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## Exploring the Route to 1,3,5-Triazine-2,4,6-triisocyanate ( $C_6N_6O_3$ ), a Hydrogen-Free Molecular Precursor for Polymeric C–N–(O) Materials

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We report on the synthesis of 1,3,5-triazine-2,4,6-triisocyanate  $[C_3N_3(NCO)_3]$ . The hydrogen-free compound, a new molecular precursor for the realisation of C-N-(O) networks (e.g.,  $C_2N_2O$ ,  $C_3N_4$ ), has been obtained in a five-step reaction sequence with well-defined intermediates. Starting from cyanoformiate, triethyl 1,3,5-triazine-2,4,6-tricarboxylate (C12O6N3H15) was prepared and identified by means of spectroscopic and thermal methods. In addition, the crystal structures of two modifications were solved [high temperature (HT):  $P6_3/m$  (no. 176), a = 11.07(2) Å, c = 6.83(4) Å,  $\gamma = 120^\circ$ ,  $V = 725.80(2) \text{ Å}^3$ , Z = 2; low temperature (LT):  $P2_1/n$  (no. 14), a = 21.75(2) Å, b = 6.54(5) Å, c = 21.81(0) Å,  $\beta = 119.81(0)^{\circ}$ , V = 2693.98(6) Å<sup>3</sup>, Z = 8]. Hydrolysis of the ester under alkaline conditions (KOH) yielded the corresponding salt of 1,3,5-triazine-2,4,6-tricarboxylic acid,  $C_3N_3(COO)_3K_3\cdot 2H_2O$  [P1 (no. 2), a = 6.95(0) Å, b = 17.45(8) Å, c = 17.54(1) Å,  $a = 119.76(0)^{\circ}$ ,  $\beta = 92.04(0)^{\circ}$ ,  $\gamma = 93.92(0)^{\circ}$ Å; V = 1837.63(0)Å<sup>3</sup>, Z = 6]. The dried salt was converted into 1,3,5-triazine-2,4,6-tricarbonyl trichloride  $[C_3N_3(COCl)_3]$  by reaction with POCl<sub>3</sub>. The tri-

#### Introduction

Molecular isocyanates are important building blocks for the preparation of polyisocyanates and polycarbodiimides.<sup>[1]</sup> Starting from isocyanates, the corresponding carbodiimides are simply prepared by thermal treatment, thus releasing  $CO_2$ ; see Equation (1).

$$2R-NCO \rightarrow R-N=C=N-R + CO_2 \tag{1}$$

Keeping this process in mind, the title compound, 1,3,5triazine-2,4,6-triisocyanate [C<sub>3</sub>N<sub>3</sub>(NCO)<sub>3</sub>] (Figure 1) appears to be an interesting molecular precursor to the stillelusive crystalline "carbon nitride" C<sub>3</sub>N<sub>4</sub>. A network that consists of triazines interlinked by carbodiimide bridges only would fulfil the desired stoichiometry for a preceramic polymeric precursor as predicted by some research groups.<sup>[2]</sup> In addition, the molecular title compound con-

chloride was also studied by means of single-crystal structure analysis  $[P2_1/c \text{ (no. 14)}, a = 9.73(6) \text{ Å}, b = 11.21(1) \text{ Å}, c =$ 17.03(1) Å,  $\beta = 91.91(1)^{\circ}$ , V = 1857.87(23) Å<sup>3</sup>, Z = 8]. Further reaction of the molecular acid chloride with AgN<sub>3</sub> gave the acyl azide, which was converted in situ into the product 1,3,5-triazine-2,4,6-triisocyanate by means of a thermally induced Curtius rearrangement. The final product was studied by thermal and spectroscopic methods. Owing to the high chemical reactivity of the isocyanate groups, oligomerisation/ polymerisation of the molecular compound occurred immediately at room temperature, thus forming amorphous uretdione-type coordination compounds. The uretdione-based network has been converted into the corresponding molecular carbamates (R-NH-CO-OR) by reaction with ethanol  $[P6_3/m \text{ (no. 176)}, a = 14.873(12) \text{ Å}, c = 6.605(7) \text{ Å}, \gamma = 120^\circ, Z$ = 2, V = 1265(2) Å<sup>3</sup>] and 2-propanol [P4<sub>3</sub> (no. 78), a =13.526(8) Å, c = 12.956(2) Å, Z = 4, V = 2370.5(3) Å<sup>3</sup>]. The potential of this new precursor in the field of carbon nitrides as well as carbon oxynitrides is discussed briefly.

sists of the elements C, N and O, and thus the difficulties in removing hydrogen from CNH-based molecules (cyanamide, dicyandiamide, melamine, melem) and polymers (melon) to produce  $C_3N_4$  are avoided. In fact, a lot of work has been reported in which polymeric melon<sup>[3]</sup> {i.e.,  $[C_6N_7(NH)(NH_2)]_n$ , the long-known final condensation product of many hydrogen-containing precursors,<sup>[4]</sup> was prepared and subsequently misinterpreted as a "carbon nitride" or "carbonitride"-based network. However, these hydrogen-containing polymeric amide-imides have nothing in common with the still elusive hydrogen-free crystalline " $C_3N_4$ ", which is expected to exhibit interesting physical properties. Nevertheless, recently some polymeric (organic) C-N-H networks based on polytriazines and polyheptazines have shown interesting features as porous supports for catalysts, for optoelectronic conversions as well as photocatalysts for water splitting and degradation of organic pollutants.<sup>[5]</sup> These systems, which have been sometimes classified as "carbon nitrides", cover a very broad range of chemical compositions and comprise a large family of related amorphous networks  $C_x N_v$  (e.g., "C<sub>3</sub>N<sub>2</sub>", "C<sub>3</sub>N", "C<sub>5</sub>N", " $C_{10}N_3$ ") as well as even more numerous defective  $C_x N_y H_z$ variants.

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Figure 1. 1,3,5-Triazine-2,4,6-triisocyanate might be regarded as the trimer of cyanogen isocyanate (NC–NCO).

In recent years, several attempts at new synthetic approaches towards preceramic C–N networks have been reported.<sup>[6]</sup> Functionalised triazines as well as heptazines of various kinds have been tested and important intermediates have been structurally characterised. So far, all of these approaches have failed to yield a crystalline nitride of carbon and therefore new preparative concepts towards hypothetical  $C_3N_4$  need to be evaluated.

Recently, we started an investigation in this field by analysing hydrogen-free C–N–O compounds for their suitability as precursors for the synthesis of binary C–N compounds.<sup>[7a–10]</sup> Molecular cyanogen isocyanate (NC–NCO)<sup>[8]</sup> might form the title compound, 1,3,5-triazine-2,4,6-triisocyanate, by means of trimerisation of the nitrile function (Figure 1). However, when studying the polymerisation reactions, the reactivity of monomeric NC–NCO was found to be different and resulted in a linear cyamelide- or nylonlike polymer.<sup>[9]</sup> Upon further thermal treatment, another polymeric resinlike solid resulted that had the correct overall composition of "C<sub>3</sub>N<sub>4</sub>" and did not contain any hydrogen.<sup>[10]</sup> The exact connectivity of this inorganic network has not been fully settled yet.

We have suggested that 1,3,5-triazine-2,4,6-triisocyanate might be another promising precursor.<sup>[7a,10]</sup> In this case, the triazine ring is preshaped and, unlike monomeric NC– NCO, one of the sites (–CN) would be inactive. This would reduce the number of possible reaction paths and would make the analysis of the underlying reaction mechanisms and of the final (amorphous) product more convenient. Indeed, spectroscopy on  $C_3N_4$  prepared by means of NC– NCO gave hints of the presence of triazine groups.<sup>[10]</sup> This fact points towards regioselective reactions at defined functional groups. Therefore, we consider free isocyanate functions to be a prerequisite for the formation of polycarbodiimides under mild conditions.

However, free isocyanates are known to exhibit several undesired side reactions. Besides hydrolytic degradation, which is commonly observed, oligomerisation/polymerisation reactions that give rise to the formation of polymeric macromolecules are a crucial issue.<sup>[1]</sup> As known from organic isocyanate chemistry, uretdione-like products of polyaddition are formed quite easily (Figure 2).<sup>[1,11]</sup>

To summarise, for efficient control of the reactivity of (molecular) isocyanate compounds that consist of the elements C, N and O only, a blocked isocyanate function would be required, from which the isocyanate function should be generated easily by simple deblocking reactions.



Figure 2. Organic isocyanates are capable of forming uretdione-like polyadducts in the course of autopolymerisation.

The acyl azide function  $(-CON_3)$  might serve this purpose, which means it could be considered a "masked isocyanate".

The transformation of the acyl azide to the isocyanate by simple abstraction of gaseous  $N_2$  is known as the Curtius rearrangement; see Equation (2).<sup>[12]</sup>

$$R-CON_3 \rightarrow R-N=C=O + N_2$$
 (2)

For the preparation of the targeted molecule 1,3,5-triazine-2,4,6-triisocyanate, we have developed a five-step synthesis protocol. A reasonable reaction sequence is presented in Figure 3. This article is organised according to the synthesis sequence given; it reports the individual syntheses and characterisations of the intermediates.



Figure 3. Five-step synthesis protocol for the synthesis of 1,3,5-triazine-2,4,6-triisocyanate.

#### **Results and Discussion**

#### Step 1: Synthesis and Characterisation of Triethyl 1,3,5-Triazine-2,4,6-tricarboxylate (C<sub>12</sub>O<sub>6</sub>N<sub>3</sub>H<sub>15</sub>)

The ester (see the Exp. Section) was characterised by single-crystal X-ray structure analysis of its two polymorphs 1 Exploring the Route to 1,3,5-Triazine-2,4,6-triisocyanate (C<sub>6</sub>N<sub>6</sub>O<sub>3</sub>)



	1	2	3	4	5	6
Formula	HT-	LT-	C <sub>3</sub> N <sub>3</sub> (COO) <sub>3</sub> K <sub>3</sub> ·	C <sub>3</sub> N <sub>3</sub> (COCl) <sub>3</sub>	C <sub>3</sub> N <sub>3</sub> (NHCOOCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ·	C <sub>3</sub> N <sub>3</sub> [NHCOOCH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> ·
	C12O6N3H15	C <sub>12</sub> O <sub>6</sub> N <sub>3</sub> H <sub>15</sub>	$2H_2O$		3CH <sub>3</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHOH
Symmetry	<i>P</i> 6 <sub>3</sub> / <i>m</i> (no. 176)	$P2_1/n$ (no. 14)	<i>P</i> 1 (no. 2)	$P2_1/c$ (no. 14)	<i>P</i> 63/ <i>m</i> (no. 176)	P43 (no. 78)
a [Å]	11.07(2)	21.75(2)	6.950(0)	9.735(6)	14.873(12)	13.526(8)
b [Å]		6.54(5)	17.4577(7)	11.210(8)		
c [Å]	6.83(4)	21.81(0)	17.5414(6)	17.034(1)	6.605(7)	12.956(2)
a [°]			119.76(0)			
β [°]		119.81(0)	92.04(0)	91.91(1)		
γ [°]			93.92(0)			
V[Å <sup>3</sup> ]	725.80(2)	2693.98(6)	1837.63	1857.87(23)	1265(2)	2370.5(3)
Formula units	2	8	6	8	2	4
T [K]	293	173	296	173	293	273
Final R indices	R1 = 0.1238,	R1 = 0.0631,	R1 = 0.0581,	R1 = 0.0520,	R1 = 0.1336,	R1 = 0.0975,
	wR2 = 0.1528	wR2 = 0.1287	wR2 = 0.1104	wR2 = 0.0990	wR2 = 0.3180	wR2 = 0.2402

Table 1. Crystal data of compounds 1-6.

and 2 (see Table 1; relevant data concerning the structural solution are documented in Tables S1 and S2 of the Supporting Information). The structural metric and symmetry derived from single-crystal studies at room temperature were verified by powder X-ray diffraction of the bulk material (see the Supporting Information). The Le Bail fit for 1 yielded the parameters for a hexagonal lattice: a = 10.993 Å, c = 6.773 Å. The crystal structures of the two phases of the triethyl ester are shown in Figure 4. The differences between the crystal structures of the two polymorphs are mainly related to packing effects.



Figure 4. The crystal structure of the high-temperature (HT) phase of the triethyl ester along [001] (left) and the crystal structure of the low-temperature (LT) phase along [010] (right).

The catalytic trimerisation of CN-containing molecules to the corresponding aromatic triazines is a well-known reaction. The influence of the solvent toluene seemed to be in keeping intermediates long enough in solution to allow the slow reaction to complete. Without cosolvent, the overall yield was very low. The product originally contained large amounts of chlorine, which was impossible to remove during the washing procedure, thus pointing towards a stable adduct. The product from the reaction along our modified procedure was found to be free of chlorine and, contrary to the used reactant, stable toward moisture. With the analytic methods applied, no impurities could be detected.

# Step 2: Synthesis and Characterisation of the (Hydrated) Potassium Salt of 1,3,5-Triazine-2,4,6-tricarboxylic Acid $[C_3N_3(COO)_3K_3\cdot 2H_2O]$

The potassium salt 3 was obtained by hydrolysis of the ester (see the Exp. Section). Its crystal structure<sup>[7a,7b]</sup> is

shown in Figure 5; for crystallographic data, see Table 1 (and Table S3 in the Supporting Information). The triazine moieties are arranged in columns along the [100] direction. Each triazine group is surrounded by three K<sup>+</sup>. The metal ions and the triazine groups connect to form a layer. Between two layers, water molecules are inserted. In one case, the triazines are arranged ecliptically; in the other case, they are staggered. This special arrangement appears to be forced by the coordinated by seven atoms (six oxygen and one nitrogen atom) in a 5+2 coordination geometry.



Figure 5. The crystal structure of the potassium salt of 1,3,5-triazine-2,4,6-tricarboxylic acid dihydrate ( $C_6O_6N_3H_3M_3\cdot 2H_2O$ ). The structure consists of four "building blocks": K<sup>+</sup> cations, water molecules, and two sets of columns that extend along the *a* axis of 1,3,5-triazine-2,4,6-tricarboxylic acid anions.

The other oxygen atoms came from the water molecules and other carboxyl groups. The K–N distances vary between 2.79 and 2.81 Å, whereas the K–O distances vary over a larger range (2.74-2.86 Å). All distances are in expected ranges.

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#### Step 3: 1,3,5-Triazine-2,4,6-tricarbonyl Trichloride [C<sub>3</sub>N<sub>3</sub>(COCl)<sub>3</sub>]

The trichloride 4 was obtained by treating the dried potassium salt with POCl<sub>3</sub> (see the Exp. Section). A Le Bail fit of a recorded X-ray diffraction pattern (data not shown) revealed a monoclinic symmetry [a = 9.78 Å, b = 10.97 Å,c = 17.12 Å,  $\beta = 91.91(1)^{\circ}$ ]. No high-quality X-ray powder patterns could be recorded on account of the waxy nature of the material. The obtained acid chloride is a highly moisture-sensitive, waxy solid. Besides the common analytics (IR, NMR, GC-MS; see the Exp. Section) no further experiments were performed. From these analyses, this product was found to be in a pure form. A suitable crystal was measured at low temperature (T = -100 °C), thus confirming the symmetry information derived from the powder (see Table 1 and also Table S4 in the Supporting Information). The packing of this molecule is shown in Figure 6. In the solid-state, the molecule is not flat, and the three planar COCl ligands are rotated against the plane of the triazine ring. The torsion angles between the Cl atoms and the *cis*-N atoms of the aromatic ring for the two crystallographically independent molecules are 44.72, 14.30, 6.66 and 41.76, 14.81, 2.85°, respectively. The intermolecular contact between an O atom and a C atom of the triazine ring is 2.79 Å. Interestingly, 4 does not feature the common 2D character for the packing of triazine-based molecules in the solid state.



Figure 6. The packing of 1,3,5-triazine-2,4,6-tricarboxyl chloride in the solid state.

#### Step 4: 1,3,5-Triazine-2,4,6-tricarbonyl Triazide/1,3,5-Triazine-2,4,6-triisocyanate

No analytical data of the acyl azide was recorded. It was prepared and treated in situ only (see the Exp. Section). Due to the extreme sensitivity of the acid chloride, standard azide formation reactions could not be applied. Excessive hydrolysis of molecular triazines was observed with oxalic acid dihydrate (COOH)<sub>2</sub>·2H<sub>2</sub>O as a crystalline product. It has to be noted that this sensitivity towards moisture is a special feature of triazine chemistry.<sup>[21]</sup> With the corresponding phenyl acyl azides, the reaction could be successfully performed in water.<sup>[15]</sup> Therefore, a solid–solute biphasic reaction was used. This reaction was so slow that heating was needed. This, however, introduced a Curtius rearrangement at once. As a summary, the molecular acyl azide was not isolated. It is certain that this compound exists. But since it was not in the focus of this work, further experiments towards its isolation were postponed. The Curtius rearrangement was indirectly substantiated to occur by gas formation during reaction (detected by means of a gas bubbler).

The obtained isocyanate was further studied. The slightly yellow solid was X-ray amorphous and highly moisture-sensitive. By means of IR spectroscopy, the presence of the isocyanate function (strong band at 2251 cm<sup>-1</sup>) was proven (Figure 7). After short exposure to humidity, this band vanishes (see Figure S5 in the Supporting Information). Also, the uretdione  $(1755 \text{ cm}^{-1})^{[11]}$  and triazine bands (1520, 1289 and 1258 cm<sup>-1</sup>) were observed.



Figure 7. IR spectrum of C<sub>3</sub>N<sub>3</sub>(NCO)<sub>3</sub>.

By using GC-MS (Figure 8), the molar mass was identified  $(m/z \ 204)$ . In addition, a complex pattern of signals was detected. The signals were found to be separated by a constant value of m/z 14. If we take the pattern as a whole, it is typical for a polymeric compound, from which nitrogen is released during thermal degradation. The solid-state <sup>13</sup>C NMR magic-angle spinning (MAS) spectrum (Figure 9) shows, in addition to side bands, four signals. Two strong ones ( $\delta = 167.28$  and 131.92 ppm) belong to the 1.3.5-triazine-2,4,6-triisocyanate. We assigned the first signal to the triazine ring and the second to the NCO group. In the related mono- and bifunctionalized triazines, the signals were found at similar positions.<sup>[13]</sup> In addition, two weaker signals were recorded ( $\delta$  = 144 and 153 ppm). These two latter signals were assigned to entities formed by means of isocyanate homopolymerisation (see Figure 2). In fact, the signal at  $\delta = 153$  ppm is close to the signal of a uretdione group

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(around  $\delta = 151 \text{ ppm}$ ).<sup>[14]</sup> The signal at  $\delta = 144 \text{ ppm}$  is within a region ( $\delta = 120$ –145 ppm) that is known for several overlapping peaks of macromolecular polyisocyanates.



Figure 8. GC–MS of  $C_3N_3(NCO)_3$ : the molecular peak is found at m/z 204.



Figure 9. <sup>13</sup>C NMR MAS spectrum of [C<sub>3</sub>N<sub>3</sub>(NCO)<sub>3</sub>].

This specific kind of homopolymerisation as sketched in Figure 2 found further support by the results of the calculation of the Mulliken charges of molecular 1,3,5-triazine-2,4,6-triisocyanate. It turned out that the highest atomic charges are found within the isocyanate (NCO) group (see Table 2). As seen from the calculated values, the point of highest chemical reactivity is the N=C bond of the isocyanate. There, a high polarity is ensured (-0.485 on the N atom, +0.684 on the C atom). This result is in accord with the proposed reactivity.

Table 2. Mulliken charges of the atoms of 1,3,5-triazine-2,4,6-triisocyanate.

Atom	Mulliken charges				
$\overline{C_3N_3}$	+0.618				
$C_3N_3$	-0.467				
NCO	-0.485				
NCO	+0.684				
NCO	-0.350				

Taken all together (see Figure 10), a more substantiated model for the chemical connectivity of the polymerised 1,3,5-triazine-2,4,6-triisocyanate (the polytriazine **2**) can be provided (sketch 3).



Figure 10. The "free" molecule 1,3,5-triazine-2,4,6-triisocyanate (1) rapidly polymerises and oligomerises to form ill-defined polyisocyanates (2). For the linkages we suggest uretdione units (3).

Finally, the thermal behaviour of the polyisocyanate was studied. The compound starts decomposing at T > 100 °C. CO<sub>2</sub> is the only gaseous product, thereby substantiating Equation (1). To substantiate the evolution of CO<sub>2</sub>, a gas bubbler filled with a diluted Ba(OH)<sub>2</sub> solution was used. A solid was formed; however, mass loss was far too high for a simple CO<sub>2</sub> abstraction reaction. Therefore we assume that depolymerisation simultaneously occurs and the monomer sublimes. In a separate experiment, the sublimation process was indeed observed. The polymer was heated and the evolving gas solidified at the colder part of the apparatus. The solid was colourless. After a certain time at room temperature, the material turned yellow again. Most likely, as also known from monomeric NCNCO,<sup>[8]</sup> the monomer is only stable at low temperatures or in the gas phase.

To substantiate the (molecular) structure of 1,3,5-triazine-2,4,6-triisocyanate, the amorphous product was treated with dry alcohols. It is known that isocyanates easily react with alcohols to form organic amides or, more specifically, carbamates (Figure 11). When storing a solution of the isocyanate at T = -4 °C in ethanol, colourless crystals of C<sub>3</sub>N<sub>3</sub>(NHCOOCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>·3CH<sub>3</sub>CH<sub>2</sub>OH formed (5) (see Table 1). The crystal structure is shown in Figure 12 (for crystallographic data see Table S5 in the Supporting Information). The most important result is the identification of the carbamate function R-NH-CO-OR. This proves the initial presence of the molecule 1,3,5-triazine-2,4,6-triisocyanate. The reaction of amorphous C<sub>3</sub>N<sub>3</sub>(NCO)<sub>3</sub> with an excess amount of isopropanol gave needles of crystalline  $C_3N_3[NHCOOCH(CH_3)_2]_3$ ·(CH\_3)<sub>2</sub>CHOH (6) (see Table 1). The crystal structure is presented in Figure 13 (crystallo-

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graphic details are listed in Table S6 of the Supporting Information). Also in this case, the presence of the carbamate function is unambiguously proven.



Figure 11. The formation of the corresponding carbamates by reaction of (poly)isocyanates with alcohols (ethanol, 2-propanol).



Figure 12. The molecular geometry of the 1,3,5-triazine-2,4,6-triethylamide–ethanol adduct (view along the [001] direction).



Figure 13. Packing motive of two molecules in the solid state. Steric interactions seem to prevent flat packing.

It is worth mentioning that the R indices for the structural solution of compounds **5** and **6** are poor. Nevertheless, there is no doubt about the chemical connectivity.

As a summary, polymeric 1,3,5-triazine-2,4,6-triisocyanate was identified by IR spectroscopy (isocyanate and triazine absorption bands), GC-MS analysis (correct molar mass) and solid-state MAS <sup>13</sup>C NMR spectroscopy (signals for triazine and isocyanate groups). Therefore, although no crystallographic data of this compound is available up to now, we give sufficient evidence that the targeted molecule has been prepared in reasonable purity. Autopolymerisation reactions rapidly turn the molecular triazine into a macromolecular network. Further evidence for the title compound has been derived by isolation of the reaction products of the polyisocyanate network with dry alcohols. The corresponding carbamates have been obtained and each case studied. In fact, the solvolysis of an amorphous crosslinked inorganic network and the subsequent crystallographic studies on molecular products obtained has been used with great success in the course of structural studies on amorphous melon.<sup>[16]</sup>

Autopolymerisation of 1,3,5-triazine-2,4,6-triisocyanate occurs by means of the reactive isocyanate groups. These are capable of forming uretdione-like adducts.<sup>[1,11]</sup> Experimental indications for these adducts were obtained from IR and NMR spectroscopic analysis from which hints for the presence of uretdione-bridges have been deduced. In addition, this common reactivity found further support by the analysis of the Mulliken charges of 1,3,5-triazine-2,4,6-triisocyanate (Table 2) from which we have deduced that the highest chemical reactivity is found with the N=C bond of the isocyanate group.

In addition, the rather weak uretdione bonding system was broken by thermal treatment with the formation of  $CO_2$ . At T = 100 °C, depolymerisation occured and a white volatile solid (the free 1,3,5-triazine-2,4,6-triisocyanate) was isolated. Overall, the thermal behaviour of the molecular precursor appears to be comparable to the reactivity found for NC–NCO (cyanogen isocyanate).<sup>[8]</sup> The product of such a thermal treatment above 100 °C (a new hydrogen-free C–N network) will be studied in the near future.

The white solid 1,3,5-triazine-2,4,6-triisocyanate is soluble in dry acetone. In solution, polymerisation of this white material occurs much faster than in the solid state, and a vellow amorphous solid precipitates. 1,3,5-Triazine-2,4,6triisocyanate (C<sub>6</sub>N<sub>6</sub>O<sub>3</sub>) might be an interesting compound in itself since it could be equally seen as an amorphous variant of elusive crystalline C2N2O (carbon oxynitride). Crystallisation experiments under high-pressure conditions [diamond anvil cell (DAC) technique] appear promising for the preparation of a new crystalline "low-Z solid",<sup>[17]</sup> as was recently shown for CO<sub>2</sub> (carbon dioxide).<sup>[18]</sup> The latter gaseous molecular compound was transformed into a SiO2like extended crystalline solid at T > 1500 °C and p >40 GPa. Application of lower pressures (and temperatures) is most likely not suited to overcome the tendency of C-N polymers to decompose to nitrogen and graphite or diamond.[19]

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#### Conclusion

In this work, the total synthesis of (polymeric) 1,3,5-triazine-2,4,6-triisocyanate has been discussed. First, the triazine ring was formed by a nitrile trimerisation. In this context, the triazine triethyl ester has been isolated. Hydrolysis of the ester under alkaline conditions gave the corresponding potassium carboxylate. This salt was converted into the acid chloride by reaction with POCl<sub>3</sub>. The compounds were fully characterised by spectroscopic methods and all of them gave well-crystallised samples for structural studies in the solid state. The acyl azide was prepared in situ by reaction with AgN<sub>3</sub>. This intermediate compound was converted into the isocyanate by Curtius rearrangement. The product obtained was analysed by thermal, theoretical and spectroscopic methods as well as crystallographic studies on products of chemical conversion reactions (carbamates). It turned out that intermolecular reaction of the isocyanate functionality of 1,3,5-triazine-2,4,6-triisocyanate occurred rapidly, thus forming an amorphous 3D polymer interlinked by uretdione functions. The free-molecule 1,3,5-triazine-2,4,6-triisocyanate can be recovered for a short time by depolymerisation at T > 100 °C. It is a white volatile solid that can be solved in dry acetone. Upon storage at room temperature polymerisation will set in again, thus forming a yellow amorphous solid after some minutes.

In terms of chemical and thermal behaviour, a striking analogy with previously studied NC–NCO has been obtained. With the polymer (or monomer) described in this article, a new C–N–O precursor is available. As already shown, these hydrogen-free networks are capable of forming pure  $C_3N_4$ . Further studies in the near future will include the chemical reactivity of this interesting compound. As a long-term goal, the directed synthesis of a hydrogen-free and crystalline C–N or C–N–O network is a primary focus.

### **Experimental Section**

Triethyl 1,3,5-Triazine-2,4,6-tricarboxylate: The triester was prepared by using the (slightly modified) procedure as given by Ott.<sup>[20]</sup> Briefly, ethyl cyanoformate (10 g) was mixed with absolute toluene (50 mL) and this solution was stirred and kept under a stream of Ar and HCl. The latter was prepared by dropping  $H_2SO_4$  (96%) into NaCl for one hour. The mixture was stored without further agitation for two weeks under Ar. The triethyl ester slowly crystallised from this solution. The product was washed several times with toluene until the washing liquid remained colourless. The solid was first dried under dynamic vacuum at room temp. and finally stored over KOH pellets for several days. Absence of Cl was checked by means of energy-dispersive X-ray (EDX) analysis. For bulk studies, the large crystals obtained were ground to a colourless powder. This was found to be insoluble in certain polar (H<sub>2</sub>O) and nonpolar (pentane, toluene) solvents but showed good solubility in CHCl<sub>3</sub>. The yield was nearly quantitative (9.82 g, 98%). FTIR (25 °C):  $\tilde{v}$  = 1745 (C=O), 1533, 1380 cm<sup>-1</sup> (C<sub>3</sub>N<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 4.51 (q), 1.15 (t) ppm. <sup>13</sup>C NMR:  $\delta$  = 14.29 (s), 64.21 (s), 161.52 (s), 167.17 (s) ppm. <sup>13</sup>C NMR MAS:  $\delta$  = 14.77 (*C*H<sub>3</sub>-), 64.47 (-CH2-), 161.07 (C-C=O), 166.15 (C-C=O) ppm. GC-MS (EI): m/z = 298. Thermal data: DSC: signal at T = -3 °C (phase transition), melting point:  $T = 166 \,^{\circ}\text{C}$ .

Potassium 1,3,5-Triazine-2,4,6-tricarboxylate: The salt was prepared by hydrolysis of the triethyl ester under basic conditions.<sup>[21]</sup> Solid KOH (1.67 g) was dissolved in water (50 mL) and the triethyl ester (3.01 g) was added. To prevent KOH as an impurity, an excess amount of triethyl ester was used. After 1 h agitation at room temp. the remaining solid ester was removed by filtration. The aqueous solution was concentrated at 80 °C and the recovered slightly yellow K salt solid was dissolved in a 50:50 mixture of ethanol and water. The solution was stored at T = -4 °C in the refrigerator for single-crystal growth. An isolated batch of single crystals was dried at room temp., mortared and used for bulk studies. The yield was quantitative (3.66 g). Storing the crystals at temperatures higher than 40 °C gave rise to a product of reduced crystallinity as seen visually (the initial clear crystals became opaque) as well as from X-ray diffraction studies on the bulk samples. For the next step, the hydrated salts were dried under dynamic vacuum up to T =150 °C for 12 h. FTIR (25 °C):  $\tilde{v}$  = 3435 (H<sub>2</sub>O), 1645 (C=O), 1311, 1554 cm<sup>-1</sup> (C<sub>3</sub>N<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O, 25 °C):  $\delta$  = 170.57 (C-C=O), 169.14 (C-C=O) ppm. GC-MS (EI): m/z = 363.

1,3,5-Triazine-2,4,6-tricarbonyl Trichloride: The dried salt (2.0 g) was suspended in neat POCl<sub>3</sub> (50 mL freshly distilled), and the mixture was stirred for 12 h at room temp. and then for an additional 12 h at 80 °C. The reaction was very slow and could be monitored visually by the gradual change in colour. The suspension became vellow-brownish and a solid residue was formed. After filtration, the solvent was removed, the remaining brown-yellow solid was dried in vacuo at room temp. and finally dissolved in ethyl ether or THF (50 mL). It should be mentioned that residual POCl<sub>3</sub> has to be completely absent since neither ether nor THF is stable in the presence of POCl<sub>3</sub>, thus leading to autopolymerisation of the solvent molecules. The acid chloride is a yellow semi-solid mass (1.08 g, 73%). Crystals were grown by storing a solution of the product in ether at T = -4 °C. FTIR (25 °C):  $\tilde{v} = 1766$  (C=O), 1350, 1527 cm<sup>-1</sup> (C<sub>3</sub>N<sub>3</sub>). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 164.6 (*C*-C-Cl), 167.7 ppm (C-*C*=O). GC-MS (EI): *m*/*z* = 268.

1,3,5-Triazine-2,4,6-tricarbonyl Triazide/1,3,5-Triazine-2,4,6-triisocyanate (Polymer): So far, only the reaction of the acyl chloride (1 g) with a suspension of dried AgN<sub>3</sub> (1.66 g) in dry acetone (50 mL) was successful. However, the reaction was not complete at room temp. The suspension was finally stirred at elevated temperatures. With this approach, however, the acyl azide could not be isolated before the Curtius rearrangement set in. Gas formation was observed visually. Finally, the polyisocyanate was obtained in quantitative yield (0.76 g). It settled from the solution as a slightly yellow solid. The solid was isolated by filtration and dried under dynamic vacuum at room temp. It turned out that under the conditions applied, AgCl was obtained as a side product in a very fine dispersion. By using a coarse frit, we separated the insoluble polymer (the product) from the solution (i.e., the dispersion that contained AgCl). The reason for the high degree of dispersion of the AgCl is not clear and has not been analysed.

The polyisocyanate (0.5 g) was dispersed and treated with an excess amount of alcohol (ethanol or isopropanol, 50 mL) to form the corresponding carbamates  $C_3N_3(NHCOOCH_2CH_3)_3$ ·  $3CH_3CH_2OH$  as well as  $C_3N_3[NHCOOCH(CH_3)_2]_3$ ·(CH<sub>3</sub>)<sub>2</sub>-CHOH. The solids were obtained by concentrating the solutions under dynamic vacuum.

To prepare the monomeric (molecular) 1,3,5-triazine-2,4,6-triisocyanate, the polyisocyanate solid (0.5 g) was placed in a glass flask, which was connected to a glass funnel. The flask was placed completely in a hot oil bath (T = 100 °C) and dynamic vacuum was applied. The yellow solid depolymerised (and partly decomposed).

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A colourless volatile solid formed on the cold wall of the glass funnel. This colourless solid was not stable at room temp. After a short time (<10 min) the solid turned yellow, thereby restoring the polyisocyanate. The overall yield of this depolymerisation reaction was between 30 and 50%.

**Single-Crystal X-ray Diffraction:** For single-crystal studies, the crystals were isolated directly from the solution. The collection of the diffraction intensities was performed with a SMART-APEX CCD X-ray diffractometer (Bruker AXS Inc.) with graphite-mono-chromated Mo- $K_{\alpha}$  radiation. Low-temperature measurements were carried out with a 700 series cryostream cooler (Oxford Cryosystems). The reflection intensities were integrated with the SAINT subprogram<sup>[22]</sup> contained in the SMART software package.<sup>[23]</sup> An empirical absorption correction (SADABS)<sup>[24]</sup> was applied. The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures with the SHELXTL software package.<sup>[25]</sup>

CCDC-879853 (for 1), -879856 (for 2), -879857 (for 5) and -879858 (for 6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Further details of the crystal-structure investigations for **3**  $[C_3N_3(COO)_3K_3\cdot 2H_2O]$  and **4**  $[C_3N_3(COC)_3]$  can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-424611 (for **3**) and -424610 (for **4**).

**X-ray Powder Diffractometry:** For the XRD analysis, the samples were carefully placed between plastic foil and measured in transmission geometry. X-ray diffraction studies have been performed with a STOE STADI P instrument with a linear PSD detector and with Mo- $K_{\alpha 1}$  as well as Cu- $K_{\alpha 1}$  radiation from a curved Johansson-type monochromator using Ge(111).

**Spectroscopy:** Infrared spectroscopy was performed with a FTIR spectrometer (IFS 113v, Bruker) from 400 to  $4000 \text{ cm}^{-1}$  with KBr as the solid matrix. The substance (1–2 mg) was mixed with KBr (300 mg) and the powder pressed to pellets (diameter 1 cm, pressed at 300 MPa).

**Energy-Dispersive X-ray Analysis:** EDX analysis was performed with a XL30 TMP (Philips Electron Optics GmbH). An energy-dispersive detector S-UTW(Li) (EDAX) was used. The powder sample stored in a glovebox filled with argon was placed on a sample holder. The sample was attached to the machine with a transfer chamber to provide inert conditions.

**Thermal Analysis:** Simultaneous DTA/TG/MS (STA 409, Netzsch) was performed on a sample placed in a corundum crucible under flowing argon (100 mLmin<sup>-1</sup>) at a heating rate of 10 Kmin<sup>-1</sup>. For the differential scanning calorimetry (DSC) analysis (DSC 404, Netzsch), the sample was heated in a corundum crucible with a heating rate of 10 Kmin<sup>-1</sup> under argon; the cooling rate was  $2 \text{ Kmin}^{-1}$ .

**NMR Spectroscopy:** Liquid NMR spectra of the dissolved samples were recorded with a Bruker Avance DPX-300 SB operating at 7.05 T. MAS NMR studies were performed with a Bruker DSX-400 spectrometer operating at 9.4 T. The sample was filled in a 7 mm  $ZrO_2$  rotor. The spinning frequency was 100557 MHz.

**Mass Spectroscopy:** MALDI-TOF mass spectra were obtained in reflection mode with a Bruker Daltonics (Bremen) Reflex VI (337 nm nitrogen laser). The 1,3-dichloro-2,4,6-trinitrobenzene (DCTB) served as a matrix for analysis of oligomers in the positive

mode. The samples were prepared by mixing DMSO solutions of the oligomer and the matrix in the ratio 1:50. The GC–MS data was recorded with a TSQ 700 (Fa. Finnigan MAT, Bremen).

**Theory:** Atomic-charge calculations were performed using the Gaussian program.<sup>[26]</sup> Calculations have been performed using DFT with the hybrid functional B3LYP/6-31G(d). The geometrical parameters used were obtained from recent structural studies.<sup>[8]</sup>

**Supporting Information** (see footnote on the first page of this article): Crystallographic data and details of the refinement procedures for the structurally characterised molecular intermediates (Tables S1–S6). In addition, further experimental data is presented (Figures S1–S5).

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In this work, the five-step synthesis of 1,3,5-triazine-2,4,6-triisocyanate  $[C_3N_3-(NCO)_3]$  is reported. This product was studied by thermal and spectroscopic methods as well as chemical transformation reactions. Due to high chemical reactivity of the isocyanate groups, oligomerisation/polymerisation of the molecular compound occurred easily at room temperature to form amorphous uretdione-type polymers.



#### **Carbon Nitride Precursors**

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C. L. Schmidt, M. Jansen\* ..... 1-10

Exploring the Route to 1,3,5-Triazine-2,4,6-triisocyanate ( $C_6N_6O_3$ ), a Hydrogen-Free Molecular Precursor for Polymeric C–N–(O) Materials

**Keywords:** Structure elucidation / Oligomerization / Polymers / Nitrogen heterocycles / Isocyanates