# Condensation of Substituted Phenols with Hexakis(methoxymethyl)melamine: Synthesis, Characterization, and Properties of Substituted 2,4,6-Tris[3,4-dihydro-1,3-(2*H*)-benzoxazin-3-yl]-*s*-triazine Derivatives

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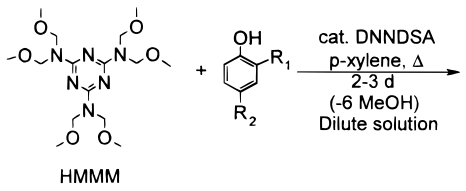
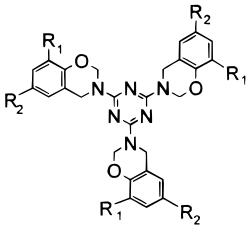
Condensation of hexakis(methoxymethyl)melamine (HMMM) with 2,4-disubstituted and 4-substituted phenols in refluxing *p*-xylene catalyzed by dinonylnaphthalenedisulfonic acid (DNNDSA) gives substituted 2,4,6-tris[3,4-dihydro-1,3-(2*H*)-benzoxazin-3-yl]-*s*-triazine derivatives (**1**−**4**). These tris(benzoxazine) derivatives are characterized by infrared, $^1$H and $^{13}$C NMR, mass spectroscopy, and elemental analysis. Differential scanning calorimetry (DSC) studies suggest thermal cross-linking reactions of benzoxazines made from 4-substituted phenols but not for the one made from a 2,4-disubstituted phenol.

## Introduction

Phenolic resins are often cross-linked with melamine−formaldehyde (MF) cross-linkers to give laminates and coatings.[1] In this paper, we describe our attempts to identify the structure of the condensation products of phenols with MF resins by studying model compounds. In the course of this work, an excellent syntheses of tris-(1,3-benzoxazines), a new class of compositions of matter, was found. The syntheses were carried out using substituted phenols and a monomeric methylolated MF resin, idealized as hexakis(methoxymethyl)melamine (HMMM, eq 1).




HMMM

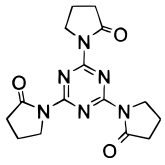


(1)

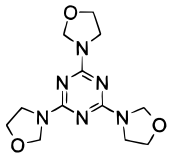
$R_1 = CH_3$; $R_2 = CH_3$ (**1**, 81%)
$R_1 = H$; $R_2 = CH_3CH_2$ (**2**, 66%)
$R_1 = H$; $R_2 = COOCH_3$ (**3**, 95%)
$R_1 = H$; $R_2 = (CH_3)_3CCH_2(CH_3)_2C$ (**4**, tert.octyl, 99%)

In the literature, there are several reports of the cocondensation of phenols with MF resins where 1,3-benzoxazines are considered to be the reaction intermediates.[2] For example, Schreiber[3] mentioned the possible formation of benzoxazine systems in the cocondensation of phenol and MF resins in the patent literature. However, benzoxazine formation has not been unequivocally established.

Besides the melamine-containing benzoxazine systems, there are only a few other reports of melamine-based trifunctional resins. These include 2,4,6-tris(2-oxopyrrolidin-1-yl)-*s*-triazine (**5**)[4] and 2,4,6-tris(1,3-oxazolidin-3-yl)-*s*-triazine (**6**).[5]



**5**



**6**

The formation of 1,3-benzoxazine systems occurs not only in the condensation of phenols and MF resins but also in the reactions of phenols with ammonia and formaldehyde. Thus, Hotta *et al.*[6] studied the condensation of 2,4-dimethylphenol, formaldehyde, and am-

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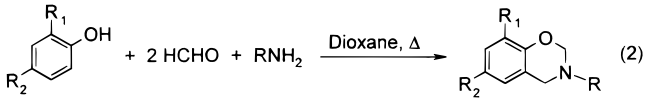
monia using NMR spectroscopy. They identified the initial product to be tris(2-hydroxy-3,5-dimethylbenzyl)-amine which gradually reacted further to give bis(2-hydroxy-3,5-dimethylbenzyl)amine and 1,3-benzoxazine. Maciel and co-workers[7] identified benzoxazine intermediates in the curing of phenolic resins by hexamethylenetetramine, using $^{13}C$ and $^{15}N$ CP/MAS NMR spectroscopy. Similar NMR studies by Whittaker et al.[8] also showed the formation of substituted benzoxazines.

Synthesis of a 1,3-benzoxazine group is accomplished by various procedures, as discussed below.

**Synthesis of 1,3-Benzoxazines.** 1,3-Benzoxazines are generally synthesized by the condensation of a 4-substituted phenol and a primary amine with formaldehyde.[9] The reaction occurs at the phenolic oxygen (O-alkylation) and also at the *ortho* carbon of the phenol (C-alkylation) as shown in eq 2.



(2)

Thackeray et al.[10] studied the reaction of excess HMMM with 4-ethylphenol, using $^{13}C$ NMR in DMSO at 140 °C and 48% HBr catalyst for 20 min, and identified that, under these reaction conditions, the transetherification of the methoxy groups of HMMM takes place with the O group of the phenol (O-alkylation) and not the *ortho* carbon (C-alkylation) of the phenol. They rationalized this reaction as kinetically controlled. In general, C-alkylation is thermodynamically favored over O-alkylation. Apparently, in our synthesis, the longer reaction time might have enabled the C-alkylation followed by the O-alkylation to give the benzoxazine ring.

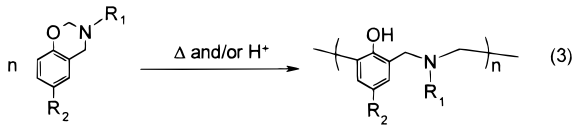
In other methods for synthesis of 1,3-benzoxazines, Vilkas et al.[11] reported the condensation of 4-substituted phenols with 1,3,5-trimethylhexahydro-*s*-triazine in the presence of oxalyl chloride, giving *N*-methyl-3,4-dihydro-2*H*-1,3-benzoxazines, and Campi *et al.*[12] reported that the reactions of 2-(allyloxy)benzylamine with $H_2$/CO in the presence of rhodium catalysts also give 1,3-benzoxazines. The reaction mechanism involves an allylic cleavage followed by regioselective carbonylation and subsequent reduction. Aversa *et al.*[13] reported an unusual dehydration of *N*-(2-hydroxybenzyl)-3-aminopropanoic acid using sulfuric acid at room temperature giving a 1,3-benzoxazine derivative.

**Syntheses of Poly(1,3-benzoxazines).** Among the class of poly(1,3-benzoxazines), syntheses of several bis-(1,3-benzoxazines) and a tetrakis(1,3-benzoxazine) have been reported.

Bis(1,3-benzoxazines) are of considerable interest as they are difunctional and provide alternatives to phenolic resins. They are synthesized either by the condensation of bisphenol A with an amine and formaldehyde or by the condensation of a diamine with a phenol and formaldehyde.[14]

Arnecke *et al.*[15] reported a similar synthesis of the tetrakis(1,3-benzoxazine) by the condensation of resorcarene with primary amines and excess formaldehyde.

**Applications of 1,3-Benzoxazines.** Upon heating, 1,3-benzoxazines undergo polymerization reactions to give substituted polyphenols (eq 3). Further reactions



(3)

may occur, leading to formation of crosslined materials. Thus, Shreiber[16] obtained a brittle, insoluble polymer by heating a benzoxazine derived from aniline, phenol, and formaldehyde at 180 °C.

For polybenzoxazines the reaction shown in eq 3 can lead to cross-linking even when no side reactions occur. Ishida and Rodriguez[14] showed that bis(1,3-benzoxazine) precursors, synthesized from bisphenol A, formaldehyde, and methylamine, can be cross-linked. These cross-linked derivatives can overcome most of the shortcomings of the traditional phenolic molding resins, since these cross-linking reactions do not involve the evolution of volatile materials, a potential advantage over phenol−formaldehyde or amino resins. Molding compounds containing benzoxazines do not contain free phenols, reducing the environmental and health risks of phenols. Ishida et al.[17] also reported that unlike many thermoset resins, the polymerized benzoxazine-based materials may expand upon curing.

Polybenzoxazines offer greater flexibility than conventional novolac or resole resins in terms of molecular design.[18] For example, composites based on benzoxazine materials exhibit excellent mechanical integrity with glass transition temperatures over 200 °C. Schreiber obtained several patents for the use of benzoxazines that find use in heat-hardenable resins as adhesives in the manufacture of paper laminates and

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for fiber-reinforced moldings (synthesized from phenol, bis(4-aminophenyl)methane, and formaldehyde),[19] fire- and heat-resistant plastics [derived from 3,3′-(methylenedi-*p*-phenylene)bis(3,4-dihydro-1,3-benzoxazine)],[20] and flame-resistant resins that have good processability and negligible toxicity.[21]

Higginbottom *et al.*[22] obtained patents for a benzoxazine monomer, prepared from bisphenol A, aniline, and 50% aqueous formaldehyde. This monomer can be formulated with a polyamine cross-linker to give a composition which can be coated on zinc phosphate-treated steel panels. The panels could be cured to give coatings having excellent mechanical and protective properties. These compositions are also useful for corrosion inhibition of metals and as potting and laminating resins.

Benzoxazine derivatives obtained by the condensation of bisphenol A, aniline, and formaldehyde find use in self-curable cathodic electrocoat resins and processes.[23] Audebert *et al.*[24] reported the electro-oxidative polymerization of *N*-methylbenzoxazines in acetonitrile and methanol solutions either in neutral or alkaline media. Coatings obtained by the polymerization of these benzoxazines in the alkaline medium find use in corrosion protection. Benzoxazine derivatives also find use in toner related applications in recording processes.[25] Polymers containing benzoxazine groups also find use in the manufacture of resinoid wheels[26] and antiknock additives.[27]

In this paper, we report the syntheses of the new melamine-based resin systems with three 1,3-benzoxazine groups (eq 1). This method also opens up a potentially economical route to the synthesis of melamine based benzoxazine resins. Formation of these resins also unequivocally establishes the pathway for the reaction of melamine−formaldehyde resins with phenols.

## Experimental Section

Hexakis(methoxymethyl)melamine (HMMM) was obtained from Monsanto Chemical Co. (now Solutia Inc.) as Resimene HM 2612. 2,4-Dimethylphenol, 4-ethylphenol, 4-*tert*-octylphenol, and *p*-toluenesulfonic acid were purchased from Aldrich Chemical Co. Dinonylnaphthalenedisulfonic acid (DNNDSA, Nacure 155) was obtained from King Industries. 4-Hydroxybenzoic acid was obtained from Mobay (now Bayer) Corp. Solvents were purchased from Aldrich Chemical Co. and were used as received; *p*-xylene, rather than a mixture of xylenes, was used. "Brine" is a saturated solution of sodium chloride in water.

Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 5DX spectrometer in the form of KBr pellets. NMR spectra were recorded using a Bruker AC-250 spectrometer. Chemical shifts are reported relative to tetramethylsilane (TMS) in $CDCl_3$. Each spectrum was recorded using a solution of approximately 0.08 g of sample in 1 mL $CDCl_3$ containing 5 wt % TMS. Nominal mass spectra were recorded at the University of Michigan on a Finnigan model 4021 mass spectrometer using a desorption chemical ionization (DCI) probe. High-resolution mass spectra were recorded on a VG analytical model 70-250S mass spectrometer. Elemental analysis was performed at the University of Michigan on a Perkin-Elmer 2400 CHN analyzer. Differential scanning calorimetry (DSC) experiments were performed on a TA 2920 modulated differential scanning calorimeter where the downward peak is the exothermic response and the upward peak is the endothermic response. The heating rate was 20 °C/min under nitrogen.

**Synthesis of Methyl 4-Hydroxybenzoate.** A suspension of 4-hydroxybenzoic acid (103.71 g, 0.75 mol) in anhydrous methanol (600 mL, 14.83 mol) was prepared in a 1-L round-bottomed flask, and the acid catalyst (*p*-toluenesulfonic acid, 0.5 g, 0.09 wt %) was added to the suspension. The reaction mixture was refluxed for 3 days. A clear solution was obtained upon heating. The reaction solution was cooled to room temperature, and the excess methanol was removed under vacuum. A white crystalline solid was obtained which was dissolved in ethyl acetate (500 mL). The ethyl acetate solution was washed four times with 100 mL of a 10% aqueous NaOH solution and once with brine. The ethyl acetate solution was dried using anhydrous $MgSO_4$, and the solvent was removed in a vacuum to give a white crystalline solid. The solid was recrystallized from ethanol and subsequently dried in the oven at 100 °C for 6 h. Yield: 84.34 g (74%). Mp: 124−126 °C (lit. mp 126−128 °C). $^1$H NMR ($CDCl_3$): $\delta$ 7.97, 7.93 (d, $J$ = 7.5 Hz, 2H), 6.91, 6.87 (d, $J$ = 7.5 Hz, 2H), 3.90 (s, 3H). $^{13}$C NMR($CDCl_3$): $\delta$ 167.55, 160.39, 131.99, 122.25, 115.34, 52.11.

**Tris(1,3-benzoxazine) Derivative from HMMM and 2,4-Dimethylphenol: 2,4,6-Tris[3,4-dihydro-6,8-dimethyl-1,3-(2*H*)-benzoxazin-3-yl]-*s*-triazine (1).** A solution of HMMM (41.14 g, 0.11 mol) and 2,4-dimethylphenol (40.09 g, 0.33 mol) was prepared in 250 mL of *p*-xylene in a 500-mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. Approximately 0.15 g of DNNDSA (1.85 wt %) was also added to the solution, and the solution was refluxed for 72 h. A white solid precipitated after 48 h of refluxing, and more solid precipitated 24 h later. When the reaction mixture was cooled to room temperature more solid precipitated. The solid precipitates were collected by filtration, combined, and stirred vigorously with 200 mL of 10% aqueous NaOH solution for 2 h to dissolve any unreacted phenol. The insoluble product was filtered again and was suspended in 200 mL of brine for another 2 h. The suspended product was filtered from the aqueous medium, and the filtrate was crystallized from dichloromethane and hexane using the diffusion method inside a desiccator. The crystallized product (**1**) was filtered off and dried in an oven at 100 °C for 4 h. Yield: 47.88 g (81%). Mp: >230 °C. IR (KBr): 3015, 2980, 1555, 1500, 1498, 1475, 1447, 1388, 1333, 1310, 1259, 1228, 1202, 1193, 1161, 1153, 1134, 1120, 1052, 1006, 1001, 983, 892, 846, 802, 753, 725, 606, 586, 562,483, 454 cm$^{-1}$. $^1$H NMR($CDCl_3$): $\delta$ 6.80−6.78 (d, $J$ = 5 Hz, 6H), 5.69 (s, 6H, >N$CH_2$O−), 4.93 (s, 6H, >N$CH_2$Ph), 2.25 (s, 12H), 2.19 (s, 12H). $^{13}$C NMR($CDCl_3$): $\delta$ 164.76, 150.20, 129.91, 129.42, 126.10, 124.47, 119.96, 72.54 (>N$CH_2$O−), 43.10 (>N$CH_2$Ph), 20.45, 15.46. MS(EI/70 eV) [*m*/*z* (relative intensity)]: 564 (100%), 552 (13),

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429 (51), 418 (21), 295 (15), 162 (9), 134 (28), 106 (15), 91 (34), 73 (25), 58 (8), 44 (8).

**Tris(1,3-benzoxazine) Derivative from HMMM and 4-Ethylphenol: 2,4,6-Tris[3,4-dihydro-6-ethyl-1,3-(2*H*)-benzoxazin-3-yl]-*s*-triazine (2).** A solution of HMMM (1.05 g, 2.69 mmol) and 4-ethylphenol (1.04 g, 8.52 mmol) was prepared in 10 mL of *p*-xylene in a 50 mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. Approximately 0.02 g of DNNDSA (1.0 wt %) was added to the solution, and the solution was refluxed for 48 h. No precipitate was formed in this reaction, and the reaction mixture remained clear throughout. The reaction mixture was cooled to room temperature, and the contents of the reaction flask were dissolved in approximately 20 mL of methylene chloride. The methylene chloride solution was washed with 10 wt % aq NaOH solution (5 mL × 4) to remove any unreacted phenol. The organic layer was finally washed with brine (5 mL × 4). Water was removed from the methylene chloride solution using anhydrous $MgSO_4$. The solvents, methylene chloride and *p*-xylene, were removed from the organic solution using a rotary evaporator. An amber yellow oily product was obtained upon solvent removal which upon cooling gave an off-white solid. The product (**2**) was crystallized from dichloromethane and hexane using the diffusion method inside a desiccator. An off-white microcrystalline product (**2**) was crystallized in approximately 24 h. The product **2** was filtered off and dried inside the oven at 100 °C for 12 h. Yield: ~1 g (66%). Mp: 107−113 °C (softens). IR (KBr): 3018, 2963, 1589, 1549, 1482, 1447, 1426, 1313, 1274, 1246, 1233, 1199, 1189, 1140, 1114, 1063, 1042, 1004, 998, 980, 890, 877, 822, 807, 756, 745, 686, 580 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 6.95−6.94 (br, m, 6H), 6.83−6.72 (d, 3H), 5.68 (s, 6H, >N$CH_2$O−), 4.97 (s, 6H, >N$CH_2$Ph), 2.58 (q, $J$ = 7.5 Hz, 6H), 1.22 (t, $J$ = 7.5 Hz, 9H). $^{13}C$ NMR($CDCl_3$): $\delta$ 164.97, 152.03, 137.10, 127.01, 125.87, 120.45, 116.98, 72.57 (>N$CH_2$O−), 43.21 (>N$CH_2$Ph), 27.99, 15.72. MS (EI/70 eV) [*m*/*z* (% intensity)]: 564 ($M^+$, 100), 446 (6), 429 (69), 418 (17), 311 (4), 295 (19), 283 (16), 269 (5), 255 (3), 214 (3), 181 (8), 162 (11), 135 (17), 106 (9), 91 (31), 73 (33), 55 (8), 44 (19).

**Tris(1,3-benzoxazine) Derivative from HMMM and Methyl 4-Hydroxybenzoate: 2,4,6-Tris[3,4-dihydro-6-methoxycarbonyl-1,3-(2*H*)-benzoxazin-3-yl]-*s*-triazine (3).** A solution of HMMM (52.08 g, 0.14 mol) and methyl 4-hydroxybenzoate (62.38 g, 0.41 mol) was prepared in 500 mL *pof* -xylene in a 1000 mL round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. Approximately 0.25 g of DNNDSA (0.22 wt %) was added to the solution, and the solution was refluxed for 72 h. The clear solution became transparent, milky-white after 12 h. A white precipitate was formed around the flask after 48 h. The reaction mixture was cooled to room temperature, and the solid was filtered off. The filtered solid was washed with 10% aqueous NaOH solution followed by brine. The product **3** was dried in the oven at 100 °C for 6 h. Yield: 72.64 g (95%): Mp: >150 °C (dec). IR (KBr): 3014, 2968, 1715, 1619, 1545, 1478, 1455, 1434, 1390, 1320, 1290, 1261, 1251, 1210, 1194, 1168, 1130, 1112, 1088, 986, 892, 836, 802, 766, 730, 702, 622, 580, 519 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.88−7.81 (m, 6H), 6.96−6.88 (d, $J$ = 8.5 Hz, 3H), 5.75 (s, 6H, >N$CH_2$O−), 5.04 (s, 6H, >N$CH_2$Ph), 3.90 (s, 9H). $^{13}C$ NMR ($CDCl_3$): $\delta$ 166.61, 165.09, 157.96, 129.48, 129.03, 123.22, 120.43, 117.30, 72.84 (>N$CH_2$O−), 51.96 (−O$CH_3$) 43.13 (>N$CH_2$Ph). MS (EI/70 eV) [*m*/*z* (% intensity)]: 654 ($M^+$, 76), 623 (9), 534 (14), 489 (100%), 325 (25), 192 (9), 165 (13), 133 (12), 105 (6), 84 (50), 49 (66).

**Tris(1,3-benzoxazine) Derivative from HMMM and 4-*tert*-Octylphenol: 2,4,6-Tris[3,4-dihydro-6-(1,1,3,3-tetramethylbutyl)-1,3-(2*H*)-benzoxazin-3-yl]-*s*-triazine (4).** A solution of HMMM (51.80 g, 0.13 mol) and 4-*tert*-octylphenol (83.79 g, 0.41 mol) was prepared in 600 mL of *p*-xylene in a 1-L round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. Approximately 0.11 g of DNNDSA (0.08 wt %) was added to the solution, and the solution was refluxed for 72 h. The solution remained clear throughout the reaction period. The reaction mixture was cooled to room temperature, and the *p*-xylene was removed in a vacuum using a rotary evaporator. An amber yellow, oily product was obtained which upon cooling gave an off-white solid. The solid obtained was dissolved in 200 mL of ether. The ether solution was washed with 10 wt % aq NaOH solution (100 mL × 4) to remove any unreacted phenol present. The organic layer was finally washed with brine (50 mL × 4). Water was removed from the ether solution using anhydrous $MgSO_4$. Ether was removed from the solution using a rotary evaporator to give a colorless, oily but viscous product. The solid was poured into an aluminum pan and was kept overnight in a stream of air at room temperature to remove any remaining solvent. A white solid was obtained. Yield: 95.92 g (99%). Mp: 182−185 °C. IR (KBr): 2964, 2905, 2858, 1619, 1552, 1483, 1447, 1416, 1385, 1362, 1341, 1308, 1248, 1217, 1184, 1153, 1127, 1088, 1042, 1008, 980, 921, 905, 887, 828, 820, 805, 779, 753, 727, 658, 614, 588 $cm^{-1}$. $^1H$ NMR($CDCl_3$): $\delta$ 7.15 (s, 6H), 6.80 (d, $J$ = 8.5 Hz, 3H), 5.71 (s, 6H, >N$CH_2$O−), 4.98 (s, 6H, >N$CH_2$Ph), 1.71 (s, 6H), 1.36 (s, 18H), 0.74 (s, 27H). $^{13}C$ NMR-($CDCl_3$): $\delta$ 165.06, 151.76, 143.23, 125.52, 124.17, 119.74, 116.44, 72.68 (>N$CH_2$O−), 56.90, 43.50 (>N$CH_2$Ph), 38.04, 32.32, 31.80, 31.57. MS (EI/70 eV) [*m*/*z* (% intensity)]: 818 (56), 817 ($M^+$, 84), 747 (10), 598 (15), 528 (7), 381 (12), 337 (13), 309 (8), 163 (90), 161 (100), 151 (18) 147 (35), 135 (34), 86 (28), 84 (38), 57 (36), 51 (28), 48 (11), 41 (17).

## Results and Discussion

The syntheses of tris(1,3-benzoxazines) **1**−**4** were performed by the condensation of hexakis(methoxymethyl)melamine (HMMM) with 4-substituted or 2,4-disubstituted phenols using dinonylnaphthalenedisulfonic acid (DNNDSA) catalyst in refluxing *p*-xylene. The benzoxazines **1** and **4** precipitated during the course of the reaction, whereas products **2** and **3** remained in solution, due to the increased solubility brought about by the longer alkyl chains.

As a precedent to this synthetic scheme, Reynolds and Cossar[28] reported that bis(methoxymethyl)amine reacts with substituted hydroquinone to give 1,3-benzoxazine hydrochlorides. Stronger acid catalysts, such as methanesulfonic acid (MSA), generally favor cross-linking reactions involving the available *ortho* position of the phenol group (see eq 3), especially in higher concentration. Attempts to scale-up these reactions met with similar cross-linking reactions, which were overcome by considerably diluting with the solvent.

Synthesis of **4** from *p*-*tert*-octylphenol and HMMM was carried out in order to synthesize tris(1,3-benzoxazines) that might have better solubility in common organic solvents.

**Characterization of Compounds 1−4.** The compounds synthesized were characterized by infrared and $^1H$ and $^{13}C$ spectroscopy similar to the reported characterization of 1,3-benzoxazines by Proponet *et al.*[29] Further characterizations were made using high-resolution mass spectroscopy and elemental analysis. The relevant assignments in each technique are described below.

Dunkers and Ishida[30] assigned the fundamental vibrational bands of a series of 3-alkyl-3,4-dihydro-6-methyl-2*H*-1,3-benzoxazines in the fingerprint region of their IR and Raman spectra. Among these, the impor-

(28) Reynolds, D. D.; Cossar, B. C. *J. Heterocycl. Chem.* **1971**, *8*, 611.

(29) Proponet, C.; Laude, B.; Ramah, M.; Riess, G. *Spectrochim. Acta, Part A* **1982**, *38A*, 323.

(30) Dunkers, J.; Ishida, H. *Spectrochim. Acta, Part A* **1995**, *51A*, 1061.

**Table 1. Tentative Vibrational Band Assignments for 1−4[a]**

| compd | C−N−C antisym bands ($cm^{-1}$) | C−N−C sym bands ($cm^{-1}$) | C−O−C antisym bands ($cm^{-1}$) | C−O−C sym bands ($cm^{-1}$) | benzoxazine radial ring mode ($cm^{-1}$) |
|---|---|---|---|---|---|
| **1** | 1202 (s), 1193 (m), 1153 (s), 1134 (m) | 846 (m) | 1228 (m) | 1052 (m) | 753 (w) |
| **2** | 1199 (w), 1189 (w) | 823 (w) | 1233 (m) | 1063 (w) | 756 (w) |
| **3** | 1194 (w), 1168 (w), 1130 (w) | 836 (w) | 1210 (m) | 1050 (w) | 766 (s) |
| **4** | 1184 (w), 1127 (w) | 820 (m) | 1217 (w) | 1088 (w) | 753 (w) |

[a] Relative intensities of the bands are listed in parentheses: w, weak; m, medium; s, strong.

**Table 2. $^1H$ and $^{13}C$ NMR Chemical Shifts for the $>NCH_2O-$ and $>NCH_2Ph$ Groups in $CDCl_3$**

| | $^1H$ NMR data (ppm) | | $^{13}C$ NMR data (ppm) | |
|---|---|---|---|---|
| compd | $>NCH_2O-$ | $>NCH_2Ph$ | $>NCH_2O-$ | $>NCH_2Ph$ |
| **1** | 5.69 | 4.93 | 72.54 | 43.10 |
| **2** | 5.68 | 4.97 | 72.57 | 43.21 |
| **3** | 5.75 | 5.04 | 72.84 | 43.13 |
| **4** | 5.71 | 4.98 | 72.68 | 43.50 |

tant peaks for the benzoxazine moiety include the C−N−C and C−O−C antisymmetric and symmetric stretching bands. The reported C−N−C antisymmetric bands appear at 1240−1020 $cm^{-1}$, and symmetric bands appear at 830−740 $cm^{-1}$.[30] Similarly, C−O−C antisymmetric bands appear at 1240−1210 $cm^{-1}$, whereas the C−O−C symmetric bands appear at 1040−1020 $cm^{-1}$. In addition, the benzoxazine rings also show uniform, radial displacement of the atoms. These ring mode vibrations generally appear at 770−760 $cm^{-1}$. Upon comparison of these data to the corresponding wavenumbers in the infrared spectra of **1**−**4**, tentative assignments were made for various bands which are listed in Table 1.

The infrared spectroscopic data for compounds **1**−**4** are consistent with benzoxazine ring systems.

$^1H$ and $^{13}C$ NMR spectroscopy provides more conclusive evidence for the structures of compounds **1**−**4** than the infrared spectra. The $^1H$ and $^{13}C$ chemical shifts of $>NCH_2O-$ and $>NCH_2Ph$ groups are listed in Table 2.

The reported $^1H$ NMR chemical shifts for the methylene protons in $-(CH_2)(H_5C_6)NCH_2O-$ and $-(OCH_2)(H_5C_6)NCH_2Ph$ groups are ca. 5.4 and 4.6 ppm, respectively.[31] The chemical shifts of the $-CH_2-$ protons in **1**−**4** appear slightly downfield, perhaps due to the melamine moiety. Besides, the integration results also confirm the number of different protons present in these compounds.

The $^{13}C$ NMR peak assignments were confirmed by distortionless enhancement by polarization transfer (DEPT) techniques for the $-CH_2-$ carbons and also for the aromatic carbons. The $>NCH_2OCH_2N<$ carbons in self-condensed melamine−formaldehyde resins appear at ca. 73 ppm.[32] Therefore the new peak at ca. 73 ppm in the benzoxazine products must be due to the $>NCH_2O-$ carbon. Tomita and Hse[33] reported that the chemical shift of the $>NCH_2Ph$ carbon in phenol−melamine formaldehyde cocondensates is at ca. 43 ppm. This confirms our peaks assignments for the $>NCH_2Ph$ carbons.

In addition to the methylene carbons, the $^{13}C$ NMR spectra of **1**−**4** did not show the aromatic carbons corresponding to the starting materials. Instead, there were six new peaks for the six aromatic carbons of the tri- or tetrasubstituted phenols. DEPT spectra also showed three C−H carbons for the phenol moiety of **2**−**4** and two C−H carbons for **1**.

Compounds **1**−**4** were further characterized by mass spectroscopy and elemental analysis. The molecular weights of compounds **1**−**4** were obtained by high-resolution mass spectroscopy (HRMS). The HRMS and elemental analysis data are listed in Table 3.

These results confirm the compositions and molar masses of benzoxazines **1**−**4**.

**Reactions of Benzoxazines.** Many of the reported reactions of 1,3-benzoxazines involve opening of the oxazine ring to give aminomethylphenol derivatives (eq 3). The ring-opening reaction is either activated by a nucleophile or it is thermally catalyzed. Thus, benzoxazines undergo hydrolysis when heated with an acid catalyst giving 2-(aminomethyl)phenols.[34] For example, acid-catalyzed hydrolysis of the 1,3-benzoxazine obtained by the condensation of 2,4-di-*tert*-butylphenol and 2,4-di-*tert*-butylaniline with formaldehyde gives *N*-(3,5-di-*tert*-butyl-2-hydroxybenzyl)-2,4-di-*tert*-butylaniline.[35] Moloney et al.[36] used NMR to study the hydrolytic stability at ambient temperatures in DMSO solution of the oxazine ring in benzoxazines and pyridooxazines having N-phenyl substituents. They found that the ring stability is enhanced by the electron-donating substituents at the *meta* position of the *N*-phenyl substituent of the benzoxazine group.

Among the compounds synthesized in this study, only **1** has its *ortho* and *para* positions substituted. Therefore, **1** could be used for model studies. When an aqueous suspension of **1** was refluxed with 10% (v/v) aqueous HCl solution for 4 h, the resulting product was not soluble even in dimethyl sulfoxide (DMSO). When the concentration of the acid was lowered to 2% (v/v), no change was detectable by $^1H$ NMR. This suggests that **1** might have undergone an acid-catalyzed cross-linking reaction. It is possible that the benzoxazine rings might have been hydrolyzed to give the expected product, $Tr[N(CH_2OH)CH_2Ar]_3$, where Tr is the *s*-triazine ring and Ar is the phenol moiety. This product could undergo acid-catalyzed self-condensation reactions similar to the self-condensation of melamine−formaldehyde resins.[37]

Alternately, to effect alcoholysis, **1** was refluxed in excess methanol along with catalytic amount of meth-

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(34) McDonagh, A. F.; Smith, H. E. *J. Org. Chem.* **1968**, *33*, 8.

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(36) Moloney, G. P.; Craik, D. J.; Iskander, M. N. *J. Pharm. Sci.* **1992**, *81*, 692.

(37) (a) Wicks, Z. W.; Jones, F. N.; Pappas, S. P. *Organic Coatings Science and Technology*; Wiley-Interscience: New York, 1992; Vol. 1, pp 83−103. (b) Jones, F. N.; Subrayan, R. P. *Polym. Mater. Sci. Eng.* **1997**, *77*, 389 and references therein.

**Table 3. High-Resolution Mass Spectral Data (*m/e*) and Elemental Analysis Data (%) for Compounds 1−4**

| | | HRMS | | anal. data | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | calcd | | | found | | |
| compd | formula | calcd | found | C | H | N | C | H | N |
| **1** | $C_{33}H_{36}N_6O_3$ | 564.2849 | 564.2862 | 70.19 | 6.43 | 14.88 | 70.10 | 6.50 | 14.82 |
| **2** | $C_{33}H_{36}N_6O_3$ | 564.2849 | 564.2837 | 70.19 | 6.43 | 14.88 | 70.23 | 6.70 | 15.13 |
| **3** | $C_{33}H_{30}N_6O_9$ | 654.2074 | 654.2070 | 60.55 | 4.62 | 12.84 | 59.98 | 4.69 | 12.71 |
| **4** | $C_{51}H_{72}N_6O_3$ | 816.5666 | 816.5651 | 74.96 | 8.88 | 10.28 | 74.93 | 8.77 | 10.56 |

anesulfonic acid for 36 h. As noted above, **1** did not dissolve in methanol. According to $^1H$ and $^{13}C$ NMR spectra, only the starting material was isolated. Perhaps, the temperature of the reaction was not high enough for the reaction to proceed.

These observations show that melamine-based tris(benzoxazines) might react analogously to other benzoxazines reported in the literature, but isolation of the reaction products is difficult possibly due to the competing reactions from the self-condensation of the melamine-formaldehyde moiety.

**Thermal Polymerization and Cross-linking Reactions of Benzoxazines.** As described above, polyfunctional 1,3-benzoxazines have potential utility as components of thermoset molding compounds. As shown in eq 3, 1,3-benzoxazine derivatives can polymerize when heated, and di- and polyfunctional 1,3-benzoxazines can cross-link when heated. Note that this reaction requires that the position *ortho* to the oxygen group of the benzoxazine be unsubstituted. Of the benzoxazines synthesized in this study, **2**−**4** have unsubstituted *ortho* positions, but **1** does not. We performed preliminary studies of the thermal behavior of benzoxazines **1**−**4**. The results were somewhat equivocal but are described briefly here.

When benzoxazines **1** and **2** were heated to 300 °C in a forced air oven for 10 min, they became yellow to light brown materials that were partly soluble in $CDCl_3$. $^1H$ NMR analysis of the soluble fraction showed a decrease in the $>NCH_2O-/>NCH_2Ph$ proton ratio from 1.0/1.0 to 0.7/1.0, suggesting loss of formaldehyde. When benzoxazines **2**−**4** were heated for 10 min inside a muffle furnace preheated to 300 °C, these white solids became black, hard, brittle solids. All three materials lost 10−20% of their weight and expanded in volume, indicating partial decomposition with outgassing. The black materials were not soluble in chloroform or DMSO suggesting that cross-linking occurred along with degradation. The infrared spectra of the black products did not show the asymmetric and symmetric $\nu_{C-O-C}$ bands at 1210−1233 and 1050−1088 $cm^{-1}$. Also, there was a new broad $\nu_{OH}$ band at ca. 3500 $cm^{-1}$ attributable to the phenol moiety. Its position and broadness suggest that the −OH group is hydrogen bonded.[38] These observations are consistent with a combination of cross-linking by the reaction shown in eq 3 and thermal degradation reactions.

DSC plots of benzoxazines **1**−**4** from 80−200 °C are shown in Figure 1. The plots of benzoxazines **2**−**4** appear to show exotherms with maxima at 151, 157, and 123 °C, respectively. The DSC traces of **3** and **4** had additional features at 170 − 200 °C. Literature reports,[14,31] attribute similar exotherems in other 1,3-benzoxazines to cross-linking reactions. However, benzoxazines **2**, **4**, and probably **3** all melt within the temperature range studied, so no definite conclusions can be drawn from their DSC plots.

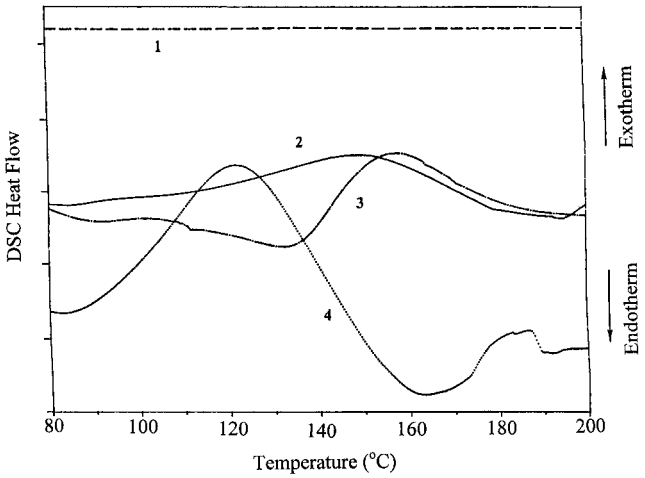


**Figure 1.** Differential scanning calorimetric (DSC) data for melamine-based tris(1,3-benzoxazines) **1**−**4**. Heating rate: 20 °C/min under $N_2$(g).

When the DSC study was extended to 300 °C, compound **1** showed two sharp endothermic transitions around 230 and 265 °C whereas **2**−**4** showed exotherms attributable to chemical reactions that might include cross-linking or degradation. The endotherms observed for compound **1** may be associated with melting transition(s).

Grabarnik *et al.*[39] reported a comparative study of the curing of a blend of phenol−formaldehyde and hexamethylenetetramine and also 3,3′-ethylenebis(2*H*-3,4-dihydro-6-methyl-1,3-benzoxazine) using thermogravimetry (TGA), differential thermogravimetry (DTG), differential thermal analysis (DTA), and pyrolysis gas chromatography. They concluded that, at low temperatures, ammonia is not evolved during curing of the benzoxazine derivative, and weight loss in the curing of the benzoxazine derivative is significantly lower than the curing of the blend. In a separate study,[40] they also found that blending benzoxazines with phenol−formaldehyde oligomer decreases the gas evolution and improves the dielectric properties of the cured oligomers.

When combined with previously reported behavior of benzoxazines, the preliminary results reported here strongly suggest that when benzoxazines **2**−**4** are heated they undergo cross-linking via the reaction

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(39) Grabarnik, L. G.; Leonova, M. B.; Korotin, M. M.; Vorosova, T. G.; Osetrova, E. N. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **1990**, 65; *Chem. Abstr.* **1990**, *113*, 133439.

(40) Grabarnik, L. G.; Puryga, T. V.; Matveev, V. A.; Glebov, A. V. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **1989**, 64; *Chem. Abstr.* **1989**, *111*, 195985.

shown in eq 3. Cross-linking is accompanied by other reactions and partial degradation, especially as temperatures reach 300 °C.

## Summary and Conclusions

We have synthesized substituted 2,4,6-tris[3,4-dihydro-1,3-(2*H*)-benzoxazin-3-yl]-*s*-triazine derivatives (**1**−**4**) in 66−99% yield from readily available substituted phenols and hexakis(methoxymethyl)melamine resin. Such compositions were not previously reported. The synthesis of these benzoxazines provides strong evidence that cyclic benzoxazine structures are formed when resins having pendant or terminal phenol groups are cross-linked with melamine−formaldehyde (MF) resins. While 1,3-benzoxazines can be hydrolyzed, the C−C bond is expected to remain intact. Thus, the benzoxazine cross-links are expected to provide superior hydrolytic stability than the ether cross-links formed by aliphatic hydroxyl groups cross-linked with MF resins. Formation of cyclic cross-links is also expected to add rigidity to the network, increasing $T_g$. Preliminary studies of the thermal behavior of the benzoxazines produced in this study suggest that benzoxazines **2**−**4** are capable of thermal cross-linking at temperatures less than 200 °C, while benzozazine **1** is not. This conclusion is reasonable in view of the structural difference between benzoxazines **1** and **2**−**4**. Thus, the synthetic route demonstrated here may prove useful as a potentially low-cost route to cross-linkable benzoxazines. On the other hand, the potential for thermal polymerization and other thermal reactions may complicate the cross-linking process when MF resins are used to cross-link phenolic resins.

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