

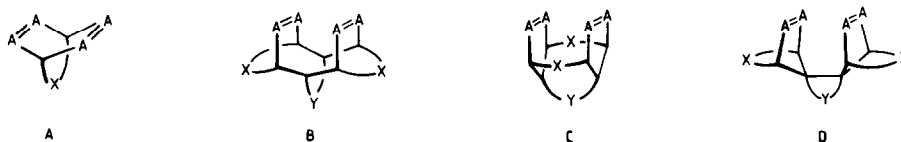
[6+6]-BENZO/BENZO - PHOTOCYCLOADDITION REACTIONS**

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SUMMARY: Cyclobutane-formation between "face-to-face" oriented benzenoid chromophoric units has been observed in 1,6-diene- (B) (1b-d/4a-d), not, however, in 1,5-diene-derived (C) (7a-c) skeletons.

The polycyclic skeletons A-D generalize a large arena in which a wide variety of transannular interactions/bond formations between various A=A-chromophoric units can be studied. Reactions between two benzenoid chromo-



phors have been investigated in several dibenzo-substrates A²⁾, where no [6+6]-photoaddition products could be identified directly. The first³⁾ syn-o,o-dibenzo-photoproduct (2a) was isolated in the series B upon direct excitation of 1a ($\lambda = 254 \text{ nm}$ (ca. 7:3 photoequilibrium)⁵⁾). The remarkable thermal stability of 2a allowed its use as an intermediate in the synthesis of pagodane, a potential precursor of dodecahedrane⁶⁾. As part of a programme to elucidate the geometry dependence and preparative scope of such [6+6]-cycloaddition reactions (e.g. modified pagodanes⁷⁾, pagodane-dications⁸⁾ additional examples of dibenzo-substrates B (1b-e, 4a-e) and C (7a-c) have been studied⁹⁾.

In Fig. 1 the relevant structural data (X-ray) for 1a⁵⁾/4e¹⁰⁾ and 7a,b⁹⁾. d¹¹⁾ as prototypes of structures B and C are compared.

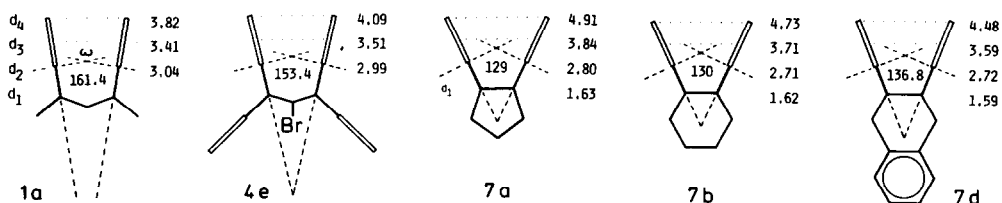
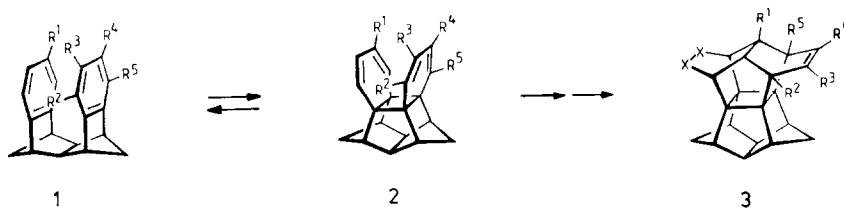


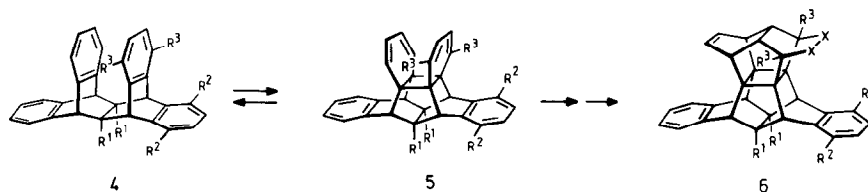
Fig. 1. Transannular Distances (Å) and Interorbital Angles ω (°)

Under the conditions applied to 1a⁵⁾ (monochromatic 254 nm light, low pressure Hg-lamp, r.t., 10^{-3} - 10^{-4} M iso-octane or iso-octane/THF 4:1 solutions), clean photoequilibria ranging from 1:1 to 5:2 (Table 1) were estab-

blished for 1b-d and 4a-c. Only polymerisation occurred with the dinitro-compound 1e - independent of the mode of excitation ($\lambda = 254$ nm, $\lambda \geq 280$ nm, high pressure Hg-lamp, pyrex filter; acetone sensitization). With 4d the equilibrium was not observed because of a rapid conversion of 5d (products unknown). There was no indication of any interference by photoprocesses typical for dibenzo(dihydro)barrelenes, the structural subunits present in 4a-d²). The thermally stable syn-o,o-dibenzo-compounds 2/5 ($t_{1/2}$ for the reversions (C_6D_6) 2b \rightarrow 1b and 5a \rightarrow 4a ca. 30 min (200°C) and 25 min (160°C)) were isolated by crystallization/chromatography or by formation of "domino"-cycloadducts 3 and 6 (and regioisomers) with NMTD, MA and DMAD directly out of the photolysis-mixtures. In no case could the primary [4+2]-adduct be observed.



	a	b	c	d	e
R ¹	H	H	H	Br	NO ₂
R ²	H	CH ₃	CH ₃	H	H
R ³	H	C ₆ H ₅	C ₆ H ₅	Br	H
R ⁴	H	C ₆ H ₅	(CH ₂	H	NO ₂
R ⁵	H	CH ₃	C ₆ H ₄)	H	H



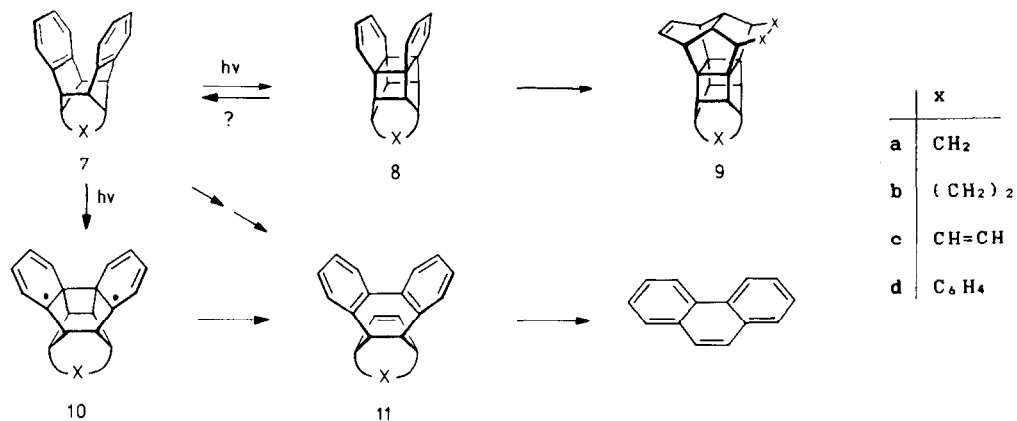
	a	b	c	d	e
R ¹	H	OCOCO	H	H	Br
R ²	H	H	OAc	H	H
R ³	H	H	H	OAc	H

Table 1 Selected UV-Data and Photoequilibria

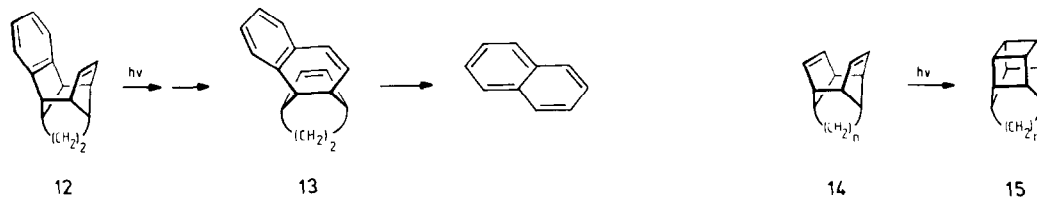
	$\epsilon_{254}(\text{educt})$	$\epsilon_{254}(\text{product})$	Isosbestic Points	Ratio
1b/2b	14700	6425	264	1:1 (5:1)*
1c/2c	12200	2000	323, 258, 224	2:1
1d/2d	2700	2000	258	5:2
4a/5a	2000	4500		2:1 (8:1)*
4c/5c	1400	1950		2:1

*equilibrium composition at irradiation with high-pressure Hg-lamp, vycor filter

In the dibenzohypostrophene homologues 7a,b, the transannular distances d_2 are even shorter but the π -orbitals are less aligned than in 1a. By qualitative judgement of the chromophors involved, similar photoequilibria for 7a,b \rightleftharpoons 8a,b were expected as for 1a \rightleftharpoons 2a. In the corresponding dienes 14b,c ($n=1$ ¹²), $n=2$ ⁵), but not 14a ($n=0$)¹³), four-membered ring-formation by sensitized excitation is an efficient process. Direct irradiation of 7a-c in ca. 10^{-3} M iso-octane solutions between -70° and $+20^\circ\text{C}$ furnished no indications for the formation of syn-o,o-dibenzenes 8a-c. After addition of NMTD to the photolysis solutions between -70° and -40°C no adducts 9a-c could be detected (TLC, $^1\text{H-NMR}$). After ca. 48 h irradiation time (20°C), 7a remained unchanged, 7b transformed to ca. 60% 11b and 7c to ca. 10% phenanthrene/benzene based on recovered starting material. Formation of equivalent amounts



of phenanthrene/naphthalene had been reported as a result of direct excitation (Hanovia 125 W, 25°C) of 7d, arising via thermal [4+2]-cycloreversion of 11d¹⁴). With the benzo/ene-system 12 again no four-membered ring product was detected (direct excitation ($\lambda = 254$ nm), -70 to $+20^\circ\text{C}$) and, instead, only naphthalene (>85%) was produced. On shorter irradiation time, a small



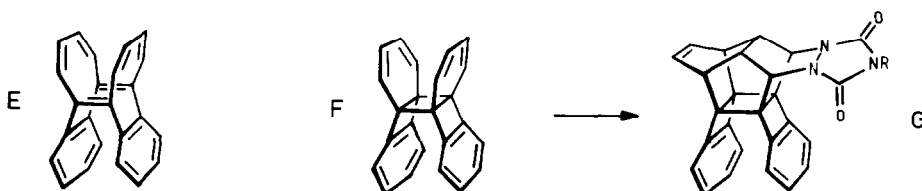
amount of presumably 13 was detected (NMR). Clearly, the situation is similar to that with the (di)benzo-compounds A insofar as the formation of (highly labile) cycloadducts (8) cannot be excluded with certainty.

This paper is dedicated to Prof. Dr. T. GÄUMANN on the occasion of his 60th birthday as an expression of our good wishes and a mark of our esteem.

Financial support by the "Deutsche Forschungsgemeinschaft", the "Fonds der Chemischen Industrie" and the BASF AG is gratefully acknowledged. P. R. S. thanks the Alexander von Humboldt Foundation for a fellowship.

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(Received in Germany 9 January 1986)