

¹H AND ¹³C NMR SPECTRA OF TECHNICALLY IMPORTANT SODIUM 1- AND 2-AMINONAPHTHALENESULFONATES

Josef JIRMAN

*Research Institute of Organic Syntheses,
532 18 Pardubice-Rybitví, The Czech Republic*

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The ¹H and ¹³C NMR spectra of twenty-one technically important sulfonated 1- and 2-naphthylamines have been measured in deuterium oxide. The substituent chemical shifts (SCS) of a sulfonic acid group on naphthylamine skeleton have been calculated from the chemical shifts assigned.

Sulfonylation in the naphthalene series is a very important operation in preparation of intermediates in dyestuff industry. The sulfonation products from naphthylamines are useful components for synthesis of azo dyestuffs^{1,2}.

The sulfonation products obtained from 1- and 2-naphthols were characterized by means of the ¹³C NMR spectra³. For the sulfonation products obtained from 1- and 2-naphthylamines it seems helpful to complement the ¹³C NMR data by the ¹H NMR data measured on a spectrometer with high working frequency (400 MHz).

The aim of the present paper was to measure the ¹H and ¹³C NMR spectra of available technically important sodium 1- or 2-aminonaphthalene-X-sulfonates and assign their signals to their structures. Another aim was to calculate the substituent chemical shifts (SCS) of SO₃Na group on naphthylamine skeleton for use in predictions of ¹H and ¹³C NMR spectra of the sulfonated derivatives of 1- and 2-naphthylamines not yet measured.

EXPERIMENTAL

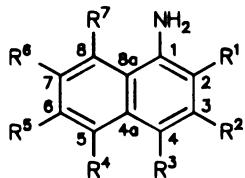
The sulfonated naphthylamines were obtained as standard samples from a collection of Research Institute of Organic Syntheses, Pardubice-Rybitví, and were transformed into the corresponding sodium salts by a treatment with anhydrous sodium carbonate. Saturated solutions of these salts in deuterium oxide were used for the measurements. Sodium 3-(trimethylsilyl)propanesulfonate was added as the standard for the ¹H NMR spectra ($\delta = 0.05$), and tetramethylsilane in a coaxial capillary was used for the ¹³C NMR spectra ($\delta = 0.00$). This standard was removed during the measurements of *J*-modulated and H,C-correlated spectra. The ¹H and ¹³C NMR spectra were measured at 305 K with an AM 400 (Bruker) apparatus at 400.13 and 100.62 MHz, respectively, using a 5 mm H,C dual probe. The onedimensional NMR spectra were obtained with a digital resolution of ca 0.2 Hz/point (¹H) and 1 Hz/point (¹³C). The *J*-modulated ¹³C NMR spectra for differentiation between CH and quaternary carbon atoms were measured with the use of

the program of pulse sequence JMODXH.AU; for the H,H- and H,C-correlated spectra we used the programs COSY.AU and XHCORRDC.AU, respectively, supplied by the manufacturer of the spectrometer⁴.

RESULTS AND DISCUSSION

The ¹H and ¹³C NMR spectra of sodium 1-aminonaphthalenesulfonates *I* – *X* are given in Tables I and II and those of sodium 2-aminonaphthalenesulfonates *XI* – *XXI* in Tables III and IV. The proton signals were assigned directly from the onedimensional spectrum in the cases when the compounds exhibit spectra characteristical of the so-called 1,2,4-trisubstitution of benzene (e.g. compounds *IV*, *VI*, *VII*, and *XVII*). In most cases the assignment was carried out by combining the results of the H,H-COSY spectra with the known substituent chemical shifts (SCS) of amino and SO₃CH₃ groups⁵ (the SCS value of sulfonic acid group was not found in literature).

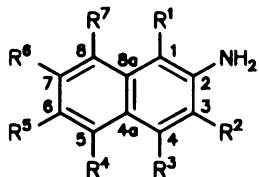
Interestingly, the naphthalene nucleus exhibits the proton long-range interactions (through up to five bonds) not observed in a normal proton spectrum, not even after a mathematical line narrowing before Fourier's transformation. In the homocorrelated spectrum H,H-COSY there appear off-diagonal peaks due to the interactions between the H-4 and H-8 protons or between the H-5 and H-1 protons. A similar type of



	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷
<i>I</i>	H	SO ₃ Na	H	H	H	H	H
<i>II</i>	H	H	SO ₃ Na	H	H	H	H
<i>III</i>	H	H	H	SO ₃ Na	H	H	H
<i>IV</i>	H	H	H	H	SO ₃ Na	H	H
<i>V</i>	H	H	H	H	H	H	SO ₃ Na
<i>VI</i>	SO ₃ Na	H	H	H	SO ₃ Na	H	H
<i>VII</i>	H	SO ₃ Na	H	H	SO ₃ Na	H	H
<i>VIII</i>	H	SO ₃ Na	H	H	H	H	SO ₃ Na
<i>IX</i>	H	H	SO ₃ Na	H	H	H	SO ₃ Na
<i>X</i>	H	SO ₃ Na	H	H	SO ₃ Na	H	SO ₃ Na

TABLE I
¹H NMR chemical shifts (in ppm) of compounds *I* – *X* in D₂O

Compound	H-2	H-3	H-4	H-5	H-6	H-7	H-8
<i>I</i>	7.25	–	7.82	7.92	7.59	7.61	7.92
<i>II</i>	6.79	8.10	–	8.83	7.78	7.53	7.87
<i>III</i>	6.89	7.55	8.37	–	8.29	7.44	7.95
<i>IV</i>	6.85	7.26	7.30	8.33	–	7.94	7.94
<i>V</i>	7.10	7.50	7.50	8.06	7.50	8.32	–
<i>VI</i>	–	7.75	7.22	8.09	–	7.81	7.98
<i>VII</i>	7.33	–	7.82	8.30	–	7.93	7.93
<i>VIII</i>	7.45	–	7.87	8.06	7.55	8.44	–
<i>IX</i>	7.07	8.17	–	9.01	7.81	8.53	–
<i>X</i>	7.66	–	8.12	8.73	–	8.93	–



	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷
<i>XI</i>	SO ₃ Na	H	H	H	H	H	H
<i>XII</i>	H	H	H	H	SO ₃ Na	H	H
<i>XIII</i>	H	H	H	H	H	SO ₃ Na	H
<i>XIV</i>	H	H	H	H	H	H	SO ₃ Na
<i>XV</i>	SO ₃ Na	H	H	SO ₃ Na	H	H	H
<i>XVI</i>	H	SO ₃ Na	H	H	SO ₃ Na	H	H
<i>XVII</i>	H	H	SO ₃ Na	H	H	H	SO ₃ Na
<i>XVIII</i>	H	H	H	SO ₃ Na	H	SO ₃ Na	H
<i>XIX</i>	H	H	H	H	SO ₃ Na	H	SO ₃ Na
<i>XX</i>	SO ₃ Na	H	H	SO ₃ Na	H	SO ₃ Na	H
<i>XXI</i>	H	SO ₃ Na	H	H	SO ₃ Na	H	SO ₃ Na

TABLE II
 ^{13}C NMR chemical shifts (in ppm) of compounds *I* – *X* in D_2O

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
<i>I</i>	143.26	105.96	140.20	116.77	129.44	127.41	127.28	121.24	133.00	125.35
<i>II</i>	146.30	107.53	127.54	128.15	125.05	127.54	125.27	121.65	129.10	123.46
<i>III</i>	142.35	111.54	127.90	116.34	137.96	126.06	123.24	126.31	128.71	124.42
<i>IV</i>	141.45	112.73	127.50	120.17	125.75	139.33	120.66	122.34	132.64	124.24
<i>V</i>	144.08	116.30	128.60	121.10	135.26	125.31	128.60	138.00	139.05	119.98
<i>VI</i>	141.02	121.67	124.96	118.37	125.69	140.58	121.60	123.29	133.99	124.32
<i>VII</i>	143.44	107.69	141.22	117.22	126.84	140.63	122.85	122.64	132.09	125.24
<i>VIII</i>	144.05	109.48	140.32	116.42	134.55	125.19	128.99	135.84	137.53	119.69
<i>IX</i>	147.43	111.09	128.54	132.05	129.98	125.75	127.54	138.78	132.05	118.65
<i>X</i>	144.37	111.46	141.57	117.21	131.65	139.35	124.72	135.37	138.61	120.04

long-range interactions was observed in homocorrelated spectra of azo dyestuffs with a naphthylamine section^{6,7}.

The differentiation between CH and quaternary carbon atoms was carried out on the basis of measurement of *J*-modulated ¹³C NMR spectrum where the phases of signals are separated for CH and quaternary carbons. The CH carbons were assigned unambiguously after measuring the heterocorrelated spectrum. The quaternary carbons were assigned on the basis of the calculation of their chemical shifts from the ¹³C chemical shifts of 1- and 2-naphthylamines⁸ and the substituent chemical shifts of sulfonic acid group at naphthalene nucleus⁹ using the same method as in ref.³.

The heterocorrelated spectrum of 1-aminonaphthalene-8-sulfonate was not measured because of the low solubility of this substance. All the signals were assigned on the basis of the above-mentioned calculation after differentiation between CH and quaternary carbons.

For reproducibility of results and agreement between experimental and calculated values of ¹³C NMR signals it is important to keep neutral to slightly alkaline reaction of the sample solution in which the amino group is not protonated and the sulfonic acid group is deprotonated. In acidic samples the respective dipolar ions are formed, which markedly changes the character of the ¹H spectrum. Also in the ¹³C NMR spectra relatively large changes are observed, and it is naturally impossible to assign the signals by a calculation using the shifts of naphthylamines. Moreover, the inner salts of aminonaphthalenesulfonic acids exhibit very low solubilities in water. Nevertheless, they can be dissolved and measured in hexadeuteriodimethyl sulfoxide. The data given in the

TABLE III
¹H NMR chemical shifts (in ppm) of compounds *XI* – *XXI* in D₂O

Compound	H-1	H-3	H-4	H-5	H-6	H-7	H-8
<i>XI</i>	–	7.01	7.74	7.77	7.39	7.62	8.59
<i>XII</i>	6.99	7.06	7.72	8.20	–	7.76	7.66
<i>XIII</i>	7.19	7.18	7.76	7.88	7.64	–	8.13
<i>XIV</i>	7.95	7.13	7.73	7.85	7.33	7.15	–
<i>XV</i>	–	7.14	8.80	–	8.15	7.82	9.02
<i>XVI</i>	7.04	–	8.44	8.36	–	7.91	7.58
<i>XVII</i>	8.35	8.15	–	9.03	7.75	8.44	–
<i>XVIII</i>	7.21	7.40	8.64	–	8.44	–	8.38
<i>XIX</i>	7.99	7.08	7.76	8.53	–	8.70	–
<i>XX</i>	–	7.57	8.89	–	8.63	–	9.65
<i>XXI</i>	8.20	–	8.78	8.75	–	8.68	–

TABLE IV
 ^{13}C NMR chemical shifts (in ppm) of compounds *XI* – *XXI* in D_2O

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
<i>XI</i>	115.09	143.89	120.65	133.02	128.66	122.87	127.76	123.95	127.87	130.66
<i>XII</i>	109.21	146.49	120.09	130.30	125.61	135.68	122.45	126.91	126.41	130.20
<i>XIII</i>	110.38	145.55	121.03	129.11	128.92	118.71	140.13	123.56	128.60	133.60
<i>XIV</i>	106.99	145.85	119.23	130.22	132.34	121.00	126.57	135.70	128.61	129.55
<i>XV</i>	115.58	144.03	122.09	129.37	138.72	122.47	126.20	128.08	122.47	131.95
<i>XVI</i>	111.30	142.50	136.25	128.78	126.36	136.67	123.82	126.36	124.40	130.34
<i>XVII</i>	110.12	144.58	119.34	140.27	129.26	112.32	127.06	136.54	123.27	130.74
<i>XVIII</i>	111.23	145.35	121.94	126.12	139.29	118.60	138.56	127.76	122.91	134.69
<i>XIX</i>	106.31	147.91	119.77	131.04	129.59	134.34	122.60	136.54	127.15	130.62
<i>XX</i>	115.75	144.78	123.99	131.51	139.51	118.30	139.87	125.08	123.20	131.51
<i>XXI</i>	108.79	144.44	136.54	130.14	130.67	131.83	124.40	135.32	125.81	125.81

present paper, however, cannot be used for interpretation of their spectra just because of the protonation of amino nitrogen atom.

Tables V – VIII present the substituent chemical shifts of SO_3Na group at naphthylamine skeleton. The SCS values for a given position of naphthylamine skeleton slightly differ depending on which of the monosulfonated or disulfonated derivatives was used for the calculation. The chemical shifts of naphthylamines could not be used for the calculation of SCS's because naphthylamines are practically insoluble in water. The data given are applicable to calculations of ^1H NMR spectra of aminonaphthalene-sulfonates in water and to those of ^{13}C NMR spectra in other solvents too (with reduced accuracy). Moreover, it must be stressed that they are unsuitable for calculation of NMR spectra of compounds having a protonated amino group.

When comparing the ^{13}C SCS values of sulfonate group at naphthalene skeleton calculated from the spectra of sulfonation products of naphthylamines, naphthols³, naphthalene⁹, and naphthalenesulfonates⁹ one can see an agreement between the ^{13}C SCS values calculated from the spectra of sulfonation products of naphthylamines, naphthols, and naphthalenesulfonates. That means that a substituent at naphthalene skeleton affects the ^{13}C SCS value of sulfonate group, and this effect is comparable for amino group, hydroxyl group, as well as sulfonic acid group, although they are substituents very different from the standpoint of their proper ^{13}C SCS's or of the Hammett σ constants.

TABLE V
 ^1H SCS values of SO_3Na group at "X" position of 1-naphthylamine in D_2O at 305 K

X	Compounds used for calculation	H-2	H-3	H-4	H-5	H-6	H-7	H-8
2	VI, IV	–	0.49	–0.08	–0.24	–	–0.13	0.04
3	VII, IV	0.48	–	0.52	–0.03	–	–0.01	–0.01
3	VIII, V	0.35	–	0.37	0.00	0.05	0.12	–
4	IX, V	–0.03	0.67	–	0.95	0.31	0.21	–
6	VII, I	0.08	–	0.00	0.38	–	0.32	0.01
6	X, VIII	0.21	–	0.25	0.67	–	0.49	–
8	VIII, I	0.20	–	0.05	0.14	–0.04	0.83	–
8	IX, II	0.28	0.07	–	0.18	0.03	1.00	–
8	X, VII	0.33	–	0.30	0.43	–	1.00	–

TABLE VI
 ^{13}C SCS values of SO_3Na group at "X" position of 1-naphthylamine in D_2O at 305 K

X	Compounds used for calculation	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
2	<i>V, IV</i>	-0.43	8.94	-2.54	-1.80	-0.06	1.25	0.94	0.95	1.35	0.08
3	<i>VII, IV</i>	1.99	-5.04	13.72	-2.95	1.09	1.30	2.19	0.30	-0.55	1.00
3	<i>VII, V</i>	-0.03	-6.82	11.72	-4.68	-0.71	-0.12	0.39	-2.16	-1.52	-0.29
4	<i>IX, V</i>	3.35	5.21	-0.06	10.95	-5.28	0.44	-1.06	0.78	-7.00	-1.33
6	<i>VII, I</i>	0.08	1.73	1.02	0.45	-2.60	13.22	-4.43	1.40	-0.91	-0.11
6	<i>X, VIII</i>	0.32	1.98	1.25	0.79	-2.90	14.16	-4.27	-0.47	1.08	0.35
8	<i>VII, I</i>	0.69	3.52	0.12	-0.35	5.11	-2.22	1.71	14.60	4.53	-5.66
8	<i>IX, II</i>	1.13	3.56	1.00	3.90	4.93	-1.79	2.27	17.13	2.95	-4.81
8	<i>X, VII</i>	0.93	3.77	0.35	-0.01	4.81	-1.28	1.87	12.73	6.52	-5.20

TABLE VII
 ^{13}C SCS values of SO_3Na group at "X" position of 2-naphthylamine in D_2O at 305 K

X	Compounds used for calculation	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
1	<i>XI, XVII</i>	4.52	-0.57	2.05	5.39	0.22	-0.30	1.31	-2.68	0.29	-3.18
3	<i>XVI, XII</i>	2.09	-3.99	16.16	-1.52	0.75	0.99	1.37	-0.55	-2.01	0.14
3	<i>XII, XIX</i>	2.48	-3.47	16.77	-0.90	1.08	-2.51	1.80	-1.22	-1.34	-4.81
4	<i>XVII, XIV</i>	3.13	-1.27	0.11	10.05	-3.08	-8.68	0.49	0.84	-5.34	1.19
5	<i>XVIII, XIII</i>	0.85	-0.20	0.91	-2.99	10.37	-0.11	-1.57	4.20	-5.69	1.09
5	<i>XV, XI</i>	0.49	0.14	1.44	-3.65	10.06	-0.40	-1.56	4.13	-5.40	1.29
6	<i>XIX, XIV</i>	-0.68	2.06	0.54	0.82	-2.75	13.34	-3.97	0.84	-1.46	1.07
7	<i>XIX, XV</i>	0.17	0.75	1.90	2.14	0.79	-4.17	13.67	-3.00	0.73	-0.44
8	<i>XIX, XII</i>	-2.90	1.42	-0.32	0.74	3.98	-1.34	0.15	9.63	0.74	0.42
8	<i>XII, XVI</i>	-2.51	1.94	0.29	1.36	4.31	-4.84	0.58	8.96	1.41	-4.53

TABLE VIII
 ^1H SCS values of SO_3Na group at "X" position of 2-naphthylamine in D_2O at 305 K

X	Compounds used for calculation	H-1	H-3	H-4	H-5	H-6	H-7	H-8
3	<i>XVI, XII</i>	0.05	—	0.72	0.16	—	0.15	-0.08
3	<i>XXI, XIX</i>	0.21	—	1.02	0.22	—	-0.02	—
4	<i>XVII, XIV</i>	0.40	1.02	—	1.18	0.42	1.29	—
5	<i>XV, XI</i>	—	0.13	1.06	—	0.76	0.20	0.43
5	<i>XVIII, XIII</i>	0.02	0.22	0.88	—	0.80	0.00	0.25
6	<i>XIX, XIV</i>	0.04	-0.05	0.03	0.68	—	1.55	—
7	<i>XX, XV</i>	—	0.43	0.09	—	0.48	—	0.63
8	<i>XIX, XII</i>	1.00	0.02	0.04	0.33	—	0.94	—
8	<i>XXI, XVI</i>	1.16	—	0.34	0.39	—	0.77	—

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