

# A $^{13}\text{C}$ n.m.r. study of the sulphonation of novolacs\*

Allan H. Fawcett

Department of Pure and Applied Chemistry, The Queen's University of Belfast, Northern Ireland

and John Guthrie and Kwong-Wing Lo

Department of Chemical Engineering, The Queen's University of Belfast, Northern Ireland

H. Pyszora

British Petroleum Research Centre, Sunbury-on-Thames, Middlesex, UK

(Received 15 January 1985; revised 6 February 1985)

A parameter scheme has been devised for predicting the  $^{13}\text{C}$  shifts of atoms in the aromatic rings of phenols substituted with  $-\text{SO}_3^-$ ,  $-\text{CH}_2-\text{Ar}$  and  $-\text{CH}_3$  in an alkaline medium, from the measured shifts of 30 different substituted benzene rings. The application of the scheme to novolacs is considered before the scheme is used to interpret the changes of chemical shift that occur upon sulphonation of one such sample. In the aromatic carbon region the sites of substitution on the rings are identified. In the upfield region of the spectrum a substantial alteration to the pattern of shifts from the bridging methylene groups was noted: once a ring had been sulphonated the methylene bridge might break to yield methylol groups, which then to a large extent reformed as methylene and dimethylene ether ( $-\text{CH}_2-\text{O}-\text{CH}_2-$ ) links, but with an increased proportion of abutments on sites *para* with respect to the phenolic group.

(Keywords:  $^{13}\text{C}$  n.m.r. parameter scheme; novolac; sulphonation)

$^{13}\text{C}$  n.m.r. spectroscopy is the latest of a number of techniques used in industry to characterize novolacs and resoles. While reports on the chemical shifts of carbons in novolacs and resoles have appeared<sup>1,2</sup>, here we describe the application of the n.m.r. method to elucidate the structures obtained when a novolac is sulphonated. Such products, polymeric phenols rendered soluble in water by the presence of the sulphonic acid group, have been used as synthetic tanning agents<sup>3</sup>. To eliminate any variation of ring carbon shift that would derive from a variable degree of dissociation of the phenolic group, the shifts of a series of model compounds have been studied in a strongly alkaline medium – to ensure that the phenolic group was always completely dissociated – prior to an examination of a novolac before and after sulphonation.

## EXPERIMENTAL

Standard methods were used for the preparation of 2,4-dimethylphenol-6-sulphonic acid<sup>4</sup>, and a mixture of di-, tri- and tetranuclear novolacs with an almost completely *o,o* type of linkage<sup>5</sup>. Samples of the three dimeric isomers were provided by British Petroleum (BP). A commercial novolac (5.0g, 0.047 mol), with an *o:p* ratio of 8.2:1, according to its i.r. spectrum, was sulphonated in 10 ml of dioxane with 9.5 ml (0.09 mol) of 98%  $\text{H}_2\text{SO}_4$  at 60°C. Two reaction times of 15 and 30 min were used. After cooling, the excess acid was neutralized with sodium carbonate. The products were dried under vacuum at 60°C.

\* Permission to publish this paper has been given by British Petroleum P.L.C.

$^{13}\text{C}$  n.m.r. spectra were obtained on a Bruker WH90 or a Jeol FX 200 instrument, using 0.5 g samples dissolved in 2 ml of a mixture of 3.0 g of NaOH, 0.4 ml of dioxane, 2.0 ml of  $\text{D}_2\text{O}$  made up to 10.0 ml with water.  $T_1$  values were 1.2 to 1.8 s (CH) and 0.8 to 1.2 s ( $\text{CH}_2$ ) in the dimer. The chemical shift of dioxane was adopted as an internal standard, at 66.60 ppm.

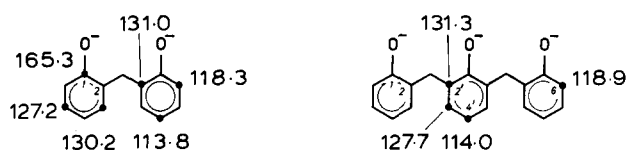
## RESULTS AND DISCUSSION

To establish the pattern of substitution effects upon the  $^{13}\text{C}$  chemical shifts of the aromatic nucleus, molecules in which the benzene ring contained one or more of the substituents  $-\text{O}^-$ ,  $-\text{CH}_3$ ,  $-\text{SO}_3^-$  and  $-\text{CH}_2-\text{Ar}$  were examined by  $^{13}\text{C}$  n.m.r. in aqueous alkali. The molecules included phenol, the three cresols, the six xylenols, the three phenol-formaldehyde dimers and the *o,o,o,o* trimer, phenyl sulphonic acid, *p*-toluene sulphonic acid, *o*- and *p*-phenol sulphonic acid, *o*-phenol-*p*-sulphonate, 2,4-dimethylphenol-6-sulphonate, and 2,6-dimethylphenol-4-sulphonate. Diphenylmethane-4,4'-disulphonic acid, being insoluble in alkali, was examined in acetone, which was assumed to be sufficiently polar to allow the strong acid to dissociate.

Assignment of the aromatic shifts was straightforward, for they usually suffered additive effects, as has been found for other groups<sup>6</sup>, but off-resonance experiments were needed to clarify cases where there were difficulties, such as arose from coincidences of shifts. Many of these shifts have already been reported<sup>7</sup>, and these, including some revised assignments, together with a supplementary number, may be obtained upon request. A parameter

scheme was devised for 149 ring carbon shifts in 25 of such molecules, the four rings of the three phenol-formaldehyde dimers and three shifts of the central ring of the entirely *o*-linked trimer. The values of the parameters were adjusted to obtain a minimum in the sum of squares of residuals, the difference between experimental and predicted shifts<sup>8</sup>. Besides the 14 parameters of Table 1, two further parameters were adopted: the shift of a substituted carbon should be reduced by 1.6 ppm if one or more *ortho* sites is occupied by  $-O^-$ ,  $-CH_2-$  or  $-CH_3$ , but be increased by that amount when  $-SO_3^-$  is in an *ortho* position, and if  $-O^-$  and  $-SO_3^-$  are neighbours the shift of a C-H *ortho* to the  $-O^-$  is 3.8 ppm more. Though this factor was based on only two experimental shifts, its value was much greater than the standard deviation of the fit (1.16 ppm). The situation may arise in sulphonated phenol-formaldehyde resins.

To illustrate the use of the shift parameter scheme we consider the <sup>13</sup>C n.m.r. spectrum of the mixture of high *ortho* oligomers. In the methylene region the dimer shift was seen at 30.9 ppm, the shift of the terminal methylene group of higher oligomers was seen at 31.6 ppm and the shift of interior methylene groups was at 32.5 ppm. From the height of these intensity peaks, and neglecting oligomers higher than the tetramer, the molar ratio of the first three oligomers was approximately 12:2:1. In the region between 110 and 140 ppm (Figure 1) the underlined shifts were assigned to the *o,o* dimer, being coincident with the shifts of a pure sample, as is indicated below, where the remaining shifts are also assigned to positions in the *o,o,o,o* trimer. Regarding the trimer as being obtained by substitution of the six position of the right-hand ring of the dimer, the shifts of atoms 2' and 4' were expected near 131 and 114 ppm, and were found at 131.3 and 114.0 ppm.



(When the two parameters omitted from Table 1 were allowed as variables, a factor of 0.10 was obtained for carbons at position 3 relative to the site of substitution by a benzyl derivative.)  $\delta_3$  was predicted to be either  $\delta_3(\text{dimer}) - 1.5 = 128.7$  ppm or  $\delta_5(\text{dimer}) + 0.9 =$

Table 1 <sup>13</sup>C n.m.r. chemical shift parameters for substitution to the benzene ring<sup>a</sup>

Substituent	Position relative to site of attachment				No. of molecules
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	
$-O^-$	37.6	-9.6	1.1	-14.7	24
$-SO_3^-$	13.1	-1.4	-0.8	3.7	13
$-CH_3$	9.8	0.9	-	-2.8	20
$-CH_2-Ph$	14.7	0.9	-	1.5	7

<sup>a</sup> Under alkali conditions shifts may be predicted by adding these parameters to the shift of benzene, taken to be 128.3 ppm, according to the pattern of substitution. For a substituted site an extra factor of 1.6 ppm is added if the adjacent site is occupied by an  $-SO_3^-$  group, but is subtracted if one or more adjacent sites is occupied by  $-O^-$ ,  $-CH_3$  or  $-CH_2-Ph$ . When  $O^-$  and  $-SO_3^-$  are adjacent, a C-H site next to the  $-O^-$  has an extra factor of 3.8 ppm. The standard deviation of the fit was 1.16 ppm; the least-square fit was obtained with a NAG routine<sup>8</sup>

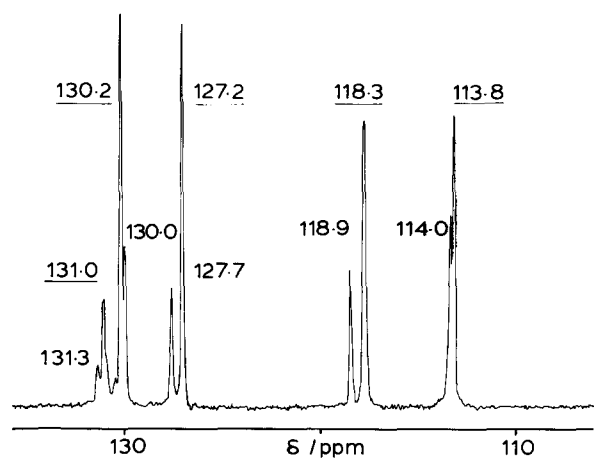


Figure 1 Part of the <sup>13</sup>C n.m.r. spectrum at 50.1 MHz of a mixture of dimeric, trimeric and higher oligomers of a high *ortho*-linked novolac. Pulse width 10  $\mu$ s (50°); acquisition time 0.82 s; pulse delay 5 s; 500 scans. Shifts were measured in ppm from the internal dioxane line, taken to be at 66.60 ppm in the aqueous alkali used. Assignments are indicated in the scheme alongside

128.1 ppm, both of which are in good agreement with the shift at 127.7 ppm. The remaining distinct shift at 118.9 ppm was assigned by default to C<sub>6</sub> of the end ring of a trimer (and tetramer), but the difference of 0.6 ppm

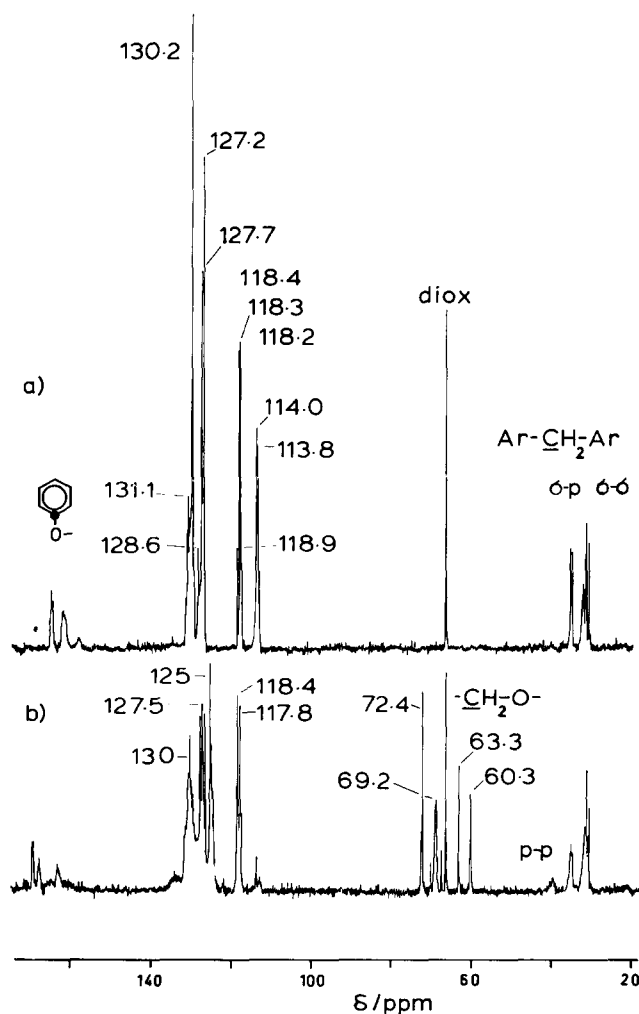
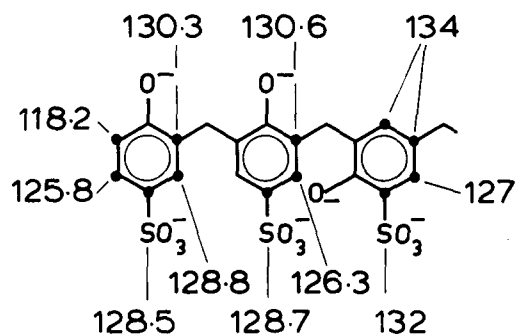


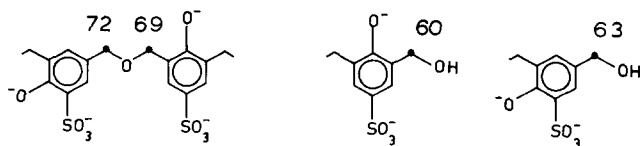
Figure 2 The <sup>13</sup>C n.m.r. spectrum at 50.1 MHz of a novolac with a high *ortho* content: (a), before, and (b) after sulphonation with sulphuric acid for 30 min. (Spectrometer settings as for the spectrum in Figure 1)

between that shift and the corresponding shift in the dimer (118.3 ppm) was not part of the parameter scheme. Such a variation was also seen at the end rings of these oligomers in neutral THF<sup>1</sup>, but was not observed at the end rings of the similar series of furfural oligomers<sup>9</sup>. Shift differences of this size and type lie outside the scope of this parameter scheme.

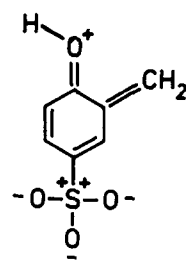
The <sup>13</sup>C n.m.r. spectra of a high *ortho* novolac resin before (a) and after (b) a 30 min sulphonation reaction are shown in Figure 2. While noting that sulphonation has produced a group of new resonances in the 60.0–75.0 ppm range near the dioxane reference peak, we first examine the region between 100 and 140 ppm. The most obvious change was the decrease in the intensities of the peaks at 113.8 and 114.0 ppm, from C<sub>4</sub> atoms of *o* end groups and of *o,o* interior rings that were the sites of sulphonation. (If sulphonation had occurred at other sites, for example at the 6 position of a 2-*ortho* end group, a shift would have appeared upfield of 114 ppm.) According to the scheme below, the appearance of a group of shifts at 125 ppm in Figure 2b is associated with 4-sulphonation of *o*-linked end groups. The appearance of the region below that is complicated, but consistent with the shift predictions that were made with the aid of the parameter set for –SO<sub>3</sub><sup>-</sup>. The predictions made in the scheme for a sulphonated *o,p* ring were made using 2,4-dimethyl phenol as the reference\*.



On each side of the dioxane reference peak is a set of new lines which are attributed to methylol groups, –CH<sub>2</sub>–OH, and to dimethylene ether links, –CH<sub>2</sub>–O–CH<sub>2</sub>–. In support of these assignments is their proximity to the dioxane shift<sup>2</sup>, and the similarity of the shift differences in this case to those between the corresponding groups in the furfural oligomers: methylol 19.5 ppm below bridging methylene, and dimethylene-ether a further 6.5 ppm downfield<sup>9</sup>. Such groups *para* to the –O<sup>-</sup> group are a further 3 ppm downfield.



The occurrence of methylol groups under acidic conditions was unexpected: usually a species such as



readily forms and quickly attacks another aromatic ring, but this particular species is prevented from forming by the presence of the electron-withdrawing sulphonic group that disrupts such a pattern of  $\pi$ -electrons. In the spectrum of the sample that had been sulphonated for the intermediate period of 15 min, the peaks near 114 ppm had diminished in intensity and the peaks at 125 ppm appeared, yet the methylol and methylene ether peaks had not appeared. This supported the view that methylene bridges might readily begin to breakdown only when at least one of the abutment rings has become sulphonated.

On the basis of the areas of the upfield peaks, 56% of the methylene bridges were broken, and under the dehydrating influence of the sulphuric acid formed ether links with 45% of the carbons concerned. The proportion of the methylol groups in the *ortho* position was less than in the *para* position (5 to 6%) and the proportion of dimethylene ether carbons in the *para* position was less than in the *ortho* position (20 to 25%), but these proportions were much more in favour of the *para* position than in the original resin. Perhaps some of the methylene carbons became detached, and later recombined to occupy *para* sites preferentially.

## REFERENCES

- 1 Sojka, S. A., Wolfe, R. A., Dietz, E. A. and Dannels, D. F. *Macromolecules* 1979, **12**, 767; and references cited therein
- 2 Kim, M. G., Tiedeman, G. T. and Amos, M. W. *Weyerhaeuser Sci. Symp.*, pp. 263–289, 1979 (1980); (CA 96: 182065n)
- 3 Kuntzel, A. and Schwank, M. *Collegium* 1940, **441**, 445
- 4 Katscher, E. and Lehr, H. *Monatsh.* 1934, **64**, 242
- 5 Dradi, E., Casiraghi, G., Sartori, G. and Casnati, G. *Macromolecules* 1978, **11**, 1295
- 6 Wehrli, F. W. and Wirthlin, T., 'Interpretation of Carbon-13 NMR Spectra', Heyden, London, 1976
- 7 Guthrie, J., Fawcett, A. H. and Kwong-Wing Lo *J. Soc. Leather Tech. Chem.* 1982, **66**, 107
- 8 The program has been used before: Fawcett, A. H., Ivin, K. J. and Stewart, C. D. *Org. Mag. Res.* 1978, **11**, 360
- 9 Fawcett, A. H. and Ddamba, W. A. *Makromol. Chem.* 1982, **183**, 2799

\* The ring shifts of this molecule were in order from position 1 to 6: 163.0, 128.6, 134.1, 118.9, 125.5 and 130.1 ppm