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RIGID FACE-TO-FACE [3.3]-*o,o'*-CYCLOPHANES ARENE/ALKENE AND ARENE /ARENE PHOTOCYCLOADDITION REACTIONS[1]

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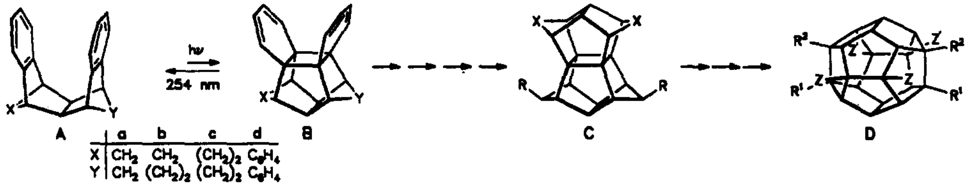
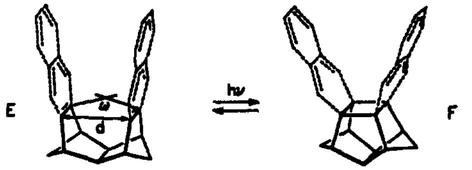
Summary. Proximity as origin of unusual photoreactivity is being explored: In the naphtho/ene **5** (X-ray analysis), direct or sensitized photoexcitation induce an efficient *meta*-addition to the naphthalene nucleus; *ortho*-(2,3)-addition is not enforced. Naphtho/benzo cyclophane **10**, however, is photochemically "inert". Structurally related benzo/enes **4** and **17** undergo photoequilibration (2:1) with the respective [6+2]-cycloadducts.

Cycloadditions to aromatic rings, particularly arene/arene photodimerizations, make up a synthetically as well as theoretically attractive chapter of organic photochemistry.[2] To us, the discovery of the benzo/benzo-photoequilibration **Aa** ⇄ **Ba**[3] became of utmost importance as key step in our pagodane → dodecahedrane route (**C** → **D**).[4] Subsequent studies uncovered a very delicate structure dependancy for this *o,o'*-photocycloaddition: It similarly occurred in **Ab,d** (→ **Bb,d**) but not in **Ac**.[5]



	a	b	c	d
X	CH_2	CH_2	$(CH_2)_2$	C_6H_4
Y	CH_2	$(CH_2)_2$	$(CH_2)_2$	C_6H_4

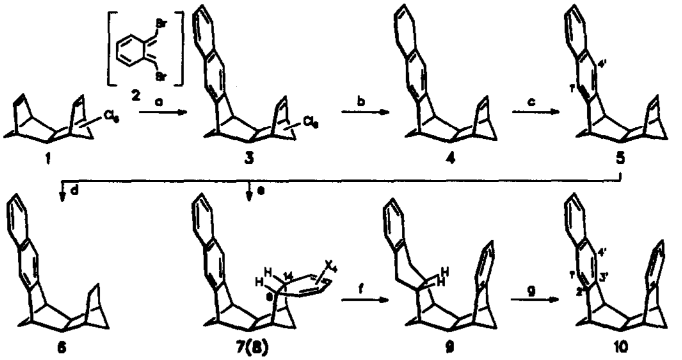
The question was raised whether specific properties of the **Aa** skeleton - *inter alia* very short π,π-distance, almost perfect *syn*-periplanar alignment of the orbitals involved - could be exploited for the realization of other unusual arene cycloaddition modes such as **Ec,e,f** → **Fc,e,f**.[6] There are good reasons why the known *o*-additions to the naphthalene nucleus involve the 1,2-bond.[2,3] It could be although speculated that in **Ec,e,f** substrates steric constraint or exciplex formation could outweight the orbital symmetry restrictions and enforce the participation of the naphthalene-2,3-bond as formulated in Table 1. The kinetic stability of the respective naphtho/benzo (**Fe**) and naphtho/naphtho "dimers" (**Ff**) should profit, similarly to the benzo/benzo "dimers" **B** (≡ **Fd**)[7], from skeletal rigidity. Yet, the uncertainty with respect to the photoreactivity of the σ-coupled polyenes **F** remained.[8]



	chromophores		d [Å]	ω [°]	$\Delta\Delta H_f^\circ$	ΔE_{str}
a	Ene	Ene	2.84	175.2	-31.7	10.0
b	Benzo	Ene	2.93	169.5	5.1	7.6
c	Naphtho	Ene	2.93	170.3	21.5	7.4
d	Benzo	Benzo	3.02	161.0	36.7	9.5
e	Naphtho	Benzo	3.02	160.5	52.1	9.4
f	Naphtho	Naphtho	3.10	160.6	68.1	9.2

Table 1: Calculated (MMX, version 87.200) transannular π,π-distances d [Å], interorbital angles ω [°], and differences in enthalpy and strain [kcal/mol] for the photoisomers **E** and **F**.

The synthesis of naphtho/ene **5** and of naphtho/benzo substrate **10** as presented in Scheme 1[9] follows proven procedures but needs comments with respect to complications arising from given proximity and cage situations. During the reaction of **1** with **2** (prepared *in situ* from tetrabromo-*o*-xylene),[10] the primary adduct looses HBr spontaneously to give **3** (31%, not optimized). For dehalogenation of **3**, Li/NH_3/THF was the only productive reagent but also caused Birch reduction, thus necessitating an additional oxidation step [**5**: colorless crystals, mp 112°C, λ_{max} (ε) = 226 nm (61410), 265 (8120), 275 (6790), 285 (3750), 312 (660), 326 (800), ε_{254} = 11940]. In the addition of tetrachlorothiophene dioxide (TCTD) to **5**, conversion had to be restricted to ca. 60% in order to avoid substantial material loss by secondary reactions. The standard procedure to transform **7** (X = Cl) into **10**, sequential base-catalyzed isomerization, HCl elimination and dehalogenation, had to be modified, when **7** with its effective protection through the opposite naphtho ring [$\delta_{9(14)\text{-H}}$ = 2.66; $CDCl_3$] withstood all attempts for aromatization (KOH/CH_3OH, reflux; KOH/DMSO, 160°C). Prior dehalogenation to **8** (X = H) was expected to provide remedy. Yet, after exposure of **7** to the conditions applied to **3**, the isolated product was not **8** but **9**; Birch reduction in the naphthalene part and subsequent dyotropic hydrogen transfer reasonably explain the event. Oxidation with DDQ povided **10** [colorless crystals, mp 178°C, λ_{max} (ε) = 208 nm (54400), 249 (18540), 272 (6470), 278 (6180; sh), 292 (4120; sh), 328 (650), ε_{254} = 15860].



Scheme 1: (a) 3 eq **2**, NaI, DMF, 4 h, 31%; (b) NH_3/Li/THF, -78°C, 15 min, 61%; (c) DDQ, benzene, 25°C, 15 min, 99%; (d) Pd/C, H_2, ethyl acetate, 25°C, 96%; (e) tetrachlorothiophene dioxide, toluene, 110°C, 2 h, 54%; (f) NH_3/Li/THF, -78°C, 1.5 h, 43%; (g) DDQ, toluene, 110°C, 20 h, 78%.

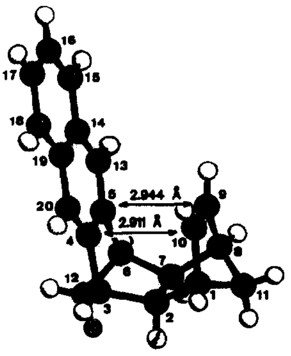
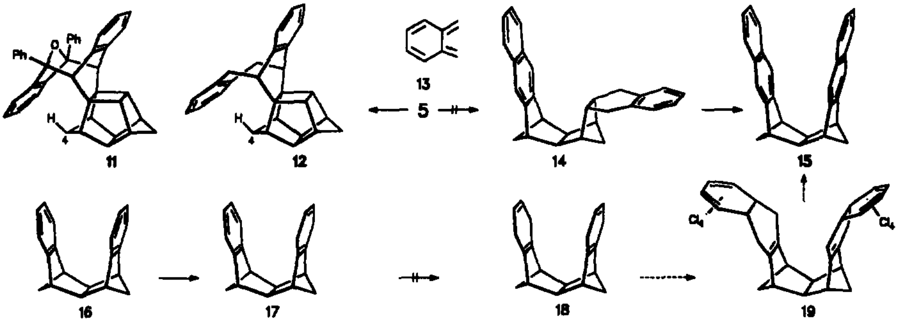


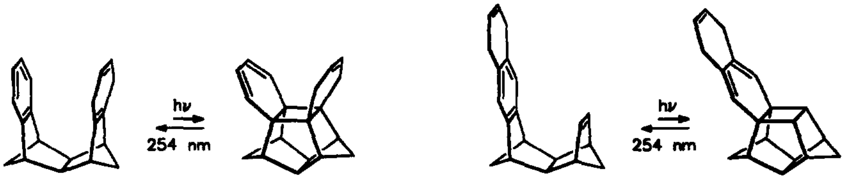
Figure 1: Schakal plot of **5** [Å]
C4-C5: 1.427(4); C4-C20: 1.352(4);
C5-C13: 1.347(4); C13-C14: 1.420(4);
(C4C5C13C14C19C20)/(C1C10C9C8) ca. 8°

o,o'-Naphtho/naphtho cyclophane **15** became not available along these lines since naphtho/ene **5** resisted the addition of **2**. With the sterically less demanding unsubstituted *o*-quinodimethane **13** (prepared from 1,4-dihydro-5,6-benzoxathiin-3-oxide)[10] a 1:1 adduct was indeed generated (54%, mp 178°C) which turned out to be not the wanted **14** but **12**, presumably the result of a proximity-assisted four-step radical - formal [4+4+2] - addition. An analogous addition mode was established for the reaction of **5** with diphenylisobenzofuran (88% **11**, mp 252°C). In another futile approach to **15**, implying a double benzanellation to well available **16**, *via* double TCTD addition to **18** to give **19**, the general difficulty in bringing about twofold Birch reduction in **16**, and the evasion of **17** (26% isolated) to be reduced to **18**, are further manifestations of the prize to be paid for "proximity".[11]



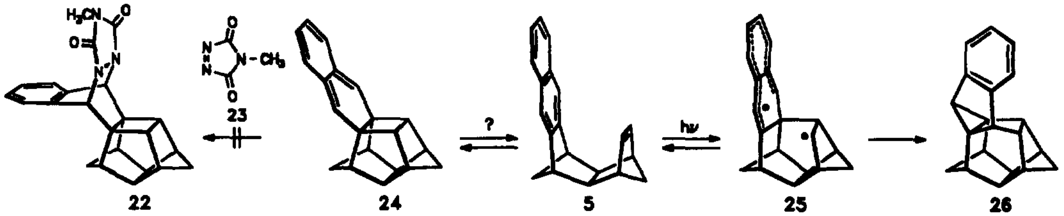
The X-ray structure of **5** (Figure 1, distortion from C_s-symmetry)[12] demonstrates very good agreement with the calculated data (Table 1) and thus the very favorable geometrical situation for transannular bond formation [cf. the d/ω values for the benzo/benzo structure **16**: 3.04 Å; 161.4°]. The proximity of the *syn*-periplanar π-chromophores in **5** and **10** finds its standard spectral expressions: e. g. a diamagnetic shift of the 1'(4')-^{1}H NMR signal (0.26 and 0.69 ppm, resp.) and a charge transfer maximum (a longer-wavelength absorption, 4 - 6 nm) in the UV spectra (**6** as reference compound: λ_{max} = 322 nm).[3,13]

The photochemical behavior of benzo/enes **17** and **4** (cf. **Eb** → **Fb**) is unexceptional for rigid photosubstrates.[1,3,14,15] After irradiation of ca. 10^{-4} M deoxygenated etheral solutions of **17** with monochromatic 254 nm light (Hanau TNN 15/32 low pressure Hg lamp), a 2:1 equilibrium with **20** is established; the latter is chromatographically separated [mp 45°C, λ_{max} = 288 nm (ε = 1600)]. Analogously, benzo/ene **4** forms an 2:1 equilibrium mixture with **21**, from which the latter is isolated by chromatography [mp 69°C, λ_{max} = 291 nm (ε = 2230)]. In preparative runs (100 mg scale) material loss up to 20% is due to polymerization.



17 20 4 21

Irradiation of naphtho/ene **5**, direct with polychromatic or monochromatic light (λ = 254 nm, > 270 nm, > 300 nm; ether; -78°, 0°, 25°C) or sensitized (acetone), exclusively (NMR, TLC) produced an isomeric, colorless compound (MS, 80-85% isolated, mp 126°C) for which the NMR analysis (NOE, two-dimensional correlation) unequivocally confirmed the non-symmetrical benzenoid structure **26** (ΔH_f° ca. 20 kcal/mol smaller than that of **24**), the result of an unusually selective intramolecular *m*-addition of an alkene to the naphthalene nucleus.[2,16] At direct irradiation (room temp.), a yellow coloration of the reaction solution appears momentarily which survives for ca. 1 min in the dark (for ca. 10 min at -78°C). The absence of an adduct **22** when **5** is irradiated (254 nm) in the presence of **23** makes, however, **24** highly improbable as a low-percentage equilibrium component (for comparison, the photoisomer **Ba** could be quantitatively intercepted).[1]



22 24 5 25 26

A formidable substituent effect upon the course of this photoreaction surfaces from the direct (254 nm) and sensitized (acetone) excitation of the hexachloro naphtho/ene **3** (-20°, 0°, 25°C). The latter stays intact for hours and after long irradiation times (5-10 h) ends up in polymers. Naphtho/benzo cyclophane **10** (**Ee**), in contrast to **5** and **16**, under multiply varied conditions of direct and indirect excitation, proved photostable for long irradiation times - in spite of d/ω values close to that of **5** (**16**) and of strong transannular π,π-interaction as measured by PE spectroscopy.[17] Still, it cannot be excluded that a diradical resulting from transannular bond formation (cf. **25**) does not close for thermodynamic reasons (cf. $\Delta\Delta H_f^\circ$ = 52.1 kcal/mol for **Ee** → **Fe**). More insight into the fate of the non-productive excited states of these rigid *o,o'*-cyclophanes is expected from photophysical studies.[18]

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References and Notes

1) Photochemical Transformations 78. - 77: M. Wollenweber, D. Hunkler, M. Keller, L. Knothe, H. Prinzbach, *Bull. Soc. Chim. Fr.* **1993**, *130*, 32.

2) G. Kaupp, Angew. *Chem. Int. Ed. Engl.* **1980**, *19*, 243; J. McCullough, *Chem. Rev.* **1987**, *87*, 811; J. Mattay, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 825; Essentials of Molecular Photochemistry (A. Gilbert, J. Baggott), *Blackwell Scientific Publications, London*, **1991**, chapter 8.

3) H. Prinzbach, G. Sedelmeier, C. Krüger, R. Goddard, H.-D. Martin, R. Gleiter, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 297; J. Mattay, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 825; G. Sedelmeier, W.-D. Fessner, C. Grund, P.R. Spurr, H. Fritz, H. Prinzbach, *Tetrahedron Lett.* **1986**, *27*, 1277.

4) W.-D. Fessner, B.A.R.C. Murty, P. Spurr, R. Pinkos, J.-P. Melder, H. Fritz, H. Prinzbach, *Chem. Ber.* **1992**, *125*, 1697; J.-P. Melder, R. Pinkos, H. Fritz, J. Wörth, H. Prinzbach, *J. Am. Chem. Soc.* **1992**, *114*, 10213.

5) J.-P. Melder, *Dissertation*, University of Freiburg, **1990**; F. Wahl, *Dissertation*, University of Freiburg, **1993**.

6) R. Thiergardt, *Dissertation*, University of Freiburg, **1992**; M. Wollenweber, *Dissertation*, University of Freiburg, **1993**.

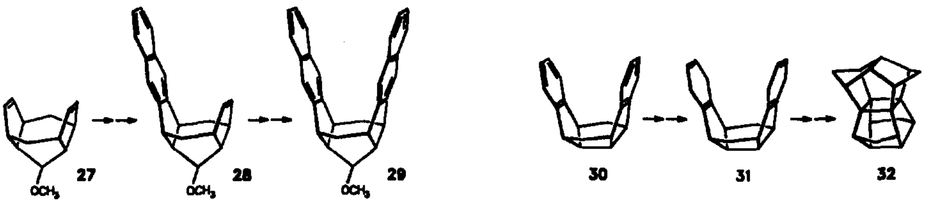
7) W.v.E. Doering, W.R. Roth, R. Breuckmann, H.J. Figge, L. Figge, H.W. Lennartz, W.-D. Fessner, H. Prinzbach, *Chem. Ber.* **1988**, *121*, 1.

8) R. Gleiter, H. Zimmermann, W.-D. Fessner, H. Prinzbach, *Chem. Ber.* **1985**, *118*, 3856.

9) The new compounds are characterized by elemental analysis and spectral data (IR, ^{1}H-,^{13}C-NMR, MS).

10) M.D. Hoey, D.C. Dittmer, *J. Org. Chem.* **1991**, *56*, 1947; cit. lit.

11) Slightly larger π,π-distances and higher skeletal mobility in trishomohypostrophene **27** make the construction of the naphtho/naphtho cyclophane **29** from **28** unproblematical, which are, however, photostable under various conditions. For similar reasons, double Birch reduction of **30** provided **31**, an intermediate on the way to isopagodane **32**.[6]

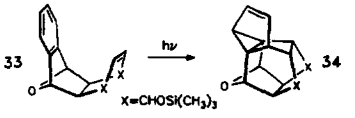


12) Crystallographic details: cell constants: $a = 6.102(3)$, $b = 17.379(4)$, $c = 6.960(3)$ Å, $\beta =$ 111.01, crystal system: monoclinic, space group: P2$_1$(No. 4), Z = 2, Mo-K_α-radiation, 2226 reflections measured, 1695 reflections observed [$I > 2\sigma(I)$], 180 parameters. All computations were done with MOLEN program package. [MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands (1990)]. Further details of the crystal structure investigation are available on request from Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-400068, the authors, and the journal citation.

13) J.-L. Lim, S. Chirayil, R.P. Thummel, *J. Org. Chem.* **1991**, *56*, 1492; S. Mataka, K. Takahashi, T. Mimura, T. Hirofa, K. Takuma, H. Kobayashi, M. Tashiro, K. Imada, M. Kuniyoshi, *ibid.* **1987**, *52*, 2653.

14) W.D. Klobucar, R.L. Burson, L.A. Paquette, *J. Org. Chem.* **1981**, *46*, 2680; R.D. Miller, J. Kolc, J. Michl, *J. Am. Chem. Soc.* **1976**, *98*, 8510; W. Grimme, P. Hörner, H.T. Kämmerling, R. Waldraff, J. Wirz, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1355.

15) In **33** with its less proximate and less rigid benzo/ene arrangement, 254 nm irradiation causes nearly quantitative formation of **34** (*m*-addition); C. Grund, *Dissertation*, University of Freiburg, **1990**.



16) H.E. Zimmermann, M. Viriot-Villaume, *J. Am. Chem. Soc.* **1973**, *95*, 1274; A.Gilbert, A. Kashoulis-Koupparis, C.R. Ellis-Davies, M. Firth, *J. Chem. Soc. Perkin Trans. 1*, **1988**, 31; Y. Kubo, T. Inoue, H. Sakai, *J. Am. Chem. Soc.* **1992**, *114*, 7660; N. Zupancic, B. Šket, *J. Chem. Soc. Perkin Trans. 1*, **1992**, 179; D. Döpp, A.W. Erian, G. Henkel, *Chem. Ber.* **1993**, *126*, 239.

17) D. Elsässer, H.-D. Martin, B. Mayer, G. Lutz, H. Prinzbach, *Chem. Ber.* **1991**, *124*, 2863.

18) K. Schaffner, S.E. Braslavsky, H. Prinzbach, M. Wollenweber, R. Thiergardt, in preparation.

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