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Proximate, *syn*-Periplanar, Rigid Imine(Nitrone)/Ene-, and Diazene(Diazeneoxy)/Ene Systems: Syntheses, Homoconjugate Reactivity and Photochemistry

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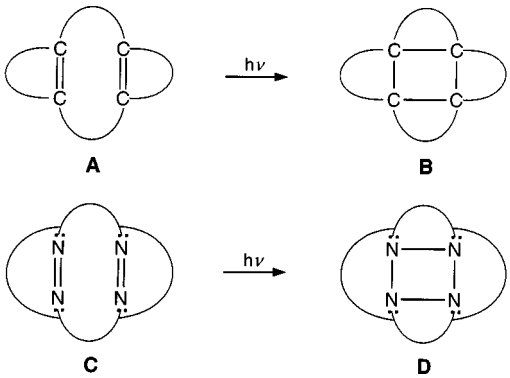
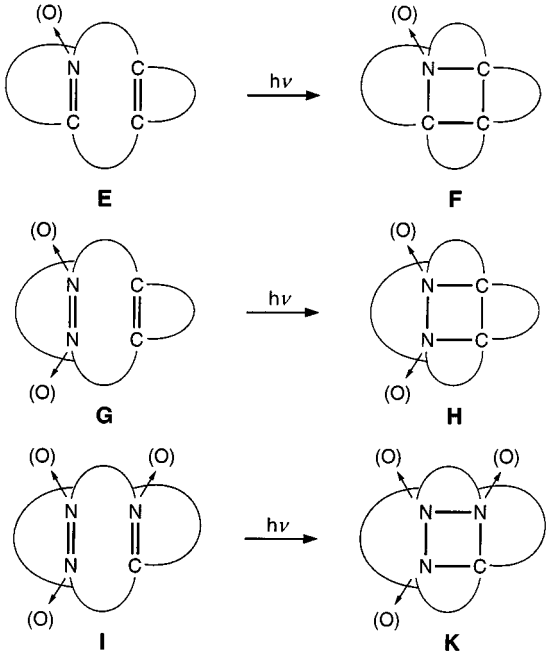
The chances for intramolecular imine/ene (→ azetidines), diazene/ene (→ 1,2-diazetidines), diazeneoxy/ene (→ 1,2-diazetidine oxides) and diazenedioxiene (→ 1,2-diazetidine dioxides) [2+2]photocycloadditions and for the isolation of the respective photoproducts, have been probed with specifically designed substrates. Upon direct or sensitized excitation, [2+2]cycloaddition was found to be the exclusive or at least dominant chemical process for the C=N/C=C, N=N/C=C and ON=N(O)/C=C systems featuring very small π,π-distances of 2.8–3.0 Å and large π,π-interorbital angles of 160–170° (**7** → **51**, **17** → **55**, **33** → **58** (competing N_2 elimination), **22** → **62**). This is not the case, however, in ON=NO/C=C (**23**, where electron transfer is a possibility), or in the more flexible, less "proximate" C=N/C=N (**57**) and C=NO/C=N (**63**) systems (π,π-distances of >3.8 Å). While the corseted 1,2-diazetidine photoadducts (**55**, **58**) proved to be thermally stable, their *N*-oxides (**62**, **65**) were thermally too labile to be directly observable above –65 °C. For the latter's only fleeting existence, electronic rather than strain effects are held responsible (B3LYP/6–31G* calculations). Very facile C=NO/C=C (**12** → **13**) and N=NO/C=C (**22** → **24**) [3+2]cycloadditions, homoconjugate addition of H_2 and of dienophiles ([2+2+2]) to the diazene/ene **17** (→ **39**, **41**, **45**) are manifestations of "proximity" in these bichromophoric skeletons.

Introduction

The ene/ene photocycloaddition to generate cyclobutanoid structures (**A** → **B**) is a standard method in the repertoire of synthetic chemistry;[2] extensive photophysical and theoretical studies have contributed to a good understanding of its scope and limitations.[2,3] In contrast, to date no such [2+2]photocycloaddition has been observed between two N=N double bonds (diazene/diazene, **C** → **D**); the subsequent two papers are devoted to this subject.[4,5]



A project – originally started with the intention of gaining experience in dealing with the ubiquitous complications met around the tetraaza systems **C** and **D**, and also of gaining complementary experimental and analytical knowledge – had been focused on structurally analogous proximate and rigid imino/ene-(**E**), diazene/ene-(**G**), diazene/imine (**I**) systems and the respective combinations with *N*-oxidized (nitrone, diazene (di)oxide) chromophores.[6] Renewed interest in proximate bichromophoric systems as potential precursors of a class of nonclassical ions featuring novel types of cyclic electron delocalization,[5] prompted us to



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write this detailed account of our findings so far presented only in preliminary communications.[7] The synthesis of representative substrates, the chemical peculiarities associated with the spatial arrangement of the two "proximate" chromophoric subunits, the photochemistry, and selected properties of the respective photoproducts (**F**, **H**) are discussed.

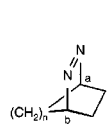
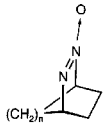
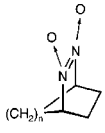
Choice of Substrates – General Aspects

In the vast area of homoconjugational (laticyclic) effects[8] in ground and excited states of C=C/C=C systems **A**, the tetracyclic 1,6-dienes **A'$_{mn}$** consisting of bicyclo[2.2.2]-hept(oct)-2-ene chromophores [*m*, *n* = 1(2); 3,10;4,9;5,8-bridged 1,6-cyclodecadienes] make up[4,9] for a still very popular playing ground.[10] With highly proximate ($d_{\pi,\pi}$ = 3.0–3.15 Å) and nearly *syn*-periplanar (ω = 160–175°) π-bonds embedded in rather rigid molecular skeletons (cf. Table 1 in ref.[4]), these dienes undergo – irrespective of direct or sensitized excitation – efficient [2+2]photocycloaddition. The bishomoprismanes **B'** are thermally stable, and only the most strained **B'$_{11}$**, skeletons could, under flash-vacuum pyrolysis conditions (500–650 °C), be transformed into the more flexible metathesis isomers of type **A''$_{11}$**.[11,12] The latter, in spite of less favorable stereoelectronic prerequisites ($d_{\pi,\pi}$ ca. 3.5 Å, ω ca. 140°), efficiently underwent [2+2]photocycloaddition (**B'$_{11}$**).[9]

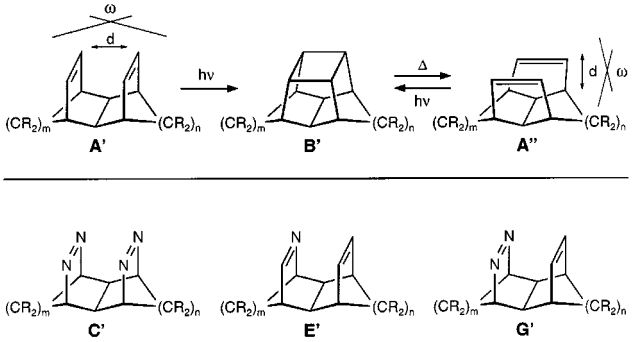
Conceptualized as a comparative study with (*N*-oxidized) N=N/N=N systems **C**, which are only available with *m* = *n* = 2 (**C$_{22}$**) and *m* = 1, *n* = 2 (**C$_{12}$**), incorporation of the C=N/C=C (**E**) and N=N/C=C (**G**) bichromophoric combinations into analogous molecular skeletons (**E'**, **G'**) became the obvious synthetic program.

Under stereoelectronic aspects (cf. Table 1 in ref.[4]) **E'$_{11}$** and **G'$_{11}$** substrates (*m* = *n* = 1) were best suited for [2+2] photocycloaddition, but the **G'$_{11}$**-systems should also, as judged by the quantum yields (Φ_{-N2}, Table 1), be most amenable to competitive N_2 elimination. However, in an early paper by Hünig and Berning[13] it was demonstrated that even in a DBH-N=N/C=C system cycloaddition can win over N_2 elimination.[14] In the respective *N*-oxides, elimination of NO, N_2O and N_2O_2 is generally, if it occurs at all, only a very slow process. For reference purposes, throughout this series of papers[4,5] the pertinent photophysical properties of DBH, DBO and their oxides are listed together with characteristic spectral data in Table 1 (ref.[15]).

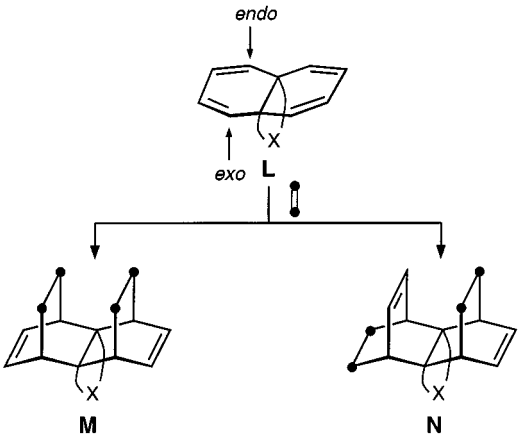
Table 1. Selected photophysical properties and spectral data for DBH, DBO and their oxides (ref.[15])

	 DBH / DBO	 DBH-O / DBO-O	 DBH-O_2 / DBO-O_2
$\phi_{-N_2(N_2O,\ N_2O_2)}$ (nm)	1.00(350) / 0.01(350) ~0(254) / ~0(254)	~0(254) / ~0(254)	~0(254) / ~0(254)
λ_{max} (nm, ε)	341(420)* / 377(193)* 340** 376**	228(6200) / 230(7300)** 226(6100) / 228(7400)***	266(10100) / 267(8300)** 260(7400) / 261(8700)***
IR (cm^{-1})	1495, 1445 / 1534, 1461	1508 / 1500	1475, 1423 / 1437, 1443
$\delta_{^{13}C\ (^1H)}$	75.9 (5.16) / 61.0(5.13)	67.0(4.66) / 56.6(4.47) 80.4(4.66) / 70.4(4.56)	73.7(4.79) / 70.0(4.76)
IP_{vert}(eV)	8.96 / 8.32	9.37 / 9.16	/ 8.04

* *n*-hexane ** CH_3CN *** H_2O

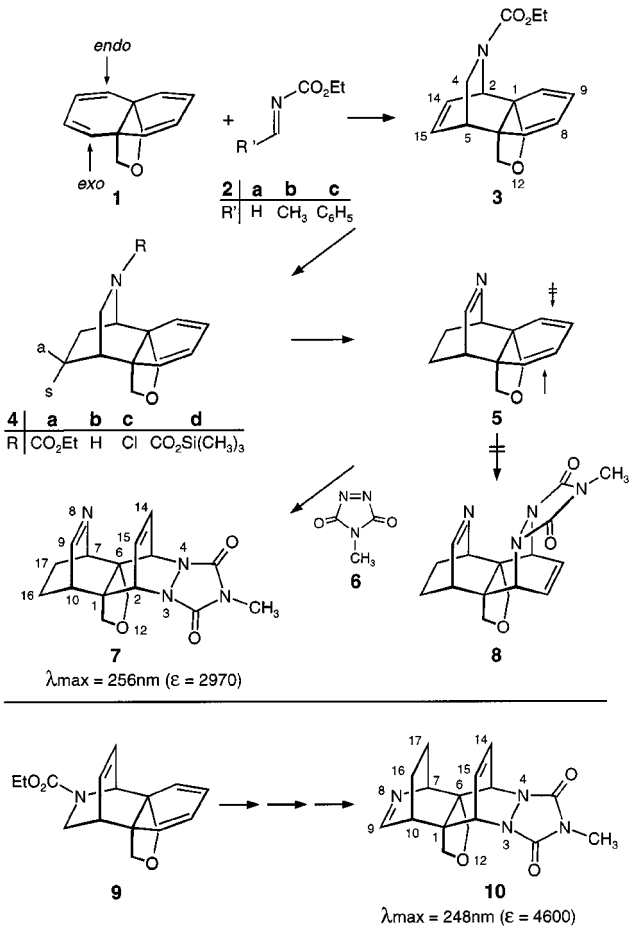


With no practical access to the parent **E'$_{22}$** and **G'$_{22}$** structures in sight, the construction of derivatives with photochemically acceptable substituents has been pursued with the propellatetraenes **L** as more readily accessible starting materials.[16] There was hope that the additional bridges X thus introduced would be helpful in directing the two [4+2]cycloadditions involved [e.g. *endo*,*endo* (**M**), *exo*,*endo* (**N**)][17] and in stabilizing intrinsically labile photocycloadducts. It was understood that a considerable molecular strain, inherent in such polycyclic skeletons, would pose limitations as to the applicability of the dienophiles. Specifically for the installation of N=N bridges, the ease of N_2 loss from 2,3-diazabicyclo[2.2.2]octa-2,5-diene part had to be taken into consideration.[18]



Syntheses

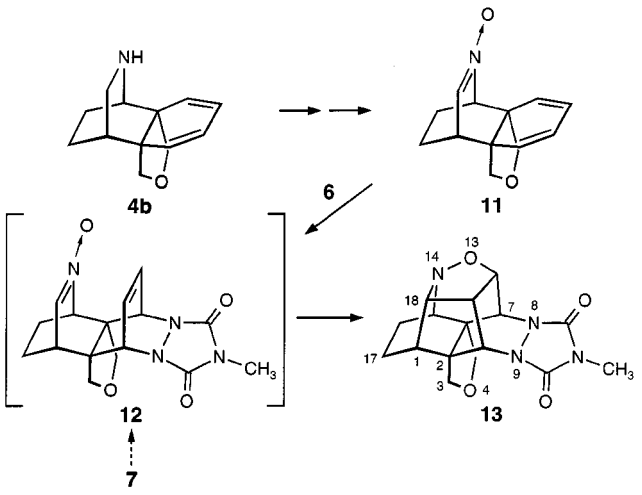
*C=N(O)/C=C Skeletons **E'** (7,12):*[6,7b] The introduction of a C=N bridge into the tetracyclic propellatetraene



Scheme 1

1[17] (Scheme 1) by a [4+2]cycloaddition of a nitrile was appealing, but proved to be impractical when [4+2]cycloreversion of such adducts with expulsion of pyridine fragments occurred too rapidly. Of several nitrile-equivalents tested, e. g. *N*-acyl-/sulfonyl-imines, alkylideneurethanes,[19] the latter were given preference. There was, however, a limitation in that only imines **2** with sterically undemanding R-substituents added to **1** with sufficient ease (not e.g. **2b**,**c**). From the unoptimized reaction with imine **2a** (generated from the methylenebisurethane with BF_3[20]) a 10:1 mixture of the *endo*-/*exo*-monoadducts **3**/**9** was obtained in 61% yield (76% based on consumption of **1**), and fractional crystallization delivered pure **3**. For the selective catalytic hydrogenation of the isolated, rather strained C=C double bond of **3** (Scheme 1), prior protection of the cyclohexadiene part in the form of a $Fe(CO)_3$-complex had been suggested,[21] and has, in fact, been successful. However, treatment of **3** with N_2H_2 [prepared *in situ* from $N_2(CO_2K)_2$,[22]] as reagent of choice for strained C=C double bonds, proved more convenient as well as more efficient (85% of **4a**). Given the half-cage situation and the reactivity of the strained C=N bond of **5**, saponification of the urethane part of **4a** and chlorination of the secondary amine **4b** as well as dehydrohalogenation of the chloroamine **4c** posed problems – to be ultimately circumvented with the trimethysilylcarbamate **4d** and the use of either the P1 Schwesinger base[23] or *tert*-BuOK for the β-elimination to give **5**. Pure aldimine **5** was found to be surprisingly stable; even in highly concentrated solutions at room temperature there was no tendency for trimerization.[24] In line with prior experience,[25] cycloaddition experiments with **5** – with approaches to the diene ring from both sides being sterically hindered and high-pressure facilities[26] not yet being available – were only successful with the extremely reactive triazolinedione **6** (NMTD). The very fast reaction (even at –60 °C) proceeded stereospecifically in an *exo* fashion and led quantitatively to **7**. Obviously the formation of the *endo*-isomer **8** as a promising precursor of a N=N/C=N substrate of type **I** would have been much welcomed.[27] After recrystallization of **7**, the UV absorption curve reached 320 nm, the maximum [$\lambda_{max}(\varepsilon)$ = 256 nm (2970)] representing the n → π* absorption of an alkylimine;[28] it is influenced by laticyclic conjugation (cf. 248 nm for **10**) redshifted by 8 nm relative to **10**. The high extinction coefficient reflects the absorption of the diazabicyclooctene-dicarboximide part (continuously declining from 220 –320 nm).

For spectral comparison, the *anti*-C=N/C=C isomer **10** had been prepared by reacting the minor component **9** (as a sample enriched with **3**, ca. 1:2) with **6** to give an inseparable mixture of **10**/**7**. After photolysis, colorless crystalline **10** could be separated chromatographically from the azetidine derived from **7** (**51**, Scheme 8).



Scheme 2

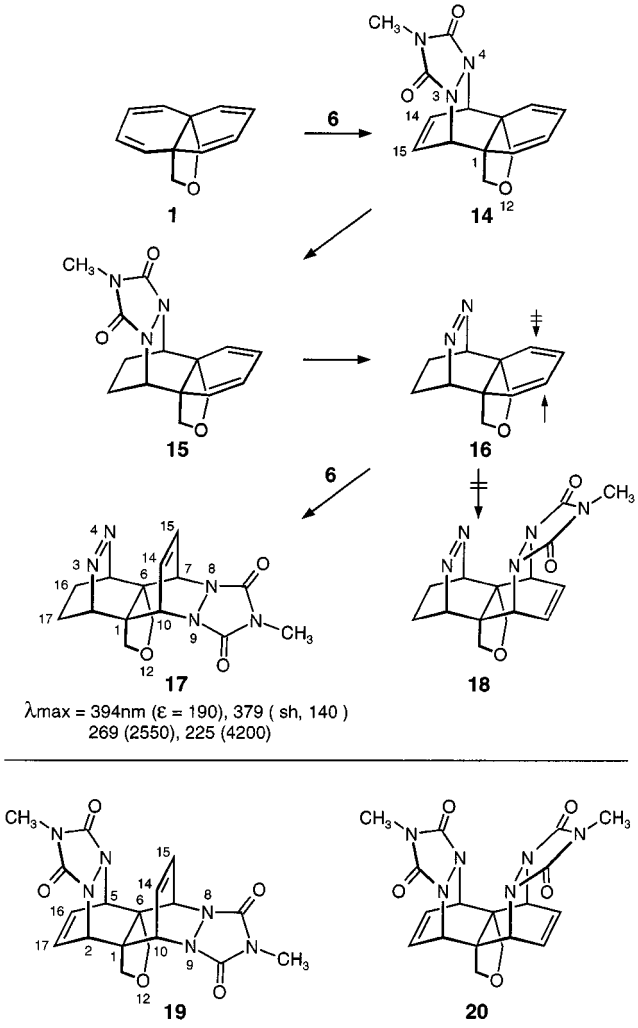
The C=NO/C=C system **12** (Scheme 2), much wanted for the photochemical study, proved to be unattainable. Given the positioning of the two functional groups and the high tendency of nitrones for [3+2]cycloaddition, ready transformation into the isoxazolidine **13**[29] had to be expected. Indeed, even when triazolinedione **6** was added at –78 °C to nitrone **11**, the primary cycloadduct **12** was not observed and only **13** was formed quantitatively. The nitrone, a high melting (m.p. 213 °C), colorless, crystalline compound, which had been conveniently prepared by ox-

idation of amine **4b** with Na_2WO_4/H_2O_2,[30] did also not dimerize.

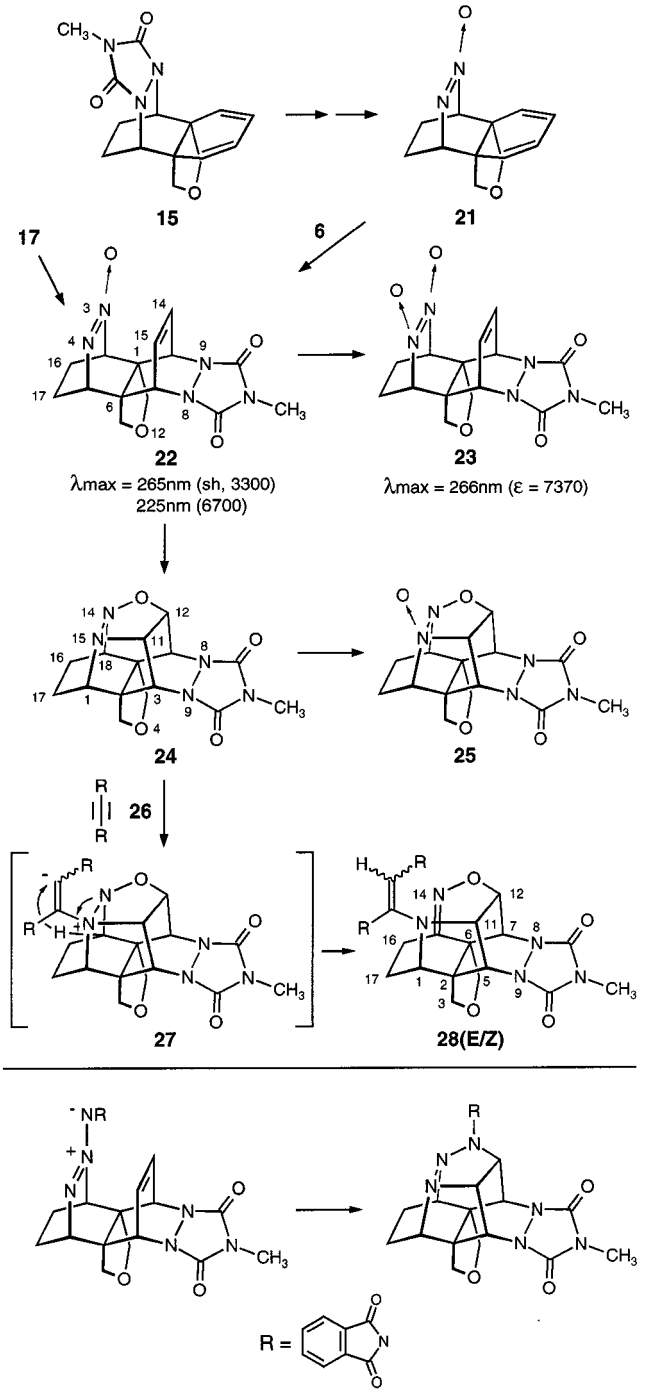
Typical MS/IR/^{1}H NMR data for imine **5** [*m/z* = i. a. 201 (M^+)] are the C=N frequency at 1610 cm^{-1} and the aldimine 4-H NMR doublet at δ = 8.42 ($J_{4,5}$ = 4.0 Hz). In the case of the intermediates **3**(**9**) as well as of the imino/enes **7** and **10**, the NMR assignments were not unequivocal [**7**: $\delta_{9\text{–H}}$ = 8.31, $\delta_{14(15)\text{–H}}$ = 6.08 (6.38); $J_{9,10}$ = 4.0 Hz. – **10**: $\delta_{9\text{–H}}$ = 7.99, $\delta_{14(15)\text{–H}}$ = 6.08 (6.36)]. The definite differentiation came from the photocycloaddition of **7** to **51** (see Scheme 8). The *N*-inversion barriers in the urazole moieties of **7** and **10** are too low (<10 kcal mol^{-1})[31] to make isomers distinguishable. Nitrone **11** shows a strong C=NO IR frequency at 1575 cm^{-1}, an intensive π → π* absorption at 244 nm (ε = 12300) and a typical upfield shift at 1.22 ppm for 4-H with respect to **5**. Structure **11** was confirmed by a UV end absorption (ε_{220} = 6350) and a completely assigned ^{1}H NMR spectrum with δ = 3.43 (11-H), 3.97 (18-H) and 4.50 (12-H, $J_{11,12}$ = $J_{11,18}$ = 7.0 Hz).

N=N(O)/C=C Skeletons ***G*** *(**17** (**22,23**); **33** (**36**)). – N=NO/C=C Cycloadditions:*[6,7a] For the construction of diazene/ene **17** from tetraene **1** (Scheme 3), it was essential that the first addition of triazolinedione **6** – as with imine **2a** – proceeded selectively from the *endo*-side and that it was kinetically sufficiently distinguished from the second addition. In fact, along Ginsburg's protocol,[32] monoadduct **14** was obtained in nearly quantitative yield. The much slower addition of **6** to **14** – as with **3** – did not produce even traces of *endo,endo*-bisadduct **20**, which was desired as potential precursor of a *syn*-bisdiazene **C**. Instead, the *exo*-adduct **19** was generated exclusively, but was of no use for the preparation of **17** since no conditions were found for the selective hydrogenation of the C16=C17 double bond. Hydrogenation at the stage of **14** (→ **15**) was the alternative. Presumably due to steric protection of the C14=C15 double bond by the rapidly inverting urazole ring, the reaction was much slower than in **3**. However, in spite of a vast excess of the $N_2(CO_2K)_2$ reagent being needed for total conversion (95 equivalents), the yield achieved for **15** was better than 80%. After standard degradation of the urazole ring, the diazene **16** (71% based on **1**) was reacted instantaneously with triazolinedione **6** to deliver, as with **5**, exclusively the *exo*-adduct **17**. Once again, less selectivity with the formation of *endo*-isomer **18** would have been welcomed. For **17**, isolated in the form of yellowish, high melting crystals (m.p. 282 °C), the UV/Vis spectrum showed an n → π* absorption at 394 nm (ε = 190) with a shoulder at 379 nm (140), π → π* absorptions at 269 (2550) and 225 nm (4200); the former is bathochromically displaced by 17 nm with respect to the isolated DBO chromophore (377 nm, ε = 193, Table 1). When exposed to daylight, crystalline **17** and its solutions slowly decolorized (cycloaddition to **55**, Scheme 9).

Literature precedence[33] existed to bring about exclusive *N*-oxidation of **17** to diazene oxide **22** (Scheme 4) with standard peracids, and of **22** to diazene dioxide **23** with stronger oxidants. The normally sensitive bicyclo[2.2.2]octene unit is sterically and inductively deactivated. The problem was again the relative rate of the entropically assisted N=NO/C=C [3+2]cycloaddition **22** → 1,2,3-oxadiazolidine **24**. With *m*-chloroperbenzoic acid (*m*-CPBA), monoxide **22** was indeed selectively generated, but unavoidable small amounts of **24** necessitated a tedious low-temperature chromatographic separation. The alternative sequence **15** → **21** → **22** proved more convenient. One-pot hydrolysis/*N*-oxidation, with some modification of the original protocol,[34] gave an 80% yield of **21**, which below –10 °C rapidly added triazolinedione **6** to give a quantitative yield of practically pure **22**. The latter isomerized quantitatively to **24** ($t_{1/2}$ ca. 65 min) at room temperature in acid-free $CDCl_3$.[35] In dealing with the rigid polycyclic diazene dioxides such as **23**, equilibration with the deeply blue dinitroso isomers was not a problem; after all, the parent DBO dioxide survived heating up to 250 °C.[36] When diazene/ene **17** was exposed at 0 °C to a vast excess of CF_3CO_3H in highly concentrated solution, epoxidation of the C=C double bond did not occur at all. Yet, in spite of various experimental modifications, competition by the the cycloaddition **22** → **24** (with the latter's oxidation to **25**) and polymer formation could not be avoided. Rather unfavorable mixtures of dioxide **23** together with oxadiazolidine oxide **25** had to be accepted; from a typical run, 25% of **23** and 43% of **25** could be separated from polymers. In



Scheme 3



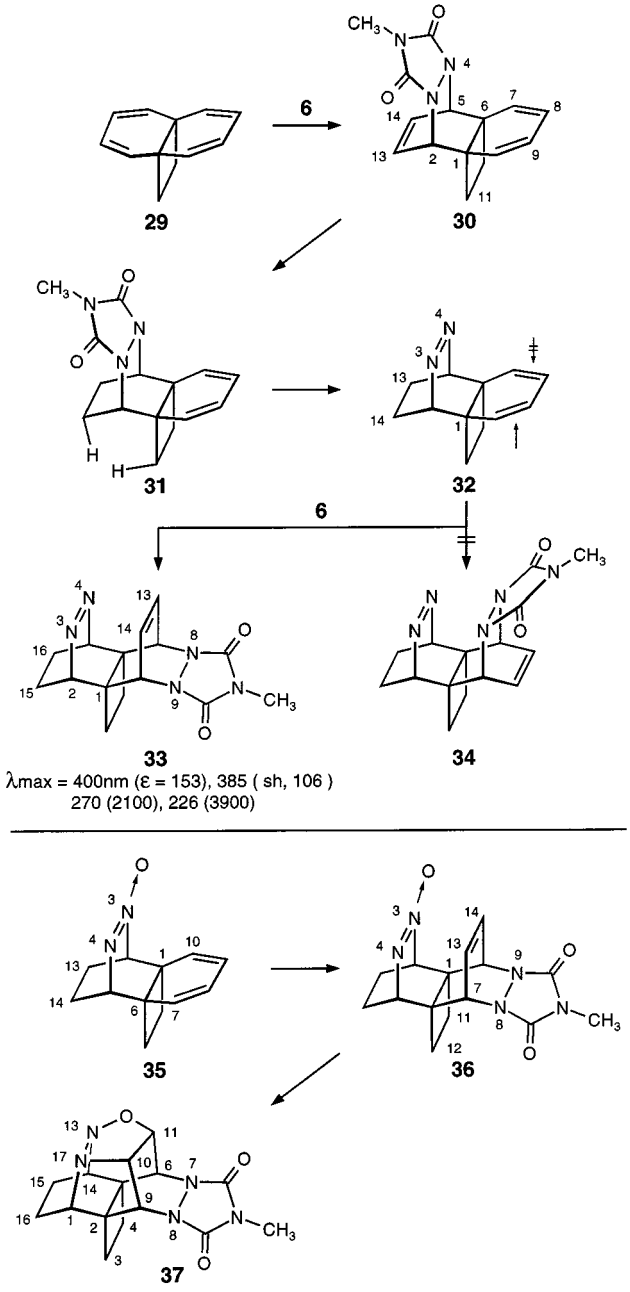
Scheme 4

the electronic spectrum of **22** [$\lambda_{max}(CH_3CN)$ = 265 nm (sh, ε = 3000), 227 (6700), ε_{254} = 3600)[37]] the π → π*$_{N=NO}$ maximum at 227 nm with its shoulder at 265 nm (cf. 230 nm for the DBO oxide[3]) is presumably a manifestation for through-space charge transfer.

The response of oxadiazolidine **24** to dimethyl acetylenedicarboxylate (**26**)[38] is notable: when the reaction and separation procedures were executed below –5 °C, a crystalline 1:1 adduct (MS) was obtained in a nearly 80% yield, and identified as *E*/*Z*-mixture **28**. The ylide **27** resulting from attack at the more nucleophilic N-18 (cf. the oxidation **24** → **25**) is a plausible primary product which, along a six-membered transition state, rearranges into *E*-**28** ($\delta_{2'-H}$ = 5.42). The latter, upon standing at room temperature, slowly isomerizes into *Z*-**28** ($t_{1/2}$ ca. 2.5 d, $\delta_{2'-H}$ = 4.92).

For completion and as reference for the analogously attempted preparation of a particularly desired pentazolidine,[4] it is added without details that like oxide **22**, the pictured azimine/ene quantitatively and rapidly ($t_{1/2}$ ca. 15 min at 20 °C) undergoes [3+2]cycloaddition to give the rather persistent triazolidine ($t_{1/2}$ ca. 30 h at 20 °C).[6]

From the cyclobutane ring in propellane **29**[39] (Scheme 5), particularly at the stage of the intermediate **32**,



Scheme 5

a stronger steric protection of the *exo*-face was assumed, giving a better chance for the formation of the *endo*,*endo*-

bisadduct **34,** and hence for a *syn*-bisdiazene of type **C**. In practice, however, the reaction of **29** with triazolinedione **6** gave quantitatively *endo*-monoadduct **30**, from which the *endo*,*endo*-bisadduct was not accessible. In the case of the diazene/ene **33**, for steric or electronic[40] reasons, the diimide hydrogenation of **30** occurred differently to that of **14,** and under varied conditions led to mixtures consisting of desired **31** and four components resulting from hydrogenation of the cyclohexadiene ring (cf. **31a**–**d** in the Experimental Section). Labour-intensive separations were needed to obtain modest amounts of pure **31**. In **32**, obtained after oxidative hydrolysis, the addition of **6** again occurred unexpectedly and exclusively from the *exo*-face to yield diazene/ene **33**, isolated as slightly yellowish crystals melting at 226 °C with decomposition. Its n → π* absorption with 400 nm (ε = 153) with a shoulder at 385 nm (106) is even more redshifted than for **17** (23 nm with respect to DBO). Like **17**, crystalline **33** turned colorless slowly on exposure to daylight (→ **58**, Scheme 10).

Rather than by *N*-oxidation of **33**, diazeneoxi/ene **36** was approached by the proven one-pot saponification/oxidation sequence **31** → **35** (72%), followed once more by the *exo*-specific addition of **6** to **36** (100%). The ^{1}H NMR-controlled [3+2]cycloaddition **36** → **37** with $t_{1/2}$ (20 °C) ca. 80 min turned out to be roughly as fast as **22** → **24**.

For **17** and **33**, when compared to the bi(tri)cyclic reference structures (Table 1) the signals of the olefinic protons are diamagnetically shifted by 0.30 (0.35) ppm,[41] whilst the ^{15}N shifts are practically identical. These could be indications of laticyclic conjugation. A typical spectral feature of the diazene (di)oxides **22**, **23** and **36** is the diamagnetic displacement of the two α-protons by 0.3–0.9 ppm, the downfield signal generally being assigned to the α-NO proton.[42] In the dioxide **23**, the olefinic protons ($\delta_{14(15)-H}$ = 6.46) are deshielded relative to those of **17** ($\delta_{14(15)-H}$ = 6.13); obviously the ONNO double bond exerts an anisotropic influence. In **28a(b)** the rather tilted oxime C15=NO double bond is confirmed by the IR band at 1570 cm^{-1} and by the signal at δ = 157.9 (157.1) in the ^{13}C NMR spectra. The oxadiazolidines **24** (**25**) and **37** are characterized i.a. by the disappearance of the long-wavelength UV absorption (**24**: ε_{220} = 6100; **25**: ε_{220} = 5700; **37**: ε_{220} = 6000); the original olefinic protons have nearly identical chemical shifts and coupling constants, the latter showing a good agreement with the experimental H/H dihedral angles derived from the X-ray structure of **24** [**24**: δ_{11-H} = 4.17 (t), δ_{12-H} = 4.70 (dd), $J_{7,12}$ = 3.0, $J_{10,11}$ = $J_{11,12}$ = 6.0 Hz; **37**: δ_{10-H} = 4.06 (t), δ_{11-H} = 4.73 (dd), $J_{6,11}$ = 2.5, $J_{9,10}$ = $J_{10,11}$ = 6.5 Hz].

With a crystal of oxadiazolidine **24** obtained from methanol, an X-ray crystal structure analysis was performed.[43] Though protected by an Araldit Rapid coating, the crystal partially decomposed during the measurement. The structure which featured two molecules in the asymmetric unit was solved by direct methods; block diagonal least squares refinements (BDLS) with anisotropic refinement of the 48 non-H atoms converged at R = 0.132. (Figure 1). Remarkably, the tetrahydrofuran and triazolinedione rings are tilted toward each other; the oxadiazolidine ring adopts an envelope conformation with the oxygen lying 0.58 (0.64) Å above the C11–C12–N14–N15 plane.

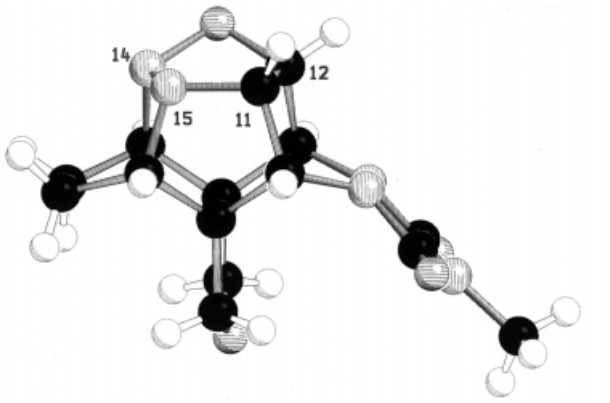


Figure 1. X-ray structural analysis of **24**; selected bond lengths (Å): C11–C12 1.552 (1.565), N14–N15 1.488 (1.464), C12–O 1.415 (1.477), N15–C11 1.480 (1.502), O–N14 1.389 (1.377)

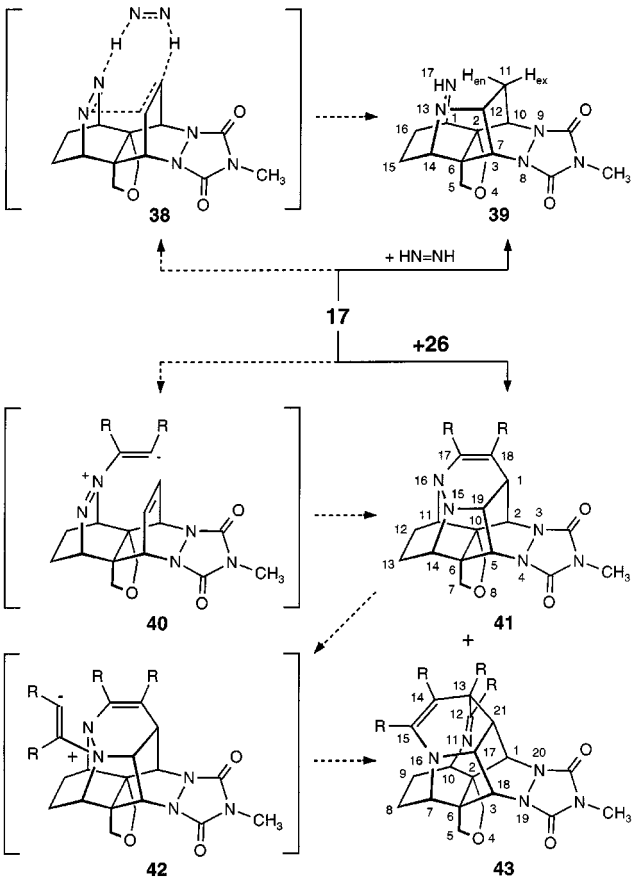
Homoconjugate Additions[6,7a,44]

In *syn*-periplanar dienes of type **A'** the *syn*-periplanar π,π-alignment is set up for homoconjugate additions,[45] not amenable, however, to [2+2+2]cycloadditions as e.g. routinely observed with tilted homodienes such as norbornadiene.[46] In the **A'** analogous N=N/C=C structures **G** (**17**, **33**) with participation of the n-electron pairs at nitrogen, [n_2+n_2+π_2] additions seemed feasible and were explored with DMAD (**26**), tetrachlorothiophene dioxide **46**, and triazolinedione **6** as π_2 components.

A first example for possible homoconjugate reactivity was the attempt to bring about the selective reduction of diazene **17** to the respective hydrazine. Catalytically, as well as with N_2H_2, the 1,4-dihydro-derivative **39** had been produced exclusively instead. This could possibly occur concertedly via **38** and a primary 1,2-addition cannot be strictly excluded.[47]

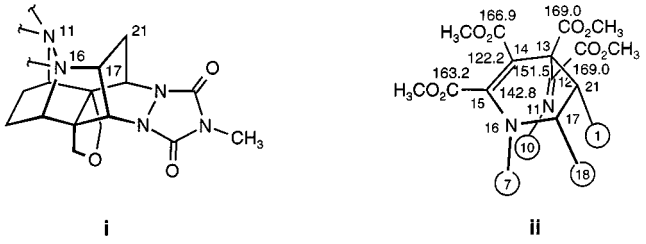
From the reaction of **17** with DMAD (**26**) (Scheme 6), conducted at room temperature with equivalent amounts and stopped after 5 h, besides some oligomeric material the yellowish crystalline 1:1 adduct **41** ($C_{21}H_{23}N_5O_7$, MS, 23%) and the rather complex-looking, colorless, crystalline 1:2 adduct **43** ($C_{27}H_{29}N_5O_{11}$, MS, 62%) resulted and were separated chromatographically. It was established that the latter arises from the former with the ylide **42** as plausible intermediate. With a large excess of DMAD only **43** (>80%) was formed. No efforts were made to decide between the stepwise (via **40**) or concerted alternatives en route to the [2+2+2]cycloadduct **41**.

A remarkable detail in the ^{1}H NMR spectrum of **39** is the shift difference of ca. 2 ppm for $11_{en(ex)}$-H [δ = 3.41 (1.30)]. The structure **41** was mainly confirmed by totally analyzed NMR spectra based on selective H/H (e.g. $J_{1,2}$ = 0, $J_{1,19}$ = 5.5, $J_{5,19}$ = 6.0 Hz) and ^{13}C/H decoupling experiments – e.g. of 1-H (δ = 2.90) with total or partial decoupling of the signal for C-18 (d, ^2J = 6.0 Hz), C-17 (br d, ^3J = 6.0 Hz) and C18–*C*O (dq, ^3J = 4.0 Hz). The ester-substituted enehydrazine chromophore is responsible for

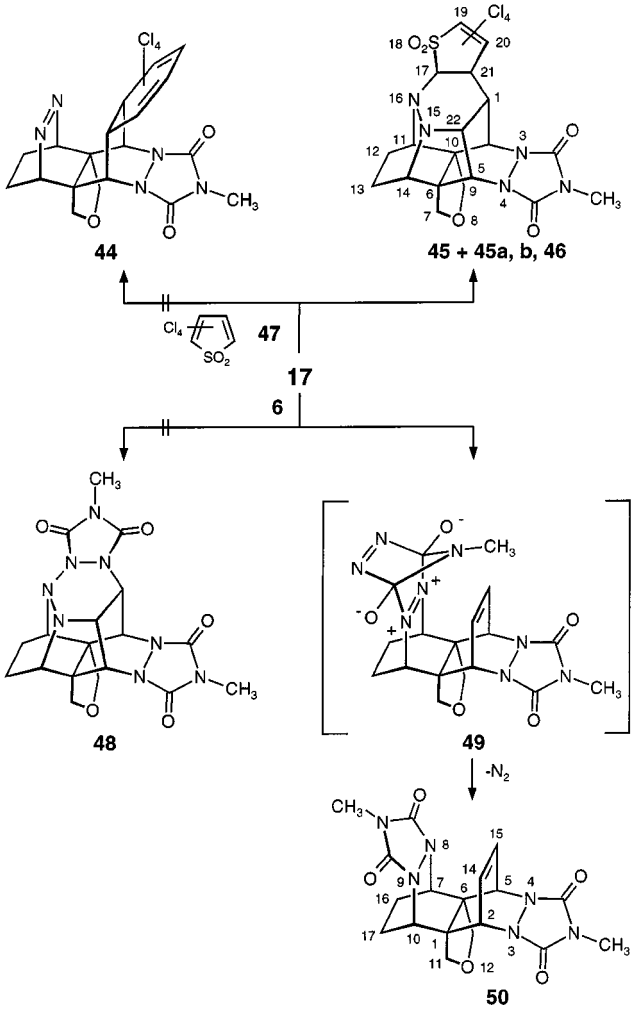


Scheme 6

the UV absorption reaching into the visible region [λ_{max} (CH_3CN) = 350 nm (ε = 1200), 274 (sh, 2400)].[48] In the case of **43**, the identification of subunit **i** was straightforward: According to COSY experiments the basic propellane skeleton with the substitution pattern present in **17** had been retained. Shift and multiplicity of the δ_H = 3.69 signal (17-H) suggested the transannular C–N bond between the ethano bridge and one of the nitrogen atoms (C17–N16). For the structural element **ii** bridging N11–N16–C21, the distinction of 9 ^{13}C signals between δ = 169 and 122 belonging to twofold substituted sp^2-carbons and of two enamine/imine nitrogens (N-16, δ = 87.1, N-11, δ = 344.6) was decisive. Of these nine ^{13}C signals, six arose from C=O groups of which one (δ = 169) showed a coupling of J = 7.0 Hz to a proton separated by 3 bonds. Of the other 3 signals, the one at δ = 151.3 is split by coupling to two protons (J = 5.0, 9.0 Hz), while the remaining two (δ = 142.8, 122.2) appear as singlets. ^{13}C-^{13}C coupling constants[49] together with the ^{15}N- shifts gave additional helpful information [e.g. CO,C-12 = 87.9; CO,C-13 = 61.0; CO,C-14 = 82.5; CO,C-15 = 82.9 Hz; δ = 344.6 for imine N-11, δ = 87.1 for enamine N-16 besides δ = 118.8, 126.7 (N–CH_3), 133.4 for the urazole nitrogens]. In line with the NMR analyses was λ_{max}(CH_3CN) = 360 nm (ε = 3800) for the π → π* absorption of the ester-substituted enamine double bond and the IR band with ν = 1565 cm^{-1} for the ester-substituted C=N double bond.



The addition of tetrachlorothiophene dioxide (TCTD, **47**, Scheme 7) to the C=C double bond in **17** had been pursued as a step en route to a benzo/diazene system (**44**).[50] In structurally rather similar substrates such TCTD additions have been reported.[51] Yet, even in the presence of a large excess of TCTD at 100 °C (acid free $CHCl_3$, ampoule), it took ca. 2 days for complete consumption of **17**, and none of the four isolated products turned out to be **44**. After a tedious separation procedure, three components were identified as [2+2+2]adducts, mainly (55%) **45**, and isomers **45a**,**b**; cf. Experimental Section); a small fourth component (4%, **46**, 2(TCTD):1 adduct – SO_2) was most probably a result of TCTD addition to the C19=C20 double bond in **45**, followed by SO_2 extrusion.

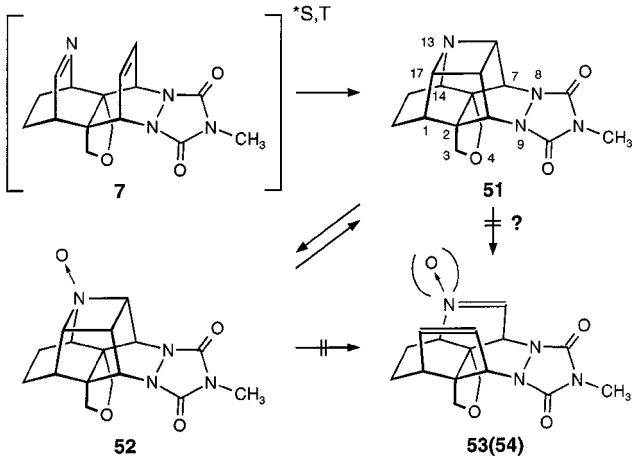


Scheme 7

Triazolinedione **6** added very rapidly to **17**. ^{1}H NMR and TLC control confirmed the formation of a single product. This was readily shown not to be the perhydro-1,2,3,4-tetrazine **48**, but triazolinedione **50** (= dihydro-**19**). Obviously, the N=N double bond in **17** serves as a 1,2-dinucleophile – with **49** as a formal intermediate.

Photochemistry

Imino/ene 7:[6,7a,52] The imine chromophore is only poorly photoreactive and cycloadditions to alkenes are scarce.[53] Direct excitation of **7** (Scheme 8) with monochromatic 254 nm light (Hanau TNN 15 low-pressure Hg lamp, ca. 10^{-2} M, CH_3CN), close to the absorption maximum of 256 nm (n → π*), as well as sensitized (acetone) excitation of **7** (Hanau TQ 150 high-pressure Hg lamp, ca. 10^{-2} M), selectively generated azetidine **51**, isolated as a colorless crystalline compound in 80–85% yield, the missing 15–20% being polymeric material.



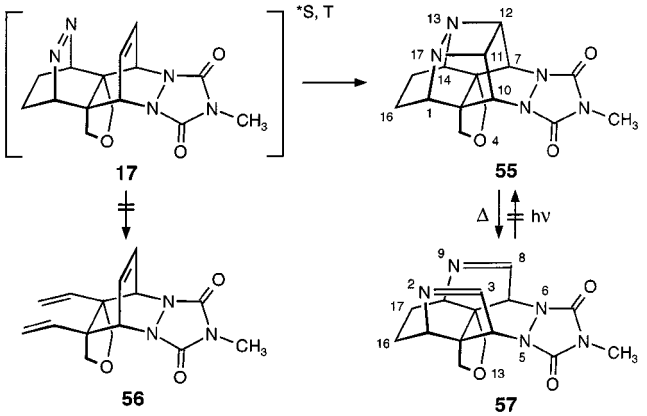
Scheme 8

Highly strained azetidine **51** proved to be thermally very stable. Upon heating of degassed [D_5]pyridine/[D_6]benzene solutions, only at ca. 240 °C ($t_{1/2}$ ca. 4 h) did slow decomposition start; there was no hint of the metathesis isomer **53**, rapid polymerization of this highly reactive imine being a possible explanation (cf. the rapid polymerization of **57**). Similarly, the azetidine oxide **52** (not accessible from **12** (Scheme 2) but obtained from **51** through oxidation with ozone or *m*-CPBA) dissolved in CD_3OD did not undergo a metathesis isomerization (to **54**, ^{1}H NMR).[11] Instead, oxygen was lost above 160 °C ($t_{1/2}$ ca. 50 min) to give back **51** (73%), a behavior not unusual for tertiary amine oxides.[54]

For **51**, the ^{1}H- and ^{13}C NMR spectra ($CDCl_3$) were fully assigned with the help of ^{13}C/^{1}H decoupling experiments – the planar azetidine ring gave rise to signals at δ = 4.25 ("t", 12-H), 4.17 ("t", 17-H), 3.12 ("q", 11-H) with $J_{11,12}$ = 6.0, $J_{11,10(17)}$ = 5.5 Hz and δ = 62.4 (C-17), 60.0 (C-12), 36.1 (C-11); for *N*-oxide **52** the 11-, 12-, 17-H signals show the typical paramagnetic displacement of 0.3–0.5 ppm.

Diazene/ene 17:[6,7a,55] Expectations based on the prior examples,[13] on the poor reactivity of the DBO-chromophore in **17** (Table 1) and on the sensitivity of **17** to daylight, were fully confirmed: Irradiation of ca. 10^{-2} M CH_3CN solutions (–20 °C) under three sets of direct and sensitized irradiation generated in practically quantitative yield 1,2-diazetidine **55** (ε_{220} = 5400). In the TLC and ^{1}H NMR controlled experiments, N_2 elimination products such as **56** (cf. **59**, Scheme 10) would have been detected even in trace quantities (1%). Under the three sets of conditions: (i) with continuous light of λ >280 nm (TQ 150 lamp, pyrex vessel); (ii) light of λ >360 nm [Cu(II)nitrate filter solution]; and (iii) acetone sensitized [280< λ <350 nm, Co(II)sulfate/Ni(II)sulfate filter solution], total conversion was achieved after 20, 5, and 10 min, respectively.

Compared with azetidine **51**, colorless, crystalline, high-melting (>350 °C) 1,2-diazetidine **55** (cf. the elongated N–N bond of 1.540 Å for model **H'** in Table 2) is thermally much less stable. Above 100 °C [$t_{1/2}$ (140 °C) ca. 20 min] 2σ → 2π cleavage occurs, resulting in bispyrroline **57**



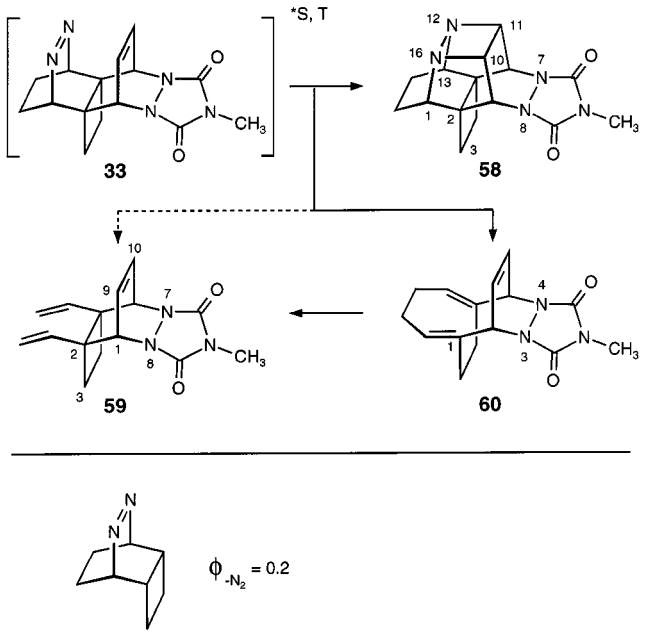
Scheme 9

(Scheme 9), which polymerizes rapidly and therefore can only be characterized (NMR) *in situ*.[11,55]

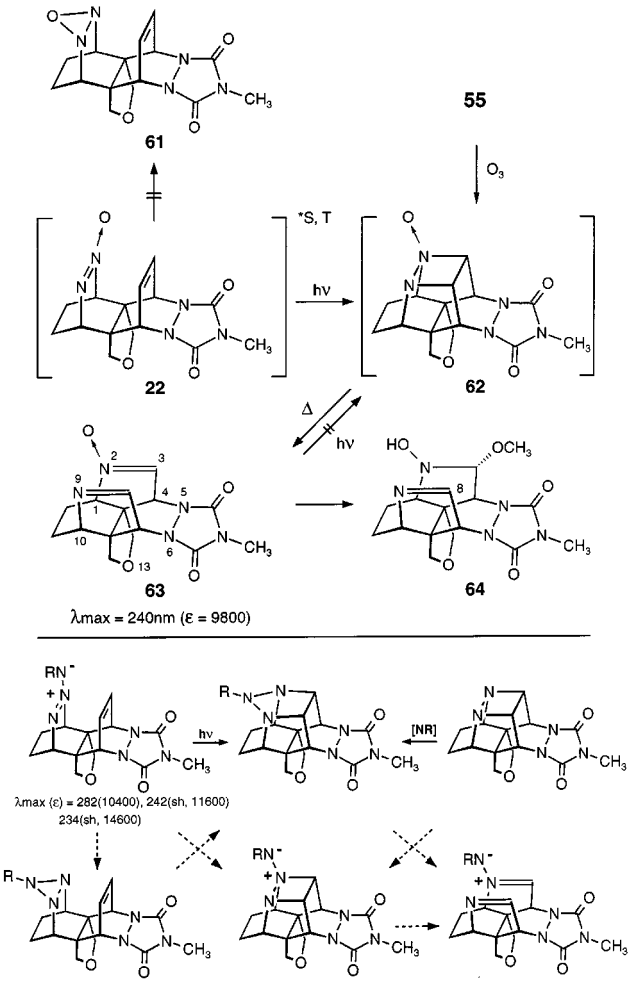
As a notable distinction to the presumably more "proximate" **A"$_{11}$** dienes, triplet excitation (acetone) of **57** [transannular π,π-distance ca 5 Å (Table 2)], did not notably induce C=N/C=N cycloaddition back to **55**. Polymers were formed instead.

A characteristic feature in the ^{1}H NMR analysis of **55** ($CDCl_3$) [δ = 4.51 (11-, 12-H), 60.2 (C-11, -12)] is the relatively large ^{13}C/^{1}H coupling constant $J_{C11(12)-H}$ = 164 Hz (cf. $J_{C,H}$ = 134 Hz for cyclobutane.[56])

Diazene/ene 33:[6,7a] The situation with **33** (Scheme 10) differed from that of **17** in that N_2 elimination became a significant competition for cycloaddition, due to the anellated cyclobutane ring. After all, for the the cyclobuta-anellated DBO, a significant tendency for N_2 elimination (Φ_{-N2} = 0.20) had been reported.[57] As it turned out, upon direct n → π* excitation (λ >280 nm, –30 °C) [2+2]cycloaddition to 1,2-diazetidine **58** remained the dominant pathway (70%), but N_2-elimination accounted for the 20–25% of isolated **59** and **60** (ca. 1:1, the former arising from the latter by means of a Cope rearrangement). The same product composition was established after **33** had been exposed to daylight.



Scheme 10



Scheme 11

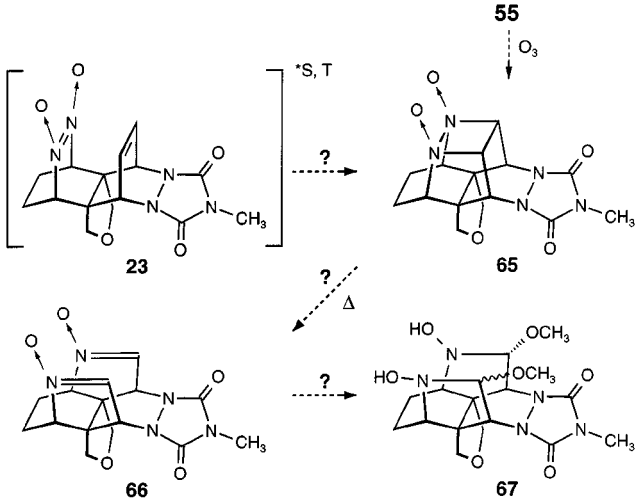
Diazeneoxylene **22**.[6,7a] Structurally related diazeneoxides respond to photoexcitation by cyclization to oxadiaziridines,[58,59] deoxygenation and N_2O-elimination.[60] With thermally labile **22**, the irradiation and workup experiments (Scheme 11) had to be performed at low temperatures (–30 to –50 °C; –10 to –20 °C). After irradiation of ca. 10^{-3} M CH_3CN solutions with the monochromatic 254 nm light (quartz vessel, TNN) until ca. 40% conversion had taken place (5 min), only one monomeric photoproduct was observed (TLC, ^{1}H NMR), chromatographically purified and isolated (78% based on conversion) in the form of colorless crystals. It was identified not as C_s-symmetrical oxadiaziridine **61**[61] but as nitrone/imine **63** [λ_{max} = 240 nm (ε = 2800)]. When such an irradiation experiment was taken to ca. 85% conversion (2 h) only traces of **63** were left [under the given conditions highly photoreactive as well as thermally labile (cf. bisimine **57**]. Besides presumably thermally formed oxadiazolidine **24** (15%), at least 7 inseparable monomeric components derived from **63** (HPLC, ^{1}H NMR) and polymers were found. In line with the short-wavelength absorption of **63**, the relatively slow reaction at > 280 nm irradiation provided after ca. 75% conversion 83% of **63**. Sensitized excitation of **22** (ca. 10^{-3} M acetone solution, TQ 150, pyrex vessel) led to **63** with similar selectivity. In CH_3OH as solvent and with 254 nm light, **63** could be efficiently intercepted in the form of the colorless, crystalline 1:1 adduct **64** [86% after 60% conversion (5 min)].

Probing the thermal stability of **62** through oxidation of diazetidine **55** (Scheme 11), the latter was treated with O_3 at –90 °C in methanol (ca. 10 min). With the proviso that the excess oxidant was removed before warming up, nitrone/imine **63** was practically the exclusive product (85% isolated); when this oxidation experiment was repeated at –65 °C the complex product mixture was found to be very similar in composition to that obtained from ozonolysis of **63**. The opening **62** → **63** is obviously already fast at –65 °C. A one-step mechanism is plausible. However, as in case of the tetrazetidine oxides, a primary N–NO homolysis to aminyl-[62]/aminyloxy-radicals[63] is not ruled out. In control experiments with nitrone/imine **63**, it was confirmed that, as with imine **57**, neither sensitized (acetone, λ >280 nm) nor direct excitation (CH_3CN or MeOH; λ = 254 nm) causes [2+2]cycloaddition (**62**, **22**); in CH_3OH only **64** was generated.

Mechanistically remarkable[12] is the contrasting photobehaviour of the azimine/ene shown in Scheme 4: after its total conversion with light > 280 nm (CH_3CN, –30 °C) the C_s-isomeric triazolidine was separated in good yield (ca. 70%) from several small components (in total 10%) and polymers; it was independently prepared (ca. 80%) by addition of the (RN) nitrene to diazetidine **55**. However, azimine → triaziridine cyclization followed by [π_2 + σ_2]photocycloaddition remains an alternative (see Remarks in ref.[4]).

For the C=NO/C=N elements[20] in structure **63**, typical spectral data are the IR bands at 1590 and 1470 cm^{-1}, the UV absorption with $\lambda_{max}(CH_3CN)$ = 240 nm (ε = 9800, ε_{254} = 5700, ε_{280} = 290) and the ^{1}H NMR signals at δ = 7.67 (8-H) and 7.16 (3-H); for the relatively flexible skeleton

the coupling constants $J_{3,4}$ = 2.5 and $J_{7,8}$ = 0 Hz allow for an estimate of the π,π distance of > 3.8 Å. It can be speculated that the relatively downfield 8-H signal for **64** (δ = 9.34) indicated the presence of an intramolecular O–H–N9 bond.



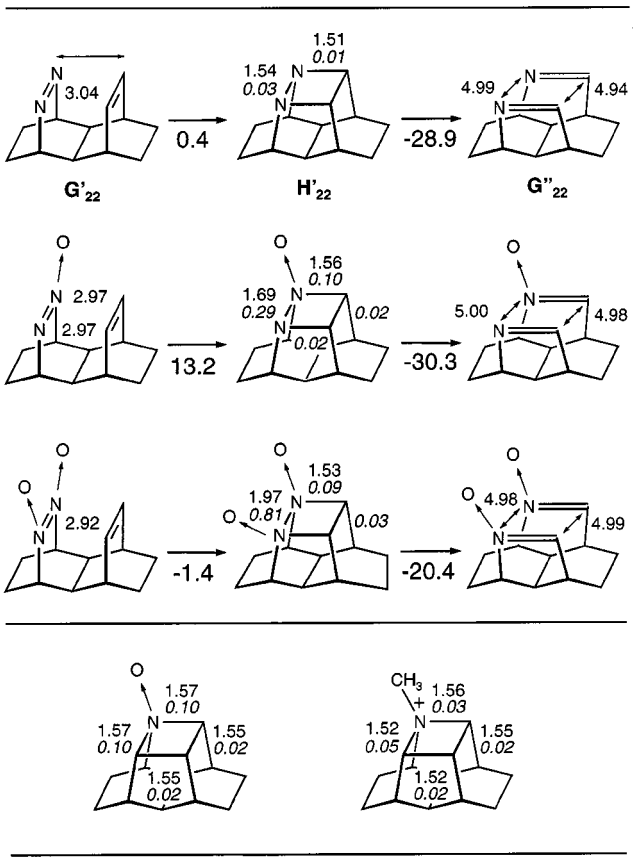
Scheme 12

Diazenedioxylene ***23*** *(Scheme* 12*):* N=O cleavage with formation of nitroxyl radicals or complete loss of the ON=NO unit are known photoprocesses for diazene dioxides.[64] Under the conditions causing the highly selective transformations **22** → **62**(→ **63**) (λ = 254 nm, acetone sensitization), already after very small conversions (10–15%) a complex, inseparable mixture of 5–8 components was present (TLC, ^{1}H NMR, N–CH_3 signal as sensitive probe). Efforts to intercept the expectedly very light-sensitive bisnitrone **66** e.g. through working in CH_3OH (e.g. **67**) were not rewarding; differently from the results with **22**, no single assignment could be made in very complex product mixtures. When the ozonolysis experiment described above for diazetidine **55** (CH_3OH, –90 °C) was executed extending the reaction time to ca. 60 min, with the hope that at least some of oxide **62** would be oxidized to dioxide **65** before opening to **63**, again a highly complex mixture of products was produced, which could not be analyzed (several OCH_3 NMR signals, indicate that **67** could be a possibility). Well-separated nitrone(imine) ^{1}H NMR signals (δ = 7.67, 7.16 for **63**) would have been detected, even if only trace components were present.

Comments and Calculations

Photochemical transformations of the type **E** → **F** (imino/ene → azetidine) and **G** → **H** (diazene/ene → 1,2-diazetidine) were known at the beginning of our project. What we wanted to gain from the polycyclic systems $\mathbf{E'_{22}}$ and $\mathbf{G'_{22}}$ (**7**, **17**, **33**) and the respective *N*-oxides (**12**, **22**, **23**, **36**) was a better understanding of the influence of the specific polycyclic framework on the course of the photoreactions (direct and sensitized excitation), and on the thermal and photochemical stability of the photoproducts, thus providing a basis for extrapolations to the unknown N=N/N=N cycloadditions of type **C** → **D**.[4,5] To summarize: (i) For the studied C=N/C=C and N=N/C=C bichromophoric systems, after singlet (n → π*, π → π*) as well as triplet excitation, [2+2]photocycloaddition proceeded highly selectively (**7** → **51**, **17** → **55**), with only competitive loss of N_2 when this latter process was electronically assisted (**33** → **58**). (ii) For the N=NO/C=C combination **22**, metathesis (→ **63**) was the dominant process. Deoxygenation and particularly oxadiaziridine formation were not significant. There are good reasons to assume that this metathesis proceeds via the diazetidine oxide **62**, which thermally undergoes rapid opening to **63**. Given a weak π → σ* transition[65] for the NO group in **62**, a rapid phototransformation is highly improbable. For the only fleeting existence of **62**, electronic rather than strain effects are responsible; the *N*-methylated diazetidine **55** was found to be stable up to 100 °C. (iii) The rather remote possibility of a primary [3+2]photocycloaddition in **22** was dismissed when in separate irradiation experiments (254 nm) with oxadiaziridine **24** no metathesis (nitrone/imine **63**) was effected. (iv) The response of the ON=NO/C=C substrate (**23**) to direct as well as sensitized excitation is not understood. With reference to the ON=NO/N=N case,[5] internal electron transfer

Table 2. Calculated structure and energy data (B3LYP/6–31G*, $\Delta\Delta H_R$ [kcal mol^{-1}]) for the model diazene/ene $\mathbf{G'_{22}}$, its oxides, the respective diazetidines, metathesis isomers $\mathbf{G''_{22}}$, the *N*-oxidized and *N*-methylated azetidines; selected distances and occupancies of σ* orbitals (B3LYP/6–31G*)



is invoked as the initiating process. (v) For none of the "metathesis" bichromophoric systems (C=N/C=N **57**, C=NO/C=N **63**) was photocycloaddition (back to **7**, **22**) observed, due to unfavorable stereoelectronic rather than for energetic reasons.

B3LYP/6–31G* calculations (Table 2)[66] were performed after completion of the experimental work for reference purposes (Table 1 in ref [5]) and as part of the recent study with cyclically delocalized, nonclassical (σ-bishomoaromatic) 4*N*-ions (Summary and outlook in ref.[5]). There is full agreement with the experiments. In short: For the **G'$_{22}$** N=N/C=C model and the two *N*-oxides the transannular π,π-distances, decreasing with the oxidation state, are even smaller than in the parent **A'$_{22}$** diene (3.13 Å; **I$_{22}$** in Table 1 of ref.[4]). Of the three photocycloadditions, only the N=NO/C=C case is significantly endothermic and the openings into the respective metathesis isomers **G"$_{22}$** are highly exothermic. Upon *N*-oxidation, the N–N bonds, broken in the intermediate diazetidines, undergo a remarkable lengthening from 1.54 Å to 1.69 Å in the monooxide to 1.97 Å in the dioxide. According to NBO analyses, there is a strong interaction of O lone pairs with the adjacent N–N σ* orbitals, with occupancies of 0.29e for the N–NO bond (cf. the very facile fragmentation of **62**) and of 0.81e for the ON–NO bond. With ca. 2 Å length this ON–NO bond is best described as a loosely bonded nitroxyl dimer.[67] As exemplified by the model azetidine oxide, the C–N(O) bonds are notably less influenced by this effect (cf. the thermal stability of **51**); *N*-methylation is predicted to shorten the C–N bonds.

Experimental Section

General Aspects: Melting points were determined on a Monoskop IV (Fa. Bock) and are uncorrected. – Elemental analyses were performed by Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. – IR spectra were measured with a Perkin–Elmer 457 or a Philips PU 9706. – ^{1}H NMR spectra were measured with a Bruker AC 250, AM 400 and ^{13}C NMR spectra with a Bruker AM 400 spectrometer. Chemical shifts are given relative to TMS (δ = 0), coupling constants are reported in Hz; unless otherwise specified, 250 MHz ^{1}H and 100.6 MHz-^{13}C spectra recorded in $CDCl_3$ are given; values marked with an asterisk are interchangeable; assignments have been confirmed by homo- and hetero-nuclear decoupling experiments, H'H, H'X correlation spectroscopy. – Mass spectra were run on a Finnigan MAT 44S spectrometer (EI, 70 eV, unless otherwise specified). – The silica gel used for column chromatography was Merck (0.040–0.063 mm) or ICN Biomedicals GmbH (0.032–0.063 mm). The purity of oily compounds has generally been confirmed by TLC. The irradiation experiments were performed in high-grade solvents, carefully dried and saturated with N_2.

(±)-Ethyl (1*R,2*R**)-12-Oxa-3-azatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-7,9,14-triene-3-carboxylate (3):** A solution of **1** (5.0 g, 29.0 mmol) in anhydrous benzene (30 mL) was added dropwise within 15 min to a refluxing solution of **2a** (5.5 g, 29.0 mmol) and $BF_3{\cdot}Et_2O$ (1.2 g, 8.5 mmol) in anhydrous benzene (70 mL). After refluxing for 20 h and cooling to room temp. it was washed with saturated aqueous $NaHCO_3$ (3 × 100 mL), water (2 × 100 mL), and dried ($MgSO_4$). After concentration in vacuo the solid residue was purified by chromatography on silica gel (PE 60–70/ether, 4:1) to isolate first residual **1** (R_f = 0.50, 1.0 g, 20%), then with cyclohexane/ethyl acetate (3:1) the mixture **3/9** (R_f = 0.25, 10:1, ^{1}H NMR; 4.8 g, 76% on conversion). Upon concentration of the second fraction, the residue was crystallized from cyclohexane/ethyl acetate to give practically pure **3**, as colorless crystals (3.5 g), m.p. 77 °C. – IR (KBr): ṽ = i.a. 1690 cm^{-1} (C=O). – UV (CH_3CN): λ_{max} (ε) = 273 nm (sh, 1910), 262 (3240), 254 (3230), 244 (sh, 2400). – ^{1}H NMR: δ = 6.59–6.42 (m, 14-, 15-H), 6.08–5.88 (m, 8-, 9-H), 5.64 (d, 7- or 10-H, rel. int. 3), 5.55 (d, 7- or 10-H, rel. int. 2), 5.47 (str. d, 10- or 7-H), 4.62 (dd, 2-H, rel. int. 3), 4.48 (dd, 2-H, rel. int. 2), 4.10 (q, $CO_2CH_2CH_3$, rel. int. 2), 4.06 (q, $CO_2CH_2CH_3$, rel. int. 3), 3.88, 3.78, 3.62, 3.57 (4 AB, 11-, 11'-, 13-, 13'-H, rel. int. 2), 3.87, 3.80, 3.62, 3.57 (4 AB, 11-, 11'-H, 13-, 13'-H, rel. int. 3), 3.36 (dd, 4_{en}-H, rel. int. 2)*, 3.34 (dd, 4_{en}-H, rel. int. 3)**, 2.71 (dd, 4_{ex}-H, rel. int. 2)*, 2.68 (dd, 4_{ex}-H, rel. int. 3)** 2.58 (m, 5-H), 1.25 (t, $CO_2CH_2CH_3$, rel. int. 2), 1.20 (t, $CO_2CH_2CH_3$, rel. int. 3); $J_{2,15}$ = 10.5, $J_{4en,4ex}$ = 10.5, $J_{4en,5}$ = $J_{4ex,5}$ = 1.5, $J_{11,11'}$ = $J_{13,13'}$ = 9.5, $J_{CH2,CH3}$ = 7.0 Hz; 3:2 mixture of invertomers. – $C_{16}H_{19}NO_3$ (273.4): calcd. C 70.31, H 7.01, N 5.12; found: C 69.95, H 7.02, N 5.05.

(±)-Ethyl (1*R,2*R**)-12-Oxa-3-azatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-7,9-diene-3-carboxylate (4a):** To a stirred solution of **3** (1.0 g, 3.7 mmol) and $N_2(CO_2K)_2$ (5.0 g, 26 mmol) in CH_2Cl_2 (35 mL), acetic acid (32 g, 54 mmol)/anhydrous CH_3OH (10 mL) was added dropwise within 15 min. After 7 h, the yellow color had disappeared, and water was added (40 mL). After standard workup (extraction of the water-phase with $CHCl_3$, drying ($MgSO_4$) of the organic phase and concentration in vacuo) the residue was crystallized from cyclohexane/ethyl acetate (2:1). 855 mg (85%) of **4a** were obtained as colorless crystals, m.p. 89 °C. – IR (KBr): ṽ = i.a. 1690 cm^{-1} (C=O). – UV (CH_3CN): λ_{max}(ε) = 276 nm (sh, 1690), 263 (3370), 256 (3380). – ^{1}H NMR: δ = 5.96–5.78 (m, 4 H), 5.49 (d, 1 H), 5.43–5.29 (d, 3 H), 4.36 (d, 2 H), 4.25–4.00 (m, 6 H), 3.87 (mc, 1 H), 3.77 (mc, 1 H), 3.56–3.39 (m, 6 H), 3.19 (dd, 2 H), 2.14–1.92 (m, 5 H), 1.83–1.59 (m, 5 H), 1.56–1.40 (m, 2 H), 1.25 (t, 6 H); 1:1 mixture of invertomers. – $C_{16}H_{21}NO_3$ (275.4): calcd. C 69.75, H 7.65, N 5.09; found: C 69.52, H 7.74, N 4.86.

(±)-(1*R,2*R**)-12-Oxa-3-azatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-7,9-diene (4b):** A solution of **4a** (5.1 g, 18.5 mmol) and trimethylsilyl iodide (4.2 mL, 29.4 mmol) in anhydrous $CHCl_3$ (20 mL) was warmed up to 60 °C (N_2 atm.). After total conversion (TLC, 3 h), the solution was cooled to 0 °C, and anhydrous CH_3OH (3 mL) was added dropwise. After concentration in vacuo, the residue was dissolved in ether (50 mL) and extracted with 2 N HCl (2 × 20 mL). The aqueous phase was brought to pH 9 by addition of solid NaOH and extracted with ether (3 × 20 mL). The combined organic phases were dried (Na_2CO_3) and concentrated in vacuo. The residue was practically pure **4b** (2.9 g, 78%) (^{1}H NMR, TLC). Colorless crystals, m.p. 149 °C (ether). – IR (KBr): ṽ = i.a. 3500–3300 cm^{-1} (NH). – UV (CH_3CN): λ_{max}(ε) = 277 nm (sh, 1800), 266 (sh, 3040), 256 (3330). – ^{1}H NMR: δ = 6.01 (dd, 8-H)*, 5.93 (dd, 9-H)* 5.35 (d, 7-, 10-H), 4.29, 4.18, 3.52, 3.46 (4 AB, 11-, 11'-, 13-, 13'-H), 4.01 (br. m, NH), 3.06 (td, 4_{ex}-H)**, 2.81 (dd, 4_{en}-H)**, 2.52 (br. s, 2-H), 2.12–1.88 (m, 2 H), 1.79 (mc, 1 H), 1.53 (mc, 1 H), 1.39 (br. s, 5-H), $J_{4en,ex}$ = 10.5, $J_{4en,5}$ = $J_{4ex,5}$ = 2.0, $J_{7,8}$ = 9.5, $J_{8,9}$ = 4.5, $J_{9,10}$ = 9.5, $J_{11,11'}$ = $J_{13,13'}$ = 9.5 Hz. – $C_{13}H_{16}ClNO_5$ (301.8): C 51.41, Cl 11.67, H 5.97, N 4.61; found: C 51.34, Cl 11.62, H 6.04, N 4.50.

(±)-(1*R,2*R**)-3-Chloro-12-oxa-3-azatetracyclo[4.4.3.2^{2,5}.0^{1,6}]-pentadeca-7,9-diene (4c):** To a solution of **4b** (700 mg, 3.4 mmol)

in anhydrous ether (40 mL) was added *N*-chlorosuccinimide (460 mg, 3.4 mmol). After stirring for 30 min, filtration (succinimide) and concentration in vacuo, the residue was filtered through silica gel (cyclohexane/ethyl acetate, 3:1) to give pure **4c** (R_f = 0.65) as colorless crystals (695 mg, 85%), m.p. 73 °C (ether). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 275 nm (sh, 2770), 265 (4220), 256 (4080), 247 (sh, 3170), 238 (sh, 2330). – ^{1}H NMR: δ = 6.01–5.87 (m, 8-, 9-H), 5.50 (m, 7-H)*, 5.31 (m, 10-H)*, 4.28, 4.20, 3.50, 3.43 (4 AB, 11-,11' 13-, 13'-H), 3.76 (td, 4_{en}-H)**, 3.00 (dd, 4_{ex}-H)**, 2.85 (''t'', 2-H), 2.34 (mc, 1 H), 2.15–1.83 (m, 2 H), 1.62 (mc, 1 H), 1.46 (mc, 5-H), $J_{4en,ex}$ = 12.0, $J_{4en,5}$ = $J_{4ex,5}$ = 2.5, $J_{11,11'}$ = $J_{13,13'}$ = 9.5 Hz. – $C_{13}H_{16}ClNO$ (237.7): calcd. C 65.68, H 6.78, Cl 14.91, N 5.89; found C 65.33, H 6.72, Cl 14.70, N 5.83.

(±)-(1*R,2*R**)-12-Oxa-3-azatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-3,7,9-triene (5):** A solution of **4c** (180 mg, 0.86 mmol) and freshly sublimed *tert*-BuOK in anhydrous 1,2-dimethoxyethane (4 mL) was stirred at room temp. until total conversion (30 min, TLC). After addition of water (15 mL) and extraction with CH_2Cl_2 (3 × 30 mL) the organic phase was dried ($MgSO_4$) and concentrated in vacuo. Chromatography (silica gel, $CHCl_3$/methanol, 12:1) gave pure **5** (TLC, 107 mg, 62%), colorless crystals, m.p. 107 °C (ether). – IR (KBr): $\tilde{\nu}$ = i.a. 1610 cm^{-1} (C=N). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 281 nm (sh, 1490), 267 (2830), 259 (3000). – ^{1}H NMR: δ = 8.42 (d, 4-H), 5.80–5.66 (m, 8-, 9-H), 5.60 (m, 7-H)*, 5.42 (m, 10-H), 4.26, 4.19, 3.39, 3.37 (4 AB, 11-, 11'-, 13-, 13'-H), 4.06 (mc, 2-H), 2.52 (mc, 5-H), 2.06–1.85 (m, 14s-, 15s-H), 1.35–1.00 (m, 14a-, 15a-H), $J_{4,5}$ = 4.0, $J_{11,11'}$ = $J_{13,13'}$ = 9.0 Hz. – MS; *m/z* (%): i.a. 202 (M^+ + 1, 2), 201 (M^+, 7), 129 (8). – $C_{13}H_{15}NO$ (201.3): C 77.58, H 7.51, N 6.96; found: C 77.21, H 7.45, N 6.73.

(±)-(1*R,2*S**,7*R**)-12-Oxa-3,4,8-triazapentacyclo[4.4.3.2^{2,5}.2^{7,10}.0^{1,6}]-heptadeca-8,14-diene-3,4-methyldicarboximide (7):** A solution of **5** (320 mg, 1.6 mmol) and freshly sublimed **6** (180 mg) in anhydrous CH_2Cl_2 was stirred for 30 min at room temp. (exclusion of moisture). After concentration in vacuo, 500 mg (100%) of uniform **7**, colorless crystals, m.p. 89 °C (ethyl acetate/$CHCl_3$, 10:1) were obtained. – IR (KBr): $\tilde{\nu}$ = i.a. 1730–1650 cm^{-1} (C=O, C=N). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 256 nm (2970), ε_{280} = 640. – ^{1}H NMR: δ = 8.31 (d, 9-H), 6.38 (ddd, 14-H)*, 6.08 (ddd, 15-H)*, 4.63 (dd, 2-H)**, 4.50, (dd, 5-H)**, 4.32, 4.31, 4.07, 3.95 (4 AB, 11-, 11'-, 13-, 13'-H), 4.21 (br. s, 7-H), 2.98 (s, $NHCH_3$), 2.52 (br. s, 10-H), 2.22–2.05 (m, 16s-, 17s-H), 1.29–0.95 (m, 16a-, 17a-H), $J_{2,14}$ = 1.5, $J_{2,15}$ = $J_{5,14}$ = 6.0, $J_{5,15}$ = 1.5, $J_{9,10}$ = 4.0, $J_{11,11'}$ = $J_{13,13'}$ = 9.5, $J_{14,15}$ = 6.5 Hz. – $C_{16}H_{18}N_4O_3$ (314.3): calcd. C 61.14, H 5.77, N 17.82; found: C 60.68, H 5.72, N 17.59.

(±)-(1*R,2*S**,7*S**)-12-Oxa-3,4,8-triazapentacyclo[4.4.3.2^{2,5}.2^{7,10}.0^{1,6}]-heptadeca-8,14-diene-3,4-methyldicarboximide (10):** A 2:1 mixture of **7**/**10** (620 mg, 2.0 mmol) was irradiated in acetone (220 mL, 1.5 h, –60 °C) with a 150 W Hg high pressure lamp in a pyrex vessel (TLC control, silica gel, $CHCl_3$/CH_3OH 12:1, R_f (**10**) = 0.35, R_f (**7**) = 0.30), R_f (azetidine **51**) = 0.21). After workup the residue was chromatographically separated (silica gel, $CHCl_3$/CH_3OH, 12:1) to give first **51** (339 mg, 82% based on **7**), then **10** (195 mg, 94% based on primary **10**). Colorless crystals, m.p. 260 °C (ethyl acetate). –IR (KBr): $\tilde{\nu}$ = i.a. 1720 cm^{-1} (C=O), 1655 (C=N). – UV (CH_3CN): λ_{max} (ε) = 248 nm (4600). – ^{1}H NMR: δ = 7.99 (s, 9-H), 6.36 (ddd, 14-H)*, 6.08 (ddd, 15-H)*, 4.58 (dd, 2-H)**, 4.55 (dd, 5-H)**, 4.18, 4.14, 3.94, 3.90 (4 AB, 11-, 11'- 13-, 13'-H), 3.56 (br. s, 7-H), 3.07 (br. s, 10-H), 2.99 (s, NCH3), 2.29–2.00 (m, 2 H), 1.71 (mc, 1 H), 1.50 (mc, 1 H); $J_{2,14}$ = 1.5, $J_{2,15}$ = $J_{5,14}$ = 6.0, $J_{5,15}$ = 1.5, $J_{9,10}$ 0.5, $J_{11,11'}$ = $J_{13,13'}$ = 9.5, $J_{14,15}$ = 6.0. – $C_{16}H_{18}N_40_3$ (314.3): calcd. C 61.14, H 5.77, N 17.82; found C 60.79, H 5.62, N 17.75.

(±)-(1*R,2*R**)-12-Oxa-3-azatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-3,7,9-triene 3-Oxide (11):** To a stirred suspension of **4b** (780 mg, 3.8 mmol) and $Na_2WO_4{\cdot}2H_2O$ in methanol/H_2O (4:1, 20 mL) at 0 °C, aqueous H_2O_2 (30%, 6 mL) was added dropwise. After 3 h, satd. aqueous $NaHSO_3$ (1 mL) was added and the mixture concentrated in vacuo. **Caution:** test for peroxide has to be negative before concentration. The residue was extracted with $CHCl_3$ (3 × 10 mL). After drying ($MgSO_4$) and concentration in vacuo, the solid residue was filtered through silica gel ($CHCl_3$/CH_3OH, 12:1). 635 mg (76%) colorless crystals, m.p. 213 °C (dec.; ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i.a. 1575 cm^{-1} (C=NO). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 244 nm (12300). – ^{1}H NMR: δ = 7.20 (dd, 4-H), 5.96 (ddd, 8-H)*, 5.80 (ddd, 9-H)*, 5.63 (d, 7-H)**, 5.43 (d, 10-H)**, 4.32, 4.22, 3.49, 3.46 (4 AB, 11-, 11'-, 13-, 13'-H), 3.94 (mc, 2-H), 2.73 (mc, 5-H), 2.23 (m, 1 H), 2.15 (m, 1 H), 1.83 (mc, 1 H), 1.451 (mc, 1 H); $J_{2,4}$ = 1.0, $J_{4,5}$ = 6.0, $J_{7,8}$ = 9.5, $J_{7,9}$ = 1.0, $J_{8,9}$ = 9.5, $J_{8,10}$ = 1.0, $J_{9,10}$ = $J_{11,11'}$ = $J_{13,13'}$ = 9.5 Hz. – $C_{13}H_{15}NO_2$ (217.3): calcd. C 71.87, H 6.96, N 6.45; found: C 71.45, H 6.78, N 6.39.

(±)-4,13-Dioxa-8,9,14-triazaheptacyclo[9.6.1.0^{2,6}.0^{2,10}.0^{6,15}.0^{7,12}.0^{14,18}]-octadecan-8,9-methyldicarboximide (13): A solution of **11** (380 mg, 1.7 mmol) and **6** (198 mg, 1.7 mmol) in anhydrous CH_2Cl_2 (5 mL) was stirred at room temp. until the color had disappeared (ca. 10 min). After concentration in vacuo, the residue was pure **13** (560 mg, 100%), colorless crystals (ethyl acetate/$CHCl_3$, 10:1), m.p. 240 °C. When the reaction was monitored at –50 °C (TLC, ^{1}H NMR) no **12** could be detected. UV (CH_3CN): ε_{220} = 6350. – ^{1}H NMR: δ = 4.50 (dd, 12-H), 4.34 (d, 10-H), 4.13 (d, 7-H), 3.97 (dd, 18-H), 3.87, 3.78, 3.73, 3.63 (4 AB, 3-, 3'-, 5-, 5'-H), 3.43 ("q", 11-H), 3.14 (s, NCH_3), 3.12 (mc, 15-H), 1.93- 1.76 (m, 3 H), 1.74–1.55 (m, 2 H); $J_{1,18}$ = 4.5, $J_{4,5}$ = 6.0, $J_{3,3'}$ = $J_{5,5'}$ = 10.0, $J_{7,12}$ = 3.0, $J_{10,11}$ = 6.5, $J_{11,12}$ = $J_{11,18}$ = 7.0 Hz. – $C_{16}H_{18}N_4O_4$ (330.3): calcd. C 58.17, H 5.49, N 16.96; found: C 58.12, H 5.43, N 16.87.

(1*R,2*R**)-12-Oxa-3,4-diazatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-7,9-diene-3,4-methyldicarboximide (15):** (cf. **4a**): **14**[32] (2.34 g, 8.2 mmol), $N_2(CO_2K)_2$ (152.0 g, 0.78 mol), acetic acid (103.6 g, 1.73 mol), CH_3OH (150 mL); the solid residue was crystallized from ethyl acetate; 1.69 g (83%) of colorless crystals, m.p. 249 °C. – IR (KBr): $\tilde{\nu}$ = i.a. 1680 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 274 nm (sh, 2020), 261 (2850), 252 (3120). – ^{1}H NMR: δ = 5.78 (AA', 7-, 10-H)*, 5.42 (BB', 8-, 9-H)*, 4.23 (AB, 11-, 13-H), 4.07 (m, 2-, 5-H), 3.38 (BA, 11'-, 13'-H), 2.18 (m, 14s-, 15s-H), 1.84 (m, 14a-, 15a-H), $J_{11,11'}$ = $J_{13,13'}$ = 9.5 Hz. – $C_{15}H_{17}N_3O_3$ (287.3): calcd. C 62.72, H 5.96, N 14.62; found: C 62.54, H 5.82, N 14.62.

(1*R,2*R**)-12-Oxa-3,4-diazatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-3,7,9-triene (16):**[21] Compound **15** (2.35 g, 8.2 mmol) and KOH (3.18 g, 56.7 mmol) were heated at reflux in 2-propanol (150 mL) under exclusion of air (TLC monitoring, silica gel, ethyl acetate, R_f(**15**) = 0.35; R_f (semicarbazide of **15**) = 0.20) for 10 h. After acidification with 2 N HCl (30 mL), $CuCl_2$ (7.50 g) dissolved in water (120 mL) was added at 0 °C (solution turned black). After stirring for 2 h, conc. aqueous NH_3 was added to give a clear, deeply blue solution. It was extracted with CH_2Cl_2 (3 × 200 mL), the organic phase washed with water (100 mL), dried ($MgSO_4$) and concentrated in vacuo. After filtration through silica gel (ethyl acetate/CH_2Cl_2, 1:1) **16** (1.41 g, 85%) was obtained, physical data identical to ref.[21].

(1*R,2*S**,7*R**)-12-Oxa-3,4,8,9-tetraazapentacyclo[4.4.3.2^{2,5}.2^{7,10}.0^{1,6}]-heptadeca-3,14-diene-8,9- methyldicarboximide (17)** (cf. **7**): Compound **16** (1.18 g, 5.8 mmol), **6** (660 mg, 5.8 mmol), in CH_2Cl_2 (10 mL), were stirred for 30 min. After concentration in vacuo, ca. 1.8 g (100%) of pure **17** were obtained. Yellowish crystals, m.p. 282 °C

(ethyl acetate). **17** has to be kept in the dark; if exposed to daylight, in solution (10^{-3} M, CH_3Cl) as well as in crystalline form (2 d), it is quantitatively transformed into **55**. – IR (KBr): $\tilde{\nu}$ = i.a. 1710 cm^{-1} (C=O), 1455 (N=N). – UV (CH_3CN): = $\lambda_{max}(\varepsilon)$ = 394 nm (190), 379 (sh, 140), 269 (2550), 225 (4200), ε_{280} = 1800, ε_{254} = 1900. – UV (CH_3OH): $\lambda_{max}(\varepsilon)$ = 388 nm (125), 269 (2300), 226 (3800); ε_{280} = 1900, ε_{254} = 1700. – ^{1}H NMR (400 MHz): δ = 6.13 (AA', 14-, 15-H), 5.12 (br. s, 2-, 5-H), 4.63 (XX', 7-, 10-H), 4.28 (AB, 2 H), 3.96 (BA, 2 H), 2.97 (s, NCH_3), 2.04 (m, 2 H) 1.00 (m, 2 H), $J_{3,3'}$ = $J_{5,5'}$ = 10.0 Hz. – ^{13}C NMR: δ = 157.8 (2 CO), 129.1 (C-14, –15), 70.9 (C-11, –13), 66.6 (C-7, –10), 55.4 (C-2, –5), 47.4 (C-1, –6), 25.5 (NCH_3), 17.4 (C-16, –17), $J_{C-2,H}$ = $J_{C-5,H}$ = $J_{C-7,H}$ = $J_{C-10,H}$ = 153.0, $J_{C-11,H}$ = $J_{C-13,H}$ = 148.0, $J_{C-16,H}$ = $J_{C-17,H}$ = 136.0, $J_{C-14,H}$ = $J_{C-15,H}$ = 175.0, J_{NCH3} = 141.0 Hz. – ^{15}N NMR ($CDCl_3$, 44.55 MHz): δ = 530.3 (N-8, –9), 131.6 (NCH_3), 131.3 (N-3, –4). – $C_{15}H_{17}N_5O_3$ (315.3): calcd. C 57.14, H 5.43, N 22.2; found: C 56.92, H 5.24, N 22.23.

(±)-(1*R,2*R**)-12-Oxa-3,4-diazatetracyclo[4.4.3.2^{2,5}.0^{1,6}]pentadeca-3,7,9-triene 3-Oxide (21):** To a stirred solution of **15** (845 mg, 2.9 mmol) in ethanol (150 mL) at room temp. KOH (30 g, 0.53 mol), water (30 mL), and 30% H_2O_2 (10 mL) were added. The solution was heated to 80 °C and 30% H_2O_2 (110 mL) was added within 2 h (TLC control, silica gel, ethyl acetate, R_f(**15**) = 0.38; R_f(**21**) = 0.52). Addition of H_2O_2 was interrupted shortly after 1 h to replenish KOH (30 g, 0.53 mol). After standard workup and filtration through silica gel (ethyl acetate) **21** was isolated as colorless crystals (513 mg, 80%), m.p. 222 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i.a. 1490 cm^{-1} (N=NO). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 277 nm (sh, 1300), 267 (sh, 2420), 232 (9000). – ^{1}H NMR: δ = 5.98 (ddd, 8-H)*, 5.84 (ddd, 9-H)*, 5.58 (d, 7-H)**, 5.52 (d, 10-H)**, 4.38 (mc, 2-H)***, 4.36, 4.27, 3.38, 3.47 (4 AB, 11-, 11'-, 13-, 13'-H), 4.28 (d, 3.0 Hz, 5-H)***, 2.34–2.08, (m, 14s-, 15s-H), 1.83 (m, 14a-H)****, 1.63 (m, 15a-H)****, $J_{7,8}$ = 9.5, $J7_{,9}$ = 0.5, $J_{8,9}$ = 5.5, $J_{8,10}$ = 0.5, $J_{7,8}$ = $J_{9,10}$ = 9.5, $J_{11,11'}$ = $J_{13,13'}$ = 10.0 Hz. – $C_{12}H_{14}N_2O_2$ (218.3): calcd. C 66.04, H 6.47, N 12.84; found: C 65.72, H 6.35, N 12.91.

(±)-(1*R,2*S**,7*R**)-12-Oxa-3,4,8,9-tetraazapentacyclo[4.4.3.2^{2,5}.2^{7,10}.0^{1,6}]-heptadeca-3,14-diene-8,9-methyldicarboximide 3-Oxide (22):** (cf. **17**) **a)**: Compound **21** (680 mg, 3.1 mmol), **6** (320 mg, 3.1 mmol) were dissolved in CH_2Cl_2 (5 mL). After stirring for 20 min at –10 °C and concentration in vacuo pure **22** (1.02 g, 100%) was obtained. The product has to be kept at –20 °C since in solution ($t_{1/2}$ ca. 20 °C ca. 65 min) as well as in the solid state ($t_{1/2}$ at 20 °C ca. 50 h) cycloaddition to **24** occurs. – **b) Oxidation of 17:** To a stirred solution of **17** (185 mg, 0.59 mmol) in CH_2Cl_2 (10 mL) at –10 °C 85% *m*-CPBA (131 mg, 0.64 mmol) was added. After 40 min of stirring (total conversion, TLC, silica gel, $CHCl_3$/CH_3OH 12:1, R_f (**22**) = 0.45, R_f (**17**) = 0.55) it was worked up at –10 °C. The solid residue was separated over a short, cooled (-10 °C) silica gel column ($CHCl_3$/CH_3OH, 12:1); first **22** (148 mg, 76%), then **24** (10 mg, 5%, R_f = 0.33) were eluted. **22**: Colorless crystals, m.p. >350 °C (ethyl acetate/$CHCl_3$ 10:1). – IR (KBr): $\tilde{\nu}$ = i.a. 1700 cm^{-1} (C=O), 1500 (N=NO). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 265 (sh, 3300), 227 nm (6700), ε_{280} = 1400, ε_{254} = 3600. – UV (CH_3OH): $\lambda_{max}(\varepsilon)$ = 265 (sh, 3000), 225 nm (6700), ε_{280} = 1400, ε_{254} = 3600. – ^{1}H NMR: δ = 6.43 (ddd, 14-H)*, 6.20 (ddd, 15-H)*, 4.81 (str. d, 7-, 10-H)**, 4.64 (str. d, 10-H)**, 4.51 (mc, 2-H)***, 4.32, 3.99, 3.99, 3.95, (4 AB, 11-, 11'-, 13-, 13'-H), 4.26 (mc, 5-H)***, 3.02 (s, NCH_3), 2.38–2.15 (m, 16s-, 17s-H), 1.90–1.57 (m, 16a-, 17a-H), $J_{7,14}$ = 1.5, $J_{7,15}$ = $J_{10,14}$ = 6.0, $J10_{,15}$ = 1.5, $J_{11,11'}$ = $J_{13,13'}$ = 10.0, $J_{14,15}$ = 7.0 Hz. – $C_{15}H_{17}N_5O_4$ (331.3): calcd.C 54.38, H 5.17,N 21.14: found: C 54.22, H 5.01, N 21.03.

(1*R,2*S**,7*R**)-12-Oxa-3,4,8,9-tetraazapentacyclo[4.4.3.2^{2,5}.2^{7,10}.0^{1,6}]-heptadeca-3,14-diene-8,9-methyldicarboximide 3,4-Dioxide (23):** Trifluoroacetic acid anhydride (3.75 g, 17.9 mmol) and 85% H_2O_2 (580 mg, 17.1 mmol) in CH_2Cl_2 (10 mL) were stirred at 0 °C for 10 min. Then KH_2PO_4 (3.31 g, 19.0 mmol) and **17** (280 mg, 0.89 mmol) dissolved in CH_2Cl_2 (10 mL) were added. After stirring for 30 h at 0 °C, aqueous $NaHSO_3$ (5 mL) was added. The aqueous phase was concentrated to dryness, the solid extracted with boiling $CHCl_3$ (5 × 50 mL). The combined organic phases were dried, concentrated in vacuo, and the residue chromatographically separated ($CHCl_3$/CH_3OH, 1:2) to give **23** (76 mg, 25%, R_f = 0.39), then after changing to $CHCl_3$/CH_3OH 4:1 **25** (131 mg, 43%, R_f = 0.26). **23**: Colorless crystals, m.p. 210 °C ($CHCl_3$/ethyl acetate 2:1). – IR (KBr): $\tilde{\nu}$ = i.a. 1705 cm^{-1} (C=O), 1420 (ON=NO). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 266 nm (7370), ε_{280} = 5230, ε_{254} = 6200. – ^{1}H NMR: δ = 6.46 (4 AA', 14-, 15-H), 4.81 (XX', 2-, 5-H), 4.54 (br. s, 7-, 10-H), 4.32 (AB, 11-, 13-H), 4.00 (BA, 11'-, 13'-H), 3.03 (s, NCH_3), 2.50 (m, 16s-, 17s-H), 2.18 (m, 16a-, 17a-H), $J_{11,11'}$ = $J_{13,13'}$ = 10.0 Hz. – $C_{15}H_{17}N_5O_5$ (347.3): calcd. C 51.87, H 4.93, N 20.16; found: C 51.56, H 4.81, N 20.03.

(±)-4,13-dioxa-8,9,14,18-tetraazaheptacyclo[9.6.1.0^{2,6}.0^{2,10}.0^{6,15}.0^{7,12}.0^{14,18}]-octadecane-8,9-methyldicarboximide (24): A solution of **22** (88 mg, 0.27 mmol) in anhydrous $CDCl_3$ (0.4 mL) was kept at room temp.: ^{1}H NMR control showed the quantitative transformation into **24** ($t_{1/2}$ 65 min). In crystalline state the isomerization was much slower ($t_{1/2}$ ca. 50 h). Colorless crystals, m.p. >350 °C (ethyl acetate/$CHCl_3$, 10:1) (Table 3). – IR (KBr): $\tilde{\nu}$ = i.a. 1700 cm^{-1} (C=O). – UV (CH_3CN): ε_{220} = 6100. – ^{1}H NMR (400 MHz): δ = 4.70 (dd, 12-H), 4.64 (d, 10-H), 4.23 (d, 7-H), 4.17 ("t", 11-H), 3.85 (2 AB, 2 H), 3.75, 3.67 (2 AB, 2 H), 3.18 (str. d, J = 3.0 Hz, 1-H), 3.11 (s, NCH_3), 3.10 (m, 15-H)*, 2.05–1.90, (m, 2 H), 1.85–1.67 m, 2 H), $J_{3,3'}$ = $J_{5,5'}$ = 10.0, $J7_{,12}$ = 3.0, $J_{10,11}$ = $J_{11,12}$ = 6.0 Hz. – ^{13}C NMR: δ = 153.4 (CO), 153.0 (CO), 77.6 (C-12), 69.9, 67.2 (C-3, –5), 65.0 (C-11), 59.9, 56.3 (C-1, –15), 54.0 (C-10), 51.3 (C-2)*, 49.8 (C-7), 46.6 (C-6)*, 25.4 (NCH_3), 18.0, 15.7 (C-16, –17). – $C_{15}H_{17}N_5O_4$ (331.3): calcd. C 54.38, H 5.17,N 21.14; found: C 54.14, H 5.13, N 20.99.

(±)-4,13-Dioxa-8,9,14,18-tetraazaheptacyclo[9.6.1.0^{2,6}.0^{2,10}.0^{6,15}.0^{7,12}.0^{14,18}]-octadecane-8,9-methyldicarboximide 18-Oxide (25). – a) Thermolysis of 23: After heating a solution of **23** (35 mg, 0.10 mmol) in anhydrous $CDCl_3$ to 50 °C, ^{1}H NMR control showed quantitative conversion into **25** with $t_{1/2}$ 150 min. – **b) Oxidation of 24:** To a solution of **24** (300 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) at 0 °C 85%, *m*-CPBA (193 mg, 0.95 mmol) dissolved in CH_2Cl_2 (5 mL) was added within 10 min under stirring. After 30 min aqueous $NaHSO_3$ (0.5 mL), then aqueous $NaHCO_3$ were added (basic pH). After concentration in vacuo to dryness, the residue was extracted with boiling $CHCl_3$ (5 × 20 mL). Evaporation of the organic solvent and filtration through silica gel ($CHCl_3$/CH_3OH, 4:1) provided **25** as colorles crystals (254 mg, 81%, R_f = 0.26), m.p. 210 °C (CH_3OH). – IR (KBr): $\tilde{\nu}$ = i.a. 1690 cm^{-1} (C=O). – UV (CH_3CN): ε_{220} = 5700. – ^{1}H NMR: δ = 5.24 (dd, 12-H), 4.94 (d, 10-H), 4.60 ("t", 11-H), 4.34 (d, 7-H), 3.97, 3.92, 3.87, 3.83 (4 AB, 3-, 3'-, 5-, 5'-H), 3.62 (m, 1-H)*, 3.36, (str. d, J = 3.0 Hz, 15-H)*, 3.13 (s, NCH_3), 2.67 (m, 1 H), 2.27 (m, 1 H), 2.10–1.80 (m, 2 H), $J_{3,3'}$ = $J_{5,5'}$ = 10.0, $J_{7,12}$ = 2.5, $J_{10,11}$ = $J_{11,12}$ = 5.5 Hz. – ^{1}H NMR (CD_3OD): δ = 5.48 (dd, 12-H), 5.24 (d, 10-H), 4.60 ("t", 11-H), 4.58 (d, 7-H), 4.07, 3.97, 3.81, 3.77 (4 AB, 3-, 3'-, 5-, 5'-H), 3.84 (m, 1-H)*, 3.55 (m, 15-H)*, 3.06 (s, NCH_3), 2.38 (m, 1 H), 2.18–1.86 (m, 3 H), $J_{3,3'}$ = $J_{5,5'}$ = 10.0, $J_{7,12}$ = 3.0, $J_{10,11}$ = $J_{11,12}$ = 6.0 Hz. – $C_{15}H_{17}N_5O_5$ (347.3): calcd. C 51.87, H 4.93, N 20.16; found: C 51.79, H 4.89, N 20.03.

Table 3. X-ray structural analysis of **24**

Formula	$C_{15}H_{20}N_5O_4$
Molecular mass	334.36
Crystal system	triclinic
Space group	*P*–1
a (Å)	7.586(1)
b (Å)	13.652(1)
c (Å)	16.761(2)
α (°)	106.74(1)
β (°)	93.14(1)
γ (°)	103.73(1)
V (Å^3)	1600.5(6)
Z	4
D_{calc} (g·cm^{-3})	1.388
Crystal size (mm)	0.70 × 0.70 × 0.50
Crystal habit	cube
Diffractometer	Philips PW1100
Radiation	graphite-monochromated, Cu-K_α
Wavelength (Å)	1.54178
Scan mode	θ/2θ
Scan range (2θ)	6–134
No. of observed refl. ($I>2\sigma(I)$)	4794
R(int)	0.031
Refinement method	full matrix
Hydrogen atoms calculated	not refined
No. of parameteres	217
R	0.098
Rw	0.106
(Δ/σ)max.	0.02
S	1.88
Max density in final differ. map (eA^{-3})	0.631

(±)-18-(*E*-1',2'-Dimethoxycarbonyl-vinyl)-4,13-dioxa-8,9,14,18-tetraazahexacyclo [9.6.1.0^{2,6}.0^{2,10}.0^{6,15}.0^{7,12}]octadec-14-ene-8,9-methyldicarboximide (28E): A solution of **24** (470 mg, 1.4 mmol) and freshly distilled **26** (4.0 g, 28.2 mmol) in CH_2Cl_2 (5 mL) was stirred under N_2 at –5 °C. After total conversion of **24** (3 h, TLC control, silica gel, $CHCl_3$/CH_3OH, 12:1, R_f (**28E**) = 0.76, R_f (**24**) = 0.33) solvent and excess **26** were distilled off (<10 °C, 0.05 Torr), and the residue filtered through silica gel (ethyl acetate) to give **28E** (530 mg 79%), colorless crystals, m.p. 285 °C (ethyl acetate/cyclohexane 3:1). – IR (KBr): ṽ = i.a. 1705 cm^{-1} (C=O), 1570 (C=N). – ^{1}H NMR: δ = 5.42 (s, 2'-H), 5.39 (dd, 11-H), 4.60 (dd, 12-H), 4.55 (d, 10-H), 4.50 (str. d, *J* = 4.5, 1-H), 4.29, 4.10, 3.95, 3.90 (4 AB, 3-, 3'-, 5-, 5'-H), 4.28 (d, 7-H), 3.85 (s, OCH_3), 3.64 (s, OCH_3), 3.13 (s, NCH_3), 2.68 (m, 16a-H)*, 2.45 (str. t, 16s-H)*, 2.12 (m, 17a-H)**, 1.69 (m, 16s-H)*, $J_{3,3'} = J_{5,5'} = 10.0$, $J_{7,12} = 2.5$, $J_{10,11} = 5.5$, $J_{11,12} = 7.0$ Hz. – ^{13}C NMR (20.2 MHz): δ = 165.9, 165.7 (2 CO, ester), 157.9 (C-15), 153.9, 153.7 (2 CO, imide), 143.3 (C-1'), 94.6 (C-2'), 73.7 (C-12), 70.0, 68.8 (C-3,-5), 59.8 (C-2)*, 59.6 (C-11), 59.0 (C-1), 53.0 (OCH_3), 52.0 (C-10), 51.2 (OCH_3), 46.7 (C-6)*, 46.6 (C-7), 25.6 (NCH_3), 22.9, 19.7 (C-16, –17). – $C_{21}H_{23}N_5O_8$ (473.4): calcd. C 53.28, H 4.90, N 14.79; found C 53.16, H 4.91, N 14.89.

(±)-18-(*Z*-1',2'-Dimethoxycarbonyl-vinyl)-4,13-dioxa-8,9,14,18-tetraazahexacyclo [9.6.1.0^{2,6}.0^{2,10}.0^{6,15}.0^{7,12}]octadec-14-ene-8,9-methyl-dicarboximide (28Z): A solution of **28E** (142 mg, 0.60 mmol) in acid-free $CDCl_3$ (0.4 mL) was kept at room temp (^{1}H NMR control). After 5 d, conversion into **28Z** was quantitative; colorless crystals, m.p. 285 °C (ethyl acetate/cyclohexane, 3:1). – IR (KBr): ṽ = i.a. 1700 cm^{-1} (C=O), 1570 (C=N). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 287 nm (17900), 223 (10300). – ^{1}H NMR: δ = 4.92 (s, 2'-H), 4.66 (dd, 12-H), 4.49 ("t", 11-H), 4. 47 (d, 10-H), 4. 36 (d, 7-H), 4.34, 4.07, 3.95, 3.85 (4 AB, 3-, 3'-, 5-, 5'-H), 3.91 (s, OCH_3), 3.69 (str. d, *J* = 4.0 Hz, 1-H), 3.64 (s, OCH_3), 3.13 (s, NCH_3), 2.78 (m, 16a-H)*, 2.60 (m, 16s-H)*, 2.27 (m, 17a-H)**, 2.00 (m, 17s-H)**; $J_{3,3'} = J_{5,5'} = 10.0$, $J_{7,12} = 2.5$, $J_{10,11} = J_{11,12} = 5.5$ Hz. – ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 4.88 (dd, 12-H), 4.71 (s, 2'-H), 4.67 (d, 10-H), 4.37 (dd, 11-H), 4.32, 4.11, 3.70, 3.66 (4 AB, 3-, 3'-, 4-, 4'-H), 4.31 (d, 7-H), 3.81 (mc, 1-H), 3.76 (s, OCH_3), 3.52 (s, OCH_3), 2.94 (s, NCH_3), 2.65 (m, 16a-H)*, 2.30 (mc, 16s-H)*, 2.00 (m, 17a-, 17s-H); $J_{3,3'} = J_{4,4'} = 10.0$, $J_{7,12} = 2.0$, $J_{10,11} = 5.0$, $J_{11,12} = 6.5$ Hz. – ^{13}C NMR ([D$_6$]DMSO): δ = 166.3 (CO-2'), 164.2 (CO- 1'), 157.1 (C-15), 154.0, 153.1 (2 CO, imide), 150.8 (C-1'), 88.2 (C-2'), 71.7 (C-12), 69.0, 67.6 (C-3, –5), 60.1 (C-2)*, 59.7 (C-11), 57.2 (C-1), 52.6 (OCH_3), 50.1 (C-10), 50.4 (OCH_3), 46.2 (C-7), 46.1 (C-6)*, 25.2 (NCH_3), 22.9, 19.7 (C-16, –17); $J_{CO-1',2'-H} = 10.0$ Hz. – $C_{21}H_{23}N_5O_8$ (473.4): calcd C 53.28, H 4.90, N 14.79: found: C 53.26, H 4.78, N 14.57.

(1*R,2*S**)-3,4-Diazatetracyclo[4.4.2.2^{2,5}.0^{1,6}]tetradeca-7,9,13-triene-3,4-methyldicarboximide (30):** (*cf.* **7**, **17**): Compound **29** (5.60 g, 35.9 mmol)/CH_2Cl_2 (20 mL) and **6** (4.06 g, 35.9 mmol) in CH_2Cl_2 (50 mL) were stirred for 30 min at 0 °C. After evaporation **30** (9.66 g, 100%) was obtained, colorless crystals, m.p. 210 °C (dec., ethyl acetate). – IR (KBr): ṽ = i.a 1705 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 256 nm (5350). – ^{1}H NMR (90 MHz): δ = 6.57 (AA', 13-, 14-H), 5.87 (AA', 8-, 9-H)*, 5.45 (BB', 7-, 10-H)*, 4.45 (XX', 2-, 5-H), 2.90 (s, NCH_3), 2.17 (AA', 11-, 12-H), 1.83 (BB', 11'-, 12'-H). – $C_{15}H_{15}N_3O_2$ (269.3): calcd. C 66.90, H 5.61, N 15.60; found: C 67.11, H 5.50, N 15.64.

Diimide Reduction of 30: To a solution of **30** (4.50 g, 16.7 mmol) in CH_2Cl_2 (350 mL) finely powdered $N_2(CO_2K)_2$ (105.0 g, 0.54 mol) was added. Under vigorous stirring within 4 h at 0 °C acetic acid (68.0 g, 1.13 mol)/CH_3OH (100 mL) was added dropwise. After 14 h at room temp. the yellowish color had disappeared; water (400 mL) was added, the organic phase separated, and the aqueous phase extracted with $CHCl_3$ (3 × 150 mL). After washing (satd. aqueous $NaHCO_3$, 100 mL) and drying ($MgSO_4$) the combined organic phases were concentrated in vacuo, the complex solid residue (TLC) separated chromatographically on silica gel (ethyl acetate). First (R_f = 0.67) a 61:7:32 mixture (^{1}H NMR) of **30**, **31a** (7,8-dihydro-**30**), and **31b** (7,8,9,10-tetrahydro-**30**) (2.21 g, ca. 46%)was eluted; after repeated chromatography (silica gel, ether/cyclohexane 4:1) pure **31b** (R_f = 0.42, 690 mg, 15%), pure **31a** (R_f = 0.33, 155 mg, 3%) and residual **30** (R_f = 0.25, 1.28 g, 28%) were isolated. The second fraction (R_f = 0.32, 1.72 g, ca. 37%) consisted of a 88:11:1 mixture (^{1}H NMR) of **31**, **31c** (6,8,13,14-tetrahydro-**30**), and **31d** (hexahydro-**30**), from which through crystallization (ethyl acetate/cyclohexane 2:1) 420 mg (9%) of pure **31** was obtained.

(1*R,2*S**)-3,4-Diazatetracyclo[4.4.2.2^{2,5}0^{1,6}]tetradeca-7,9-diene-3,4-methyldicarboximide (31):** Colorless needles, m.p. 145 °C (ethyl acetate). – IR (KBr): ṽ = i.a. 1690 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 267 nm (1960). – ^{1}H NMR: δ = 5.70 (AA'-, 7-, 10-H)*, 5.30 (BB', 8-, 9-H)*, 4.00 (mc, 2-, 5-H)*, 2.97 (s, N–CH_3), 2.48 (m, 13s-, 14s-H), 2.46 (m, 11-, 12-H), 2.30 (m, 11'-, 12'-H), 2.02 (m, 13a-, 14a-H). – $C_{15}H_{17}N_3O_2$ (271.3): calcd. C 66.40, H 6.32, N 15.49; found: C 66.12, H 6.20, N 15.27.

(±)-(1*R,2*S**)-3,4-Diazatetracyclo[4.4.2.2^{2,5}0^{1,6}]tetradeca-7,13-diene-3,4-methyldicarboximide (31a):** Colorless needles, m.p. 165 °C (ethyl acetate). – IR (KBr): ṽ = i.a. 1690 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 252 nm (3500). – ^{1}H NMR: δ = 6.70–6.51

(m, 13-, 14-H), 6.10 (m, 8-H), 5.94 (d, 7-H), 4.66 (dd, 2-H)*, 4.53 (dd, 5-H)*, 2.98 (s, N–CH_3), 2.36–2.18 (m, 2 H), 1.91–1.42 (m, 6 H). – $J_{2,13}$ = 2.0, $J_{2,14}$ = 5.5, $J_{5,13}$ = 5.0, $J_{5,14}$ = 1.5, $J_{7,8}$ = 9.5 Hz. – $C_{15}H_{17}N_3O_2$ (271.3): calcd. C 66.40, H 6.32, N 15.49; found: C 66.17, H 6.29, N 15.42.

(1*R,2*S**)-3,4-Diazatetracyclo[4.4.2.2^{2,5}0^{1,6}]tetradec-13-ene-3,4-methyldicarboximide (31b):** Colorless crystals, m.p. 143 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 1755 cm^{-1}, 1690 (C=O). – ^1H NMR: δ = 6.43 (AA', 13-, 14-H), 4.30 (XX', 2-, 5-H), 2.00–1.27 (m, 12 H). – $C_{15}H_{19}N_3O_2$ (273.3): calcd. C 65.91, H 7.01, N 15.37; found: C 65.78, H 6.95, N 15.33.

(1*R,2*S**)-3,4-Diazatetracyclo[4.4.2.2^{2,5}0^{1,6}]tetradeca-3,7,9-triene (32):** *cf.* (**15**): Compound **31** (1.30 g, 4.8 mmol) and KOH (1.55 g, 17.6 mmol) were stirred in 2-propanol (50 mL). After 10 h reflux (total conversion, TLC) and workup, filtration of the solid residue through silica gel (cyclohexane/ethyl acetate, 3:1) yielded colorless crystals (685 mg, 77%), m.p. 182 °C (ether). – IR (KBr): $\tilde{\nu}$ = i.a. 1480 cm^{-1} (N=N). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 390 nm (90), 375 (70), 285 (1540), 235 (1830). – ^1H NMR: δ = 5.55 (AA'-, 7-, 10-H)*, 5.40 (BB', 8-, 9-H)*, 5.03 (mc, 2-, 5-H)*, 2.38 (AA', 11-, 12-H), 2.25 (BB', 11'-, 12'-H), 2.20, (m, 13s-, 14s-H), 1.27 (m, 13a-, 14a-H). – $C_{12}H_{14}N_2$ (186.3): calcd. C 77.38, H 7.58, N 15.04; found: C 77.12, H 7.73, N 15.06.

(1*R,2*R**,7*S**)-3,4,8,9-Tetraazapentacyclo[4.4.2.2^{2,5}.2^{7,10}.0^{1,6}]-hexadeca-3,13-diene-8,9-methyldicarboximide (33):** (*cf.* **7**): **32** (510 mg, 2.7 mmol), **6** (309 mg, 2.7 mmol), CH_2Cl_2 (5 mL). 810 mg (100%) yellowish crystals, m.p. 226 °C (dec.). – IR (KBr): $\tilde{\nu}$ = i.a. 1705 cm^{-1}, (C=O), 1450 (N=N). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 400 nm (153), 385 (sh, 106), 270 (2100), 226 (3900), ε_{280} = 1700, ε_{254} = 1380. – ^1H NMR: δ = 6.08 (AA', 13-, 14-H), 5.00 (br. s 2-, 5-H), 4.64 (XX', 7-, 10-H), 2.97 (s, NCH_3), 2.66 (AA', 11-, 12-H), 2.31 (BB', 11'-, 12'-H and m, 15s-, 16s-H), 1.13 (m, 15a-, 16a-H). – ^1H NMR (CD_3CN): δ = 5.97 (AA', 13-, 14-H), 4.95 (d, J 2.0 Hz, 2-, 5-H), 4.40 (XX', 7-, 10-H), 2.85 (s, NCH_3), 2.52 (AA', 11-, 12-H), 2.32 (BB', 11'-, 12'-H), 2.30 (m, 15s-, 16s-H), 0.97 (m, 15a-, 16a-H). – $C_{15}H_{17}N_5O_2$ (299.3): calcd. C 60.19, H 5.72, N 23.40; found: C 59.91, H 5.57, N 23.27.

(±)-(1*R,2*S**)-3,4-Diazatetracyclo[4.4.2.2^{2,5}0^{1,6}]tetradeca-3,7,9-triene 3-Oxide (35):** (*cf.* **21**): Compound **31** (395 mg, 1.5 mmol) was stirred in ethanol (80 mL), with KOH (15.5 g, 0.28 mol)/water (15 mL)/30% H_2O_2 (6 mL), warmed to 80 °C, with the addition of 30% H_2O_2 (60 mL) within 90 min (TLC control, silica gel, ethyl acetate, R_f (**31**) = 0.50, R_f (**55**) = 0.25). After 45 min addition was stopped and additional KOH (15.0 g, 0.27 mol) was added. After addition of water (60 mL), standard workup and filtration: 212 mg (72%) of **55**, colorless crystals, m.p. 254 °C (ethyl acetate/cyclohexane, 3:1). IR (KBr): $\tilde{\nu}$ = i.a. 1475 cm^{-1} (N=NO). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 280 nm (sh, 1640), 231 (7200). – ^1H NMR: δ = 5.83 (ddd, 8-H)*, 5.70 (ddd, 9-H)*, 5.42 (dd, 7-H)**, 5.36 (dd, 10-H)**, 4.30 (m, 2-H)***, 4.25 (d, J = 3.5 Hz, 5-H)***, 2.64–2.28 (m, 11-, 11'-, 12-, 12'-, 13s-, 14s-H), 1.98 (m, 13a-H)****, 1.79 (m, 14a-H)****, $J_{7,8}$ = 10.0, $J_{7,9}$ 1.0, $J_{8,9}$ = 6.5, $J_{8,10}$ = 1.0, $J_{9,10}$ = 9.5 Hz. – $C_{12}H_{14}N_2O$ (202.3): calcd. C 71.26, H 6.98, N 13.85; found: C 70.91, H 7.03, N13.97.

(±)-(1*R,2*R**,7*S**)-3,4,8,9-Tetraazapentacyclo[4.4.2.2^{2,5}.2^{7,10}.0^{1,6}]-hexadeca-3,13-diene-8,9-methyldicarboximide 3-Oxide (36):** A solution of **35** (245 mg, 1.2 mmol) and **6** (137 mg, 1.2 mmol) in CH_2Cl_2 was stirred at –10 °C. After total conversion (10 min) it was concentrated in vacuo at –10 °C. The residue (245 mg, 100%) was pure **36**, colorless crystals, m.p. 265 °C (ethyl acetate/CH_2Cl_2, 10:1). The product has to be kept below –20 °C, in solution [$t_{1/2}$(20 °C) ca. 80 min] and in the crystalline state [$t_{1/2}$(20 °C) ca. 60 h] [3 + 2]cycloaddition to **37** occurs. – IR (KBr): $\tilde{\nu}$ = i.a. 1700 cm^{-1}, (C=O), 1490 (N=NO). – ^1H NMR: δ = 6.38 (mc, 13-H)*, 6.14 (mc 14-H)*, 4.85 (d, 7-H)**, 4.73 (d, 10-H)**, 4.48 (m, 2-H)***, 4.27 (d, J = 3.0 Hz, 5-H)***, 3.03 (s, NCH_3), 2.76 –2.50 (m, 11-, 11'-, 12-, 12'-H), 2.41 –2.18 (m, 15s-, 16s-H), 1.92 –1.70 (m, 15a-, 16a-H), $J_{7,14}$ = $J_{10,13}$ = $J_{13,14}$ = 6.5 Hz. – $C_{15}H_{17}N_50_3$ (315.3): calcd.: C 57.14, H 5.43, N 22.21; found: C 56.94, H 5.36, N 22.05.

(±)-12-Oxa-7,8,13,17-tetraazaheptacyclo[8.6.1.0^{2,5}.0^{2,9}.0^{5,14}.0^{6,11}.0^{13,17}]-heptadecane-7,8-methyldicarboximide (37): A solution of **36** (105 mg, 0.34 mmol) in acid-free $CDCl_3$ (0.4 mL) was kept at room temp. ^1H NMR control showed quantitative conversion into **37** [$t_{1/2}$ (20 °C) ca. 80 min]. In a crystalline form this conversion was complete after ca. 4 d. Colorless crystals, m.p. 265 °C (ethyl acetate/$CHCl_3$, 10:1). IR (KBr): $\tilde{\nu}$ = i.a. 1690 cm^{-1} (C=O). – UV(CH_3CN): ε_{220} = 6000 nm. – ^1H NMR: δ = 4.73 (dd, 11-H), 4.50 (d, 9-H), 4.18 (d, 6-H), 4.06 ("t", 10-H), 3.20 (s, NCH_3), 3.10, (d, J 3.0 Hz, 1-H)*, 2.99 (m, 14-H)*, 2.42–1.95, (m, 8 H); $J_{6,11}$ = 2.5, $J_{9,10}$ = $J_{10,11}$ = 6.5 Hz. – $C_{15}H_{17}N_50_3$ (315.3): calcd. C 57.14, H 5.43, N 22.21; found: C 56.91, H 5.32, N 22.00.

(±)-4-Oxa-8,9,13,17-tetraazahexacyclo[11.3.1.0^{2,6}.0^{2,10}.0^{6,14}.0^{7,12}]-heptadecane-8,9-methyldicarboximide (39). – a) Catalytically: A solution of **17** (100 mg, 0.32 mmol) in ethyl acetate (35 mL) was exposed to H_2 (1 bar, 10% Pd/C, 20 mg) at 20 °C until the theoretical amount of H_2 was consumed. After standard workup and filtration through silica gel ($CHCl_3/CH_3OH$, 12:1, R_f (**39**) = 0.31) 78 mg (77%) of **39** was obtained. – **b) With Diimide:** (*cf.* **4a**, **15**): Compound **17** (125 mg, 0.40 mmol) and $N_2(CO_2K)_2$ (350 mg, 1.80 mmol) in CH_2Cl_2 (5 mL), was stirred with acetic acid (230 mg, 3.43 mmol)/CH_3OH (2 mL). After 3 h the yellowish coloration had disappeared. After standard workup and filtration of the solid crude product through silica gel ($CHCl_3/CH_3OH$, 12:1) colorless crystals were obtained (93 mg, 73%), m.p. 250 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i.a. 3280 cm^{-1} (N–H), 405. – UV (CH_3CN): ε_{220} = 6500. – ^1H NMR (400 MHz): δ = 4.43 (d, 7-H), 4.15 (d, 10-H), 4.03 ("t", 12 H), 3.95, 3.90, 3.84, 3.64, (3-, 3'-, 5-, 5'-H), 3.41 (dd, 11en-H), 3.22 (br. s, NH), 3.13 (s, NCH_3), 3.01 (d, 14-H), 2.92 (mc, 1-H), 2.03–1.83 (m, 3 H), 1.53 (m, 1 H), 1.30 (dd, 11ex-H), $J_{3,3'}$ = $J_{5,5'}$ = 10.0 Hz, $J_{7,12}$ = 6.0, $J_{10,11en}$ = 5.0, $J_{10,11ex}$ 0, $J_{11en,ex}$ = 14.0, $J_{11ex,12}$ = 5.0, $J_{11en,12}$ 0 Hz. – ^{13}C NMR (62.8 MHz): δ = 154, 153.2 (2 CO), 72.2, 66.9 (C-3, –5, $^1J_{(C-H)}$ = 148 Hz), 62.3 (d, $^1J_{(C-H)}$ = 158), 56.6 (d, $^1J_{(C-H)}$ = 146 Hz), 55.6 (d, $^1J_{(C-H)}$ = 155 Hz), 54.9 (d, $^1J_{(C-H)}$ = 154 Hz), 52.7, 52.3 (C-2, –6), 50.1 (d, $^1J_{(C-H)}$ = 145 Hz), 28.3 (C-11, $^1J_{(C-H)}$ = 137 Hz), 25.4 (NCH_3, $^1J_{(C-H)}$ = 143 Hz), 21.7, 17.0 (C-15, –16, $^1J_{(C-H)}$ = 132 Hz). Picrate: $C_{21}H_{22}N_8O_{10}$ (546.5): calcd. C 46.16, H 4.06, N 20.51; found: C 46.02, H 4.02, N 20.45.

(±)-Dimethyl 3,4-Methyl-dicarboximido-8-oxa-3,4,15,16-tetraaza-heptacyclo[13.3.1.0^{2,10}.0^{5,19}.0^{6,10}.0^{6,14}.0^{11,16}]nonadec-17-ene-17,18-dicarboxylate (41): A solution of **17** (770 mg, 2.4 mmol) and freshly distilled **26** (347 mg, 2.4 mmol) in CH_2Cl_2 (10 mL) was stirred at room temp. until total consumption of **26** (5 h, TLC). After concentration in vacuo, the solid residue (3 components, TLC) was purified by chromatography on silica gel ($CHCl_3/CH_3OH$, 12:1). After 453 mg (62%) of **43** (R_f = 0.45), 223 mg (29%) of **17** (R_f = 0.55), and 255 mg (23%) of **41** (R_f = 0.68) were eluted. **41**: Colorless crystals, m.p. 218 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 1660 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 350 nm (1200), 274 (sh, 2400). – ^1H NMR (400 MHz): δ = 4.62 (d, 5-H), 4.23 ("t", 19-H), 4.02 (s, 2-H), 3.93, (2 AB, 7-,9-H), 3.84 (s, OCH_3), 3.81, 3.75 (2 BA, 7'-, 9'-H), 3.79 (s, OCH_3), 3.27 (mc, 14-H)*, 3.23 (d, J = 6.0 Hz, 11-H)*, 3.13 (s, NCH_3), 2.96 (d, 1-H), 2.20 (m, 1 H), 1.98–1.78 (m, 3 H), $J_{1,2}$ = 0, $J_{1,19}$ = 5.5, $J_{5,19}$ = 6.0, $J_{7,7'}$ = $J_{9,9'}$ = 10.0 Hz. – ^1H NMR ([D_6]DMSO, 400 MHz): δ = 4.77 (d, 5-H), 4.19 (s, 2-H), 4.09 (''t'', 19-H), 3.89, 3.75, 3.64, 3.52 (4 AB, 7-, 7'-, 9-, 9'-H), 3.72

(s, OCH_3), 3.69 (s, OCH_3), 3.31 (m, 11-, 14-H), 2.96 (s, NCH_3), 2.90 (d, 1-H), 1.88 (m, 1 H), 1.75–1.62 (m, 3 H), $J_{1,2}$ = 0, $J_{1,19}$ = 5.5, $J_{5,19}$ = 6.0, $J_{7,7'}$ = $J_{9,9'}$ = 10.0 Hz. – ^{13}C NMR (20.2 MHz): δ = 164.3, 164.0 (2 CO, ester), 153.4, 153.2 (2 CO, imide), 151.3 (C-17), 128.2 (C-18), 72.7, 66.9 (C-7, –9), 66.3 (C-19), 59.2 (C-6)*, 58.6, 55.0 (C-11, –14), 54.2, 54.1 (C-2, –5), 52.8, 52.7 (2 OCH_3), 52.5 (C-10)*, 37.3 (C-1), 25.6 (s, NCH_3), 22.4, 17.2 (C-12, –13); $J_{C-1,H}$ = 139, $J_{C-2,H}$ = $J_{C-5,H}$ = 156, $J_{C-7,H}$ = $J_{C-9,H}$ = 148, $J_{C-12,H}$ = $J_{C-13,H}$ = 132, $J_{C-19,H}$ = 162, J_{NCH3} = 143 Hz. – ^{13}C NMR ([D_6]DMSO): δ = 164.8 (CO, C-18), 163.4 (CO, C-17), 152.9, 152.4 (2 CO, imide), 148.8 (C-17), 130.2 (C-18), 72.1, 66.3 (C-7, –9), 66.0 (C-19), 58.6 (C-6)*, 57.4, 57.0 (C-11, –14), 53.9 (C-5), 53.4 (C-2), 52.4, 52.3 (2 OCH_3), 51.5 (C-10)*, 36.9 (C-1), 25.1 (s, NCH_3), 21.9, 16.7 (C-12, –13); $J_{C-1,H}$ = 139.0, $J_{C-2,H}$ = $J_{C-5,H}$ = 156.0, $J_{C-7,H}$ = $J_{C-9,H}$ = 148.0, $J_{C-11,H}$ = 148.5, $J_{C-12,H}$ = $J_{C-13,H}$ = 134.0, $J_{C-14,H}$ = 148.5, $J_{C-19,H}$ = 162.0, J_{NCH3} = 142.= Hz; $^2J_{C-18,1-H}$ = 6.0, $^3J_{C-17,1-H}$ 6.0, $^3J_{CO,C-18,1-H}$ = 4.0 Hz. – $C_{21}H_{23}N_5O_7$ (457.4): calcd. C 55.14, H 4.88, N 15.31; found: C 54.85, H 5.01, N 15.17.

(±)-Tetramethyl 19,20-Methyldicarboximid 4-oxa-11,16,19,20-tetraazahexacyclo[11.7.1.0^{2,6}.0^{2,10}.0^{7,16}.0^{17,21}]henicosa-11,14-diene-12,13,14,15-tetracarboxylate (43): Compound **41** (130 mg, 0.32 mmol) and **26** (70 mg, 0.49 mmol), dissolved in CH_2Cl_2 (5 mL), were stirred under N_2 at room temp. for 2 h (TLC control). After workup and filtration through silica gel (ethyl acetate/acetone, 5:1) 156 mg (82%) of **43** (R_f = 0.33) were obtained, yellow crystals, m.p. 275 °C (ethyl acetate). – IR (KBr): ṽ = i.a. 1715 cm^{-1} (C=O), 1565 (C=N). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 360 nm (3800). – ^{1}H NMR: δ = 4.76 (d, 1-H), 4.73 (d, 18-H), 4.52 (mc, 10-H), 4.45, 4.09, 3.67, 3.43 (4 AB, 3-, 3'-, 5-, 5'-H), 4.09 (str. d, *J* 4.5 Hz, 7-H), 3.85 (s, 2 OCH_3), 3.81 (s, OCH_3), 3.74 (s, OCH_3), 3.69 ("t", 17-H), 3.22 (dd, 21-H), 3.08 (s, NCH_3), 2.10 (m, 1 H), 2.00–1.82 (m, 2 H), 1.17 (m, 1 H), $J_{1,21}$ = 1.5, $J_{3,3'}$ = $J_{5,5'}$ = 10.0, $J_{17,18}$ = 6.0, $J_{17,21}$ = 7.0 Hz. – ^{1}H NMR ([D_6]DMSO, 400 MHz): δ = 4.84 (d, 18-H), 4.56–4.50 (m, 1-, 10-H), 4.17 (d, *J* 6.5 Hz, 7-H), 4.08, 3.93, 3.50, 3.43 (4 AB, 3-, 3'-, 5-, 5'-H), 3.73 (s, OCH_3), 3.69 (s, OCH_3), 3.66 (s, OCH_3), 3.58 (''t'', 17-H), 3.64 (s, OCH_3), 3.30 (str. d, 21-H), 2.89 (s, NCH_3), 2.01 (m, 1 H), 1.91 (m, 1 H), 1.62 (m, 1 H), 0.82 (m, 1 H); $J_{1,21}$ 1.0, $J_{3,3'}$ = $J_{5,5'}$ = 10.0, $J_{17,18}$ = 6.0, $J_{17,21}$ = 7.0 Hz. – ^{13}C NMR (20.2 MHz): δ = 169.8 (CO, C-13), 167.4 (CO, C-14), 164.2 (CO, C-14), 163.4 (CO, C-15), 154.0 (CO), 152.5 (CO, and C-12), 142.2 (C-15), 123.9 (C-14), 80.4, 72.4 (C-3, –5), 59.2 (d), 56.7 (d), 56.1 (d), 55.0 (s), 54.9 (d), 53.3, 53.2, 52.9 (3 OCH_3), 52.6 (s and d), 52.4 (OCH_3), 52.1 (s), 50.9 (s), 25.3 (s, NCH_3), 20.8, 20.6 (C-8, –9). – ^{13}C NMR ([D_6]DMSO): δ = 169–0 (CO, C-13), 166.9 (CO, C-14), 163.9 (CO, C-12), 163.2 (CO, C-15), 153.2, 152.0 (2 CO, imide), 151.3 (C-12), 142.8 (C-15), 122.2 (C-14), 79.4, 71.5 (C-3, –5, $^1J_{(C-H)}$ = 148), 58.3 (d, $^1J_{(C-H)}$ = 146 Hz), 55.7 (d, $^1J_{(C-H)}$ = 158 Hz), 55.5 (d, $^1J_{(C-H)}$ = 158 Hz), 54.4 (s), 54.0 (d, $^1J_{(C-H)}$ 140 Hz), 52.8, 52.5, 52.2, (3 OCH_3), 52.1 (d, $^1J_{(C-H)}$ 152 Hz), 51.9 (s), 51.8 (OCH_3), 51.2 (s), 50.4 (d, $^1J_{(C-H)}$ 152 Hz), 24.9 (NCH_3, $^1J_{(C-H)}$ = 140 Hz), 20.2, 20.0 (C-8, –9, $^1J_{(C-H)}$ = 130 Hz); $^3J_{CO,\ C-13,21-H}$ = 7.0, $^3J_{C-12,21-H}$ = 5.0, $^3J_{C-12,10-H}$ = 9.0 Hz; $J_{CO,\ C-13}$ = 61.0, $J_{CO,C-14}$ = 82.5, $J_{CO,C-15}$ = 82.9, $J_{CO,C-12}$ = 87.9, $J_{C-14,C-15}$ = 78.5 Hz. – ^{15}N NMR ([D_6]DMSO, 44.65 MHz): δ = 344.6 (N-11), 133.4 (N-19)*, 126.7 (NCH_3), 118.8 (N-20)*, 87.1 (N-16). – MS *; m/z* (%): = i.a. 599 (M^+, 4%), 540 ($M^+ - CO_2CH_3$, 4), 514 (41), 455 (54), 398 (31), 222 (24), 196 (24), 130 (26), 118 (26), 117 (26), 91 ($C_7H_7^+$, 57), 77 ($C_6H_5^+$, 25), 59 ($CO_2CH_3^+$, 100), 42 (31), 41 ($C_3H_5^+$, 24). – $C_{27}H_{29}N_5O_{11}$ (599.6): calcd. C 54.09, H 4.88, N 11.68; found: C 53.75, H 4.71, N 11.75.

(±)-(17*R,21*S**)-17,19,20,21-Tetrachloro-8-oxa-18-thia-3,4,15,16-tetraazaoctacylo [13.6.1.0^{2,10}.0^{5,22}.0^{6,10}.0^{6,14}.0^{11,16}.0^{17,21}]docos-18-ene-3,4-methyldicarboximide 18,18-Dioxide (45):** Compound **17** (470 mg, 1.5 mmol) and **47** (800 mg, 3.2 mmol) dissolved in anhydrous $CHCl_3$ (10 mL) were kept at 100 °C in a thick-walled glass ampoule (N_2 atm.). After 20 h (ca. 50% conversion, ^{1}H NMR) another 850 mg (3.3 mmol) of **47** was added. After an additional 30 h at 100 °C and concentration in vacuo, the solid residue was purified by chromatography on silica gel ($CHCl_3$/CH_3OH, 12:1): after residual **47** (90 mg, R_f = 0.95), **45a** (150 mg, 18%, R_f = 0.50), then a mixture of **45**, **45b** and **46** (380 mg, R_f = 0.37; 88:8:4; ^{1}H NMR) were eluted. By crystallization of the mixture from ethyl acetate pure **45** (250 mg, 29%) was isolated. By HPLC of the mother liquor (Merck Si 100, $CHCl_3$/CH_3CN, 7:5, 15 mL/min) 12 mg (1%) of **46**, then 65 mg (8%) of **45** and 30 mg (4%) of **45b** were isolated. **45**: Colorless crystals, m.p. >350 °C ($CHCl_3$). IR (KBr): ṽ = i.a. 1695 cm^{-1} (C=O), 500. – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 225 nm (12400). – ^{1}H NMR: δ = 5.59 (br. s, 2-H), 4.56 (d, 5-H), 4.12 ("t", 22-H), 3.94 (2 AB, 2 H), 3.88 (BA, 1 H), 3.86 (br. s, 11-H), 3.66 (BA, 1 H), 3.11 (s, NCH_3), 3.08 (dd, 1-H), 3.07 (obscured, 14-H), 2.21–1.71 (m, 12a-, 12s-, 13a-, 13s-H); $J_{1,2}$ = 1.0, $J_{1,22}$ = 5.5, $J_{5,22}$ = 6.0, $J_{7,7'}$ = $J_{9,9'}$ = 10.5 Hz. – MS (CI, NH_3); *m/z* (%): = i.a. 572 (M^+ + 3, 53), 571 (M^+ + 2, 31), 570 (M^+ + 1, 100), 569 (M^+, 31), 568 (M^+ – 1, 76), 536 (M^+ + 2-Cl, 59), 535 (M^+ + 1-Cl, 53), 470 (21), 321 (19), 273 (21), 203 (17), 145 (17). – $C_{19}H_{17}Cl_4N_5O_5S$ (569.3): calcd. C 40.09, H 3.01, Cl 24.91, N 12.30, S 5.63; found: C 40.05, H 2.62, Cl 24.89, N 12.19, S 5.62.

(±)-(17*R,21*S**)-17,19,20,21-Tetrachloro-8-oxa-18-thia-3,4,15,16-tetraazaoctacylo[13.6.1.0^{2,10}.0^{5,22}.0^{6,10}.0^{6,14}.0^{11,16}.0^{17,21}]docos-19-ene-3,4-methyldicarboximide 18,18-Dioxide (45a):** Colorless crystals, m.p. >350 °C (ethyl acetate/$CHCl_3$). – IR ($CHCl_3$): ṽ = i.a. 1855 cm^{-1} (C=O), 645. – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 224 nm (13000). – ^{1}H NMR: δ = 5.63 (mc, 2-H), 4.92 (str. t, 22-H), 4.56 (d, 5-H), 3.95 (2 AB, 2 H), 3.90 (BA, 1 H), 3.80 (d, *J* = 5.0 Hz, 11-H)*, 3.76 (BA, 1 H), 3.25 (mc, 14-H)*, 3.13 (s, NCH_3), 3.11 (dd, 1-H, *partially obscured*), 2.27 (m, 1 H), 2.08 (m, 1 H), 2.00–1.81 (m, 2 H), $J_{1,2}$ = 1.5, $J_{1,22}$ = 5.5, $J_{2,22}$ = 1.5, $J_{5,22}$ = 6.0, $J_{7,7'}$ = $J_{9,9'}$ = 10.5 Hz. – ^{13}C NMR (20.2 MHz): δ = 154.2, 154.1 (2 C=O), 132.4 (C-19), 94.9 (C-17), 84.5 (C-21), 70.4, 67.1 (C-7, –9), 64.1 (C-22), 56.8 (d), 54.1 (d), 53.8 (d), 51.8 (C-6)*, 50.1 (d), 48.5 (C-10)*, 47.2 (d), 25.6 (NCH_3), 18.9, 16.1 (C-12, –13); C-20 could not be detected. – $C_{19}H_{17}Cl_4N_5O_5S$ (569.3): calcd. C 40.09, H 3.01, Cl 24.91, N 12.30, S 5.63; found: C 40.35, H 2.73, Cl 24.88, N 12.05, S 5.76.

(±)-(17*R,21*R**)-17,18,19,21-Tetrachloro-8-oxa-20-thia-3,4,15,16-tetraazaoctacylo[13.6.1.0^{2,10}.0^{5,22}.0^{6,10}.0^{6,14}.0^{11,16}.0^{17,21}]docos-18-ene-3,4-methyldicarboximide 20,20-Dioxide (45b):** Colorless crystals, m.p. >350 °C (ethyl acetate/$CHCl_3$, 4:1). – IR (KBr): ṽ = i.a. 1700 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 228 nm (12300). – ^{1}H NMR: δ= 5.64 (br. s, 2-H), 4.58 (d, 5-H), 4.43 (str. t, 22-H), 3.87 (2AB, 2 H), 3.82 (BA, 1 H), 3.69 (BA, 1 H), 3.43 (dd, 1-H), 3.17 (s, NCH_3), 3.03 (mc, 11-, 14-H), 2.09 (m, 1 H), 1.96–1.69 (m, 3 H), $J_{1,2}$ = 1.5, $J_{1,22}$ = 5.5, $J_{2,22}$ 1.0, $J_{5,22}$ = 6.0, $J_{7,7'}$ = $J_{9,9'}$ = 10.5 Hz. – $C_{19}H_{17}Cl_4N_5O_5S$ (569.3): calcd. C 40.09, H 3.01, Cl 24.91, N 12.30, S 5.63; found: C 40.37, H 2.82, Cl 24.81, N 12.13, S 5.65.

(±)-(17*R,21*S**)-17,19,20,21,22,23,24,25-Octachloro-8-oxa-18-thia-3,4,15,16-tetraazanonacylo[13.10.1.0^{2,10}.0^{5,26}.0^{6,10}.0^{6,14}.0^{11,16}.0^{17,25}.0^{19,24}]hexacosa-20,22-diene-3,4-methyldicarboximide 18,18-Dioxide (46):** Colorless crystals, m.p. >350 °C (ethyl acetate/$CHCl_3$, 5:1). – IR ($CHCl_3$): ṽ = i.a. 1700 cm^{-1} (C=O). – ^{1}H NMR: δ = 5.63 (br. s, 2-H), 4.97 (str. t, 26-H), 4.57 (d, 5-H), 3.96 (2 AB, 2 H), 3.91 (BA, 1 H), 3.80 (d, *J* 5.0 Hz, 11-H)*, 3.77 (BA, 1 H), 3.25 (mc, 14-H)*, 3.14 (s, NCH_3), 3.10 (dd, 1-H), 2.28 (m, 1 H), 2.15–1.80 (m, 3 H); $J_{1,2}$ 1.5, $J_{1,26}$ = 5.5, $J_{2,26}$ 1.0, $J_{5,22}$ = 6.0,

$J_{7,7'} = J_{9,9'} = 10.5$ Hz. – $C_{23}H_{17}Cl_8N_5O_5S$ (759.1): calcd. C 36.39, H 2.26, Cl 37.34, N 9. 23, S 4. 22; found: C 36.03, H 2.15, Cl 37.48, N 9.08, S 4.09.

(1*R,2*R**,7*S**)-12-Oxa-3,4,8,9-tetraazapentacyclo[4.4.3.$2^{2,5}$.$2^{7,10}$.$0^{1,6}$]-heptadec-14-ene-3,4;8,9-bis(methyldicarboximide) (50):** (*cf.* **14**, **30**): Compound **17** (470 mg, 1.5 mmol) and **6** (1.70 g, 15.0 mmol) were dissolved in $CHCl_3$ (15 mL), and kept in an ampoule at 100 °C for 20 h. After concentration in vacuo, excess **6** was sublimed off (80 °C, 0.05 Torr), the residue filtered through silica gel (acetone/$CHCl_3$, 2:1). 465 mg (78%) of colorless crystals was isolated, m.p. 296 °C (ethyl acetate/CH_2Cl_2 2:1). – IR (KBr): $\tilde{\nu}$ = i.a. 1700 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 255 (sh, 4500), 228 nm (10700). – ^1H NMR δ = 6.17 (AA', 14-, 15-H), 4.71 (XX', 7-, 10-H), 4.31 (br. s, 2-, 5-H), 4.26 (AB, 11-, 13-H), 3.97 (BA, 11'-, 13'-H), 3.06 (s, NCH_3), 3.03 (s, NCH_3), 2.22 (m, 16s-, 17s-H), 1.85 (m, 16a-, 17a-H); $J_{11,11'} = J_{13,13'} = 10.0$ Hz. – $C_{18}H_{20}N_6O_5$ (400.4): calcd C, 54.00; H, 5.03; N, 20.99; found: C, 53.77; H, 5.00; N, 20.78.

Photolysis of 7. – a) Direct Irradiation: Low-pressure TNN 15/32 lamp; quartz vessel. A solution of **7** (40 mg, 0.13 mmol) in CH_3CN (120 mL) kept at –20 °C was irradiated to total conversion (ca. 30 min, TLC monitoring, silica gel, $CHCl_3/CH_3OH$, 12:1, R_f (**7**) = 0.30; R_f (**51**) = 0.21, only one monomeric product). After evaporation to dryness, the solid residue consisting of **51** and polymers (TLC, ^1H NMR) was filtered through silica gel: 32 mg (80%) of **51**. – **b) Acetone-Sensitized Irradiation:** High pressure TQ 150 lamp; pyrex vessel. A solution of **7** (345 mg, 1.1 mmol) in acetone (200 mL) kept at –60 °C was irradiated to total conversion. TLC monitoring as above showed the formation of only one monomeric product. After evaporation to dryness, the solid residue consisting of **51** and polymers (TLC, ^1H NMR) was filtered through silica gel: 286 mg (83%) of **51**.

(±)-4-Oxa-8,9,13-triazaheptacyclo[9.5.1.$0^{2,6}$.$0^{2,10}$.$0^{6,14}$.$0^{7,12}$.$0^{11,17}$]-heptadecane-8,9-methyldicarboximide (51): Colorless crystals, m.p. 254 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i.a. 1705 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 223 nm (4370). – ^1H NMR (C_5D_5N/C_6D_6 1:1): δ = 4.48 (d, 7-H)*, 4.20 (d, 10-H)*, 4.08 (br. s, 12-H)**, 3.94, 3.89, 3.62, 3.49 (4 AB, 3-, 3'-, 5-, 5'-H), 3.78 (br. s, 17-H)**, 2.97 (s, NCH_3), 2.74 (″q″, 11-H), 2.50 (br. s, 14-H), 1.40 (m, 3 H), 1.30–1.09 (m, 2 H); $J_{3,3'} = J_{5,5'} = 9.5$, $J_{7,12} = J_{10,11} = J_{11,12} = J_{11,17} = 6.0$ Hz. – ^1H NMR (400 MHz): δ = 4.42 (d, 7-H)*, 4.25 ("t", 12-H), 4.24 (d, 10-H), 4.17 ("t", 17-H), 3.94, 3.88, 3.87, 3.83 (4 AB, 3-, 3'-, 5-, 5'-H), 3.12 ("q" 11-H), 3.11 (s, NCH_3), 2.68 (br. s, 14-H), 1.84–1.72 (m, 2 H), 1.69–1.09 (m, 1 H), 1.66 (m, 1-H), 1.54 (mc, 1 H); $J_{3,3'} = J_{5,5'} = 10.0$, $J_{7,12} = J_{10,11} = J_{11,17} = 5.5$, $J_{11,12} = 6.0$, $J_{1,17} = 3.0$ Hz. – ^{13}C NMR: δ = 153.9 (CO), 153.7 (CO), 69.6, 68.2 (C-3, –5), 62.4 (C-17), 60.0 (C-12), 55.2 (C-7), 54.1 (C-10), 53.3 (C-14), 53.0, 52.4 (C-2, –6), 36.1 (C-11), 33.7 (C-1), 25.3 (NCH_3), 15.9, 13.2 (C-15, –16). Picrate: $C_{22}H_{21}N_7O_{10}$ (543.5): calcd. C 48.62, H 3.89, N 18.04; found: C 48.55, H 3.81, N 17.89.

(±)-4-Oxa-8,9,13-triazaheptacyclo[9.5.1.$0^{2,6}$.$0^{2,10}$.$0^{6,14}$.$0^{7,12}$.$0^{11,17}$]-heptadecane-8,9-methyldicarboximide 13-Oxide (52): Into a solution of **51** (430 mg, 1.4 mmol) in anhydrous CH_3OH (100 mL) kept at –78 °C O_3 gas was blown until the bluish coloration persisted. With N_2 gas, the excess O_3 was blown out, the solution was concentrated to dryness; the residue was pure **52** (100%). – Colorless crystals (ethyl acetate/$CHCl_3$, 10:1) m.p. 254 °C. – IR (KBr): $\tilde{\nu}$ = i.a. 1690 cm^{-1} (C=O). – UV (CH_3CN): ε_{220} = 5860. – ^1H NMR: δ = 4.83 (d, 7-H), 4.73 (''t'', 12-H), 4.54 (dd, 17-H), 4.39 (d, 10-H), 3.98, 3.96, 3.92, 3.85 (4 AB, 3-, 3'-, 5-, 5'-H), 3.48 ("q'', 11-H), 3.17 (mc, 14-H), 3.13 (s, NCH_3), 2.39 (m, 1 H), 2.04 (mc, 1-H), 1.94–1.63 (m, 3 H); $J_{1,17} = 3.5$, $J_{3,3'} = J_{5,5'} = 9.5$, $J_{7,12} = J_{10,11} = J_{11,12} = J_{11,17} = 5.5$ Hz. – $C_{16}H_{18}N_4O_4$ (330.3): calcd. C 58.17, H 5.96, N 16.96; found C 57.92, H 5.78, N 16.72.

Thermolysis of 51: Upon heating the melt of **51**, no change was noted up to 350 °C.

Thermolysis of 52: A solution of **52** (65 mg, 0.20 mmol) in anhydrous CD_3OD (0.4 mL) was heated in a sealed NMR tube (N_2 atm.) to 160 °C (internal standard CH_3OH, $t_{1/2}$ ca. 50 min). After filtration through silica gel ($CHCl_3/CH_3OH$, 12:1) 45 mg of **51** (73%) was isolated. In the ^1H NMR analysis even trace amounts of olefinic products (**53**, **54**) would have been detected.

Photolysis of 17. – a) Direct Irradiations: i) Hg high pressure TQ 150-W lamp, pyrex vessel. After irradiation of a solution of **17** (550 mg, 1.7 mmol) in CH_3CN (210 mL) kept at –20 °C for 20 min (total conversion, TLC) and evaporation, 550 mg (100%) of pure **55** was isolated. **ii)** Hg high pressure Hanovia 679 A lamp, pyrex vessel, filter: aqueous solution of $Cu(NO_3)_2$, 2 M, 1 cm, λ >360 nm. After irradiation of a solution of **17** (330 mg, 1.1 mmol) in CH_3CN (180 mL) kept at –20 °C for 5 min (total conversion, TLC) and evaporation, 360 mg (100%) of pure **55** was isolated. **iii)** Daylight, λ >400 nm, pyrex vessel. After keeping a solution of **17** (180 mg, 0.57 mmol) in CH_3OH (50 mL) exposed to daylight, after 6 d uniform and complete conversion into **55** had occurred. **b) Sensitized irradiation:** Hg high pressure TQ 150-W lamp, pyrex vessel; aqueous filter solution $NiSO_4 \cdot 7\ H_2O$ (492 g/l)/$CoSO_4 \cdot 7\ H_2O$ (141 g/l); 280 < λ > 350 nm. After irradiation of a solution of **17** (520 mg, 1.6 mmol) in acetone (220 mL) kept at –20 °C for 10 min (TLC control, silica gel, $CHCl_3/CH_3OH$, 12:1, R_f (**17**) = 0.55, R_f (**55**) = 0.20) quantitative conversion into **55** (520 mg, 100%) had taken place.

4-Oxa-8,9,13,17-tetraazaheptacyclo[9.5.1.$0^{2,6}$.$0^{2,10}$.$0^{6,14}$.$0^{7,12}$.$0^{13,17}$]-heptadecane-8,9-methyl-dicarboximide (55): Colorless crystals, m.p. > 350 °C (ethyl acetate/$CHCl_3$, 5:1). – IR (KBr): $\tilde{\nu}$ = i. a. 1700 cm^{-1} (C=O). – UV (CH_3CN): ε_{220} = 5400. – ^1H NMR (400 MHz): δ = 4.51 (AA', 11-, 12-H), 4.49 (BB', 7-, 10-H), 3.96 (AB, 3-, 5-H), 3.91 (BA, 3'-, 5'-H), 3.13 (s, NCH_3), 2.84 (br. s, 1-, 14-H), 1.80 (m, 15a-, 15s-, 16a-, 16s-H), $J_{3,3'} = J_{5,5'} = 9.5$ Hz. – ^{13}C NMR: δ = 154.0 (2 CO), 68.4 (C-3, –5), 60.2 (C-11, –12), 55.4 (C-1, –14), 53.8 (C-7, –10), 52.1 (C-2, –6), 25.5 (NCH_3), 14.2 (C-15, –16); $J_{C-1,H} = J_{C-14,H} = 143$, $J_{C-3,H} = J_{C-5,H} = 148$, $J_{C-7,H} = J_{C-10,H} = 154$, $J_{C-11,H} = J_{C-12,H} = 164$, $J_{C-15,H} = J_{C-16,H} = 132$ Hz. – $C_{15}H_{17}N_5O_3$ (315.3): calcd. C 57.14, H 5.43, N 22.21; found: C 56.88, H 5.28, N 22.13.

Thermolysis of 55: A solution of **55** (10 mg, 3×10^{-5} mmol) in acid-free $CDCl_3$ (0.4 mL) was heated in a sealed NMR tube to 140 °C. Up to ca. 50% conversion (ca. 20 min), **57** remained the sole product (^1H NMR). The latter's high tendency for polymerization prohibited isolation and further characterization.

(1*R,4*S**)-13-Oxa-2,5,6,9-tetraazapentacyclo[8.5.2.$0^{4,15}$.$0^{7,11}$.$0^{11,15}$]-heptadeca-2,8-diene-5,6-methyldicarboximide (57):** ^1H NMR: δ = 7.72 (d, 3-, 8-H), 4.51 (d, 4-, 7-H), 4.09 (m, 1-, 10-H), 3.98 (AB, 12-, 14-H), 3.87 (BA, 12'-, 14'-H), 3.16 (s, NCH_3), 2.14–1.91 (m, 16a-, 16s-, 17a-, 17s-H), $J_{12,12'} = J_{14,14'} = 9.5$ Hz.

Photolysis of 33: Hg high pressure TQ 150 W lamp, pyrex vessel. After irradiation of a solution of **33** (370 mg, 1.2 mmol) in CH_3CN kept at –30 °C until total conversion (15 min, TLC), and concentration in vacuo, the solid residue was purified by chromatography on silica gel. With ether/petroleum ether (60–70) (5:1), 37 mg (11%) of **59** (R_f = 0.59) and 35 mg (10%) of **60** (R_f = 0.33), then with $CHCl_3/CH_3OH$ (8:1) 260 mg (70%) of **58** (R_f = 0.30) were eluted.

The same product composition was found when **32** in $CHCl_3$ solution or as crystalline solid was exposed to daylight.

7,8,12,16-Tetraazaheptacyclo[8.5.1.0^{2,5}.0^{2,9}.0^{5,13}.0^{6,11}.0^{12,16}]-hexadecane-7,8-methyldicarboximide (58): Colorless crystals, m.p. 190 °C (ethyl acetate/$CHCl_3$ 5:1). – IR (KBr): $\tilde{\nu}$ = i.a. 1695 cm^{-1} (C=O). – ^{1}H NMR: δ = 4.48 (m, 6-, 9-H)*, 4.34 (m, 10-, 11-H)*, 3.18 (s, NCH_3), 2.69 (br. s, 1-, 13-H), 2.48 (s, 3-, 3'-, 4-, 4'-H), 2.10 (m, 14s-, 15s-H)**, 1.91 (m, 14a-, 15a-H)**. – ^{1}H NMR (CD_3CN): δ = 4.29 (m, 6-, 9-H)*, 4.22 (m, 10-, 11-H)*, 3.04 (s, NCH_3), 2.57 (mc, 1-, 13-H), 2.46 (m, 3-, 4-H), 2.36 (m, 3'-, 4'-H), 2. 08 (m, 14s-, 15s-H)**, 1.69 (m, 14a-, 15a-H)**. – $C_{15}H_{17}N_5O_2$ (299.3): calcd. C 60.19, H 5.72, N 23.40; found: C 59.95, H 5.65, N 23.28.

(1*R,2*R**)-2,5-Divinyl-7,8-diazatricyclo[4.2.2.0^{2,5}]dec-9-ene-7,8-methyldicarboximide (59):** Colorless crystals, m.p. 195 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i.a. 1715 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 248 nm (4190). – ^{1}H NMR: δ = 6.43 (AA', 9-, 10-H), 5.66 (dd, 1'-, 1''-H), 5.16 (dd, 2'c-, 2''c-H), 5.07 (dd, 2't-, 2''t-H), 4.70 (XX', 1-, 6-H), 3.07 (s, NCH_3), 2.49 (AA', 3-, 4-H), 2.14 (BB', 3'-, 4'-H), $J_{1',2't} = J_{1'',2''t}$ = 16.5, $J_{1',2'tc} = J_{1'',2''tc}$ = 10.5, $J_{2't,2'c} = J_{2''t,2''c}$ =1.0 Hz. – $C_{15}H_{17}N_3O_2$ (271.3): calcd. C 66.40, H 6.32, N 15.49; found: C 66.28, H 6.10, N 15.39.

(1*Z*,6*Z*)-3,4-Diazatricyclo[4.4.2.2^{2,5}]tetradeca-1(10),6,13-triene-3,4-methyldicarboximide (60): Colorless crystals, m.p. 195 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i.a. 1695 cm^{-1} (C=O). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 245 nm (4540). – ^{1}H NMR: δ = 6.46 (mc, 13-, 14-H), 5.59 (mc, 2-, 5-H), 5.34 (mc, 7-, 10c-H), 3.10 (s, NCH_3), 2.59–2.34 (m, 6 H), 2.17 (mc, 2-H). – $C_{15}H_{17}N_3O_2$ (271.3): calcd. C 66.40, H 6.32, N 15.49; found: C 66.07, H 6.24, N 15.40.

Photolysis of 22. – a) Direct Irradiations: i) Hg low pressure TNN 15/32 lamp, quartz vessel. A solution of **22** (154 mg, 0.46 mmol) in CH_3CN (230 mL) was irradiated at –30 °C for 5 min (ca. 40% conversion, TLC, ^{1}H NMR). After evaporation below –10 °C the residue (two components besides polymers) was separated on a silica gel column cooled to –20 °C ($CHCl_3$/CH_3OH 12:1). First residual **22** (R_f = 0.50, 90 mg, 58%) then **63** (R_f = 0.27, 50 mg, 78% on conversion) were eluted. From a run (83 mg, 0.25 mmol) taken to ca. 85% conversion (ca. 2 h), a complex mixture (ca. 75%) consisting of at least 7 components was separated (silica gel, $CHCl_3$/CH_3OH, 12:1) from polymers (traces of **63**?). Through HPLC only **24** (12 mg, 15%) could be obtained in pure form. **ii)** Hg high pressure TQ 150-W lamp, pyrex vessel. A solution of **22** (85 mg, 0.26 mmol) in CH_3OH (220 mL) was irradiated at –50 °C for 2 h (ca. 75% conversion, TLC, ^{1}H NMR). Workup led to 20 mg (24%) of residual **22** and 54 mg (83% based on conversion) of **63**. **iii)** Hg low pressure TNN 15/32 lamp, quartz vessel. A solution of **22** (80 mg, 0.24 mmol) in CH_3OH (200 mL) was irradiated at –40 °C for 5 min (ca. 60% conversion, TLC, ^{1}H NMR). After workup 30 mg (38%) of residual **22** and 43 mg (86% based on conversion) of **63** resulted. From a run (83 mg, 0.25 mmol) taken to ca. 90% conversion after workup (chromatography below –20 °C), 9 mg (11%) of residual **22** (R_f = 0.50), 20 mg (27% based on conversion) of **63** (R_f = 0.27) and 37 mg (46% based on conversion) of **64** were obtained. **b) Sensitized irradiation:** Hg high pressure TQ 150-W lamp, pyrex vessel. Compound **22** (110 mg, 0.33 mmol) in acetone (250 mL) at –50 °C for 7 min (ca. 70% conversion, TLC, ^{1}H NMR) afforded, after workup, 33 mg (30%) of residual **22**, and 64 mg (83% based on conversion) of **63**.

Ozone Oxidation of 55: Into a solution of **55** (125 mg, 0.40 mmol) in CH_3OH (20 mL) at –90 °C a stream of O_3 was blown until the appearance of a bluish colour. Excess O_3 was blown out at –90 °C, the solution was concentrated in vacuo, and the solid residue (one monomeric product, TLC) filtered through silica gel ($CHCl_3$/CH_3OH 12:1) to give 112 mg (85%) of **63**.

(±)-(1*R,4*S**,7*R**,10*S**)-13-Oxa-2,5,6,9-tetraazapentacyclo-[8.5.2.0^{4,15}.0^{7,11}.0^{11,15}]heptadeca-2,8-diene-5,6-methyldicarboximide 2-Oxide (63):** Colorless crystals, m.p. 170 °C (CH_3OH/ether 2:1). – IR (KBr): $\tilde{\nu}$ = i. a. 1715 cm^{-1} (C=O), 1590 (C=NO, C=N), 1470. – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 240 nm (9800), ε_{280} = 290, ε_{254} = 5700. – ^{1}H NMR: δ = 7.67 (d, 8-H), 7.16 (dd, 3-H), 4.71 (s, 7-H), 4.55 (d, 4-H), 4.15 (mc, 10-H), 4.08, 4.06, 3.94, 3.93 (4 AB, 12-, 12'-, 14-, 14'-H), 3.97 (m, 1-H), 3.12 (s, NCH_3), 2.13–1.91 (m, 3 H), 1.77 (m, 1 H), $J_{1,3}$ = 2.0, $J_{3,4}$ = 2.5, $J_{7,8}$ 0, $J_{8,10}$ = 3.0, $J_{12,12'} = J_{14,14'}$ = 9.0 Hz. – $C_{15}H_{17}N_5O_4$ (331.3): calcd. C 54.38, H 5.17, N 21.14; found: C 54.13, H 5.02, N 21.00.

(±)-(1*R,3*R**,4*S**,7*R**,10*S**)-2-Hydroxy-3-methoxy-13-oxa-2,5,6,9-tetraazapentacyclo [8.5.2.0^{4,15}.0^{7,11}.0^{11,15}]heptadeca-2,8-diene-5,6-methyldicarboximide (64):** Colorless crystals, m.p. 226 °C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = i. a. 1695 cm^{-1} (C=O), 1475 (C=N). – UV (CH_3CN): ε_{220} = 8100. – ^{1}H NMR: δ = 9.34 (s, 8-H), 4.43, 3.89, 3.66, 3.61 (4 AB, 12-, 12'-, 14-, 14'-H), 4.34 (s, 7-H, d, 3-H)*, 4.09 (d, 4-H)*, 4.01 (br. s, OH), 3.41, (s, OCH_3), 3.27 (str, d, 1-H)**, 3.17 (s, NCH_3), 3.02 (mc, 10-H)**, 2.14–1.92 (m, 3 H), 1.74 (m, 1 H), $J_{3,4}$ = 3.0, $J_{7,8}$ 0, $J_{12,12'} = J_{14,14'}$ = 9.5 Hz. – MS (CI, isobutane); *m/z* (%): i.a. 366 (M^++3, 10), 365 (M^++2, 38), 364 (M^++1, 100), 3.63 (M^+, 10), 333 (5), 332 (15), 127 (10). – $C_{16}H_{21}N_5O_5$ (363.4): calcd. C 52.89, H 5.83, N 19.27; found: C 52.55, H 5.66, N 19.01.

Photolysis of 23: Direct and acetone sensitized irradiations performed as with **22** even at as low as 15% conversion led to product mixtures consisting of more than five components. Their separation and isolation was not possible due to their instability.

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[43] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133157 (**24**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

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