Examination of some melamine—formaldehyde adducts by ^{13}C nuclear magnetic resonance

M. Dawbarn, J. R. Ebdon and S. J. Hewitt
Department of Chemistry, University of Lancaster, Lancaster, UK
and J. E. B. Hunt, I. E. Williams and A. R. Westwood
Formica Products Research Centre, Maidenhead, UK
(Received 15 May 1978)

The ^{13}C n.m.r. spectra of mixtures of melamine–formaldehyde adducts exhibit several azine carbon peaks. These peaks have been assigned to six of the nine possible methylolmelamines. The areas of the peaks may be used to estimate the relative proportions of mono-, di- and trimethylolmelamines in the mixtures. Melamine–formaldehyde resins show an additional characteristic resonance.

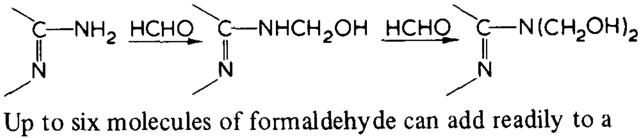
INTRODUCTION

^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy is now used routinely as a method for examining the microstructures of soluble natural and synthetic polymers. Recently it has been shown that the method can be used to identify many of the adducts formed in the initial stages of the reaction of urea with formaldehyde and also to follow the course of the subsequent stages which lead to the formation of urea–formaldehyde resins[1,2]. Of comparable commercial importance to the urea–formaldehyde resins are resins based on melamine (2, 4, 6-triaminotriazine) and formaldehyde. As yet, there has been only one brief report of the characterization of melamine–formaldehyde materials by ^{13}C n.m.r.[3].

In this paper, we report the examination by ^{13}C n.m.r. of several mixtures of low molecular weight adducts of melamine and formaldehyde. It will be seen that the ^{13}C n.m.r. technique can give valuable qualitative and quantitative information regarding the compositions of such mixtures of adducts.

Chemistry of melamine–formaldehyde addition and condensation

Formaldehyde adds readily to melamine in aqueous solution under neutral or basic conditions to yield a mixture of methylolmelamines with an overall composition which depends upon the initial formaldehyde to melamine ratio. The possible reactions are indicated below:



$$\overset{\diagdown}{\underset{\diagup\,\overset{\|}{N}}{C}}\text{—NH}_2 \xrightarrow{\text{HCHO}} \text{C—NHCH}_2\text{OH} \xrightarrow{\text{HCHO}} \text{C—N(CH}_2\text{OH)}_2$$

Up to six molecules of formaldehyde can add readily to a molecule of melamine to make adducts ranging from mono- to hexamethylolmelamine. In all, nine methylolmelamines are possible since di-, tri- and tetramethylolmelamine may each exist in two isomeric forms, e.g. dimethylolmelamine may contain two amine groups both singly substituted with methylol groups or one doubly substituted amine group. The presence of many of these adducts in melamine–formaldehyde mixtures has been demonstrated; for example, Braun and Legradic[4] identified six methylolmelamines by gel permeation chromatography after treatment of mixtures of adducts with *N*-diethyltrimethylsilylamine and, more recently, Tomita[5] separated and identified all nine methylolmelamines by high pressure liquid chromatography and was able also to measure rate constants and equilibrium constants governing the interconversions of these methylolmelamines. Of the adducts, only hexamethylolmelamine appears to be sufficiently stable to allow it to be separated from melamine–formaldehyde mixtures without the need for chromatographic techniques.

At high temperatures, methylolmelamines react further by condensation to form polynuclear species of high molecular weight containing methylene and methylene ether linkages:

$$\text{R–NHCH}_2\text{OH} + \text{HOCH}_2\text{NH–R}' \rightarrow$$
$$\text{R–NHCH}_2\text{OCH}_2\text{NH–R}' + \text{H}_2\text{O}$$

$$\text{R–NHCH}_2\text{OH} + \text{H}_2\text{N–R}' \rightarrow \text{R–NHCH}_2\text{NH–R}' + \text{H}_2\text{O}$$

EXPERIMENTAL

Preparation of melamine–formaldehyde adducts

Various mixtures of melamine–formaldehyde adducts were prepared by dissolving the requisite amount of melamine in 44% w/v aqueous formaldehyde previously adjusted to pH 9.5 by the addition of 2 N aqueous sodium hydroxide. The mixtures were heated to 70°C to assist dissolution and were maintained at this temperature until all the melamine had dissolved. They were then allowed to cool and the white precipitates which separated were filtered off, washed with dilute ammonium hydroxide solution to remove unreacted formaldehyde and dried. Adducts were prepared from aqueous solutions containing from 0.8 to 8.0 mol of formaldehyde per mol of melamine.

^{13}C nuclear magnetic resonance

^{13}C n.m.r. spectra of the adducts were recorded using a Varian CFT20 Fourier transform n.m.r. spectrometer on solutions in DMSO (20% w/v) with 20% d_6-DMSO added to provide the necessary deuterium locking frequency. Spectra

0032–3861/78/111309–04$02.00

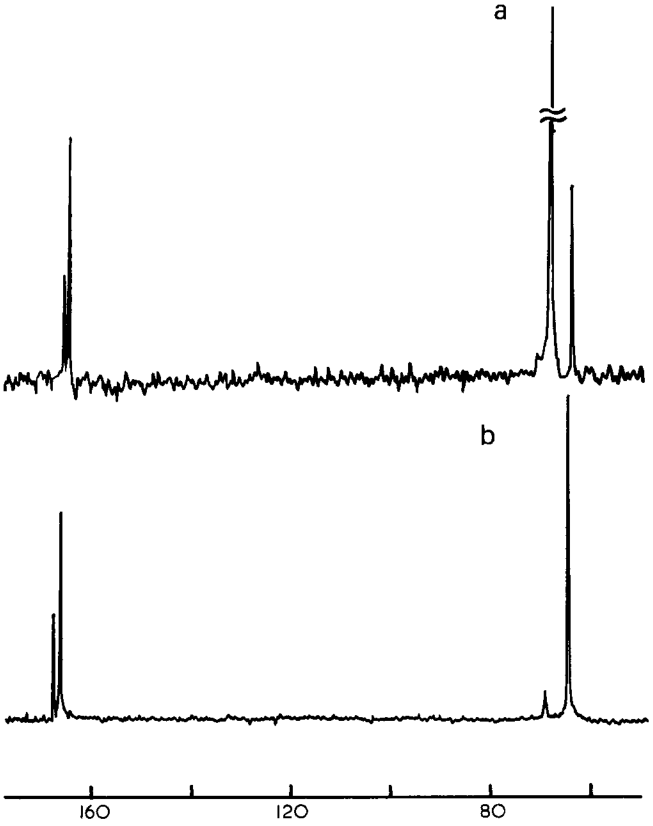


Figure 1 ^{13}C n.m.r. spectra of adduct mixtures prepared at: (a) 4.0:1; and (b) 2.2:1 formaldehyde/melamine ratios

were recorded over a spectral width of 4000 Hz using a pulse width of 12 μsec (corresponding to a nuclear tip angle of about 52°). In each case approximately 30 000 pulses were employed with no delay between pulses other than the acquisition time of 0.5 sec. 'White-noise' proton decoupling was employed throughout. When improved resolution of certain carbon signals was required, spectra were recorded over the region of interest at the reduced spectral width of 1000 Hz with a pulse width of 21 μsec (corresponding to a tip angle of 90°) and with an acquisition time of 2.0 sec. For both types of experiment, 4096 data points were used in the accumulation of the spectra.

Gel filtration chromatography

Some of the adducts were analysed by gel filtration chromatography on a Pharmacia SR 25/100 column packed with 400 cm^3 of Sephadex LH-20 gel following essentially the method of Tsuge *et al.*[6] DMF was used as solvent at a flow rate of 2 cm^3/min and the melamine–formaldehyde fractions in the eluent were detected using an Applied Research Labs. differential refractometer maintained at 30° ± 0.5°C. Typically, the samples were injected into the column as 0.5 cm^3 aliquots of 4% w/v solutions in DMF. In some cases, notably for adducts prepared at low formaldehyde/melamine ratios, complete dissolution of the sample in DMF was not possible. This problem was overcome by first dissolving the adduct in a small amount of DMSO and then diluting this solution to the required concentration with DMF. The DMSO did not interfere with the analyses of the adducts.

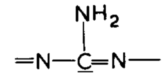
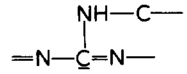
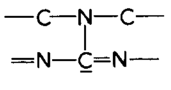
RESULTS AND DISCUSSION

^{13}C n.m.r. spectra

The ^{13}C n.m.r. spectra of the adducts all exhibit peaks in two main regions: at around 165 ppm (relative to TMS at 0 ppm) are a series of peaks arising from the azine carbons of the melamine units whilst between 60 and 90 ppm are several peaks arising from methylene carbons. The complete ^{13}C n.m.r. spectra of two of the adducts, prepared at 2.2:1 and 4.0:1 formaldehyde/melamine ratios, respectively, are shown in *Figure 1*. Close inspection of the spectra reveals that the azine carbon signals are grouped into three sets of peaks. The methylene signals for the adducts prepared at the lower formaldehyde/melamine ratios show the presence of methylol groups attached to secondary and to tertiary nitrogen and of free formaldehyde. For the adducts prepared at high formaldehyde/melamine ratios (>6) there are some additional methylene peaks which are believed to arise from hemiformal groups. The complete assignments are given in *Table 1*.

Figure 2 shows the azine carbon regions obtained at

Table 1 Assignments of ^{13}C signals in melamine–formaldehyde adduct mixtures

Assignment	Chemical shift (ppm)
 $=N-\overset{NH_2}{\overset{\vert}{\underline{C}}}=N-$	167.4–167.0 (3 components)
 $=N-\overset{NH-C-}{\overset{\vert}{\underline{C}}}=N-$	166.3–165.8 (3 components)
 $\begin{array}{c}-C-N-C-\\ \vert \\ =N-\underline{C}=N-\end{array}$	165.2
$HO\underline{C}H_2OH$ (free formaldehyde)	84.4
$-NHCH_2O\underline{C}H_2OH$ $-N-CH_2O\underline{C}H_2OH$	85.6
$-N-\underline{C}H_2OCH_2OH$	71.6
$-NH\underline{C}H_2OCH_2OH$	67.4
$-N-\underline{C}H_2OH$	68.7
$-NH\underline{C}H_2OH$	64.5

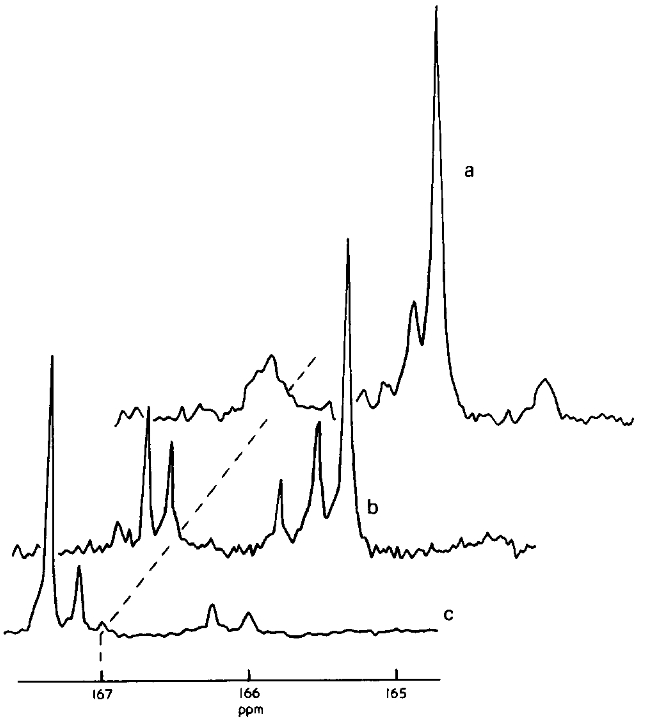
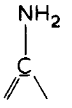
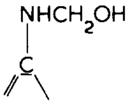
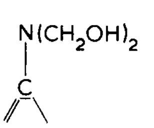


Figure 2 Azine carbon peaks in ^{13}C n.m.r. spectra of adduct mixtures prepared at (a) 2.8:1; (b) 1.8:1; and (c) 0.8:1 formaldehyde/melamine ratios. [Spectra (a) and (b) are offset to the right relative to (c)]

Table 2 Assignments of azine carbon signals in melamine-formaldehyde adducts

	Assignment		
Carbon type	Compound	Designation	Chemical shift (ppm)
	Melamine	A	167.4
	Monomethylol-melamine	B	167.2
	N,N′-dimethylol-melamine	C	167.0
	Monomethylol-melamine	D	166.3
	N,N′-dimethylol-melamine	E	166.0
	N,N′,N″-trimethylol-melamine	F	165.8
	*N,N,N′,N″*-tetra-methylolmelamine	G	~165.2
	Pentamethylol-melamine		
	Hexamethylol-melamine		

higher resolution of adducts prepared at 0.8:1, 1.8:1 and 2.8:1 formaldehyde/melamine ratios. In all, seven distinct azine carbon signals can be seen. It is believed that the three peaks at lowest field (A, B and C) arise from the azine carbons bearing unsubstituted amine groups in melamine, monomethylol–melamine and *N,N′*-dimethylolmelamine, and that the adjacent three peaks (D, E and F) arise from azine carbons bearing singly substituted amine groups in monomethylol-, *N,N′*-dimethylol- and *N,N′,N″*-trimethylol-melamine, respectively. (Melamine alone gives a single azine carbon signal at position A). The azine signal at highest field (*G*) which is the predominant peak in adducts prepared at formaldehyde/melamine ratios greater than 4, is non-Lorentzian in shape and may contain three closely overlapping components arising from azine carbons bearing doubly substituted amine groups in *N,N,N′,N″*-tetramethylol-, pentamethylol- and hexamethylolmelamine, respectively. The full assignments are given in *Table 2*.

The assignments in *Table 2* differ from the more limited assignments of de Breet *et al.*[3] in that they assigned the azine carbon signal at highest field to free melamine. However, our studies of a range of adducts show that this particular assignment cannot be correct. The work of Gordon, Halliwell and Wilson[7] and more recently of Tomita[5] indicates that the adducts listed in *Table 2* are the most readily formed but that small quantities of *N,N*-dimethylolmelamine, *N,N,N′*-trimethylolmelamine and *N,N,N′,N′*-tetramethylolmelamine are formed also at the appropriate formaldehyde/melamine ratios. It is not clear whether such compounds contribute significantly to the azine carbon resonance described here, although some evidence for an additional component is provided by a small peak at 166.4 ppm visible in some of the spectra.

The self-consistency of the assignments made in *Table 2* can be checked to a limited extent by calculating the ratios of monomethylolmelamine (MMM) to *N,N′*-dimethylolmelamine (DMM) first from the ratios of the areas of peaks B to peaks C and then from the areas of peaks D and E. This procedure is based on the assumption that the relative areas of the azine signals are proportional to the relative concentrations of the carbon atoms giving rise to them. Since small changes in acquisition time and pulse width did not appreciably affect the relative areas of the relevant peaks, this assumption is justified. The ratios of MMM to DMM obtained from the spectra are recorded in *Table 3*. The equations used to calculate the relative concentrations are:

$$\text{MMM/DMM} = A_{\text{B}}/2A_{\text{C}} \text{ (from peaks B and C)}$$

and

$$\text{MMM/DMM} = 2A_{\text{D}}/A_{\text{E}} \text{ (from peaks D and E)}$$

where MMM and DMM represent the concentrations of mono- and *N,N′*-dimethylolmelamine and A_{B}, A_{C}, A_{D} and A_{E} represent the areas of peaks B, C, D and E, respectively.

For reactions which give adduct mixtures containing only free melamine, monomethylolmelamine, *N,N′*-dimethylolmelamine and *N,N′,N″*-trimethylolmelamine, the areas of the azine carbon peaks can be used also to calculate the overall ratio of formaldehyde to melamine incorporated in the mixture of adducts. Such ratios calculated for adduct mixtures prepared from reaction mixtures containing from 0.8 to 3.2 mol of formaldehyde per mol of melamine are given in *Table 4* together with the corresponding ratios obtained by C, H and N analysis.

Gel filtration chromatography

Gel filtration chromatograms for three of the adduct mixtures prepared at formaldehyde/melamine ratios of 1.0, 2.0 and 3.2, respectively, are shown in *Figure 3*. Consideration of these and chromatograms for the other adduct mixtures together with the patterns of azine peaks arising in the ^{13}C n.m.r. spectra leads to the following assignments for the chromatogram peaks (*Table 5*).

Adducts prepared at formaldehyde/melamine ratios of 4.0, 5.0 and >6 and which were expected to correspond in overall composition to tetramethylolmelamine, pentamethylolmelamine and hexamethylolmelamine, respectively, gave only a single broad chromatogram peak at 147 counts.

Table 3 Relative concentrations of monomethylolmelamine and *N,N′*-dimethylolmelamine from azine carbon peak areas

Formaldehyde/ melamine ratio in reaction mixture	[MMM]/[DMM]	
	From peaks B and C	From peaks D and E
0.8	4.5	3.8
1.0	2.1	1.6
1.2	1.6	1.1
1.4	1.4	0.9
1.8	0.5	0.6
2.0	0.6	0.4
2.2	0.7	0.5
2.8	0.3	0.4

Table 4 Formaldehyde/melamine ratios in adducts, obtained from ^{13}C n.m.r. spectra

Formaldehyde/ melamine ratio in reaction mixture	Formaldehyde/melamine ratio in adduct mixture	
	^{13}C n.m.r.	C, H and N Analysis
0.8	0.4	0.6
1.0	1.2	0.8
1.2	1.7	1.6
1.4	1.7	1.6
1.8	2.2	2.0
2.0	2.3	2.2
2.2	2.1	2.1
2.8	2.5	2.5
3.0	2.7	2.5
3.2	2.8	2.6

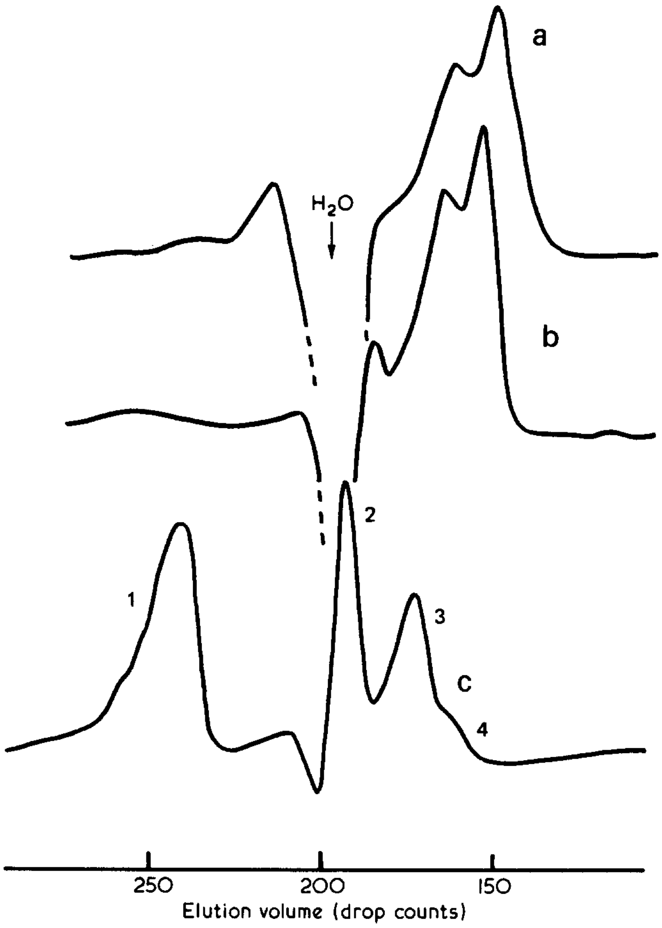


Figure 3 Gel filtration chromatograms for adduct mixtures prepared at (a) 3.2:1; (b) 2.0:1; and (c) 1:1 formaldehyde/melamine ratios. Peak 1 = melamine; peak 2 = monomethylolmelamine; peak 3 = dimethylolmelamine and peak 4 = trimethylolmelamine

A pure sample of hexamethylolmelamine (American Cyanamid Co.) gave a single sharp peak at 140 counts. Thus it would seem that under the preparative conditions described here even at formaldehyde/melamine ratios of ~6, mixtures of adducts are formed.

Melamine–formaldehyde resins

Prolonged heating of melamine–formaldehyde mixtures under alkaline conditions leads to some condensation of methylol groups and to the formation of liquid resins of moderate molecular weight. Condensation is accompanied by small changes in the ^{13}C n.m.r. spectra of the mixtures and in particular by the appearance of an additional azine carbon peak at 165.6 ppm. *Figure 4* shows the azine carbon resonances of a sample withdrawn after 65 min from a resin preparation carried out at pH 9 and 100°C with a formaldehyde/melamine ratio of 6:1. The new peak is assigned to azine carbon atoms bearing methylol-substituted amine groups that have reacted to form ether linkages. Under these conditions of resin preparation, no methylene linkages are found, i.e. there are no resonances visible in the region 47–54 ppm where the carbon atoms within the methylene groups of methylene linkages would be expected to absorb[1]. The methylene groups within the ether linkages give rise to signals very close to those from methylol carbons at 68.7 ppm.

◆

Table 5 Assignments of peaks in gel filtration chromatograms

Peak No.	Elution Volume in drop counts (arbitrary units)	Assignment
1	250	Melamine
2	184–190*	Monomethylolmelamine
3	162–169*	Dimethylolmelamine
4	151–158*	Trimethylolmelamine
5	~150	Tetramethylolmelamine

* Positions vary slightly from sample to sample

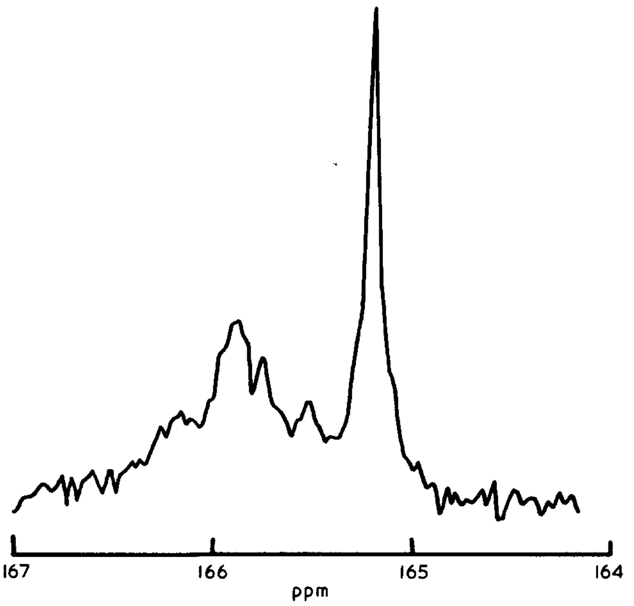


Figure 4 Azine carbon peaks in ^{13}C n.m.r. spectrum of a melamine-formaldehyde resin. (F/M = 6:1, 65 min at 100°C and pH 9)

ACKNOWLEDGEMENTS

We thank the Science Research Council for the award of an Advanced Course Studentship to S. J. H. and the American Cyanamid Co. for the gift of hexamethylolmelamine.

REFERENCES

1 Ebdon, J. R. and Heaton, P. E. *Polymer* 1977, **18**, 971
2 Heaton, P. E. *Thesis* University of Lancaster, 1977
3 de Breet, A. J. J., Dankelman, W., Huysmans, W. G. B. and de Wit, J. *Angew. Makromol. Chem.* 1977, **62**, 7
4 Braun, D. and Legradic, V. *Angew. Makromol. Chem.* 1972, **25**, 398; 1973, **34**, 499; 1974, **35**, 504; 1974, **36**, 529
5 Tomita, B. *J. Polym. Sci. (Polym. Chem. Edn)* 1977, **15**, 2347
6 Tsuge, M., Miyakayashi, T. and Taraka, S. *Jpn Anal.* 1974, **23**, 1141
7 Gordon, M., Halliwell, A. and Wilson, T., SCI Monograph No. 20, 1966, p. 187