KEYNOTE

A short survey of bicyclic diamines–syntheses and properties of *N*,*N*′-bridged-1,10-diazabicyclooctadeca-5,14-diynes

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The conformations and properties of 1,(k + 2)-diazabicyclo[$k.l.m$]alkanes are reviewed briefly. In these species the alkane chains allow inside protonation but no metal complexation. Inside metal complexation is made possible if the alkane chains incorporate alkyne units. The preparation and structures of bridged 1,10-diazacyclooctadeca-5,14-diynes are reported. As bridges we use simple alkyl chains from $(CH_2)_2$ to $(CH_2)_{10}$, di- and triethyleneglycol, but-2-yne, hex-3-yne, and oct-4-yne chains. The resulting bicyclic systems, **34**–**47**, adopt in the solid state either the *in*/*in* or the *out*/*out* conformations. By means of dynamic NMR spectroscopy a homeomorphic isomerism in **34** was uncovered. A second dynamic process, a "wagging" motion of the alkyne bridges, could be studied in case of **35**. The molecular dimensions in the solid state reveal N · · · N distances between 3.16 Å and 6.52 Å. The intramolecular distances between the triple bonds vary between 4.25 Å and 7.31 Å.

In 1,(k + 2)-diazabicyclo[$k.l.m$]alkanes there are three isomers possible which are equilibrated by nitrogen inversion: the *out*/*out*, *out*/*in* and *in*/*in* isomers[1–3] as shown in Fig. 1. If the

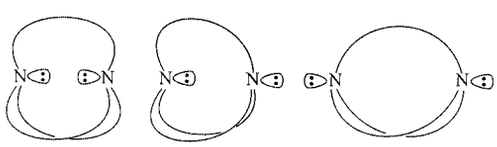
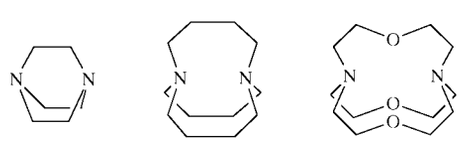


Fig. 1 Schematic representation of the *in*/*in*, *in*/*out* and *out*/*out* conformations of bicyclic 1,(k + 2)-diazabicyclo[$k.l.m$]alkanes.

chain lengths k, l and m are between 1 and 3 atoms or groups the *out*/*out* isomer is the most stable one. For k, l, m = 3–6 we expect the *in*/*in* conformer to be more stable than the other two isomers. This anticipation is supported by the observation that 1,4-diazabicyclo[2.2.2]octane (DABCO, **1**) adopts the *out*/*out* and 1,6-diazabicyclo[4.4.4]tetradecane (**2**) the *in*/*in* conformation.[3]



1 **2** **3**

Molecular models suggest that medium sized bicyclic systems with k, l, m = 4 or 5 should provide the molecular frame for a rather strong through space interaction between the inside directed lone pairs. This was supported by photoelectron spectroscopic studies on a series of bridgehead diazabicyclo[$k.l.m$]-alkanes.[4] The resulting small cavity in the inside of the molecule acts as a proton sponge.[5,6] A detailed study of the protonation of the [1.1.1]cryptand **3** reveals that it binds one or two protons inside or outside.[7] In Fig. 2 the *in*/*in* conformation and its mono- and diprotonated forms are shown. The study of the protonation of **3** shows that proton transfer from outside to inside and *vice versa* is a very slow process. Interestingly the inside protonated ion **3** H^+ (*in*/*in*$^+$) reveals no strong hydrogen bond between NH and N. This has been detected for the inside protonated **2**.

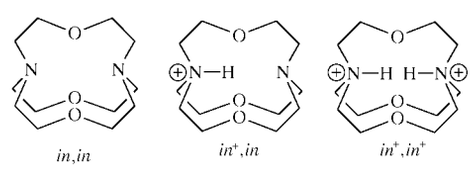


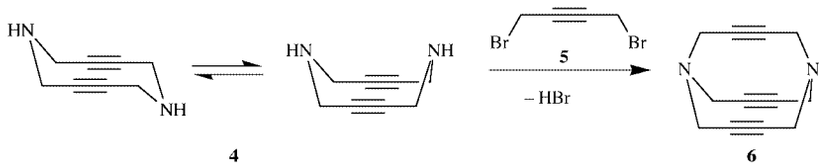
Fig. 2 [1.1.1]Cryptand in its *in*/*in* conformation and in its mono and diprotonated forms.

The examples for the complexation of metals by cryptands are legion by now.[8] Even for the [1.1.1]cryptand **3** complexation of lithium ions has been reported.[9] These findings on cryptands are contrasted by the observation that no reports are known of 1,(k + 2)-diazabicyclo[$k.l.m$] alkanes that form complexes with metal ions.[5,6] We ascribe this lack to the alkane chains which make a penetration of ions rather difficult and the fact that the molecules might not provide enough suitable coordination sites. To test this hypothesis we started to synthesize a series of bridgehead diazabicyclic systems in which the flexible alkane chains are replaced by at least two alkyne units.

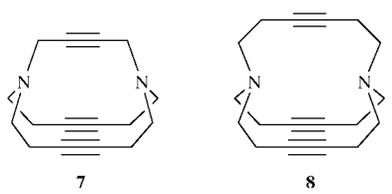
In this paper we review briefly earlier work on bicyclic diazadiynes and diazatriynes and describe in detail the synthesis and properties of bridged derivatives of 1,10-diazacyclooctadeca-5,14-diyne.

Bridged 1,6-diazacyclodeca-3,8-diynes and bridged 1,8-diazacyclotetradeca-4,11-diynes

The synthesis of 1,6-diazabicyclo[4.4.4]tetradeca-3,8,12-triyne **6**[10] could be achieved by bridging 1,6-diazacyclodeca-3,8-diyne **4**[11] with 1,4-dibromobut-2-yne **5**. The success of this rather simple procedure is probably due to the fact that in **4** the chair and boat conformations are present at room temperature.[12] This observation was rationalized by assuming a reduction of the torsional strain between the CH_2 groups. For the synthesis of DABCO **1** a stepwise approach is necessary because in piperazine the boat conformation is prevented due to the torsional strain between the CH_2 groups of the ethano bridges. Molecular models suggest for **6** the *out*/*out* conformation of the nitrogen lone pairs. The simple synthesis of **6** could be extended to derive 1,8-diazabicyclo[6.6.4]octadeca-4,11,16-triyne **7**[13,15] and 1,8-diazabicyclo[6.6.6]icosa-4,11,17-triyne **8**.[14] X-Ray

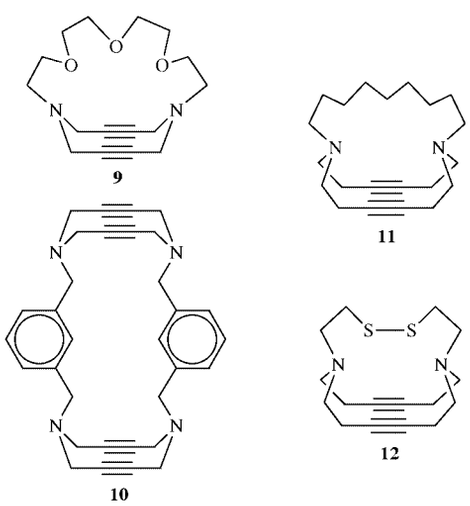


Scheme 1



investigations on **7**[13] reveal almost flat nitrogen atoms with CNC bond angles of 119.6°. For **8**[13] the nitrogen lone pairs adopt the *in*/*in* conformation. For this cage system mono- and diprotonation as well as complexation with Cu^+ and Ag^+ have been encountered.[16] It is interesting to note that the distance between the nitrogen atoms in **8** is shortened from 5.05 Å in **8** to 4.85 Å in **8**·$2H^+$, 4.23 Å in **8**·Cu^+ and 4.61 Å in **8**·Ag^+.[16]

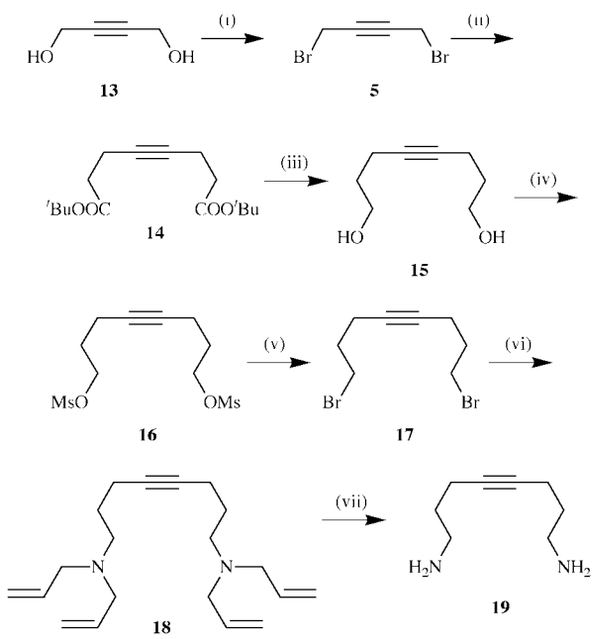
1,6-Diazacyclodeca-3,8-diyne **4** as well as 1,8-diazacyclotetradeca-4,11-diyne have also been bridged by alkane chains and polyethylene glycol units, and have been incorporated as binding blocks in other main cyclic ring systems such as **9**–**12**[10,17] to mention only a few.



Synthesis and properties of bridged 1,10-diazacyclooctadeca-5,14-diyne

The synthesis of *N*,*N*′-bridged 1,10-diazacyclooctadeca-5,14-diynes was accomplished by a three component cyclization of an α,ω-diamine with 1,8-dibromooct-4-yne **17** in the ratio of 1:2. The synthesis of the latter was achieved in a straightforward manner as shown in Scheme 2. The starting point of this protocol is but-2-yne-1,4-diol **13** which was brominated with PBr_3–pyridine in dry ether to get 1,4-dibromobut-2-yne **5**. The latter was added to the dilithium salt of *tert*-butyl acetate to yield di-*tert*-butyl oct-4-yne-1,8-dicarboxylate **14**. Reduction of **14** with $LiAlH_4$ yielded oct-4-yne-1,8-diol **15** which was transformed to the bismesylate **16** by reaction with methanesulfonyl chloride in the presence of triethylamine. The 1,8-dibromooct-4-yne **17** was obtained from **16** *via* a Finkelstein reaction with LiBr in acetone.

For the preparation of 1,10-diazabicyclo[8.8.8]hexacosa-5,14,22-triyne **40** we needed oct-4-yne-1,8-diamine **19**. Its preparation (Scheme 2) could be accomplished in good yields from *N*,*N*,*N*′,*N*′-tetraallyloct-4-yne-1,8-diamine **18**. The four allyl groups could be removed by treating **18** with *N*,*N*′-dimethylbarbituric acid and $Pd(PPh_3)_4$ using a protocol described by Guibé *et al.*[18]



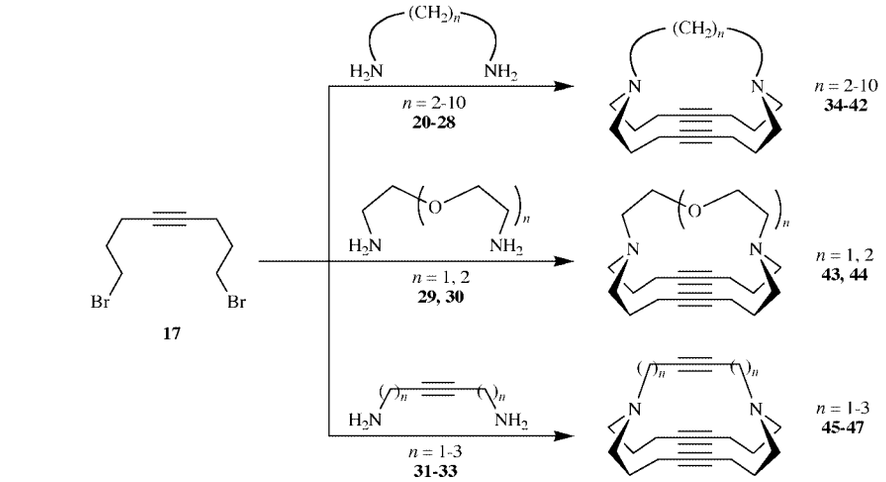
Scheme 2 *Reagents and conditions*: (i) PBr_3, pyridine, Et_2O, 80%; (ii) (CH_3COO^tBu and LDA), THF, −78 °C, 97%; (iii) $LiAlH_4$, Et_2O, 90%; (iv) $MeSO_2Cl$, NEt_3, CH_2Cl_2, 0 °C, 80%; (v) LiBr, acetone, 92%; (vi) diallylamine, K_2CO_3, acetonitrile, 80 °C, 90%; (vii) NDMBA, $Pd(PPh_3)_4$, CH_2Cl_2, 35 °C, 70%.

To achieve the tricyclic systems we reacted the dibromide **17** with a number of α,ω-amines containing simple alkane chains (**20**–**28**), ethyleneglycol chains (**29**, **30**), and alkyne bridges (**31**–**33**). This leads to the bicyclic systems **34**–**47** in yields between 40% and 80%. In two cases, in the reactions of **23** and **26**, we also could isolate the dimers **48** and **49**.

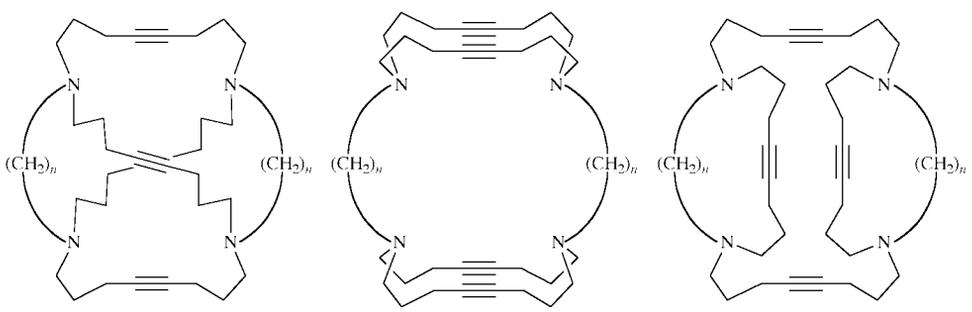
The ^1H NMR spectra of **34**–**36** indicate a dynamic behavior. As an example we show in Fig. 3 the ^1H NMR spectrum of **34** at room temperature, −20 °C and −70 °C in deuterochloroform.

At −70 °C we assume a rigid structure on the NMR time-scale with C_2 symmetry. This assumption is supported by the ^{13}C NMR spectrum of **34** which shows seven signals for the methylene groups and two for the sp carbon atoms. The ^1H NMR spectrum of **34** shows ten signals (A–J). The integration of the area below the signals yields a contribution of two hydrogen atoms for A, B, D, and F–J. For C the integration yields four and for E eight hydrogen atoms.

The assignment to the various methylene groups follows from the H,H- and HMQC spectra of **34**. The result of this study is summarized in Fig. 4. The correlation reveals that the CH_2 groups in α-position to the nitrogens (C2, C9, C11, C18, C19, and C20) contribute to the signals C, E, G, I, and J in Fig. 4. The CH_2 groups in α-position to the alkyne groups (C4, C7, C13, and C17) contribute to E, F, and H. The hydrogen atoms at C3, C8, C12 and C17 contribute to the signals A, B, D, and E. It is interesting to note that the chemical shift of the diastereotopic hydrogens at the α-position to the nitrogen atoms differ considerably. To elaborate this we have shown in Fig. 4 (bottom) the Newman projections along the C2–N1, C19–N1 and C18–N1 axes. It is seen that the hydrogens H_I and H_J are positioned in an *antiperiplanar* arrangement to the lone



Scheme 3



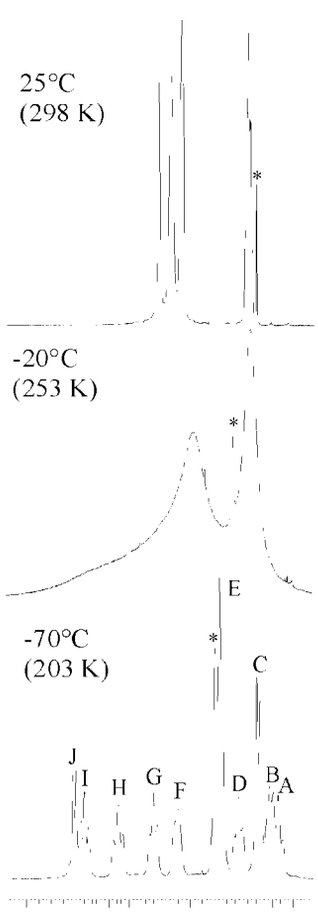


Fig. 3 ^{1}H NMR spectrum of **34** at room temperature, −20 °C and −70 °C (* = water).

pair at the nitrogen atom. In the case of the hydrogen atoms H_E and H_G at C18 the lone pair at the nitrogen atom is oriented in a *gauche* conformation. The *antiperiplanar* situated hydrogen atoms H_I and H_J are strongly shifted to lower field as compared to H_C, H_E and H_G.

Molecular models of **34** suggest at least two dynamic processes for the skeleton: an inversion of the nitrogen centers which causes a butterfly like movement in which the ethano bridge and the C_8H_{12} bridges move in opposite directions as shown in (a) of Fig. 5. A second movement is shown in (b) of Fig. 5 in which a kind of wagging movement of the C_8H_{12} bridges lead to a racemisation of the two enantiomers. In both movements the signals for the diastereotopic hydrogens H_C and H_J of the ethano bridge at δ 1.54 and 3.33 at −70 °C (Fig. 3) should coalesce. The same holds of course also for the signals of the other diastereotopic hydrogens; however H_C and H_J are those with the largest shift difference.

To freeze out the dynamic processes shown in Fig. 5 we recorded the ^{1}H NMR spectrum of **34** in $CDCl_3$ between 25 °C and −70 °C (300 MHz). As shown in Fig. 3 the coalescence of the H_C and H_J signals is estimated to occur at $T_c \approx -20$ °C. From $T_c = 253 \pm 10$ K and $\Delta\nu = 540$ s^{-1} we estimate $\Delta G^{\ddagger}$ for the dynamic process of **34** to be *ca.* 11 kcal mol^{-1}.[19]

To decide between the butterfly and wagging motion of **34** we reasoned that in **37** the pentamethylene bridge should prevent a butterfly like motion but not the wagging one. To freeze out the wagging motion in **37** we recorded the ^{1}H NMR spectrum of **34** in CD_2Cl_2 between 25 °C and −100 °C (500 MHz). The coalescence temperature could be estimated to be $T_c \approx -90$ °C. This allowed us to estimate $\Delta G^{\ddagger}$ for the wagging process of **37** to be *ca.* 7–8 kcal mol^{-1} by adopting $T_c = 183 \pm 10$ K.

X-Ray investigations

For several of the bicyclic diazadiynes **34**–**47** we could study the molecular structure in the solid state by X-ray diffraction on

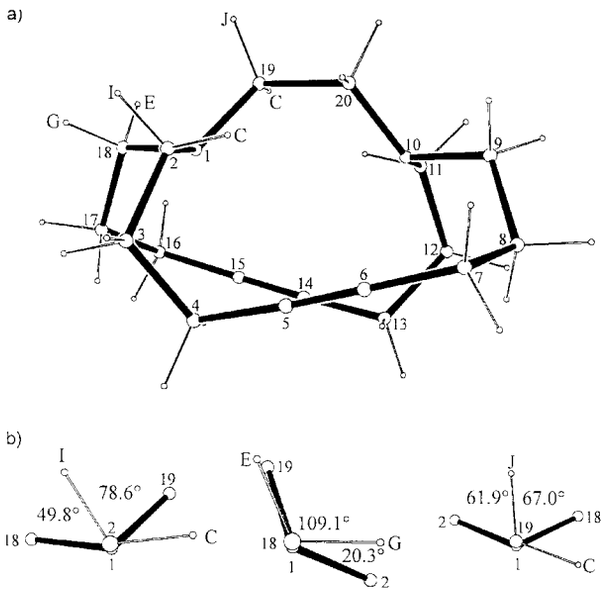


Fig. 4 (a) Numbering of carbons of **34** (RHF/32-1G optimised structure[22]). The hydrogens are denoted according to the signals of the ^{1}H NMR spectrum (see Fig. 3). (b) Newman projection along the C2–N1 (left), C18–N1 (center) and C19–N1 (right) axis to show the conformation of the hydrogens relative to the lone pair at nitrogen.

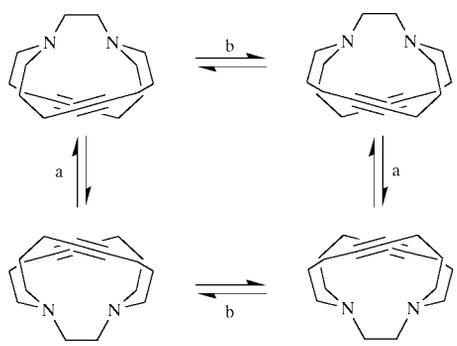


Fig. 5 Schematic drawing to visualize the dynamic processes observed for **34**. The path a implies a passage of the ethano bridge through the large ring (homeomorphic isomerism); path b represents a "wagging" motion of the two alkyne bridges.

single crystals. As examples we show in Fig. 6 the molecular structures of **34**, **37**, **39** and **47**. It is found that most of the molecules (**34**, **37**, **38**, **39** and **47**) adopt a structure with C_2 symmetry. Only in the case of **35** was a zig-zag arrangement of the chains connecting the triple bonds found. The *in*/*in* conformation is adopted for **34**, **37**, **38**, **42**, **44** and **47**; the others (**35**, **39**, **43** and **46**) adopt the *out*/*out* arrangement. The preference for one or the other conformation does not depend on the length of the bridges. This can be seen by comparing **37** and **43**. In both cases the shortest bridges between the nitrogen atoms are nearly of the same length (C_5H_{10} *vs.* C_4H_8O). We found no evidence for the presence of an *in*/*out* isomer.

In Table 1 we have compared the distances between the bridgehead nitrogens, the sum of the C–N–C angles and the distances of the triple bonds of **34**, **35**, **37**, **38**, **39**, **42**, **43**, **44**, **46**, and **47**. As anticipated the distance between the bridgehead nitrogen atoms is shortest (3.16 Å) in **34** which has the smallest bridge. The sum of the CNC angles varies only slightly between 330° (**34**) and 340° (**47**).

In Fig. 7 we show the molecular structure of the "dimer" **48** as found in the solid state.

The same connectivity is also encountered in the solid state of **49**. It is noteworthy that the alternative connectivities which would have given **50**–**53**, respectively, were not observed.

Table 1 Most relevant distances and angles in **34**, **35**, **37**, **38**, **39**, **42**, **43**, **44**, **46** and **47**

Compound	d(N···N)/ Å	d(C≡C)[a]/ Å	d(sp···sp)[b]/ Å	Σ(∠CNC)[a]/°
34	3.16	1.19	4.25	330
35[c]	5.02	1.19	7.31	332
	5.02	1.19	7.31	331
37[c]	5.40	1.19	4.49	333
	5.32	1.18	4.46	330
38	4.93	1.19	5.74	335
39	5.86	1.19	6.72	337
42	6.52	1.20	4.33	335
43[c]	5.20	1.19	6.70	336
	5.25	1.18	6.76	334
44	6.12	1.19	4.34	337
46	5.57	1.19	6.93[a]	338
47	5.70	1.18	5.57[a]	340

[a] Averaged values. [b] Transannular distance between the center of the triple bonds of the eight-membered bridges. [c] Values correspond to two independent molecules in the unit cell.

Conclusions and outlook

The three component condensation between the α,ω-dibromide **17** and different α,ω-diamines has proved to be a simple and efficient method to obtain 1,10-diazabicyclo[8.8.*m*]alkanes. The high yield of the bicyclic diamines **34**–**47** is striking. We assume that the potassium ion acts as a template. This is supported by the very high yields of **34**, **35** and **44**. Another interesting observation is that no derivatives of 1-azacyclonon-5-yne could be detected. The cages spanned by the 1,10-diazacyclooctadeca-5,14-diyne scaffold should provide enough space for one or even more metal ions. It remains to be seen if the molecules share our optimistic view in this respect.

Experimental

General

All reactions were carried out under argon atmosphere with magnetic stirring. The solvents were purified and dried using standard procedures. The ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with Bruker AS 200, WH 300, and Avance 500 instruments, respectively. *J* values are given in Hz. High resolution (HR) mass spectra were obtained with a ZAB-2F (Vacuum Generators) and a JEOL JMS 700 high-resolution mass spectrometer. The UV–VIS spectra were recorded on a Hewlett-Packard HP 8452 diode array spectrometer in CH_2Cl_2. Microanalyses were performed at the Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

Di-*tert*-butyl oct-4-yne-1,8-dicarboxylate 14

Lithium diisopropylamide (LDA) (0.3 mol) was formed by the addition of 30 ml of *n*-BuLi (10 M in hexane, 0.3 mol) to a stirred solution of diisopropylamine (47 ml, 0.3 mol) in dry tetrahydrofuran (THF) (500 ml) at −10 °C under argon. After cooling (dry ice–MeOH) *tert*-butyl acetate (40 ml, 0.3 mol) was added slowly keeping the temperature below −70 °C and the mixture was stirred for 40 minutes. Compound **5** (11 ml, 0.1 mol) was then added dropwise to the mixture *via* syringe while the temperature was kept below −70 °C. After additional

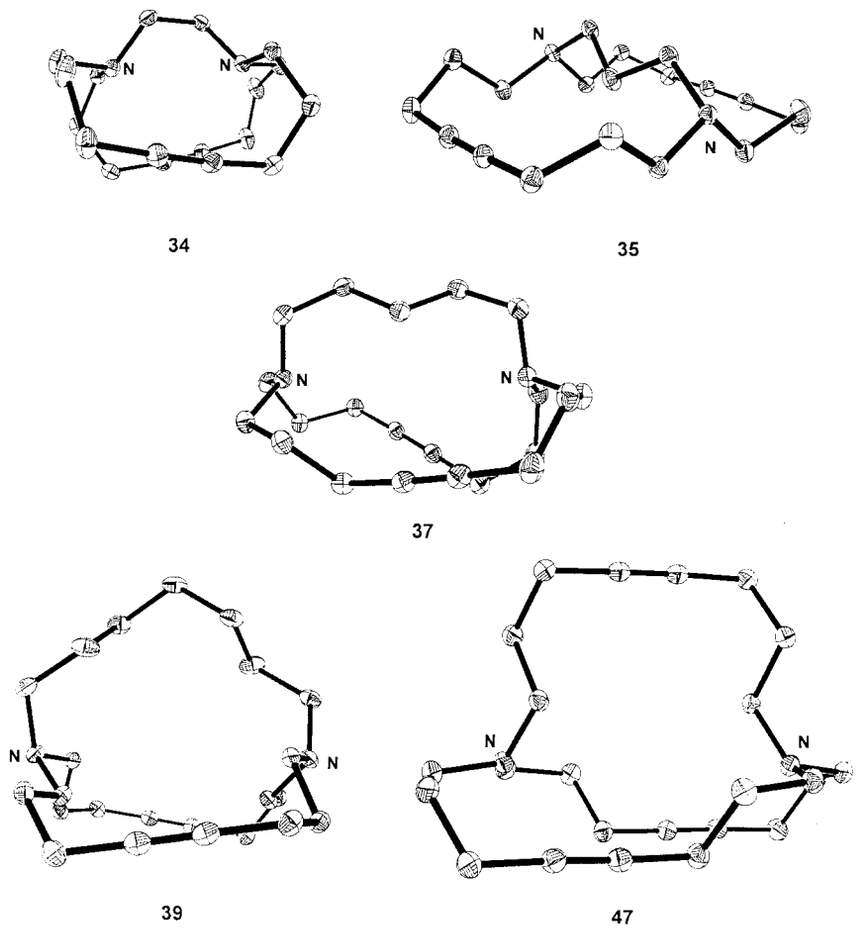


Fig. 6 Molecular structures of **34**, **35**, **37**, **39** and **47** in the solid state. The thermal ellipsoids are of 25% probability and the hydrogen atoms and the crystal water molecules in **35** have been omitted for clarity. For **35** and **37** only one molecule of the independent unit is shown.

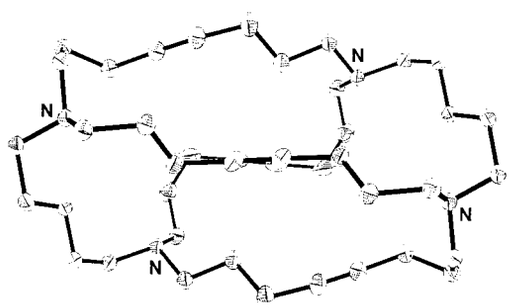


Fig. 7 Molecular structure of **48** in the solid state. The thermal ellipsoids are of 25% probability and the hydrogen atoms have been omitted for clarity.

stirring for two hours at −78 °C the reaction was quenched with saturated aq. ammonium chloride (100 ml) and the mixture allowed to warm up to room temperature. The phases were separated and the aqueous layer was extracted with ether (3 × 100 ml) while the organic layer was concentrated *in vacuo*. The residue was taken up with ether (500 ml) and the combined organic layers were washed with water (75 ml) and brine (75 ml), dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography (silica, cyclohexane–ethyl acetate, 15:1) or distilled *in vacuo* to yield **3** (27.4 g, 97%) as a colorless crystalline solid [mp 30 °C; bp (0.3 mbar): 116 °C] (Calc. for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.16; H, 9.35%). UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 230 (2.02); IR (KBr) ν_{max}/cm^{-1} 3427 (br), 3003 (m), 2979 (s), 2922 (s), 1722 (vs), 1464 (m); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43 (s, 18H, CH_3); 2.38 (s, 8H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 14.94 (CH_2); 28.19 (CH_3), 35.21 (CH_2); 79.10 (CMe_3); 80.63 (C≡C); 171.50 (C=O).

Oct-4-yne-1,8-diol 15

A solution of **14** (25.4 g, 90 mmol) in dry ether (100 ml) was added to a stirred solution of $LiAlH_4$ (100 ml, 1 M in ether, 100 mmol) in dry ether (200 ml) just as fast as the reaction could be controlled at smooth reflux; subsequently the mixture was refluxed for an additional hour. The mixture was cooled in an ice bath and carefully hydrolyzed with water until no further evolution of hydrogen was observed; finally dilute H_2SO_4 was added to dissolve the precipitated salts. The phases were separated and the aqueous layer was extracted with ether (3 × 100 ml). The organic layers were combined, washed with brine (100 ml) and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica, ether) or distillation *in vacuo* to obtain **15** (11.5 g, 90%) as a colorless, viscous liquid [bp (0.025 mbar): 133 °C] which solidifies on ice (Calc. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.18; H, 10.07%). UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 232 (1.92); IR (film) ν_{max}/cm^{-1} 3332 (br), 2944 (vs), 2877 (s), 1436 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65–1.75 (m, 4H, CH_2); 2.20–2.28 (m, 4H, CH_2); 2.54 (s, 2H, OH); 3.70 (t, J 6.3, 4H, CH_2OH); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 15.43, 31.60, 61.80 (CH_2); 80.22 (C≡C).

Oct-4-yne-1,8-diyl bis(methanesulfonate) 16

Methanesulfonyl chloride (11.5 g, 100 mmol, 1:1 in dry CH_2Cl_2) was added to a stirred solution of **15** (4.9 g, 34.5 mmol) and triethylamine (10.2 g, 100 mmol) in dry CH_2Cl_2 (150 ml) while the temperature was kept below 5 °C. After stirring for one hour at 0 °C the mixture was hydrolyzed with ice–water. After addition of NaCl the layers were separated and the organic layer was washed with a solution of phosphate buffer (5%, 3 × 50 ml), saturated aq. ammonium chloride (50 ml) and

water (50 ml), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica, cyclohexane–ethyl acetate, 1:1) and recrystallized from methanol to give **16** (8.3 g, 80%) as a colorless crystalline solid (mp 42 °C) (Calc. for $C_{10}H_{18}O_6S_2$: C, 40.25; H, 6.08; S, 21.49. Found: C, 40.22; H, 5.96; S, 21.29%). UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 230 (1.04); 258 (0.87); IR (KBr) ν_{max}/cm^{-1} 3426 (br),3052 (s), 2972 (s), 2942 (s), 2921 (s), 1462 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.85–1.97 (m, 4H, CH_2); 2.28–2.37 (m, 4H, CH_2); 3.01 (s, 6H, CH_3); 4.32 (t, *J* 6.1, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 15.07, 28.36 (CH_2); 37.44 (CH_3); 68.60 (CH_2); 79.44 (C≡C).

1,8-Dibromooct-4-yne 17

A solution of **16** (25.8 g, 86 mmol) in acetone (520 ml) was refluxed with LiBr (45.2 g, 520 mmol) for two hours and stirred overnight at room temperature. Water was added to dissolve the precipitated salt, the phases were separated and the aqueous layer extracted with ethyl acetate (3 × 100 ml) while the organic layer was concentrated *in vacuo*. The residue was taken up with ethyl acetate (300 ml) and the combined organic layers dried over $MgSO_4$. The solvent was removed quickly *in vacuo* and the crude product purified by column chromatography (alumina, cyclohexane–ethyl acetate, 2:1) to yield **17** (21.45 g, 92.4%) as a colorless viscous liquid. An analytical sample was purified by kugelrohr distillation [bp (0.2 mbar): 110 °C] (Calc. for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.63. Found: C, 35.85; H, 4.50; Br, 59.43%). UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 222 (3.55); IR (KBr) ν_{max}/cm^{-1} 2962 (s), 2940 (s), 2912 (s), 2841 (m), 1432 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.95–2.07 (m, 4H, CH_2); 2.30–2.34 (m, 4H, CH_2); 3.51 (t, *J* 6.5, 4H, CH_2Br); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 17.59, 31.87, 32.56 (CH_2); 79.35 (C≡C).

N,*N*,*N*′,*N*′-Tetraallyloct-4-yne-1,8-diamine 18

A mixture of **17** (5.4 g, 20 mmol) and diallylamine (4.3 g, 44 mmol) in acetonitrile (200 ml) with powdered K_2CO_3 (5.55 g, 80 mmol) was refluxed overnight. After filtration the solvent was removed *in vacuo* and pure **18** (5.28 g, 90%) obtained by distillation [bp 0.045 mbar): 119–120 °C] as a colorless viscous and hygroscopic liquid (Calc. for $C_{20}H_{32}N_2$: C, 79.94; H, 10.73; N, 32.17. Found: C, 78.42; H, 10.61; N, not measured%). UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 222 (3.55); IR (KBr) ν_{max}/cm^{-1} 3076 (m), 2934 (s), 2800 (s), 1849 (w), 1643 (s), 1418 (m); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55–1.69 (m, 4H, CH_2); 2.01–2.19 (m, 4H, CH_2); 2.44–2.54 (m, 4H, CH_2); 3.07 (d, *J* 6.5, 8H, CH_2); 5.07–5.20 (m, 8H, H_2C=CH); 5.75–5.91 (m, 4H, H_2C=C*H*); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 16.80, 26.78, 52.42, 57.07 (CH_2); 80.14 (C≡C); 117.31 (H_2C=CH); 136.01 (H_2C=*C*H).

Oct-4-yne-1,8-diamine 19

A solution of **18** (3.0 g, 10 mmol) in dry degassed CH_2Cl_2 (10 ml) was added *via* syringe to a solution of $Pd(PPh_3)_4$ (462 mg, 0.4 mmol) and *N*,*N*′-dimethylbarbituric acid (NDMBA) (18.74 g, 120 mmol) in dry degassed CH_2Cl_2 (100 ml) under argon and the mixture was refluxed for five hours. The product precipitated in the form of its barbiturate and was filtered off, dissolved in water and brought to pH 14 with aq. NaOH (5 M). After extraction with $CHCl_3$ (5 × 100 ml) the organic phase was washed with brine and the solvent removed *in vacuo*. Pure **19** (965 mg, 70%) was obtained by kugelrohr distillation [bp (0.040 mbar): 90–100 °C] as a colorless viscous and very hygroscopic liquid which solidifies on ice (Calc. for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98. Found: C, 67.91; H, 11.47; N, not measured%). UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 232 (1.75); 302 (0.51); IR (KBr) ν_{max}/cm^{-1} 3366 (m), 2934 (vs), 2856 (s), 1600 (m), 1436 (m); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (s, 4H, NH_2); 1.47–1.63 (m, 4H, CH_2); 2.11–2.21 (m, 4H, CH_2); 2.73 (t, *J* 6.9, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 16.22, 32.86, 41.33 (CH_2); 79.92 (C≡C).

General procedure for the preparation of the bicyclic diazaalkynes 34–47

A solution of **17** (2.0 g, 7.5 mmol) and of the corresponding α,ω-diamine (3.4 mmol) in acetonitrile (750 ml) together with powdered K_2CO_3 (5.0 g, 72 mmol) was refluxed for four days. After filtration the solvent was removed *in vacuo* and pure product obtained by column chromatography (alumina, cyclohexane–ethyl acetate mixtures or acetone) and (if possible) recrystallized from ethyl acetate.

1,10-Diazabicyclo[8.8.2]icosa-5,14-diyne 34 (*n* = 2). Eluent: acetone; yield: 722 mg, 78% (colorless crystalline solid), mp 93–94 °C (Calc. for $C_{18}H_{28}N_2$: C, 79.36; H, 10.36; N, 10.28. Found: C, 79.24; H, 10.27; N, 10.23%); HRMS, EI *m*/*z* 272.2268, Calc. for $C_{18}H_{28}O_2$ (M^+): 272.2252; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 222 (4.22); IR (KBr) ν_{max}/cm^{-1} 3445 (br), 2981 (vs), 2960 (vs), 2862 (vs), 2789 (vs), 2241 (w), 1638 (w), 1457 (vs), 1436 (s); ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 1.57–1.71 (m, 8H); 2.29 (s, br, 8H); 2.39 (s, br, 8H); 2.51 (s, 4H); ^{1}H NMR ($CDCl_3$, 300 MHz, −70 °C) δ 1.23–1.63 (m, 8H); 1.64–1.82 (m, 2H); 1.83–2.04 (m, 8H); 2.23–2.44 (m, 2H); 2.47–2.67 (m, 2H); 2.82–3.03 (m, 2H); 3.15–3.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 125.76 MHz, 25 °C) δ 17.62, 25.54, 50.82, 52.82 (CH_2); 81.82 (C≡C); ^{13}C NMR ($CDCl_3$, 75.47 MHz, −60 °C) δ 15.09, 19.38, 24.13, 25.23, 48.03, 49.94, 55.60 (CH_2); 80.29, 82.94 (C≡C).

1,10-Diazabicyclo[8.8.3]henicosa-5,14-diyne 35 (*n* = 3). Eluent: ethyl acetate; yield: 747 mg, 77% (colorless wax-like solid, hygroscopic); HRMS, EI *m*/*z* 286.2404, calc. for $C_{19}H_{30}N_2$ (M^+): 286.2408; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.57–1.72 (m, 8H); 1.73–1.89 (m, 2H); 2.15–2.25 (m, 8H); 2.58–2.71 (m, 12H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 18.10, 26.10, 27.23, 54.04, 54.65 (CH_2); 81.77 (C≡C).

1,10-Diazabicyclo[8.8.4]docosa-5,14-diyne 36 (*n* = 4). Eluent: ethyl acetate; yield: 431 mg, 40.5% (colorless wax-like solid, hygroscopic); HRMS, EI *m*/*z* 300.2580, calc. for $C_{20}H_{32}N_2$ (M^+): 300.2565; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 224 (4.08); IR (KBr) ν_{max}/cm^{-1} 3439 (br), 2917 (vs), 2804 (vs), 2238 (w), 1638 (w), 1457 (s), 1432 (s); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52–1.74 (m, 12H); 2.15–2.26 (m, 8H); 2.32–2.41 (m, 4H); 2.61 (t, *J* 6.4, 8H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 17.92, 23.62, 24.42, 52.62, 54.00 (CH_2); 80.77 (C≡C).

1,10-Diazabicyclo[8.8.5]tricosa-5,14-diyne 37 (*n* = 5). Eluent: cyclohexane–ethyl acetate, 5:1; yield: 679 mg, 63.7% (colorless crystalline solid), mp 82 °C (Calc. for $C_{21}H_{34}N_2$: C, 80.20; H, 10.90; N, 8.91. Found: C, 80.00; H, 10.80; N, 8.83%); HRMS, EI *m*/*z* 314.27215, calc. for $C_{21}H_{34}N_2$ (M^+): 314.27219; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 222 (3.89); IR (KBr) ν_{max}/cm^{-1} 3444 (br), 2956 (vs), 2914 (vs), 2844 (vs), 2799 (vs), 2739 (s), 2669 (m), 2233 (w), 1651 (w), 1457 (vs), 1429 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.40–1.49 (m, 4H); 1.53–1.65 (m, 8H); 1.66–1.75 (m, 2H); 2.05–2.14 (m, 4H); 2.23–2.37 (m, 8H), 2.37–2.48 (m, 4H); 2.66–2.76 (m, 4H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.68, 26.48, 26.72, 28.78, 54.90, 55.39 (CH_2); 81.40 (C≡C).

1,7,16,22-Tetraazatetracyclo[14,14,8,8^{7,22}]hexatetraconta-11,26,34,42-tetrayne 48. Eluent: cyclohexane–ethyl acetate, 5:1; yield: 260 mg, 24.4% (colorless, crystalline solid), mp 71 °C HRMS, EI *m*/*z* 628.5411, calc. for $C_{42}H_{68}N_4$ (M^+): 628.5444; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 232 (3.87); IR (KBr) ν_{max}/cm^{-1} 3444 (br), 2930 (vs), 2854 (s) 2803 (vs), 2749 (m), 1633 (w), 1462 (vs); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.35–1.45 (m, 4H); 1.47–1.65 (m, 24H); 2.12–2.24 (m, 16H); 2.44–2.54 (m, 16H), 2.54–2.60 (m, 8H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 16.37, 16.65, 23.79, 26.39, 26.92, 27.01, 52.44, 53.57, 53.69 (CH_2); 80.38, 80.81 (C≡C).

1,10-Diazabicyclo[8.8.6]tetracosa-5,14-diyne 38 (n = 6). Eluent: cyclohexane–ethyl acetate, 5:1; yield: 459 mg, 41.2% (colorless crystalline solid), mp 78 °C (Calc. for $C_{22}H_{36}N_2$: C, 80.43; H, 11.04; N, 8.53. Found: C, 80.28; H, 11.08; N, 8.53%); HRMS, EI *m*/*z* 328.28794, calc. for $C_{22}H_{32}N_2N_2$ (M^+): 328.28784; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 232 (3.68); IR (KBr) ν_{max}/cm^{-1} 3445 (br), 2953 (vs), 2926 (vs), 2899 (vs), 2854 (s), 2787 (vs), 2739 (s), 2670 (w), 1652 (w), 1454 (m), 1428 (m); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42–1.54 (m, 8H); 1.54–1.70 (m, 8H); 2.05–2.34 (m, 8H); 2.40–2.67 (m, 12H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 17.19, 26.04, 26.51, 27.61, 52.76, 53.65 (CH_2); 80.80 (C≡C).

1,10-Diazabicyclo[8.8.7]pentacosa-5,14-diyne 39 (n = 7). Eluent: cyclohexane–ethyl acetate, 5:1; yield: 628 mg, 54.1% (colorless crystalline solid), mp 42 °C (Calc. for $C_{23}H_{38}N_2$: C, 80.64; H, 11.18; N, 8.18. Found: C, 80.57; H, 11.12; N, 8.13%); HRMS, EI *m*/*z* 342.30359, calc. for $C_{23}H_{38}N_2$ (M^+): 342.303050; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 234 (3.57); IR (KBr) ν_{max}/cm^{-1} 3445 (br), 2932 (vs), 2857 (s), 2813 (s), 1651 (w), 1460 (m), 1432 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32–1.40 (m, 2H); 1.42–1.56 (m, 8H); 1.56–1.74 (m, 8H); 2.13–2.23 (m, 4H); 2.26–2.36 (m, 4H); 2.56–2.71 (m, 12H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.38, 25.09, 26.33, 26.98, 28.63, 53.51, 54.06 (CH_2); 80.83 (C≡C).

1,10-Diazabicyclo[8.8.8]hexacosa-5,14-diyne 40 (n = 8). Eluent: cyclohexane–ethyl acetate, 5:1; yield: 725 mg, 60.0% (colorless crystalline solid), mp 61 °C (Calc. for $C_{24}H_{40}N_2$: C, 80.84; H, 11.31; N, 7.71. Found: C, 80.49; H, 11.22; N, 7.75%); HRMS, EI *m*/*z* 356.3189, calc. for $C_{24}H_{40}N_2$ (M^+): 356.3132; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 234 (3.67); IR (KBr) ν_{max}/cm^{-1} 3446 (br), 2935 (vs), 2914 (vs), 2853 (s), 2790 (vs), 2739 (m), 2666 (w), 1652 (w), 1456 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.30–1.40 (m, 4H); 1.41–1.91 (m, 4H); 1.43–1.59 (m, 4H); 1.56–1.74 (m, 8H); 2.22–2.28 (m, 8H); 2.36–2.55 (m, 12H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.28, 26.26, 26.80, 28.33, 29.46, 53.19, 54.29 (CH_2); 80.88 (C≡C).

1,11-Diazabicyclo[9.8.8]heptacosa-15,23-diyne 41 (n = 9). Eluent: cyclohexane–ethyl acetate, 5:1; yield: 637 mg, 50.7% (colorless viscous liquid); HRMS, EI *m*/*z* 370.33563, calc. for $C_{25}H_{42}N_2$ (M^+): 370.33481; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27–1.39 (m, 10H), 1.39–1.52 (m, 4H), 1.53–1.74 (m, 8H), 2.16–2.31 (m, 8H), 2.42–2.49 (m, 4H), 2.50–2.63 (m, 8H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 17.21, 25.19, 26.44, 26.52, 26.90, 28.44, 53.27, 54.02 (CH_2); 80.80 (C≡C).

1,12-Diazabicyclo[10.8.8]octacosa-16,24-diyne 42 (n = 10). Eluent: cyclohexane–ethyl acetate, 5:1; yield: 392 mg, 30.0% (colorless crystalline solid), mp 48 °C (Calc. for $C_{26}H_{44}N_2$: C, 81.19; H, 11.53; N, 7.28. Found: C, 80.96; H, 11.53; N, 7.21%); HRMS, EI *m*/*z* 384.34982, calc. for $C_{26}H_{44}N_2$ (M^+): 384.35046; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 224 (3.79); IR (KBr) ν_{max}/cm^{-1} 3441 (br), 2926 (vs), 2853 (s), 2789 (vs), 2741 (w), 1632 (w), 1459 (s), 1427 (w); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28–1.38 (m, 12H); 1.40–1.49 (m, 4H); 1.56–1.70 (m, 8H); 2.14–2.23 (m, 4H); 2.26–2.34 (m, 4H); 2.37 (t, *J* 6.7, 4H); 2.46–2.53 (m, 8H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.06, 25.85, 26.45, 26.54, 27.36, 28.11, 52.99, 53.70 (CH_2); 80.72 (C≡C).

21-Oxa-1,10-diazabicyclo[8.8.5]tricosa-5,14-diyne 43 (n = 1). Eluent: ethyl acetate; yield: 342 mg, 32.0% (colorless crystalline solid), mp 74 °C (Calc. for $C_{20}H_{32}N_2O$: C, 75.90; H, 10.19; N, 8.85. Found: C, 75.50; H, 10.09; N, 8.77%); HRMS, EI *m*/*z* 316.25159, calc. for $C_{20}H_{32}N_2O$ (M^+): 316.25146; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 230 (3.45); IR (KBr) ν_{max}/cm^{-1} 3424 (br), 2931 (vs), 2897 (vs), 2866 (vs), 1652 (w), 1461 (m), 1435 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.55–1.79 (m, 8H); 2.13–2.34 (m, 8H); 2.84–2.96 (m, 12H); 3.64 (t, *J* 5.5, 4H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.54, 26.53, 52.94, 53.39, 69.68 (CH_2); 81.04 (C≡C).

4,7-Dioxa-1,10-diazabicyclo[8.8.8]hexacosa-14,22-diyne 44 (n = 2). Eluent: cyclohexane–ethyl acetate, 2:1; yield: 956 mg, 78.3% (colorless crystalline solid), mp 81 °C (Calc. for $C_{22}H_{36}N_2O_2$: C, 73.29; H, 10.06; N, 7.77. Found: C, 73.03; H, 10.03; N, 7.69%); HRMS, EI *m*/*z* 360.2780, calc. for $C_{22}H_{36}N_2O_2$ (M^+): 360.27768; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 222 (3.64); IR (KBr) ν_{max}/cm^{-1} 3444 (br), 2943 (vs), 2891 (vs), 2782 (vs), 2716 (s), 2236 (w), 1651 (w), 1452 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.56–1.72 (m, 8H); 2.16–2.31 (m, 8H); 2.70–2.84 (m, 8H); 2.86 (t, *J* 5.5, 4H); 3.62–3.68 (m, 8H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.09, 27.37, 53.46, 53.76, 67.82, 71.75 (CH_2); 80.53 (C≡C).

1,10-Diazabicyclo[8.8.4]icosa-5,14,20-triyne 45 (n = 1). Eluent: ethyl acetate; yield: 724 mg, 72.0% (colorless crystalline solid), mp 165 °C (Calc. for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.45. Found: C, 79.75; H, 9.55; N, 9.45%); HRMS, EI *m*/*z* 296.2231, calc. for $C_{20}H_{28}N_2$ (M^+): 296.2252; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 230 (2.69); IR (KBr) ν_{max}/cm^{-1} 3426 (br), 2947 (vs), 2903 (vs), 2840 (vs), 2792 (w), 1638 (w), 1437 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.53–1.63 (m, 4H); 1.66–1.77 (m, 4H); 2.00–2.11 (m, 4H); 2.30–2.39 (m, 4H); 2.50–2.60 (m, 4H); 2.98–3.07 (m, 4H); 3.50 (s, 4H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.18, 25.56, 39.13, 54.87 (CH_2); 78.43, 81.40 (C≡C).

1,10-Diazabicyclo[8.8.6]tetracosa-5,14,21-triyne 46 (n = 2). Eluent: cyclohexane–ethyl acetate, 5:1; yield: 426 mg, 38.6% (colorless crystalline solid), mp 115 °C (Calc. for $C_{22}H_{32}N_2$: C, 81.43; H, 9.94; N, 8.63. Found: C, 81.29; H, 9.80; N, 8.62%); HRMS, EI *m*/*z* 324.25770, calc. for $C_{22}H_{32}N_2$ (M^+): 324.25770; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 239 (3.42); IR (KBr) ν_{max}/cm^{-1} 3433 (br), 2949 (vs), 2928 (vs), 2897 (vs), 2862 (vs), 2839 (vs), 1632 (w), 1423 (m); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.55–1.72 (m, 8H); 2.12–2.33 (m, 8H); 2.34–2.40 (m, 4H); 2.95–3.05 (m, 8H); 3.16–3.26 (m, 4H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 15.91, 17.20, 27.46, 52.78, 54.02 (CH_2); 80.79, 81.83 (C≡C).

1,10-Diazabicyclo[8.8.8]hexacosa-5,14,22-triyne 47 (n = 3). Eluent: cyclohexane–ethyl acetate, 10:1; yield: 485 mg, 40.6% (colorless crystalline solid), mp 92 °C (Calc. for $C_{24}H_{36}N_2$: C, 81.76; H, 10.29; N, 7.95. Found: C, 81.36; H, 10.21; N, 7.90%); HRMS, EI *m*/*z* 352.28808, calc. for $C_{24}H_{36}N_2$ (M^+): 352.28784; UV–VIS (CH_2Cl_2) λ_{max}/nm (log ε) 224 (3.79); IR (KBr) ν_{max}/cm^{-1} 3441 (br), 2928 (vs), 2886 (vs), 2808 (vs), 2771 (vs), 2700 (w), 2236 (w), 1738 (w), 1638 (w), 1462 (s), 1441 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.62–1.78 (m, 8H); 2.19–2.25 (m, 8H); 2.54 (t, *J* 7.0, 8H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 17.51, 26.14, 53.42 (CH_2); 81.22 (C≡C).

X-Ray structural analysis of 34–48

The measurements on **34**, **35**, **38**, **39**, **42**, **44** and **48** were recorded on a Siemens X-ray diffractometer equipped with a SMART CCD detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The SMART software package[20] was used for data collection as well as frame integration. Structure solution was carried out using the SHELXTL V5.10 software package.[21] The data for **37**, **43**, **46** and **47** were collected with a Nonius-CAD4 diffractometer (Mo-Kα radiation, graphite monochromator, ω–2θ-scan). Intensities of all structures were corrected for Lorentz and polarisation effects. Structure solution was carried out using the SHELXS-97 software package.[22] All structures were solved by direct methods. Full matrix least squares refinement was carried out against F^2. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically for **39**, **42**, **46**, **47** and **48** or

Table 2 Crystallographic data

	34	**35**	**37**	**38**	**39**	**42**	**43**	**44**	**46**	**47**	**48**
Empirical formula	$C_{18}H_{28}N_2$	$C_{19}H_{30}N_2$ (·4H_2O)	$C_{21}H_{34}N_2$	$C_{22}H_{36}N_2$	$C_{23}H_{38}N_2$	$C_{26}H_{44}N_2$	$C_{20}H_{32}N_2O$ (·6H_2O)	$C_{22}H_{36}N_2O_2$	$C_{22}H_{32}N_2$	$C_{24}H_{36}N_2$	$C_{42}H_{68}N_4$
Formula weight	272.42	356.91	314.5	328.53	342.55	384.63	316.5	360.53	324.50	352.55	125.80
Temperature/K	200(2)	200(2)	223(2)	200(2)	200(2)	200(2)	223(2)	200(2)	223(2)	293(2)	200(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12$	$P\bar{1}$	$C2/c$	$Fdd2$	$Fdd2$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_12_12$	$C2/c$
Z	2	4	12	8	8	4	4	4	4	2	4
a/Å	10.7545(2)	11.1299(9)	30.67(1)	16.5939(8)	16.0954(4)	9.8034(1)	8.899(3)	8.9706(1)	9.569(1)	12.177(2)	25.4676(3)
b/Å	11.0123(2)	12.4995(10)	12.356(2)	28.3186(13)	33.2375(9)	11.9812(2)	12.364(2)	20.6147(3)	12.697(2)	9.875(2)	10.5968(2)
c/Å	6.8433(1)	15.5200(13)	15.188(7)	8.6029(4)	7.8746(2)	20.9007(3)	20.155(6)	11.4614(1)	16.052(5)	8.532(5)	14.8576(2)
α/°	90	101.348(1)	90	90	90	90	104.35(3)	90	90	90	90
β/°	90	93.019(2)	91.13(3)	90	90	91.531(1)	94.56(3)	94.86	98.82(2)	90	93.620(1)
γ/°	90	102.137(1)	90	90	90	90	99.02(3)	90	90	90	90
U/Å^3	810.46(2)	2059.6(3)	5754(4)	4042.6(3)	4212.7(2)	2454.05(6)	2106(1)	2111.90(4)	1927.2(7)	1026.0(3)	4001.7(1)
Absorption coefficient, μ/mm^{-1}	0.065	0.080	0.06	0.062	0.062	0.060	0.09	0.072	0.07	0.07	0.060
Reflections collected	6016	15475	7036	7363	7681	17751	10779	15586	4910	1441	14473
Independent reflections	1408 R(int) = 0.028	6862 R(int) = 0.058	6913 R(int) = 0.013	1750 R(int) = 0.024	1749 R(int) = 0.017	4249 R(int) = 0.022	10134 R(int) = 0.036	3668 R(int) = 0.025	4641 R(int) = 0.025	1441	3478 R(int) = 0.026
Final R indices [$I > 2\sigma(I)$]	$R(F) = 0.031$ $R_w(F^2) = 0.071$	$R(F) = 0.061$ $R_w(F^2) = 0.128$	$R(F) = 0.050$ $R_w(F^2) = 0.133$	$R(F) = 0.041$ $R_w(F^2) = 0.107$	$R(F) = 0.031$ $R_w(F^2) = 0.071$	$R(F) = 0.040$ $R_w(F^2) = 0.100$	$R(F) = 0.055$ $R_w(F^2) = 0.159$	$R(F) = 0.035$ $R_w(F^2) = 0.084$	$R(F) = 0.039$ $R_w(F^2) = 0.093$	$R(F) = 0.035$ $R_w(F^2) = 0.093$	$R(F) = 0.038$ $R_w(F^2) = 0.089$

calculated in the cases of **34**, **35**, **37**, **38**, **43** and **44**. In the structures of **37**, **38** and **43** some disorder was found and considered in the structure model. For **37** we found a complete (see Fig. 6) and a half molecule as independent unit. Six of the carbon atoms of the half molecule were disordered over two positions with an occupancy of 50%. In **38** a disorder was found for the two central methylene groups of the hexamethylene bridge creating a crystallographic C_2 axis. One of the two independent molecules which were found in compound **43** was disordered at the oxygen and five of the carbon atoms. The crystallographic data are listed in Table 2.†

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