DOI: 10.1002/ejoc.200601075

[6+6]Photocycloadditions in Face-to-Face Benzo/Pyridazino Substrates – En Route to Azapagodanes[‡]

Thomas Mathew,*[a] Joern Tonne,[b] Gottfried Sedelmeier,[b] Clemens Grund,[b] Manfred Keller,[b] Dieter Hunkler,[b] Lothar Knothe,[b] and Horst Prinzbach*[b]

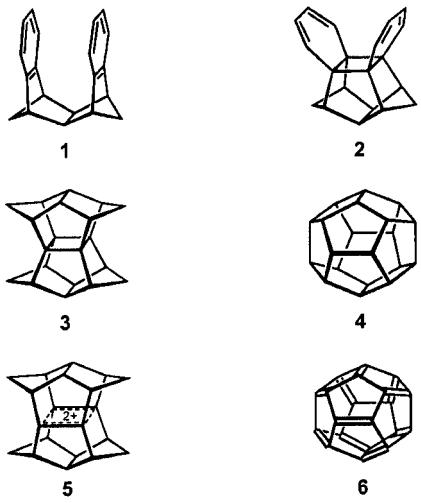
Dedicated to Prof. Dr. George A. Olah

Keywords: Photocycloadditions / Polycycles / Polyelectron cycloadditions / Heterocycles

In two specifically constructed rigid, proximate, "face-to-face" benzo/pyridazino systems (shortest π,π distances ca. 3 Å) photoequilibration with the photo[6+6]cycloadducts has been established by 254-nm irradiation (ratios ca. 2:1). The failure to observe such "benzene/heteroarene" photodimers for differently substituted benzo/pyridazino analogues is related to unfavorable UV absorption characteristics of the respective pair of photoisomers as determined by their acceptor/donor substituents. The highly strained photo-[6+6]cycloadducts are sufficiently thermally persistent to enable the addition of standard dienophiles, thus opening access to novel azapagodane-type cage molecules.

Introduction

When the [6+6]photodimerization of 3,3′-*o*,*o*′-cyclophane **1** to give **2** was reported in 1978,[2,3] the formation of a highly strained four-membered ring between two benzenoid rings, combined with a significant loss of aromaticity, constituted a new addition to "aromatic photochemistry".[4] The shortest π,π distance between the face-to-face oriented benzenoid chromophores (d_{exp} = 3.04 Å) is far below the sum of the van der Waals radii (3.4 Å), the close-to-rigid sandwich-type geometry between the chromophoric units causing significant pyramidalization of the quaternary carbon atoms (interorbital angle ω_{exp} = 161.4°). This unusual degree of enforced "proximity" was denoted by significantly red-shifted charge-transfer absorptions in the UV/Vis spectra and significant through-space π,π interactions determined by photoelectron spectroscopy. Upon direct (254 nm) and xanthone-sensitized excitation, photoequilibria were established at ratios of 70:30 and 87:13, respectively. Under the given geometric restraint, the strongly through-space and through-bond homoconjugated[5] "*syn*-*o*,*o*′-benzene dimer" **2** proved to be highly stable kinetically ($\Delta H^{\#}$ = 38.8 kcal mol^{-1} for the cycloreversion to **1**[6]) and thus conveniently amenable to physical and chemical studies. Most importantly, the equilibration **1** ⇄ **2** became a key step in the pagodane (**3**) → dodecahedrane (**4**) design[7,8] and ultimately in the vapor-phase generation of the C_{20} fullerene **6**.[9] A theoretically highly intriguing offspring of our assorted attempts to effect the isomerization **3** → **4** was the discovery of the surprisingly persistent 4C/2e in-plane bis(homoaromatic) dication **5**, which triggered multifaceted investigations.[10]

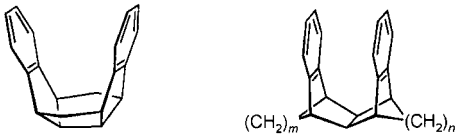


Subsequent explorations disclosed a perplexing dependence of the photoreaction, as well as of the dications of type **5**, on seemingly small structural differences.[11] Only with one of nearly a dozen variously functionalized deriva-

[‡] Photochemical Transformations, 86. Part 85: Ref.[1]

[a] Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA
[b] Chemisches Laboratorium der Universität Freiburg i. Br., Institut für Organische Chemie und Biochemie, Albertstr. 21, 79104, Freiburg, i. Br., Germany
Fax: +49-761-203-6048
E-mail: horst.prinzbach@orgmail.chemie.uni-freiburg.de

tives of **1** and the homolog **8** could [6+6]photoequilibria be observed. Isomer **7** and the higher homolog **9** remained unchanged.[1,12,13]



7 **8**: $m = 1$ $n = 2$; **9**: $m = 2$ $n = 2$

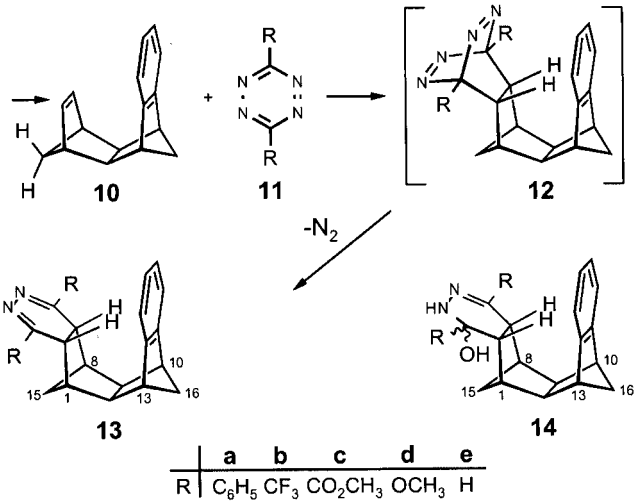
Replacement of one or both[12c] benzene rings in **1** by variously substituted pyridazine rings was part of our continuing efforts to correlate structural and electronic substrate properties with the photochemical response and hopefully extend the preparative-synthetic potential of the respective *syn*-*o*,*o*-(hetero)arene/(hetero)arene dimers as intermediates to azacages of type **3**, **4** and **5**.[2] Here we detail our photochemical study with the benzo/pyridazino systems (Scheme 2) and present explorative experiments directed at novel (aza)cage molecules.[14]

Results and Discussion

Syntheses

The construction of the benzo/pyridazino-*o*,*o*′-cyclophanes **24** (Scheme 2) commenced from the benzo/ene **10**, which had been prepared in the pagodane-dodecahedrane project in kg-quantities (from isodrin, at that time a bulk chemical)[8] (Scheme 1). The annelation of the pyridazino chromophore was approached in a standard way[15] utilizing the 1,2,4,5-tetrazines **11a**–**e**[16] whose functionalization (R) provides access to a number of target oriented variations. It was expected that the sterically only feasible *exo* addition to **10** (→) would have to overcome skeletal strain and steric compression between the benzene ring and the vinylic hydrogen atoms during rehybridization en route to the extremely labile cycloadducts **12** and that in the derived dihydropyridazines **13**, the two sterically highly protected inner hydrogen atoms (2-,7-H, Figure 1) would be hardly open to normally rapid tautomerization,[17] deprotonation or oxidative elimination.

In practice, benzoene **10** reacted rather smoothly with the tetrazines **11a**–**c**,**e** in comparison to the very sluggish addition of the electron-demanding diene (tetrachlorocyclopentadienone dimethyl acetal) in the model case.[8] When exposed at room temperature to equimolar amounts of reagent under strictly anhydrous, aprotic conditions, **10** was totally consumed within minutes (**11b**) or hours (**11a**,**c**,**e**). Only with **11d** was high pressure (9.5 kbar) needed, basically in line with the expected tendency in inverse Diels–Alder additions.[18] Of the practically quantitatively formed 4,5-dihydropyridazines (Figure 1), **13b**,**c** proved particularly prone to hydration; under not perfectly anhydrous conditions the *exo*-/*endo*-hydrates **14b**,**c** were isolated in addition.



Scheme 1.

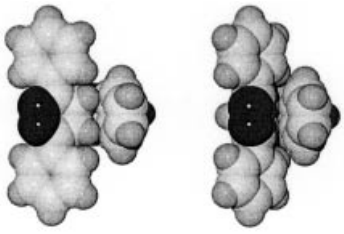
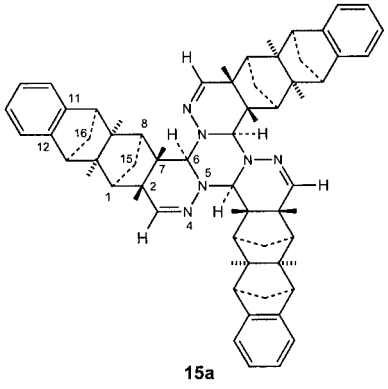


Figure 1. Space filling models of **13a** and **24a** (AM1, Schakal).

The reaction with parent **10e** proved exceptional in that instead of **13e** a ca. 2:1 mixture of the C_3 symmetric trimer, **15a**, and an unsymmetrical, non-identified trimer, **15b**, were isolated, the rapid trimerization being in line with a number of prior reports.[18,19] For **15a** an X-ray crystal structural analysis performed at 100 K (Figure 2, numbering scheme of **15a**)[20] provided the ultimate structural proof and stereochemical details such as the dihedral angles H2–C2–C7–H7 = 40.3°, H6–C6–C7–H7 = 91.4° ($J_{2,7}$ = 6.2, $J_{6,7}$ = 2.0 Hz) and N4–N4 transannular distance [d = 3.187(3) Å].



15a

The use of equimolar amounts of **10** and the reagents **11** was suggested when it was found that **13b** reacted smoothly with an excess of **10** to give virtually exclusively (TLC) the C_s symmetrical cycloadduct **16**. The latter, isolated in 80% yield also after treating **11b** with two equivalents of **10**,

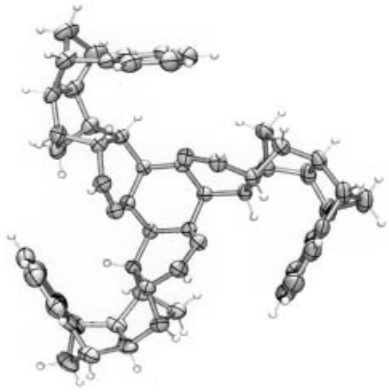
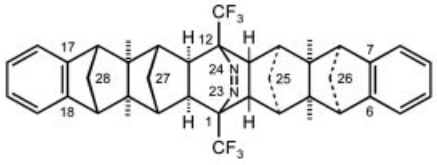
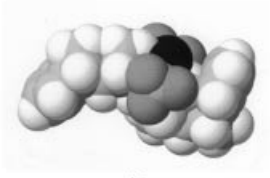


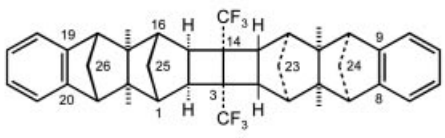
Figure 2. ORTEP diagram of trimer **15a** (T = 100 K).

proved thermally highly stable (m.p. 310–312 °C) and, like diazabicyclooctene {λ_{max} (ε) = 375 nm (85)}, typically "photoreluctant".[21] After exposure to the Pyrex®-filtered polychromatic light of a Hanau TQ 125-Watt lamp ($\lambda >$ 280 nm) and ca. 50% conversion (2.5 h irradiation time), the likewise thermally stable bicyclo[2.2.0]hexane derivative **17** (m.p. 289–291 °C) was the sole product. Typical for the highly congested steric situation in the decacycle **16** are inter alia the diamagnetic shielding effects of the N=N double bond upon the proximate CH_2 group (δ_{27a}-H = –0.24, δ_{27s}-H = –0.36, J = 12.6 Hz!) and of the 6,7-anellated benzene ring upon the 2(11)-H hydrogen atoms (δ = 0.97 ppm). The inversion of the combining radical centers implied by structure **17**, though, has not been unequivocally established.



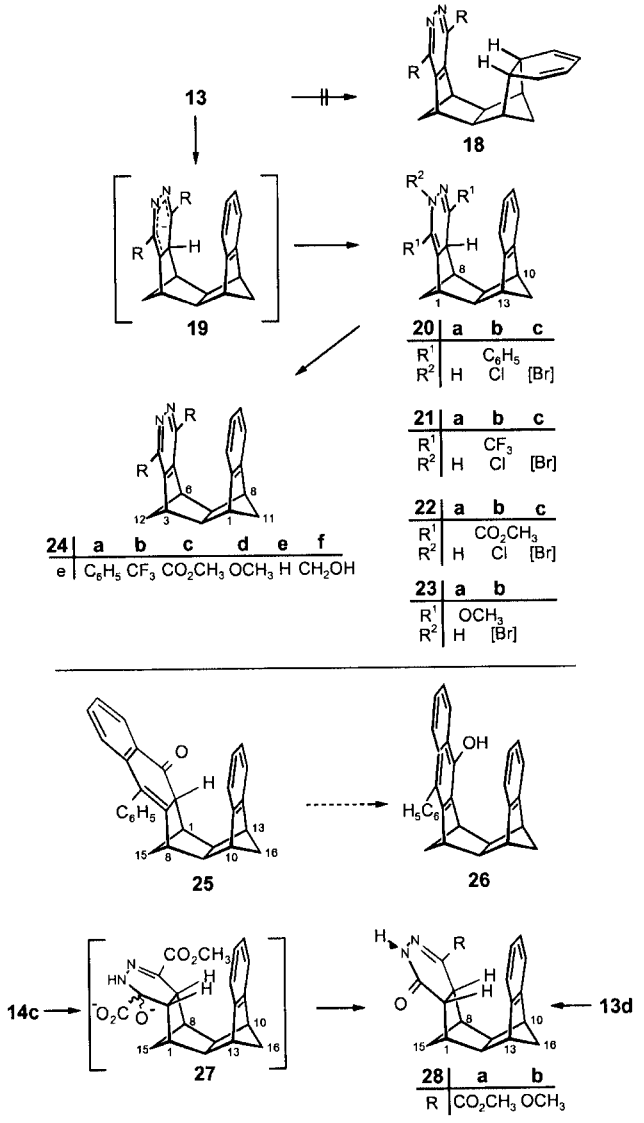


16



17

In the dihydropyridazines **13a**–**d**, the two inner hydrogen atoms immersed into the π face of the opposing benzene ring (Figure 1, $\delta_{2(7)H}$ = 2.68–2.25) indeed proved hardly accessible making dehydrogenation of the heterocyclic rings a critical step (Scheme 2). Attempts with numerous common oxidants (e.g. MnO_2, CrO_3, chloranil) under forcing conditions, and likewise with our standard drastic catalytic dehydrogenation procedure (Pd/C, 250 °C) successfully applied to the dihydrobenzene/benzene systems,[8] led to total decomposition. Only from the CrO_3 oxidation of **13a** the $C_{30}H_{24}O$ (MS) compound **25** surfaced as a defined, minor degradation product (ca. 10%); the isomer **26** most probably formed upon longer heating a [D_5]pyridine solution of **25** to 100 °C was of interest in our search for proximate "face-to-face" benzo/naphtho system.[22]



Scheme 2.

For **24a**,**b** the desired aromatization was originally[14] achieved when the normally rapid tautomerization of 4,5-dihydro-1,2-pyridazines in **13a**,**b** could be neatly brought-about through extended boiling in *p*-dichlorobenzene (174 °C) providing **20a** and **21a** (notably no H-transfer to give **18**), followed by *N*-chlorination (**20b**, **21b**) and 1,4-HCl

elimination, in the case of **20b** with *t*BuOK, in case of **21b** only with Schwesinger's very small and strong "naked" F^- base (P_2F).[23] Later,[24] the overall yields of 53% for **24a** and 69% for **24b** (based on **10**) could be considerably improved to ca. 90% and the synthetic procedure considerably shortened into a "one-pot" protocol {**13a**–**c** → **24a**–**c**} when it was found that generation of the anions **19a**–**c** with P_2F followed by quenching with methanol and bromine neatly yielded **20a**–**22a** and **20c**–**22c**, respectively, and that the latter in the presence of excess base rapidly lost HBr to give nearly quantitatively **24a**–**c**. It is stressed that, particularly for **24c**, total exclusion of moisture was necessary for this result. A second product occasionally isolated besides **24c** was identified as **28a** and was related to the formation of the hydrates **14** that were decarboxylated via **27** . For **24d** this highly economical procedure failed, when in **13d**, possibly with the assistance of bromine, the nucleophilic substitution of one methoxy group by F^- was much faster than the formation of **24a** (**b**). After flash chromatography, **28b** was isolated in high yield (88%). Reduction of **24c** with LAH generated smoothly bismethylol **24f** (77%, not optimized), a close substitute of **24e**.

The single-crystal X-ray analyses of **24a** (Figure 3)[20] and **24c** reveal nearly identical proximity effects, very close to that of **1**: Closest through-space π,π distances (*d*) of 3.003 (3.03) Å, with the two (hetero)aromatic rings nevertheless remaining planar and with the π,π repulsion being levied by 7–8° outward pyramidalization at the four annelated positions and by widening of the interplanar angles (ω).

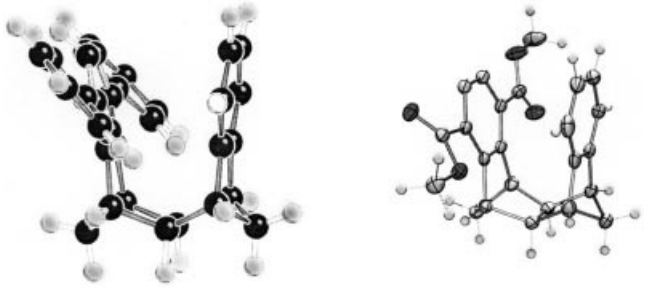
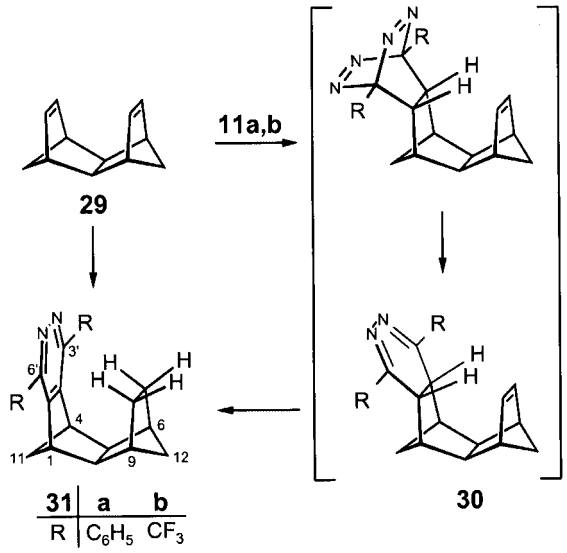


Figure 3. ORTEP diagrams of **24a** and **24c**.

Thus the intrinsic deviations from perfect parallel orientation of the two chromophores by ca. 9° (MM2, interorbital angles ω ca. 171°, Schakal plots) are enlarged by these pyramidalizations to ca. 20° resulting in ω = 163° (161° in **1**). This "face-to-face" orientation is clearly expressed in the ^1H NMR spectra. The signals of the four benzenoid protons appear at significantly higher field than those of the respective precursor **13** {e.g. $\Delta\delta$ = +0.5 – +0.9 (ca. 0.5) for **24a**(**b**)}. The UV spectra of **24a**,**b** (Figure 4), on the other hand, do not show the remarkable bathochromic shift of the long-wavelength absorption which was noted for the dibenzo compound **1** (charge-transfer effect between the benzene rings).[8] Compared to the UV spectra of the model pyridazines **31a**,**b** only the intensities of the long-wavelength absorptions are significantly enhanced. To obtain **31a**,**b**, diene **29** was treated with equimolar amounts of **11a** and **11b**. At room temperature, the adducts **30a**,**b** underwent quantitatively, presumably dyotropic, hydrogen transfer (Scheme 3).[8,25]

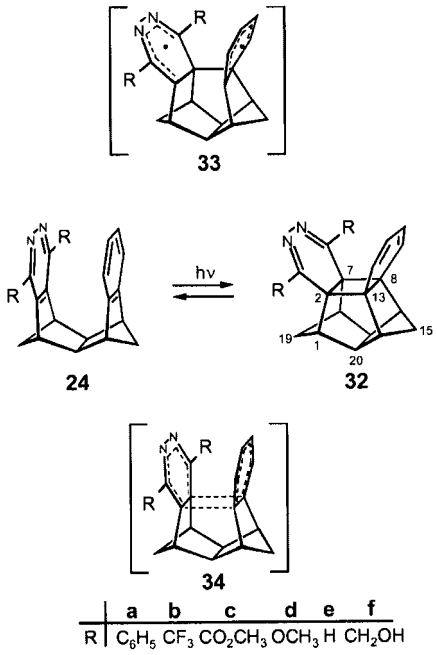


Scheme 3.

Benzo/Pyridazino[6+6]Photocycloadditions

From a thorough photomechanistic study with **1**, **7**, **8** and **9** it has been concluded that the tendency of such *o*,*o*′-cyclophanes to undergo [6π+6π]photocycloaddition depends on whether the geometry of the S_1 state is close enough to the geometry of the photoproduct. A heuristic trend for this tendency is seen in the relative strain energies of substrate and photoproduct.[13b,24] It was recognized, that the installation of preparatively useful photostationary equilibria would depend much on the UV absorption characteristics of the respective pair of photoisomers as determined by their acceptor/donor substituents. As in case of **1** no other reaction pathway (such as photometathesis to the respective [12]diazaannulenes) would supposedly interfere.[26]

As it turned out, **24a** and **24b** behaved as expected with respect to rate and specificity of the photoreaction (Scheme 4). Irradiation of ca. $10^{-3(-4)}$ M carefully dried and degassed acetonitrile solutions at 0 °C with λ = 254 nm light of low-pressure Hg lamps (Rayonet chamber, quartz tubes, room temperature, Figure 4) established neat ca. 2:1 equilibria with **32a** and **32b**, respectively (isosbestic points at 296 nm and 228, 249 nm, respectively). Prolonged irradiation had no further measurable effect and NMR control shown for **24a** in Figure 5, proved the neatness of these photoequilibrations. Irradiation of such solutions or of solutions of pure **32a** or **32b** with polychromatic light (λ > 280 nm, high-pressure Hg lamp, a Pyrex® vessel) caused complete cycloreversion to **24a** and **24b**, respectively. Particularly, the UV absorption curves (CH_3CN) of **24a**/**32a** (λ_{max} = 277/304 nm) displayed the degree of bathochromic displacement as seen for **1**/**2** and ascribed to cyclobutane-



Scheme 4.

mediated σ-homoconjugation between the two dienic chromophores.[5] In clear contrast, UV and NMR control of irradiation experiments with **24c** and **24f** in carefully degassed solvents using monochromatic (254 nm) and polychromatic light ($\lambda > 280$ nm) furnished no evidence for the formation of **32c** and **32f**, only slow polymerization.

The benzo/pyridazino cyclodimers **32a** and **32b** are extremely acid-sensitive. Chromatography of the photoequilibrium mixtures even on deactivated silica gel (triethylamine), unproblematic with benzo/benzo dimers,[1] caused

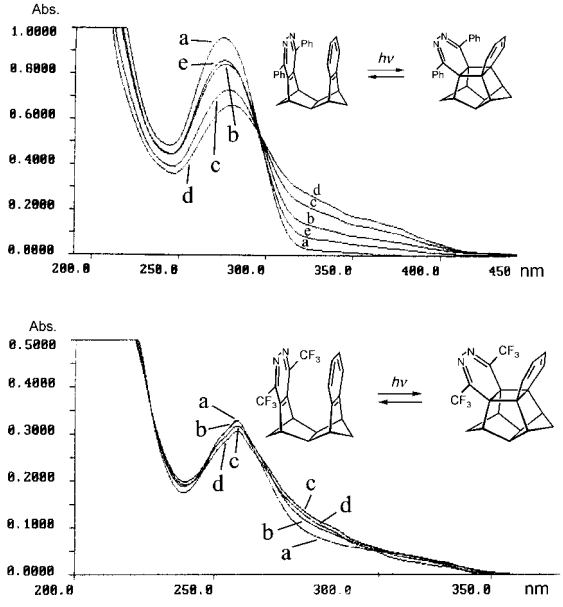


Figure 4. UV (254 nm) control of the equilibrations **24a** ⇄ **32a** and **24b** ⇄ **32b**. Top: a: start, b: 10 s, c: 30 s, d: 2 min, e: change to 300 nm, 8 min. Bottom: a: start, b: 20 s, c: 2 min, d: 4 min.

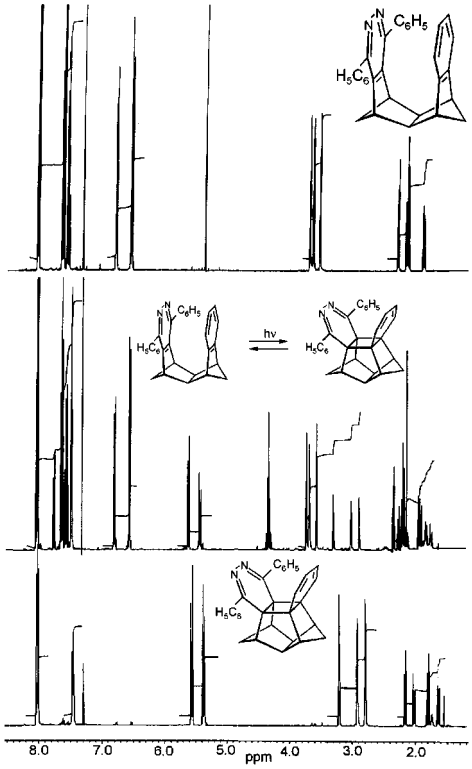


Figure 5. ^{1}H NMR control of the equilibration **24a** ⇄ **32a**.

appreciable isomerization back to **24a**(**b**) [typically ca. 25% of pure **32a**(**b**) isolated]. After crystallization the slightly colored crystals melted upon rapid heating without noticeable change at 183–185 °C and 140 °C, respectively.

Thermal Cycloreversions

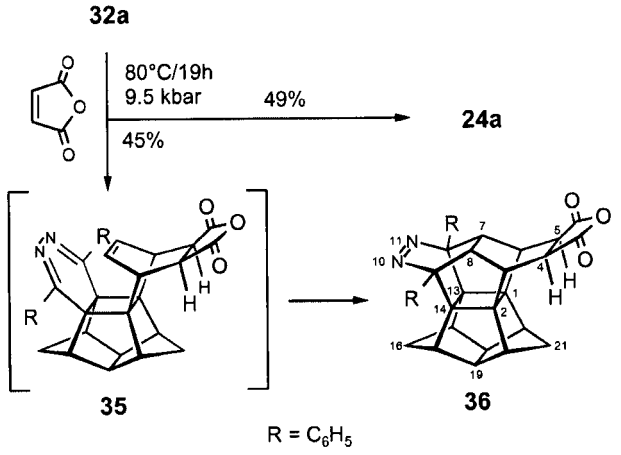
To account for the above cited high kinetic stability of parent **2**, an explanation in terms of a structurally enforced concerted but symmetry-forbidden cycloreversion mechanism via an antiaromatic transition state (cf. **34**) – as opposed to a stepwise one (cf. **33**) – has been presented.[6] For **32a** a qualitative, ^{1}H NMR monitored kinetic study in [D_6]-benzene at 140 °C (sealed tube) confirmed a neat cycloreversion to **24a** with a half-life time of ca. 13 h. The fragmentation patterns in the 70-eV MS spectra of the pairs **24a**/**32a** and **24b**/**32b** indicate the rapid cycloreversion of the **32a**$^{\cdot+}$ and **32b**$^{\cdot+}$ ions.

Cycloadditions

Inverse and standard [4+2]-additions to the dihydropyridazine and cyclohexadiene parts of the photoproducts **32** were explored with novel cage structures as target molecules. The attempts aiming at inverse additions can be briefly summarized: not in the least for steric reasons (3,6-disubstitution), with no electron-rich dienophile, not even with the sterically rather undemanding (dimethylamino)ethylene,[27] could addition be achieved, even under high pres-

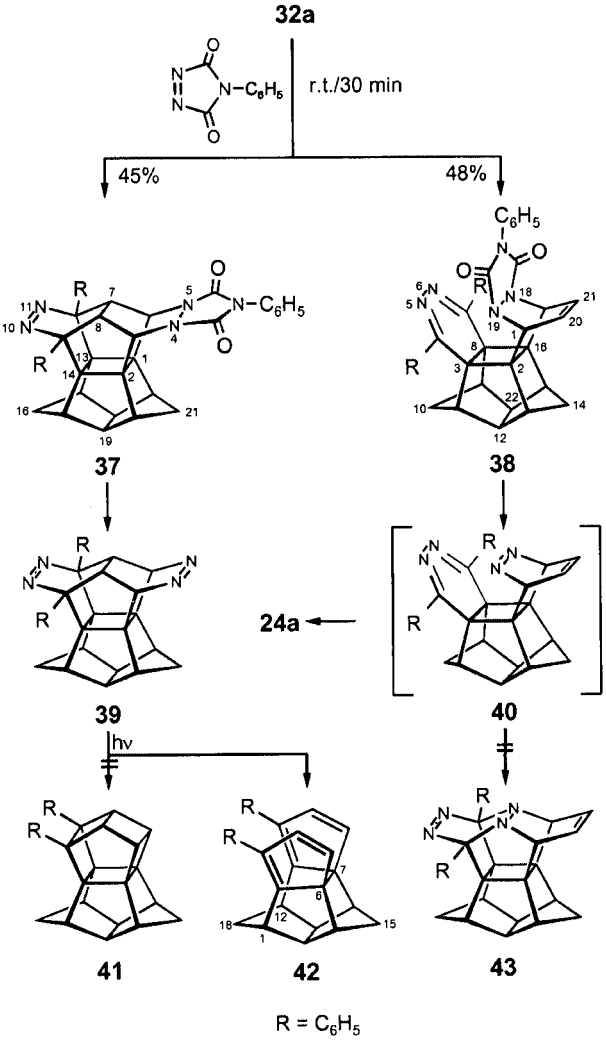
sure (9.5 kbar). Selected standard additions performed with **32a** are listed in Scheme 5, Scheme 6, and Scheme 7.

The *syn-o,o'*-dibenzene **2** is thermally stable enough to allow the sterically demanding addition of maleic anhydride (MA) and after prolonged boiling (12 h) of a benzene solution, the 1:1 "domino" adduct arising from external attack was quantitatively secured. For **32a** it was expected that its lower thermal stability would complicate matters. In fact, a ^{1}H NMR-controlled experiment with a solution of **32a** and MA in [D_6]benzene kept at 100 °C for 15 h in a sealed NMR tube revealed the presence of only ca. 10% of the 1:1 "domino" product **36** besides **24a** (no evidence for intermediate **35**). The yield of **36** was raised to 45% when the reaction solution was subjected to 9.5-kbar pressure at 80 °C for 19 h.



Scheme 5.

In contrast, *N*-phenyl-triazoline-3,5-dione (NPTD) added rapidly at room temperature to **32a** providing after chromatographic separation 45–48% of the colorless "domino" adduct **37** and the yellow "pincer" isomer **38**.[28] Because **24a** neither interfered with NPTD nor with the separation of **37** and **38**, it was preparatively advantageous to use **32a** as the original ca. 2:1 photoequilibrium mixture with **24a**. The principal features of the C_s-symmetrical skeletons **37** and **38** were unambiguously derived from the NMR spectra. In this context, the at first sight surprising structural assignment of **38** was confirmed by an X-ray structural analysis (Figure 6) with crucial details such as the through-space distance C4(7)–N19(18) = 2.9354 (2.8314) Å.[20] Oxidative hydrolysis of **37** to provide with the bisazo[2.2.1.1]pagodane **39** a potential precursor of the much desired [1.1.0.0]pagodane **41** required forcing conditions. The highly strained yet thermally rather stable **39** was nevertheless isolated in high yield {80%, colorless crystals, λ_{max} = 389 nm (ε = 129), 367 (106), 276 (1170), 246 (8700). MS: *m*/*z* = 412 ([M – N_2]$^+$), 384 ([M – 2 N_2]$^+$)}. Analogous or even somewhat milder treatment of **38** did not result in **40** or the tetraaza[2.2.1.1]pagodadiene **43** but in **24a**. In spite of the seemingly very favorable steric situation in **40** (intermediacy admittedly questionable) for a cycloaddition to give **43**, the expulsion of N_2 from the diazabicyclo[2.2.2]-



Scheme 6.

octadiene unit,[29] presumably promoted by the concerted opening of the annelated cyclobutane ring, was too fast. For probably similar reasons, the photoelimination of N_2

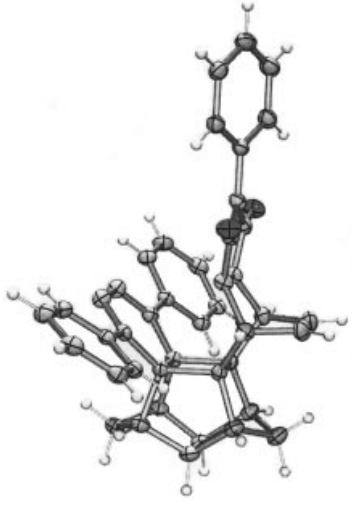
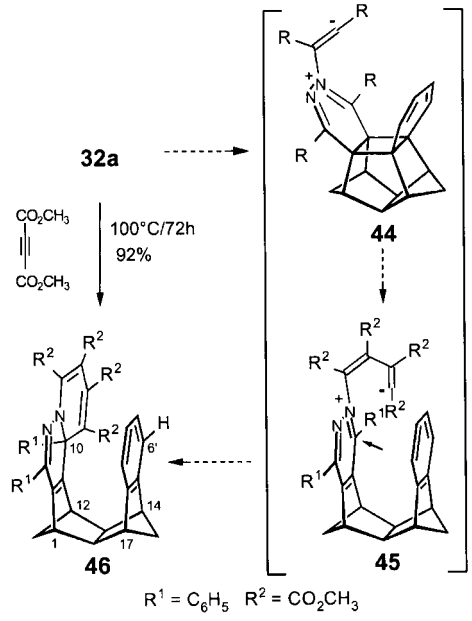


Figure 6. X-ray structure of **38**.

from **39** did not give access to **41**. Hopes, that in both N_2-elimination steps 1,4-radical recombination (cf. **16** → **17**) could at least compete with ring-opening events[30] were not substantiated. Irradiation of "photoreluctant" **39** with 254 nm light in dilute, deoxygenized CH_3CN at room temperature ended in a mixture of products (at least 3, TLC, no **41**) of which the major (80%), oxygen-sensitive component was isolated through crystallization (hexane/CH_2Cl_2, 4:1) and identified as tetraene **42**.

The slim dimethyl acetylene dicarboxylate (DMA) has been shown to expeditiously undergo "domino" – and "pincer"-type additions to **2** (ratio 97:3).[28] **32a**, in contrast, like other *N*-heterocycles,[31] behaved towards DMA as nucleophile producing with an excess of reagent nearly quantitatively the yellowish [λ_{max} (CH_3CN) = 395 nm], crystalline 1:2 adduct (MS, TLC, 92% isolated besides **24a** and another trace component). Structure **46** arising from the interception of the primary dipole **44** and *endo*-cyclization in **45** is in line with the spectroscopic data. The high-field chemical shift of (presumably) 6′-H (δ = 4.68 ppm) and *m*/*z* = 619 [M – C_6H_5]$^+$ as mother peak in the MS spectrum are prominent features.

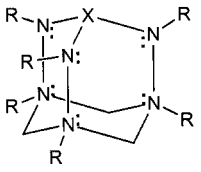


Scheme 7.

Concluding Remarks

With the photoequilibrations **24a**,**b** ⇄ **32a**,**b**, the primary objective of this study was accomplished, the scope of arene/(hetero)arene [6+6]photocycloaddition reaction could be extended. The limitations met with **24c**,**f** are, as in case of a dibromo-derivative of **2**,[12a] primarily ascribed to the absorption characteristics of starting materials and potential products. The preparative-synthetic utility of the *syn*-[6+6]arene/(hetero)arene cyclodimers for the construction of (aza)pagodane-type cage molecules has been further substantiated.

With the C_{3v} symmetrical trimer **15a** in hand, a potential tripodal N-donor ligand,[32] a chance was seen to arrive at hexaazaadamantanes (**47**) which, with their rigid-parallel fixation of three neighboring –NR–NR– bonds (through-space N···N distances of ca. 3.2 Å), could have meant a highly attractive extension of our search for proximate, *syn*-periplanar bishydrazines and the derived (radical) ions.[33] In explorative experiments, however, the C=N double bonds in **15a** proved resistant to their hydrogenative saturation and bridging interconnections.[34]



47

With this 86th report on "Photochemical Transformations", a series comes to an end which began in 1962,[35] in the earlier days of preparative, particularly mechanistic organic photochemistry.[36] Over the years, the use of light for the construction of molecules with unusual architecture, with unusual photophysical and chemical properties, has remained a major area of research performed in the group of the senior correspondence author (H. P.). The latter takes this opportunity to express his gratitude and sincere thanks to all the students, technicians, postdoctoral fellows and colleagues who along this long road have contributed their time, skills, enthusiasm, advice and expertise, and to all the institutions and agencies having generously provided financial support.

Experimental Section

General: Melting points (m.p.) were determined with a Monoskop IV (Fa. Bock) and are uncorrected. Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. Analytical TLC: Merck silica gel plates with F_{254} indicator with detection by UV, $KMnO_4$ or phosphomolybdic acid solution. IR spectra were recorded with Perkin–Elmer 457 (KBr pellets), UV spectra with Perkin–Elmer Lambda 15, Mass spectra with Finnigan MAT 44S and MAT 8200, ^{1}H NMR spectra with Bruker WM 250 and AM 400, ^{13}C NMR spectra with Bruker AM 400. If not specified otherwise, EI (70 eV) MS, 400/100.6 MHz ^{1}H/^{13}C NMR spectra in $CDCl_3$ are given. Chemical shifts were recorded relative to TMS (δ = 0 ppm). Assignments were confirmed by homo- and hetero-nuclear decoupling and H′H, H′X correlation experiments; assignments indicated with an asterisk can be interchanged. In the glove box used (M. Braun Labmaster 130), the O_2 and H_2O values were below 1 ppm. The silica gel used for column chromatography was Merck (0.040–0.063 mm) or ICN Biomedicals GmbH (0.032–0.063 mm).

(1α,2α,7α,8α,9β,10α,13α,14β)-3,6-Diphenyl-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-3,5,11-triene (13a): A solution of **11a** (234 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **10** (208 mg, 1.0 mmol) in CH_2Cl_2 (10 mL). After 12 h, the color of the reaction mixture had changed from violet to yellow (total conversion, TLC). Following concentration in vacuo, the residue was chromatographed (silica gel, 12 × 2 cm,

CH_2Cl_2), 380 mg (92%) of yellow crystals were isolated (R_f = 0.17); m.p. 167–168 °C. UV (CH_3CN): λ_{max} (ε) = 358 nm (sh, 3700), 345 (sh, 8400), 327 (sh, 14400), 315 (16100), 280 (sh, 8200), 273 (sh, 7000), 259 (sh, 6000), 220 (sh, 4400). IR: $\tilde{\nu}$ = i.a. 3032, 2952, 2882, 1580, 1553, 1460 cm^{-1}. ^1H NMR: δ = 7.85–7.80 (m, 4 H), 7.50–7.40 (6 H), 7.45 (m, 4′-, 5′-H), 7.14 (3′-,6′-H), 3.43 (s, 10-,13-H), 2.76 (m, 9-,14-H), 2.68 (br. s, 2-,7-H), 2.43 (m, 1-,8-H), 2.18 (dm, 16a-H), 2.02 (dm, 16s-H), 1.56 (dm, 15a-H), 1.47 (dm, 15s-H) ppm; $J_{15a,s}$ = 9.4, $J_{16a,s}$ = 8.6 Hz. ^{13}C NMR: δ = 159.5 (C-3,-6), 143.7 (2 C), 136.3 (C-11,-12), 130.2, 128.3, 127.0 (10 C), 126.2 (C-4′,-5′), 122.8 (C-3′,-6′), 60.9 (C-16), 48.3 (C-2,-7), 47.5 (C-10,-13), 46.4 (C-9,-14), 42.8 (C-15), 33.8 (C-1,-8) ppm. MS: *m/z* (%) = 415 (23) [M + 1]$^+$, 414 (70) [[M]$^+$], 233 (46), 165 (22), 116 (100). $C_{30}H_{26}N_2$ (414.6): calcd. C 86.82, H 6.32; found: C 86.84, H 6.35.

(1α,2α,7α,8α,9β,10α,13α,14β)-3,6-Bis(trifluoromethyl)-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-3,5,11-triene (13b): Upon addition of an orange-red, dry solution of **11b** (312 mg, 1.5 mmol) in CH_2Cl_2 (5 mL) to a stirred dry solution of **10** (327 mg, 1.5 mmol) in CH_2Cl_2 (5 mL) the color rapidly disappeared. After 15 min of concentration in vacuo, the greenish residue crystallized from CH_2Cl_2/petroleum ether (1:9). 540 mg (90%) of light green crystals were collected, m.p. 110 °C (R_f = 0.39, CH_2Cl_2/petroleum ether, 1:1). UV (CH_3CN): λ_{max} (ε) = 282 nm (1100), 275 (1530), 268 (1560), 250 (1670), 243 (sh, 1550), 213 (sh, 7530). IR: $\tilde{\nu}$ = i.a. 2948 cm^{-1}, 1464, 1201, 1142, 1125. ^1H NMR: δ = 7.18 (m, 4′,-5′-H)*, 7.05 (m, 3′-,6′-H)*, 3.35 (s, 10-,13-H), 2.88 (m, 9-,14-H), 2.68 (m, 1-,8-H), 2.25 (br. s, 2-,7-H), 2.12 (dm, 16a-H), 1.98 (dm, 16s-H), 1.84 (dm, 15a-H), 1.35 (dm, 15s-H) ppm; $J_{15a,s}$ = 10.8, $J_{16a,s}$ = 8.8 Hz. ^{13}C NMR: δ = 156.8 (q, J = 32.4 Hz, C-3,-6), 145.8 (C-11,-12), 126.6 (C-4′,-5′), 123.3 (C-3′,-6′), 120.3 (q, J = 279.1 Hz, 2 CF_3), 60.4 (C-16), 47.7 (C-2,-7), 46.2 (C-10,-13), 46.0 (C-9,-14), 43.3 (C-15), 33.0 (C-1,-8) ppm. MS: *m/z* (%) = 398 (12) [M]$^+$, 143 (33), 141 (12), 117 (23), 116 (100), 115 (31), 67 (22). $C_{20}H_{16}F_6N_2$ (398.4): calcd. C 60.31, H 4.05; found: C 60.37, H 4.06

Occasionally, if moisture was not completely excluded, besides **13b**, two hydrates were isolated chromatographically (silica gel, 12 × 2 cm, CH_2Cl_2/petroleum ether, 1:1), which resulted from *exo*/endo addition of H_2O to a C=N double bond (**14b**$_{endo/exo}$).

Dimethyl (1α,2α,7α,8α,9β,10α,13α,14β)-11,12-Benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-3,5,11-triene-3,6-dicarboxylate (13c): Upon stirring a deeply red solution of **10** (107 mg, 0.52 mmol) and **11c** (104 mg, 0.52 mmol) in benzene (4 mL) for 1 h, conversion was complete (TLC). Concentration in vacuo and flash chromatography (silica gel, ethyl acetate, R_f = 0.48) delivered 191 mg (98%) of yellowish crystals. ^1H NMR: δ = 7.35 (m, 4′-,5′-H), 7.12 (m, 3′-,6′-H), 3.86 (s, 2 OCH_3), 3.38 (br. s, 10-,13-H), 2.85 (m, 9-,14-H), 2.48 (br. s, 2-,7-H), 2.42 (m, 1-,8-H), 2.12 (dm, 16a), 1.98 (dm, 16s-H), 1.79 (dm, 15a-H), 1.29 (dm, 15s-H) ppm; $J_{15a,s}$ = 10.6, $J_{16a,s}$ = 9.0 Hz. MS: *m/z* (%) = 379 (9) [M + 1]$^+$, 378 (18) [M]$^+$, 320 (13), 319 (58) [M – $COOCH_3$]$^+$, 318 (14), 260 (4) [M – 2 $COOCH_3$]$^+$, 203 (13), 197 (85), 188 (17), 181 (12), 165 (27), 143 (14), 128 (18), 117 (30), 116 (100). $C_{22}H_{22}N_2O_4$ (378.4): calcd. C 69.83, H 5.86; found C 69.44, H 5.50. **13c** remained unchanged after refluxing a solution in *p*-dichlorobenzene (174 °C) for 8 h. Occasionally, if moisture was not completely excluded, chromatographically (silica gel, 12 × 2 cm, CH_2Cl_2/petroleum ether, 1:1), besides **13c** a mixture of two hydrates (**14c**$_{endo/exo}$) was isolated resulting from *exo*/*endo* addition of H_2O to a C=N double bond (MS, NMR). $C_{22}H_{24}N_2O_5$ (396.4): calcd. C 66.65, H 6.10; found C 66.25, H 6.21.

(1α,2α,7α,8α,9β,10α,13α,14β)-3,6-Dimethoxy-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-3,5,11-triene (13d): A deeply red, dry solution of **10** (51 mg, 0.22 mmol) and **11d** (51 mg, 0.25 mmol) in toluene (1 mL) was sealed into a small Teflon® hose. Using PE 60/70 as a pressure source, the sample was exposed to 9.5 kbar at 65 °C for 2 d in a 10-cm^3 high-pressure autoclave. Concentration in vacuo yielded colorless crystals (69 mg, 97%). ^1H NMR: δ = 7.25 (m, 4′-,5′-H), 7.10 (m, 3′-,6′-H), 3.68 (s, 2 OCH_3), 3.35 (m, 10-,13-H), 2.79 (m, 9-,14-H), 2.52 (br. s, 2-,7-H), 2.22 (m, 1-,8-H), 2.18 (dm, 16s-H), 2.09 (dm, 15s-H), 1.63 (dm, 16a-H), 1.60 (dm, 15a-H) ppm. ^{13}C NMR: δ = 174.2 (C-3,-6) 147.0 (C-11,-12), 126.0 (C-4′,-5′), 123.3 (C-3′,-6′), 60.4 (C-16), 51.4 (C-2,-7), 46.9 (C-10,-13), 46.3 (C-9,-14), 44.1 (C-15), 44.0 (2 OCH_3), 43.2 (C-1,-8) ppm. HRMS: calcd. for $C_{20}H_{22}N_2O_2$ 322.1683; found 322.1678. Compound **13d** remained unchanged after refluxing a solution in *p*-dichlorobenzene (174 °C) for 8 h.

(1α,2α,7α,8α,9β,10α,13α,14β)-3,6-Bis(trifluoromethyl)-3-hydroxy-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-5,11-diene (14b$_{endo/exo}$). 14b$_{endo}$: Colorless crystals (R_f = 0.20, CH_2Cl_2). UV (CH_3CN): λ_{max} (ε) = 276 nm (610), 268 (770), 261 (sh, 980), 240 (sh, 2880), 215 (sh, 11050). IR: $\tilde{\nu}$ = inter alia 3450 cm^{-1} (br., O–H), 2962, 1499 (C=C), 1463, 1146 (C-F). ^1H NMR: δ = 7.27–7.18 (m, 3′-,4′-,5′-,6′-H), 6.03 (br. s, D_2O-exch. NH), 3.33 (s 10-H)*, 3.31 (s, 13-H)*, 2.81–2.70 (m, 9-,14-H), 2.55 (s, 1-H)*, 2.58 (s,8-H)*, 2.17–2.09 (m, 2-,7-H), 1.97 (d, 16a-H), 1.67–1.58 (m, 16s-,15a-H) 1.56 (br. s, D_2O-exch. OH), 1.52 (dm, 15s-H) ppm; $J_{15a,s}$ = 10.4, $J_{16a,s}$ = 8.6 Hz. ^{13}C NMR: δ = 147.6, 146.1 (C-11, C-12), 146.2 (q, J = 32.4 Hz, C-6), 126.1, 125.8 (C-3′,-4′), 125.0 (q, J = 335.1 Hz, CF_3) 123.5 (q, J = 286.0 Hz, CF_3), 123.3 (C-5′,-6′), 80.0 (q, J = 30.0 Hz, C-3), 60.3 (C-16), 47.7 (C-13), 47.0 (C-10), 46.3 (C-7), 46.2, 46.1 (C-9,-14), 42.4 (C-15), 40.7 (C-2), 40.4 (C-8), 34.2 (C-1) ppm. MS: *m/z* (%) = 416 (15) [M]$^+$, 181 (15), 167 (9), 166 (9), 165 (11), 143 (87), 142 (21), 141 (19), 130 (28), 128 (15), 117 (32), 116 (100). $C_{20}H_{18}N_2O$ (416.4): calcd. C 57.70, H 4.36; found C 57.68, H 4.40.

14b$_{exo}$: Colorless crystals (R_f = 0.16, CH_2Cl_2). UV (CH_3CN): λ_{max} (ε) = 276 nm (575), 268 (815), 261 (sh, 1170), 241 (3040), 215 (sh, 10430). IR: $\tilde{\nu}$ = i.a. 3430 cm^{-1} (br., O–H), 2954, 2880, 1462 (C=C), 1180 (C-F). ^1H NMR: δ = 7.23–7.05 (m, 3′-,4′-,5′-,6′-H), 5.94 (br. s, D_2O-exch. NH), 3.35 (s, 10-H)*, 3.30 (s, 13-H)*, 2.87–2.72 (m, 9-,14-H), 2.57 (1-H)*, 2.64 (s, 8-H)*, 2.37 (br. s, D_2O-exch -OH), 2.12 (dm, 16a-H), 2.06–2.01 (m 2-,7-H), 1.99 (dm, 16s-H), 1.62 (dm, 15a-H), 1.55 (dm, 15s-H) ppm; $J_{15a,s}$ = 10.2, $J_{16a,s}$ = 8.6 Hz. ^{13}C NMR: δ = 146.8, 146.0 (C-11, C-12) 144.5 (q, J = 32.3 Hz, C-6), 126.2, 126.1 (C-3′,-4′), 124.4 (q, J = 286.4 Hz, CF_3) 124.4 (q, J = 290.4 Hz, CF_3), 123.3 (C-5′,-6′), 78.5 (q, J = 29.3 Hz, C-3), 60.4 (C-16), 47.3 (C-13), 47.0 (C-10), 46.3 (C-7), 46.2, 46.0 (C-9,-14), 43.7 (C-15), 40.0 (C-2), 36.9 (C-8), 35.3 (C-1) ppm. MS: *m/z* (%) = 416 (20) [M]$^+$, 347 (8), 283 (6), 165 (15), 143 (74), 142 (20), 130 (27), 128 (17), 118 (5), 117 (39), 116 (100), 115 (52), 91 (10), 83 (5), 77 (6), 69 (6), 67 (13). $C_{20}H_{18}N_2O$ (416.4): calcd. C 57.70, H 4.36; found: C 57.63, H 4.39.

Dimethyl (1α,2α,7α,8α,9β,10α,13α,14β)-3-Hydroxy-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-5,11-diene-3,6-dicarboxylate (14c$_{endo(?)}$): Colorless crystals, 182 °C. ^1H NMR: δ = 7.40 (br. s, NH), 7.32 (m, 1 H), 7.15 (m, 3 H), 6.08 (s, OH), 3.90 (s, OCH_3), 3.80 (s, OCH_3), 3.40 (br. s, 7-H)*, 3.31 (br. s, 2-H)*, 2.75–2.70 (m, 2 H), 2.45–2.38 (m, 2 H), 2.15 (m, 1-H), 1.95–1.90 (m, 2 H), 1.70 (m, 1 H), 1.65 (m, 1 H), 1.40 (1 H) ppm. MS (EI): *m/z* (%) = 396 (58) [M]$^+$, 278 (14) [M – H_2O]$^+$, 337 (100) [M – CO_2CH_3]$^+$, 197 (30), 116 (29).

(1α,2α,7α,8α,9β,10α,13α,14β)-11,12-Benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-3,5,11-triene [13e ($C_{18}H_{18}N_2$, 262.4)]-Trimer (15a): A red solution of **10** (107 mg, 0.52 mmol) and **11e**

(43 mg, 0.52 mmol) in CH_2Cl_2 (5 mL) was stirred at room temp., and the color disappeared after 5 h to give two products (TLC). Concentration in vacuo and crystallization of the residue from CH_2Cl_2 provided 85 mg (62%) of pure trimer **15a**. These crystals proved suitable for the X-ray structural analysis (Figure 2). The second product (**15b**, MS) could not be obtained pure, because under various separation procedures it rapidly equilibrated with **15a** and (protonated) **13e**.

15a: Colorless crystals, melting with decomposition ≥195 °C. ^{1}H NMR (C_6D_6): δ = 7.15 (m, 1 H), 7.05 (m, 1 H), 6.95–6.85 (m, 2 H), 6.50 (d, 3-H), 3.37 (d, 6-H), 3.04 (m, 10-H), 3.01 (m, 13-H), 2.5–2.4 (m, 9-,14-H), 2.37 (m, 2-H), 2.15 (br. s, 8-H), 2.08 (br. s, 1-H), 1.91 (dq, 16s-H), 1.81 (dq, 15s-H), 1.64 (dt, 16a-H), 1.53 (dt, 7-H), 1.32 (dm, 15a-H) ppm; $J_{2,3}$ = 2.0, $J_{2,7}$ = 6.2, $J_{6,7}$ = 2.0, $J_{7,8}$ = 1.5 Hz. ^{13}C NMR: δ = 147.2, 146.3, 146.3 (C-3,-11,-12), 125.9, 125.5, 123.6, 122.9 (C-3′,-4′,-5′,-6′), 78.8 (C-6), 60.5 (C-16), 48.3 (C-14), 47.7 (C-9), 46.8 (C-13), 46.7 (C-10), 45.9 (C-1), 45.7 (C-8), 43.9 (C-15), 35.9 (C-2), 35.4 (C-7) ppm. MS: *m*/*z* (%) = 787 (5) [M + 1]$^+$, 786 (9) [M]$^+$, 525 (8), 524 (17) [**15a** – **13e**]$^+$, 379 (21), 263 (50), 262 (71) [**13e**, HR], 208 (39), 167 (36), 165 (25), 143 (26), 142 (39), 141 (45), 117 (56), 116 (100). $C_{54}H_{54}N_6$ (648.6): calcd. C 82.41, H 6.92; found C 82.01, H 6.77.

1,12-Bis(trifluoromethyl)-6,7;17,18-dibenzo-23,24-diazadecacyclo[10.10.2.1^{3,10}.1^{5,8}.1^{14,21}.1^{16,19}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]octacosa-6,17,23-triene (16): Cf. **13b**; upon addition of a deeply orange-red, dry solution of **11b** (109 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) to a stirred dry solution of **10** (208 mg, 1.0 mmol)/P_2O_5 (100 mg) in CH_2Cl_2 (5 mL), the color rapidly disappeared. The mixture was concentrated in vacuo for 30 min, the colorless residue crystallized after addition of CH_2Cl_2/petroleum ether (1:1). 240 mg (80%, not optimized) of colorless crystals (CH_2Cl_2) were isolated, m.p. 310–312 °C. UV (CH_3CN): λ_{max} (ε) = 375 nm (85), 278 (sh, 860), 273 (1800), 267 (1820), 262 (sh, 1400), 216 (sh, 16400). IR: $\tilde{\nu}$ = i.a. 3000, 2946, 2896, 1487, 1461, 1333, 1275, 1214, 1153, 1057, 939 cm^{-1}. ^{1}H NMR: δ = 7.28 (m, 2 H) 7.17 (m, 2 H), 6.98 (br. s, 4 H), 3.27 (m, 5-,8-H), 3.23 (m, 16-,19-H), 2.65 (m, 4-,9-H), 2.52 (m, 15-, 20-H), 2.11 (m, 26-Ha,s), 2.09 (dm, *J* = 8.6 Hz, 28-Ha), 1.88 (dm, *J* = 8.6 Hz, 28-Hs), 1.79 (m, 14-,21-H,), 1.77 (m, 3-,10-H), 1.75 (dm, *J* = 8.3 Hz, 25-Ha), 1.57 (dm, *J* = 8.3 Hz, 25-Hs), 1.25 (m, 13-,22-H), 0.97 (m, 2-,11-H), –0.24 (dm, *J* = 12.6 Hz, 27-Ha), –0.36 (dm, *J* = 12.6 Hz, 27-Hs) ppm. ^{13}C NMR: δ = 147.6 (C-6,-7)*, 145.2 (C-17,-18)*, 126.3 (q, *J* = 282.1 Hz, 2 CF_3), 126.2 (2 C′), 125.6 (2 C′), 123.4 (2 C′), 122.0 (2 C′), 76.8 (q, *J* = 25.4 Hz, C-1,-12), 60.1 (CH_2), 52.8 (CH_2), 50.7 (C-3,-10), 50.3 (C-14,-21), 47.9 (C-4,-9), 47.5 (C-15,-20), 46.1 (C-5,-8), 43.3 (C-16,-19), 41.9 (CH_2), 41.5 (C-13,-24), 39.6 (C-2,-11), 27.4 (CH_2) ppm. MS (FAB): *m*/*z* (%) = 607 (25) [M + 1]$^+$, 606 (3) [M]$^+$, 400 (19), 399 (70) [**13b** + H]$^+$, 307 (23), 304 (27), 289 (25), 273 (11), 257 (13), 246 (13), 242 (11), 217 (100). $C_{36}H_{32}F_6N_2$ (606.7): calcd. C 71.28, H 5.32; found C 71.06, H 5.27. Occasionally, if moisture was not completely excluded, chromatographically (silica gel, 12 × 2 cm, CH_2Cl_2/petroleum ether, 1:1), besides **16** the two hydrates of **13b** were found.

3,14-Bis(trifluoromethyl)-8,9;19,20-dibenzodecacyclo-[14.6.1.1^{5,12}.1^{7,10}.1^{18,21}.0^{2,15}.0^{3,14}.0^{4,13}.0^{6,11}.0^{17,22}]hexacosa-8,19-diene (17): A degassed solution of **16** (61 mg, 0.1 mmol) in CH_3CN (150 mL) was irradiated in a Pyrex® vessel with polychromatic light from a Hanau TQ 125-W high-pressure lamp (λ >280 nm) until ca. 50% conversion (TLC, 2.5 h, one product). After concentration in vacuo, the residue was chromatographed (silica gel, CH_2Cl_2/petroleum ether, 1:3) giving 30 mg (52%) of colorless crystals, m.p. 289–291 °C (CH_2Cl_2/petroleum ether, 1:9, R_f = 0.83), and then residual **16**. UV (CH_3CN): λ_{max} (ε) = 277 nm (sh, 400), 273 (1280), 267 (1330), 261 (sh, 990), 217 (9300). IR: $\tilde{\nu}$ = i.a. 3000 cm^{-1}, 2950, 2890, 1450, 1345, 1300, 1260, 1214, 1120, 1065. ^{1}H NMR: δ = 7.24 (m, 2 H), 7.13 (m, 2 H), 7.04 (br. s, 4 H), 3.27 (m, 2 H), 3.23 (m, 2 H), 2.72 (m, 2 H), 2.40 (m, 2 H), 2.23 (dm, *J* = 11.1 Hz, 1 H), 2.06 (dm, *J* = 8.1 Hz, 1 H), 1.95–1.88 (m, 2+2+1 H), 1.76 (m, 2 H), 1.73 (dm, *J* = 8.5 Hz, 1 H), 1.58 (dm, *J* = 11.1 Hz), 1.53 (dm, *J* = 8.1 Hz, 1 H), 1.48 (m, 2 H), 0.96 (dm, *J* = 12.5 Hz, 1 H), –1.13 (dm, *J* = 12.5 Hz, 1 H) ppm. ^{1}H NMR (C_6D_6): δ = 6.55 (m, 4 H), 6.52 (m, 4 H), 2.69 (m, 7-,10-H)*, 2.51 (m, 18-,21-H)*, 2.13 (dm, *J* = 11.3 Hz, 1 H), 2.06 (br. s, 2 H), 1.93 (m, 2 H), 1.77 (m, 2 H), 1.62 (m, 2 H), 1.48 (dm, *J* = 7.8 Hz, 1 H), 1.33 (m, 2 H), 1.30 (m, 2 H), 1.25–1.20 (m, 2+1 H), 1.15 (dm, *J* = 8.6 Hz, 1 H), 1.08 (dm, 1 H), 1.01 (dm, 1 H), 0.95 (dm, *J* = 12.8 Hz, 1 H), –1.13 (dm, *J* = 12.8 Hz, 1 H) ppm. ^{13}C NMR: δ = 148.1 (C-8,-9)*, 145.7 (C-19,-20)*, 126.1 (2 C′), 126.2 (q, *J* = 282.1 Hz, CF_3), 125.0 (2 C′), 123.5 (2 C′), 122.1 (2 C′), 76.7, (q, *J* = 25.4 Hz, C-3,-14), 60.4 (CH_2), 54.3 (2 CH), 52.4 (CH_2), 48.9 (2 CH), 47.9 (2 CH), 47.7 (2 CH), 47.6 (2 CH), 46.3 (2 CH), 42.0 (CH_2), 41.8 (2 CH), 39.5 (2 CH), 26.8 (CH_2) ppm. MS: *m*/*z* (%) = 578 (8) [M]$^+$, 149 (10), 143 (16), 142 (22), 141 (10), 129 (7), 128 (6), 117 (25), 116 (100). $C_{36}H_{32}F_6$ (578.7): calcd. C 74.73, H 5.57; found C 74.67, H 5.69.

(1α,7α,8α,9β,10α,13α,14β)-3,6-Diphenyl-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-2,5,11-triene (20a): A mixture of **13a** (207 mg, 0.5 mmol) and carefully dried *p*-dichlorobenzene (1.0 g) was refluxed for 2 h (total conversion, TLC). After removal of *p*-dichlorobenzene in vacuo, the residue was chromatographed (silica gel, 9 × 2 cm, CH_2Cl_2, R_f = 0.25). With crystallization (CH_2Cl_2), 155 mg (74%) of light yellow, oxygen-sensitive crystals were isolated, m.p. 161–162 °C. UV (CH_3CN): λ_{max} (ε) = 300 nm (5500), 292 (5800), 285 (6300), 278 (4200), 258 (1800), 251 (950), 243 (11800). IR: $\tilde{\nu}$ = i.a. 3296 cm^{-1}, 3040, 2954, 1659, 1590, 1488, 1460. ^{1}H NMR: δ = 7.45 (br. s, N–H), 7.40–7.15 (m, 10 H, 3′-,6′-H), 6.90–6.85 (m, 4′-,5′-H), 3.40–3.43 (m, 10-,13-H), 2.95–2.80 (m, 8-,9-,14-H), 2.70 (d, 7-H), 2.14 (dm, 16a-H), 2.04 (dm, 16s-H), 1.72 (m, 1-H), 1.52 (dm, 15a-H), 0.93 (dm, 15s-H) ppm; $J_{7,8}$ = 3.2, $J_{15a,s}$ = 8.9, $J_{16a,s}$ = 8.3 Hz. ^{13}C NMR: δ = 159.5, 154.3 (C-3,-6), 142.6, 141.6 (C-11,-12), 136.3, 136.2, 134.4, 131.2, 131.1, 128.6, 128.4, 128.1, 127.9, 127.5, 126.6, 125.7, 124.8, 123.2, 121.7 (10 C, C-2,-3′,-4′,-5′,-6′), 60.0 (C-16), 49.3 (C-15), 48.4 (C-7), 47.0, 46.7 (C-10,-13), 46.3, 43.8 (C-9,-14), 41.0, 37.8 (C-1,-8) ppm. MS: *m*/*z* (%) = 415 (31) [M + 1]$^+$, 414 (96) [M]$^+$, 348 (42), 298 (79), 297 (100), 271 (38). $C_{30}H_{26}N_2$ (414.6): calcd. C 86.90, H 6.32; found C 86.79, H 6.29

(1α,7α,8α,9β,10α,13α,14β)-3,6-Bis(trifluoromethyl)-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-2,5,11-triene (21a): Cf. **20a**; A solution of **13b** (398 mg, 1.0 mmol) in *p*-dichlorobenzene (1.5 g) was refluxed for 2 h. After removal of the solvent the solid residue was chromatographed (silica gel, 10 × 2 cm; CH_2Cl_2/petroleum ether, 1:4). 340 mg (85%) of **21a** (R_f = 0.15) were isolated after crystallization from CH_2Cl_2/petroleum ether (1:9) as colorless needles, m.p. 167 °C. UV (CH_3CN): λ_{max} (ε) = 288 nm (sh, 1880), 278 (2250), 274 (sh, 2180), 238 (sh, 4200), 216 (sh, 10920). IR: $\tilde{\nu}$ = inter alia 3328 cm^{-1} (N–H), 2960, 1468, 1399, 1372, 1198, 1150. ^{1}H NMR: δ = 7.35 (br. s, N–H), 7.3–7.25 (m, 3′-,4′-H), 7.2–7.1 (m, 5′-,6′-H), 3.35 (m, 10-H), 3.30 (m, 13-H), 3.19 (br. s, 1-H), 2.92–3.03 (m, 9-,14-H), 2.88 (d, 7-H), 2.09 (dm, 16a-H), 2.01 (dm, 16s-H), 1.93 (dm, 15a-H), 1.60 (m, 8-H), 1.19 (dm, 15s-H) ppm; $J_{7,8}$ = 1.6, $J_{15a,s}$ = 9.9, $J_{16a,s}$ = 8.6 Hz. ^{13}C NMR: δ = 147.1, 144.7 (C-11,-12), 129.8 (q, *J* = 34.2 Hz, C-6), 127.0, 125.3, 125.2, 122.4 (C-2,-3′,-4′,-5′,-6′), 121.2 (q, *J* = 273.4 Hz, CF_3)*, 120.7 (q, *J* = 272.3 Hz, CF_3)*, 120.9 (q, *J* = 35.0 Hz, C-3), 59.6 (C-16), 49.3 (C-15), 47.1 (C-7), 46.6, 46.3 (C-10,-13), 46.1, 43.4 (C-9,-14), 39.5, 35.5 (C-1,-8) ppm. MS: *m*/*z* (%) = 399 (13) [M + 1]$^+$, 398 (59) [M]$^+$, 329

(87), 213 (27), 167 (16), 143 (33), 142 (22), 141 (36), 129 (32), 128 (43), 117 (55), 116 (100). $C_{20}H_{16}F_6N_2$ (398.4): calcd. C 60.31, H 4.05; found C 60.38, H 4.10.

(1α,7α,8α,9β,10α,13α,14β)-3,6-Bis(trifluoromethyl)-4-chloro-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-3,5,11-triene (21b): *t*BuOCl (0.13 mL, 1.0 mmol) was added dropwise to a stirred solution of **21a** (250 mg, 0.63 mmol) in anhydrous toluene (3 mL) at room temperature (under N_2). After 30 min *t*BuOK (220 mg) was added and stirring was continued for 30 min. After concentration in vacuo the residue was dissolved in $CHCl_3$ (20 mL), washed with water and dried ($MgSO_4$). The product obtained after concentration in vacuo was chromatographed (silica gel, 10 × 2 cm, petroleum ether, R_f = 0.25). After crystallization from petroleum ether 245 mg (90%) of yellow needles were isolated, m.p. 97–98 °C. UV (CH_3CN): λ_{max} (ε) = 438 nm (210), 317 (2140), 270 (sh, 1970), 255 (2450), 217 (sh, 5840). IR: $\tilde{\nu}$ = i.a. 3052 cm^{-1}, 2960, 2913, 2873, 1469, 1375, 1330, 1269, 1196, 1175. ^{1}H NMR: δ = 7.11 (m, 3′-,4′-H), 6.95 (m, 5′-,6′-H), 3.37 (m, 10-H), 3.34 (m, 13-H), 3.29 (m, 1-H), 3.21 (m 9-H)*, 3.02 (m, 14-H)*, 2.70 (d, 7-H), 2.65 (dm, 16a-H), 2.34 (m, 8-H), 2.16 (dm, 16s-H), 2.0–2.1 (dm, 15s-,15a-H) ppm; $J_{7,8}$ = 2.1, $J_{16a,s}$ = 9.8 Hz. ^{13}C NMR: δ = 147.7, 143.4 (C-11,-12), 128.0 (q, J = 34.8 Hz, C-3)*, 123.0 (q, J = 35.0 Hz, C-6)*, 126.9, 126.7, 125.6, 122.9 (C-2,-3′,-4′,-5′,-6′), 123.9 (q, J = 281.8 Hz, CF_3), 121.0 (q, J = 272.2 Hz, CF_3), 58.6 (C-16), 48.8 (C-7), 48.2, 46.0 (C-10,-13), 47.3 (C-15), 45.8, 43.0 (C-9,-14), 39.0, 34.45 (C-1,-8) ppm. MS: *m*/*z* (%) = 432 (5) [M]$^+$, 143 (12), 142 (38), 141 (43), 129 (23), 128 (19), 117 (37), 116 (100). $C_{20}H_{15}ClF_6N_2$ (432.2): calcd. C 55.51, H 3.49; found C 55.64, H 3.54.

Dimethyl (1α,7α,8α,9β,10α,13α,14β)-11,12-Benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-2,5,11-triene-3,6-dicarboxylate (22a): P_2F (488 mg, 1.36 mmol) was added to a stirred solution of **13c** (243 mg, 0.64 mmol) in benzene (10 mL) in a glove box. After 3 min the reaction was quenched with methanol (5 mL), the clear yellowish solution concentrated in vacuo, and the residue was flash-chromatographed (silica gel, 10 × 2 cm, cyclohexane/ethyl acetate, 1:1); 231 mg (95%) of colorless crystals (R_f = 0.60) were isolated. ^{1}H NMR (C_6D_6): δ = 8.3 (br. s, N–H), 7.00 (m, 3′-H)*, 6.86 (m, 4′-H)*, 6.83–6.72 (m, 5′-,6′-H)*, 3.75 (br. s, 1-H), 3.47 (d, 7-H), 3.40 (s, OCH_3),3.42 (m, 13-H), 3.32 (s, OCH_3), 3.10 (br. s, 10-H), 2.98 (br. s, 14-H), 2.56–2.60 (8-,9-H), 1.92 (dm, 16s-H), 1.85 (dm, 15s-H), 1.65 (dm, 16a-H), 1.58 (dm, 15a-H) ppm; $J_{7,8}$ = 2.6 Hz. ^{13}C NMR: δ = 164.5 (CO), 161.3 (CO), 147.4, 145.3 (C-11,-12), 130.0 (C-6), 128.6 (C-2), 126.2, 125.1, 124.0, 123.0 (C-3′,-4′,-5′,-6′), 124.1 (C-3), 59.5 (C-16), 51.5 (OCH_3), 51.2 (OCH_3), 49.8 (C-15), 47.8 (C-7), 46.7, 46.5 (C-10,-13), 46.5, 45.5 (C-9,-14), 40.0, 38.2 (C-1,-8) ppm. MS: *m*/*z* (%) = 379 (4), 378 (17) [M]$^+$, 329 (56), 318 (19), 218 (16), 203 (26), 202 (14), 189 (17), 188 (36), 165 (15), 128 (40), 116 (98), 115 (100). HRMS: calcd. for $C_{22}H_{22}N_2O_4$ (378.4): 378.1580; found: 378.1574.

Dimethyl (1α,7α,8α,9β,10α,13α,14β)-4-Chloro-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-2,5,11-triene-3,6-dicarboxylate (22b): After stirring a solution of **22a** (26 mg, 0.07 mmol) and sodium dichloroisocyanurate (16 mg, 0.07 mmol) in benzene (10 mL) and six drops of water (clear solution) for 12 h at 70 °C, conversion was complete (TLC). MS: *m*/*z* (%) = 414 (21), 413 (77), 412 (10) [M]$^+$, 377 (100) [M – Cl]$^+$, 295 (13), 294 (17), 279 (23), 245 (12), 243 (11). HRMS: calcd. for $C_{22}H_{21}ClN_2O_4$ (412.9): 412.1191; found 412.1181.

(1α,2β,3α,6α,7β,8α)-4,5-(3′-,6′-Diphenyl-4′,5′-pyridazino)-9,10-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (24a): a) *t*BuOCl (0.13 mL, 0.1 mmol) was added to a stirred solution of **20a** (414 mg, 1.0 mmol) in anhydrous toluene (5 mL). After 30 min (total conversion, **20b**, MS) *t*BuOK (220 mg) was added and stirring continued for 30 min. Upon standard workup the product was crystallized from CH_2Cl_2/petroleum ether (1:4), 345 mg (84%) of light-yellow crystals were collected, m.p. 205–206 °C. UV (CH_3CN): λ_{max} (ε) = 338 nm (sh, 390), 274 (19800), 214 (sh, 25100). IR: $\tilde{\nu}$ = inter alia 3032 cm^{-1}, 2948, 1548, 1488, 1463. ^{1}H NMR: δ = 8.00–7.90 (m, 4 H), 7.60–7.45 (m, 6 H), 6.72 (m, 3′-,6′-H), 6.50 (m, 4′-,5′-H), 3.61 (br. s, 3-,6-H), 3.56 (br. s, 2-,7-H), 3.45 (br. s, 1-,8-H), 2.19 (dm, 12a-H), 2.05 (dm, 11a-H), 2.03 (dm, 12s-H), 1.80 (dm, 11s-H) ppm; $J_{11a,s}$ = 8.8, $J_{12a,s}$ = 9.1 Hz. ^{13}C NMR: δ = 152.8 (C-3′,-6′), 143.3 (2 C), 142.4 (C-4,-5), 136.6 (C-9,-10), 128.9, 128.7, 128.4 (10 C), 126.5 (C-4′′,-5′′), 122.0 (C-3′′,-6′′), 58.9, 58.8 (C-11,-12), 46.2 (C-3,-6), 46.0 (C-2,-7), 45.2 (C-1,-8) ppm. MS: *m*/*z* (%) = 413 (33) [M + 1]$^+$, 412 (100) [M]$^+$, 295 (75), 116 (70). HRMS: calcd. for $C_{30}H_{24}N_2$ 412.1939; found 412.1946. $C_{30}H_{24}N_2$ (412.6): calcd. C 87.34, H 5.86; found: C 86.57, H 6.85. Crystal structural analysis, Figure 3.

b) cf. **24c**: **13a** (212 mg, 0.5 mmol)/benzene (30 mL)/P_2F (1.6 g, 4.5 mmol)/benzene (15 mL)/Br_2 (320 mg, 2.0 mmol). 190 mg (92%) of **24a**.

(1α,2β,3α,6α,7β,8α)-4,5-(3′,6′-Bis(trifluoromethyl-4′,5′-pyridazino)-9,10-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (24b): a) Cf. **24a**; in a glove box, P_2F (520 mg, 1.45 mmol) was added to a solution of **21b** (150 mg, 0.35 mmol) in anhydrous benzene (5 mL). After being stirred for 2 min, the now colorless solution was washed with water, dried ($MgSO_4$), and concentrated in vacuo. Chromatographically (silica gel, 8 × 2 cm, CH_2Cl_2/petroleum ether, 1:1), 130 mg (95%) were recovered (R_f = 0.25) and crystallized from CH_2Cl_2/petroleum ether (1:8); m.p. 208–210 °C. UV (CH_3CN): λ_{max} (ε) = 312 nm (sh, 440), 293 (sh, 560), 258 (2520), 252 (sh, 2200), 223 (sh, 3610), 217 (sh, 8270). IR: $\tilde{\nu}$ = inter alia 3004 cm^{-1}, 2968, 1455, 1403, 1259, 1215, 1200, 1180. ^{1}H NMR: δ = 6.77, 6.66 (3′′-,4′′-,5′′-,6′′-H), 3.65 (m, 1-,8-H), 3.50 (q, 2-,7-H), 3.29 (q, 3-,6-H), 2.23 (dt, 12a-H), 2.08 (dt, 11a-H), 1.97 (dq, 11s-H), 1.90 (dq, 12s-H) ppm; $J_{11a,s}$ = $J_{12a,s}$ = 9.4, $J_{11a(s),1(8)}$ = 1.5, $J_{12a(s),3(6)}$ = 1.6 Hz. ^{13}C NMR: δ = 147.4 (q, J = 34.8 Hz, C-3′,-6′), 145.7 (C-4,-5), 143.4 (C-9,-10), 127.2 (C-3′′,-6′′), 123.6 (C-4′′,-5′′), 121.5 (q, J = 275.0 Hz, C–CF_3), 59.1 (C-12), 58.5 (C-11), 45.8 (C-1,-8)*, 45.9 (C-2,-7), 44.6 (C-3,-6)* ppm. MS: *m*/*z* (%) = 396 (11) [M]$^+$, 167 (12), 143 (31), 142 (37), 141 (100). $C_{20}H_{14}F_6N_2$ (396.3): calcd. C 60.61, H 3.56; found C 60.41, H 3.55.

b) Cf. **24c**; compound **13b** (200 mg, 0.5 mmol)/benzene (30 mL)/P_2F (1.6 g, 4.5 mmol)/benzene (15 mL)/Br_2 (320 mg, 2.0 mmol). 180 mg (90%) of **24b**.

Dimethyl (1α,2β,3α,6α,7β,8α)-4′,5′-Pyridazino-9,10-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene-3′,6′-dicarboxylate (24c): A deeply red solution of **11c** (285 mg, 1.44 mmol) in CH_2Cl_2 (50 mL) was added to a solution of **10** (294 mg, 1.41 mmol) in CH_2Cl_2 (10 mL) within 20 min. After concentration in vacuo, the yellowish residue (525 mg, 1.4 mmol, of **13c**) was transferred into a glove box and dissolved in benzene (30 mL). Within 3 min, a solution of P_2F (3.52 g, 9.80 mmol) in benzene (40 mL) was added, then the resulting brown solution was removed from the glove box. Under N_2 bromine (684 mg, 4.28 mmol) was added, and the orange solution was extracted with water (4 × 50 mL) after 10 min. The organic phase was dried (Na_2SO_4), concentrated in vacuo, and the solid residue flash-chromatographed (silica gel, CH_2Cl_2/ethyl acetate, 2:1); 510 mg, (96%) of colorless crystals were isolated. UV (CH_3CN, qual.): λ_{max} (ε) = 340–330 nm (br. sh, ca. 200), 310–260 (ca. 600). ^{1}H NMR: δ = 6.68, 6.55 (3′′-,4′′-,5′′-,6′′-H), 4.10 (s, 2 OCH_3) 4.00 (m, 3-,6-H), 3.50 (m, 2-,7-H), 3.32 (m, 1-,8-H), 2.15

(dm, 11a-H), 2.05 (dm, 12a-H), 1.92 (dm, 11s-H), 1.90 (dm, 12s-H) ppm; $J_{11a,s} = J_{12a,s} = 9.2$ Hz. HRMS: calcd. for $C_{22}H_{20}N_2O_4$ 376.1423; found 376.1401. X-ray crystal structure, Figure 3.

Under not totally anhydrous conditions a second product besides **24c** was isolated in various amounts and identified as **28a**.

(1α,2β,3α,6α,7β,8α)-4,5-[3′,6′-Bis(hydroxymethyl)pyridazino]-9,10-benzotetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (24f): At room temperature and under N_2, **24c** (103 mg, 0.27 mmol) was added to a suspension of $LiAlH_4$ (78 mg, 2.05 mmol) in anhydrous THF (5 mL). After being stirred for 45 min at 50 °C, the suspension was cooled to 0 °C, hydrolyzed with water (0.5 mL)/NaOH (0.1 mL, 10%), and the stirring was continued for 15 min at room temp. Following concentration in vacuo, the residue was extracted with CH_2Cl_2 (5 × 10 mL), the organic phase dried (Na_2SO_4), concentrated in vacuo, and the residue flash-chromatographed (silica gel, ethyl acetate/methanol, 7:1); 64 mg (73%) of crystals were isolated. ^{1}H NMR (CD_3OD): δ = 6.76, 6.54 (3′′-,4′′-,5′′-,6′′-H), 4.70 (d, 2 CH_2OH), 3.60 (m, 3-,6-H), 3.48 (m, 2-,7-H), 3.30 (t, 2 OH), 3.2 (m, 1-,8-H) 2.15 (dm, 11a-H)*, 2.10 (dm, 12a-H)*, 1.98–194 (dm, 11s-,12s-H) ppm. ^{13}C NMR (CD_3OD): δ = 156.3 (C-3′,-6′), 146.4 (C-4,-5), 145.2 (C-9,-10), 127.5 (C-3′′,-6′′), 123.3 (C-4′′,-5′′), 63.6 (CH_2OH) 60.3 (C-12), 59.3 (C-11), 47.4 (C-1,-8), 46.8 (C-2,-7), 44.8 (C-3,-6) ppm. MS: *m*/*z* (%) = 320 (4) [M]$^+$, 291 (10), 179 (6), 161 (8), 142 (18), 141 (38), 129 (19), 128 (28), 127 (11), 117 (18), 116 (67), 115 (100). HRMS: calcd. for $C_{20}H_{20}N_2O_2$ 320.1525; found 320.1508.

(1α,2α,8α,9β,10α,13α,14β)-6-Phenyl-4,5;11,12-dibenzopentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadeca-4,6,11-trien-3-one (25): Yellowish crystals (CCl_4), m.p. 205–207 °C. IR: $\tilde{\nu}$ = inter alia 2980 cm^{-1}, 2900, 2880, 1690, 1590, 1460, 1440, 1220, 775 cm^{-1}. ^{1}H NMR: δ = 7.58 (m, 2 H), 7.50 (m, 1 H), 7.41 (m, 1 H), 7.36–7.31 (m, 3 H), 7.16 (m, 1 H), 7.07 (m, 1 H), 7.01 (m, 1 H), 6.89 (m, 1 H), 6.75 (m, 2 H), 3.48 (m, 10-H), 3.34 (m, 13-H), 3.0–2.9 (m, 1-,9-,14-H), 2.81 (m, 8-H), 2.47 (br. s, 2-H), 2.17 (dm, 16s-H), 2.06 (dm, 16a-H), 1.77 (dm, 15a-H), 1.50 (dm, 15s-H) ppm; $J_{15a,s} = 10.5$, $J_{16a,s} = 11.0$ Hz. ^{1}H NMR ([D$_5$]pyridine): δ = 7.79–6.74 (m, 13 H), 3.34 (m, 1 H), 3.20 (m, 1 H), 3.15 (m, 1 H), 2.85 (m, 2 H), 2.72 (m 1 H), 2.02 (dm, 16s-H), 1.89 (dm, 16a-H), 1.63 (dm, 15a-H), 1.50 (dm, 15s-H) ppm. ^{13}C NMR: δ = 203.2 (C=O) 148.0, 147.1, 145.1, 144.8, 140.7, 138.2, 132.9, 131.2, 130.3, 129.0, 128.9, 128.3, 128.0, 126.9, 126.3, 126.1, 126.0, 125.6, 125.0, 124.6, 122.2, 59.3, 53.9, 48.9, 47.7, 46.8, 46.7, 46.5, 46.2, 37.4 ppm. MS (EI): *m*/*z* (%) = 400 (100) [M]$^+$, 285 (22), 284 (64), 283 (45), 259 (20), 258 (32), 257 (21). $C_{30}H_{24}O$ (400.5): calcd. C 89.96, H 6.03; found C 89.29, H 6.25. Dissolved in [D$_5$] pyridine, **25** at 100 °C was slowly transformed (completely after 5 h) to (most probably) **26**. ^{1}H NMR ([D$_5$]pyridine): δ = 8.51 (m, 1 H), 7.97 (m, 1 H), 7.8–7.3 (m, 8 H), 6.82 (d, 1 H), 6.42 (m, t, 1 H), 6.06 (t, 1 H), 5.6 (br., OH), 3.85 (m, 1 H), 3.37 (m, 1 H), 3.20 (m, 1 H), 3.16–3.0 (3 H), 2.10–1.85 (m, 3 H), 1.81 (dm, 1 H) ppm.

(1α,2α,7α,8α,9β,10α,13α,14β)-6-Methoxycarbonyl-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-5,11-dien-3-one (28a): Colorless crystals. ^{1}H NMR: δ = 7.52 (br. s, NH), 7.32 (m, 1 H), 7,25 (m, 1 H), 7.06 (m, 2 H), 3.54 (s, OCH_3), 3.30 (m, 10-, 13-H), 2.85–2.70 (m, 2-,7-,8-H), 2.66 (m, 1-H), 2.1–2.0 (m, 9-,14-H), 1.98 (dm, 16s-H) 1.6–1.4 (m, 15s-,16a-H), 1.52 (dm, 15a-H) ppm. ^{13}C NMR: δ = 167.5 (C-6), 163.8 (CO), 146.6, 146.0 (C-11,-12), 126.1, 126.0, 123.8, 123.4 (C-3′,-4′,-5′,-6′), 60.5 (C-15), 52.7, 47.8 (C-2,-7), 47.0, 46.9 (C-10,-3), 46.4 (C-9,-14), 46.3, 46.2 (C-15), 43.2, 40.1 ppm. MS (EI): *m*/*z* (%) = 336 (58) [M]$^+$, 323 (14), 277 (26) [M – CO_2CH_3]$^+$, 193 (18), 155 (95), 116 (100). $C_{20}H_{22}N_2O_3$ (336.4): calcd. C 71.41, H 5.99; found: C 71.02, H 5.81.

(1α,2α,7α,8α,9β,10α,13α,14β)-6-Methoxy-11,12-benzo-4,5-diazapentacyclo[6.6.1.1^{10,13}.0^{2,7}.0^{9,14}]hexadeca-5,11-dien-3-one (28b): Cf. **24c**. A solution of P_2F (710 mg, 2.0 mmol) in benzene (5 mL) was added over 3 min to a solution of **13d** (97 mg, 0.30 mmol) in benzene (5 mL) in a glove box . The brownish solution (**19d**) was removed from the box and under N_2, bromine (218 mg, 1.36 mmol) was added. After 30 min the orange solution (one product, TLC) was thoroughly washed with water, dried (Na_2SO_4) and concentrated in vacuo. The solid residue was flash-chromatographed (silica gel, CH_2Cl_2/ethyl acetate, 3:1) and 81 mg (88%) of crystalline **28b** were isolated. ^{1}H NMR: δ = 7.52 (br. s, NH), 7.32 (m, 1 H), 7.25 (m, 1 H), 7.06 (m, 2 H), 3.54 (s, OCH_3), 3.30 (m, 10-,13-H), 2.85–2.70 (m, 2-,7-,8-H), 2.66 (m, 1-H), 2.1–2.0 (m, 9-,14-H), 1.98 (dm, 16s-H) 1.6–1.4 (m, 15s-,16a-H), 1.52 (md, 15a-H) ppm. ^{13}C NMR: δ = 167.7 (C-6), 157.1 (C-3), 146.7, 146.5 (C-11,-12), 126.0, 126.1, 123.9, 123.2 (C-3′,-4′,-5′,-6′), 60.6 (C-15), 53.7, 47.0 (C-2,-7), 46.7, 46.3 (C-10,-3), 46.3 (C-9,-14), 46.2 (OCH_3), 43.3 (C-16), 40.2, 37.5 (C-1,-8) ppm. MS (EI): *m*/*z* (%) = 308 (100) [M]$^+$, 307 (4), 267 (12), 179 (13), 167 (11), 166 (16), 165 (34), 128 (10), 127 (45). $C_{19}H_{20}N_2O_2$ (308.4): calcd. C 74.00, H 6.54; found C 73.79, H 6.33.

(1α,4α,5β,6α,9α,10β)-2,3-(3′,6′-Diphenyl-4′,5′-pyridazino)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2-ene (31a): A carefully dried, violet solution of **29** (158 mg, 1.0 mmol) and **11a** (234 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was stirred until total conversion (TLC, 12 h, a single product, TLC). After standard workup 320 mg (88%) of colorless crystals were isolated. UV (CH_3CN): λ_{max} (ε) = onset ca. 330 nm, 327 (450), 272 (2600), 249 (2100). ^{1}H NMR: δ = 8.05 (m, 4 H), 7.65 (m, 4 H), 7.53 (m, 2 H), 3.55 (m, 3-,6-H), 3.00 (m, 2-,7-H), 2.48 (1-,8-H), 1.94 (m, 12-Ha,s), 1.83 (dm, 11-Ha), 1.55 (dm, 11-Hs), 1.15 (m, 9-,10-Ha), 0.72 (m, 9-,10-Hs) ppm; $J_{11a,s} = J_{12a,s}$ = 9.2 Hz. ^{13}C NMR: δ = 156.6 (C-3′,-6′), 144.5 (C-4,-5), 135.4 (2 C), 128.5 (4 C), 127.3 (4 C), 59.8 (C-12), 46.8 (2 C), 46.4 (C-11), 46.2 (2 C), 44.2 (2 C), 39.2 (2 C), 21.8 (C-9,-10) ppm. MS: *m*/*z* (%) = 365 (22) [M + 1]$^+$, 364 (100) [M]$^+$, 323 (15), 283 (32). $C_{26}H_{24}N_2$ (364.5): calcd. C 85.68, H 6.64; found C 85.62, H 6.70.

(1α,4α,5β,6α,9α,10β)-2,3-(3′,6′-Trifluoromethyl-4′,5′-pyridazino)tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (31b): Preparation according to compound **31a** from **29** (158 mg, 1.0 mmol) and **11b** (218 mg, 1.0 mmol) in CH_2Cl_2 (10 mL); after stirring for 15 min provided 310 mg (89%) of colorless crystals. UV (CH_3CN): λ_{max} (ε): onset ca. 345 nm, 313 (450), 257 (sh, 1460), 233 (4050). ^{1}H NMR: δ = 3.70 (m, 3-,6-H), 2.99 (m, 2-,7-H), 2.30 (1-,8-H), 2.19 (br. s, 12-Ha,s), 1.72 (dm, 11-Ha), 1.42 (dm, 11-Hs), 1.05 (m, 9-,10-Ha), 0.07 (m, 9-,10-Hs) ppm; $J_{11a,s}$ = 9.5 Hz. ^{13}C NMR: δ = 149.4 (C-4,-5), 148.5 (q, J = 33.9 Hz, C-3′,-6′), 120.8 (q, J = 285.7 Hz, CF_3), 57.7 (C-12), 46.8 (2 C), 46.4 (1 C), 45.6 (1 C),44.4 (2 C), 39.3 (2 C), 21.8 (C-9,-10) ppm. MS: *m*/*z* (%) = 340 (85) [M]$^+$, 320 (27), 280 (31), 95 (100). $C_{16}H_{14}F_6N_2$ (340.3): calcd. C 55.18, H 4.05; found C 55.08, H 4.05.

3,6-Diphenyl-4,5-diazaoctacyclo[12.5.1.0^{2,7}.O^{2,13}.0^{7,18}.0^{8,13}.O^{8,16},0^{17,20}]eicosa-3,5,9,11-tetraene (32a): A degassed solution of **24a** (206 mg, 0.5 mmol) in CH_3CN (150 mL) was irradiated with monochromatic 254 nm light (Rayonet reactor, quartz tubes) for 3 h (ratio **24a/32a** ca. 2:1, no further change, ^{1}H NMR control, see Figures 4 and 5). After concentration in vacuo, the residue was chromatographically (deactivated silica gel, 10 × 2 cm, CH_2Cl_2/petroleum ether, 1:5) separated into **32a** (R_f = 0.1, 62 mg, 30%) and, after changing to CH_2Cl_2/CH_3OH (2%), residual **24a** (150 mg). Compound **32a** crystallized from CH_2Cl_2/petroleum ether (1:5) in orange needles, melting at 183–185 °C without change. UV (CH_3CN): λ_{max} (ε) = 351 nm (sh, 5460), 304 (sh, 11300), 294 (sh,

11700), 286 (sh, 11500), 214 (sh, 7000). IR: $\tilde{\nu}$ = inter alia 3046 cm^{-1}, 2934, 2858, 1534, 1503, 1447, 1434. ^1H NMR: δ = 8.12–7.90 (m, 4 H), 7.50–7.35 (m, 6 H), 5.51 (m, 9-,12-H), 5.34 (m, 10-,11-H), 3.17 (m, 1-,18-H), 2.88 (m, 17-,20-H), 2.75 (m, 14-,16-H), 2.10 (dm, 15a-H), 1.99 (dm, 15s-H), 1.74 (dm, 19a-H), 1.60 (dm, 19s-H) ppm; $J_{15a,s}$ = 10.7, $J_{19a,s}$ = 11.3 Hz. ^{13}C NMR: δ = 156.7 (C-3,-6), 135.9, 130.5, 128.4, 128.1 (10 C), 124.7 (C-10,-11), 123.7 (C-9,-12), 64.0 (C-2,-7), 59.9 (C-8,-13), 54.9 (C-1,-8), 54.8 (C-17,-20), 54.6 (C-14,-16), 38.4, 38.1 (C-15,-19) ppm. MS: *m/z* (%) = 413 (6) $[M + 1]^+$, 412 (34) $[M]^+$, 295 (55), 116 (100). HRMS: calcd. for $C_{30}H_{24}N_2$ (412.55) 412.1939; found 412.1942.

3,6-Bis(trifluoromethyl)-4,5-diazaoctacyclo-[12.5.1.0^{2,7}.O^{2,13}.0^{7,18}.0^{8,13}.O^{8,16},0^{17,20}]eicosa-3,5,9,11-tetraene (32b): Cf. **32a**. Compound **24b** (65 mg, 0.16 mmol) in CH_3CN (150 mL) was irradiated with 254 nm light for 2 h: ratio **24b**/**32b**, ca. 2:1 (^1H NMR). The residue was chromatographed (deactivated silica gel, 8 × 2 cm, CH_2Cl_2/petroleum ether, 1:1). First **32b** (R_f = 0.25, 18 mg, 28%), then residual **24b** (R_f = 0.40, 45 mg) were eluted. Compound **32b** crystallized from CH_2Cl_2/petroleum ether (1:9) in light-green needles, melting at 140 °C without change. UV (CH_3CN): λ_{max} (ε) = 354 nm (120), 304 (sh, 780), 291 (sh, 1715), 278 (sh, 2440), 266 (2725), 212 (sh, 3400). IR: $\tilde{\nu}$ = inter alia 3040 cm^{-1}, 2976, 2940, 2872, 1577, 1347, 1278, 1243, 1197, 1174, 1156. ^1H NMR: δ = 5.80 (m, 9-,12-H), 5.38 (m, 10-,11-H), 3.04 (m, 1-,18-H), 2.82 (m, 17-,20-H), 2.51 (m, 14-,16-H), 2.04 (dm, 19a-H), 1.96 (dm, 15a-H), 1.97 (dm, 15s-H), 1.57 (dm, 19s-H) ppm; $J_{15a,s}$ = 11.7, $J_{19a,s}$ = 11.4 Hz. ^{13}C NMR: δ = 155.9 (q, J = 33.5 Hz, C-3,-6), 126.0 (C-10,-11), 121.9 (C-9,-12), 120.1 (q, J = 278.8 Hz, CF_3), 66.4 (C-2,-7), 58.7 (C-8,-13), 55.2 (C-1,-8), 54.7 (C-17,-20), 52.3 (C-14,-16), 38.8, 36.6 (C-15,-19) ppm. MS: *m/z* (%) = 397 (2) $[M + 1]^+$, 396 (6) $[M]^+$, 143 (12), 142 (41), 141 (100). $C_{20}H_{14}F_6N_2$ (396.3): calcd. C 60.61, H 3.56; found C 60.55, H 3.54.

9,12-Diphenyl-10,11-diazaundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docos-10-ene-*anti*-4,*anti*-5-dicarboxylic Anhydride (36): A solution of **32a** (103 mg, 0.25 mmol) and freshly sublimed maleic anhydride (62 mg, 0.63 mmol) in anhydrous toluene (2 mL) was heated to 80 °C under a pressure of 9.5 kbar for 19 h. After concentration in vacuo, residual maleic anhydride was sublimed away at 10^{-3} Torr and the residue chromatographed (silica gel, 8 × 2 cm, ethyl acetate/petroleum ether, 3:7). First **36** (R_f = 0.3, 58 mg, 45%), then **24a** (R_f = 0.8, 50 mg, 49%) were eluted. Compound **36** crystallized from CH_2Cl_2/petroleum ether (1:4) in colorless needles, m.p. 258 °C. ^1H NMR: δ = 7.69 (m, 4 H), 7.53 (m, 4 H), 7.43 (m, 2 H), 3.05 (m, 4-,5-H), 2.96 (m, 3-,6-H),2.93 (m, 7-,8-H), 2.79 (m, 20-,22-H), 2.69 (m, 18-,19-H), 2.03 (m, 15-,17-H), 1.93 (dm, 21a-H), 1.52 (dm, 21s-H), 1.42 (dm, 16a-H), 0.98 (dm, 16s-H) ppm; $J_{16a,s}$ = $J_{21a,s}$ = 10.5 Hz. ^{13}C NMR: δ = 172.4 (CO), 141.8 (2 C), 129.2, 128.6, 127.9 (10 C), 75.4 (C-9,-12), 62.9 (C-1,-2), 59.6 (2 C), 57.4 (C-13,-14), 49.8 (2 C), 42.5 (2 C), 42.1 (2 C), 41.8 (C-21), 39.6 (C-16), 37.4 (2 C), 30.6 (2 C) ppm. MS: *m/z* (%) = 513 (29), 512 (39), 511 (100) $[M + 1]^+$, 510 (9) $[M]^+$, 482 (8) $[M - N_2]^+$ (HR: calcd. 482.1882; found 482.1880), 483 (17), 440 (10), 439 (22), 104 (10), 85 (15). $C_{34}H_{26}N_2O_3$ (510.6): calcd. C 79.98, H 5.13; found C 79.77, H. 5.01.

9,12-Diphenyl-4,5,10,11-tetrazaazaundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docos-10-ene-4,5-dicarbox-*N*-phenylimide (37) and 4,7-Diphenyl-5,6,18,19-tetraazadecacyclo[15.2.2.1^{9,15}.0^{2,13}.0^{2,13}.0^{3,11}.0^{8,16}.0^{9,22}.0^{12,22}.0^{15,22}]docosa-4,6,20-trien-18,19-dicarbox-*N*-phenylimide (38): A solution of **32a** (82 mg, 0.20 mmol) and *N*-phenyltriazoline-3,5-dione (36 mg, 0.20 mmol) in CH_2Cl_2 (6 mL) was stirred for 30 min (total conversion, two products, TLC). After concentration in vacuo, the residue was chromatographed (silica gel, 8 × 1.5 cm, CH_2Cl_2). First 52 mg (45%) of **37** (R_f = 0.85), then, 56 mg (48%) of **38** [with CH_2Cl_2/CH_3OH (2%)] were eluted.

37: Colorless crystals, m.p. 234–236 °C. UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 388 nm (90), 376 (80), 258 (sh, 5200). IR (KBr): $\tilde{\nu}$ = inter alia 3050, 2968, 2864, 1762, 1716, 1497, 1440 cm^{-1}. ^1H NMR: δ = 7.75–7.50 (10 H), 7.40–7.30 (5 H, *N*-phenyl), 4.92 (m, 3-,6-H), 2.98 (m, 18-,19-H), 2.84 (m, 20-,22-H), 2.81 (m, 15-,17-H), 2.46 (m, 7-,8-H), 1.94 (dm, 21s-H), 1.65 (dm, 21a-H), 1.43 (dm, 16s-H),0.96 (dm, 16a-H) ppm; $J_{16a,s}$ = $J_{21a,s}$ = 11.0 Hz. ^{13}C NMR: δ = 165.9 (C=O), 151.4, 140.6, 131.4, 129.2, 129.0, 128.8, 128.2, 125.5 (15 C), 73.7 (C-9,-12), 61.2 (C-13,-14), 59.4 (C-3,-6), 58.6 (C-1,-2), 52.1 (C-18,-19), 49.1 (C-20,-22), 42.7 (C-15,-17), 42.0 (C-7,-8), 41.8 (C-21), 39.6 (C-16) ppm. MS (FAB): *m/z* (%) = 589 (45) $[M + 2]^+$, 588 (100) $[M + 1]^+$, 587 (3) $[M]^+$, 560 (58), 559 (99) $[M - N_2]^+$, 441 (21), 440 (12) $[M - N_2 - PhNCO]^+$, 413 (31), 307 (39), 289 (37), 279 (16), 271 (21), 258 (17). MS (EI): *m/z* (%) = 559 (100) $[M - N_2]^+$, 440 (14) $[M - N_2 - PhNCO]^+$, 303 (21). $C_{38}H_{29}N_5O_2$ (587.7): calcd. C 77.66, H 4.97; found C 77.59, H 4.80.

38: Colorless crystals, m.p. 331–332 °C. UV (CH_3CN): λ_{max} (ε) = 342 nm (5450), 392 (4700), 241 (4150). 204 (sh, 10050). IR (KBr): $\tilde{\nu}$ = inter alia 3068 cm^{-1}, 2986, 1769, 1706, 1530, 1490. ^1H NMR: δ = 8.1–7.4 (10 H), 7.32–7.20 (5 H, *N*-phenyl), 6.32 (m, 20-,21-H), 4.97 (m, 1-,17-H), 3.03–3.07 (m, 12-,22-H), 3.0–2.9 (m, 9-,11-H), 2.79 (m, 13-,15-H), 2.1–1.95 (m, 10a-,10s-,14a-H), 1.79 (dm, 14s-H) ppm; $J_{14a,s}$ = 11.3 Hz. ^{13}C NMR: δ = 170.0 (C=O), 157.3, 134.7, (C-20,-21), 130.9, 128.8, 128.7, 128.6, 127.8, 127.7, 125.2 (14 C), 77.2 (C-4,-7), 63.36 (C-3,-8), 54.9 (C-1,-17), 53.8 (C-2,-16), 52.3 (C-12,-22), 52.0 (C-13,-15), 47.6 (C-9,-11), 40.3 (C-10)*, 40.2 (C-14)* ppm. MS: *m/z* (%) = 588 (20) $[M + 1]^+$, 587 (33) $[M]^+$, 297 (17), 296 (32), 295 (68), 271 (16), 202 (16), 165 (19), 141 (29), 128 (18), 119 (24), 117 (23), 116 (100). $C_{38}H_{29}N_5O_2$ (587.7): calcd. C 77.66, H 4.97; found C 77.55, H 4.75. X-ray crystal structure, Figure 6.

3,6-Diphenyl-4,5,10,11-tetraazaundecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosa-4,10-diene (39): A solution of **37** (20 mg, 0.035 mmol) and NaOH (24 mg) in dry *i*PrOH (2 mL) was heated under reflux for 22 h (N_2, total conversion, TLC). The solution was cooled to 0 °C, then HCl (10%, 0.4 mL) and a solution of $CuCl_2$ (45 mg) in water (2.5 mL) were added. After stirring at room temp. for 2 h, concd. NH_4OH solution was added dropwise till a blue color persisted. The solution was extracted with CH_2Cl_2, the organic phase washed and dried ($MgSO_4$), then concentrated in vacuo. The solid residue crystallized from CH_2Cl_2 in colorless needles (12 mg, 80%). UV (CH_3CN): λ_{max} (ε) = 389 nm (130), 367 (110), 276 (1170). 246 (8700). ^1H NMR: δ = 7.9–7.5 (10 H), 6.06 (9-,12-H), 2.88 (m, 18-,19-H), 2.70 (m, 15-,17-H), 2.64 (m, 20-,22-H), 1.65 (m, 7-,8-H), 1.58 (dm, 21s-H), 1.37 (dm, 16s-H), 1.14 (dm, 21a-H), 0.96 (dm, 16a-H) ppm. ^{13}C NMR: δ = 141.4, 128.9, 128.8, 128.0 (10 C), 74.6 (C-9,-12), 65.1 (C-3,-6), 61.3 (C-13,-14), 59.6 (C-7,-8), 56.7 (C-1,-2), 50.2 (C-15,-17), 42.6 (C-18,-19), 41.7 (C-20,-22), 40.8 (C-16), 39.8 (C-21) ppm. MS (FAB): *m/z* (%) = 441 (9) $[M + 1]^+$, 413 (100) $[M + 1 - N_2]^+$, 385 (22), 384 (95) $[M + 1–2\ N_2]^+$, 318 (12), 307 (29), 289 (21). MS (EI): *m/z* (%) = 412 (9) $[M - N_2]^+$, 385 (33), 384 (100) $[M - 2\ N_2]^+$, 319 (19), 318 (54), 317 (21), 241 (15), 239 (12), 215 (11), 202 (11), 191 (14), 178 (14), 165 (12), 115 (17). $C_{30}H_{24}N_4$ (440.6): calcd. C 81.79, H 5.49; found C 81.51, H 5.36.

3,10-Diphenylheptacyclo[10.5.1.0^{2,6}.0^{6,16}.0^{7,11}.0^{7,14}.0^{13,17}]octadeca-2,4,8,10-tetraene (42): A degassed solution of **39** (50 mg, 0.11 mmol) in CH_3CN (50 mL) was irradiated with monochromatic light (254 nm, quartz tube) for 1 h (complete conversion, one major product, two traces, TLC). After concentration in vacuo, the resi-

due was crystallized from hexane/CH_2Cl_2 (4:1); 30 mg (80%) of colorless, oxygen-sensitive crystals were isolated. ^{1}H NMR: δ = 7.5–7.2 (10 H), 6.56 (d, 4-,9-H), 6.22 (d, 5-,8-H), 3.48 (m, 1-,12-H), 3.25 (m, 13-,17-H), 2.56 (m, 18a-H), 2.46 (m, 18s-H), 2.37 (m, 15a-H), 2.22 (m, 14-,16-H), 2.15 (m, 15s-H) ppm; $J_{4,5} = J_{8,9}$ = 5.4 Hz. ^{13}C NMR: δ = 162.0 (2 C), 135.7 (C-3,-10), 138.5, 132.5, 128.3 (10 C), 126.6 (C-4,-9), 126.3 (C-5,-8), 75.6 (C-2,-11), 62.1 (C-1,-,12), 50.3 (C-13,-17), 43.4 (C-18), 42.4 (C-14,-16), 41.1 (C-15) ppm. MS: *m/z* (%) = 385 (12) $[M + 1]^+$, 384 (9) $[M]^+$, 319 (16), 318 (37), 317 (14), 241 (13), 239 (9), 191 (9), 178 (10), 165 (7), 115 (9), 91 (12). HRMS: calcd. for $C_{30}H_{24}$ 384.1878; found 384.1855.

Tetramethyl (1α,12α,13β,14α,17α,18β)-3,10-Diphenyl-15,16-benzo-4,5-diazahexacyclo[10.6.1.1^{14,17}.0^{2,11}.0^{5,10},0^{13,18}]eicosa-2(11),3,6,8,15-pentaene-6,7,8,9-tetracarboxylate (46): A mixture of **32a** (206 mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (2 mL, 16.3 mmol) was heated at 100 °C for 72 h (total conversion, one major product two traces, TLC). Excess reagent was removed in vacuo, the residue was chromatographed (silica gel, petroleum ether/ethyl acetate, 7:3); 320 mg of yellow crystals (92%) were isolated, m.p. 214–216 °C. UV (CH_3CN): λ_{max} (ε) = 395 nm (10760), 302 (sh, 4780), 265 (sh, 11900), 236 (sh, 20680), 222 (21080). ^{1}H NMR: δ = 7.75–7.35 (10 H), 6.55 (m, 1 H), 6.45 (m, 1 H), 6.32 (m 1 H), 4.68 (m, 1 H), 4.0 (s, OCH_3), 3.74 (s, OCH_3), 3.71 (dm, J = 3.5 Hz, 12-H), 3.65 (s, OCH_3), 3.60 (s, OCH_3), 3.38 (dt, 19a-H), 3.35 (dm, J = 3.2 Hz, 1-H), 3.25 (dt, 19s-H), 3.23 (br. d, J = 3.8 Hz, 14-H)*, 2.70 (br. d, J = 3.7 Hz, 17-H)*, 2.03 (dt, 20s-H), 1.98–1.94 (m, 13-,18-H), 1.82 (dt, 20a-H) ppm; $J_{19a,s}$ = 10.5, J_{20as} = 9.8 Hz. ^{13}C NMR: δ = 166.9 (CO), 166.3 (CO), 164.5 (CO), 163.6 (CO), 147.3 (C=N), 146.5, 143.8, 143.2, 142.3, 138.0, 134.6, 131.1, 129.1, 128.5, 128.0, 127.9, 127.8, 127.1 126.5, 124.8, 123.1, 122.7, 121.7, 101.9, 65.6, 60.6, 60.2, 53.0 (OCH_3), 52.8 (OCH_3), 52.5 (OCH_3), 51.8 (OCH_3), 48.2, 47.5, 46.4, 46.1, 46.0 ppm. MS: *m/z* (%) = 696 (4) $[M]^+$, 638 (11), 637 (15) $[M - CO_2CH_3]^+$, 621 (7), 619 (100) $[M - C_6H_5]^+$, 477 (2), 445 (2), 141 (2), 116 (2), 77 (3). $C_{42}H_{36}N_2O_8$ (696.8): calcd. C 72.40, H 5.21; found C 72.01, H 5.09.

Acknowledgments

Support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and BASF AG is gratefully acknowledged. We thank Prof. Dr. J. Sauer for valuable information, Prof. Dr. R. Schwesinger for generous gifts of bases, Dr. J. Geier for calculations, C. Warth for help with MS analyses, G. Fehrenbach for artwork, and Dr. P. R. Spurr for help with the manuscript. T. M. sincerely thanks Professor Dr. George A. Olah and Professor Dr. G. K. Surya Prakash for their constant encouragement, the Alexander von Humboldt Foundation and the Loker Hydrocabon Research Institute for financial support.

[1] M. Wollenweber, M. Etzkorn, J. Reinbold, F. Wahl, T. Voss, J.-P. Melder, C. Grund, R. Pinkos, D. Hunkler, M. Keller, J. Wörth, L. Knothe, H. Prinzbach, *Eur. J. Org. Chem.* **2000**, 3855, and cited references.

[2] a) G. Sedelmeier, Dissertation, University of Freiburg, **1978**; b) C. Grund, Diplomarbeit, University of Freiburg, **1984**.

[3] H. Prinzbach, G. Sedelmeier, C. Krüger, R. Goddard, H.-D. Martin, R. Gleiter, *Angew. Chem.* **1978**, *90*, 297; *Angew. Chem. Int. Ed.* **1978**, *17*, 271.

[4] a) G. Kaupp, *Angew. Chem.* **1980**, *92*, 245; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 243; b) J. McCullough, *Chem. Rev.* **1987**, *87*, 811; c) J. Mattey, *Angew. Chem.* **2007**, *119*, 674; *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 663.

[5] a) R. Gleiter, H. Zimmermann, W.-D. Fessner, H. Prinzbach, *Chem. Ber.* **1985**, *118*, 3856; b) H. Gan, G. Horner, B. Hrnjez, T. A. McCormack, J. L. King, Z. Gasyna, G. Chen, R. Gleiter, N. C. Yang, *J. Am. Chem. Soc.* **2000**, *122*, 12098.

[6] W. v. E. Doering, W. R. Roth, R. Breuckmann, L. Figge, H.-W. Lennartz, W.-D. Fesner, H. Prinzbach, *Chem. Ber.* **1988**, *121*, 1; for the thermolytic cleavage of the parent *syn-o,o′*-dibenzene an activation enthalpy of 27.2 ± 0.6 kcal mol^{-1} has been reported: H. Gan, G. Horner, B. Hrnjez, T. A. McCormack, J. L. King, Z. Gasyna, G. Chen, R. Gleiter, N. C. Yang, *J. Am. Chem. Soc.* **2000**, *122*, 12098.

[7] a) W.-D. Fessner, H. Prinzbach, G. Rihs, *Tetrahedron Lett.* **1983**, *24*, 5857; b) W.-D Fessner, H. Prinzbach, *The Pagodane Route to Dodecahedrane in Cage Carbons*, G. A. Olah (Ed.), Wiley, New York, **1990**; c) H. Prinzbach, K. Weber, *Angew. Chem.* **1994**, *106*, 2329; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2239.

[8] a) W.-D. Fessner, G. Sedelmeier, P. R. Spurr, G. Rihs, H. Prinzbach, *J. Am. Chem. Soc.* **1987**, *109*, 4226; b) J.-P. Melder, H. Prinzbach, *Chem. Ber.* **1991**, *124*, 1271.

[9] a) H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J. Wörth, L. T. Scott, M. Gelmont, D. Olevano, B. v. Issendorff, *Nature* **2000**, *407*, 60; b) H. Prinzbach, F. Wahl, A. Weiler, P. Landenberger, J. Wörth, L. T. Scott, M. Gelmont, D. Olevano, B. Sommer, B. v. Issendorff, *Chem. Eur. J.* **2006**, *12*, 6268.

[10] a) H. Prinzbach, B. A. R. C. Murty, W.-D. Fessner, J. Mortensen, J. Heinze, G. Gescheidt, F. Gerson, *Angew. Chem.* **1987**, *99*, 488; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 457; b) G. K. S. Prakash, V. V. Krishnamurty, R. Herges, R. Bau, H. Yuan, G. A. Olah, W.-D. Fessner, H. Prinzbach, *J. Am. Chem. Soc.* **1988**, *110*, 7764.

[11] a) T. Drewello, W.-D. Fessner, A. J. Kos, C. B. Lebrilla, H. Prinzbach, P. v. R. Schleyer, H. Schwarz, *Chem. Ber.* **1988**, *121*, 187; b) R. Herges, P. v. R. Schleyer, M. Schindler, W.-D. Fessner, *J. Am. Chem. Soc.* **1991**, *113*, 3649; c) K. Weber, H. Prinzbach, R. Schmidlin, F. Gerson, G. Gescheidt, *Angew. Chem.* **1993**, *105*, 1376; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 875; d) H. Prinzbach, G. Gescheidt, H.-D. Martin, R. Herges, J. Heinze, G. K. S. Prakash, G. A. Olah, *Pure Appl. Chem.* **1995**, *67*, 673; e) A. A. Trifunac, D. W. Werst, R. Herges, H. Neumann, H. Prinzbach, M. Etzkorn, *J. Am. Chem. Soc.* **1996**, *118*, 9444; f) M. Etzkorn, F. Wahl, M. Keller, H. Prinzbach, F. Barbosa, V. Peron, G. Gescheidt, J. Heinze, R. Herges, *J. Org. Chem.* **1998**, *63*, 6080; g) G. K. S. Prakash, K. Weber, G. A. Olah, H. Prinzbach, M. Wollenweber, M. Etzkorn, T. Voss, R. Herges, *Chem. Commun.* **1999**, 1929; h) A. Weiler, E. Quennet, M. Keller, K. Exner, H. Prinzbach, *Tetrahedron Lett.* **2000**, *41*, 4763; i) J. Reinbold, M. Bertau, T. Voss, D. Hunkler, L. Knothe, H. Prinzbach, D. Neschadin, G. Gescheidt, B. Mayer, H.-D. Martin, J. Heinze, G. K. S. Prakash, G. A. Olah, *Helv. Chim. Acta* **2001**, *84*, 1518; j) K. Weber, T. Voss, D. Heimbach, A. Weiler, M. Keller, J. Wörth, L. Knothe, K. Exner, H. Prinzbach, *Tetrahedron Lett.* **2005**, *46*, 5471.

[12] a) G. Sedelmeier, W.-D. Fessner, C. Grund, P. R. Spurr, H. Fritz, *Tetrahedron Lett.* **1986**, *27*, 1277; b) G. Sedelmeier, W.-D. Fessner, R. Pinkos, C. Grund, B. A. R. C. Murty, D. Hunkler, G. Rihs, H. Fritz, C. Krüger, H. Prinzbach, *Chem. Ber.* **1986**, *119*, 3442; c) B. A. R. C. Murty, P. R. Spurr, R. Pinkos, C. Grund, W.-D. Fessner, D. Hunkler, H. Fritz, W. R. Roth, H. Prinzbach, *Chimia* **1987**, *41*, 32; d) W.-D. Fessner, G. Sedelmeier, L. Knothe, H. Prinzbach, G. Rihs, Z.-z. Yang, B. Kovac, E. Heilbronner, *Helv. Chim. Acta* **1987**, *70*, 1816; e) M. Wollenweber, D. Hunkler, M. Keller, L. Knothe, H. Prinzbach, *Bull. Soc. Chim. Fr.* **1993**, *130*, 32.

[13] a) For a [6+6]cycloaddition as part of a more complex photoisomerization in layered cyclophanes s. H. Higuchi, K. Takatsu, T. Otsubo, Y. Sakata, S. Misumi, *Tetrahedron Lett.* **1982**, *23*, 671; b) H. Higuchi, E. Kobayashi, Y. Sakata, S. Misumi, *Tetrahedron* **1986**, *42*, 1731; c) The formation of saturated, functionalized (OH,Cl,MeO) polycyclic skeletons upon direct irradiation of multibridged [3$_n$]cyclophanes (n = 3–6) in CH2Cl_2/H_2O (MeOH/2 N HCl) has been - speculatively - re-

lated to the intermediate formation of hexaprismanes along not further commented photochemical addition steps: R. Nogita, K. Matohara, M. Yamaji, T. Oda, Y. Sakamoto, T. Kumagai, C. Lim, M. Yasutake, T. Shimo, C. W. Jefford, T. Shinmyozu, *J. Am. Chem. Soc.* **2004**, *126*, 13732, and cited references; d) The dependence of benzo/benzo photoreactions on subtle structural differences was recently further demonstrated when a nitrogen-bridged [3.3]parayclophane, but not the carbon-bridged analogue, underwent photodimerizations: H. Okamoto, K. Satake, H. Ishida, M. Kimura, *J. Am. Chem. Soc.* **2006**, *128*, 16508, and cited references.

[14] Preliminary communication: T. Mathew, M. Keller, D. Hunkler, H. Prinzbach, *Tetrahedron Lett.* **1996**, *37*, 4491.

[15] a) D. L. Boger, *Chem. Rev.* **1986**, *86*, 781; b) J. Sauer, *Comprehensive Heterocycl. Chem. II* **1996**, *6*, 1901.

[16] **11a:** R. Huisgen, J. Sauer, M. Seidel, *Liebigs Ann. Chem*. **1962**, *654*, 146; **11b:** T. Klindert, P. v. Hagel, L. Baumann und G. Seitz, J. Prakt. Chem. 330 (1997) 623; and cit references; **11c**,**e:** D. L. Boger, R. S. Coleman, J. S. Panek, F. X. Huber, J. Sauer *J. Org. Chem.* **1985**, *50*, 5377; **11d**: F. A. Neugebauer, H. Fischer *Liebigs Ann. Chem.* **1982**, 387; **11e:** J. Sauer, D. K. Heldmann, J. Hetzenegger, J. Krauthan, H. Sichert, J. Schuster, *Eur. J. Org. Chem.* **1998**, 2885. These tetrazines were part of a study correlating reduction potentials with the respective LUMO energies and the tendency to undergo inverse Diels–Alder cycloaddition: R. Gleiter, V. Schehlmann, J. Spanget-Larsen, H. Fischer, F. A. Neugebauer, *J. Org. Chem.* **1988**, *53*, 5756.

[17] a) W. Friedrichsen, H. v. Wallis, *Tetrahedron* **1978**, *34*, 2509; b) G. Seitz, T. Kämpchen, W. Overhen, *Arch. Pharm.* **1978**, *311*, 786.

[18] a) J. Sauer, R. Sustmann, *Angew. Chem.* **1980**, *92*, 773; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 779; b) J. Sauer, *Acta Chim. Slovenica* **1994**, *41*, 235; c) J. Sauer, J. Breu, U. Holland, R. Herges, H. Neumann, S. Kammermeier, *Liebigs Liebigs Ann./ Recueil* **1997**, 1473; d) J. Sauer, P. Bäuerlein, W. Ebenbeck, C. Gousetis, H. Sichert, T. Troll, F. Utz, U. Wallfahrer, *Eur. J. Org. Chem.* **2001**, 2629.

[19] a) e.g.B. Albert, W. Berning, C. Burschka, S. Hünig, F. Prokschy, *Chem. Ber.* **1984**, *117*, 1465; b) G. Fischer, E. Beckmann, H. Prinzbach, G. Rihs, J. Wirz, *Tetrahedron Lett.* **1986**, 1273.

[20] CCDC-630112 (for **15a**), -405092 (for **24a**), -630113 (for **24c**) and -630111 (for **38**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] a) Rev.: W. Adam, O. DeLucchi, *Angew. Chem.* **1980**, *92*, 815; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 762; b) P. S. Engel, *Chem. Rev.* **1980**, *80*, 99.

[22] R. Thiergardt, M. Keller, M. Wollenweber, H. Prinzbach, *Tetrahedron Lett.* **1993**, *34*, 3397.

[23] R. Schwesinger, R. Link, P. Wenzel, S. Kossek, *Chem. Eur. J.* **2006**, *12*, 438, and cited references.

[24] a) J. Tonne, Dissertation, University of Freiburg, **2001**; b) J. Tonne, H. Prinzbach, J. Michl, *J. Photochem. Photobiol. Sci.* **2002**, *1*, 105.

[25] a) K. Mackenzie, G. J. Proctor, D. J. Woodnutt, *Tetrahedron Lett.* **1984**, *25*, 977; b) K. Mackenzie, G. J. Proctor, D. J. Woodnutt, *Tetrahedron* **1987**, *24*, 5981.

[26] See also footnote (40) in ref.[8a].

[27] J. Krauthan, Dissertation, University of Regensburg, **1995**; cf.J. Laue, G. Seitz, *Liebigs Ann.* **1996**, 773.

[28] a) W.-D. Fessner, C. Grund, H. Prinzbach, *Tetrahedron Lett.* **1989**, *30*, 3133; b) F.-G. Klärner, U. Artschwager-Perl, W.-D. Fessner, C. Grund, R. Pinkos, J. P. Melder, H. Prinzbach, *Tetrahedron Lett.* **1989**, *30*, 3137; c) W.-D. Fessner, K. Scheumann, H. Prinzbach, *Tetrahedron Lett.* **1991**, *32*, 5939.

[29] The parent diazabicyclo[2.2.2]octadiene has a half life ($t_{1/2}$) at –78 °C of ≤ 30 s: N. Rieber, J. Alberts, J. A. Lipsky, D. M. Lemal, *J. Am. Chem. Soc.* **1969**, *91*, 5668.

[30] a) Cf. chapter 3 in ref.[21a]; b) J. Sauer, P. Bäuerlein, W. Ebenbeck, H.-D. Fühlhuber, C. Gousetis, K. Werntahler, *Eur. J. Org. Chem.* **2001**, 3999. We had failed, however, to arrive along photochemical N_2 elimination strategies at similary corsetted [2.1.1.0]pagodane (T. Pracht, K. Weber, H. Fritz, L. Knothe, H. Prinzbach, *Chin. Chem. Soc.* **1994**, *41*, 1) and hexaprismane skeletons[1].

[31] a) R. M. Acheson, N. F. Elmore, *Adv. Heterocycl. Chem.* **1976**, *19*, 279; b) R. Riebel, A. Weber, T. Troll, J. Sauer, J. Breu, H. Nöth, *Tetrahedron Lett.* **1996**, *37*, 1587.

[32] For a recent "Highlight" (C_3-Symmetry: Molecular Design Inspired by Nature) see: S. E. Gibson, M. P. Castaldi, *Angew. Chem.* **2006**, *118*, 4834; *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 4718.

[33] K. Exner, M. Heizmann, M. Kegel, M. Keller, L. Knothe, H.-D. Beckhaus, B. Großmann, J. Heinze, H. Prinzbach, *Eur. J. Org. Chem.* **2005**, 1311.

[34] H. Stetter, J. Bremen, *Chem. Ber.* **1973**, *106*, 2523.

[35] H. Prinzbach, J. H. Hartenstein, *Angew. Chem.* **1962**, *74*, 506; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 507 ("Zur 1,3- bzw. 1,4-Addition photochemisch erzeugter Carbene an Diene"); H. Prinzbach, J. H. Hartenstein, *Angew. Chem.* **1962**, *74*, 651 ("Photoisomerisierung von 1,3-Cyclohexadienen").

[36] Still expected is the detailed report of the photoacoustic measurements by S. Braslavsky and S. Bertolotty conducted at the MPI für Kohlenforschung in Mülheim/Ruhr, of the Diplomarbeit of M. Schottelius and the Dissertation of J. Tonne performed in J. Michel's laboratory (Boulder, Colorado, USA).[24] In the latter, the above-cited kinetic analysis of the photophysical properties of the [3.3]cyclophanes **1**,**7**,**9** and of appropriate reference compounds (absorption, transient absorption, fluorescence emission, fluorescence excitation, fluorescence lifetimes, fluorescence quantum yields, phosphorescence, picosecond-resolved transient absorption measurements) and of the photochemical characteristics of the reversible reaction **1** ⇄ **4** (quantum yields, triplet sensitization) allowed the formulation of kinetic models and of the respective potential energy surface diagrams.

Received: December 12, 2006
Published Online: March 13, 2007

