

# N-Methylmelamines: Synthesis, Characterization, and Physical Properties

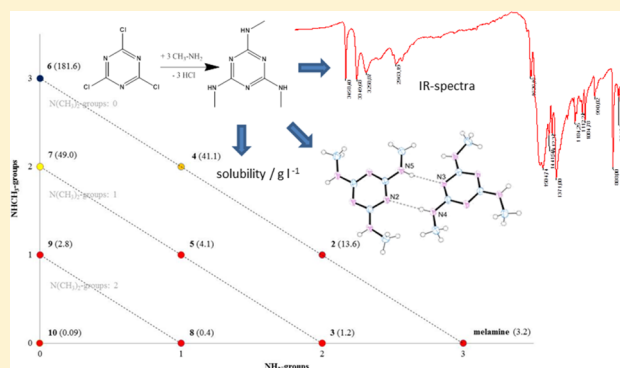
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## S Supporting Information

**ABSTRACT:** N-Methylmelamines have recently gained importance as valuable compounds for manufacturing modified melamine formaldehyde resins and other polymer building blocks. A great advantage of these polymers is the reduction of the carcinogenic formaldehyde. Selecting the polymerization processes (e.g., substance polymerization, polymerization in solution) and controlling the polymerization reaction and properties of these novel materials requires knowledge of the properties of the individual melamine derivatives used as new building blocks. All possible permutations of N-methylmelamines were prepared, and reaction progress was monitored by GC/MS. 2,4,6-Tris(dimethylamino)-1,3,5-triazine was prepared to complete the series; this is, however, also a possible byproduct in various synthesis routes. The reaction conditions were optimized to obtain high yields of each derivative with the highest possible purity. The substances were characterized by NMR and IR spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray diffraction. In addition, physical properties, such as solubility, melting points, and  $pK_b$  values, were determined. The number of amino-, methylamino-, and dimethylamino groups has a significant effect on these properties. In summary, we found that by increasing the number of amino- and methylamino groups, solubility and  $pK_b$  increase. With increasing number of amino groups, the compounds tend to form hydrogen bonds, and thus, the melting point shifts to higher temperature ranges where they start to decompose.



## 1. INTRODUCTION

Methylated melamines are widely used as antitumor drugs, insect sterilants, and also as monomers for modified melamine-formaldehyde<sup>1–3</sup> and vinyl melamine polymers.<sup>4</sup> Hydroxymethyl(methylmelamines) are metabolites of antitumor agents such as altretramine (hexamethylmelamine) and trimelamol (trimethylol(trimethylmelamine)), formed by oxidation of a methyl group and subsequent elimination of formaldehyde.<sup>1,5,6</sup> These monomers offer a broad range of industrial applications, not only homopolymerized but also copolymerized with other monomers currently under investigation. Recent studies have used methylmelamines as building blocks for the synthesis of functional monomers and coating materials or as fine chemicals.<sup>7–14</sup> More information about applications of N-methylmelamines were summarized by Bretterbauer and Schwarzinger.<sup>14</sup>

To control and understand the properties of novel polymers, it is important to use starting material with high purity and not a mixture, which is currently the only commercially available form. Possible routes for preparing N-methylmelamines are transamination of melamine with methylamines;<sup>15–18</sup> direct methylation with methanol or tetramethylammonium hydroxide;<sup>19,20</sup> catalytic hydrogenation of melamine-formaldehyde resins;<sup>21,22</sup> reaction of carbon monoxide with ammonia/methylamine;<sup>23</sup> catalytic synthesis of methylmelamines from melamine and

methanol;<sup>24–27</sup> reaction of melamine with dimethyl sulfate and strong bases;<sup>28</sup> reaction of cyanoguanidine with dimethyl sulfate, methylamine, or methyl cyanamides;<sup>29–32</sup> and trimerization of substituted nitriles.<sup>33,34</sup> All these methods involve very complex mixtures of starting materials and thus also of products, whose properties are therefore very difficult to predict. Hence, it is crucial to understand the behavior of pure monomers, which can be prepared by successive substitution of the chlorine atoms in cyanuric chloride **1** with ammonia, methylamine, and/or dimethylamine.<sup>2,35–37</sup> In the published general procedures, the preparations are carried out in water, acetone, toluene, or chloroform, using the amine in gaseous form or as a solution in acetone or as hydrochlorides.

In this work, we present the selective synthesis of each methylmelamine using **1** as starting material with the addition of aqueous amine solutions, list the optimized reaction conditions to obtain high yields, and finally describe a general synthesis method usable for each individual derivative. A general structure and the prepared N-methylmelamines are listed in Table 1.

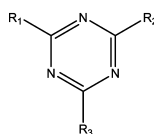
In the literature<sup>2,35,36</sup> characterization has so far been limited to elemental analyses and melting points. We compare our results to

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Table 1. List of Prepared *N*-Methylmelamines

	number	compound name	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
	1	cyanuric chloride	Cl	Cl	Cl
	2	2,4-diamino-6-methylamino-1,3,5-triazine	NH <sub>2</sub>	NH <sub>2</sub>	NH(CH <sub>3</sub> )
	3	2,4-diamino-6-dimethylamino-1,3,5-triazine	NH <sub>2</sub>	NH <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>
	4	2-amino-4,6-bis(methylamino)-1,3,5-triazine	NH <sub>2</sub>	NH(CH <sub>3</sub> )	NH(CH <sub>3</sub> )
	5	2-amino-4-methylamino-6-dimethylamino-1,3,5-triazine	NH <sub>2</sub>	NH(CH <sub>3</sub> )	N(CH <sub>3</sub> ) <sub>2</sub>
	6	2,4,6-tris(methylamino)-1,3,5-triazine	N(CH <sub>3</sub> )	NH(CH <sub>3</sub> )	NH(CH <sub>3</sub> )
	7	2,4-bis(methylamino)-6-dimethylamino-1,3,5-triazine	NH(CH <sub>3</sub> )	NH(CH <sub>3</sub> )	N(CH <sub>3</sub> ) <sub>2</sub>
	8	2-amino-4,6-bis(dimethylamino)-1,3,5-triazine	NH <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>
	9	2-methylamino-4,6-bis(dimethylamino)-1,3,5-triazine	NH(CH <sub>3</sub> )	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>
	10	2,4,6-tris(dimethylamino)-1,3,5-triazine	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>



those published and indicate any differences. Further, we provide additional data from IR, NMR, MS, and single-crystal X-ray diffraction experiments, and list solubilities, melting points, and  $pK_b$  values, which are important for choosing a polymerization process.

## 2. RESULTS AND DISCUSSION

**2.1. Synthesis of Methylmelamines.** For substitution of the first chlorine atom of cyanuric chloride **1**, it is crucial to stir the reaction mixture vigorously and cool it with crushed ice in order to dissipate the heat of reaction as fast as possible. The second chlorine atom reacts at around room temperature, and the third at 90–100 °C.<sup>36</sup>

The reaction temperature necessary for the substitution reaction also depends on the reactivity of the reagents: it increases from ammonia to methylamine and dimethylamine ( $\text{NH}_3 < \text{H}_2\text{N}(\text{CH}_3) < \text{HN}(\text{CH}_3)_2$ ). Generally, rigorous temperature control is important to avoid byproduct formation, in particular methylmelamine dimers. In the first reaction step, the easiest way of removing reaction heat is addition of crushed ice directly to the mixture under vigorous stirring. These conditions are limited to aqueous systems. After completion of the reaction, the products were filtered, washed several times with deionized water, and recrystallized if necessary. Some possible reaction routes for the preparation of different methylmelamines are shown in Scheme 1. The intermediates **1b**, **1d**, **1f**, **1g**, and **1h** were washed with deionized water to remove excess amines and, after GC/MS analysis, used directly without drying for the further synthesis of methylmelamine derivatives.

Advantages of the synthetic methods to previous studies are that the production of all *N*-methylmelamines was carried out in water as reaction medium and the use of aqueous solutions of ammonia, methylamine, and dimethylamine instead of the corresponding gases as reactant. The monitoring of the reaction with gas chromatography/mass spectrometry shows the complete turnover and also the optimized reaction times. The final products are isolated in good to excellent yield; for purifying, only minimal workup is necessary.

**2.2. Thermogravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC) Results.** In the DSC experiments, some of the methylmelamines (**2**, **3**, **4**, **5**, **8**) showed no clearly observable melting point, and the samples changed color, which

indicates further processes aside from simple melting. This is in contrast to reports from some previous studies,<sup>2,37</sup> describing only a melting point. The onset of this DSC measurement coincides with the values given in the literature. The additional processes were investigated by a combination of TGA and DSC. Compound **4** shows a 8% decrease in weight before melting starts, which indicates minor decomposition of the methylmelamine (Figure 1).

The methylmelamines without amino group at the triazine ring (**6**, **7**, **9**, **10**) show a sharp melting point without degradation. As an example, the TGA of **6** is shown in Figure 2, where the melting point is far below the decomposition temperature.

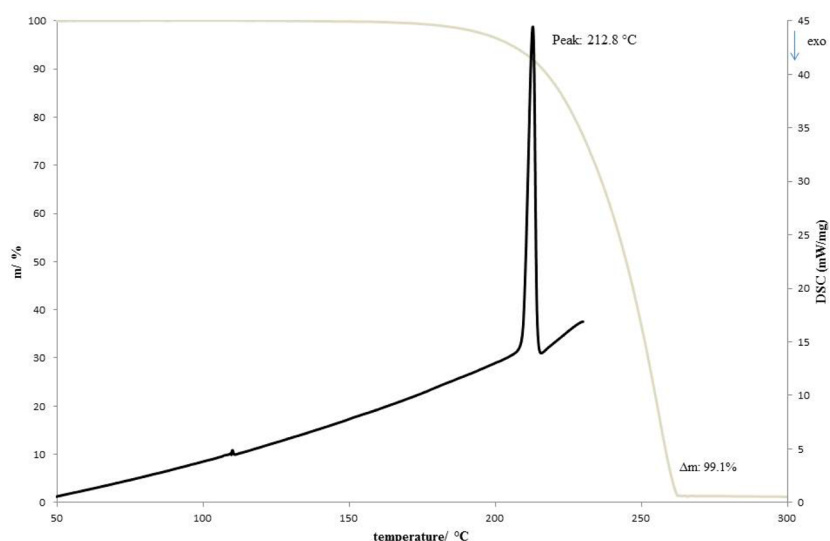
The presence of a free amino group at the triazine ring increases the number of possible hydrogen bonds and thus also the melting point to temperatures where the compound starts to decompose. The compounds that possess only methylamino- and dimethylamino groups at the triazine ring do not form an extended hydrogen bond system, and thus, their melting points are at considerably lower temperatures where no degradation takes place. The melting points and other physical properties of all methylmelamines are summarized in Table 2.

**2.3. Solubility.** The conclusions drawn from the TGA experiments are further supported by the water solubilities. For example, the water solubility of **6** is 45 times higher than that of **5**, which is a remarkable difference, given that both are trimethylmelamines. This can be explained by the number of amino-, methylamino-, and dimethylamino groups.

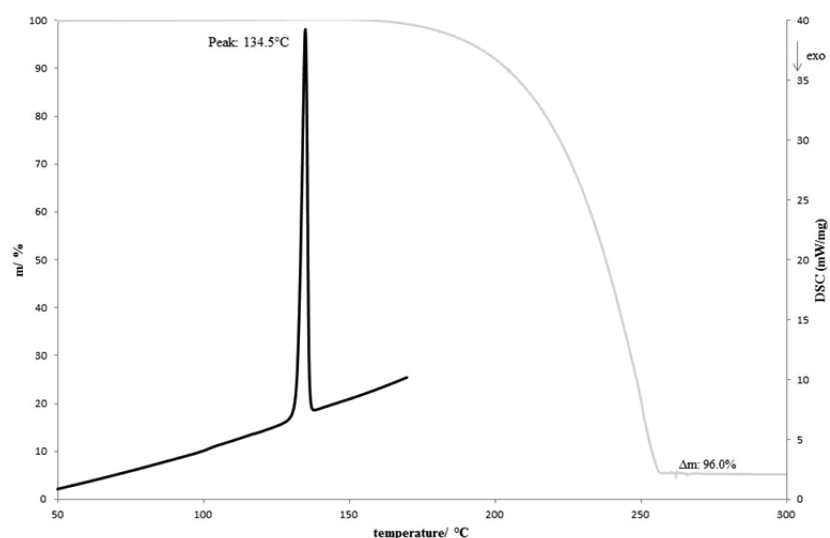
Increasing the number of methylamino groups has the greatest effect on water solubility (see ordinate in Figure 3). Accordingly, methylmelamines with two (**4**, **7**) and three methylamino groups (**6**) have the highest water solubility. With increasing number of amino groups, the water solubility also increases, but their influence is not as pronounced as that of the methylamino groups (see abscissa in Figure 3). Exceptions are compounds **4** and **7**: the solubility of **4** is somewhat lower than that of **7**, although **4** has one additional amino group. The number of diaminomethyl groups is indicated by dashed lines in Figure 3, and the higher number of diamino groups, the lower the solubility.

**2.4.  $pK_b$  Values.** In melamine, chemical reactions take place at the amino group,<sup>38</sup> whereas protonation occurs at the nitrogen atom in the ring.<sup>39</sup> According to calculations by Wang,<sup>40</sup> the  $pK_b$  value for the protonation of an amino group would be 17.8.





**Figure 1.** TGA/DSC of compound 2-amino-4,6-bis(methylamino)-1,3,5-triazine **4**. About 5% decrease in weight before melting indicates decomposition.



**Figure 2.** TGA/DSC of compound 2,4,6-tris(methylamino)-1,3,5-triazine **6**. The compound exhibits a sharp melting point, far below its decomposition temperature.

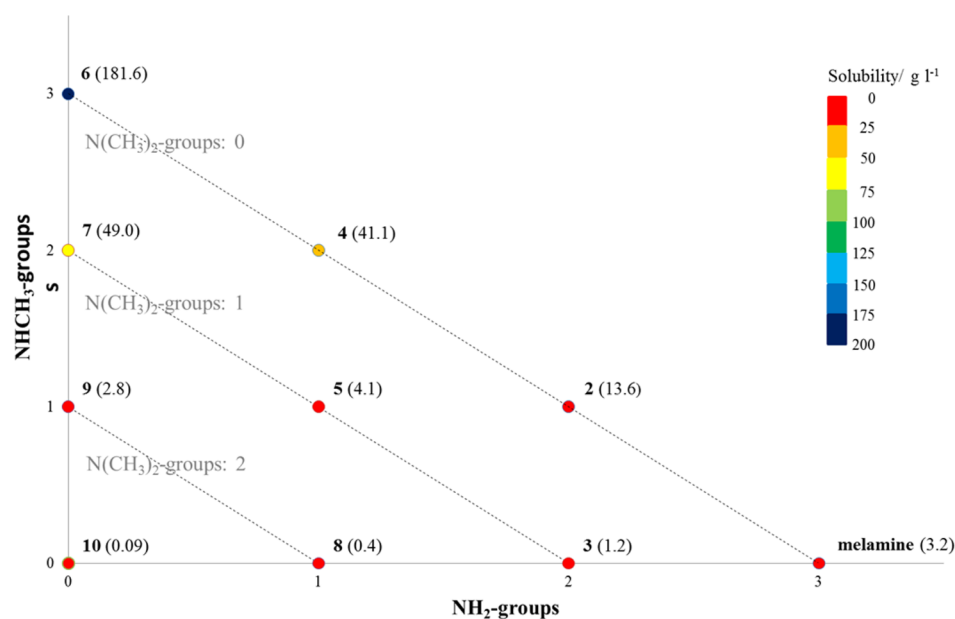
**Table 2. Melting Point (Onset), Solubility at 20 °C in Water,  $pK_b$ , of Different Methylmelamines, and Starting Temperature of Decomposition**

substance	mp/°C onset	solubility at 20 °C in H <sub>2</sub> O/g L <sup>-1</sup>	$pK_b$	starting temperature of decomposition/°C
<b>2</b>	270	13.6	8.65	220
<b>3</b>	256	1.2	8.44	180
<b>4</b>	210	41.1	8.42	174
<b>5</b>	182	4.1	8.23	164
<b>6</b>	132	181.6	8.14	162
<b>7</b>	93	49.0	8.01	150
<b>8</b>	215	0.4	8.16	146
<b>9</b>	103	2.8	8.01	128
<b>10</b>	172	0.09	7.92	184

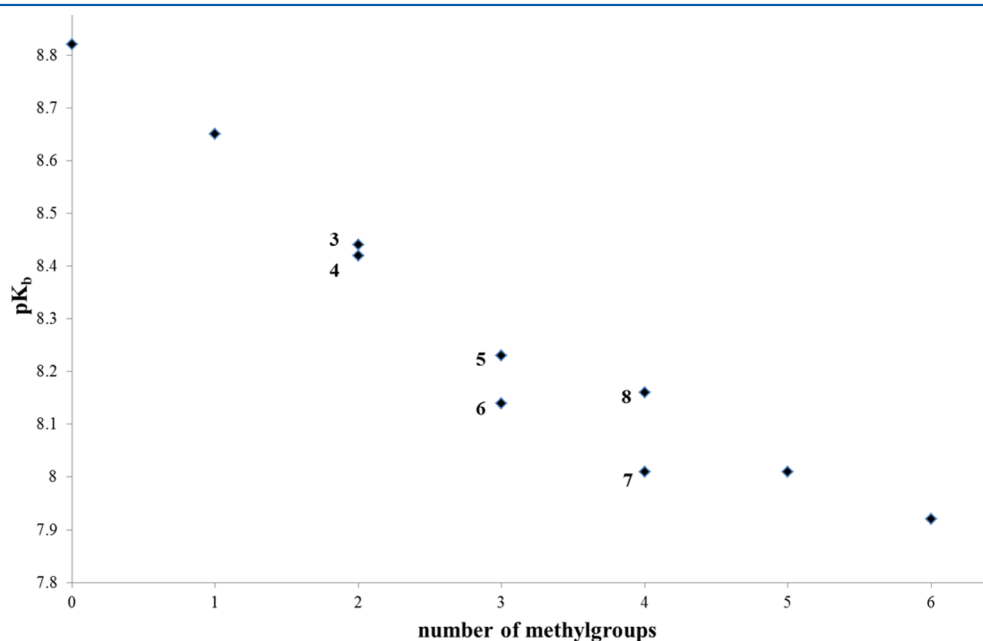
Replacing amino groups with stronger electron-donating methyl amino groups increases the electron density in the triazine system and concomitantly also the basicity. The  $pK_b$  values we determined are in accordance with this correlation (Table 2 and Figure 4).

A more detailed diagram is given in Figure 5, which illustrates the influence of the degree of substitution with amino groups on the  $pK_b$  value. Generally, the basicity increases with the number of methyl groups on the exocyclic nitrogen atoms. The  $pK_b$  decreases with decreasing number of both amino (abscissa) and methylamino groups (ordinate). The lowest  $pK_b$  was determined for **10**, which contains exclusively dimethylamino groups at the triazine ring.

**2.5. Structural Studies.** The triazine moiety is a popular template for supramolecular assemblies and multidentate ligands, because substituted melamines are easily accessible and facilitate a variety of interactions, such as hydrogen bonds, coordination bonds, and  $\pi\pi$ -stacking. Hence, it is surprising that simple alkyl-substituted melamines have so far not been investigated systematically. Although some solid-state structures of simple alkyl melamines have been determined by single-crystal X-ray diffraction,<sup>42–45,48</sup> methyl-substituted derivatives remain almost unexplored. The only reported example of a solid-state structure is hexamethylmelamine, **10**, which was published as early as in 1972.<sup>49</sup>



**Figure 3.** Solubility: correlation between amino-, methylamino-, and dimethylamino groups at the triazine ring; the number indicates the methylmelamine derivative; the solubility is given in  $\text{g L}^{-1}$  in brackets.



**Figure 4.**  $\text{pK}_b$  value as a function of the number of methyl groups.

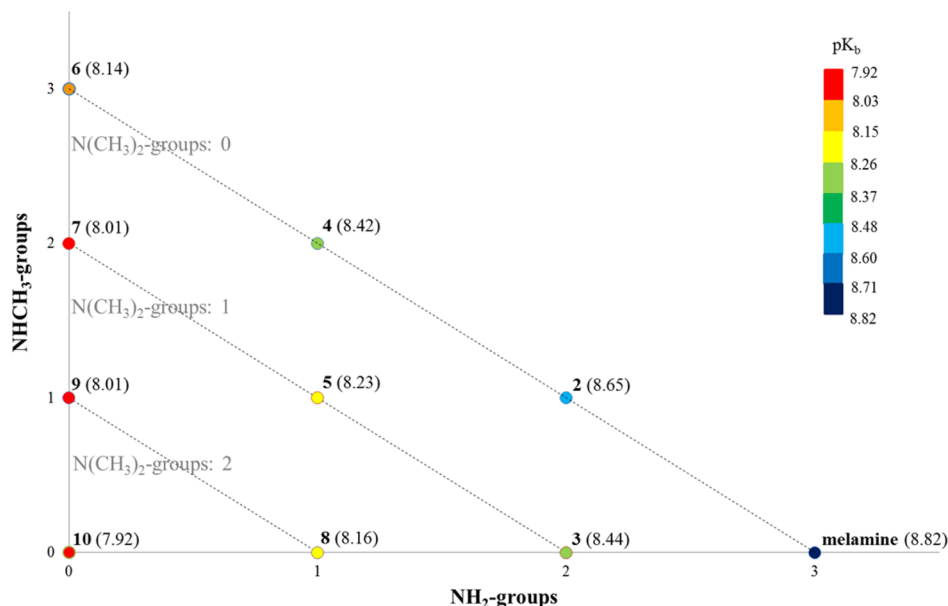
In contrast, the solid-state structure of the parent compound melamine has been determined several times, for the first time in 1941.<sup>50–55</sup> We were able to determine the molecular structures of almost all possible methyl-derivatives with the exception of **5** and **7**, which resisted repeated attempts to form suitable crystals in various solvents. Due to the high symmetry of most of the compounds, the symmetry of the space groups is also high: **2** and **8** crystallize in the orthorhombic space group  $P2_12_12_1$ , **3** in the tetragonal (and chiral) space group  $P4_32_12$ , **4** in the trigonal space group  $R\bar{3}c$ , and **6** and **9** in the monoclinic space groups  $P2_1/n$  and  $C2/c$ .

The molecular structures of all structurally characterized compounds are shown in Figure 6. The central triazine moiety forms a distorted but mostly planar hexagon. The outer-cycle nitrogen atoms and the methyl substituents lie largely in the

triazine plane. Bond lengths and angles of all melamines together with the reported parameters of melamine and hexamethylmelamine are summarized in Table S2 in the Supporting Information. Substitution with methyl groups alters the structural parameters of the triazine moiety of this series of melamines only slightly. For all derivatives, the inner-cycle C–N bond lengths are  $\sim 1.335\text{--}1.350$  Å. The C–N–C and N–C–N angles are  $\sim 113.5\text{--}114.5^\circ$  and  $\sim 125\text{--}126^\circ$ , respectively. The outer-cycle C–N bond lengths are also around  $\sim 1.34$  Å, which indicates bonding orders of both types of C–N bond that are, in principle, identical.

All compounds maintain an in part complex network of hydrogen bonds. Though a detailed discussion of the hydrogen bond system is beyond the scope of this contribution, Figure 7 shows an example of the bonding system between molecules of





**Figure 5.**  $pK_b$  value in relation to the number of amino-, methylamino-, and dimethylamino groups at the triazine ring. The number indicates the methylmelamine derivative; the  $pK_b$  is given in brackets.

compound **6**, which only dimerize due to the limited number of possible amine hydrogen atoms able to bond to an N-acceptor atom. Our as well as the previously published structural data of melamine derivatives suggest that  $\pi\pi$ -stacking does not play a major role in the aggregation of the molecules in the solid state, which is somewhat surprising, considering the flat structure of the melamine core moiety.<sup>43–47</sup>

### 3. CONCLUSIONS

Various methylated melamine derivatives that can be used as starting materials for modified melamine-formaldehyde resins or vinylmelamines were prepared in high purity and in high yields.

The information we gathered on the solubility of the presented melamine derivatives in water, their melting points, and the  $pK_b$  values are crucial for further processing, for instance, for the preparation of new melamine-formaldehyde resins with lower formaldehyde content, or the production of novel monomers and polymers. For example, the excellent water solubility of **6**, which is 45 times higher than that of melamine, makes it an ideal candidate for modified aqueous melamine formaldehyde resins. For further processing in molten state only **6**, **7**, and **9** can be used as they are the only derivatives having melting points below their decomposition temperature. The knowledge of  $pK_b$  values is very important especially when using the compounds in the manufacture of formaldehyde resins, as the procedure of hydroxymethylation is best performed in a pH range of 8–9, whereas higher or lower pH promotes the condensation reaction, thus buffering effects have to be taken into account.

The number of dimethylamino, methylamino, and amino groups significantly influences both solubility and  $pK_b$  values: solubility and  $pK_b$  increase with increasing number of methylamino and amino groups and decrease with increasing number of dimethylamino groups.

Higher numbers of amino groups increase the formation of hydrogen bonds and thus shift the melting point to temperatures at which the compounds start to decompose.

Our study of these compounds concluded with comprehensive chemical characterization based on IR, NMR, MS, and single crystal X-ray structures.

### 4. EXPERIMENTAL SECTION

**4.1. Material.** All chemicals and reagents were of p.a. quality and used without further purification.

**4.2. TGA/DSC.** Melting point and degradation temperatures were determined with DSC and TGA under nitrogen atmosphere. The temperature program was 40 °C (2 min), then heating at a rate of 10 °C min<sup>-1</sup> to 350 °C (2 min), and cooling at 10 °C min<sup>-1</sup> to 30 °C.

**4.3. GC/MS.** Reaction progress was determined with gas chromatography/mass spectrometry system. The samples were dissolved in water/acetone. Products were separated by means of an RTX 35 column (30 m, 0.32 mm i.d., 0.25  $\mu$ m) with He 4.6 as carrier gas (2 mL min<sup>-1</sup>), and identified by interpretation of their EI mass spectra and comparison to literature data and data from the NIST 2002, Wiley, and NBS electronic libraries. The GC/MS interface was kept at 280 °C. The GC was programmed from 5 °C (2 min) to 300 °C (10 min) at a rate of 20 °C min<sup>-1</sup>. The mass spectrometer was operated in EI mode (70 eV) at a source temperature of 200 °C.

**4.4. Elemental Analysis.** The elemental analysis was carried out with a CHNS/O-analyzer.

**4.5. Determining the  $pK_b$  Value.** Generally, potentiometric and spectroscopic methods are employed to determine  $pK_b$  values;<sup>56</sup> we used the former method. Solutions of each substance with concentrations ranging from 0.001 to 0.01 mol L<sup>-1</sup> were prepared. For concentrations above 0.01 mol L<sup>-1</sup>, the activity had to be considered. For concentrations below 0.001 mol L<sup>-1</sup>, potentiometry is too imprecise and spectrometry is the method of choice. The solutions were first adjusted with 0.1 N hydrochloric acid to a pH value of 2 and subsequently titrated with 0.1 N NaOH at 25 °C while being monitored using a glass electrode. The equivalence point corresponds to an inflection point of the curve and can thus be calculated by setting the second derivative of the titration curve equal to zero. For polyvalent bases, more than one equivalence point can be obtained.

**4.6. Determining the Solubility in Water.** To determine the solubility, a saturated aqueous solution of each compound was prepared at 20 °C. The solutions were homogenized for about 10 min in an ultrasonic bath and subsequently stirred for about 1 h. Undissolved compound was separated via filtration, and water was removed from the solution under vacuum. The residue substance was dried at 40 °C and weighed.

**4.7. IR Spectroscopy.** FTIR analyses were performed on an IR-microscope using the attenuated total reflection (ATR) mode. Spectra were recorded in the range from 650 to 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

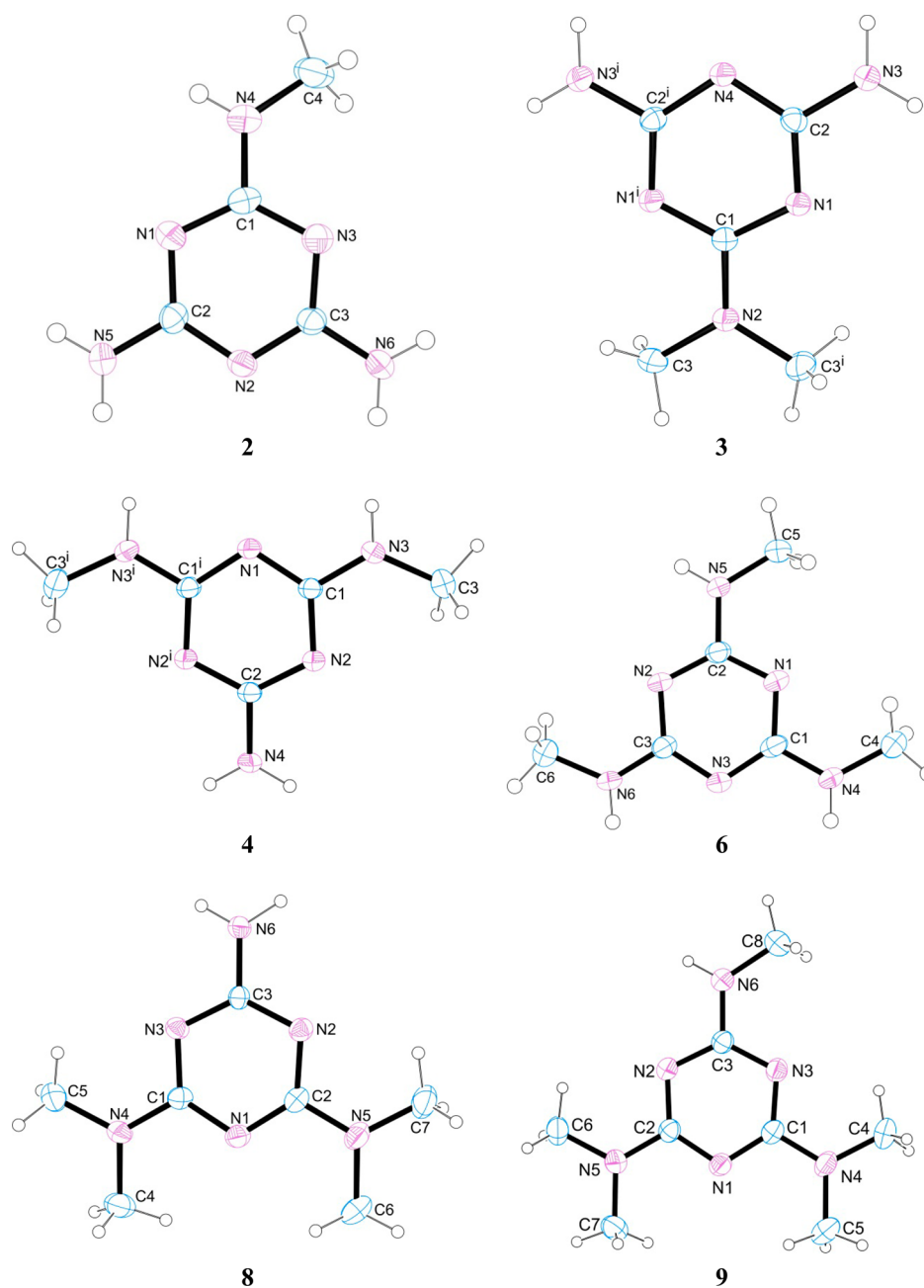


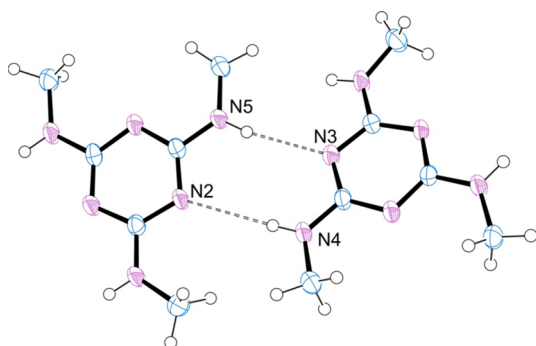
Figure 6. Molecular structures of compounds 2–4, 6, 8, 9 (ellipsoids drawn at the 50% probability level).

**4.8. NMR Spectroscopy.**  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were measured with a 300 MHz spectrometer using standard pulse sequences as provided by the manufacturer. The  $^1\text{H}$  signals of the deuterated solvents were used as internal calibration standards for NMR spectroscopy.  $^1\text{H}$  and  $^{13}\text{C}$  NMR of compounds 2–10 are included in the Supporting Information as Figure S9–S26. There are  $^1\text{H}$  spectra for substance 7<sup>57</sup> and 8,<sup>58</sup> but their results are not comparable with our results because different solvents were used. The  $^1\text{H}$  and  $^{13}\text{C}$  spectra of 10<sup>59</sup> and  $^{13}\text{C}$  spectra of 6<sup>60</sup> and 9<sup>61</sup> are according to literature.

**4.9. Single-Crystal X-ray Diffraction Experiments.** Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallization from ethanol. Single-crystal structure analysis was carried out on a diffractometer operating with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Further crystallographic and refinement data can be found in Table S1 in the Supporting Information. The structures were solved by direct methods (SHELXS-97)<sup>62</sup> and refined by full-matrix least-squares on  $F^2$  (SHELXL-97).<sup>63</sup> The H atoms were calculated geometrically, and a riding model was applied in the refinement process. Due to the absence

of a strong anomalous scatterer in compound 3, the Flack parameter is meaningless. Thus, Friedel opposites were merged, and the structure was refined in the space group  $P4_32_12$ . Refinement in the enantiomeric space group  $P4_12_12$  resulted in comparable crystallographic parameters. CCDC 1048857–1048862 contain the supplementary crystallographic data for the hitherto unpublished 2, 3, 4, 6, 8, 9. These data can be obtained free of charge from “The Cambridge Crystallographic Data Centre” via <https://summary.ccdc.cam.ac.uk/structure-summary-form>.

**4.10. Procedures for Synthesizing Precursors and Methylmelamines.** **1a:** 2-Amino-4,6-chloro-1,3,5-triazine. A hot suspension of 100 g (0.54 mol) of 1 in 250 mL of acetone was added under stirring to 500 g of crushed ice in water. The temperature should not exceed  $0^\circ\text{C}$ . To avoid a temperature increase, further ice was added as needed. While maintaining a temperature below  $0^\circ\text{C}$ , 110 g of 25 wt % aqueous ammonia solution was added. The suspension was stirred until the temperature increased to  $5^\circ\text{C}$  and then filtrated. The product was recrystallized in water and dried at room temperature. Yield: 79.7–82.3 g (90–93%), white solid. The product was used without analysis for further reaction steps.



**Figure 7.** Hydrogen bonds in crystal of **6** (N4–N2 3.401(3) Å, N4–H–N2 171°; N5–N3 3.051(3) Å, N5–H–N3 171°).

**1d:** 2,4-Bis(dimethylamino)-6-chloro-1,3,5-triazine. A suspension of 100 g (0.54 mol) of **1** in hot acetone was added very slowly to crushed ice. Then, 162.3 g (2.16 mol) of 60 wt % aqueous dimethylamine was added dropwise so that the temperature did not exceed 0 °C. After complete addition, the mixture was allowed to warm to room temperature and filtered. The product was recrystallized from isopropyl alcohol/water. Yield: 87.1–92.5 g (80–85%), white solid. MS EI:  $m/z = 203$  (40), 201 (100), 185 (85), 171 (76), 157 (21), 143 (23), 123 (26), 96 (71), 71 (50), 69 (64), 55 (42), 44 (48), 42 (98). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 202.4$  [**1d** + H]<sup>+</sup>.

**1f:** 2,4-Diamino-6-chloro-1,3,5-triazine. Under stirring, a hot suspension (lowers the temperature very quickly) of 100 g (0.54 mol) of **1** in acetone was added to 230 g (4.30 mol) of 32 wt % aqueous ammonia solution in about 500 g of crushed ice while the temperature did not exceed 10 °C. After complete addition, the temperature was raised to 40–45 °C for 4 h. After the mixture cooled to room temperature, it was filtered and the solid was washed with water and dried in vacuo at 40 °C. Yield: 70.2–74.1 g (90–95%), white solid. MS EI:  $m/z = 145$  (1), 126 (1), 101 (2), 68 (5), 62 (10), 43 (20), 42 (100). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 146.2$  [**1f** + H]<sup>+</sup>.

**1g:** 2-Amino-4-methylamino-6-chloro-1,3,5-triazine. At 0 °C, 9.3 g of a 40 wt % aqueous methylamine solution and 4.8 g of sodium hydroxide in water were added dropwise to 20 g of **1a** in 500 g of crushed ice. After complete addition, the mixture was stirred for 1 h at 0–5 °C and then for another hour at room temperature. The mixture was filtered, and the product washed with water and dried. Yield: 17.1–17.8 g (88–92%), white solid. MS EI:  $m/z = 159$  (1), 130 (1), 116 (1), 102 (1), 95 (3), 82 (4), 68 (21), 62 (55), 55 (50), 53 (29), 43 (32), 42 (100). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 160.2$  [**1g** + H]<sup>+</sup>.

**1h:** 2,4-Bis(methylamino)-6-chloro-1,3,5-triazine. Under stirring, a hot suspension of 100 g (0.54 mol) of **1** in 250 mL of acetone was added to 500 g of crushed ice in water. The temperature should not exceed 0 °C. Then, 84.0 g of 40 wt % methylmelamine in water and an aqueous solution of 43.2 g of sodium hydroxide were added at a temperature below 0 °C. The suspension was heated to 45 °C for 2 h. After it had cooled to room temperature, the product was filtered off, washed with water, and dried under vacuum at 40 °C. Yield: 84.4–89.1 g (90–95%), white solid. MS EI:  $m/z = 173$  (1), 155 (2), 129 (4), 105 (4), 99 (3), 77 (5), 62 (17), 55 (70), 41 (7). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 174.3$  [**1h** + H]<sup>+</sup>.

**2:** 2,4-Diamino-6-methylamino-1,3,5-triazine. To 60 g of **1f** suspended in water were added 64 g of 40 wt % aqueous methylamine solution and 16.4 g of sodium hydroxide in water. The mixture was heated to reflux for 2 h. After the mixture had cooled to room temperature, the solid was filtered off, washed with water, and dried under vacuum at 40 °C. Yield: 37.8–40.7 g (65–70%), white solid. Anal. Calcd for C<sub>4</sub>N<sub>6</sub>H<sub>8</sub> (140.15 g mol<sup>-1</sup>): C, 34.3; H, 5.8; N, 60.0. Found C, 34.4; H, 5.8; N, 59.7. MS EI:  $m/z = 140$  (46), 111 (24), 69 (24), 68 (34), 55 (26), 43 (100), 42 (45). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 141.2$  [**2** + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 30 °C):  $\delta = 2.67, 5.94, 6.12, 6.34$  ppm; <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 30 °C)  $\delta = 166.9, 167.3, 27.2$  ppm. IR (ATR):  $\bar{\nu} = 3442, 3318, 3153, 2954, 1675, 1645, 1535, 1462, 1442, 1406, 1369, 1287, 1174, 1063, 983, 813, 639$  cm<sup>-1</sup>.

**3:** 2,4-Diamino-6-dimethylamino-1,3,5-triazine. Fifty grams of **1f** was mixed with water; 51.7 g of 60 wt % aqueous dimethylamine solution and 13.6 g of sodium hydroxide in water were added. To avoid foaming, the mixture was heated very slowly to reflux for 4 h. After the mixture cooled, it was filtered. The product was washed with water and recrystallized from ethanol. Yield: 50.1–51.2 g (94–96%), white solid. Anal. Calcd for C<sub>5</sub>N<sub>6</sub>H<sub>10</sub> (154.17 g mol<sup>-1</sup>): C, 39.0; H, 6.5; N, 54.5. Found C, 39.2; H, 6.5; N, 54.2. MS EI:  $m/z = 154$  (32), 139 (16), 125 (13), 111 (18), 97 (4), 69 (32), 68 (35), 55 (9), 43 (100), 42 (92). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 155.2$  [**3** + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 30 °C):  $\delta = 2.97, 6.07$  ppm; <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 30 °C)  $\delta = 167.0, 166.1, 35.6$  ppm. IR (ATR):  $\bar{\nu} = 3324, 3178, 1665, 1636, 1549, 1504, 1445, 1399, 1275, 1109, 1064, 1028, 899, 811, 752, 625$  cm<sup>-1</sup>.

**4:** 2-Amino-4,6-bis(methylamino)-1,3,5-triazine. Under stirring, 57 g of 40 wt % aqueous methylamine solution and 14.8 g of sodium hydroxide in water were added to 30 g of **1a** suspended in water. The mixture was heated to reflux for 2 h and cooled to room temperature, and the product was filtered and dried. Yield: 22.6–24.0 g (80–85%), white solid. Anal. Calcd for C<sub>5</sub>N<sub>6</sub>H<sub>10</sub> (154.17 g mol<sup>-1</sup>): C, 39.0; H, 6.5; N, 54.5. Found C, 38.7; H, 6.5; N, 54.9. MS EI:  $m/z = 154$  (54), 125 (21), 98 (10), 83 (11), 82 (21), 68 (26), 57 (44), 55 (61), 43 (59), 42 (25); ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 155.2$  [**4** + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 30 °C):  $\delta = 2.68, 6.06, 6.29$  ppm; <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 30 °C)  $\delta = 166.5, 27.1$  ppm. IR (ATR):  $\bar{\nu} = 3203, 2958, 1663, 1547, 1459, 1414, 1379, 1178, 1044, 807, 726$  cm<sup>-1</sup>.

**5:** 2-Amino-4-methylamino-6-dimethylamino-1,3,5-triazine. At room temperature, 13.5 g of 40 wt % aqueous dimethylamine and 4.8 g of sodium hydroxide in water were added to 19 g of **1g** suspended in water. The mixture was heated under reflux for 2 h. The product was filtered, washed with water, and dried. Yield: 10.1–10.9 g (50–54%), white solid. Anal. Calcd for C<sub>6</sub>N<sub>6</sub>H<sub>12</sub> (168.20 g mol<sup>-1</sup>): C, 42.8; H, 7.2; N, 50.0. Found C, 42.8; H, 7.1; N, 49.9. MS EI:  $m/z = 168$  (59), 153 (32), 139 (19), 125 (15), 124 (13), 111 (6), 98 (9), 96 (10), 82 (31), 71 (20), 69 (29), 68 (36), 57 (38), 55 (66), 43 (79), 42 (100). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 169.2$  [**5** + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 30 °C):  $\delta = 2.70, 2.98, 5.17, 5.99, 6.40$  ppm; <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 30 °C)  $\delta = 166.7, 166.4, 165.7, 35.5, 27.1$  ppm. IR (ATR):  $\bar{\nu} = 3269, 3138, 2961, 1663, 1520, 1482, 1442, 1405, 1368, 1288, 1256, 1151, 1061, 999, 880, 808, 735, 630$  cm<sup>-1</sup>.

**6:** 2,4,6-Tris(methylamino)-1,3,5-triazine. To 93.5 g of **1h** in about 100 mL of water were added 83.8 g of 40 wt % aqueous methylamine and 21.6 g of sodium hydroxide in water. The mixture was heated very slowly to reflux and was refluxed for 2 h. When the mixture became clear, it was cooled down. Half the amount of water was removed by distillation. The solid was filtered off, washed with water, and dried. Yield: 75.2–77.0 g (83–85%), white solid. Anal. Calcd for C<sub>6</sub>N<sub>6</sub>H<sub>12</sub> (168.20 g mol<sup>-1</sup>): C, 42.8; H, 7.2; N, 50.0. Found C, 42.5; H, 6.9; N, 49.7. MS EI:  $m/z = 168$  (60), 139 (26), 138 (13), 124 (16), 83 (10), 82 (45), 68 (13), 57 (100), 55 (74), 43 (8), 42 (13). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 169.2$  [**6** + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 30 °C):  $\delta = 2.92, 4.88$  ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 30 °C)  $\delta = 166.8, 27.7$  ppm. IR (ATR):  $\bar{\nu} = 3458, 3349, 3258, 2963, 1626, 1510, 1504, 1441, 1412, 1371, 1184, 1112, 1084, 990, 808, 754, 728, 680$  cm<sup>-1</sup>.

**7:** 2,4-Bis(methylamino)-6-dimethylamino-1,3,5-triazine. Under stirring, 82.6 g of 60 wt % aqueous dimethylamine and 22 g of sodium hydroxide in water were added at room temperature to 95.3 g (0.55 mol) of **1h** suspended in water. The suspension was refluxed for 2 h. After the mixture was cooled to room temperature, the product was filtered, washed several times with water, and dried under vacuum at 40 °C. Yield: 82.0–87.0 g (82–87%), white solid. Anal. Calcd for C<sub>7</sub>N<sub>6</sub>H<sub>14</sub> (183.23 g mol<sup>-1</sup>): C, 46.1; H, 7.7; N, 46.1. Found C, 46.2; H, 7.5; N, 46.1. MS EI:  $m/z = 182$  (64), 167 (34), 153 (20), 138 (21), 124 (10), 96 (23), 82 (58), 71 (21), 69 (26), 57 (100), 55 (89), 44 (36), 43 (26), 42 (78). ESI pos (H<sub>2</sub>O/acetonitrile):  $m/z = 182.2$  [**7** + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 30 °C):  $\delta = 2.92, 3.09, 4.80$  ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 30 °C)  $\delta = 166.8, 165.8, 36.0, 27.7$  ppm; IR (ATR):  $\bar{\nu} = 3470, 3268, 2935, 1630, 1519, 1438, 1376, 1264, 1178, 1108, 1032, 900, 805, 751$  cm<sup>-1</sup>.



**8: 2-Amino-4,6-bis(dimethylamino)-1,3,5-triazine.** To 30 g of **1a** suspended in water was added 14.4 g of sodium hydroxide in water. Under stirring, 82.4 g of 40 wt % aqueous dimethylamine was added. To avoid foaming, the mixture was heated very slowly to reflux. After 2 h of refluxing, the mixture was cooled to room temperature. The product was filtered and dried. Yield: 30.0–30.7 g (90–92%), white solid. Anal. Calcd for  $C_7N_6H_{14}$  (182.23 g mol<sup>-1</sup>): C, 46.1; H, 7.7; N, 46.1. Found C, 46.0; H, 7.6; N, 46.8. MS EI:  $m/z$  = 182 (32), 167 (26), 153 (8), 138 (12), 124 (13), 112 (6), 111 (5), 96 (14), 82 (11), 71 (39), 69 (32), 55 (32), 44 (41), 43 (46), 42 (100). ESI pos ( $H_2O$ /acetonitrile):  $m/z$  = 183.2 [8 + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 30 °C):  $\delta$  = 3.09, 4.76 ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 30 °C)  $\delta$  = 167.2, 166.1, 36.1 ppm. IR (ATR):  $\bar{\nu}$  = 3336, 3172, 2933, 1659, 1506, 1380, 1298, 1244, 1217, 1033, 974, 929, 854, 808, 747, 656 cm<sup>-1</sup>.

**9: 2-Methylamino-4,6-bis(dimethylamino)-1,3,5-triazine.** To 100.5 g of **1d** suspended in water were added 87.0 g of 60 wt % aqueous dimethylamine and 23.2 g of sodium hydroxide in water. The mixture was heated to reflux for 2 h. After the mixture cooled, the product was filtered, washed with water, and dried. Yield: 80.2–85.1 g (82–87%), white solid. Anal. Calcd for  $C_8N_6H_{16}$  (196.25 g mol<sup>-1</sup>): C, 49.0; H, 8.2; N, 42.8. Found C, 48.7; H, 8.0; N, 42.9. MS EI:  $m/z$  = 196 (39), 181 (33), 167 (11), 152 (19), 138 (18), 123 (3), 107 (4), 96 (23), 82 (28), 71 (43), 69 (36), 57 (23), 55 (47), 44 (53), 43 (26), 42 (100). ESI pos ( $H_2O$ /acetonitrile):  $m/z$  = 197.2 [9 + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 30 °C):  $\delta$  = 2.92, 3.10, 4.69 ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 30 °C)  $\delta$  = 166.9, 165.8, 36.0, 27.6 ppm. IR (ATR):  $\bar{\nu}$  = 3269, 2931, 1514, 1370, 1297, 1240, 1221, 1136, 1049, 1008, 913, 853, 806, 607 cm<sup>-1</sup>.

**10: 2,4,6-Tris(dimethylamino)-1,3,5-triazine.** Under stirring, 7.5 g of 60 wt % aqueous dimethylamine and 2 g of sodium hydroxide in water were added to a suspension of 10 g of **1d** in water. The mixture was heated to reflux for 2 h. After the mixture has cooled, the solid was filtered, washed with water, and dried. Yield: 9.9–10.1 g (95–97%), white solid. Anal. Calcd for  $C_9N_6H_{18}$  (210.28 g mol<sup>-1</sup>): C, 51.4; H, 8.6; N, 40.0. Found C, 51.4; H, 8.4; N, 39.7. MS EI:  $m/z$  = 210 (30), 195 (30), 181 (7), 167 (7), 166 (11), 152 (20), 138 (2), 123 (7), 107 (4), 96 (38), 82 (11), 71 (36), 69 (41), 55 (27), 44 (57), 43 (26), 42 (100). ESI pos ( $H_2O$ /acetonitrile):  $m/z$  = 211.2 [10 + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 30 °C):  $\delta$  = 3.10 ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 30 °C)  $\delta$  = 166.0, 36.0 ppm. IR (ATR):  $\bar{\nu}$  = 2919, 2862, 1625, 1519, 1381, 1300, 1211, 1048, 854, 803, 570 cm<sup>-1</sup>.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00355. The corresponding CIF files were deposited at the Cambridge Crystallographic Data Center (1048857–1048862).

The <sup>1</sup>H, <sup>13</sup>C NMR, and the thermal plot for the structures (PDF)

Crystallographic data for compound **2** (CIF)

Crystallographic data for compound **3** (CIF)

Crystallographic data for compound **4** (CIF)

Crystallographic data for compound **6** (CIF)

Crystallographic data for compound **8** (CIF)

Crystallographic data for compound **9** (CIF)

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### Notes

The authors declare no competing financial interest.

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