Tetrahedron Vol. 46, No. 10, pp. 3613-3620, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF REGIO-CONTROLLED OLIGOMERS FROM 2-NAPHTHALENSULFONIC ACID AND FORMALDEHYDE

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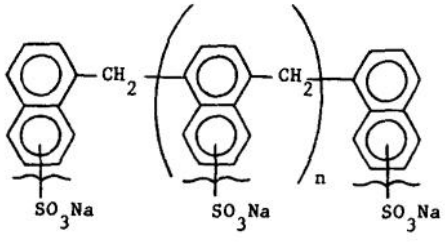
(*Received in UK* 5 *March* 1990)

Abstract - Regiocontrolled synthesis of symmetrical dinuclear products 4 and 8 derived from condensation of 2-naphthalensulfonic acid and formaldehyde was afforded. Acid catalyzed reaction of 4 with formaldehyde gave a mixture of regiocontrolled oligomers with even number of naphthalenic nucleus from which tetranuclear 9 and hexanuclear 10 products were separated. NMR Studies of all these products were carried out, obtaining both the structural characterization and useful informations for the identification of more complex mixtures.

Polymers from 2-naphthalensulfonic acid formaldehyde condensation, which have wide industrial applications, are mixtures of oligomeric products with linear structure and methylene bridge in 5- and 8-position of naphthalene nucleus.[1]



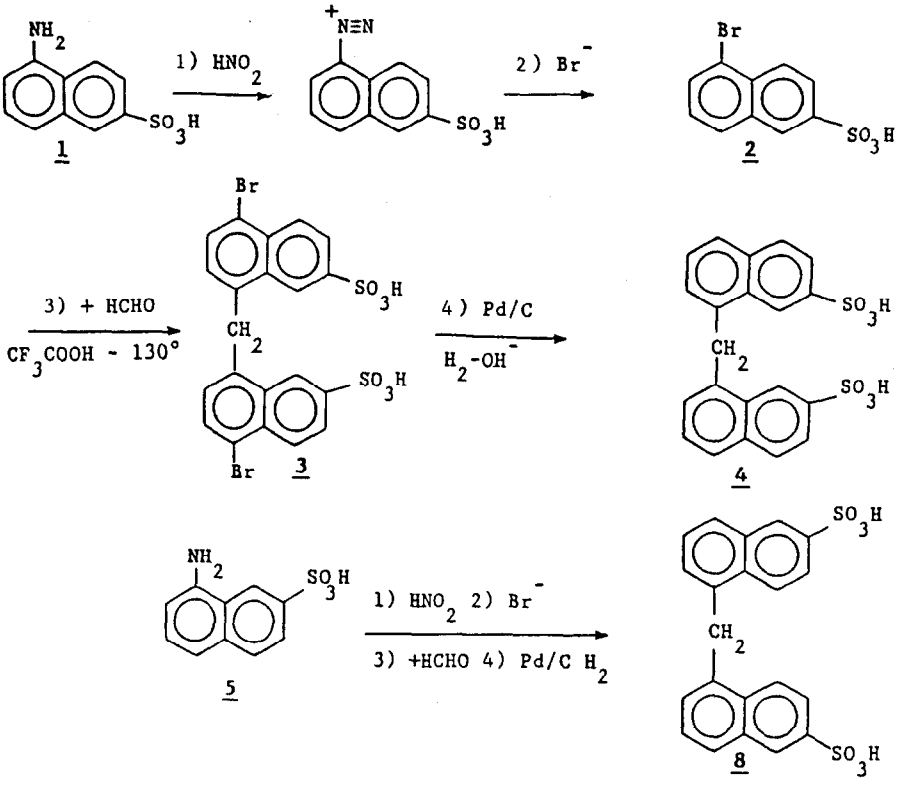
To study the physico-chemical properties of pure oligomeric products up to hexanuclear one we undertook the synthesis of these compounds.[2]

Previous studies showed that chromatographic separation of regioisomers from oligomeric mixtures obtained by 2-naphthalenicsulfonic acid-formaldehyde condensation was too difficult[1]. Moreover the number of possible regioisomers increases rapidly with the oligomers molecular weight. So a regiocontrolled synthesis of these oligomeric products was attempted.

In this paper we report the regiocontrolled synthesis of the two symmetric dinuclear products (5,5'- and 8,8') and the oligomerization of 8,8' isomer with formaldehyde to obtain products with even number of naphthalenic nucleus.

Synthesis of 5,5'- and 8,8'-methylenbis-2-naphthalensulfonic acids

Regiocontrolled synthesis was performed using a protective group for one of the two electrophilic position, 5 or 8 position, of 2-naphthalensulfonic acid.[3]



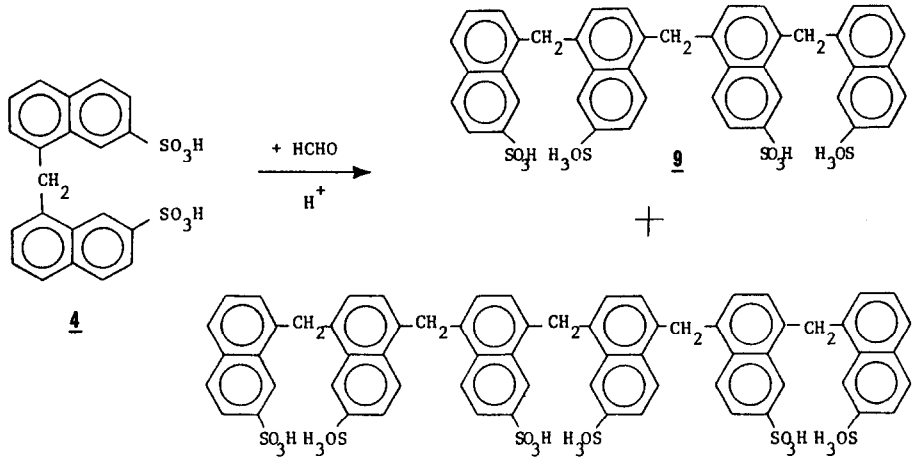
As protective group bromine was chosen. Starting from commercial Cleve acid 5-amino-2-naphthalensulfonic acid 1, 5-bromo derivative 2 is easily prepared.

Although bromide is a deactivating group for electrophilic reactions, the condensation with formaldehyde in suitable conditions gives with good yield 8,8'-methylenebis-5-bromo-2-naphthalensulfonic acid 3.

Removal of protective group, performed by hydrogen and Pd/C in basic condition[4], gives pure 8,8'-methylenebis-2-naphthalensulfonic acid 4. By a similar pathway, starting from 8-amino-2-naphthalensulfonic acid 5, pure 5,5'-methylenbis-2-naphthalensulfonic acid 8 was obtained.

Synthesis of tetranuclear and hexanuclear oligomeric products

Reaction of 8,8'-methylenbis-2-naphthalensulfonic acid 4 with formaldehyde in suitable conditions, gives with good yield a oligomeric mixture of products with even number of naphthalenic nucleus. Chromatographic separation of this mixture affords to tetranuclear 9 and hexanuclear product 10.



4 9 10

^{1}H and ^{13}C NMR structural determination of polynuclear products

^{1}H NMR spectra of 8,8'-methylenbis-2-naphthalensulfonic acid 4 were assigned on the base of chemical shifts and coupling constants (see Fig. 1 and Table)[5].

More complex was the assignment of ten signals observed in the aromatic region of ^{13}C NMR spectrum of this product (see Fig 2 and Table).[6] Six aromatic carbons were assigned by ^{1}H-^{13}C HETCOR. The last four quaternary carbon (2,8,9,10) were assigned by COLOC (correlation spectroscopy via long range couplings - see Fig. 3)[7].

Using the same procedure we performed the ^{1}H and ^{13}C NMR spectra assignements of 5,5'-methylenbis-2-naphthalensulfonic acid 8 (see Table).

Table. ^{1}H and ^{13}C NMR data for dinuclear products 4 and 8.

	Chemical shifts δ (ppm)								Coupling constants (Hz)				
Comp.	H-1	H-3	H-4	H-5	H-6	H-7	H-8	CH_2	$J_{1,3}$	$J_{3,4}$	$J_{5,6}$	$J_{6,7}$	$H_{7,8}$
4	8.69	7.97	8.04	7.88	7.47	7.15	--	5.01	1.52	8.84	8.19	7.15	--
8	8.40	7.87	8.13	--	7.12	7.40	7.85	4.97	1.58	8.88	--	7.16	8.17

	Chemical shifts δ (ppm)										
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_2
4	122.5	143.3	123.8	130.1	127.9	128.1	128.9	138.1	132.5	135.7	36.3
8	125.7	143.1	124.3	125.2	137.6	129.6	127.3	129.1	134.0	134.3	36.4

Fig. 1 - ^{1}H NMR aromatic region spectrum of di-, tetra- and hexanuclear products 4, 9 and 10.

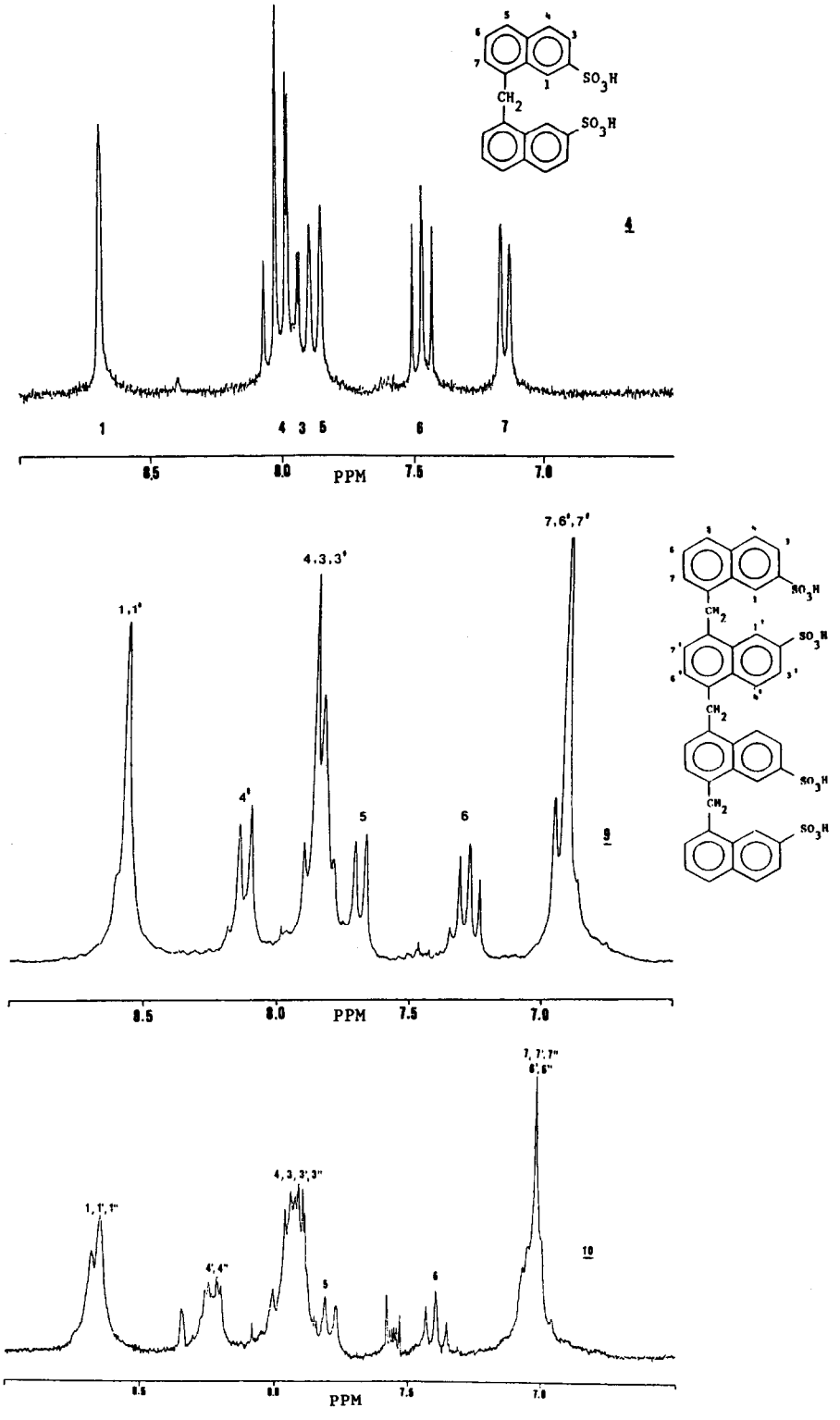


Fig. 2 - ^{13}C NMR aromatic region spectrum of di-, tetranuclear products 4 and 9.

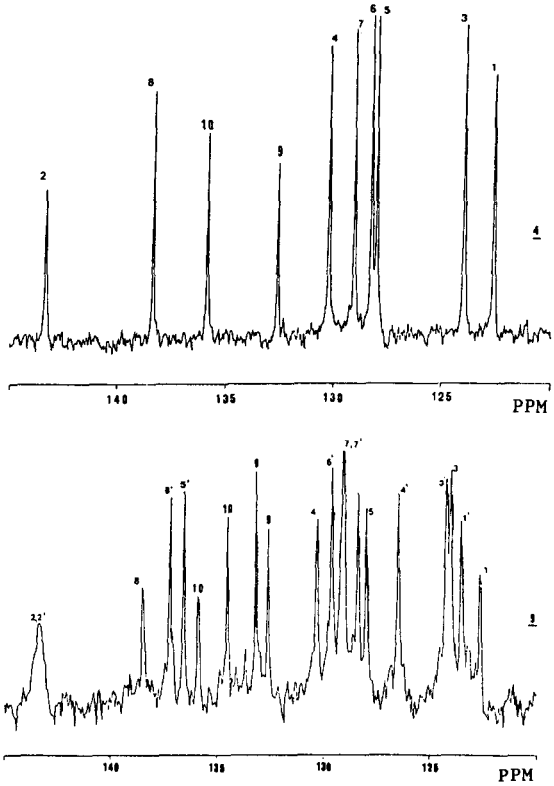
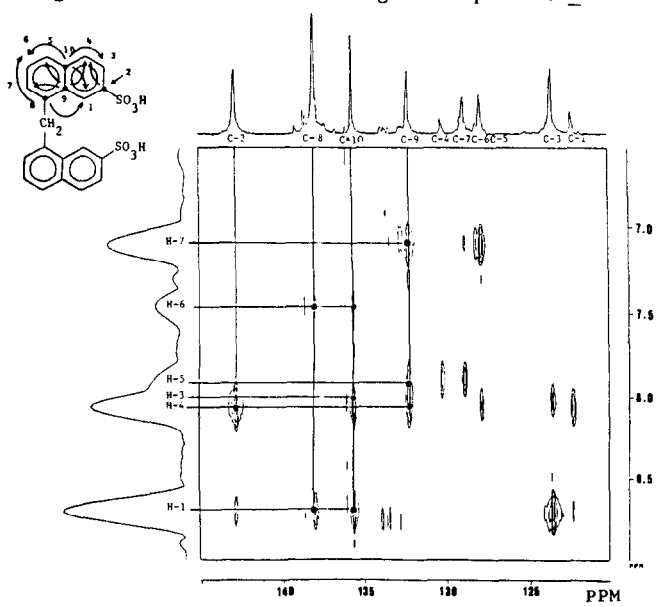


Fig. 3 - COLOC on aromatic region of product 4.



^{1}H and ^{13}C NMR aromatic region spectrum of tetranuclear product 9 with methylene bridges respectively in 8,8'- 5',5"- and 8", 8"'-position are reported respectively in Fig. 1 and Fig. 2.

^{1}H NMR spectra is in good agreement with the tetranuclear structure. In fact the intensity ratio of aromatic and methylene protons[8] is 3.60 (calculated for dinuclear = 6, for tetranuclear = 3.67, for hexanuclear = 3.20). Comparing the chemical shifts of aromatic protons and carbons of dinuclear and tetranuclear products a remarkable difference in ^{1}H NMR spectra is observed while in ^{13}C NMR spectra ten signals of dinuclear product are practically superimposable with ten of the eighteen aromatic signals of tetranuclear product.[9]

Differences in ^{1}H NMR spectra are probably due to a diamagnetic effect of aromatic rings of tetranuclear product, not relevant in ^{13}C NMR spectra. By this way ten carbon atoms of terminal naphthalenic units could be easily assigned. ^{1}H-^{13}C heteronuclear correlation and COLOC experiment gave a complete assignement of ^{1}H and ^{13}C signals.

Hexanuclear product 10 presents a ^{1}H NMR spectrum in agreement with the proposed structure (see Fig. 1) but there are some minor signals at 7.6 δ (multiplet) and 8.35 (singlet) due to an impurity of 2-naphthalensulfonic acid. This product both for the chemical preparation and the chromatographic separation can derive from a decomposition[10] of hexanuclear product probably due to the strong acidity of sulfonic groups of this product in which it is possible to hypothesize the formation of strong acidic hydrogen-bonded polysulfonic acids[11] with consequent aromatic dealkylation.[12]

Conclusions

Using protective groups regiocontrolled synthesis of symmetrical dinuclear products from 2-naphthalensulfonic acid and formaldehyde was obtained.

Condensation of one of these compounds with formaldehyde afforded linear oligomers with even number of naphthalenic nucleus and with defined structure.

So e.g. only one isomer of ten possible tetranuclear isomeric products, obtained from 2-naphthalensulfonic acid-formaldehyde condensation, was synthesized.

NMR Studies of these oligomers showed that ^{1}H but expecially ^{13}C NMR spectra seem particularly interesting in structural definition of more complex mixtures as that obtained from 2-naphthalensulfonic acid-formaldehyde condensation.[1]

Last but non least these oligomers seem very promising both as cation binding agents and after cyclization and salification as synthetic cyclodestrin models for complexation in water of neutral molecules.

EXPERIMENTAL

Reagents were used without further purification. Thin layer chromatography analyses were performed on Merck 60 F 254 silica gel plates (0.2 mm thicknes). Column chromatography was performed using silica gel 60 (Merck, 230-400 mesh).

^{1}H NMR experiments were performed on a Bruker AC200 (200 MHz) instruments from CD_3OD solutions at room temperature.

5-bromo-2-naphthalensulfonic acid, sodium salt 2.

To a solution of 5-amino-2-naphthalensulfonic acid (6.70 g - 32 mmol) dissolved in 36 ml of NaOH 0.85 M, 12 ml of 40% hydrobromic acid were added. The resulting suspension was cooled at -5° C and a solution of 2.4 g (35 mmol) of $NaNO_2$ in 4.5 ml of H_2O was added dropwise with stirring in 20 min. mantaining the temperature below 2° C. The reaction mixture was stirred at - 5° C for 30 min. and the excess of nitrite was decomposed with urea.

The diazonium salt was added in small portions (1 h) with stirring to a heated (70° C) solution of CuBr (4.6 g - 32 mm) dissolved in 24 ml of 40% HBr.

The reaction mixture was then stirred at 80° C for 30 min., cooled at room temperature, saturated with solid NaCl and filtered. The solid sodium salt was recrystallized from water and, after drying, 6.15 g (60% yield) of compound 2 were obtained.

^{1}H NMR (CD_3OD) δ 7.40 (dd, H-7, $J_{6,7}$=7.53, $J_{7,8}$=7.40 Hz), 7.84 (dd, H-6, $J_{6,8}$=1.16 Hz), 7.95 (broad d, H-8), 8.02 (dd, H-3, $J_{3,4}$=8.88, $J_{1,3}$=1.75 Hz), 8.27 (broad d, H-4), 8.39 (broad d, H-1).

8,8'-methylenbis-5-bromo-2-naphthalensulfonic acid 3

In a closed thick wall glass tube 5 g (16 mmol) of sodium 5-bromo-2-naphthalensulfonate, 1.05 g (35 mmol) of paraformaldehyde and 5.2 g of Amberlyst 15 ion-exchange resin were poured into 25 ml of trifluoroacetic acid. The reaction was stirred at 130° C for 5 h. After cooling at room temperature the solvent was removed in vacuo. Soxhlet extraction with ethyl acetate gave 3.56 g (70% yield) of pure compound.

^{1}H NMR (CD_3OD) : δ 4.90 (s, CH_2), 7.00 (d, H-7, $J_{6,7}$=7.58 Hz), 7.76 (d, H-6), 8.03 (dd, H-3, $J_{3,4}$=8.85, $J_{1,3}$=1.26 Hz), 8.38 (d, H-4), 8.63 (d, H-1).

8,8'-methylenbis-2-naphthalensulfonic acid 4

1 g (1.7 mmol) of dibromo compound 3 was hydrogenated (1 atm) at room temperature in a solution of methanol (60 ml) and 0.3 g (5.3 mmol) of KOH, using 1 g of Pd/C 10% as catalyst.

Warning: Mixing the catalyst and methanol in air atmosphere bring out the self ignition of the mixture.

After filtration the dipotassium salt solution was exchanged over IRA 120 resin to give 0.51 g (69% yield) of pure compound 4. ^{1}H and ^{13}C NMR data are reported in Table.

8-bromo-2-naphthalensulfonic acid, sodium salt 6.

This compound was prepared as previously reported for product 2 with 45% yield.

^{1}H NMR (D_2O) : δ 7.10 (broad t, H-6, $J_{6,7}$=$J_{5,6}$=7 Hz), 7.49 (broad d, H-5 and H-7), 7.80 (broad d, H-3, $J_{3,4}$=8.2 Hz), 7.99 (d, H-4), 8.62 (broad s, H-1).

5,5'-methylenbis-8-bromo-2-naphthalensulfonic acid 7

Starting from product 6, as previously reported for product 3, 7 was prepared with a 60% yield.

^{1}H NMR (100 MHz, CD_3OD) : 4.88 δ (S, CH_2), 6.97 (d, H-6, $J_{6,7}$=7.6 Hz), 7.72 (d, H-7),

7.97 (dd, H-3, $J_{3,4}$=9, $J_{1,3}$=1.5 Hz), 8.17 (d, H-4), 8.83 (d, H-1).

5,5'-methylenbis-2-naphthalensulfonic acid 8

Product 8 was prepared with 70% yield from 7 as previously reported for compound 4. ^{1}H and ^{13}C NMR data are reported in Table.

Oligomerization of 8,8'-methylenbis-2-naphthalensulfonic acid.

4 (1 g, 2.3 mmol) was reacted at 50° C for 5 h with 0.75 g of paraformaldehyde in 10 ml of CF_3COOH and 1 ml of H_2O in a closed tube. After evaporation of the solvent the oligomeric mixture was separated on silica gel column chromatography (ethyl acetate : isopropanol : water = 4:2:1) to remove the unreacted dinuclear compound (0.18 g) and than with 3:2:1 mixture and gave 0.36 g of tetranuclear compound 9 and 0.28 g of hexanuclear 10 compound and 0.10 g of likely octanuclear compound.

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8.- Methylene hydrogen signals of tetra- and hexanuclear products 9 and 10 are at 5.0 ppm (broad singlet).

9.- Methylene carbons signals of tetranuclear product 9 are present at 35.74 and 35.93 ppm.

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