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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.

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