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Azo Bridges from Azines. XV [1]

Oxygenation of Unsaturated Cyclic Azo Compounds with Peracids

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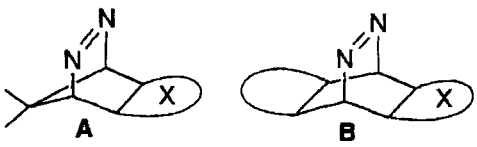
Abstract. Azo bridges in compounds **3**, **6**, **11**, **16**, **20** and **22** are chemospecifically oxidized with MCPBA to the corresponding azoxy derivatives **4**, **7**, **12**, **17**, **21**, and **23** in the presence of one or two (**20**, **22**) double bonds even if these are located in a close parallel position to the azo bridge (**6**, **11**, **20**, **22**). The order of reactivity of different olefinic moieties towards MCPBA was found to be bicycloheptene > bicyclooctene, cyclopentene. Thus, epoxy/azoxides **5**, **8**, **13**, **14**, and **19** as well as bisepoxy/azoxides **10** and **15** were obtained. If both the azo and the olefinic bridge are part of a bicycloheptane system (**24**) the azo group can be no longer oxidized chemospecifically (**25** + **26**).

In preceding papers of this series we reported on a general route to new derivatives of 2,3-diazabicyclo-[2.2.1]heptenes (DBH-type **A**) and 2,3-diazabicyclo-[2.2.2]octenes (DBO-type **B**) in which the heterocyclic moiety is annulated to saturated or unsaturated mono- or bicyclic systems [3].



X = saturated/unsaturated mono-/bicyclic rings

Clean transformation of both DBH and DBO into their azoxy derivatives by peracids has already been described [4] and seems to be a rather general reaction [5].

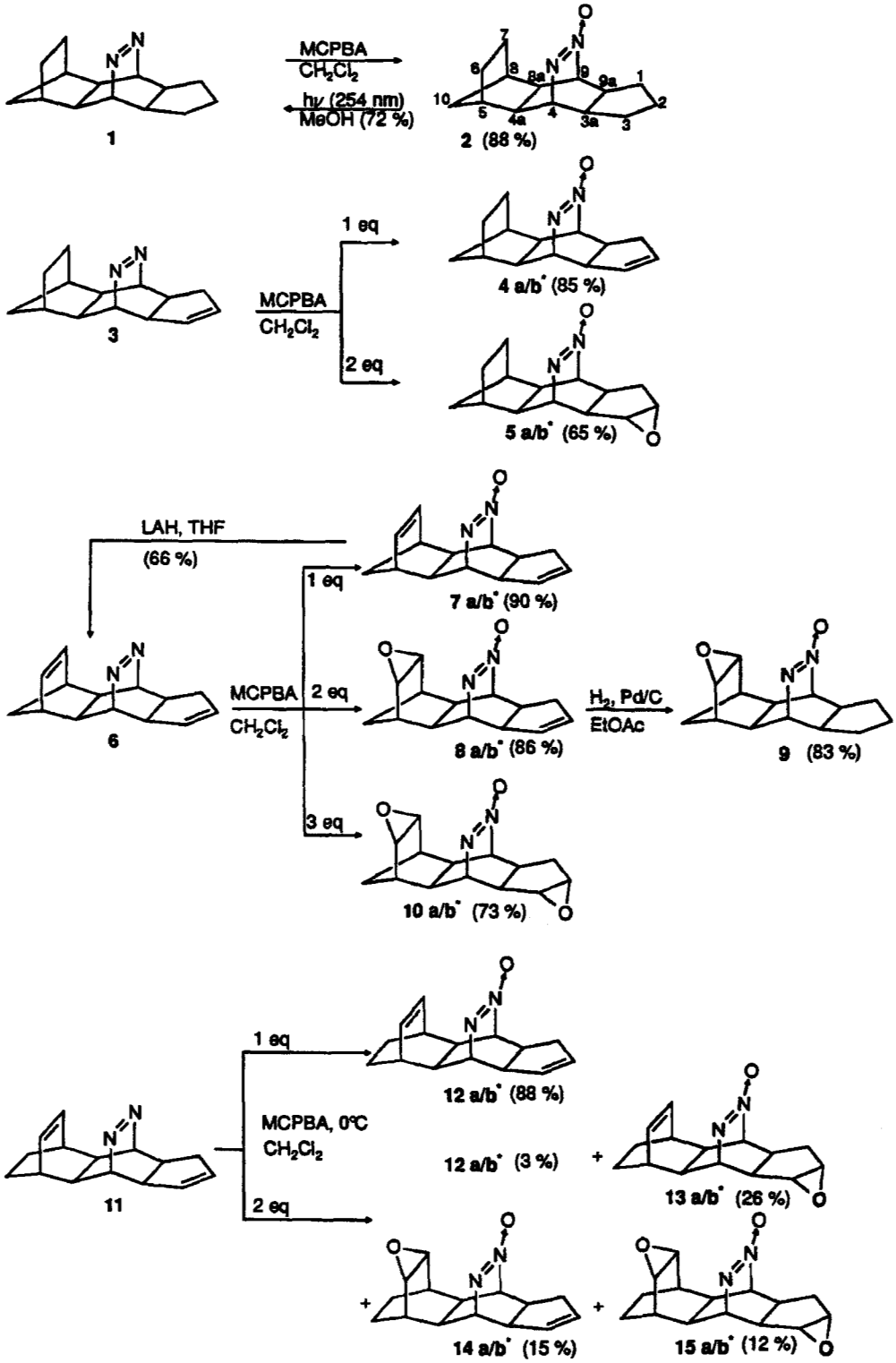
We wondered wether this reaction would occur chemospecifically in systems **A** and **B** which contain olefinic bonds.

The prospects were rather good, since a variety of α,ß-unsaturated azo compounds add oxygen delivered from peracids specifically at the azo group [6]. As most of the compounds discussed in this paper contain double bonds in a parallel position to the azo group and/or in a strained ring system, however, the selectivity of the oxidation was questionable.

We now [7] present the results of various peroxidations together with some spectroscopical properties of the products. Intramolecular [3+2] cycloadditions of some of the azoxides will be discussed in the subsequent paper [8].

Reaction of MCPBA with Azo-Bridged Compounds

Apart from **24**, all the azo-bridged compounds can be regarded as derivatives of DBO. Consequently, **1**, being void of any other functionality, is smoothly transformed into its azoxy derivative **2**. Even if the same skeleton contains one (**3**) or two (**6**) olefinic functions, high chemoselectivity is observed. With one equivalent of MCPBA in both **3** and **6**, only the azo group is attacked and the corresponding azoxy derivatives **4a/b** and **7a/b** are isolated in high yield. With two equivalents of MCPBA in the case of **3** the product to be expected is **5a/b**. However, with **6** having two slightly different double bonds present, attack occurs preferentially at the norbornene moiety as demonstrated by the high yield of **8a/b**. When three equivalents of MCPBA are used, the stepwise oxidation of **6** finally comes to its end by forming the azoxybis-oxirane **10a/b**.



* in isomer "b" the oxygen atom at the azo group is attached to the other nitrogen atom

This pronounced chemoselectivity between the CC double bonds is no longer observed with **11**, in which the norbornene moiety of **6** has been replaced by a bicyclo[2.2.2]octene unit. Again, the first equivalent of MCPBA definitely prefers to oxygenate the azo group in **11** producing **12a/b**.

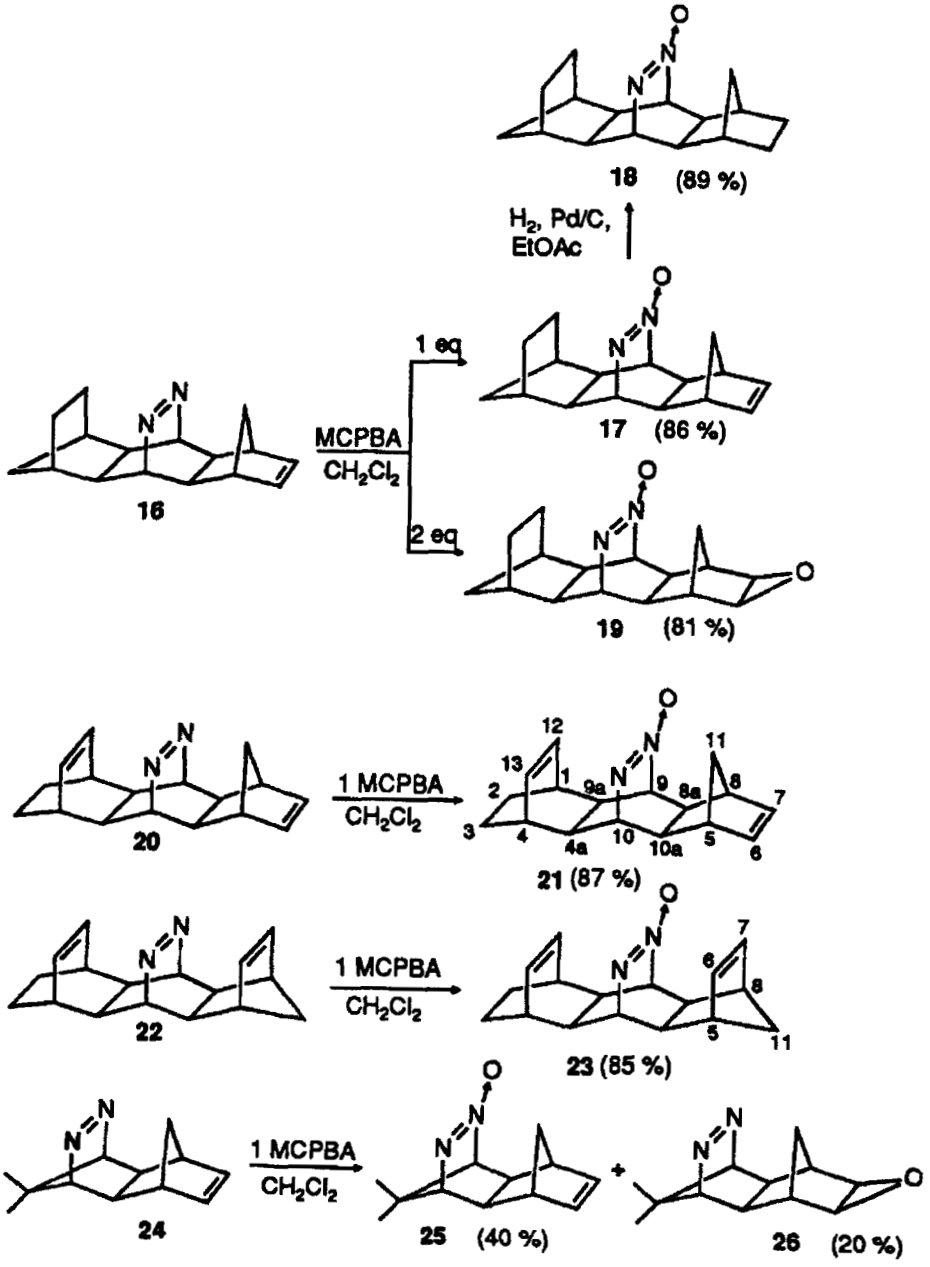
However, the second equivalent of MCPBA no longer discriminates between the two different double bonds

in **11**: Now the two isomeric oxiranes **13a/b** and **14a/b** together with bisoxirane **15a/b** are formed in comparable yields.

In azo compounds **16**, **20**, and **22** the cyclopentene unit of **3**, **6**, and **11** has been replaced by a norbornene moiety, attached to the central DBO moiety with differing geometry. As to be expected already from the reaction sequence **6** → **7a/b** one equivalent of MCPBA cleanly transforms **16**, **20** and **22** into the corresponding azoxy derivatives **17**, **21** and **23**, even if the azo bridge is flanked by two olefinic bridges as in **22**. As in the transformation **6** → **8a/b** the azoxy-oxirane **19** is produced from **16** by two equivalents of MCPBA. But obviously, the reactivity of the azo group in **24**, being enclosed in a DBH system, is definitely reduced. Now both unsaturated functionalities in **24** compete favorably for the peracid, as can be judged from the formation of azoxy derivative **25** and azo-oxirane **26**.

Reduction of Some Products

Of the few methods available for the reduction of aliphatic azoxy compounds to their azo derivatives, the reaction with lithium aluminium hydride in ether or THF seems to be the only one gaining preparative accept-



ance [4a, 9]. Application of this procedure to **7a/b** leads to regeneration of **6** in 66% yield. As a minor side reaction, probably catalyzed by lithium ions (Lewis acid) 10% of the intramolecular [3+2] cyclization product of **7a/b** is formed. This [3+2] cycloaddition will be discussed in the following paper [8].

As exemplified by the transformation **2** → **1**, even aliphatic azoxy compounds can readily be photoreduced. So far, only the photoreduction of aromatic azoxy compounds has been described [9]. There it is interesting to note that hydrogen from the solvent is transferred into the triplet state of the azoxy group obtained by photolysis sensitized with benzophenone [10], whereas direct excitation (λ = 254 nm) gives rise to *cis/trans* isomerization of the azo group only [11]. By contrast, clean photoreduction of **2** leading to **1** is observed from the excited singlet state (λ = 254 nm) either in methanol (72%) or hexane (91%). Obviously, a protic solvent is no prerequisite for hydrogen transfer. In the presence of a sensitizer, however, either decomposition (methanol/acetone, 1:1) or very sluggish reduction (hexane/benzophenone) is observed.

Catalytic hydrogenation of the olefinic bonds occurs smoothly without affecting azoxy or oxirane functionalities as exemplified by the transformations **8a/b** → **9** and **17** → **18**.

Spectroscopic Properties of the Azoxy Compounds

The structure and physical properties of DBON-oxide were thoroughly elucidated and compared with those of DBO. Since all DBON-oxides discussed here contain the azoxide function as a central unit, very similar features were found:

1) The ^{1}H-NMR signals of the two protons adjacent to the azoxy bridge are shifted upfield by ca. δ = 1.5 compared to those in the corresponding azo compounds [4a, 12, 13]. Despite the asymmetry of the azoxy group the chemical shifts of these protons differ only by δ = 0.02–0.2 from each other, a surprising phenomenon [4a, 12] for which a theoretical analysis has been provided [12].

The effect of the azoxide function on the chemical shift in the ^{13}C-NMR spectra, however, is sufficiently strong to detect that a (1:1) mixture of the regioisomers **4a,b**, **5a,b**, **7a,b**, **8a,b**, and **12–15, a,b** is formed in the oxidation of the corresponding azo compound.

2) Again the ^{13}C-NMR signals of the two bridgehead C atoms agree with those of DBON-oxide [12]. As expected, they differ by 13–17 ppm. The resonance of the C atom attached to the trivalent nitrogen matches that of the corresponding azo compounds whereas the presence of oxygen at the other N atom causes the downfield shift of the ^{13}C signal in the range mentioned above.

3) In the IR spectrum bicyclic azoxy derivatives are characterized by a sharp and intense vibration band at 1510–1500 cm^{-1} [12,14] which is also observed with all the newly prepared derivatives.

4) In most of the azoxides (**2**, **4**, **5**, **8–10**, **14**, **15**, **17–19**) described here the UV absorption of DBON-oxides at 230 nm (ε = 6 680) [12] is shifted to 236–238 nm. Transannular interactions as found in the case of the corresponding azo compounds [15] cannot be derived safely from these rather small bathochromic effects which are displayed by both saturated and unsaturated bridges in positions parallel to the azoxy group. Possibly, subtle structural differences may account for these shifted bands since with unsaturated bridges of the norbornene type, the UV maxima are found at 232 nm (**7**) or even at 224 nm (**21**, **23**). As with DBHN-oxide [12] the absorption band of **25** is found at 226 nm.

5) The 70-eV mass spectra of the new azoxides are by no means uniform. Although in all cases primary fragmentation occurs with loss of oxygen, nitrogen monoxide, and dinitrogen monoxide, the strength of the signal for the molecular ion changes dramatically: Most compounds give a M^+ signal intensity of 0.5–10%, but **7**, **12**, **13**, and **23** were found to give 55–100% M^+. These azoxides probably undergo an intramolecular [3+2] cycloaddition, to be discussed in the subsequent paper [8] either prior to or during ionisation.

Conclusions

The known high yield oxidation of aliphatic azo compounds by peracids [4, 5] occurs chemospecifically in the presence of double bonds of different energy and position in the same molecule. As demonstrated by **6**, **11**, **20**, and **22**, the sequence of reactivity for the different moieties is found to be as follows: azo >> bicycloheptene > bicyclooctene, cyclopentene.

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Experimental

Melting points corrected: Kofler heated microscope. – IR: Perkin-Elmer 157 G, Beckman IR 33. – UV/VIS: Beckman DB-GT, Perkin-Elmer 330. – ^{1}H NMR: Varian T 60 (60 MHz), EM 390 (90 MHz), Bruker WM 200 (200 MHz), WM 400 (400 MHz). Internal standard TMS (δ = 0.00 ppm) or $CHCl_3$ (δ = 7.26 ppm). – ^{13}C NMR: Bruker WM 200 (50.3 Hz), WM 400 (100.6 Hz). – MS: Varian MAT CH7 (70 eV).

General Oxidation Procedure (GOP):

A solution of 1–3 equivalents of m-chloroperbenzoic acid [MCPBA, Janssen 80%, 1.15–3.45 mmol (200–600 mg)] in 5–15 ml of dichloromethane is slowly added (15 min) to a solution of 1.00 mol of the azo compound in 10 ml of dichloromethane at 0 °C. Any precipitate formed is dissolved by adding more dichloromethane. The reaction is monitored by TLC (silica, cyclohexane/ethyl acetate, 1:1).
Isolation of products:
GOP 1: The mixture is stirred for 12 h with potassium carbonate (2.5 g per equiv. of MCPBA), filtered, the filtrate is washed with dichloromethane and the solvent removed in a rotary evaporator.
GOP 2: The mixture is stirred with 1M sodium hydroxide (15 ml per equiv. of MCPBA) for 2 min. The separated organic phase is dried with potassium carbonate and the solvent removed in a rotary evaporator.

(t-3a,t-4a,t-8a,t-9a)-Perhydro-r-4,c-9-azo-t-5,t-8-methano-1H-cyclopenta[b]-naphthalene-11-oxide (**2**):

GOP 2: 400 mg (2.00 mmol) of **1**, 400 mg (2.30 mmol) of MCPBA, 1.5 h. Sublimation (120 °C, 0.01 Torr) of the crude product yields 410 mg (88%) of **2**. Colorless crystals, m.p. 256–257 °C. – IR (CCl_4): ν = 2960, 2870 cm^{-1} (-C-H), 1500 (NNO), 1450, 1260. – UV (CH_3CN): λ_{max} (lg ε) = 238 nm (3.73). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.10–2.10 (m, 12 H, 1-H_2, 2-H_2, 3-H_2, 6-H_2, 7-H_2, 10-H_2), 2.16 (br.s, 2 H, 3a-H, 9a-H), 2.39 (br.s, 4 H, 4a-H, 8a-H, 5-H, 8-H), 4.43, 4.48 [2 s (1:1), 2 H, 4-H, 9-H] ppm. – ^{13}C NMR(100.6 MHz, $CDCl_3$): δ = 77.57, 61.93 (2 d, C-4, C-9), 46.83 (d), 45.08 (d), 44.54 (d), 44.44 (d), 42.19 (t, C-10), 40.53 (d), 40.29 (d), 29.47, 28.92 (2 t, C-1, C-3*), 26.75 (t, C-2*), 25.96, 22.55 (2 t, C-6, C-7) .– *: Assignment unsure.– $C_{14}H_{20}N_2O$ (232.3): calcd. C 72.38, H 8.68, N 12.06; found C 72.11, H 8.74, N 11.92.

Photochemical Deoxygenation of N-oxide 2:

A degassed solution of 100 mg (0.43 mmol) of **2** in 150 ml of solvent is irradiated at λ = 254 nm (rayonet reactor, quartz filter, T = 20 °C). When the reaction is complete (TLC monitoring) the solvent is evaporated under reduced pressure. The solid residue is purified by filtration through a short chromatographic column (silica gel, 63 - 200 μm (Woelm), 2 x 6 cm, EtOAc) and characterized by means of IR and ^{1}H-NMR spectroscopy.
a) Irradiation in 200 ml of hexane, 120 min, yield 85 mg (91%) of **1**, purity > 95% (^{1}H-NMR).
b) Irradiation in 150 ml of methanol, 105 min, yield 80 mg (86%) of **1**, purity about 80% (^{1}H-NMR).

(t-3a,t-4a,t-8a,t-9a)-Δ²-Decahydro-r-4,c-9-azo-t-5,t-8-methano-1H-cyclopenta[b]naphthalene-11(12)-oxide (**4ab**)

GOP 2: 643 mg (3.00 mmol) of **3** [3b], 600 mg (3.45 mmol) of MCPBA,3 h. Sublimation (120 °C, 0.01 Torr) of the crude product affords 590 mg (85%) **4a/b**. Colorless crystals, m.p. 162–164 °C.– IR (KBr): ν = 3050 cm^{-1} (=C-H), 2990, 2950, 2910, 2880, 2840 (-C-H), 1500 (NNO), 1450. – UV (CH_3CN): λ_{max} (lg ε) = 238 nm (3.74). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.10–1.85 (m, 6 H, 6-H_2, 7-H_2, 10-H_2), 2.05–2.90 (m, 7 H, 1-H_2, 4a-H, 5-H, 8-H, 8a-H, 9a-H), 3.17 (m, 1 H, 3a-H), 4.43, 4.53, 4.57 (3 s, 2 H, 4-H, 9-H), 5.43 - 5.90 (m, 2 H, 2-H, 3-H). - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 134.37, 132.48, 129.39, 127.66 (4 d, C-2, C-3), 78.77, 77.34, 63.18, 61.92 (4d, C-4, C-9), 53.30 (d), 51.79 (d), 46.94 (d), 46.63 (d), 44.61 (d, 2C), 42.27 (t, 2C, C-10), 41.39 (d), 40.98 (d), 40.90 (d), 40.74 (d), 40.63 (d), 40.49 (d), 37.23, 35.56 (2 t, C-1), 27.16, 27.04, 22.92, 22.82 (4 t, C-6, C-7). – MS (70 eV); m/z (%): 230.1 (5.8) [M^+], 200.0 (29.2) [M^+ – 30], 165.1 (100) [M^+ – 65] .– $C_{14}H_{18}N_2O$ (230.3): calcd. C 73.01 H 7.87 N 12.16; found C 72.89 H 8.04 N 11.86.

(t-3a,t-4a,t-8a,t-9a)-Δ²-Decahydro-r-4,c-9-azo-t-5,t-8-methano-t-2,t-3-epoxy-1H-cyclo-penta[b]naphthalene-11(12)-oxide (**5a/b**):

GOP 1: 429 mg (2.00 mmol) of **3** [3b], 8.00 mg (4.60 mmol) of MCPBA, 1 h (0 °C), 3 d (5 °C). The crude product is sublimed (120 °C/0.01 Torr) and recrystallized from cyclohexane. 300 mg (65%) of **5a/b**, colorless crystals, m.p. 218–220 °C). – IR (KBr): ν = 2945 cm^{-1}, 2870 (-C-H), 1500 (NNO), 1450, 835 (oxirane). – UV (CH_3CN): λ_{max} (lg ε) = 238 nm (3.77). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.21–1.85 (m,6 H, 6-H_2, 7-H_2, 10-H_2), 1.85–2.69 (m, 8 H, 1-H_2, 3a-H, 4a-H, 5-H, 8-H, 8a-H, 9a-H), 3.40 (m, 2 H, 2-H, 3-H), 4.39, 4.52, 4.67 [3 s (2:1:1), 2 H, 4-H, 9-H] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 78.43, 74.82, 62.51, 60.54 (4 d, C-4, C-9), 60.21 (d), 60.03 (d), 59.86 (d, 2C, C-2, C-3), 48.35 (d), 47.52 (d), 47.14 (d), 45.31 (d), 44.81 (d), 43.59 (d), 42.83 (d), 42.57 (d), 42.26 (t, 2C, C-10), 40.89 (d, 2C), 40.74 (d), 40.57 (d), 31.37, 30.35 (2 t, C-1), 27.13, 26.95, 23.11, 22.44 (4 t, C-6, C-7) ppm. – MS (70 eV); m/z(%): 247.1 (0.86) [M^+ +1], 246.1 (0.37) [M^+], 216.1 (100) [M^+–30]. – $C_{14}H_{18}N_2O_2$ (246.3): calcd. C 68.26, H 7.36, N 11.37; found C 68.00; H 7.38; N 10.98.

(t-3a, t-4a, t-8a, t-9a)-Δ²- Octahydro-r-4, c-9-azo-c-5,c-8-methano-1H-cyclopenta[b]naphthalene-10(11)-oxide (**7a,b**)

GOP2: 424 mg (2.00 mmol) of **6**, 400 mg (2.30 mmol) of MCPBA, 3 h. Filtration through a short chromatographic column (silica gel, 63–200 μm (Woelm), 2 × 6 cm, EtOAc) yields 410 mg (90%) of **7a,b**. Colorless crystals m.p. 144–146 °C. IR (KBr): ν = 3050 cm^{-1} (=C-H), 2995, 2940, 2890, 2840 (-C-H), 1500 (NNO), 1450 (NN). – UV (CH_3CN): λ_{max} (lg ε) = 232 nm (3.91). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35, 1.47 (AB, $J_{10,10'}$ = 8.5 Hz, 2 H, 10-H_2), 2.10–2.75 (m, 5 H, 1-H_2, 4a-H, 8a-H, 9a-H), 2.89, 2.96 (2 br, s, 2 H, 5-H, 8-H), 3.10, 3.21 (2 m, 1 H, 3a-H), 4.27, 4.33, 4.42, 4.53 [4s (1:1:1:1)], 2 h, 4-H, 9-H), 5.48, 5.62, 5.78 [3 m (2:1:1)], 2 H, 2-H, 3-H, 5.84, 5.98 (2 m, 2 H, 6-H, 7-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 136.57 (d, 2C), 126.78, 126.58 (2 d, C-6, C-7), 134.73, 132.53, 129.18, 127.42 (4 d, C-2, C-3), 78.89, 77.41, 63.00, 61.64 (4 d, C-4, C-9), 52.96 (d), 51.99 (t, 2C, C-10), 51.13 (d), 45.70 (d), 45.56 (d, 2C), 45.50 (d), 45.21 (d), 44.85 (d), 41.17 (d), 40.37 (d), 40.17 (d), 39.80

(d), 37.03 (d), 35.58 (2 t, C-1) ppm.– MS (70 eV): m/z = 228.3 (100.0) [M+], 199.3 (27.31) [M+– 29], 163.3 (11.37) [M+– 65].– $C_{14}H_{16}N_2O$ (228.3): calcd. C 73.65; H 7.06; N 12.27; found C 73.89; H 7.23; N 12.27.

Chemical Deoxygenation of N-Oxide 7a,b:

114 mg (0.50 mmol) of **7a,b** are dissolved in 7 ml of THF and 600 mg (15 mmol) of $LiAlH_4$ is added in portions to the solution with vigorous stirring. The mixture is refluxed for 5 h. After hydrolysis by addition of 20 ml of water, the mixture is extracted with CH_2Cl_2. The separated organic phase is dried with potassium carbonate and the solvent removed in a rotary evaporator. Sublimation (120 °C, 0.01 Torr) of the solid residue yields 70 mg (66%) of **6** (purity > 90%, ^1H NMR).

(t-3a, t-4a, t-8a, t-9a)-Δ^2- Octahydro-r-4, c-9-azo-t-5, t-8-methano-t-6, t-7-epoxy-1H-cyclopenta(b)naphthalene-11(12)-oxide (**8a,b**):

GOP2: 424 mg (2.00 mmol) of **6,** 800 mg (4.60 mmol) of MCPBA, 1 d at 5 °C. Sublimation (120 °C, 0.01 Torr) of the crude product yields 420 mg (86%) of **8a,b**. Colorless crystals m.p. 136-139 °C. IR (KBr): ν = 3050 cm^{-1} (=C-H), 2960, 2900, 2840 (-C-H), 1500 (NNO), 1450 (NN), 850 (oxirane). — UV (CH_3CN): λ_{max} (lg ε) = 237 nm (3.68). – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.77, 1.49 (AB, $J_{10,10'}$ = 11.0 Hz, 2 H, 10-H_2), 2.37 (br.s, 2 H, 4a-H, 8a-H), 2.16–2.58 (m, 3 H, 1-H_2, 9a-H), 2.67 (br.s, 2 H, 5-H, 8-H), 2.98 [d, $J_{6,7}$ = 3.0 Hz, 1 H, 6-H (7-H)], 3.12 (mc, 1 H, 3a-H), 3.43 [d, 1 H, 7-H (6-H)], 4.45, 4.51, 4.58 [3 s (2:1:1)], 2 H, 4-H, 9-H), 5.33–5.76 (m, 2 H, 2-H, 3-H) ppm. – MS (70 eV); m/z (%): 244.3 (10.6) [M+], 228.3 (21.7) [M+ – 16], 179.3 (100) [M+ – 65]. – $C_{14}H_{16}N_2O_2$ (244.3): calcd. C 68.83, H 6.60, N 11.46; found C 69.05, H 6.74, N 10.99.

(t-3a, t-4a, t-8a, t-9a)-Perhydro-r-4, c-9-azo-t-5, t-8-methano-t-6, t-7-epoxy-1H-cyclopenta[b]naphthalene-11-oxide (**9**):

244 mg (1.00 mmol) of **8a,b** is dissolved in 30 ml of EtOAc and hydrogenated with 80 mg of Pd/C (Merck, 10% Pd) under atmospheric pressure. After filtration and evaporation of the solvent, the crude product is sublimed (120 °C, 0.01 Torr). Yield 200 mg (83%) of **9**, colorless crystals m.p. >205 °C (decomp.). – IR (KBr): ν = 2950 cm^{-1}, 2860 (-C-H), 1500 (NNO), 1450, 850 (oxirane). – UV (CH_3CN): λ_{max} (lg ε) = 238 nm (3.70). – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.78 (d, $J_{10,10'}$ = 9.9 Hz, 1 H, 10-H), 1.31 (mc, 2 H, 1-H, 3-H), 1.43 (m, 1 H, 2-H), 1.53 (dt, J = 10.0, 1.7 Hz, 1 H, 10-H'), 1.59 (m, 1 H, 2-H'), 1.84 (mc, 2 H, 1-H', 3-H'), 2.29 (br.s, 2 H, 4a-H, 8a-H), 2.34 (mc, 2 H, 3a-H, 9a-H), 2.69 (br. s, 2 H, 5-H, 8-H), 3.04 [br. d, $J_{6,7}$ = 3.3 Hz, 1 H, 6-H (7-H)], 3.51 [br. d, 1 H, 7-H (6-H)], 4.49, 4.54 (2 s, 2 H, 4-H, 9-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 77.38, 62.08 (2 d, C-4, C-9), 50.66, 46.08 (2d, C-6, C-7), 45.14 (d), 44.77 (d), 44.35 (d), 44.11 (d), 41.35 (d), 41.24 (d), 29.73 (t, C-10), 29.46, 28.40 (2t, C-1, C-3), 26.28 (t, C-2) ppm. – MS (70 eV); m/z (%): 247.2 (1.2) [M+ + 1], 216.3 (5.2) [M+–30], 202.3 (33.2) [M+–44]. – $C_{14}H_{18}N_2O_2$ (246.3): calcd. C 68.26, H 7.36, N 11.37; found C 67.91, H 7.53, N 10.89.

(t-3a, t-4a, t-8a, t-9a)-Δ^2-Octahydro-r-4, c-9-azo-t-5, t-8-methano-t-6, t-7: t-2, t-3-diepoxy-1H-cyclopenta(b) naphthalene-11(12)-oxide (**10a,b**):

GOP1: 212 mg (1.00 mmol) of **6**, 600 mg (3.45 mmol) of MCPBA, 2 d at 5 °C. Sublimation of the crude product yields 190 mg (73%) **10a,b**. Colorless crystals mp 163-165 °C. – IR (KBr): ν = 2960 cm^{-1}, 2940, 2920, 2840 (-C-H), 1500 (NNO), 1440, 840, 830 (oxirane). – UV (CH_3CN): λ_{max} (lg ε) = 238 nm (3.72).– ^1H NMR (90 MHz, $CDCl_3$): δ = 0.76 (AB, $J_{10,10'}$ = 10.5 Hz, 1 H, 10-H), 1.55 (AB, 1 H, 10-H') 1.72–2.90 (m, 8 H, 1-H_2, 3a-H, 4a-H, 5-H, 8-H, 8a-H, 9a-H), 3.02 [br. s, 1 H, 7-H (6-H)], 3.47 [br. s, 3 H, 2-H, 3-H, 6-H (7-H)], 4.46, 4.52, 4.72 [3 s (1:1:2), 2 H, 4-H, 9-H] ppm. – MS (70 eV); m/z = 261.3 (0.62) [M+ + 1], 260.2 (0.23) [M+], 230.1 (2.26) [M+ – 30], 215.3 (4.91) [M+ – 45]. – $C_{14}H_{16}N_2O_3$ (260.3): calcd. C 64.60, H 6.19, N 10.76; found C 64.53, H 6.29, N 10.51.

(t-3a, t-4a, t-8a, t-9a)-Δ^2- Decahydro-r-4, c-9-azo-c-5, c-8-etheno-1H-cyclopenta[b]naphthalene-12(13)-oxide (**12a,b**):

GOP2: 452 mg (2.00 mmol) of **11**, 400 mg (2.30 mmol) of MCPBA, 3 h. Filtration through a short chromatographic column (silica gel, 63–200 µm (Woelm), 2 × 6 cm, EtOAc) and evaporation of the solvent from the filtrate yields 425 mg (88%) of **12a,b**. Colorless crystals m.p. 154-156 °C. – IR (KBr): ν = 3050 cm^{-1} (=C-H), 2940, 2900, 2860(-C-H), 1500 (NNO), 1440. – UV (CH_3CN): λ_{max} (lg ε) = 232 nm (3.72). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.37 (mc, 4 H, 6-H_2, 7-H_2), 2.20 (br. s, 2 H, 4a-H, 8a-H), 2.30–2.90 (m, 5 H, 1-H_2, 5-H, 8-H, 9a-H), 3.13 (mc, 1 H, 3a-H), 4.13, 4.21, 4.37, 4.47 [4 s (1:1:1:1)], 2 H, 4-H, 9-H), 5.40–5.83 (m, 2 H, 2-H, 3-H), 6.07 (mc, 2 H, 10-H, 11-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 133.60 (2C), 126.39, 126.30 (2 d, C-10, C-11), 134.72, 132.51, 129.30, 127.56 (4 d, C-2, C-3), 79.90, 78.30, 65.67, 64.06 (4 d, C-4, C-9), 52.21 (d), 50.44 (d), 43.96 (d), 43.71 (d), 41.31 (d), 41.14 (d), 40.43 (d), 39.11 (d), 37.40, 36.01 (2 t, C-1), 33.57 (d, 4C), 25.82, 25.77, 25.57, 25.50 (4 t, C-6, C-7) ppm. – MS (70 eV); m/z(%): 242.3 (55.1) [M+], 213.3 (25.8) [M+–29], 163.3 (37.1) [M+–79]. – $C_{15}H_{18}N_2O$ (242.3): calcd. C 74.35, H 7.49, N 11.56; found C 74.52, H 7.55, N 11.14.

(t-3a, t-4a, t-8a, t-9a)-Δ^2-Octahydro-r-4, c-9-azo-t-1, t-2-epoxy- t-5, t-8-etheno-1H-cyclopenta[b]naphthalene-12(13)-oxide (**13a,b**),

(t-3a, t-4a, t-8a, t-9a)- Δ^2-Octahydro-r-4, c-9-azo-t-6, t-7-epoxy- t-5, t-8-etheno-1H-yclopenta(b)naphthalene-12(13)-oxide (**14a,b**),

(t-3a, t-4a, t-8a, t-9a)- Δ^2-Octahydro-r-4, c-9-azo-t-1, t-2, t-6, t-7-diepoxy-c-5, c-8-etheno-1H-cyclopenta(b)-naphthalene 12(13)-oxide (**15a,b**):

GOP2: 1.05 g (4.64 mmol) of **11**, 1.86 g (10.7 mmol) of MCPBA, 2 d at 5 °C. Purification of the crude product by means of MPLC (LiChrosorb, 15–25 µm (Merck), N = 4900; CH_2Cl_2, EtOAc 5:3; Det. -nD), four main fractions are

collected (A.D):
Fraction A: 33 mg (3%) of **12a,b** (^{1}H-NMR spectroscopically pure).
Fraction B: 305 mg (26%) of **13a,b**, colorless crystals m.p.158–159 °C.
Fraction C: 172 mg (15%) of **14a,b**, colorless crystals, m.p.169–172 °C.
Fraction D:159 mg (12%) of **15a,b**, colorless crystals, m.p. > 192 °C (decomp.).
The ratios of isomers **a/b** given below may have been affected by the chromatographic purification.

13a,b (B, **a/b** = 4:1): IR (KBr): n = 3040 cm^{-1}, 3020 (=C-H), 2940, 2900, 2860 (-C-H), 1500, 1460, 1445, 1400, 1385, 1365, 1260, 1030, 930, 900, 850, 840, 820. – UV (CH_3CN): λ_{max} (lg ε) = 229 nm (3.60). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (mc, 2H, 9-H, 10-H), 1.48 (mc, 2 H, 9-H', 10-H'), 1.68 [ddd, J = 15.3, 5.1, 2.1 Hz, 0.8 H, 1-H(a)], 1.85 [dd, J = 15.0 Hz, 4.8 Hz, 0.2 H, 1-H(b)], 2.12 (m, 3H, 1-H', 4a-H, 8a-H), 2.35 [mc, 0.2 H, 9a-H(b)], 2.41 [mc, 0.8 H, 9a-H(a)], 2.60 (m, 3 H, 3a-H, 5-H, 8-H), 3.39 (m, 2 H, 2-H, 3-H), 4.06, 4.32, 4.35, 4.50 [4 s (4:1:1:4), 2 H, 4-H, 9-H], 5.98, 6.05 (2 ps.-t, J = 7.3 Hz, 6-H, 7-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$) **a**: δ = 133.54, 126.20 (2 d, C-6, C-7), 79.24, 61.90 (2 d, C-4, C-9), 60.40, 59.95 (2 d, C-2, C-3), 45.96, 43.71 (2 d, C-3a, C-9a), 41.33, 39.96 (2 d, C-4a, C-8a), 33.29, 33.14 (2 d, C-5, C-8), 30.50 (t, C-1), 25.40, 25.34 (2 t, C-10, C-11). – **b**: δ = 133.54, 126.20 (2 d, C-6, C-7), 75.68, 64.69 (2 d, C-4, C-9), 59.95, 59.85 (2 d, C-2, C-3), 42.36 (d), 41.03 [d, (2C?)] 31.23 (t, C-1), 25.78, 25.01 (2 t, C-10, C-11). – missing signals of isomer **b** are overlapped by signals of **a**. – MS (70 eV); m/z (%): 259.2 (14.04) [M$^+$ + 1], 258.1 (76.16) [M$^+$], 257.1 (8.32) [M$^+$–1], 229.3 (27.44) [M$^+$ – 29], 91.1 (84.27), 80.0 (100) [$C_4H_4N_2^+$]. – $C_{15}H_{18}N_2O_2$ (258.3): calcd. C 69.74, H 7.02, N 10.84; found C 69.85, H 7.04, N 10.63.

14a,b (C, **a/b** = 2:1): IR (KBr): ν = 3020 cm^{-1} (=C-H), 2960, 2930, 2910, 2900, 2850 (-C-H), 1500 (NNO), 1390, 1370, 1300, 1280, 1270, 1250, 980, 940, 910, 850, 800, 720, 660. – UV (CH_3CN): λ_{max} (lg ε) = 236 nm (3.73). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (mc, 2H, 10-H, 11-H), 1.76 (mc, 2 H, 10-H', 11-H'), 2.16–2.32 (m, 4 H, 4a-H, 5-H, 8-H, 8a-H), 2.44 (ps.-d, J = 17.0 Hz, 1 H, 1-H), 2.59 (m, 1 H, 1-H'), 2.72 [ps.-t, J = 9.5 Hz, 0.6H, 9a-H(a)], 2.79 [ps.-t, J = 9.5 Hz, 0.4H, 9a-H(b)], 3.02 [dd, $J_{6,7} = J_{6,5}$ = 4.8 Hz, 1 H, 6-H(7-H)], 3.17 [ps.-d, J =9.0 Hz, 0.4 H, 3a-H(b)], 3.28 [ps.-d, J = 9.0 Hz, 0.6 H, 3a-H(a)], 3.38 [t, 1 H, 7-H(6-H)), 4.42, 4.58 [2 s, 0.8 H, 4-H(b), 9-H(b)], 4.45, 4.48 [2 s, 1.2H, 4-H(a), 9-H(a)], 5.49, 5.65 [2 m, 1.2 H, 2-H(a), 3-H(a)], 5.51, 5.80 [2 m, 0.8 H, 2-H(b), 3-H(b)] ppm.- ^{13}C NMR (100.6 MHz, $CDCl_3$): **a**: δ = 134.81, 127.45 (2 d, C-2, C-3), 78.58, 65.72 (2 d, C-4, C-9), 52.18, 51.85, 48.39 (3 d, C-9a, C-6, C-7), 41.81, 40.09 (2 d, C-4a, C-8a), 39.14 (d, C-3a), 37.36 (t, C-1), 32.32, 32.02 (2 d, C-5, C-8), 24.50, 24.34 (2 t, C-10, C-11). – **b**: δ = 132.72, 129.11 (2 d, C-2, C-3), 80.24, 64.14 (2 d, C-4, C-9), 51.85, 50.49, 48.28 (3 d, C-9a, C-6, C-7), 40.36, 40.26 (2 d, C-4a, C-8a), 36.05 (t, C-1), 32.32, 32.02 (2 d, C-5, C-8), 24.52, 24.30 (2 t, C-10, C-11) ppm. – signal of C-3a is overlapped by **a**. – MS (70 eV); m/z(%): 259.2 (3.26) [M$^+$ + 1], 258.3 (15.81) [M$^+$], 257.2 (1.58) [M$^+$–1], 229.3 (7.94) [M$^+$–29], 193.1 (100.0) [M$^+$–65], 177.3 (63.10), 97.1 (59.89), 91.1 (55.87), 79.1 (47.49), 67.00 (38.83), 66.0 (32.29) [$C_5H_6^+$]. – $C_{15}H_{18}N_2O_2$ (258.3): calcd. C 69.75 H 7.02 N 10.84; found C 70.07 H 7.09 N 10.96.

15a,b (D, **a/b** = 2/1): IR (KBr): ν = 3020 cm^{-1}, 2940, 2920, 2860 (-C-H), 1500 (NNO), 1480, 1450, 1400, 1390, 1380, 1280, 1270, 1260, 1160, 1030, 950, 930, 910, 860, 840, 815, 810. – UV (CH_3CN): λ_{max} (lg ε) = 236 nm (3.72) nm. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (mc, 2 H, 10-H, 11-H), 1.74 (m, 2 H, 10-H', 11-H'), 2.05–2.34 (m, 6 H, 1-H_2, 4a-H, 5-H, 8-H, 8a-H), 2.43 [m, 0.3 H, 9a-H(b)], 2.52 [m, 0.7 H, 9a-H(a)], 2.66 (m, 1 H, 3a-H), 2.99 [br. t, $J_{6,7} = J_{6,5}$ = 4.5 Hz, 1 H, 6-H (7-H)], 3.32 [br. t, $J_{6,7} = J_{7,8}$ = 4.5 Hz, 1 H, 7-H (6-H)], 3.43 [m, 2 H, 2-H, 3-H), 4.34, 4.61 [2 s, 1.4 H, 4-H(a), 9-H(a)], 4.44, 4.59 [2 s, 0.6 H, 4-H(b), 9-H(b)] ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$) **a**: δ = 79.57, 62.11 (d, C-4, C-9), 60.32, 59.85 (2 d, C-2, C-3), 51.62, 46.00 (2 d, C-6, C-7), 48.28 (d, C-9a), 41.48 (d, C-3a), 40.54, 40.26 (2 d, C-4a, C-8a), 32.14, 31.84 (2 d, C-5, C-8), 30.62 (t, C-1), 24.27 (t, 2C, C-10, C-11) ppm. – **b:** δ = 76.06, 64.79 (2 d, C-4, C-9), 59.90, 59.71 (2 d, C-2, C-3), 51.62, 47.06 (2 d, C-6, C-7), 47.85 (d, C-9a), 41.93 (d), 41.24 (d), 38.72 (d), 31.23 (t, C-1), 24.53, 24.01 (2 t, C-10, C-11). – missing signals of isomer **b** are overlapped by signals of **a**. – MS (70 eV); m/z(%): 275.3 (0.97) [M$^+$ + 1], 274.3 (1.93) [M$^+$], 273.4 (2.51) [M$^+$–1], 258.4 (20.85) [M$^+$–16], 244.3 (23.41) [M$^+$–30, NO], 91.1 (100), 81.1 (83.11), 67.0 (62.84). – $C_{15}H_{18}N_2O_3$ (274.3): calcd. C 65.68 H 6.61 N 10.21; found C 66.09, H 6.84, N 10.51.

(t-4a, t-8a, t-9a, t-10a)-Δ^2- Dodecahydro-c-9,c-10-azo-r-1,c-4, t-5, t-8-dimethano-anthracene-13-oxide (**17**):

GOP2: 120 mg (0.50 mmol) of **16**, 100 mg (0.57 mmol) of MCPBA, 4.5h. Filtration through a short chromatographic column (silica gel, 63–200 µm (Woelm), 2 × 6 cm, EtOAc) yields 110 mg (86%) of **17**. Colorless crystals > 295 °C decomp. – IR (KBr): ν = 3060 cm^{-1}, 3020 (=C-H), 2970, 2950, 2900, 2880 (-C-H), 1505 (NNO), 1480, 1460, 1390, 1375, 1265, 975, 710, 690. – UV (CH_3CN): λ_{max} (lg ε) = 237 nm (3.76). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (AB, $J_{11,11'}$ = 10.2 Hz, 1 H, 11-H), 1.22 (m, 1 H, 7-H [a)]), 1.35 (dt, $J_{12,12'}$ = 9.5, 1.6 Hz, 1 H, 12-H), 1.44 (d, 1H, 12-H'), 1.46 [m, 2 H, 7-H' [a)], 6-H [a)]], 1.58 (AB, 1 H, 11-H'), 1.80 (m, 1 H, 6-H' [a)]), 1.82 [dt, J = 8.4, 1.5 Hz, 1H, 10a-H [b)]], 1.94 [d, J = 8.4 Hz, 1 H, 4a-H [b)]], 2.18 [ddt, J = 11.8, 4.2, 1.5 Hz, 1 H, 8a-H [c)]], 2.25 (dd, J = 11.8, 4.0 Hz (broad), 1 H, 9a-H [c)]), 2.35, 2.39 (2 br.s, 2 H, 5-H, 8-H), 2.84 (br. s, 2 H, 1-H, 4-H), 4.51, 4.57 (2 s, 2 H, 9-H, 10-H), 6.17, 6.22 (2 m, 2 H, 2-H, 3-H) ppm.– [a)],[b)],[c)]): Assignment unsure. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 140.00, 139.33 (2 d, C-2, C-3), 76.24, 61.33 (2 d, C-9, C-10), 48.29 (d), 46.69 (d), 46.21 (d), 45.73 (d), 44.91 (d), 44.65 (d), 42.49 (t, C-12*), 41.90 (t, C-11*), 40.78 (d), 40.57 (d), 27.10, 22.58 (2 t, C-6, C-7) ppm. – *): Assignment unsure. – MS (70 eV); m/z (%): 257.3 (0.46) [M$^+$ + 1], 256.3 (0.23) [M$^+$], 255.3 (0.20) [M$^+$–1], 239.3 (5.68) [M$^+$–17], 226.3 (100) [M$^+$–NO], 79.1 (22.99), 66.1 (31.60) [$C_5H_6^+$]. – $C_{16}H_{20}N_2O$ (256.4): calcd. C 74.97, H 7.86, N 10.93; found C 74.73, H 8.12, N 10.61

(t-4a, t-8a, t-9a, t-10a)-Perhydro-c-9,c-10-azo-r-1,c-4, t-5, t-8-dimethano-anthracene-13-oxide (**18**):

A solution of 100 mg (0.39 mmol) of **17** in 60 ml of EtOAc is vigorously stirred with 50 mg of Pd/C (Merck, 5% Pd) under hydrogene. After filtration and evaporation of the solvent the crude product is sublimed (120 °C, 0.01 Torr). Yield 90 mg (89%) of **18**, colorless crystals > 320 °C decomp. – IR (KBr): ν = 3000 cm^{-1}, 2960, 2920, 2890, 2880 (-C-H), 1500, 1490 (NNO), 1460, 1450, 1375, 1370, 1260. – UV (CH_3CN): λ_{max} (lg ε) = 239 nm (3.80). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.89 (d, J = 11.5 Hz, 1 H, 11-H), 0.97–1.27 (m, 3 H), 1.27–1.37 (m, 2 H), 1.37–1.52 (m, 5 H), 1.73 (mc, 1 H) (2-H_2, 3-H_2, 6-H_2, 7-H_2, 11-H', 12-H_2), 1.77, 1.86 (AB, $J_{4a,10a}$ = 8.6 Hz, 2 H, 4a-H, 10a-H), 2.14 (br. s, 2 H, 8a-H, 9a-H), 2.24 (s, 1 H, 8-H*)), 2.31 (br. s, 3 H, 1-H, 4-H, 5-H*)), 4.50, 4.53 (2 s, 2 H, 9-H, 10-H) ppm. – *) assignment unsure. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 75.99, 62.39 (2 d, C-9, C-10), 49.71 (d), 48.76 (d), 47.61 (d), 45.09 (d), 42.00 (t, C-12), 40.85 (d), 40.64 (d), 39.75 (d), 39.29 (d), 34.00 (t, C-11), 30.77, 29.76 (2t, C-2, C-3), 27.10, 22.60 (2t, C-6, C-7) ppm. – MS (70 eV); m/z (%): 259.1 (0.40) [M^+ + 1], 258.1 (0.60) [M^+], 241.1 (7.06) [M^+–17], 228.1 (100.0) [M^+–NO]. – $C_{16}H_{22}N_2O$ (258.4): calcd. C 74.38, H 8.58, N 10.84; found C 74.15. H 8.83. N 10.52.

(t-4a, t-8a, t-9a, t-10a)-Perhydro-c-9,c-10-azo-c-2,c-3-epoxy-r-1,c-4, t-5,t-8-dimethano-anthracene-13-oxide (**19**):

GOP1: 120 mg (0.50 mmol) of **16**, 200 mg (1.15 mmol) of MCPBA, 3d at 5 °C. Filtration through a short chromatographic column (silica gel, 63–200 µm (Woelm), 2 × 6 cm, EtOAc) yields 110 mg (81%) of **19**. Colorless crystals > 300 °C decomposition. – IR (KBr): ν = 3020 cm^{-1}, 2990, 2950, 2910, 2870 (-C-H), 1510 (NNO), 1460, 1455, 1380, 1260, 860 (Oxirane). – UV (CH_3CN): λ_{max} (lg ε) = 237.5 nm (3.67). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (br. s, 2 H, 11-H2), 1.21 (m, 1 H, 7-H*), 1.33 (d, J = 9.5 Hz, 1 H, 12-H), 1.42 (m, 3 H, 6-H*, 12-H', 7-H*), 1.74 (m, 1 H, 6-H'*), 1.89 (mc, 2 H, 4a-H, 10a-H), 2.20 (br. s, 2 H, 8a-H, 9a-H), 2.37, 2.39 (2 br. s, 2 H, 5-H, 8-H), 2.52, 2.60 (2 s, 2 H, 1-H, 4-H), 3.01, 3.07 (2 d, J = 3.5 Hz, 2 H, 2-H, 3-H), 4.52 (s, 2 H, 9-H, 10-H) ppm.– *): Assignment unsure. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 75.38, 61.63 (2 d, C-9, C-10), 51.32 (d, 2 C, C-2, C-3), 47.88, 46.46, 45.52, 45.40 (4 d, C-4a, C-8a, C-9a, C-10a), 42.18 (t, C-12), 40.85, 40.65, 40.55, 40.27 (4 d, C-1, C-4, C-5, C-8), 27.08, 22.56 (2 t, C-6, C-7), 20.45 (t, C-11) ppm. – MS (70 eV); m/z (%): 273.3 (0.46) [M^+ + 1], 272.2 (0.84) [M^+], 271.3 (0.17) [M^+–1], 242.3 (100) [M^+–NO], 81.1 (30.33), 67.1 (49.58). – $C_{16}H_{20}N_2O_2$ (272.4): calcd. C 70.56, H 7.40, N 10.28; found C 70.93, H 7.74, N 9.86.

(t-4a, t-8a, t-9a, t-10a)-Δ^6-Dodecahydro-c-9,c-10-azo-r-1,c-4-etheno-c-5,c-8-methano-anthracene-14-oxide (**21**):

GOP2: 480 mg (1.90 mmol) of **20**, 380 mg (2.18 mmol) of MCPBA, 7 h. Filtration through a short chromatographic column (silica gel, 63–200 µm (Woelm), 2 × 6 cm, EtOAc) yields 460 mg (87%) of **21.** Colorless crystals > 215 °C decomposition. – IR (KBr): ν = 3050 cm^{-1} (=C-H), 3000, 2960, 2930, 2900, 2860 (-C-H), 1500 (NNO), 1390, 1370, 1420, 1280, 1260, 700, 680, 635. – UV (CH_3CN): λ_{max} (lg ε) = 224 nm (3.61). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (AB, $J_{11,11'}$ = 10.1 Hz, 1 H, 11-H), 1.17 (mc, 2 H, 2-H, 3-H), 1.46 (m, 3 H, 2-H', 3-H', 11-H'), 1.82 (s, 2 H, 8a-H, 10a-H), 2.07, 2.12 (AB, J = 9.9 Hz, 2 H, 4a-H, 9a-H), 2.55, 2.62 (2 d, J = 5.0 Hz, 2 H, 1-H, 4-H), 2.75, 2.79 (2 s, 2 H, 5-H, 8-H), 4.18, 4.44 (2 s, 2 H, 9-H, 10-H), 5.94, 6.06 (2 ps.-t, J = 7.2 Hz, 2 H, 12-H, 13-H), 6.10, 6.18 (2dd, J = 3.0, 5.6 Hz, 2 H, 6-H, 7-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 139.48, 138.94 (2d, C-6, C-7), 133.30, 126.05 (2 d, C-12, C-13), 76.67, 63.62 (2 d, C-9, C-10), 44.99 (d, 3C (2C?)), 44.91 (d), 44.70 (d), 42.18 (t, C-11), 42.06 (d, (2C?)), 33.34 (d, 2C), 25.83, 25.34 (2t, C-2, C-3) ppm. – MS (70 eV); m/z (%): 269.3 (19.78) [M^+ + 1], 268.3 (100) [M^+], 267.3 (1.45) [M^+–1], 239.3 (4.27) [M^+–29], 225.3 (2.16) [M^+–43], 80.1 (84.10), 66.1 (43.66) [$C_5H_6^+$]. – $C_{17}H_{20}N_2O$ (268.4): calcd. C 76.09, H 7.51, N 10.43; found C 76.26, H 7.69, N 10.20.

(t-4a, t-8a, t-9a, t-10a)-Δ^6-Dodecahydro-c-9,c-10-azo-r-1,c-4-etheno-t-5,t-8-methano-anthracene-14-oxide (**23**):

GOP2: 85.0 mg (0.34 mmol) of **22**, 68.0 mg (0.39 mmol) of MCPBA, 1 h. Filtration through a short chromatographic column (silica gel, 63–200 µm (Woelm), 2 × 6 cm, EtOAc) yields 80 mg (85%) of **23**. Colorless crystals, > 220 °C decomp. – IR (KBr): ν = 3040 cm^{-1} (=C-H), 2980, 2930, 2900, 2880 (-C-H), 1500 (NNO), 1420, 1280, 1210, 1300, 1085, 1010, 860, 850, 750, 740, 680, 670, 620. – UV (CH_3CN): λ_{max} (lg ε) = 223 nm (3.61). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (mc, 2 H, 2-H, 3-H), 1.26, 1.41 (AB, 2 H, 2-H', 3-H'), 1.48 (m, 2 H, 2-H_2), 2.12 (br. s, 2 H, 4a-H, 9a-H), 2.43 (br. s, 2 H, 8a-H, 10a-H), 2.55, 2.63 (2 d, J = 6.0 Hz, 2 H, 1-H, 4-H), 2.84, 2.91 (2 s, 2 H, 5-H, 8-H), 4.08, 4.39 (2 s, 2 H, 9-H, 10-H), 5.77, 5.92 (2 dd, J = 3.0, 5.5 Hz, 2 H, 6-H, 7-H), 5.93, 6.05 (2ps.-t, J = 4.4 Hz, 2 H, 12-H, 13-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 136.15, 126.38 (2 d, C-6, C-7), 133.11, 126.17 (2 d, C-12, C-13), 76.36, 62.47 (2 d, C-9, C-10), 51.65 (t, C-11), 45.79 (d), 45.54 (d), 45.49 (d), 45.40 (d), 43.37 (d), 41.54 (d), 33.26 (d, 2C), 25.86, 25.25 (2 , C-2, C-3) ppm. – MS (70 eV); m/z (%): 269.2 (5.32) [M^+ + 1], 268.2 (25.13) [M^+], 267.1 (6.79)[M^+–1], 239.3 (91.95) [M^+ + 1 – NO], 90.9 (70.62), 80.0 (100.0) [$C_4N_2H_4^+$], 79.0 (71.83), 65.9 (45.36) [$C_5H_6^+$], 27.9 (37.21) [N_2]. – $C_{17}H_{20}N_2O$ (268.4): calcd. C 76.09, H 7.51, N 10.43; found C 76.11, H 7.78, N 9.94 .

10,10-Dimethyl-(c-4a, c-8a)-1,4,4a,5,8,8a-hexahydro-r-1,c-4, t-5,t-8-dimethanophthalazine- 2-oxide (**25**) ,

10,10-Dimethyl-(c-4a, c-8a)-1,4,4a,5,8,8a-hexahydro-c-6,c-7-epoxy-r-1,c-4,t-5,t-8-dimethanophthalazine (**26**):

GOP2: 139 mg (0.74 mmol) of **24**, 130 mg (0.75 mmol) of MCPBA, 1 d at 5 °C. Purification of the crude product by MPLC (LiChrosorb, 15–25 µm (Merck), N = 4900; CH_2Cl_2,

EtOAc 5:3; Det. -nD), three main fractions can be collected (A–C):
Fraction A: 30 mg (21%) of **24** (starting material, ^{1}H-NMR spectroscopically pure).
Fraction B: 60 mg (40%) of **25**, colourless crystals, m.p. 114–115 °C.
Fraction C: 30 mg (20%) of **26**, colourless crystals, m.p. 149–152 °C

25: IR (KBr): $\nu = 3050\ cm^{-1}$, 3020 (=C-H), 3000, 2960, 2940, 2900, 2860 (-C-H),1510 (NNO), 1300, 1370, 1310, 1280, 1250, 1220, 1150, 1020, 830, 810, 720, 690, 660. – UV (CH_3CN): λ_{max} (lg ε) = 226 nm (3.56). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09, 1.15 [2 s, 6 H, 10-$(CH_3)_2$], 1.22, 1.70 (AB, $J_{9,9'}$ = 10.5 Hz, 2 H, 9-H_2), 2.43, 2.49 (2 dd, J = 7.8, 2.5 Hz, 2 H, 4a-H, 8a-H), 2.75, 2.81 (2 s, 2 H, 5-H, 8-H), 3.94, 4.03 (2 s, 2 H, 1-H, 4-H), 6.23, 6.28 (2 dd, J = 3.1, 5.6 Hz, 2H, 6-H, 7-H) ppm. – ^{13} C NMR (100.6 MHz, $CDCl_3$): δ = 141.18, 141.03 (2 d, C-6, C-7), 87.91, 74.15 (2 d, C-1, C-4), 60.44 (s, C-10), 47.96, 45.00 (2 d, C-4a, C-8a), 41.73 (t, C-9), 41.51, 41.39 (2 d, C-5, C-8), 20.01, 19.58 (2 q, 10-$(CH_3)_2$) ppm. – MS (70 eV); m/z (%): 205.2 (2.64) [M^+ + 1], 204.2 (16.47) [M^+], 97.1 (100), 79.1 (54.41), 66.0 (40.88) [$C_5H_6^+$], 65.1 (24.92) [$C_5H_5^+$]. – $C_{12}H_{16}N_2O$ (204.3): calcd. C 70.59 H, 7.89 N, 13.71; found C 70.74, H 8.16, N 13.36

26: IR (KBr): $\nu = 3080\ cm^{-1}$, 3040, 3000, 2980, 2940, 2920, 2880 (-C-H), 1470, 1460 (NN), 1380, 1300, 1285, 1250, 1220, 1025, 860 (epoxide), 840. – ^{1}H NMR (400 MHz, $CDCl_3$):δ = 0.67, 1.09 [2 s, 6 H, 10-$(CH_3)_2$], 0.85, 1.32 (AB, J = 11.7 Hz, 2 H, 9-H_2), 2.28 (s, 2 H, 4a-H, 8a-H), 2.51 (s, 2 H, 5-H, 8-H), 2.94 (s, 2 H, 6-H, 7-H), 4.76 (ps.-t, J = 1.4 Hz, 2 H, 1-H, 4-H) ppm. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 86.37 (d, 2C, C-1, C-4), 59.62 (s, C-10), 52.10 (d, 2C, C-6, C-7), 43.85 (d, 2C, C-4a, C-8a), 37.63 (d, 2C, C-5, C-8), 21.74 (t, C-9), 19.49, 19.37 [2 q, 10-$(CH_3)_2$] ppm. – MS (70 eV); m/z (%): 205.1 (0.22) [M^+ + 1], 204.0 (0.32) [M^+], 79.1 (100). – $C_{12}H_{16}N_2O$ (204.3) calcd. C 70.59, H 7.89, N 13.71; found C 70.77, H 8.03, N 13.26.

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