

THE BENZO- AND AZO(AZOXY)-CHROMOPHORS AS $\pi 6/\pi 2$ -COMPONENTS IN PHOTOCYCLOADDITION REACTIONS**

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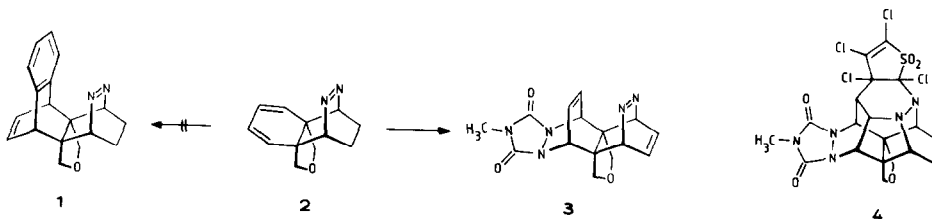
SUMMARY: In cage substrates (15/16) with specifically designed and favourable geometry (X-ray), no [6+2]-photocycloaddition between benzo/azo(azoxy) chromophors could be effected.

In the benzo/ene-skeletons A ($X=CH_2$)² as well as in the basic ene/ene-³ and benzo/benzo-analogues⁴, favourable geometrical and stereoelectronic



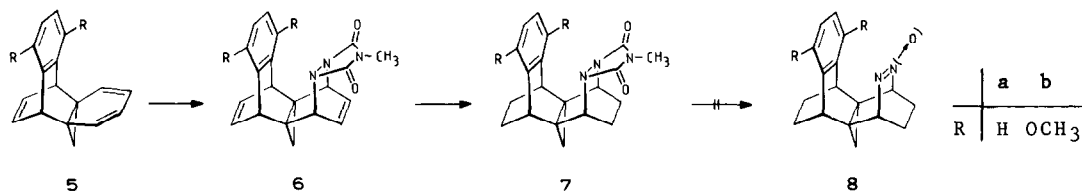
prerequisites for efficient transannular cyclobutane formation are given - with the additional bonus, that the highly strained photoproducts show high kinetic stability⁵). Seeking further information with respect to the relative ability of (C_6H_4) -, $N=N(O)$ and $C=N(O)$ chromophoric units to function as $\pi 6/\pi 2$ -components in photocycloaddition reactions - comparative studies with the structurally similar benzo/imine(nitrone)- and benzo/azo(azoxy)-compounds C and D were an obvious extension. Synthesis, X-ray structural analysis and the photobehaviour of the benzo/azo(azoxy)-substrates 15(16) are described in this paper.

The construction of substrates with suitably oriented benzo/azo(azoxy)-chromophors posed some problems⁶). Addition of benzyne to the azopropellane 2 failed (maleic anhydride added only at temp. $>160^\circ C$)⁸) as did attempts to effect



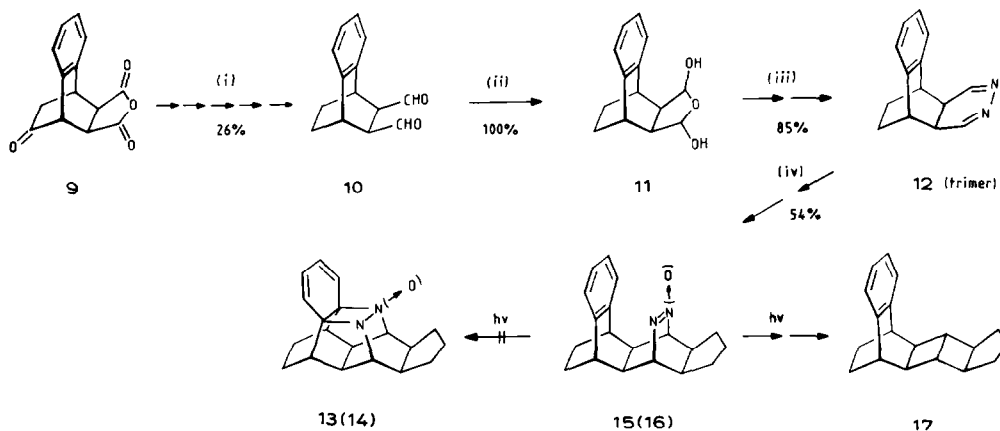
benzo-annellation of its N-methyl-triazolinedione(NMTD)-adduct 3. Tetrachlorothiophenedioxide⁹) added sluggishly ($200^\circ C$, 2d), not, however, in the expected

[4+2]-sense to the C=C-double bond, but in a formal [2+2+2]-sense¹⁰⁾ to give a mixture of stereoisomeric 1:1-adducts (e.g. 4). Alternatively, the installation of an azo-bridge syn to the benzene-unit in substrates of type 5 was pursued. In this way specific variations in the benzene-unit seemed feasible. 5a (45%, m.p. 122°C) was prepared by addition of benzyne to 1,6-methano [10]annulene¹¹⁾, 5b (yellow needles, 22%, m.p. 173°C) by addition of quinone (refl. chlorobenzene, yellow plates, 23%, m.p. 167-168°C) followed by deprotonation/methylation (NaH/DMSO, CH₃I). NMTD addition to 5a,b was rapid and regioselective (100% 6a, m.p. 250°C; 100% 6b, m.p. 252°C (dec.)), hydrogenation (10%



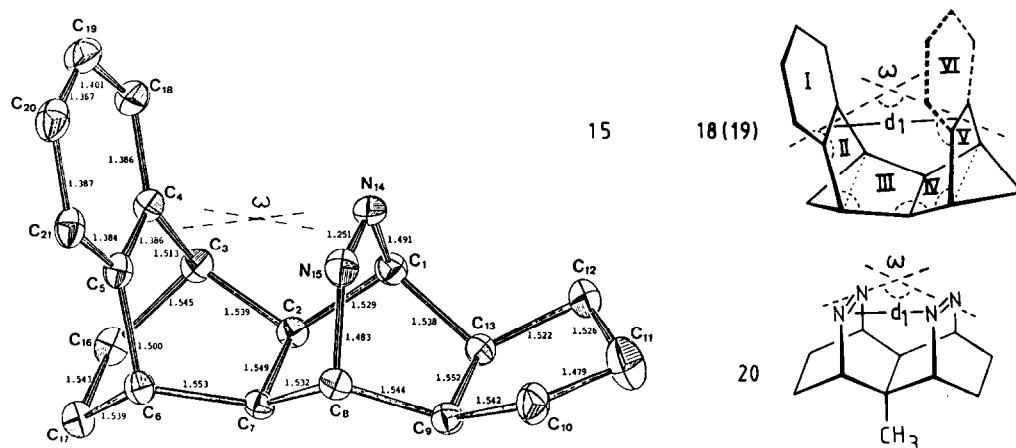
Pd/C) to 7a,b was quantitative (7a: colourless crystals, m.p. 271°C, 7b: colourless crystals, m.p. 260-261°C). Unfortunately (oxidative) hydrolysis to 8a,b could not be effected, presumably for steric reasons. Even under forcing conditions 7a,b remained intact.

In the route, which finally proved successful, we took advantage of experiences by Hünig et al.^{12,14)}. The moderate overall yield in the five-step transformation 9→10 was acceptable in view of the ready availability of 9, the exo-adduct of 2-naphthol with maleic anhydride¹³⁾. The final work-up with CuCl₂ leading to the benzo/azo-substrate 15 was necessitated by the partial N=N-reduction in the C=C-hydrogenation of the intermediate cyclopentadiene-adduct. 15 (m.p. 215°C; λ_{max} (CH₃CN) = 392 nm (ϵ = 145), 381 (sh, 195), 353 (sh, 250), 272 (sh, 240), 263 (375)) was oxidized (*m*-CPBA) to 16 (m.p. 250°C; λ_{max} (CH₃CN) = 274 nm (sh, ϵ = 790), 247 (sh, 2300)).



(i): HOCH₂CH₂OH (benzene, TsOH(cat.)); LAH/THF, refl., 1h; acetone/H₂SO₄, 20°C; KOH/hydrazine, 200°C; (COCl)₂/DMSO/CH₂Cl₂, -45°C, work up with (C₂H₅)₃N; (ii): H₂O; (iii): anhydrous hydrazine/CH₂Cl₂; (iv): cyclopentadiene/TFA¹⁴⁾, 0°C; 10% Pd/C; CH₃CO₂C₂H₅, 1 atm. H₂, 20°C; work up with CuCl₂.

In Fig.1 structural details for 15 are presented¹⁵⁾ and the relevant interplanary angles, through space distances d_1 and interorbital angles ω are compared with the experimental and calculated (MND0)¹⁶⁾ values of the syn-benzo/ene-, syn-benzo/benzo- and syn-azo/azo-structures 18, 19 and 20, for which transannular [6+2]/[6+6]-photocycloadditions have been observed^{3,4)}. Clearly, there are only minimal differences and as evidenced by the d_1/ω -values the geometrical situation for [6+2]-additions seems at least as favourable in 15 as in 18/19 (20). In contrast to the findings with 18/19 however, PE-studies do not reveal a significant benzo/azo(azoxy) through-space interaction¹⁷⁾.



	I/II	II/III	III/IV	IV/V	V/VI	ω	d_1
15	182 (181.6)	124 (123.7)	127 (129.7)	123 (122.7)		164 (162)	2.97 (3.079)
18	(183.5)	(118.9)	(132.5)	(118.3)		(167)	
19	184.7 (185.4)	119.0 (119.4)	133.1 (133.4)	118.4 (119.4)	183.7 (185.4)	161 (157)	3.04 (3.113)
20						167	2.82/2.88

Fig.1 Structure of 15. Interplanary/Interorbital Angles ($^{\circ}$), Transannular Distances (\AA) (calculated values in brackets)

Irradiation of 15 under the conditions employed for the conversion A \rightarrow B, (10^{-3} M degassed methanol (acetonitrile) or acetone solution, -50°C , $\lambda = 254$ nm (Hanau Hg TNN 15 low pressure lamp) or $\lambda \geq 280$ nm, Hanau TQ 150 high pressure lamp, solidex filter) or with light of $\lambda > 350$ nm ($\text{Cu}(\text{NO}_3)_2$ -filter solution, TQ 150) led only to very slow N_2 -elimination to give 17 (m.p. 117°C , up to 70% isolated based on ca. 60% conversion (ca. 2d irradiation)). When the oxide 16 was irradiated under similar conditions again no cyclization (to the diazeti-dine-N-oxide 14) was observed and instead, slow deoxygenation to 15 (up to 60%) and subsequent elimination to 17 took place in addition to polymeriza-tion. On direct excitation of 15(16) under various conditions in the presence of TCNE or NMTD (-30 to 0°C) or MA (up to $+80^{\circ}\text{C}$) or by rapid addition of NMTD

to irradiated solutions at -70°C , no [4+2]-adducts with 13(14) (as exemplified with the hydrocarbon B ($\text{X}=\text{CH}_2$) at -70°C) were detected. Irradiation of 15(16) at 77 K ($\lambda = 254$ nm, EPA) caused only minimal changes of the UV-spectra; after warming to $+10^{\circ}\text{C}$ a weak UV-absorption at 340(325) nm was recorded, which disappeared (decreased) on standing at r.t.. No new product could be isolated. According to our experiences in the A-series the chances for cycloaddition in D-systems might be improved by shortening the X-bridges.

Financial support by the "Deutsche Forschungsgemeinschaft", the "Fonds der Chemischen Industrie" and the BASF AG is gratefully acknowledged. For the MNDO-calculations we thank Dipl.Chem. W.-D.Fessner, for experimental help cand. rer. nat. B.Fischer.

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- 6) G. Fischer, dissertation, Univ. Freiburg 1986. - All new compounds are fully analyzed by elemental analysis and spectral data (IR, UV, MS, ^1H -, ^{13}C -NMR), e.g. 15 (1R*, 2S*, 3S*, 9S*)-4,5-Benzo-14,15-diazapentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]heptadeca-4,14-diene: ^1H -NMR (400 MHz, CDCl_3): $\delta = 7.18$ (m, ZH-m), 7.05 (m, 2H-O), 5.16 (s, 1-, 8-H), 2.97 (br. s, 3-, 6-H), 2.27 (br. s, 2-, 7-H), 2.25 (m, 9-, 13-H), 1.71 (m, 16-, 17-H), 1.63 (m, 10-, 12-H), 1.36 (m, 16'-, 17'-H), 1.17 (m, 10'-, 12'-H), 1.14 (m, 11-H), 1.04 (m, 11'-H); ^{13}C -NMR (CDCl_3): $\delta = 140.3$ (C-4, -5), 126.9 (2C-m), 124.1 (2C-O), 70.9 (C-1, -8), 44.0 (C-9, -13), 42.7 (C-2, -7), 38.2 (C-3, -6), 30.5 (C-10, -12), 26.4 (C-16, -17), 25.7 (C-11); ^{15}N -NMR (CDCl_3): $\delta = 536.6$ (N-14, -15).
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- 15) Crystals are monoclinic, space group $\text{P}2_1/\text{c}$ (Nr. 14), $a = 6.460$ Å, $b = 9.792$ Å, $c = 23.000$ Å, $\beta = 90.13^{\circ}$. Number of reflections used in least squares refinement = 3833. Final R-factor: 0.069. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EH, UK. Any request should be accompanied by the full literature citation for this communication.
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(Received in Germany 28 October 1985)