suspension of 2.0 g **II** in 40 ml acetonitrile was added dropwise into 0.6 g *N,N*-dimethylethylenediamine, 1.0 g K_2CO_3, and 30 ml acetonitrile. This mixture was stirred at 35–40 °C for 4 h and refluxed for further 2 h. After extraction with ethyl acetate and recrystallization from acetonitrile, **III** was obtained in white color with a yield of 36.2%. Mass spectral analysis (Atmospheric Pressure Ionization-Electrospray Ionization positive): *m/z* 615.1 ($[M+H]^+$, 66.9%), 637.1 ($[M+Na]^+$, 100%).

Results and Discussion

Because of the analogy of the substituted groups and their positions on the two naphthalene rings, it is impossible to elucidate the structure of **III** solely by its MS, 1D ^{1}H NMR, and 1D ^{13}C NMR spectra. The assignments of the resonances to individual protons and carbons are based on 2D NMR spectra including gCOSY, TOCSY, gHSQC, and gHMBC.

Compared with other aromatic hydrogens, the resonance signals of H2 and H15 should appear in a higher field because of the *p*–π conjugation interactions between the *ortho*-oxygen atom and the naphthalene ring. As a hydroxyl group is present in the *ortho*-position of H2, its chemical shift should appear in a higher field (δ 7.09), whereas as a strong electron-withdrawing group sulphonyl (–SO_2–) is present in the *ortho*-position of H15, its chemical shift should appear in a lower field (δ 7.44).

The gCOSY spectrum indicates the coupling interactions between H2 and H4 and between H15 and H17; consequently, chemical shifts δ 7.90 and 8.20 are assigned to H4 and H17, respectively. The gCOSY spectrum also suggests the coupling interactions among H5, H7, and H8 and among H18, H20, and H21, although it is not possible to assign the accurate chemical shift to individual H.

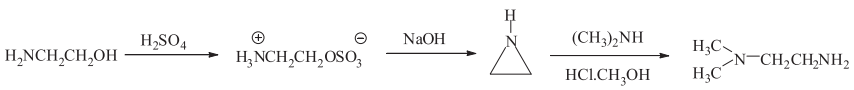
The TOCSY spectrum demonstrates a weak connectivity between H4 and H5 and between H17 and H18; consequently, the chemical shifts δ 8.32 and 8.45 are assigned to H5 and H18, respectively. Then, in reference to gCOSY, chemical shifts δ 7.73 and 8.11 are assigned to H7 and H8, respectively; chemical shifts δ 7.67 and 7.88 are assigned to H20 and H21, respectively.

The assignment of ^{1}H NMR signals of **III** was further completed with gHMBC and gHSQC. It is worth noting that the difference in chemical shifts between H11 and H29 is fairly marginal, only δ 0.04 (δ 12.30, 12.26), which suggests the complexity in assigning the NMR resonance signals. GHMBC indicates the connectivity among H11 and C5, C6, C7, C12; thus, the chemical shift δ 10.26 is assigned to H11. As H29 and C18, C19, C20, C30 are also coupling related in gHMBC, the chemical shift δ 10.30 is assigned to H29. Concurrently, the assignment of ^{13}C NMR signals could be completed, and this in turn supports the assignment of ^{1}H NMR signals. Strikingly, δ 169.1 and 168.9 are assigned unambiguously to C12 and C30, respectively; the difference in chemical shifts is only δ 0.2.

In essence, the ^{1}H and ^{13}C NMR signals of **III** were assigned, and the ^{1}H–^{1}H coupling constants are listed in Table 1.

Conclusions

A convenient approach was developed to prepare 6-acetamido-3-(*N*-(2-(dimethylamino) ethyl) sulfamoyl) naphthalene-1-yl 7-acetamido-4-hydroxynaphthalene-2-sulfonate, through which the condensation of sulfonyl chloride with *N,N*-dimethylethylenediamine and the condensation of naphtholic hydrogen with sulfonyl chloride take place concurrently. The ^{1}H and ^{13}C NMR spectra were interpreted unambiguously, and the ^{1}H–^{1}H coupling constants and the chemical shifts of ^{1}H and ^{13}C were reported for the first time.



Scheme 2. Synthesis route for *N,N*-dimethylethylenediamine.

Table 1. NMR data of 6-acetamido-3-(*N*-(2-(dimethylamino) ethyl) sulfamoyl) naphthalene-1-yl 7-acetamido-4-hydroxynaphthalene-2-sulfonate (**III**)

No.	δ_H	δ_C	^1H–^1H coupling constants (Hz)	TOCSY	gCOSY cross signal	gHSQC ^1J(C,H) cross signal	gHMBC
1	/	154.9	/	/	/	/	2[^2J(C,H)] 8[^3J(C,H)]
2	7.09	102.4	$^4J(H_2,H_4)$:1.4	2,4,5,7,8	2,4	+	4[^3J(C,H)]
3	/	131.9	/	/	/	/	2[^2J(C,H)] 4[^2J(C,H)]
4	7.90	120.0	$^4J(H_2,H_4)$:1.4	2,4,5,7,8	2,4	+	2[^3J(C,H)]
5	8.32	115.9	$^4J(H_5,H_7)$:1.5	2,4,5,7,8	5,7	+	4[^3J(C,H)] 7[^3J(C,H)] 11[^3J(C,H)]
6	/	139.1	/	/	/	/	5[^2J(C,H)] 8[^3J(C,H)] 11[^2J(C,H)]
7	7.73	122.3[a]	$^4J(H_5,H_7)$:1.5 $^3J(H_7,H_8)$: 9.1	2,4,5,7,8	5,7 7,8	+	5[^3J(C,H)] 11[^3J(C,H)]
8	8.11	123.2	$^3J(H_7,H_8)$: 9.1	2,4,5,7,8	7,8	+	7[^2J(C,H)]
9	/	123.4	/	/	/	/	2[^3J(C,H)] 4[^3J(C,H)] 5[^3J(C,H)] 7[^3J(C,H)]
10	/	133.6	/	/	/	/	8[^3J(C,H)]
11	10.26	/	/	/	/	/	/
12	/	168.9	/	/	/	/	11[^2J(C,H)] 13[^2J(C,H)]
13	2.09[a]	24.1	/	/	/	+	/
14	/	145.4	/	/	/	/	15[^2J(C,H)] 17[^4J(C,H)] 21[^3J(C,H)]
15	7.44	112.9	$^4J(H_{15},H_{17})$:1.3	15,17,18,20,21	15,17	+	17[^3J(C,H)]
16	/	138.0	/	/	/	/	15[^2J(C,H)] 17[^2J(C,H)]
17	8.20	125.6	$^4J(H_{15},H_{17})$:1.3	15,17,18,20,21	15,17	+	15[^3J(C,H)] 18[^3J(C,H)]
18	8.45	115.6	$^4J(H_{18},H_{20})$:1.4	15,17,18,20,21	17,18,20	+	17[^3J(C,H)] 20[^3J(C,H)] 29[^3J(C,H)]
19	/	139.1	/	/	/	/	18[^2J(C,H)] 21[^3J(C,H)] 29[^2J(C,H)]
20	7.67	123.0	$^4J(H_{18},H_{20})$:1.4 $^3J(H_{20},H_{21})$:9.1	15,17,18,20,21	18,20 20,21	+	18[^3J(C,H)] 29[^3J(C,H)]
21	7.88	122.2[a]	$^3J(H_{20},H_{21})$:9.1	15,17,18,20,21	20,21	+	20[^2J(C,H)]
22	/	123.9	/	/	/	/	15[^3J(C,H)] 17[^3J(C,H)] 18[^3J(C,H)] 20[^3J(C,H)]
23	/	133.9	/	/	/	/	17[^2J(C,H)] 21[^3J(C,H)]
25	2.69	40.5	$^3J(H_{25},H_{26})$:6.6	26	25,26	+	26[^2J(C,H)]
26	2.16	57.9	$^3J(H_{25},H_{26})$:6.6	25	26,25	+	25[^2J(C,H)] 27[^3J(C,H)] 28[^3J(C,H)]
27	2.01	44.8	/	/	/	+	26[^3J(C,H)] 27[^3J(C,H)]
28	2.01	44.8	/	/	/	+	26[^3J(C,H)] 27[^3J(C,H)]
29	10.30	/	/	/	/	/	/

(Continues)

Table 1. *(Continued)*

No.	δ_H	δ_C	^1H–^1H coupling constants (Hz)	TOCSY	gCOSY cross signal	gHSQC ^1J(C,H) cross signal	gHMBC
30	/	169.1	/	/	/	/	29[^2J(C,H)] 31[^2J(C,H)]
31	2.10[a]	24.1	/	/	/	+	/

[a]These peaks are assigned tentatively.

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