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# **Spectral Assignments and Reference Data**

## A <sup>13</sup>C NMR study of the methylol derivatives of 2,4'- and 4,4'-dihydroxydiphenylmethanes found in resol phenol-formaldehyde resins

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Received 19 April 2002; revised 15 July 2002; accepted 25 July 2002

A total of 13 of the 16 possible methylol derivatives of 2,4'- and 4,4'-dihydroxydiphenylmethane have been synthesized, isolated, and identified. These compounds are found as intermediates in the cure process of resol phenol-formaldehyde (PF) resins. Analysis of the  $^{13}$ C NMR spectra (in acetone- $d_6$ ) of these compounds provided a way to evaluate the seven methylolphenol ring types (methylol derivatives of 2-hydroxyphenyl and 4-hydroxyphenyl rings) found in typical resol PF resins using the ipso carbon region from 150 to 160 ppm. A simple diagnostic test was developed using the chemical shift values of the methylol methylene carbon atoms to identify the presence of intermediates containing either a 2-hydroxyphenyl or a 4-hydroxyphenyl ring. Using these data it is now possible to analyze the major components in extracted prepreg PF resins. Copyright © 2002 John Wiley & Sons, Ltd.

**KEYWORDS:** NMR; <sup>1</sup>H NMR; <sup>13</sup>C NMR; phenol-formaldehyde resins; dihydroxydiphenylmethanes

### INTRODUCTION

Phenol-formaldehyde (PF) resins, the first totally synthetic polymers, have wide commercial applications as molding compounds, coatings, wood binders, and high-temperature ablatives.<sup>1</sup> Several kinetic studies of the condensation reactions of phenol and formaldehyde have been reported,<sup>2–6</sup> but clear experimental verification of the major intermediates formed in the PF cure process has been difficult to obtain. The first compounds formed in base-catalyzed PF condensation reactions are mono-, di-, and tri-methylol (CH<sub>2</sub>OH) derivatives of phenol. Condensation of these methylolphenols with themselves or with another molecule of phenol results in dihydroxydiphenylmethanes (HO–Ar–)<sub>2</sub>CH<sub>2</sub> that contain methylol groups.<sup>6,7</sup> Additional methylol groups can be added to these dihydroxydiphenylmethanes by further condensation reactions with formaldehyde.<sup>4,8</sup>

Earlier, we reported a <sup>13</sup>C NMR method for the analysis of resol PF prepolymer resins based on nine model compounds.<sup>9</sup> In order to analyze the next cure stage (called prepreg) more comprehensively, it was necessary to extend the range of model compounds to include the methylol derivatives of the dihydroxydiarylmethanes, which are common intermediates found in this cure stage.

In this work we report <sup>1</sup>H and <sup>13</sup>C NMR data on 13 of the 16 possible methylol derivatives of 4,4'-dihydroxydiphenylmethane (4,4'methylenebisphenol) and 2,4'-dihydroxydiphenylmethane (2[(4hydroxyphenyl)methyl]phenol); see Fig. 1. Analysis of these data led to an improved NMR method for the analysis of methylolphenol dimers and oligomers found in the cure process of PF resins.

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Contract/grant sponsor: NASA/MSFC.



2,4'-Dihydroxydiphenylmethanes (7-18)

4,4'-Dihydroxydiphenylmethanes (1 - 6)  $[A = CH_2OH \text{ (methylol) (m) or }H]$ 

Compa	3	5	3	5
1 =	н	Н	Н	н
2 =	m	Н	Н	н
3 =	m	Н	m	Н
4 =	m	m	Н	Н
5 =	m	m	m	н
6 =	m	m	m	m

Co	mpd	<u>3</u>	<u>5</u>	<u>3′</u>	<u>5′</u>
7	=	н	Н	н	н
8	=	m	Н	Н	н
9	=	Н	m	Н	н
10	=	Н	Н	m	н
11	=	m	m	Н	н
12	=	Н	н	m	m
13	=	m	н	m	Н
14	=	Н	m	m	н
15	=	m	m	m	н
16	=	m	Н	m	m
17	=	Н	m	m	m
18	=	m	m	m	m



### EXPERIMENTAL

#### Materials

4,4'-Dihydroxydiphenylmethane (1), formaldehyde (37%), phenol, and acetone- $d_6$  were used as purchased from Aldrich Chemical Co. 2,4'-Dihydroxydiphenylmethane (7) was used as purchased from TCI America.

#### Syntheses of compounds 2-6

4,4'-Dihydroxydiphenylmethane (1), 0.797 g (4.0 mmol), 1.2 ml of 37% formaldehyde, and 2.0 ml of 0.6 M NaOH were heated for 1 h at 60 °C. Products **2–6** were separated by preparative thin-layer chromatography (TLC) on silica gel using methanol(8)/chloroform(60).  $R_f$  values found for compounds **2–6** are for this solvent system; if additional elution solvent systems were used, then their  $R_f$  values are also given: compound **6** has an  $R_f = 0.19$ ; compound **7**,  $R_f = 0.25$ ; compound **3**,  $R_f = 0.36$ , then with chloroform(9)/ethanol(0.7),  $R_f = 0.23$ ; compound **4**,  $R_f = 0.36$ ; then with chloroform(9)/ethanol(0.6)/methanol(0.7),  $R_f = 0.28$ ; compound **2**,  $R_f = 0.48$ .

### Syntheses of compounds 8, 10-13, 15, and 18

2,4'-Dihydroxydiphenylmethane (7), 0.892 g (4.4 mmol), 1.34 ml of 37% formaldehyde, and 2.0 ml of 1.4 M NaOH were heated for 1 h. at 60 °C. The products were separated by preparative TLC on silica gel using methanol(1)/chloroform(10).  $R_f$  values given for compounds 8, 10–13, 15, and 18 are for this solvent system. If additional elution solvent systems were used, then their  $R_f$  values are also given: compound 18 has an  $R_f = 0.12$ ; compound 15,  $R_f = 0.19$ , then with chloroform(2)/ethanol(2.5)/methanol(0.7),  $R_f = 0.55$ ; compound 11,  $R_f = 0.31$ ; compound 12,  $R_f = 0.43$ ; compound 13,  $R_f = 0.49$ ; compound 10,  $R_f = 0.56$ ; compound 8,  $R_f = 0.64$ .

### Synthesis of 9

5-Methylol-2,4'-dihydroxydiphenylmethane (9) was prepared by the LiAlH<sub>4</sub> reduction of 5-carboxy-2,4'-dihydroxydiphenylmethane, which was obtained from 5-bromo-2,4'-dihydroxydiphenylmethane using the procedure of Carpenter and Hunter<sup>10</sup> and collected by preparative TLC on silica gel using methanol(1)/chloroform(9). 5-Bromo-2,4'-dihydroxydiphenylmethane was prepared from the dehydration reaction of 5-bromo-2-methylolphenol with phenol under acid conditions.

Contract/grant sponsor: Hercules Aerospace Company.



### NMR experiments

All spectra were obtained on a General Electric QE-300 NMR spectrometer at 25 °C observing <sup>1</sup>H and <sup>13</sup>C at 300.67 MHz and 75.61 MHz respectively. <sup>1</sup>H NMR spectra were collected into 32K data sets over a spectral width of 6 kHz using a 30° pulse. <sup>13</sup>C spectra were collected into 32K data sets over a spectral width of 20 kHz using a 40° pulse and were processed using exponential multiplication with 1 Hz line broadening. Acetone- $d_6$  containing (TMS) tetramethylsilane was the solvent used for all compounds.

### **RESULTS AND DISCUSSION**

In resol PF polymerization, only methylol derivatives of 2,4'and 4,4'-dihydroxydiphenylmethanes are formed as intermediates in the cure process, and no methylol derivatives of 2,2'dihydroxydiphenylmethane are found.<sup>6,9,11–14</sup> To develop further our comprehensive <sup>13</sup>C NMR method<sup>9</sup> to monitor the early stages of resol PF polymerization, each of the individual methylol isomers of 2,4'- and 4,4'-dihydroxydiphenylmethanes were needed as model compounds. To this end, an attempt was made to synthesize and isolate each of these compounds, 1-18, shown in Figure 1.

All five methylol derivatives (2-6) of 4,4'-dihydroxydiphenylmethane (1) were prepared by the reaction of 1 with excess formaldehyde and base at 60 °C for 1 h. Each compound was isolated by preparative TLC on silica gel. The <sup>1</sup>H and <sup>13</sup>C NMR assignments of compounds 1-6 are given in Table 1. It should be emphasized that all of the <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values reported here are specific for the NMR solvent acetone- $d_6$ . Chemical shift values from other NMR solvents cannot be used in our correlation, as discussed previously.<sup>9</sup> A recent study<sup>15</sup> found both acetone-d<sub>6</sub> and DMSO-d<sub>6</sub>

to be good quantitative solvents for <sup>13</sup>C NMR analysis of PF resins with shorter acquisition times available using added Cr(acac)<sub>3</sub>.

Reaction of 2,4'-dihydroxydiphenylmethane (7) with excess formaldehyde and base at 60 °C for 1 h resulted in seven (8, 10-13, 15, 18) of the 11 possible methylol derivatives of 7. Each compound was isolated by preparative TLC on silica gel and identified by <sup>1</sup>H and <sup>13</sup>C NMR. A trace of 16 was isolated and identified by <sup>1</sup>H NMR, but not enough was isolated to obtain a <sup>13</sup>C NMR spectrum.

5-Methylol-2,4'-dihydroxydiphenylmethane (9) was prepared by the by LiAlH<sub>4</sub> reduction of 5-carboxy-2,4'-dihydroxydiphenylmethane, which was prepared from 5-bromo-2-methylolphenol by condensation with phenol, lithiation with BuLi, and carbonation using the procedure of Carpenter and Hunter.<sup>10</sup> The only methylol derivatives of 2,4'-dihydroxydiphenylmethane that could not be synthesized and identified were 14, 16, and 17. The <sup>1</sup>H and <sup>13</sup>C NMR assignments of compounds 7-13, 15, and 18 are given in Table 2.

There are seven different methylolphenol ring types found in dihydroxydiphenylmethanes 1-18, as shown in Fig. 2. These methylolphenol ring types are called A-G here for discussion purposes. Types A, B, and C all have the 4-hydroxyphenyl ring system, whereas types D, E, F, and G all have the 2-hydroxyphenyl ring system.

The most diagnostic carbon atoms found in the <sup>13</sup>C NMR spectra of compounds 1-18 are the ring carbon atoms, which are directly bonded to a hydroxyl group. There is only one such carbon per phenol ring, and this carbon is often referred to as the 'ipso' carbon. The ipso carbon atoms in 2,4'-dihydroxydiphenylmethane (7) are C-2 and C-4'. The chemical shifts of ipso carbon atoms are found in the  $^{13}\mbox{C}$  NMR spectra of phenolic compounds between 150 and 160 ppm. The second most diagnostic kind of carbon atom found in the <sup>13</sup>C NMR spectra of 1-18 are the bridge methylene carbon

C or (H)	<b>1</b> <sup>a</sup>	2	3	4	5	<b>6</b> <sup>a</sup>
1	133.71	133.68	133.70	133.40	133.44	133.42
2	130.45 (7.01, d, 8.1)	130.45 (7.08, d, 2.1)	128.06 (6.97, s)	127.39 (6.97, s)	127.42 (6.97, s)	127.48 (6.97, s)
3	115.93 (6.74, d, 8.1)	128.70	128.79	127.74	127.60	127.60
4	156.36	154.38	154.35	152.82	152.74	152.73
5	115.93 (6.74, d, 8.1)	115.94 (6.71, d, 8.1)	115.87 (6.73, d, 8.4)	127.74	127.68	127.60
6	130.45 (7.01, d, 8.1)	128.07 (6.92, dd, 2.1, 8.1)	128.87 (7.01, d, 8.4)	127.39 (6.93, s)	127.42 (6.97, s)	127.48 (6.97, s)
1′	133.71	133.73	133.70	133.73	133.62	133.42
2′	130.45 (7.01, d,	128.98 (7.03, d,	128.06 (6.97, s)	130.46 (7.08, d, 8.1)	128 <sup>b</sup> (7.10, d, 2.1)	127.48 (6.97, s)
3′	8.1) 115.93 (6.74, d, 8.1)	8.4) 115.94 (6.73, d, 8.4)	128.79	115.94 (6.71, d, 8.1)	128.10	127.60
4′	156.36	156.42	154.35	156.42	154.25	152.73
5′	115.93 (6.74, d, 8.1)	115.94 (6.73, d, 8.4)	115.87 (6.73, d, 8.4)	115.94 (6.71, d, 8.1)	115.85 (6.71, d, 8.1)	127.60
6'	130.45 (7.01, d, 8.1)	128.98 (7.03, d, 8.4)	128.87 (7.01)	130.46 (7.08, d, 8.1)	128 <sup>b</sup> (6.92, dd, 2.1, 8.1)	127.48 (6.97, s)
ArCH <sub>2</sub> Ar	40.72 (3.76)	40.90 (3.76, s)	41.07 (3.77, s)	41.00 (3.76, s)	41.15 (3.75, s)	41.09 (3.74, s)
ArCH <sub>2</sub> OH		61.99 (4.69, s)	61.95 (4.69, s)	62.28 #3,5 (4.72, s, #3,5)	62.18 #3,5 (4.71, s, #3,5) 61.73 # 3' (4.67, s, #3')	62.12 (4.71, s)
Unassigned					128.62 128.94	

Table 1. <sup>13</sup>C and (<sup>1</sup>H, J, Hz) chemical shift values (ppm) for 4,4'-dihydroxydiphenylmethanes 1-6 in acetone-d<sub>6</sub> solvent

<sup>a</sup> See Ref. 9.

<sup>b</sup> See unassigned peaks at bottom of table.



Table 2. <sup>13</sup> C	and ( <sup>1</sup> H, <i>J</i> , Hz)	chemical shift v	/alues (ppm) for 2,4′-c	dihydroxydiphe	nylmethanes 7-	- <b>13, 15, 18</b> in ac∈	stone-d <sub>6</sub> solvent		
C or (H)	7 <sup>a</sup>	8	6	10	11	12	13	15	18
1	129.26	129.82	128.88	129.21	128.97	129.47	129.15	128.02	129.41
7	155.68	155.02	154.73	155.74	153.96	155.72	154.88	153.95	153.87
ю	115.80	126.37	115.55	115.83	129.46	115.86	129.86	129 <sup>b</sup>	129.00
	(6.84, d, 7.5)		(6.80, d, 8.1)	(6.84, d, 7.5)		(6.84, d, 7.4)			
4	127.82	126.07	126.61	127.79	124.92	127.82	126.08	124.92	124.93
	(6.99, t, 7.5)	(6.92, d, 7.4)	(7.01, dd, 2.1, 8.1)	(7.01)	(6.98, d, 1.5)	(7.00, t, 7.4)	(66.9)	(6.98, s)	(6.98, d, 1.9)
5	120.34	119.95	132.99	120.27	132.93	120.30	119.96	132.92	132.59
	(6.74, t, 7.5)	(6.71, t, 7.4)		(6.73, t, 7.5)		(6.73, t. 7.4)	(6.70, t, 7.5)		
6	131.18	130.17	130.09	131.19	126.05	131.22	130.12	126.08	126.17
	(7.06, d, 7.5)	(6.97, d, 7.4)	(7.04, d, 2.1)	(66.9)	(6.92, d, 1.5)	(7.02, d, 7.4)	(66.9)	(6.98, s)	(6.92, d, 1.9)
1'	132.92	132.79	134.29	132.90	133.99	132.62	132.66	133.96	133.83
2′	130.62	130.66	130.60	129.30	130.65	127.67	128.06	129 <sup>b</sup>	127.54
	(7.08, d, 8.3)	(7.05, d, 8.4)	(7.08, d, 8.4)	(7.13, d, 2.0)	(7.08, d, 8.4)	(7.03, s)	(7.13, d, 2.1)	(7.13, d, 1.6)	(7.03, s)
3′	115.80	115.83	115.79	128.94	115.81	127.58	129.00	127.66	127.70
	(6.73, d, 8.3)	(6.73, d, 8.4)	(6.72, d, 8.4)		(6.72, d, 8.4)				
4′	156.27	156.39	156.32	154.32	156.34	152.80	154.21	154.35	152.74
5'	115.80	115.83	115.79	115.83	115.81	127.6 <sup>b</sup>	115.75	115.84	127.70
	(6.73, d, 8.3)	(6.73, d, 8.4)	(6.72, d, 8.4)	(6.70, d, 8.4)	(6.72, d, 8.4)		(6.73, d, 7.8)	(6.70, d, 8.2)	
6'	130.62	130.66	130.60	131.19	130.65	127.6 <sup>b</sup>	129.86	128.96	127.54
	(7.08, d, 8.3)	(7.05, d, 8.4)	(7.08, d, 8.4)	(7.02, d, 8.1)	(7.08, d, 8.4)	(7.03, s)	(96.9)	(7.01, d, 8.2)	(7.03, s)
$ArCH_2Ar$	35.39	35.12	35.45	35.48	35.20	35.53	35.23	35.28	35.32
		(3.86, s)	(3.86, s)	(3.86, s)	(3.86, s)	(3.86, s)	(3.86, s)	(3.85, s)	
ArCH <sub>2</sub> OH		64.22 #3	64.66 #5	62.10 #3′	64.33 #3	62.36 #3′, 5′	63.72 #3	64.61 #5	64.56 #5
		(4.83, s, #3)	(4.45, s, #5)	(4.69, s, #3')	(4.83, s, #3)	(4.71, s, #3',5')	(4.83, s, #3)	(4.44, s, #5)	(4.44, s, #5)
					64.61 #5		61.66 #3'	64.30 #3	64.11 #3
					(4.44, s, #5)		(4.69, s, #3')	(4.83, s, #3)	(4.81, s, #3)
								62.14 #3/	62.26 #3', 5'
								(4.69, s, #3')	(4.70, s, #3', 5')
Unassigned								129.46, 129.26	
<sup>a</sup> See Ref. 9. <sup>b</sup> See unassi£	med peaks at b	ottom of table.							





750

**Figure 2.** Methylol-substituted phenolic ring types, A-G, found in 2,4'- and 4,4'-dihydroxydiphenylmethanes. Ipso <sup>13</sup>C chemical shifts shown above OH groups, methylene <sup>13</sup>C chemical shift shown to left of CH<sub>2</sub> groups and methylol <sup>13</sup>C chemical shift shown above CH<sub>2</sub>OH groups.



**Figure 3.** Ipso <sup>13</sup>C chemical shift ranges **A**–**G** for diarylmethanes (top), and for methylolphenols (bottom) using compound numbers from Ref. 9.

atoms, Ar–CH<sub>2</sub>–Ar, which bond the two phenol rings together. Such aryl-connecting methylene carbon atoms are found in  $^{13}$ C NMR spectra in the region 30–41 ppm. The methylene carbon atoms of methylol groups, Ar–CH<sub>2</sub>–OH, can also give further diagnostic information about the ring types **A–G**. The methylol methylene carbon atoms in **1–18** are found in their  $^{13}$ C NMR spectra between 60 and 65 ppm.

A summary of the <sup>13</sup>C NMR chemical shift values of the ipso, bridge methylene, and methylol methylene carbon atoms on methylolphenolic ring types A-G is given in Fig. 2.

The <sup>13</sup>C chemical shifts of ipso carbon atoms of methylolphenols were discussed in our previous work.<sup>9</sup> Here, we add to that list the <sup>13</sup>C chemical shifts of the ipso carbon atoms of methylol derivatives of 2,4'- and 4,4'-dihydroxydiphenylmethanes given in Tables 1 and 2. Ipso ring carbon types **A**, **B**, and **C** are found in both 2,4'- and 4,4'-dihydroxydiphenylmethanes, since each contains at least one 4-hydroxyphenyl ring. The presence of one *ortho*-methylol group causes a 4-ipso carbon to be shielding by 2.1 ppm; the addition of a second *ortho*-methylol group causes an additional 1.5 ppm upfield shift. The effects of methylol substituents on the <sup>13</sup>C chemical shifts of the ipso carbon atoms in 2-hydroxyphenyl ring types **D**–**G** are in the same direction, but of a smaller magnitude.

a smaller magnitude. The ipso <sup>13</sup>C chemical shift region for phenolic ring types A-Gare shown in Fig. 3 above the chemical shift scale. The ipso chemical shifts of the methylolphenols studied earlier<sup>9</sup> are also given in Fig. 3 below the chemical shift scale. Figure 3 can be used to assign the ipso region of various stages of cure found in PF resins up to and including the prepreg stage.

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The bridge methylene chemical shift values have been used<sup>4,8,9</sup> as the easiest way to evaluate the amount and type of diphenylmethanes present in the various stages of cure found in PF resins. A methylene between two 4-hydroxyphenyl rings comes at 40.97  $\pm$  0.14 ppm, a methylene between a 4-hydroxyphenyl ring and a 2-hydroxyphenyl ring comes at 35.32  $\pm$  0.14 ppm, and a methylene between two 2-hydroxyphenyl rings comes at 30.5 ppm in acetone- $d_{6}$ .

The methylol methylene chemical shift data from 60 to 65 ppm in acetone- $d_6$  solvent can by used in a diagnostic manner. If there is a methylol carbon peak in this region that is less than 63.0 ppm, then this methylol is on a 4-hydroxyphenyl ring. If a peak in this region is greater than 63.0 ppm, then it represents a methylol group on a 2-hydroxyphenyl ring. If there is no peak in the 60 to 65 ppm region but there is a peak near 35 ppm or 41 ppm, then there is an unsubstituted 2-hydroxyphenyl- or 4-hydroxyphenyl-containing compound respectively in the resin mixture. This correlation also holds for trimeric and oligomeric PF methylolarylmethane derivatives.

Using the <sup>13</sup>C NMR data presented here, it is now possible to evaluate the chemical components in extracted prepreg PF resins. This information is also being used to evaluate cured PF resins using solid-state <sup>13</sup>C NMR.

### Acknowledgements

The authors acknowledge support for this research from NASA/MSFC and Hercules Aerospace Company. We also like to thank the Mississippi Magnetic Resonance Facility at Mississippi State University for use of GE-QE 300 NMR.

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