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Keywords:	Heterocycle, Tri-s-triazine , Hydrazine, Azide, Phosphazene



2,5,8-Trihydrazino-s-heptazine: a precursor for heptazine-based iminophosphoranes

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Keywords: Heterocycle; s-Heptazine; Hydrazine; Azide; Phosphazenes; Crystal structure

Abstract: The title compound **1** $C_6N_7(NHNH_2)_3$ was obtained from melem $C_6N_7(NH_2)_3$ or melon $[C_6N_7(NH_2)NH]_n$ and hydrazine via an autoclave synthesis. Upon treatment with a 10 % HCl solution it is transformed into the trihydrochloride **2**, $[C_6N_7(NHNH_3)_3]Cl_3$. Compounds **1** and **2** were analysed with ^{13}C NMR, ^{15}N NMR, FTIR- and Raman-spectroscopy. Furthermore, the single crystal X-ray structure of the pentahydrate of **2** is reported (*P-1*, $a = 674.96(3)$, $b = 1214.17(6)$, $c = 1272.15(6)$ pm, $\alpha = 66.288(2)^\circ$, $\beta = 75.153(2)^\circ$, $\gamma = 80.420(2)^\circ$, $V = 920.30(8) \cdot 10^6$ pm³, $Z = 2$, $T = 90(2)$ K). The thermal decomposition of **1** and **2** was investigated with TG/DTA. Reaction of **1** with $NaNO_2/HCl$ yields triazido-s-heptazine, $C_6N_7(N_3)_3$ **3**. Tris(triⁿbutylphosphinimino)-s-heptazine **4** was synthesized from **3** and characterised by means of ^{13}C , ^{31}P , 1H NMR, FTIR and MALDI-TOF spectroscopy. Similar to s-heptazine derivative **3**, compounds **1** and **4** are precursors for graphitic carbon nitrides, which have attracted considerable attention recently, and to various potential applications, such as flame retardants and (photo)catalysis.

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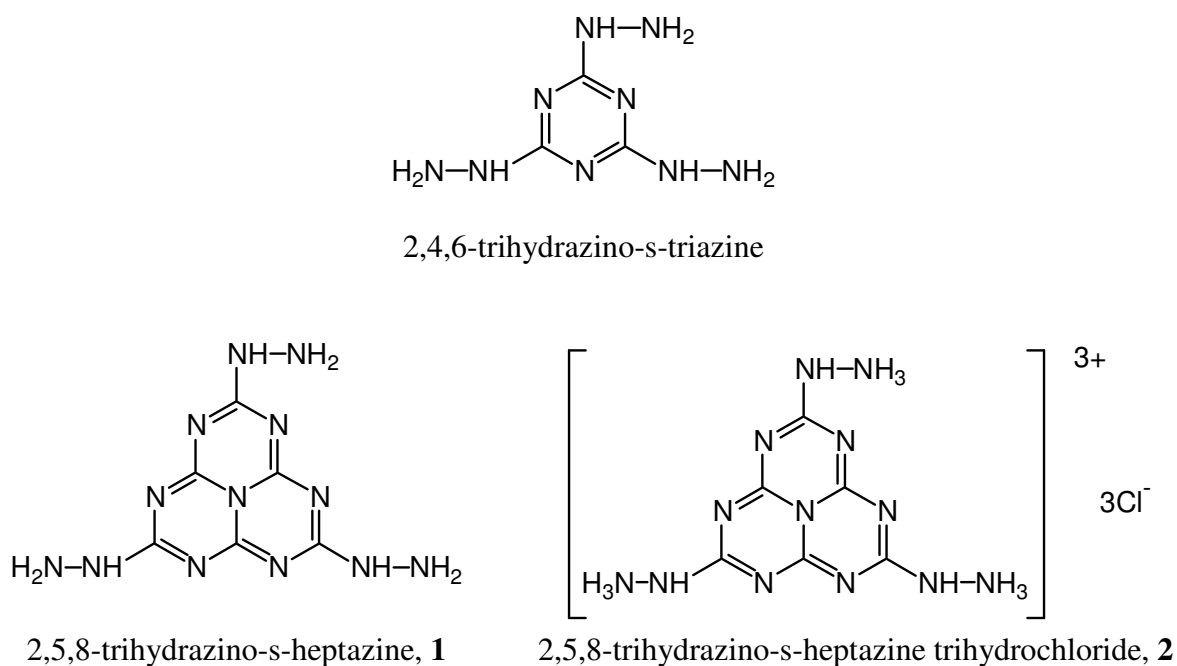
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Introduction

Within the last decade numerous publications addressed the preparation of carbon nitride materials.^[1] Binary compounds with C₃N₄ stoichiometry and 3D structure are postulated to exhibit very specific physicochemical properties, in particular their hardness is expected to exceed that of diamond.^[2]

Among potential precursors for graphitic CN_x materials, s-heptazine^[3] based compounds, such as trichloro-s-heptazine,^[4,5] triazido-s-heptazine,^[6] melem^[7] and melon^[1g,8] attracted considerable interest in recent years. Here we report on the melem-related nitrogen-rich substance 2,5,8-trihydrazino-s-heptazine **1** (Scheme 1). Although the synthesis of **1** has been described in a patent in 1965,^[9] its further characterization was missing yet.



Scheme 1.

This fact becomes especially intriguing, when compared to the s-triazine derivative the 2,4,6-trihydrazino-s-triazine (Scheme 1). The latter is a well known substance (its crystal structure has been determined already in 1976)^[10] which found broad application in synthetic and coordination chemistry. For instance, a variety of compounds combining the triazine core and different functional groups, such as CN, COOR, CH₂OH, CONH₂,^[11] N=N-R (R = alkyl, aryl)^[12,13] can be obtained from 2,4,6-trihydrazino-s-triazine. Furthermore, it can act as a

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3 poly-dentate ligand, giving complexes with transition metals, such as Co(II), Ni(II), Cu(I),
4 and Zn(II).^[14] Zn(II) complexes of $C_3N_3(NHN=C(CH_3)_2)_3$ were investigated for their non-
5 linear optic (NLO) properties.^[15] The industrial application of 2,4,6-trihydrazino-s-triazine as
6 a blowing agent in polymer industry for producing plastic foams is a consequence of its
7 ability to produce gaseous products by thermal decomposition.^[16]
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11 Contrary to 2,4,6-trihydrazino-s-triazine, compound **1** exhibits poor solubility in water and
12 organic solvents (dmf, dmsO). In addition, chemical inactivity of its hydrazine groups (see
13 Results and Discussion) and relatively low yield of the reported procedure (27 %) are the
14 possible reasons for scant knowledge about **1**.
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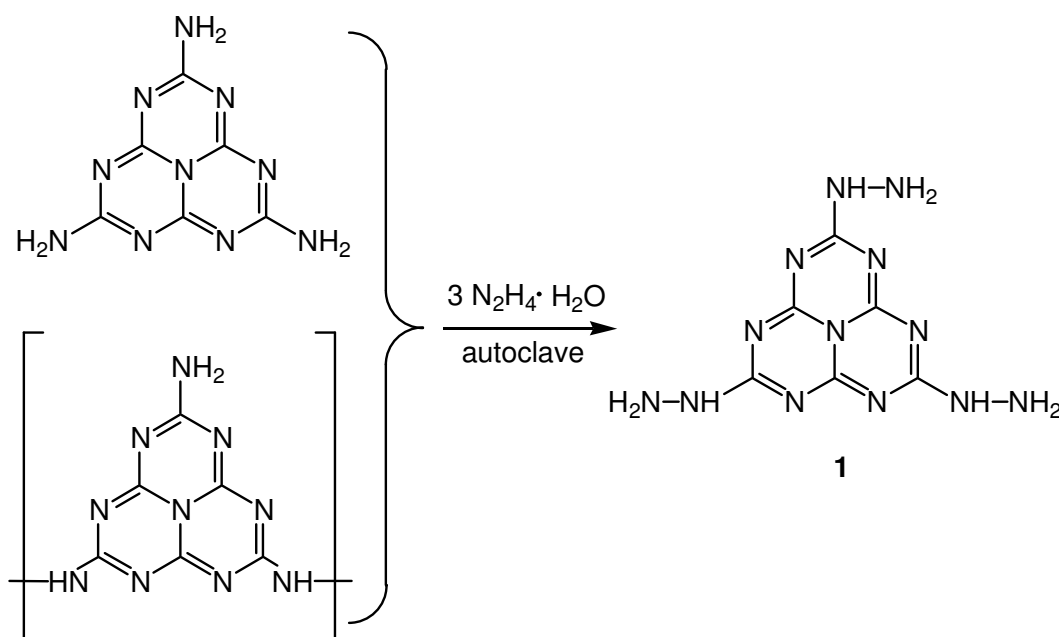
19 During our investigation we improved the synthesis procedure of **1** (yield 47 %). The
20 crystal structure of 2,5,8-trihydrazino-s-heptazine trihydrochloride pentahydrate **2** was
21 determined by X-ray single crystal diffraction. Furthermore, the 2,5,8-triazido-s-heptazine **3**,
22 an important intermediate to CN_x -compounds and chemically-interesting substance, was
23 obtained by reaction of **1** with sodium nitrite in HCl-solution. One of the applications of **3** is a
24 synthesis of heptazine-based iminophosphoranes via the Staudinger reaction;^[17] the latter
25 were suggested as halogen-free flame retardants for plastics.^[18,20] In this context, compound **4**,
26 tris(triⁿbutylphosphinimino)-s-heptazine, was synthesized by the Staudinger reaction of **3** with
27 triⁿbutylphosphine.
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38 Results and Discussion

39 The 2,5,8-trihydrazino-s-heptazine **1** was synthesized analogously to the reported
40 procedure,^[9] while the reaction conditions were slightly modified (see Experimental Section).
41 The reaction was carried out according to Scheme 2. Two types of heptazine-containing
42 starting materials, i. e. melem and melon, can be engaged. This variation of starting materials
43 does not have any influence on the purity and yield of product **1**.
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48 2,5,8-trihydrazino-s-heptazine is a yellowish solid, which decomposes (changes its
49 colour to dark-brown) without melting at about 300°C and proved soluble in diluted mineral
50 acids, such as HCl, H_3PO_4 , H_2SO_4 , HNO_3 . Contrary to our expectations, the nucleophilicity of
51 the terminal amino groups of hydrazine substituents in **1** is somewhat lower than in melem.
52 Besides Uhl et al. have performed several attempts to investigate reactivity of **1** towards
53 aluminium alkyls, aiming for alkylaluminium hydrazides.^[19] Unfortunately, all reactions to
54 yield the expected product failed. Furthermore, our attempt to perform the Kirsanov reaction
55 between **1** and PCl_5 failed, whereas this reaction route proceeds perfectly with melem.^[18,20]
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One possible explanation is an involvement of the amino groups of **1** into strong hydrogen bonding.



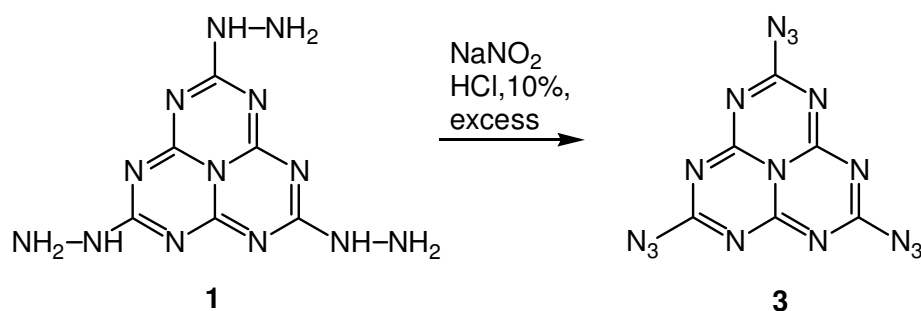
Scheme 2.

Thin colourless needle-like crystals of 2,5,8-trihydrazino-s-heptazine trihydrochloride pentahydrate [C₆N₇(NHNH₃)₃]³⁺3Cl⁻·5 H₂O (**2**) were obtained by recrystallisation of **1** from 10 % HCl solution and were characterised by single crystal X-ray diffraction. During air-drying on a filter paper at room temperature compound **2** partially loses its water of crystallization and HCl molecules. Thus, determining Cl⁻ concentration in different samples of 2,5,8-trihydrazino-s-heptazine hydrochloride by potentiometric titration with AgNO₃ solution, we found the chloride content to vary between 10 and 30 %, what can be interpreted as one, two or three HCl molecules per one C₆N₇(NHNH₂)₃ unit. Therefore, further characterization of 2,5,8-trihydrazino-s-heptazine hydrochloride **2** (IR, Raman, TG) reported here, were performed with a mixture of mono-, di- and trihydrochlorides of **1**. Repeated treatment of this mixture with 10 % NaOH solution and following drying of the precipitate under vacuum at 110-115°C gives 2,5,8-trihydrazino-s-heptazine **1**.

Surprising is the mode of protonation of C₆N₇(NHNH₂)₃ by HCl, which takes place on the terminal NH₂ groups of hydrazine-substituents, resulting in the cationic species [C₆N₇(NHNH₃)₃]³⁺ (Scheme 1, Figure 3a). Such proton position is very unusual for cyanuric and cyameluric derivatives, which prefer ring-protonation, as in case of melemium sulphate or

perchlorate^[21,22] and different melaminium salts.^[23] The compounds **1** and **2** have been characterized by means of vibrational spectroscopy (FTIR and Raman), NMR-spectroscopy and elemental analyses. Additionally, **2** has been studied by single crystal X-ray diffraction (vide infra).

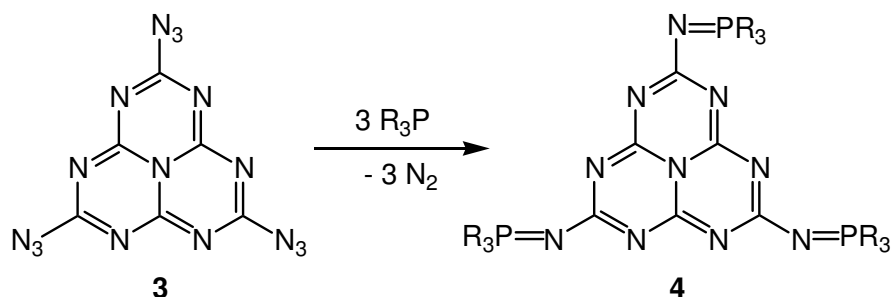
One of the interesting potential applications of **1** is its further derivatisation with sodium nitrite and 10 % hydrochloric acid to 2,5,8-triazido-s-heptazine **3** (Scheme 3). A similar procedure has been reported for 2,4,6-trihydrazino-s-triazine,^[12] whereas triazido-s-heptazine C₆N₇(N₃)₃ **3** has previously been synthesized via reaction of C₆N₇Cl₃ with Me₃SiN₃.^[6] However, C₆N₇Cl₃ is a highly air sensitive compound, which is difficult to obtain in large amounts, thus rendering diazotation of **1** an attractive goal.



Scheme 3.

Indeed, the synthesis of **3** from **1**, taking place under mild conditions, provides an easy and uncomplicated alternative to the known approach. The reaction results in yellow-orange compound **3** (with a yield of 60 %), which was characterized by elemental analysis and vibrational spectroscopy.

In a related study^[20] we investigated the synthesis of s-triazine- and s-heptazine based iminophosphoranes by the Kirsanov reaction and tested their fire-retarding activity. As an alternative we employed the Staudinger reaction to synthesize heptazine-based iminophosphoranes C₆N₇(N=PR₃)₃ (R = Me, Et, ⁱPr, ⁿBu, Ph, m-Kresyl) from triazido-s-heptazine **3** and tertiary phosphines R₃P (Scheme 4).^[18] Here we describe in detail the synthesis and spectroscopic properties of tris(triⁿbutylphosphinimino)-s-heptazine **4**, illustrating versatile application of **3**.



Scheme 4.

Spectroscopy

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Compounds **1** and **2** were characterised by solid state ^{13}C and ^{15}N CP/MAS NMR spectroscopy. The ^{13}C CP/MAS NMR signals of $\text{CN}_2(\text{NHNH}_2)$ carbons are observed at 164.2 and 162.2 ppm, and the resonance of CN_3 groups appeared at 154.5 ppm. The positions of the signals are similar to those of melem and melon.^[7,8] The ^{13}C CP/MAS NMR spectrum of **2** exhibits the three broad signals of $\text{CN}_2(\text{NHNH}_3)$ at 165.3, 163.4 and 162.1 ppm. The CN_3 group signal appeared similarly to that of **1** at 154.1 ppm. The position of these signals is near to that in **1**, being evidence, that protonation does not have any significant influence on the heptazine ring. Additionally, a solution of compound **2** in HCl was investigated by ^{13}C NMR spectroscopy. The spectrum exhibits two heptazine ring signals at 163.5 and 156.3 ppm.

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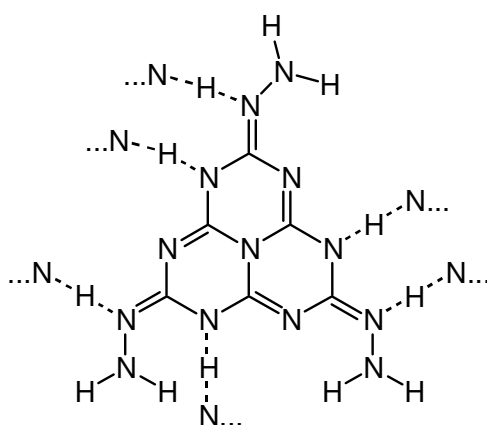
The ^{15}N CP/MAS NMR spectrum of **1** exhibits four signals with different intensity. The heptazine ring signals appear at -207.0 ppm (NC_2) and at -233.3 (NC_3) ppm. In case of melem these signals were observed at -201 and -234 ppm, respectively. The other two strong signals at -256.4 ppm (NH_2) and -320.1 ppm (NH) belong to the hydrazine groups. A very weak signal at -222.3 ppm was assigned to an impurity. The ^{15}N CP/MAS NMR spectrum of compound **2** exhibits similar chemical shifts of heptazine ring N atoms at -206.7 (NC_2) and at -233.8 (NC_3) ppm. The signals of side-chain nitrogen atoms were observed at -252.5 (NH_3^+) and -318.2 (NH) ppm. As expected, the signal of the NH_3^+ group of **2** is significantly shifted downfield in comparison with the amino-group signal of **1**, being in agreement with the crystal structure data.

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The ^{13}C NMR spectrum of a dmsO-solution of **4** exhibits two characteristic heptazine-ring signals at 164.4 and 154.7 ppm and four signals of the triⁿbutylphosphine substituents (27.0, 23.5, 23.3, 13.5 ppm). ^1H and ^{31}P NMR spectra of **4** reveal typical signals of ⁿ $\text{Bu}_3\text{P}=\text{N}$ groups (see Experimental Section).

The infrared and Raman spectra of compounds **1** and **2** are represented in Figure 1. For the X–H stretching modes ($2600 - 3400 \text{ cm}^{-1}$, X = N, O) the IR spectra of **1** and **2** exhibit several broad bands. These bands incorporate an N–H stretching of hydrazine-substituents, as well as O–H stretching vibrations of the coordinated water molecules. Positions of some of these bands at relative low wavenumbers, as well as their multiplicity and broadness, indicate strongly hydrogen bonded NH and OH groups in **1** and **2**. The Raman spectra exhibit two broad vibrations in the indicated region ($2897(\text{w})$ and $3230(\text{m}) \text{ cm}^{-1}$) in case of **1**, and one very broad band of weak intensity ($2660 - 3300 \text{ cm}^{-1}$) in case of **2**. The heptazine core vibrations of **1** and **2** appear at similar positions: $1640, 1520, 1400, 793 \text{ cm}^{-1}$ and $1660, 1550, 1400, 812 \text{ cm}^{-1}$, respectively. Additionally, in the region $1650 - 1450 \text{ cm}^{-1}$ deformation vibrations of N–H bonds occur, but they are partially overlapped by the absorption bands of heptazine rings. Only in case of salt **2**, strong bands at 1620 and 1480 cm^{-1} , which are assigned to deformation vibrations of NH_3^+ groups, were observed. The same range in the Raman spectra exhibits several weak vibrations between 1653 and 1000 cm^{-1} , which belong to the C=N stretching and N–H deformation.

Surprising is the presence of a very strong signal at 1620 cm^{-1} in the Raman spectrum of **1**, which is completely absent in the spectrum of **2**. This signal was assigned to the stretching vibration of an exocyclic C=N bond, which is a result of strong intermolecular N–H...N hydrogen bonding, as shown in Scheme 5.



Scheme 5.

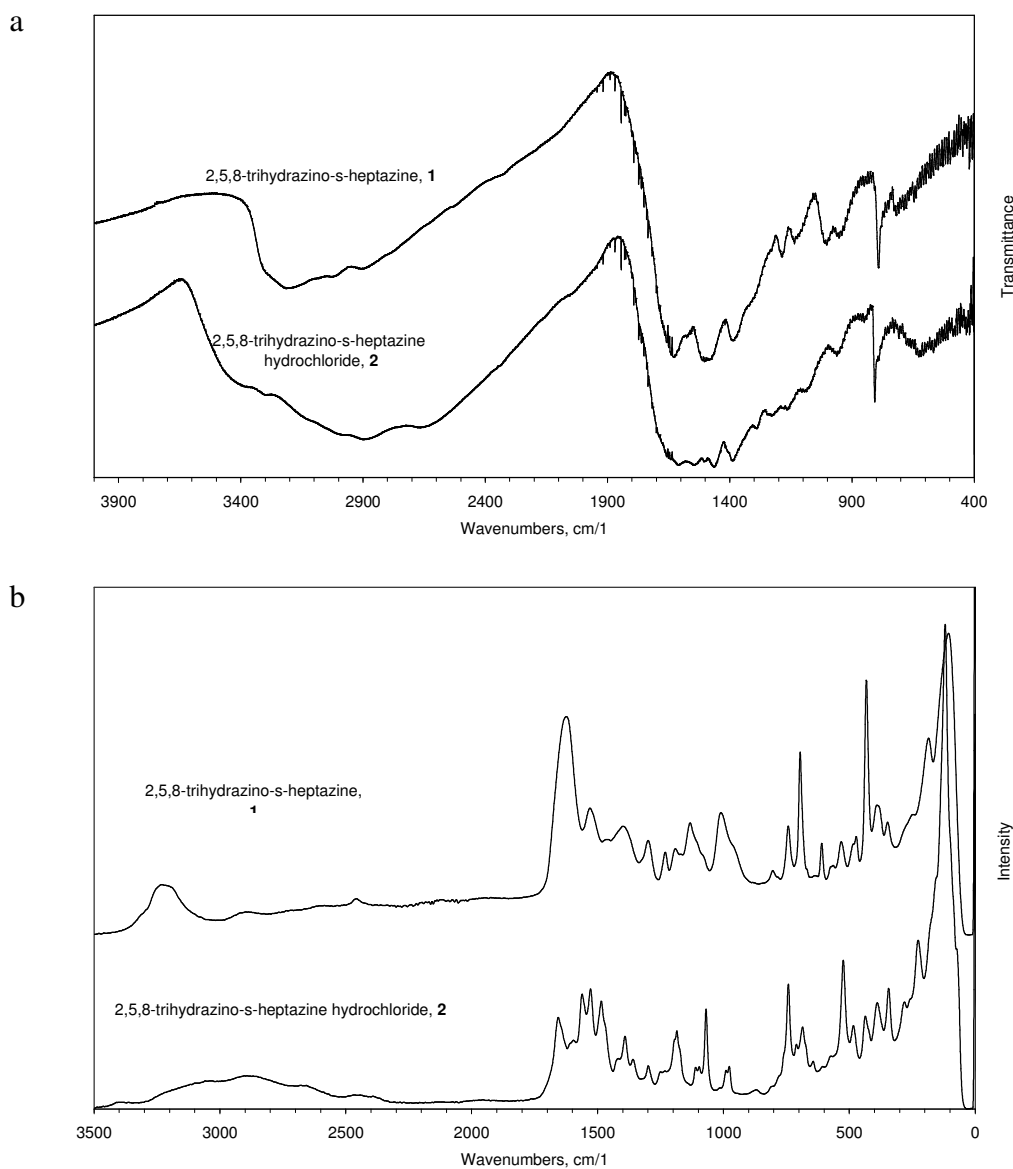


Figure 1. IR (a) and Raman (b) spectra of **1** and **2**.

The FTIR spectrum of **3** (see Supplementary Material, Figure S1) exhibits four typical vibrations of the s-heptazine ring at 1608, 1529, 1359 and 818 cm^{-1} . The azido-group in **3** is represented by a vibration band at 2260 – 2140 cm^{-1} . The obtained spectra are identical with those reported by Miller and co-workers.^[6]

The FTIR spectrum of **4** is represented in Supplementary Material as well (Figure S2). The $\nu(\text{C}=\text{N})$ vibrational bands of the heptazine-ring of compound **4** appeared at 1617, 1457, 1380 and 811 cm^{-1} . The $\text{P}=\text{N}$ stretching vibration is found at 1395 cm^{-1} , the position is in agreement with those observed for similar compounds.^[20,24] The signals at 2955, 2928 and

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3 2869 cm^{-1} were assigned to the C–H stretching vibrations of the t Bu groups. Additionally, **4**
4 has been characterized by means of MALDI-TOF mass spectrometry. Although a molecular
5 ion $[\text{M}+\text{H}]^+$ was not detectable, signals, were observed at 419.2 $[\text{M}-2\text{PBU}_3+5\text{H}]^+$, 441.3 $[\text{M}-$
6 $2\text{PBU}_3+4\text{H}+\text{Na}]^+$, 619.6 $[\text{M}-\text{PBU}_3+3\text{H}]^+$ and 657.4 $[\text{M}-\text{PBU}_3+2\text{H}+\text{K}]^+$ m/z, illustrating the
7 splitting of trialkylphosphine groups.
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16 *Thermal stability*

17 Since many CN_x materials were produced via solid state thermolysis techniques,^[1f,25]
18 the thermal behaviour of hydrazine derivatives **1** and **2** is of considerable interest. In order to
19 examine the thermal stability of compounds **1** and **2** thermogravimetric analyses were
20 performed. The TG curve of **1** shows two successive steps in the temperature range 20-900°C
21 with finally complete decomposition of the sample (Figure 2a). The first mass loss, which was
22 attributed to evaporation of the residual water, occurs between 30 and 290°C and comprises
23 2.8 %. It is followed by a very steep weight loss at 294°C, which illustrates a rupture of N–N
24 bonds of the hydrazine groups. During this endothermic process 18 % of the mass are lost,
25 matching well with calculated value for three NH_3 molecules (19.4 %). The region between
26 310 and 700°C represents a smooth slope of the TG curve, illustrating further condensation
27 accompanied by NH_3 formation and decomposition of the heptazine ring. The mass
28 degradation is an endothermic process, with a minimum of the DTA curve at 697°C.
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39 The TG curve of **2** (Figure 2b) exhibits three successive steps. Contrary to **1**, the first
40 mass loss appears already at 87°C and comprises 15 %. This strongly endothermic process
41 can be related to evaporation of three water molecules ($3 \text{H}_2\text{O} = 14 \%$). The next step at
42 226°C is due to the elimination of HCl, with experimental TG data (18.8 %) corresponding to
43 two HCl molecules (18.7 %). Furthermore, compound **2** keeps losing weight from 230 to
44 700°C, showing an endothermic character of the DTA curve. The process terminates,
45 similarly to **1**, between 700 and 900°C, indicating complete decomposition of the sample. The
46 temperature range for the heptazine ring decomposition, which in both cases takes place
47 between 500 and 700°C, is in agreement with data reported for related s-heptazine
48 compounds.^[26,27,28]
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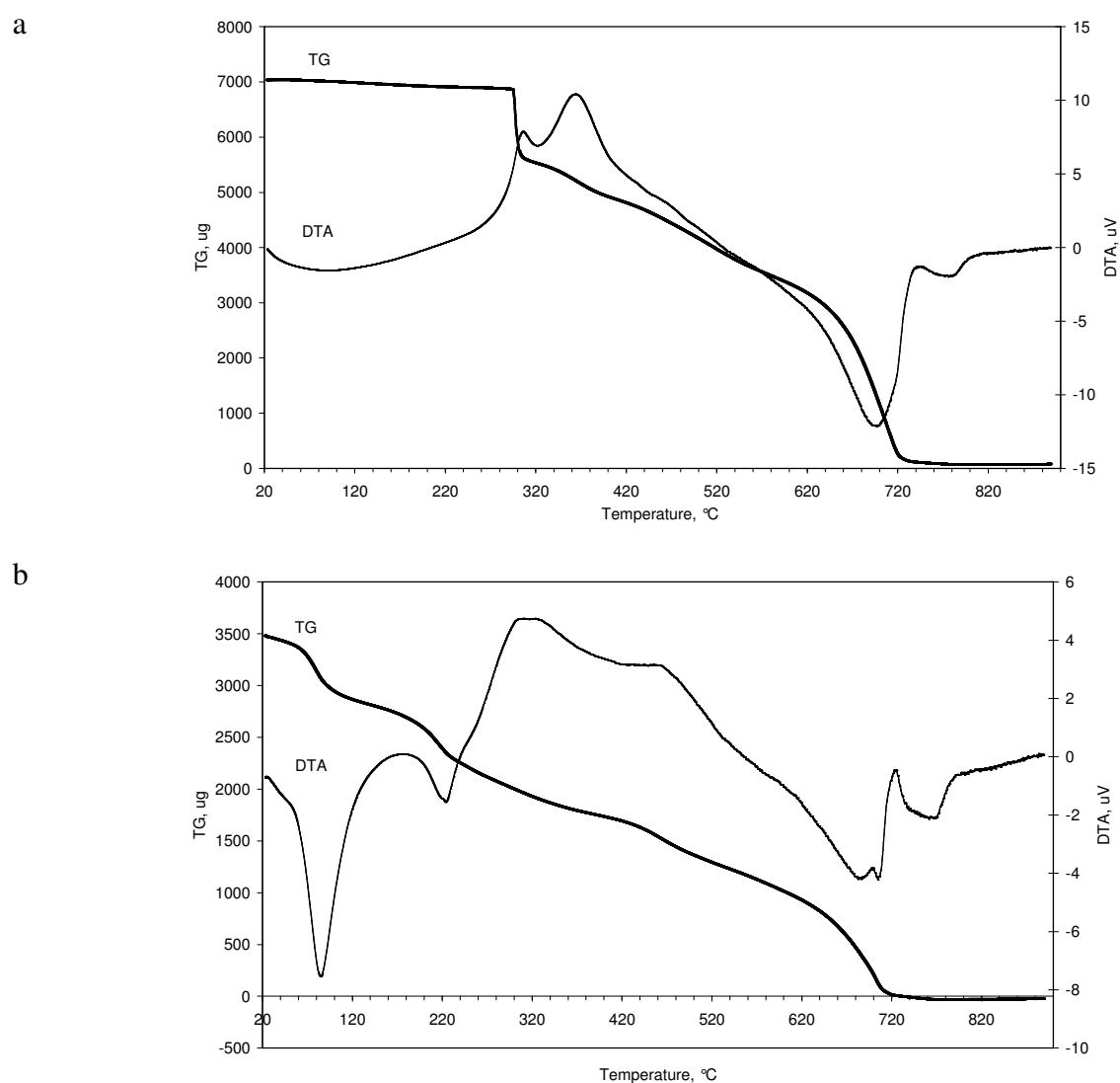


Figure 2. TG and DTA plots of (a) 2,5,8-trihydrino-s-triazine **1** and (b) 2,5,8-trihydrino-s-triazine hydrochloride **2**.

X-ray diffraction data

Details of the crystal parameters, data collection and structure refinement for **2** are listed in the Experimental Part. Compound **2** crystallizes in the triclinic space group *P*-1 with five water molecules per asymmetric unit. All H-atoms were localized from residual electron density and refined isotropically. The water molecule O5 is disordered over two sites with a population ratio 83 to 17 %.

Compound **2** consists of the cationic unit $[\text{C}_6\text{N}_7(\text{NHNH}_3)_3]^{3+}$ and three chloride anions (Figure 3a). The cationic unit is linked to adjacent anions and to neighbour cations by several hydrogen bonds of the types N–H \cdots Cl and N–H \cdots N, respectively. Additionally, the cations and anions are surrounded by water molecules, forming several N–H \cdots O and O–H \cdots Cl

hydrogen bridges. Parameters of the hydrogen bonding are summarized in Supplementary Material, Table S1.

The hydrogen bonding between hydrazine-*s*-heptazine units is shown in Figure 3b. Similar interaction between amino-substituents and *s*-heptazine cores was reported for melem (2,5,8-triamino-*s*-heptazine).^[7] The crystal structure of **2** represents a layered structure with an AB order, while an interaction between the layers occurs via the above mentioned hydrogen bridges to chloride ions and water molecules. The molecules of A and A' layers are situated directly one above another with a distance of about 6 Å.

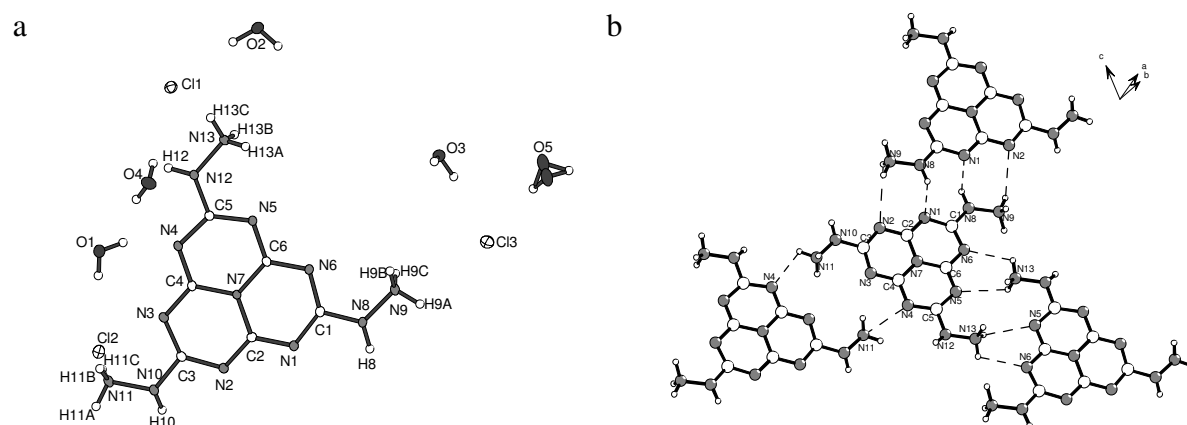


Figure 3. (a) Molecular structure and the atom numbering scheme of trihydrazino-*s*-heptazine trihydrochloride pentahydrate **2** (thermal ellipsoids at 50 % probability level) and (b) intermolecular hydrogen bonds between cations $[(C_6N_7(NHNH_3)_3)]^{3+}$ in **2** (the chlorine atoms and water molecules are omitted for clarity).

The heptazine motif is almost planar: the sums of corresponding NCN and CNC angles are nearly equal to 360°. A slight distortion of hexagon rings, as well as their structural parameters are similar to those in triazido-tri-*s*-triazine,^[6] melem,^[7] melonates,^[29] tri-*s*-triazine^[30], cyamelurates,^[27] cyameluric acid^[31] and its esters^[32] and amides^[33] as well as trichloro-tri-*s*-triazine.^[4,5]

The three NH₂-groups lie almost in the same plane with the heptazine ring, with a maximum deviation of the N_{hydraz.} atoms from the plane of 0.186(1) Å. The exocyclic C–N bonds are slightly longer than those in melem (1.35 Å vs 1.32 Å), but their bond lengths are in agreement with the typical value reported for C_{ar}–NH(sp²): 1.355 Å.^[34]

The torsion angles between hydrazine-substituents N9–N8…N12–N13, N9–N8…N10–N11 and N11–N10…N12–N13 are of 3.92(8)°, 11.82(21)° and 154.71(13)°, respectively. The

N–N bond lengths in the hydrazine groups of **2** (average 1.415 Å) exhibit similar values as reported for $R_3N^+–NR_2$ (1.414 Å).^[34] Comparable bond lengths were found for the corresponding triazine derivative as well (1.409 Å).^[12]

Table 1. Selected bond lengths (Å) and bond angles (°) of compound **2**.

Bond lengths, (Å)		Bond angles, (°)	
N1-C2	1.322(1)	C2-N1-C1	116.20(9)
N1-C1	1.339 (1)	C2-N2-C3	115.75(9)
N2-C2	1.324(1)	C4-N3-C3	115.35(9)
N2-C3	1.340(1)	C4-N4-C5	115.55(9)
N3-C4	1.330(1)	C6-N5-C5	115.97(9)
N3-C3	1.336(1)	C6-N6-C1	115.30(9)
N4-C4	1.323(1)	C6-N7-C4)	120.26(8)
N4-C5	1.343(1)	C6-N7-C2	119.48(8)
N5-C6	1.329(1)	C4-N7-C2	120.22(8)
N5-C5	1.334(1)	C1-N8-N9	120.85(9)
N6-C6	1.325(1)	C5-N12-N13	117.65(9)
N6-C1	1.345(1)	N1-C1-N8	113.76(9)
N7-C6	1.391(1)	N1-C1-N6	128.26(9)
N(7)-C(4)	1.400(1)	N(8)-C(1)-N(6)	117.98(9)
N(7)-C(2)	1.401(1)	N(1)-C(2)-N(2)	120.65(9)
N(8)-C(1)	1.342(1)	N(1)-C(2)-N(7)	119.83(9)
N(8)-N(9)	1.411(1)	N(2)-C(2)-N(7)	119.52(9)
N(10)-C(3)	1.352(1)	N(3)-C(3)-N(2)	129.27(9)
N(10)-N(11)	1.417(1)	N(3)-C(3)-N(10)	117.58(9)
N(12)-C(5)	1.354(1)	N(2)-C(3)-N(10)	113.12(9)
N(12)-N(13)	1.416(1)	N(4)-C(4)-N(3)	120.42(9)
N(8)-H(8)	0.87(2)	N(4)-C(4)-N(7)	119.80(9)
N(9)-H(9A)	0.90(2)	N(3)-C(4)-N(7)	119.78(9)
N(9)-H(9B)	0.96(2)	N(5)-C(5)-N(4)	128.69(9)
N(9)-H(9C)	0.88(2)	N(5)-C(5)-N(12)	117.22(9)
		N(4)-C(5)-N(12)	114.08(9)
		N(6)-C(6)-N(5)	119.79(9)
		N(6)-C(6)-N(7)	120.70(9)
		N(5)-C(6)-N(7)	119.49(9)

Conclusions

Compound **1** and its hydrochloride **2** were obtained from melem or melon and hydrazine in satisfactory yield. These air stable species were characterized by means of NMR and FTIR spectroscopy as well as by X-ray diffraction (**2**), showing the typical structural and spectroscopic characteristics of heptazine derivatives. By treatment of **1** with NaNO₂ in HCl solution triazido-s-heptazine **3** was obtained. This procedure significantly simplifies the synthesis of **3**, which in turn has been used as a building block for carbon nitride materials^[35] and for the synthesis of heptazine-based iminophosphanes.^[18,20] Compound **4**, tris(triⁿbutylphosphinimino)-s-heptazine, has been synthesised and characterized spectroscopically to illustrate applicability of **3** as a useful starting material for the Staudinger reaction.

Experimental Section

Reagents and instrumentation

All chemicals were used in p.a. quality as obtained from the suppliers. 2,5,8-triamino-s-heptazine (melem) was synthesized according to a published procedure.^[26] In brief, preparation of melem was performed by annealing melamine at 345°C under ambient atmosphere for two days. Melon was obtained in crude form from Durferrit GmbH (Hanau, Germany) and purified either by annealing and/or extraction of impurities with water. Melem, melon as well as melem-melon mixtures were dried in air at 140 °C for 10 h. The identity and purity of both starting materials were checked using elemental analyses, FTIR-spectroscopy, powder XRD and thorough solid state ¹³C- and ¹⁵N-NMR studies.

The synthesis was performed in a self-constructed steel autoclave (wall thickness of about 1 cm) equipped with a Teflon lining of about 1 cm thickness (V = 35 ml).

The solution ¹³C NMR spectra were recorded on an Inova 400 (400 MHz) Varian spectrometer at 300 K (University of Konstanz). The chemical shifts are reported relative to TMS. Solid-state ¹⁵N and ¹³C CP/MAS NMR spectra were measured with a conventional impulse spectrometer DSX Avance 400, Bruker.

FTIR spectra were recorded in a range from 400 to 4000 cm⁻¹ at room temperature using Nicolet 380, Varian 3100 (TU Freiberg) and Perkin Elmer (Konstanz) FTIR spectrometers. The Raman spectra were recorded on a Bruker RFS 100/S, Neodym YAG Laser instrument. Thermogravimetry measurements were performed using a TG/DTA (Seiko

Instruments) with a heating rate of 10 K / min, argon flowing rate of 300 ml/min, maximum temperature 900°C.

Elemental analyses were performed with the “vario Micro cube”, Elementar (TU Freiberg) and CHN-O-Rapid, Heraeus (University of Konstanz) elemental analyzers.

MALDI-TOF spectra were recorded using Kompact MALDI II, Kratos Analytical spectrometer (University of Konstanz).

Titration experiments for determination of chlorine contents were performed according to Mohr's method at room temperature. A digital pH-meter MV 870 was used. The endpoint was determined potentiometrically using an Ag-sensitive electrode and a normal pH electrode. 0.1N AgNO₃ solution was used for titration. Samples (~ 0.6 g) were dissolved in 100 ml of diluted H₂SO₄ (~ 2 %). Aliquots of 10 ml were used for titration.

2,5,8-trihydrazino-s-heptazine (1)

20 ml (0.5 mol) of 80 % hydrazine solution in water and 3.2 g (0.015 mol) of melem were mixed in a 35 ml Teflon lined autoclave. The tightly closed set-up was placed in a drying oven and heated up to 140 °C. After 24 h at this temperature the autoclave was cooled down to room temperature and the obtained yellowish, ammonia-smelling suspension was placed in a 100 ml beaker. To this suspension a 10 % solution of HCl was added until the pH of the solution was between 1 and 2. By the following filtration of the mixture the unreacted solid residue was separated and the filtrate was treated with 10 % NaOH solution. The product was precipitated at a pH value of the solution of 7.5 – 8.5 and washed with water. The obtained solid was dissolved in 10 % HCl again (pH = 1), filtered once more, and precipitated with NaOH-solution (pH = 8). This procedure was repeated three times, and then the yellowish solid was washed with ethanol and dried under vacuum. Yield: 1.9 g, 47 %. The same route was performed with melon as well as melon-melem mixtures, giving the 2,5,8-trihydrazino-s-heptazine **1** with a similar yield.

NMR (CP/MAS, ppm): ¹³C: 164.2, 162.2, 154.5. ¹⁵N: -207.0, s; -223.3, s; -233.3, s; -256.4, s; -320.1.

IR (KBr): 3305(w), 3153(m), 3032(m), 2917(m), 1636(s), 1509(s), 1391(s), 1327(m), 1188(w), 1129(w), 1107(w), 1001(w), 790(m), 723(w), 650(w), 497(w).

Raman: 3230 (m, broad), 2896 (w), 2459 (w), 1620 (s), 1530 (m), 1400 (m), 1298 (m), 1232 (m), 1170 (m), 1131 (m), 1004 (m), 802 (w), 742 (m), 694 (m), 609 (w), 575 (m), 532 (w), 489 (s), 432 (m), 396 (m), 350 (m), 186 (s), 106 (s).

Elemental analysis calcd. (%) for $C_6H_9N_{13}$: C 27.38, H 3.45, N 69.18; found: C 31.82, H 2.66, N 68.25.

Potentiometric titration: Cl^- was not detected.

2,5,8-trihydrazino-s-heptazine hydrochloride (2)

500 mg (1.9 mmol) of 2,5,8-trihydrazino-s-heptazine **1** were dissolved in ~ 15 ml of 10 % HCl by slight heating. The solution was cooled down to room temperature within several hours. Single crystals suitable for X-ray analysis were obtained. The precipitate was filtered off and dried between two sheets of filter paper at room temperature.

Yield (calculated for average HCl content: 2,5,8-trihydrazino-s-heptazine dihydrochloride): 519 mg (81 %).

NMR (CP/MAS, ppm): ^{13}C : 165.3, 163.4, 162.1, 154.1; ^{15}N : -206.7, -233.8, -252.4, -318.2.

^{13}C NMR (10 % HCl, ppm): 163.5, s; 156.3, s.

IR (KBr): 3420(s), 3200 – 2800 (s), 2660 (s), 1660 (vs), 1620 (vs), 1550 (vs), 1480 (vs), 1400 (vs), 1290 (s), 1230 (s), 1180 (s), 988 (m), 875 (m), 812 (s), 638 (m).

Raman: 2893 (w), 1656 (m), 1562 (m), 1527 (m), 1485 (m), 1391 (w), 1360 (w), 1299 (w), 1185 (m), 1096 (w), 1069 (m), 977 (m), 747 (m), 686 (m), 644 (w), 524 (m), 483 (w), 436 (m), 389 (m), 344 (m), 281 (m), 226 (m), 119 (s).

Elemental analysis calcd. (%) for $[C_6N_7(NHNH_3)_3]Cl_3 \cdot 4H_2O$, $C_6H_{20}N_{13}O_4Cl_3$: C 16.21, H 4.53, N 40.95; found: C 16.20, H 3.61, N 40.75.

Potentiometric titration: depending on drying conditions (air humidity, temperature) and sample age (from 5 days to several month) the chloride content varies between 1 and 3 HCl molecules per one $C_6N_7(NHNH_2)_3$ unit. The higher the temperature and the longer the time of drying, the less HCl content was found.

2,5,8-triazido-s-heptazine (3)

500 mg (1.9 mmol) of compound **1** were dissolved in 20 ml 10 % HCl and this solution was slowly dropped to a 5°C cold solution of 655 mg (9.5 mmol) of $NaNO_2$ in 10 ml of 10 % HCl. The reaction mixture was stirred in a light-protected flask for 3 hours. A precipitate formed, which was filtered off, washed with water and ethanol and dried in vacuum at 90 – 100°C. Yield: 340 mg, 60.5 %.

IR (KBr): 2500 (w), 2400 (w), 2280 (w), 2220 (m), 2170 (m), 2140 (m), 2120 (m), 1606 (vs), 1530 (s), 1537 (vs), 1250 (s), 1170 (m), 1110 (m), 1090 (m), 819 (m), 721 (m), 651 (w), 549

(w). These data as well as the ^{13}C NMR spectra determined in acetone- d_6 correspond well with the data reported in [6].

*Tris(tri-*n*-butylphosphinimino)-*s*-heptazine (4)*

Route A: To a solution of 300 mg (1 mmol) of **3** in DMSO 0.85 ml (3.4 mmol) of tri-*n*-butylphosphine was added dropwise. During addition the mixture changes its color to orange and gas liberation (N_2) was observed. The orange solution was stirred for 14 h. A precipitate, which formed at the interphase between DMSO and phosphine, was filtered off, washed with DMSO and dried under vacuum. The product was recrystallized from THF. Yield: 0.53 g, 65 %.

Route B: 400 mg (1.35 mmol) of **3** were carefully powdered and dissolved in DMF. To the yellow solution 1.1 ml (4.3 mmol) of tri-*n*-butylphosphine were added dropwise under stirring. During addition gas liberation and change of color to orange was observed. The mixture was stirred until N_2 evolution stopped. Thereafter DMF was removed under vacuum at 60°C and the white solid was isolated. Yield: 0.78 g, 71 %.

NMR (400MHz, DMSO, ppm): ^{13}C : 13.5 (s, $-\text{CH}_3$); 23.3 (d, $-\text{CH}_2-(\text{CH}_3)$); 23.5 (d, $-\text{CH}_2-(\text{CH}_2)$); 27.0 (d, $-\text{CH}_2-(\text{P})$); 154.7 (s, $\text{C}_{\text{hept.}}$); 164.4 (s, $\text{C}_{\text{hept.}}$); ^1H : 0.83 (t, $-\text{CH}_3$); 1.32 (m, $-\text{CH}_2\text{CH}_2-(\text{CH}_3)$); 1.52 (m, $-\text{CH}_2-(\text{P})$); ^{31}P : 47.43 (s).

IR (KBr, cm^{-1}): 2956 (s), 2867 (m), 1617 (vs), 1558 (w), 1437 (vs), 1398 (vs), 1296 (m), 1219 (w), 1138 (w), 1011 (w), 911 (w), 809 (m).

Elemental analysis, %: calcd. for $\text{C}_{42}\text{H}_{81}\text{N}_{10}\text{P}_3$: C 61.59, N 15.84, H 9.97; found: C 59.24, N 17.10, H 9.67.

MALDI-TOF: m/z : 657.4 (18 $[\text{M}-\text{PBu}_3+2\text{H}+\text{K}]^+$), 619.6 (100 $[\text{M}-\text{PBu}_3+3\text{H}]^+$), 441.3 (17 $[\text{M}-2\text{PBu}_3+4\text{H}+\text{Na}]^+$), 419.2 (100 $[\text{M}-2\text{PBu}_3+5\text{H}]^+$).

X-ray analysis

2,5,8-trihydrazino-*s*-heptazine trihydrochloride pentahydrate **2**: $\text{C}_6\text{H}_{22}\text{Cl}_3\text{N}_{13}\text{O}_5$, $M_r = 462.72$, colourless crystal, $0.40 \times 0.24 \times 0.10$ mm, triclinic space group *P*-1, $a = 6.7496(3)$ Å, $b = 12.1417(6)$ Å, $c = 12.7215(6)$ Å, $\alpha = 66.288(2)^\circ$, $\beta = 75.153(2)^\circ$, $\gamma = 80.420(2)^\circ$, $V = 920.30(8)$ Å³, $Z = 2$, $\rho_{\text{calcd.}} = 1.670$ mg/m³, $\Theta_{\text{max}} = 33^\circ$, $F(000) = 480$, $\mu = 0.551$ mm⁻¹, absorption correction: semi-empirical from equivalents, $\lambda = 0.71073$ Å, $T = 90(2)$ K, 32575 recorded reflections ($-10 \leq h \leq 10$, $-18 \leq k \leq 18$, $-19 \leq l \leq 19$), 6755 unique reflections, 336 parameters, $R_1 = 0.0314$, $wR_2 = 0.0895$ ($I > 2\sigma(I)$), $R_1 = 0.0393$, $wR_2 = 0.0934$ (all data), residual electron density (highest peak and deepest hole) 0.894 and -0.545 eÅ⁻³.

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3 Crystallographic data for the structure reported in this paper have been deposited with the
4 Cambridge Crystallographic Centre as supplementary publication no. CCDC-737044. Copies
5 of the data can be obtained free of charge on application to CCDC, 12 Union Road,
6 Cambridge CB2 1EZ, UK. [Fax: (internat.) +44-1223/336-033; E-mail:
7 deposit@ccdc.cam.ac.uk].
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