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Letter

Tri-*s*-triazine derivatives. Part I. From trichloro-tri-*s*-triazine to graphitic C_3N_4 structures†

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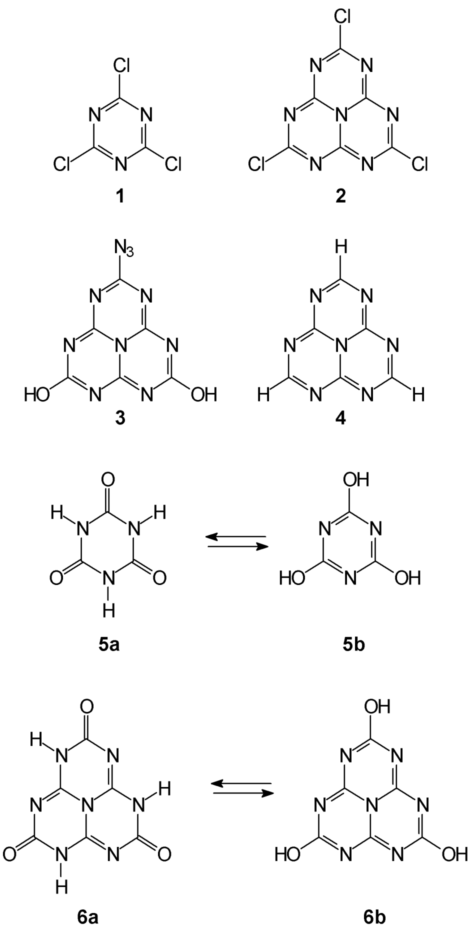
The first detailed structural characterisation of a functionalised tri-*s*-triazine derivative, trichloro-tri-*s*-triazine, is reported, which is a promising starting material for numerous compounds including graphitic C_3N_4 phases. DFT calculations show that a C_3N_4 structure based on tri-*s*-triazine should exist and that it is ~30 kJ mol^{-1} more stable than the previously reported C_3N_4 phase of lowest energy.



Scheme 1 Comparison of the triazine and tri-*s*-triazine derivatives cyanuric chloride **1**, trichloro-tri-*s*-triazine **2**, as well as cyanuric acid **5ab** and cyameluric acid **6ab**. The parent tri-*s*-triazine molecule **4** and an unknown azido derivative **3**, which was found on the chalkboard of Linus Pauling after his death, are also depicted.

Acid chlorides are important starting materials.[1] For example, cyanuric chloride (trichloro-*s*-triazine) **1** in Scheme 1 the trichloride of cyanuric acid **5ab**, is used to produce many triazine containing compounds.[2]

The *sym*-heptazine[3] nucleus C_6N_7 consists of three fused *s*-triazine rings. A compound structurally analogous to cyanuric acid, cyameluric acid **6ab**, has been reported in the literature.[4] Its chemical properties have been examined several decades ago, but no detailed spectroscopic and physical data except IR spectra are known.[5] The acid chloride of cyameluric acid **6ab**, trichloro-tri-*s*-triazine **2**, is a useful starting material to introduce the *sym*-heptazine unit, an electron-poor and thermally extremely stable fragment. In fact, tri-*s*-triazine is the most stable member of the azacycl[3.3.3]azine series of compounds, which are isoelectronic to the phenalene anion.[6] The *sym*-heptazine unit is most likely contained in melon, melem and similar C/N/H materials, which also posses high thermal stability, sometimes even to >500 °C. Investigations on these compounds date back to the 1830s.[7] Not only then were investigators challenged by the insolubility and chemical inertness—possibly one reason why their structures remained unclear until today. Pauling and Sturdivant were the first to suggest a coplanar tri-*s*-triazine unit as the basic structural motif of these compounds.[8] Pauling apparently maintained an interest in tri-*s*-triazine, for reasons unknown, as the molecular formula of compound **3** was preserved on his office chalkboard at the time of his death in 1994.[9]

To our knowledge, there is only one tri-*s*-triazine compound described in the literature that has been comprehensively characterised, namely the molecule tri-*s*-triazine, $C_6N_7H_3$ **4**. It was synthesised by a three-step route starting from 2,4-diamino-1,3,5-triazine and methyl *N*-cyanomethanimidate.[6] Its structural and spectroscopic properties including an X-ray crystal structure analysis were discussed. UV photoelectron spectra were taken and *ab initio* calculations performed in order to explain the low basicity and the high stability.[6]

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† Part II: Alkalicyamelurates $M_3[C_6N_7O_3]$, M = Li, Na, K, Rb, Cs, manuscript in preparation.

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A search in the CAS Registry database gave 129 substances containing the tri-*s*-triazine unit.[10] However, many of these compounds have been only briefly mentioned in communications or patents and were not characterised at all.[5] Some have been examined by the determination of melting points, C/H/N analysis and IR spectroscopy. This is also true for trichloro-tri-*s*-triazine **2**, which was first prepared by Redemann and Lucas in 1940 by chlorination of cyameluric acid **6ab** or its tripotassium salt with PCl$_5$.[5d] The product was not characterised except for its N and Cl content. It was reported to be impure, containing small amounts of phosphorus. According to the authors compound **2** could not be purified by sublimation or re-crystallisation from organic solvents.[5d] Schroeder and Kober tried to improve this synthesis using C$_6$H$_5$PCl$_4$ instead of PCl$_5$, which was unsuccessful.[5b] Therefore, they treated an excess of PCl$_5$ with the tripotassium salt of cyameluric acid and purified the product by washing it very rapidly with ice water. The dried product was characterised without further purification by determination of its melting/decomposition point and the chlorine content. It was claimed in a patent that the chlorination of potassium cyamelurate can be performed in an organic solvent like *o*-dichlorobenzene.[5e] Another patent describes a different route to **2** that is based on a high temperature transformation of **1** or cyanogen chloride ClCN using charcoal as a solid phase catalyst.[5f]

We prepared **2** by a modified method similar to those described in ref. 5(*b*–*d*), followed by purification through sublimation and recrystallisation (see Experimental). The bright yellow crystalline product was characterised using MS, FTIR, ^{13}C-NMR, UV/Vis absorption and photoluminescence (PL) spectroscopy as well as elemental analysis and single crystal X-ray diffraction. The C/N element content was in excellent agreement with the theoretical values, and IR data correspond well with the reported spectra, including three characteristic vibrations for the tri-*s*-triazine unit at 1610, 1505 and 825 cm^{-1}. The ^{13}C NMR signal at 159 ppm is due to the C atoms bonded to three N neighbours, which is almost identical to the value reported for tri-*s*-triazine. A resonance for the Cl-bonded C atoms was detected at 176 ppm, which is at lower field compared to the unsubstituted molecule as expected. The yellow colour of compound **2** is caused by an absorption band with a maximum at 310 nm. Photoluminescence was detected at 468 nm.

For X-ray structure analysis, suitable crystals were grown by slow diffusion of diethyl ether vapour into a solution of **2** in acetone (see Experimetal). The structure solution in the monoclinic space group *C*2/*c* revealed the expected molecule with an asymmetric unit comprised of $3\frac{1}{2}$ molecules of **2**, half a molecule of diethyl ether and a molecule of acetone. Since $Z = 8$ there are thus 28 molecules of **2**, four of diethyl ether and eight of acetone in the unit cell. All trichloro-tri-*s*-triazine molecules are planar as indicated by the sums of bond angles at each C and N atom bonded to three neighbours being 360°($\pm$0.2°). This is due to the aromaticity of **2** based on the 14 π electrons. However, the three triazine units of **2** are considerably distorted (Fig. 1 and Table 1). The average C–N bond lengths to the central N atom of 1.397 Å are longer than the (Cl)C–N bonds (1.328 Å) as well as the remaining C–N bonds (1.334 Å). Besides, the endocyclic N–C–N angles of the C atoms bonded to the chlorine atoms are larger (≈130°) than the endocyclic C–N–C angles of ≈115° at the peripheral N atoms, which is to be expected due to the lone pair sp^2 orbitals located on these nitrogen atoms.

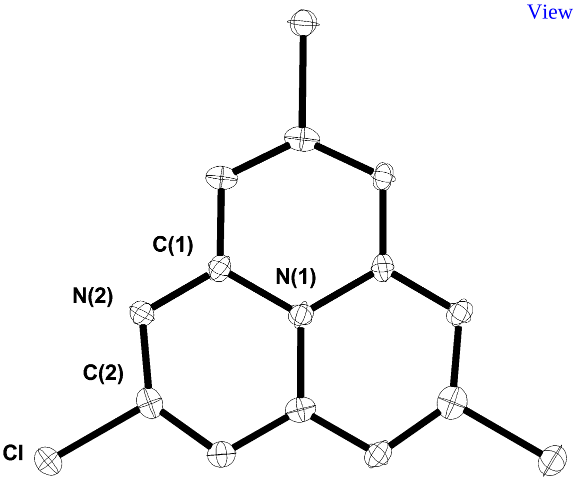


Fig. 1 Ortep plot of **2** (50% probability) indicating the distortion of the six-membered triazine rings. However, the molecule is completely planer as shown by the sum of bond angles of 360° for all C and N atoms.

Table 1 Average bond lengths and bond angles for molecule **2** (see Fig. 1)

Bond length	d^a/Å (σ/Å)^b	Bond angle	∠^{a}/° (σ/°)^b
N(1)–C(1)	1.397 (0.004)	C(1)–N(1)–C(1)′	120.0 (0.6)
C(1)–N(2)	1.334 (0.004)	N(1)–C(1)–N(2)	119.7 (0.5)
C(2)–N(2)	1.328 (0.008)	C(1)–N(2)–C(2)	115.1 (0.4)
C(2)–Cl	1.716 (0.004)	N(2)–C(2)–N(2)′	130.2 (0.4)
		Cl–C(2)–N(2)	114.9 (0.4)

[a] Avarage values for all equivalent bond lengths and angles of molecules 1 through 3 (see Experimental). [b] The sigma values refer to the calculated mean values (the experimental sigma values for each bond length and angle are available together with the crystallographic data as ESI.

Table 2 Intermolecular Cl···N distances found in the crystals of **2** with $d < 3.5$ Å. The first twelve lines refer to molecules within layer B, while the last two lines are related to N···Cl contacts between the layers A and B (see Fig. 2)

Cl···N contact^a	d/Å	Bond angle^a	∠/°
Cl(3)···N(9)	3.070	C(6)–Cl(3)···N(9)	150.4
Cl(4)···N(18)	3.091	C(8)–Cl(4)···N(18)	164.0
Cl(8)···N(7)	3.111	C(16)–Cl(8)···N(7)	148.6
Cl(4)···N(5)	3.257	C(8)–Cl(4)···N(5)	98.6
Cl(8)···N(11)	3.344	C(16)–Cl(8)···N(11)	93.7
Cl(9)···N(12)	3.369	C(18)–Cl(9)···N(12)	67.6
Cl(9)···N(14)	3.373	C(18)–Cl(9)···N(14)	93.3
Cl(7)···N(7)	3.387	C(14)–Cl(7)···N(7)	120.4
Cl(2)···N(17)	3.456	C(4)–Cl(2)···N(17)	95.0
Cl(1)···N(9)	3.458	C(2)–Cl(1)···N(9)	121.0
Cl(6)···N(19)	3.492	C(12)–Cl(6)···N(19)	105.3
Cl(4)···N(24)	3.411	C(8)–Cl(4)···N(24)	118.9
Cl(2)···N(23)	3.429	C(4)–Cl(2)···N(23)	138.0

[a] The atom numbering refers to the crystallographic data available as ESI.

Azaaromatic chlorides, which are aromatic compounds containing many N=C–Cl subunits, are a remarkable class of compounds.[11] Like cyanuric chloride **1** they frequently show short intermolecular Cl···N contacts of 3.0 to 3.5 Å displaying extensive donor-acceptor networks in the solid state.[11] We therefore examined the intermolecular distances in the crystals of **2** and found indeed several such contacts (Table 2). The arrangement of the molecules in the unit cell can be described by ABAB layers that are parallel to the *ab*-plane (Fig. 2). Within layer A the molecules of **2** are almost coplanar forming thin sheets. Since solvent molecules separate these molecules there are no Cl···N interactions within these layers. Twelve

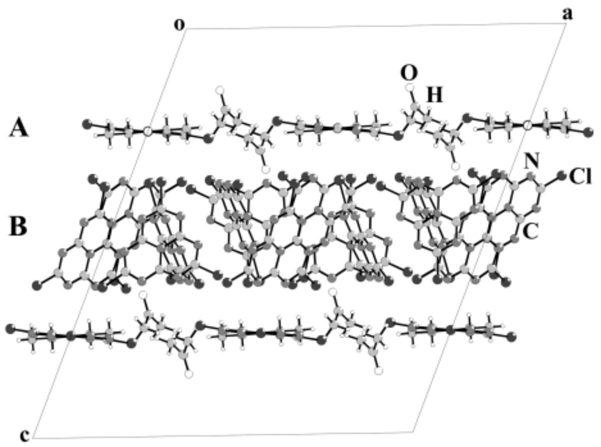


Fig. 2 View along the *b*-axis of the unit cell. The layers A and B can clearly be distinguished (further layers have been omitted for clarity and space limitations). Due to the solvent molecules in layer A there are no Cl···N interactions found within this layer. A close packing of molecules of **2** in layer B corresponds to several weak Cl···N contacts of 3.0 to 3.5 Å.

different Cl···N contacts of 3.070 to 3.492 Å with C–Cl···N angles of 67.6° to 164.0° are present within the layer B. This is due to the absence of solvent molecules. Interestingly, there are only two rather long Cl···N contacts between the two layers. Based on *ab initio* calculations it was suggested that the strength of each of the weak contacts is about 5 kJ mol^{-1}.[11]

Several compounds may be prepared from **2**, for example graphitic C_3N_4 structures.[12] These materials are expected to be suitable precursors for the high pressure synthesis of superhard C_3N_4 phases in analogy with the conversion of graphite and h-BN to diamond and c-BN, respectively. Theoreticians have proposed several structural models of C_3N_4 to have properties comparable to diamond.[13,14] This motivated numerous experimentalists to try to synthesise these phases.[12] Typical products of most attempts are "graphite-like" materials, which are believed to be based on the *s*-triazine network **7** (Scheme 2). Another carbon(IV) nitride structure **13**, also derived from triazine rings connected by N-atoms, has been suggested recently.[15] Alternatively, the C_3N_3 rings may be interconnected with carbodiimide (N=C=N) or cyanamide (N–C≡N) groups to form the (soft) 2D or 3D networks **9** and **10** with C_3N_4 stoichiometry and an alternating C–N arrangement.[16] Analogous 2D or 3D C_3N_4 materials are formed by connecting the tri-*s*-triazine units with N atoms (**8**, **14**), carbodiimide (**11**) or cyanamide (**12**) groups (Scheme 2). Furthermore, C_3N_4 structures based on both triazine and tri-*s*-triazine units may be postulated, as indicated by the networks **15** and **16**. To our knowledge, none of the authors discussing graphitic C_3N_4 structures have ever tried to explain the experimental results in terms of these tri-*s*-triazine containing structures.

To access the likeliness of such structures we performed total energy calculations of various structures using density functional theory.[17] We used a standard *ab initio* total energy and molecular dynamics program (VASP, Vienna *Ab-initio* Simulation Package) for this purpose, which combines ultra-soft pseudo-potentials with a plane-wave basis set.[18] The exchange correlation energy of the electrons is treated within the local density approximation (LDA). The generalised-gradient approximation (GGA) yields almost identical results for energy differences, since no significant changes in co-ordination (*e.g.*, tetrahedral *vs.* octahedral co-ordination) are present among the investigated structures. All structures we considered were completely optimised using a cut-off of 400 eV for the expansion of the wavefunction into the plane-wave basis set. For the integration over the Brillouin zone we used the *k*-point scheme of Monkhorst and Pack.[19] Forces were relaxed to values below 1×10^{-2} eV A^{-1} and stresses below 1 kbar. We confirmed the achieved structural properties at this level of accuracy by using finer grids for the *k*-point sampling and larger plane-wave basis sets. The total energy differences are found to be converged to values better than 1 kJ mol^{-1}. The approach we used has been proven to successfully calculate structure, relative energies, and properties of solid-state materials, defect structures, and surfaces.[20] Our own experience in this field stems from several nitride systems, such as carbon nitride,[16] silicon nitride,[21] and phosphorous nitride.[22]

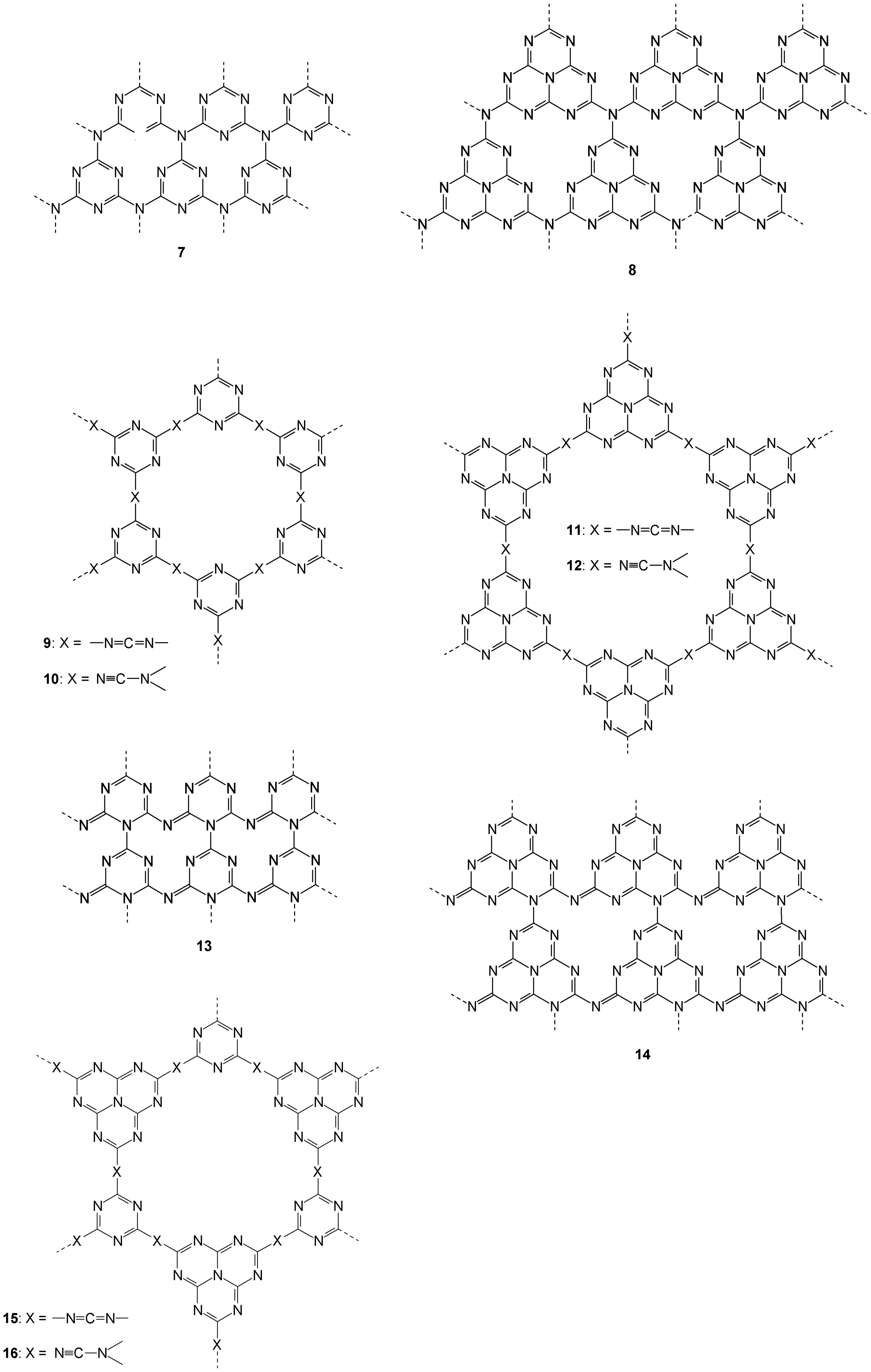
Previously, it was shown that **7** is the C_3N_4 structure with lowest energy.[14,15a] While we do reproduce all the relative energies of diamond-like and graphitic-C_3N_4 structures previously suggested, we now find that a tri-*s*-triazine based layered structure **8** is energetically more favorable, by ~30 kJ mol^{-1} in comparison to **7**, and thus should exist. We tested for several different stacking variants of the layered structure **8**, and found the structure with lowest energy to have space group *Cmc*21, for which an ortho-hexagonal setting is due to the stacking sequence. Similar to hexagonal boron nitride, nitrogen atoms avoid being stacked on top of each other so as to reduce repulsive interactions along the stacking direction. Due to the size of the structural building block, however, there exists at least three different stacking variants based on the motif **8**, all separated by an energy difference of less than 10 kJ mol^{-1}. We, therefore, suggest that in many cases, because of the high temperatures usually used to prepare carbon nitrides by CVD, PVD or bulk synthesis, tri-*s*-triazine based structures are formed. The experimental data should be re-examined carefully, comparing them to the data of tri-*s*-triazine and tricholoro-tri-*s*-triazine **2**.

Currently, we are trying to use compound **2** for reactions with nitrogen sources like Li_3N or $N[Si(CH_3)_3]_3$ to form **8**. Varying and very interesting results have been reported for similar attempts to obtain **7** from **1**.[12] Similarly, **11** (or **12**) may be obtained by reacting **2** with 1.5 equiv of bis(trimethylsilyl)carbodiimide for example, as was tried for **9**.[23] Besides, we have prepared a single source precursor for **8** by reacting **2** with 1 equiv of $LiN[Si(CH_3)_3]_2$, again similar to analogous triazine compounds.[24] The C_3N_4-structures **15** (or **16**), containing hepatzin and triazin units, may be synthesised from tricyanmelamiates[25] like $Na_3[C_6N_9]$ and the title compound **2**. A detailed report about these studies will be published elsewhere. Very recently similar approaches to carbon(IV) nitrides have been reported by Komatsu.[26] However, none of the attempts was successful so far, since elemental analyses indicated that all products contained significant amounts of residual hydrogen.

Experimental

Synthesis of 2

Potassium cyamelurate was synthesised by refluxing a suspension of 50 g melon powder (obtained from Degussa AG, Germany) in 500 ml of a 2.5 molar aqueous KOH solution for 45 min. The hot reaction mixture was filtered and upon slow cooling to 0 °C fine needles precipitated from the filtrate. The potassium cyamelurate was separated, washed with EtOH, dried and identified by IR spectroscopy and C/H/N analysis. The potassium cyamelurate (18.7 g) was intimately mixed with 42.27 g of PCl_5. The mixture was filled in a thick walled Schlenk tube that was subsequently evacuated to 10^{-1} mbar. The closed tube was heated to 130 °C **(caution!)**. The pressure generated inside the tube was carefully released several times followed by evacuation. After 10 h the solid reaction product was quickly washed with ice water. Drying



7

8

9: X = —N=C=N—

10: X = N≡C—N

11: X = —N=C=N—

12: X = N≡C—N

13

14

15: X = —N=C=N—

16: X = N≡C—N

Scheme 2 Triazine and tri-*s*-triazine based C_3N_4 structures, which can be considered as "graphitic" carbon(IV) nitrides containing an alternating arrangement of C and N atoms. None of these phases has been unambiguously proven to exist. Most authors tried to explain experimental results in terms of **7**. DFT calculations indicate that the tri-*s*-triazine based structure **8** seems to be more stable than **7**.

over P_2O_5 afforded 14 g (91%) of **2**. The crude product was purified by sublimation at 10^{-2}–10^{-3} mbar and 240–290 °C. We also found that Soxhlet extraction with toluene may be used to purify **2**. EA (Labor Pascher, Remagen, Germany): C: 26.22 (calcd: 26.07), N: 35.5 (calcd: 35.46); MS (EI) m/z: 277.5 (100%, MH^+), 276.5 (M^+), 240 ($MH^+ - Cl$); ^{13}C NMR (D_8-THF, 300 MHz): δ 158.23 (CN_3), 175.00 ($CClN_2$); FTIR (KBr pellet, cm^{-1}): 1610(vs), 1505(vs), 1310(s), 1205(s), 941(s), 825(m); PLS ($T = 290$ K) $\lambda_{max,abs}$ 310, $\lambda_{max,emission}$ 466 nm ($\tau < 700$ ns).

Crystal structure determination

For X-ray diffraction a plate-shaped crystal was placed under Exxon Paratone N oil, mounted onto a glass fiber, and moved to the goniometer head of a Siemens SMART CCD diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.[27] A detailed examination of the refined data revealed that molecules 1 through 3 all have well-behaved displacement parameters, while the half molecule that is located on the twofold rotational axis shows somewhat larger ellipsoids elongated in the direction perpendicular to the symmetry axis. Therefore, we carefully re-examined the experimental data for possible supercells. Besides, the system was re-refined in space group Cc, the only sensible second choice. Geometry was distorted, a common result when refining a centrosymmetric system in a non-centrosymmetric space group. The 2-fold symmetry was readily apparent. PLATON found 100% fit in the original space group $C2/c$. Therefore, we suppose that static disorder of the molecule on the rotational axis is the reason for its slightly elongated ellipsoids. The structural parameters presented in Table 1 are confined to molecules 1 through 3 and exclude the half molecule 4, although the deviations of bond lengths and bond angle values are smaller than 0.02 Å and 1°, respectively. Crystal data for $3\frac{1}{2}$ **2**· acetone·$\frac{1}{2}$ diethyl ether: $C_{26}H_{11}Cl_{10.50}N_{24.50}O_{1.50}$, $M = 1062.82$, monoclinic, space group $C12/c1$, $a = 23.2550(3)$, $b = 13.4512(2)$, $c = 26.8143(4)$ Å, $\beta = 111{,}4770(10)°$, $U = 7805.31(19)$ Å^3, $T = 142$ K, $Z = 8$, $D_c = 1.809$ g cm^{-3}, μ(Mo-Kα) $= 0.815$ mm^{-1}, 40 278 reflections measured, 8520 unique ($R_{int} = 0.0997$). The final R values were $R_1 = 0.1148$, $wR_2 = 0.1511$ [for all data] and $R_1 = 0.0798$, $wR_2 = 0.1360$ [for 6354 data with $I > 2\sigma(I)$].

CCDC reference number 175532. See http://www.rsc.org/suppdata/nj/b1/b111062b/ for crystallographic data in CIF or other electronic format.

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