

# Crystal and Molecular Structures, IR Absorption Spectra and Thermal Behaviour of Sodium 3-Hydroxy-7-sulfonato-2-naphthoic Acid Trihydrate and Sodium 1-Hydroxy-4-sulfonato-2-naphthoic Acid Dihydrate

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The crystal structures, IR spectra and thermal behaviour of monosodium salts of 3-hydroxy-7-sulfonato-2-naphthoic acid (abbreviated here as 372HSN) and 1-hydroxy-4-sulfonato-2-naphthoic acid (142HSN) have been investigated. In solid state the former acid contains three and the latter two hydrate water molecules. The crystal structures have been determined by X-ray diffraction methods. The crystals are monoclinic, space group  $P2_1/c$ , with unit cell dimensions:  $a = 5.487(2)$ ,  $b = 30.432(10)$ ,  $c = 7.839(3)$  Å and  $\beta = 93.57(3)^\circ$  for sodium 3-hydroxy-7-sulfonato-2-naphthoic acid trihydrate, and  $a = 7.069(1)$ ,  $b = 18.558(3)$ ,  $c = 10.464(2)$  Å and  $\beta = 108.63(1)^\circ$  for sodium 1-hydroxy-4-sulfonato-2-naphthoic acid dihydrate. There are four formula units in the unit cell. Final  $R$ -values are 0.055 and 0.041 for 372HSN and 142HSN, respectively.

The non-isothermal studies on the thermal behaviour of the two sodium *o*-hydroxynaphthoic acid sulfonates revealed that their decomposition mechanisms are similar. The decomposition reactions have four stages. The first is dehydration at 90–150 °C, the second is the decomposition of the carboxyl group at 200–300 °C, the third is the formation of naphthol (1- or 2-naphthol depending on the compound) and sodium sulfate at 300–380 °C, and the fourth is the sublimation of naphthol at 400–480 °C.

The IR spectra were recorded using the KBr pellet technique.

The present solid state studies are part of our investigation of the chemistry of sulfo-substituted aromatic *o*-hydroxycarboxylic acids. In earlier

papers we have studied the protonation and metal complex formation equilibria of seven different *o*-hydroxysulfonocarboxylic acids in aqueous solutions by potentiometric, UV-absorption spectrophotometric and spectrofluorometric methods.<sup>1</sup> In addition, we have reported structural investigations of these compounds by <sup>13</sup>C NMR spectrometry.<sup>2</sup>

In the present work we have determined the crystal and molecular structures of sodium 3-hydroxy-7-sulfonato-2-naphthoic acid trihydrate (abbreviated as 372 HSN) and sodium 1-hydroxy-4-sulfonato-2-naphthoic acid dihydrate (142HSN) by X-ray diffraction methods, and studied the thermal behaviour and IR absorption spectra of these compounds.

## EXPERIMENTAL

*Crystal preparation.* The monosodium salts of 3-hydroxy-7-sulfonato-2-naphthoic and 1-hydroxy-4-sulfonato-2-naphthoic acids were prepared and purified as described earlier.<sup>1</sup> The yellow crystals of 372HSN and opaque crystals of 142HSN were grown by gradual cooling from a dilute, aqueous solution of the salts.

*Unit cell determination and data collection.* The crystal data for the present compounds are given in Table 1. A computer controlled Syntex P2<sub>1</sub> (Fortran version) fully automated four-circle diffractometer with graphite monochromatized MoK $\alpha$  radiation was utilized in the unit cell determination and data collection. The lattice constants at 25 °C

were calculated by least squares refinement of angular settings of selected reflections.

The  $\omega$ -scan mode was used for data collection with different scan rates. The intensity of each reflection was calculated by subtracting the total background count, BC, from the total scan count, SC. The standard deviation,  $\delta_c(I)$ , was calculated from the equation  $\delta_c(I) = (SC + BC)^{1/2}$ . The values were then multiplied by the scan rate to compensate for different scan speeds. All intensities were corrected for Lorentz and polarization effects.

A semiempirical absorption correction was made for 142HSN only. The reflections were measured for a full flat cone rotation around the diffraction vector in steps of  $10^\circ$ . The largest measured relative reduction in the intensity was from 1.00 to 0.86 (for 372HSN from 1.00 to 0.97).

The structures were solved by the MULTAN 78 programme package and refined with the XRAY 76 programme package.<sup>3,4</sup> Scattering factors for neutral atoms were taken from Cromer and Mann.<sup>5</sup> All the calculations were carried out on a Univac 1108 computer.

After refinement with isotropic temperature factors the  $R$  value was about 10 % for both compounds, and after block diagonal matrix refinement with anisotropic temperature factors the final  $R$  value was 5.5 % for 372HSN and 4.1 % for 142HSN. The positions of the hydrogen atoms were found from a difference Fourier map, but it was not possible to refine their atomic parameters.

**Thermal analyses.** Thermal decomposition was studied with a Mettler TA-1 thermoanalyzer recording the TG, DTG and DTA curves simultaneously. The heatings were carried out in a dynamic air atmosphere with an air flow rate of  $100 \text{ cm}^3 \text{ min}^{-1}$ . The heating rates were 2 and  $6^\circ \text{C min}^{-1}$ , and the sample weights were 22 and 55 mg, respectively. The sample holder was a standard platinum crucible (diam. 7 mm and depth 19 mm). In the DTA measurements alumina was used as reference.

**IR measurements.** IR spectra were recorded on a Perkin-Elmer 521 instrument using the KBr pellet technique.

## RESULTS AND DISCUSSION

**Crystal and molecular structures.** The crystal data, positional and thermal parameters are listed in Tables 1–4, and the schematic figures of both compounds with atomic numbering and interatomic distances are presented in Fig. 1. Their structures are shown in Fig. 2.

There is only one hydroxyl, one carboxyl and one sulfonato group attached to the naphthalene ring in both compounds, and in both cases the anions are joined together by sodium atoms forming infinite three-dimensional networks.

There are six oxygen atoms around each sodium atom forming octahedra: two oxygen atoms from the sulfonato group, one oxygen atom from the carboxyl group and three oxygen atoms from the hydrate water molecules in 372HSN, and two oxygen atoms from the sulfonato group, one oxygen atom from the carboxyl group, one oxygen atom from the hydroxyl group and two oxygen atoms from the hydrate water molecules in 142HSN. The average sodium–oxygen distances in the former and latter compound are 2.430 and 2.461 Å, respectively. The octahedron around the sodium atom for 372HSN is only slightly distorted, whereas for 142HSN the corresponding octahedron is strongly distorted (the sodium–oxygen distances vary between 2.304 and 2.627 Å). The bond distances and angles in both compounds are in good agreement with those given in the literature for the related compounds 1-naphthoic acid, 2-naphthoic acid, 1-hydroxy-2-naphthoic acid and

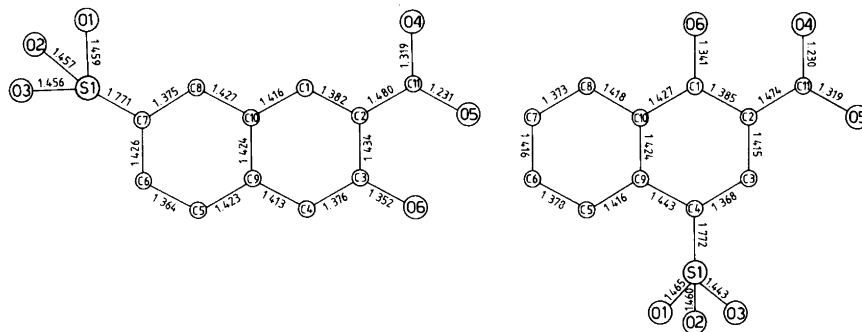


Fig. 1. Schematic figures of 372HSN (left) and 142HSN (right). Estimated standard deviations are equal or less than 0.002 Å.

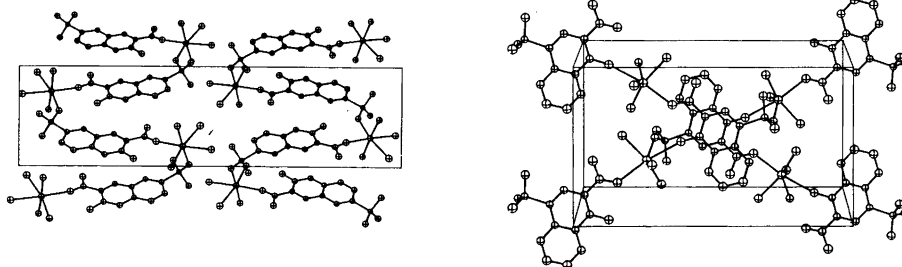


Fig. 2. The unit cell contents of 372HSN (left) and 142HSN (right).

3-hydroxy-2-naphthoic acid.<sup>6-9</sup> The average carbon-carbon bond lengths in naphthalene ring are 1.405 and 1.406 Å for 372HSN and 142HSN, respectively, and there is a normal distribution of short and long C-C bonds. The observed carbon-hydrogen distances were also normal. The average values were 0.92 and 0.98 Å for 372HSN and 142HSN, respectively.

The anions of both compounds are approximately planar. The angles between the planes of six-membered carbon rings are 2.6 and 0.7° for 372HSN

and 142HSN, respectively. The maximum atomic distances from the least square planes of naphthalene rings are 0.04 Å in 372HSN and 0.01 Å in 142HSN. The carboxyl group is slightly twisted out from the naphthalene plane in both compounds, and the angles between the naphthalene ring and carboxyl group are 6.5 and 3.9° for 372HSN and 142HSN, respectively. In literature the values between 0 and 11° are reported.<sup>6-9</sup>

Sodium atoms are coordinated to 3-hydroxy-7-sulfonato-2-naphthoic acid and 1-hydroxy-4-sulfo-

Table 1. Crystal data for 372HSN and 142HSN.

Code	372HSN	142HSN
Formula	$\text{Na}[\text{C}_{10}\text{H}_5(\text{COOH})(\text{OH})(\text{SO}_3)] \cdot 3\text{H}_2\text{O}$	$\text{Na}[\text{C}_{10}\text{H}_5(\text{COOH})(\text{OH})(\text{SO}_3)] \cdot 2\text{H}_2\text{O}$
<i>a</i> (Å)	5.487(2)	7.069(1)
<i>b</i> (Å)	30.433(10)	18.558(3)
<i>c</i> (Å)	7.839(3)	10.464(2)
$\beta$ (°)	93.57(3)	108.63(1)
<i>V</i> (Å <sup>3</sup> )	1306.5(8)	1300.8(4)
<i>Z</i>	4	4
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
$D_m$ (g cm <sup>-3</sup> ) (flot)	1.75	1.67
$D_x$ (g cm <sup>-3</sup> )	1.750	1.666
$\mu$ (cm <sup>-1</sup> )	3.1	3.1
Number of reflections in unit cell determination	24	25
$2\theta$ interval in unit cell determination (°)	5.35–14.40	20.28–33.39
$2\theta$ interval in data collection (°)	5–60	5–60
Scan speed (° min <sup>-1</sup> )	5.9–19.5	2.0–9.8
Number of collected reflections	3974	3780
Number of refined reflections		
$I > 3\delta(I)$	2755	2195
Final <i>R</i> value (%)	5.5	4.1

Table 2. Positional and thermal ( $\times 10^2$ ) parameters for 372 HSN compound. Estimated standard deviations are given in parentheses. The temperature coefficients are of the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$ .

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S	.9129(1)	.9188(1)	.4343(1)	1.51(1)	0.99(1)	1.76(1)	.10(1)	.25(1)	-.12(1)
Na	.5514(1)	.0709(1)	.2702(1)	2.15(3)	1.46(3)	2.70(3)	-.09(2)	.40(2)	-.19(2)
C1	.0529(2)	.7517(1)	.3245(2)	1.67(6)	1.09(5)	2.27(6)	.05(5)	.44(5)	.03(5)
C2	.1927(2)	.7177(1)	.2663(2)	1.70(6)	1.17(5)	2.00(6)	.12(5)	.09(5)	-.15(5)
C3	.4064(2)	.7273(1)	.1766(2)	1.78(6)	1.56(6)	1.99(6)	.57(5)	.35(5)	-.23(5)
C4	.4731(2)	.7702(1)	.1491(2)	1.64(6)	1.62(6)	2.52(7)	.09(5)	.69(5)	-.34(5)
C5	.4019(2)	.8496(1)	.1851(2)	1.77(6)	1.44(6)	2.76(7)	-.22(5)	.70(5)	-.01(5)
C6	.2710(2)	.8830(1)	.2503(2)	1.81(6)	1.40(6)	2.79(7)	-.19(5)	.69(5)	-.07(5)
C7	.0631(2)	.8736(1)	.3445(2)	1.66(6)	1.09(5)	2.16(7)	.11(5)	.41(5)	-.12(5)
C8	-.0147(2)	.8312(1)	.3682(2)	1.56(6)	0.96(5)	2.29(7)	.05(5)	.60(5)	-.11(5)
C9	.3327(2)	.8051(1)	.2101(2)	1.33(6)	1.37(5)	1.93(6)	.00(5)	.32(5)	-.13(5)
C10	.1201(2)	.7960(1)	.2994(2)	1.46(6)	1.08(5)	1.99(6)	.13(4)	.43(5)	-.04(5)
C11	.1317(2)	.6719(1)	.3037(2)	2.26(6)	1.37(6)	2.11(6)	.21(5)	.10(5)	.01(5)
O1	.1956(2)	.4438(1)	.2134(1)	2.75(5)	1.73(5)	2.41(5)	-.78(4)	-.12(4)	-.22(4)
O2	.1026(2)	.5554(1)	.0261(1)	2.38(5)	1.59(5)	2.83(5)	.19(4)	-.52(4)	.63(4)
O3	.7318(2)	.5983(1)	.0431(1)	2.46(5)	1.97(5)	3.23(6)	.06(4)	1.64(4)	.30(4)
O4	.0698(2)	.1661(1)	.1152(1)	2.46(5)	1.36(5)	3.81(6)	-.01(4)	.90(4)	-.39(4)
O5	.2608(2)	.6404(1)	.2645(1)	3.55(6)	1.16(4)	3.62(6)	.67(4)	.82(5)	-.10(4)
O6	.4533(2)	.1954(1)	.3868(1)	2.63(5)	1.85(5)	3.71(6)	-1.08(4)	1.32(4)	.38(4)
O7	.2031(2)	.0833(1)	.0558(1)	2.75(5)	1.68(4)	2.88(5)	.07(4)	.32(4)	-.04(4)
O8	.2096(2)	.5267(1)	.4206(2)	3.01(6)	2.38(5)	4.04(7)	-.24(4)	1.27(5)	.24(5)
O9	.6296(2)	.4975(1)	.2112(2)	3.09(6)	2.04(5)	4.42(7)	.47(4)	.78(5)	-.50(5)

Table 3. Positional and thermal ( $\times 10^2$ ) parameters for 142 HSN compound. Estimated standard deviations are given in parentheses.

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S	.8135(1)	.1848(1)	.1445(1)	2.28(2)	1.87(2)	2.59(2)	-.08(2)	.74(1)	-.37(2)
Na	.3090(1)	.2437(1)	.1572(1)	3.61(4)	3.40(4)	3.15(4)	-.10(4)	1.19(4)	.01(4)
C1	.7364(3)	.9496(1)	.0060(1)	2.05(9)	2.11(9)	3.12(10)	-.17(7)	.88(8)	.17(8)
C2	.7613(3)	.9691(1)	.1382(2)	2.59(10)	2.14(9)	2.88(10)	.17(7)	1.16(8)	.31(8)
C3	.7882(3)	.0423(1)	.1776(2)	2.37(10)	2.22(9)	2.93(10)	.42(8)	.77(8)	.07(8)
C4	.7907(3)	.0946(1)	.0859(2)	2.55(10)	1.91(9)	2.44(9)	.01(7)	.73(8)	-.22(07)
C5	.7726(3)	.1286(1)	.8489(2)	3.03(10)	2.90(10)	2.84(10)	.52(9)	.95(9)	.51(9)
C6	.7484(3)	.1074(1)	.7184(2)	3.92(13)	3.42(12)	3.06(11)	.48(10)	1.05(10)	.48(9)
C7	.7172(3)	.0342(1)	.6797(2)	4.10(13)	4.11(13)	2.76(11)	.16(10)	1.08(10)	-.18(10)
C8	.7136(3)	.9829(1)	.7735(2)	3.35(11)	3.10(10)	3.01(11)	.02(9)	1.06(9)	-.63(10)
C9	.7680(3)	.0769(1)	.9475(2)	2.06(10)	2.19(9)	2.46(9)	.13(7)	.62(7)	.06(7)
C10	.7399(3)	.0031(1)	.9088(2)	2.04(9)	2.28(9)	2.71(9)	-.06(7)	.83(8)	-.21(8)
C11	.7594(3)	.9132(1)	.2379(2)	2.78(10)	2.83(10)	3.26(11)	.19(9)	1.00(9)	.24(9)
O1	.8530(2)	.1795(1)	.2904(1)	3.57(8)	3.14(8)	2.55(7)	.24(7)	.49(6)	-.52(6)
O2	.6213(2)	.2196(1)	.0802(1)	2.88(8)	2.12(7)	3.19(7)	.42(6)	.67(6)	.14(6)
O3	.9745(2)	.2184(1)	.1097(1)	3.55(9)	3.47(8)	5.24(10)	-1.33(7)	2.24(8)	-1.23(8)
O4	.7242(2)	.8494(1)	.2079(2)	4.61(9)	2.31(8)	3.87(9)	-.31(7)	1.56(8)	.39(7)
O5	.2049(2)	.0631(1)	.6376(2)	5.81(11)	3.46(9)	2.81(8)	-.37(8)	1.59(8)	.13(7)
O6	.7088(2)	.8807(1)	.9655(2)	4.79(9)	1.91(7)	3.72(8)	-.58(7)	1.84(8)	-.82(6)
O7	.5106(2)	.1934(1)	.3608(2)	3.43(8)	4.23(9)	2.82(7)	-.40(7)	1.21(7)	-.64(7)
O8	.2207(2)	.1698(1)	.4778(2)	3.44(8)	3.98(7)	2.56(7)	-.27(7)	.94(7)	.41(7)

Table 4. The unrefined positional parameters of hydrogen atoms.

	372HSN			142HSN		
	x	y	z	x	y	z
H1	.9098	.7452	.3820	.8037	.4474	.7691
H2	.3782	.2800	.3961	.7996	.1790	.8777
H3	.4574	.3600	.3593	.7556	.3567	.1528
H4	.6794	.0900	.7632	.6982	.4816	.0843
H5	.1526	.3300	.0767	.2984	.4338	.7538
H6	.1053	.3600	.6083	.2915	.1460	.9614
H7	.5513	.1766	.3352	.2098	.3992	.0803
H8	.2079	.0780	.9502	.6178	.1800	.3372
H9	.0985	.0700	.0782	.5587	.2768	.9188
H10	.7589	.4783	.4793	.3079	.1653	.4401
H11	.8029	.5000	.6397	.1190	.3188	.9227
H12	.7312	.0092	.6392			
H13	.5102	.0188	.6841			

nato-2-naphthoic acid anions in different ways: the first anion acts as a tridentate and the latter acts as tetradentate ligand. In the case of 142HSN the sodium atom is connected to the oxygen atom of the hydroxyl group, whereas in the case of 372HSN it is not. Therefore the molecular structures of these two compounds are different as can be seen in Fig. 2.

The sulfonato groups are similar in both compounds: the sulfur-carbon distances are 1.771 and

Table 5. Sodium atom environment (distances (Å) and selected angles (°)).

372HSN		142HSN	
Na-O2	2.450(1)	Na-O2	2.620(2)
O3	2.353(1)	O3	2.304(2)
O5	2.376(1)	O4	2.471(2)
O7	2.493(1)	O6	2.627(2)
O8	2.452(1)	O7	2.346(2)
O9	2.453(1)	O8	2.396(2)
O2-Na-O7	177.24(4)	O4-Na-O6	168.36(8)
O3-Na-O8	166.67(5)	O7-Na-O8	155.38(7)
O5-Na-O9	176.15(5)	O2-Na-O3	143.77(7)
O2-Na-O5	85.53(4)	O4-Na-O2	123.68(6)
O2-Na-O3	100.24(5)	O4-Na-O8	82.42(6)
O3-Na-O5	93.67(5)	O2-Na-O8	84.67(6)

1.772 Å for 372HSN and 142HSN, respectively, and the average sulfur-oxygen distances are 1.461 and 1.456 Å, respectively.

In both compounds the O-Na-O bonds join the molecules together in infinitive three-dimensional network, which are strengthened by hydrogen bonds (Table 6). The positions of the hydrogen atoms were located from a difference Fourier map, but it was not possible to refine these parameters. Still all distances and angles involving hydrogen are normal. The hydrogen bond O5-H7-O6 in 372HSN and the hydrogen bond O4-H6-O6 in

Table 6. Bond lengths (Å) and angles (°) in hydrogen bonds. The positions of hydrogen atoms are unrefined.

O-H...O	O-H	H...O	O...O	∠O-H...O
372HSN compound				
O4-H6...O7	.82	1.86	2.672(2)	170.2
O6-H7...O5	.90	1.73	2.627(2)	179.9
O7-H8...O1	.85	1.97	2.806(2)	170.5
O7-H9...O8	.73	2.14	2.860(2)	166.1
O8-H10...O9	.81	2.25	3.024(2)	172.5
O8-H11...O1	.94	2.06	2.998(2)	174.4
O9-H12...O2	.84	2.15	2.924(2)	152.1
O9-H13...O1	.84	2.09	2.888(2)	158.6
142HSN compound				
O6-H6...O4	.93	1.70	2.568(2)	153.8
O5-H7...O8	.93	1.69	2.619(2)	175.3
O7-H8...O1	.90	1.88	2.758(2)	162.5
O7-H9...O2	.83	1.92	2.709(2)	158.6
O8-H10...O7	.89	1.89	2.736(2)	160.5
O8-H11...O1	.89	1.89	2.715(2)	155.4

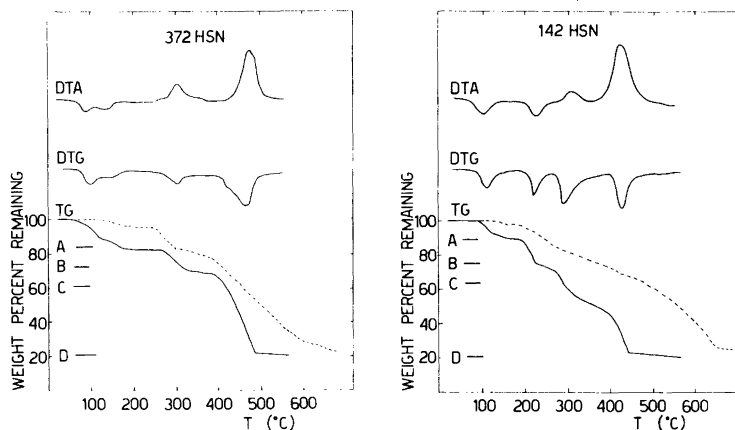


Fig. 3. DG, DTG and DTA curves from the thermal decomposition of 372HSN (left) and 142HSN (right) in air. Heating rate  $2^{\circ}\text{C}/\text{min}$ .

142HSN are intramolecular hydrogen bonds between hydroxyl and carboxyl groups. Other hydrogen bonds exist between the crystal water molecules

Table 7. Bond angles ( $^{\circ}$ ) in 372HSN and 142HSN ligands. Estimated standard deviations are given in parentheses.

	372HSN	142HSN
C10–C1–C2	120.8(1)	120.3(2)
C1–C2–C3	119.8(1)	120.3(2)
C2–C3–C4	120.3(1)	120.5(2)
C3–C4–C9	120.2(1)	121.4(2)
C4–C9–C10	120.1(1)	117.7(2)
C9–C10–C1	118.7(1)	120.0(2)
C7–C8–C10	118.7(1)	120.2(1)
C8–C10–C9	120.0(1)	120.0(2)
C10–C9–C5	119.0(1)	118.6(2)
C9–C5–C6	120.4(1)	120.2(2)
C5–C6–C7	120.1(1)	121.1(2)
C6–C7–C8	121.5(1)	119.9(2)
C1–C2–C11	120.6(1)	119.8(2)
C2–C11–O4	114.8(1)	122.9(2)
O4–C11–O5	122.6(1)	122.1(2)
O5–C11–C2	122.6(1)	114.9(2)
C2–C3–O6	122.4(1)	–
O6–C3–C4	117.3(1)	–
C2–C1–O6	–	121.5(2)
O6–C1–C10	–	118.2(2)
C6–C7–S1	117.2(1)	–
S1–C7–C8	121.3(1)	–
C3–C4–S1	–	116.5(2)
S1–C4–C9	–	122.1(2)

and oxygen atoms of the sulfonato groups.

*Thermal analysis.* Both compounds were heated in air under two different experimental conditions, *viz.* sample weight 55 mg with a heating rate of  $6^{\circ}\text{C min}^{-1}$ , and 22 mg with  $2^{\circ}\text{C min}^{-1}$ . The thermoanalytical curves are presented in Fig. 3.

The decomposition reaction mechanisms cannot be determined from the TG curves obtained with a heating rate  $6^{\circ}\text{C min}^{-1}$ . Only the loss of the water molecules (between 100 and  $300^{\circ}\text{C}$ ) and the anhydrous phase of 372HSN can be identified. The other reactions occur simultaneously so that no other plateaus can be seen in TG or DTG curves.

With a slow heating rate ( $2^{\circ}\text{C min}^{-1}$ ) all reactions occur, as expected, at much lower temperatures. In addition, the different stages of the decomposition reactions can be observed. The first decomposition stage for both compounds is the release of water. With regard to 372HSN the loss of the two first water molecules and subsequently the loss of the third one, and for 142HSN the loss of the two different water molecules, can be clearly distinguished. The next stage in the decomposition is the loss of carbon dioxide from the carboxyl group at  $200\text{--}250^{\circ}\text{C}$ , followed by the formation of sodium sulfate and 1- or 2-naphthol. Thus, half a molecule of sulfur oxide is released, but it was not possible to determine whether it was di- or trioxide. The final and greatest weight loss occurs in range  $380\text{--}500^{\circ}\text{C}$  and is due to naphthol sublimation. The temperature range corresponds well to the values found in literature for the sublimation of naphthols.<sup>10,11</sup> The end-product is pure sodium

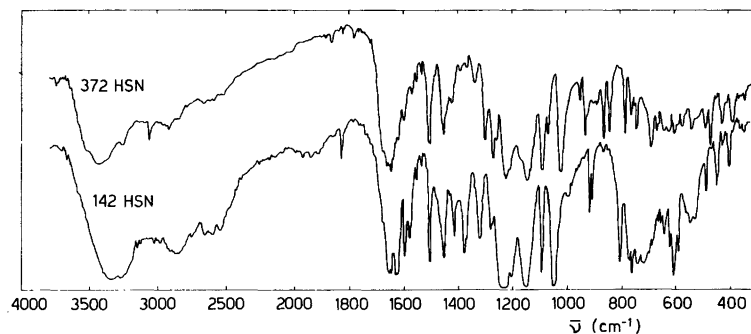


Fig. 4. The IR absorption spectra of 372HSN (A) and 142HSN (B).

sulfate which was identified by X-ray powder diffraction.

The comparison of the TG curves of 372HSN and 142HSN shows that their decomposition mechanism are similar. Only the anhydrous phase of 372HSN is somewhat more stable than that of 142HSN. In both cases the oxidation of the sulfonato groups readily begins after the loss of  $\text{CO}_2$  and no clear plateaus can be observed between the two last decomposition stages.

The interpretation of the DTA curves is not easy. The first reaction stages, the loss of water and carbon dioxide, are endothermic. The oxidation of sulfur is exothermic and almost at the same time the endothermic sublimation of naphthol begins. After sublimation a part or all of the naphthols is burning, causing a strong exothermic effect. The sum peak which can be seen from these thermal occurrences is strongly exothermic.

**IR spectra.** The results from the IR spectral measurements are presented in Fig. 4. As can be surmised from the figure the spectra are very complicated and over 50 peaks are observed. To aid in the interpretation of spectra the IR absorption spectra of naphthalene, sodium 1-hydroxy-naphthalene-4-sulfonato and 1-hydroxy-2-naphthoic acid were also recorded. The assignments in the text are based on the reference spectra and literature.<sup>12,13</sup>

The spectra consist of broad bands in the 3200–3500  $\text{cm}^{-1}$  region due to the O–H stretching of water molecules and many sharp peaks at 1700–400  $\text{cm}^{-1}$ . Between these strong absorption regions there are some weak bands in the 2880–1700  $\text{cm}^{-1}$  region which may be overtones and combinations from stronger ones.

The characteristic strong bands of the sulfonato group can be observed at 1150–1250  $\text{cm}^{-1}$  and

weaker ones at 950, 620–660 and 450–470  $\text{cm}^{-1}$ . The carboxyl group has strong absorption bands (C=O, C–O and O–H stretches) in the region of 1640–1670, 1550–1570, 1300–1320 and 1085–1095  $\text{cm}^{-1}$  and weaker ones at 2600–2900 and 915–930  $\text{cm}^{-1}$ .

The strong C–H bendings of the naphthalene skeleton are situated at 1000–1280 (in plane) and 800–950 (out of plane)  $\text{cm}^{-1}$ . The C–C stretching absorb at 1570–1590, 1500, 1450, 1365–1375, 1280–1300, 575–685, 485–515 and 340–360  $\text{cm}^{-1}$ . The bending absorptions of the hydroxyl group are at 1390–1420, 1355 and 720–740  $\text{cm}^{-1}$ .

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Received January 6, 1981.