

**$^{13}\text{C}$  NMR SPECTRA OF SODIUM NAPHTHALENESULPHONATES**

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$^{13}\text{C}$  NMR spectra of thirteen sodium naphthalenesulphonates have been measured in deuterium oxide. The  $^{13}\text{C}$  chemical shifts have been assigned, and the  $^nJ(^{13}\text{C}^1\text{H})$  coupling constants have been measured. Effect of  $\text{SO}_3^-$  group on the  $^{13}\text{C}$  NMR parameters is discussed.

The  $^{13}\text{C}$  chemical shifts of substituted naphthalenes and other polynuclear systems are given in ref.<sup>1</sup>. So far little attention has been paid to naphthalene derivatives carrying sulphonic groups. Refs<sup>2-6</sup> give the  $^{13}\text{C}$  NMR spectra of hydroxynaphthalenemono- and disulphonic acids and hydroxynaphthoic acids, *i.e.* compounds used as analytical reagents<sup>2</sup>. A summary of the  $^{13}\text{C}$  chemical shifts of these compounds is published in ref.<sup>7</sup>.

Naphthalenesulphonates find very broad technical applications<sup>8</sup>. The aim of the present communication was to measure the  $^{13}\text{C}$  NMR spectra of sodium naphthalenesulphonates, to assign the  $^{13}\text{C}$  chemical shifts, to determine the  $^nJ(^{13}\text{C}^1\text{H})$  coupling constants, and to discuss the effects of sulphonic group on the  $^{13}\text{C}$  NMR parameters.

**EXPERIMENTAL**

The sodium 1- and 2-naphthalenesulphonates, 1,2-, 1,4-, 1,5-, 1,6-, 1,7-, 2,6-, and 2,7-naphthalenedisulphonates, 1,3,5-, 1,3,6-, and 1,3,7-naphthalenetrisulphonates, and 1,3,5,7-naphthalenetetrasulphonate were prepared by known procedures<sup>9</sup>.

The  $^{13}\text{C}$  NMR spectra were recorded with a JNM-FX 100 (JEOL) spectrometer at 25.047 MHz. The substances were measured as 10% (w/v) or saturated solutions in deuterium oxide (used as internal lock) in 10 mm NMR test tubes at 300 K with external tetramethylsilane in a coaxial capillary. The following apparatus parameters were used: the spectral width of 5 000 Hz; 8 K; the pulse width of 9  $\mu\text{s}$  (23  $\mu\text{s}$   $\sim 90^\circ$ ); pulse repetition 3 s; the proton noise decoupling. For evaluation of the coupling constants the spectra were recorded with digital resolution of 0.244 Hz/point and with gated decoupling (the proton noise decoupling beside the acquisition time) in saturated solutions at 320 K; in the case of sodium 2-naphthalenesulphonate at 350 K. The  $^{13}\text{C}$  chemical shifts related to external tetramethylsilane were converted to the  $\delta$  scale by subtracting a correction of 1.00 ppm found from the difference of the  $^{13}\text{C}$  chemical shifts of dioxane dissolved in deuterium oxide with external tetramethylsilane and that dissolved in hexadeuteriodimethyl sulphoxide ( $\delta = 39.6$ ). Positive values of chemical shifts denote downfield shifts.

## RESULTS AND DISCUSSION

The  $^{13}\text{C}$  chemical shifts,  $^{13}\text{C}$  substituent chemical shifts (SCS), and coupling constants  $^1J(^{13}\text{C}^1\text{H})$  and/or  $^3J(^{13}\text{C}^1\text{H})$  are given in Tables I–IV. It was verified that the  $^{13}\text{C}$  chemical shifts of aqueous solutions of the naphthalenesulphonates are independent of concentration and temperature: the  $^{13}\text{C}$  chemical shifts of sodium 1,5-naphthalenedisulphonate and 1,3,6- and 1,3,7-naphthalenetrisulphonates (concentrations, 50, 100, 250 mg/ml or saturated solutions) showed random differences of  $\pm 0.1$  ppm at 300 K. The  $^{13}\text{C}$  NMR spectra of sodium 2-naphthalenesulphonate were recorded at 300 and 350 K: the value of chemical shift of the C(2) atom increased by 0.8 ppm, whereas the differences of the other carbon atoms were below 0.2 ppm.

The set of data obtained by measurements of the proton-decoupled, proton-coupled, off-resonance, and selectively decoupled  $^{13}\text{C}$  NMR spectra of the mono- to tetrasulphonated naphthalenes at comparable conditions was sufficient for assignment of all the signals even without selective deuteration of the naphthalene nucleus. Some signals could be assigned directly and unambiguously according to the values  $^1J(^{13}\text{C}^1\text{H}) = 0$  Hz,  $^3J(^{13}\text{C}^1\text{H}) = 0$  Hz and according to results of the selective decoupling. Additive combination of SCS values of these carbon atoms gave orientation SCS values of the first and the other sulphonic groups entering the  $\alpha$  or  $\beta$  positions of the non-substituted or substituted part of naphthalene nucleus. The SCS sets (Table V) were made more accurate by further check comparison

TABLE I

$^{13}\text{C}$  chemical shifts ( $\delta$  scale;  $\pm 0.1$  ppm) of the atoms in sodium naphthalene-X-sulphonates in deuterium oxide

X	1	2	3	4	5	6	7	8	4a	8a
1-	137.8	126.0	124.5	132.5	128.8	126.6	127.6	124.9	133.8	127.9
2-	125.6	139.4	121.8	129.1	127.7	128.1	127.3	128.8	133.9	131.9
1,2-	138.6	135.6	130.7	131.5	128.5	126.7	127.9	125.6	132.6	129.8
1,4-	141.7	124.9	124.9	141.7	126.0	128.2	128.2	126.0	129.0	129.0
1,5-	139.1	126.8	126.4	129.5	139.1	126.8	126.4	129.5	129.2	129.2
1,6-	138.2	128.0	126.1	133.5	126.5	140.3	123.6	126.5	133.2	129.1
1,7-	138.9	127.1	126.6	132.2	130.1	122.5	140.9	122.9	134.6	127.1
1,3,5-	140.6	122.9	139.9	126.9	140.1	127.8	128.5	129.4	128.6	130.1
1,3,6-	139.8	124.0	139.8	130.7	127.5	141.3	125.6	126.7	132.8	130.0
1,3,7	140.7	123.3	140.4	129.6	131.4	123.9	142.8	123.0	134.4	128.3
1,3,5,7-	141.8	124.0	141.8	126.8	141.8	123.0	141.8	126.8	129.8	129.8
2,6-	125.5	141.4	123.2	130.3	125.5	141.4	123.2	130.3	133.0	133.0
2,7-	126.5	140.7	124.0	129.2	129.2	124.0	140.7	126.5	134.8	131.1

of the assignment of all the signals using both calculation from SCS and splitting of the individual signals by long-range interactions, as well as according to absolute values of the coupling constants and their trends depending on position. With application of these SCS sets, the differences between the calculated and found values of the  $^{13}\text{C}$  chemical shifts do not exceed  $\pm 0.2$  ppm within the whole range of the sodium naphthalene sulphonates studied (the only, expected, exception being sodium 1,2-naphthalenedisulphonate – sterical reasons).

The  $^{13}\text{C}$  chemical shifts of *ipso* carbon atoms are always distinctly higher than those of C(4a) and C(8a) atoms. In the coupled spectra, the  $\alpha$  *ipso* carbon atoms differ from the  $\beta$  *ipso* carbons by a greater width of non- or badly resolved multiplets (effect of greater  $^4J(^{13}\text{C}^1\text{H})$  values). The signals of two carbon atoms of the same type in the naphthalenetrisulphonic acids differed by multiplicity (given by number of the  $^3J(^{13}\text{C}^1\text{H})$  coupling constants): in sodium 1,3,5-naphthalenetrisulphonate the signal with the chemical shift of 140.6 is split by a single coupling constant  $^3J$  and was assigned to the C(1) atom, whereas the signal at 140.1 is split by two  $^3J$  and is due to the C(5) atom. For the assignment of C(4a) and C(8a) atoms it was fundamentally important to find that both  $\alpha$  and  $\beta$  sulphonic acid groups decrease the chemical shift value of the nearer carbon atom of this pair, *i.e.* introduction of sulphonic group into 1 or 2 position causes an upfield shift of the C(8a) atom. This regularity was also observed<sup>1</sup> with other substituents showing predominant inductive effects

TABLE II

$^{13}\text{C}$  substituent chemical shifts<sup>a</sup> (ppm) of the atoms in sodium naphthalene-X-sulphonates in deuterium oxide

X	1	2	3	4	5	6	7	8	4a	8a
1-	9.7	0.0	-1.5	4.4	0.7	0.7	1.7	-3.2	0.1	-5.8
2-	-2.5	13.5	-4.2	1.0	-0.4	2.2	1.4	0.7	0.2	-1.8
1,2-	10.5	9.7	4.8	3.4	0.4	0.8	2.0	-2.5	-1.1	-3.9
1,4-	13.6	-1.1	-1.1	13.6	-2.1	2.3	2.3	-2.1	-4.7	-4.7
1,5-	11.0	0.9	0.5	1.5	11.0	0.9	0.5	1.5	-4.5	-4.5
1,6-	10.1	2.1	0.2	5.4	-1.6	14.4	-2.4	-1.6	-0.5	-4.6
1,7-	10.8	1.2	0.7	4.1	2.0	-3.5	15.0	-5.2	0.9	-6.6
1,3,5-	12.5	-3.1	14.0	-1.2	12.0	1.9	2.6	1.3	-5.1	-3.6
1,3,6-	11.7	-2.0	13.9	2.6	-0.6	15.4	-0.4	-1.4	-0.9	-3.7
1,3,7-	12.6	-2.7	14.5	1.5	3.3	-2.1	16.9	-5.1	0.7	-5.4
1,3,5,7-	13.7	-2.0	15.9	-1.3	13.7	-2.0	15.9	-1.3	-3.9	-3.9
2,6-	-2.6	15.5	-2.8	2.2	-2.6	15.5	-2.8	2.2	-0.7	-0.7
2,7-	-1.6	14.8	-2.0	1.1	1.1	-2.0	14.8	-1.6	1.1	-2.6

<sup>a</sup> Naphthalene:  $\delta(\text{C}_1) = 128.1$ ;  $\delta(\text{C}_2) = 126.0$ ;  $\delta(\text{C}_{4a}) = 133.7$ .

TABLE III

The  $^1J(^{13}\text{C}^1\text{H})$  coupling constants (Hz,  $\pm 0.3$  Hz) in sodium naphthalene-X-sulphonates in deuterium oxide

X	1	2	3	4	5	6	7	8
1-	0	167.8	166.3	162.1	162.4	162.8	161.8	162.9
2-	165.3	0	165.4	163.3	163.2	162.2	162.4	163.2
1,2-	0	0	167.9	163.6	162.7	162.0	161.7	164.0
1,4-	0	169.1	169.1	0	162.6	163.0	163.0	162.6
1,5-	0	166.7	165.5	164.5	0	166.7	165.5	164.5
1,6-	0	167.5	167.2	164.0	166.0	0	167.5	166.5
1,7	0	168.7	167.0	164.2	165.6	166.7	0	166.6
1,3,5-	0	169.3	0	168.9	0	167.5	166.3	165.3
1,3,6-	0	168.7	0	167.7	167.5	0	167.7	168.7
1,3,7-	0	169.2	0	167.7	166.3	167.2	0	168.7
1,3,5,7-	0	170.7	0	169.8	0	170.7	0	169.8
2,6-	165.8	0	166.0	164.7	165.8	0	166.0	164.7
2,7-	166.7	0	166.3	165.5	165.5	166.3	0	166.7

TABLE IV

The  $^3J(^{13}\text{C}^1\text{H})$  coupling constants (Hz,  $\pm 0.3$  Hz) in sodium naphthalene-X-sulphonates in deuterium oxide

X	C 1	2	3	4	5	6	7	8
1-	<sup>a</sup>	9.0	0	4.5; 7.1	4.5; 7.2	8.2	8.2	6.8
2-	4.3; 6.8	7.0	6.6	4.8	<sup>b</sup>	8.4	8.1	<sup>b</sup>
1,2-	<sup>a</sup>	10.0	0	4.5	<sup>b</sup>	8.5	8.5	5.7
1,4-	<sup>a</sup>	0	0	<sup>a</sup>	<sup>a</sup>	8.4	8.4	<sup>a</sup>
1,5-	<sup>a</sup>	8.9	0	7.1	<sup>a</sup>	8.9	0	7.1
1,6-	<sup>a</sup>	8.5	0	5.0; 7.1	5.1; 5.1	9.2	6.5	0
1,7-	<sup>a</sup>	7.4	0	5.1; 7.2	4.6	6.5	9.0	5.0
1,3,5-	5.4	6.6	0	5.4	<sup>a</sup>	8.5	0	6.8
1,3,6-	<sup>b</sup>	6.6	0	4.9; 6.4	4.9; 5.4	9.3	6.3	0
1,3,7-	<sup>a</sup>	6.8	0	5.4; 5.4	4.8	6.6	9.3	5.7
1,3,5,7-	0	6.6	0	5.6	0	6.6	0	5.6
2,6-	4.6; 5.3	9.8	6.3	4.9	4.6; 5.3	9.8	6.3	4.9
2,7-	3.7; 4.6	7.5	6.6	3.5	3.5	6.6	7.5	3.7; 4.6

<sup>a</sup> A complex multiplet; <sup>b</sup> overlapped signals.

on naphthalene nucleus. In several cases the assignment was verified by differences in the multiplicity of the signals.

It was directly possible to assign the signals of all methine carbon atoms which have  ${}^3J({}^{13}\text{C}^1\text{H}) = 0$ . Only in the case of 1,6-naphthalenedisulphonate it was necessary to apply selective irradiation of H(8) atom so that the signals at 126.5 and 126.1 might be assigned to C(8) and C(3), respectively. Signals of the remaining methine carbon atoms were assigned as follows: Sodium 1-naphthalenesulphonate: the signal at 126.0 with the maximum values of both  ${}^1J({}^{13}\text{C}^1\text{H})$  and  ${}^3J({}^{13}\text{C}^1\text{H})$  was assigned to C(2). The broadened (due to three  ${}^4J({}^{13}\text{C}^1\text{H})$ ) signal at 124.9 ppm with the lowest value of  ${}^3J({}^{13}\text{C}^1\text{H})$  was assigned to C(8). Sodium 2-naphthalenesulphonate: the assignment of the signal at 125.6 ppm to C(1) atom was verified by selective decoupling. The signal at 121.8 ppm with the maximum value of  ${}^1J({}^{13}\text{C}^1\text{H})$  and the minimum value of  ${}^2J({}^{13}\text{C}^1\text{H})$  corresponds to C(3) atom. The signal at 129.1 was assigned to C(4) atom with regard to the small  ${}^3J({}^{13}\text{C}^1\text{H})$  value from *peri* position. Sodium 1,2-naphthalenedisulphonate: the signal at 125.6 was assigned to C(8) atom after selective decoupling. The signal with chemical shift of 131.5 with the value  ${}^3J({}^{13}\text{C}^1\text{H})$  corresponding to an effect from *peri* position belongs to the C(4) atom. The only signal at 128.5 ppm is split by two  ${}^3J({}^{13}\text{C}^1\text{H})$  and is due to C(5) atom.

TABLE V

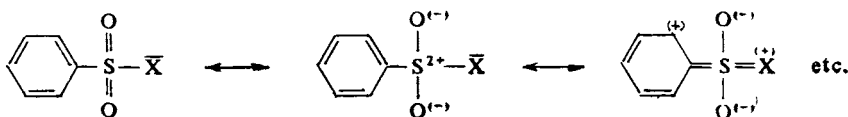
Values of  ${}^{13}\text{C}$  substituent chemical shifts (SCS) for calculation of  ${}^{13}\text{C}$  chemical shifts in sodium naphthalenesulphonates ( $\delta(\text{Ci}) = 128.1$  ( $i = 1; 4; 5; 8$ );  $\delta(\text{Ci}) = 126.0$  ( $i = 2; 3; 6; 7$ );  $\delta(\text{Ci}) = 133.7$  ( $i = 4a; 8a$ ))

Ci	(SCS) $_{\alpha}$			Ci	(SCS) $_{\beta}$		
	A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>		A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>
1 <sup>b</sup>	9.7	10.3	10.5	1	-2.5	-2.2	-2.6
2	0.0	0.0	0.2	2 <sup>b</sup>	13.5	13.4	13.6
3	-1.5	-1.3	-1.0	3	-4.2	-4.1	-4.0
4	4.4	4.6	4.0	4	1.0	1.5	1.7
4a	0.1	1.1	1.5	4a	0.2	1.0	1.0
5	0.7	1.1	1.1	5	-0.4	0.0	0.0
6	0.7	0.7	0.7	6	2.2	2.1	2.0
7	1.7	1.7	1.8	7	1.4	1.4	1.1
8	-3.2	-2.8	-2.7	8	0.7	1.1	1.1
8a	-5.8	-4.7	-4.7	8a	-1.8	-0.8	-0.4

<sup>a</sup> A denotes SCS for the first  $\text{SO}_3^{(-)}$  group, B denotes SCS for the second  $\text{SO}_3^{(-)}$  group introduced into the not yet substituted nucleus, and C denotes SCS for the next  $\text{SO}_3^{(-)}$  group introduced into the same nucleus; <sup>b</sup> C— $\text{SO}_3^{(-)}$ .

Sodium 1,4- and 1,5-naphthalenedisulphonates: they were differentiated by application of selective decoupling. Sodium 1,6-naphthalenedisulphonate: the signals corresponding to C(2) and C(7) atoms are split by one  $^3J(^{13}\text{C}^1\text{H})$  coupling constant. The signal (128.0) with higher  $^3J(^{13}\text{C}^1\text{H})$  value was assigned to C(2), that at 123.6 to C(7). The signals at 133.5 ppm (C(4)) and at 126.5 ppm (C(5)) are split by two different coupling constants  $^3J$ . Sodium 1,7-naphthalenedisulphonate: the shifts of C(5) and C(8) atoms at 130.1 ppm were assigned on the basis of selective decoupling. The signal with the maximum value of both  $^1J(^{13}\text{C}^1\text{H})$  and  $^3J(^{13}\text{C}^1\text{H})$  was assigned to C(2) atom. The signal of C(4) atom (132.2) is the only signal of CH groups which exhibits two  $^3J(^{13}\text{C}^1\text{H})$  coupling constants. The other signals were assigned on the basis of comparison with the calculated values of the  $^{13}\text{C}$  chemical shifts, the appearance of the proton-coupled spectrum being taken into account. The assignment of signals of the other compounds, which show higher symmetry and, hence, smaller number of non-equivalent signals (1,4-, 1,5-, 2,6-, 2,7-naphthalenedisulphonates and 1,3-, 5,7-naphthalenetetrasulphonate) or simpler  $^1\text{H}$  NMR spectra (the naphthalenetrisulphonates), was carried out with the use of selective decoupling and different number and different magnitudes of the  $^3J(^{13}\text{C}^1\text{H})$  coupling constants.

Analysis of  $^{13}\text{C}$  chemical shifts of a series of benzenesulphonyl derivatives<sup>10</sup> showed that the  $-\text{SO}_2\text{X}$  group represents a distinctly electronegative substituent which strongly polarizes the  $\sigma$  bond to aromatic nucleus and, at the same time, affects the distribution of  $\pi$  electron density in the nucleus by both inductive (+I) and mesomeric (+M) effects. Moreover it was found<sup>10</sup> that the acceptor effect is increased with increasing donor character of the X substituent. The described influence of sulphonyl group can be understood if it is presumed that a) the system of bonding electrons also involves those in  $d$  orbitals of sulphur atom, b) oxygen atoms of sulphonyl group draw off the partial negative charge shifted from the donor atom X by mesomeric effect, c) the increased acceptor effect of oxygen atoms is transferred equally also to the aromatic nucleus so that symmetry of valence electrons of the central atom might be maintained as much as possible. These presumptions can be schematically represented *e.g.* by the following valence bond structures:



The first presumption is supported *e.g.* by results of calculations carried out by Craig and coworkers<sup>11-13</sup> which show that participation of sulphur  $d$  orbitals in a bond is the more probable the more electronegative are the atoms bound thereon. In the case of sulphonyl group these atoms are oxygen atoms. The second and the third presumptions are supported by results of studies carried out by Hargittai<sup>14-15</sup>.

Comparisons of S=O bond lengths and O=S=O bond angles determined by electron diffraction method for a series of sulphones type  $XSO_2X$  or  $XSO_2Y$  showed that these bond lengths are increased and the bond angles are decreased with increasing donor ability of the substituents X, Y. Also unambiguously proved was mutual influence of the substituents X—S and Y—S.

For axially symmetrical nuclei of benzenesulphonyl derivatives<sup>10</sup> it was possible to show the existence of both the types of electromeric shifts which could only be differentiated from each other by comparison of SCS values of C(1)—C(4) in a series of derivatives with various X's, because the two effects (+I & +M) act in the same direction. In the case of non-symmetrical naphthalenesulphonate molecules, however, the two effects can be distinctly proved and differentiated even in the case of a single X ( $X = O^{(-)}$ ).

Table VI compares the orders of carbon atoms in the 1- and 2-naphthalenesulphonates according to increasing SCS values and the expected distribution of  $\pi$  electron density in the naphthalene molecule as a result of introduction of sulphonic group into 1 and 2 position, resp. A higher SCS value corresponds to a greater decrease of  $\pi$  electron density.

For the *ipso* carbon atoms the observed order distinctly differs from the expected one, and differences are also found between the absolute SCS values of the *ipso* carbon atom and other carbons. These differences represent evidence for the fact that dominant effect of sulphonic group consists in polarization of its  $\sigma$  bond to the naphthalene nucleus. The SCS value of the  $\beta$  *ipso* carbon atom is practically equal to that of *ipso* carbon atom in benzenesulphonate, being by 3.8 ppm greater than that of the  $\alpha$  *ipso* carbon atom. Obviously this difference is due to a greater share of mesomeric shifts in the case of  $\alpha$  substitution than in  $\beta$  substitution. This result agrees with chemical experience: reactivity of naphthalene resembles that of 1,4-diphenylbutadiene more than that of a purely aromatic hydrocarbon.

The effect of mesomeric shifts in the substituted nucleus is obvious. The negligible probability of resonance structures involving two quinoid nuclei (Table VI) also corresponds to the tendency of naphthalene to maintain benzenoid structure of one nucleus, if symmetry of the molecule is disturbed. The only obvious exception is the resonance structure of 2-naphthalenesulphonate with increased positive charge at C(6). In this case, however, the both nuclei have *para*-quinoid structures.

High positive SCS value at C(7) is the same in the two naphthalenemonosulphonates, hence it is probably connected not with mesomeric but with inductive shifts transferred predominantly *via* C(1)  $\rightarrow$  C(8a)  $\rightarrow$  C(8)  $\rightarrow$  C(7) path.

Strikingly, the bond between C(4a) and C(8a) atoms does not practically transfer electromeric effects. Therefore, the SCS differences between the first and the next sulphonic groups introduced are considerably greater just in the case of the C(4a) and C(8a) atoms, and that is why also a better agreement between the observed and the expected order (according to the inductive effect) of the carbon atoms was

achieved in the case when the distance of the carbon atom considered from the *ipso* carbon atom was expressed exclusively by the number of peripheral bonds.

Out of other acceptor substituents, trifluoromethyl group has very similar effects (except for the *ipso* carbon atom). Also the trends in the set of SCS's of nitro group are analogous to those in the set of sulphonic group. With nitro group, however, the inductive effect is more important due obviously to the lower length of C—N bond.

Excellent SCS additivity in naphthalenepolysulphonic acids series (with the exception of 1,2-disubstitution — sterical reasons) is due to the same acceptor character of the substituents and minor importance of their electromeric effects.

The survey of  $^1J(^{13}\text{C}^1\text{H})$  coupling constants given in Table III indicates that introduction of sulphonic group into the naphthalene molecule is connected with overall increase in the  $^1J(^{13}\text{C}^1\text{H})$  value which are 158.8 and 159.5 Hz for  $\text{C}_\alpha\text{—H}$  and  $\text{C}_\beta\text{—H}$ , respectively, in the non-substituted naphthalene<sup>1</sup>. The  $^1J(^{13}\text{C}^1\text{H})$  values of the substituted nucleus show the regularity  $^1J(\textit{ortho}) > ^1J(\textit{meta}) > ^1J(\textit{para})$  observed with the benzene nucleus<sup>16</sup>. Obviously, for a given type of hybri-

TABLE VI

Comparison of Ci order according to the increasing value of substituent chemical shifts in sodium 1-naphthalenesulphonate (SCS) <sub>$\alpha$</sub>  and 2-naphthalenesulphonate (SCS) <sub>$\beta$</sub>  and according to the expected influence of electromeric effects on the  $\pi$  electron density

(SCS) <sub><math>\alpha</math></sub>	Ci			(SCS) <sub><math>\beta</math></sub>	Ci		
	A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>		A <sup>a</sup>	B <sup>a</sup>	C <sup>a</sup>
—5.8	8a	2; 8a	—	—4.2	3	1; 3	—
—3.2	8	3; 8	—	—2.5	1	—	—
—1.5	3	—	(5; 7; 8a)	—1.8	8a	4; 8a	—
0.0	2	4; 7	—	—0.4	5	—	—
0.1	4a	4a; 6	—	0.2	4a	4a; 8	(3; 4a; 8)
0.7	5; 6	5	—	0.7	8	—	—
1.7	7	—	—	1.0	4	—	—
4.4	4	—	2; 4	1.4	7	5; 7	(6)
9.7	1	—	—	2.2	6	6	1
				13.5	2	—	—

<sup>a</sup> A denotes number of the carbon atom which corresponds to the experimental SCS value; B denotes number of carbon atom in the order according to the distance from C *ipso* expressed by number of peripheral bonds of the molecule ( $\approx +1$ ); C denotes number of the carbon atom according to the mesomeric influence (the values without brackets apply to the benzenoid non-substituted nucleus and those in brackets to the quinoid non-substituted nucleus).



dization of the carbon bonding orbital, the increase of  $^1J(^{13}\text{C}^1\text{H})$  values is proportional predominantly to the magnitude of the partial positive charge induced at the individual carbon atoms by polarization of  $\sigma$  bonds by sulphonic group.

The values of  $^2J(^{13}\text{C}^1\text{H})$  coupling constants could be reliably determined in several favourable cases only, particularly from the spectra recorded at higher temperatures:  $^2J(\text{C}_\alpha\text{H}_\beta) = 1.8$  Hz (1,5-naphthalenedisulphonate),  $^2J(\text{C}_\beta\text{H}_\alpha) = 0.9$  Hz (2-naphthalenesulphonate),  $^2J(\text{C}_\beta\text{H}_\beta) = 1.2$  Hz (1,4-naphthalenedisulphonate), 1.7 Hz (1,5-naphthalenedisulphonate), and 1.8 Hz (1,3,6-naphthalenetrisulphonate). Number of these values is insufficient for a discussion of the effect of substitution position of naphthalene molecule on the  $^2J(^{13}\text{C}^1\text{H})$ .

Introduction of sulphonic group into naphthalene molecule causes both increase and decrease of values of the  $^3J(^{13}\text{C}^1\text{H})$  coupling constants. The  $^3J(\text{C}_\beta\text{H}_\alpha)$  value found for naphthalene<sup>1</sup> is 8.4 Hz. This value is considerably smaller (6.3–6.8 Hz) with naphthalenesulphonates in the cases of negative SCS values at the respective carbon atoms. In most cases this applies to carbon atoms in *ortho* positions with respect to a sulphonic group in  $\beta$  position. If the respective carbon atom has a positive SCS value, then the  $^3J(^{13}\text{C}^1\text{H})$  value is greater (up to 10 Hz) than or equal to that of naphthalene. In average the  $^3J(\text{C}_\alpha\text{H}_\beta)$  values of naphthalenesulphonates are lower than those in the previous case. Again the regularity is observed that lower values (5.7 to 4.6 Hz) are found in the cases of a  $\beta\text{-SO}_3^-$  group bound at *ortho* position and higher values (7.2 Hz) in the cases of positive SCS values at the both interacting positions.

The value  $^3J = 4.9$  Hz was found<sup>1</sup> for the pair ( $\text{C}_\alpha; \text{H}_\alpha$ ), *i.e.* for interaction of *peri* positions of naphthalene. The values observed with naphthalenesulphonates are 3.5 to 5.4 Hz. No obvious dependence, however, can be seen between these values and the position with respect to the substituents, number of substituents, or SCS values.

The values  $^3J(^{13}\text{C}^1\text{H}) = 5.9$  and 8.1 Hz were found<sup>1</sup> for C(4a) and C(8a) atoms, resp., and  $\text{H}_\alpha$  and  $\text{H}_\beta$  in naphthalene. The values 6.1 and 6.5 Hz were found for interaction with  $\text{H}_\alpha$  in 1,3,6- and 1,3,7-naphthalenetrisulphonates, respectively, and the value 8.2 Hz for the interaction with  $\text{H}_\beta$  in 1,3,7-naphthalenetrisulphonate.

From the survey of regularities observed in the effects of sulphonic group on the  $^3J(^{13}\text{C}^1\text{H})$  values it can be deduced that a decisive role is played by the density of  $\pi$  electron cloud at the both interacting positions but especially at the carbon atom whose signal is followed. Lowering of  $\pi$  electron density is accompanied by increase in  $^3J(^{13}\text{C}^1\text{H})$  and *vice versa*.

The  $^4J(^{13}\text{C}^1\text{H})$  coupling constants, which attain the value of 0.6 Hz in naphthalene<sup>1</sup>, could not be reliably evaluated. Their influence, however, makes itself felt distinctly by broadening of signals of carbon atoms at  $\alpha$  positions in the proton-coupled spectrum. This broadening is particularly striking with the signals  $\text{C}_\alpha\text{-SO}_3^-$  as compared with those of  $\text{C}_\beta\text{-SO}_3^-$ .

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