

Review

Tri-*s*-triazines (*s*-heptazines)—From a “mystery molecule” to industrially relevant carbon nitride materials

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ABSTRACT

This review provides a comprehensive overview about the fascinating history and chemistry of s-heptazines in its ionic, molecular and polymeric forms – their synthesis, structure, properties and (potential) applications. The very stable aromatic s-heptazine (tri-s-triazine) C_6N_7 moiety has been discovered as early as in the 1830s, when Liebig, Berzelius and Gmelin independently synthesized the first s-heptazine derivatives. However, the correct tricyclic molecular structure was first proposed by L. Pauling about 100 years later. He obviously was intrigued by selected C_6N_7 -derivatives until he died since the structure of a so-called “mystery molecule” $C_6N_7(OH)_2N_3$, which has not been synthesized so far, was later found on the chalkboard in his office. Very few s-heptazines including the parent molecule $C_6N_7H_3$ (**6**) were synthesized and unambiguously analysed until the beginning of the 21st century. Due to the proposed ultrahardness of 3D carbon(IV) nitride networks C_3N_4 in the 1980/90s several researchers became interested in s-heptazines as precursors for novel carbon(IV) nitrides. Besides, in the patent literature numerous claims for the application of s-heptazines (and s-triazines $C_3N_3X_3$) as flame retardants and for other applications are found. Thus, the formation, structure and properties of key molecular derivatives such as cyameluric chloride $C_6N_7Cl_3$ (**4**), melem $C_6N_7(NH_2)_3$ (**1**), cyameluric acid $C_6N_7(OH)_3$ (**2**), selected symmetric and asymmetric amides $C_6N_7(NR^1R^2)_3-x(NR^3R^4)_x$, cyameluric esters $C_6N_7(OR)_3$ and s-heptazine triazide $C_6N_7(N_3)_3$ (**5**) have been reported in recent years. In addition, various metal melonates $M^{(I)}_3[C_6N_7(NCN)_3]$, metal cyamelurates $M^{(I)}_3[C_6N_7(O)_3]$, s-heptazine-based metal-organic frameworks (MOFs) and melon $[C_6N_7(NH_2)(NH)]_n$ were analysed in detail. Also, numerous reports on so-called carbon nitrides, which are in fact melon-related C/N/H-oligomers and polymers, have been reported recently. Although the structure of these materials is not known in detail, their properties as well as the properties of the above mentioned thoroughly analysed compounds provide a very promising outlook for various applications of carbon nitrides and C/N/H materials including s-heptazines, especially in the field of novel semiconducting materials, (photo)catalysts e.g. for hydrogen generation and carbon dioxide fixation, luminescent and in other ways optically active materials. Many of the latter characteristics have been investigated very recently and in most cases supported by experimental and theoretical studies.

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1. Introduction and historical overview

The research fields dealing with the class of compounds entitled as carbon nitrides is very broad. It spans from the theoretical and experimental investigation of extremely nitrogen-rich binary molecular compounds such as unstable tetraazido methane CN_{12} [**1**], relatively stable commercially available triazido-s-triazine C_3N_{12} [**2**], which may be useful as green primary explosives [**3**], via postulated diamond-like as well as graphitic carbon(IV) nitrides C_3N_4 structures [**4,5**] to binary molecular compounds such as tetracyanoethylene (TCNE) and cyano acetylenes $NC-(CC)_x-CN$ [**6**], nitrogen-doped diamond [**7**], nitrogen-doped fullerenes [**8**], nitrogen-doped nanotubes [**9**] or nitrogen-doped graphene [**10**] with relatively low N-contents. Furthermore, there are ternary C/N/H and multinary C/N/E/H materials related to or derived from the said binary C/N compounds, showing very interesting properties and being also frequently denominated as carbon nitrides in the current literature. Especially the semiconductivity and (photo)catalytic activity [**11**] of the 1D polymer melon $[C_6N_7(NH_2)(NH)]_n$ and related C/N/H materials have recently found strong recognition in the scientific community. Although it is well beyond the scope of this review to comprehensively cover all of these classes of carbon nitrides, a summary and discussion on binary carbon nitrides and melon-related ternary and multinary materials is provided in Section 6.

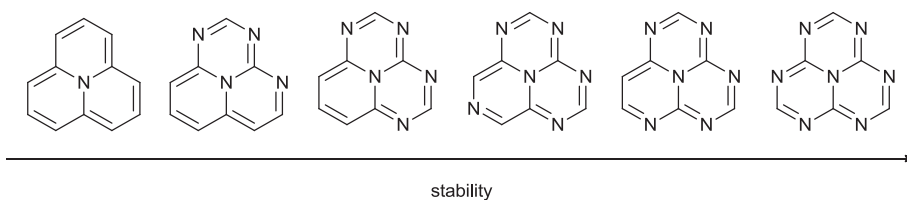
The major focus of the present review lies on molecular, ionic and polymeric compounds containing the aromatic tricyclic unit

C_6N_7 , frequently denoted as s-heptazine or tri-s-triazine [**12**]. This N-rich heterocyclic unit is surprisingly thermally stable, e.g. when compared with related aromatic motives containing less nitrogen (Scheme 1) [**13,14,15**].

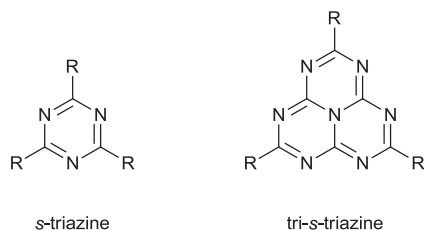
A high thermal stability of the C_6N_7 -unit is also indicated by the very efficient formation of melem $C_6N_7(NH_2)_3$ (Section 2.1) and the polymeric melon $[C_6N_7(NH_2)(NH)]_n$ by simple annealing of various molecular precursors such as cyanamide, cyanoguanidine or melamine (see Section 6.3). Therefore, the synthesis of nearly all s-heptazine derivatives is based on reactions using one of these solids containing melem and/or melon as starting materials. This very simple access to s-heptazine-based compounds is also the reason for early reports in the beginning of the 19th century of the synthesis of cyamelurates and melonates as stable ionic derivatives. Some of the interesting historical aspects of s-heptazine chemistry will be discussed in the following paragraphs, after a comparison with the well examined 1,3,5-triazines.

1.1. The heterocyclic systems s-triazine C_3N_3 and s-heptazine C_6N_7 – a brief comparison

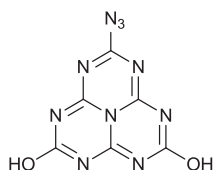
The aromatic six-membered ring of s-triazines with an alternating order of C- and N-atoms is part of numerous compounds. Some of them, such as melamine $C_3N_3(NH_2)_3$, cyanuric chloride $C_3N_3Cl_3$ or cyanuric acid $C_3N_3(OH)_3$ and various derivatives are produced industrially on very large scales [**16**]. The tremendous



Scheme 1. Azacycl-[3.3.3]azines with alternating C- and N-atoms: it was reported that the reactivity decreases and the thermal stability increases within this series of heteroaromatic systems, which are isoelectronic to the phenallen anion.



Scheme 2. Structure of 1,3,5-triazine (*s*-triazine) and tri-*s*-triazine (*s*-heptazine) derivatives.



Scheme 3. Pauling's "mystery molecule" found on the chalkboard in his office after his death in 1994.

importance of the C_3N_3 moiety becomes also obvious when looking for commercially available compounds via the Chemical Abstracts Registry File, indicating that more than 5600 of such derivatives are offered with more than 125,000 references reporting on these compounds [17]. To the contrary, *s*-heptazine and its derivatives have to be considered as a still relatively exotic and not well-known class of compounds, as only five derivatives are listed as commercially available with 402 related references [17].

The similarity of both molecular motives includes features such as the C_{3h} -symmetry, the aromaticity or the donor-properties of the ring-N-atoms (see Scheme 2, Table 1). Furthermore, it is intriguing that the thermal (and thermodynamic) stability of the C_6N_7 -unit is reported to be significantly higher in most cases than for the C_3N_3 -unit, which leads to the formation of the former upon thermal treatment of many organic C/N/H compounds, especially melamine and its monomer cyanamide (see below). The general interest in the various fields of *s*-triazine chemistry continues and keeps growing due to the said properties and applications [18,19]. This is even more pronounced for the *s*-heptazines (Scheme 4).

In contrast to *s*-heptazines, the synthesis of substituted 1,3,5-triazines seems to be more efficient and easier. For *s*-triazines one

option is the functionalization of an organic nitrile followed by a cyclisation (2+2+2-cycloaddition) of three CN groups, another is the substitution of the halogen atoms of cyanuric halides $C_3N_3X_3$ and related derivatives [18,19]. The synthesis of substituted tri-*s*-triazines usually requires the generation of the *s*-heptazine core and afterwards its functionalization. In contrast to benzene, *s*-triazine and *s*-heptazine are electron poor aromatic compounds and therefore undergo a nucleophilic substitution instead of an electrophilic one. In addition, the poor solubility of many *s*-heptazine derivatives reduces the successful synthesis of new compounds in high yields.

With regard to the electronic structure of *s*-triazine and *s*-heptazine a striking difference has been reported. While in typical *s*-triazines the HOMO is dominated by a strong contribution of the lone pair n -electron at the nitrogen atoms (with no π -orbital influence), for *s*-heptazines it was found that the HOMO is mainly comprised of the p -orbitals on the outer ring N-atoms (see Section 5). Nevertheless, the very recently discovered semiconductive properties of the linear *s*-heptazine-based polymer melon $[C_6N_9H_3]_n$ and related C/N/H materials is due to p -orbitals of the C- and N-atoms forming delocalised π -orbitals of the conduction as well as the valence band (see Section 5). Besides, in several compounds the lone pair electrons at the N-atoms may be protonated, or substituted to form exocyclic N–E bonds or can be involved as donor electron pairs coordinating main group or transition metal cations (see Section 3). These latter possibilities hold true for both, the *s*-triazine and the *s*-heptazine unit.

1.2. Heptazines – a historical sketch

According to J. Liebig, J. J. Berzelius reported on the ignition of $Hg(SCN)_2$ to get H_2S , HCN and a pale yellow solid residue [29]. Later Liebig on his own came to the same results and named the obtained residue melon and defined its composition as $(C_2N_3H)_n$ [29]. These and related studies by Gmelin in the 1830s lead to the discovery of melamine, cyanuric acid and cyanuric chloride as well as the corresponding *s*-heptazine derivatives melem, cyameluric acid and cyameluric chloride (see Table 1). The early studies were challenged by the insolubility and low reactivity of the *s*-heptazine derivatives [20,22,29]. Hence, analyses of resulting products were difficult and mainly focused on the CHN elemental analysis of the products.

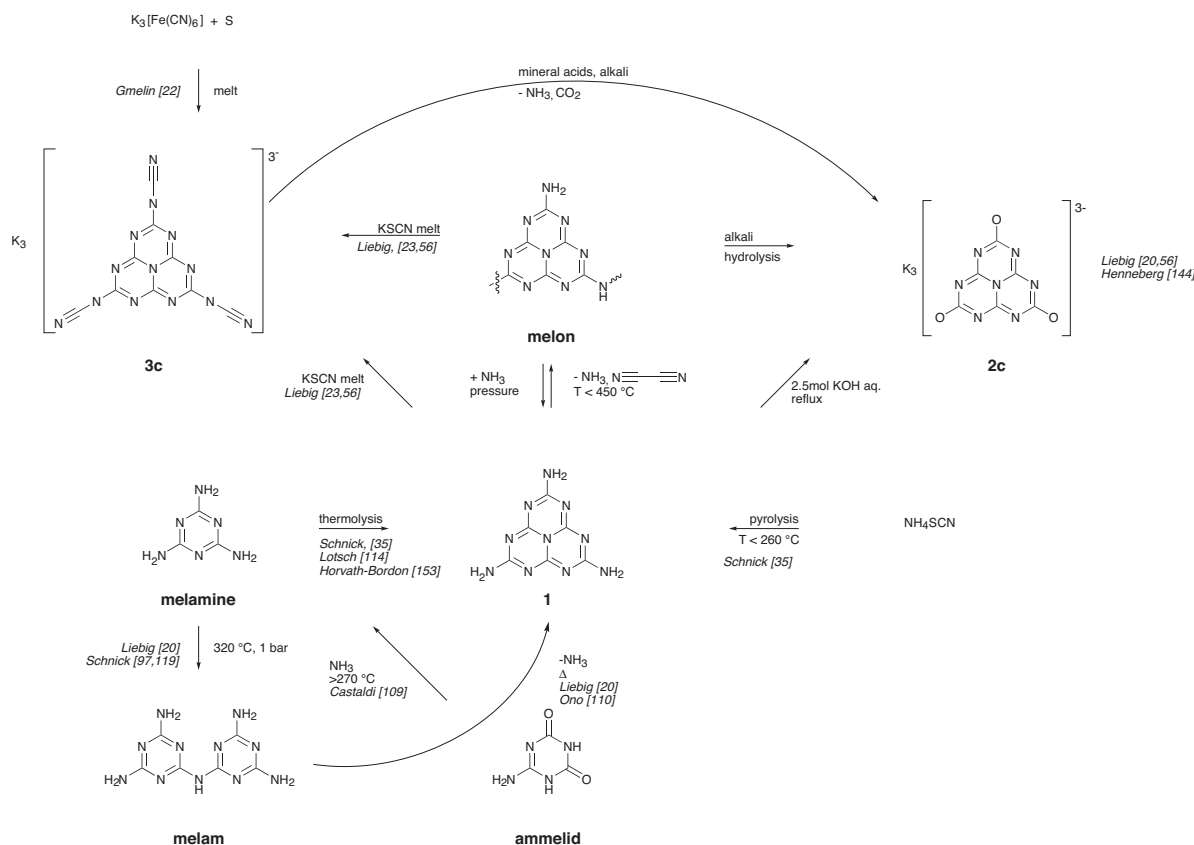
Table 1
Selected *s*-triazines and heptazines, year of discovery and corresponding authors.

R	<i>s</i> -Triazine	First reported	<i>s</i> -Heptazine	First reported/mentioned
NH ₂	Melamine	Liebig, 1834 [20]	Melem (1)	Liebig, 1834 [20] ^a
OH	Cyanuric acid	Liebig, 1834 [20]	Cyameluric acid (2)	Liebig, 1834 [20] ^b
NCN [−]	Tricyanomelamine	Bannow, 1871 [21]	Melonates (3a–q)	Gmelin, 1835 [22]
Cl	Cyanuric chloride	Liebig, 1834 [20]	Cyameluric chloride (4)	Liebig, 1844 [23]
N ₃	Triazido triazine	Finger, 1907 [24]	Tri-azido tri- <i>s</i> -triazine (5)	Pauling, 1937 [25–27] ^c
H	Triazine		Tri- <i>s</i> -triazine (6)	Hosmane, 1982 [28]

^a According to Liebig, J.J. Berzelius first reported on the reaction of $Hg(SCN)_2$ to get a *s*-heptazine-based compound.

^b In detail, Liebig reported on the potassium cyamelurate.

^c Miller et al. first reported on the tri-azido-tri-*s*-triazine, but on Pauling's chalkboard a monoazido derivative was drawn, see Scheme 3 [53,54].



Scheme 4. Overview of the formation processes and reactions of mellem **1**.

The structure of the *s*-heptazine unit remained unclear for a long time. In 1886 Klason mentioned the formula $C_3N_3(NH)_3C_3N_3$, which was not explained any further [30]. Franklin discussed a similar NH-group bridged di-triazine structure in 1922 [31]. More than 100 years after the discovery of the first *s*-heptazine derivatives Pauling and Sturdivant suggested the correct planar tricyclic structure [25]. They had used X-ray crystallography to show that the core of that molecule consists of three fused 1,3,5-triazine rings. Much later, in 1982 the first comprehensive analysis of *s*-heptazine $C_6N_7H_3$ (**6**) was published, followed by reports of the crystal structures of the chloride $C_6N_7Cl_3$ (**4**) in 2002 and selected further derivatives in the past decade. Komatsu [32] and Schnick and Lotsch et al. [98] confirmed the structure of Berzelius's melon. Relatively few reports on systematically and fully characterised *s*-heptazine derivatives were published so far. This becomes obvious when the structurally analysed neutral *s*-heptazine molecules are

considered, i.e. the compounds investigated by single crystal (or powder) X-ray diffraction as shown in Table 2.

In the time from 1960 to 1992, Finkel'shtein and co-workers [45–51] as well as Schroeder and Kober [52] synthesised several tri-*s*-triazine derivatives which were characterised via CHN analyses, melting points and IR spectroscopic measurements.

Although Pauling did not publish on tri-*s*-triazines after the structural study mentioned above he obviously stayed interested in this class of compounds. After his death on the chalkboard in his office a molecular structure among other notes was found, and later described as a so-called “mystery molecule” [53,54] (Scheme 3).

Some of the first investigations in the field of *s*-heptazines included the synthesis of the salts of cyameluric and hydromelonic acid, cyamelurates $M^{(I)}_3[C_6N_7O_3]$ and melonates $M^{(I)}_3[C_6N_7(NCN)_3]$, correspondingly [23,55–57]. Similar to the neutral tri-*s*-triazine molecules structural analyses of these

Table 2
Structurally analysed neutral *s*-heptazine molecules.

Compound	Formula	Year reported	Reference
Tri- <i>s</i> -triazine (6)	$C_6N_7H_3$	1982	[28]
2,5,8-Trichloro-tri- <i>s</i> -triazine (4)	$C_6N_7Cl_3$	2002	[33]
2,5,8-Triamino-tri- <i>s</i> -triazine (melem, 1)	$C_6N_7(NH_2)_3$	2003	[34,35]
2,5,8-Triazido-tri- <i>s</i> -triazine (5)	$C_6N_7(N_3)_3$	2004	[25,27]
2,5,8-tris(Diethylamino)-tri- <i>s</i> -triazine (13)	$C_6N_7(NEt_2)_3$	2004	[36]
2,5,8-Triphenoxy-tri- <i>s</i> -triazine (7)	$C_6N_7(OPh)_3$	2006	[37]
Cyameluric acid (2)	$C_6N_7H_3O_3$	2006	[38,39]
2,5,8-tris(Trimethylsilyl)cyamelurate (10)	$C_6N_7(OSiMe_3)_3$	2007	[40]
2,5,8-tris(Trichlorophosphinimino)-tri- <i>s</i> -triazine	$C_6N_7(NPCl_3)_3$	2010	[41]
5,8-bis(Diphenylamino)-8-chloro-tri- <i>s</i> -triazine (17)	$C_6N_7(NPh_2)_2Cl$	2010	[42]
2,5-bis(Diphenylamino)-8-(diethylamino)-tri- <i>s</i> -triazine (20)	$C_6N_7(NPh_2)_2NEt_2$	2011	[43]
2-(Diphenylamino)-5,8-bis(diethylamino)-tri- <i>s</i> -triazine (21)	$C_6N_7(NEt_2)_2NPh_2$	2011	[43]
2,5,8-tris(Diphenylamino)-tri- <i>s</i> -triazine (14)	$C_6N_7(NPh_2)_3$	2011	[43]
2,5,8-Triphthalimido-tri- <i>s</i> -triazine	$C_6N_7(phtal)_3$	2012	[44]

Table 3
Structurally analysed ionic tri-*s*-triazine molecules.

Compound	Formula	Counter ion	Year reported	Reference		
Melemium salts	$C_6N_7H[(NH_2)_2NH_2]^+ \cdot C_6N_7H[NH_2(NH_2)_2]^{2+}$	$MeSO_3^-$	2010	[58]		
	$C_6N_7^{3+}H_3[(NH_2)_3]$	$HOSO_3^-$	2010	[59]		
	$C_6N_7[NH_2(NH_2)_2]^{2+}$	$MeSO_3^-$	2010	[58]		
	$C_6N_7^{2+}H_2[(NH_2)_3]$	SO_4^{2-}	2005	[60]		
	$C_6N_7^+H[(NH_2)_3]$	ClO_4^-	2005	[60]		
	$C_6N_7^+H(NH_2)_3 \cdot C_6N_7H(NH_2)_3$	ClO_4^-	2005	[61]		
Melonates	$C_6N_7[NCN]_3^{3-}$	Li^+	2010	[62]		
		K^+	2005	[63]		
		Rb^+, Cs^+	2009	[64]		
		Ca^{2+}	2009	[65]		
		Cu^{2+}	2011	[66]		
		Ag^+	2012	[67]		
		$La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}$	2012	[68]		
		Cyamelurates	$C_6N_7O_3^{3-}$	Li^+	2004	[69]
Na^+	2004			[69]		
K^+	2004			[69]		
Rb^+	2004			[69]		
$C(NH_2)NH_2^+$	2008			[70]		
$Me_2NH_2^+/Cl^-$	2008			[71]		
Cu^{2+}	2009			[72]		
Zn^{2+}	2009			[72]		
2,5,8-Trihydrazino- <i>s</i> -heptazine-trihydrochloride	$C_6N_7[NHNH_3^+]_3$			Cl^-	2009	[73]
2,5,8-Tris(trichlorophosphinimino)-heptazinium	$C_6N_7^+H[NPCl_3]_3$			Cl^-	2010	[41]

compounds based on single crystal and powder X-ray diffraction analysis were reported first in 2004, followed by several papers in recent years (Table 3).

By now, several *s*-heptazine derivatives are described in scientific and patent literature in the field of oligomer and polymer formation, especially carbon nitrides. The latter field can be separated in true binary C/N compounds and more complex polymers which contain stoichiometric amounts of hydrogen (and sometimes further elements such as oxygen). The latter compounds are frequently based on the *s*-heptazine structural motive since they are prepared at elevated temperatures between 350 and 650 °C. They can contain both C_3N_3 and C_6N_7 moieties. Several reports appeared on C/N(H) coatings [4,5], membranes [74], nanoparticulate [75–78] and mesoporous [79,80] materials. Treatment of other materials such as TiO_2 [77,81–84] or sulphur [85] leads to photocatalytically active composites [74,79,81,86–89]. These and many other studies on C/N(H) compounds have recently been discussed in reviews [5,90–93,257] and are briefly summarized in Section 6.

In Sections 2–5, we focus on the developments and achievements in the field of well analysed tri-*s*-triazines, their preparation, characteristic features and applications.

2. Melem, and melemium salts

2.1. Melem

2.1.1. Formation

The thermal condensation of various C- and N-containing species, which leads to C/N(H)-polymers and to the formation of extended carbon nitride networks, was and still is currently studied by material scientists and solid state chemists. Series of publications dedicated to the basic principles of the solid state formation of CN_x and CN_xH_y materials, qualitative and quantitative aspects of the reaction mechanisms, and investigation of the related molecular systems have appeared during the last decades [4,5,94–110] (Section 6). A precise study of solid state reactions of various CN-compounds resulted in a number of new substance classes such as different metal dicyanamides $M^{n+}[N(CN)_2]_n$ (M = alkaline,

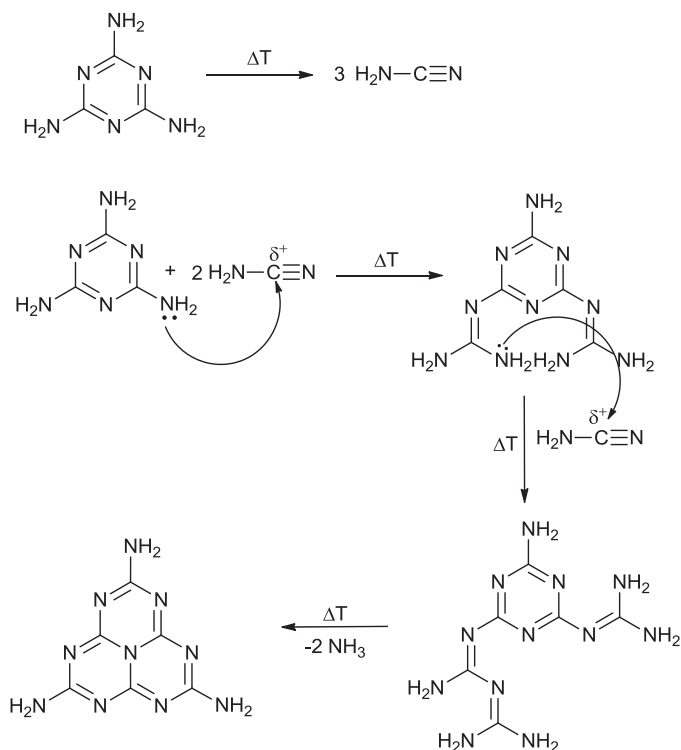
alkaline-earth, transition metals, lanthanides) [111,112], or triazine derivatives $C_3N_3Cl_3 \cdot AlCl_3$, $C_3N_3(N_3)Cl_2$, $N(C_3N_3Cl_2)_3$ [113]. These investigations indicate that the thermal treatment of *s*-triazine and *s*-heptazine-based compounds is one of the most promising ways to graphitic CN_x phases [4,5]. Two representatives of these classes of compounds, melamine $C_3N_3(NH_2)_3$ and melem $C_6N_7(NH_2)_3$, play an important role in this field of solid state chemistry as stable and readily available CN_x and C/N(H) precursors.

Whereas melamine is a very well investigated commercial product and can be purchased from suppliers, melem needs to be synthesized in sufficient amounts. According to the literature, melem can be obtained by heating of cyanamide H_2N-CN or ammonium dicyanamide $NH_4[N(CN)_2]$ or dicyandiamide $(NH_2)_2C=N-CN$ or melamine [5,35]. However, in the doctoral thesis of B. Lotsch it is demonstrated that any one of these precursors transforms into melamine during thermal treatment [114]. This fact is an evidence of high thermodynamic stability of melamine, whereas at higher temperatures the formation of the *s*-heptazine nucleus is favourable. Therefore, melamine was utilized as a starting material for the synthesis of melem. The thermal treatment of melamine was performed in a sealed glass ampoule at 450 °C for 5 h yielding 60% of melem [35]. Schemes 5 and 6 represent two suggested mechanisms of melem formation. According to the melem formation proposed by May [115], some melamine molecules decompose into cyanamide H_2N-CN at about 300–320 °C followed by condensation of cyanamide with melamine, leading to melem formation under elimination of two ammonia molecules (Scheme 5).

The formation of melem from melamine and dicyandiamide was described by Lotsch et al. [98] and represents a variation of Hosmane's mechanism of tri-*s*-triazine synthesis [14,15]. Dicyandiamide may form in parallel with the monomer cyanamide by thermal decomposition of melamine (Scheme 6).

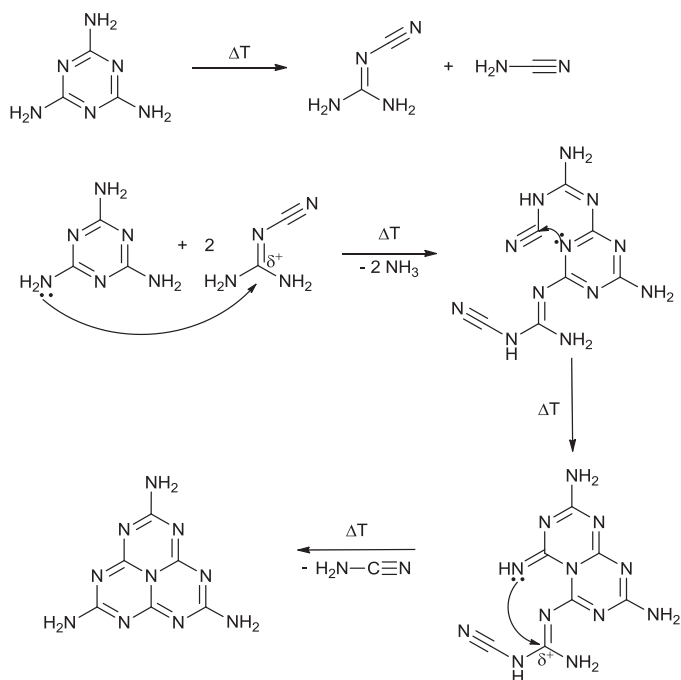
Some authors postulated a formation of melam $HN(C_3N_3(NH_2)_2)_2$ during the melamine-to-melem route, as a direct intermediate in the thermal condensation of melamine (Scheme 7, Route B) [115,116].

The pyrolysis of C/N(H) substances in the presence of acids supports the formation of melam and melamine containing species [118].

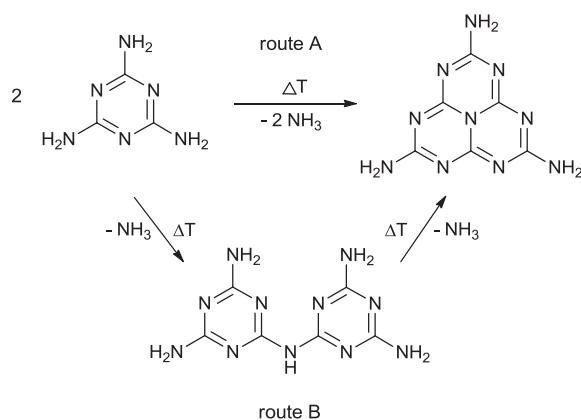


Scheme 5. Formation of melem from melamine suggested by May [115].

Melam was first prepared in 1834 upon heating of potassium thiocyanate with ammonium chloride [20], whereas its crystal structure and spectroscopic characterisation were completed only recently [97,119]. Crystal structures of some melam derivatives were established some time ago [98,120,121]. Melam and its derivatives were suggested as flame retarding materials, owing to their thermal stability and decomposition properties [122,123], and recently, the structure of a protonated melaminium salt was reported [119].



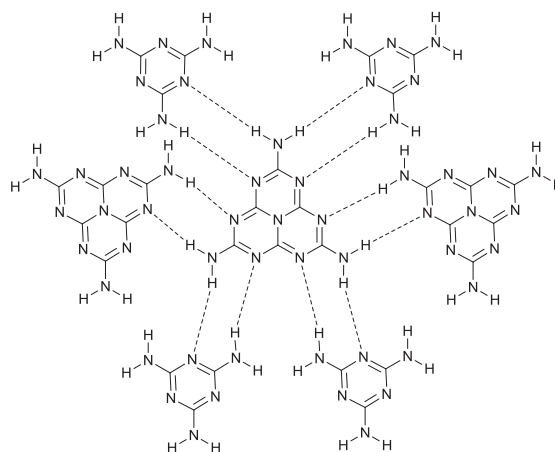
Scheme 6. Formation of melem from melamine according to Hosmane et al. [14,15].



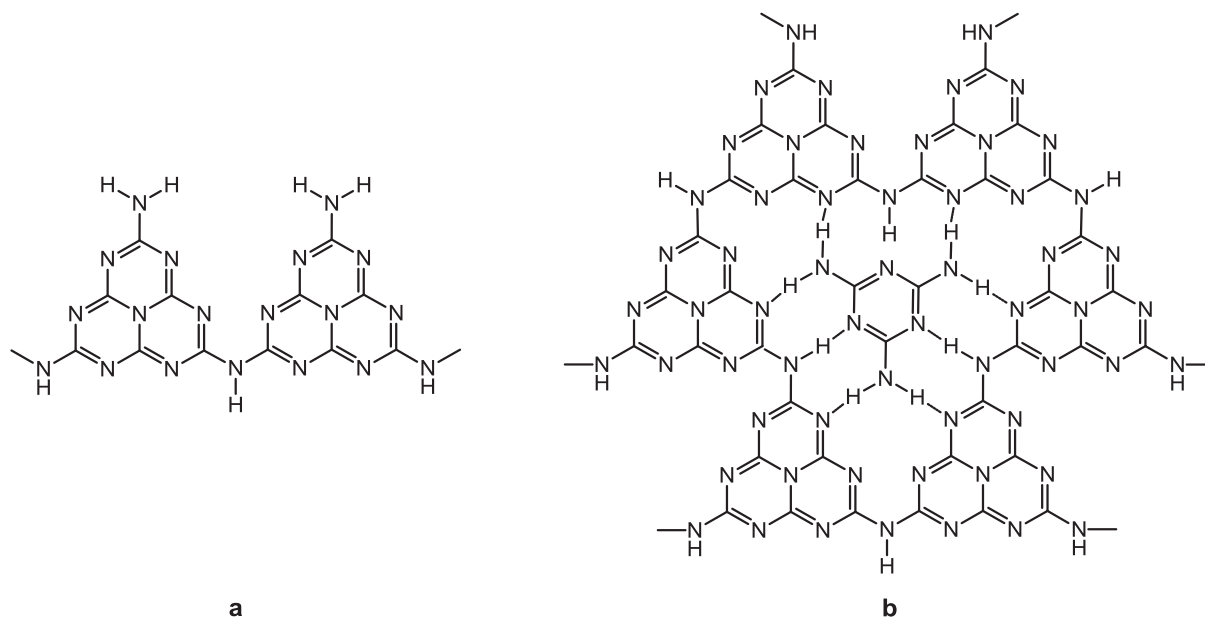
Scheme 7. Two proposed routes for the melamine-to-melem condensation process [114,117].

However, only trace amounts of melam were found among the products of thermal treatment of melamine. Recent investigations suggest that melam may form only at certain heating conditions (temperature, time, pressure) and is stable only for a short time [97]. Therefore, it is questionable if melam is a crucial intermediate in the melamine-to-melem thermal condensation. It may be a minor by-product which is detectable only in small amounts under specifically tuned reaction conditions. Several of the intermediates were isolated and characterised recently in the melamine-to-melem condensation process [97,114,117,124]. A modified preparation of melam using thiourea or melamine and ammonium chloride and using longer reaction times is described. Mixtures of melam and melamine, NH_3 and a large amount of the starting materials were identified [119]. The obtained crystalline intermediates represent stoichiometric mixtures of melem and melamine molecules with the following three different compositions: $2\text{C}_3\text{N}_3(\text{NH}_2)_3 \cdot \text{C}_6\text{N}_7(\text{NH}_2)_3$, $\text{C}_3\text{N}_3(\text{NH}_2)_3 \cdot \text{C}_6\text{N}_7(\text{NH}_2)_3$ and $\text{C}_3\text{N}_3(\text{NH}_2)_3 \cdot 3\text{C}_6\text{N}_7(\text{NH}_2)_3$ (see also Fig. 4, Section 6.3). The existence of such melamine-melem adducts was suggested already in 1981 by van der Plaats et al. who proposed the formation of mixed crystals of melamine with the condensation product at 320–400 °C [125]. Melamine and melem molecules in the represented intermediates are held together via extensive hydrogen bonding (Scheme 8).

Furthermore, in 2011 Uemura et al. reported on formation of self-assembled structures of melem or melamine on a Au(111) surface under electrochemical control [126]. These 2D structures



Scheme 8. Hydrogen bonding in the melamine-melem co-crystal $\text{C}_3\text{N}_3(\text{NH}_2)_3 \cdot \text{C}_6\text{N}_7(\text{NH}_2)_3$ [124].



Scheme 9. Fragments of the structures of melon (a) and polyheptazine imide with the incorporated melamine molecule (b) [129].

are formed by the corresponding molecules, whereas the interaction between the structural motifs proceeds due to the hydrogen bonds between amino-groups and nitrogen atoms of the heterocyclic cores [126]. Independently, Eichhorn et al. reported in the same year on the self-assembly of melem on a Ag(1 1 1) surface [75]. Using STM analyses five porous and two dense packed but different mono layered polymorphs were characterised in detail [75].

Strong non-covalent interactions play a significant role in *s*-triazine as well as *s*-heptazine chemistry. For instance, the melamine-cyanuric acid adduct, where the separate molecules interact via hydrogen bonds, is stable up to 350 °C [127,128]. The crystal structures of melem [35] and polyheptazine imide with built-in melamine molecules [129] are strongly influenced by hydrogen bonding as well. The latter example is quite astonishing, since polyheptazine imide is synthesized by thermal treatment of melamine at 630 °C and represents 2D polymeric layers of *s*-heptazine cores bridged by NH groups. According to the structure elucidation [129], melamine molecules are tightly fixed in the voids of the polyheptazine imide layers via hydrogen bonds (Scheme 9). The retention of the *s*-triazine structural motif despite of high temperature treatment illustrates the crucial factor of hydrogen bonding in the structural chemistry of melem and related *s*-heptazine compounds.

Just recently, a hydrated melem phase was described [130]. It was achieved by hydrothermal treatment of melem at 200 °C and shows a hexagonal rosette like arrangement of the molecules. The channels with a diameter of about 8.9 Å are filled with water molecules being desorbed over a large temperature range. The hexagonal layer structure of the melem moieties remains though a shift can be observed resulting in closed channels. Surprisingly, the hydrated melem does not transform to the solvent-free melem phase after the release of the guest molecules at higher temperatures [130].

It should be mentioned that the formation of melam, melem, melon and related condensation products starting from melamine is relevant for the application of the latter as a flame retardant, e.g. for polyurethane foams [131]. Although the details of these reactions and the flame retardancy mechanisms are not fully understood, it is supposed that both ammonia evolution and the formation non-volatile *s*-heptazine-containing polymeric products enhance the performance of melamine as a flame retardant.

2.1.2. Melem – structure and properties

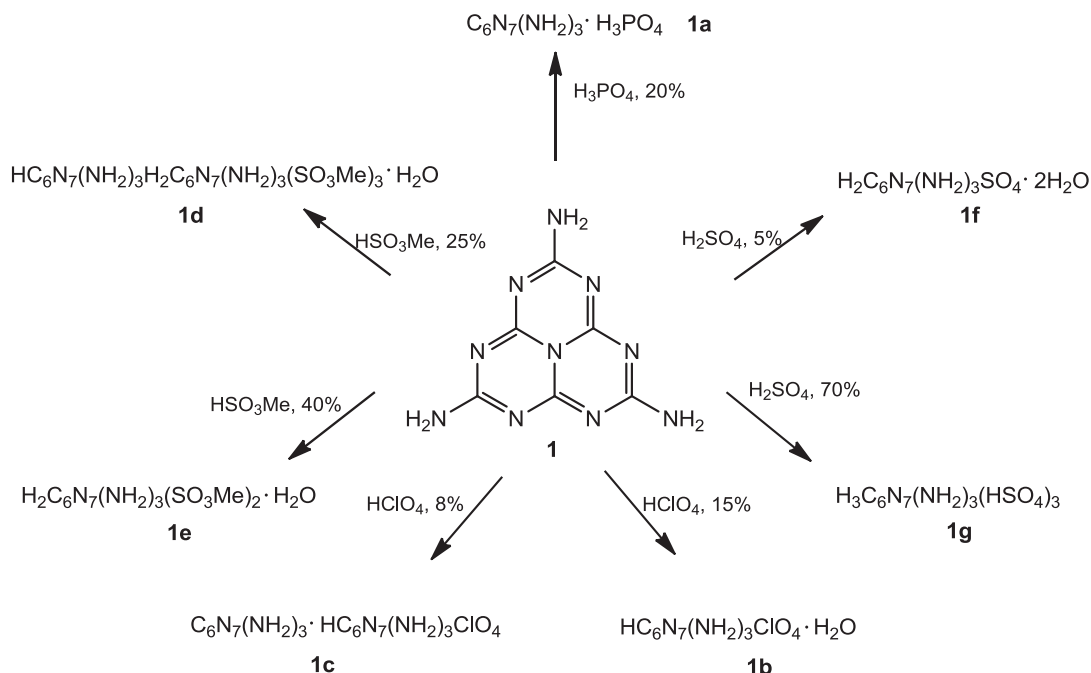
The structure of melem was elucidated by means of powder and later also single crystal X-ray diffraction [34,35]. Similar to other *s*-heptazine-based compounds, melem represents planar C₆N₇(NH₂)₃ molecules arranged in layers. Intra- and interlayered interactions between the molecules proceed via a system of hydrogen bonds. The interlayer distances in melem (3.27 Å) were found to be of similar order as those in melamine (3.2–3.4 Å) and in graphite (3.34 Å). Such short distances between the layers may be explained by the π–π interaction and stacking of the planar cyameluric cores [132–135]. However, the nature, strength and role of these weak interactions are still not completely understood and under continued investigation.

The C₆N₇-ring in melem is planar with the sum of the bonding angles around each atom of 360°. There are two types of CN bonds in its structure. The C–N bond lengths of the central N atom vary around 1.4 Å, being typical for single bonds of this type. The other C–N bond length values differ around 1.33–1.35 Å, similar to *s*-triazine. It was determined experimentally and theoretically (see below), that the lone pair of the central nitrogen atom in *s*-heptazine participates in the conjugated system of the ring, making the latter a 14-π-electron aromatic system being very stable against hydrolysis, oxidation and reduction [5,13–15].

The chemical behaviour of melem is much less studied than that of its triazine analogue melamine. So far, only a few examples concerning the reactivity of the NH₂-groups in melem were reported. For instance, tris(trimethylsilylamino)-*s*-heptazines and tris(tri-*n*-butylstannylamino)-*s*-heptazines were synthesized from melem and various organyl silyl- and stannylamines [136], and trimethylolmelem was prepared by reaction of melem with 50% formalin [137]. Besides, trihydrazino-*s*-heptazine C₆N₇(NH–NH₂)₃, iminophosphoranes C₆N₇(N=PR₃)₃ and imides C₆N₇(N-phthal)₃ have been obtained directly from melem (see Sections 4.7.1 and 4.7.2).

Bidevkina and Ivanov reported first preliminary toxicological properties of melem [138]. Adverse effects were found for female rats, mouse and rabbits when melem was intraperitoneal applied. Besides, melem dust was found to exhibit effects on the nerve system and behaviour of female rats.

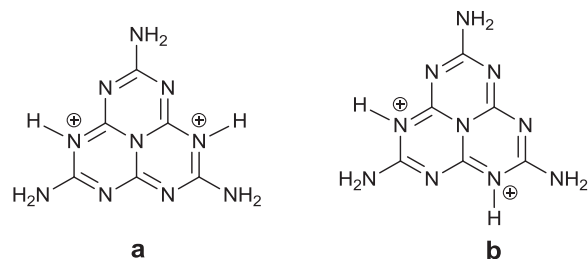
Due to the relatively high nitrogen content of melem and other *s*-heptazine derivatives these compounds may be used for gas generating, detonating or explosive mixtures as recently claimed in a



Scheme 10. Melemium salts **1a–1g** isolated by treating melem **1** with mineral acids.

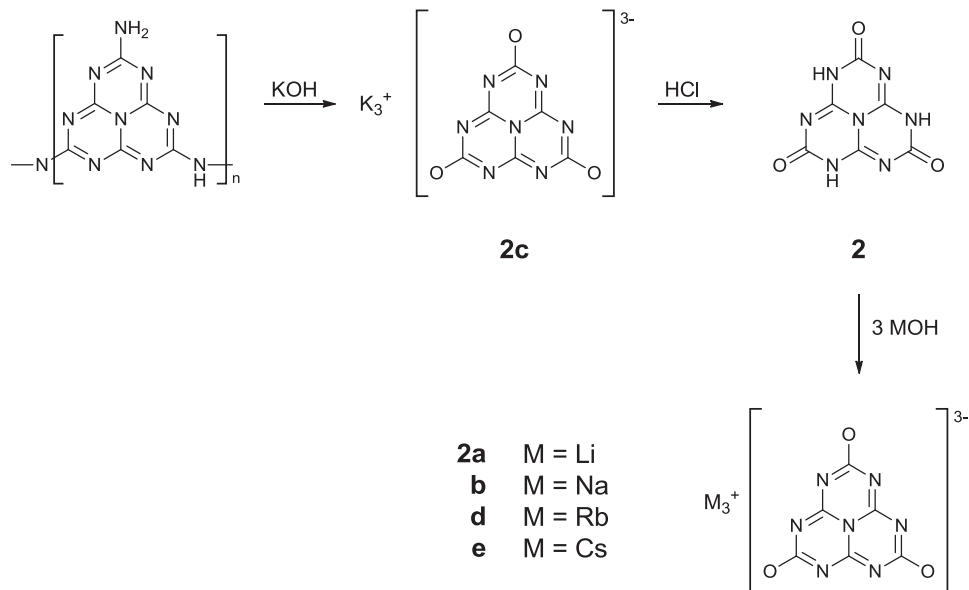
patent application [139]. Besides, melem is mentioned in numerous patents on flame retardants for polymers and related formulations [140]. The number of patents in this field appears to increase in recent years [141], which may be due to the search for halogen-free compounds with high flame retardant activity and good polymer compatibility.

By heating melem or melamine at temperatures higher than 450 °C, the formation of melon [$C_6N_7(NH)(NH_2)$] $_n$ takes place (see Section 6.3). The structure of melon has been proven recently [98] and reveals a 1D polymer constructed from *s*-heptazine building blocks connected via the imido function NH, whereas one NH_2 group remains at each *s*-heptazine nucleus (Scheme 9a). Melon as well as melem are known to offer a range of further derivatisation reactions to various *s*-heptazine-based compounds (cyameluric acid and its salts, melonates, chloride, azide, see below).

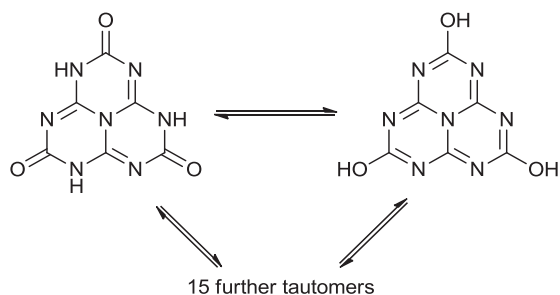


Scheme 11. C_{2v} (a) and C_s (b) tautomers of diprotonated melemium cation [$H_2C_6N_7(NH_2)_3$] $^{2+}$.

Melem can be deposited, adsorbed and 2D-crystallized on gold and silver (1 1 1)-surfaces as mentioned above [75,126]. Ishii et al. prepared fluorescing Langmuir–Blodgett-layers containing melem and tri-stearyl-praesodymium(III) complexes [142]. They found



Scheme 12. Synthesis of cyameluric acid, **2**, and alkali cyamelurates from melon.

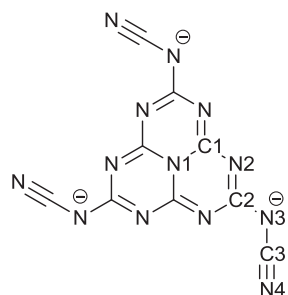


Scheme 13. Tautomeric forms of cyameluric acid (**2**).

an alternating melem-Pr(SA)₃-arrangement, but no praseodymium coordination by the melem molecules.

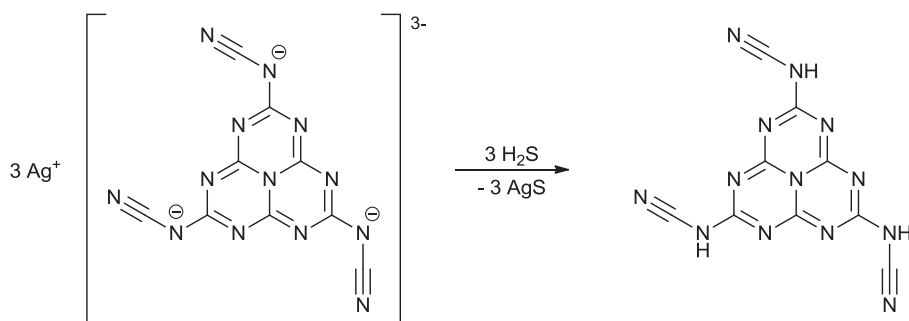
2.2. Melemium salts

By dissolving melem (**1**) in mineral acid solutions melemium salts **1a–1g** were isolated. Depending on acid concentration and acidity, different types of compounds can be obtained. For instance, melem-phosphoric acid adduct C₆N₇(NH₂)₃·H₃PO₄ **1a** [60], was obtained by dissolving melem in 20% phosphoric acid (Scheme 10). Interestingly, acid–base interaction in **1a** is based on strong hydrogen bonds without protonation of the heterocycle. In contrast, perchloric acid, HClO₄, builds two types of monoprotonated

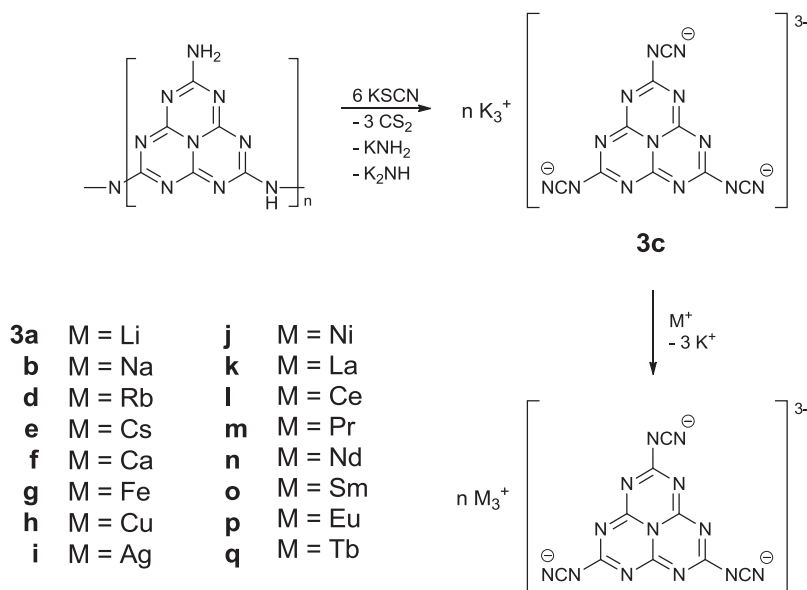


Scheme 14. Structure and atom numbering scheme of melonate anion [C₆N₇(NCN)₃]³⁻.

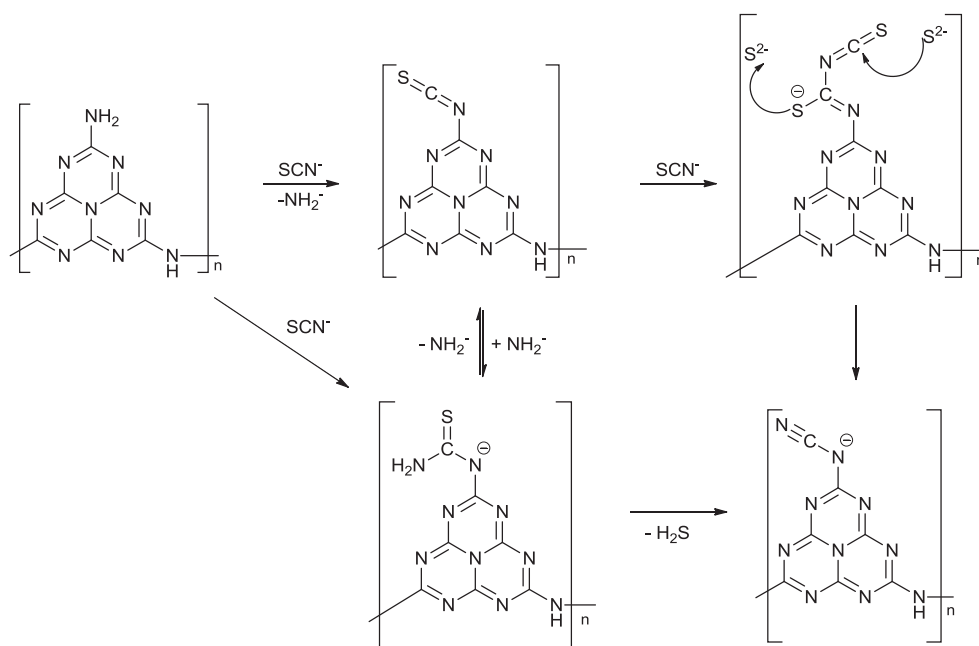
salts: melemium perchlorate [HC₆N₇(NH₂)₃]ClO₄·H₂O **1b** [60] and melemium–melem perchlorate HC₆N₇(NH₂)₃ClO₄·C₆N₇(NH₂)₃, **1c**, [61] by treating melem with 15% and 8% acid solutions respectively. In case of methylsulfonic acid two salts were isolated as well [58]. Compound **1d** includes mono- and diprotonated melem moieties HC₆N₇(NH₂)₃H₂C₆N₇(NH₂)₃(SO₃Me)₃·H₂O and was obtained from a 25% acid solution, whereas **1e** is represented by diprotonated melemium di(methylsulfonate) H₂C₆N₇(NH₂)₃(SO₃Me)₂·H₂O isolated from 40% methylsulfonic acid [58]. Dissolving of melem in diluted sulphuric acid yields melemium sulphate [H₂C₆N₇(NH₂)₃]SO₄·2H₂O **1f** [60]. Triprotonated H₃C₆N₇(NH₂)₃(H₃SO₄)₃ **1g** was obtained by mixing melem



Scheme 15. Synthesis of hydromelonic acid, as reported by Burdick in 1925 [161]. However, the free acid is most likely not stable and tends to polymerize und ambient conditions.



Scheme 16. Synthesis of potassium melonate, **3c** and other melonates **3a–b** and **3d–j** from **3c** and **3k–q** prepared from ammonium melonate.



Scheme 17. Two possible reaction mechanisms of melonate formation presented by Sattler and Schnick [162].

and 70% H_2SO_4 [60]. In the sulphuric acid concentration range 40–60%, two other salts were isolated but not characterised up to now (Scheme 10).

As follows from the represented examples, the strength of the acid and the concentration are the determining factor for the degree of protonation of melon. Increasing the acid strength and/or concentration leads to a higher degree of protonation of melon. Additionally, the solubility increases with the acid concentration due to the stepwise protonation of melon.

Melemium salts **1a–1g** represent white air-stable solids. Triprotonated salt **1g** is highly hygroscopic. NMR and IR spectroscopic investigations of the salts show the typical signals of melon and the corresponding acids. Like melon, all melemium cations are almost planar. The protonation occurs on the terminal nitrogen atoms of the C_6N_7 moiety and leads to some elongation of the C–N bonds adjacent to the protonated atom.

Since compounds **1a–1g** were obtained from the aqueous solutions of acids, almost all of them were isolated as hydrates. Water molecules play an important role in the building of systems of hydrogen bonds which leads to layered structures of melemium salts. The interaction between layers occurs via mineral acid anions and water molecules. However, melon – phosphoric acid adduct **1a** and salts **1c** and **1g** were isolated without crystal water in their structures, representing layered arrangement as well.

Cation $\text{H}_2\text{C}_6\text{N}_7(\text{NH}_2)_3^{2+}$ in salts **1d**, **1e** and **1f** occurs in two tautomeric forms (Scheme 11). Thus, in case of compound **1e** and **1f** the higher symmetric form (C_{2v}) was observed. In case of **1d** the cation with a lower symmetry C_s was found. A similar effect was observed in case of dihydrogencyamelurates [40,72,143]. The stability of these two tautomeric forms evidences quite a low energetic difference between them.

3. s-Heptazine-based salts and acids

3.1. Cyameluric acid and cyamelurates

The first description of cyameluric acid, **2**, $\text{H}_3\text{C}_6\text{N}_7\text{O}_3$, and its most abundant salt tripotassium cyamelurate $\text{K}_3[\text{C}_6\text{N}_7\text{O}_3]$, **2c**, dates back to 1850, as well as the determination of their quantitative composition [20,56,144].

3.2. Preparation

The syntheses of cyameluric acid (**2**) and potassium cyamelurate (**2c**) reported by Liebig [20,56] and Henneberg [144] are in use up to nowadays [38,39,40]. Cyameluric acid, **2**, is usually prepared by acidifying of potassium cyamelurate, **2c**, with strong acids, whereas the former can be obtained by the alkaline hydrolysis of melon, melon (**1**) or of potassium melonate (**3c**) [144] (Scheme 12). Sodium cyamelurate (**2b**) can be also prepared from **1** and sodium hydroxide in water, while Li, Cs and Rb cyamelurates were obtained by reacting cyameluric acid with corresponding metal hydroxides in water [69].

The formation of di- and trivalent metal salts of cyameluric acid by the exchange reaction between potassium cyamelurate (**2c**) and the corresponding metal salt was reported in 1970th by Zhagrova et al. [47] without complete characterisation.

Recently, it was reported that the reaction of cyameluric acid with strong organic bases such as guanidine in aqueous solution yields triguanidinium cyamelurate hydrate $[\text{C}(\text{NH}_2)_3]_3[\text{C}_6\text{N}_7\text{O}_3] \cdot 3\text{H}_2\text{O}$ [70]. The first di- and mono-protonated cyamelurates were $\text{K}[\text{H}_2\text{C}_6\text{N}_7\text{O}_3] \cdot 2\text{H}_2\text{O}$ and $\text{K}_2[\text{HC}_6\text{N}_7\text{O}_3] \cdot \text{H}_2\text{O}$ [40]. Calcium-ammonium cyamelurate $\text{NH}_4\text{Ca}[\text{H}_2\text{C}_6\text{N}_7\text{O}_3] \cdot [\text{HC}_6\text{N}_7\text{O}_3] \cdot 6\text{H}_2\text{O}$ is the first example of a structurally characterised cyamelurate with anions in mono- and di-protonated form at the same time [72].

3.2.1. Physical and chemical properties

Alkali metal cyamelurates are white, air-stable crystalline solids, well soluble in water. Cyameluric acid, **2**, is only poorly soluble in water exhibiting weak acidic reactions. Investigations of the acidity of cyameluric acids were reported already by Pauling and Sturdivant in 1937 [25]. At about the same time, Redemann and Lucas [57] performed the titration of potassium cyamelurate with hydrochloric acid. The dissociation constants of cyameluric acid obtained from this experiment are in good agreement with the data reported later by Takimoto [145], Huyge-Tiprez et al. [146] and El Gamel et al. [40]. The latter investigations included the acid–base titration experiments providing the three pK_s values (pK_{s1} 3.0–3.1, pK_{s2} 6.1–6.6, pK_{s3} 8.4–9.1).

A remarkable property of cyameluric acid is its ability to keto-enol tautomerism that leads to the formation of 17 tautomeric structures [40], while cyanuric acid has only five tautomeric forms (Scheme 13).

For instance, some derivatives of cyanuric acid, $\text{H}_3\text{C}_3\text{N}_3\text{O}_3$, are able to transform from one isomer to another simply under heating [147]. This rearrangement reaction of cyanuric acid has been used in preparative organic chemistry, e.g. for the synthesis of pharmaceutical intermediates [148].

Although in solution the equilibrium between different tautomers of **2** is established, the stable tautomeric forms in the solid state have been the subject of controversial discussions for many years.

In the 1960s Finkel'shtein suggested the domination of the hydroxy-tautomers of cyameluric acid in the solid state [46]. This suggestion was based on UV and IR spectroscopic data as well as on the magnetic susceptibility measurement. Furthermore, Dergunov et al. reported about reactions of cyameluric acid with hexamethyldisilazane (HMDS) or tributylmethoxystannate [149]. IR investigations of the obtained products indicated the presence of hydroxy-derivative with $-\text{C}-\text{O}-\text{SiMe}_3$ groups (**10**) in case of HMDS and the formation of the oxo-derivative with characteristic $\text{C}=\text{O}$ and $\text{N}-\text{SnBu}_3$ group vibrations in case of the tin-containing compound. Additionally, mono- and di-potassium salts were investigated crystallographically indicating the oxo-tautomer [40]. The X-ray structure of $\text{C}_6\text{N}_7\text{O}_3[\text{Sn}(\text{C}_2\text{H}_5)_3]_3$ (**11**) reveals the trihydroxy-tautomer [40].

The first data about structural analysis of alkali metal cyamelurates appeared in 2004 including their vibrational spectroscopy (IR, Raman), thermal stability, photoluminescence and UV/vis investigations [69]. Cyamelurates exhibit a planar $[\text{C}_6\text{N}_7\text{O}_3]^{3-}$ -ring. All four examples **2a–d** crystallize as hydrates and show a π -stacking of the anions. The hydrogencyamelurates are derivatives of the keto-tautomer of cyameluric acid, whereas the residual hydrogen atoms were found to be bound to nitrogen atoms of the cyameluric nucleus. Similarly to cyamelurates, hydrogencyamelurate and dihydrogencyamelurate represent a layer-like structure with an extensive hydrogen bonding network in the solid state [40].

In 1981 the reactions between cyanuric or cyameluric acids and 1-chlorohexamethylene-6-isocyanate with triethylamine as base were elaborated [150]. In both cases the formation of oxo-derivatives were reported.

The recent theoretical calculations of the hydroxyl-oxo tautomerism of cyameluric acid have shown that the formation of oxo-form is preferred in the gas phase [151]. Additionally, two crystal structures of cyameluric acid solvates **2**·3DMSO [38] and **2**·3H₂O [39] were reported, in both cases the C_3 -symmetrical oxo-isomers were isolated. Furthermore, the structure elucidation of solid **2** by means of solid state NMR spectroscopy and X-ray powder diffraction have shown that the protons are localised on the outer ring nitrogen atoms [152].

In summary, most of the structurally characterised neutral and ionic species containing cyameluric acid nucleus are derived from the trihydroxy tautomer, whereas the crystal structures of cyameluric acid and its mono- and dipotassium salts represent the tri-carbonyl tautomeric form [38–40].

3.2.2. Thermal stability and spectroscopic properties

The cyamelurate salts investigated so far decompose at 470–540 °C, producing cyanates and metal oxides [153]. Cyameluric acid **2** is stable up to 480 °C and decomposes under formation of *s*-heptazine-based polymers [48].

In the 1970s several cyamelurates (Na, K, Ba, Ca, Mg, Co, Ni, Zn, Mn, Pb, Cu, Ag, Fe, Al, Bi, and Cr and Cd) were investigated using IR spectroscopy and thermogravimetry [47,49]. All metal cyamelurates lose their crystal water at 100–180 °C decomposing in the

temperature range of 420–540 °C. While the anhydrous salts of K, Na, Mg decompose to cyanates and Ba and Ca to their carbonates, the Mn, Zn, Cd, Co, Ni, Pb, Cu cyamelurates decompose to their oxides [49].

Systematic investigations of IR spectra of cyamelurates showed typical vibrational bands of the *s*-heptazine ring (around 1650, 1530 and 1450 cm^{-1}) not much affected by the cation type [47,69,145,153].

The partially protonated cyamelurate anions were investigated recently. Compounds $\text{Na}[\text{H}_2\text{C}_6\text{N}_7\text{O}_3]\cdot 4\text{H}_2\text{O}$ [143], $\text{K}[\text{H}_2\text{C}_6\text{N}_7\text{O}_3]\cdot 2\text{H}_2\text{O}$ and $\text{K}_2[\text{HC}_6\text{N}_7\text{O}_3]\cdot \text{H}_2\text{O}$ [40] were obtained by the neutralisation of the aqueous solutions of corresponding cyamelurates with strong mineral acids [40,143].

The titration experiment of potassium cyamelurate, **2c**, with hydrochloric acid was monitored by the UV/vis spectroscopy [40] allowing to detect the formation of all protonation stages of cyameluric anions $[\text{H}_2\text{C}_6\text{N}_7\text{O}_3]^-$ and $[\text{HC}_6\text{N}_7\text{O}_3]^{2-}$ and $[\text{C}_6\text{N}_7\text{O}_3]^{3-}$ in the pH range 0.5–11.5.

3.2.3. Applications

Cyameluric acid, **2**, and cyamelurates have been suggested for a wide application spectrum in scientific and industrial fields. For example, **2** may be used for the preparation of resins, polymers, photographic materials and thermally insulating coatings [154–157]. Some time ago, the adsorption properties of **2** were investigated by gas chromatography [50]. The ability of cyameluric acid to form hydrogen bonds allows to use this acid as an adsorbent for gas-chromatographic analysis of compounds with active functional groups. Similar properties were observed for other *s*-heptazine-based compounds such as melem, **1**, and dimelemone (*N,N*-bis(5,8-diamino-*s*-heptazin-2-yl)urea) [158]. Recently, the syntheses of group II and III-metal containing compounds from cyameluric acid were reported as potential flame retarding compounds [159].

Recent theoretical calculations have shown that **2** is a potent receptor of anions such as NO_3^- and ClO_4^- via anion- π interaction [160]. The planar D_{3h} symmetric C_6N_7 nucleus of cyameluric acid with electron-withdrawing oxygen atoms can be regarded as new type of tripodal and cylindrophane receptors for the selective recognition of trigonal-planar and tetrahedral anions [160].

As the most of *s*-heptazine-based materials, cyameluric acid is a starting material for many molecular *s*-heptazine derivatives and a precursor for the synthesis of carbon nitrides, C/N/H materials and related microporous or non-porous (interpenetrating) 2D and 3D polymers such as COFs (see Section 6).

3.3. Melonates and hydromelonic acid

3.3.1. Introduction

Melonates which are also called tricyanomelates or tricyanamido-*s*-heptazines represent salts of the hydromelonic acid $\text{H}_3[\text{C}_6\text{N}_7(\text{NCN})]$ (**3**) containing the anionic structural motif $[\text{C}_6\text{N}_7(\text{NCN})]^{3-}$ (Scheme 14).

The name hydromelonic acid was introduced on the mistaken assumption that the acid was a hydrate of melon. In 1835, Leopold Gmelin, found that when potassium ferricyanide, $\text{K}_3[\text{Fe}(\text{CN})_6]$, was heated with sulphur, a species called potassium hydromelionate, $\text{K}_3\text{C}_9\text{N}_{13}$ is generated [22].

The factual composition and formula of melonate anion $[\text{C}_6\text{N}_7(\text{NCN})]^{3-}$ was determined by Pauling and Sturdivant in 1937 [25], which introduced the cyameluric nucleus C_6N_7 and proposed this nucleus to be present in hydromelonic and cyameluric acid.

Redeman and Lucas extended the work of Pauling and Sturdivant by investigation of K_α values of hydromelonic acid $\text{C}_6\text{N}_7(\text{HNCN})_3$. Hydromelonic acid is stronger than cyameluric acid, and the latter is even stronger than cyanuric acid [57].

The electronic structure of the NCN side groups in melonates was controversially discussed in literature. Two tautomeric forms, the carbodiimide ($-\text{N}=\text{C}=\text{N}$) and cyanamide ($-\text{N}-\text{C}\equiv\text{N}$) were supposed. The recent crystal structure investigations of melonates showed the prevalence of the cyanamide tautomers.

3.3.2. Preparation

The synthesis of hydromelonic acid from silver melonate and H_2S was reported by Burdick in 1925 [161] (Scheme 15).

However, the polymerization of $\text{C}_6\text{N}_7(\text{NHCN})_3$ in water solutions [46], hinders the isolation of pure hydromelonic acid. Due to the same reason, hydromelonic acid cannot be obtained by reactions of potassium melonate and mineral acids HCl or HNO_3 .

Potassium melonate, **3c**, a precursor for almost all known melonate derivatives, was among the first synthesized *s*-heptazine compounds reported by Gmelin [22] and thoroughly investigated by Liebig [20] in 1834. Since those times, a wide variety of metal melonates was synthesized. Thus, Fedoruk et al. reported about thermal decomposition of group II, IV, VII and VIII metal melonates [51]. Moreover, Burdick investigated in 1925 the synthesis of silver melonate $\text{Ag}_3(\text{C}_6\text{N}_7(\text{NCN})_3) \cdot 6\text{NH}_3$ from sodium melonate in liquid ammonia [161]. Recently, our group reported on the synthesis of a silver melonate from an ethylenediamine solution including the comprehensive analysis as well as on the syntheses of silver and nickel melonates (**3j**) in water, ammonia and ethylenediamine solution [67] (Scheme 16).

Also recently, Makowski et al. reported on rare-earth melonates **3k–p** prepared from ammonium melonate which is accessible by ion exchange from potassium melonate **3c** [68]. The other known metal melonates were prepared by cation exchange reactions from potassium melonate, **3c**. The latter is usually prepared by a classical method from melon and potassium thiocyanate [23,56,57,63]. Sodium melonate, **3b**, can be obtained by a similar procedure with sodium thiocyanate. Alternatively, K and Na melonates were prepared by Burdick from corresponding metal thiocyanates and SbCl_3 or BiCl_3 [161] (Scheme 17).

The reaction of melon and KSCN is characterised by high yield and high purity of the product. However, the reaction mechanism is still under consideration. One of the first suppositions was made by Horvath-Bordon et al. [63], whereby CS_2 , and potassium amides are evolved. Recently, Sattler and Schnick proposed three possible reaction courses in the thiocyanate melt [162].

Two of them, which combination is most likely to take place in the reaction process are in accordance with the observed CS_2 formation and other reaction by-products described by Horvath-Bordon et al. [63].

Komatsu and Nakamura investigated a pyrolysis of *s*-heptazine-based compounds aiming to obtain graphite-like carbon nitrides [163]. Thus, anhydrous copper (II) melonate **3h**, $\text{Cu}_3(\text{C}_6\text{N}_7(\text{NCN})_3)_2$, was obtained by the exchange reaction of $\text{K}_3[\text{C}_6\text{N}_7(\text{NCN})_3]$ and copper acetate. The pyrolysis of the former at 550°C resulted in a hydrogen-containing carbon nitride phase $\text{CH}_{0.1}\text{N}_{0.83}$ [163].

Recently, synthesis, crystal structures and thermal behaviour of alkali metal melonates with Li (**3a**) [62], K (**3c**) [162], Rb (**3d**) and Cs (**3e**) [64] as well as and protonated calcium derivative **3f** [65] were reported. Furthermore, Fe(III) melonate $\text{Fe}[\text{C}_6\text{N}_7(\text{NCN})_3]$ was obtained and characterised by spectroscopic methods [164]. By pyrolysis of the latter in a microwave formation of tubular carbon nanostructures was observed. Very recently, our group reported on copper melonate, **3h**, and a copper melonate crystallizing with ethylenediamine as bridging agent [66].

3.3.3. Physical properties

Alkali metal melonates **3a–e** represent white air-stable hygroscopic powders. These crystalline substances are soluble in water and in diluted aqueous acid solutions. Transition metal melonates

are coloured due to colour of the corresponding cations. Melonates exhibit quite high thermal stability. Thus, alkali metal melonates **3a–e** and iron melonate **3g** [164] decompose at above 500°C . Protonated calcium melonate **3f** decomposes at rather low temperatures starting at 250°C [65].

Additionally, **3c** was investigated by means of electron spectroscopy. The photoluminescence measurements have shown excitation and emission spectra similar to those of alkali metal cyamelurates [69]. Additionally, the UV spectra and the extinction coefficient ($\epsilon = 0.75 \times 10^2 \text{ mol}^{-1} \text{ cm}^{-1}$) indicate the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [69]. Among the rare-earth melonates **3k–q** reported only the Tb melonate **3q** shows luminescence under UV excitation [68].

3.3.4. Vibrational and NMR spectroscopy

Table 4 shows the data of spectroscopic investigations of metal melonates **3a**, **3c–k** [62–66,164]. The IR spectra of these substances are similar, showing the characteristic vibrations of the *s*-heptazine core at the expected values (see also Section 4.8). Even in case of protonated *s*-heptazine rings in calcium melonate **3f**, the *s*-heptazine vibrations are similar to other salts, showing the ability of the large *s*-heptazine system delocalizing the positive charge. Only the E–H (E=O, N) stretching region in **3d** represents a more complex system of vibration bands including not only OH stretch, but also NH vibrations.

Compounds **3a** and **3c** were investigated by means of solution ^{13}C NMR spectroscopy, whereas the calcium melonate **3f** was investigated by solid state ^{13}C CP/MAS spectroscopy. The solution spectra and the solid state spectra of **3a** and **3c** are quite similar. Signals of *s*-heptazine-nucleus appear around 170 (C2) and 155 (C1) ppm being in the same range as in case of the other *s*-heptazine derivatives (see Table 4). Signals of carbon atoms of the cyano-groups arise at 120 ppm for all compounds studied so far. The investigations of calcium melonate **3f** by solid state NMR allows estimating of the proton influence on the *s*-heptazine ring. Thus, the C2-atom, adjacent to the protonated N, was found at 160 ppm, being shifted upfield in comparison with the non-protonated equivalent C-atoms.

^{15}N CP/MAS NMR spectroscopy was employed to characterize the positions of N atoms in melonates. The cross-polarisation CPPI experiment allows detection of H-containing N atom in the heptazine ring of **3d**. The NH atom was observed at -255 ppm. The other signals were observed and unambiguously assigned with the following chemical shift values: N_{tert} and $\text{C}=\text{N}$: -183 to -203 ppm; NC_3 : -233 ppm; $\text{N}(\text{CN})$: -250 to -261 ppm [162].

3.3.5. Crystal structures

The crystal structures of all alkali metal melonates, except sodium, are known. On the other hand, the poor solubility of heavy metal melonates in water hinders their investigation with single crystal X-ray diffraction.

Lithium, potassium, rubidium and caesium melonates were crystallized from the water solutions as hydrates **3a**· H_2O [62], **3c**· $5\text{H}_2\text{O}$ [63], **3d**· $3\text{H}_2\text{O}$ and **3e**· $3\text{H}_2\text{O}$ [64]. Besides, the structure of solvent-free potassium melonate **3c** was reported by Sattler and Schnick [162]. Furthermore, the first crystal structure of protonated melonate, calcium salt **3f**· $7\text{H}_2\text{O}$ was investigated [65]. The crystal structure of copper melonate containing ethylenediamine, **3h**· $(\text{CH}_2\text{NH}_2)_2$, shows the only example of a coordination of a metal to the terminal nitrogen atoms of the exocyclic cyanamide groups [66].

Recently, we reported on the crystal structure of an ethylenediamine adduct of silver melonate, **3i**, [67]. The complexing agents water, ethylenediamine and ammonia decrease the thermal stability compared to other known *s*-heptazine derivatives. The ethylene diamine leads to a stacked structure with $\text{Ag}(\text{I})-\text{Ag}(\text{I})$ contacts and

Table 4
Selected IR and NMR data of melonates **3a**, **3c–k**.

	3a	3c	3d/3e	3f	3g	3h	3i	3j-NH₃	3k^f
Reference	[62]	[63]	[64]	[65]	[164]	[66]	[67]	[67]	[68]
$\delta_{\text{C6N7-unit}}$	805	756	795	790	800	800	795	807	807
$\nu_{\text{C6N7-unit}}$	1628, 1414, 1497	1195, 1432, 1578, 1638	1634–1418	1200–1700	1280–1650	1641, 1426	1650, 1447	1632, 1427	1700–1200 ^g
ν_{NCN}	2157	2183	2170–2140	2179	2186	2207	2181	2197	2184
$\nu_{\text{OH}}^{\text{a}}$	2600–3600	3400	3000–3600	2600–3600 ^b 3000–3600	3400–3600	3403	3190	3341	3600–3000 ^g
¹³ C NMR [ppm]									
C(NCN)	172.2	174.3	/	170–171; 160 ^c	/	175 ^d	164; 169	/	/
CN ₃	155.6	158.6	/	149–154	/	157 ^d	155	/	/
C≡N	120.3	124.8	/	119–122	/	~125 ^d	120	/	/
¹⁵ N NMR ^e [ppm]									
N _{tert} C≡N	/	/	/	–183 to –203	/	/	/	/	/
N–H	/	/	/	–255	/	/	/	/	/
NC ₃	/	/	/	–233	/	/	/	/	/
N(CN)	/	/	/	–261 to –250	/	/	/	/	/

^a From H₂O molecules.^b NH stretching.^c Carbon atom near protonated nitrogen atom.^d Unpaired electrons of Cu²⁺ lead to extremely broad signals.^e CP/MAS measurements.^f La melonate represents all other reported Ln melonates [68].^g Not assigned in detail.

hydrogen bonds between the layers [67]. A copper melonate, **3h**, crystallizing with ethylenediamine as bridging agent [66] shows a coordination of the metal ion only to the terminal nitrogen atoms of the cyanamide and is the first structurally analysed transition metal melonate. On the other hand, the melonate–ethylenediamine complex **3h**·(CH₂NH₂)₂ shows less thermal stability than **3h** [66]. The Ln melonates **3k–q** were characterised by means of single crystal structure analysis (**3k**) and powder X-ray diffraction with Rietveld refinement (**3l–q**) [68]. The lanthanide melonates represent the first melonates with trivalent cations showing a different thermal behaviour. As the authors assume, the incomplete dehydration leads to a reaction between the remaining water and the heptazine core resulting in another decomposition mechanism [68].

In all presented cases, the [C₆N₇(NCN)₃]^{3–} moieties are almost planar – including the cyanamide side arms – and arranged in layers. In case of K, Rb and Cs melonates, the AB stacking of the layers was observed, where melonate moieties are situated in A layers and the B layers are represented by water and cations. These layers interact via hydrogen bonds. In case of Li and Ca melonates, the cations are coplanar with anions and the B layers are represented only by water molecules. This can be explained by relative small ionic radii of Li⁺ and Ca²⁺. In case of anhydrous potassium melonate, the H-bonds are absent, whereas the intermolecular interaction is represented by the π–π stacking of *s*-heptazine nuclei with a distance of 3.28 Å. Such heptazine–heptazine interaction

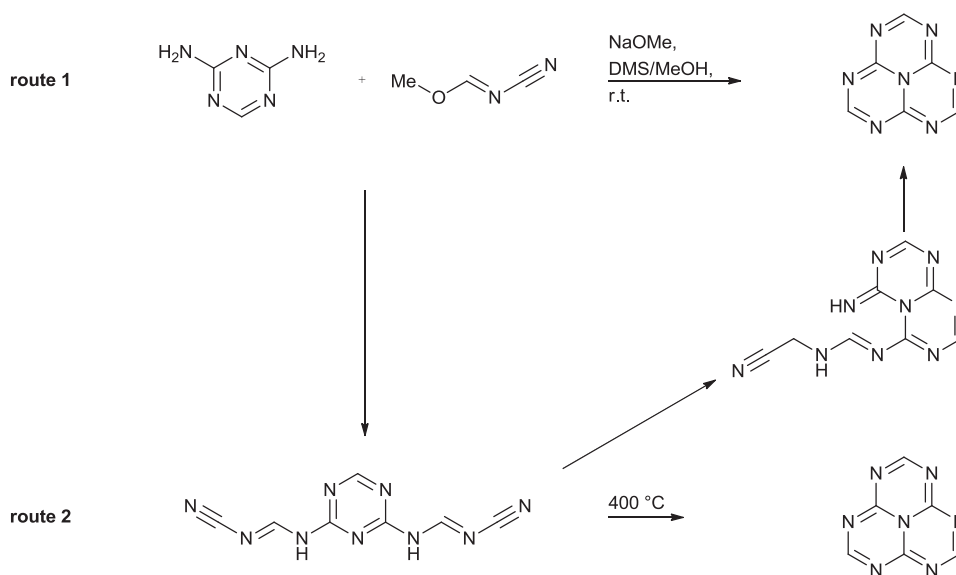
was observed in the hydrated **3c–e** as well, with centre-to-centre distances of 2.6–3.3 Å. In case of **3a** and **3f**, the distance between heptazine nuclei is >6 Å not supporting any interlayer interaction. Whereas the adjacent anions of Li (**3a**) and K (**3c**) melonates situated in one plane, the anions in Rb (**3d**) and Cs (**3e**) melonates are inclined towards each other by an angle of 12.3°. In case of anhydrous K melonate (**3c**), the anion is present as a C_s-rotamer. Thus the anion is not completely planar, since one NCN “arm” is significantly deviated from the plane of the *s*-heptazine core.

In principle, the melonate anion can appear in various rotamers: several C_s geometries (reduced molecular symmetry), C_{3v} and the planar and most symmetric C_{3h} form. In the majority of all known melonates conjugated [C₆N₇(NCN)₃]^{3–} anions exhibit the C_{3h} symmetry.

The NCN side arms of the melonate anion can show two mesomeric forms, the symmetric carbodiimide and the asymmetric cyanamide. The latter was suggested by Pauling and Sturdivant and proven by crystal structure determinations. Thus, the observed terminal C3–N4 bond lengths of 1.15 Å is slightly shorter than that suggested by Pauling (1.20 Å). The inner C3–N3 bond of the NCN unit equals to 1.32 Å being in agreement with the typical value of cyanamides. The bond lengths of the exocyclic C2–N3 and the C3–N3 bonds of the NCN substituents are in the range between single and double-bonds illustrating the π conjugation over the whole [C₆N₇(NCN)₃]^{3–} ion. These bond lengths correspond well with the planarity of the system usually found in the solid state.

Table 5
Comparison of structural properties of selected *s*-heptazine derivatives. Numbering as depicted in Fig. 2.

X=	1 NH ₂	4 -Me ₂ CO, Et ₂ OCl	4 Cl	5 N ₃	6 H	7 OPh	10 OSiMe ₃	20 -3H ₂ O	13 NEt ₃
Reference	[34,35]	[33]	[173]	[27]	[28]	[37]	[40]	[39]	[36]
d (N1–C1) [Å]	1.40	1.40	1.39	1.40	1.38	1.41	1.41	1.39	1.40
d (C1–N2) [Å]	1.33	1.33	1.34	1.33	1.35	1.31	1.33	1.34	1.33
d (N2–C2) [Å]	1.35	1.34	1.33	1.33	1.31	1.33	1.34	1.38	1.36
d (C2–X) [Å]	1.33	1.71	1.72	1.40	1.05	1.32	1.31	1.23	1.34
∠ (N2–C2–N2) [°]	127.0	129.6	130.4	128.8	128.3	129.1	127.9	119.0	126.9
∠ (C1–N2–C2) [°]	117.5	115.1	115.0	115.4	116.3	114.9	116.9	124.5	116.2
∠ (N2–C1–N1) [°]	119.0	119.8	119.0	120.1	119.2	121.4	119.0	114.6	120.3
∠ (N2–C1–N2) [°]	120.5	120.2	120.7	120.8	120.7	117.9	121.2	121.2	119.9
∠ (N2–C2–X) [°]	115.7	114.9	115.1	113.4	107.9	120.6	117.5	119.0	116.1
∠ (C1–N1–C1) [°]	119.8	119.8	119.2	120.0	119.4	118.1	119.9	119.9	120.8



Scheme 18. Synthesis of the parent *s*-heptazine $C_6N_7H_3$ **6** by Hosmane et al. [14,28].

3.3.6. Applications

s-Triazine-based analogues of melonates, tricyanomelaminates $[C_3N_3(NCN)]^{3-}$, have been thoroughly investigated in the recent years [99,112,165,166]. It was found that a pyrolysis of metal-free tricyanomelaminates yielded *s*-heptazine-based substances prior to formation of CN_x phases. From this point of view, melonates represent promising precursors for graphitic carbon nitrides. Indeed, it has been observed that pyrolysis or polycondensation of hydromelonic acid lead to the formation of C/N/H compounds [163]. Furthermore, a pyrolysis of boron compounds with copper(II) melonates leads to the formation of graphite-like B–C–N materials which are used as precursors for cubic hard B–C–N compounds and as semiconductors [167].

4. Other molecular tri-*s*-triazine derivatives

In addition to the described molecular compounds melem (**1**), cyameluric acid (**2**) and the highly reactive and therefore still elusive hydromelonic acid (**3**), several other molecular *s*-heptazine derivatives have been reported. These are described in the following subchapters.

4.1. $C_6N_7H_3$ – the parent *s*-heptazine

The parent molecule, the H-substituted tri-*s*-triazine **6**, was first mentioned in theoretical predictions [25,168] before Hosmane et al. prepared and analysed **6** comprehensively [14,28]. The synthesis of tri-*s*-triazine was carried out either via reaction of (*E*)-methyl *N*-cyanoformimidate, 2,4-diamino-1,3,5-triazine and sodium methanolate in $(CH_3)_2SO/CH_3OH$ at room temperature or via sublimation of 2,4-bis(*N*-cyano-*N'*-formamido)-1,3,5-triazine at $\sim 400^\circ C$ and <0.025 mm Hg. The latter starting material occurs during the reaction of the first indicating a related mechanism via tautomerisation, ring closure and elimination (Scheme 18).

The yellow coloured compound shows a UV absorbance at $\lambda_{max} = 443$ nm in acetonitrile and weak fluorescence activity, while the crystal structure analysis reveals the planar structure of the molecule [14,28].

It is interesting to compare chemical and physical properties of the aromatic *s*-triazine $C_3N_3H_3$ with its counterpart *s*-heptazine. A summary is provided in Fig. 1.

The authors also performed a reactivity study treating *s*-heptazine $C_6N_7H_3$ under various conditions with nucleophiles and electrophiles as well as other reactive reagents such as elemental halogens. They reported hydrolytical sensitivity in aqueous environments. Under non-aqueous conditions relative low reactivity was observed. No *s*-heptazine derivative was isolated or identified [28].

4.2. Cyameluric halides – tri-chloro-tri-*s*-triazine

Since melem (**1**) or cyameluric acid (**2**) do hardly react with common nucleophiles or electrophiles the access to several new *s*-heptazine derivatives is based on the synthesis of cyameluric chloride, $C_6N_7Cl_3$ (**4**) being extremely reactive towards O and N nucleophiles.

Cyameluric chloride (**4**) was first synthesized by Redemann and Lucas in 1940 by heating either tripotassium cyamelurate, **2c**, or cyameluric acid, **2**, with phosphorous pentachloride in a large bomb tube [169] (Scheme 19). This solid phase reaction releases toxic phosphoryl trichloride ($POCl_3$) among the other volatile compounds making the synthesis difficult and dangerous. In addition, the product was contaminated with small amounts of phosphorous. Schroeder and Kober tried to optimize the synthesis of **4** by replacing PCl_5 with $C_6H_5PCl_4$ but were not successful [52]. Redemann and Lucas improved the solid phase reaction by using an excess of PCl_5 and **2** or the tripotassium salt (**2c**). Rapid cleaning with



mp > 300°C
soluble in organic solvents
hydrolysis in H_2O
yellow, $\lambda_{max} = 443$ (ϵ : 270), 305 (22700)
 λ_{em} 517 (τ : 9–14 ns, ϕ : 0.014 rel. fluorescein)
 1H NMR: $\delta = 8.3$ ppm
HOMO: π -orbital

mp = 86°C; bp = 114°C; dec. > 600°C
soluble in organic solvents
hydrolysis in H_2O
colorless
 1H NMR: $\delta = 9.2$ ppm
HOMO: n-orbital

Fig. 1. Comparison of selected characteristics of *s*-heptazine, **6** and *s*-triazine.

ice water gives the chloride **4** in good yields and without any further purification after drying over phosphorus pentoxide in vacuo. In a patent Neef describes a non-solid phase synthesis of **4** [170]. Tripotassium cyamelurate, **2c**, is treated with an excess of PCl_5 in *ortho*-dichlorobenzene at 160°C for 1 h, removing of the solvent and the phosphoryl trichloride gives the raw product. The latter was used without purification in situ for further derivatisation. Another synthesis is based on a high temperature transformation of cyanuric chloride or cyanogen chloride CICN using charcoal as a solid phase catalyst [171]. Kroke et al. described the purification of **4** obtained by solid phase reaction from PCl_5 and **2c** using sublimation at 10^{-2} – 10^{-3} bar and 240 – 290°C and also via Soxhlet extraction with toluene [25,33,172].

Schroeder and Kober characterised the chloride **4** by the melting–decomposition point and the chlorine content [52]. We published a comprehensive characterisation of this heptazine derivative including ^{13}C NMR, FTIR, UV–vis absorption and photoluminescence spectroscopy, elemental analysis and a X-ray structure determination [25,33]. Cyameluric chloride, **4**, shows the characteristic vibrations of the *s*-heptazine core (1610 , 1505 , 825 cm^{-1}) and typical chemical shift values in the ^{13}C NMR (159 ppm for CN_3 , 176 ppm for CN_2Cl) [33]. An absorption band with a maximum at 310 nm is in accordance with the yellow colour of the compound, while a photoluminescence signal of **4** occurs at 468 nm [33]. The first single crystal structure of a solvate of the chloride **4**, namely $\text{C}_6\text{N}_7\text{Cl}_3 \cdot \text{Me}_2\text{CO} \cdot \text{Et}_2\text{O}$, indicated a completely planar $\text{C}_6\text{N}_7\text{Cl}_3$ molecule, arranged in ABAB layers in the crystal [33]. Acetone and diethyl ether are part of layers A, while layers B being free of solvent molecules show a number of $\text{Cl} \cdots \text{N}$ intermolecular interactions [33]. A solvent-free structure of **4** was published by Tragl et al. [173]. Again, the planar molecule crystallizes in layers parallel to the *ab* plane [173]. Here, the synthesis of the cyameluric chloride was done via a solid state reaction of 2,4,6-trichloro-1,3,5-triazine and sodium dicyanamide in an ampule at 250 and 390°C for several hours leading to a sublimed product **4** [173].

To the best of our knowledge, no other fully halogen substituted tri-*s*-triazine was synthesized or analysed until now, i.e. the trifluoride, -bromide and -iodide are not known. Zheng et al. used density functional theory to study the geometries, electronic structures, harmonic vibrational frequencies for the cyameluric fluoride, chloride and bromide and suggested the azide substituted derivative **5** (see below) to be a material with good high-energy density properties [174–176].

4.3. The azide $\text{C}_6\text{N}_7(\text{N}_3)_3$

Gillan and co-workers reported the preparation, characterisation and crystal structure of the triazide **5**, $\text{C}_6\text{N}_7(\text{N}_3)_3$ [27,177]. Synthesis of **5** was carried out via the preparation of the chloride **4** synthesized from **2c** with PCl_5 and purified via Soxhlet extraction. Reaction of **4** with trimethylsilyl azide for 12 h and Soxhlet extraction in acetone gives the orange-tan azide **5** quantitatively. The same synthesis was independently used in our laboratory providing the same analytical data [25]. Besides, an alternative synthesis based on the reaction of 2,5,8-trihydrazino-*s*-heptazine (**22**) with NaNO_2 was reported [73]. The FTIR analyses of **5** reveal the typical *s*-heptazine vibrations (see Table 6) and a characteristic azide group vibration at 2168 cm^{-1} . The presence of these azide groups leads to energetic instability of compound **5** decomposing at 185°C to N_2 and nitrogen-rich CN_x materials [177]. Due to the azide group an extended illumination below 270 nm leads to photolytic decomposition. The theoretical HOMO–LUMO gap of 4.14 eV (300 nm) [174] is in good agreement with the spectroscopic data of Miller et al. reporting an absorption maximum of **5** at 295 nm in ethanol [27]. Photoluminescence occurs at 430 nm in ethanol with an excitation of 290 nm . The solvent-free crystal structure analysis proves the

Table 6
Comparison of general and spectroscopic properties of selected *s*-heptazine derivatives $\text{C}_6\text{N}_7\text{X}_3$.

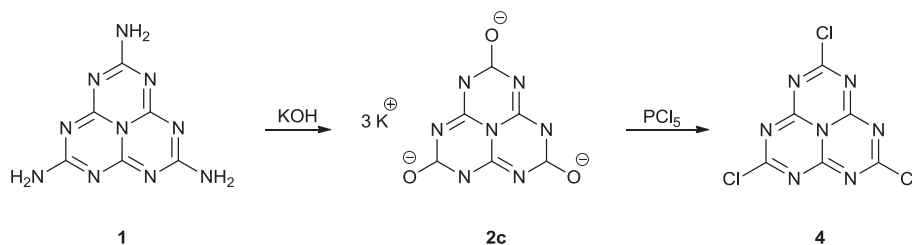
X=	1	2	4	5	6	7	10	13	22	23	24
	NH_2	=O	Cl	N_3	H	OPh	OSiMe_3	NEt_2	NHNH ₂	$\text{N}=\text{P}(\text{n-Bu})_3$	Phthalimide
Reference	[34,35]	[39,46]	[33,173]	[25,27]	[14,28]	[37]	[40,149]	[36]	[73,195]	[73]	[44]
Colour	White	White	Yellow	Orange	Yellow	White	White	White	Yellow	/	Yellow
M.P. [$^\circ\text{C}$]	560, decomp.	/	366	180, decomp	>360	285	198–199	218	/	/	>300
^{13}C NMR δ C1/C2 [ppm]	560, decomp.	156.5/150.6 ^d	175.0/158.2 ^a	171.4/158.7 ^b	171.6/159.7 ^b	/	169.5/158.9 ^d	162.4/155.0 ^c	164.2(162.2)/154.5 ^d	164.4/154.7 ^b	163.1/161.5 ^b
IR [cm^{-1}] of C_6N_7 -unit	1606 (vs)	1648 (vs)	1610 (vs)	1606 (vs)	/	1634 (vs)	1658 (vs)	1639	1636	1617	1618
	1469 (vs)	1540 (vs)	1505 (vs)	1530 (vs)	/	1476 (w)	1451 (vs)	1539	1509	1437	1470
	1304 (vs)	1426 (vs)	1310 (vs)	1362 (vs)	/	1392 (vs)	812 (w)	807	1391	1398	1329
	802 (m)	817 (m)	825 (m)	820 (m)	/	816 (m)	812 (w)	271	790	809	812
$\lambda_{\text{max, abs}}$ [nm]	245	217	310	295	443	/	/	386	/	/	236
$\lambda_{\text{max, emission}}$ [nm]	/	/	366	430	517	/	/	/	/	/	416

^a Solvent: THF-d⁸.

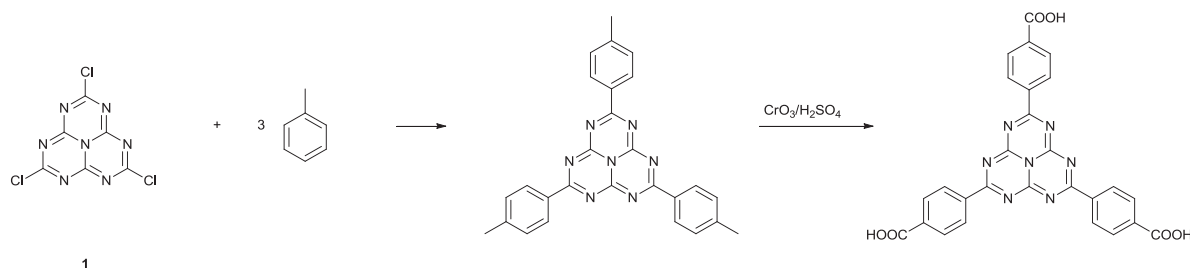
^b Solvent: DMSO-d⁶.

^c Solvent: CDCl_3 .

^d Solid state ^{13}C MAS NMR.



Scheme 19. Synthesis of cyameluric chloride, **4**, from potassium cyamelurate, **2c**, and PCl_5 .



Scheme 20. Preparation of a benzoic acid derivative of *s*-heptazine as linker for metal-organic frameworks [178,179].

planar geometry of the molecule with C_{3h} symmetry analogous to the above mentioned melonate anions. In addition to the synthesis of extended amorphous carbon nitrides the triazide **5** has been used as a starting material for *s*-heptazine-based phosphazenes as described further in Section 4.7.1.

4.4. $\text{C}_6\text{N}_7\text{R}_3$ – alkyl- and aryl *s*-heptazine derivatives

The azide $\text{C}_6\text{N}_7(\text{N}_3)_3$ (**5**) and the chloride $\text{C}_6\text{N}_7\text{Cl}_3$ (**4**) are currently the most reactive tri-*s*-triazine derivatives and therefore important as starting materials for further derivatisation of the cyameluric nucleus. One of the most extensive studies on molecular heptazine derivatives was presented by Schroeder and Kober in the early 1960s [52]. Based on several reactions of cyameluric chloride, **4**, with different nucleophilic reagents such as phenols, alcohols, amines and even aryl substituents they proved the high reactivity of tri-*s*-triazine chloride (see below). The authors also tried a Wurtz reaction with *s*-heptazine chloride using the Grignard reagents phenyl- and propyl-magnesium bromide. Unfortunately these attempts failed as well as the Wurtz–Fittig reaction with sodium and *n*-butyl bromide [52]. This reaction behaviour of **4** is unexpected. The only report on a methyl-substituted derivative was published by Finkel'shtein without any analytic data [46]. In fact, there are no characterised *s*-heptazines with aliphatic substituents reported so far.

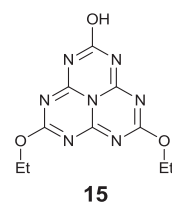
The only known C–C coupling reaction was realized by Ke et al. using **4**, toluene and AlCl_3 in a Friedel–Crafts reaction [178]. Oxidation and reaction with $\text{Zn}(\text{ClO}_4)_2$ [178] and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ [179] yielded tri-*s*-triazine-based metal-organic frameworks (MOFs) (Scheme 20).

4.5. Symmetric and asymmetric cyameluric esters

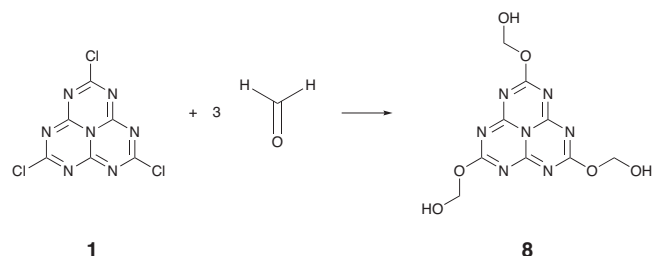
Cyameluric chloride $\text{C}_6\text{N}_7\text{Cl}_3$ may be used to prepare esters of the type $\text{C}_6\text{N}_7(\text{OR})_3$. While the reaction of cyameluric chloride with alcohols leads to the formation of cyameluric acid and the corresponding alkyl chloride, the reaction with sodium alkylates forms the desired trialkylcyamelurates. Phenols can react with **4** without being converted into the sodium derivative to the corresponding triarylcymelurates, e.g. phenol to $\text{C}_6\text{N}_7(\text{OC}_6\text{H}_5)_3$ (**7**) [37].

Apart from the non-successful reactions of cyameluric chloride with Grignard reagents and sodium organyls, Schroeder and Kober synthesized and characterised nine cyameluric esters including one asymmetrically substituted compound analysed with IR spectroscopy, melting point and CHNX elemental analysis [52]. They show the typical in-plane vibration of the triazine rings in the range of $1631\text{--}1642\text{ cm}^{-1}$. The attempt to synthesize monochloro-tri-*s*-triazine by reaction of cyameluric chloride with sodium ethylate yielded the diethyl cyamelurate (**15**) as the only reported asymmetric cyameluric ester so far (Scheme 21). This cyamelurate **15** was achieved in moderate yields (59%) and shows a relatively low melting point of $192\text{--}196^\circ\text{C}$.

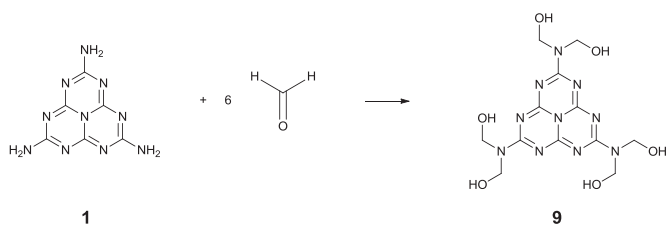
In the 1970s Strukov et al. described investigations on the *s*-heptazine derivative **8** [180] showing the inhibiting properties of **8** in an aqueous solution on the corrosion of steel (Scheme 22).



Scheme 21. Diethyl cyamelurate (**15**) as reported by Schroeder and Kober in its hydroxyl form. It was analysed with IR spectroscopy and elemental analysis. Based on the crystal structures of cyameluric acid (see text) and the mono- and deprotonated salts it is expected that compound **15** crystallizes in the carbonyl tautomeric form.



Scheme 22. Reaction of formaldehyde with **1** according to Strukov et al. [180].



Scheme 23. Reaction of formaldehyde with melem, **1**, according to Sprasskaya et al. [137].

Gordetsov et al. synthesized group 14 derivatives of cyameluric acid using OSiMe_3 [149], OSnBu_3 [136] and OGeEt_3 [181] substituents. Later the molecular structure of **10** with $\text{R} = \text{OSiMe}_3$ revealed the expected trihydroxy tautomeric form of the cyameluric acid ester [40,182,183], while the tin atoms in **11** with $\text{R} = \text{OSnEt}_3$ show the Sn-typical hexacoordination [40].

4.6. Symmetric and asymmetric cyameluric amides

Symmetric compounds of the type $\text{C}_6\text{N}_7(\text{NR}^1\text{R}^2)_3$ as well as asymmetric derivatives such as $\text{C}_6\text{N}_7\text{X}(\text{NR}^1\text{R}^2)\text{NR}^3\text{R}^4$ or $\text{C}_6\text{N}_7\text{X}_2(\text{NR}^1\text{R}^2)$ may be considered as cyameluric acid amides. Alternatively, these compounds can formally be derived from melem.

The reaction of melem, **1**, with formaldehyde leads to the formation of **9** [137]. The hydroxyl-methyl substituent is interesting in triazine chemistry used as starting material for Bakelite derivatives (Scheme 23).

Schroeder and Kober synthesized and characterised 11 tri-*s*-triazine derivatives based on the cyameluric amid form including three asymmetrically substituted derivatives with IR spectroscopy, melting point and CHNX elemental analysis [52]. Again, the derivatives show the typical in-plane vibration of the heptazine ring in the range of $1631\text{--}1640\text{ cm}^{-1}$ (Scheme 24).

Reactions with secondary amines lead to tri-*s*-triazine amide derivatives. Some of these compounds reported by Schroeder and Kober with e.g. $\text{N}(n\text{-C}_7\text{H}_{15})_2$ -trisubstitution (**12**) show a gelatinizing effect upon alkanes forming stable gels at room temperature for several months or occur in different polymorphs [52]. According to a patent application [197], hexaaryl substituted melem derivatives

are supposed to be used in organic electroluminescent devices, but comprehensive analyses of the reported compounds are missing.

In 2004, the NEt_2 -substituted tri-*s*-triazine $\text{C}_6\text{N}_7(\text{NEt}_2)_3$ (**13**) was the first reported crystal structure of a organo melem derivative [36]. Moreover, the NEt_2 -substitution at the heptazine core leads to the new nonlinear optically active molecule **13** showing a high absorbance coefficient in the UV. In 2011 the hexaphenyl melem **14** was found to crystallize as inclusion compound with nitromethane [43].

Using diphenylamine and di-*n*-heptylamine in different ratios leads to the corresponding *s*-heptazine derivatives **18–19** as shown in Scheme 24. Synthesis and separation of a monochloro derivative **16** was successful for the weak base α -dipyridylamine [52].

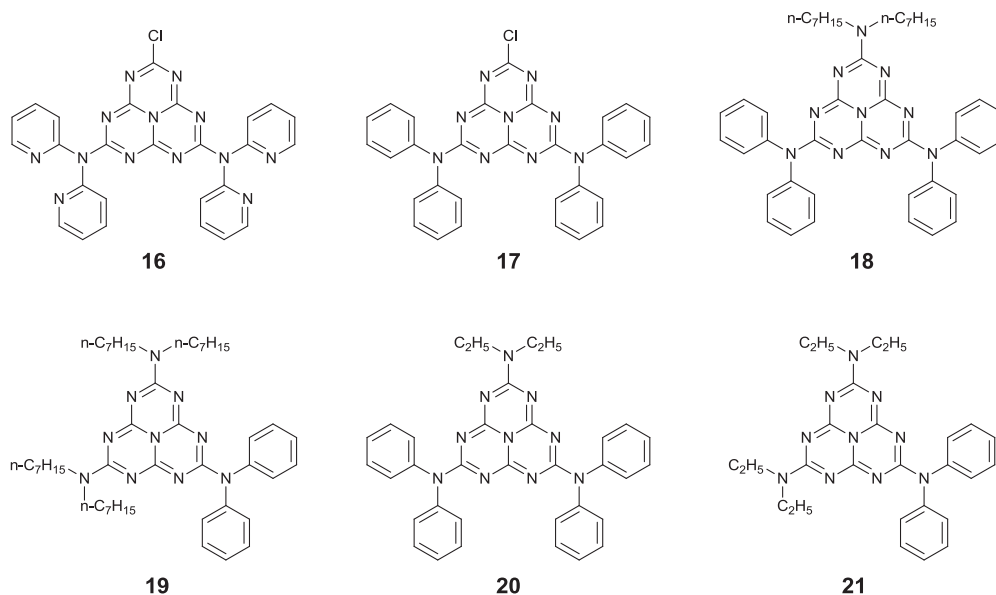
Recently, Schwarzer and Kroke reported the first crystal structure of the monochloro-tri-*s*-triazine **17**, derived from the hexaphenylmelem as inclusion compound with *p*-xylene. The comprehensive analysis and the reaction with diethylamine prove the reactivity of **17** [42]. The series of melem derivatives **12**, **14**, **18** and **19** [52], especially NEt_2 - and NPh_2 -substituted compounds **13**, **14**, **20** and **21** were investigated in detail [43]. While **18** forms stable gels, **19** occurs in different polymorphs, **20** and **21** were found to crystallize as inclusion compounds including nitromethane, *p*-xylene and water clathrates. The synthesis of these compounds depends on the molecular ratio of the educts. The differently substituted melem derivatives **20–21** occur in both syntheses requiring column chromatography for purification. Hence, the NPh_2 substitution at the tri-*s*-triazine **4** leads to a lower reactivity of the remaining chlorine atoms.

4.7. Further molecular derivatives of melem

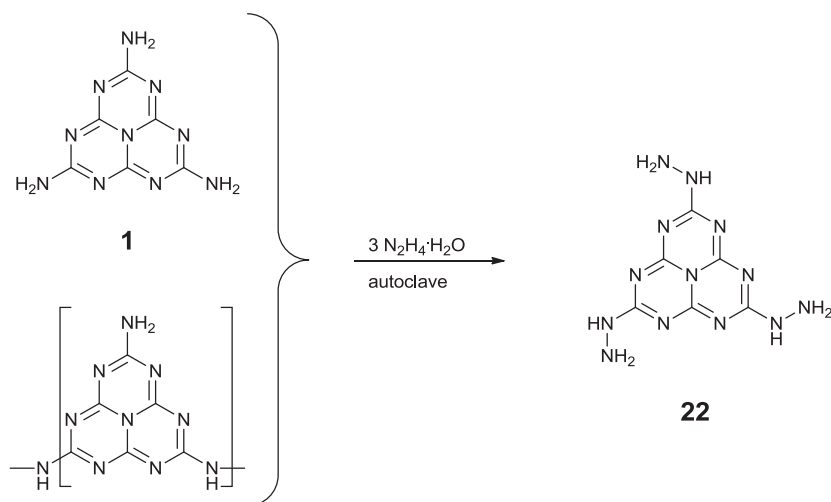
4.7.1. Trihydrazino-*s*-heptazine and melem derived iminophosphoranes

2,5,8-Trihydrazino-*s*-heptazine (**22**) was first described by Wright in 1965 in a patent without any further characterisation [195]. Recently, Saplinova et al. reported on the synthesis, comprehensive analysis and reaction of **22** [73] (Scheme 25).

The hydrazine derivative **22** is a yellow solid melting with decomposition at about 300°C . It is poorly soluble in water and common organic solvents e.g. DMF and DMSO. Two crystal structures, **22** and **22**·3HCl were reported showing an unusual



Scheme 24. Asymmetrically substituted tri-*s*-triazine derivatives reported by Schroeder and Kober [52] and Schwarzer and Kroke [42,43].



Scheme 25. Synthesis of the hydrazine derivative **22** as reported by Saplinova et al. [73].

protonation at the terminal N atoms [73]. The protonated form **22**·3HCl is a main product of the reaction between melem (**1**) and N_2H_4 , for deprotonation of which a sodium hydroxide solution is required.

Iminophosphoranes were investigated in detail in our group [41,184–186] (Scheme 26). They can be obtained by the Staudinger reaction [187], using tertiary phosphines and the azides **5** or by Kirsanov reactions [188,189] of phosphorus(V)-halides of the type R_nPX_{5-n} and **1** [41]. The Kirsanov reaction seems to be a better alternate route to compounds of the type $C_6N_7(N=PR_3)_3$ with R = methyl, ethyl, *i*-propyl, *n*-butyl, phenyl, *m*-cresyl. Starting materials for the Staudinger reaction are explosive (**5**) and difficult to access (**4**) [73,177,190]. On the other hand, the Kirsanov reaction requires melem and phosphorus(V)-halides of the type R_nPX_{5-n} . The resulting iminophosphoranes were successfully tested for applications as halogen-free flame retardants in polymers [41].

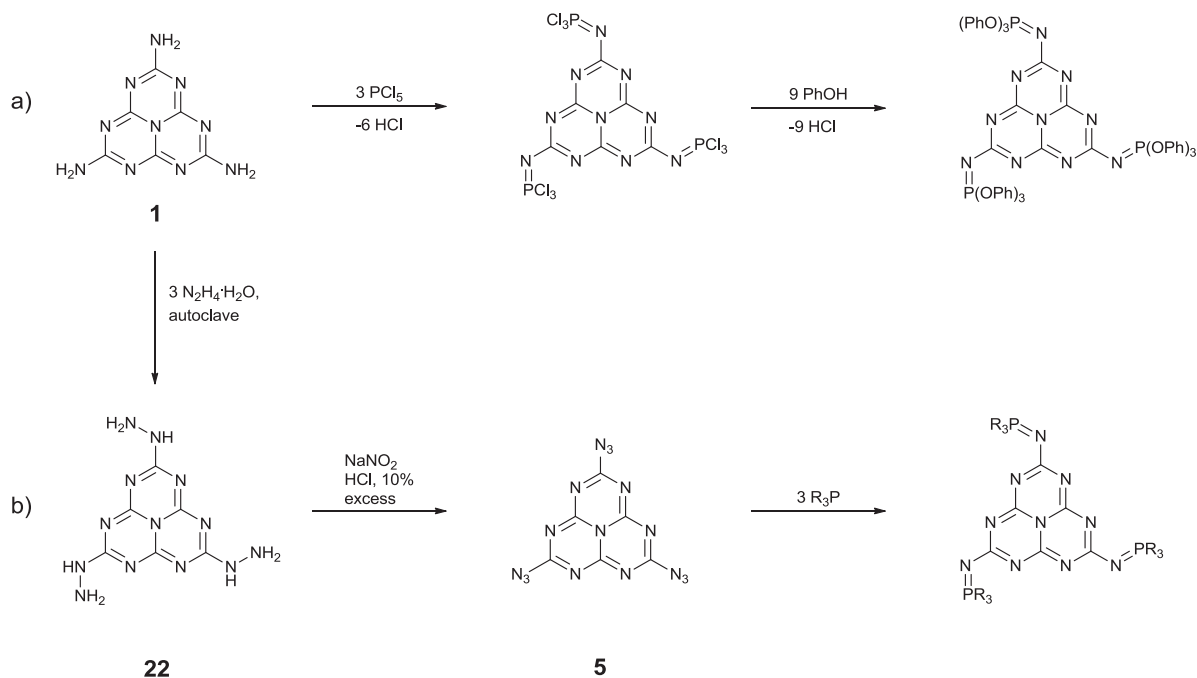
4.7.2. Imides

Recently, we reported on the syntheses of a new type of a heptazine-based compounds, the 2,5,8-triphthalimido-tri-*s*-triazine [44] (Scheme 27). Melem was utilized as a nucleophilic reagent towards phthalic anhydride and phthalic dichloride in various solvents, at different temperatures as well as in the solid state. Though the yields are very low, this compound shows high thermal stability up to 500 °C in air and argon atmosphere. Even more promising is the strong photoluminescence with a maximum emission of $\epsilon_{Em} = 1,07,500 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 416 nm excitation [44,191].

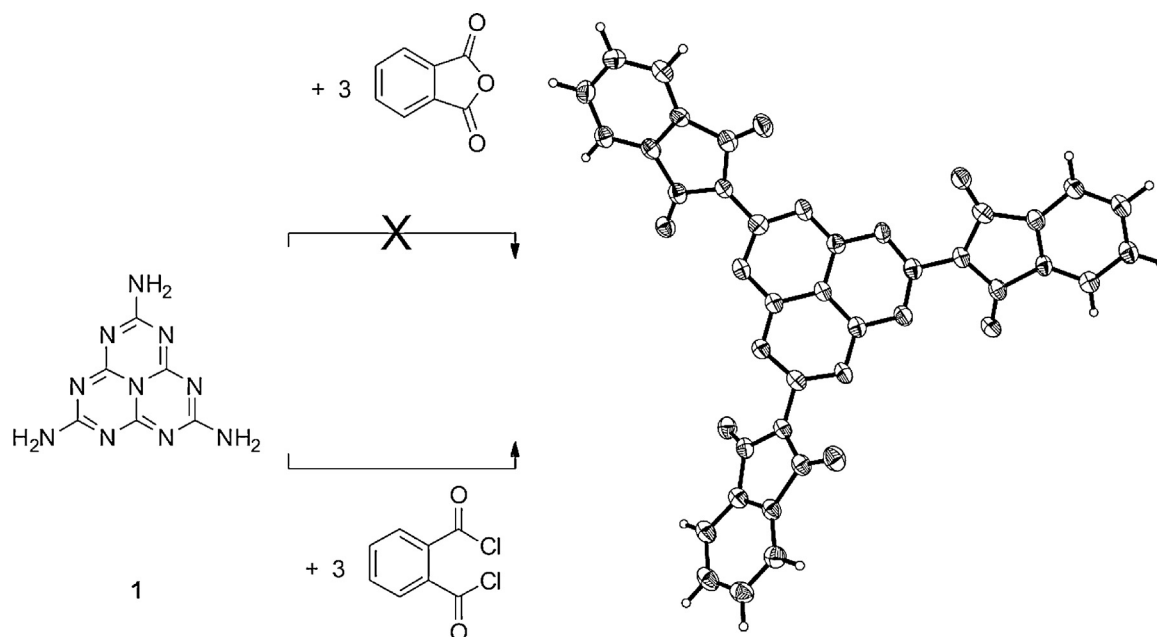
4.8. Comparative reflections on spectroscopic properties and crystal structures of molecular tri-*s*-triazine derivatives

4.8.1. Crystal structures

The first crystal structure of a *s*-heptazine derivative was reported by Hosmane et al. in 1982 [28]. More than 20 years later



Scheme 26. a) Synthesis of the 2,5,8-tris(trichlorophosphinimino)-*s*-heptazine by the Kirsanov reaction followed by a further transformation with phenol; b) synthesis of iminophosphoranes using the Staudinger reaction [41,73].



Scheme 27. Synthesis of 2,5,8-triphthalimido-tri-*s*-triazine from melem (**1**) and phthaloyl dichloride (PACl). The analogous reaction with phthalic acid anhydride (PAA) was not successful [44,191].

when carbon nitriles, especially carbon(IV) nitriles [4,5,90–93], came into the focus of many researchers further *s*-heptazine derivatives were structurally characterised. In the past decade the number of studies strongly increased (Tables 2 and 3). Currently, these are a total number of 50 single crystal structures reported in the CSD databases [192]. These X-ray structure analyses prove the molecular structure generally characterised by the planarity of the *s*-heptazine core. In addition, nine further crystal structures, i.e. a total number of 59 structures, were used for the following comparative reflections [193].

All seven N atoms as well as all six C-atoms are sp^2 hybridised. Significant π delocalisation is found for all 13 atoms, especially the 12 peripheral C and N atoms. A comparison of the reported crystal structures reveals the main deviations by introducing different substituents for the C–X bond lengths [192,193] (Table 5). The outliers in the terminal C2–X bonds are due to the different substituents at the *s*-heptazine core, e.g. 0.809 Å for C–H in **6** [28] and 1.742 Å for the C–Cl bond in **17** [42]. The inner C1–N1 bonds are usually about 1.396 Å and therefore show a single bond character (for atom numbering see Fig. 2). Typical bond lengths of a C–N single bond are in the range of 1.417 Å, while a C=N bond is 1.300 Å and C≡N 1.140 Å

[194]. On the other hand, all outer C–N bonds are 1.34 Å in average being conjugated C=N bonds.

A main feature of cyameluric acid, **2**, is the keto-enol tautomerism. As presented above, e.g. the potassium cyamelurates show C–O bond lengths indicating the keto-tautomer of cyameluric acid including the positioning of the residual hydrogen atoms at the *s*-heptazine core [40]. In contrast, organometallic derivatives such as $C_6N_7O_3[Sn(C_2H_5)_3]_3$ and $C_6N_7O_3[Si(CH_3)_3]_3$ represent the trihydroxy-tautomer [40].

For melonates (**3a–q**) the NCN side arms have to be considered. As mentioned above, crystal structure analyses have finished the controversy about the electronic structure of the NCN groups in literature. The CSD search gives an average bond length for the inner N3–C3 bond of 1.322 Å while the outer C3–N4 bond is about 1.155 Å and therefore a typical C–N triple bond (1.140 Å). Hence, the cyanamide (–N–C≡N) tautomer was proven as prevalent in contrast to the carbodiimide (–N=C=N) tautomer.

Out of the 59 tri-*s*-triazine containing crystal structures 43 were found to crystallize with solvent molecules. For instance, cyamelurates tend to crystallize as hydrates forming networks of hydrogen bonds.

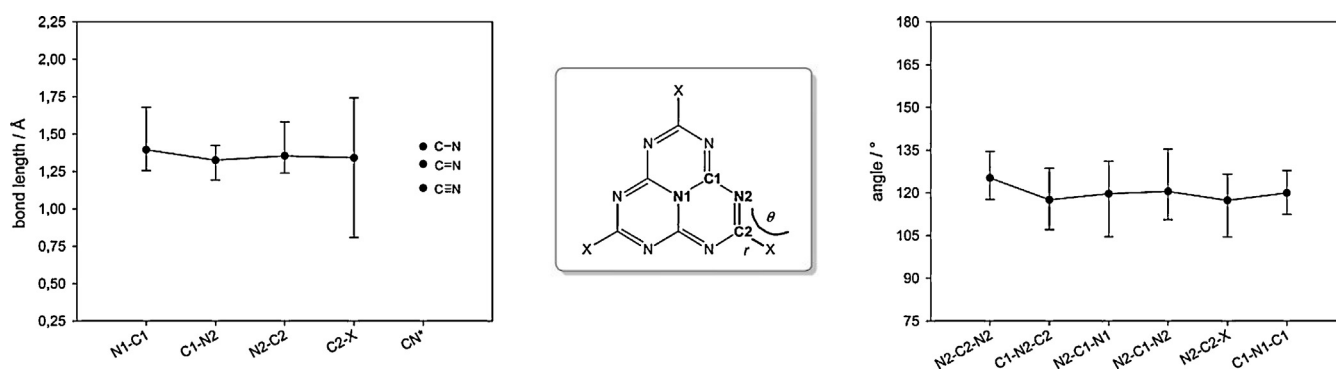


Fig. 2. Comparison of average, minimum, and maximum bond lengths and angles of the C_6N_7 -core as observed in all molecular crystal structures [192,193]. CN* indicates the typical C–N (1.417 Å), C=N (1.300 Å) and C≡N (1.140 Å) bond lengths [194] (see Table 5).

4.8.2. Spectroscopic and thermal properties

Table 6 shows typical spectroscopic properties of selected non-ionic heptazine derivatives. Most of these compounds are white or yellow, only the azide **5** is orange.

The thermal decomposition behaviour depends on the substituents but is usually above 300 °C. Only the azide **5** decomposes at 180 °C, the silyl ester **10** and the amide **13** around 200 °C.

Due to the poor solubility of most tri-*s*-triazine derivatives the IR spectroscopic analyses is one of the most important tools for their characterisation. Typical stretching vibrations of the *s*-heptazine moiety occur in the range of 1650–1600, 1540–1470, 1425–1300 and 825–790 cm⁻¹. NMR spectroscopic data of the tri-*s*-triazines show a typical signal for the inner C-atoms at about 155 ppm, while the shift of the outer C atom depends on the substituent and therefore ranges between 162 and 176 ppm. Only, in case of the acid **2**, the outer carbon atom is close to 155, while the inner shows a chemical shift at 150 ppm.

Only minor investigation on the emission and UV/vis spectroscopic properties were reported in literature. Though typical trends are not obvious, several patents and work show the potential application as photo stabilizer and sensitiser [36,63,69], as functional (semiconducting) components for organic electronics [196] or luminescent devices [197].

5. Theoretical considerations

The initial work which triggered several new investigations in the field of carbon nitrides and later also *s*-heptazine compounds were the theoretical reports of Cohen as well as Liu and Cohen [198–200] and Sung and Sung [201] revealing extraordinary high bulk moduli of sp³-hybridised α - and β -C₃N₄ compounds. Many further important theoretical studies on these silicon nitride analogous structures, related cubic phases and *s*-triazine-based graphitic carbon nitride (*g*-C₃N₄) structures followed, e.g. by Ortega and Sankey [202], Lowther [203] and Teter and Hemley [204], who completed the predictions by Sung, Liu and Cohen. The predicted incompressibility of α - and β -C₃N₄ is larger than that of diamond. Some of the proposed *g*-C₃N₄ structures are based on the *s*-heptazine motifs [4,5,33,90–96]. Therefore, the nitrogen-rich C₆N₇-based compounds such as melem, melon and further derivatives were brought to the forefront of modern material science and inspired several new works in the field of molecular *s*-heptazine chemistry. Most of the earlier theoretical work has been comprehensively summarized in 2004 [5]. However, the theoretical work on carbon(IV) nitride structures with *s*-heptazine units continued in past decade [4], and gained renewed interest since 2008, when the electronic and catalytic properties of *g*-C₃N₄ structures came into focus (see below).

Apart from the experimental work described above, several theoretical studies were reported and inspire to synthesize the predicted molecular substances and check their properties. For instance, Tian and co-workers used the electron distribution in the tri-*s*-triazine molecule by the molecular electrostatic potential to show the influence of different substituents on the heptazine core and the properties of the respective derivatives [151,174,205,259]. Electron-donating groups and substituents with a π bond (except CN) expand the negative spatial domain softly. On the other hand, electron-withdrawing groups can even cause a negative spatial domain in the molecule [174]. Zheng et al. studied the geometries, electronic structures, harmonic vibrational frequencies for several tri-*s*-triazines [174–176]. Ferrighi et al. derived and implemented the solvent contribution to the cubic response function for the polarizable continuum model in its integral equation formulation for *s*-triazine, three *s*-heptazine derivatives and related heterocyclic compounds. The different functionals employed have

been used to investigate the effect of a better description of the long-range Coulomb interactions. However, definitive determination of the quality of the results compared to experimental data was not possible because all functionals yield results within the experimental error [260].

Nevertheless, the first quantum mechanical calculations dealing with the cyameluric nucleus was reported by Pauling and Sturdivant [25]. The authors calculated the electronic structures to get a hint of the resonance energies. They used several substituents such as NH₂, NCNH, NNH and OH while comparing the cyameluric nucleus with the cyanuric nucleus. One of the interesting results they published is the conjugation π electrons in the cyameluric nucleus which was reported to be 8% more effective than for the cyanuric nucleus [25].

Other quantum chemical calculation aimed to explain the low basicity and high stability via the description of the electronic structure [13–15]. Properties such as structural and vibrational features of molecular melem were investigated and are in good agreement with the experimental results [35]. It was reported that a tri-*s*-triazine-based graphitic C₃N₄ should not only exist but should be 30 kJ mol⁻¹ more stable than the analogous *s*-triazine-based graphitic C₃N₄ phases [33]. Gracia and Kroll later investigated *s*-heptazine based C₃N₄ graphene structures and nanotubes reporting that puckered layers are more stable than completely planar structures [100,101]. Senker et al. focused on the elucidation of *s*-heptazine-based graphitic structures using ab initio calculations in combination with very comprehensive solid state NMR investigations [35,98,129,206].

Very interesting are the electronic properties of *s*-triazine and *s*-heptazine-based *g*-C₃N₄ structures, which were analysed in more detail recently. Thus, structure and properties of 2D single *g*-C₃N₄ layers were investigated by Deifallah et al. [207]. The band gaps were calculated and reported to be 2.97, 0.93 and 2.88 eV for *g*-*h*-triazine, *g*-*o*-triazine and *g*-*h*-heptazine phases respectively [208]. This leads to various applications (and further theoretical investigations) of extended *s*-triazine and *s*-heptazine-based carbon nitrides and C/N/H materials in catalysis, which continue to be actively investigated (see also Section 6). Current issues studied theoretically in the latter fields are the control and narrowing of the band gap of *s*-triazine and *s*-heptazine based *g*-C₃N₄ in order to control and design the semiconducting properties and/or to increase the electrical conductivity or provide absorption of visible light, e.g. by doping with non-metal elements such as sulphur or phosphorous [209], by doping with other non-metals or self-doping with carbon (see Table 7 in Section 6 and references cited there), by combining single graphene layers to multi-layers [210], by fabricating heterojunctions [211] or by combining the *g*-C₃N₄ layers with wide gap molecules such as 1,2,4,5-benzene tetracarboxylic dianhydride [212].

In order to design *s*-heptazine-based *g*-C₃N₄ electronic devices the interaction with a single graphene layer was studied recently by hybrid density functional theory [213]. The *g*-C₃N₄ promotes electron- and hole-rich regions forming a well-defined electron-hole puddle on the graphene layer. The composite displays significant charge transfer from graphene to the *g*-C₃N₄.

Ghule et al. used quantum chemistry to search for connectivity between the molecular structure and the probabilities of novel tri-*s*-triazine derivatives [214]. Aiming to predict novel high energetic materials the authors calculated the heat of formation in the gas phase and the crystal density in the solid state. Finally, the authors showed that the amino substituted di- and triazol derivatives of the tri-*s*-triazine are little stable and insensitive. Analogous nitro derivatives were predicted to be good candidates for gas generators and smoke-free pyrotechnic fuels [214].

Even in the field of metal-organic frameworks (MOFs) molecular dynamic calculations were performed to determine diffusion

Table 7
Overview on doped g-C₃N₄, their C/N precursors, heteroatom source and reaction conditions.

Doping material	C/N precursor and heteroatom source	Temperature/°C	Time/h	Pressure	Heating rate/K/min	Reference
Carbon self-doping	Melamine, ethanol	1.) 200 2.) 520	1.) 24 2.) 4	1.) Autoclave 2.) Normal	2.) 20	[245]
TiO ₂ doped with C ₃ N ₄ Water vapour	Melamine, rutil Melamine	550 1.) 500 2.) 520	4 1.) 2 2.) 2	Normal	5 20	[246] [238]
Water vapour	Melamine hydrochloride	1.) 500 2.) 520	1.) 2 2.) 2		20	[238]
g-C ₃ N ₄ with reduced graphene oxide (rGO)	Dicyanamide, graphene oxide	1.) 150 2.) 550	1.) Concentrated to paste 2.) 4	1.) Normal 2.) Normal		[247]
Boron	Dicyandiamide, BH ₃ NH ₃	1.) 80 2.) 600	1.) Water removal 2.) 4	1.) Normal 2.) Normal	2.) 2.5	[248]
Au	Urea, HAuCl ₄	1.) 80 2.) 300 3.) 550	1.) 4 2.) 4 3.) 1	1.) Normal 2.) Normal 3.) Normal		[249]
Boron	Melamine, ethanol, B ₂ O ₃	1.) 80 2.) 500 3.) 520, 550, 580, 600	1.) 3 2.) 2 3.) 2	1.) Normal 2.) Normal 3.) Normal	2.) 20	[250]
Sulphur	Dicyandiamide, H ₂ S	1.) 550 2.) 450	1.) 4 2.)	1.) Normal 2.) H ₂ S atmosphere	1.) 2.3	[251]
Aniline	Cyanamide, aniline	1.) 550 2.) 0	1.) 4 1.) 8	1.) Normal 2.) Normal	1.) 10	[252]
NH ₄ F	Dicyandiamide, NH ₄ F	1.) 60 2.) 550	1.) Water removal 2.) 4	1.) Normal 2.) Normal	2.) 2.3	[253]
Sulphur	Trithiocyanuric acid	Different temperatures (500, 550, 600, 650, 700)	2	Normal		[254]
Boron and fluorine	Dicyandiamide, ionic liquid (BmimBF ₄ , 1-butyl- 3- methylimidazolium tetrafluoroborate)	1.) 100 2.) 350 3.) 550	1.) Water removal 2.) 4 3.) 4	1. Normal 2. Normal 3. Normal	2.) 2.9 3.) 3.3	[255]
Phosphorus	Dicyandiamide, ionic liquid (BmimPF ₆ , 1-butyl- 3- methylimidazolium hexafluorophos- phate,)	550	4	Normal	2.3	[256]

rates of methane depending on the gas pressure [215]. Several different kinds of MOFs were tested including the heptazine-based tri-benzoate reported by Zhou et al. earlier [178,179]. The heptazine derivative showed a remarkably good storage capacity and adsorption of methane compared to the other investigated MOFs [215]. In another recent theoretical study the CO₂ capture properties of several different MOFs including the said *s*-heptazine-based coordination polymers were investigated [216]. The latter are not the most promising candidates according to these calculations.

The absorption of water on the surface of a tri-*s*-triazine-based graphitic C₃N₄ catalyst for photocatalytic processes was also studied recently. Charge density distribution analysis reveals an absorption of water with the proton to the twofold coordinated N atom of the C₃N₄, whereas the second O–H bond is orientated parallel to the surface [74].

In a DFT study by Aspera et al. it was reported that O₂ physically adsorbs on *s*-heptazine-based graphitic C₃N₄ layers. This interaction is stronger than the interaction with graphene sheets and provides hints for catalytic applications of graphitic carbon nitrides, e.g. the oxygen reduction reaction on the cathode of proton exchange membrane fuel cells [261]. In another recently published DFT study by Koh et al. the interaction of graphitic carbon(IV) nitride nanotubes with H₂ molecules is analysed. A comparatively low barrier (~0.54 eV) for a passage through the pores, a relatively large storage capacity of 4.66 wt.% for isolated tubes and 5.45 wt.% for bulk bundles and a hydrogen adsorption energy of –0.22 eV are reported [262].

As described above, the melonate anions usually do not coordinate cations with the terminal N atoms. On the other hand, Cu and Ag were shown to use exclusively or additionally coordinate to

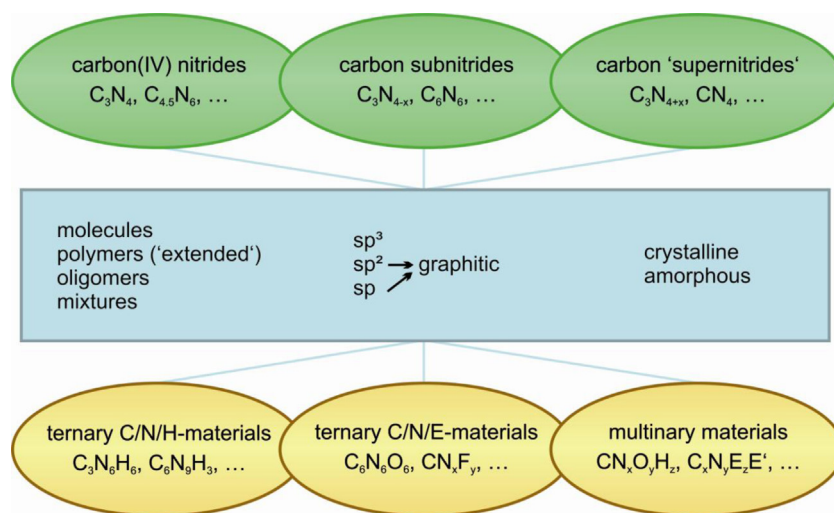


Fig. 3. The term 'carbon nitride' should be used for binary CN_x compounds. In the current literature numerous authors use the denomination carbon nitride also for various ternary, quarternary and multinary materials. All these classes of substances include molecular, oligomeric and polymeric substances. They may be of amorphous or (partially) crystalline nature. Especially the polymeric (extended) materials may further be distinguished into 1-, 2- and 3D structures, i.e. linear (1D) polymers like (idealized) melon $C_6N_9H_3$, layered or graphitic (2D) structures and 3D networks.

these terminal N atoms. To get deeper insight in the coordination modes of melonate anions quantum chemical calculations were performed [67]. The natural atomic charges of all non-equivalent nucleophilic N atoms of the $[C_6N_7(NCN)_3]^{3-}$ anion were calculated to be -0.596 , -0.619 , -0.675 and -0.644 indicating little differences in charges. A metal coordination found in silver melonate matches this as well as the HSAB concept. An explanation for the favoured coordination of the copper ion to the terminal N atom could not be given. Following the *ab initio* calculations, the single protonation of the melonate anion occurs at the terminal N atom as indicated also by the crystal structure of the calcium melonate reported by Makowski et al. [65].

Very recently, it was even reported by Li et al. that nonmagnetic *g*- C_3N_4 becomes ferromagnetic when the 2D structure is patterned in the form of a kagome lattice. Its magnetic properties are further enhanced by applying external strain [263].

6. Carbon nitrides – from binary CN_x compounds to ternary and multinary polymers

From a chemical point of view the term 'carbon nitride' should be used exclusively for binary compounds containing the elements carbon and nitrogen, and other elements only in very small (non-stoichiometric or trace) amounts. With respect to the maximum oxidation number of four for carbon the stoichiometry for carbon(IV) nitride is C_3N_4 , which may be compared to carbon(IV) oxide CO_2 [5]. An additional requirement for a true carbon(IV) nitride with carbon in the oxidation state +4 is that the material should not contain any C–C and/or N–N bonds. As mentioned above, the molecular formula C_3N_4 is now used in numerous publications to denominate ternary and multinary polymers such as melon. Further binary carbon nitrides may be distinguished, i.e. carbon subnitrides with a composition C_3N_{4-x} and carbon 'supernitrides' C_3N_{4+x} containing excessive nitrogen, e.g. in the form of azo or azido units. These three groups of binary C/N compounds should be distinguished from ternary and multinary compounds containing additional elements, in many cases hydrogen (Fig. 3).

The latter ternary C/N/H materials span from very well-known molecular compounds such as melamine $C_3N_6H_6$ or cyanamide CN_2H_2 via the *s*-heptazine derivatives melem $C_6N_{10}H_6$ (see Section 2.1) and the 1D polymer melon $C_6N_9H_3$ (see below) or the 2D

polymer poly-*s*-heptazine imide $C_{12}N_{17}H_3$ (see Scheme 9) to less well characterised polymeric materials.

A few extended ternary and multinary compounds derived from binary carbon nitride materials are known, which are very well structurally characterised. These include the crystalline *s*-triazine-based graphitic structures $C_6N_9H_3 \cdot HCl$ reported by McMillan et al. [217] and $C_{12}N_{17.5}H_{6.3}Cl_{1.5}Li_{3.2}$ described by Wirnhier et al. [222].

The synthesis routes to both binary carbon nitrides and multinary C/N/H/E materials reported in literature include numerous approaches such as classical chemical reactions with aqueous or organic solvents, solvent-free solid state transformation including mechanochemical techniques, application of medium, high and ultrahigh pressure as well as numerous vapour phase deposition approaches belonging to CVD and PVD methods usually performed under reduced pressure and frequently providing amorphous products [4,5].

It should be pointed out that both large classes of compounds, i.e. the binary CN_x materials and the ternary and multinary substances may be subdivided into molecular and polymeric materials with sp , sp^2 and/or sp^3 hybridised carbon and nitrogen atoms. In case of solids it is possible to distinguish between layered graphitic structures with sp^2 (and sometimes sp) hybridisation of C- and N-atoms, and 3D structures based on full or partial sp^3 hybridisation (Fig. 3).

Other fundamental aspects to distinguish different materials from each other and to comprehensively identify and characterise binary carbon nitride solids as well as ternary and multinary materials are of course the amount of certain functional groups present in the bulk and at the surface. Typical examples are the different structures of fully symmetric carbodiimides $-N=C=N-$ or the isomeric cyanamides $>N-CN$ [218]. Another example is the question if a certain carbon nitride or C/N/H material is based on *s*-triazine and/or *s*-heptazine units (see Section 1.1 and below). Nitrogen atoms may possess the coordination number one (in nitriles and azides), two (in so-called Schiff-bases $C=N=C$ or as pyridinic N-atoms), three (in planar and non-planar forms) and four in tetrahedral mode bearing a positive charge (ammonium groups). Besides, if hydrogen is present it is crucial to distinguish between $>N(sp^2)H$, $-N(sp^2)H_2$, $>N(sp^3)H$, $-N(sp^3)H_2$, and CH-units with sp , sp^2 or sp^3 hybridised C-atoms, CH_2 moieties with sp^2 or sp^3 hybridised C-atoms and CH_3 groups.

Finally, at least from the viewpoint of materials science and various applications of solid carbon nitrides and C/N/H materials it is very important to consider their morphology. In many cases materials with the same chemical composition *and* structure exhibit very differing properties depending on particle size distributions, particle shapes, porosity, density and the pore structure and surface chemistry. In the past few years various dense and porous C/N/H materials have been described and successfully applied in many adsorption and (photo)catalysis applications. Although this field of carbon nitride research is only covered since about 5 years, first review articles appeared very recently [90–93].

6.1. Carbon(IV) nitrides C_3N_4

6.1.1. Known and postulated C_3N_4 phases

There are several possibilities to design C_3N_4 modifications which obey the above mentioned criteria of alternating C–N-arrangement. These have been discussed in reviews over the past decade [4,5] and are therefore only briefly considered here. Known molecular carbon(IV) nitrides include the highly reactive molecular compounds tricyanamine $N(CN)_3$ and dicyanocarbodiimide $NC-NCN-CN$. The latter has been experimentally investigated in a solid matrix at 20 K [219]. Oligomers and polymers derived from both molecules, e.g. via cycloaddition reactions of the cyano groups, also may be formed [5].

Numerous attempts have been performed to synthesize diamond-like C_3N_4 modifications, which were first predicted as analogous to the well-known α - and β - Si_3N_4 modifications [198–201]. Due to the expected ultrahardness of these novel and still unknown carbon(IV) nitrides a multitude of methods including many different PVD and CVD techniques, solid state, solvothermal and mechanochemical approaches have been applied. Although there are numbers of papers reporting on the successful synthesis of the said ultrahard C_3N_4 phases, none of these studies included a reliable determination of the composition AND structure. Besides, it appears that the reproducibility is questionable in many cases [4,5]. Nevertheless, the original paper reporting the semi-empirical model to predict the potential ultrahardness of Si_3N_4 -analogous C_3N_4 by Liu and Cohen [199] initiated a “harder-than-diamond” fever as can be seen from the fact that this paper has been cited more than 1500 times (see also Section 5). It is now accepted by most materials scientists who thoroughly investigated carbon nitrides that all reported CN_x phases with stoichiometries close to C_3N_4 show a relatively low thermal stability. They decompose and loose nitrogen at temperatures below 750 °C. Therefore, carbon(IV) nitride are most likely not suitable as diamond substitutes for cutting, grinding or drilling applications. However, it should be pointed out that materials harder than single crystal diamond can be made by nano-structuring, as several researchers have proved for coating and bulk materials [220], but at the same time it is important to note that hardness measurements should be performed very carefully [220a] and that many reported data for ultrahard coatings are over-estimated by a factor of approximately two [221].

In addition to 3D diamond-like C_3N_4 phases various graphitic modifications may be postulated (see Section 6.1.2). There are reports on the successful synthesis of these structures. However, in many cases the data published for characterisation of these phases were incomplete or misinterpreted. An example is a report on the synthesis of the *s*-heptazine-based *g*- C_3N_4 structure $[(C_6N_7)N]_n$, which has been described to be obtained from a LiCl/KCl salt melt [96]. Later it turned out that a *s*-triazine-based ionic structure, which has the composition $C_{12}N_{17.5}H_{6.3}Cl_{1.5}Li_{3.2}$ [222] is the correct formulation for the product. It can be concluded that no fully characterised graphitic C_3N_4 phase has been reported so far.

Finally, it should be stated that for both – diamond-like and even more so for the graphitic carbon(IV) nitrides – it is expected that one or more of these phases are (meta)stable and exist under ambient conditions. It is a matter of time that successful and reproducible experimental routes to these phases will be reported allowing comprehensive analyses with respect to structure and properties.

6.1.2. Postulated carbon(IV) nitrides containing the C_6N_7 nucleus

The numerous different possibilities to design carbon(IV) nitrides have been discussed [4,5]. With respect to the C_6N_7 -unit it should be pointed out that there are molecular compounds like hexacyano melem $[C_6N_7(N(CN)_2)_3]$ and oligomers derived from this molecule (Scheme 28). Besides, there are extended structures such as *s*-heptazine units connected by carbodiimide $-N=C=N-$ or its isomeric cyanamide form $>N-CN$ which would also be forms of carbon(IV) nitrides. There have been attempts to prepare the latter compounds, which were so far unsuccessful [223].

The thermodynamically most stable C_3N_4 modification is $[(C_6N_7)N]_n$ according to theoretical considerations [33,208]. However, this stability order might change when very small nano-sized structures are considered [224]. It is more important to note that for a $[(C_6N_7)N]_n$ structure not only a layered graphitic arrangement is possible. Different types of *s*-heptazine-based C_3N_4 -nanotubes and related puckered structures have been investigated theoretically [100,101,225] and large fullerene-like structures might also be formed. Upon tilting the disc-shaped C_6N_7 -units it is also possible to construct 3D networks. Examples are 3D-srs- and 3D-ths $[(C_6N_7)N]_n$ discussed in [5].

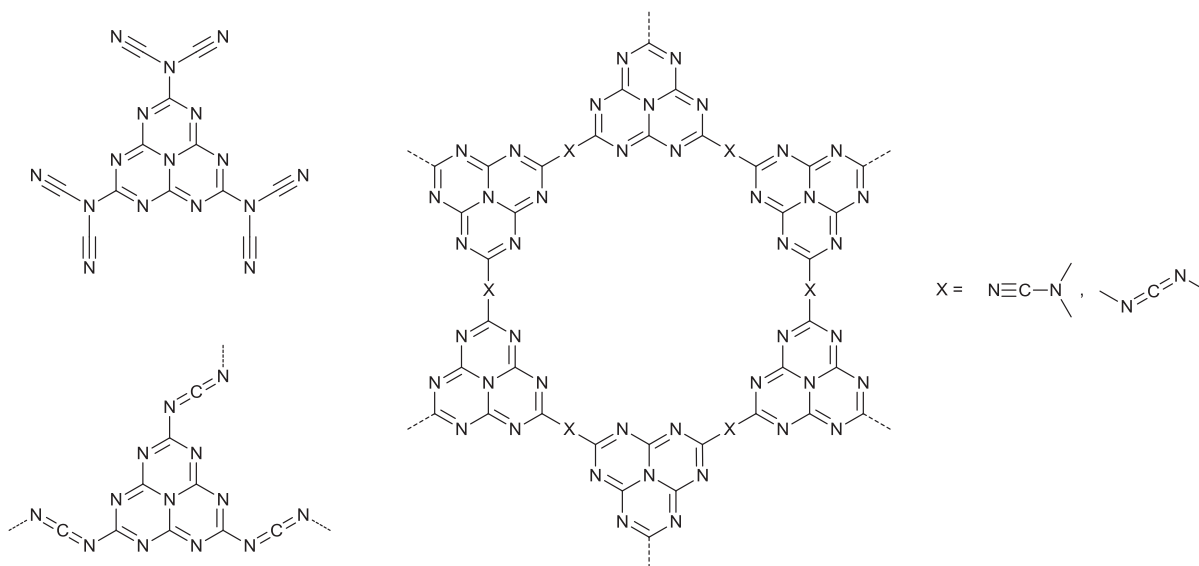
6.2. Carbon subnitrides and carbon ‘supernitrides’ with the C_6N_7 -unit

6.2.1. Carbon subnitrides

An unlimited number of binary carbon subnitrides C_3N_{4-x} can be designed with and without the *s*-heptazine motif. In fact there are numerous reports on attempts to prepare C_3N_4 phases resulting in sub-stoichiometric materials (see above and [4,5]). It cannot be excluded that some of these solids contain the C_6N_7 moiety, especially when the synthesis was performed at relatively high temperatures around 400 °C and above, where melem and melon are known to form. However, in order to unambiguously prove the presence of *s*-heptazine groups it is not sufficient to use vibrational spectroscopy, for example. Solid state NMR (^{15}N and ^{13}C) should be applied, at least if amorphous or nanocrystalline phases or mixtures are obtained, in order to prove if *s*-triazine, *s*-heptazine and/or related structural motifs are present [98,129,222,206].

For a rational approach to (hypothetical) C_6N_7 -based carbon subnitrides it is possible to combine the *s*-heptazine unit directly via C–C bonds (see Scheme 29, A). An alternative is to connect the C_6N_7 -unit via carbon atoms, acetylene or diacetylene groups. Another interesting hypothetical carbon subnitride with the stoichiometry C_9N_{10} consists of a network of alternating *s*-triazine and *s*-heptazine groups (Scheme 29, D). These layered structures may of course be not necessarily planar, they may form puckered structures, single and multi-walled tubes and fullerene-like modifications. 3D networks similar to 3D-srs- and 3D-ths $[(C_6N_7)N]_n$ or 3D-srs- and 3D-ths $[(C_3N_3)N]_n$ are possible as well [5].

Needless to say that carbon nitrides with very low N-contents may also contain the *s*-heptazine group. For example, CN_x -nanotubes with relatively low N-contents are known to form bamboo-morphologies [226]. The nitrogen atoms may accumulate in certain regions of a graphite network in various including pyridinic forms [227], thus possibly also incorporating aromatic C_6N_7 moieties.

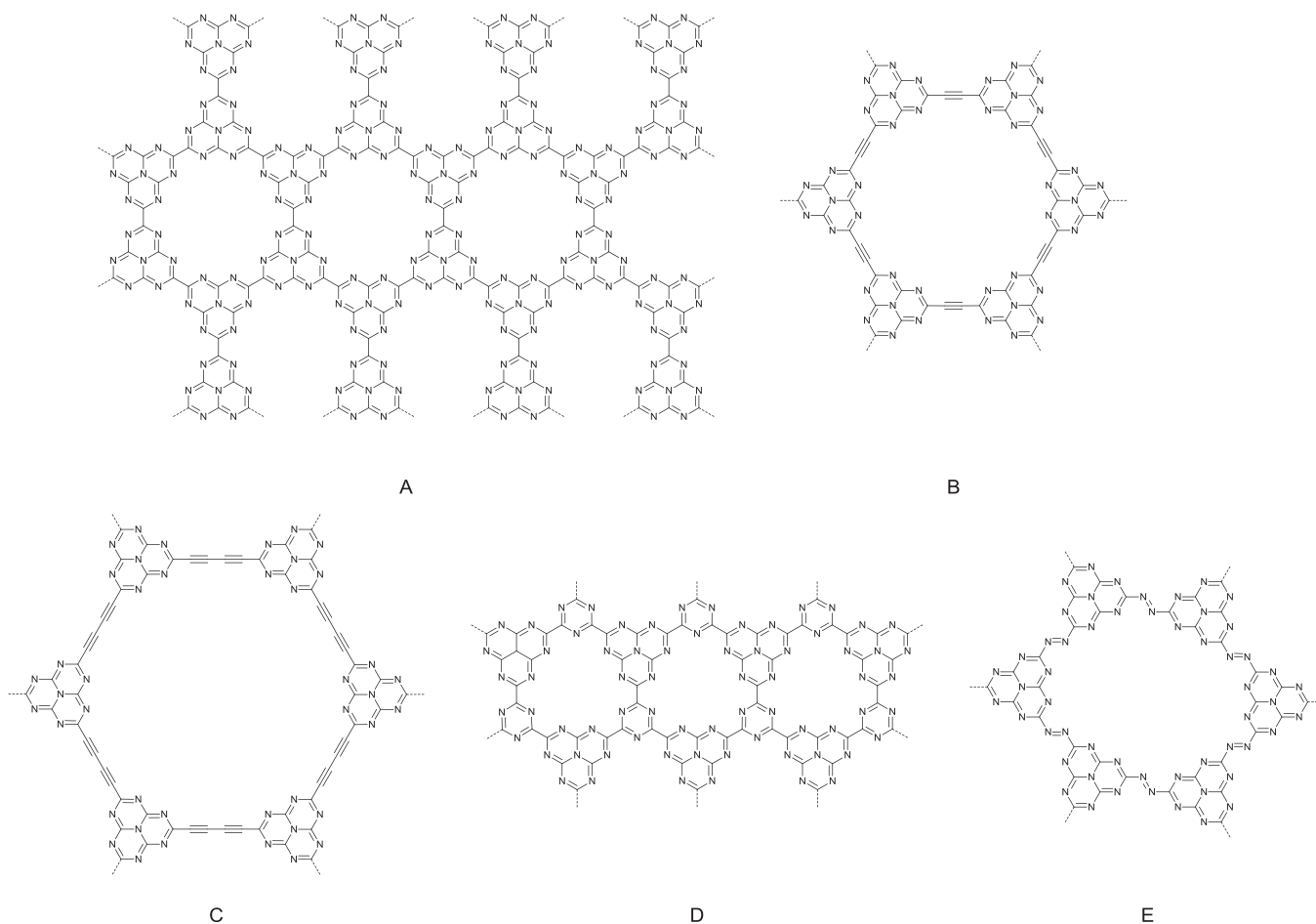


Scheme 28. Molecular structures of hexacyano melem and s-heptazine units connected by carbodiimide —N=C=N— or its isomeric cyanamide form.

6.2.2. Carbon 'supernitrides'

Complementary to the briefly discussed subnitrides carbon nitrides with superstoichiometric amounts of nitrogen C_3N_{4+x} may be formed. The most important example for compounds containing the C_6N_7 -unit is the triazide $\text{C}_6\text{N}_7(\text{N}_3)_3$, which was in detail

discussed in Section 4.3. Careful thermal decomposition of this molecular compound yields different polymeric carbon nitride networks including carbon supernitrides, as demonstrated by Miller et al. [177]. Similar s-triazine-based disordered carbon supernitrides were obtained by careful decomposition at



Scheme 29. Molecular structure of heptazine-based oligomers and polymers. Hypothetical structures $(\text{C}_6\text{N}_7)_n$ **A**, $[\text{C}_6\text{N}_7(\text{C}_2)_{1.5}]_n$ **B**, $[\text{C}_6\text{N}_7(\text{C}_4)_{1.5}]_n$ **C** and $[\text{C}_6\text{N}_7(\text{C}_3\text{N}_3)]_n$ **D** are carbon subnitrides connected via C–C bonds. The hypothetical network $[\text{C}_6\text{N}_7(\text{N}_2)_{1.5}]_n$, **E** is an example for a carbon 'supernitride'.

temperatures <200 °C of the corresponding triazide $C_3N_3(N_3)_3$ [228], while fast (detonative) reactions leads to carbon subnitrides, carbon nanotubes and related carbon nanostructures with low N-content [229].

Networks such as $[C_6N_7(N_2)_{1.5}]_n$ or $[(C_6N_7)(C_3N_3)(N_2)_3]_n$ interconnected by diazo bridges are examples for idealized, simple hypothetical carbon ‘super-nitride’ networks, which contain the *s*-heptazine group (see Scheme 29, E). In general, all of these nitrogen-rich materials are expected to be thermally less stable compared to carbon(IV) nitrides. Nevertheless, they may be useful materials. Potential applications include “green” smoke-free explosives and propellants, gas generators as already mentioned above, or (photo)catalysis and related field as recently reported for different C/N/H materials (see below).

6.3. The C/N/H-polymers melon and polyheptazine imide

6.3.1. Composition and molecular structure(s)

Melon $[C_6N_7(NH_2)NH]_n$ is probably the most important *s*-heptazine-based polymeric compound. However, although it has a CAS-number (32518-77-7) and although it has been studied thoroughly, it should be pointed out that this material may occur in various forms. It is well-known for polymers with a linear structure having very different properties depending on the molecular weight distribution. Besides, it may be distinguished in cyclic oligomers and macrocyclic linear structures. In case of the polymer melon, it appears to be even more complicated, since the overall composition can be constant $[C_6N_7(NH_2)NH]_n$ while the distribution of NH_2 -groups, NH -groups and threefold-linked N-atoms (which are not present in the pure form of melon $[C_6N_7(NH_2)NH]_n$), may vary. Thus, the degree of crosslinking, and the dimensionality (linear 1D, sheet-like 2D and 3D network structures) can be different depending on the way of preparation.

In some cases under careful and prolonged annealing of melon further evolution of ammonia has been observed. The formally 2D or graphitic network polyheptazine imide which is formed can be described with the idealized structure $[C_6N_7(NH)_{1.5}]_n$, i.e. does not contain any NH_2 groups. Interestingly, it was found that the voids of this polymer can perfectly accommodate melamine [129] (see Section 2.1 and Scheme 9).

6.3.2. Synthesis

No rational chemical synthesis except for pyrolytically induced condensation of molecular starting materials is known for melon. As already mentioned in Section 2 melon is formed upon thermal treatment of various organic compounds containing the three elements carbon, nitrogen and hydrogen – and even further elements which can form volatile side products such as oxygen or sulphur. Thus, melon is typically obtained upon annealing cyanamide H_2N-CN or its dimer or trimer cyanoguanidine, $H_2N-CN-NH-CN$, or melamine, $C_3N_3(NH_2)_2$, respectively. The formation steps and intermediate products such as melam $(H_2N)_2(C_3N_3)NH(C_3N_3)(NH_2)_2$, melem $C_6N_7(NH_2)_3$ and the co-crystalline materials have been studied in detail by Schnick et al. (see Section 2). For example, melon was reported to be formed upon annealing melamine at 490 °C for 4 days [162]. Alternatively, melamine may be heated in a sealed quartz ampule to 630 °C for 12 h [98,129]. Starting from $(NH_4)SCN$ melon is obtained upon heat treatment a dimer of melem is formed at 300 °C which was further annealed in an autoclave at 700 °C for 2 h to give a polymeric melon with the correct elemental composition [27]. A yield of 38% was reported for this approach [27].

According to our own experience it is crucial to adjust the thermolysis temperature, ammonia partial pressure and pyrolysis time in a suitable range in order to obtain pure melon $[C_6N_7(NH_2)NH]_n$ in high yield. Therefore, the type of furnace, the amount of

starting material, the dimensions of the reaction vessel as well as gas flow rates have to be taken into account and controlled for a reproducible synthesis. We have analysed the thermolysis of different batch sizes of melamine and other molecular compounds. It turned out that in our case melon is formed in a Schlenk tube at a temperature of 470–520 °C. We found that further annealing at 580 °C yields polyheptazine imides.

Many other polymers containing the *s*-heptazine unit have been prepared. In some cases composition and structure are close to melem, melon or polyheptazine imides. A well analysed polymer which contains the C_6N_7 group was obtained by Holst and Gillan via rapid exothermic decomposition of trichloromelamine $C_3N_3(NHCl)_3$, which gives at temperatures around 400 °C a C/N/H polymer predominantly consisting of *s*-heptazine groups being comparable to melon [230]. Gibson et al. used another triazine-based precursor, namely 1,3-dichloro-5-amino-*s*-triazine $C_3N_3(NH_2)(Cl)_2$ and also obtained a polymer upon annealing at 500 °C in sealed tubes and under dynamic vacuum [231]. The products again contain the *s*-heptazine group and may be comparable to melon.

6.3.3. Analysis

It should be pointed out that although semi-crystalline graphitic products are generally obtained upon the thermolysis route described above that in most cases standard powder XRD analysis is not sufficient to distinguish between melon and polyheptazine imide as well as related phases. The only information provided is the graphitic stacking of 2D structures with a distance around 3.4 Å in most reports published so far. However, in case of relatively well crystallized samples and in combination with other methods such as HR-TEM, NMR etc. (see below) powder XRD provides the key to resolve the corresponding structures.

Partially suitable for the characterisation is a thorough interpretation of vibrational spectra, which can provide information on the presence or absence of NH and NH_2 groups and further structural details. Ultraviolet and near-infrared Raman spectroscopy has e.g. been applied by Zinin et al. [232] and McMillan et al. [217] in order to analyse graphitic carbon nitrides.

Vibrational as well as other spectroscopic investigations should further be supported by careful elemental analyses using the combustion method (C/H/N-analysis). However, in many studies it was found that reliable CNH-contents are very difficult to be obtained. Nevertheless, the hydrogen content gives at least additional information on the respective structure of the solids, although the total amounts are very small, e.g. 1.5 weight-% in case of melon and 0.8 weight-% in case of polyheptazine imide, and it is sometimes difficult to get reliable and reproducible data.

X-ray photoelectron spectroscopy (XPS or ESCA) has also frequently been used to get additional information on the composition and bonding situation of carbon nitride materials, for example in the recent studies by Foy et al. [264] or Dante et al. [265]. It should be kept in mind that XPS is primarily a surface analysis method, therefore it is used for the investigation of coatings in many cases. It appears to be not a suitable method to distinguish between melon and closely related polyheptazine imide for example.

Another useful analytical tool for a differentiation and direct comparison between C/N/H-polymers obtained from molecular precursors by annealing methods are thermal analysis techniques. A simple comparison of the TG curves of melamine pyrolysates indicates distinctly different results as shown in Fig. 4 [233].

Most suitable for a detailed analysis of the structure of melem adducts, melon, polyheptazine imide and related materials are solid state NMR studies as reported by Senker et al. [98,129,222,206]. Chemical shifts in the ^{15}N NMR spectra provide information on the presence of *s*-triazine and *s*-heptazine groups (see Table 4) and

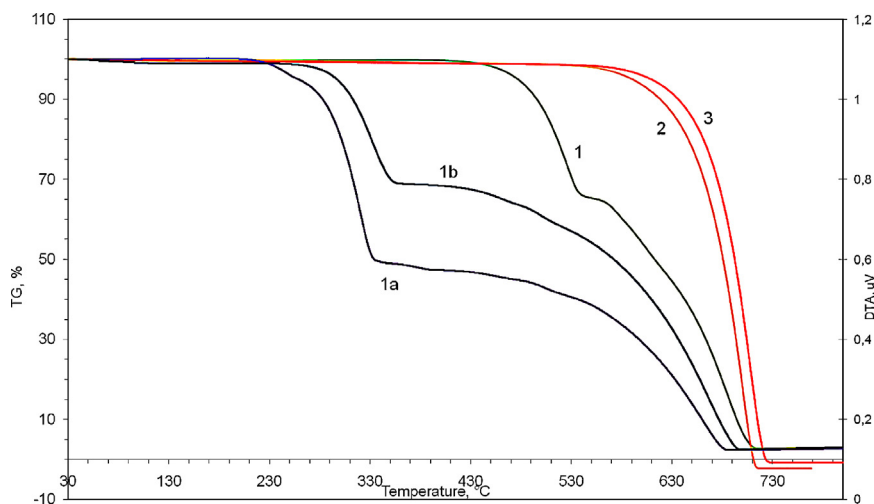


Fig. 4. Thermal gravimetric analysis (TGA) of melamine-melem adducts $[\text{C}_3\text{N}_3(\text{NH}_2)_3]_3[\text{C}_6\text{N}_7(\text{NH}_2)_3]$ (**1a**), $[\text{C}_3\text{N}_3(\text{NH}_2)_3]_2[\text{C}_6\text{N}_7(\text{NH}_2)_3]$ (**1b**), melem (**1**), melon (**2**) and polyheptazine imide (**3**).

cross-polarisation measurements allow to unambiguously identify the presence and location of the hydrogen atoms.

A comprehensive structural analysis of melon reported by Senker and Schnick et al. relied on several techniques including electron diffraction, solid state NMR and theoretical calculations [98]. Polyheptazine imide was similarly analysed and unambiguously identified by the same research group [129] (see also Section 2).

Many further analytical methods may be used to get additional information about the structures and properties of carbon nitrides, melon and other C/N/H materials. These include optical spectroscopy, electrical conductivity measurements and numerous more specialised techniques such as electron paramagnetic resonance (EPR), which has to be applied for radicals and conducting materials like polyaniline nanotubes [266]. Similarly, more tools need to be used for the analysis of selected (structural) properties and applications (see below). However, a comprehensive survey of analysis methods for carbon nitrides is beyond the scope of this review.

6.3.4. Applications

Originally, melon and similar nitrogen-rich C/N/H-polymers were used for the regeneration of steel hardening baths [234]. This application does not require any high purity or well-defined chemical compounds, but has been applied industrially for many years [235].

Another very important application of melon and similar *s*-heptazine-containing C/N/H compounds including melem is the use as starting materials for cyamelurates, melonates and practically all molecular *s*-heptazine derivatives described in this review and investigated so far.

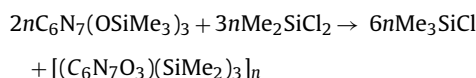
Recently, it was discovered that melon and related graphitic C/N/H materials are semiconductors. They proved to be efficient (photo)catalyst, especially when they are doped or combined with other elements [93–96]. The latter doping leads to novel composites or multinary materials (see Section 6.4), which are in many cases chemically inhomogeneous. Nevertheless, they proved to be efficient photocatalysts for the splitting of water and hydrogen evolution as well as metal-free catalysts for several different organic reactions such as selective C–H oxidation [236], transerifications [237], or CO_2 activation [238]. The presence of the *s*-heptazine unit may not be essential for these catalytic properties. Nevertheless, numerous papers are currently published in this area.

6.4. Further C/N/H materials and *s*-heptazine-containing polymers

In Section 6.3 we focused on the well described graphitic C/N/H compounds melon and poly-*s*-heptazine imide. There are also numerous non-graphitic solids which have been prepared, especially amorphous materials generated by vapour phase deposition techniques (CVD and PVD) and other approaches leading to amorphous or nanocrystalline products, see e.g. [4,5]. To the best of our knowledge there are only two *crystalline* extended 3D C/N/H solids described in literature so far. These are the carbon nitride imide $\text{C}_2\text{N}_2(\text{NH})$ [239] and the closely related compound $\text{C}_2\text{N}_2(\text{CH}_2)$ [240]. Both of these crystalline phases have been synthesized in very small amounts under extremely high pressure in diamond anvil cells. The structures are comprised of CN-layers consisting of saturated and fully condensed C_3N_3 -rings in chair conformation interconnected either by NH or CH_2 groups. This is analogous to the well-known silicon compounds Sinoite $\text{Si}_2\text{N}_2\text{O}$ [241] and silicon nitride imide $\text{Si}_2\text{N}_2(\text{NH})$ [242], with SiN-layers interconnected by oxygen atoms or NH groups, respectively.

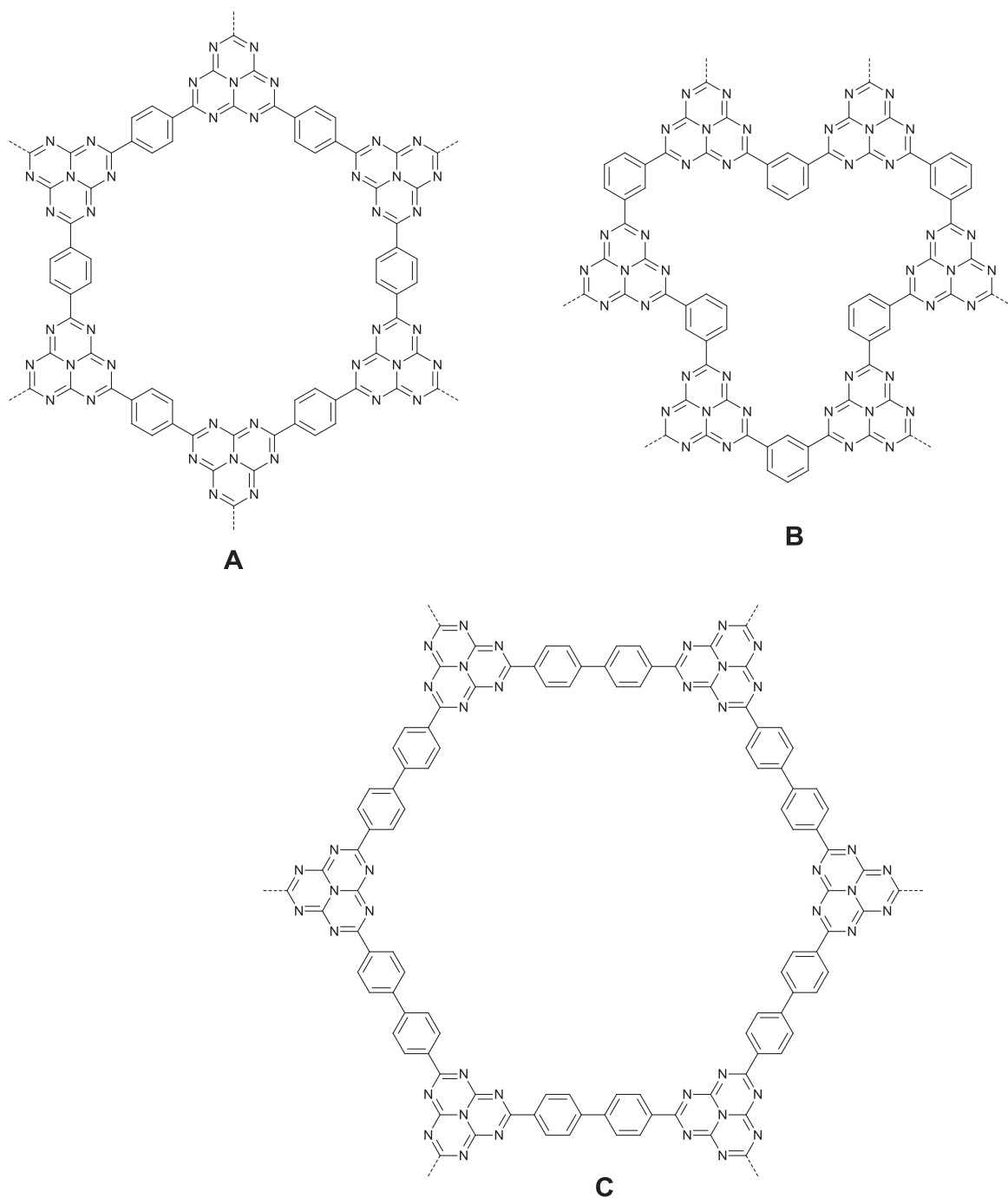
Coming back to *s*-heptazine-containing networks it is obvious that it should be possible to introduce the very stable C_6N_7 -unit into many kinds of organic and inorganic polymers. Thus, the *s*-heptazine moiety may be bridged with rigid or flexible organic linkers. The former approach was recently reported applying a so-called “ionothermal synthesis”, which refers to reactions of *s*-triazine precursors in molten LiBr/KBr mixtures at 400–430 °C [243]. Solid state ^{13}C NMR spectra indicate the formation of *s*-heptazine-based C/N/H-polymers with the idealized structure depicted in Scheme 30. Similarly, organic spacers containing oxygen and other hetero elements or flexible organic groups may be used in future.

An amorphous polymer which contains trifunctional cyamelurate groups and difunctional dimethylsilyl units has been obtained from the silyl ester $\text{C}_6\text{N}_7(\text{OSiMe}_3)_3$ according to the following idealized equation [183].



The analogous reaction is also observed when the *s*-heptazine group is replaced by the *s*-triazine group. Both networks are formed via a sol–gel transition in organic solvents [183].

In several recent publications the surface modification of TiO_2 with *s*-heptazine-containing polymers is reported. Urea may



Scheme 30. Idealized structures of the C/N/H-polymers using organic linkers based on reference [243].

be used as a precursor and it was proved that it is transformed into compounds which contain the C_6N_7 -unit. These surface treated titania powders show enhanced optical and photo(electro)chemical properties [81–84,244].

Another class of C/N/H materials are the so-called “tholins”, which are usually prepared by plasma discharge in gaseous N_2 - CH_4 mixtures. They are considered to provide materials that are analogous to those found responsible for the haze in Titan’s atmosphere [257]. The CASSINI mission has shown that these tholins contain hydrogen, carbon and nitrogen. Numerous studies with many different analytical methods have been applied to elucidate the structure of tholins. Recent solid state ^{13}C and ^{15}N NMR investigations indicate that *s*-triazine and/or *s*-heptazine and/or other sp^2 -hybridised N-containing groups may be present, as well

as hydrogen-containing moieties such as $=NH$, $-NH_2$ and $-CH_x$ groups [258].

In addition to the numerous C/N/H-polymers mentioned in literature and discussed in Section 6.3 there have been reports of “doped” carbon nitrides, i.e. C/N/H materials containing various amounts of further elements such as oxygen, or sulphur, or boron. The term doping was introduced due to the fact that the graphitic carbon nitrides as well as melon were reported to be semiconductors. These semiconductive properties can be exploited using the doped materials as catalyst for visible light induced splitting of water and related applications as catalysts (see Table 7). Despite various investigations and clear indications that the *s*-heptazine unit is usually present in these multinary materials, the chemical structure is still largely unknown. Not only the amount

of *s*-heptazine groups in these solids but also their bonding mode need to be clarified. The C₆N₇ moiety may be bonded via the terminal carbon and/or nitrogen atoms to carbon, hydrogen, oxygen, nitrogen or other elements. This is due to the tautomeric behaviour as observed and studied in detail for several molecular *s*-triazine and *s*-heptazine derivatives in the solid state and in solution. Nevertheless, despite these open questions these *s*-heptazine-containing polymeric compounds and composites have been proved to possess very interesting and useful properties leading to several (potential) applications of these materials in the future.

7. Conclusions and outlook

s-Heptazine (or tri-*s*-triazine) derivatives have a long history. They were first discovered by the very famous chemists Liebig and Gmelin in the 1830s. About 100 years later Linus Pauling suggested the correct planar heteroaromatic structure for the C₆N₇ moiety. He obviously remained interested in this class of compounds until much later in his life, since the structure of an unsymmetric azide derivative C₆N₇O₂H₂(N₃) was found on the chalkboard in his office after his death. This so-called 'mystery molecule' is still elusive, although the symmetric azide C₆N₇(N₃)₃ (**5**) as well as asymmetric amides C₆N₇(NR₂)(NR'₂)₂ and cyameluric acid C₆N₇O₃H₃ (**2**) have recently, i.e. in the past decade, been synthesized and comprehensively characterised.

In spite of the almost 200 years of *s*-heptazine research there are still relatively few fully analysed compounds described in the literature. A major reason for this fact is the low solubility and in some cases also relatively low reactivity of important *s*-heptazine derivatives, in particular melem C₆N₇(NH₂)₃ (**1**). On the other hand it should be noted that melem (**1**) as well as the closely related polymer melon [C₆N₇(NH)(NH₂)]_n are easily obtained via one-step syntheses simply by annealing melamine, cyanamide or similar starting materials to temperatures above 350 °C. An interesting and diverse structural chemistry was recently reported for melem, melon and hydromelonic imide [C₆N₇(NH)_{1.5}]_n, which also involves crystalline melem-melamine adducts and the inclusion of molecular melamine. It is generally based on layered structures with π -stacking and strong hydrogen bonding. Both compounds melem and melon are the primary educts for practically all known and comprehensively analysed *s*-heptazine derivatives, except the parent tri-*s*-triazine C₆N₇H₃ (**6**) which was obtained by a four-step organic synthesis approach in the 1980s.

A very important starting material for many molecular *s*-heptazine compounds is the trichloride C₆N₇Cl₃ (**4**). This molecule is characterised by a high reactivity towards nucleophiles and may be considered as a very useful reagent comparable to cyanuric chloride C₃N₃Cl₃. The said triazide **5**, all reported symmetric and asymmetric amides, the tri-*p*-tolyl derivative C₆N₇(C₆H₄-CH₃)₃ and a few cyameluric esters C₆N₇(OR)₃ have been obtained from it. Further molecular *s*-heptazine derivatives include the trihydrazine C₆N₇(NH-NH₂)₃ (**22**), the tri-imide C₆N₇(phthal)₃ and phosphazenes C₆N₇(N=P(OR)₃)₃ and C₆N₇(N=PR₃)₃.

Also usually obtained from melem and/or melon are the ionic *s*-heptazine compounds, namely cyamelurates M^(I)₃[C₆N₇O₃], melonates M^(I)₃[C₆N₇(NCN)₃], melemium salts [C₆N₇(NH₂)₃H]X and further protonated derivatives. In almost all cases mono- and di-protonation occurs at the outer ring nitrogen atoms of the *s*-heptazine unit and not at the N- and O-containing substituents. The cyamelurate and melonate salts are soluble in water, at moderate pH-values also up to the boiling point.

In addition to melon and poly-*s*-heptazine imide numerous polymeric materials containing the *s*-heptazine group have been reported, which are generally completely insoluble and in most cases non- or only partially crystalline. Therefore, structural

analyses are more challenging than for the molecular and ionic compounds. Besides, there are some still hypothetical carbon(IV) nitride phases C₃N₄, which are based on the C₆N₇-units. These are expected to be very stable, especially in the case of the network [C₆N₇N]_n, and may occur as nanotubes, graphene-like sheets and many further forms. It is unfortunate that recently various C/N/H-polymers which are in many cases comparable to melon, are denominated as graphitic carbon nitrides or even C₃N₄ phases in the current literature.

Many of the mentioned molecular, ionic and polymeric *s*-heptazine derivatives have interesting properties. The thermal stability of the C₆N₇-unit is usually found to be very high when compared with most organic or other C/N-moieties, i.e. decomposition starts above 500 °C. This property may be useful for many applications, e.g. for catalysts or polymer additives or components, it is also related to the use of melamine as a flame retardant. Further useful properties include photo- and electroluminescence, as reported for selected *s*-heptazine derivatives. Besides, NLO active *s*-heptazine-based materials have been found. Several theoretical and in some cases experimental studies suggest further applications in fields such as adsorption or sensors. However, one of the most intriguing and promising future application of *s*-heptazine-based materials seems to be the semiconducting behaviour of ordered and disordered C/N/H-polymers such as melon. Numerous reports on their application as (visible light) photocatalysts for water splitting as well as metal-free catalysts for various organic reactions appeared recently. These proved and theoretically predicted properties together with the large field of completely unexplored *s*-heptazine derivatives (of molecular, ionic and especially polymeric types) provides a very promising outlook for the future of this branch of chemistry and materials science.

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