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METHYLENE BRIDGE POSITION IN 2-NAPHTHALENSULFONIC ACID-FORMALDEHYDE CONDENSATION PRODUCTS: A NMR INVESTIGATION

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Abstract - Low molecular weight oligomers from acid catalyzed condensation of 2-naphthalensulfonic acid and formaldeyde were obtained. Spectroscopic (NMR) studies of dinuclear mixture verified the presence of 5,5'- 8,8'- and 5,8'-methylenebis-2-naphthalensulfonic acid, with a predominance of products derived from 5-attack. Trinuclear product confirmed the presence of a linear structure of these condensate. Similar results were also obtained from dinuclear product separated from commercial product (Daxad 15-Grace).

Oligomers derived from the acid-catalyzed condensation of 2-naphthalensulfonic acid and formaldehyde are widely used for the preparation of industrial dispersants,[1] pharmaceutical products [2] and for lather tanning.[3] In spite of their large use there is up to now a great confusion in the literature on the structure of these compounds. Until few years ago they were described as methylenebis-2-naphthalensulfonic acid. Sometime also the position of the methylene bridge was indicated, generally the more reactive of non sulfonated aromatic nucleus (5,5'-6,6' etc) but in other cases[2] also the more unlikely 3,3' position. Only in the last few years, for example in Chemical Abstract, most of these have been correctly indicated as a mixture of 2-naphthalensulfonic acid-formaldehyde olygomers.

However, because of the complex composition, very few fundamental research has been carried out on the structure of these condensation products. After their discovery around 1911[4] the only reliable reports concerning the structure of these polymers were published by K. Hattori in 1963.[5] On the basis of these results it was extablished that the product obtained from the condensation of 2-naphthalensulfonic acid and formaldehyde was not the dinuclear compound, which was not even the main component, but rather a mixture ranging from mono- to decanuclear compound. Infrared studies allowed Hattori to conclude that the methylene bridge of dinuclear compound was present mainly in 8-position of 2-naphthalensulfonate while trinuclear products had the bridge at the 5- or 8-position of the naphthalenesulphonate.

On this basis a linear structure of the polynuclear condensate was hypothesized.

The linear structure hypothesis, although not completely supported by experimental data, seems to be correct on the basis of the reported data of the regioselectivity of electrophilic attacks on 2-naphthalensulfonic acid.[6] However the Hattori's hypothesis of 8,8'-dinuclear product does not seem correct, on the basis of the reported partial rate factors for the sulfonation of this compound which are: 0.133 for 5; 0.032 for 8 and 0.007 for 4-position.[6]

In order to obtain conclusive informations on the structure of oligomeric products, we have undertaken a chemical study to obtain pure di and trinuclear fractions and a spectroscopic (NMR) research to clarify the structure of these compounds. These results are the first step to understand the correlation between properties and structure of these oligomers.[7]

Synthesis and separation of oligomeric products

To semplify the work-up of the reactions an acidic ion-exchange resin was employed as catalyst instead of sulfuric acid. By a careful choice of the experimental conditions we succeed to prepare low molecular weight oligomeric mixtures. Analyses of these mixtures were performed on TLC (silica gel) and preparative separations using column chromatography. For comparison a dinuclear oligomeric mixture was also separated from the commercial product DAXAD 15 (Grace).

After silica gel chromatographic separation of the oligomeric mixture, sulfonic groups are partially salified and, owing to the better resolution in ^{1}H NMR spectra of the free acids, the cromatographic fractions were desalted by ion-exchange resins.

NMR structure determination of dinuclear fraction.

A first structural insight was obtained from the intensity ratio of the aromatic and methylene protons.[8] In fact the calculated ratio is 6 for dinuclear, 4.25 for trinuclear and 3.67 for tetranuclear fraction and gives a good idea of the molecular weight for the low molecular weight fractions.

The observed ratio for the isolated compound resulted to be 5.95 which indicated its dinuclear nature.

The aromatic protons region, reported in Fig. 1, shows a very complex pattern.

Results of a "J resolved" experiment of this region (see Fig. 2) evidenced the presence of three sets of signals and of a fourth one with a lower intensity. Each set consists of one singlet, four doublets and one triplet, the coupling constants being of the order of 8 Hz (ortho coupling).

Excluding meta and para coupling constant, this pattern is expected only with methylene bridge in 5 or 8 position.

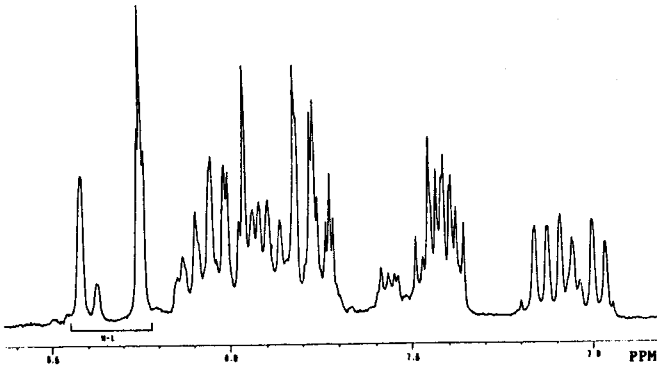


Fig. 1 - ^{1}H NMR of aromatic protons of dinuclear fraction.

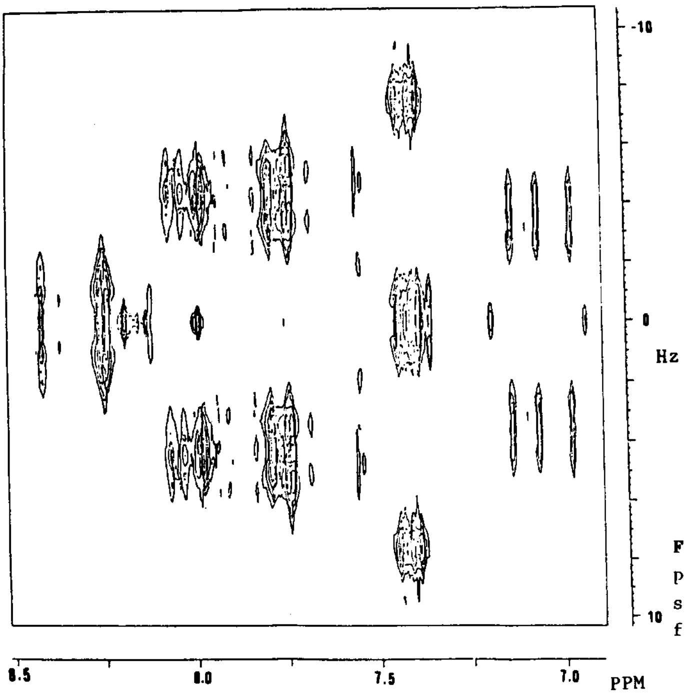
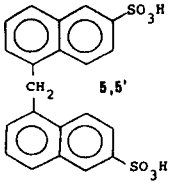
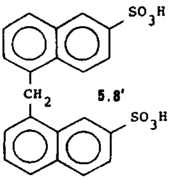


Fig. 2 - Aromatic protons J resolved spectrum of dinuclear fraction.

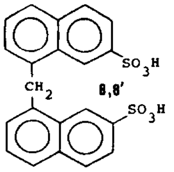
To explain the presence of four sets of signals, we must consider the three possible isomers derived from electrophilic attack in 5 or 8 position: 5,5'-, 8,8'- and 5,8'-methylenebis-2-naphthalensulfonic acid. The first two products are symmetric and the two aromatic nuclei are equivalent.



5,5'



5,8'



8,8'

However, 5,8'-isomer has two non equivalent aromatic nuclei and should be characterized by two sets of signals with the same intensity. A tentative complete assignement was obtained by 2D-Cosy ^{1}H-^{1}H experiment (Fig. 3). Further support was obtained by a comparison with the spectra of pure 5,5'- and 8,8'-isomers prepared by a regiocontrolled synthesis.[9]

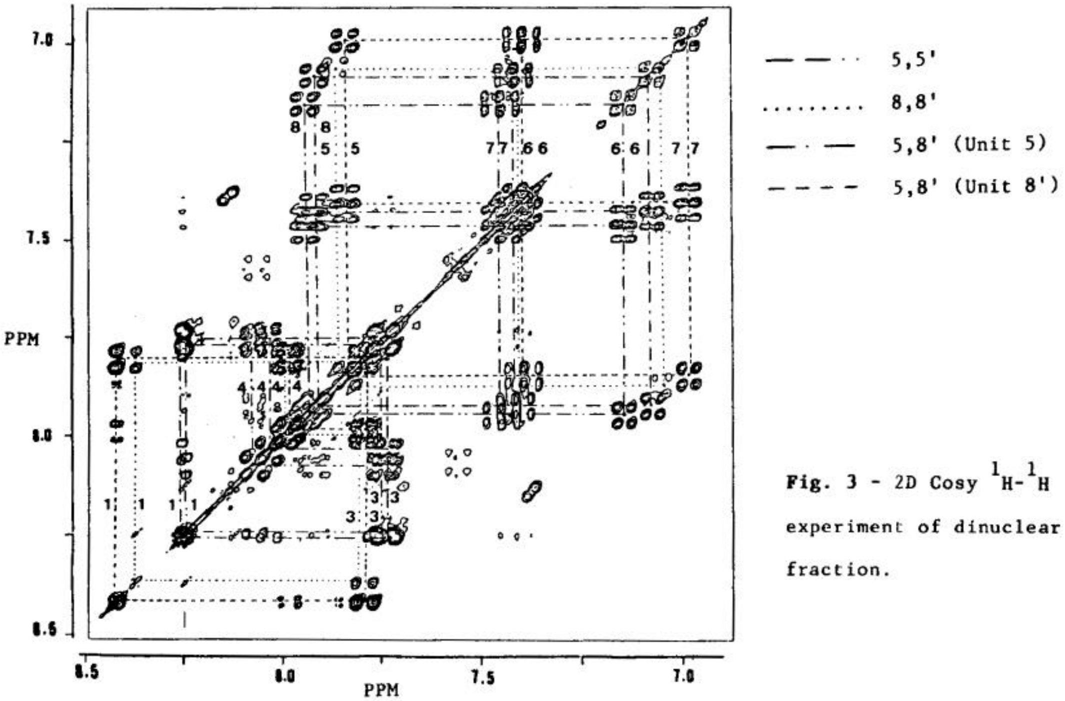


Fig. 3 - 2D Cosy ^{1}H-^{1}H experiment of dinuclear fraction.

Using the assignements of H-1 proton signals of monodimensional spectra the relative percentages of the three isomers present in this chromatographic fraction were obtained: 5,5' = 29%, 5,8' = 62%, 8,8' = 9%.

^{1}H NMR analysis of the dinuclear fraction, obtained from the commercial desalified Daxad 15, showed a similar pattern. The only observed difference was a variation of the isomers percentage with a slight decrease of those arising from 5-position attack.

^{1}H NMR of trinuclear fraction

Intensities ratio of aromatic and methylene protons of a fraction eluted after dinuclear one is 6.33 in agreement with a trinuclear product ^{1}H NMR of aromatic region is reported in Fig. 4.

Assuming an electrophilic attack on 5- and 8-position the expected isomers are four. No one is symmetric, so owing to the complexity of NMR spectroscopic pattern, it is not possible to recognize the different isomers. However the spectrum pattern of dinuclear and trinuclear fractions are very similar. The only difference is the presence of high field signals, at around 7 ppm, that is the zone of aromatic protons in ortho position to CH_2. 2D Cosy spectrum shows in 6.8-7.0 zone an AB system due to the 6 and 7 protons of internal unity, which, as expected, are magnetically very similar (J = 8 Hz).

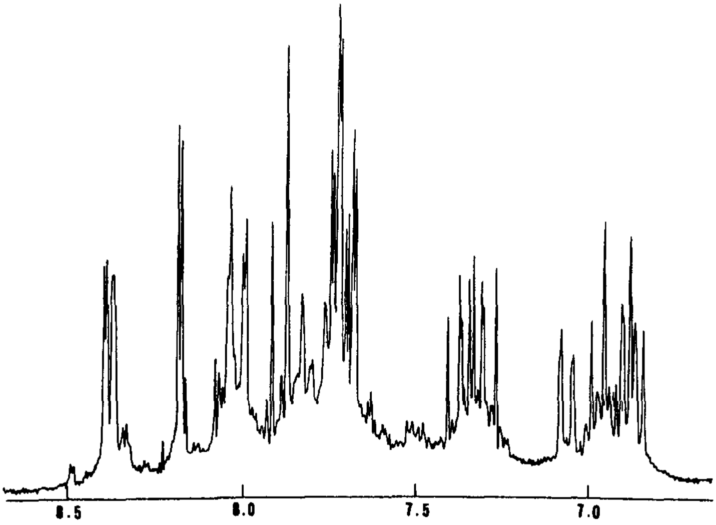


Fig. 4 - ^{1}H NMR of trinuclear fraction.

These signals are specific for internal naphthalenic units and may be useful for the evaluation of chain length in oligomeric mixtures.

Conclusions

Synthesis and separation of low molecular weight oligomeric mixtures from 2-naphthalensulfonic acid-formaldehyde were obtained.

^{1}H NMR spectra of the dinuclear and trinuclear fractions obtained from these mixtures are in agreement with a linear structure. Methylene bridges are present in 5 and 8 position of 2-naphthalensulfonic acid. As expected, in dinuclear products 5-position attack of methylene bridges is favoured.

However, commercial products are not prepared from purified 2-naphthalensulfonic acid so their structures may strongly depend from sulfonation stage of naphthalene. For example starting from not completely sulfonated naphthalenic mixture a branched structure arises.[10] Unsulphonated naphthalene with more than two reactive positions becomes infact the branching point of the polymer.

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) instrument from DMSO D_6 solutions at room temperature.

2D-COSY H1-H1 parameters were SW2 = 400 Hz, NE = 256, NS = 16.

2-Naphthalensulfonic acid-formaldehyde polymer.

2-Naphthalensulfonic acid (0.05 moles), formaldehyde (40% in water, 0.025 or 0.05 moles), Amberlyst 15 (2.5 g) were reacted in water (6 ml) in a closed vesses at 95° for 14 h. Filtration and vacuum drying gave the polymeric mixture.

Chromatographic analyses and preparative separations.

TLC analysis were performed on silica gel plates using ethyl acetate-isopropanol-water (4:2:1 or 2:4:1) and tetrahydrofuran-isopropanol-water (3:1:1 or 5:1:1). Increasing molecular weight a decrease of Rf is observed. E.g. R_f with THF-iPrOH-H_2O (5-1-1):2-naphthalensulfonic acid (2NSA) 0.67; dinuclear fraction 0.44; trinuclear fraction 0.31; tetranuclear fraction 0.20; hexanuclear fraction 0.06.

Preparative separations were performed by silica gel flash-chromatography using previously reported solvents. Pure polynuclear fractions were obtained by a second flash-chromatography. After chromatography water solutions of pure products were desalified by ion-exchange (IRA 120).

Typical results after separations of a reaction with a ratio 2NSA/HCHO = 2/1 are: 2NSA - 6.4 g, dinuclear fraction - 1,2 g, trinuclear fraction - 0.7 g, polinuclear fraction - 1.0 g; with 2NSA/HCHO = 1/1: 2NSA-4.5 g, dinuclear fraction - 1.4 g, trinuclear fraction - 1.2 g, tetranuclear fraction - 0.8 g, polynuclear fraction - 1.7 g.

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