Photochemical Transformations, 84[‡]

Proximate, *syn*-Periplanar Diazene/Diazene(di)oxy, Diazeneoxy/Diazene(di)oxy, and Diazenedioxy/Diazenedioxy Skeletons: Syntheses, [2+2]Photocycloadditions, Metathesis

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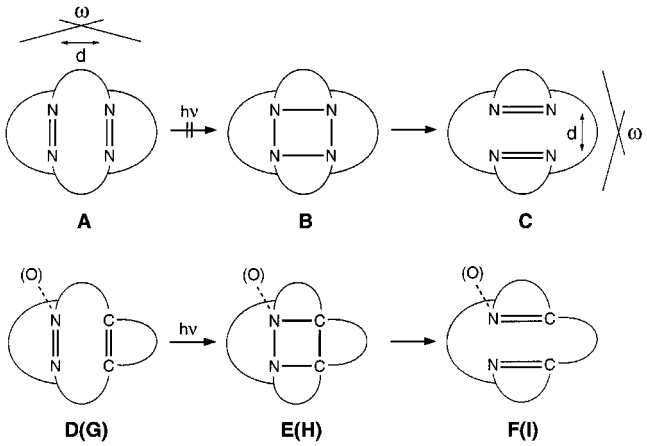
Dedicated to Professor Wolfgang Lüttke on the occasion of his 80th birthday

Keywords: Photochemistry / Heterocycles / Diazenes

Of two very proximate *syn*-periplanar bisdiazenes (**1**,**2**) mono-, di-, tri- and tetra-*N*-oxides were prepared, representing six combinations of the individual N=N/N=NO/ON=NO chromophores. According to DFT calculations (B3LYP/6–31G*), [2+2]photocycloaddition to the respective oxidized tetrazetidines is significantly to moderately endothermic. The metathesis isomerization of the oxidized tetrazetidines is generally highly exothermic and kinetically increasingly favorable with increasing oxidation state. In practice, four out of the six bichromophoric combinations undergo selectively, in competition with N_2 elimination from a DBH unit (**13**) still partially, metathesis isomerization upon $\pi \rightarrow \pi^*$ excitation (monochromatic 254 nm light). In the case of the *syn*-N=NO/N=NO combinations (**5**/**6**, **14**), the photoaddition is thermally reversed. For a ON=NO/N=N combination (**30**), internal electron transfer is responsible for a complex reaction pattern. The preparative value of the metathesis reactions, though, is limited: The metathesis-derived bis[diazene mono(di)oxides] undergo relatively fast secondary photoreactions, while the tri(tetra)oxides undergo rapid thermal transformations. For the N=N/N=NO systems (**12**), of three potential pathways for its metathesis isomerization, the one that takes place via σ-symmetric intermediates (**63**, **64**) is excluded by virtue of the retention of optical purity in the photometathesis of a highly enriched enantiomer [(–)-**12**]. Matrix irradiation experiments (12 K, IR control) with **12** result in the appearance of a kinetically highly labile transient. Supported by DFT calculations it is concluded that in the metathesis reactions, the respective tetrazetidine oxides (increasingly destabilized by interactions between oxygen lone pairs and NNσ* orbitals) function as vibrationally excited transients. That thermal reversion of these transients might be a general, nonproductive competition, is suggested by the experimental verification of a "reversed photometathesis" (**51** → **15**) and by the generally low rates in product formation upon irradiation. The question remains to be answered why in structurally analogous molecular skeletons, [2+2]photocycloaddition occurs in the C=C/N=N and variously oxidized N=N/N=N, and not, however, in the parent N=N/N=N combinations.

Introduction

To date, all attempts to demonstrate the occurrence of N=N/N=N photocycloadditions and thus to generate still elusive N_4 (tetrazetidine) rings (**A** → **B**) have met with failure. Even under the seemingly optimal circumstances offered with the *syn*-bisdiazenes presented in the preceding paper (**1**, Scheme 1; **2**, Scheme 2), elimination of N_2 remained the exclusive product-forming reaction. That the thermodynamically much more stable and photochemically less reactive metathesis isomers (**C**) were not observed is one of the arguments against the intervention of the respective tetrazetidines (**B**).[1] In contrast, in the closely related model N=N/C=C (**D**) and N=NO/C=C (**G**) systems the (oxidized) 1,2-diazetidines **E** (**H**) were found to be the preferred if not exclusive photoproducts, with the notable distinction that the diazetidines remained intact upon heating up to 200 °C whilst their oxides, even at –70 °C, could not be observed and had to be indirectly assessed from the isolation of the metathesis (ON=C/C=N) isomers **I**.[2]



[‡] Part 83: Ref.[1]

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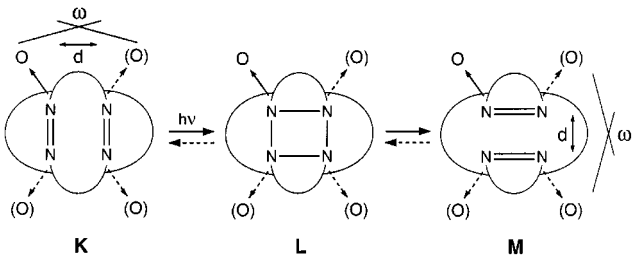
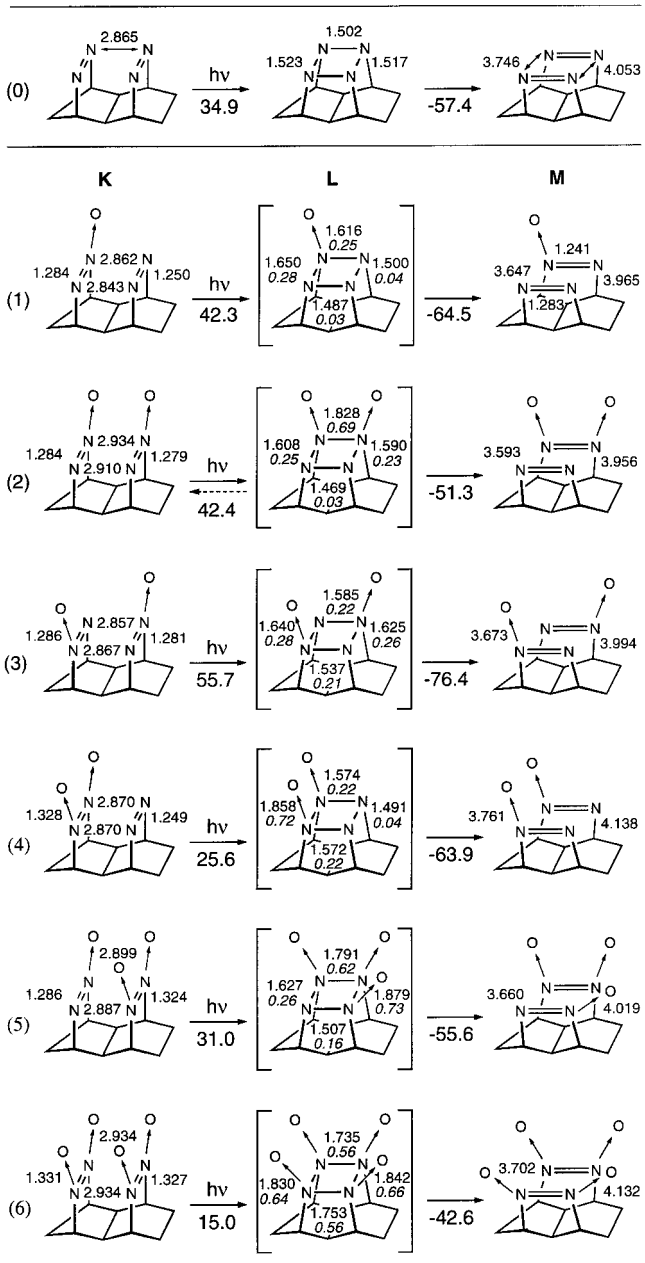
With the assumption that oxidation of one of the two electronically "coupled" N=N units in the bisdiazenes **A** would not only protect one of the N=N chromophores, as in the diazeneoxy/enes **G** and in the parent DBH and DBO oxides ($\Phi_{-N2O(N2O2)} \approx 0$, Table 1 in ref.[2]), but would also inhibit loss of N_2, it was very likely that the N=N/N=NO photocycloaddition in N=N/N=NO substrates **K** to give the tetrazetidine oxides **L** would occur,[3–8] if only at the expense that the latter would very readily undergo ring-opening to the metathesis isomers **M** and thus most probably would not be directly observable.[1][2] This project was extended to the higher (di-, tri-, tetra-)oxides **K** in order to explore the scope of this type of photocycloaddition and to broaden the experimental basis for mechanistic interpretation.[3–10]



As a first test of the above hypotheses, this paper presents the photochemistry of the *N*-oxides of types **K** as derived from the ″very proximate″ bisdiazenes **1** and **2** (Schemes 1–4)[1] – in principle making up for six different bichromophoric combinations (Table 1): diazene/diazeneoxy (N=N/N=NO: **3/4**; **12/13**), *syn*- and *anti*-diazeneoxy/diazeneoxy (N=NO/N=NO: **5/6**, **7**; **14**, **15**), diazene/diazenedioxy (N=N/ON=NO: **8**; **16/17**), diazeneoxy/diazenedioxy (N=NO/ON=NO: **9/10**; **18/19**), diazenedioxy/diazenedioxy (ON=NO/ON=NO: **11**; **20**). For all six combinations featuring (oxidized) DBH/DBO substructures (cf. $\mathbf{F_{12}}$/$\mathbf{H_{12}}$ in Table 1, ref.[1]) and for the respective tetrazetidines and metathesis isomers, the calculated (B3LYP/6–31G*)[1][2][7] energy and structure data are listed in Table 1. The reliability of these calculations has already been commented on.[1][2] Compared to the 2.865 Å for the reference bisdiazene (Entry 0), the transannular π,π distances in the oxidized derivatives **K** are similar for Entries 1, 3 and 4, but somewhat larger for Entries 2, 5 and 6, presumably due to transannular O/O repulsion. The reaction enthalpies for the photochemical steps (→ **L**) are larger by some 30 kcal mol^{-1} than in the corresponding N=N/C=C cases (Table 2 in ref.[2]), while for the thermal steps (→ **M**) they are once again significantly more negative. As noted for the oxidized diazetidines (Table 2 in ref.[2]) the markedly elongated ON–N and ON–NO bonds in the tetrazetidine oxides reflect the strong interactions of O lone pairs with NNσ* orbitals (NBO analysis) – giving particularly the ON–NO bonds the character of loosely bonded nitroxyl dimers. Concerning the isolability of the tetrazetidine oxides, it should be noted that photochemical and subsequent thermal steps belong

Table 1. Selected calculated structure and energy data (B3LYP/6–31G*, $\Delta\Delta H_R$ [kcal mol^{-1}]) for the transformations **K** → **L** → **M** (Entry 0, ref.[1] for comparison); occupancies of N–N σ* orbitals in italics

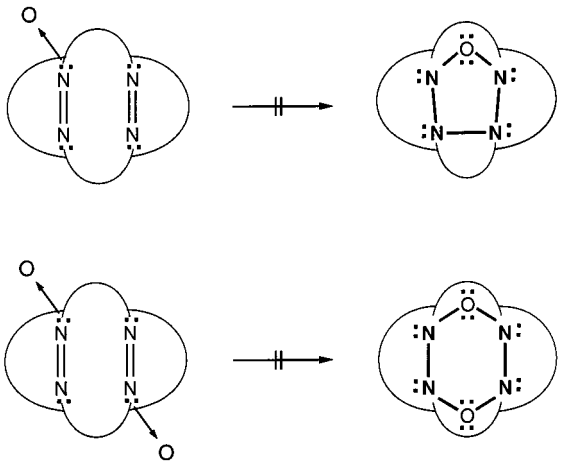


to directly connected sections of the very same trajectory; vibrationally excited photoproducts may therefore be converted before reaching thermal equilibrium. Only in case of Entry 2 is the relative length of the bonds in the tetrazetidinedioxide suggestive of preferential thermal isomerization back to the starting material. For the more flexible metathesis isomers **M** π,π distances >3.6 Å make transannular bond formation highly improbable. To recall, for the $\mathbf{M_{12}}$ compounds at hand (Scheme 2), as pointed out for the parent bisdiazene (**2**),[1] the π,π distances are, due to the anellated cyclopentane ring, considerably shorter (ca. 3.0

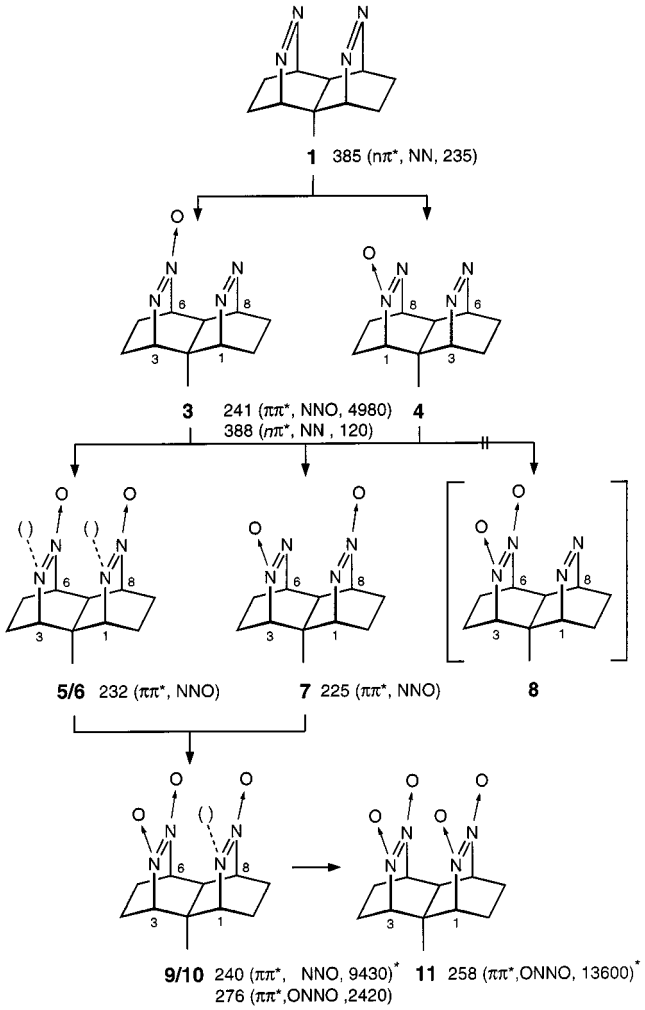
Å). Our early PE analysis (Heilbronner)[4] for DBO/DBO-O and DBO-O/DBO-O combinations (**3/4**, **7**, Scheme 1) showed N=N and N=NO ionisation energies hardly different from the energies of the parent DBO/DBO-O chromophores (Table 1, ref.[2]).[7][11] As in case of the N=N/N=N bichromophoric systems[1] the split due to through-space/through-bond interactions is not significant – a notable distinction from the analogous C=C/C=C[12] and N=N/C=C bichromophoric substrates.[2][13][14]

Preparation of Substrates

For the oxidation of the bisdiazenes **1** and **2** (Scheme 1 and Scheme 2) to their mono-, di-, tri-, and tetroxides (with reference to the oxidation of the N=N/C=C models[2]), selectivity could be expected in the sense that the diazene/diazene oxides should be much more rapidly oxidized to bis(diazene oxides) than to the diazene/diazenedioxides and, specifically in **2** [judged by the relative ionization potentials of DBH (8.96 eV) and DBO (8.32)[3] as well as by the respective transition states (DMDO)[16]] that the DBO part should be oxidized faster than the DBH part. As pointed out in the preceding paper (Table 2), in the N=N/N=NO systems, dipolar cycloaddition (to give oxatetrazolidines – kinetically and thermodynamically very favorable in the structurally related C=C/N=NO systems) as well as ON=N/N=NO-cycloadditions in the *anti*-bis(diazene oxides) (to give tetraalkylated 1,4-dioxatetrazines) should not interfere with the preparation of these oxides.



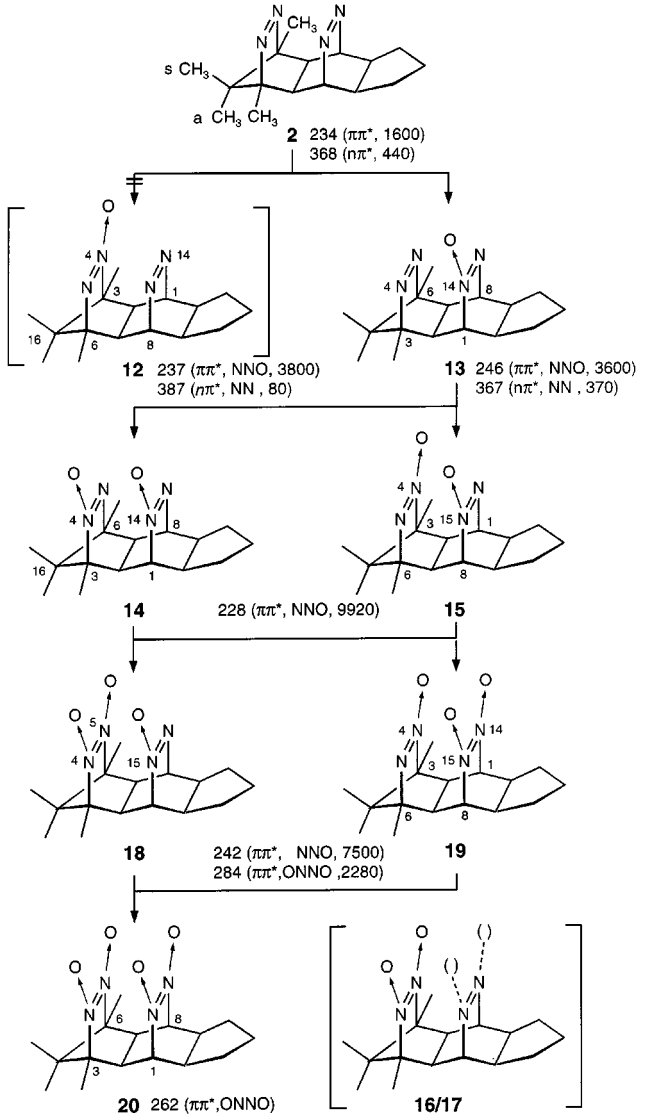
For bisdiazene **1** (Scheme 1, λ_{max}[nm], ε) the synthetically unavoidable CH_3 group caused complications in that poorly separable mixtures of monoxides (**3/4**), *syn*-bis(diazene monoxides) (**5/6**) and trioxides (**9/10**) had to be accepted. Thus, treatment of **1** with equimolar amounts of *m*-chloroperbenzoic acid (*m*-CPBA) as relatively mild oxidant at 0 °C provided, after ca. 70% conversion and chromatographic separation, ca. 70% of monoxides **3/4** (1:1.3), ca. 19% of



Scheme 1

syn-(**5/6**) and *anti*-bis(monoxides) (**7**) (1:1:1), with no trace of diazene/diazene dioxide **8** being detectable. With the stronger oxidant CF_3CO_3H/CH_2Cl_2 in a moderate excess (3.1 equivalents) at 0–20 °C after ca. 70% conversion, 42% of trioxides **9/10** could be chromatographically separated from small quantities (4–6%) of dioxides **5–7** and tetroxide **11**. Separation of **9/10** through fractional crystallization or chromatography was not possible. Tetroxide **11** was quantitatively obtained under somewhat more forcing conditions (13 equivalents of oxidant) and was crystallized from water. So far, the thin plates of **11** also obtained from other solvents (MeOH, CF_3CO_2H, CH_3NO_2), have proved to be unsuitable for X-ray structural analysis. Upon heating (m.p. >320 °C) no equilibration with deeply colored nitroso compounds was noted.

When solutions of **2** (Scheme 2, λ_{max} [nm], ε) in CH_2Cl_2 were "titrated" with dimethyldioxirane (DMDO),[17] momentarily and exclusively "DBO monoxide" **13** was formed (TLC, ^{1}H NMR, 100% isolated as colorless crystals). It took hours to achieve the latter's total conversion into a mixture of the *syn*- and *anti*-bis(monoxides) **14/15** (their ratio of 1.0:3.9 does not express the relative thermodynamic stability); correspondingly, with the sterically less de-



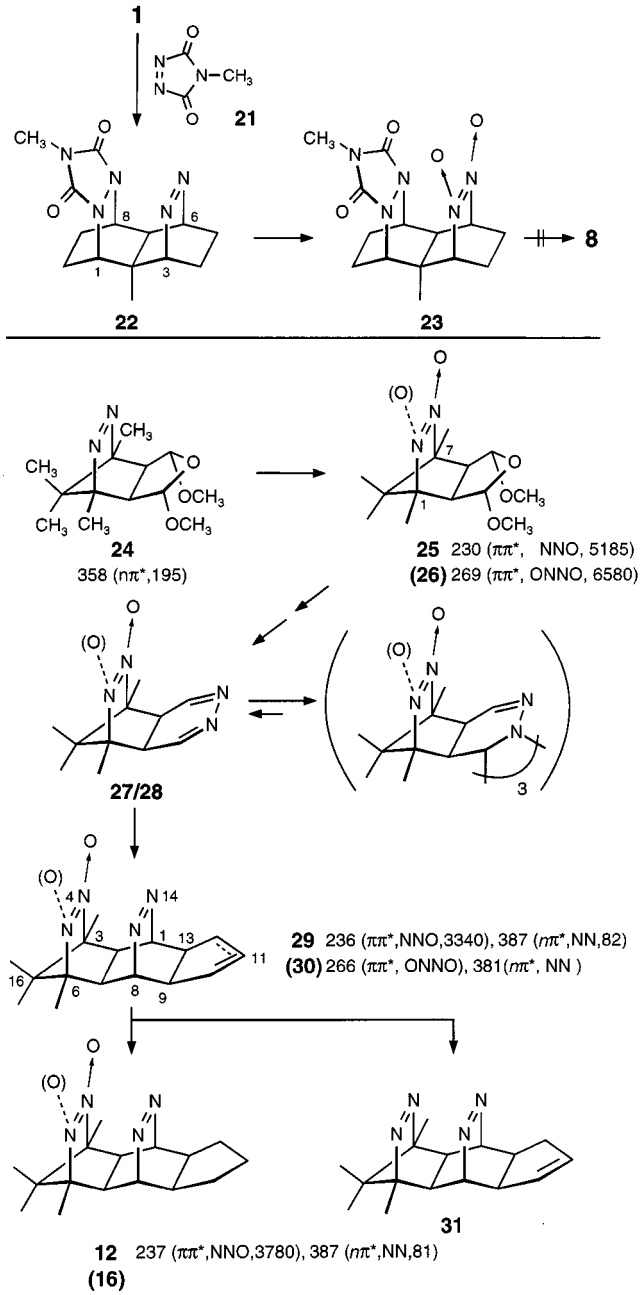
Scheme 2

manding *m*-CPBA preferably used for larger scale preparations, the ratio changed to 1.0:2.2, again with no trace of diazene dioxides (**16/17**) being present. Of the mixture of colorless crystals, m.p. >320 °C, 10–15 mg are soluble in 1 mL CH_3OH or CH_3CN. Separation through HPLC or fractional crystallization was once again not possible. Pure *anti*-isomer **15** could, however, be secured by taking advantage that in the subsequent oxidation, the *syn*-isomer **14** was more rapidly consumed. Following an unoptimized protocol for the highly polar, hardly soluble and hence difficult to handle trioxides **18/19** (trying to avoid an inseparable mixture with even less soluble tetroxide **20**) the mixture of **2** and a very large excess of DMDO (165 equivalents) was kept for a long period of time at room temperature (14 d). Through a sequence of extraction and chromatography, ca. 40% of a 1.0:8.5 mixture of **18/19** was separated from ca. 50% of **15**. Repeated HPLC provided some pure **19** and a highly enriched sample of **18** (ca. 80% of a microcrystalline solid, m.p. >320 °C, solubility ca. 5–6 mg mL^{-1} of CH_3CN). Tetroxide **20** was quantitatively produced after exposure of the mixture **14/15** to a large excess of $CF_3CO_3H/CH_2Cl_2/CF_3CO_2H$ at room temperature for 1–2 days. The microcrystalline **20** is only sparingly (< 1 mg mL^{-1}) soluble in CH_3CN or MeOH and somewhat better only in CF_3CO_2H (ca. 20 mg mL^{-1}). As noted for **11**, no melting and particularly no coloration due to nitroso isomers took place upon heating up to 320 °C.

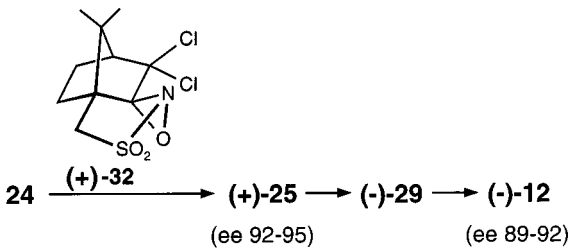
The N=N/ON=NO and N=N/N=NO substrates **8** (**16**) and **12**, the latter in optically active form, were desired for the mechanistic argument (vide infra) but belonged to the class of oxides not accessible along Scheme 1 and Scheme 2. For their preparation, the routes pictured in Scheme 3 and Scheme 4 (λ_{max} [nm], ε) were explored.

For **8**, a convenient access was seen in the protection of one N=N unit of **1** in form of **22** (conveniently obtained from **1** and triazolinedione **21**), oxidation to diazene dioxide **23** and oxidative saponification. Yet, after efficient realization of the first two steps, the route came to an end when the urazole ring of **23**, contrary to that of **22**, even under very forcing conditions proved resistant to all saponification methods successfully applied before to such sterically demanding cases.[18] For monoxide **12** and dioxide **16**, the DBH oxidation was effected in **24**, the latter was available as an early intermediate in the synthesis of parent **2** (Scheme 1 in ref.[1]). Monoxide **25** (98%) and dioxide **26** (90%, 100 mg scale) were then introduced into the original sequence consisting of hydrolysis, condensation with hydrazine (**27**, **28** present as trimers), and then with cyclopentadiene. After some modifications of the original protocol as necessitated by the retarding effect due to the *N*-oxidation, the overall yields achieved for **29** (72–73%) and **30** (25%) were in the expected range. In the saturation of the cyclopentene rings of **29** and **30** to give **12** and **16**, it was unavoidable, as en route to **2**, that catalytic hydrogenation (Pd/C, 10%) as well as reduction with diimide were accompanied not only by partial saturation of the N=N double bond, readily reversed by air oxidation, but also by partial deoxygenation (i.a. **2**, **31**), particularly in case of dioxide **30**. Thus, after chromatographic workup and crystallization only of monoxide **12** a pure sample (53–66%) was available.

For optically active **12** (Scheme 4), after futile efforts to oxidize **24** enantioselectively by making use of Sharpless[19] and Jacobsen[20] methods, with percamphanic acid according to Greene/Hecht[21] or the chiral oxaziridine (+)-**32** (Davies),[22] the application of high pressure to the reaction of **24** with **(+)-32** provided the solution. Chiral oxide **25** was isolated with up to 95% *ee*. For practical reasons (corrosion of the high pressure cell after potential lesion of the teflon tube) the g-scale preparations were performed in ethyl acetate with 65% yield and 92–95% *ee* (Chiracell AD, 2-propanol/*n*-hexane 1:9). The absolute configuration of (+)-**25** (1*R*) predicted on the basis of the known absolute configuration of (+)-**32**, was established by CD measurements (see Experimental Section). After transformation to (–)-**12**, the optical purity could not be reliably determined by HPLC, but supported by the *ee* value for the ultimately



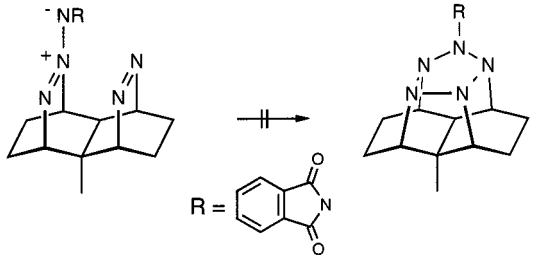
Scheme 3



Scheme 4

analyzed (–)-**38** (89–92% *ee*, Scheme 8), preservation of the optical purity (92–95% *ee*) could be assumed.

The predictions with respect to the intervention of dipolar cycloadditions in N=N/N=NO and ON=N/N=NO systems were fully confirmed. Of the monoxides, neither **3**/**4** nor the more proximate **12** and **13** showed any tendency for cycloaddition. With the latter pair, a fleeting oxatetrazolidine intermediate would have been recognized through their equilibration. A DSC experiment with **13** only demonstrated the exothermic extrusion of N_2 above the melting point, (to give **39**, Scheme 6). For isomer **12**, no defined DSC signal was recorded up to 280 °C (decomposition). Cycloaddition could not be catalyzed: Heating of **12** in CF_3CO_2H up to 120 °C had no effect at all, while heating of **13** caused neat [4+2]cycloreversion (MS). Similarly, for none of the *anti*-(bismonoxides) (**7**, **15**) was [3+3]cycloaddition noted. It can also be noted that an imine derivative of **1** – again contrasting the azimine/ene → 1,2,3-triazolidine addition[2] – did not cyclize to the respective pentazolidine.[5]



As a standard qualitative test for homoconjugational interaction between the N=N, N=NO and ON=NO chromophores in their various combinations, the UV/Vis absorptions[23] of the newly prepared bichromophoric compounds were compared with those of parent DBO (376 nm, CH_3CN), DBH (341 nm, CH_3CN) and their oxides [DBO-O (230 nm, CH_3CN), DBH-O (228 nm, CH_3CN)]. The n → π^*_{NN} maxima (CH_3CN) of the monoxides **3**/**4** are bathochromically shifted by 12 nm, those of **12** by 11 nm, and those of **13** by 27 nm (9 nm relative to **24**). The π → π^*_{NNO} maxima of **3**/**4** are shifted by 11 nm, those of **12** by 9 nm, and those of **13** by 16 nm (9 nm relative to **24**). In the N=NO/N=NO substrates (**5**/**6**,**7**; **14**,**15**), however, the π → π^*_{NNO} maxima are pretty much those of the reference compounds, and if at all, are only slightly blueshifted for the *anti*-isomers (**7**,**15**). For the trioxides (**9**/**10**); (**19**/**18**), the bathochromic shift for the π → π^*_{NNO} transition amounts again to 10(12) nm. The π → π^*_{ONNO} transition is shifted by 9(17) nm relative to DBO-O_2/DBH-O_2 (267/266 nm, CH_3CN). For both tetroxides **12** and **20**, the lowest HOMO → LUMO transitions are of low intensity due to poor spatial overlap and are covered by the intensive HOMO → LUMO+1 transitions expected in a region comparable to the absorption of the undisturbed ON=NO transitions.

All new compounds presented in this section were characterized by spectral data (IR, ^1H, ^{13}C NMR, UV, MS)[24] and, in part, by elemental analysis or HRMS. The individual ^1H and ^{13}C NMR assignments have been corroborated by comparison with the data of DBH and DBO (Table 1 in ref.[2]), if necessary, by homo/hetero decoupling and NOE experiments, in a few cases by making resort to the

calculated data. The PMSE-GIAO/B3LYP/6–3lG* ^{13}C shifts are generally in very good agreement with the experimental ones. This point is emphasized with the analyses of **15** and **51** pictured in Figure 1. Characteristic MS (CI) fragmentation patterns such as [4$^+$+2] cycloreversions were e.g. helpful in the differentiation of **12** and **13**, with intensive signals for 4*H*-tetramethylpyrazole or its oxide.

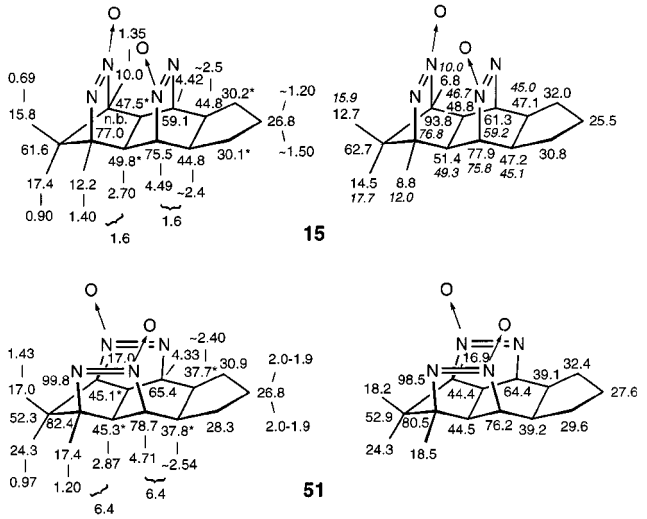


Figure 1. ^1H and ^{13}C NMR shifts (CD_3CN, δ) and vicinal coupling constants (Hz) for *anti*-bis(diazene oxides) **15** and **51** (left), calculated ^{13}C shifts (B3LYP/6–31G*; PMSE-GIAO/B3LYP/6–31G*) (right)

In spite of the high confidence into the DFT-calculated structural details (see Table 1), an experimental check was highly desired, particularly for the trioxides and tetroxides. After all, it was for the latter that one- and two-electron oxidation was predicted to cause significant positional reorientations, even dramatic ones for the oxygen atoms.[2] Up to now, though, only for the diazenedioxide **26** could suitable crystals for an X-ray structural analysis be obtained from CHC_3.[25] For **26** as well as its parent diazene (**18**, in Scheme 2 of ref.[1]) there is generally good agreement with the B3LYP/6–31G* data (Figure 2) and with the known structure of DBH dioxide.[26] The elongation of the methyl-substituted, strained C-1(7)/C-10 bonds by 0.030 Å points to a slight buttressing effect. In the crystal, the symmetry is reduced from $P2_1/m$ to $P2_1/n$; in the unit cell with four molecules, the packing is governed by short CH–O and CH–ONNO distances as had been observed for the DBH-/DBO oxides.[26][27]

Photochemistry[28]

Of the bichromophoric combinations presented in Scheme 1 and Scheme 2, all have been made part of the photochemical study – except the unavailable N=N/ON=NO systems (**8**,**16**,**17**). Given the minimal perturbation caused by the methyl substituent, the utilization of the mixtures **3/4** and **5/6** meant complications in the reaction control, but no detraction from the desired information. The light sources were those used in the two preceeding papers: 150-W Hg high pressure lamp, Hanau TQ 150, solidex filter

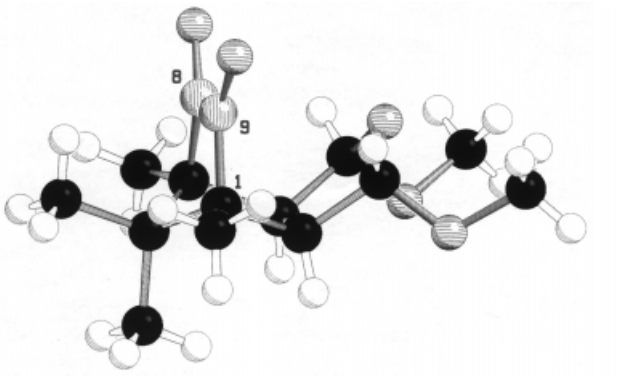
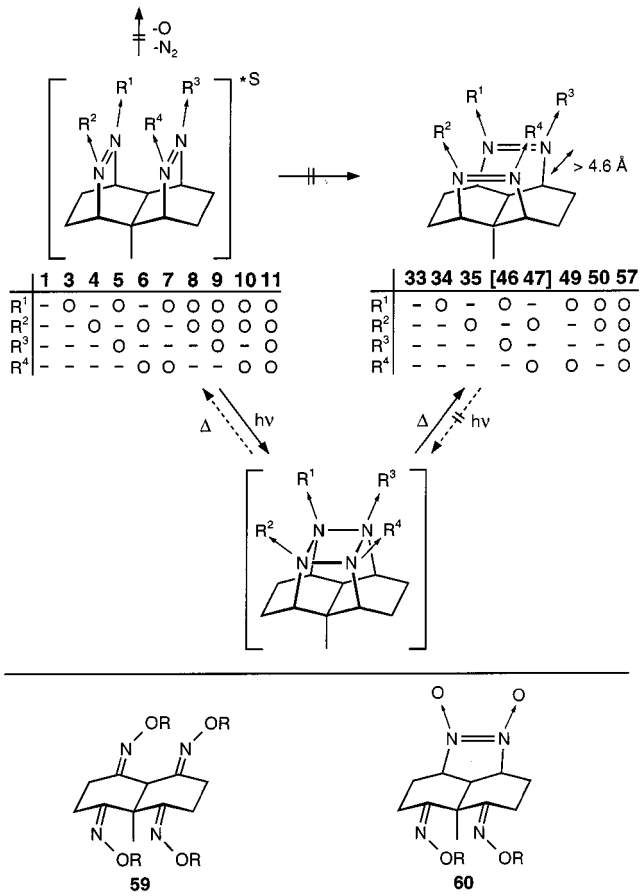


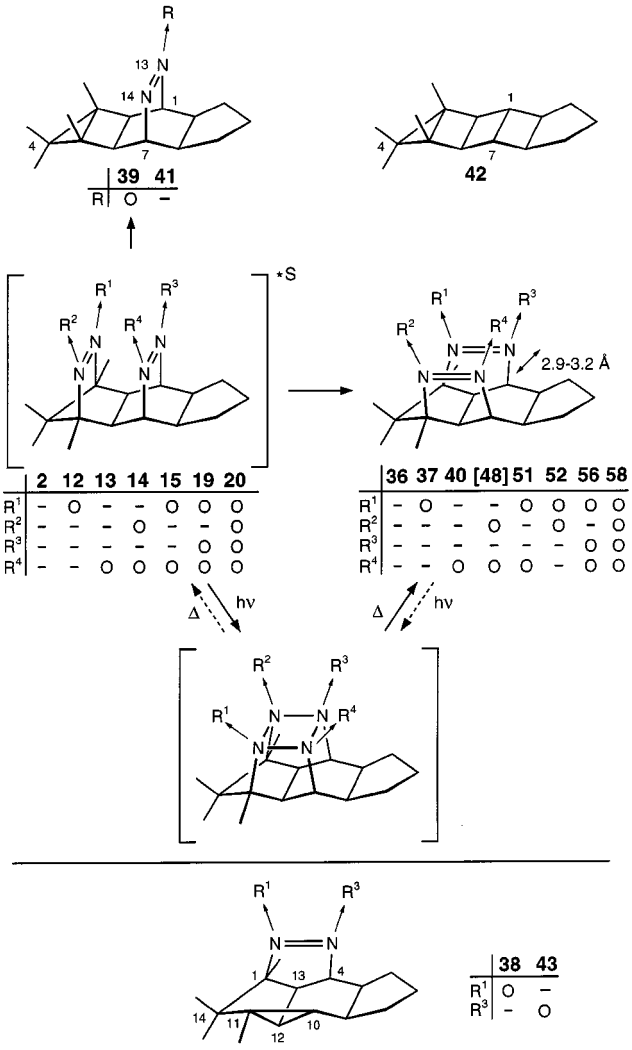
Figure 2. X-ray crystal structure analysis of diazene dioxide **26** (selected bond lengths and transannular distances, Å, in brackets the B3LYP/6–31G* data): N8–N9 1.304 (1.316), N8···CH_{3s} 2.838 (2.888), N9···CH_{3s} 2.841 (2.888), CH_{3s}···CH_{3s} 2.485 (2.489), CH_2–H_a···2-H 2.231 (2.244), CH_2–H_a···6-H 2.211 (2.244); for comparison selected distances are given for parent diazene of **26** (**18** in ref.[1]): N8–N9 1.2553 (1.249), N8···CH_{3s} 2.905 (2.927), N9···CH_{3s} 2.903 (2.927), CH_{3s}···CH_{3s} 2.478 (2.486), CH_2–H_a···2-H 2.313 (2.222), CH_2H_a···6-H 2.234 (2.222)

for the n → π^*_{NN}, 15-W Hanau TNN low pressure lamp, quartz filter for π → π^*_{NN}, π → π^*_{NNO}, and π → π^*_{ONNO} excitation. To recall, even n → π^*_{NN} excitation of bisdiazenes **1** and **2** had led to preferential loss of N_2,[1] and π → π^*_{NNO}, excitation of the C=C/N=NO model substrates even at –60 °C led to metathesis isomerization, of a C=C/ON=NO substrate to a complex reaction pattern (presumably due to initial internal electron transfer),[2] and the quantum yields for $N_2O(N_2O_2)$ elimination upon irradiation of the DBH/DBO oxides with 254 nm light are practically zero (Table 1 in ref.[2]).

1. N=N/N=NO Systems (3/4, 12, 13; *cf. Entry 1, Table 1):* The monoxides **3/4** (Scheme 5) with their DBO/DBO-O subunits proved typically "reluctant": Irradiation of the original 1:1.3 mixture [λ_{max} = 388 nm ($n\pi^*_{NN}$), 241 ($\pi\pi^*_{NNO}$), ε_{254} = 3450] as a ca. 10^{-2} molar CH_3CN solution with λ > 280 nm light had no effect at all. Even after irradiation for 2–4 days the substrates were quantitatively reisolated; they are obviously even more "reluctant" than DBO – in marked contrast to the DBO/DBO-bisdiazene **1**.[1] For the 254 nm light-induced albeit slow reaction, with very small (ca. 10%) conversions, the metathesis isomers **34/35** [$\lambda_{max}(\varepsilon)$ = 325 nm (320), 227 (7050)] remained the only products observed; by careful TLC and MS control, more than 2% of competitive loss of N_2 or deoxigenation (**1**) would have been detected. With increasing reaction time, secondary reactions became notable: deoxygenation of **34/35** to the common bisdiazene **33** [$\lambda_{max}(\varepsilon)$ = 325 nm (630)] and the latters relatively rapid transformation mainly to polymeric material (no cyclopropanoid component, cf. **38**) was observed. From runs taken to ca. 40, 60 and 100% conversion ca. 45, 20 and 14%, respectively of **34/35** (ratio 2.3:1, reactivity differences of the involved pairs of isomers is expected), 5 – 7% of **33** and ca. 15% of unidentified, less polar (deoxygenated) components (presumably derived mainly from **33**) were isolated besides polymers. In control experiments with "distant" **34/35** [$\lambda_{max}(\varepsilon)$ = 325 nm (320, 227 (7050)] deoxygenation (**33**) and N_2 elimination were es-



Scheme 5

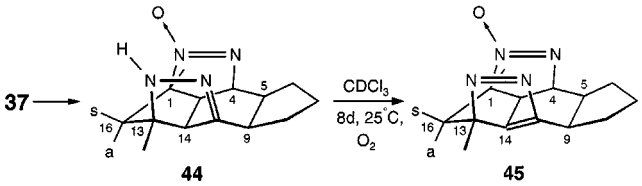


Scheme 6

tablished as parallel pathways; reformation of **3**/**4** was safely excluded (< 2%).

DBO/DBH-O substrate **12** (Scheme 6) [$\lambda_{max}(\varepsilon)$ = 387 nm (80), 237 (3800), CH_3CN] turned out to be as unreactive to >280 nm light as **3**/**4**, but when irradiated with 254 nm light with up to ca. 10% conversion, **12** neatly underwent metathesis to form **37** (TLC, ^1H NMR). With increasing irradiation time, the cyclopropane/diazene oxide **38** and deoxygenated components appeared as secondary products. Bisdiazene **36** was only isolated in trace amounts, if at all. On a preparative scale (ca. 0.1 mmol), irradiation was stopped after ca. 30% conversion, the substrate separated and irradiated again. After three such cycles (88% conversion) 51% of **37** [$\lambda_{max}(\varepsilon)$ = 346 nm (170), 239 (5500), 202 (3200), CH_3CN] and 20% of **38** [$\lambda_{max}(\varepsilon)$ = 232 nm (5400), CH_3CN] could be isolated in the form of colorless crystals. In the control experiment with "proximate" **37**, not even traces of **12** were found: deazatization to **38** proved faster than deoxygenation to **36**. Isomer **13** with its DBH subunit [$\lambda_{max}(\varepsilon)$ = 367 nm (370), 246 (3600), CH_3CN], contrary to **12**, reacted to the λ >280 nm light by rapid and selective N_2 elimination to give pentacyclic **39**. Even during 254 nm irradiation, photometathesis to **40** evolved only into a minor pathway: After ca. 75% conversion, the ratio of elimination:metathesis amounted to ca. 4:1. Besides small amounts of polymers, 49% of **39**, 2–4% of **40** as primary photoproducts, ca. 7% of **41**, a trace of **42** and 10% of **43** as secondary products (^1H NMR) were observed. Through TLC and HPLC, samples of pure crystalline **39** [$\lambda_{max}(\varepsilon)$ = 235 nm (4700)] and of highly enriched **40** (λ_{max} = 238, 343 nm) were collected. The other components were identified as mixtures by spectral comparison. Analogously to **37**, **40** (254 nm light) underwent elimination of N_2 (**43**) much faster than deoxygenation (**36**) and, of particular relevance, no reversion to **13**.

In the context of the "*anti*-Bredt protection" of bisdiazenes (bisdiazene oxides) of type **A**(**K**) and **C**(**M**), it is remarkable that **37**, on standing in $CDCl_3$ solution (^1H NMR), slowly isomerized into hydrazone **44** which itself, with partial decomposition in the presence of oxygen (air), transformed into (presumably) 3*H*-pyrazole **45**.

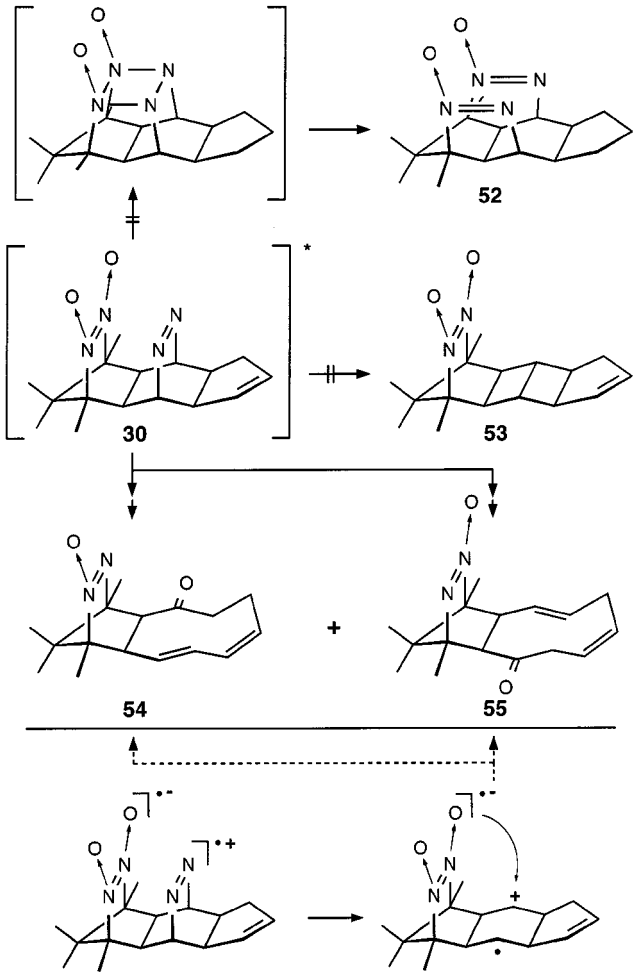


***2. syn-N=NO/N=NO Systems (5/6;14** – cf. Entry 2, Table 1):* For *syn*-monoxides **5/6** (Scheme) [$\lambda_{max}(\varepsilon)$ = 232 nm (11700)], in an analytical experiment (254 nm, CH_3OH) performed with the mg-batches of pure material available (as a ca. 1:1 mixture), as well as in preparative runs with the original mixture of **5/6/7** (2.3 mmol, ratio 8:24:68), no metathesis (<2% of **46/47**), but only slow deoxygenation (**3**,**4**) and generation of polymers was noted (TLC, ^{1}H NMR). Analogously, in experiments with **14** (Scheme 5) analyzed at several intervals, there was no sign for metathesis (< 2% of **48**). Slow deoxygenation delivered **12/13** and ultimately traces of **37/40** besides polymers.

***3. anti-ON=N/N=NO Systems (7, 15;** cf. Entry 3, Table 1): anti*-Bis(monoxide) **7** [$\lambda_{max}(\varepsilon)$ = 225 nm (16200); ε_{254} = 2100] (Scheme 5), only studied on a mg-scale, differed from the *syn*-isomers **5/6** in that metathesis did occur (**49**). Bis(monoxide) **7** also differed from the monoxides **3/4** in that metathesis was accompanied by deoxygenation. As a secondary product of **49**, the C_s-isomer **50** appeared, both being slowly deoxygenated to **34/35**. Like **7**, *anti*-dioxide **15** (Scheme 6), studied on a larger scale as a 1:1 mixture with **14** [λ_{max} (ε) = 228 nm (9920)], primarily underwent metathesis to 2,11-dioxide **51** and only to a minor extent deoxygenation of the DBO part (**14** remained unchanged). For an experiment stopped after ca. 50% conversion, the ^{1}H NMR analysis showed in total 80% metathesis (29–31% of **51**, 1–2% of 1,12-dioxide **52**, 4–7% of **37** and traces of **12**). Repeated HPLC separations provided crystalline **51** for full spectral characterization. Independently, monoxide **37** was oxidized with DMDO to give a 63:27 mixture of **51** and **52**. Of central importance, in the irradiation of "proximate" bis(diazene oxide) **51** [$d_{\pi,\pi}$ = 2.91/3.08 Å (calc.), 2.788/2.955 Å (exp., Figure 4) after total conversion, besides mainly **52** and **37** (and secondary products) up to 5% of original starting material **15** were firmly identified.

***4. N=N/ON=NO Systems** (cf. Entry 4, Table 1):* With neither **8** (from **1**) nor **16/17** (from **2**) at hand, explorative experiments were restricted to **30** as substitute for **16** (Scheme 7). There was no hint for metathesis: **30**, like **3/4**, and **12**, was unreactive towards light of λ >280 nm. With 254 nm light, only expulsion of N_2 took place (MS) – not, however, to give the pentacyclic diazenedioxide **53** (cf. **39**), but a mixture (1:1) of most probably tricyclic diazeneoxy ketones **54** and **55**, the results of N_2 elimination, O-migration and skeletal C–C cleavage. Electron transfer from the DBO- to the DBN-O_2 chromophore – cf. the behaviour of the related ON=NO/C=C system[2] – is assumed to be the initiating event.

***5. N=NO/ON=NO Systems** (9/1, 18, 19; cf. Entry 5, Table 1):* Because of the high oxidation potential of the N=NO unit, electron transfer as formulated above for **30** should not intervene. Of the trioxides **9/10**, **18** and **19**, only with the latter [$\lambda_{max}(\varepsilon)$ = 242 nm, 284, CH_3CN] ^{1}H NMR-controlled explorative experiments (CD_3CN) with 254 nm light were performed (Scheme 55% conversion, the metathesis isomer **56** made up 70–80% of the crude product mixture with polymers, but could only be isolated with severe losses before characterization by ^{1}H NMR and MS.



Scheme 7

***6. ON=NO/ON=NO Systems** (11, 20; cf. Entry 6, Table 1):* Analytical UV-controlled experiments (254 nm, ca. 10^{-4} M) with tetroxides **11** [Scheme 4, $\lambda_{max}(\varepsilon)$= 258 nm (13600), H_2O] and **20** (Scheme 5, λ_{max} = 262 nm, CH_3CN) showed only marginal differences between the absorption maxima of substrates and products, neatly expressed isosbestic points indicating nevertheless uniform transformations into tetroxides **57** (Figure 3) and **58**, respectively. Only **11** was sufficiently soluble in water for experiments under ^{1}H NMR control (5 mg mL^{-1}). Up to ca. 50% conversion, ca. 90% of **57**, and after total conversion (ca. 10 h) still ca. 70% of **57** (λ_{max} = 259 nm, H_2O) was present. More mobile tetroxide **57** proved to be stable in acidified aqueous solution, but in marked contrast to isomer **11**, was too base-sensitive to be isolated in pure form. During chromatographic workup at room temperature (silica gel, CH_3OH/H_2O, 10:1), and even during freeze-drying of the aqueous reaction solution, **57** was partially transformed along a complex sequence of ON=NO cleavages[29] and tautomerizations, via strongly UV active intermediates (e.g. **60**), mainly into the tetroxime **59**, which was once again unstable.

Like the photosubstrates, and with the help of their spectra, the photoproducts of Schemes 5–6 were spectroscop-

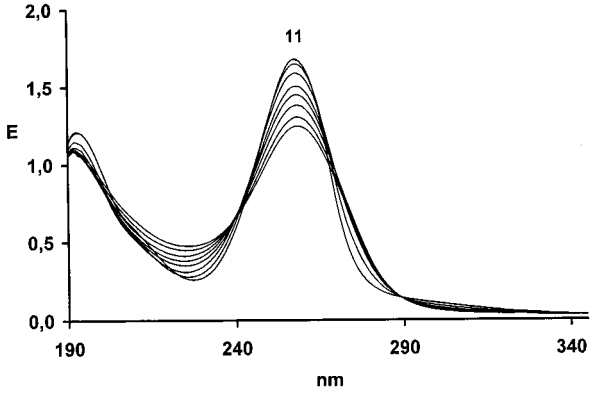


Figure 3. UV control of the reactions **11** → **57**

ically characterized (IR, ^{1}H, ^{13}C NMR, UV, MS). Some NMR assignments were made on the basis of the GIAO/B3LYP/6–31G* calculations. For example the C_s-2,12-dioxide **51** was distinguished from its C_s-3,11-isomer by making recourse to the calculated shifts, e.g. δ_{C-4} = 65.5 (exp.) versus 65.4 (calcd., **51**) and 76.8 (calcd.). Nicely reflected is the exchange of the highly strained DBN/DBO chromophores by the relatively unstrained pyrazoline rings as parts of more flexible "open" (Scheme 5) and rigid "closed" (Scheme 6) frameworks. The NMR anisotropy effects exerted by the chromophoric units, and the tendency for [4+2]cycloreversions (MS) typical for the starting materials, are no longer evident. A prototypical NMR analysis (**51**) is given in Figure 1. Tetroxime **60** is not totally, but reliably characterized by ^{13}C NMR signals at δ = 160.0/157.4, IR signals at 3400 (OH), 1644 (C=N), 968 cm^{-1} (NO), and the MS fragmentation pattern.

An X-ray structural analysis performed with crystals of *anti*-bis(monoxide) **51** (Figure 4, R = 4.7), though disordered due to spontaneous not total resolution during crystallisation from methanol (85:15, *ee* = 59), confirmed a "closed" conformation, with an averaged transannular π,π distance (2.871 Å) close to that of **1a** (av. 2.849 Å) and **2** (2.822 Å), primarily due to the annelated cyclopentane ring.

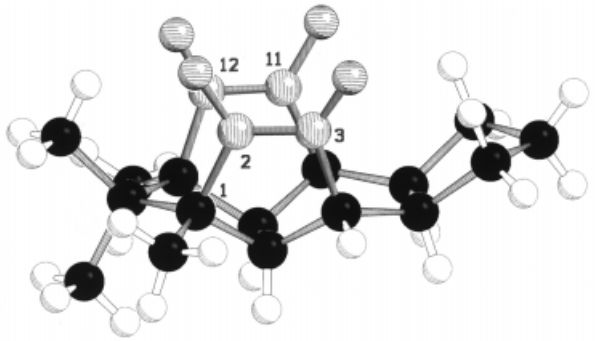
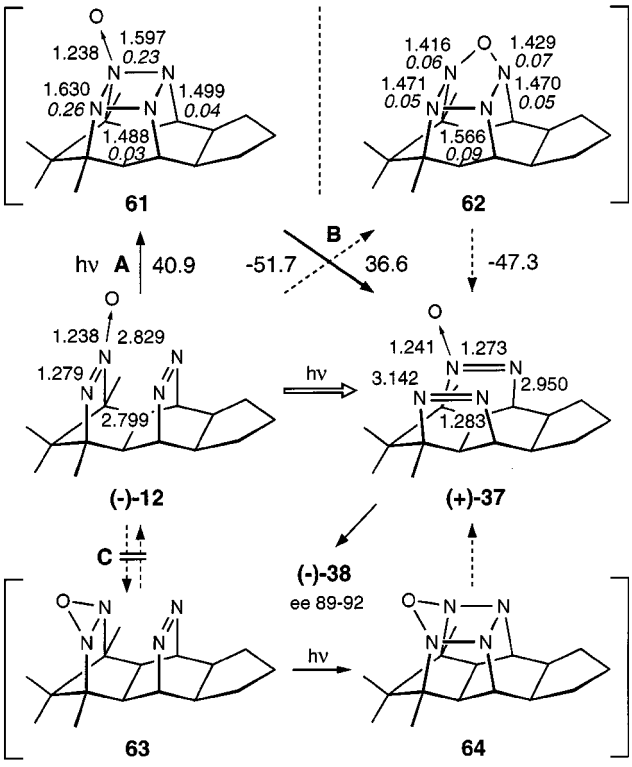


Figure 4. X-ray crystal structure analysis of metathesis *anti*-bis(diazene oxide) **51** (selected bond lengths and transannular distances, Å): N2–N3 1.263(3), N2–O 1.11(2), N11–N12 1.266(3) [N12 – O 1.246(3)], N2–N12 2.788, N11–O 1.112(9), N3···N11 2.955 [N3–O 1.238(3)]

Mechanistic Aspects

For the metathesis of the N=N/N=NO system **12** (Scheme 6), the tetrazetidine oxide (**61**) had been formulated as intermediate (route **A**, Scheme 8). An alternative[3][4] to this [2+2]cycloaddition discussed earlier, was [3+2]cycloaddition to the oxatetrazolidine **62** (route **B**); clearly, the transformation **62** → **37** would need a rather complicated multistep procedure, hardly in line with the selectivity in product formation. For the analogous N=NO/C=C photometathesis, the thermally accessible oxadiazolidine was unequivocally excluded as intermediate. A third alternative to be considered (route **C**) involves cyclization to C_s-symmetrical oxaziridine **63**, [2_π+2_σ]photocycloaddition (C_s-**64**), and [3+2]cycloreversion. In fact, efficient diazene oxide → oxadiaziridine cyclizations had been observed in structurally related systems,[9][10][28][30] and for the subsequent photostep, there are also a number of related examples.[14][31]

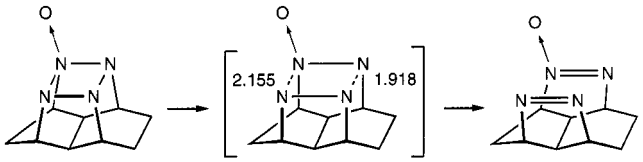


Scheme 8

For the distinction of the routes **A** and **C**, the highly optically enriched (–)-**12** had been prepared (Scheme 4). After its irradiation up to various degrees of conversion, quantitative HPLC separation of the enantiomers **37** proved impossible and NMR methods for the determination of optical purity were not applicable to **37** because of its instability (tautomerization). The *ee* determination was postponed to the secondary photoproduct **38**; *ee* values of 89–92% for samples of (–)-**38** neatly separated by HPLC from photolysis mixtures or from samples independently prepared from isolated (+)-**37**, allow for route **C** to be safely

excluded. A fast equilibration **12** ⇄ **63** is dismissed by the retention of optical purity in reisolated (–)-**12**.

In cooperation with G. Maier and H.-P. Reisenauer (Giessen), samples of **12** in argon matrices (12 K) were irradiated (>310, 254 nm light) under IR control.[32] For the transformation into **61**, the DFT calculations (B3LYP/6–21G*, scaling factor for IR frequencies = 0.963[33]) had predicted the replacement of the intensive valence vibration of **12** (1533 cm^{-1}, exp.) by an intensive N=NO (**37**, 1560 cm^{-1}) or intensive N–O vibration (**61**, 1431 cm^{-1}); for **62** no such intensive absorption was calculated. As in the solution experiments, light of $\lambda > 310$ nm had no effect, whilst 254 nm light caused rapid conversion (66% within 30 min). Yet, the new N=NO band observed at 1524 cm^{-1}, reduced to 42% of its intensity only after 40 h of irradiation time, is not that of **61**. In a separate experiment with matrix-isolated **37**, the strong N=NO band at 1527 cm^{-1} was totally replaced within 15 min – again by the ominous 1524 cm^{-1} band. Irradiation (254 nm) of **12** in a EtOH/Et_2O glass (2:1, 77 K)[34] confirmed the formation first of **37**, then of **38**. Obviously, even at temperatures as low as 12 K, no intermediate between **12** and its metathesis isomer **37** is observable. On the B3LYP/6–31G* level (Scheme 8), the essential points on the S_0-potential hypersurface have been calculated [reaction energies (kcal mol^{-1}), distances (Å), σ* occupancies]. Particularly for tetrazetidine oxide **61** and oxatetrazolidine **62**, an essential discrepancy is disclosed. For **62** a very long NN–NN bond (1.566 Å) points to [3+2]cycloreversion to **12(13),** in **61** the longer of the two very long N–N bonds geminal to the NO bond imposes a distortion towards **37**. For the calculationally less demanding parent DBH-O/DBO case (Entry 2, Table 2) with its nearly identical geometrical changes, a transition state for the opening of the tetrazetidine oxide could be localized ($\tilde{\nu}_{imag} = -1736$ cm^{-1}, $E_a = 23.3$ kcal mol^{-1}) featuring effective participation of N and O lone pairs and distances of 2.155 and 1.918 Å for the N–N bonds to be broken. Such a transition structure with exactly one eigenfrequency on the B3LYP-6–31G* hypersurface is suggestive of a continuously transforming wavefunction in this section of the ground state hypersurface – then the cleavage **61** → **37** would not be a symmetry forbidden [2+2]cycloreversion.



In preliminary mechanistic scenarios, awaiting support from photophysical measurements and more detailed calculations (CASSCF), the tetrazetidine oxide **61** appears as a vibrationally excited transient which, due to the low activation barrier even at 12 K, rapidly transforms into **37**. The generally slow product formation, however, suggests that thermal reversion of the transient tetrazetidine oxide back to **12** is occurring – as experimentally verified for **51** (→ **15**).

Summary and Outlook

Four of the six N=N/N=NO/ON=NO combinations **K** listed in Table 1 (Entries 1, 3, 5, 6) selectively undergo metathesis isomerization upon direct excitation (254 nm). Under preparative aspects there are limitations, though, due to relatively rapid secondary photochemical (N=N/N=NO) or chemical (ON=N(O)/ON=NO) reactions.[35] No photophysical data are available yet, but a good amount of experimental as well as calculation evidence justifies the conclusion that, as formulated in Scheme 5, Scheme 6 and Scheme 8, [2+2]photocycloaddition in these four bichromophoric combinations does occur, but that the respective *N*-oxidized tetrazetidines function as vibrationally excited transients which even at temperatures as low as 12 K very rapidly undergo $2\sigma \rightarrow 2\pi$ cleavage. Particularly the response of the N=N/N=NO substrates [for which cycloaddition is the dominant pathway when the N=N double bond is part of the DBO substructure (**3/4**, **13**), and still a minor pathway when the N=N double bond is part of the DBH substructure (**12**)], lends credit to the postulate made in the preceeding paper, that N=N/N=N → tetrazetidine photocycloaddition in the parent bisdiazenes **1** and **2** should have become observable through metathesis isomerization.[1] The lack of metathesis products in the irradiation of the *syn*-N=NO/N=NO substrates **5/6** and **14** (cf. the length of the formed ON–NO bond of 1.828 Å, Entry 2) can be accounted for by the facile reversion of the photocycloaddition rather than unfavorable dipole/dipole interactions. Thermal reversion of the [2+2]photocycloaddition, a potentially general, nonproductive competition to metathesis cleavage, could be experimentally confirmed for a relatively "proximate" N=NO/N=NO metathesis substrate (**51**). In the exceptional ON=NO/N=N combination (**30**, Scheme 7, cf. Entry 4), as in case of the ON=NO/C=C model compound,[2] it is assumed that internal electron transfer from the N=N to the ON=NO unit initiates complex molecular transformations which are not understood in detail. Still, the question remains to be answered why in the N=N/C=C and N=N/N=NO, but not, however, in the N=N/N=N bichromophoric combinations (embedded in geometrically analogous molecular corsets), [2+2]photocycloaddition wins over, or at least can compete with, N_2 elimination.[36] Non-concerted reaction pathways[37] for **1** and **2**, with the intervention of tetrazane-type 1,4-diradicals featuring costly in-line fixation of the four *n*-electron pairs (•NR-NR-NR-NR•) which undergo *retro*-(2,3)-NR,NR cleavage rather than 1,4-cyclization is just one of the mechanistic speculations.[38]

The work detailed in this series of three papers had been originated by the search for N=N/N=N photocycloadditions when not a single such example could be found. The usefulness of the specifically constructed substrates for a novel and successful project is highly appreciated. In fact,

it was the access to more or less proximate N=N/C=C, N=N/N=N systems and their *N*-oxides that catalyzed our recent study of homoconjugate ππ-interactions after one- or two-electron reductions and oxidations. For us this meant a continuation of a prominent precedent: The oxidation of similarly preoriented C=C/C=C substrates (pagodadienes, dodecahedradienes) to *in-plane* delocalized 4C/3e radical cations and σ-bishomoaromatic 4C/2e dications.[39] As recently reported, the same type of nonclassical bonding was ascertained for 4N/5e radical anions and 4N/6e dianions,[39] simply by addition of electrons to the bisdiazenes **1** and **2**. After the protection of **1** and **2** in form of their tetra-*N*-oxides **11/12**, one- or two-electron oxidation led to cations with presumably highly intriguing cubic electron delocalization (4N4O/11e; 4N4O/10e).[40] With the availability of the conformationally immobilized *cis*-peralkylated tetrazolidines and perhydro-1,2,4,5-tetrazines (cf. **36**, **44**; **39**, **47** in ref.[1]) additional bonding features in this family of 4N-ions could be uncovered.[41] After repeated failures with the photocycloaddition approach, finally some isolated "N_4-heterocycles"!

Experimental Section

General: 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, and if necessary by GIAO/B3LYP/6–31G* calculations. – Mass spectra were run on a Finnigan MAT 44S spectrometer (EI, 70 eV, unless specified differently). – 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.

(±)-(1*R,2*S**,3*S**)-2-Methyltetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-tetradeca-4,9-diene 5-Oxide (3) and 4-Oxide (4) (Mixture of Isomers), (1*R**,2*S**,3*S**)-2-Methyl-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene 5,9-Dioxide (5), ... 4,10-Dioxide (6), and ... 4,9-Dioxide (7) (Mixture of Isomers):** To a solution of **1** (0.5 g, 2.45 mmol) in CH_2Cl_2 (10 mL) at 0 °C, a solution of *m*-CPBA (0.5 g, 2.32–2.60 mmol, 80–90%) in CH_2Cl_2 (20 mL) was added dropwise (TLC control). After ca. one third of the solution had been added, a white precipitate was formed, which did not disappear while the reaction proceeded. After addition of phosphate buffer solution (pH 7.5, 0.2 M equiv. KH_2PO_4, 31 mL, 0.2 M Na_2HPO_4, 69 mL, water, 100 mL) it was stirred for 1 h at room temp. Any remaining peracid was destroyed by the addition of 2 M aq. $Na_2S_2O_5$ (KI/starch). Na_2CO_3 was added until pH 9 and the organic layer was separated and dried over $MgSO_4$. After concentration in vacuo chromatographic workup ($CHCl_3$/CH_3OH) yielded **1** (R_f = 0.47, 80 mg, 16%), **3/4** (mixture of isomers, 1:1.3, ^{1}H NMR, assignment interchangeable, R_f = 0.38, 315 mg, 70% based on conversion), and **5/6/7** (mixture of isomers, 1:1:1, ^{1}H NMR, R_f = 0.23, 90 mg, 19% based on conversion). By preparative HPLC (silica gel Merck Si 100, CH_3CN, 15 mL/min) after several runs, small amounts (50 mg) of **7** (retention vol. 120 mL) could be separated from **5/6** (retention vol. 135 mL). – **3/4 (Mixture of Isomers):** M.p. 250–252 °C. – IR (KBr): ṽ = i.a. 1505 cm^{-1} (N=NO). – UV (CH_3OH): λ_{max} (ε) = 388 nm (120), 241 (4980), ε_{254} = 3450. – ^{1}H NMR: δ = 2.20 (m_c, 7-, 11-, 12-, 13-, 14-H, total 18 H), 2.0–1.3, 1.00, 1.30 (s, CH_3, rel. intensity 1.3, 1.25 (s, CH_3, relative intensity 1.0); isomer of rel. intensity 1.0: δ = 5.31 (m, 1 H), 5.00 (pt, 1 H), 4.52 (m, 1 H), 4.18 (pt, 1 H); isomer of rel. intensity 1.3: δ = 5.22 (m, 1 H), 4.97 (pt, 1 H), 4.34 (m, 1 H), 4.15 (pt, 1 H). – $C_{11}H_{16}N_4O$ (220.2): calcd. C 59.98, H 7.32, N 25.43; found C 59.73, H 7.60, N 25.55. – **5/6 (Mixture of Isomers, 1*:3*):** Colorless crystals, m.p. >350 °C (CH_3OH). – IR (KBr): ṽ = i.a. 1510 cm^{-1} (N=NO). – UV (CH_3CN) λ_{max} (ε) = 232 nm (11700). – ^{1}H NMR: δ = 4.68 (str. d., *J* ≈ 4.0 Hz, 1-, 3-H, rel. int. 3)*, 4.56 (m, 1-, 3-H, rel. int. 1)**, 4.48 (m, 6-, 8-H, rel. int. 1)**, 4.25 (″t″, *J* ≈ 2.0 Hz, 6-, 8-H, rel. int. 3)*, 2.38–2.17, 2.15–1.95, 1.93–1.70, 1.68–1.52 (m, 9H), 1.43 (s, CH_3, rel. int. 3), 1.35 (s, CH_3, rel. int. 1). – ^{1}H NMR (CD_3OD): δ = 4.60 (str. d., *J* ≈ 4.0 Hz, 1-, 3-H, rel. int. 3)*, 4.49 (m, 1-, 3-H, rel. int. 1)**, 4.22 (″t″, *J* ≈ 2.0 Hz, 6-, 8-H, rel. int. 3)*, 2.41–2.24, 2.10–1.53, 1.51–1.36 (m, 9H), 1.43 (s, CH_3, rel. int. 3), 1.38 (s, CH_3, rel. int. 1); the signals of 6-, 8-H, rel. int. 1, are hidden by the solvent. – **Compound 7:** Colorless crystals, m.p. > 350 °C (CH_3OH). – IR (KBr): ṽ = i.a. 1470 cm^{-1} (N=NO). – UV (CH_3CN): λ_{max} (ε) = 225 nm (16200). – ^{1}H NMR: δ = 4.63 (m, 6-H)*, 4.53 (str. d., *J* = 4.5 Hz, 8-H)*, 4.37 (″t″, *J* = 2.0 Hz, 1-H)^2*, 4.32 (″t″, *J* = 2.0 Hz, 3-H)^2*, 2.33–2.17 (m, 11s, 14s-H), 2.01 (m, 12s-H)^3*, 1.97 (mc, 7-H), 1.92 (m, 13s-H)^3*, 1.86–1.70 (m, 11a^4*-, 12a-, 13a-H), 1.66 (m, 14a-H)^4*, 1.36 (s, CH_3).

7/5/6 (Mixture of Isomers): ^{1}H NMR ([D_6]DMSO): δ = 4.41 (m_c, total 6 H), 2.4–1.4 (m_c, total 27 H), 1.32 (s, CH_3), 1.27 (s, CH_3), 1.25 (s, CH_3) (all CH_3 groups of equal intensity). – **Mixture of 5/6:** δ = 4.34 (pt, 1 H, *J* = 2.0 Hz), 4.22 (pt, 2 H, *J* = 2.0 Hz). – **Compound 7:** δ = 4.53 (m, 1 H), 4.11 (pt, 1 H, *J* = 2.0 Hz). – $C_{11}H_{16}N_4O_2$ (236.3): calcd. C 55.92, H 6.83, N 23.71; found C 55.65, H 6.85, N 23.77.

(±)-(1*R,2*S**,3*S**)-2-Methyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-tetradeca-4,9-diene 4,5,9-Trioxide (9) and ... 4,5,10-Trioxide (10):** To a solution of **1** (273 mg, 1.34 mmol) in CH_2Cl_2 (9 mL), was added at 0 °C with stirring a solution of H_2O_2 (0.42 mL, 30% in H_2O, 4.1 mmol, 3.1 equiv.) and $(CF_3CO)_2O$ (3.1 mL) in CH_2Cl_2 (5 mL). After warming to room temp. over 12 h and removing of the volatile components in vacuo, the colorless residue was purified by chromatography over silica gel (2 × 20 cm) twice with CH_3OH/H_2O = 10:1, then with CH_3OH/H_2O = 10:3 to give dioxides (12 mg, 4%), trioxides (142 mg, 42%, ratio of isomers 1:1), and tetroxide (20 mg, 6%), all as colorless, microcrystalline solids. The trioxides are soluble in H_2O and CF_3COOH, only in traces in CH_3OH and CH_3CN. Purification by fractional precipitation or extraction (CH_3OH, CH_3OH/H_2O mixtures) was not possible. – **9/10 (1:1):** 142 mg (42%) colorless, microcrystalline powder, m.p. 320 °C (H_2O), R_f = 0.33 (CH_3OH/H_2O, 10:1; UV). – IR (KBr): ṽ = i.a. 1499, 1425 cm^{-1}. – UV (H_2O): λ_{max}(ε) = 276 nm (ππ*, ONNO, 2400), 240 (π → π*, NNO, 9400), 207 (580). – UV (CH_3CN): λ_{max}(ε_{rel}) = 283 nm (1), 240 (3.45), 200 (2.92); the solubility in CH_3CN is too low to determine reliable ε values. – ^{1}H NMR (D_2O, dioxane, 400 MHz): δ = 4.55 (dt, *J* = 4.55 Hz, *J* = 0.80 Hz, 1 H), 4.63–4.58 (m, 3 H), 4.51–4.46 (m, 3 H, superposed by HDO), 4.28 (t, *J* = 2.68 Hz, 1 H), 2.47–2.36 (m, 3 H), 2.34–2.25 (m, 2 H), 2.20–

2.12 (m, 1 H), 2.10–1.68 (m, 9 H), 1.65–1.46 (m, 2 H), 1.35–1.22 (m, 1 H), 1.24 (s, CH_3), 1.23 (s, CH_3). – ^{13}C NMR (D_2O/dioxane): δ = 78.5 (CH), 78.5 (CH), 78.1 (CH), 74.6 (CH), 74.5 (CH), 74.1 (CH), 66.0 (CH), 61.5 (CH), 48.5 (CH), 47.2 (CH), 42.6 (C), 41.2 (C), 24.6 (CH_2, 2 signals), 24.4 (CH_2), 23.9 (CH_3), 23.7 (CH_2), 23.1 (CH_3), 22.9 (CH_2), 22.2 (CH_2), 21.3 (CH_2), 21.0 (CH_2); calculated chemical shifts: – **Compound 9:** δ = 78.3 (C-1), 76.2 (C-3), 72.2 (C-6), 59.6 (C-8), 49.6 (C-7), 43.8 (C-2), 27.8 (C-14), 27.0 (C-12, C-13), 25.7 (C-11), 23.5 (2-CH_3). – **Compound 10:** δ = 76.6 (C-3), 73.9 (C-8), 71.8 (C-6), 64.0 (C-1), 50.9 (C-7), 42.6 (C-2), 27.6 (C-13), 26.7 (C-7), 26.0 (C-12), 25.2 (C-11), 24.9 (2-CH_3). – MS; *m/z* (%): 252 [M^+] (25), 253 [M^+ – OH] (9), 222 [M^+ – NO] (6), 192 [M^+ – 2 NO] (4), 191 [M^+ – 2 NO – H] (13), 160 (12), 145 (21), 131 (28), 117 (21), 99 (100). – HRMS: calcd. 252.122241; found 252.122292 (+0.2 ppm). – $C_{11}H_{16}N_4O_3$ (252.3).

(1*R,2*S**,3*S**)-2-Methyl-4,5,9,10-tetraazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]-tetradeca-4,9-diene 4,5,9,10-Tetroxide (11):** To a solution of **1** (124 mg, 0.304 mmol) in CH_2Cl_2 (4 mL), was added at 0 °C with stirring a solution of H_2O_2 (30%, 0.80 mL, 7.90 mmol, 13 equiv.) and $(CF_3CO)_2O$ (6.00 mL) in CH_2Cl_2 (8 mL). Warming to room temp. over 12 h and removal of the volatile components in vacuo, gave a colorless, microcrystalline, uniform (DC and ^{1}H NMR) residue (163 mg, 100%), which can be crystallized from H_2O or precipitated from H_2O with CH_3OH, m.p. > 320 °C (H_2O/CH_3OH), R_f = 0.14 (CH_3OH/H_2O = 10/1; UV). – IR (KBr): $\tilde{\nu}$ = i.a. 1490 cm^{-1}, 1427. – UV: (H_2O): $\lambda_{max}(\varepsilon)$ = 258 nm π → π*, ON=NO, 13600). – UV (CH_3CN): λ_{max} = 263 nm (ππ*, ON=NO).); the solubility in CH_3CN is too low to determine reliable ε values. – ^{1}H NMR: (D_2O/dioxane, 400 MHz): δ = 4.84 (ddd, 6-H, 8-H), 4.73 (dd, 1-H, 3-H), 2.64 (t, 7-H), 2.49 (dddd, 11a-H, 13a-H), 2.16–1.95 (m, 12s-H, 12a-H, 14s-H, 14a-H), 1.84 (dddd, 11s-H, 13s-H), 1.32 (s, 2-CH_3); $J_{1,11s} = J_{1,11a} = J_{3,13s} = J_{3,13a}$ = 2.8, $J_{6,7} = J_{6,14a} = J_{7,8} = J_{8,12a}$ = 1.7, $J_{6,14s} = J_{8,12s}$ = 4.3, $J_{11s,11a} = J_{13s,13a}$ = 15.0, $J_{11a,12a} = J_{13a,14a}$ =9.4, $J_{11a,12s} = J_{13a,14s}$ =3.5, $J_{11s,12s} = J_{13s,14s}$ = 11.5, $J_{11s,12a} = J_{13s,14a}$ = 6.6 Hz. – ^{13}C NMR (D_2O/dioxane): δ = 78.2 (C1, C3), 74.0 (C-6, C-8), 48.2 (C-7), 43.3 (C-2), 24.8 (C-12, C-14), 24.5 (C-11, C-13), 21.2 (2-CH_3). – MS; *m/z* (%): 268 [M^+] (18), 252 [M^+ – O] (22), 251 [M^+ – OH] (12), 238 [M^+ – NO] (13), 236 [M^+ – 2 NO] (33), 220 [M^+ – 2 NO – O] (15), 191 (65), 99 (100). – MS (CI, isobutane); *m/z* (%): 269 [M + H^+] (6), 253 [M – O + H^+] (100), 238 [M^+ – NO] (75), 222 (99). – HRMS: calcd. 268.117156; found 268.117241 (+0.3 ppm). – $C_{11}H_{16}N_4O_4$ (268.3).

(±)-(1*R,2*S**,3*R**,9*S**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-diene 14-Oxide (13):** A solution of **2** (100 mg, 0.37 mmol) in CH_2Cl_2 (50.0 mL) was titrated with a ca. 0.1 M solution of DMDO in acetone (TLC control, $CHCl_3$/CH_3OH, 10:1). The weakly UV-active starting material (R_f = 0.48, spontaneous coloration to brown with $CuCl_2$ solution) was oxidized immediately to the UV-active diazene oxide 13 (R_f = 0.43, no reaction with $CuCl_2$ solution at room temp.). Concentration in vacuo gave 13 as colorless crystals (100%), m.p. 265 °C ($CHCl_3$/Et_2O), R_f = 0.43 ($CHCl_3$/CH_3OH = 10/1). – IR (KBr): $\tilde{\nu}$ = i.a. 1500, 1467 cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 367 nm (370), 246 (3600). – ^{1}H NMR (400 MHz): δ = 4.50 (s, 1-H*), 4.40 (AB*X*, $J_{AX} = J_{BX}$ = 1.5 Hz, 8-H*), 2.27 (m, 9-H, 13-H), 2.23 (center of *AB*X, J_{AB} = 9.9 Hz, 2-H, 7-H), 3.65 (m, 10-H_a, 12-H_a), 1.70 (s, 3-CH_3**), 1.70 (m, hidden, 12-H_s***), 1.67 (s, 6-CH_3**), 1.58 (m, 10-H_s***), 1.44 (m, 11-H_a****), 1.32 (m, 11-H_s****), 0.83 (s, 16-CH_{3a}), 0.47 (s, 16-CH_{3s}). – ^{1}H NMR (CD_3CN, 400 MHz): δ = 4.38 (s, 1-H*), 4.29 (AB*X*, $J_{AX} = J_{BX}$ = 1.6 Hz, 8-H*), 2.39 (center of A*B*X, J_{AB} = 9.9 Hz, J_{BX} = 1.6 Hz, 2-H**), 2.32 (m, 9-H, 13-H), 2.28 (center of *A*BX, J_{AB} = 9.9 Hz, J_{AX} = 1.6 Hz, 7-H**) 1.78 (m, 10-H_a, 12-H_a), 1.62 (s, 3 H, 3-CH_3***), 1.58 (s, 6-CH_3***), 1.47 (m, 12-H_s****), 1.25 (m, 10-H_a, 11-H_s****), 1.11 (m, 11-H_s), 0.81 (s, 16-CH_{3a}), 0.39 (16-CH_{3s}). – ^{13}C NMR: δ = 88.6 (C-6), 88.4 (C-3), 74.0 (C-1), 60.5 (C-16), 58.1 (C-8), 46.0 (C-2), 45.4(C-7), 44.3 (C-13), 44.2 (C-9), 29.3 (C-10, C-12), 26.2 (C-11), 17.1 (16-CH_{3a}), 15.4 (16-CH_{3s}), 11.6 (6-CH_3), 11.4 (3-CH_3). Assignment secured by calculation. – MS; *m/z* (%): 245 (4) [M^+ –N_2 – CH_3], 230 (5) [M^+ – N_2–2 CH_3], 201 (4), 139 (100). – MS (CI); *m/z* (%): 413 (2) [M + tetramethyl-4*H*-pyrazole + H^+], 306 (100) [M + NH_4^+], 289 (13) [M + H^+], 273 (8) [M + H^+ – O], 261 (13) [M + H^+ – N_2], 125 (9) [tetramethyl-4*H*-pyrazole + H^+]. – $C_{16}H_{24}N_4O$ (288.4).

(±)-(1*R,2*S**,3*R**,9*S**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-diene 4,14-Dioxide (14) and ... 4,15-Dioxide (15):** To a solution of **2** (240 mg, 0.882 mmol) in CH_2Cl_2 (40 mL), was added a solution of DMDO (0.1 M in acetone, 60 mL, 6.0 mmol, 6.8 equiv.) and the mixture was stirred at 25 °C for ca. 2 h (TLC control). Removal of all volatile components in vacuo left a uniform product (TLC, ^{1}H NMR), which could be purified by chromatography over silica gel ($CHCl_3$/CH_3OH, 10:1). Colorless crystals (268 mg, 100%), mixture of isomers **14/15** (1.0:3.9, ^{1}H NMR, CD_3CN).

As an alternative, to a solution of **2** (240 mg, 0.882 mmol) in CH_2Cl_2 (40 mL), was added with stirring a solution of *m*-CPBA (346 mg, 80–90%, 1.764–1.985 mmol, 2.00–2.22 equiv.) in CH_2Cl_2 (80 mL). After 14 d at 25 °C, conversion was practically total. The organic phase was extracted with diluted K_2CO_3 solution (50 mL) and the aqueous phase was reextracted with CH_2Cl_2 (50 mL). The combined organic phases were dried (K_2CO_3), concentrated in vacuo, and purified by chromatography over silica gel ($CHCl_3$/CH_3OH, 10:1). 241 mg, 90%, mixture of isomers **14/15** (1.0:2.2, ^{1}H NMR, CD_3CN) was obtained. Attempts to separate the isomers by fractional crystallization or HPLC failed. Small amounts of pure **15** were obtained by oxidation of the mixture with DMDO. – **Mixture of 14/15:** M.p. > 330 °C (Precipitation from CH_3OH by addition of Et_2O up to a ratio CH_3OH/Et_2O, 1:6), R_f = 0.38 ($CHCl_3$/CH_3OH, 10:1; UV). – IR (KBr): $\tilde{\nu}$ = i.a. 1516 cm^{-1} (N=NO), 1500 (N=NO). – UV (CH_3CN, **14/15** = 1.0:3.9): λ_{max} (ε) = 228 nm (9917). – UV (CH_3CN, **14/15** = 1.0:1.0): λ_{max} (ε) = 228 nm (10602). – MS; *m/z* (%): 304 [M^+] (4), 288 [M^+ – O] (0.6), 274 [M^+ – NO] (17), 260 (5), 245 (5), 230 (9), 165 (8), 141 (38), 139 (95). – MS (CI); *m/z* (%) (isobutane): 343 [M + H^+ + isobutene – H_2O] (4), 305 [M + H^+] (100), 289 [M + H^+ – -O] (31), 273 [M + H^+ – 2 O] (7), 261 [M + H^+ – N_2O] (4), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (2), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (5). – $C_{16}H_{24}N_4O_2$ (304.40): calcd. C 63.13, H 7.94, N 18.40; found C 61.83, H 7.75, N 17.98. The substance has a high tendency for static electrification, the values observed deviate therefore systematically from the calculated ones (here C –2.1%, H -2.4%, N –2.3%). This problem was met with several probes. – **Compound 14:** ^{1}H NMR (CD_3OD, 400 MHz): δ = 4.56 (q, 1-H, 8-H), 2.92 (d*A*B, 2-H), 2.72 (dA*B*, 7-H), 2.66–2.59 (m, 9-H*), 2.55–2.47 (m, 13-H*), 1.95–1.78 (m, 10-H_a, 12-H_a), 1.59–1.50 (m, 11-H_a), 1.43 (s, 3-CH_3), 1.39 (s, 6-CH_3), 1.40–1.22 (m, 10-H_s, 11-H_s, 12-H_s), 1.06 (s, 16-CH_{3a}), 0.73 (s, 16-CH_{3s}); $J_{1,2} = J_{1.13} = J_{7,8} = J_{8,9}$ = 1.6, $J_{2,7}$ = 10.4 Hz. – ^{1}H NMR (CD_3CN, 400 MHz): δ = 4.46 (app. br. dd, 8-H), 4.43 (app. dd, 1-H), 2.70 (d*A*B, 2-H), 2.56 (dA*B*, 7-H), 2.56–2.47 (m, $J_{app.}$ = 8.3 Hz, 9-H*), 2.45–2.37 (m, 13-H*), 1.95–1.75 (m, 10-H_a, 12-H_a), 1.55–1.45 (m, 11-H_a), 1.37 (s, 6-CH_3), 1.31 (s, 3-CH_3), 1.35–1.25 (m, 10-H_s, 12-H_s), 1.25–1.12 (m, 11-H_s), 0.98 (s, 16-CH_{3a}), 0.67 (s, 16-CH_{3s}). – ^{1}H NMR (CD_3COCD_3, 400 MHz): δ = 4.45 (m, 2 H, 8-H), 2.88–2.86 (m, hidden, 2-H), 2.74–2.70 (m, hidden, 7-H), 2.67–2.58 (m, 9-H*), 2.54–2.46 (m, 13-H*), 1.87–1.73

(m, 10-H_a, 12-H_a), 1.55–1.46 (m, 11-H_a), 1.39 (s, 6-CH_3), 1.34 (s, 3-CH_3), 1.33–1.20 (m, 10-H_s, 11-H_s, 12-H_s), 1.07 (s, 16-CH_{3a}), 0.70 (s, 16-CH_{3s}). – ^{13}C NMR (CD_3CN): δ = 75.4 (C-1), 59.7 (C-8), 46.3 (C-7), 45.9 (C-13), 45.0 (C-9), 44.2 (C-2), 30.1 (C-11), 29.9 (C-12), 26.8 (C-11), 17.5 (16-CH_{3a}), 16.0 (16-CH_{3s}), 12.3 (6-CH_3), 10.0 (3-CH_3). The signals of the quaternary C-atoms were not observed. The following C/H-correlations confirm the differentiation C-2/C-7 vs. C-9/C-13: 44.2 (C-2)2.70 (2-H), 46.3 (C-7)2.56 (7-H). Correlations at positions 9 and 13 were not observed because of the width of the ^{1}H-signals. Calculations confirm further differentiation: δ = 91.0 (C-3), 76.3 (C-1), 76.0 (C-6), 62.1 (C-16), 61.0 (C-8), 49.1 (C-13), 49.0 (C-7), 47.7 (C-9), 46.0 (C-2), 33.8 (C-10), 32.7 (C-12), 27.7 (C-11), 18.9 (16-CH_{3a}), 17.4 (16-CH_{3s}), 14.4 (6-CH_3), 11.9 (3-CH_3). **15**: ^{1}H NMR (CD_3OD, 400 MHz) δ = 4.62 (dd, 8-H), 4.53 (dd, 1-H), 2.89 (d*A*B7-H), 2.78 (dA*B*, 2-H), 2.66–2.59 (m, 9-H*), 2.46–2.38 (m, 13-H*), 1.95–1.78 (m, 10-H_a, 12-H_a), 1.59–1.50 (m, 11-H_a), 1.48 (s, 6-CH_3), 1.40 (s, 3-CH_3), 1.40–1.22 (m, 10-H_s, 11-H_{syn}, 12-H_s), 1.03 (s, 16-CH_{3a}), 0.74 (s, 16-CH_{3s}); $J_{1,2} = J_{1,13} = J_{7,8} = J_{8,9}$ = 1.6, $J_{2,7}$ = 10.4 Hz – ^{1}H NMR (CD_3CN, 400 MHz): δ = 4.49 (dd, 8-H), 4.42 (dd, 1-H), 2.70 (d*A*B, 7-H), 2.59 (dA*B,* 2-H), 2.56–2.47 (m, 9-H*), 2.36–2.39 (m, 13-H*), 1.95–1.75 (m, 10-H_a, 12-H_a), 1.55–1.45 (m, 11-H_a), 1.40 (s, 6-CH_3), 1.35 (s, 3-CH_3), 1.35–1.25 (m, 10-H_s, 12-H_s), 1.25–1.12 (m, 11-H_s), 0.96 (s, 16-CH_{3a}), 0.69 (s, 16-CH_{3s}); $J_{9,13}$ = 8.3 Hz. – ^{1}H NMR (CD_3COCD_3, 400 MHz): δ = 4.51 (app. dd, 8-H), 4.42 (app. dd, 1-H), 2.91–2.88 (d*A*B, hidden, 7-H), 2.70 (dA*B*, 2-H), 2.67–2.58 (m, 9-H*), 2.46–2.38 (m, 13-H*), 1.87–1.73 (m, 10-H_a, 12-H_a), 1.55–1.46 (m, 11-H_a), 1.43 (s, 6-CH_3), 1.36 (s, 3-CH_3), 1.33–1.20 (m, 10-H_s, 11-H_s, 12-H_s), 1.04 (s, 16-CH_{3a}), 0.71 (s, 16-CH_{3s}). – ^{13}C NMR (CD_3CN): δ = 77.0 (C-6), 75.5 (C-8), 61.6 (C-16), 59.1 (C-1), 49.8 (C-7), 47.5 (C-2), 44.8 (2 signals! C-9, C-13), 30.2/30.1 (C-10/C-12), 26.8 (C-11), 17.4 (16-CH_{3a}), 15.8 (16-CH_{3s}), 12.2 (6-CH_3), 10.0 (3-CH_3). The signal of C-3 (quaternary) was not observed. The following C/H-correlations confirm the differentiation C-2/C-7 vs. C-9/C-13: 47.5 (C-2)2.59 (2-H), 49.8 (C-7)2.70 (7-H). Calculated values: δ = 91.0 (C-3), 76.3 (C-1), 76.0 (C-6), 62.1 (C-16), 61.0 (C-8), 49.1 (C-13), 49.0 (C-7), 47.7 (C-9), 46.0 (C-2), 33.8 (C-10), 32.7 (C-12), 27.7 (C-11), 18.9 (16-CH_{3a}), 17.4 (16-CH_{3s}), 14.4 (6- CH_3), 11.9 (3-CH_3).

(±)-(1*R,2*S**,3*R**,9*S**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-diene 4,5,15-Trioxide (18) and ... 4,14,15-Trioxide (19):** A solution of **2** (23 mg, 0.085 mmol) in a solution of DMDO (0.1 M in acetone, 140 mL, 165 equiv.) was kept at 25 °C for 14 d with exclusion of light. After concentration in vacuo, the residue was dissolved in CH_3OH (5 mL) and adsorbed on silica gel (2.5 g). The gel was dried and put on a silica gel column preconditioned with $CHCl_3$ (3.0 g silica gel, diameter 0.5 cm). Elution with $CHCl_3/CH_3OH$ (30:1) gave pure **15** (13 mg, 51%). Subsequent elution with $CHCl_3/CH_3OH$ (10:1) gave the trioxides, ratio **18/19** = 1.0:8.5 (^{1}H NMR). By preparative HPLC **19** can be obtained in pure form, **18** enriched to 80% (^{1}H NMR). – **Compound 19:** colorless crystals (13 mg, 37%), m.p. > 320 °C (CH_3CN), R_f = 0.11 ($CHCl_3/CH_3OH$ 10:1; UV); 0.42 (CH_3OH; UV). – IR (KBr): ṽ = i.a. 1515 cm^{-1}, 1473. – UV (CH_3CN): λ_{max} (ε) = 284 nm (2282), 242 (7495). – ^{1}H NMR (CD_3CN, 400 MHz): δ = 4.58 (dd, 1-H*), 4.57 (dd, 8-H*), 2.85 (*A*BX, 2-H**), 2.79 (A*B*X, 7-H**), 2.65–2.56 (m, 9-H, 13-H), 1.92–1.82 (m, 1 H), 1.55–1.45 (m, 1 H), 1.40 (s, 3-CH_3***), 1.40–1.38 (m, hidden, 2 H), 1.36 (s, 6-CH_3***), 1.25–1.10 (m, 2 H), 1.00 (s, 16-CH_{3a}), 0.71 (s, 16-CH_{3s}); $J_{1,2} = J_{1,13} = J_{7,8} = J_{8,9}$ = 1.6, $J_{2,7}$ = 10.4 Hz. – ^{13}C NMR (CD_3CN): δ = 73.6/73.4 (C-1/C-8), 47.8/47.0/45.8/45.6 (C-2/C-7/C-9/C-13), 29.9/29.6 (C-10/C-12), 26.5 (C-11), 17.3 (16-CH_{3a}), 15.9 (16- CH_{3s}), 12.1 (6-CH_3), 9.9 (3-CH_3); signals of **18** and of the quaternary C-atoms could not be observed. – MS; *m*/*z* (%): 320 [M^+) (2), 290 [M^+ – NO] (3), 201 (4), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (100), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (24), 91 (20), 67 (27). – MS (CI, isobutane); *m*/*z* (%): 321 [M + H^+] (45), 305 [M + H^+ – O] (100), 289 [M + H^+ – 2O] (25), 261 [M – 2NO + H^+] (20), 259 (23), 246 (18), 231 (10), 215 (29), 213 (18), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (54), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (32). – HRMS: calcd. 320.184369; found 320.184841 (-1.5 ppm). $C_{16}H_{24}N_4O_3$ (320.4). 18: Laborious HPLC enrichment gave only ca. 0.7 mg of pure **18**. – **Compound 18:** – ^{1}H NMR (CD_3CN, 400 MHz): δ = 4.52 (m, 1-H, 8-H), 2.87 (*A*BX, 2-H**), 2.68 (A*B*X, 7-H**), 2.63–2.53 (m, 9-H*), 2.44–2.32 (m, 13-H*), 1.55–1.45 (m, 1 H), 1.40 (s, 3-CH_3***), 1.39 (s, 6-CH_3***), 1.06 (s, 16-CH_{3a}), 0.75 (s, 16-CH_{3s}); $J_{1,2} = J_{7,8}$ = 1.6, $J_{2,7}$ = 11.0 Hz. Signals not mentioned were hidden by solvent signals. – MS; *m*/*z* (%): 320 [M^+] (15), 304 [M^+ – O] (7), 290 [M^+ – NO] (43), 260 [M^+ – 2NO] (7), 230 [M^+ – 3NO] (10), 157 [3,4,4,5-tetramethyl-4*H*-pyrazole dioxide + H^+] (10), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (34), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (14). – MS (CI, isobutane); *m*/*z* (%): 321 [M + H^+] (5), 289 [M + H^+ – 2O] (20), 261 [M – 2NO + H^+] (10), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (12), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (16).

(1*R,2*S**,3*R**,9*S**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-diene 4,5,14,15-Tetroxide (20):** To a suspension of **14/15** (20 mg, 0.066 mmol) in CH_2Cl_2 (1 mL), was added at 0 °C a solution of H_2O_2 (30% in H_2O, 0.10 mL, 15 equiv.) and trifluoracetic anhydride (0.72 mL) in CH_2Cl_2 (5 mL). After 2 d at 25 °C, all volatile compounds were removed in vacuo to leave a uniform (TLC, ^{1}H NMR), colorless, crystalline residue (22 mg, 100%), m.p. > 320 °C (CH_3CN), R_f = 0.20 (CH_3OH, UV). – IR (KBr): ṽ = i.a. 1496 cm^{-1}, 1472. – ^{1}H NMR (CF_3COOH, 400 MHz): δ = 5.40 (br. s, 2 H, 8-H), 3.40 (br. s, 2-H, 7-H), 2.94 (s, 9-H, 13-H), 2.09 (br. s, 10-H_a, 12-H_a), 1.73 (s, 3-CH_3, 6-CH_3), 1.32 (s, 16-CH_{3a}), 1.04 (s, 16-CH_{3s}); the signals of 10-H_s, 11-$H_{s/a}$ and 12-H_s between 1.80–1.00 are hidden by the signals of the methyl groups. – ^{13}C NMR (CF_3COOH): δ = 87.8 (C-3, C-6), 75.9 (C-1, C-8), 61.5 (C-16), 49.7 (C-2, C-7), 48.0 (C-9, C-13), 30.6 (C-10, C-12), 27.1 (C-11), 17.8 (16-CH_{3a}), 15.8 (16-CH_{3s}), 9.5 (3-CH_3, 6-CH_3); the assignment of the signals is secured by APT measurement. – MS; *m*/*z* (%): 336 [M^+] (0.2), 320 [M^+ – O] (0.7), 304 [M^+ – 2O] (0.3), 290 [M^+ – O – NO] (1.6), 190 (3), 173 (44), 157 [3,4,4,5-tetramethyl-4*H*-pyrazole dioxide + H^+] (3), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (15), 127 (15), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (5), 100 (38), 44 [N_2O] (100). – MS (CI, isobutane); *m*/*z* (%): 321 [M + H^+ –O] (20), 308 (43), 305 [M + H^+ –2O] (100), 289 (38), 277 (34), 261 (31), 246 (67), 230 (22), 215 (18), 163 (30), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (54), 127 (4), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (76), 121 (22). – MS (CI, NH_3); *m*/*z* (%): 338 (12), 322 (100), 308 (39), 290 (22), 277 (24), 261 (16), 246 (39), 230 (23), 228 (23), 215 (15), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (20), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (84). – MS (FAB, NBA); *m*/*z* (%): 359 [M + Na^+] (4), 337 [M + H^+] (15), 321 [M + H^+ – O] (2), 307 [M + H^+ – NO] (29), 289 [M + H^+ – 3 O] (17), 273 [M + H^+ –4 O] (5), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (2), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (3). $C_{16}H_{24}N_4O_4$ (336.4)

(±)-(1*R,2*R**,3*S**,5*R**)-3,5-Dimethoxy-1,7,10,10-tetramethyl-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene 8-Oxide (25):** To a solution of **24** (1.50 g, 5.91 mmol) in $CHCl_3$ (28 mL), was added a solution of DMDO (0.1 M in acetone, 90 mL, 1.5 equiv.). After 12

h the solvent was removed in vacuo and the residue purified by chromatography on silica gel (cyclohexane/ethyl acetate 1:1) to give colorless crystals (1.56 g, 98%), m.p. 153 °C, dec. >145 °C (*n*-hexane), R_f = 0.23 (cyclohexane/ethyl acetate, 2:1; UV), 0.72 ($CHCl_3$/CH_3OH, 10:1; UV). – IR (KBr): $\tilde{\nu}$ = i.a. 1506 cm^{-1}(N=NO). – UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 230 nm (5984), 200 (2377, sh). – ^1H NMR: δ = 4.99 (s, 3-H, 5-H), 3.40 (s, 3-OCH_3, 5-OCH_3), 2.97 (s, 2-H, 6-H), 1.49 (s, 1-CH_3*), 1.43 (s, 7-CH_3*), 0.97 (s, 10-CH_{3a}), 0.79 (s, 10-CH_{3s}). – ^{13}C NMR: δ = 105.9 (C-3), 105.0 (C-5), 93.5 (C-7), 75.6 (C-1), 59.8 (C-10), 56.1 (C-2), 55.4 (C-6), 55.4/55.3 (3-OCH_3, 5-OCH_3), 17.4 (C-10_a), 15.7 (C-10_s), 12.6 (1-CH_3), 10.4 (7-CH_3). Calculated values: δ = 104.6 (C-3), 103.3 (C-5), 93.0 (C-7), 75.3 (C-1), 61.4 (C-10), 57.6 (C-2), 57.2 (C-6), 53.5 (3-OCH_3), 53.4 (5-OCH_3), 18.9 (C-10_a), 17.5 (C-10_s), 14.6 (1-CH_3), 12.4 (7-CH_3). – MS; *m/z* (%): 253 [M^+ – O – H] (11), 239 [M^+ – OCH_3] (6), 180 (11), 167 (19), 151 (64), 141 (96), 135 (25), 125 (19), 124 (16), 123 (32), 122 (35), 121 (37), 119 (30), 107 (45), 91 (31). – MS (CI, isobutane); *m/z* (%): 271 [M + H^+] (49), 239 [M^+ – OCH_3] (100), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (59), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (30). – $C_{13}H_{22}N_2O_4$ (270.3)**:** calcd. C 57.76, H 8.20, N 10.36; found C 57.63, H 8.15, N 10.25.

(+)-(1*R*,2*R*,3*S*,5*R*)-3,5-Dimethoxy-1,7,10,10-tetramethyl-4-oxa-8,9-diazatricyclo [5.2.1.$0^{2,6}$]dec-8-ene 8-Oxide ((+)-25): A solution of **24** (1.2 g, 4.7 mmol) and (+)-**32** (1.6 g, 5.3 mmol, 1.1 equiv.) in ethyl acetate (20.0 mL) was heated for 12 d at 14.3 kbar at 65 °C. Concentration in vacuo and chromatography of the colorless residue on silica gel (250 g, $CHCl_3$/CH_3OH, 30:1gave **25** (0.95 g, 75%), *ee* = 92–95%. The enantiomeric excess was determined by HPLC with a Chiralcell AD column [2-propanol/*n*-hexane, 20:10, 0.9 mL min^{-1}, retention times (+)-**25**: 7.32 min, (–)-**25**: 9.79 min, or as an alternative: 2-propanol/*n*-hexane, 25:75, 0.9 mL min^{-1}, retention times (+)-**25**: 7.94 min, (–)-**25**: 10.99 min]. Further enrichment by crystallization was not possible. – ORD (CH_3CN, 0.413 g/100 cm^3): $[\alpha]_\lambda^{24}(\lambda)$ = +67.2 (589 nm), +70.7 (578), +82.2 (546), +162.0 (436), +339.0° (365). – CD (CH_3CN, 0.5 mg/mL): $\Delta\varepsilon_{max}$ (λ) = +0.6 (285 nm), –3.2 (251), +3.4 (226); calcd. with ZINDO// B3LYP/6–31G*: $\Delta\varepsilon_{max}$ (λ) = +0.9 (405 nm, n → π*), –2.3, (270, π → π*), +2.2 (251, n → π*).

(±)-(1*R,2*R**,3*S**,5*R**)-3,5-Dihydroxy-1,7,10,10-tetramethyl-4-oxa-8,9-diazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene 8-Oxide:** A solution of (±)-**25** (317 mg, 1.17 mmol) in 1 M H_2SO_4 (45 mL) was heated at reflux for 10 min. The aqueous solution was saturated with NaCl and extracted continuously for 24 h with CH_2Cl_2. Concentration in vacuo and chromatography on silica gel ($CHCl_3$/acetone, 1:1) left an amorphous solid (210 mg, 80%), R_f = 0.27 ($CHCl_3$/acetone, 1:1; UV, anisaldehyde). – IR (KBr): $\tilde{\nu}$ = 3366 cm^{-1} (br., OH), 1509 (N=NO). – ^1H NMR**:** δ = 5.43 (s, 3-H*), 5.41 (s, 5-H*), 4.89 (br. s, OH), 3.08 (*A*B, 2-H**), 3.03 (A*B*, 6-H**), 1.49 (s, 1-CH_3***), 1.42 (s, 7-CH_3***), 1.00 (s, 10-CH_{3a}), 0.76 (s, 10-CH_{3s}); $J_{2,6}$ = 8.2 Hz. – ^{13}C NMR: δ = 99.4/98.6 (C-3/C-5), 93.7 (C-7), 75.9 (C-1), 60.0 (C-10), 56.9/56.3 (C-2/C-3/C-5/C-6), 17.4 (C-10_a), 15.8 (C-10_s), 12.5 (1-CH_3*), 10.4 (7-CH_3*). – MS; *m/z* (%): 225 [M^+ – OH] (2), 178 (14), 163 (43), 150 (24), 135 (37), 107 (92), 91 (100). – MS (CI, isobutane); *m/z* (%): 243 [M + H^+] (14), 225 [M^+ – OH] (27), 179 (86), 165 (28), 151 (41), 141 [tetramethyl-4*H*-pyrazole oxide + H^+] (100), 125 [tetramethyl-4*H*-pyrazole + H^+] (41). – MS (CI, NH_3); *m/z* (%): 260 [M + NH_4^+] (83), 243 [M + H^+] (25), 242 (100), 225 [M^+ – OH] (2), 196 (21), 179 (71), 141 [tetramethyl-4*H*-pyrazole oxide + H^+] (14), 125 [tetramethyl-4*H*-pyrazole + H^+] (18). – MS (FAB); *m/z* (%) (NBA): 243 [M + H^+] (69), 225 [M^+ – OH] (100). – $C_{11}H_{18}N_2O_4$ (242.3)

(±)-(1*R,2*S**,3*R**,9*S**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,10,14-triene 4(5)-Oxides (29, Mixture of Isomers, a/b = 1:1.3):** A solution of **25** (1.56 g, 5.8 mmol) in 1 M H_2SO_4 (90.0 mL) was heated at reflux until total conversion into the 3,5-diol [ca. 10 min, TLC control, $CHCl_3$/CH_3OH 10:1; UV, anisaldehyde, 0.72 (starting material), 0.48 (monohydroxy compound), 0.28 (product)] had occurred. Then the solution was cooled to room temp., saturated with NaCl and extracted continuously with CH_2Cl_2 (250 mL) for 8 h. To the organic phase was added anhydrous K_2CO_3 (30.0 g) and then at 0 °C anhydrous N_2H_4 (3.0 mL). The mixture was stirred at 0 °C for 20 min, filtered and concentrated in vacuo. The excess hydrazine was completely removed under high vacuum. To a suspension of the residue in CH_2Cl_2 (70 mL) was added freshly distilled cyclopentadiene (70 mL), and then at –78 °C with vigorous stirring a solution of trifluoracetic acid [0.48 mL, 710 mg, 6.2 mmol, precooled to –78 °C in CH_2Cl_2 (60 mL)] was added dropwise over 5 min. With stirring, the mixture was warmed to 4 °C, and stirring continued at this temp. for 16 h. Then it was diluted with CH_2Cl_2 (100 mL) and washed with satd. $NaHCO_3$ solution (50 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL), the combined organic phases dried (K_2CO_3) and concentrated in vacuo. The residue was purified by chromatography on silica gel (4 × 27 cm). Non-polar by-products were eluted with $CHCl_3$ (300 mL), further elution with $CHCl_3$/CH_3OH 30:1 (ca. 1200 mL). As an alternative, the raw material can be dissolved in a small amount of $CHCl_3$ and **29** is precipitated by addition of Et_2O. Polymeric contaminations can be separated by dissolving in CH_3OH. This product can be directly hydrogenated to **12**; from the combined residues, additional 10–20% product can be obtained by chromatography. Total yield 1.19–1.21 g (72–73%), colorless crystals, m.p. 276 °C (dec.) ($CHCl_3$/Et_2O), R_f = 0.44 ($CHCl_3$/CH_3OH, 10:1; UV). – IR (KBr): $\tilde{\nu}$ = i.a. 1512 cm^{-1} (N=NO), 1470. – UV (CH_3CN): λ_{max} (ε) = 387 nm (82), 236 (3339), 206 (4500). – ^1H NMR (400 MHz): δ = 5.54–5.48 (m, 5 H, alkene-H, 1-H^{a*}), 5.46 (app. t, *J* = 1.6 Hz, 1-H^{b**}), 5.35 (app. t, *J* = 1.6 Hz, 8-H^{b**}), 5.31 (app. t, *J* = 1.6 Hz, 8-H^{a*}), 3.04 (app. ddd, $J_{9,8}$ = 1.6 Hz, $J_{9,10}$ = 3.8 Hz, $J_{9,13}$ = 10.7 Hz, 9-H^b), 2.95–2.90 (app. dddd, $J_{9,8}$ = 1.6 Hz, $J_{9,11}$ = 2.0 Hz, $J_{9,10}$ = 3.6 Hz, $J_{9,13}$ = 9.1 Hz, 9-H^a), 2.62–2.55 (m, 13-H^a), 2.52–2.28 m, 8 H), 1.48 (s, 6-CH_3^a), 1.47 (s, 6-CH_3^b), 1.41 (s, 3-CH_3^b), 1.39 (s, 3-CH_3^a), 0.93 (s, 16-$CH_{3a}^{a,b}$), 0.72 (s, 16-CH3s^{a,b}). – ^{13}C NMR: δ = 133.0 (alkene^a), 132.9 (alkene^b), 129.2 (alkene^b), 128.8 (alkene^a), 91.0 (C-3^b), 90.9 (C-3^a), 75.6 (C-6^b), 75.6 (C-6^a), 64.4 (C-8^{a*}), 64.1 (C-8^{b*}), 62.6 (C-1^{b*}), 61.9 (C-1^{a*}), 59.5 (C-16^{a,b}), 51.8 (a), 50.9 (b), 48.0 (b), 47.9 (a), 43.2 (a), 43.0 (b), 39.9 (b), 38.9 (a), 37.0 (a), 36.88 (b), 17.4 (16-$CH_{3a}^{a,b}$), 15.6 (16-$CH_{3s}^{a,b}$), 12.1 (3-CH_3^a), 12.1 (3-CH_3^b), 9.7 (6-CH_3^b), 9.7 (6-CH_3^a). – MS; *m/z* (%): 287 [M + H^+] (1), 229 [M – N_2 – NO + H^+] (12), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (100), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (72). – MS (CI, isobutane); *m/z* (%): 411 [M + 3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (13), 287 [M + H^+] (49), 271 [M – O + H^+] (20), 243 [M – N_2 – O + H^+] (12), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (15), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (100). – MS (CI, NH_3); *m/z* (%): 573 [2 M + H^+] (79), 411 [M + 3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (80), 370 (7), 304 [M + NH_4^+] (54), 287 [M + H^+] (91), 271 [M – O + H^+] (7), 256 (2), 243 [M – N_2 – O + H^+] (3), 158 (3), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (21), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (100). – $C_{16}H_{22}N_4O$ (286.4): calcd. C 67.11, H 7.74, N 19.56; found C 67.17, H 7.77, N 19.41.

(±)-(1*R,2*S**,3*R**,9*S**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-diene 4-Oxide (12)**: A solution of **29** (1.20 g, 4.2 mmol) in CH_3OH (40 mL) was hydro-

genated over Pd/C (10%, 20 mg, TLC control). At ca. 80% conversion, the following product composition was determined [^{1}H NMR, 400 MHz): **29** (20.1%), **12** (66.0%), **2** (11.0%), **31** (2.8%). – R_f ($CHCl_3/CH_3OH$, 10:1): 0.42 (**29**), 0.49 (**12**), 0.53 (**2**), 0.48 (**31**); R_f ($CHCl_3/CH_3OH$, 30:1): 0.21 (**29**), 0.29 (**12**), 0.29 (**2**), 0.25 (**31**); R_f (cyclohexane/2-propanol, 1:1): 0.33 (**29**), 0.41 (**12**), 0.63 (**2**), 0.51 (**31**); R_f (cyclohexane/2-propanol, 2:1): 0.16 (**29**), 0.21 (**12**), 0.42 (**2**), 0.28 (**31**); R_f (cyclohexane/2-propanol, 3:1): 0.10 (**29**), 0.18 (**12**), 0.30 (**2**), 0.21 (**31**). Separation of the reaction mixture is possible chromatographically on a 300 mg scale (silica gel, 1 × 40 cm, cyclohexane/2-propanol, 3:1). With larger quantities (up to 1.20 g of the mixture) a separation of **2** and **31** by chromatography with cyclohexane/2-propanol, 3:1 (4 × 27 cm silica gel) and subsequent separation of **29** and **12** by chromatography with $CHCl_3/CH_3OH$, 30:1 (silica gel, 4 × 40 cm) is preferable. Separation of **12** and **2** by preparative HPLC (silica gel) is possible with cyclohexane/2-propanol, 2:8. Retention times (analytical HPLC): cyclohexane/2-propanol, 1:9 (1.5 mL min^{-1}): 5.74 min (**2**), 6.86 min (**12**); cyclohexane /2-propanol, 2/8 (1.5 mL min^{-1}): 6.88 min (**2**), 8.58 min (**12**). – **Compund 12:** colorless crystals (640–798 mg, 53–66%), m.p. 264 °C ($CHCl_3$/*n*-hexane), R_f = 0.29 ($CHCl_3/CH_3OH$, 30:1; UV). – IR (KBr): $\tilde{\nu}$ = i.a. 1509 cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 387 nm (80), 237 (3800). – ^{1}H NMR (400 MHz): δ = 5.47 (t, 8-H), 5.31 (t, 1-H), 2.35 (ABX, 7-H), 2.27 (ABX, 2-H), 2.32–2.25 (m, dddd, hidden, 9-H), 2.23–2.15 (dddd, 13-H), 1.80–1.70 (m, 10-H_a, 12-H_a), 1.47 (s, 6-CH_3), 1.45–1.35 (m, hidden, 10-H_s, 11-H_a, 12-H_{syn}), 1.39 (s, 3-CH_3), 1.23–1.10 (m, 11-H_s), 0.92 (s, 16-CH_{3s}), 0.72 (s, 16-CH_{3s}); $J_{1,2} = J_{1,13} = J_{7,8} = J_{8,9}$ = 1.6, $J_{2,7}$ = 10.4 Hz. The correlation of the measured and the calculated data was better than 2 ppm, fixation relative to the ^{13}C shifts of C-3/C-6 was done with a shift difference of Δδ = 15.39. – ^{1}H NMR (CD_3OD, CD_2HOD = 3.30, 400 MHz): δ = 5.44 (app. d, 0.8 Hz, 8-H), 5.26 (s, 1-H), 2.60 (AB, 2-H, 7-H), 2.48–2.40 (m, 9-H), 2.39–2.31 (m, 13-H), 1.85–1.76 (m, 10-H_a, 12-H_a), 1.45 (s, 6-CH_3), 1.36–1.15 (m, 10-H_s, 11-H_s, 11-H_a, 12-H_s), 1.35 (s, 3-CH_3), 0.96 (s, 16-CH_{3a}), 0.68 (s, 16-CH_{3s}); the central signals of the AB systems coalesce at 2.60 ppm. – ^{13}C NMR: δ = 91.0 (C-3), 75.6 (C-6), 64.0 (C-8), 63.6 (C-1), 59.8 (C-16), 48.3 (C-7), 44.6 (C-13), 43.7 (C-9), 43.3 (C-2), 30.2 (C-10*), 29.9 (C-12*), 26.2 (C-11), 17.4 (16-CH_{3a}), 15.6 (16-CH_{3s}), 12.1 (6-CH_3), 9.7 (3-CH_3). The correlation of the measured and the calculated data was better than 2 ppm. – MS; *m/z* (%): 288 [M^+] (0.9), 201 [$M^+ - N_2O - N_2 - CH_3$] (5), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (100), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (26), 91 (39). – MS (CI, isobutane); *m/z* (%): 577 [2 M + H^+] (5), 289 [M + H^+] (100), 273 [M – O + H^+] (7), 261 [M – N_2 + H^+] (6), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H^+] (2), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H^+] (2). – $C_{16}H_{24}N_4O$ (288.4): calcd. C 66.64, H 8.39, N 19.43; found C 66.59, H 8.27, N 19.24.

(–)-(1*S*, 2*R*, 3*S*, 9*R*)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,14-diene 4-Oxide ((–)-12): (–)-**12** was prepared starting with (+)-**25** analogously to the racemate. The enantiomeric excess of (–)-**12** could not be determined by HPLC. Racemisation in the course of the synthesis is excluded (*ee* of (+)-**25** = 92–95%). – ORD (CH_3CN, 0.323 g/100 cm^3): $[\alpha]_\lambda^{24}$ (λ) = –195.0 (589 nm), –39.2 (578), –30.5 (546), –28.2 (436). – CD (CH_3CN, 2.14 mM): $\Delta\varepsilon_{max}$ (λ) = –2.2 (390 nm), +6.2 (290), –16.6 (251), +12.3 (213).

(1*R,2*R**,3*S**,5*R**)-3,5-Dimethoxy-1,7,10,10-tetramethyl-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene 8,9-Dioxide (26):** To a solution of **24** (103 mg, 0.41 mmol) in CH_2Cl_2 (30 mL), was added anhydrous Na_2HPO_4 (11.0 g) and then at 0 °C, dropwise with stirring, a solution of H_2O_2 (95% in H_2O, 1.0 mL, CAUTION) and trifluoracetic anhydride (10.0 mL) in CH_2Cl_2 (100 mL). After stirring at 25 °C for 12 h, H_2O (150 mL) was added and the aqueous phase made slightly alkaline by addition of K_2CO_3. It was extracted with CH_2Cl_2 (2 × 100 mL), the combined organic phases dried (K_2CO_3) and concentrated in vacuo. Chromatography on silica gel (1 × 15 cm, $CHCl_3/CH_3OH$, 30:1) gave colorless crystals (104 mg, 90%), m.p. 264–266 °C ($CHCl_3$/*n*-hexane), R_f = 0.59 ($CHCl_3/CH_3OH$, 10:1; UV) (Table 3). – IR (KBr): $\tilde{\nu}$ = i.a. 1494 cm^{-1} (ON=NO). – UV (CH_3CN): λ_{max}(ε) = 269 nm (π → π*, ON=NO, 6600), 195 (4200). – UV (H_2O): λ_{max}(ε) = 264 nm (π → π*, ON=NO, 7300), 194 (4600). – ^{1}H NMR: δ = 5.06 (s, 3-H, 5-H), 3.41 (s, 3-OCH_3, 5-OCH_3), 3.07 (s, 2-H, 6-H), 1.54 (s, 1-CH_3, 7-CH_3), 1.07 (s, 10-CH_{3a}), 0.91 (s, 10-CH_{3s}); assignment relative to the ONNO unit. – ^{13}C NMR: δ = 104.4 (C-3, C-5), 83.6 (C-1, C-7), 56.6 (C-10), 55.5 (C-2, C-6), 55.0 (3-OCH_3, 5-OCH_3), 17.0 (10-CH_{3a}), 15.4 (10-CH_{3s}), 9.8 (1-CH_3, 7-CH_3). – MS; *m/z* (%): 286 [M^+] (17), 269 [M^+ – OH] (21), 196 (14), 179 (40), 164 (38), 151 (83), 141 (30), 121 (100), 95 (45). – $C_{13}H_{22}N_2O_5$ (286.3): calcd. C 54.53, H 7.75, N 9.78; found C 54.41, H 7.71, N 9.64.

Table 2. Crystal structure of **26**

Identification code	mk115al1
Empirical formula	$C_{13}H_{22}N_2O_5$
Formula mass	286.33
Temperature [K]	293(2)
Wavelength [Å]	0.71069
Crystal system	Monoclinic
Space group	*P*1 2_1/*n* 1
Unit cell dimensions	*a* = 7.7476(12) Å
	b = 19.023(2) Å
	c = 10.190(2) Å
	α = 90°
	β = 94.697(7)°
	γ = 90°
Volume [Å^3]	1496.8(4)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.271
Absorption coefficient [mm^{-1}]	0.098
F(000)	616
Crystal size [mm]	0.4 × 0.3 × 0.2
Theta range for data collection	2.27 to 26.33°.
Index ranges	0 *h* 9, 0 *k* 23, –12 *l* 12
Reflections collected	3269
Independent reflections	3047 [*R*(int) = 0.0240]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3046/0/182
Goodness-of-fit on F^2	1.052
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0468, *wR*2 = 0.1374
R indices (all data)	*R*1 = 0.1194, *wR*2 = 0.1690
Extinction coefficient	0.007(3)
Largest diff. peak and hole	0.221 and –0.189 eÅ^{-3}

(±)-(1*R,2*R**,5*R**)-5-Hydroxy-1,7,10,10-tetramethyl-4-oxa-8,9-diazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3-one 4,5-Dioxide:** To a solution of **24** (30 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was added a solution of H_2O_2 (30% in H_2O, 0.10 mL, 8.3 equiv.) and trifluoracetic anhydride (0.75 mL) in CH_2Cl_2 (2 mL). After 45 min, H_2O (1 mL) was added and the mixture was stirred at room temp. for 2 d. Concentration in vacuo and chromatography on silica gel (1 × 8 cm, $CHCl_3/CH_3OH$, 10:1) gave pure oily dioxide (16 mg, 53%), R_f =

Table 3. Crystal structure of parent diazene of **26** (**18** in ref.[1])

Identification code	mk114al
Empirical formula	$C_{16}H_{24}N_4O_2$
Formula mass	304.39
Temperature (K]	293(2)
Wavelength [Å]	0.71069
Crystal system	Monoclinic
Space group	*P*1 2_1/*n* 1
Unit cell dimensions [Å, °]	*a* = 7.057(2) *b* = 10.5096(10) *c* = 20.525(4) α = 90 β = 96.609(11) (= 90
Volume [Å^3]	1512.1(5)
Z	4
$D_{calcd.}$ [g cm–3]	1.337
Absorption coefficient [mm^{-1}]	0.091
F(000)	656
Crystal size	0.5 × 0.3 × 0.2 mm
Theta range for data collection	2.78 to 26.29°
Index ranges	–8≤ *h* 8, –13 ≤ *k* 0, 0 *l* ≤ 25
Reflections collected	3130
Independent reflections	3048 [*R*(int) = 0.0315]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3048/0/218
Goodness-of-fit on F^2	1.013
Final *R* indices [*I*>2σ(*I*)]	*R*1 = 0.0472, *wR*2 = 0.1293
R indices (all data)	*R*1 = 0.1263, *wR*2 = 0.1637
Extinction coefficient	0.005(3)
Largest diff. peak and hole	0.263 and –0.207 eÅ^{-3}

0.18 ($CHCl_3$/CH_3OH, 10:1; UV). – IR (KBr): ṽ = 3351 cm^{-1} (br., OH), 1773 (C=O), 1498 (ON=NO), 1427 (ON=NO), 1380 (ON=NO). – ^{1}H NMR (CD_3CN): δ = 5.70 (br. s, OH), 5.59 (s, 5-H), 3.66 (d, 2-H), 3.22 (dd, 6-H), 1.55 (s, 1-CH_3*), 1.51 (s, 7-CH_3*), 1.06 (s, 10-CH_{3a}), 0.85 (s, 10-CH_{3s}); $J_{2,6}$ = 8.9, $J_{5,6}$ = 1.2 Hz. – MS; *m*/*z* (%): 240 [M$^+$ – O] (2), 226 [M$^+$ – NO] (26), 194 (38), 176 (49), 161 (48), 150 (97), 135 (55), 107 (100). – MS (CI, isobutane); *m*/*z* (%): 257 [M + H$^+$] (49), 241 [M + H$^+$ – O] (73), 226 (36), 195 (95), 177 (95), 151 (100), 135 (28), 122 (48), 107 (47). – $C_{11}H_{16}N_2O_5$ (256.3).

(±)-(1*R,2*S**,3*R**,9*S**)-3,6,16,16-Tetramethyl-4,5,14,15-tetraazapentacyclo[6.5.2.1^{3,6}.0^{2,7}.0^{9,13}]hexadeca-4,10,14-triene 4,5-Dioxide (30):** A solution of **26** (34 mg, 0.12 mmol) in TFA (2 mL), after addition of H_2O (1 mL), was heated to 90 °C for 18 h. After concentration in vacuo and dissolution in CH_2Cl_2 (5 mL), anhydrous K_2CO_3 (1.7 g) and at 0 °C anhydrous N_2H_4 (0.2 mL) were added. After 30 min, the mixture was filtered, and solvent and excess hydrazine were thoroughly removed in vacuo. To a suspension of the colorless residue in CH_2Cl_2 (5 mL), freshly distilled cyclopentadiene (10 mL) and at –78 °C a solution of TFA (16 mg) in CH_2Cl_2 (5 mL) were added. The mixture was warmed with stirring to 4 °C and, after 16 h at this temp., washed with satd. $NaHCO_3$ solution (10 mL), dried (K_2CO_3), filtered, and concentrated in vacuo. Chromatography (0.5 × 12 cm, silica gel, $CHCl_3$/CH_3OH, 10:1) gave colorless crystals (9 mg, 25%), R_f = 0.18 ($CHCl_3$/CH_3OH, 10:1; UV, $KMnO_4$). – IR (KBr): ṽ = i.a. 1491 cm^{-1}(ON=NO), 1424 (ON=NO). – UV (CH_3CN): λ_{max} (ε) = 381 nm (NN, ε_{rel} = 1.0), 266 (ONNO, ε_{rel} = 87.9). – ^{1}H NMR (CD_3OD, 400 MHz): δ = 5.60 (s, 8-H), 5.58 (t, 1-H), 5.53–5.47 (m, 10-H, 11-H), 3.17–3.12 (ddddd, 9-H), 3.05 (7-H**), 2.78 (*A*BXY, 2-H**), 2.76–2.69 (dddd, 13-H), 2.55–2.46 (ddddd, 12-H_a), 2.23–2.16 (ddddd, 12-H_s), 1.50 (s, 6-CH_3**), 1.49 (s, 3-CH_3**), 1.08 (s, 16-CH_{3a}), 0.75 (s, 16-CH_{3s}). $J_{1,2}$ = $J_{7,8}$ = 1.3, $J_{1,13}$ = 2.0, $J_{2,7}$ = 10.7, $J_{9,10}$ = $J_{9,11}$= $J_{11,12s}$ ≈ 4.0, $J_{9,12s}$ = $J_{9,12a}$ = $J_{10,12s}$ = $J_{11,12a}$ ≈ 2.0, $J_{9,13}$ = 9.1, $J_{12s,12a}$ = 17.7, $J_{12s,13}$ = 4.3, $J_{12a,13}$ = 10.7 Hz. – ^{13}C NMR (CD_3OD): δ = 133.7/130.3 (C-10/C-11), 85.2/85.1 (C-3/C-6), 66.5/64.5 (C-1/C-8), 59.6 (C-16), 51.9 (C-9), 49.2 (C-7*), 48.5 (C-2*), 39.8 (C-12**), 38.0 (C-13**), 16.9 (C-16_a), 15.1 (C-16_s), 9.14/9.09 (3-CH_3/6-CH_3). – MS; *m*/*z* (%): 302 [M$^+$] (36), 274 [M$^+$ – N_2] (2), 272 [M$^+$ – NO] (26), 244 [M$^+$ – NO – N_2] (5), 212 (12), 199 (24), 157 [3,4,4,5-tetramethyl-4*H*-pyrazole dioxide + H$^+$] (20), 141 [3,4,4,5-tetramethyl-4*H*-pyrazole oxide + H$^+$] (96), 133 (100), 125 [3,4,4,5-tetramethyl-4*H*-pyrazole + H$^+$] (41). – $C_{16}H_{22}N_4O_2$ (302.4).

(1*R,4*S**,11*S**)-11-Methyl-2,3,8,9-tetraazatetracyclo[8.2.2.0^{4,12}.0^{7,11}]tetradeca-2,8-diene (33) and (±)-(1*R**,4*S**,11*S**)-11-Methyl-2,3,8,9-tetraazatetracyclo[8.2.2.0^{4,12}.0^{7,11}]tetradeca-2,8-diene 2-Oxide and ... 8-Oxide (34/35, Mixture of Isomers):** A solution of **3/4** (150 mg, 0.68 mmol) in CH_3OH (120 mL), saturated with N_2 was irradiated in a quartz tube (diam. 2.5 cm, Rayonet reactor, 8 lamps 254 nm) for 6 h. After concentration in vacuo, filtration through a short column (silica gel, $CHCl_3$/CH_3OH 12/1) furnished a deeply red eluate, which was then purified by chromatography on silica gel (20 g, 2 × 29 cm, CH_2Cl_2/acetone, 4:1). According to HPLC analysis the first fraction (10 mg, R_f = 0.85–0.90) consisted of at least three compounds. Then 35 mg of fraction 2 (R_f = 0.55) and **3/4** (35 mg, R_f = 0.20) were obtained. The main products (R_f = 0.55) were separated by preparative HPLC (silica gel Merck Si 100, ethyl acetate, 12 mL/min.): 1) retention vol. 96 mL: **33** (6 mg, 5% based on conversion), 2) retention vol. 130 mL: **34/3**5 [26 mg, 20% based on conversion, ratio **34/35** = 2.3:1.0 (^{1}H NMR)]. Photolysis under identical conditions to total conversion of **3/4** (450 mg, 2.0 mmol) in CH_3OH (450 mL) produced **34/35** (60 mg, 14% based on conversion) and **33** (30 mg, 7%, based on conversion) besides polymers. – **Compound 33:** M.p. 164 °C. – UV (CH_3OH): λ_{max} (ε) = 325 (630). – ^{1}H NMR (360 MHz): δ = 4.62 (dddd, 1-, 4-H), 4.18 (ddd, 7-, 10-H), 2.21 (dddd, 5a-, 14a-H), 2.11 (t, 12-H), 2.09 (dddd, 6a-, 13a-H), 1.90 (m, 6s-, 13s-H), 1.18 (m, 5s-, 14s-H), 1.10 (s, CH_3); $J_{1,12}$ = 10.5, $J_{4,5s}$ = $J_{4,5a}$ = 6.5, $J_{a5,\ 5a}$ = $J_{6s,6a}$ = 13.5 Hz, $J_{5s,\ 6a}$ = 10.0, $J_{5a,6s}$ = 8.0, $J_{5a,6a}$ = 2.5, $J_{6a,7}$ = 6.0 Hz. – ^{13}C NMR: δ = 94.6, 87.6 (C-1, –4, –7, –10), 36.0, 34.8 (C-12, CH_3), 22.6, 22.0 (C-5, –6, –13, –14). – MS (CI, isobutane); *m*/*z* (%): 207 (6), 206 (15), 205 (100) [M + 1], 195 (8), 193 (8), 163 (6). – **34/35 (Mixture of Isomers):** M.p. 189 °C (dec.). – IR ($CHCl_3$): ṽ = i.a. 1515 cm^{-1} (N=NO), 1455. – UV (CH_3OH): λ_{max} (ε) = 325 nm (320), 227 (7050). – MS (CI, isobutane); *m*/*z* (%): 222 (15) [M + 1], 221 (100) [M], 207 (12), 205 (20), 193 (9), 175 (15). – **Compound 34:** ^{1}H NMR (360 MHz): δ = 4.53 (m, 10-H)*, 4.44 (m, 7-H)*, 4.33 (dt, 4-H)$^+$, 4.25 (ddd, 1-H)$^+$, 2.77 (t, 14-H), 2.30 (m, 5-, 12a-H), 2.2–1.8 (m, CH_2), 1.36, 1.31 (m, 5s-H, 12s-H), 1.17 (s, CH_3); $J_{1,4}$ = 1.0, $J_{10,11s}$ = 8.5, $J_{1,12a}$ = 8.5 $J_{1,12s}$ = 9.5, $J_{4,5a}$ = $J_{4,5s}$ = 5.5, $J_{6s,7}$ = 6.0, $J_{7,14}$ = $J_{10,14}$ = 10.5 Hz. – **Compound 35:** ^{1}H NMR (360 MHz): δ = 4.72 (m, 10-H)*, 4.64 (m, 7-H)*, 3.94 (dt, 4-H)$^+$, 3.87 (ddd, 1-H)$^+$, 2.35 (m, 5-, 12a-H), 2.17 (t, 14-H), 2.2 –1.8 (m_c, CH_2), 1.35 (s, CH_3), 0.94 (m, 5s-H); $J_{1,4}$ = 2.0, $J_{4,5}$ = $J_{10,11s}$ = 8.0, $J_{1,12s}$ = 10.0, $J_{4,5a}$ = $J_{1,12a}$ = 8.5, $J_{6a,7}$ = $J_{6s,7}$ = $J_{10,11a}$ = 6.0 Hz.

(1*R,4*S**,11*S**)-11-Methyl-2,3,8,9-tetraazatetracyclo[8.2.2.0^{4,12}.0^{7,11}]tetradeca-2,8-diene 2,3,8,9-Tetroxide (57):** A solution of **11** (50 mg, 0.19 mmol) in H_2O (10 mL) was purged with Ar for 20 min and irradiated in a quartz tube (= 1.4 cm) at 25 °C with 254 nm light (Hanau TNN 15, distance probe/lamp 6 cm) to total conversion (TLC control, ca. 10 h). After concentration at room temp. under high vacuum, purification is possible by flash chromatography on silica gel (CH_3OH/H_2O, 10:1). Tetroxide **57** is extremely unstable in the presence of traces of base and above 40 °C. Spectro-

scopic characterization is carried out directly after irradiation in a NMR tube. Yield: 90% at 52% conversion and 100% after total conversion (TLC, ^{1}H NMR). R_f = 0.36 (CH_3OH/H_2O, 10:1; UV). – UV (H_2O): λ_{max} = 259 nm. – ^{1}H NMR (D_2O/dioxane): δ = 4.70 (dt, 1-H, 4-H), 4.31 (t, 7-H, 10-H), 3.14 (t, 12-H), 2.10–1.90 (m, 4 H), 1.80–1.55 (m, 4 H), 1.39 (s, 11-CH_3); $J_{1,12(4,12)}$ = 10.8, $J_{1,13s(4,5s)} = J_{1,13a(4,5a)}$ = 6.4, $J_{7,6s(10,14s)} = J_{7,6a(10,14a)}$ = 6.0 Hz. – ^{13}C NMR (D_2O/dioxane): δ = 73.7 (C-1*, C-4*), 66.4 (C-7*, C-10*), 33.8 (C-12), 32.2 (C-11), 20.7 (C-5**, C-13**), 20.1 (C-6**, C-14**), 19.9 (11-CH_3). – $C_{11}H_{16}N_4O_4$ (268.3).

(±)-(1*R,4*S**,11*S**)-11-Methyl-2,3,8,9-tetraazatetracyclo[8.2.2.2^{4,12}.0^{7,11}]tetradeca-2,8-diene 2,8-Dioxide (49) and ... 2,9-Dioxide (50) (mixture of isomers, ratio 5:3):** A mixture of **5/6/7** (8*:24*:68, 550 mg, 2.3 mmol) in CH_3OH, (550 mL) was irradiated in quartz tubes (ϕ = 2.5 cm, λ = 254 nm, Rayonet) at 30 °C for 2.5 h. After concentration, chromatographic workup (silica gel, $CHCl_3/CH_3OH$ 12/1) yielded several fractions, the first (R_f = 0.80–0.95, 30 mg) consisting of at least four components (analyt. HPLC, RP-C-18, 100% CH_3OH), the second (R_f = 0.55–0.65, 30 mg) of **34/35** and **49/50**, which could be separated chromatographically (silica gel, CCl_4/acetone, 1:1) to give **7** (30 mg, 6%), **34/35** (R_f = 0.45, 30 mg) and **49/50** (R_f = 0.32, 80 mg, 63:37 (^{1}H NMR). Additional **3/4** (R_f = 0.30, 30 mg, 12%) and **5/6/7** (R_f = 0.20, 170 mg, 31%, **5/6** = 9%, 24*:70*:6) were obtained. Crystallization of **49/50** from ethyl acetate/CH_3OH gave colorless crystals, m.p. 182 °C (dec.). – IR (KBr): ṽ = i.a. 1520 cm^{-1} (N=NO). – UV (CH_3CN): λ_{max} (ε) = 225 (14500) nm. – ^{1}H NMR (360 MHz): δ = 4.64 (ddd, 1-H, rel. int. 5)*, 4.57 (m, 4-H, rel. int. 5)*, 4.50 (m, 1-H, rel. int. 3)**, 4.49 (ddd, 4-H, rel. int. 5)*, 4.06 ("t", 7-H, rel. int. 3)****, 4.04 ("t", 10-H, rel. int. 3)****, 4.12 ("t", 7-H, rel. int. 5)*, 4.57 (m, 4-H, rel. int. 5)*, 4.57 (m, 4-H, rel. int. 5)***, 3 .98 (dd, 10-H, rel. int. 5)***, 2.85 ("t", 12-H, rel. int. 5)*, 2.83 ("t", 12-H, rel. int. 3)*, 2.5–2.4/2.3–1.8/1.6–1.5/1.4–1.3 (multiplets of the ethano-bridges, 8 H); rel. int. 5: $J_{4,12} = J_{1,12}$ = 10.5, $J_{6a,7}$ = 6.5*, $J_{6s,7}$ = 10.0*, $J_{10,14a} = J_{10,14s}$ = 6.5 Hz; rel. int. 3: $J_{1,12}$ = 10.0*, $J_{4,12}$ = 11.0, $J_{6a,7} = J_{6s,7} = J_{10,14a} = J_{10,14s}$ = 6.5 Hz. – $C_{11}H_{16}N_4O_2$ (236.3): calcd. C 55.92, H 6.83, N 23.71; found C 55.88, H 7.02, N 23.65.

(±)-(1*R,2*R**,3*R**,8*S**)-3,4,4,5-Tetramethyl-13,14-diazapentacyclo[5.5.2.0^{2,6}.0^{3,5}.0^{8,12}]tetradec-13-ene 13-Oxide (39). A) Thermolysis: 13** (2.070 mg, 7.19 μmol) was sealed in an Al capsule and heated in a DSC system (Perkin–Elmer thermal analysis system 7) with 5 K min^{-1} to 260 °C. The probe melted at 234 °C and decomposed at 242–243 °C endothermically. After cooling, pure **39** was obtained as colorless crystals. – **B) Photolysis:** A solution of **13** (40 mg, 0.14 mmol) in CH_3CN (5.0 mL), was purged with Ar for 20 min and irradiated in a quartz tube (= 1.4 cm) for 30 min in a Rayonet reactor with 253.7 nm light. At ca. 77% conversion the following product mixture was obtained (^{1}H NMR): **39:** 49%, **43:** 10%, **41:** 7%, **40:** 2–4%, **42:** trace. With TLC (silica gel, $CHCl_3$/CH_3OH, 10:1, R_f = 0.50) **40** could be enriched. A further (partial) separation was possible by preparative HPLC (Merck SiO_2_100, cyclohexane/2-propanol/CH_3CN, 88:7:5, 15 mL min^{-1}, detection at 235 nm), but only **39** could be obtained in pure form (49%, ^{1}H NMR), R_f = 0.57 ($CHCl_3/CH_3OH$, 30:1; UV). – IR (KBr): ṽ = i.a. 1500 cm^{-1}(N=NO). – UV (CH_3CN): λ_{max} (ε) = 235 nm (4700). – ^{1}H NMR (400 MHz) δ = 4.57 (dd, 1-H*), 4.51 (br. dd, 7-H*), 2.38–2.31 (dddd, 12-H**), 2.25–2.14 (dddd, 12-H**), 2.06 (dd, 6-H***), 1.96 (dd, Hz, 2-H***), 1.95–1.80 (m, 9-H_a, 11-H_a), 1.65–1.50 (m, 9-H_s, 11-H_s), 1.49–1.40 (m, 10-H_a), 1.34–1.23 (m, 10-H_s), 1.10 (s, CH_3), 1.08 (s, CH_3), 1.05 (s, CH_3), 0.88 (s, CH_3); $J_{1,2} = J_{1,12}$ = 2.1, $J_{2,6}$ = 5.4, $J_{6,7} = J_{7,8}$ = 2.1, $J_{8,9}$ = 10.2, $J_{8,9}$ = 8.3, $J_{8,12}$ = 10.0, $J_{11,12}$ = 10.0, $J_{11,12}$ = 8.5 Hz. – ^{13}C NMR: δ = 78.4 (C-1), 61.2 (C-7), 42.8, 42.1, 41.8, 41.6, 32.7 (Cq), 30.1, 29.8, 25.8, 24.7 (Cq), 19.4, 14.8, 9.9, 7.5. – MS; *m*/*z* (%): 260 [M$^+$] (2), 230 [M$^+$ – NO] (9), 139 (100). – MS (CI, isobutane); *m*/*z* (%): 261 [M + H$^+$] (100), 245 [M + H$^+$ – O] (5). – $C_{16}H_{24}N_2O$ (260.4)

(±)-(1*R,4*R**,5*R**,14*R**)-1,13,16,16-Tetramethyl-2,3,11,12-tetraazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadeca-2,11-diene 2-Oxide (37) and (±)-(1*R**,4*R**,5*R**,12*S**)-1,11,14,14-Tetramethyl-2,3-diazapentacyclo[9.2.1.04,13.05,9.010,12]tetradec-2-ene 2-Oxide (38):** A solution of **12** (275 mg, 0.955 mmol) in CH_3OH (100 mL), purged with N_2, was irradiated in an immersion apparatus with continued purging with N_2 with a 15-W Hg low-pressure lamp (Hanau TNN 15) for 15 min. After concentration in vacuo, the photoproducts were separated from starting material by chromatography on silica gel (2 × 20 cm, $CHCl_3/CH_3OH$, 30:1). The recovered starting material was again irradiated twice. The following was obtained: **12:** 34 mg (0.12 mmol, 12%), **37:** 145 mg (0.503 mmol, 51%), **38:** 58 mg (0.20 mmol, 20%); **37** could be obtained pure by crystallization from $CHCl_3/Et_2O$, 1:4, **38** from Et_2O/*n*-hexane, 3:4. – **Compound 37:** Colorless crystals [145 mg, 51%, 58% based on conversion (88%)], m.p. 198–199 °C (dec., slow, unspecific dec. already above 150 °C) ($CHCl_3/Et_2O$, 1:4), R_f = 0.56 ($CHCl_3$/CH_3OH, 30:1; UV). – IR (KBr): ṽ = i.a. 1509 cm^{-1}(N=NO). – UV (CH_3CN): λ_{max} (ε) = 346 nm (170), 239 (5500), 202 (3250). – ^{1}H NMR (400 MHz): δ = 4.38 (dd, 10-H), 4.10 (dd, 4-H), 2.79–2.69 (dddd, *J* = 9.6, 9.6, 9.9 Hz, 9-H), 2.58 (dd, 15-H), 2.45–2.35 (m, 5-H, 6-H), 2.25–2.19 (m, 8-H), 2.15 (dd, 14-H), 2.11–1.96 (m, 6-H, 8-H), 1.93–1.85 (m, 7-H), 1.84 (s, CH_3), 1.59–1.48 (m, 7-H), 1.40 (s, 13-CH_3), 1.05 (s, CH_3), 1.02 (s, CH_3); $J_{4,5} = J_{4,15}$ = 5.9, $J_{9,10}$ = 9.2, $J_{10,14}$ = 6.4, $J_{14,15}$ = 10.4 Hz. – ^{1}H NMR (CD_3OD, CD_2HOD = 3.30, 400 MHz): δ = 4.46 (dd, 10-H), 4.18 (dd, 4-H), 2.85–2.75 (m, 9-H), 2.73 (dd, 15-H), 2.50–2.42 (m, 5-H), 2.30 (dd, 14-H), 2.35–2.16 (m, 6-H, 8-H), 2.11–1.96 (m, 6-H, 8-H), 1.90–1.80 (m, 7-H), 1.78 (s, 13-CH_3), 1.63–1.50 (m, 7-H), 1.40 (s, CH_3), 1.06 (s, CH_3), 1.05 (s, CH_3). – ^{13}C NMR: δ = 105.4 (C-13), 98.5 (C-1), 86.5 (C-10), 65.7 (C-4), 49.3 (C-16), 45.4 (C-15), 41.0 (C-14), 37.2 (C-9), 36.7 (C-5), 31.5 (CH_2), 30.1 (CH_2), 26.1 (CH_2), 25.2 (CH_3), 17.2 (CH_3), 16.9 (CH_3), 15.0 (CH_3). – MS; *m*/*z* (%): 288 [M$^+$] (2), 243 [M$^+$ – N_2 –OH] (4), 230 (13), 216 [M$^+$ –N_2 – N_2O] (28), 201 (100), 133 (60). – MS (CI, isobutane); *m*/*z* (%): 289 [M + H$^+$] (100), 273 [M + H$^+$ –O] (12), 261 [M + H$^+$ – N_2] (13), 245 [M + H$^+$ – N_2O] (5), 217 [M + H$^+$ – N_2 – N_2O] (2). – $C_{16}H_{24}N_4O$ (288.4): calcd. C 66.64, H 8.39, N 19.43; found C 66.74, H 8.33, N 19.29. – **Compound 38:** Colorless needles [58 mg, 20%, 23% on conversion (80%)], m.p. 146–162 °C, when repeated 152–155 °C (Et_2O/*n*-hexane, 3:4), R_f = 0.80 ($CHCl_3/CH_3OH$, 30:1; UV), 0.20 ($CHCl_3$; UV). – IR (KBr): ṽ = i.a. 1512 cm^{-1} (N=NO). – UV (CH_3CN): λ_{max} (ε) = 232 nm (5400). – ^{1}H NMR (400 MHz): δ = 4.25 (dd, 4-H), 3.04 (ddd, 13-H), 2.58 (dddd, 9-H), 2.09–2.02 (m, 6-H), 2.02–1.95 (m, 5-H), 1.85–1.65 (m, 6-H, 7-H, 8-H_a), 1.58 (s, 1-CH_3), 1.60–1.45 (m, 7-H), 1.35–1.22 (m, 12-H), 1.30–1.18 (m, 10-H), 1.22–1.10 (m, 8-H_s), 1.21 (s, 14-CH_{3s}), 1.16 (s, 14-CH_{3a}), 1.10 (s, 11-CH_3); $J_{4,5}$ = 6.3, $J_{4,13}$ = 10.4, $J_{5,9} = J_{8a,9}$ = 7.8, $J_{8s,9}$ = 13.7, $J_{9,10}$ = 10.9, $J_{10,13}$ = 1.6, $J_{12,13}$ = 7.0 Hz. – ^{13}C NMR: δ = 101.4 (C-1), 66.0 (C-4), 47.7 (C-14), 47.0 (C-13), 43.9 (C-11), 39.6 (C-5), 36.7 (C-9), 30.8 (C-8), 30.0 (C-10), 28.0 (C-1), 26.5 (12-CH_{3s}), 26.0 (C-6), 25.2 (12-CH_{3a}), 24.7 (C-7), 23.9 (11-CH_3), 23.7 (C-12); the assignment is confirmed by NOE measurements, decoupling experiments and ^{1}H/^{1}H- and ^{13}C/^{1}H-correlations. – MS; *m*/*z* (%): 260 [M$^+$] (2), 244 [M$^+$ – O] (2), 243 [M$^+$ – OH] (8), 230 [M$^+$ – NO] (32), 216 [M$^+$ – N_2O] (26), 201 [M$^+$ – N_2O – CH_3] (55), 133 [M$^+$ – N_2O – CH_3 - cyclopentene] (45). – MS (CI, NH_3); *m*/*z* (%): 278 [M + NH_4^+] (6), 261 [M + H$^+$] (100), 245 [M + H$^+$ – O] (29), 215 [M + H$^+$ – O – 2 CH_3] (8). – $C_{16}H_{24}N_2O$ (260.4).

(+)-(1*S*,4*S*,5*S*,14*S*)-1,13,16,16-Tetramethyl-2,3,11,12-tetraazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadeca-2,11-diene 2-Oxide ((+)-37) and (–)-(1*S*,4*S*,5*S*,12*R*)-1,11,14,14-Tetramethyl-2,3-diazapentacyclo[9.2.1.04,13.05,9.010,12]tetradec-2-ene 2-Oxide [(–)-38]: (+)-**37** and (–)-**38** were obtained by photolysis of (–)-**12** as described for the racemic precursor. The enantiomeric excess of **38** was determined by HPLC (Chiralcell AD, 2-propanol/*n*-hexane, 10:90, 0.8 mL min^{-1}, retention times (+)-**38**: 9.23 min, (–)-**38**: 11.06 min) to be 89–92% starting with (–)-**12** with 92–95% *ee*. A separation of the enantiomers of **38** was not possible with probes of *ee* > 90%. – **Compound (+)-37:** 89–95% *ee*. – ORD (CH_3CN, 0.189 g/100 cm^3): $[\alpha]_{(}^{24}$ (λ) = +54.5 (589 nm), +57.2 (578), +63.0 (546), +44.5 (436). – **Compound (–)-38:** 89–92% *ee*. – ORD (CH_3CN, 0.140 g/100 cm^3): $[\alpha]_{(}^{24}$ (λ) = –39.3 (589 nm), –40.0 (578), –44.3 (546), –55.7 (436), –9.3 (365).

(±)-(1*R,4*R**,5*R**,14*S**)-1,13,16,16-Tetramethyl-2,3,11,12-tetraazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadeca-2,10-diene 2-Oxide (44):** In solution, **40** (60 mg, 0.21 mmol) in $CHCl_3$ (0.8 mL) rearranged at 25 °C within 2–3 d completely to the unstable hydrazone **44**. – IR (KBr): ṽ = i.a. 3323 cm^{-1} (br.), 1502 (N=NO). – ^{1}H NMR (400 MHz): δ = 4.89 (br. s, NH), 4.07 (dd, $J_{4,5}$ = 4.3 Hz, $J_{4,15}$ = 5.4 Hz, 4-H), 3.02 (*A*BX, $J_{AB\ app.}$ = 10.4 Hz, $J_{15,4}$ = 5.4 Hz, 15-H), 2.96–2.90 (m, hidden, 9-H), 2.94 (A*B*X, $J_{AB\ app.}$ = 10.4 Hz, $J_{x,y}$ = 1.1 Hz, 14-H), 2.83 (m, 5-H), 2.16 (m, 6-H$_s$, 6-H$_a$, 8-H), 1.95 (m, 7-H, 8-H), 1.56–1.48 (m, 7-H), 1.44 (s, CH_3), 1.41 (s, CH_3), 1.24 (s, CH_3), 0.95 (s, CH_3); *J4,15* = 5.4 Hz, *J*1$_{4,15}$ = 10.4 Hz. – ^{13}C NMR: δ = 155.8 (C-10), 98.5 (C-1), 74.4 (C-13), 56.6 (C-14), 54.6 (C-16), 52.3 (C-15), 43.7 (C-5), 39.6 (C-9), 30.6 (C-6), 28.7 (8), 26.3 (C-7), 25.9 (CH_3), 22.1 (CH_3), 17.9 (CH_3), 16.0 (CH_3). The following correlations of methyl signals were observed: 1.44 17.9, 1.41 16.0, 1.24 22.1, 0.95 25.9. – MS; *m*/*z* (%): 288 [M$^+$] (20), 262 (17), 260 [M$^+$ – N_2] (8), 246 (16), 244 [M$^+$ – N_2O] (18), 231 (27), 230 (33), 216 (12), 215 (47), 201 (21), 135 (31), 133 (30), 124 (100), 123 (77), 122 (48), 121 (42). – $C_{16}H_{24}N_4O$ (288.4).

(±)-(1*R,4*R**,5*R**,15*S**)-1,13,16,16-Tetramethyl-2,3,11,12-tetraazapentacyclo[11.2.1.0$^{4.15}$.0^{5,9}.0^{10,14}]hexadeca-2,10(14),11-triene 2-Oxide (45):** In solution, **40 (**60 mg, 0.21 mmol) in $CHCl_3$ (0.8 mL) rearranged at 25 °C within 8 d completely to give the sensitive **45**, accompanied by increasing decomposition. – ^{1}H NMR (400 MHz): δ = 4.45 (dd, 4-H), 3.59 (dq, 15-H), 2.86 (ddd, 5-H), 2.68 (dd, 9-H), 1.99 (d, 13-CH_3), 1.53 (s, 1-CH_3), 1.40 (s, 16-CH_{3s}), 1.05 (s, 16-CH_{3a}); $J_{4,5}$ = 8.0, $J_{4,15}$ = 6.2, $J_{5,6a}$ ≈ 8.0, $J_{5,9}$ = 15.0, $J_{8a,9}$ = 7.5, $J_{15,13\text{-}CH3}$ = 2.4 Hz. 6-H, 7-H and 8-H between 2.0 and 0.9 ppm. – ^{13}C NMR: δ = 159.5, 126.4, 109.8, 98.0, 64.6, 54.5, 52.8, 52.0, 41.3, 29.1, 27.5, 25.2, 22.9, 19.8, 15.2, 11.4.

(±)-(1*R,4*S**,11*S**)-11-methyl-2,3,8,9-tetraazatetracyclo-[8.2.2.0^{4,12}.0^{7,11}]tetradecane 2,8-Dioxide (49) and ... 2,9-Dioxide (50):** A solution of **5/6/7** (8*:24*:68, 550 mg, 2.3 mmol) in CH_3OH (550 mL) was irradiated in quartz tubes (2.5 cm) in a Rayonet reactor with 254 nm light at 30 °C for 2.5 h) to give 97% conversion of **7** and 9% conversion of **5/6**. Concentration in vacuo and chromatography (silica gel, CH_3Cl/ CH_3OH, 12:1) gave 4 fractions: R_f = 0.8–0.95, complex mixture of at least 4 substances (30 mg); R_f = 0.55–0.65, **34/35/49/50** (155 mg); R_f = 0.3, **3/4** (75*:25*, 60 mg, 12%, 18% based on **7**), R_f = 0.20, **5/6/7**, (24*:70*:6, 170 mg, 31%). The mixture of the second fraction could be separated by chromatography (silica gel, CCl_4/acetone, 1:1) to give 2 fractions: R_f = 0.45, **34/35** (30 mg, 6%, 9% based on **7**) and R_f = 0.32 (**49/50** (63:37, 15%, 22% based on **7**). On irradiation of **7** (6 mg, 0.03 mmol) in CD_3OD (0.5 mL), purged with N_2 (^{1}H NMR), after only 10 min signals of **7**, **49/50**, and **3/4** (65:25:5) could be observed, and after 40 min (total conversion) signals of **49/50**, **3/4**, **34/35** (45:36:19) were registered. After irradiation of **5/6** (3*:1*, 5 mg, 0.02 mmol) in CD_3OD (0.5 mL), purged with N_2 (^{1}H NMR control after 10, 20, 40, and 90 min), besides undefined upfield signals, only signals of the starting materials were observed. – **49/50 (Mixture of Isomers, 5:3):** colorless crystals, m.p. 182 °C, dec.) (ethyl acetate/ CH_3OH, 1:1). – IR (KBr) : ṽ = i.a. 1520 cm^{-1} (N=NO). – UV (CH_3CN): λ_{max} (ε) = 225 nm (14500). – ^{1}H NMR (360 MHz): δ = 4.64 (ddd, 1-H, rel. int. 5)*, 4.57 (m, 4-H, rel. int. 5)*, 4.50 (m, 1-H, rel. int. 3)^2*, 4.49 (ddd, 4-H, rel. int. 3)^2*, 4.06 (″t″, 7-H, rel. int. 3)^4*, 4.04 (″t″, 7-H, rel. int. 3)^4*, 4.12 (″t″, 7-H, rel. int. 5)^3*, 3.98 (dd, 10-H, rel. int. 5)^3*, 2.85 (″t″, 12-H, rel. int. 5), 2.83 (″t″, 12-H, rel. int. 3), 2.50–2.40; 2.27–1.76; 1.60–1.48; 1.40–1.28 (m of the ethano bridges, 8 H); rel. int 5: $J_{1,2}$ = $J_{4,12}$ = 10.5*, $J_{6a,7}$ = 6.5*, $J_{6s,7}$ = 10.0, $J_{10,14a}$ = $J_{10,14s}$ = 6.5 Hz; rel. int. 3: $J_{1,12}$ = 10.0*, $J_{4,12}$ = 11.0*, $J_{6a,7}$ = $J_{6s,7}$ = $J_{10,14a}$ = $J_{10,14s}$ = 6.5 Hz.

(±)-(1*R,4*R**,5*R**,14*R**)-1,13,16,16-Tetramethyl-2,3,11,12-tetraazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadeca-2,11-diene 2,11-Oxide (51) and ... 2,12-Oxide (52):** A solution of **14/15** (1:1, 50 mg, 0.16 mmol) in CH_3OH or CH_3CN (10 mL) in a quartz tube (= 1.4 cm), purged with Ar, was irradiated in a Rayonet reactor with 253.7 nm light for 30 min. With a conversion of **15** of ca. 50% (**14** remained unchanged, 97%) the following mixture was obtained (^{1}H NMR, based on conversion): **51**: 29–31%, **52**: 1–2%, **37**: 4–7%, **12**: traces. The first chromatographic separation (silica gel, $CHCl_3$/ CH_3OH, 10:1, R_f = 0.45–0.55) gave two fractions, one (R_f = 0.45) containing **14/15**, the other (R_f = 0.55) containing **37**, **51** and **52**. Separation of **51** and **52** was possible by repeated preparative HPLC (silica gel Merck 100, 2-propanol, 1.5 mL min^{-1}, detection at 237 nm, retention times: **52**: 11.2 min., **51**: 12.0 min). – **Compound 51:** Colorless crystals (29–31%, ^{1}H NMR), m.p. > 320 °C (CH_3OH), R_f = 0.59 ($CHCl_3$/CH_3OH, 10:1; UV) (Table 4). – IR (KBr): ṽ = i.a. 1509 cm^{-1}(N=NO), 1499 (N=NO). – UV (CH_3CN): λ_{max} (ε) = 225 nm (11570). – ^{1}H NMR (CD_3CN, 400 MHz): δ = 4.71 (dd, 10-H), 4.33 (dd, 4-H), 2.87 (m, 14-H, 15-H), 2.70–2.61 (m, 8-H$_s$), 2.58–2.49 (m, 9-H), 2.44–2.35 (m, 5-H), 2.00–1.79 (m, 4 H), 1.48–1.36 (m, 1 H), 1.43 (s, 16-CH_{3s}), 1.39 (s, 1-

Table 4. Crystal structure of **51**

Identification code	mk116 ml1
Empirical formula	$C_{13}H_{22}N_2O_3$
Formula mass	254.33
Temperature [K]	293(2)
Wavelength [A]	0.71073
Crystal system, space group	Monoclinic, *P*1 2$_1$/*n* 1
Unit cell dimensions [Å, °]	*a* = 9.8718(2), *b* = 10.2542(2) *c* = 14.5020(3) α = 90 β = 108.8910(10) γ = 90
Volume [Å^3]	1388.93(5)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.216
Absorption coefficient [mm^{-1}]	0.086
F(000)	552
Crystal size	0.70 × 0.49 × 04.6 mm
Theta range for data collection	2.20 to 26.49°
Index ranges	–10 ≤ *h* 12, –10 *k* 12, –18 ≤ *l* 18
Reflections collected/unique	11478/2816 [*R*(int) = 0.1078]
Completeness to 2Θ	26.49 92.4%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2816/0/251
Goodness-of-fit on F^2	1.018
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0464, *wR*2 = 0.1200
R indices (all data)	*R*1 = 0.0611, *wR*2 = 0.1278
Largest diff. peak and hole	0.395 and –0.448 eÅ^{-3}

CH_3), 1.20 (s, 13-CH_3), 0.97 (s, 16-CH_{3a}). $J_{4,5} = J_{4,15} = 6.3$, $J_{9,10} = J_{10,14} = 6.4$ Hz, – ^{1}H NMR (CD_3OD): δ = 4.87 (dd, 10-H), 4.43 (dd, 4-H), 3.01–2.88 (m, 14-H, 15-H), 2.80–2.39 (m, 5-H, 8-H, 9-H), 2.05–1.82 (m, 4 H), 1.57–1.34 (m, 1 H), 1.48 (s, 16-CH_{3s}), 1.47 (s, 1-CH_3), 1.27 (s, 12-CH_3), 1.04 (s, 16-CH_{3a}). – ^{1}H NMR (400 MHz): δ = 4.64 (dd, 10-H), 4.34 (dd, 4-H), 3.71–3.10 (m, 1 H), 2.86–2.69 (m, 3 H), 2.55–2.46 (m, 9-H), 2.42–2.33 (m, 1 H), 2.16–2.07 (m, 1 H), 2.04–1.89 (m, 2 H), 1.56 (s, 16-CH_{3s}), 1.48–1.41 (m, 1 H), 1.47 (s, 1-CH_3), 1.27 (s, 13-CH_3), 1.23 (s, 16-CH_{3a}). – ^{13}C NMR (CD_3CN): δ = 99.8 (C-1), 82.4 (C-13), 78.7 (C-10), 65.4 (C-4), 52.3 (C-16), 45.3/45.1 (C-14/C-15), 37.8/37.7(C-5/C-9), 30.9 (C-6), 28.3 (C-8), 26.8 (C-7), 24.3 (16-CH_{3a}), 17.4/17.0/17.0 (16-CH_{3s}, 1-CH_3, 13-CH_3). – MS (CI, isobutane); *m/z* (%): 343 [M + H^+ + isobutene – H_2O] (4), 305 [M + H^+] (100), 289 [M + H^+ – O] (21), 274 (9), 261 [M + H^+ – N_2O] (8), 245 [M + H^+ – O – N_2O] (3). – MS (CI, NH_3); *m/z* (%): 322 [M + NH_4^+] (100), 306 [M + H^+] (23), 289 [M + H^+ – O] (13). – $C_{16}H_{24}N_4O_2$ (304.4). – **52:** Yield 1–2% (^{1}H NMR), R_f = 0.59 ($CHCl_3/CH_3OH$, 10:1; UV). – IR (KBr): $\tilde{\nu}$ = i.a. 1513 cm^{-1} (N=NO). – UV (CH_3CN): λ_{max} (ε) = 228 nm (9775). – ^{1}H NMR (400 MHz): δ = 4.32–4.29 (m, 4-H, 10-H), 2.82–2.76 (m, 14-H, 15-H), 2.50–2.40 (m, 5-H, 9-H), 2.15–2.06 (m, 2 H), 2.01–1.92 (m, 2 H), 1.90–1.82 (m, 1 H), 1.78 (s, 16-CH_{3s}), 1.51 (s, 1-CH_3, 13-CH_3), 1.04 (s, 16-CH_{3a}). (1 H is hidden). – ^{1}H NMR (CD_3CN, 400 MHz): δ = 4.31–4.28 (m, 4-H, 10-H), 2.90–2.88 (m, 14-H, 15-H), 2.50–2.44 (m, 5-H, 9-H), 2.20–1.70 (m, 5 H), 1.63 (s, 16-CH_{3s}), 1.55–1.45 (m, 1 H), 1.43 (s, 1-CH_3, 13-CH_3), 1.00 (s, 16-CH_{3a}). The signals of the five protons between δ = 2.20 and 1.70 are hidden by solvent signals. – ^{13}C NMR (CD_3CN): δ = 66.5 (C-4, C-10), 45.6 (C-5, C-9), 37.3 (C-14,C-15), 31.6 (C-6, C-8), 26.8 (C-7), 26.6 (16-CH_{3s}), 17.8 (1-CH_3, 13-CH_3), 16.2 (16-CH_{3a}). – MS (CI, isobutane); *m/z* (%): 343 [M + H^+ + isobutene – H_2O] (4), 305 [M + H^+] (100), 289 [M + H^+ – O] (39), 274 (9), 261 [M + H^+ – N_2O] (23), 245 [M + H^+ – O – N_2O] (8). – $C_{16}H_{24}N_4O_2$ (304.4).

Photolysis of (±)-(30): A solution of **30** (9 mg, 0.03 mmol) in CH_3OH (4.5 mL), was purged with Ar (15 min), irradiated in a quartz tube (= 1.4 cm) with monochromatic 254 nm light (Hanau TN 15 or Rayonet RUL2537) and purified by chromatography on silica gel ($CHCl_3/CH_3OH$, 10:1, starting material R_f = 0.20 (UV), product 0.32 (UV) to give a uniform product fraction (53% with 31% conversion; 18% with 79%conversion, ^{1}H NMR) consisting of a mixture of isomers **54/55** (^{1}H NMR). – UV (CH_3CN): λ_{max} = 247 nm. – ^{1}H NMR (CD_3CN, 100 MHz): δ = 5.57–5.44 (m, 4 H), 3.16–3.10 (m, 1 H), 2.87–2.78 (AB, 1 H), 2.74–2.65 (m, 2 H, AB), 2.57–2.47 (m, 1 H), 2.28–2.20 (m, 1 H), 1.70+1.68 (2 s, ges. 3 H), 1.42+1.40 (2 s, ges. 3 H), 1.10 (s, 3 H), 0.72 (s, 3 H).

(±)-(1*R,4*R**,5*R**,14*R**)-1,13,16,16-Tetramethyl-2,3,11,12-tetraazapentacyclo[11.2.1.0^{4,15}.0^{5,9}.0^{10,14}]hexadeca-2,11-diene 2,3,11-Trioxide (56):** A solution of **19** (8 mg, 0.03 mmol) in CD_3CN (0.8 mL) in a quartz NMR tube, purged with Ar for 20 min and sealed, was irradiated with monochromatic 254 nm light (Hanau TNN 15, NMR control). The photoproduct was purified by chromatography (silica gel, 2 g, $CHCl_3/CH_3OH$, 10:1) with severe losses. R_f = 0.18 ($CHCl_3/CH_3OH$, 10:1, UV). – ^{1}H NMR (CD_3CN, 100 MHz): δ = 4.87 (dd, 4-H), 4.49 (dd, 10-H), 3.02 (center of ABXY, 14-H, 15-H), 2.60–2.35 (m, 3 H), 1.41 (s, CH_3), 1.39 (s, CH_3), 1.21 (s, CH_3), 1.01 (s, CH_3); $J_{4,5} = J_{4,15} = 7.2$, $J_{9,10} = 4.6$, $J_{10,14} = 6.4$, $J_{14,15} = 10.7$ Hz. – MS; *m/z* (%): 290 [M^+ – NO] (8), 274 [M^+ – NO – O] (1), 243 (4), 176 (13), 162 (14). – MS (CI, isobutane); *m/z* (%): 321 [M + H^+] (28), 305 [M + H^+ – O] (100), 290 (96), 274 (97), 261 (66), 246 (80), 230 (68), 208 (51), 192 (61), 176 (279), 165 (32).

(1*R,4*S**,11*S**)-11-Methyl-2,3,8,9-tetraazatetracyclo[8.2.2.0^{4,12}.0^{7,11}]tetradeca-2,8-diene 2,3,8,9-Tetroxide (57):** A solution of **11** (50 mg, 0.19 mmol) in H_2O (10 mL) was purged with Ar for 20 min and irradiated in a quartz tube (= 1.4 cm) at 25 °C with 254 nm light (Hanau TQ 15) to total conversion (TLC control, ca. 10 h). Concentration in high vacuum at room temp. and flash chromatography (silica gel, CH_3OH/H_2O, 10:1) gave a product extremely sensitive to traces of base and temp. >40 °C. Spectroscopic characterization was carried out in an NMR tube. Yield 90% at 52% conversion (NMR); 100% after complete conversion (TLC, ^{1}H NMR), R_f = 0.36 (CH_3OH/H_2O, 10:1; UV). – UV (H_2O): λ_{max} = 259 nm. – ^{1}H NMR (D_2O/dioxane): δ = 4.70 (dt, 1-H, 4-H), 4.31 (t, 7-H, 10-H), 3.14 (t, 12-H), 2.10–1.90 (m, 4 H), 1.80–1.55 (m, 4 H), 1.39 (s, 11-CH_3); $J_{1,12(4,12)} = 10.8$, $J_{1,13s(4,5s)} = J_{1,13a(4,5a)} = 6.4$, $J_{7,6s(10,14s)} = J_{7,6a(10,14a)} = 6.0$ Hz. – ^{13}C NMR (D_2O/dioxane): δ = 73.7 (C-1*, C-4*), 66.4 (C-7*, C-10*), 33.8 (C-12), 32.2 (C-11), 20.7 (C-5**, C-13**), 20.1 (C-6**, C-14**), 19.9 (11-CH_3). – $C_{11}H_{16}N_4O_4$ (268.3).

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG. We thank Dr. D. Hunkler for NMR, Dr. J. Wörth for MS analyses, Prof. A. W. Frahm for CD measurements, Prof. J. Wirz, Dr. H.-P. Reisenauer and Prof. G. Maier for the matrix irradiation experiments.

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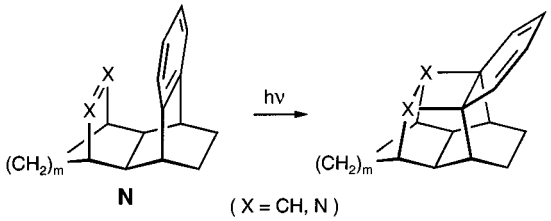

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Received May 25, 1999
[O99294]