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Preparation and Structure of Novel Hexaazaisowurtzitane Cages

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Abstract: Hexaazaisowurtzitane or cage molecules have attracted attention concerning their synthesis because hexanitrohexaazaisowurtzitane (HNIW or CL20) is presently the most powerful energetic compound. The synthesis of hexaazaisowurtzitanes was considered to be limited solely to the condensation of certain benzylamines with glyoxal. Here, we present the synthesis and characterization of seven novel non-benzylic hexaazaisowurtzitanes, such as hexapropargylhexaazaisowurtzitane. The substituents on the six nitrogen atoms are different to those of the benzyl or substituted benzyl groups to which previous syntheses were limited. X-ray structures are given for the hexapropargyl and hexa-2-thienylmethylene derivatives. Steric strains limit the synthesis with α-substituted benzyl and allyl derivatives. The reaction mechanism and the role of the intermediate diimines are discussed. Some of the novel hexaazaisowurtzitanes are potential precursors of hexanitrohexaazaisowurtzitane.

Keywords: cage compounds · CL20 · condensation reactions · glyoxal · hexaazaisowurtzitane

Introduction

Organic chemists have always been attracted by fascinating molecules, many of which are cyclic and striking because of their geometry and symmetry.[1] The wurtzitane (iceane), from the series of cage compounds having 12 atoms, was identified in 1974.[2] Later, Nielsen et al. reported the synthesis of a new polyazapolycyclic ring system: the 2,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane,[3] commonly named hexaazaisowurtzitane, owing to its similarity with the isowurtzitane structure. The synthesis of hexabenzylhexaazaisowurtzitane (HBIW) is remarkable because it builds a 12-atom polyclic cage compound in a one-pot cascade reaction with three glyoxal and six benzylamines.[3] In addition, this elegant molecule proved to be a precursor of one of the best modern energetic materials: hexanitrohexaazaisowurtzitane (HNIW or CL20).[4a–d] However, the replacement of the six benzyl groups by nitro functions, to give the six nitramides in HNIW, could not be carried out directly, but required three steps involving debenzylation–acylation, nitrosation, and nitration.[5] A more efficient one-step synthesis would be valuable for the industrial development of the reaction; however, no direct displacement of a benzyl moiety by a nitro function on HBIW has been reported,[6] despite the potential interest of the reaction. On the other hand, several functional groups are suitable for nitrolysis of secondary amines (transformation $R_2N{-}Y \rightarrow R_2N{-}NO_2$),[7a–f] which could hopefully give the HNIW from the corresponding hexafunctional-hexaazaisowurtzitane. The major difficulty, however, is that the synthesis described by Nielsen and co-workers,[3] despite several attempts, seems limited to benzylamines, as stated in reference [3]: "apparent uniqueness of benzylamines in the condensation with glyoxal, which leads to hexabenzylhexaazaisowurtzitane". To the best of our knowledge, since the work of Nielsen, no amine other than benzylamine (or substituted benzylamine) has been reported to give this reaction. As confirmation, a recent publication about the synthesis of new substituted hexabenzylhexaazaisowutzitane from Klapötke et al.[8] recalled that "the formation of hexaazaisowurtzitane cage system is limited to certain benzylamines that condense in an acid-catalyzed reaction with glyoxal". We took these statements as a challenge and describe here the preparation of novel

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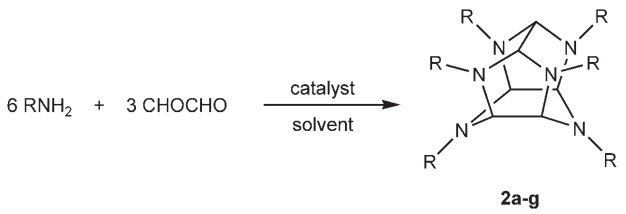
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: ^{1}H, ^{13}C NMR and DEPT 135 spectra of cage compounds **2a–g** and elemental analyses of **2a–g** are available.

hexaazaisowurtzitane molecules, made from primary amines other than benzylamines (or substituted benzylamines), together with the study of their structure and of the mechanism of synthesis of these cage compounds.

Results and Discussion

The seven novel hexaazaisowurtzitane cage compounds **2a–g** were prepared by reacting glyoxal with seven primary amines **1a–g** (Scheme 1).



Scheme 1. Condensation of primary amines **1a–g** on glyoxal; **a**: R = 2-thienyl−CH_2, **b**: R = PhCH=CH−CH_2, **c**: R = 3-pyridyl−CH_2, **d**: R = CH_2=CH−CH_2, **e**: R = 2-furfuryl, **f**: R = CH≡C−CH_2, **g**: R = 1-naphtyl−CH_2, **h**: R = CH_2=CH−CHMe, **i**: R = PhCHMe, **j**: R = CH_2=CH−CMe_2, **k**: R = $PhCMe_2$.

The reaction conditions and yields are given in Table 1.

Optimum yields were obtained by controlling kinetic parameters, such as temperature and reaction time. We observed that a longer reaction time lowered the yield and increased the ratio of the impurities as a result of reversible reactions between the cage formation and the intermediate diimine. Despite applying the best kinetic parameters for each run, significant amounts of impurities remained in the crude products and made the further isolation and purification of the cage compounds difficult. The main impurities were polymers, formed from the major side reaction, which was also mentioned by Nielsen,[3] and which prevented crystallization of the cage compounds. To purify the products, chromatographic methods specific for such compounds with low stability on acidic materials like silica gel, were required. The purification procedures are described in the Experimental Section, but no optimization of reaction parameters by experimental design[9] to increase the yields was attempted. The use of formic acid as an acidic catalyst (runs 1–7) gave yields[11] in the range of 17–40%; with runs 7 and 8, use of a water-tolerant Lewis acid catalyst [$Yb(OTf)_3$], recently proposed by Kobayashi,[10] increased notably the yield from 25 to 62%. Compounds **2a–g** were fully characterized by spectroscopic methods; compounds **2a** and **2f** by X-ray crystallographic analyses.

Table 1. Synthesis of hexasubstituted-hexaazaisowurtzitanes **2a–g**.

Run	Cpd	Catalyst	Solvent	T [°C]	t [h]	Yield[a]
1	**2a**	HCO_2H	MeCN/H_2O 10:1	20	18	40
2	**2b**	HCO_2H	MeCN/H_2O 10:1	20	18	18
3	**2c**	HCO_2H	MeCN/H_2O 10:1	20	18	19
4	**2d**	HCO_2H	MeCN	0	1	20
5	**2e**	HCO_2H	MeCN/H_2O 10:1	20	18	40
6	**2f**	HCO_2H	MeCN	0	1	17
7	**2g**	HCO_2H	MeCN/H_2O 10:1	20	36	25
8	**2g**	[$Yb(OTf)_3$]	MeCN/H_2O 30:1	20	36	62

[a] Yield of isolated, purified product (%).

The cage compounds **2a–g** were detected in their respective crude mixtures by performing NMR analyses. Results of previous NMR analyses showed that cage compounds, such as hexabenzyl- and hexa(substituted-benzyl)hexaazaisowurtzitane[3] have characteristic NMR proton and carbon signals. The cage skeleton can be seen as a six-membered boat ring and two near-planar five-membered rings linked by a C−C bridge; indeed, in the carbon and proton spectra, two different peaks for each signal appear in a 1:2 ratio, corresponding to a six-membered ring and two five-membered rings, due to the symmetry of the cage skeleton. Characteristics of the proton spectra are, for instance, two singlets for the two types of cage ring methine protons observed in a 4:2 ratio at around $\delta = 4.0$ and 3.5 ppm (see Table 2). The compounds are also recognizable by the signals for the adjacent methylene protons at δ close to 4.0 ppm in an 8:4 ratio.

Table 2. ^{1}H NMR spectral data of cage compounds **2** (20 °C) [δ in ppm].

Cpd	Solvent	Cage ring	CH_2	Aromatic	(Ac)Ethylenic
2a	$CDCl_3$	3.83 (s, 2H)	4.24 (s, 4H)	6.6–7.3 (18H)	
		4.24 (s, 4H)	4.35 (AB, 8H)		
2b	$CDCl_3$	4.20 (s, 2H)	3.9–4.1 (m, 12H)	7.3–7.6 (30H)	6.3–6.8 (12H)
		4.46 (s, 4H)			
2c	$CDCl_3$	3.89 (s, 2H)	4.34 (AB, 8H)	7.3–7.8 (24H)	
		4.24 (s, 4H)[a]	4.45 (s, 4H)[a]		
2d	$CDCl_3$	3.85 (s, 2H)	3.5–3.7 (m, 12H)		5.0–5.3 (12H)
		4.16 (s, 4H)		5.7–6.0 (6H)	
2e	$CDCl_3$	3.57 (s, 2H)	4.04 (s, 4H)[a]	5.9–6.3 (12H)	
		4.24 (s, 4H)[a]	4.08 (AB, 8H)	7.35 (6H)	
2f	$CDCl_3$	4.15 (s, 2H)	3.78 (m, 12H)		2.21 (t, 4H)
		4.47 (s, 4H)		2.28 (t, 2H)	
2g	$CDCl_3$	3.45 (s, 2H)	4.33 (AB, 8H)	5.9 (4H)	
		4.60 (s, 4H)[a]	4.69 (s, 4H)[a]	6.9 (4H)	
				7.3–8.2 (34H)	

[a] Singlet assignments may refer to either cage-ring protons or methylene protons.

However, we found that ^{13}C NMR analyses were more relevant and convenient for detecting the cage compounds in the crude mixture. The ^{13}C NMR spectrum shows two signals for the carbon atoms of the cage ring in an average 2:1 ratio in the 75–83 ppm range. The same observation was made for the carbon atoms of the adjacent methylene groups within the 50–60 ppm range, depending on the

nature of the unsaturated group, and at around 41–42 ppm for the propargyl derivative **2f** (see Table 3).

Table 3. ^{13}C NMR spectral data of cage compounds **2** (20 °C) [δ in ppm].

Cpd	Solvent	Cage ring	CH_2	Aromatic	(Ac)Ethylenic
2a	$CDCl_3$	76.4, 81.6	51.3, 52.8	125.3, 125.4, 125.5, 126.0, 126.9, 127.0, 145.0, 146.1	
2b	acetone	78.2, 82.2	55.7, 56.4	127.5, 127.6, 128.3, 128.4, 129.7, 129.8, 130.5, 130.7, 132.4, 132.6, 138.7, 138.8	
2c	$CDCl_3$	77.1, 81.8	54.3, 55.1	124.1, 124.3, 135.4, 135.6, 136.4, 137.1, 149.3, 149.4, 150.2, 151.1	
2d	$CDCl_3$	77.7, 80.8	56.4, 56.7		116.6, 117.6, 137.9, 138.4
2e	$CDCl_3$	77.2, 80.3	49.2, 50.3	108.1, 108.4, 110.7, 142.3, 142.4, 154.0, 154.8	
2f	$CDCl_3$	75.6, 81.6	41.3, 42.2		71.4, 73.3, 80.8, 80.9
2g	$CDCl_3$	77.7, 78.3	53.2, 55.2	124.8, 125.2, 125.3, 125.4, 125.6, 125.7, 125.8, 125.9, 126.6, 127.36, 127.39, 127.8, 128.5, 128.7, 132.4, 132.6, 134.0, 134.2, 135.6, 136.0	

The isolated pure products showed expected assignments, but for the methylene protons, slight differences to reference [3] were noted. For each cage compound, except for propargylic **2f**, and allylic **2b** and **2d**, a 4H singlet and an 8H AB quartet were observed for the methylene compounds, due to a complex multiplicity with the sp and sp^2 protons, respectively. This differs from Nielsen's observations because of higher resolution;[12] the phenomenon might be explained by the steric effects of heterocyclic rings. The free rotation around the methylene carbon atoms linked to the two near-planar five-membered rings may be quite limited, due to the size of the heterocyclic or aromatic ring inducing a differentiation between the two methylene protons. In contrast, a free rotation around the methylene carbon atoms linked to the six-membered boat ring seems to be easier because of the greater space available; the proton spectra indeed show a sole singlet for the two methylenes.

In addition, we reasoned that during the next anticipated nitrolysis of the bridgehead benzylamine in HBIW, the benzyl moiety should be displaced as a cationic leaving group by NO_2^+. Therefore, beside the benzyl substituted on the phenyl group, reported in previous studies,[3,8] the successive replacement of the hydrogen atoms by methyl groups in the α position of the benzyl should give secondary and tertiary cations of increased stability and ease of displacement as electrophilic leaving groups. This should also be expected for the α position of the allyl. Therefore, we prepared the amines **1h–k** by known synthetic procedures and carried out the syntheses shown in Scheme 1. Unfortunately, with amines **1h–k**, the reactions failed and no cage compounds were observed; more precisely, the reactions reached the intermediate diimines **3h–k** in good yield (see Table 4), but did not cyclize further to the cage compounds (Scheme 2).

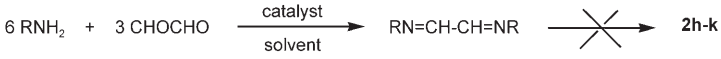
Neither extension of the reaction time for runs 9–12 to 6 or 11 days, nor the use triflate ytterbium ($[Yb(OTf)_3]$), which had proved highly efficient as a catalyst (Table 1, run 8), gave the expected cage compounds. Only diimines[13] and larger amounts of polymers were formed. The formation of polymers was evidence for diimine intermolecular additions rather than intramolecular cycloadditions.

Condensation of glyoxal with primary amines usually gives dicarbinol amines and further diimines or tetrakisaminoethane, depending on the reaction conditions and reagent structures (Scheme 3).[14]

Table 4. Synthesis of diimines **3h–k**.

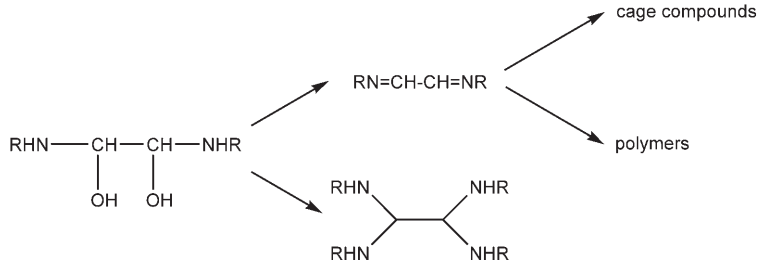
Run	Diimine	Yield[a]
9	**3h**	87
10	**3i**	80
11	**3j**	76
12	**3k**	85

[a] Yield calculated from crude product without further purification (%).



Scheme 2. Condensation of primary amines **1h–k** on glyoxal.

Nielsen has proposed a mechanism for the formation of HBIW via the dicarbinolamine, the diimine, and further cyclization to the cage compound.[3] He checked that the diimine was the reaction intermediate. As a confirmation of this result, we observed that performing the experiment of run 7 (Table 1) over 12 h afforded the corresponding diimine **3f**, which, after isolation and introduction into the reaction



Scheme 3. Formation of diimines.

medium, gave the cage compound **2f**. If diimines are indeed reaction intermediates for all isowurtzitane cage compounds,[3,8] the lack of formation of **2h–k** may be due to steric effects that have already been advocated to prevent the 1,2-dipole self-reaction of bulky imines to produce hexahydrotriazines.[3,15] The formation of polymers is proof of the inability of diimines to participate in a parallel reaction toward cyclization. To evaluate the steric strains caused by the methyl group in the α position of benzyl- or allylamines (**1h–k**), we calculated the strain energy of the hexabenzyl- and hexaallyhexaazaisowurtzitane and their corresponding α-methyl and α,α′-dimethyl derivatives by using Molecular Mechanics[16,17](Table 5).

Table 5. Strain energy of the hexasubstituted-hexaazaisowurtzitane.

Substituent	Strain energy [kcal mol^{-1}]
hexabenzyl	59.7
hexa(α-methylbenzyl)	72.0
hexa(α,α′-dimethylbenzyl)	160.0
hexaallyl	67.1
hexa(α-methylallyl)	84.5
hexa(α,α′-dimethylallyl)	100.8

This provides only a rough evaluation of the steric strains involved in the reaction because estimation of the activation energy of cyclization from the diimines to the cage compound should be made at the transition state of the rate-determining step. This would involve laborious theoretical work beyond the scope of this study, though some computational works have been performed and will be published later. They also highlight significantly different levels of energy at the transition state of the rate-determining steps between cage compounds. Data from Table 3 show a large increase in strain with one α-methyl, for both allyl and benzyl groups, and an even larger strain (more specifically with the benzyl) with the α,α′-dimethyl derivatives. Such strain energies for α-methyl derivatives clearly indicate that the activation energy to related cage compounds should be very high. This seems a reasonable explanation for the lack of formation of **2h–k**.

The stick plots of the X-ray structures of hexa(2-thienylmethylene)hexaazaisowurtzitane **2a** and hexapropargylhexaazaisowurtzitane **2f** are displayed in Figures 1 and 2, respectively.

Both cages have the same structure: a bottom six-membered boat ring, two five-membered near-planar rings, and two seven-membered rings having a chair conformation. As observed by Nielsen,[3] in the six-membered ring, the two benzyl methylene–nitrogen bonds are exocyclic, whereas in the two five-membered rings, the four benzyl methylene–nitrogen bonds are alternatively exo- and endocyclic. Lengths of the C–C single bonds for the six-membered ring are around 1.56 Å, a value slightly larger than a mean standard C–C value (1.54 Å),[18] indicating small internal strains in the cage structure. However, the highest strain in the cage structures seems to be located on the C–C bridge bond linking the two five-membered rings because of a fairly long

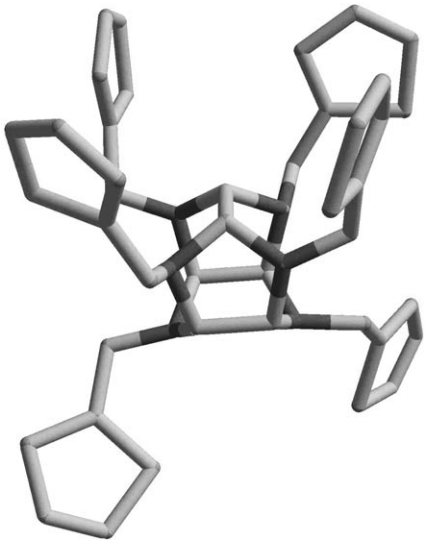


Figure 1. Stick plot of **2a**. Hydrogen atoms are omitted for clarity.

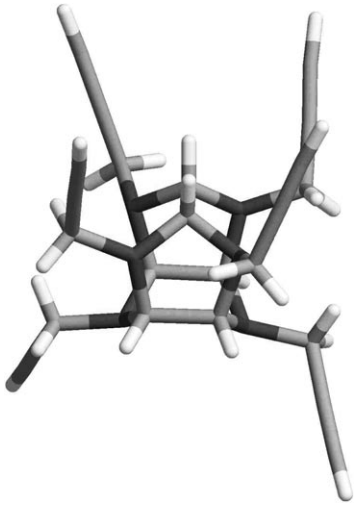


Figure 2. Stick plot of **2f**.

C–C bond (from 1.58 to 1.60 Å for the hexathienylmethylene compound **2a**). Strains inside the five-membered rings are also highlighted by torsion angles (102° between the bridge carbon and the two adjacent nitrogen atoms). The C–N bond lengths range on a larger scale, from 1.442 to 1.497 Å, flanking the usual mean standard value (1.47 Å).[18] This may be due to the difference in structure around the nitrogen atoms, exemplified by C-N-C angles in the range 123–150°.

Conclusion

Seven novel hexaazaisowurtzitanes were prepared. This synthesis of hexaazaisowurtzitanes is not limited solely to the condensation of certain benzylamines with glyoxal, as stated previously.[3,8] A water-tolerant Lewis acid catalyst is efficient for the synthesis. α-Substituted benzyl- and allylamines

afford diimines in good yield, but fail to give cage compounds, owing to steric effects, as reasonably explained by Molecular Mechanics. The direct displacement by nitronium of the substituents on the nitrogen atoms of cage compounds **2a**–**g** to yield HNIW has given favourable results[19] and was studied further here.

Experimental Section

Melting points were determined by using an Electrothermal 9100 capillary apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded by using Bruker AC 200 and Bruker Avance 400 NMR spectrometers at 20 °C. Chemical shifts were referred to tetramethylsilane (TMS) for ^{13}C and ^{1}H (δ values) and are reported in ppm. Coupling constants (J values) are given in Hz. Multiplicity is indicated by the following abbreviations: s for singlet, d for doublet, t for triplet, m for multiplet, AB for AB quartet. Infrared spectra were recorded by using an Avatar 320 FTIR Nicolet apparatus. Elemental analyses were performed in-house for compounds **2a**, **2b**, **2d**, and **2e**, and by using a Thermo Finnigan Flash EA 1112 at the University of Aix-Marseille III for the other cage structures. Mass spectra (MS) were recorded by using a Nermag R10–10H mass spectrometer by electronic impact (IE, 70 eV) and positive chemical ionization (IC^+, NH_3), except for cage compound **1g**, which was characterized by positive ion spray (IS) by using an Api 165 Applied Bio-System, with samples dissolved in methanol containing 0.1% trifluoroacetic acid. Cage compounds were purified by flash chromatography on basic aluminium oxide of 63–200 μm particle size, except for cage compound **2a**, which was purified on silica gel (Kieselgel of 70–200 μm particle size). Reagent-grade acetonitrile (solvent) was used without further purification. Commercially available chemicals, such as glyoxal (40% in water), formic acid or ytterbium catalyst, and primary amines were used as received. Cinnamylamine was prepared from commercial cinnamyl chloride by using the Gabriel method.[20] As described in the literature, α-methylallylamine,[21] α,α′-dimethylallylamine,[22] and α,α′-dimethylbenzylamine[23,24] were prepared by following known procedures.

X-ray structure determination: Compound **2f** was analyzed by M. Giorgi at the University of Aix-Marseille III. Crystal data: $M_w = 792.98$, triclinic, colorless crystal ($0.4 \times 0.4 \times 0.3$ mm^3), $a = 9.3010(4)$ $b = 12.8170(2)$ $c = 19.0050(9)$ Å, $\alpha = 96.520(3)$ $\beta = 98.121(2)$ $\gamma = 92.205(3)°$, $V = 2225.0(2)$ Å^3, space group $P\bar{1}$, $Z = 2$, $\rho_{calcd} = 1.184$ g cm^{-3}, $\mu_{MoK\alpha} = 0.073$ mm^{-1}, 10146 reflections measured at 293 K (Bruker-Nonius Kappa CCD diffractometer:[25] 180° ϕ scan, 2° rotation/frame) in the 2.22–26.31° θ range, 8020 unique reflections, 541 parameters refined on F^2 by using 6389 [$F^2 > 4\sigma F^2$] reflections [Shelxl][26] to final indices $R[F^2 > 4\sigma F^2] = 0.057$, $wR = 0.133$ [$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.9094P]$, in which $P = (F_o^2 + 2F_c^2)/3$]. Refinement details: compound **2f** crystallized with two independent molecules in the asymmetric unit. All hydrogen atoms were introduced in theoretical positions, included in the calculations, but not refined. The last residual Fourier positive and negative peaks were equal to 0.19 and −0.155, respectively. X-ray analysis was performed for compound **2a** by G. Pèpe at the University of Aix-Marseille II. Crystal data: $M_w = 745.07$, monoclinic, colorless crystal ($0.4 \times 0.3 \times 0.3$ mm^3), $a = 12.568(2)$ $b = 15.827(2)$ $c = 18.923(3)$ Å, $\beta = 106.32$ $\gamma = 92.205(3)°$, $V = 36124(9)$ Å^3, space group $P2_1/n$, $Z = 4$, $\rho_{calcd} = 1.370$ g cm^{-3}, $\mu_{MoK\alpha} = 0.415$ mm^{-1}, 6899 reflections, $R[F^2 > 4\sigma F^2] = 0.0683$. X-ray data were processed as described above.

CCDC 268281 and 265636 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

2,4,6,8,10,12-Hexasubstituted-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0.0]dodecane (hexasubstituted-hexaazaisowurtzitane): General procedure: over a 10–15 min period, glyoxal (4.5 g, 40% aqueous solution, 0.031 mol) was added dropwise to a solution of primary amine (0.093 mol), water (10 mL), formic acid (0.4 g, 9.3 mmol) in acetonitrile (100 mL), during which the temperature was maintained at between 0 and 5 °C. Reaction details and work-up are given below.

Hexa(2-thienylmethylene)hexaazaisowurtzitane (2a): The mixture was stirred for 18 h at ambient temperature and then evaporated to dryness under vacuum. The residue was dissolved in chloroform (50 mL), dried over magnesium sulfate, filtrated, and concentrated under vacuum. The crude product as a yellow resin was purified by flash chromatography on silica gel (hexane/Et_2O, 5:1). A white solid was obtained (40%). M.p. 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.83$ (s, 2H), 4.24 (s, 8H), 4.35 (AB, $J = 15$ Hz, 8H), 6.6–7.3 ppm (m, 18H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 51.3$, 52.8, 76.4, 81.6, 125.3, 125.4, 125.5, 126.0, 126.9, 127.0, 145.0, 146.1 ppm; IR (KBr): $\tilde{\nu} = 3105$, 2916, 2853, 1685, 1654, 1439, 1348, 1314, 1289, 1274, 1211, 1176, 1130, 1036, 986, 923, 832, 695 cm^{-1}; MS (CI^+): m/z (%): 745 (91) $[M+H]^+$, 650 (25) $[M+H_2-CH_2C_4H_3S]^+$; elemental analysis calcd (%): C 58.0, H 4.8, N 11.3, S 25.9; found: C 57.4, H 4.8, N 11.8, S 26.4.

Hexacinnamylhexaazaisowurtzitane (2b): The mixture was stirred for 18 h at ambient temperature. A very viscous resin was decanted off. The mixture was stored for 1 h at 0 °C. The liquid layer was removed and the remaining resin was dissolved in ether (150 mL). The organic layer was washed three times with distilled water (3 × 20 mL), dried over magnesium sulfate, filtrated, and concentrated under vacuum at 25 °C. A yellow solid was obtained and was purified further by flash chromatography on deactivated (6% H_2O) basic alumina gel (hexane/Et_2O, 5:2) giving a white solid (18%). M.p. 60 °C; ^{1}H NMR (400 MHz,$CDCl_3$): $\delta = 3.97$–4.04 (m, 12H), 4.20 (s, 2H), 4.46 (s, 4H), 6.3–6.8 (m, 12H), 7.3–7.6 ppm (m, 30H); ^{13}C NMR (200 MHz, [D_6]acetone): $\delta = 55.7$, 56.4, 78.2, 82.2, 127.5, 127.6, 128.3, 128.4, 129.7, 129.8, 130.5, 130.7, 132.4, 132.6, 138.7, 138.8 ppm; IR (KBr): $\tilde{\nu} = 3080$, 3057, 3024, 2922, 2841, 1674, 1654, 1637, 1598, 1494, 1448, 1385, 1352, 1160, 1125, 1071, 912, 742, 692 cm^{-1}; MS (CI^+): m/z (%): 865 (5) $[M+H]^+$.

Hexa(3-pyridinylmethylene)hexaazaisowurtzitane (2c): The mixture was stirred for 18 h at ambient temperature and then concentrated under vacuum ($T < 30$ °C). Diethyl ether (150 mL) was added and the organic layer was washed twice with distilled water (2 × 20 mL), dried over sodium sulfate, filtrated, and concentrated under vacuum at 25 °C. A clear orange oil was obtained and was purified further by flash chromatography on deactivated (6% H_2O) basic alumina gel. Some impurities were removed by ether/chloroform (1:1) elution. A white gummy product containing a small amount of impurities was obtained by chloroform/NEt_3 (10:0.1) elution (19%); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.89$ (s, 2H), 4.24 (s, 4H), 4.33 (AB, $J = 13$ Hz, 8H), 4.45 (s, 4H), 7.3–8.7 ppm (m, 24H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 54.3$, 55.1, 77.1, 81.8, 124.1, 124.3, 135.4, 135.6, 136.4, 137.1, 149.3, 149.4, 150.2, 151.1 ppm; IR (KBr): $\tilde{\nu} = 3030$, 2928, 2853, 1698, 1592, 1577, 1478, 1423, 1359, 1334, 1319, 1219, 1170, 1126, 1028, 994, 913, 795, 714 cm^{-1}; MS (CI^+): m/z (%): 715 (100) $[M+H]^+$.

Hexaallylhexaazaisowurtzitane (2d): The mixture was stirred for 1.5 h at 2 °C. The product precipitated in the mixture and was isolated as a white solid by filtration (25%). M.p. 47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.54$–3.63 (m, 12H), 3.85 (s, 2H), 4.16 (s, 4H), 5.0–5.3 (m, 12H), 5.7–6.0 ppm (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 56.4$, 56.7, 77.7, 80.8, 116.6, 117.6, 137.9, 138.4 ppm; IR (KBr): $\tilde{\nu} = 3075$, 2998, 2968, 2951, 2921, 2847, 2824, 1640, 1458, 1442, 1416, 1389, 1345, 1317, 1294, 1271, 1242, 1183, 1168, 1154, 1110, 1069, 993, 959, 928, 914, 897, 799, 675, 623, 588, 526, 470, 416 cm^{-1}; MS (70 eV, EI): m/z (%): 367 (100) $[M-CH_2CHCH_2]^+$, 326 (4) $[M-2(CH_2CHCH_2)]^+$, 285 (20) $[M-3(CH_2CHCH_2)]^+$, 244 (15) $[M-4(CH_2CHCH_2)]^+$; MS (CI^+): m/z (%): 409 (100) $[M+H]^+$, 368 (10) $[M+H-CH_2CHCH_2]^+$; elemental analysis calcd (%): C 70.6, H 8.8, N 20.6; found: C 70.8, H 9.0, N 20.7.

Hexafurfurylhexaazaisowurtzitane (2e): The mixture was stirred for 18 h at ambient temperature and then concentrated under vacuum ($T < 30$ °C). Chloroform (200 mL) was added and the organic layer was washed twice with distilled water (2 × 20 mL), dried over magnesium sulfate, filtrated, and concentrated under vacuum at 25 °C. An orange oil was obtained and was purified further by flash chromatography on deactivated (3% H_2O) basic alumina gel (hexane/Et_2O, 5:2) giving a white solid (40%). M.p. 97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.57$ (s, 2H),

4.04 (s, 4H), 4.08 (AB, $J=14$ Hz, 8H), 4.24 (s, 4H), 5.9–6.3 (m, 12H), 7.35 ppm (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta=49.2$, 50.3, 77.2, 80.3, 108.1, 108.4, 110.7, 142.3, 142.4, 154.0, 154.8 ppm; IR (KBr): $\tilde{\nu}=3144$, 3018, 2946, 2917, 2855, 1600, 1507, 1450, 1384, 1352, 1336, 1288, 1273, 1244, 1216, 1174, 1161, 1147, 1124, 1075, 1060, 1018, 1010, 992, 945, 918, 897, 885, 837, 810, 767, 740, 728, 670, 654, 600 cm^{-1}; MS (70 eV, EI): m/z (%): 567 (4) $[M-CH_2C_4H_3O]^+$; MS (CI^+): m/z (%): 649 (100) $[M+H]^+$, 567 (10) $[M-CH_2C_4H_3O]^+$, 487 (10) $[M+H-2(CH_2C_4H_3O)]^+$; elemental analysis calcd (%): C 66.7, H 5.5, N 13.0; found: C 66.4, H 5.6, N 12.9.

Hexapropargylhexaazaisowurtzitane (2f): The mixture was stirred for 1 h at 0 °C then concentrated under vacuum ($T<30$ °C). Dichloromethane (150 mL) was added and the organic layer was washed twice with distilled water (2×20 mL), dried over magnesium sulfate, filtrated, and concentrated under vacuum at 25 °C. A deep-red oil was obtained and was purified further by flash chromatography on deactivated (3% H_2O) basic alumina gel (hexane/Et_2O, 7:3) giving a white solid (17%). M.p. 114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.21$ (t, $J=2$ Hz, 4H), 2.28 (t, $J=2$ Hz, 2H), 3.78 (m, 12H), 4.15 (s, 2H), 4.47 ppm (s, 4H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta=41.3$, 42.2, 71.4, 73.3, 75.6, 80.8, 80.9, 81.6 ppm; IR (KBr): $\tilde{\nu}=$ 3291, 3213, 2952, 2941, 2925, 2878, 2819, 1637, 1437, 1384, 1354, 1340, 1297, 1187, 1166, 1137, 1074, 1015, 999, 925, 895, 800, 675, 659, 631 cm^{-1}; MS (70 eV, EI): m/z (%): 357 (100) $[M-CH_2CCH]^+$; MS (CI^+): m/z (%): 397 (100) $[M+H]^+$; elemental analysis calcd (%): C 72.7, H 6.1, N 21.2; found: C 72.7, H 6.2, N 19.8.

Hexa(1-naphtylmethylene)hexaazaisowurtzitane (2g): Over a 10–15 min period, glyoxal (4.61 g, 40% aqueous solution, 0.032 mol) was added dropwise to a solution of 1-aminomethylnaphtalene (14.97 g, 0.093 mol), water (5 mL), ytterbium trifluoromethylsulfonate (2.07 g, 3.2 mmol), one drop of antifoam A (Fluka supplier) in acetonitrile (150 mL), during which the temperature was maintained at between 0 and 5 °C. The mixture was stirred for three days at ambient temperature. A white solid product (62%) was filtrated and dried over P_2O_5. M.p. 244–245 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.45$ (s, 2H), 4.33 (AB, $J=$ 14 Hz, 8H), 4.60 (s, 4H), 4.69 (s, 4H), 5.90 (m, 4H), 6.89 (m, 4H), 7.3–8.2 ppm (m, 34H); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta=53.2$, 55.2, 77.7, 78.3, 124.8, 125.2, 125.3, 125.4, 125.6, 125.7, 125.8, 125.9, 126.6, 127.36, 127.39, 127.8, 128.5, 128.7, 132.4, 132.6, 134.0, 134.2, 135.6, 136.0 ppm; MS (IS): m/z: 1009; elemental analysis calcd (%): C 85.7, H 6.0, N 8.3; found: C 85.2, H 6.0, N 8.3.

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