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2,6,9-Trioxabicyclo[3.3.1]nona-3,7-dien-4-oyl and tetraoxaadamantan-9-oyl functionalized aromatic di- and triamines: synthesis, stereochemistry and complexation

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Abstract—Primary amino groups of di- or triaminoaryl compounds add a remarkably stable dioxinyl-α-oxoketene affording bis- or tris-[trioxabicyclo[3.3.1]nona-3,7-dienyl (bridged *bisdioxine*)] systems which can be converted into the corresponding bis- or tris-[2,4,6,8-tetraoxadamantanes] by acidic hydrolysis. Stereochemical peculiarities as well as preliminary host–guest abilities of these molecules are investigated with aid of NMR-spectroscopy, an X-ray analysis and ESI-mass spectrometry.

1. Introduction

Dimerization of dipivaloylketene, generated by flash vacuum pyrolysis of the corresponding furan-2,3-dione as suitable precursor,[1] affords the remarkably stable α-oxoketene **1** in quantitative yield. This oxoketene **1** smoothly adds primary aromatic amines bearing no or electron donating substituents under mild reaction conditions to furnish functionalized trioxabicyclo[3.3.1]nona-3,7-dienes **2** (bridged *bisdioxines*) in a one-step procedure.[2] From reactants having two amino- functionalities the corresponding bis- bridged bisdioxine derivatives (e.g. **3**) were obtained, which as a stereochemical peculiarity due to the concave nature of the *bisdioxine* system should be able to adopt a 'claw'-like conformation (see Chart 1),[2a] in particular in the presence of suitable guest molecules. In addition, the bridged bisdioxine unit in general may easily be converted into the 2,4,6,8-tetraoxaadamantyl scaffold (e.g. **4**) by acidic hydrolysis.[3] Furthermore, due to the axial chirality of the bridged *bisdioxine*—as well as of the tetraoxaadamantane ring system[2,3]—all compounds having two or more of those structural units should exist as a mixture of diastereomers (*R*,*R*; *S*,*S*; *S*,*R*; *R*,*S*) which might be observable by means of their NMR spectra.

Keywords: α-Oxoketene; Aromatic di- and triamines; Bridged *bisdioxines*; Tetraoxadamantanes; Complexation studies; X-ray analysis.
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2. Results and discussion

In order to determine the scope and limitations of the preparation of such potential claw-molecules several aromatic diamines as well as triamines with different molecular skeletons have been subjected to reactions with the dimeric α-oxoketene **1**. Besides the synthetic task we also wanted to investigate whether those molecules would adopt their *syn*- (claw-like) conformation when suitable guest-molecules are offered for complexation, since the unsubstituted trioxabicyclo[3.3.1]nona-3,7-diene system itself was found to coordinate transition metals (i.e. Rh^{+}, Pt^{2+}, or Pd^{2+}).[4]

2.1. 1,3-Diaminobenzene

Both amino groups of 1,4-diaminobenzene add the oxoketene **1** thus affording the bis-product **5**,[2a] while obviously due to steric hindrance only one amino group reacts, when 1,2-diaminobenzene is employed, giving **6**.[2b] On the other hand, 1,3-diaminobenzene, after a reaction time of 5 d again adds two molecules of **1** to give compound **7** in 83% yield (Scheme 1), since, as can be easily seen from molecule models, the distance between the two bulky bridged *bisdioxines* is now far enough to minimize steric interactions.

Furthermore, following the usual procedure,[3] H^{+}- catalyzed hydrolysis converts the bisdioxine-product **7** into the

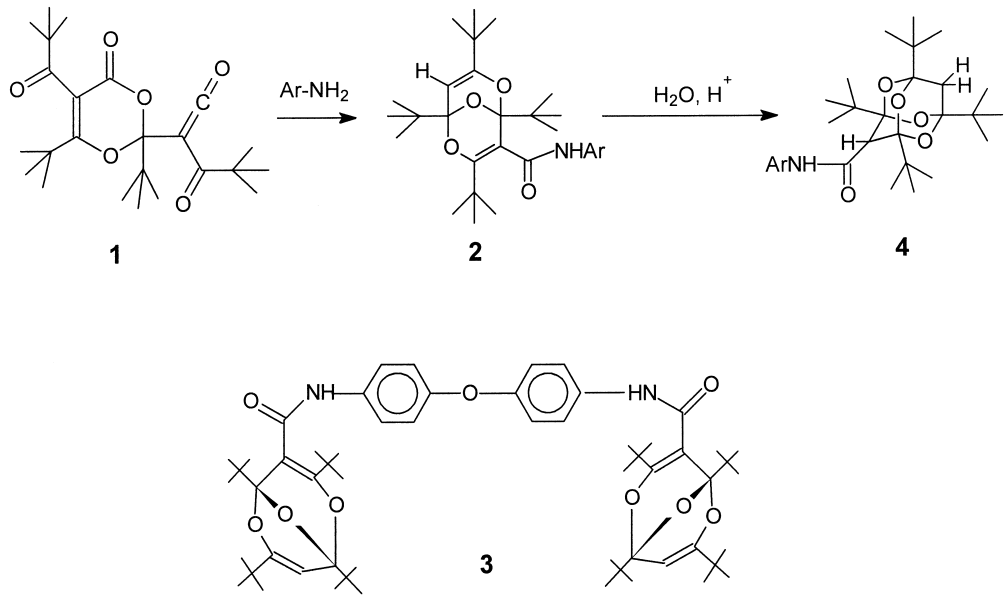
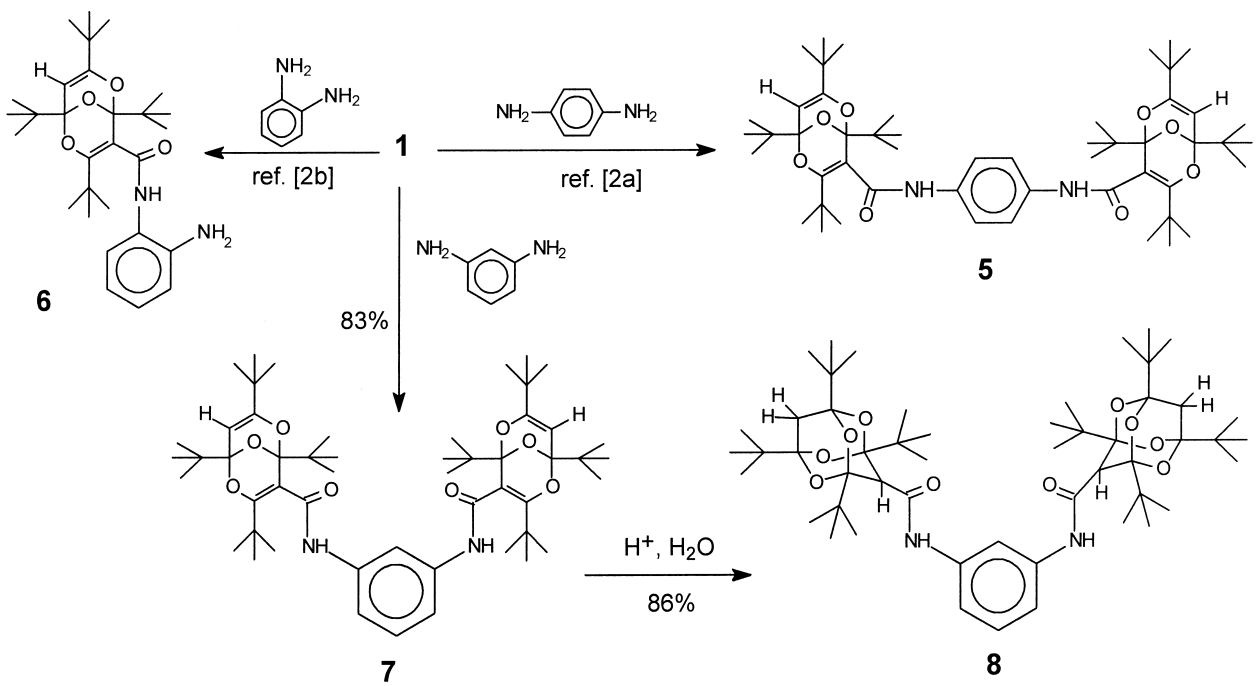


Chart 1.



Scheme 1. Reactions of diaminobenzenes with α-oxoketene **1**.

corresponding bis-tetraoxadamantanyl derivative **8**. The structural elucidation of **7** and **8** comes particularly from ^{1}H NMR data and their comparison with several analogues:[2,3] Signals at δ 4.83 (s, 2H, =CH) and at 1.05, 1.14, 1.20, 1.25 ppm (s, 18H each, rotamers, *t*-Bu) in **7**, as well as signals at δ 3.05 (s, 2CH), 1.78 (s, 2CH$_2$) and 0.98 (s, 18H, 2*t*-Bu), 1.05 (s, 36H, 4*t*-Bu), 1.28 ppm (s, 18H, 2*t*-Bu) for **8** are highly characteristic of the bridged *bisdioxine* and the tetraoxaadmantane skeletons.

There is no indication of any splitting of signals possibly coming from the presence of diastereomers. Obviously, the differences in the specific chemical shift values are too small to be detectable, at least at frequencies of 200, 360 or even 500 MHz.

2.2. Diamino-naphthalenes and -fluorenes

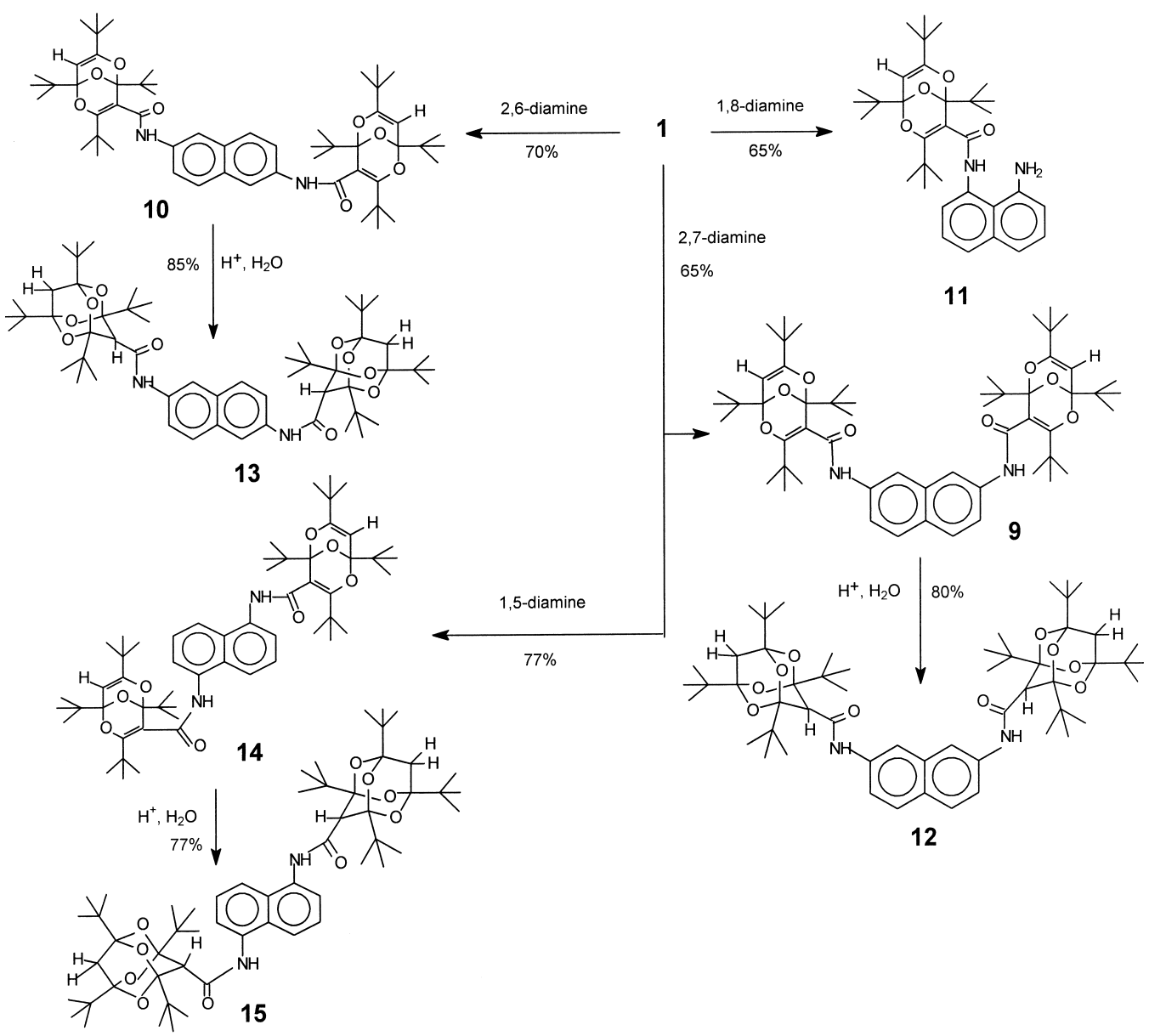
When 2,6- and 2,7-diaminonaphthalenes[5] were reacted with the dimeric oxoketene **1** the bis-bridged bisdioxine compounds **9** and **10** (2:1-ratio of reactants) were obtained as expected in yields of 65–70%. Since of all possible isomeric diaminonaphthalenes these two diamines exhibit the longest distance between the two amino functionalities, there is minimum or even no steric hindrance to be considered. On the other hand, 1,8-diaminonaphthalene

and **1** form the 1:1 adduct **11** only. Here, obviously, as in the case of 1,2-diaminobenzene (Scheme 1) the two amino groups are too close for them both to react with oxoketene **1** (Scheme 2).

The presence of the bridged *bisdioxine* unit in **9**–**11** as well as the 2,4,6,8-tetraoxaadamantane building block in **12** and **13** again is unambiguously established from characteristic NMR spectroscopic data (see discussion above).

Surprisingly, when 1,5-diaminonaphthalene was reacted with oxoketene **1**, the TLC-examination of the reaction product **14** revealed the presence of two compounds with slightly different R_f-values (0.31 and 0.28, eluent dichloromethane/*n*-hexane 3/2). With the aid of DCFC a separation was successfully achieved on a preparative scale, and the two compounds were obtained in a 2:1 (**14a** : **14b**) ratio. The results of the elemental analyses as well as the IR-spectra of **14a** and **14b** indicate the presence of isomers, most probably rotamers, since also the ^{1}H- as well as ^{13}C NMR spectra exhibited identical chemical shift values for the *t*-butyl groups (singlets at δ 1.06, 1.14, 1.24, 1.245 ppm), the olefinic protons (s, 4.92 ppm) and the carbons of the bisdioxine ring skeleton (C-1/C-5: 97.3/99.7; C-3/C-7: 162.2/162.3; C-4: 105.5; C-8: 92.0 ppm). There were only very minor differences ($\Delta\delta$=0.06–0.1 ppm) for three aromatic carbons in the ^{13}C NMR and a slightly different splitting pattern of the aromatic region in the ^{1}H NMR spectra to be observed.

In order to get some more insight into the three-dimensional structure of both isomers, NOE-experiments should be helpful: the signals at 1.06 (*t*-Bu at C-1) and 1.13 ppm (*t*-Bu at C-7) responded to the olefinic proton of the bisdioxine ring, while the signals at 1.24 (*t*-Bu at C-3) effected the CH-4 and CH-8, respectively, of the naphthalene ring. The correct assignment of all *t*-butyl groups was successfully achieved with the aid of HMBC-experiments.[6] The



Scheme 2. Reactions of diaminonaphthalenes with α-oxoketene **1**.

significant down-field shift of the *t*-butyl at C-5 (1.245 ppm) is obviously due to the anisotropic effect of nearby the amide carbonyl. The amazing result now was that all NOE's were found to be identical for both compounds. Therefore, one may conclude, that rotation around the CO–NH-bond is strongly restricted. As a consequence of that, the two isomers **14a** and **14b** could be regarded as *syn* or *anti* isomers with respect to the positions of the two bridged bisdioxines attached to the planar naphthalene ring (see Chart 2).

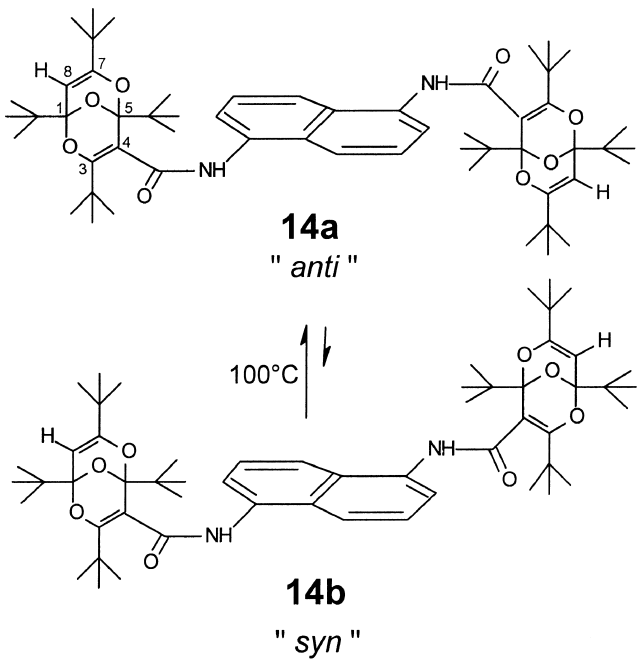


Chart 2.

Fortunately, an X-ray analysis provided unambiguous evidence that **14a** is the *anti*-isomer. In the crystal, **14a** is situated on a center of symmetry which relates the two halves of the molecule (Fig. 1). Furthermore, the structure makes evident the presence of a *R*,*S*-diastereomer. One of the four independent *tert*-butyl groups was found to be disordered over two orientations in each bisdioxine unit. The amide group is not coplanar with the naphthalene ring but is rotated out of the ring plane by approximately 50°. A packing analysis revealed a hydrogen bond between chloroform and the carbonyl oxygen of **14a** with a C···O distance of 3.0 Å.

It should further be noted, that **14b** could be quantitatively converted into the obviously more stable **14a** by heating in the solid state to 100 °C for 6 h.

2.3. Force field calculations

Since with compounds **9** and **10** no evidence was found for the formation of any kind of isomers like in case of **14**, it became highly desirable to obtain informations on the rotational barriers of the bridged *bisdioxine* moieties around the naphthalene axis in **9**, **10** and **14**.

Starting structures of isomeric diamides **9**, **10**, and **14** were generated by the Sybyl molecular modelling package[7] For the molecular mechanics calculations the MM3[8–15] as well as the Tripos[16] force fields were used. In the MM3 calculations, for the π-systems in **9**, **10** and **14** the variable electronegativity SCF (VESCF) correction[17] was applied. Gasteiger–Hückel charges[18] were used in combination with the Tripos force field. After initial minimization of these starting structures (see Fig. 2 for the lowest energy structure of **10**) a systematic conformational search was made for the two aryl –N torsional angels τ_1 and τ_2, defined by τ_1(**14**)=<(C1a–C1–N9–C10), τ_1(**9**, **10**)=<(C1–C2–N9–C10) and τ_2 (**14**)=<(C4a–C5–N9–C10), τ_2 (**10**)=<(C5–C6–N11–C12), τ_2 (**9**)=<(C8–C7–N11–C12) (for atom numbering, see Fig. 2).

2.3.1. Results. A typical conformational energy map (Tripos force field) is shown for **10** in Figure 3. As expected, these contours have an essentially symmetric appearance with potential energy minima at *s-cis* (τ_1, τ_2=±30°) and *s-trans* (τ_1, τ_2=±150°), respectively, orientations of either one of the two amide moieties in **10** and **9**. In contrast, for **14** only minima at *s-trans* (τ_1, τ_2=±150°) arrangements are calculated by both the Tripos and the MM3 force fields.

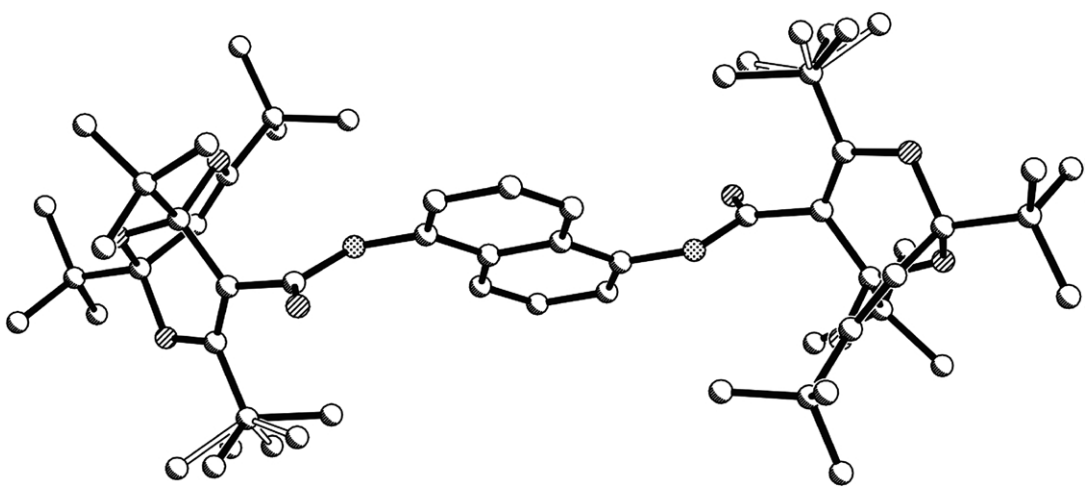


Figure 1. Perspective drawing of the molecule **14a**. Hatched circles represent oxygen atoms, dotted circles are nitrogen atoms (2*t*-butyl groups shown in two disordered orientations).

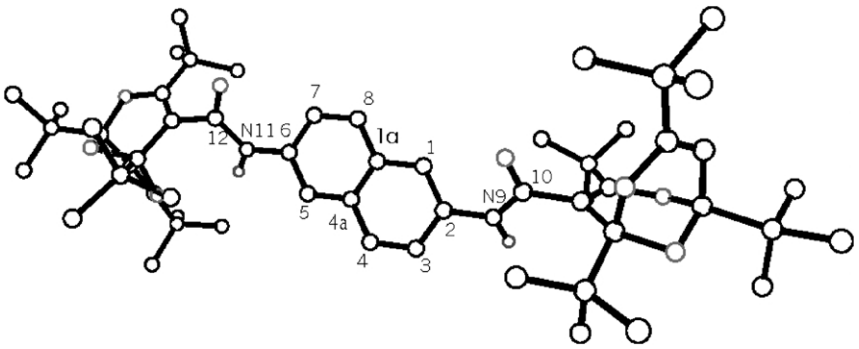


Figure 2. Calculated (Tripos force field) lowest energy structure of **10**.

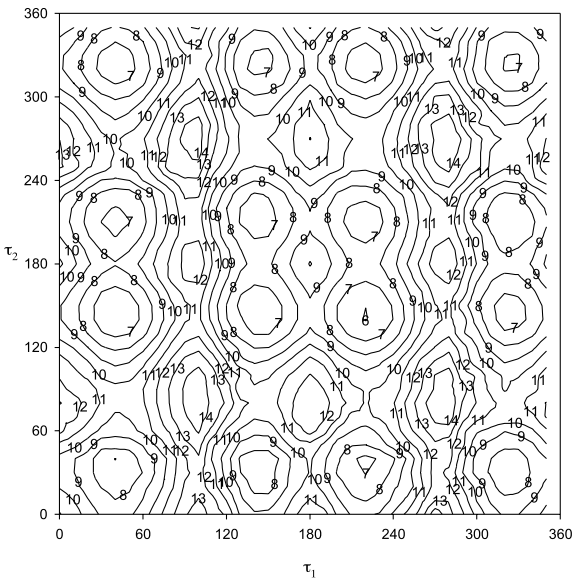


Figure 3. Contour plot (Tripos force field) for rotation of the amide groups (τ_1 and τ_2) in **10**.

Rotations around the two aryl –N bonds are more or less independent (Fig. 4) and, therefore, barriers can be estimated from potential energy curves obtained by varying τ_1 at approximately constant τ_2. For both **10** and **9** the barriers to planarity, i.e. those at 0 and 180° are considerably smaller than those at 90°. Not surprisingly, this result is especially pronounced in case of the MM3 force field with inclusion of π-conjugative effects via the VESCF procedure. For **14**, where no *cisoid* minima are calculated, the highest barrier is found at 0°. Most important, with both force fields the calculated barrier for **14** (10 kcal mol^{-1}) is twice that of either **10** and **9** (4–5 kcal mol^{-1}).

These results are in good agreement with the experimental findings and makes understandable that with compounds **9** and **10**, no rotamers could be detected. Similar results with chromatographic separation of *syn*–*anti*-rotamers of a large macrocyclic system were reported recently by Shimizu et al.[19] **14a**,**b** were also converted into the tetraoxa-adamanatane derivative **15**.

2,7-Diaminofluorene and the unsymmetrical 3,7-diamino-2-methoxyfluorene add the dimeric oxoketene **1** in the usual way to afford the bridged *bisdioxine* derivatives **16** and **17** in excellent yields (90–95%). Both again can be converted into the corresponding tetraoxaadamantanes **18** and **19**, respectively, by acidic hydrolysis. Obviously, the relatively small methoxy group in position 2 does not cause any steric hindrance on the addition of the ketene **1** to the amino group, affording **17** (Scheme 3).

As expected, due to the loss of symmetry caused by the methoxy-group, some signals in the ^{13}C NMR spectrum of **17** appear split compared to **16**, in particular those corresponding to the carbons of the bisdioxine moieties, e.g. the olefinic CH at 92.01 (**16**) and at 92.03, 91.45 ppm (**17**), the enolic C=*C*–O at 162.18, 161.75 (**16**) and at 162.49, 162.00, 161.88, 161.68 ppm (**17**) and the C=*C*–CO at 105.8 (**16**) and at 105.72, 107.01 ppm (**17**).

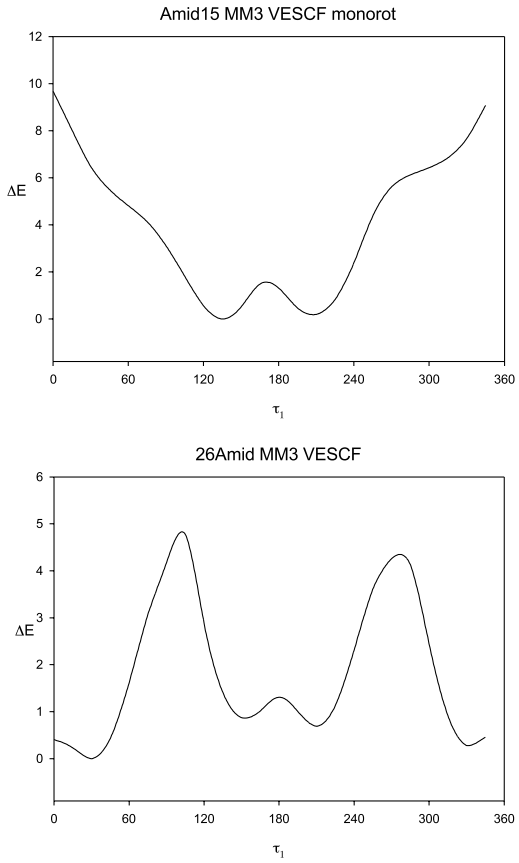
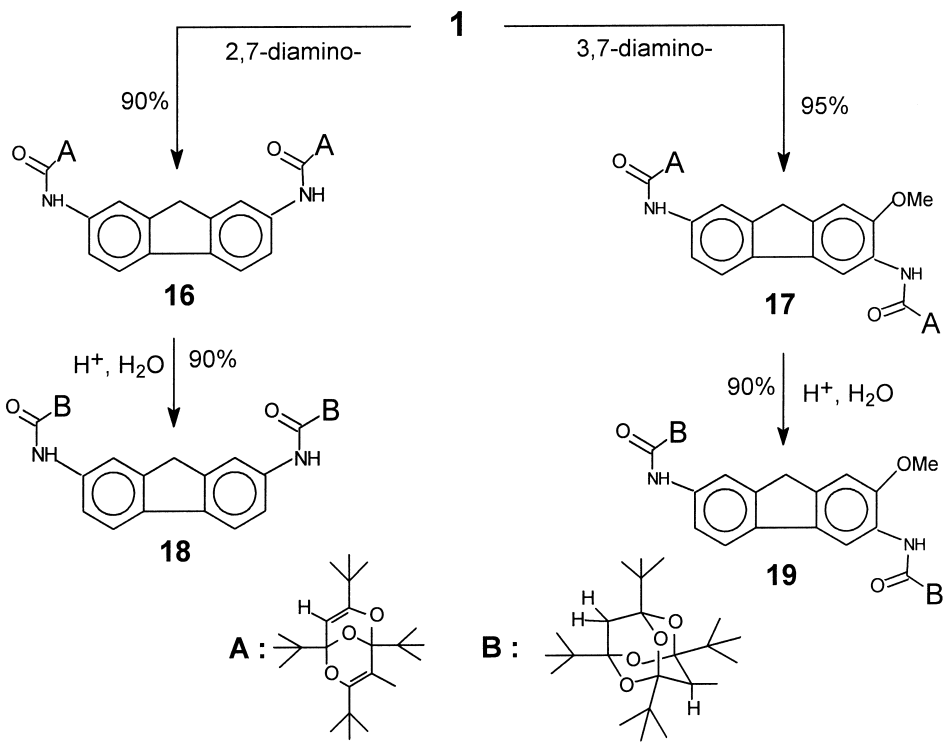
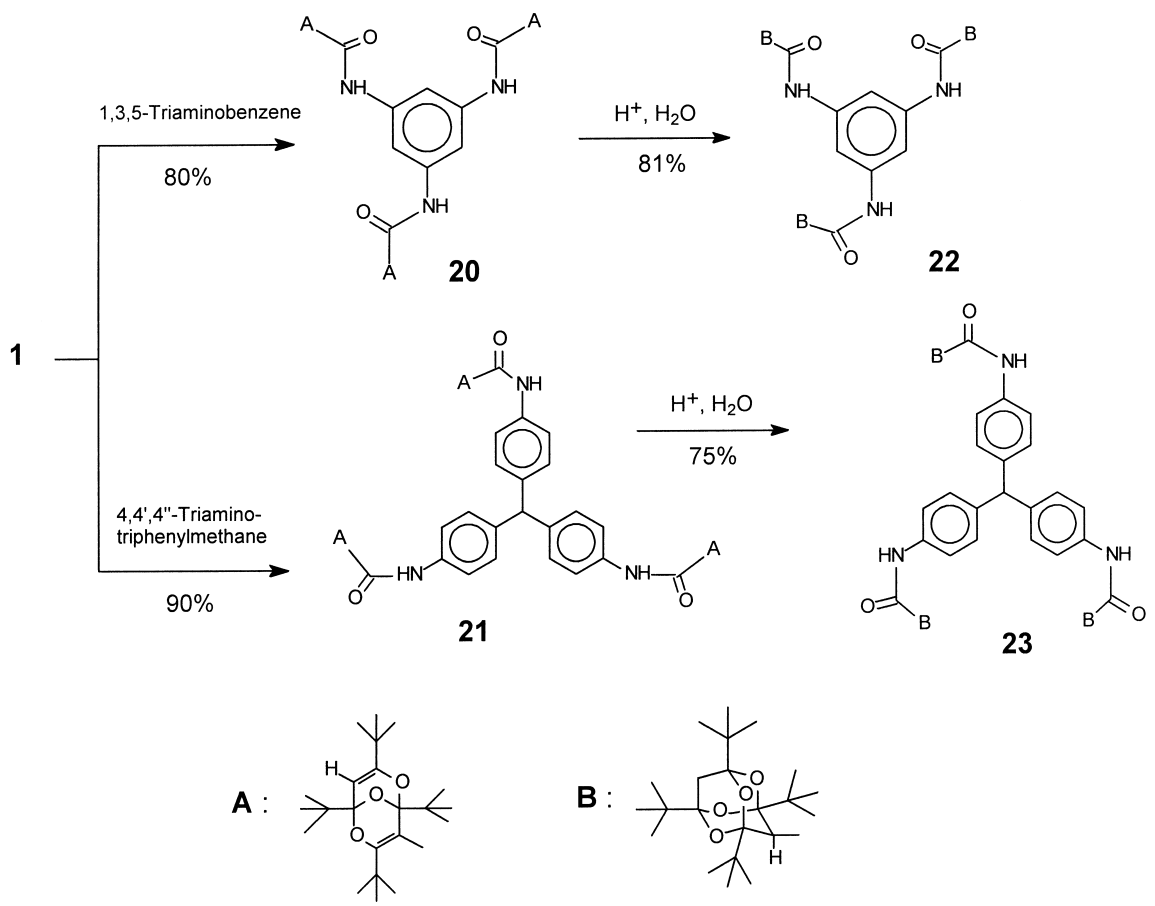


Figure 4. Rotational energy curve of **14** (upper) and **10** (lower) obtained by MM3 VESCF calculations.



Scheme 3. Reactions of diaminofluorenes with α-oxoketene **1**.



Scheme 4. Reactions of triamines with α-oxoketene **1**.

2.4. Triaminoaryl derivatives

In extension of our attempts to synthesize claw-like molecules from suitable diamines and oxoketene **1** we also tried to prepare 'bowl'-like compounds from reaction of corresponding triamines and **1** which could successfully be achieved with 1,3,5-triaminobenzene, prepared via catalytic hydrogenation of 3,5-dinitroaniline.[20] After a long reaction time (10 d) the desired 1 : 3-product **20** could be obtained in 80% yield. The size of the molecule was established by mass spectrometry (*m/z* 1252.9: $M+H^+$, FAB-mode) and elemental analysis (see Section 3 (Scheme 4)).

In a similar way the amino groups of 4,4′,4″-triaminotriphenylmethane[21] added **1** to afford compound **21** (90%, reaction time 3 d) now bearing three bridged *bisdioxines*, which again was established by FAB-mass spectrometry (*m/z*=1418.9, $M+H^+$), elemental analysis as well as by the correct ratio of aromatic to *t*-butyl protons in the ^1H NMR spectrum and correct ^{13}C NMR data, assigned with aid of H-coupling (for details, see the Section 3). Furthermore, both compounds **20** and **21** were converted into the corresponding tetraoxaadamantyl derivatives, **22** and **23** respectively, as evidenced by the presence of their characteristic CH and CH_2-signals of the tetraoxaadamantane moieties[3] at δ 3.03 and 1.75 ppm. Compounds of this type, in particular those with high molecular mass (**19**, **22**, **23**) show a strong tendency to retain water, even after a long period of drying over phosphorous pentoxide (see Section 3).

2.5. Host–guest experiments

Several samples of any type of compounds differing in size and kind of substituents (bridged *bisdioxine* or tetraoxaadamantane) were selected (**5**, **7**, **9**, **14**, **15**, **19**, **21**, and **23**) and their exact geometry was deduced from molecular (*Dreiding*) models. Organic guests were then adjusted considering their size, including estimated van der Waals radii, and their possible lipophilic affinity to the numerous bulky *t*-butyl groups present in the host system. From these considerations choline iodide, benzylammonium chloride and cholesterol were finally selected as promising guest candidates. Hosts and guests (excess) were then mixed in a 1:10 molar ratio in methanolic solution, and after stirring for 24 h at rt (for details see the Section 3) the solution as well as the residue formed were examined with aid of ESI-MS measurements. Electrospray ionization (ESI) has proven to be the method of choice for detection of supramolecular interactions by mass spectrometry in the gas phase.[22] The outcome of these experiments was, that benzylamine binds rather strongly to the host molecules **5**, **7**, **9**, **14**, **15**, **21** (intensity of the mass peaks 100%), somehow weaker to **23** (intensity 30%), choline interacts with **15**, **19** and **21** (peak intensities 20–50%), while cholesterol obviously is too big to show measurable interactions to any of the hosts. These results are summarized in Table 1.

In an attempt to gain insight into the stereochemical situation of the complexes determined by the ESI-MS, NMR-titration experiments were tried with selected

Table 1. ESI-MS data of hosts **5**, **7**, **9**, **14**, **15**, **19**, **21**, and **23** with choline iodide, benzylamine (Bzamine) hydrochloride and cholesterol as guest molecules in methanol or acetonitrile

Host	Mass (MW)	Guest	Mass (MW)	Solvent	Complexation	Mass (M+1)	Peak intensity (%)
5	861.5	Choline	104	MeOH	No		
	861.5	Bzamine	107	MeOH	Yes	968.5	100
7	861.5	Choline	104	MeOH	No		
	861.5	Bzamine	107	MeOH	Yes	968.5	100
9	911.5	Choline	104	MeCN	No		
	911.5	Bzamine	107	MeOH	Yes	1018.8	100
	911.5	Cholesterol	386.6	MeOH	No		
		Cholesterol	386.6	MeCN	No		
14	911.5	Choline	104	MeCN	No		
	911.5	Bzamine	107	MeOH	Yes	1018.5	100
	911.5	Cholesterol	386.6	MeOH	No		
	911.5	Cholesterol	386.6	MeCN	No		
15	947.5	Choline	104	MeOH	Yes	1051.5	20
	947.5	Bzamine	107	MeOH	Yes	1055.5	100
	947.5	Cholesterol	386.6	MeOH	No		
	947.5	Cholesterol	386.6	MeCN	No		
19	1014.5	Choline	104	MeOH	Yes	1119.8	50
	1014.5	Bzamine	107	MeOH	No		
	1014.5	Bzamine	107	MeCN	No		
	1014.5	Cholesterol	386.6	MeOH	No		
	1014.5	Cholesterol	386.6	MeCN	No		
21	1417.8	Choline	104	MeOH	Yes	1522.7	10
	1417.8	Bzamine	107	MeOH	Yes	1526.8	100
	1417.8	Cholesterol	386.6	MeOH	No		
23	1471.8	Choline	104	MeCN	No		
	1471.8	Bzamine	107	MeOH	Yes	1579.8	30
	1471.8	Cholesterol	386.6	MeOH	No		

examples (e.g. **7** with benzylamine hydrochloride, **19** with choline, both in d_4-methanol). No change in the chemical shift values was found when comparing the spectra of the host molecule **7** with those of a mixture of **7** and benzylamine hydrochloride (up to a molar ratio 1:20). Thus, obviously the host–guest interaction in solution here seems to be much weaker than in the gas phase. However, in case of **19** and choline iodide, the NMR titration exhibited a distinct down-field shift of the two NH-protons of 0.04 ppm ($\Delta\delta$ from 7.703 to 7.743 ppm). The aromatic protons H-1, H-4, H-5 and H-6 also move sligthly downfield (0.004–0.008 ppm), while H-8 of the fluorene ring after the final addition of choline is found slightly up-field shifted (0.007 ppm) Participation of both NH-functionalities gets understandable since complexation certainly must be regarded as a dynamic equilibrium with obviously no preference to one of the two opposite sites of the fluorene moiety. The significant deshielding of the NH-protons may be the result of a cation/π-electron complexation between the trimethylammonium part of the choline and the aromatic π-electrons of the fluorene moiety. Interactions of this type are well documented and found to be an important noncovalent binding force in host–guest chemistry in general.[23]

3. Experimental

3.1. General

All chemicals, in particular the diamino-compounds were purchased from Sigma-Aldrich Chemical Co. and used without further purification. 1,3,5-Triaminobenzene was prepared according to Ref. 20, and 4′,4″,4‴-triaminotriphenylmethane was obtained following Ref. 21. Solvents were dried according to standard protocols. α-Oxoketene **1** was prepared according to Ref. 1b. Melting points were determined on a Tottoli- or Gallenkamp Apparatus and are uncorrected. Microanalyses were performed on a C,H,N-Automat Carlo Erba 1106; IR Spectra (KBr pellets) were recorded with a Perkin–Elmer 298. ^{1}H and ^{13}C NMR spectra were measured on a Varian XL 200 MHz, a Bruker AMX 360 MHz and a Bruker Avance 500 MHz spectrometer. Mass spectra were recorded on a HP-LC/MSD 1100 (ESI or APCI-mode) or a VG ZAB-2SEQ (FAB-mode).

3.2. Synthesis of the bridged bisdioxine bis-amides 7, 9–11, 14a,b, 16, 17. General procedure

0.24 mmol of the corresponding diamine is added to a stirred solution of 200 mg (0.48 mmol) of oxoketene **1** in dry acetonitrile (4 mL). The clear solution is kept at rt for 4–5 d with stirring and permanent TLC-monitoring of reactants and the new product formed. Then the solvent is partially evaporated until the product starts to precipitate. After suction filtration the crude products are recrystallized from methanol or ethylacetate/acetonitrile (**14**).

3.2.1. 1,3-Bis-(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxabicyclo-[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-benzene (7). Yield 170 mg (85%); mp: 100 °C; IR (KBr): 3440 (NH), 3000–2860 (CH), 1680, 1660 (C═O), 1600 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.05 (s, 18H), 1.14, 1.15 (2s, 18H), 1.20, 1.21 (2s, 18H), 1.24, 1.25 (2s, 18H), 4.85 (s, 2H), 7.18–7.31 (m, 3H), 7.60 (sb, 1H). Anal. calcd for $C_{52}H_{80}N_2O_8$: C, 72.52; H, 9.36; N, 3.25. Found: C, 72.55; H, 9.44; N, 3.15.

3.2.2. 2,7-Bis-(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxabicyclo-[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-naphthalene (9). Yield 140 mg (65%); mp: 235 °C; IR (KBr): 3440 (NH), 3000–2860 (CH), 1680, 1660 (C═O), 1600 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.06 (s, 18H), 1.14 (s, 18H), 1.24 (s, 18H), 1.25 (s, 18H), 4.88 (s, 2H), 7.30 (d, 2H, *J*=8 Hz), 7.38 (s, 2H), 7.69 (d, 2H, *J*=8 Hz), 8.15 (s, 2H). Anal. calcd for $C_{56}H_{82}N_2O_8$: C, 73.81; H, 9.07; N, 3.07. Found: C, 73.43; H, 9.35; N, 3.03.

3.2.3. 2,6-Bis-(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxabicyclo-[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-naphthalene (10). Yield 150 mg (70%); mp: 245 °C; IR (KBr): 3440 (NH), 3100–2840 (CH), 1680, 1655 (C═O), 1600 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.06 (s, 18H), 1.14 (s, 18H), 1.22 (s, 18H), 1.28 (s, 18H), 4.89 (s, 2H), 7.22 (d, 2H; *J*=8 Hz), 7.35 (s, 2H), 7.72 (d, 2H, *J*=8 Hz), 8.29 (s, 2H). Anal. calcd for $C_{56}H_{82}N_2O_8$: C, 73.81; H, 9.07; N, 3.07. Found: C, 73.40; H, 9.21; N, 3.03.

3.2.4. 8-Amino-(-1-naphthyl-aminocarbonyl)-1,3,5,7-tetra-*t*-butyl-2,6,9-trioxabicyclo[3.3.1]nona-3,7-diene (11). Yield 130 mg (60%); mp: 160 °C; IR (KBr): 3440 (NH), 3350–3320 (NH_2), 3000–2860 (CH), 1660 (C═O), 1600 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.05, 1.12, 1.20, 1.25 (4s, 9H each), 3.92 (b, 2H), 4.82 (s, 1H), 6.75 (d, 1H, *J*=7.5 Hz), 7.18–7.58 (m, 5H), 8.38 (b, 1H). Anal. calcd for $C_{33}H_{46}N_2O_4$: C, 74.12; H, 8.67; N, 5.24. Found: C, 73.81; H, 8.82; N, 5.20.

3.2.5. 1,5-Bis(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxabicyclo-[3.3.1]nona-3,7-diene-4-yl-aminocarbonyl)-naphthalene (14). Yield: 165 mg (77%); mp: 243 °C; separation of rotamers **14a/14b** was achieved by dry-column flash chromatography (silicagel 60H, eluent: dichloromethane/petrolether=3/2; R_f **14a**: 0.31; R_f **14b**: 0.23); IR (KBr): 3440 (NH), 3000–2860 (CH), 1685, 1660 (C═O), 1600 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.06, 1.14, 1.24, 1.245 (4s, 18H each), 4.92 (s, 2H), 7.45–7.67 (m, 4H, 2NH), 8.08 (d, 2H, *J*=8 Hz, **14a**), 8.10 (d, *J*=8 Hz, **14b**); ^{13}C NMR ($CDCl_3$): 24.20, 25.15, 28.43, 29.25 (C(CH_3)$_3$), 35.13, 37.90, 38.27, 40.17 (C(Me)$_3$)$_3$, 91.99 (C-8), 97.26, 99.70 (C-1, C-5), 105.44 (C-4), 117.28, 120.11 (**14a**), 120.02 (**14b**), 126.08 (**14a**), 126.03 (**14b**), 127.25 (**14a**), 127.18 (**14b**) (Ar-C), 132.82 (Ar-CN), 162.20, 162.25 (C-3, C-7), 167.38 (C═O). Anal. calcd for $C_{56}H_{82}N_2O_8$: C, 73.81; H, 9.07; N, 3.07. Found: C, 73.92; H, 9.35, N, 3.05 (**14a**); C, 73.99; H, 9.24; N, 2.81 (**14b**).

3.2.6. 2,7-Bis-(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxabicyclo-[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-fluorene (16). Yield: 225 mg (92%); mp: 212°C; IR (KBr): 3440 (NH), 3000–2860 (CH), 1680, 1660 (C═O), 1600 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.06 (s, 18H), 1.14 (s, 18H), 1.22 (s, 18H), 1.25 (s, 18H), 3.85 (s, 2H), 4.83 (s, 2H), 7.22 (s, 2H), 7.28 (d, 2H, *J*=8 Hz), 7.60 (d, 2H, *J*=8 Hz), 7.85 (sb, 2H); ^{13}C NMR ($CDCl_3$): 24.08, 24.94, 28.15, 28.95 (C(CH_3)$_3$), 37.74, 38.09, 40.09 (C(Me)$_3$), 40.90 (CH_2),

92.01 (C-8), 97.2, 99.51 (C-1, C-5), 105.8 (C-4), 116.62, 118.20, 118.81, 119.67 (Ar-CH), 136.60, 137.64 (Ar-C), 144.35 (Ar-CN), 161.76, 162.18 (C-3, C-7), 166.96 (C═O). Anal. calcd for $C_{59}H_{84}N_2O_8$: C, 74.65; H, 8.91; N, 2.95. Found: C, 74.38; H, 9.00; N, 2.94.

3.2.7. 3,7-Bis-(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxabicyclo-[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-2-methoxy-fluorene (17). Yield: 210 mg (95%); mp: 242 °C; IR (KBr):3430 (NH), 3000–2870 (CH), 1680, 1655 (C═O), 1600 (C═C) cm^{-1}; ^1H NMR ($CDCl_3$): 1.04, 1.14, 1.16, 1.20, 1.28 (5s, 72H), 3.83 (s, 2H), 3.85 (s, 3H), 4.84 (s, 1H), 4.88 (s, 1H), 7.28 (s, 1H); 7.40 (d, 1H, *J*=9.3 Hz), 7.30 (s, 1H); 7.63 (d, 1H, *J*=9.3 Hz), 7.79 (s, 1H), 8.0 (s, 1H), 8.72 (s, 1H); ^{13}C NMR ($CDCl_3$): 24.16, 25.03, 28.26, 28.43, 28.94, 29.03 ($C(CH_3)_3$), 34.99, 35.07, 37.23, 37.81, 38.16 ($C(Me)_3$)$_3$, 40.06 (CH_2), 55.54 (CH_3), 91.45, 92.03 (C-8), 97.15, 99.50, 99.68 (C-1, C-5), 105.72, 107.01 (C-4), 111.75, 116.57, 118.04, 119.93, 125.83 (Ar-CH), 134.32, 136.11, 138.40, 138.93 (Ar-C), 144.07 (Ar-CN), 147.46 (Ar-CO), 161.88, 162.49 (C-3, C-7), 166.92 (C═O). Anal. calcd for $C_{60}H_{86}N_2O_9$: C, 73.59; H, 8.85; N, 2.86. Found: C, 73.30; H, 8.89; N, 2.80.

3.3. X-ray crystallographic analysis of 14a

Colorless crystals were grown by the slow vapor diffusion of acetonitrile into a chloroform solution of **14a**. The crystal was monoclinic, space group $P2_1/n$, with cell dimension a=9.708(4) Å, b=19.962(7) Å, c=16.587(6) Å, β=93.87(3)° and V=3207 Å^3. Z=2 molecules ($C_{56}H_{82}N_2O_8$·2$CHCl_3$, M_W=1150) in the unit cell (D_c=1.19 g cm^{-3}). Intensity data were measured for 4769 reflections (3646 unique, R_{int}=0.0386, $2\theta_{max}$=105°) at rt on a Siemens P4 diffractometer using a crystal with dimensions 0.3×0.3×0.2 mm [$F(000)$=1224, λ(Cu Kα)=1.54178 Å, μ=2.8 mm^{-1}]. The structure was solved by direct methods and refined by full-matrix least-squares analysis with SHELXL-97[24] minimizing the residuals for F^2. All hydrogen atoms were calculated at their theoretical position and were treated as 'riding' on the respective heavy atom. Convergence was reached at $R1$=0.0876 [for 1642 reflections with $I>2\sigma(I)$] and $wR2$=0.3010 (for all unique data). The Goodness-of-fit on F^2 was 0.975. The structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 228819).

3.4. Synthesis of the bridged *bisdioxine* tris-amides 20 and 21. General procedure

0.15 mmol of 1,3,5-triaminobenzene (or 4, 4′,4″-triamino-triphenylmethane), dissolved in dry THF (2 mL) are added dropwise to a solution of **1** (200 mg) in dry acetonitrile (4.5 mL) with stirring at rt. After 10d (**20**) or 3d (**21**), respectively, at rt, the solvent is evaporated to half of its volume. The precipitate formed over night is isolated by suction filtration and recrystallized from acetonitrile or ethanol.

3.4.1. 1,3,5-Tris-(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxa-bicyclo[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-benzene (20). Yield: 150 mg (80%); mp: 230 °C; IR (KBr): 3440 (NH), 3000–2860 (CH), 1680, 1660 (C═O), 1600 (C═C) cm^{-1}; ^1H NMR ($CDCl_3$): 1.06, 1.14, 1.24, 1.25 (4s, 27H each), 4.83 (s, 3H), 7.20 (b, 3H), 7.60 (s, 3H); MS (FAB-mode, NOBA): *m/z* 1252.9 [M+H$^+$]. Anal. calcd for $C_{75}H_{117}N_3O_{12}$: C, 71.91; H, 9.41; N, 3.35. Found: C, 71.93; H, 9.57; N, 3.26.

3.4.2. 4,4′,4″-Tris(1,3,5,7-tetra-*t*-butyl-2,6,9-trioxa-bicyclo[3.3.1]nona-3,7-diene-4-yl-carbonylamino)-triphenylmethane (21). Yield: 190 mg (90%); mp: 350–352°C; IR (KBr): 3440 (NH), 3000–2860 (CH), 1680, 1660 (C═O), 1600 (C═C) cm^{-1}; ^1H NMR ($CDCl_3$): 1.04, 1.14, 1.24, 1.26 (4s, 27H each), 4.86 (s, 3H), 5.40 (s, 1H), 7.05 (d, 6H, *J*=8.5 Hz), 7.20 (s, 3H), 7.38 (d, 6H, *J*=8.5 Hz); ^{13}C NMR ($CDCl_3$): 24.1, 25.0, 28.39, 28.98 ($C(CH_3)_3$), 35.02, 37.78, 38.13, 40.02 ($C(Me)_3$), 55.36 (CH, *J*=126 Hz), 92.07 (C-8, *J*=162 Hz), 97.11, 99.62 (C-1, C-5), 105.58 (C-4), 119.65, 129.94 (Ar-CH, *J*=156 Hz), 136.35, 139.70 (Ar-C), 161.79, 162.16 (C-3, C-7), 166.98 (C═O); MS (FAB, NOBA): *m/z* 1419.0 (M+H$^+$). Anal. calcd for $C_{88}H_{127}N_3O_{12}$: C, 74.49; H, 9.02; N, 2.96. Found: C, 74.03; H, 9.16; N, 2.82.

3.5. Synthesis of the 2,4,6,8-tetraoxaadamantanes 8, 12, 13, 15, 18, 19, 22 and 23. General procedure

200 mg of the corresponding bridged bisdioxine derivatives 7–21 are dissolved in a mixture of dichloromethane (2 mL) and acetic acid (2 mL). After addition of aqeuous HCl (150 μl) gaseous HCl is passed through the solution for 30 s and the reaction mixture is stirred for 12 h at rt. Whilst the dichloromethane is then allowed to slowly escape, a colorless residue precipitates, which after suction is recrystallized from acetonitrile.

3.5.1. 1,3-Bis(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-carbonylamino)-benzene (8). Yield: 180 mg (86%); mp: 300–302 °C; IR (KBr): 3410 (NH), 3005–2865 (CH), 1675 (C═O), 1625 cm^{-1}; ^1H NMR ($CDCl_3$): 0.98 (s, 18H), 1.05 (s, 36H), 1.28 (s, 18H), 1.78 (s, 4H, CH_2), 3.05 (s, 2H), 7.22–7.38 (m, 3H), 7.49 (s, 1H), 8.30 (s, 2H, NH). Anal. calcd for $C_{52}H_{84}N_2O_{10}$: C, 69.61; H, 9.43; N, 3.12. Found: C, 69.51; H, 9.74; N, 2.90.

3.5.2. 2,7-Bis(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-carbonylamino)-naphthalene (12). Yield: 165 mg (80%); mp: 210 °C; IR (KBr): 3410 (NH), 3010–2860 (CH), 1680 (C═O), 1600 cm^{-1}; ^1H NMR ($CDCl_3$): 0.98 (s, 18H), 1.08 (s, 36H), 1.20 (s, 18H), 1.79 (s, 4H, CH_2), 3.10 (s, 2H), 7.38 (d, 2H, *J*=8.5 Hz), 7.68 (d, 2H, *J*=8.5 Hz), 8.08 (s, 2H), 8.42 (s, 2H). Anal. calcd for $C_{56}H_{86}N_2O_{10}$: C, 71.00; H, 9.15; N, 2.96. Found: 71.35; H, 9.26, N, 3.18.

3.5.3. 2,6-Bis(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-carbonylamino)-naphthalene (13). Yield: 175 mg (85%); mp: >350 °C; IR (KBr): 3400 (NH), 3100–2860 (CH), 1680 (C═O), 1610 cm^{-1}; ^1H NMR ($CDCl_3$): 1.00 (s, 18H), 1.06 (s, 36H), 1.22 (s, 18H), 1.79 (s, 4H), 3.10 (s, 2H), 7.40 (d, 2H, *J*=9.5 Hz), 7.72 (d, 2H, *J*=9.5 Hz), 8.12 (s, 2H), 8.40 (s, 2H). Anal. calcd for $C_{56}H_{86}N_2O_{10}$: C, 71.00; H, 9.15; N, 2.96. Found: C, 69.69; H, 9.09; N, 2.99.

3.5.4. 1,5-Bis(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-carbonylamino)-naphthalene (15).

Yield: 160 mg (77%); mp: >350°C; IR (KBr): 3410 (NH), 3100–2860 (CH), 1675 (C═O), 1540 cm^{-1}; ^1H NMR ($CDCl_3$): 1.01 (s, 18H), 1.18 (sb, 54H), 1.81 (s, 4H), 3.23 (s, 2H), 7.50–8.05 (m, 6H), 8.45 (s, 2H). Anal. calcd for $C_{56}H_{86}N_2O_{10}$: C, 71.00; H, 9.15; N, 2.96. Found: C, 70.45; H, 9.19; N, 2.92.

3.5.5. 2,7-Bis(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-aminocarbonyl)-fluorene (18). Yield: 195 mg (90%); mp: 210 °C; ^1H NMR ($CDCl_3$): 0.95 (s, 18H), 1.08 (s, 36H), 1.21 (s, 18H), 1.79 (s, 4H), 3.10 (s, 2H), 3.85 (s, 2H), 7.25 (d, 2H, *J*=8.5 Hz), 7.60 (d, 2H, *J*=8.5 Hz), 7.85 (s, 2H), 8.37 (s, 2H). Anal. calcd for $C_{59}H_{88}N_2O_{10}$: C, 71.92; H, 8.99; N, 2.84. Found: C, 71.65; H, 9.20; N, 2.74.

3.5.6. 2,7-Bis(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-carbonylamino)-2-methoxy-fluorene (19). Yield: 190 mg (90%); mp: 310 °C (sublim.); IR (KBr): 3413, 3210 (NH, OH), 3100–2860 (CH), 1676 (C═O), 1530 cm^{-1}; ^1H NMR ($CDCl_3$): 0.98 (s, 18H), 1.10 (s, 36H), 1.18 (s, 9H), 1.20 (s, 9H), 1.79 (s, 2H), 1.80 (s, 2H), 3.09 (s, 1H), 3.18 (s, 1H), 3.82 (s, 2H), 3.85 (s, 3H), 7.03 (s, 1H), 7.11 (d, 1H, *J*=8.5 Hz), 7.63 (d, 1H, *J*=8.5 Hz), 7.91 (s, 1H), 8.32 (s, 2H), 8.5 (s, 1H); ^{13}C NMR ($CDCl_3$): 25.41, 25.71, 25.96, 26.15, 26.50, 26.76 ($C(CH_3)_3$), 28.39, 28.53 (CH_2-Ada), 39.12, 40.10, 40.43, 40.77 ($C(Me)_3$), 42.95 (CH_2), 52.92, 53.70 (CH), 56.94 (CH_3), 101.24, 101.40, 103.75 (O–C–O), 109.21, 116.26, 119.20, 120.48, 121.74, 127.40, 135.98, 137.30, 140.29, 141.63, 145.80, 150.67 (Ar-C), 170.18, 170.55 (C═O). Anal. calcd for $C_{60}H_{90}N_2O_{11}\cdot H_2O$: C, 69.76; H, 8.91; N, 2.71. Found: C, 70.16; H, 8.79; N, 2.78.

3.5.7. 1,3,5-Tris(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-carbonylamino)-benzene (22). Yield: 170 mg (81%); mp: >350 °C; IR (KBr): 3410, 3390 (NH, OH), 3000–2860 (CH), 1680 (C═O), 1600 cm^{-1}; ^1H NMR ($CDCl_3$): 0.95 (s, 27H), 1.05 (s, 54H), 1.16 (s, 27H), 1.75 (s, 6H), 3.02 (s, 3H), 7.52 (s, 3H), 8.29 (s, 3H). Anal. calcd for $C_{75}H_{123}N_3O_{15}\cdot H_2O$: C, 68.00; H, 9.50; N, 3.17. Found: C, 68.19; H, 9.38; N, 3.20.

3.5.8. 4,4′,4″-Tris(1,3,5,7-tetra-*t*-butyl-2,4,6,8-tetraoxa-adamantane-9-yl-carbonylamino)-triphenylmethane (23). Yield: 155 mg (75%); mp: >350 °C; IR (KBr): 3410, 3300 (NH, OH), 3100–2860 (CH), 1677 (C═O), 1600, 1522 cm^{-1}; ^1H NMR ($CDCl_3$): 0.95 (s, 27H), 1.05 (s, 54H), 1.15 (s, 27H), 1.75 (s, 6H), 3.05 (s, 3H), 7.05 (d, 6H, *J*=8.5 Hz), 7.35 (d, 6H, *J*=8.5 Hz), 8.25 (s, 3H); ^{13}C NMR ($CDCl_3$): 23.14, 23.89, 24.50 ($C(CH_3)_3$), 29.45 (t, *J*=126 Hz, CH_2-Ada), 37.85, 38.50, 40.66 ($C(Me_3)_3$), 50.64 (d, *J*=138 Hz, CH-Ada), 55.20 (d, *J*=124 Hz, CH), 99.21, 101.55 (O–C–O), 120.03, 129.61 (d, *J*=156.5 Hz, CH-Ar), 135.4, 139.45 (C-Ar), 167.9, 168.01 (C═O). Anal. calcd for $C_{88}H_{133}N_3O_{15}\cdot H_2O$: C, 70.93; H, 8.99; N, 2.81. Found: C, 70.93; H, 9.04; N, 2.68.

3.6. Host–guest experiments

(a) ESI-MS: 0.5–1 mg of the host molecules **5**–**23** together with a ten-fold excess of the corresponding guests (choline iodide, benzylamine hydrochloride and cholesterol) were mixed in methanol (1 mL) and stirred at rt for 24 h. Then, appropriate amounts of the solutions are injected into the mass spectrometer under ESI-conditions. In case a residue is formed during stirring, this solid is separated by decantation, dissolved in acetonitrile and again injected under identical conditions. The results obtained are listed in Table 1.

(b) NMR-titration: 0.5 mg of the host molecules (**7** or **19**) were dissolved in methanol-d_4 (800 μl) and a solution of the suitable guest molecules (benzylamine hydrochloride or choline iodide) in methanol-d_4 (100 μl, 100-fold excess) is added in portions of 20 μl and after each addition a ^1H NMR spectrum is recorded and the chemical shift values compared with those of the spectrum of the pure host compound.

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