

gt-C₃N₄—The First Stable Binary Carbon(IV) Nitride

Edwin Kroke*

2D polymers · graphene · heptazine · intercalation · triazine

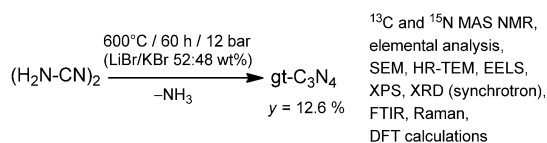
About 25 years ago Cohen et al.^[1] postulated that a Si₃N₄-analogous carbon(IV) nitride should exist. This initiated numerous attempts to synthesize carbon nitrides as well as further theoretical studies. Meanwhile more than 6000 papers about C₃N₄ and related carbon nitrides have appeared (CAS search). Among these publications are reports on successful approaches, which later turned out to be wrong or based on incomplete analyses. Bojdys et al.^[2] succeeded now in obtaining a graphitic s-triazine based C₃N₄ (gt-C₃N₄) starting from dicyanamide. The solid was formed in 12.6% yield using a LiBr/KBr melt at 600 °C and comprehensively characterized (Scheme 1). This is remarkable not only because of the many unsuccessful studies but even more due to the (predicted) properties and applications, and the close relation of the gt-C₃N₄ to graphene and graphitic ternary polymers like melon [C₆N₇(NH₂)(NH)]_n, which was recently scrutinized owing to its highly interesting semiconducting and (photo)catalytic properties (see below).

The publications of Cohen et al. attracted so much attention because he postulated that a carbon(IV) nitride with sp³-hybridized C atoms in a β-Si₃N₄-like structure (and later also further 3D networks such as α-Si₃N₄) to be extremely incompressible and harder than diamond.^[1,3] In analogy to the gas-phase deposition of diamond, many reports were published on the preparation of CN_x coatings with interesting properties as well as synthesis attempts using wet-chemical and high-pressure routes. These numerous reports were summarized and analyzed in reviews.^[4] These studies did not culminate in a successful synthesis, but yielded plenty of

other useful information. It was pointed out that the shear modulus correlates much better with the hardness than the bulk modulus. Besides, the thermal stability of CN_x phases is generally too low for applications as hard materials.^[4]

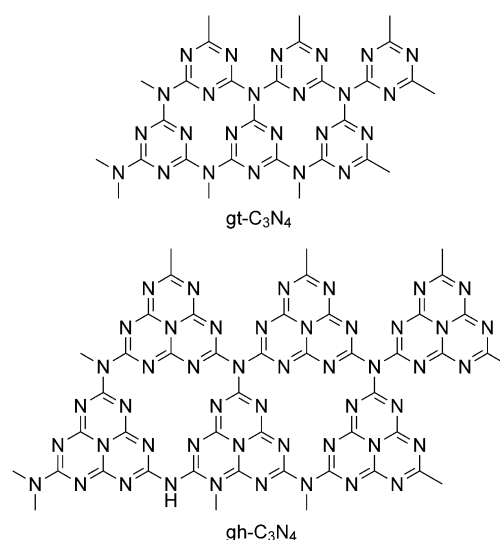
Graphitic C₃N₄ structures were also considered: A network based on s-triazine building blocks, that is, gt-C₃N₄, was suggested by Liu and Wentzcovitch (in space group *P6̄m2* (187)) as well as by Teter and Hemly (in space group *R3m* (160)) in the mid-1990s (Scheme 2 top).^[5] Further graphitic C₃N₄ modifications were postulated later.^[6] These phases are based on aromatic s-triazine units C₃N₃ as well as on the s-heptazine group C₆N₇, which is planar and aromatic as well (Scheme 2 bottom).

In 2002 it was shown by ab initio calculations on different graphitic carbon(IV) nitrides that gh-C₃N₄ should be the most stable modification under ambient conditions.^[6d] This finding is supported by observations that the C₆N₇ moiety is generally formed at higher temperatures (usually at 400–600 °C) starting from different C/N/H precursors.^[7] It has been long known that s-heptazine derivatives like melonates M(I)₃[C₆N₇(NCN)₃] and cyamelurates M(I)₃[C₆N₇O₃] (with M(I) = alkali metal) are obtained under such conditions and that these and

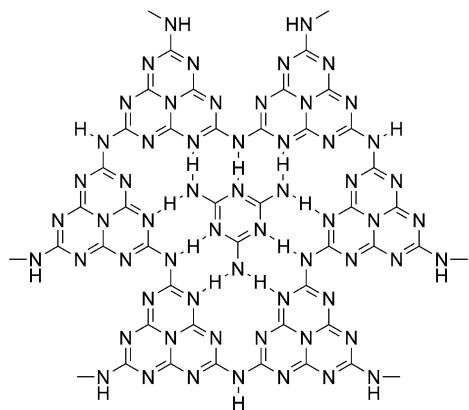


Scheme 1. Synthesis of graphitic, s-triazine-based carbon(IV) nitride (gt-C₃N₄) was performed in quartz glass ampules or (due to the pressure caused by the NH₃ formation) in small steel autoclaves.^[2] g-[(C₃N₃)N]_n is formed on the surfaces of the reactors as black layers, which can be scratched off.

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Scheme 2. The two most important graphitic carbon(IV) nitrides discussed in literature are based on s-triazine and s-heptazine units.^[7] The s-heptazine network gh-C₃N₄ should be about 30 kJ mol⁻¹ more stable than gt-C₃N₄ according to ab initio calculations.



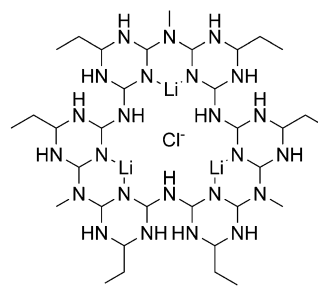
Scheme 3. The graphitic s-heptazine phase poly(heptazine imide) (PHI) $[C_6N_7(NH)_{1.5}]_n$ with the highest degree of condensation and incorporated melamine molecules.^[8d] In many cases these C/N/H phases and similar (well-characterized) compounds such as the linear polymer melon $[C_6N_7(NH_2)(NH)]_n$ are referred to as “g- C_3N_4 ” or “graphitic carbon nitrides” in the literature.

other s-heptazine compounds are surprisingly thermally stable.^[7]

The formation of graphitic C/N/H polymers by condensation reactions induced by thermolysis starting from cyanamide H_2N-CN , via dicyanamide $(H_2N-CN)_2$ and the s-triazine derivatives melamin $C_3N_3(NH_2)_3$ and melam $(C_3N_3)_2(NH)(NH_2)_4$, and the transition to the s-heptazine derivatives melem $C_6N_7(NH_2)_3$ and melon $[C_6N_7(NH_2)(NH)]_n$ were all thoroughly investigated by Schnick et al.^[8] The structures of these insoluble solids were solved by combination of NMR spectroscopy, X-ray and electron diffraction, and other analytical methods. The structures of melem and melon were confirmed and crystalline melamin–melem and melam–melem adducts as well as a polymeric heptazine imide (PHI) $[C_6N_7(NH)_{1.5}]_n$ with incorporated melamin molecules were identified and structurally investigated (Scheme 3).

Many authors speculated about a possible continued condensation (with ammonia formation) to generate binary carbon(IV) nitrides, especially gh- C_3N_4 , from melon or PHI. However, no attempts were successful so far.^[7,8] An interesting approach (similar to the gt- C_3N_4 synthesis) is based on a LiCl/KCl melt as the reaction medium.^[9] Nice hexagonal crystals were obtained, which were described to have the gh- C_3N_4 structure, although EELS spectra and elemental analyses indicated the presence of chlorine, lithium, and hydrogen. Later it was proved that a graphitic poly(triazine imide) (PTI) with intercalated lithium and chloride ions had formed (Scheme 4).^[10] A similar ternary PTI network $[C_6N_9H_3 \cdot HCl]$ which contains chlorine but no lithium has been reported before.^[11]

Binary (and multinary) nitrides have been the subject of many studies in the past decades. One might conclude from a comparison of the binary element(IV) oxides SiO_2 and CO_2 with the nitrides Si_3N_4 and C_3N_4 that molecular carbon(IV) nitrides exist; however, tricyanamide $N(CN)_3$, dicyanocarbodiimide $NC-NCN-CN$, and dicyandiazomethane $N_2C(CN)_2$ cannot be isolated under ambient conditions and were detected only at very low temperatures.^[12]



Scheme 4. Structure of the graphitic poly(triazine imide) (PTI) $[(C_3N_3)_2(NH_xLi_{1-x})_3LiCl]$ which is formed in a LiCl/KCl melt. This compound PTI/LiCl crystallizes in space group $P6_3cm$ (185), with an ABA layer in the direction of the c -axis, that is, the Li atoms and the C/N/H network comprise A layers, with alternating B layers containing the chloride ions.^[10] The occupancy factor of the Li positions is only 1/3 and combined with a Li^+/H^+ disorder. The (delocalized) π -electrons were omitted for better clarification of the symmetry.

The novel gt- C_3N_4 available now shows some interesting peculiarities. The authors report that only triple layers are obtainable by exfoliation. This is in contrast to graphene, which can be isolated in monolayers. In addition, DFT calculations and a thorough analysis of XPS measurements show that the layers are not planar but buckeled. The experimental data correlate best with a structural model in space group $P\bar{6}m2$ (187), as was suggested in 1994.^[5a] Highly interesting are the XPS, DFT, and UV/Vis investigations indicating a band gap between 1.6 and 2.0 eV, which identifies gt- C_3N_4 as a potentially promising novel semiconductor material.

It should be pointed out that also ternary graphitic C/N/H polymers like melon, which are frequently based on s-heptazine building blocks, have semiconducting properties. This fact and the interesting (photo)catalytic activity of these polymers is currently a matter of great interest.^[7,13] Unfortunately, most reports based on syntheses starting from dicyanamide or similar precursors to form C/N/H materials use the designations “graphitic carbon nitride” and/or “g- C_3N_4 ”. The structural models are sometimes based on s-triazines and in other cases on s-heptazine moieties. For a better differentiation between ternary (or multinary) materials and binary carbon nitrides the gt- C_3N_4 obtained by Bojdys et al. was therefore labeled TGCN.

Finally coming back to the postulated 3D carbon(IV) nitride structures, it should be mentioned that at a pressure of >27 GPa and with dicyanamide as a starting material the carbon(IV) nitride imide $C_2N_2(NH)$ was formed.^[14] It is a matter of time before—probably using gt- C_3N_4 as the starting material—a C_3N_4 high-pressure modification with sp^3 -hybridized C atoms will be synthesized. Similarly, the carbon(IV) nitride postulated to be most stable, gh- C_3N_4 , should be obtainable in macroscopic amounts after the identification of a suitable synthetic route. Besides, it can now be postulated that fullerene- and nanotube-like carbon(IV) nitride structures become available soon.

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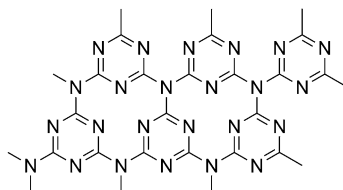
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Highlights

Carbon(IV) Nitrides

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gt-C₃N₄—The First Stable Binary
Carbon(IV) Nitride



Twenty-five years ago a diamondlike C₃N₄ phase was postulated. After many unsuccessful attempts the synthesis of an s-triazine-based modification was accomplished, which is reported to show interesting semiconducting and catalytic properties similar to that of graphene and related graphitic C/N/H phases.