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Proximate, *syn*-Periplanar Bisdiazenes/Bisdiazeneoxides - Syntheses, Photochemistry

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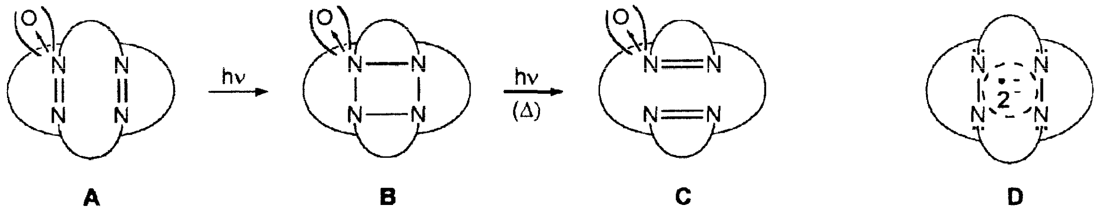
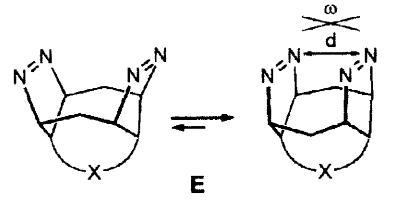
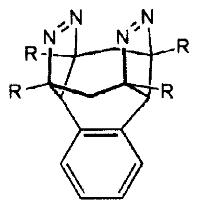
Summary. In specifically designed diazene/diazene(oxide) substrates, in spite of seemingly favorable geometrical prerequisites (**1**, d = 2.85 Å, ω = 170°), no [π2+π2] photocycloaddition, particularly no photometathesis, is observed; diazenoxide → oxadiaziridine cyclizations are the alternative photoreactions.

Elucidation of the structural prerequisites for [π2+π2] photocycloaddition (photometathesis) in *syn*-periplanar bisdiazenes/bisdiazeneoxides **A** (→ **B** → **C**)[1-4], for cyclic electron delocalization in the respective radical anions and dianions **D**[5], is bound to the availability of substrates with gradually modified geometrical parameters such as π,π-distance d and interorbital angle ω. In the bicyclo[3.3.x]diazenes **E**[6] - an addition to the originally conceptualized classes of more or less rigid, more or less proximate and *syn*-periplanar diazenes[7] - with the bridge X becoming larger (**Eo** → **E2**) these parameters (MMX) are gradually improved (distance d reduced, angle ω enlarged), in the increasingly rigid skeletons the "closed" conformers become increasingly favored.





	d(Å)	ω(°)
Eo : X = -	3.14	153
E1 : X = CH_2	3.13	158
E2 : X = $(CH_2)_2$	2.83	171
1 :	2.85	170
2 :	2.81	172



1 (R = H)
2 (R = Br)

Extending prior studies on **Eo**[2] and **E1**[3] systems, this letter deals with **E2** substrates[8]. Whilst synthetic efforts directed at the parent **E2** structure were not (yet) successful, for the benzo-derivatives **1** and **2**, with very similar d (ω) values, the route detailed in Scheme 1 proved reasonably rewarding (overall yield based on **3** up to 27%, g-scale)[9]. Starting material is the readily accessible benzo-bridged cyclooctane-3,7-dione **3**[10]. For the latter's transformation into the C_2 symmetrical diene **5** the Fetizon protocol[11] was utilized when various alternative procedures had failed, primarily due to the pronounced transannular reactivity in **3**[10]. According to careful reaction control (TLC, NMR) only the C_2 bisenolester **4** (R = PO $(OEt)_2$) had been formed, probably the result of the best possible charge-

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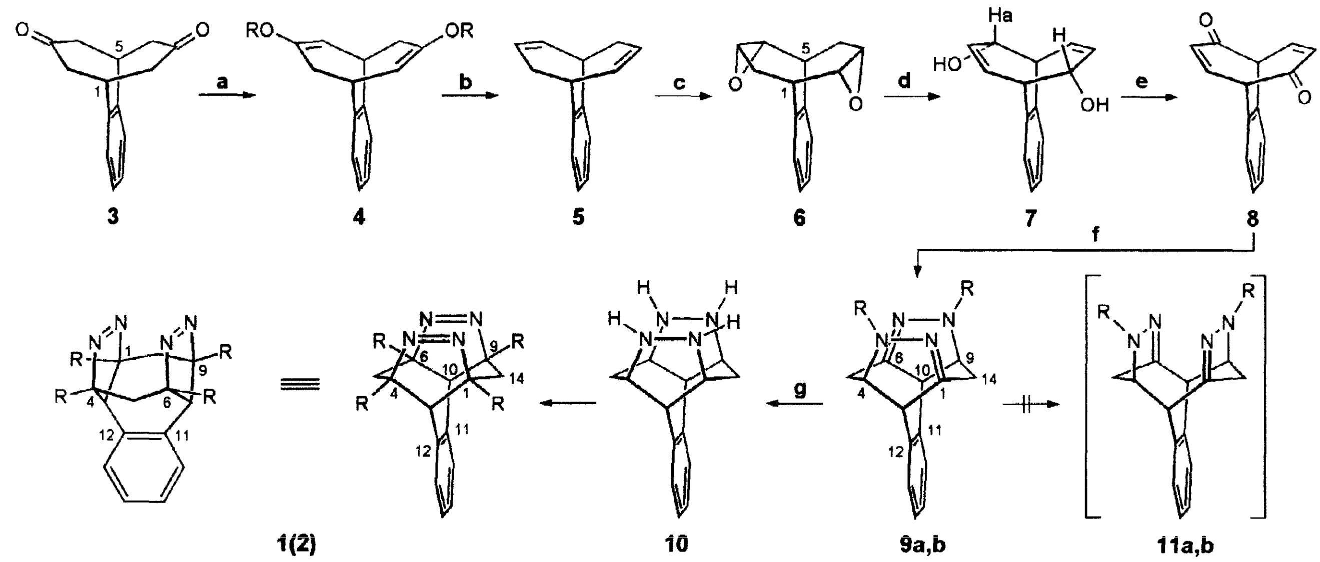
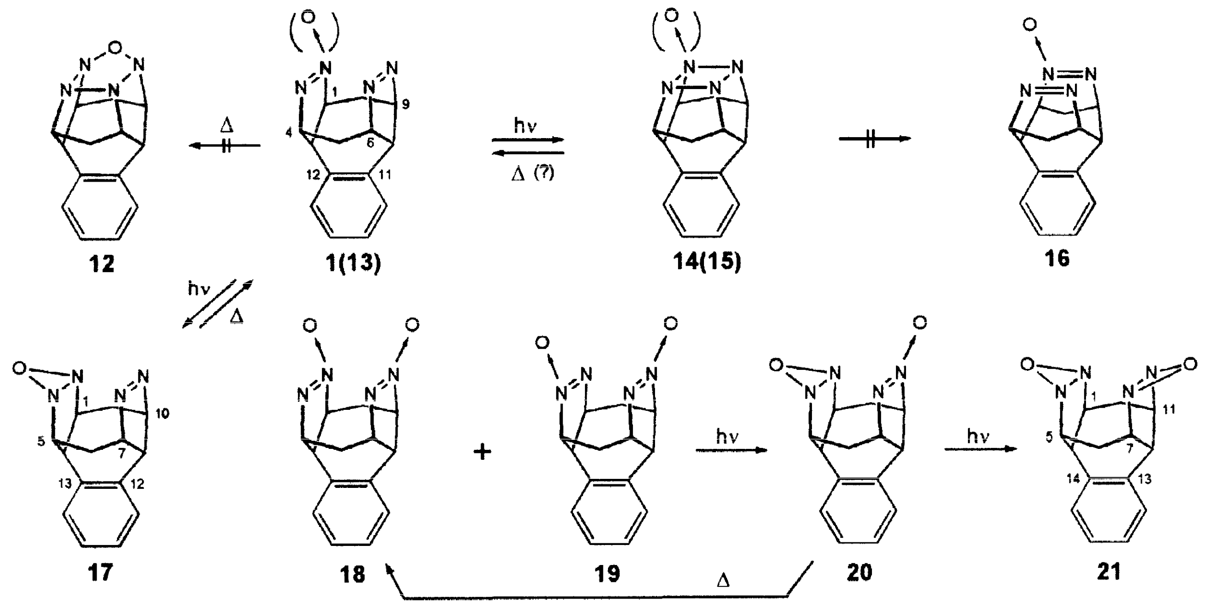
separation in the intermediate bisenolate ion. Because of overreduction the yield of step **4** → **5** is still somewhat erratic, in exceptional cases dropping to ca. 30%. For the twofold epoxidation of the waxy-solid **5** dimethyldioxirane (DMDO) proved the reagent of choice: The C_2 symmetrical *syn,syn*-diepoxide **6** made up ca. 80% of a quantitatively obtained mixture with the *syn,anti*-isomer. After this mixture had been exposed to the standard epoxide → allylic alcohol rearrangement conditions, only the *syn,syn*-diol **7** was isolated after chromatographic work-up and was oxidized to give crystalline diene-dione **8** (λ_{max} (MeOH) = 363, 236 nm; cf. 314, 230 nm (EtOH) for cyclooctene-2-one[12]). The stereochemistry formulated in **6** and **7** is based on the established *syn*-additions to the carbonyl groups in **3** and on calculations of alternative transition states for the epoxidation of **5** (with dihedral angles (AM1) of 71.2° for $1,2_{anti}$-H and 66.5° for $1,2_{syn}$-H the coupling constant $J_{1,2(5,6)}$ = 4.0 Hz measured for **7** does not allow an assignment). Treatment of **8** with 2.5 equivalents of dry hydrazine - condensation and subsequent Michael-type addition in the intermediate hydrazones - provided exclusively the air-sensitive bispyrazoline **9a** (R = H), which was completely characterized as crystalline, stable **9b** (R = Ac). In line with the respective energies (ΔH_f° (AM1), E_{str} (MM2)), the diastereomer **11a** (**11b**) was not observed (TLC, NMR). In contrast to earlier experience in the **El** series by Mellor et al. and ourselves[3], **9a** could not be isomerized into bisdiazene **1** with bases. The latter was, however, nearly quantitatively obtained through hydrogenation of **9a** to the bishydrazine **10** and oxidation. The various vicinal H,H coupling constants extracted from the ^{1}H NMR spectrum of **1**[9] reasonably fit with those calculated for the "closed" conformer (d = 2.85 Å, ω = 170°, MMX). The colorless crystals ($\nu_{N=N}$ = 1552 cm^{-1}) loose N_2 at ca. 153°C; the n, π* absorption at 336 nm (MeOH, ε = 810) - when compared with that of e.g. the **Eo** bisdiazene (339 nm (CH_3CN), ε = 650) or **17** (see below) - is not indicative of a significant transannular interaction. The fourfold bridgehead substitution present in tetrabromide **2** was conveniently achieved by treatment of **9a** with bromine inducing a sequence of bromine addition, HBr elimination and tautomerization (28%, not optimized). The colorless **2** (λ_{max} (MeOH) = 348 nm (ε = 455), stable in crystalline form, decomposes during chromatography or on

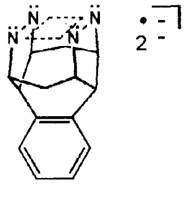


Scheme 1: a) 1. LDA, THF, - 78 °C; 2. $ClP(O)(OEt)_2$ (66%). b) Li, NH_3 (96%). c) DMDO, acetone (80%). d) $LiNEt_2$, THF, - 78°C (72%). e) PDC, HOAc, CH_2Cl_2 (45-62%). f) N_2H_4, 2.5 equiv., ethanol (98%) g) $NaBH_3CN$, MeOH, pH 4; $CuCl_2$, ethanol (98%).

standing in solution. Controlled oxidation of **1** with DMDO provided selectively monooxide **13** (colorless crystals, 87%, λ_{max} (MeOH) = 334 nm (ε = 325); the N-O bond has the typical influence upon the 1-H(C) NMR shifts[1,2]), whose separation from the dioxides **18/19** (λ_{max} (MeOH) = 223 nm (ε = 9550)) was chromatographically effected. On heating **13** up to its decomposition - differently from ene/diazeneoxides[13] - [4+2] cycloaddition (oxatetrazolidine **12**) was not noted.

The photochemistry of bisdiazene **1** closely resembles that of the **Eo/E1**[2,8] - and other *syn*-periplanar[1-3] bisdiazenes - in that after irradiation under varied conditions (light source, filter, temperature), even at low conversion (TLC, NMR), no [2+2] cycloaddition to give tetrazetidine **14** but N_2 elimination was observed, here without defined product formation. Still, a photochemically (thermally) reversible formation of **14** is not yet excluded. More surprisingly, differently from earlier studied diazene/diazeneoxides with comparable d(ω) parameters[1], but like the **E1** analogs[8], oxide **13** upon monochromatic irradiation (254 nm, MeOH) did not undergo N_2O/N_2 metathesis to give **16**. In fact, **16** is calculated to be of higher energy than **13** by ca. 50 kcal mol^{-1} (AM1, PM3). Again, with a considerable proportion of polymeric material, the intervention of tetrazetidineoxide **15**, being thermally or photochemically cleaved not to isomer **16** but back to **13**, has still to be considered. Instead, in $CHCl_3$ (not e.g. in protic MeOH), the relatively stable oxadiaziridine **17** ($t_{1/2}$ ($CHCl_3$) ca. 60 h at room temperature; λ_{max} (MeOH) = 333 nm (ε = 540)) was produced,[14] if only in modest yield (ca. 25%) besides products from denitrogenation. Analogously but much more selectively, the mixture of dioxides **18/19** was isomerized into **20**, the latter into **21** (after separation in toto 60-70%) without any hint (TLC, NMR) for transannular bond formation (metathesis). An interesting transannular electronic steering became evident when **20** upon heating was exclusively isomerized into **18**.





If there was no [π2+π2] photocycloaddition observed for **1**, the delocalized nature of its radical anion (4N/5e), and possibly its dianion (4N/6e), is an exciting discovery to be detailed in the broader context of geometrically varied ions **D**[5].

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References and Notes

1. H. Prinzbach, G. Fischer, G. Rihs, G. Sedelmeier, E. Heilbronner, Yang Z.-z., *Tetrahedron Lett.* **1982**, *23*, 1251; E. Beckmann, N. Bahr, H. Prinzbach, ibid. **1990**, *31*, 1125.
2. N. Bahr, E. Beckmann, K. Mathauer, D. Hunkler, M. Keller, H. Prinzbach, H. Vahrenkamp, *Chem. Ber.* **1993**, *126*, 429.
3. J. M. Mellor, R Pathirana, J. H. A. Stibbard, *J. Chem. Soc., Perkin Trans. I* **1983**, 2541; N. Bahr, *Dissertation*, University of Freiburg, **1994**.
4. K. Exner, D. Hochstrate, M. Keller, F.-G. Klärner, H. Prinzbach, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2256; cf. G. Ritter, G. Häfelinger, E. Lüddecke, H. Rau, *J. Am. Chem. Soc.* **1989**, *111*, 4627; E Tauer, K.-H. Grellmann, A. Heinrich, *Chem. Ber.* **1991**, *124*, 2053.
5. K. Exner, O. Cullmann, D. Hunkler, G. Gescheidt, H. Prinzbach, in preparation.
6. Calculations on various levels (MMX, AM1, HF/6-31a*, B3LYP/6-31a*) differ for the more flexible **Eo** but agree well for the **E2** (**1**,**2**) systems[5,8]
7. W. Marterer, H. Prinzbach, G. Rihs, J. Wirz, J. Lecoultre, E. Heilbronner, *Helv. Chim. Acta*, **1988**, *71*, 1937; M. Lugan, *Dissertation*, University of Freiburg, **1994**.
8. O. Cullmann, *Dissertation*, University of Freiburg, **1998**.
9. All new compounds have been fully characterized. Selected data for **1**: Colorless crystals, m.p. 153°C (dec., N_2-elimination); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.23 (dd, Ar-H), 7.15 (dd, Ar-H), 5.03 (ddd, 1-, 4-, 6-, 9-H), 3.16 (t, 10-, 13-H), 3.12 (dt, 5s-, 14s-H), 1.51 (dt, 5a-, 14a-H); $J_{5a,5s} = J_{14a,14s} = 16.1$, $J_{1,13} = J_{4,13} = J_{6,10} = J_{9,10} = 11.0$, $J_{4,5s} = J_{5s,6} = J_{1,14s} = J_{9,14s} = 3.0$, $J_{4,5a} = J_{5a,6} = J_{1,14a} = J_{9,14a} = 5.4$ Hz; ^{13}C NMR: δ = 135.3 (C-11, -12), 131.8, 127.8 (C-15, -16, -17, -18), 85.2 (C-1, -4, -6, -9), 41.3 (C-10, -13), 21.1 (C-5, -14); IR (KBr): ν = 1552 cm^{-1} (N=N), EI MS (70 eV): *m/z* (%): 238 (M^+, 3), 182 (4) (M^+ - 2 N_2), 181 (21), 167 (96), 141 (96), 128 (100), 115 (69); UV (MeOH): $\lambda_{max}(\varepsilon)$ = 336 nm (810); $C_{14}H_{14}N_4$ (238.3): calc. C 70.57, H 5.92, found C 70.84, H 6.05.- For **17**: Colorless crystals; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.32 - 7.09 (m, Ar-H), 5.13 (ddd, 7-, 10-H), 4.10 (ddd, 1-, 5-H), 3.43 (t, 14-H), 3.23 (t, 11-H), 3.22 (ddd, 6s-, 15s-H), 1.74 (ddd, 6a-, 15a-H); $J_{6s,6a} = J_{15s,15a} = 16.0$, $J_{7,11} = J_{10,11} = 11.1$, $J_{1,14} = J_{5,14} = 10.2$, $J_{5,6a} = J_{6a,7} = J_{10,15a} = J_{1,15a} = 4.8$, $J_{5,6s} = J_{6s,7} = J_{10,15s} = J_{1,15s} = 3.3$ Hz; ^{13}C NMR: δ = 132.0, 131.6, 128.9, 128.4, 127.9, 124.8 (Ar-C), 85.8 (C-7, -10), 66.2 (C-1, -5), 44.2 (C-14), 41.3 (C-11), 28.7 (C-6, -15); CI MS (NH_3): *m/z* (%): 272 (100, $M^+ + NH_4^+$), 256 (20), 255 (6, $M^+ + H^+$), 239 (7, $M^+ + H^+$ - O); UV (MeOH): $\lambda_{max}(\varepsilon)$ = 333 nm (540).
10. B. Föhlisch, U. Dukek, I. Gaeßle, B. Novotny, E. Schupp, G. Schwaiger, E. Widmann, *Liebigs Ann. Chem.* **1973**, 1839.
11. M. Fetizon, J. Jurion, N. T. Anh, *J. Chem. Soc., Chem. Commun.* **1969**, *112*; H. Müller-Bötticher, W.-D. Fessner, J.-P. Melder, H. Prinzbach, S. Gries, H. Irngartinger, *Chem. Ber.* **1993**, *126*, 2275.
12. H. O. House, R. F. Sieloff, V. Lee, M. B. DeTar, *J. Org. Chem.* **1980**, *45*, 1800.
13. G. Fischer, D. Hunkler, H. Prinzbach, *Tetrahedron Lett.* **1984**, *25*, 2459; S. Hünig, M. Schmitt, *Liebigs Ann. Chem.* **1995**; 1801 and cit. lit.
14. Review: A. Albini, M. Alpegiani, *Chem. Rev.* **1984**, *84*, 43.