DOI: 10.1002/asia.200700372

Synthesis and Structure of Monomeric, Trimeric, and Mixed Phenylcyanamides

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Abstract: In a new synthetic approach phenylcyanamide (Hpca) was synthesized by methylation of phenylthiourea followed by a basic work-up. All products along the synthetic route have been fully characterized by means of NMR, IR, and X-ray studies. The first structural report of neutral mixed crystals of phenylcyanamide containing monomeric and trimeric Hpca is presented. Examination of these intriguing mixed crystals revealed the formation of distinct layers of monomeric and trimeric Hpca. These layers are interconnected by weak hydrogen bonds. The trimer represents triphenylisomelamine, which readily isomerizes to the triphenylmelamine in the melt, in accord with computations at the B3LYP level, indicating an exothermic process ($\Delta H = -49.4$ kcal mol^{-1}). Pure trimeric Hpca (triphenylisomelamine) was obtained either by recrystallization of the mixed crystals from boiling water or by trimerization of monomeric Hpca in isopropanol for 12 h under reflux conditions. For comparison tritylcyanamide (Htca) and potassium phenylcyanamide as an [18]crown-6 complex [K([18]crown-6)pca] have been synthesized, and the solid-state structures were determined using X-ray diffraction techniques. The thermal behavior was studied by thermo-analytical experiments. In agreement with the experimental results, computations predict an exothermic cyclotrimerization process for Hpca ($\Delta H = -41.3$ kcal mol^{-1}).

Keywords: cyanamides · cyclotrimerization · isomerization · nitrogen heterocycles · structure elucidation

Introduction

As early as 1854, Cahours and Cloëz reported on cyananilide, nowadays better known as phenylcyanamide (Hpca).[1] Phenylcyanamide derivatives can be readily prepared in high yields from the corresponding anilines.[2] In a typical synthesis an aniline is treated with ammonium thiocyanate to form the thiourea,[3] which is then desulfurized using lead(II) acetate to form the phenylcyanamide derivative.[4] Other researchers have synthesized phenylcyanamides by the reaction of phenylisocyanide dihalides with ammonia,[5] or by the reaction of anilines with cyanogen bromide.[6] Scheme 1 summarizes these three common synthetic routes to phenylcyanamide derivatives.

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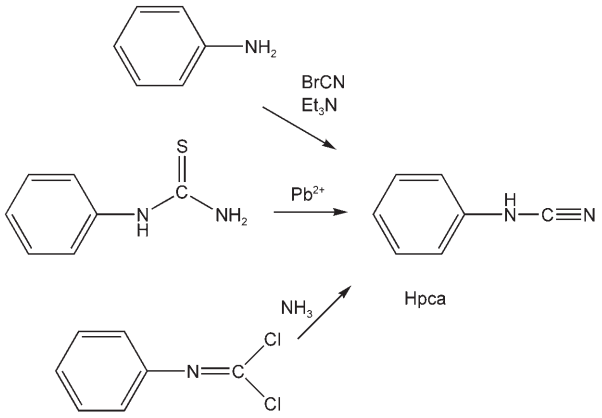
Supporting information for this article, including CIF files for all crystal structures, DSC data, and experimental details, is available on the WWW under http://www.chemasianj.org or from the author.



Scheme 1. Synthetic routes to phenylcyanamide.

Phenylcyanamides can be recrystallized in high yields from boiling acetone/water solutions. The usual procedure is to dissolve phenylcyanamides in boiling acetone and to add water until the solution just becomes cloudy while maintaining the temperature. Crystals of the product are formed from the cooling solution. Methanol and ethanol have been used in place of acetone with good results in some instances.[7] This procedure works well for substituted phenylcyanamides, while the parent phenylcyanamide tends to oligomerize under these conditions.

Cyano compounds are frequently used as starting material for the synthesis of dyes, heterocycles, organic superconductors, functional materials, etc.[8] One reason for this wide spectrum of applications is the tendency of cyano compounds to oligomerize.[9] For instance the oligomerization of cyanogen derivatives, particularly to trimers containing the 2,4,6-triazine ring system, is well known and has been studied intensively. While cyanamide H_2CN_2 is condensed easily to cyanoguanidine under a variety of conditions, the action of heat on cyanamide under pressure results in the formation of the trimer, melamine $C_3N_3(NH_2)_3$. Monomeric phenylcyanamide (m.p. 38–39 °C)[10] polymerizes slowly in any solvent and in the melt.

Although phenylcyanamide has been known for more than one century, detailed information about its crystal structure, the crystal structure of its trimer, and the isomerization process has not been available except from theoretically obtained data.[11] While metal complexes with the ambidentate phenylcyanamide anion have been discussed thoroughly,[7] no structural data of the neutral phenylcyanamide (Hpca) either as a neutral ligand in complexes or without a metal as a monomer or trimer have been published to the best of our knowledge.

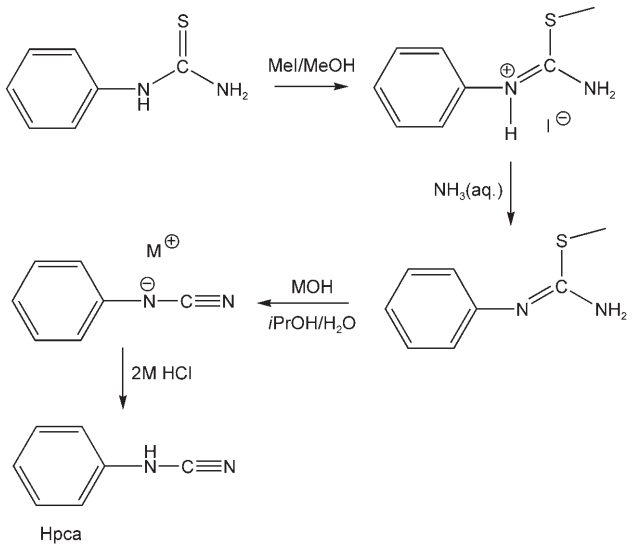
Herein we report on a new phenylcyanamide synthesis starting from phenylthiourea that avoids desulfurization using lead(II) acetate. Moreover, the crystal structures of monomeric (neutral and ionic) and trimeric phenylcyanamide as well as the structure of an intriguing mixture (monomer and trimer in one crystal) of phenylcyanamide are discussed for the first time.

Abstract in German: Eine neue Synthese für Phenylcyanamid (Hpca) wird vorgestellt. Hpca wurde durch Methylierung von Phenylthioharnstoff und anschließender basischer Aufarbeitung in großen Ausbeuten dargestellt. Alle Zwischenstufen wurden vollständig charakterisiert. Die erste Kristallstruktur eines gemischten Cyanamides, welches sowohl die monomere Spezies als auch das Trimere in einem Kristall aufweist, wird diskutiert. Diese Untersuchungen zeigen das Vorliegen von ausgeprägten Monomeren- bzw. Trimeren-Schichten, die durch schwache H-Brücken miteinander verknüpft sind. In Einklang mit B3LYP-Rechnungen konnte gezeigt werden, dass das trimere Triphenylisomelamin in der Schmelze leicht zum Triphenylmelamin exotherm isomerisiert ($\Delta H = -49.4$ kcal mol^{-1}). Reines trimeres Hpca (Triphenylisomelamin) erhält man durch Umkristallisation der Mischkristalle aus siedendem Wasser oder durch Trimerisierung von monomerem Hpca in Isopropanol. Für Vergleichszwecke wurden ebenfalls Tritylcyanamid (Htca) und Kaliumphenylcyanamid als [18]Krone-6 Komplex [K([18]Krone-6)pca] synthetisiert und kristallisiert. Das thermische Verhalten der Isomerisierung und Trimerisierung wurde in DSC-Experimenten untersucht. Im Einklang mit den experimentellen Ergebnissen wurde quantenmechanisch eine exotherme Cyclotrimerisierung für Hpca ($\Delta H = -41.3$ kcal mol^{-1}) gefunden.

Results and Discussion

Synthesis

The most frequently used methods to generate phenylcyanamide are 1) the reaction of aniline and BrCN and 2) the desulfurization of phenylthiourea using lead(II) acetate. Only recently Wong et al. described a one-pot transformation of phenylisocyanate to phenylcyanamide by use of sodium bis(trimethylsilyl)amide as a deoxygenating agent.[12] To avoid the use of larger amounts of hazardous lead(II) salts or very toxic BrCN, a new approach starting with the methylation of phenylthiourea[13] followed by a basic work-up has been introduced by us (Scheme 2). Methylation leads to crystalline



Scheme 2. New synthesis of phenylcyanamide via methylation of phenylthiourea.

N-phenyl-*S*-methylisothiouronium iodide (Figure 1),[14] and subsequent addition of aqueous ammonia gives the free S-methylated isothiourea species, *N*-phenyl-*S*-methylisothiourea[15] (Figure 2). Now the whole series of alkali phenylcyanamides (Mpca) can be isolated in high yields by treatment of *N*-phenyl-*S*-methylisothiourea with an appropriate base, for example, MOH (M = alkali metal) in isopropanol, as illustrated in Scheme 2. Differential scanning calorimetry (DSC)

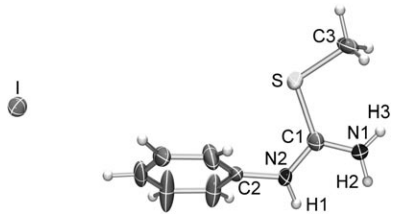


Figure 1. ORTEP drawing of the molecular structure of *N*-phenyl-*S*-methylisothiouronium iodide. Thermal ellipsoids with 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: C3–S 1.800(6), C1–S 1.739(5), C1–N1 1.307(7), C1–N2 1.329(7), N2–C2 1.437(6); C1–S1–C3 102.6(3), C1–N2–C2 127.8(5), N1–C1–N2 119.0(5), N1–C1–S 122.3(4), N2–C1–S 118.6(4).

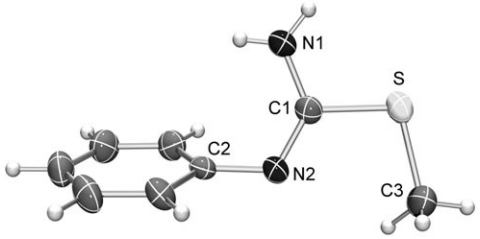


Figure 2. ORTEP drawing of the molecular structure of *N*-phenyl-*S*-methylisothiourea. Thermal ellipsoids with 50% probability at 200 K. Selected bond lengths [Å] and angles [°]: C3–S 1.789(2), C1–S 1.775(2), C1–N1 1.348(2), C1–N2 1.288(2), N2–C2 1.426(2); C1–S–C3 102.5(1), C1–N2–C2 118.2(2), N2–C1–N1 127.5(2), N2–C1–S 121.5(1), N1–C1–S 111.1(1).

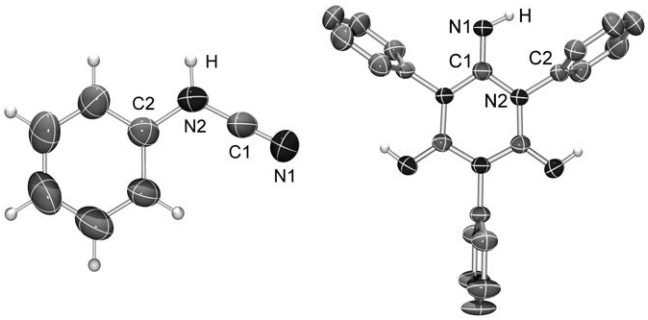


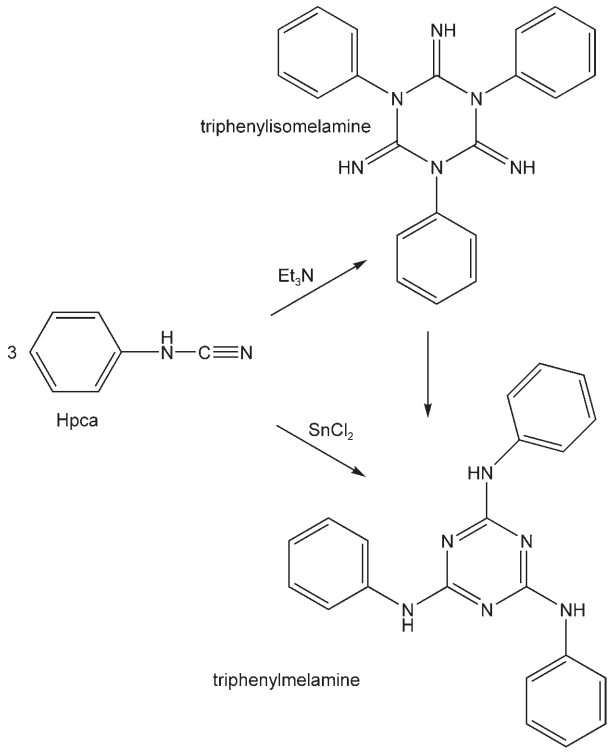
Figure 3. ORTEP drawing of the molecular structure of monomeric (links) and trimeric (right) Hpca (triphenylisomelamine) units in the mixed crystal. Thermal ellipsoids with 50% probability at 200 K (phenyl hydrogen atoms in the trimer omitted for clarity).

investigations showed that both sodium and potassium phenylcyanamide decompose above 300 °C (Na: 338 °C; K: 345 °C) without trimerization. However the cesium salt melts at 209 °C, but again no trimerization occurs, even upon further heating.

Protonation of Mpca with aqueous HCl yields the labile parent molecule phenylcyanamide (Hpca). This reaction should be carried out at temperatures not greater than 25 °C, and the final precipitation of the cyanamide should be performed as quickly as possible. Hpca is very labile with respect to cyclotrimerization and, hence, we did not succeed in isolating pure Hpca. The isolated Hpca was always contaminated with traces of oligomers. The amount of trimeric impurities clearly depends on the reaction time of the protonation reaction with HCl. As soon as Hpca is dissolved in organic solvents, trimerization can be observed even at ambient temperatures. According to a Beilstein search the published melting points of Hpca lie in the range 38–50 °C.[10,16] However, already in 1908 Baum reported on the instability of Hpca with respect to trimerization even at ambient temperatures or upon removal of solvent.[17] In agreement with Baum, we were not able to find a distinct melting point for Hpca by means of DSC.

Cyclotrimerization/Isomerization

In 1885, Hofmann obtained ethylcyanamide from the reaction of HgO (PbO) with ethylthiourea, and reported that the ethylcyanamide thus obtained trimerizes readily to triethylisomelamine.[18] Also, trimerization and isomerization of Hpca have been studied intensively.[19,20] Korshak et al. reported that, depending on the cyclotrimerization conditions, two isomeric forms of trimeric Hpca can be obtained (Scheme 3): Cyclization at 80–100 °C in the presence of a



Scheme 3. Trimerization and isomerization of Hpca.

Lewis base such as Et_3N gave triphenylisomelamine (83%), while addition of a Lewis acid ($SnCl_2$) yielded triphenylmelamine (76%). Moreover, trimerization in pure alcohols seems to slow down the conversion.

Similar to Hofmann's procedure,[18] we carried out the trimerization of Hpca and allowed it to stand at ambient temperature in isopropanol. After seven days colorless crystals (m.p. 169 °C) were obtained. Surprisingly, the melting point of 169 °C did not agree with that of triphenylisomelamine (214–215 °C; compare monomeric Hpca: 38–39 °C).[20] X-ray studies revealed the formation of intriguing mixed crystals of monomeric and trimeric Hpca with a monomer/trimer ratio of 2:1 (Figures 4 and 5). This ratio was confirmed by

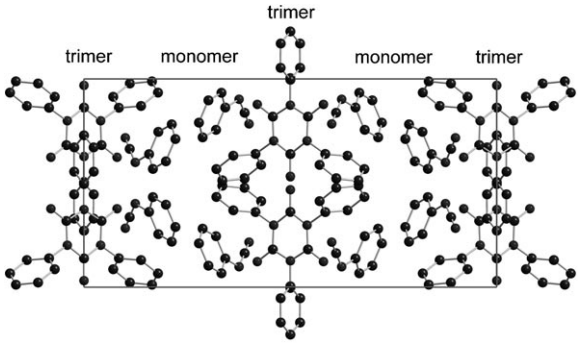


Figure 4. Cell of mixed crystals of Hpca (view along the *c* axis).

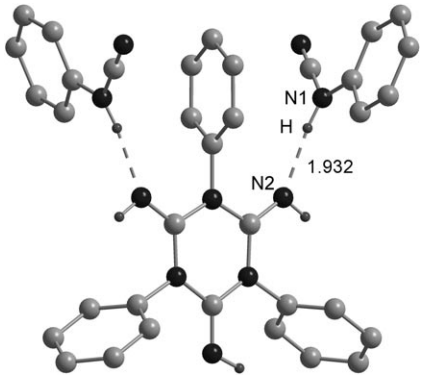


Figure 5. Hydrogen bonds between monomeric and trimeric Hpca (view along the *c* axis). Selected separations [Å] and angles [°]: N1···N2 2.817, N1–H 0.890; N1–H–N2 173.1.

^{1}H NMR spectroscopy (Experimental Section). Obviously, monomeric Hpca is stabilized by cocrystallization with trimeric Hpca (triphenylisomelamine, Scheme 3). Thus, cocrystallization prevents Hpca from further trimerization (see X-ray Crystal Structures section).

To separate monomeric from trimeric Hpca, mixed crystals of Hpca were dissolved in boiling water. After stirring for 5 min at this temperature trimeric Hpca goes into solution while monomeric Hpca remains undissolved. After filtration and cooling to 0 °C, pure trimeric Hpca (triphenylisomelamine) crystallizes from the aqueous solution (m.p. 212 °C). Another route to separate the monomeric from the trimeric species is the treatment of mixed crystals of Hpca with diluted HCl and subsequent basic work-up with aqueous ammonia. Basic triphenylisomelamine dissolves in diluted HCl, while monomeric Hpca precipitates. Addition of aqueous ammonia leads to precipitation of pure trimeric Hpca.

The fact that monomeric and trimeric Hpca (two isomers: triphenylisomelamine and triphenylmelamine, Scheme 3) possess the same chemical composition (C 71.17 %, H 5.12 %, N 23.71 %) has led to some confusion in the literature. Mistakenly, triphenylisomelamine has often been described as triphenylmelamine.[21] However, the formation of mixed crystals of Hpca with a melting point of 169 °C has not been observed so far. Interestingly, already in 1885 Hofmann reported on a "triphenylisomelamine" with a melting point of 185 °C which slowly crystallizes from a repeatedly heated solution of Hpca in ethanol,[16a] while Arndt doubted these results in 1911 and claimed that Hofmann's trimeric species is a 2:1 adduct of "triphenylmelamine" and phenylcyanamide.[21] Ever since, there has been no investigation of this cocrystallization problem.

Computations at the B3LYP/6-31G(d,p) level for the gas-phase reaction display an exothermic cyclotrimerization process with an energy gain of -41.3 kcal mol^{-1} (3 Hpca → iso-(Hpca)$_3$). Moreover, these computations also reveal that triphenylmelamine is energetically favored by 49.4 kcal mol^{-1} over the iso form. Indeed, triphenylisomelamine is readily converted into triphenylmelamine (2,4,6-triphenylamino-1,3,5-triazine) at temperatures above its melting point. In solution the isomerization of triphenylisomelamine to triphenylmelamine proceeds under milder conditions as if the reaction was run in bulk.[19] Our DSC study confirms the isomerization of triphenylisomelamine to triphenylmelamine in the melt. The isomerization represents an exothermic process which starts immediately when the melting point (212 °C, compared with m.p. 232–234 °C for triphenylmelamine[22]) of triphenylisomelamine is reached (Figure S3 in the Supporting Information).

In triphenylisomelamine all three phenyl rings are perpendicular relative to the cyanuric ring (Figure 3), and hence no significant resonance can occur. Upon isomerization all three phenyl rings shift to the adjacent exocyclic nitrogen atom with an energy release of 49.4 kcal mol^{-1} to form triphenylmelamine. In triphenylmelamine resonance between all three phenyl rings and the C_3N_3 ring is possible (Scheme 3; Figure S3 in the Supporting Information) since the C_3N_3 and the phenyl rings form a planar molecule (C_{3h} symmetry).[23] Thus, it can be assumed that increasing resonance and decreasing steric strain are the driving forces for the isomerization.

Interestingly, triphenylisomelamine can be distinguished easily from triphenylmelamine by means of mass spectrometry. The most intense peak in the spectrum of triphenylmelamine is the molecular peak, while in the spectrum of triphenylisomelamine the intensity of the molecular peak is only 4 % (100 % for the $C_6H_5^+$ fragment with m/z 77.1, only 10 % in the spectrum of triphenylmelamine), indicating a facile cleavage of $C_6H_5^+$ fragments in triphenylisomelamine.

X-ray Crystal Structures

As far as we know there are no structural data available of neutral phenylcyanamide species. Hence, we would like to focus on the discussion of monomeric (Figures 3, 4, and 5) and trimeric Hpca (Figures 3, 6, and 7) in comparison with the structures of tritylcyanamide and K([18]crown-6)pca. Since we were not able to obtain single crystals of pure Hpca, we prepared and crystallized tritylcyanamide (Htca, Figures 8, 9, and 10). Moreover, to get structural data of ionic phenylcyanamide we prepared the [18]crown-6 complex of Kpca (Figure 11). Crystallographic data of these species are summarized in Table 1 (data for *N*-phenyl-*S*-methylisothiouronium iodide and *N*-phenyl-*S*-methylisothiourea can be found in the Supporting Information).

Mixed crystals of monomeric and trimeric Hpca crystallize in the orthorhomic space group *Pbcn* with eight monomeric and four trimeric molecules (2:1 ratio) in the unit cell. A perspective view of the monomer and trimer is depicted in Figure 3, and selected structural data are listed in Table 2. In agreement with our computations (Figure S4 in the Supporting Information), the monomeric Hpca molecule adopts a *trans* configuration (phenyl group in *trans* position to the terminal N atom) with an almost trigonal-planar amide N atom ($\Sigma(\sphericalangle(N_{amide}))=359.8°$), resulting in a local C_s symmetry for the entire planar moiety. As expected the N1–C1–N2 unit is almost linear with an angle of 178°, while the C1–$N2_{amide}$–C2 angle is close to 120° (122.2(3)°), indicating a formally sp^2-hybridized nitrogen atom. Three different types of C–N bond lengths are observed: 1) a very short bond length with 1.136(5) Å (N1–C1) indicating a triple bond as expected for a cyano group, 2) a medium-sized bond length with 1.331(5) Å (C1–N2) and 3) one longer C–N bond length with d(N2–C2) = 1.409(4) Å (compare Σr_{cov}: (C–N) = 1.47, (C=N) = 1.22, (C≡N) = 1.11 Å).[24] Obviously, the lone pair (p-type atomic orbital) localized at N2 is better delocalized into the cyano group (according to natural bond orbital analysis[25] interaction with the π*-(N1–C1)) than into the phenyl ring, indicating partial double-bond character for the C1–N2 bond. The N2–C2 bond represents a typical single bond with 1.409(4) Å. The structural features of the cyanamide group are comparable to those in dicyanamide salts.[26]

Upon cyclotrimerization the structure and bonding parameters change significantly in Hpca. The main structural motif of the trimer is the well-known C_3N_3 cyanuric ring system. The CN moiety (C_3N_3 ring and exocyclic imino groups including the hydrogen atoms) is almost planar with a deviation from planarity of less than 2°. However, the phenyl groups adopt a propeller-like configuration (dihedral angles about

Table 2. Selected structural data of cyanamides (bond lengths in Å, angles in °).[c]

	Monomeric Hpca (mixed crystal)	Trimeric Hpca (mixed crystal)[b]	Trimeric Hpca[b]	Htca[a]	K([18]crown-6)pca
N1-C1	1.136(5)	1.266(5)	1.264(3)	1.144(3)	1.166(3)
		1.280(4)	1.268(2)		
C1-N2	1.331(5)	1.385(3)	1.394(2)	1.331(3)	1.301(3)
		1.393(3)	1.398(2)		
N2-C2	1.409(4)	1.451(4)	1.452(3)	1.495(2)	1.390(3)
		1.452(5)	1.452(2)		
N1-C1-N2	178.0(5)	119.3(3)	119.5(1)	179.1(3)	173.9(3)
		122.6(2)	122.4(1)		
		125.0(3)	126.0(2)		
C1-N2-C2	122.2(3)	118.6(2)	117.3(1)	121.7(2)	118.8(2)
		116.6(2)	117.6(1)		
N-C-N_{ring}	–	114.8(3)	114.5(1)	–	–
		115.7(3)	115.1(2)		
C-N-C_{ring}	–	124.3(3)	124.5(1)	–	–
		124.8(3)	124.9(2)		

[a] There are four independent Htca molecules in the cell with very similar structural data; hence, only one set is listed. [b] Local symmetry of C_3N_3 is C_2 symmetry. [c] Calculated B3LYP values can be found in the Supporting Information.

Table 1. Crystallographic data.

	Monomeric/trimeric Hpca (mixed crystal)	Trimeric Hpca[b]	Htca[a]	K([18]crown-6)pca
Formula	$C_{35}H_{30}N_{10}$	$C_{21}H_{18}N_6$	$C_{20}H_{16}N_2$	$K(C_{12}H_{24}O_6)C_7H_5N_2$
M_r	590.69	354.41	284.35	420.54
Color	colorless	colorless	colorless	colorless
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	*Pbcn* (60)	*C*2/*c* (15)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a [Å]	23.391(5)	15.674(3)	13.9368(4)	7.9349(3)
b [Å]	11.832(2)	14.061(3)	15.4251(5)	18.7805(9) 14.7125(6)
c [Å]	11.317(2)	9.6597(19)	15.7995(5)	90
α [°]	90.00	90.00	89.092(2)	92.574(2)
β [°]	90.00	125.12(3)	74.857(2)	90
γ [°]	90.00	90.00	72.409(1)	
V [Å^3]	3132.1(10)	1741.4(6)	3117.9(2)	2190.3(2)
Z	4	4	8	4
ρ_{calcd} [g cm^{-3}]	1.253	1.352	1.212	1.275
μ [mm^{-1}]	0.079	0.085	0.072	0.278
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)	200(2)
Reflections collected	22946	9794	49229	6814
Independent reflections	2191	1993	14157	3486
Obsd reflections	2106	1599	6990	2378
R_{int}	0.036	0.049	0.094	0.041
F(000)	1240	744	1200	896
R_1[a]	0.0923	0.0533	0.0628	0.0405
wR_2[b]	0.1569	0.1264	0.1426	0.1033
GooF	1.421	1.136	0.98	1.02
No. parameters/restraints	218	133	809	253
CCDC number	656411	656412	656416	656413

[a] final *R* index [$I > 2\sigma(I)$]. [b] *R* indices (all data).

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75°). Hence, the local symmetry of the trimeric species is decreased to C_2 symmetry. The exocyclic C–N bond lengths with 1.266(5) and 1.280(4) Å, respectively, are significantly shorter than the C–N bond lengths within the C_3N_3 ring (1.38–1.39 Å). The bond lengths and angles within the C_3N_3 ring are comparable to those of other cyanuric derivatives.[27]

Since the crystal contains monomeric as well as trimeric Hpca, the arrangement of both molecular species is of special interest. A view along the *c* axis is shown in Figure 4. Careful investigation of intermolecular interactions revealed no significant π stacking. Presumably, steric repulsion from the propeller-like phenyl groups prevents the molecules from coming closer in the crystal although the trimers and the monomers form layers and the C_3N_3 rings are superimposed (Figure 4). The layers exclusively composed of monomers are always interposed between two layers of trimers and vice versa. Only two close N···N contacts with 2.817 Å were found (Figure 5), indicating a weak hydrogen bond[28] between the amido H atom of the monomeric species and an exocyclic N atom of the cyanuric ring. This homonuclear N–H···N hydrogen bond is almost linear with an angle of 173.1°. Presumably, owing to the absence of N···N contacts within and between the trimer and monomer layers and the lacking of hydrogen bonds between the imino H atoms of the trimer and the nitrogen atoms of the monomer, neither chainlike structures nor sheets can be formed in the crystal in contrast to the situation found in Htca (see below).

Crystals of pure trimeric Hpca (triphenylisomelamine) crystallize in the monoclinic space group *C*2/*c* with four trimeric molecules in the unit cell. A perspective view of the trimer is illustrated in Figure 6. The X-ray study of pure trimeric Hpca revealed very similar structural features as found for the trimer in the mixed crystal (Figure 3). The C–N and C–C bond lengths and all angles do not change much when the pure compound crystallizes. The arrangement of the molecules in the crystal shows differences to the mixed crystal. Again the trimers form layers; however, the C_3N_3 rings are not superimposed anymore, yet they are still parallel to each other. A view along the *c* axis (Figure 7) shows two repeating layers. Neither hydrogen bonds nor considerable π-stacking effects could be observed.

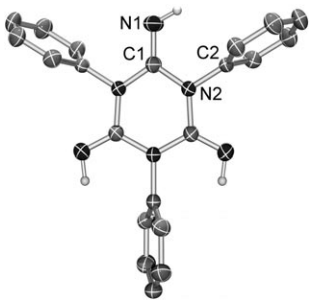

Figure 6. ORTEP drawing of the molecular structure of trimeric Hpca. Thermal ellipsoids with 50% probability at 200 K (phenyl hydrogen atoms omitted for clarity).

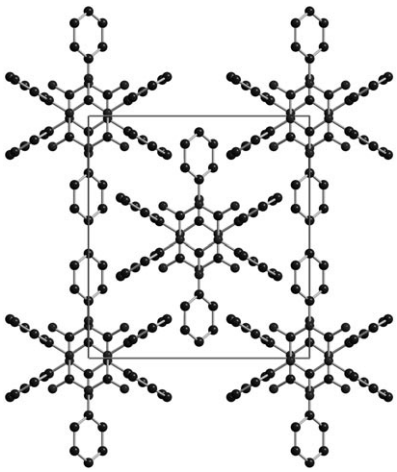

Figure 7. Cell of pure trimeric Hpca (view along the *c* axis).

Tritylcyanamide (Htca) crystallizes in the triclinic space group $P\bar{1}$ with eight molecules in the unit cell; four molecules are crystallographically different. A perspective view of the Htca is depicted in Figure 8, and a view along the *b* axis is shown in Figure 9. Interestingly, apart from the N2–C2 distance, the bond lengths and angles are very similar to those found in monomeric Hpca cocrystallized with its trimer. The N–C2 bond is elongated by 0.086 Å owing to steric strain of the bulky trityl group. A closer investigation of the homonuclear N···N

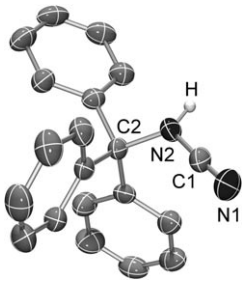

Figure 8. ORTEP drawing of the molecular structure of one of the four independent tritylcyanamide molecules in the crystal. Thermal ellipsoids with 50% probability at 200 K (phenyl hydrogen atoms omitted for clarity).

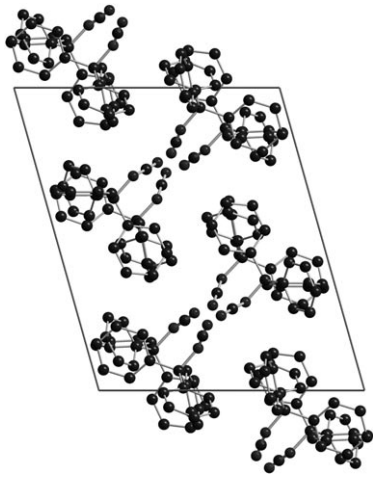

Figure 9. Cell of tritylcyanamide Htca (view along the *b* axis).

contacts shows four different weak hydrogen bonds[28] as illustrated in Figure 10. These contacts are in the range of 2.85–2.94 Å with N−H···N angles between 154 and 157° (*d*-

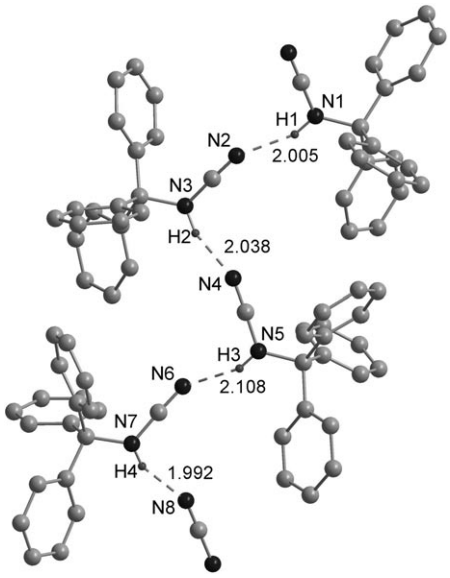

Figure 10. Hydrogen bonds in Htca. Selected distances [Å] and angles [°]: N1···N2 2.875, N3···N4 2.928, N5···N6 2.943, N7···N8 2.850; N1−H1 0.920, N3−H2 0.945, N5−H3 0.885, N7−H4 0.916; N1−H1···N2 157.1, N3−H2···N4 156.3, N5−H3···N6 156.9, N7−H4···N8 154.0.

(N-H) = 1.99–2.11 Å). Contrary to the mixed Hpca (see above) these hydrogen bonds are responsible for a zigzag chainlike structure in the crystal.

K([18]crown-6)pca crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The pca ion is an ambidentate ligand which can coordinate to a metal ion through either the nitrile or the amide nitrogen atom.[7] Astonishingly, only one nitrogen atom (amido N atom) coordinates to the K^+ ion besides the expected coordination of the crown ether oxygen atoms. Thus, as shown in Figure 11, no chainlike structure is observed although phenylcyanamide can also function as bridging ligand. Compared to

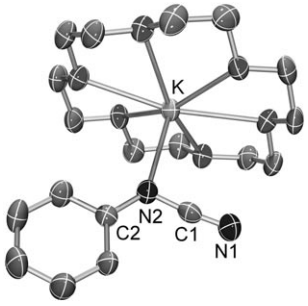

Figure 11. ORTEP drawing of the molecular structure of K([18]crown-6)pca in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: K−N2 2.749(2), N2−C1 1.301(3), C1−N1 1.166(4), N2−C2 1.390(3); N1−C1−N2 173.9(3), C1−N2−C2 118.8(2).

monomeric neutral Hpca, the N1−C1 bond in K([18]crown-6)pca is slightly elongated, while the C1−N2 bond length is decreased by about 0.03 Å.

Conclusions

A new synthetic route to phenylcyanamide has been introduced which avoids the use of hazardous lead(II) salts or very toxic BrCN. This approach starts with the methylation of phenylthiourea followed by a basic work-up. All products along the synthetic route have been fully characterized by means of NMR, IR, and X-ray studies.

For the first time structural data of neutral phenylcyanamide are available. According to X-ray studies the neutral phenylcyanamide cocrystallizes with its trimer. The trimer is triphenylisomelamine, which readily isomerizes to the triphenylmelamine upon heating in solution or in the melt, in accord with computations at the B3LYP level, which indicate an exothermic process.

X-ray studies of the intriguing mixed crystals of Hpca revealed the formation of distinct layers of monomeric and trimeric Hpca, which are connected by weak hydrogen bonds.

Experimental Section

General Information

Phenylthiourea,[13] *N*-phenyl-*S*-methylisothiouronium iodide,[14] *N*-phenyl-*S*-methylisothiourea,[15] and tritylcyanamide[29] were prepared according to the procedures given in the literature; analytical data can be found in the Supporting Information. ^{1}H, ^{13}C{^{1}H}, and ^{14}N{^{1}H} NMR spectra were obtained on a JEOL EX 400 NMR spectrometer or on a JEOL EX 270 NMR spectrometer and were referenced either to protic impurities in the deuterated solvent (^{1}H) or externally to $SiMe_4$ (^{13}C{^{1}H}) or nitromethane (^{14}N{^{1}H}). IR spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer with a DuraSampl*IR*II Diamond ATR sensor from SensIR Technologies. Raman spectra were recorded on a Perkin–Elmer Spectrum 2000 NIR FT equipped with a Nd:YAG laser (1064 nm). CHN analyses were carried out on an Analysator Elementar Vario EL. MS spectra were obtained on a Jeol MStation JMS 700. Melting points are uncorrected (Büchi B540).

X-ray Structure Determination

Crystals suitable for X-ray analysis of the mixture trimeric Hpca/Hpca (**A**; ratio 1:2, mixed crystals), of trimeric Hpca (**B**), and of K([18]crown-6)pca (**C**) were obtained by recrystallization. For *N*-phenyl-*S*-methylisothiouronium iodide (**D**), *N*-phenyl-*S*-methyl-isothiourea (**E**), and tritylcyanamide (**F**) X-ray quality crystals were grown in an analogous manner (see the Supporting Information).

X-ray quality crystals of **A, B, D**, and **E** were selected at room temperature in Kel-F oil. Suitable crystals of compounds **C** and **F** were selected in silicon oil at room temperature. All samples were mounted on a glass fiber and cooled to 200(2) K (**D**: 173(2) K) during measurement. Data for compounds **A, B, D**, and **E** were collected on an Oxford Xcalibur3 CCD diffractometer, data for compounds **C** and **F** were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$). Crystallographic data are summarized in Table 1. Selected bond lengths and angles are provided in Table 2. The structures were solved by direct methods (SHELXS-97 (**A, B, D**, and **E**), SIR-97 (**C** and **F**))[30,31] and refined by full-matrix least-squares procedures (SHELXL-97).[32] Semiempirical absorption corrections were applied for **A, B, D**, and **E** using the ABSPACK[33] program. All non-hydrogen

atoms were refined anisotropically, hydrogen atoms bound to nitrogen atoms were refined freely, and hydrogen atoms bound to carbon atoms were included in the refinement at calculated positions using a riding model.

Synthetic Procedures

Kpca: To a stirred solution of *N*-phenyl-*S*-methylisothiourea (9.59 g, 57.7 mmol) in isopropanol (30 mL) was added a solution of potassium hydroxide (3.24 g, 57.7 mmol) in water (10 mL). This mixture was heated to boiling under reflux for 10 min with stirring. Subsequently, the solvent was removed completely in high vacuum. Recrystallizing the residue from acetone yielded 6.42 g (71 %) potassium phenylcyanamide in the form of thin, colorless, shiny plates. M.p.: 345 °C (decomposition); Raman (200 mW, 25 °C): $\tilde{\nu}$ = 3065 (4), 3054 (3), 3028 (1), 2090 (3), 2077 (2), 1598 (10), 1575 (1), 1330 (4), 1177 (1), 1158 (2), 1028 (2), 995 (7), 811 (1), 676 (1), 395 (3), 258 (2), 176 cm^{-1} (3); IR (25 °C): $\tilde{\nu}$ = 3188 (w), 3065 (w), 3017 (w), 2426 (w), 2224 (w), 2129 (w), 2070 (vs), 2036 (s), 1590 (s), 1574 (m), 1480 (m), 1452 (w), 1355 (w), 1322 (m), 1312 (s), 1292 (m), 1173 (w), 1146 (w), 1113 (m), 1075 (w), 878 (w), 810 (w), 758 (w), 745 (m), 690 (m), 674 cm^{-1} (m); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): δ = 6.96–6.89 (m, 2H, Ph, *meta*), 6.64–6.59 (m, 2H, Ph, *ortho*), 6.40–6.33 ppm (m, 1H, Ph, *para*); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): δ = 155.7 (s, Ph, *ipso*), 128.9 (s, Ph, *meta*), 127.1 (s, Ph, *para*), 118.8 (s, Ph, *ortho*), 114.8 ppm (s, CN); ^{14}N NMR ([D$_6$]DMSO, 28.9 MHz, 25 °C): δ = −209 (s, $\Delta\nu_{1/2}$ = 732 Hz, CN), −325 ppm (s, $\Delta\nu_{1/2}$ = 2318 Hz, PhN); MS (FAB$^-$) *m*/*z*: 117 (100) [M]. Elemental analysis (%) calcd for $C_7H_5KN_2$ (156.23): N 17.93, C 53.82, H 3.23; found: N 17.74, C 53.27, H 3.29.

The cesium and sodium salts were prepared in an analogous manner; analytical data can be found in the Supporting Information.

K([18]crown-6)pca: Since it was not possible to grow crystals of potassium phenylcyanamide suitable for X-ray structure analysis, the potassium phenylcyanamide [18]crown-6 complex was synthesized for this purpose instead. Potassium phenylcyanamide (0.41 g, 2.65 mmol), [18]crown-6 (0.70 g, 2.65 mmol), and dried tetrahydrofuran (50 mL) were mixed and heated to reflux with stirring for 15 min. After filtering the obtained mixture, colorless crystals of the [18]crown-6 complex of potassium phenylcyanamide precipitated from the filtrate. Elemental analysis (%) calcd for $C_{19}H_{29}KN_2O_6$ (420.55): N 6.66, C 54.27, H 6.95; found: N 6.21, C 54.84, H 7.03.

Hpca: A solution of potassium phenylcyanamide (1.00 g, 6.40 mmol) in isopropanol (10 mL) and water (2 mL) was neutralized with 2 M aqueous HCl. The solvent was removed completely in high vacuum, and the residue was subsequently extracted three times with 15 mL dichloromethane. The extract was filtered and the filtrate was concentrated, yielding 0.71 g (94 %) phenylcyanamide as a colorless liquid. IR (25 °C): $\tilde{\nu}$ = 3164 (m), 3099 (m), 2986 (m), 2918 (m), 2222 (s), 1599 (s), 1498 (s), 1434 (m), 1302 (w), 1247 (m), 1176 (w), 890 (w), 745 (m), 688 cm^{-1} (m); ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 7.27–7.19 (m, 2H, Ph, *meta*), 6.99–6.94 (m, 1H, Ph, *para*), 6.78–6.72 (m, 2H, Ph, *ortho*), 5.39 ppm (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 101 MHz, 25 °C): δ = 138.4 (s, Ph, *ipso*), 129.3 (s, Ph, *meta*), 122.6 (s, Ph, *para*), 115.3 (s, Ph, *ortho*), 112.4 ppm (s, CN); ^{14}N NMR ($CDCl_3$, 28.9 MHz, 25 °C): δ = −176 (s, $\Delta\nu_{1/2}$ = 1890 Hz, CN), −329 ppm (s, $\Delta\nu_{1/2}$ = 2075 Hz, PhN); MS (DEI$^+$) *m*/*z*: 118 (84) [*M*], 117 (7) [*M*−H], 92 (13) [*M*−CN], 91 (38) [*M*−H−CN], 77 (59) [*M*−HNCN], 41 (5) [*M*−C_6H_5]. Elemental analysis (%) calcd for $C_7H_6N_2$ (118.14): N 23.71, C 71.17, H 5.12; found: N 23.24, C 70.81, H 4.69.

Mixed crystals: trimeric Hpca/Hpca: From a solution of phenylcyanamide (1.52 g, 12.9 mmol) in isopropanol (10 mL) precipitated mixed crystals of trimeric Hpca/Hpca (1.17 g, 77 %) after standing for seven days at room temperature. M.p.: 169 °C; ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C, trimeric Hpca): δ = 7.59–7.51 (m, 6H, Ph, *meta*), 7.48–7.43 (m, 9H, Ph, *para*/*ortho*), 5.65 ppm (s, 3H, NH); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C, Hpca): δ = 7.27–7.19 (m, 4H, Ph, *meta*), 6.99–6.94 (m, 2H, Ph, *para*), 6.78–6.72 (m, 4H, Ph, *ortho*), 5.39 ppm (s, 2H, HNCN); according to the ^{1}H NMR, the ratio trimeric Hpca/Hpca in the mixed crystals is 1:2. Elemental analysis (%) calcd for $C_{21}H_{18}N_6{\cdot}2C_7H_6N_2$ (590.69): N 23.71, C 71.17, H 5.12; found: N 23.82, C 71.10, H 5.17.

Trimeric Hpca from mixed crystals: A suspension of triphenylisomelamine/phenylcyanamide mixed crystals (0.73 g, 1.24 mmol) in water (10 mL) was heated to boiling for 5 min. The triphenylisomelamine went into solution while the phenylcyanamide remained undissolved. Subsequently, the solution was decanted off from the colorless, oily residue. The obtained aqueous triphenylisomelamine solution was cooled to 0 °C and kept at this temperature for 1 h. The formed precipitate was filtered, and the white residue was dried under high vacuum and recrystallized from isopropanol. Colorless crystals of 0.21 g (48 %) triphenylisomelamine were obtained. M.p.: 212 °C; IR (25 °C): $\tilde{\nu}$ = 3344 (m), 3051 (vw), 1646 (m), 1619 (vs), 1541 (w), 1491 (s), 1428 (vs), 1285 (m), 1254 (w), 1217 (w), 1198 (m), 1178 (m), 1166 (m), 1158 (m), 1094 (w), 1074 (w), 1058 (w), 1025 (s), 1002 (w), 799 (w), 752 (vs), 740 (m), 717 (m), 692 (vs), 614 cm^{-1} (w); ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): δ = 7.59–7.51 (m, 6H, Ph, *meta*), 7.48–7.43 (m, 9H, Ph, *para*/*ortho*), 5.65 ppm (s, 3H, NH); ^{13}C NMR ([D$_6$]DMSO, 101 MHz, 25 °C): δ = 148.3 (s, C=NH), 136.4 (s, Ph, *ipso*), 130.2 (s, Ph, *meta*), 129.9 (s, Ph, *para*), 129.1 ppm (s, Ph, *ortho*); MS (DEI$^+$) *m*/*z*: 354 (4) [*M*], 353 (13) [*M*−H], 235 (3) [*M*−H−H_5C_6N(H)CN], 118 (5) [*M*−2H_5C_6N(H)CN], 77 (100) [C_6H_5]. Elemental analysis (%) calcd for $C_{21}H_{18}N_6$ (354.41): N 23.71, C 71.17, H 5.12; found: N 23.27, C 71.56, H 5.34.

Trimeric Hpca from monomeric Hpca: A solution of phenylcyanamide (2.43 g, 20.6 mmol) in isopropanol 30 mL) was heated to reflux with stirring for 12 h. The solvent was removed completely in high vacuum. Recrystallizing the residue from isopropanol yielded 1.67 g (69 %) triphenylisomelamine in the form of colorless crystals. M.p.: 212 °C; Elemental analysis (%) calcd for $C_{21}H_{18}N_6$ (354.41): N 23.71, C 71.17, H 5.12; found: N 23.58, C 71.39, H 5.23. For further analytical data, see the preceding paragraph.

Computational Details

Our goal was to compare the structures and energetics of different isomers of monomeric and trimeric Hpca. Therefore, it was important to carry out the calculations in such a way that the results could be compared reliably with each other. The structural and vibrational data of all considered species and adducts were calculated by using the hybrid density functional theory (B3LYP) with the program package Gaussian 98.[34] A 6-31G(d,p) standard basis set was applied for all atoms. The computed geometrical parameters and frequency data can be found in the Supporting Information (Figure S4–S6). NBO analyses[25] were carried out to investigate the bonding in all molecules at the B3LYP level utilizing the optimized B3LYP geometry.

It should be emphasized that the computations were carried out for a single, isolated (gas-phase) molecule. However, there may be significant differences among gas-phase, solution, and solid-state data.

[1] A. T. Cahours, M. Cloëz, *Ber. Dtsch. Chem. Ges.* **1854**, *90*, 91–97.
[2] a) B. R. Hollebone, R. S. Nyholm, *J. Chem. Soc. A* **1971**, 332–337; b) B. R. Hollebone, *J. Chem. Soc. A* **1971**, 481–486; c) B. R. Hollebone, M. Stillman, *Inorg. Chim. Acta* **1980**, *42*, 169–178; d) R. J. Crutchley, M. L. Naklicki, *Inorg. Chem.* **1989**, *28*, 1955–1958.
[3] F. Kurzer, *J. Chem. Soc.* **1949**, 3033–3038.
[4] a) B. Rathke, *Ber. Dtsch. Chem. Ges.* **1879**, *12*, 772–774; b) F. Kurzer, *Org. Synth.* **1963**, *4*, 172–174.
[5] E. Kühle, *Angew. Chem.* **1969**, *81*, 18–32; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 20–34.
[6] a) A. Aumüller, S. Hünig, *Liebigs Ann. Chem.* **1986**, 142–164; b) A. Malik, N. Afza, S. Siddiqui, *Z. Naturforsch. B* **1982**, *37*, 512–518.
[7] R. J. Crutchley, *Coord. Chem. Rev.* **2001**, *219–221*, 125–155, and references therein.
[8] a) Y. Kara, PhD thesis, Heinrich-Heine-Universität Düsseldorf, **2003**; b) Y. Kubo, F. Mori, K. Komatsu, K. Yoshida, *J. Chem. Soc. Perkin Trans. 1* **1988**, 2439–2442; c) T. Chivers, D. Gates, X. Li, I. Manners, M. Parvez, *Inorg. Chem.* **1999**, *38*, 2213; d) A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, M.-H. Whangbo, *Inorg. Chem.* **1990**, *29*, 2555–2557; e) S. R. Batten, P.

Jensen, B. Moubaraki, K. S. Murray, R. Robson, *Chem. Commun.* **1998**, 439–440; f) M. Kurmoo, C. J. Kepert, *New J. Chem.* **1998**, *22*, 1515–1524; g) J. L. Manson, C. R. Kmety, Q.-Z. Huang, J. W. Lynn, G. M. Bengele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein, J. S. Miller, *Chem. Mater.* **1998**, *10*, 2552–2560; h) B. V. Lotsch, W. Schnick, *Chem. Mater.* **2005**, *17*, 3976–3982; i) B. V. Lotsch, W. Schnick, *New J. Chem.* **2004**, *28*, 1129–1136.

[9] a) W. Madelung, E. Kern, *Justus Liebigs Ann. Chem.* **1922**, *427*, 26–34; b) E. Irran, B. Jürgens, W. Schnick, *Solid State Sci.* **2002**, *4*, 1305–1311; c) B. Jürgens, E. Irran, J. Schneider, W. Schnick, *Inorg. Chem.* **2000**, *39*, 665–670; d) E. Irran, B. Jürgens, W. Schnick, *Chem. Eur. J.* **2001**, *7*, 5372–5381.

[10] H. Gotthardt, F. Reiter, *Chem. Ber.* **1979**, *112*, 1635–1649.

[11] H. M. Bassan, W. Forner, *THEOCHEM* **2004**, *673*, 223–229.

[12] F. F. Wong, C.-Y. Chun, M.-Y. Yeh, *Synlett* **2006**, *4*, 559–562.

[13] C. R. Rasmussen, F. J. Villani, Jr., L. E. Weaner, B. E. Reynolds, A. R. Hood, L. R. Hecker, S. O. Nortey, A. Hanslin, M. J. Constanzo, A. J. Molinari, *Synthesis* **1988**, *6*, 456–459.

[14] a) C. R. Rasmussen, F. J. Villani, Jr., B. E. Reynolds, J. N. Plampin, A. R. Hood, L. R. Hecker, S. O. Nortey, A. Hanslin, M. J. Constanzo, A. J. Molinari, *Synthesis* **1988**, *6*, 460–466; b) G. Toth, L. Toldy, I. Toth, B. Rezessy, *Tetrahedron* **1974**, *30*, 1219–1224.

[15] V. I. Cohen, *Synthesis* **1980**, *1*, 60–63.

[16] a) A. W. Hofmann, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 3217–3234; b) G. Heller, W. Bauer, *J. Prakt. Chem.* **1902**, *65*, 365–386; c) M. G. Seeley, R. E. Yates, C. R. Noller, *J. Am. Chem. Soc.* **1951**, *73*, 772–774; d) M. M. Aly, A. M. Fahmy, A. M. Gaber, *Phosphorus Sulfur Silicon Relat. Elem.* **1990**, *53*, 253–258; e) F. Kurzer, *J. Chem. Soc.* **1950**, 3269–3273; f) R. R. Scheline, R. L. Smith, R. T. Williams, *J. Med. Pharm. Chem.* **1961**, *4*, 109–135; g) R. C. Bertelson, K. D. Glanz, D. B. McQuain, *J. Heterocycl. Chem.* **1969**, *6*, 317–324; h) N. Vivona, S. Buscemi, S. Asta, T. Caronna, *Tetrahedron* **1997**, *53*, 12629–12636.

[17] F. Baum, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 523–524.

[18] A. W. Hofmann, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2781–2800.

[19] a) V. V. Korshak, D. F. Kutepov, V. A. Pankratov, N. P. Antsiferova, S. V. Vinogradova, *Z. Vses. Khim. Obshch. im. D. I. Mendeleeva* **1974**, *19*, 472–473; b) V. V. Korshak, D. F. Kutepov, V. A. Pankratov, N. P. Antsiferova, S. V. Vinogradova, *Izv. Akad. Nauk SSSR Ser. Khim.* **1973**, *6*, 1408–1410.

[20] R. Niwa, H. Kamada, E. Shitara, J. Horiuchi, N. Kibushi, T. Kato, *Chem. Pharm. Bull.* **1996**, *44*, 2314–2317.

[21] F. Arndt, *Justus Liebig Ann. Chem.* **1911**, *384*, 322–351.

[22] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaefer, D. Holm-Hansen, *J. Am. Chem. Soc.* **1951**, *73*, 2981–2983.

[23] B3LYP/6-31G(d,p) computations revealed C_{3h}-symmetric triphenylmelamine as the most stable isomer.

[24] N. Wiberg, E. Wiberg, A. Fr. Holleman, *Lehrbuch der Anorganischen Chemie*, 101. Aufl., de Gruyter, Berlin, **1995**, Anhang V.

[25] a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO Version 3.1*; b) J. E. Carpenter, F. Weinhold, *J. Mol. Struct. THEOCHEM* **1988**, *169*, 41–62; c) F. Weinhold, J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum, New York, **1988**, 227; d) F. Weinhold, C. Landis, *Valency and Bonding. A Natural Bond Orbital Donor–Acceptor Perspective*, Cambridge University Press, Cambridge, **2005**, and references therein.

[26] B. Jürgens, E. Irran, W. Schnick, *J. Solid State Chem.* **2001**, *157*, 241–249, and references therein.

[27] a) J. N. Varghese, A. M. O'Connell, E. N. Maslen, *Acta Crystallogr. Sect. B* **1977**, *33*, 2102–2108; b) K. C. Russell, J.-M. Lehn, N. Kyritsakas, A. DeCianb, J. Fischerb, *New J. Chem.* **1998**, *22*, 123–128; c) J. A. Zerkowski, J. C. MacDonald, Ch. T. Seto, D. A. Wierda, G. M. Whitesides, *J. Am. Chem. Soc.* **1994**, *116*, 2382–2391.

[28] a) P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **1994**, *116*, 909–915; b) T. Steiner, I. Majerz, C. C. Wilson, *Angew. Chem.* **2001**, *113*, 2728–2731; *Angew. Chem. Int. Ed.* **2001**, *40*, 2651–2654; c) A. Sattler, W. Schnick, *Z. Anorg. Allg. Chem.* **2006**, *632*, 531–533; d) R. F. M. Lange, F. H. Beijer, R. P. Sijbesma, R. W. W. Hooft, H. Kooijman, A. L. Spek, J. Kroon, E. W. Meijer, *Angew. Chem.* **1997**, *109*, 1006–1008; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 969–971.

[29] H. Bredereck, E. Reif, *Chem. Ber.* **1948**, *81*, 426–438.

[30] G. M. Sheldrick, SHELXL-97, *Program for Solution of Crystal Structures*; University of Göttingen (Germany), **1997**.

[31] "SIR97: a new tool for crystal structure determination and refinement": A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[32] G. M. Sheldrick, SHELXS-97, *Program for Refinement of Crystal Structures*; University of Göttingen (Germany), **1997**.

[33] ABSPACK, Oxford Diffraction, **2005**.

[34] M. J. Frisch, et al. Gaussian 98 (Revision A7 and A11), Gaussian, Inc., Pittsburgh, PA, **1998**.

Received: November 8, 2007
Revised: February 14, 2008
Published online: April 18, 2008

