Synthesis and Structures of Trifluoromethyl-, Fluoro-, and Azido-Substituted Hexabenzylhexaazaisowurtzitanes and Isolation of a Novel Hexaazaisowurtzitane-Based Polycycle

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Abstract: The first hexabenzylhexaazaisowurtzitane cage compounds with trifluoromethyl and azide groups, as well as those with fluorine atoms in the 3- and 4-positions, have been prepared and fully characterized. A study of the substituent influence on the benzene ring regarding the formation of the hexaazaisowurtzitane polycycle in either the 2- or 4-position with CF_3, F, and N_3 revealed an interesting difference. In all cases with CF_3, F, and N_3 substituents in the 4-position, the corresponding hexabenzylhexaazaisowurtzitanes were isolated. The corresponding hexabenzylhexaazaisowurtzitanes were also formed when these substituents were in the 2-position; however, in addition with azide in 2-position a novel type of polycycle was isolated and identified. ^{15}N NMR data and crystal structures of hexabenzylhexaazaisowurtzitane derivatives were obtained and are discussed in detail.

Keywords: azides · fluorine · NMR spectroscopy · polycycles · structure elucidation

Introduction

The condensation of amines or ammonia with aldehydes or ketones is well established to give polyazapolycyclic compounds. The oldest known reaction of this type is the formation of 1,3,5,7-tetraazaadamantane, also known as hexamethylenetetramine or urotropine. The cage structure of urotropine was identified as early as 1895.[1] Further nitrogen-containing adamantanes include mono-, di-, and triazaadamantane, as well as mixed azaadamantanes with other heteroatoms.[2] Newer, other interesting cage-type molecules that incorporate nitrogen atoms are the azawurtzitanes, with mono- and triazawurtzitanes described.[3]

More recently, Nielsen et al. discovered another new type of polyazapolycyclic ring system, the 2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecanes, referred to in the following as hexaazaisowurtzitane, because of its similarity to the wurtzitane structure (iso-analogue).[4, 5] The formation of the hexaazaisowurtzitane cage system is limited to certain benzylamines that condense in an acid-catalyzed reaction with glyoxal.[4–6] The first compound of this type, with benzyl groups attached to all nitrogen atoms, hexabenzylhexaazaisowurtzitane, is produced in the meantime on large industrial scale,[7] because it serves as an important precursor. An application of these strained cage molecules with additionally preferably higher densities is their suitability as precursors for energetic cage compounds with nitramine (R_2NNO_2) functionalities.[5] The synthesis and development of the most prominent representative, the relatively new and powerful explosive, hexanitrohexaazaisowurtzitane, with hexabenzylhexaazaisowurtzitane as the starting material, has attracted considerable interest.[8]

The influence of substituents at the phenyl ring of benzylamines on the formation of hexabenzylhexaazaisowurtzitanes has not been thoroughly examined, although some substituted examples exist. In our present study, we present an investigation on the reactivity of monosubstituted benzylamines, which bear electronegative substituents, such as trifluoromethyl, fluoro, and azido groups in the 2-, 3-, and 4-positions, towards the acid-promoted condensation with glyoxal (for fluorobenzyl in 2-position see ref. [6]).

Results and Discussion

Synthesis: Azidobenzylamines can be prepared in four-step procedures starting from the respective toluidines, following the reported synthesis of 2-azidobenzylamine.[9] The tolui-

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dines are first diazotized and then treated with azide to give the azidotoluenes. Bromination with *N*-bromosuccinimide yields the azidobenzyl bromides, which react with potassium phthalimide to the respective azidobenzylphthalimides. The phthalimides are converted with hydrazine into the azidobenzylamines [Eq. (1)].

The trifluoromethyl-, fluoro-, and azido-substituted benzylamines were treated with aqueous glyoxal in acetonitrile in the presence of catalytic amounts of formic acid [Eq. (2)].

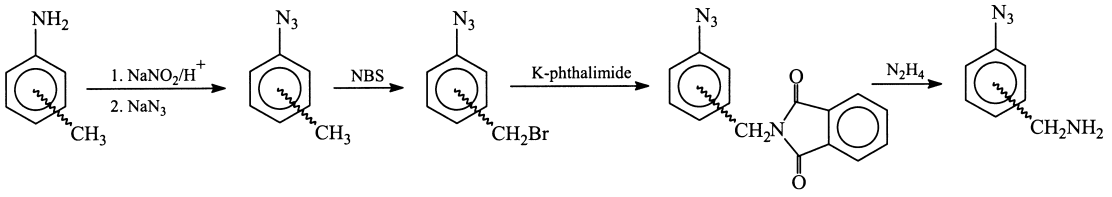
The hexabenzylhexaazaisowurtzitane derivatives with substituents in the 4-position (**1**–**3**) and those with 3-F (**4**) and 2-CF_3 (**5**) were isolated in moderate yields. However, the reaction of 3-trifluoromethyl- and 3-azidobenzylamine with glyoxal produced as yet unidentifiable viscous oils. In case of 2-azidobenzylamine, the reaction proceeded by a slightly different route, and besides the expected hexabenzylhexaazaisowurtzitane derivative **6**, a novel unusual polycyle, a 2,10,12,14-tetrakis(2-azidobenzyl)-6,7-benzo-2,4,8,10,12,14-hexaazapentacyclo[7.5.1.0.0^{3,13}.0^{8,15}]pentadecane (**7**) was obtained, both in low yields [Eq. (3)].

The exact nature of **7** was first elucidated by X-ray crystallography (see Structures section). All other spectroscopic and analytical data agree with the result obtained from X-ray crystallography.

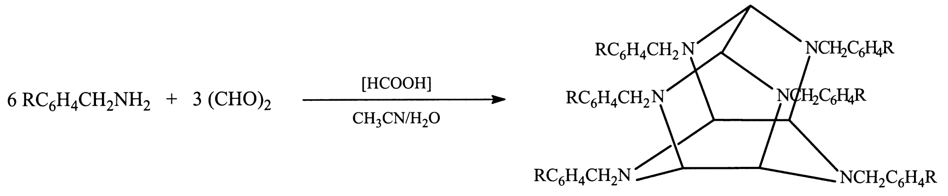
A general mechanism for the formation of the hexaazaisowurtzitane polycycle is discussed in references [4, 5]. In the case of Equation (3) resulting in the formation of **6** and **7**, it appears, as if with prolonged reaction periods, that the formation of the rearrangement product **7** occurs slowly. Both products were isolated out of a complex reaction mixture that may contain more species, but so far are unidentifiable. In any case, elimination of a 2-azidobenzyl group and an azido group must have occurred to form **7**. The sterical considerations of the 2-position are rather unlikely to be the cause of this, since the bulkier trifluoromethyl group in 2-position resulted in the formation of the corresponding hexaazaisowurtzitane derivative **5**, in addition to hexaazaisowurtzitanes with 2-chloro-[4, 6] or 2-bromobenzyl[6] groups.

During the search for further byproducts in the condensation of benzylamines with glyoxal, the formic acid salts of the respective benzylamines were isolated in small quantities, as shown by two crystal structures of 4-fluorobenzylammonium and 2-azidobenzylammonium formiate. In addition to these salts, correct elemental analysis data and NMR spectra were obtained for 4-azidobenzylammonium formiate. For a still unknown reason, some of the initially formed formiate salts, which result from the required addition of catalytic amounts of formic acid, remain unreacted for the subsequent condensation reaction.

NMR spectra: The hexabenzylhexaazaisowurtzitane derivatives **1**–**7** were characterized by all possible NMR active nuclei (^1H, ^{13}C, ^{15}N, and ^{19}F) in $CDCl_3$ (Table 1). Furthermore, previously unavailable NMR data of azidobenzyl bromides and amines[9] are listed in Table 2.

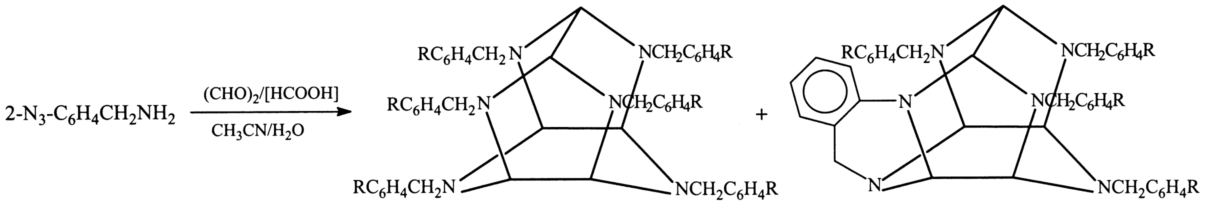


(1)



(2)

R = 4-CF_3 (**1**), 4-F (**2**), 4-N_3 (**3**), 3-F (**4**), 2-CF_3 (**5**)



(3)

R = 2-N_3 (**6**) R = 2-N_3 (**7**)

Table 1. NMR spectroscopic data of hexaazaisowurtzitane derivatives ($CDCl_3$).

	1[a]	2[b]	3	4[c]	5[d]	6	7
^1H							
Ph-H	7.54/7.30 (16H) 7.47/7.15 (8H)	7.17/6.97 (16H) 7.07/6.93 (8H)	7.20/6.94 (16H) 7.06/6.88 (8H)	7.28–6.86 (24H)	8.04–7.18 (24H)	7.42–6.97 (24H)	7.53–5.97 (20H)
CH/CH_2	4.17–3.64 (18H)	4.11–3.56 (18H)	4.08–3.59 (18H)	4.16–3.68 (18H)	4.63–4.03 (18H)	4.18–3.66 (18H)	4.72–3.18 (16H)
^{13}C							
C-6				142.9/142.8	130.5/129.7	127.9/127.6	145.6, 139.0, 138.3, 137.8,
C-5				129.7/129.5	132.0/131.5	132.0/131.9	137.6, 132.2, 131.7, 131.0,
C-4	129.6/129.4	161.9/161.8	138.7/138.5	114.0/113.8	126.7/126.5	124.4/124.3	130.9, 130.8, 130.2, 129.1,
C-3	125.4/125.2	115.0/114.9	118.8/118.7	163.0/162.9	125.6/125.5	118.0/117.9	128.6, 128.5, 127.9, 127.7,
C-2	129.3/128.1	130.5/129.5	130.4/129.5	115.7/114.8	128.0/127.9	138.6/138.0	127.6, 125.9, 125.7, 124.6,
C-1	143.9/143.8	136.0/135.8	137.1/136.9	124.5/123.5	139.0/138.7	131.0/129.4	124.4, 124.3, 119.9, 119.2, 118.1, 118.0, 117.9, 117.2
CF_3	124.2				124.7/124.4		
CH	81.4/76.7	80.6/76.5	81.1/76.4	81.4/76.7	84.8/76.3	81.2/76.9	83.6/83.4/82.1/79.0/75.4/69.5
CH_2	56.4/55.9	56.1/55.4	56.2/55.6	56.4/55.9	52.3/51.4	51.2/50.8	55.4/53.8/53.4/50.8/47.2
^{15}N							
N_β			– 138.7/ – 138.8			– 138.7/ – 138.8	– 138.6/ – 138.9/ – 139.0/ – 139.3
N_γ			– 148.6/ – 148.7			– 149.8/ – 149.9	– 149.0/ – 149.2/ – 149.5/ – 149.6
N_α			– 290.6/ – 290.8			– 292.7/ – 293.3	– 292.3/ – 292.9/ – 293.1/ – 293.4
N_4	– 298.6	– 298.0	– 298.4	– 298.9	– 302.6	– 300.6	– 292.5, – 299.8, – 300.7,
N_2	– 319.9	– 318.3	– 319.1	– 319.8	– 326.9	– 323.2	– 301.4, – 325.9, – 337.2
^{19}F							
N_4	– 62.91	– 116.3		– 113.8	– 59.8		
N_2	– 62.92	– 116.6		– 113.9	– 60.3		

[a] $^1J(C,F) = 272.1$ Hz, $^2J(C,F) = 32.3$ Hz, $^3J(C,F) = 3.8$ Hz, $^5J(C,F) = 0.8$ Hz; $^3J(H,H) = 8.0$ Hz. [b] $^1J(C,F) = 245.2$ Hz, $^2J(C,F) = 21.2$ Hz, $^3J(C,F) = 8.1$ Hz, $^4J(C,F) = 3.1$ Hz; $^3J(F,H) = 8.7$ Hz, $^4J(F,H) = 5.7$ Hz. [c] $^1J(C,F) = 246.0$ Hz, $^2J(C,F) = 21.1$, 20.8 Hz, $^3J(C,F) = 8.1$, 2.7 Hz, $^4J(C,F) = 6.9$ Hz. [d] $^1J(C,F) = 274.0$ Hz, $^2J(C,F) = 29.6$ Hz, $^3J(C,F) = 6.2$, 1.2 Hz.

Table 2. NMR spectroscopic data of azidobenzyl bromides and azidobenzylamines ($CDCl_3$).

	$4\text{-}N_3C_6H_4CH_2Br$	$3\text{-}N_3C_6H_4CH_2Br$	$2\text{-}N_3C_6H_4CH_2Br$	$4\text{-}N_3C_6H_4CH_2NH_2$	$3\text{-}N_3C_6H_4CH_2NH_2$	$2\text{-}N_3C_6H_4CH_2NH_2$
^1H						
C_6H_4	7.36, 6.98	7.52–6.81	7.36–7.10	7.26, 6.96	7.47–6.75	7.30–7.08
CH_2	4.46	4.52	4.46	3.81	3.86	3.75
NH_2				1.5	1.6	1.5
^{13}C						
C_6H_4	140.1, 134.4, 130.5, 119.3	140.0, 138.6, 134.5, 121.5, 120.6, 119.6	138.5, 131.2, 130.0, 128.8, 124.9, 118.5	140.0, 138.4, 128.5, 119.0	143.7, 139.7, 133.8, 119.4, 118.8, 118.5	137.8, 134.5, 129.1, 128.2, 124.9, 118.1
CH_2	32.8	32.5	28.3	45.8	46.6	42.7
^{14}N						
N_β	– 139.6	– 140.3	– 140.4	– 138.8	– 139.8	– 139.5
N_γ	– 148	– 145	– 148	– 149	– 148	– 149
N_α	– 290	– 294	– 293	– 292	– 296	– 294
NH_2				– 356	– 362	– 358

Due to the symmetry of the hexaazaisowurtzitane skeleton, characteristic resonances of the cage nuclei are present in all ^1H, ^{13}C, and ^{15}N NMR spectra in ratios of 4:2. Furthermore, additional resonances are observed for the substituted benzyl groups in the same ratio in the relevant spectra. The nonequivalent benzyl groups are even distinguishable in the ^{19}F NMR spectra of **1**, **2**, **4**, and **5**, with two resonances in the correct ratio. Since all derivatives **1**–**7** discussed here possess a high solubility in $CDCl_3$, their ^{15}N NMR spectra were recorded with naturally abundant ^{15}N nuclei. This beneficial property makes the reporting of the less informative ^{14}N NMR data redundant, because of the increased linewidths with ^{14}N nuclei (only three broad resonances for all species of N_α, N_β, N_γ observed). Figure 1 nicely demonstrates the usefulness of ^{15}N NMR spectroscopy in addition to ^1H and ^{13}C NMR for hexaazaisowurtzitane chemistry.

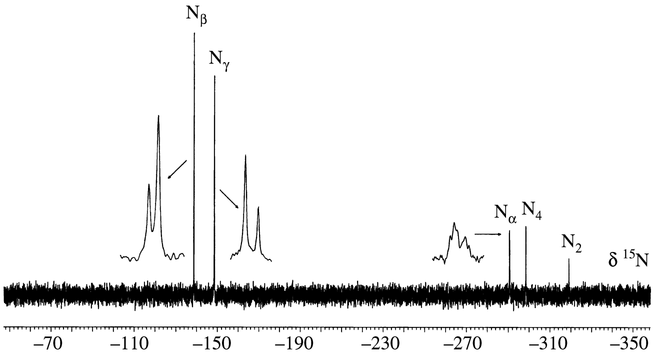


Figure 1. ^{15}N NMR spectrum of **3** ($CDCl_3$).

For the cage nitrogen atoms in **1**–**6**, two resonances are observed upfield in the range of $\delta = \sim -298$ ppm (four equivalent nitrogen atoms, denoted as N_4, see Table 1) to

-327 ppm (two equivalent nitrogen atoms, denoted as N_2, see Table 1). A high-field shift for the cage nitrogen resonances, going from the derivatives substituted in 3- and 4- position (**1**–**4**) to those substituted in 2-position (**5** and **6**) is evident (ca. 2–8 ppm). In the less symmetrical **7**, six distinct resonances at $\delta = \sim -292$ to -337 ppm are found that are assigned to the six nonequivalent nitrogen atoms. The azide resonances in **3**, **6**, and **7** appear in the typical region for carbon-bound azides ($N_\alpha \sim -292$, $N_\beta \sim -139$, $N_\gamma \sim -149$ ppm). In the ^{15}N NMR spectrum of **3** and **6**, each azide resonance is resolved into two signals with an approximate 2:1 ratio (Figure 1), because of the two nonequivalent nitrogen atoms, as already discussed above. Consequently, in the ^{15}N NMR spectrum of **7**, four signals for each set of azide resonances are visible.

Crystal structures: The isowurtzitane cage consists of two five- (C_3N_2), one six- (C_4N_2), and two seven-membered (C_4N_3) rings. Some general features are visible in all structures (Figures 2–4, below): 1) the near-planarity of the five-membered rings, 2) the boat conformation of the six-membered ring, and 3) the chair conformation of the seven-membered rings. All benzyl methylene nitrogen bonds are attached in an endocyclic fashion to the five- and six-membered ring systems. This is in agreement with the structures of the 4-CH_3O-[4] and 2-CH_3-substituted[6] hexabenzylhexaazaisowurtzitanes, but in contrast to the chloro derivative in the 4-position.[6] As a likely consequence, the orientation of the six benzyl groups are such that there is a minimum of intramolecular interactions.

The hexaazaisowurtzitane with six 4-trifluoromethylbenzyl groups (**1**) crystallizes with three molecules of acetonitrile as solvate. In order to obtain a better location of the solvent molecules the structure is displayed in a stick plot (Figure 2).

The 4-fluorobenzyl derivative **2** is shown alternatively as ORTEP plot (Figure 3) with hydrogen atoms, expressing the *endo* orientation of the benzyl methylene nitrogen bonds.

The 4-azidobenzyl derivative **3** is displayed as an ORTEP plot (Figure 4 top) and as a stick plot (Figure 4 bottom).

In the latter image, which gives a good view of the C1–C2 bridge onto the base of the structure, the six-membered ring, a *trans* orientation of azidobenzyl groups at N1/N3, N2/N4, and N5/N6, is visible. In addition, the azide groups of these three pairs are also located *trans* to each other.

In the structure of the less symmetrical hexaazaisowurtzitane **7** (Figure 5), which contains four 2-azidobenzyl groups and the additional new six-membered ring, the benzyl methylene nitrogen bonds at N3, N4, and N6 are endocyclic to their attached ring systems, while that at N1 is exocyclic.

A ring-closing reaction has occurred between two 2-azidobenzyl groups at N2 and N5, provided that the formation of **7** results from the rearrangement of **6**, forming an additional twisted six-membered ring attached to a benzo group.

Additional crystal structures of 2-azidobenzyl bromide (Figure 6), and 2-azido- (Figure 7) and 4-fluorobenzylammonium formiate (Figure 8) have been determined. A survey of the Cambridge Structural Data Base shows that crystal structures of relatively few examples of simple monosubstituted azidobenzenes exist.[10] The azide moiety in 2-azidoben-

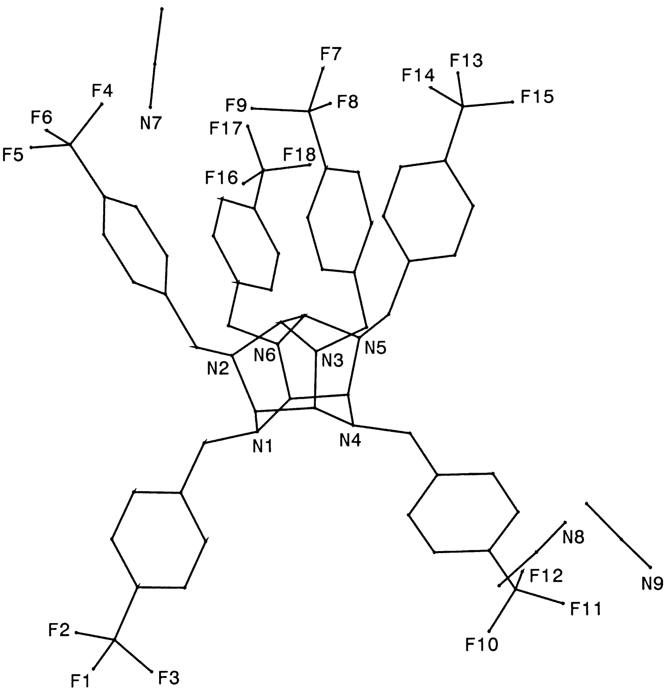


Figure 2. Stick plot of **1** · $3CH_3CN$, hydrogen atoms omitted for clarity, only N and F atoms labeled; selected bond lengths [Å] and angles [°] (ranges): cage C–N 1.440(3)–1.495(3), cage C–C 1.566(3)–1.577(3), benzyl N–C 1.448(3)–1.480(3), C–F 1.260(8)–1.333(7), solvent C≡N 1.119(8)–1.131(9), cage C-N-C 101.9(2)–112.2(2), cage N-C-N 101.6(2)–119.7(2), cage N-C-C 100.3(2)–115.7(2), benzyl N-C-C 110.0(2)–112.5(2), solvent N-C-C 176(1)–178.4(8).

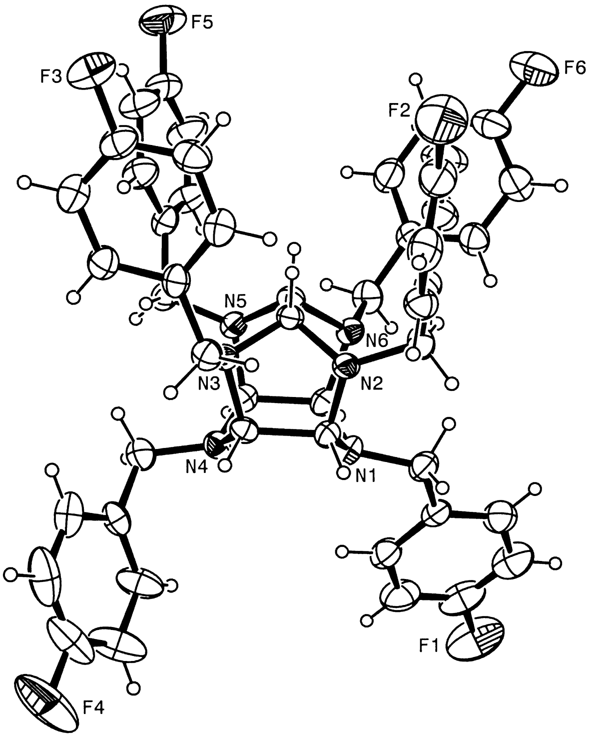


Figure 3. ORTEP plot of **2**, only N and F atoms labeled; selected bond lengths [Å] and angles [°] (ranges): cage C–N 1.437(5)–1.494(5), cage C–C 1.560(5)–1.575(6), benzyl N–C 1.453(5)–1.485(5), C–F 1.360(6)–1.375(6), cage C-N-C 102.2(3)–112.1(3), cage N-C-N 101.3(3)–120.2(4), cage N-C-C 100.4(3)–116.1(4), benzyl N-C-C 110.1(4)–113.1(4).

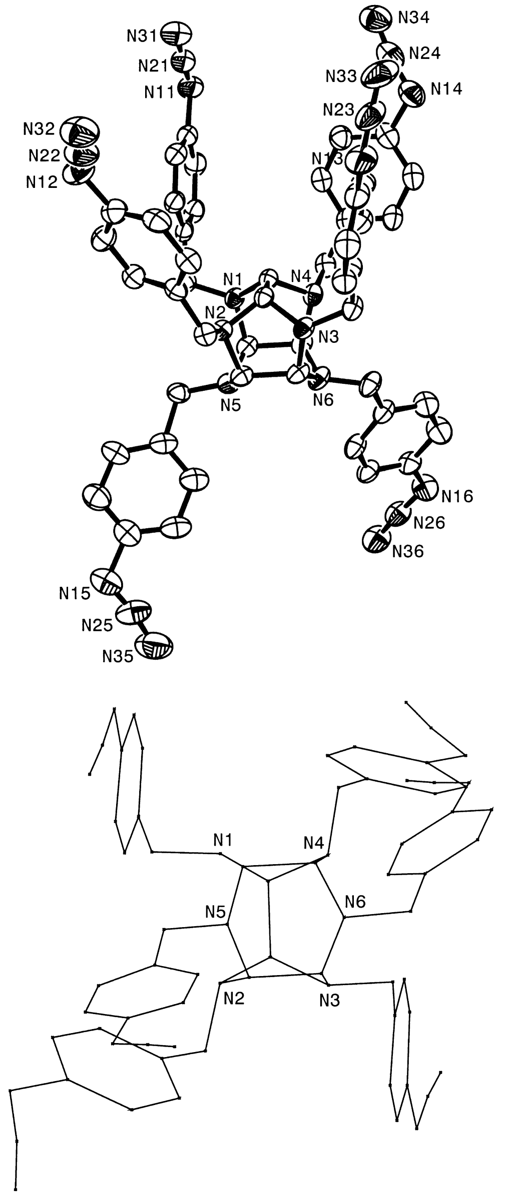


Figure 4. Top: ORTEP plot of **3**, hydrogen atoms omitted for clarity, only N atoms labeled; selected bond lengths [Å] and angles [°] (ranges): cage C–N 1.453(4)–1.492(4), cage C–C 1.566(4)–1.581(4), benzyl N–C 1.451(4)–1.478(4), C4x–N1x 1.413(5)–1.493(6), N1x–N2x 1.167(6)–1.247(6), N2x–N3x 1.118(7)–1.143(6), cage C-N-C 102.9(2)–112.1(2), cage N-C-N 100.9(2)–120.5(3), cage N-C-C 100.4(2)–116.4(2), benzyl N-C-C 110.1(2)–115.3(3), C4x-N1x-N2x 114.6(4)–117.4(4), N1x-N2x-N3x 170.1(7)–174.0(5) with $x = 1-6$. Bottom: Stick plot of **3**, view from the C1–C2 bridge onto the six-membered cycle.

zylbromide consists of a longer N1–N2 bond (1.230(5) Å) and a shorter one with more triple-bond character, N2–N3 (1.125(6) Å). The azide angle is slightly bent (N1-N2-N3 172.4(5)°).

Similar features for the azide groups are found in the structures of the azide-containing hexaazaisowurtzitanes **3** and **6**, as well as in [2-$N_3C_6H_4CH_2NH_3$][HCOO]. The structures of the formiate salts are characterized by short hydrogen bridges between ammonium hydrogen atoms and one formiate oxygen atom, that is, O11···H73 1.728 Å in [2-$N_3C_6H_4CH_2NH_3$][HCOO], and O21a···H73 1.887 Å in [4-$FC_6H_4CH_2NH_3$][HCOO].

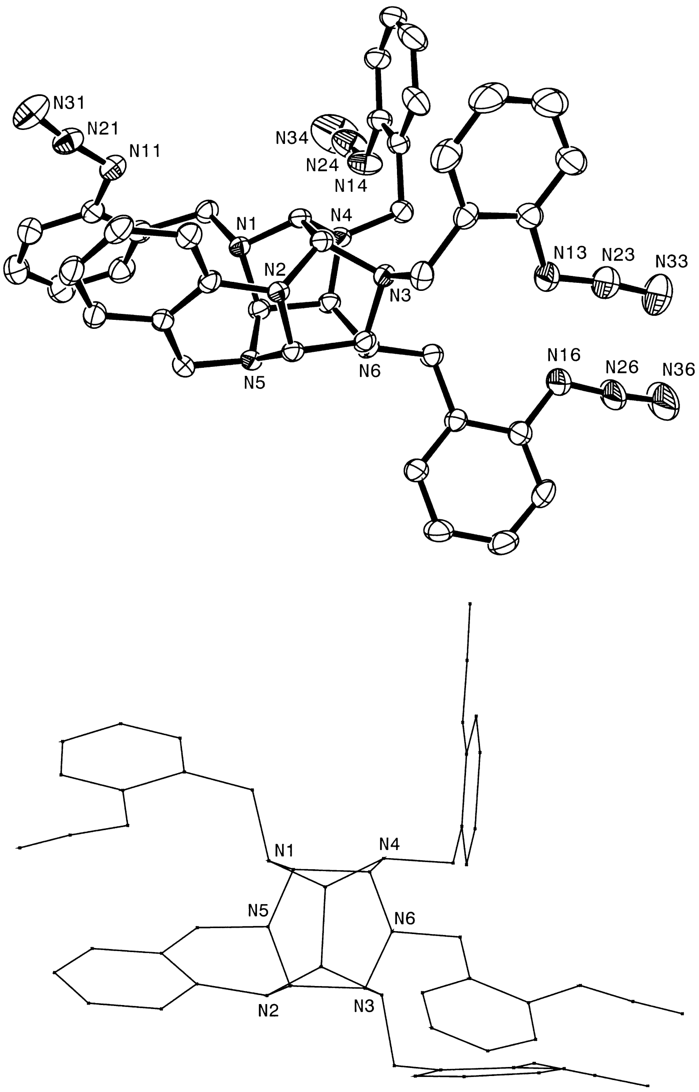


Figure 5. Top: ORTEP plot of **7**, hydrogen atoms omitted for clarity, only N atoms labeled; selected bond lengths [Å] and angles [°] (ranges): cage C–N 1.448(3)–1.492(3), cage C–C 1.547(3)–1.580(3), benzyl N–C 1.455(3)–1.482(3), N2–C65 1.419(3), N5–C75 1.473(3), C6x–N1x 1.421(4)–1.436(4), N1x–N2x 1.221(4)–1.238(3), N2x–N3x 1.119(4)–1.140(3), cage C-N-C 102.5(2)–112.9(2), cage N-C-N 101.5(2)–118.3(3), cage N-C-C 101.3(2)–116.3(2), benzyl N-C-C 110.9(2)–111.7(2), N2-C65-C15 119.5(2), N5-C75-C15 115.2(2), C6x-N1x-N2x 115.4(3)–116.6(3), N1x-N2x-N3x 171.6(4)–174.0(4) with $x = 1-4$. Bottom: Stick plot of **7**, view from the C1–C2 bridge onto the six-membered cycle.

Conclusion

New hexaazaisowurtzitanes containing benzyl groups with electron-withdrawing groups CF_3, F, and N_3 groups, were synthesized. An additional unusual byproduct was obtained, isolated and identified from the reaction of 2-azidobenzylamine with glyoxal, yielding a novel cage structure. Its crystal structure revealed a benzo-annelation at the hexaazaisowurtzitane cage, compared to the regular structures with 4-CF_3, 4-F, and 4-N_3-benzyl substitution. Future work includes studies of possible chemical modification of the attached substituted benzyl groups under retainment of the hexaazaisowurtzitane cage structure, as well as an increase of the azide content, that is, more than six azide groups per hexaazaisowurtzitane structure.

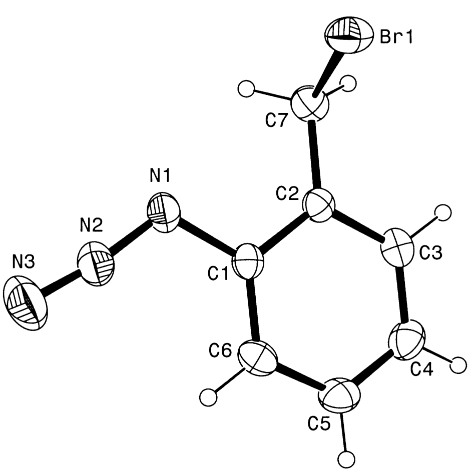


Figure 6. ORTEP plot of 2-$N_3C_6H_4CH_2Br$; selected bond lengths [Å] and angles [°]: C7–Br1 1.957(4), C1–N1 1.428(5), N1–N2 1.230(5), N2–N3 1.125(6), C2-C7-Br1 111.5(3), C2-C1-N1 115.2(4), C1-N1-N2 115.7(4), N1-N2-N3 172.4(5).

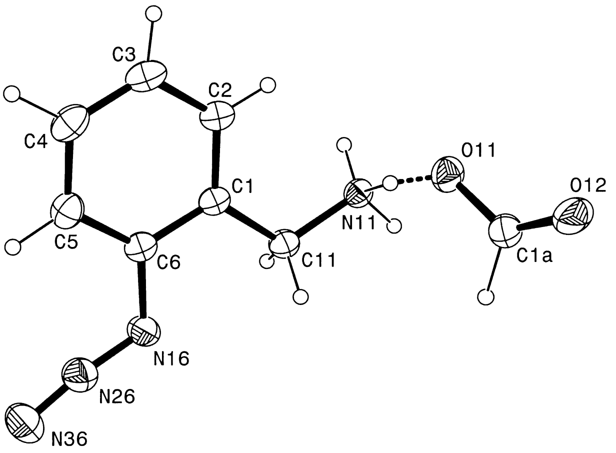


Figure 7. ORTEP plot of [2-$N_3C_6H_4CH_2NH_3$][HCOO]; selected bond lengths [Å] and angles [°]: C11–N11 1.481(3), C6–N16 1.433(3), N16–N26 1.236(3), N26–N36 1.142(3), C1a–O11 1.252(3), C1a–O12 1.232(3), O11···H73 1.728, C1-C11-N11 114.3(2), C1-C6-N16 115.1(2), C6-N16-N26 116.1(2), N16-N26-N36 172.5(3), O11-C1a-O12 125.1(2), O11···H73-N11 175.1.

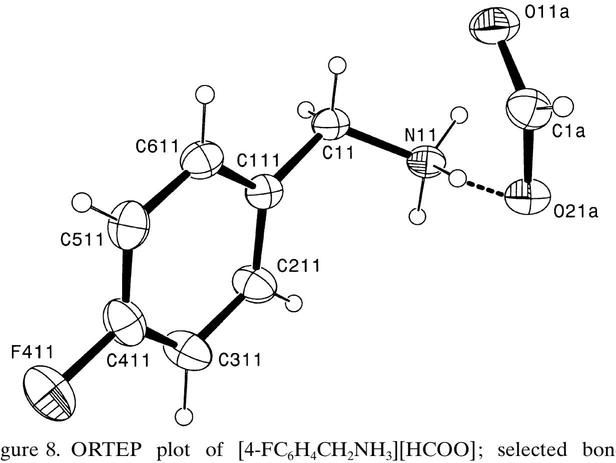


Figure 8. ORTEP plot of [4-$FC_6H_4CH_2NH_3$][HCOO]; selected bond lengths [Å] and angles [°]: C11–N11 1.481(3), C411–F411 1.369(3), C1a–O11a 1.238(3), C1a–O21a 1.258(3), O21a···H73 1.887, C111-C11-N11 114.4(2), O11a-C1a-O21a 126.1(2), O21a···H73-N11 172.2.

Experimental Section

General: Commercially available chemicals, toluidines, glyoxal (40% in water), fluoro/trifluoromethyl benzylamines were used as received. The azidobenzylamines were prepared according literature procedures, as outlined for 2-azidobenzylamine.[9] All azidotoluenes (b.p. 26–30°C/0.03 mbar), azidobenzyl bromides (b.p. 85–90°C/0.03 mbar) and azidobenzylamines (b.p. 48–52°C/0.03 mbar) were carefully distilled in vacuum prior to use. IR spectra were recorded as KBr pellets on a Nicolet 520 FT-IR spectrometer, Raman spectra on a Perkin–Elmer 2000 NIR FT-Raman spectrometer. The NMR spectra were recorded on a Eclipse 400 instrument; chemical shifts are with respect to $(CH_3)_4Si$ (^1H, ^{13}C), CH_3NO_2 (^{14}N, ^{15}N) and $CFCl_3$ (^{19}F). Mass spectral data were obtained from a Jeol Mstation JMS 700 spectrometer by using direct EI, or FAB^+ modes with 3-nitrobenzylalcohol (NBA) as matrix. Elemental analyses were performed in-house.

X-ray crystallography: For compounds **1**, **2**, and 2-$N_3C_6H_4CH_2Br$ an Enraf Nonius CAD4 diffractometer was employed for data collection using $Mo_{K\alpha}$ radiation, for compounds **3**, **7**, [2-$N_3C_6H_4CH_2NH_3$][HCOO], and [4-$FC_6H_4CH_2NH_3$][HCOO] a Nonius Kappa CCD machine was used. The structures of **1**, **2**, and 2-$N_3C_6H_4CH_2Br$ were solved by direct methods (SHELXS 86) and refined by means of the full-matrix least squares procedures by using SHELXL 93,[11] and for the structures of **3**, **7**, [2-$N_3C_6H_4CH_2NH_3$][HCOO] and [4-$FC_6H_4CH_2NH_3$][HCOO] the programs SIR97 and SHELXL97[12] were used for structure solution and refinement, respectively. Data for the solution and refinement of all structures are given in Table 3. All non-hydrogen atoms were refined anisotropically. All plots of crystal structures (Figure 2–8) are shown with 30% probability. CCDC-191312 (**1**), CCDC-191311 (**2**), CCDC-191308 (**3**), CCDC-188542 (**7**), CCDC-191313 (2-$N_3C_6H_4CH_2Br$), CCDC-191309 ([2-$N_3C_6H_4CH_2NH_3$][HCOO]), and CCDC-191310 ([4-$FC_6H_4CH_2NH_3$][HCOO]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Caution: Covalent azides are potentially explosive! Although azidotoluenes, azidobenzyl bromides and azidobenzylamines can be distilled in vacuum without decomposition in larger quantities (up to 50 grams), they should be handled with care, possible light-exclusion, and stored at 0°C.

Condensation of benzylamines ($RC_6H_4CH_2NH_2$, R = CF_3, F, N_3) with glyoxal: A solution of the benzylamine (50 mmol) in acetonitrile/water (55 mL, 10:1) was treated with catalytic amounts of formic acid at 0°C. Aqueous glyoxal (150 mmol) was then added over a period of 10 min and stirred for 2 hours at 0°C. The resulting mixture was further stirred for 3–5 days at ambient temperature. In some cases only few minutes after glyoxal addition a colorless or slightly yellowish precipitate or viscous oil was visible. This precipitate or oil was separated from the mixture and washed with cold acetonitrile to give colorless or pale yellow (**3** or **6**, non-explosive, slightly light-sensitive) crystals in yields (not optimized) of 27% (**1**), 32% (**2**), 13% (**3**), 34% (**4**), 9% (**5**) and <3% (**7**). The initially viscous oils sometimes required several weeks to crystallize. Compound **6** (ca. 5%) was not obtained analytically pure (ca. 90% purity), but was unambiguously identified by the NMR data (Table 1).

Additional spectroscopic (selected) and analytical data

4-CF_3 (1): M.p. 168–171°C; IR: $\tilde{\nu} = 1619$ (m; C=C), 1126 cm^{-1} (s; CF); Raman (100 mW): $\tilde{\nu} = 1620$ (100)/1587 (20; C=C), 1128 cm^{-1} (14; CF); EI MS: m/z (%): 1117 (9) [M^+], 1098 (2) [$M^+ - F$], 958 (82) [$M^+ - CF_3C_6H_4CH_2$], 931 (13) [$M^+ - CF_3C_6H_4CH_2 - HCN$], 159 (100)

Table 3. Crystal data and structure refinements.

	1·3 CH_3CN	**2**	**3**	**7**	2-$N_3C_6H_4CH_2Br$	[2-$N_3C_6H_4CH_2NH_3$]-[HCOO]	[4-$FC_6H_4CH_2NH_3$]-[HCOO]
formula	$C_{60}H_{51}F_{18}N_9$	$C_{48}H_{42}F_6N_6$	$C_{48}H_{42}N_{24}$	$C_{41}H_{36}N_{18}$	$C_7H_6BrN_3$	$C_8H_{10}N_4O_2$	$C_8H_{10}FNO_2$
M_r	1240.10	816.88	955.06	780.88	212.06	194.20	171.17
T [K]	293(2)	293(2)	200(2)	200(2)	293(2)	200(2)	200(2)
crystal size [mm]	0.53 × 0.47 × 0.20	0.53 × 0.43 × 0.13	0.32 × 0.08 × 0.05	0.30 × 0.08 × 0.05	0.57 × 0.43 × 0.13	0.20 × 0.20 × 0.02	0.18 × 0.16 × 0.06
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/c$	$Pbca$	$P2_1/c$
a [Å]	14.227(3)	13.606(5)	42.4133(4)	11.4159(2)	7.190(2)	13.6317(4)	16.203(2)
b [Å]	14.508(1)	16.371(4)	9.9215(1)	13.4587(3)	12.904(4)	7.4970(2)	4.8067(5)
c [Å]	14.910(2)	19.024(4)	26.0686(3)	13.9929(3)	8.773(2)	18.9349(5)	11.547(1)
β [°]	91.69(1)[a]	107.03(3)	120.497(1)	74.216(1)[b]	95.00(2)		110.091(6)
V [Å^3]	2975.9(7)	4052(2)	9452.2(2)	1915.53(7)	810.8(3)	1935.09(9)	844.6(2)
Z	2	4	8	2	4	8	4
ρ_{calcd} [g cm^{-3}]	1.384	1.339	1.342	1.354	1.737	1.333	1.346
μ [mm^{-1}]	0.123	0.099	0.089	0.088	5.004	0.100	0.111
F(000)	1272	1704	3984	816	416	816	360
θ range [°]	2.43 – 23.97	2.73 – 23.97	5.02 – 46.00	4.74 – 54.96	2.81 – 23.97	7.36 – 54.38	7.06 – 54.92
index ranges	$-16 \leq h \leq 16$	$0 \leq h \leq 15$	$-46 \leq h \leq 45$	$-14 \leq h \leq 14$	$0 \leq h \leq 8$	$-16 \leq h \leq 17$	$-20 \leq h \leq 20$
	$-16 \leq k \leq 16$	$0 \leq k \leq 18$	$-10 \leq k \leq 10$	$-17 \leq k \leq 17$	$-14 \leq k \leq 0$	$-9 \leq k \leq 9$	$-6 \leq k \leq 6$
	$0 \leq l \leq 17$	$-21 \leq l \leq 20$	$-28 \leq l \leq 28$	$-18 \leq l \leq 16$	$-10 \leq l \leq 9$	$-22 \leq l \leq 24$	$-14 \leq l \leq 14$
reflections collected	9703	6638	41904	35011	1371	26295	11421
unique reflections	9299	6345	6557	8659	1264	2134	1915
	($R_{int} = 0.0152$)	($R_{int} = 0.0224$)	($R_{int} = 0.0610$)	($R_{int} = 0.0796$)	($R_{int} = 0.0349$)	($R_{int} = 0.1297$)	($R_{int} = 0.1079$)
$R1/wR2$ [$I > 2\sigma(I)$]	0.0533/0.1236	0.0940/0.1224	0.0656/0.1866	0.0625/0.1376	0.0366/0.0818	0.0567/0.1217	0.0613/0.1386
$R1/wR2$ (all data)	0.0829/0.1426	0.1775/0.1468	0.0965/0.2084	0.1588/0.1744	0.0544/0.0911	0.1233/0.1448	0.1280/0.1648
max/min transmission	0.9986/0.8769	0.9997/0.9639	0.9968/0.9822	0.9976/0.9763	0.9975/0.6370	0.9978/0.9788	0.9932/0.9812
data/restraints/parameters	9299/72/954	6345/0/541	6557/0/649	8659/0/676	1264/0/100	2134/0/167	1915/0/149
GOOF on F^2	1.103	1.187	1.058	1.000	1.128	1.038	1.087
largest diff. peak/hole [e Å^{-3}]	0.211/ – 0.166	0.166/ – 0.195	0.531/ – 0.269	0.263/ – 0.342	0.618/ – 0.282	0.135/ – 0.240	0.189/ – 0.278

[a] $\alpha = 100.569(9)°$, $\gamma = 99.74(1)°$. [b] $\alpha = 68.356(1)°$, $\gamma = 88.7587(9)°$.

[$CF_3C_6H_4CH_2^+$]; elemental analysis calcd (%) for $C_{54}H_{42}F_{18}N_6$ (1117.02): C 58.1, H 3.8, N 7.5; found: C 58.0, H 3.3, N 7.5.

4-F (2): M.p. 153 – 155 °C; IR: $\tilde{\nu} = 3068$ (w; CH), 1603 (m; C=C), 1221 cm^{-1} (s; CF); Raman (100 mW): $\tilde{\nu} = 3073$ (100; CH), 1603 (49, C=C), 1219 cm^{-1} (49; CF); EI MS: m/z (%): 817 (12) [M^+], 708 (77) [$M^+ - FC_6H_4CH_2$], 681 (14) [$M^+ - FC_6H_4CH_2 - HCN$], 109 (100) [$FC_6H_4CH_2^+$]; elemental analysis calcd (%) for $C_{48}H_{42}F_6N_6$ (816.96): C 70.6, H 5.2, N 10.3; found: C 70.6, H 5.1, N 10.3.

4-N₃ (3): M.p. 124 °C (decomp); IR: $\tilde{\nu} = 2119$ (s)/2073 (sh; $N_{3,as}$), 1605 (m)/1581 cm^{-1} (w; C=C); Raman (100 mW): $\tilde{\nu} = 2103$ (6)/2062 (3; $N_{3,as}$), 1605 (100)/1581 cm^{-1} (17; C=C); FAB MS: m/z (%): 956 (5) [M^++H], 928 (1) [$M^+ + H - N_2$], 823 (11) [$M^+ - N_3C_6H_4CH_2$], 796 (1) [$M^+ - N_3C_6H_4CH_2$-HCN], 154 (100) [NBAH$^+$], 132 (7) [$N_3C_6H_4CH_2^+$], 104 (38) [$NC_6H_4CH_2^+$]; elemental analysis calcd (%) for $C_{48}H_{42}N_{24}$ (955.14): C 60.4, H 4.4, N 35.2; found: C 60.5, H 3.7, N 34.9.

3-F (4): M.p. 98 – 100 °C; IR: $\tilde{\nu} = 1616$ (m)/1590 (s; C=C), 1254 cm^{-1} (s; CF); Raman (100 mW): $\tilde{\nu} = 1616$ (33)/1590 (15; C=C), 1255 (19; CF), 1004 cm^{-1} (100); EI MS: m/z (%): 817 (8) [M^+], 708 (100) [$M^+ - FC_6H_4CH_2$], 681 (4) [$M^+ - FC_6H_4CH_2 - HCN$], 109 (90) [$FC_6H_4CH_2^+$]; elemental analysis calcd (%) for $C_{48}H_{42}F_6N_6$ (816.96): C 70.6, H 5.2, N 10.3; found: C 68.6, H 5.1, N 9.8.

2-CF₃ (5): M.p. 155 – 157 °C; IR: $\tilde{\nu} = 1609$ (m)/1584 (w; C=C), 1117 cm^{-1} (s; CF); Raman (100 mW): $\tilde{\nu} = 1609$ (70)/1585 (30; C=C), 1113 (13; CF), 137 cm^{-1} (100); EI MS: m/z (%): 1117 (2) [M^+], 1098 (1) [$M^+ - F$], 958 (100) [$M^+ - CF_3C_6H_4CH_2$], 931 (2) [$M^+ - CF_3C_6H_4CH_2 - HCN$], 159 (63) [$CF_3C_6H_4CH_2^+$]; elemental analysis calcd (%) for $C_{54}H_{42}F_{18}N_6$ (1117.02): C 58.1, H 3.8, N 7.5; found: C 58.0, H 3.7, N 7.5.

2-N₃ (7): M.p. 154 °C (decomp); IR: $\tilde{\nu} = 2125$ (s)/2090 (sh; $N_{3,as}$), 1600 (w)/1582 cm^{-1} (m; C=C); Raman (100 mW): $\tilde{\nu} = 2121$ (7)/2092 (6; $N_{3,as}$), 1596 (100)/1581 cm^{-1} (61; C=C); FAB MS: m/z (%): 782 (41) [M^++H], 753 (16) [$M^+ - N_2$], 649 (40) [$M^+ - N_3C_6H_4CH_2$], 622 (4) [$M^+ - N_3C_6H_4CH_2 -$ HCN], 154 (100) [NBAH$^+$], 132 (24) [$N_3C_6H_4CH_2^+$], 104 (64) [$NC_6H_4CH_2^+$]; elemental analysis calcd (%) for $C_{41}H_{36}N_{18}$ (780.95): C 63.1, H 4.7, N 32.3; found: C 62.7, H 4.4, N 31.8.

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