Photoresponsive Piperazine Macrocycles

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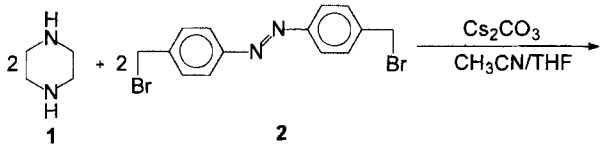
The photoresponsive macrocyclic phanes **3**, **7a**, **7b**, **10** were prepared. The (*E*) and (*Z*) isomers of **7b** could be separated from each other by column chromatography. The X-ray structure of the 31-membered cycle (*E*)-**7b** and the 54-membered cycle (*E,E*)-**10** shows a tendency toward self-assembly to a dimeric structure (**7b**) and a tubular structure (**10**) in the crystalline state. Additionally, both structures demonstrate inclusion of solvent molecules into the cavity (diameter 5 Å, **7b**) and tube (diameter 11 Å, **10**) respectively. A variable-temperature ^{1}H-NMR study of **7b** showed that the piperazine ring inversion is restricted at lower temperatures.

Macrocyclic compounds which have intramolecular cavities are expected to interact specifically with guest metal ions and molecules. As the guest selectivity is primarily governed by the size of the cavity, one may expect that if the topological ring shape can be changed reversibly, the guest-binding ability and guest selectivity may become adjustable. By the incorporation of photoresponsive units such as stilbenes and azobenzenes into the macrocycle the size and shape of the cavity can be altered by light or thermal energy, simply by triggering off (*E*) ⇌ (*Z*) isomerisation processes[1]. Photoresponsive compounds have been extensively studied because they are of great theoretical and practical interest[2], and therefore the incorporation of such groups into macrocyclic compounds is of pivotal inportance in host-guest chemistry[3]. Many examples of macromonocyclic and macrobicyclic azobenzene systems, exhibiting such behaviour, are already known[1,4]. However, recently we have prepared[5] new macrocyclic receptor molecules containing piperazine and arene units. Some of these cycles exhibit inclusion properties towards solvent molecules, which can be established by X-ray diffraction analysis. This has prompted us to prepare piperazine-based macrocycles which obtain larger arene spacer units, particularly those bearing photoresponsive groups.

Results and Discussion

In this paper we present two routes for the preparation of piperazine cyclophanes. Phane **3** was synthesised directly by a one-step reaction procedure described earlier[5]: Reaction of 4,4'-bis(bromomethyl)azobenzene (**2**) with piperazine (**1**) under high dilution conditions in the presence of caesium carbonate as a base gave after chromatographic workup and recrystallisation from acetonitrile the cyclophane **3** in 16% yield.



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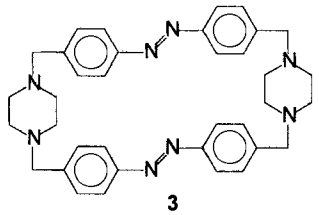

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The ^{1}H- and ^{13}C-NMR spectra of phane **3** indicate a highly symmetrical molecule, and the UV spectrum (Table 1) shows that both azobenzene units exist in the (*E*) form (strong absorption at 330 nm, λ_{max} of the $\pi \rightarrow \pi^*$ transition band)[6]. Upon exposure of **3** to 350-nm UV light, a photostationary state is established, in which the absorbance at 330 nm is reduced to 50%. When the sample is exposured to UV light, the conversions (*EE*) → (*EZ*) → (*ZZ*) → (*EZ*) → (*EE*) may reach equilibrium. On the other hand, it was found with macrocycles which contain azobenzene units that isomerisation of the (*ZZ*) form to the (*EE*) form occurred directly, without proceeding via the intermediate stage[6]. This implies that the (*ZZ*) → (*EE*) isomerisation rate is much faster than the rate via the intermediate stage and that the (*EZ*) form does not exist in the isomerisation process at all. The shape and size of the (*EE*) and (*ZZ*) forms of compound **3**, according to molecular mechanics

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calculations[7], show that the (*EE*) form seems to have a suitable cavity for small guest molecules where as (*ZZ*) form apparently has not.

Table 1. UV data (in CH_2Cl_2) of the macrocycles **3**, 7 and **10**. c(**3**) = c(**10**) = $2.5 \cdot 10^{-5}$ mol/dm^3; c(**7a**) = c(**7b**) = $5.0 \cdot 10^{-5}$ mol/dm^3

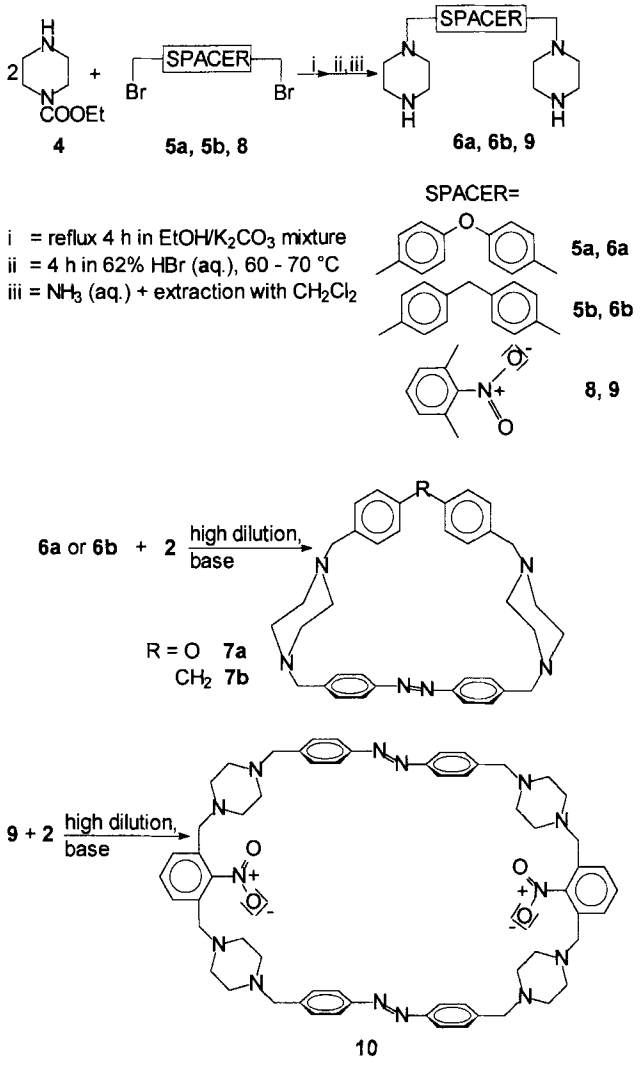
Compound	λ_{max}/nm (log ε /dm^{3}mol^{-1}cm^{-1})
3 [(EE) form]	240 (4.322), 330 (4.640), 441 (3.224)
Photostationary	
state of 3	240 (4.377), 326 (4.362), 441 (3.470)
7a [(E) form]	232 (4.426), 338 (4.250), 448 (2.953)
7c [(Z) form]	229 (4.377), 317 (3.908), 450 (3.333)
7b [(E) form]	228 (4.451), 338 (4.262), 449 (3.052)
7d [(Z) form]	229 (4.408), 310 (3.900), 447 (3.255)
10 [(EE) form]	228 (4.618), 330 (4.579)
Photostationary	
state of 10	228 (4.629), 327 (4.400)

Macrocycles **7a**, **7b**, and **10** were prepared indirectly by means of a two-step procedure. In the first step, the *N*-monosubstituted noncyclic piperazine derivatives **6a**, **6b**, and **9** were prepared by reaction of the monoprotected piperazine **4** with bis(bromomethyl)arene **5a**, **5b**, and **8**, respectively.

Subsequent deprotection of the piperazine nitrogen atom with hydrobromic acid (62%) gave the desired noncyclic products in 80–90% yield. In the second step, the macrocycles **7a**, **7b**, and **10** were obtained under high-dilution conditions by reaction of an *N*-monosubstituted noncyclic piperazine derivative (**6a** or **b**) with 4,4′-bis(bromomethyl)-azobenzene (**2**). After chromatographic workup on silica gel the desired cyclophanes **7a**, **7b**, and **10** were obtained in 20–25% yield.

Single crystals of **7b** were obtained by recrystallisation from acetonitrile. In the crystalline state, the azobenzene unit [(*E*) form] of **7b** has a slightly twisted banana shape (Figure 1), which indicates that the cycle is strained and can therefore easily be isomerised from the (*E*) to (*Z*) form by irradiation with UV light. The X-ray structure of **7b** also shows an interesting molecular recognition or self-assembly phenomenon. Two cycles form a dimeric structure, in which a corner of one of the cycles is included into the cavity of the other one, thus blocking one of the cavities. Additionally, one acetonitrile molecule is found to be incorporated into the unoccupied cavity of the second cycle [other two acetonitrile molecules are located between the three-component supramolecule giving the composition of 2:3 (**7b**: CH_3CN) to this structure]. To our knowledge this three-component supramolecular assembly is the first example of such an inclusion behaviour of an azobenzene-based macrocycle in the crystalline state. Interestingly, within the self-assembly the two cycles are enantiomeric to one another (Figure 2).

The ^{1}H-NMR spectrum of **7b** at 30°C shows two separate lines at δ = 2.24 and 2.41 originating from the piperazine moiety. Piperazine itself gives only one sharp singlet at



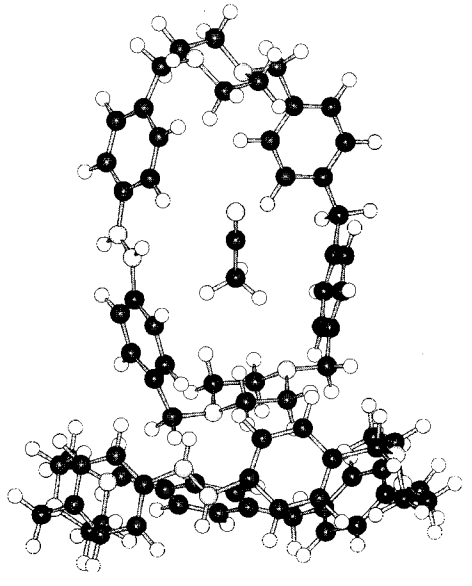


Figure 1. A view[15] of the X-ray structure of (*E*)-**7b**; only the included acetonitrile is shown

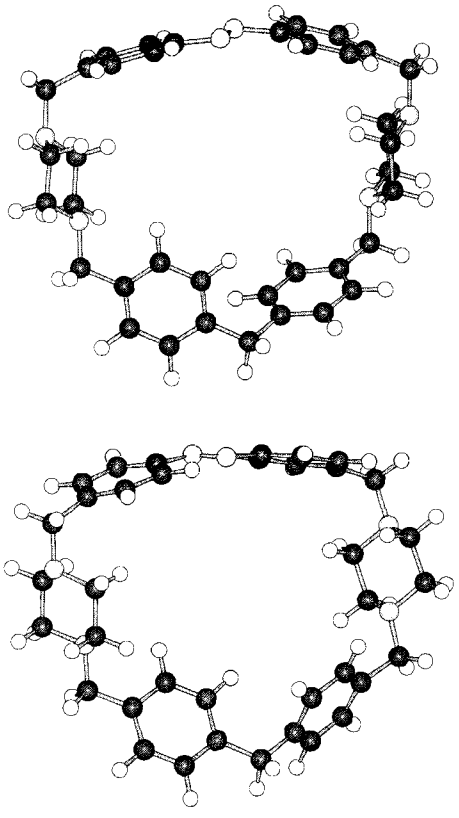
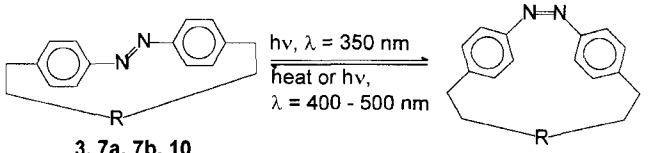


Figure 2. Two enantiomers of (*E*)-**7b** in the crystalline state

$\delta = 2.83$ under the same conditions. The nonequivalence of the piperazine protons of **7b** is due to the different spacers at the piperazine nitrogen atoms 1 and 4. The upfield shift of the signals of the piperazine protons in **7b** is caused by ring current effects of the aromatic spacers. A variable-temperature investigation of **7b** performed between 30 and −65°C showed interesting features. At −65°C there exist two pairs of resonance patterns (two doublets and two triplets) owing to a slow ring inversion (on the NMR time scale) of the piperazine moiety and subsequent nonequivalence of the piperazine protons. This means, that in this "frozen" state the geminal protons of the piperazine ring are magnetically different also giving the observed coupling patterns. Spectral coalescence of **7b** occurs at −10°C. According to the Eyring equation[8], this coalescence temperature corresponds to an energy barrier of 51 kJ/mol. For piperazine the coalescence temperature is −50°C corresponding to an energy barrier of 45 kJ/mol, same as in cyclohexane[8], but when there are substituents on the nitrogen atoms of piperazine the coalescence temperature and energy barrier of ring inversion increases. For example, the coalescence temperature of 1,4-bis(1-methylpropyl)piperazine is −20°C corresponding to an energy barrier of 50.4 kJ/mol, which is approximately the same as the energy barrier of **7b**. It seems that coalescence temperature and energy barrier depends on the *N*-substituents of piperazine, but not the strain of the macrocycle. Substitution in the piperazine unit as well as in the spacers may still further increase this barrier, thus also affecting the molecular recognition properties of systems of this type. The UV-spectral measurements show strong absorption bands at 339 (**7a**) and 337 nm (**7b**) (Table 1). Irradiation of **7a**, and **7b** with UV light (350 nm) causes the isomerisation of the (*E*) form to the (*Z*) form (Table 1). The (*Z*) form of **7b** is remarkably stable, and it was possible to separate it from the (*E*)/(*Z*) mixture by column chromatography (see Experimental).



3, 7a, 7b, 10 **3a, 7c, 7d, 10a**

Suitable single crystals of **10** were obtained by slow evaporation of a chloroform:acetonitrile (1:1) solution. The X-ray structure of **10** nicely illustrates the large ellipsoidal cavity (Figure 3) with dimensions from 8 to 14 Å. In the crystalline state **10** undergoes self-aggregation to afford "nanotubes" or "nanochannels" by stacking. Into these tubes one chloroform and one acetonitrile molecule are included. The other chloroform molecule occupies the interstices between the tubes. The packing diagram (Figure 4) shows the tubular structure, reminiscent of those found in cyclodextrins[9]. The solvent molecules inside the tube are disordered (1 acetonitrile and 1 chloroform molecule both with a population parameter of 0.5). The interaction of **10** with CH_3CN is suprisingly strong and exists also in solution, as the high-field shift in the ^{1}H-NMR spectrum ($\Delta\delta = 0.5$) proves. The UV measurements of **10** (Table 1) support the existence of a photostationary state when the sample is irradiated by UV light.

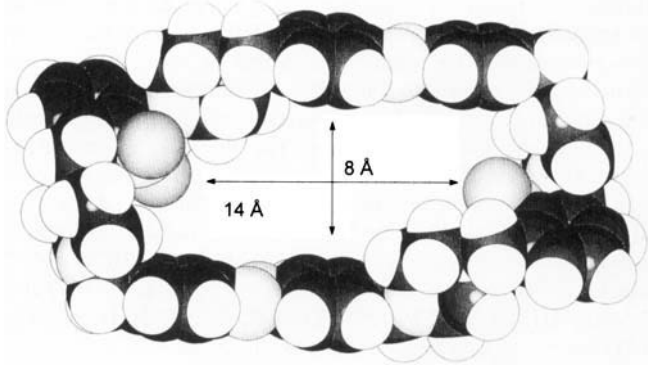


Figure 3. A view[15] with dimensions of the cavity of **10** (X-ray structure)

Piperazine macrocycles have been found to have very interesting inclusion and metal-complexing properties. When azobenzene units have been incorporated into these piperazine macrocycles, exposure to UV light causes variation of the shape and size of the cavity. In the crystalline state these photoactive macrocycles also show a novel supramolecular behaviour.

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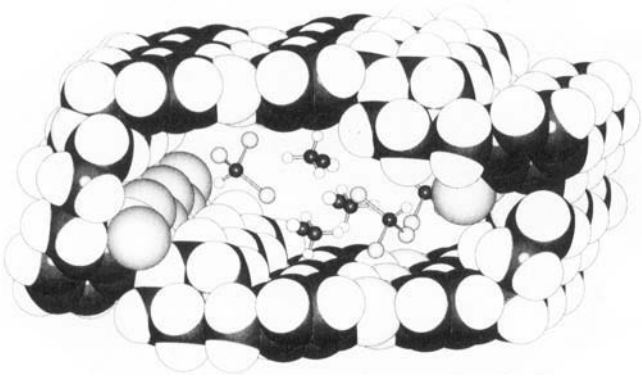

Figure 4. A view showing the tubular packing of **10** with disordered solvent molecules inside (X-ray structure)

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Experimental

Melting points: Electrothermal IA9200 (uncorrected). – UV/Vis: Perkin Elmer Lambda 5. – ^{1}H NMR: Jeol 270 GSX (270.17 MHz). – ^{13}C NMR: Jeol 270 GSX (67.94 MHz), Jeol FX 90Q (33.3 MHz). – MS: VG auto Spec HRMS. – FAB MS: Kratos Concept 1H (in *m*NBA). – Thin-layer chromatography: Silica gel 60 F_{254} (Riedel-de Haën). – Column chromatography: Silica gel S (32–63 μm) (Riedel-de Haën), Silica gel 60 F_{254} (63–200 μm) (Merck).

4,4'-Bis(bromomethyl)azobenzene (**2**)[10]: A mixture of 6.6 g (31.4 mmol) of 4,4'-dimethylazobenzene, 12.4 g (69.7 mmol) of *N*-bromosuccinimide and azobisisobutyronitrile was stirred and refluxed while illuminated with two 150-W lamps for 8 h in 500 ml of tetrachloromethane. After cooling of this mixture the solvent was evaporated. The residue was boiled in water, filtered and washed several times with hot water. The orange filter residue was dried, boiled in 250 ml of tetrachloromethane and filtered immediatelly through a hot Büchner funnel. The filter residue consisted of 5.5 g of the desired product as an orange powder. A second crop was obtained from the filtrate, which also contained small amounts of side-products which were treated with tetrachloromethane as above. The overall yield was 6.3 g (54%). M. p. 217–218°C (ref.[10] 218°C). – ^{1}H NMR ($CDCl_3$, TMS): δ = 4.55 (s, 4H, ArCH_2Br), 7.54 (d, 4H, Ar-H), 7.89 (d, 4H, Ar-H). – ^{13}C NMR ($CDCl_3$, TMS): δ = 32.63, 123.37, 129.90, 140.80, 152.32.

1,3,7,9(1,4)-Tetrabenzena-2,8-bis(diazena)-5,11(1,4)-dipiperazinacyclododecaphane (**3**)[*]: 0.234 g (2.72 mmol) of piperazine (**1**) and 1.0 g (2.72 mmol) of **2** were each dissolved in 250 m of acetonitrile/tetrahydrofuran (4:1), and the resulting solutions were dropped slowly and simultaneously during 8 h into a boiling mixture of 1.78 g (5.44 mmol) of caesium carbonate, 700 ml of acetonitrile and 70 ml of tetrahydrofuran. The mixture was kept refluxing for additional 5 h. After cooling to room temp. the inorganic salts were filtered off, the organic solvents were evaporated, and the residue was chromatographed on silica gel ($CHCl_3$/CH_3OH, 1:1). The product was recrystallised from CH_2Cl_2/hexane (1:1) to give 132 mg (16%) of an orange powder; R_f = 0.68 ($CHCl_3$/CH_3OH, 1:1), m.p. >300°C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 240 nm (4.322), 327 (4.640). – ^{1}H NMR ($CDCl_3$, TMS): δ = 2.48 [s, 16H, RN(CH_2CH_2)$_2$NR], 3.69 (s, 8H, Ar-CH_2-piperazine), 7.40 (d, 8H, Ar-H), 7.83 (d, 8H, Ar-H). – ^{13}C NMR ($CDCl_3$, TMS): δ = 52.72, 62.50, 122.68, 130.22, 140.83, 152.32. – MS (FAB, Matrix: *m*NBA), *m/z* (%): 584 (48) [M^+ + H^+]. – $C_{36}H_{40}N_8$ · 0.5 CH_2Cl_2 (627.2): calcd. C 69.89, H 6.59, N 17.86; found C 70.27, H 6.61, N 17.82.

[*] Named by using the forthcoming new IUPAC approved system for phane nomenclature, see ref.[5].

Bis[4-(1-piperazinylmethyl)phenyl] Ether (**6a**), *Bis([4-(1-piperazinylmethyl)phenyl]methane* (**6b**) *and 2-Nitro-1,3-bis(1-piperazinylmethyl)benzene* (**9**): 2.50 g (12.8 mmol) of **4** and 6.00 g (43.4 mmol) of potassium carbonate were dissolved in 30 ml of dimethylformamide. To the resulting solution was added dropwise a solution of 6.42 mmol of the respective bis(bromomethyl)arene (**5a**, **b** or **8**) in 20 ml of dimethylformamide during a period of 30 min. After the addition was complete the solution was kept in a water bath at 65–70°C for 4–7 h. The inorganic material was filtered off, and the solvent was removed from the filtrate in vacuo. To the residue 30 ml of 62% hydrobromic acid was added, and the mixture was kept at 60–70°C for 7 h. The acid was removed in vacuo (below 60°C) and the residual oil treated with 50 ml of ethanol. The precipitate formed was filtered and washed several times with ethanol. The solid was dissolved in conc. aq. NH_3, and the solution was extracted three times with dichloromethane. The combined organic layers were dried with sodium sulfate and evaporated to dryness to give the compounds **6a**, **6b**, and **9**, respectively.

6a: Yield 2.00 g (85%), m.p. 108–110°C. – ^{1}H NMR ($CDCl_3$, TMS): δ = 1.96 (s, 2H, NH), 2.42 [t, 8H, RN(CH_2CH_2)$_2$NH], 2.89 [t, 8H, RN(CH_2CH_2)NH], 3.46 (s, 4H, Ar-CH_2-piperazine), 6.94 (d, 8H, Ar-H), 7.27 (d, 8H, Ar-H). – ^{13}C NMR ($CDCl_3$, TMS): δ = 46.08, 54.37, 63.03, 118.51, 130.49, 132.87, 156.37. – MS (35 eV), *m/z* (%): 366 (30) [M^+], 281 (100) [M^+ – piperazine].

6b: Yield 2.12 g (90%), m.p. 119–122°C. – ^{1}H NMR ($CDCl_3$, TMS): δ = 2.41 [t, RN(CH_2CH_2)$_2$NH], 2.74 (s, 2H, NH), 2.88 [t, 8H, RN(CH_2CH_2)$_2$NH], 3.45 (s, 4H, Ar-CH_2-piperazine), 3.93 (s, 2H, Ar-CH_2-Ar), 7.12 (d, 4H, Ar-H), 7.22 (d, 4H, Ar-H). – ^{13}C NMR ($CDCl_3$, TMS): δ = 41.31, 45.84, 54.10, 63.30, 128.73, 129.33, 135.70, 139.95. – MS (35 eV), *m/z* (%): 364 (30) [M^+], 278 (100) [M^+ – piperazine].

9: Yield 1.63 g (80%), m.p. 97–100°C. – ^{1}H NMR ($CDCl_3$, TMS): δ = 1.64 (s, 2H, NH), 2.35 [t, 8H, RN(CH_2CH_2)$_2$NH], 2.81 [t, 8H, RN(CH_2CH_2)$_2$NH], 3.54 (s, 4H, Ar-CH_2-piperazine), 7.35 (s, 3H, Ar-H). – ^{13}C NMR ($CDCl_3$, TMS): δ = 46.00, 54.34, 59.28, 129.68, 131.35, 150.57. – MS (35 eV), *m/z* (%): 319 (10) [M^+], 233 (50) [M^+ – piperazine].

Macrocycles **7a** *and* **7b**: Both macrocycles were prepared according to the same cyclization procedure used for the synthesis of compound **3**. Compounds **7a**, and **7b** were separated by silica gel chromatography using chloroform/methanol (1:1) as the eluent and were recrystallised from acetonitrile.

1,3,7,9(1,4)-Tetrabenzena-2-diazena-8-oxa-5,11(1,4)-dipiperazinacyclododecaphane (**7a**): Starting materials: 0.510 g (1.39 mmol) of **6a** and 0.512 g (1.39 mmol) of **2**; yield after cyclization, chromatographic workup, and crystallisation 160 mg (20%) of **7a**. – TLC (silica gel): R_f = 0.59 (CH_3OH/$CHCl_3$, 1:1), m.p. >270°C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 338 nm (4.250). – ^{1}H NMR ($CDCl_3$, TMS): δ = 2.31 [s, 8H, R^1N(CH_2CH_2)$_2$NR^2], 2.46 [s, 8H, R^1N(CH_2CH_2)$_2$NR^2], 3.35 (s, 4H, Ar-CH_2-piperazine), 3.99 (s, 4H, Ar-CH_2-piperazine), 6.85 (d, 4H, Ar-H), 7.14 (d, 4H, Ar-H), 7.34 (d, 4H, Ar-H), 8.00 (d, 4H, Ar-H). – ^{13}C NMR ($CDCl_3$, TMS): δ = 50.51, 53.26, 61.18, 61.35, 118.22, 122.59, 129.97, 131.34, 134.08, 137.09, 152.26, 156.23. – MS (35 eV), *m/z* (%): 572

(100) [M^+], 363 (10) [M^+ − diazobenzene], 293 (20), 280 (10), 208 (10), 196 (30). − $C_{36}H_{40}N_6O$ (572.75): calcd. C 75.49, H 7.04, N 14.67; found C 75.34, H 7.06, N 14.56.

1,3,7,9(1,4)-Tetrabenzena-2-diazena-5,11(1,4)-dipiperazinacyclododecaphane (**7b** [(*E*) form] and **7b** [(*Z*) form]): Starting materials: 0.729 g (2 mmol) of **6b** and 0.736 g (2 mmol) of **2**; yield after separation on silica gel ($CH_3OH/CHCl_3$, 1:1) and crystallisation from acetonitrile 225 mg (20%) of **7b**. − TLC (silica gel). R_f = 0.6 ($CH_3OH/CHCl_3$, 1:1), m.p. 255−260°C. − UV: λ_{max} (lg ε) = 338 nm (4.262). − ^1H NMR ($CDCl_3$, TMS): δ = 1.99 (s, 4.5H, CH_3CN) 2.24 [s, 8H, $R^1N(CH_2CH_2)_2NR^2$], 2.41 [s, 8H, $R^1N(CH_2CH_2)_2NR^2$], 3.30 (s, 4H, Ar-CH_2-piperazine), 3.90, (s, 2H, Ar-CH_2-Ar), 3.92 (s, 4H, Ar-CH_2-piperazine), 6.95 (d, 4H, Ar-H), 7.06 (d, 4H, Ar-H), 7.27 (d, 4H, Ar-H), 7.92 (d, 4H, Ar-H). − ^{13}C NMR ($CDCl_3$, TMS): δ = 40.94, 50.80, 53.67, 61.63, 62.25, 122.71, 128.86, 129.02, 131.22, 137.04, 137.50, 139.29, 151.42. − MS (FAB, *m*NBA), *m/z* (%): 571.3 (10) [$M^+ + H^+$]. − $C_{37}H_{42}N_6 \cdot 1.5\ CH_3CN$ (632.4): calcd. C 75.98, H 7.41, N 16.61; found C 75.90, H 7.48, N 16.61.

Separation of the (E) and (Z) Form of **7b**: Exposure of 10 mg of **7b** in CH_2Cl_2 to UV light (λ = 350 nm) and chromatographic workup on silica gel ($CHCl_3/CH_3OH$, 1:1) gave 5 mg (50%) of **7d** [(*Z*) form]. − TLC (silica gel): R_f = 0.7 ($CHCl_3/CH_3OH$, 1:1). − UV (CH_2Cl_2): λ_{max} (lg ε) = 447 nm (3.255). − ^1H NMR ($CDCl_3$, TMS): δ = 2.43 [s, 16H, $RN(CH_2CH_2)_2NR$], 3.41 (s, 4H, Ar-CH_2-piperazine), 3.66 (s, 4H, Ar-CH_2-piperazine), 3.82 (s, Ar-CH_2-Ar), 6.84 (d, 4H, Ar-H), 7.10−7.18 (m, 12H, Ar-H). − ^{13}C NMR ($CDCl_3$, TMS): δ = 42.09, 51.29, 53.50, 62.50, 120.67, 128.35, 129.83, 130.22, 140.77, 151.60.

$7^2,17^2$-Nitro-1,3,11,13(1,4),7,17(1,3)-hexabenzena-2,12-bis(diazena)-5,9,15,19-tetrapiperazinacycloeicosaphane (**10**): 0.400 g (1.25 mmol) of **9**, 0.461 g (1.25 mmol) of **2**, and 0.815 mg (2.50 mmol) of ceasium carbonate were allowed to react as described above. Chromatographic workup on silica gel using $CHCl_3/CH_3OH$ (5:1) and recrystallisation from chloroform yielded 156 mg (24%) of **10**. − TLC (silica gel): R_f = 0.32 ($CH_3OH/CHCl_3$, 5:1), m.p. <300 C. − UV (CH_2Cl_2): λ_{max} (lg ε) = 330 nm (4.579). − ^1H NMR ($CDCl_3$, TMS): δ = 1.47 (s, 3H, CH_3CN), 2.33 [s, $RN(CH_2CH_2)_2N$, 32H], 3.42 (s, 8H, Ar-CH_2-piperazine), 3.54 (s, 8H, Ar-CH_2-piperazine), 7.33 (m, 14H, Ar-H), 7.75 (d, 8H, Ar-H). − ^{13}C NMR ($CDCl_3$, TMS): δ = 52.85, 53.07, 58.03, 62.63, 122.77, 129.59, 129.94, 131.05, 131.50, 141.13, 151.02, 152.29. − MS (FAB, *m*NBA), *m/z* (%): 1051.6 (10) [$M^+ + H^+$]. − $C_{60}H_{70}N_{14}O_4 \cdot CH_3CN \cdot 3\ CHCl_3$ (1450.5): calcd. C 53.82, H 5.28, N 14.48; found C 54.13, H 5.35, N 13.91.

Irradiation Experiment with **3**, **7a**, **7b**, **10**: A solution of the respective macrocycle [*all*-(*E*)] in CH_2Cl_2 [$c = 2.5 \cdot 10^{-5}$ mol dm^{-3} (**3** and **10**), $c = 5.0 \cdot 10^{-5}$ mol dm^{-3} (**7a** and **7b**)] was prepared in the dark and filled into a quartz cuvette. The cuvette was irradiated at 350 nm for 10 min, and the UV/Vis spectrum (500−200 nm) was measured immediately.

X-Ray Studies[11]: Suitable crystals of macrocycle **7b** were obtained by slow evaporation of an acetonitrile solution, which gave deep red crystals. Crystallisation of phane **10** from chloroform/acetonitrile (1:1) solution furnished yellow-orange crystals.

X-Ray Crystal Structure Analysis of **7b**: Crystal data: $C_{72}H_{80}N_{12}O_2 \cdot 3\ CH_3CN$, M_{tot} = 1268.660, monoclinic, space group $P2_1/c$ (no. 14), a = 11.089(4), b = 20.074(3), c = 36.637(7) Å, β = 116.21(2)°, V = 7317(3) Å^3, Z = 4, D_c = 1.152 g cm^{-3}, $F(000)$ = 2664, T = 296 ±1 K. Data collection and reduction: Data were collected from a deep red crystal of the size 0.2 × 0.3 × 0.5 mm. Data were recorded with an Enraf-Nonius CAD4 diffractometer by using graphite-monochromatised Mo-K_α radiation [λ(Mo-K_α) = 0.7107 Å] and ω/2θ scan mode to 2θ = 46° (h: 0 → 11, k: 0 → 20, l: −37 → 37). Of the 8327 collected reflections 4323 with $I > 1.4\sigma I$ were used for refinement. An empirical absorption correction[12] [λ (Mo-K_α) = 0.656 mm^{-1}] was applied to the data with minimum and maximum correction coefficients of 0.777 and 1.136, respectively. Structure solution and refinement: The structure was solved by direct methods[13] and subjected to full-matrix refinement[14]. All non-H atoms were refined anisotropically. The hydrogen atoms were calculated to their idealised positions (C−H distances 1.00 Å) with fixed isotropic temperature factors (U = 0.08 Å^2). The F_o/parameter ratio = 5.05 and the final R value was 0.068 and R_w = 0.070 for 856 parameters. $w = w' \cdot [1.0 - (\Delta F/6 \cdot \sigma F)^2]^2$; where w' = Chebychev polynomial for F_c with four coefficients (2.14, −0.396, 1.32, −0.451). Convergence, max. shift/error <0.10. A final difference map displayed no electron density higher than 0.23 e A^{-3}.

X-Ray Crystal Structure Analysis of **10**: Crystal data: $[C_{60}H_{70}N_{14}O_4 \cdot CH_3CN \cdot CHCl_3] \cdot CHCl_3$, M_{tot} = 1331.11, monoclinic, space group $P2_1/c$ (no. 14), a = 15.305(1), b = 6.136(1), c = 42.477(4) Å, β = 93.65(1)°, V = 3982.2(6) Å^3, Z = 4, D_c = 1.110 g cm^{-3}, $F(000)$ = 1396, T = 296 ± 1 K. Data collection and reduction: Data were collected from a yellow-orange crystal of the size 0.25 × 0.30 × 0.45 mm. Data were recorded with a SYNTEX $P2_1$ diffractometer using graphite monochromatized Cu-K_α radiation [λ(Cu-K_α) = 1.5418 Å] and ω scan mode to 2θ = 113° (h: −13 → 13, k: 0 → 6, l: 0 → 42). Of the 4779 collected reflections 1971 with $I > 1\sigma I$ were used for refinement. An empirical absorption correction[12] [λ(Cu-K_α) = 0.263 mm^{-1}] was applied to the data with minimum and maximum correction coefficients of 0.743 and 1.287, respectively. Structure solution and refinement: The structure was solved by direct methods[13] and subjected to full-matrix refinement[14]. All non-disordered non-H atoms were refined anisotropically. The disordered chloroform and acetonitrile molecules inside the channels were located from the ΔF map and then refined isotropically with the occupancy 0.5 and geometrical restraints to prevent anomalous bond distances and angles [restraints used were C−Cl, 1.770(1) Å, C−Cl−C, 110.0(1)°, C−C, 1.490(1), CN, 1.180(1) Å and C−CN, 180.0(1)°]. During the final refinements the disordered molecules were included in the final structure factor calculations, as they were after isotropic refinements, but were not refined. The hydrogen atoms were calculated to their idealised positions (C−H distances 1.00 Å, 1.05 Å for chloroform) with fixed isotropic temperature factors (U = 0.08 Å^2) and included in the final structure factor calculations, but were not refined. The F_o/parameter ratio = 5.08, final R value 0.112 and R_w = 0.123 for 388 parameters: $w = w' \cdot [1.0 - (\Delta F/6 \cdot \sigma F)^2]^2$; where w' = Chebychev polynomial for F_c with four coefficients (3.64, 5.07, 2.60, 0.457). Convergence, max. shift/error <0.02. A final difference map displayed no electron density higher than 0.82 e Å^{-3}.

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