Short Communications

Nuclear Magnetic Resonance Studies on Aromatic Compounds. Part II. ^{13}C and ^1H NMR Spectra of 1-Hydroxy-4-sulfo-2-naphthoic AcidLAURI H. LAJUNEN ^a and
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The ^{13}C NMR spectra of the following aromatic monosulfo-substituted *o*-hydroxy carboxylic acids have been reported in part I of this series:¹ 3-hydroxy-4-sulfo-2-naphthoic (342HSN), 3-hydroxy-5-sulfo-2-naphthoic (352HSN), 3-hydroxy-7-sulfo-2-naphthoic (372HSN), and 5-sulfosalicylic (5SSA) acid. A pure monomeric ^{13}C NMR spectrum could be recorded for all carboxylic acids studied except 352HSN, which was found to be partly in dimeric form in concentrated D_2O solutions. We have now completed our investigations of this type of *o*-hydroxy carboxylic acids, and report here our findings for 1-hydroxy-4-sulfo-2-naphthoic acid (142HSN). The ^1H NMR spectrum of this compound is recorded in order to verify the analysis of the ^{13}C spectrum.

Experimental. 1-Hydroxy-4-sulfo-2-naphthoic acid was prepared by sulfonation of 1-hydroxy-2-naphthoic acid with an ice-cold mixture consisting of two parts of 20 % fuming H_2SO_4 and three parts of conc. H_2SO_4 , followed by

heating to 60 °C.² The acid was converted to its monosodium salt with NaCl and the product was recrystallized several times from hot water.

Apparatus and methods. The ^{13}C and ^1H NMR spectra of 142HSN were determined on a concentrated solution (10 mg/ml) with a Jeol JNM-FX100 FT-spectrometer operating in DQD mode and at 25.06 MHz. The ^{13}C NMR spectrum was recorded with proton noise-decoupling to assess chemical shifts, and without proton noise-decoupling to assess coupling constants. In both cases the recording parameters were: spectral width 5 kHz with 16k memory points; pulse width, 10 μs ; number of pulses accumulated, about 4000. Both the normal and decoupled ^1H NMR spectra were recorded in DQD mode and at 99.6 MHz. The recording parameters were: spectral width 1 kHz for recording the whole spectrum and 200 Hz with 16k memory points for the aromatic range of the spectrum; pulse width, 12 μs ; number of pulses accumulated in the normal ^1H NMR spectrum, about 30.

The protons H-5, H-6, H-7, and H-8 of the present compound form an ABCD system. With this system as a basis, the theoretical spectrum was calculated with the program LAOCN3³ on a Univac 1108 computer. The theoretical line shapes were calculated with the program PLOTTI (a program made in this laboratory), which is based on the Lorentzian shape function. The proton H-3 was neglected in the theoretical calculations because the couplings from this proton to the other protons are smaller than the half-widths of the lines in the spectrum. All the measurements were carried out in D_2O

Table 1. ^{13}C Chemical shifts of 142HSN relative to the external standard TMS at 298 K, and one- and three-bond carbon–proton couplings ($^1J_{\text{CH}}$ and $^3J_{\text{CH}}$). The chemical shifts of naphthalene are included in the table for comparison.⁶ The coupling constants are absolute values.

Compound	Chemical shifts (ppm)									
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
Naphthalene	128.10	125.95	125.95	128.10	128.10	125.95	125.95	128.10	133.70	133.70
142HSN	163.45	105.40	127.10	132.60	127.60	124.90	126.10	131.80	125.80	131.80

$^1J_{\text{C}_8\text{H}} = 166.6$ Hz, $^1J_{\text{C}_6\text{H}} = 164.8$ Hz, $^1J_{\text{C}_8\text{H}} = 166.3$ Hz, $^1J_{\text{C}_7\text{H}} = 166.0$ Hz, $^1J_{\text{C}_6\text{H}} = 164.2$ Hz, $^3J_{\text{C}_1-\text{sH}} = ^3J_{\text{C}_9-\text{tH}} = ^3J_{\text{C}_1-\text{sH}} = 7.9$ Hz, $^3J_{\text{C}_1-\text{sH}} = 9.1$ Hz, $^3J_{\text{C}_5-\text{rH}} = ^3J_{\text{C}_7-\text{sH}} = 9.2$ Hz, $^3J_{\text{C}_6-\text{sH}} = ^3J_{\text{C}_8-\text{sH}} = 8.0$ Hz, $^3J_{\text{C}_9-\text{sH}} = ^3J_{\text{C}_9-\text{rH}} = ^3J_{\text{C}_{10}-\text{sH}} = ^3J_{\text{C}_{10}-\text{sH}} = 6.7$ Hz.

Fig. 1. The differences between the chemical shifts (in ppm) for the ^{13}C nuclei of 142HSN relative to naphthalene.

solution at 298 K, and TMS was used as an external standard for the chemical shifts. No corrections of the chemical shifts were made.

Results and discussion. The chemical shifts of the ^{13}C nuclei of 142HSN and naphthalene are given in Table 1. The changes of the chemical shifts of the corresponding carbon atoms of 142HSN do not differ significantly from those observed for the related compounds of our earlier study (Fig. 1).¹ The difference between

the chemical shift of 142HSN and that of naphthalene for the carbon C-8 is positive, whereas the corresponding difference for all the other derivatives of 1-naphthol studied in this series is negative.^{4,5} The difference between the chemical shifts for the carbon C-4 is also opposite in sign (being 4.50 ppm) to the differences for the 1-naphthol derivatives.^{4,5}

The one-bond carbon-proton couplings of 142HSN (Table 1) are between 164.2 and 166.6 Hz, and the three-bond couplings of the carbons C-1, C-3, C-4, C-5, C-6, C-7, and C-8 to the hydrogen nuclei between 8 and 9 Hz. The three-bond couplings of the bridge-end ^{13}C nuclei are about 6.7 Hz.

The recorded and calculated ^1H spectra of 142HSN are presented in Fig. 2 and the observed chemical shifts and couplings in Table 2. It is especially notable that the proton H-8 appears at lower field than the proton H-5. The positions of the corresponding ^{13}C nuclei are quite similar with respect to one another and the changes in the chemical shifts of the protons at C-6 and C-7 are similar in sign to those of the carbons C-6 and C-7, respectively.

The long-range proton couplings J_{35} must be smaller than 0.3 Hz, because the half-width

Fig. 2. The recorded ^1H spectrum (above) and calculated ^1H spectrum (below) of 142HSN. In A the protons H-5 and H-8, and in B the protons H-6 and H-7. The chemical shifts are presented in a Hz-scale relative to TMS.

Table 2. The chemical shifts (Hz) relative to the external standard TMS at 298 K and the proton-proton couplings of 142HSN derived by iteration from the 100 MHz ^1H spectrum. The coupling constants are absolute values.

H-3	H-5	H-6	H-7	H-8
872.3	859.6	795.4	817.9	890.3
$J_{56} = 8.5 \text{ Hz}$, $J_{57} = 1.3 \text{ Hz}$, $J_{58} = 0.7 \text{ Hz}$, $J_{67} = 8.4 \text{ Hz}$, $J_{68} = 1.7 \text{ Hz}$, $J_{78} = 8.2 \text{ Hz}$.				

of the lines in the recorded ^1H spectrum of 142HSN is about 0.3 Hz. The rest of the proton-proton couplings are of about the same size as in other aromatic compounds.⁷

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