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SYNTHESIS, X-RAY STRUCTURAL ANALYSIS AND PHOTOCHEMISTRY OF NOVEL SYN-PERIPLANAR BIS-AZO-SKELETONS

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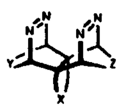
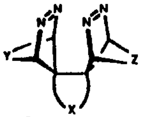
Summary: Skeletons with syn-periplanar bis-azo-chromophoric units (**8**,**18**,**19**) have been synthesized (**8**: transannular N=N/N=N-distances 2.939(2.999) Å, interorbital angle ω = 154.3°, X-ray analysis). In no case azo/azo-photocycloaddition has been observed upon direct or sensitized excitation.

For good reasons the azo-chromophor is a rare participant in [π2+π2]-photocycloaddition reactions; the thermodynamic situations are relatively unfavorable, the steric/stereoelectronic prerequisites are unusually strict and N_2-elimination is an omnipresent competition$^{1)}$. Several (intramolecular) azo/ene$^{2,3)}$, but no azo-/azo-cycloadditions have been observed and only a single case of an azoxy/azo-photometathesis reaction$^{4)}$ has been reported. A demanding aspect is the construction of appropriate substrates - with two closely oriented syn-periplanar azo-groups built into as rigid as possible frameworks as approached with the skeletons **A**-**E**.



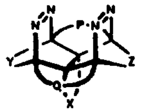
A

B



C

D



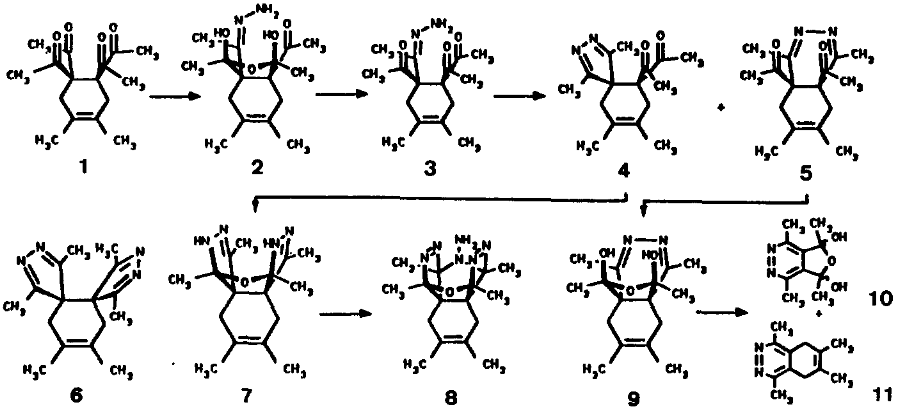
E

F

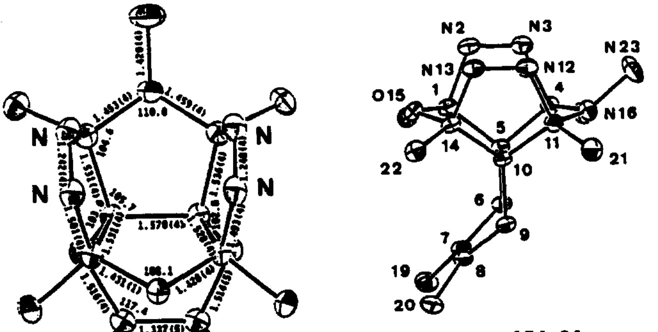
G

On our search for syn-bisazo substrates which would provide perfect orientation of the chromophors on the educt side and sufficient kinetic stabilization on the product (tetrazetidine) side, we also checked routes to structures of type **A** and **C** starting from 1,1,2,2-tetracarbonylethanes via bis-dihydropyridazines **F** and bis-isopyrazoles **G**. The original goals were not attained, yet a convenient access to syn-bisazo-substrates of general type **D** (**8**,**18**,**19**) was opened up$^{5)}$.

Starting material of the synthesis is the tetraacetyl cyclohexene **1**$^{6)}$. Upon treatment of **1** with large excess of anhydrous hydrazine (10 equiv., CH_3CN, 0°C), a single product is formed (100%) - the colourless, oxygen-bridged hydrazone **2** (m.p. 128-130° C). On drying i.vac., **2** looses water to give **3**. Cyclization of the latter in direction of isopyrazole **4** or dihydropyridazine **5** critically depends on the reaction conditions: in a carefully dried suspension of $LiClO_4/CH_2Cl_2$ isopyrazole **4** is formed preferentially and is isolated chromatographically (acetone, silica gel) in 60% yield as pale yellowish oil. In the presence of water **4** remains a minor component in a complex reaction mixture with **10** (11%) and **11** (10%) resulting from rapid cycloreversion of dihydropyridazine **9**. Under various conditions the prospected formation of the bis-isopyrazole **6** could not be accomplished; some of the complications become obvious from the reaction of **4** with 4 equivalents of anhydrous hydrazine in an O_2-atmosphere (CH_3CN, 0°C, exclusion of light, 5h): the crystalline product isolated in 80% yield is shown to be the pale-yellow transannularly O,N-bridged syn-bis-azo compound **8** (m.p. 210°C, $\nu_{N=N}$ = 1570 cm^{-1}; at 205°C N_2 elimination sets in). In the absence of oxygen NMR analysis reveals an equilibrating mixture of primarily three components (aminals etc.).



8 is stable enough to allow purification by sublimation at 160°C (10^{-3} torr). In the UV spectrum (CH_3CN) an unusually long-wavelength maximum at 394 nm (ϵ = 245) is indicative of efficient transannular interaction between the two N=N double bonds (perhaps enhanced by the neighbouring NH_2-function). The prominent geometrical details as disclosed by the X-ray structural analysis are given in Fig.1[7]. When compared with the calculated data for the energetically favorable ("closed") conformation of the model 1,6-diene **12** (d = 3.10 Å, ω = 153.3°)[8] - which efficiently undergoes [π2+π2]-photocycloaddition to give **13** - the transan-

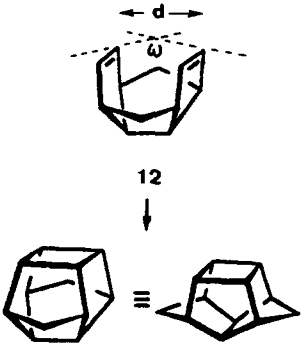


ω = 154.3°

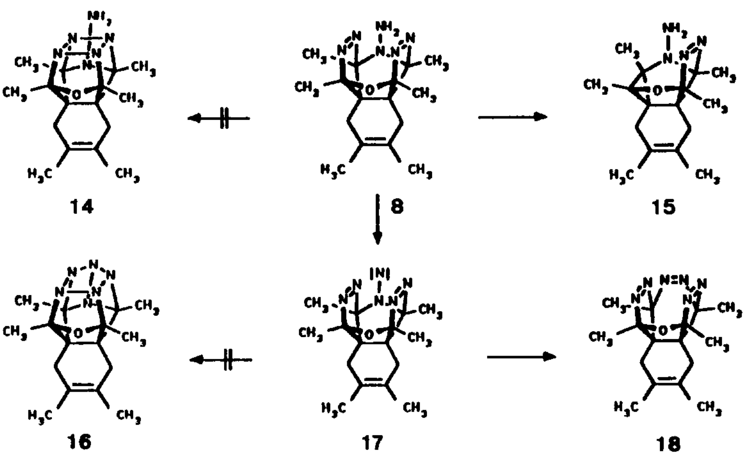
N2 - N13: 2.939 (N3 - N23: 2.926 Å)

N3 - N12: 2.999 (N12 - N23: 2.922 Å)

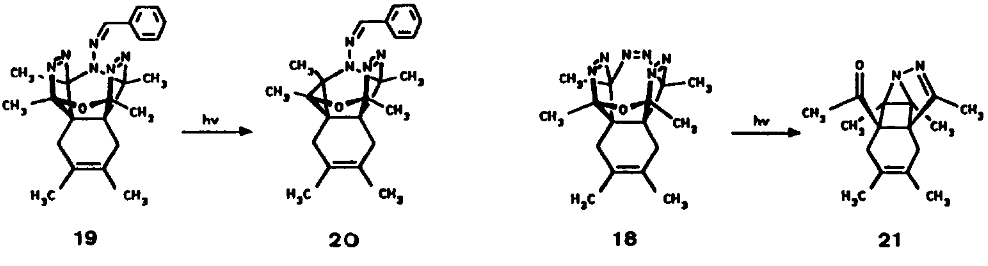
Fig. 1. X-Ray Structure of **8** (Å, °).



nular π/π-distances are even sligtly shorter, the interorbital angle ω almost identical; the length of the N=N-bonds is normal[9]. Nevertheless, for **8** on daylight or upon exposure to the light of a daylight lamp (ca. 10^{-3} M degassed CH_3CN solutions, -40°C) using a solidex filter (λ>290 nm) elimination of one N_2 unit to give "reluctant" **15** is the preferred pathway (74%, λ_{max} (CH_3CN) = 360 nm (ε = 120)); monochromatic 254 nm ligth (same conditions) produced only polymeric material. Upon irradiation in acetone **15** is again the only monomeric product. From low temperature and solid state experiments, information about the potential intervention of tetrazetidine **14** is expected. Oxidation of **8** with $Pb(OAc)_4$ or with m-chloroperbenzoic acid (CH_2Cl_2, K_2CO_3, room temp.) led in high yield (80-90%) to the yellow-crystalline pentacycle **18** featuring three homoconjugated N=N bonds (λ_{max}(CH_3CN = 365 nm (ε = 305)); nitrene (**17**) addition to give the highly strained pentazolidine **16** (homoconjugatively or stepwise)[10] can apparently not compete[11].



8 was derivatized as Schiff base **19** (73%, yellow crystals, m.p. 173°C, $\nu_{N=N}$ = 1564 cm^{-1}, λ_{max}(CH_3CN) = 410 nm (ε = 165)). When irradiated under the conditions applied to **8**, **19** behaves in much the same way (55% "reluctant" **20** with λ>290 nm)). With (twofold) N_2-extrusion ends also the direct irradiation of trisazo-substrate **18** (ca. 10^{-3} M degassed CH_3CN solution, 800 W halogen daylight lamp, solidex-filter, -40°C, total conversion, separation from polymers through filtration over silica gel); **21** was isolated as viscous oil (39%, λ_{max} (CH_3CN) (ε) = 297sh (190), 225 nm (2000)).



Clearly, the steric/stereoelectronic demands for the photocycloaddition reaction between two N=N bonds are very stringent. Preparative efforts are therefore directed towards the construction of even more rigid substrates of type **B** - with even closer orientation of the N=N/N=N units.

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6) All new compounds are fully analyzed by elemental analysis and spectra (IR, UV, MS, ^{1}H-, ^{13}C-NMR). **8**: (1R,4R,6S,9S,10S,15R)-16-Amino-1,4,6,9,12,13-hexamethyl-5-oxa-2,3,7,8,16-pentaazapentacyclo[7.6.1.0^{4,15}.0^{6,10}.0^{10,15}]hexadeca-2,7,12-triene; **18**: (1R,4R,7S,10S,11S,16R)-1,4,7,10,13,14-Hexamethyl-17-oxa-2,3,5,6,8,9-hexaazapentacyclo[8.6.1.0^{4,16}.0^{7,11}.0^{11,16}]heptadeca-2,5,8,13-tetraene.

7) Crystallographic data of **8** (crystals grown from acetonitrile): Formula $C_{16}H_{24}N_6O$; crystal size, mm 0.7 x 0.6 x 0.6; crystal system monoclinic; space group $P2_1/c$; a, Å 8.132(1); b, Å 13.516(3); c, Å 14.506(3); β, ° 93.36(2); V, Å^3 1591; Z 4; calc. density g/cm^3 1.320; No. of reflections 3560; No. of nonzero reflections ($I>2\sigma(I)$) 3369; No. of parameters 604; Final R factor (solvent disordered) 0.075. Further details are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW.

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22 **23**

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