

Determination of Methylene Bridge Type of Mixed Meta- and Para-Cresol-Formaldehyde Novolaks by ^{13}C -NMR Spectroscopy

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SYNOPSIS

Cresol-formaldehyde resins are important components of photoresists for semiconductor fabrication. The type of methylene bridge and relative amounts thereof are key structural features that determine resin properties. Several model compounds were prepared that represent the various types of methylene bridges that are possible from condensation of meta- and para-cresol with formaldehyde. The methylene bridges were characterized by ^{13}C -NMR spectroscopy, and the assignments made were used to analyze spectra of cresol-formaldehyde novolak resin and several oligomer types. The effect of complexation with metal ion on the methylene bridge chemical shift was investigated for one oligomer. The effect of bridging position on the intramolecular hydrogen bonding of the phenolic hydroxyl group was investigated by infrared spectroscopy.

INTRODUCTION

Cresol-formaldehyde novolak resins are important components of photoresists for semiconductor fabrication. The relative amounts of cresol comonomers and distribution of type of methylene bridge are key structural features that determine resin properties. A previous publication from this laboratory¹ described determination of comonomer content by ^{13}C -NMR spectroscopy. deBreet and co-workers² discussed the ^{13}C -NMR spectra of phenol, *p*-cresol, and resorcinol-formaldehyde resins and made methylene bridge assignments. Pethrick and Thompson³ made methylene bridge assignments of phenol-formaldehyde resins by synthesis and spectroscopy of lower molecular weight model compounds and oligomers.

The steric effect of the 3-methyl group in *m*-cresol formaldehyde adducts yields additional isomeric possibilities to ortho-ortho and ortho-para substituted methylene bridges, that is, hindered and unhindered bridges. This work assigns methylene

bridge type in the cresol-formaldehyde resins by preparation and NMR spectroscopy of model compounds. The effect of oligomer length and diamagnetic ions on chemical shift have also been investigated for two types of oligomers. Also, the effect of the configuration of the isomers on intramolecular hydrogen bonding was investigated by infrared spectroscopy.

EXPERIMENTAL

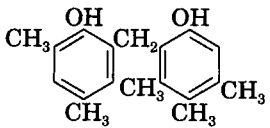
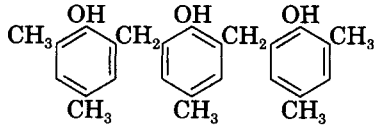
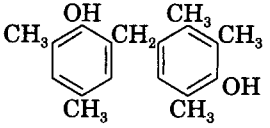
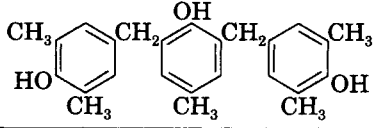
Spectroscopy

^{13}C -NMR spectra were obtained using a Bruker WP200 superconducting Fourier transform NMR spectrometer with a carbon frequency of 50.13 MHz. Approximately 1.5 g of sample was dissolved in 5 mL of DMSO-*d*₆ and spectra were recorded in 10 mm diameter sample tubes.

Spectra were recorded with a sweep width of 10,000 Hz using a pulse width of 8 μs (45° pulse angle) and broad-band proton decoupling. A read delay of 5 s was utilized between pulses and approximately 4000 transients were averaged.

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Table I Chemical Shift and Purity of Model Compounds

Compound	Delta, ppm in DMSO	LC Purity (Retention time)
I. 	27.4	90%, (3.2) ^a
II. 	30.5	82%, (5.9) ^a
III. 	33.5	95%, (5.5) ^b
IV. 	35.3	85%, (2.5) ^b

^aChromatographic conditions on octadecyl-bonded phase column at 1 mL/min. 60% CH₃CN/40% PH3 buffer.

^bChromatographic conditions on octadecyl-bonded phase column at 1 mL/min. 70% CH₃CN/30% PH3 buffer.

Synthesis

3,5,4',5',6'-Pentamethyl-2,2'-dihydroxy-diphenylmethane (I)

A solution of 5.6 g (0.3 mol) of 6-methylolated 2,4-dimethylphenol was dissolved with 5 g (.037 mol) 3,4,5-trimethyl phenol in 25 g of methanol; 2 g of 37% HCl were added and the mixture was heated for 2 h at 45°C while stirring. The mixture was cooled to room temperature and a precipitate was isolated. The product was washed with methanol and dried in a vacuum oven at 45°C.

The 6-methylolated 2,4-dimethylphenol was prepared by dissolving 30.5 g of 2,4-dimethylphenol in 102 g of methanol and adding 25 g of 85% KOH

dissolved in 102 g of water with stirring. Then 472 g of 37% formaldehyde was added and the solution was heated to 45°C for 1 h. Acetic acid was added to neutralize to pH 7 and 200 mL of water was added, and the solution was let stand. The product was separated as an oily top layer and dried under vacuum at 45°C.

2,6-Bis(2-hydroxy-3,5-dimethylbenzyl)-4-methylphenol (II)

A solution of 108.6 g (0.82 mol) of 2,4-dimethyl phenol was added to 2.5 g of 37% hydrochloric acid with stirring; 19.8 g (0.118 mole) of 2,6-bis-(methylol)-*p*-cresol was added slowly with stirring

Table II Infrared Hydroxyl Stretch Frequency of *o-o* Bridged Oligomer

Compound	Hydroxyl Frequency Maximum, cm ⁻¹
I (Table I), (<i>o-o</i>) hindered	3400
II (Table I), (<i>o-o</i>) unhindered	3200

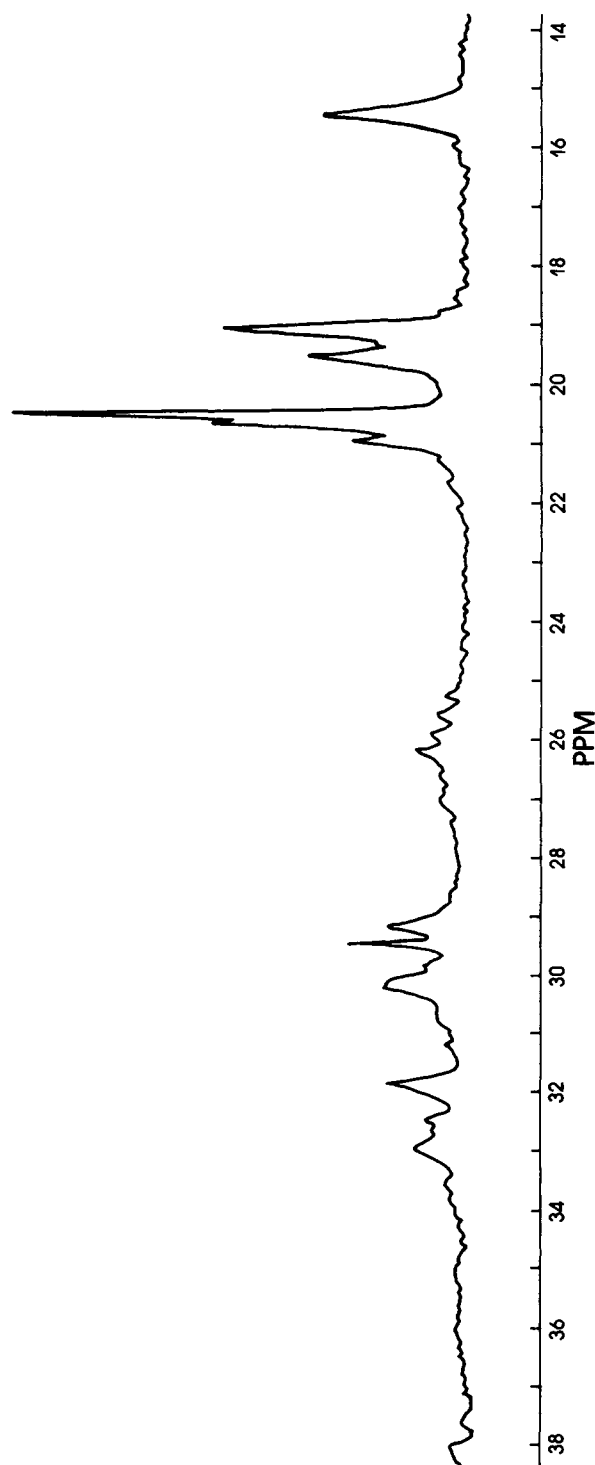


Figure 1 ^{13}C -NMR spectrum of *m*-cresol/*p*-cresol novolak in methylene region.

with the temperature increasing to 38°C. The mixture was heated at 48°C for 3 h. Xylene (100 mL) was added and the mixture heated to 55°C. The xylene solution was filtered and cooled and the product isolated after precipitation.

3,5,2',3',5'-Pentamethyl-2,4'-dihydroxydiphenylmethane (III)

A solution of 7.6 g (0.056 m) of 2,3,6-trimethylphenol was added to 2 g of sodium hydroxide dissolved in 8 g of water; 7.6 g (0.05 mol) of 6-methylolated-2,4-dimethylphenol was added and the solution was stirred for 2 h at 55°C. A heavy precipitate formed. Hydrochloric acid was added to neutralize the mixture along with 50 mL of water. The precipitate was isolated and dried at 45°C under vacuum.

2,6-Bis(4-hydroxy-3,5-dimethylbenzyl)-4-methylphenol (IV)

A solution of 25 g (0.21 mol) of 2,6-dimethylphenol was dissolved in 45 g of ethanol; 0.6 g of concentrated hydrochloric acid was added and 4.96 g (0.0295 mole) of 2,6-bis(methylol)-*p*-cresol were added slowly with stirring. Then 23 g of ethanol was added and the mixture heated at 55°C for 6 h. The ethanol was distilled at 100°C until 58 g (85%) of the ethanol was recovered in the distillate. The mixture was cooled to room temperature, and the product separated as a precipitate. The product was isolated and dried at 45°C under vacuum.

RESULTS AND DISCUSSION

Several types of methylene bridge are possible upon condensation of meta- and para-cresol with formaldehyde: *o-o*, *o-p*, and *p-p* (relative to OH) condensation can occur, the chemical shift value becoming more deshielded with para substitution.^{2,3} In addition, the methylene group can be sterically crowded by the *m*-methyl of *m*-cresol, the chemical shift becoming more shielded with steric hindrance.⁴ The model compounds I to IV (Table I) were prepared to assign chemical shifts to hindered and unhindered *o-o* and *o-p* methylenes. No *p-p* substituted standards were prepared because no chemical shifts in the 40 ppm region indicative of *p-p* substitution were found in the novolaks and oligomers analyzed. The chemical shifts were measured in DMSO (carbon multiplet at 40 ppm) rather than methanol (carbon multiplet at 49 ppm) because some of the standards were insoluble in methanol. Table I lists the chemical shifts and purity (liquid chromatography) of

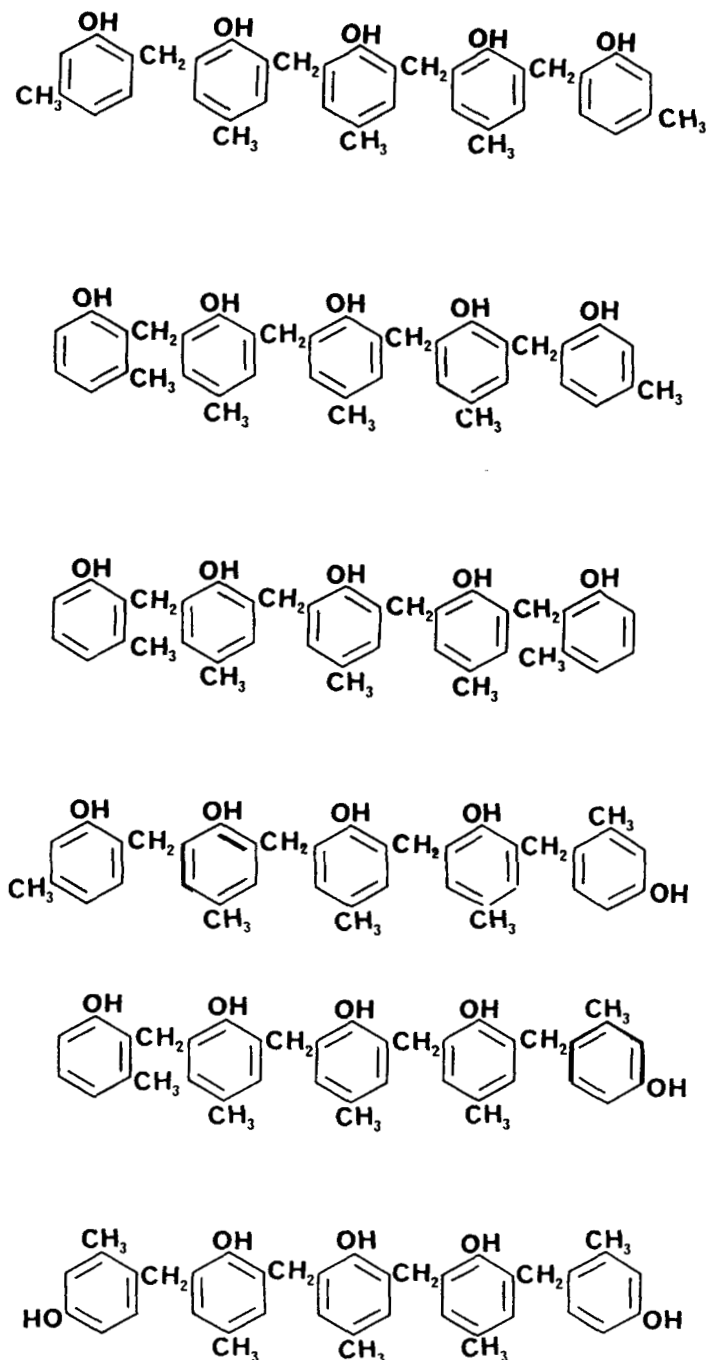


Figure 2 Isomers from *m*-cresol and bis-methylolated *p*-cresol trimer.

standards I to IV. The expected upfield shift occurs when the *o-o* and *o-p* standards were sterically crowded but not in the case of the *o-p* standard.

The ¹³C spectrum of a 60% *m*-cresol/40% *p*-cresol novolak (Fig. 1) contained peaks expected in the 26 ppm (hindered *o-o*), 29–30 ppm (unhindered *o-o*), and 32–34 ppm (ortho-para) regions. However, no

peaks were observed downfield from the *o-p* region, indicating no *p-p* bridges are formed.

Another novolak oligomer investigated was the reaction product of *m*-cresol with bismethylolated *p*-cresol trimer. Five isomeric products are possible (Fig. 2), and indeed five components were observed by liquid chromatography. The possible isomers

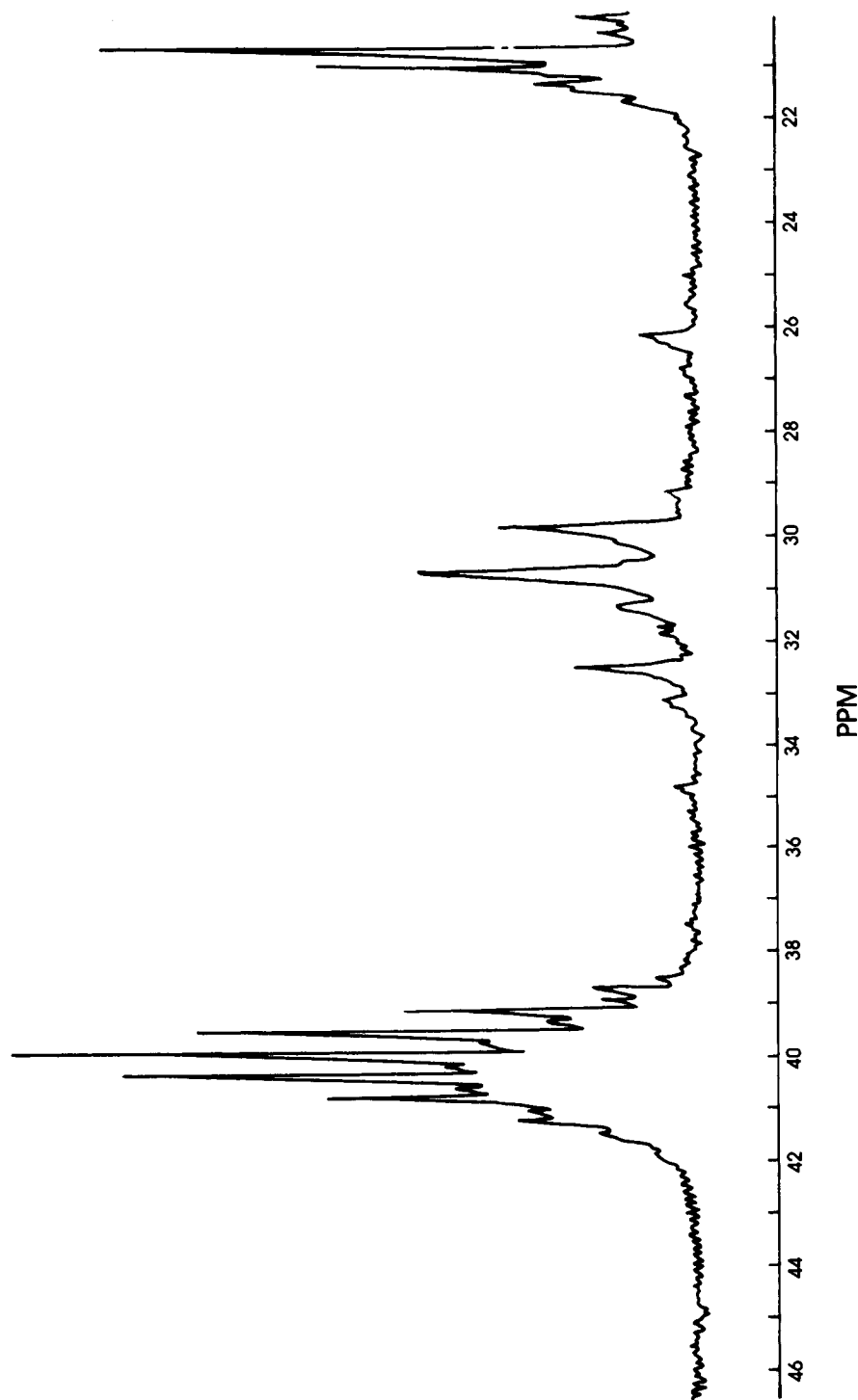


Figure 3 ^{13}C -NMR spectrum of pentamer from *m*-cresol and bis-methylolated-*p*-cresol trimer in methylene region.

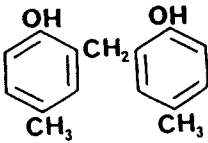
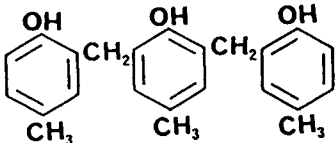
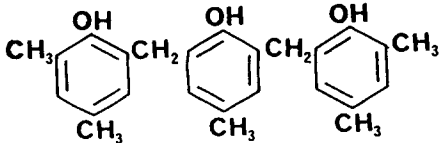
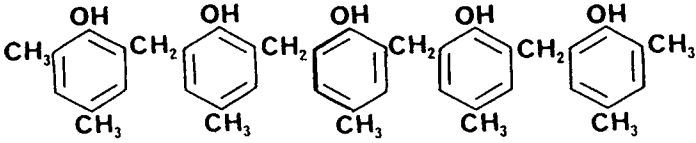
STRUCTURE	CHEMICAL SHIFT (DMSO), PPM
	29.5
	30.0
	30.5
	30.6
P-CRESOL POLYMER	29.6, 30.3, 30.7

Figure 4 Chemical shift vs. length of *o-o* substituted *p*-cresol oligomers.

contain (*o-o*) hindered, (*o-o*) unhindered, and (*o-p*) methylene bridges. The NMR spectrum (Fig. 3) contains peaks in the (*o-o*) hindered, (*o-o*) unhindered, and (*o-p*) regions.

The chemical shift value of the ortho-ortho methylene bridge was investigated as a function of oligomer length (Fig. 4). The chemical shift value increases by increments of 0.5 ppm for *p*-cresol dimer to trimer. The methyl-substituted trimer increases another 0.5 ppm, identical to that of the methyl-terminated pentamer. The chemical shift values found for *p*-cresol-formaldehyde novolac were 29.6, 30.3, and 30.7. The chemical shift of the *o-o* methylene bridge in these *p*-cresol oligomers in-

crease to 30.5, and the value is then constant. The identical values for the methyl-substituted trimer and pentamer indicate that 3-substitution from the methylene bridge has the same effect whether the substitute is a methyl or benzyl group.

Complexation of ortho-ortho bridged phenolic oligomers can shift the methylene bridge frequency. The trimer reaction product from 2,6-bismethylolated *p*-cresol and 2,3-dimethylphenol was prepared, and the three isomeric possibilities were found by liquid chromatography. The NMR spectrum of the product (Fig. 5) indicated two ortho-ortho bridges barely resolved at 30.8 ppm and an *o-p* bridge at 33.7 ppm. Addition of 3% zinc acetate to the 30% solution

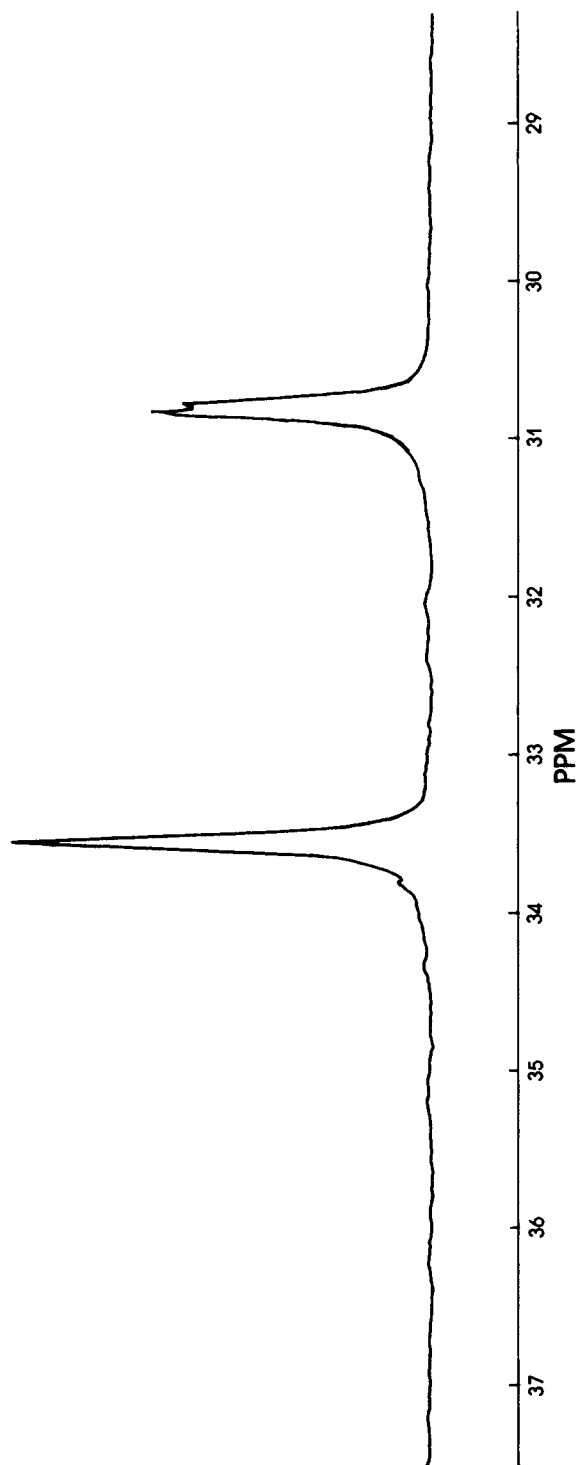


Figure 5 ^{13}C -NMR spectrum of trimer isomers from 2,3-dimethylphenol and 2,6-bis-methylolated-*p*-cresol in methylene region.

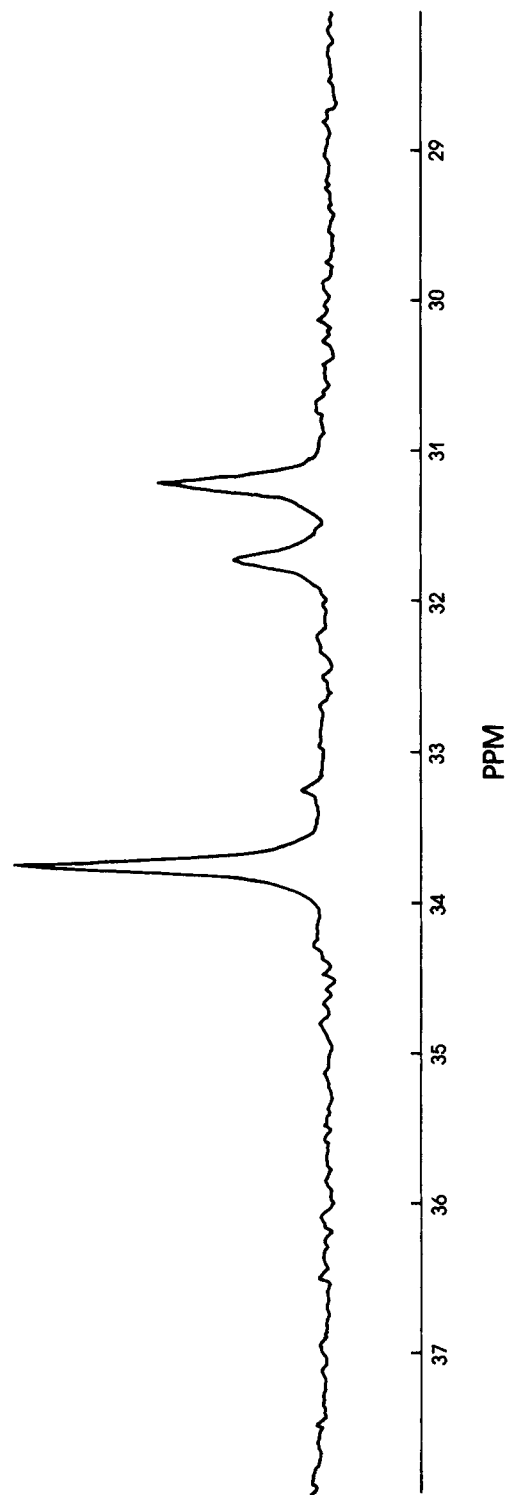


Figure 6 ^{13}C -NMR spectrum of trimer isomers with zinc acetate added.

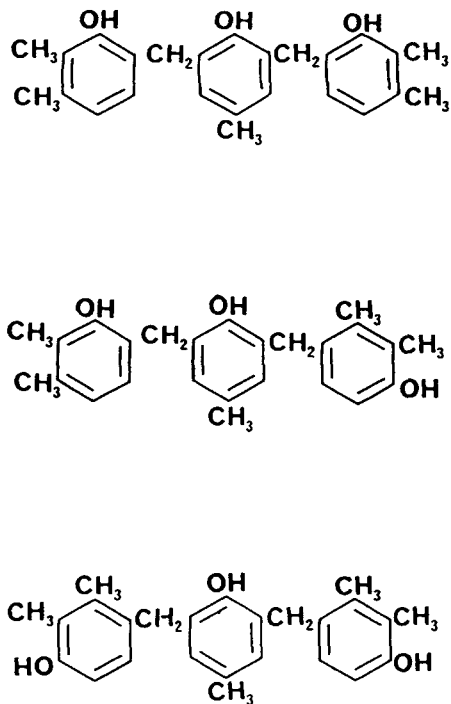


Figure 7 Trimer isomers from 2,3-dimethylphenol and 2,6-bismethylol-*p*-cresol.

in DMSO resolved the ortho-ortho peaks to 31.2 and 31.8 ppm (Fig. 6). The three isomers possible for this product (Fig. 7) contain two types of *o-o*

bridges, the *o-o*, *o-o* most likely forms a stronger complex with zinc and a larger shift results.

The effect of bridging position on the intramolecular hydrogen bonding of the phenol group can be seen by comparison of infrared spectra of the two ortho-ortho bridged model compounds. Table II shows that the OH stretching frequency of the unhindered ortho-ortho standard (structure III, Table I) is lower than that of the hindered ortho-ortho standard (structure I, Table I). The spectra were recorded in 0.1% solutions in KBr pellets, a concentration low enough to minimize intermolecular hydrogen bonding. This would indicate that the unhindered isomer participates in more intramolecular hydrogen bonding, which would be expected from the stereochemistry.

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