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[6+6]- Photocycloadditions in "Face-to-Face" Benzo/Pyridazino Systems En Route to Azapagodanes (Azadodecahedranes)[1]

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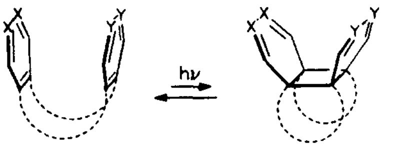
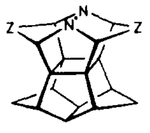
Summary: In two very proximate *syn*-periplanar ("face-to-face") benzo/pyridazino systems (shortest π,π-distances of ca. 3.0 Å, X-ray), photoequilibration (ratio ca. 2:1) with the cyclobutane-photo[6+6]cycloadducts has been installed by 254 nm irradiation. The hetarene/arene "dimers" are thermally persistent enough as to allow pagodane formation through the cycloaddition of dienophiles.

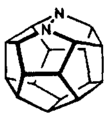
Non-covalent interaction[2] as well as covalent bond formation upon photoexcitation, specifically dimerization,[3] between more or less proximate, ordered arene units are subject of active investigation. Still, arene/arene dimerizations with cyclobutane formation (A → B, [6+6]) are very rare. In the few cases known (X = Y = CH, X = Y = N),[4,5] rigid carbon skeletons enforce a nearly optimal *syn*-periplanar orientation of the two benzenoid chromophors ("face-to-face") at distances much smaller than van-der-Waals (to the benefit of exciplex formation), and provided enough kinetic stabilization to the "*syn-o,o'*-benzene dimers"[6] to be preparatively useful - the very first example became a key step in the pagodane-dodecahedrane synthetic scheme.[7]



A B



C

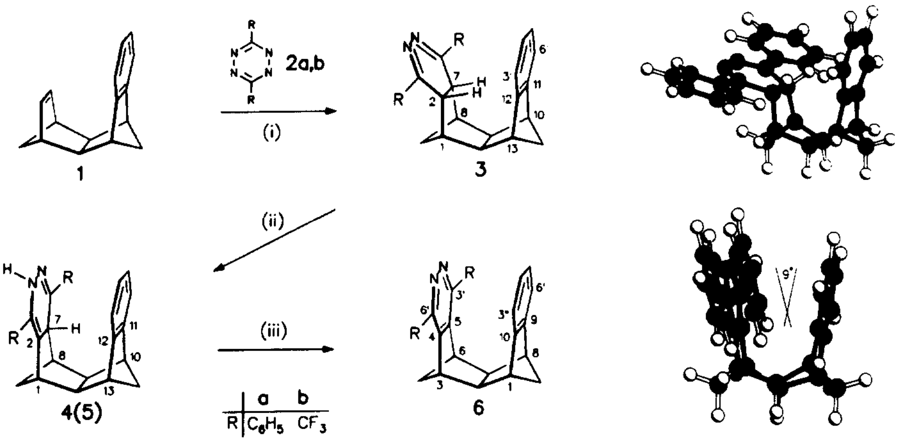


D

It is in the photophysical as well as the preparative-synthetic context that an exploration with benzo/pyridazino systems of type **A** (X = N) was started. Synthetically, the respective cycloadducts **B** are aspired as potential intermediates en route to diazapagodanes **C**/diazadodecahedranes **D** (and respective radicals/ions[8]).

The synthesis of the "face-to-face" benzo/pyridazino substrates **6**[9] shares with that of the benzo/benzo analogs[4] the benzo/ene **1** as $\pi 2$ component in the anellation of the second arene ring - here effected with the help of the tetrazines **2**[10] whose functionalization (R) allows broad, target oriented variations. With the readily available phenyl- and CF_3-disubstituted tetrazines **2a,b** exclusive *exo*-addition led to cycloadducts **3a,b**. "Aromatization" by elimination of the two "inner" hydrogens faced severe steric inhibition ($\delta_{2(7)\text{-H}}$ = 2.68 (2.25); s. Schakal plot for **3a**) and was additionally complicated by the reactivity of the heterocycles involved. After futile attempts to bring about the dehydrogenation **3a,b** → **6a,b** with standard oxidants (the necessarily forcing conditions had ended in decomposition[11]) this goal was now achieved through forcing thermal isomerization to **4a,b**, N-chlorination to **5a,b**, and 1,4-

HCl-elimination to **6a,b**; in case of **5a** the system *t*-buOK/toluene proved useful whilst **5b** only yielded to the small "naked" F^- base (P_2F).[12]



(i) 1 equiv. of **2a** (**2b**), anhydr. CH_2Cl_2, RT, 90 - 95%; (ii) *p*-dichlorobenzene, 173°C, 2h, 70% **4a**, 85% **4b**; (iii) 1 equiv. of *t*-butylhypochlorite/*t*-buOK (excess), anhydr. toluene, RT, 84% **6a**, 90% **5b**; P_2F (4 equiv.), anhydr. benzene, RT, 95% **6b**.

For the 3,3'-*o*,*o*'-cyclophane **6a** a crystal structure analysis (Fig. 1)[13] provided crucial informations; i.a. the shortest π,π-distance *d* of 3.003 (av.) Å between C4-C10, C5-C9 and the degree of pyramidalization of these four arene carbons of ca. 8° as expression of strong π,π repulsion (criterion for cyclobutane formation?). The intrinsic deviation from perfect parallel orientation of the benzenoid chromophors by ca. 9° (MM2, interorbital angle ω = ca. 171°, Schakal plot) is enlarged by this pyramidalization to ca. 20° (ω = ca. 160°). Transannular diamagnetic shielding is expressed in the ^{1}H NMR shifts.[9]

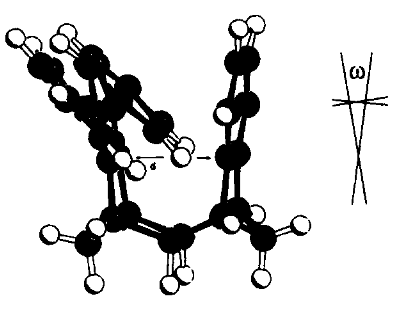
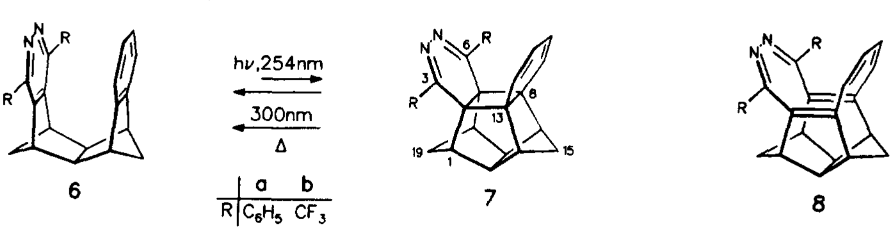


Fig. 1. X-ray crystal structure of **6a**.

With respect to the photocycloadditions **6a,b** → **7a,b**, there were a priori several uncertainties: Would there be an absorption "window" to allow selective excitation of the substrates? Could eventual photoequilibria be steered towards the cycloadducts? Would other photochemical pathways as e.g. metathesis to the [12]diazaannulenes **8** interfere?[14] Would the hetarene/arene-dimers **7a,b** be kinetically stable enough to allow their use in cycloaddition reactions? The answers to these questions were in toto rather promising. During irradiation of dilute (ca. 10^{-3} molar), degassed, carefully dried CH_3CN solutions of **6a** (**6b**) at 0°C with the polychromatic light of a high-pressure Hg lamp in a pyrex vessel (λ > 280 nm) no **7a**(**7b**) was detected; yet, with monochromatic 254 nm light (Hanau, low-pressure Hg lamp, Rayonet chamber, quartz vessel) the equilibria **6a** ⇄ **7a** and **6b** ⇄ **7b** were installed (isosbestic points at 296 nm (228, 249 nm); both ratios of ca. 2:1 not expressing the relative absorption of the equilibrium participants at 254 nm[4] ($\varepsilon_{6a(7a)}$ = 12650 (10440); $\varepsilon_{6b(7b)}$ = 2310 (2410)); the quantum yields for the two processes are different[15]). Even under prolonged irradiation no detractive competition (e.g. **8a,b**) came into play.

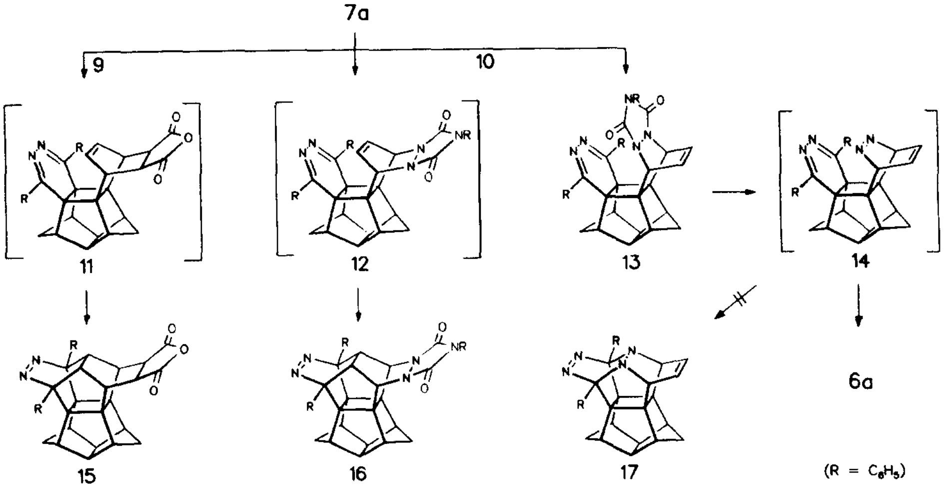
The pyridazine/benzene "dimers" **7a,b** proved thermally highly persistent ($t_{1/2}$ (140°C), benzene, ca. 10 h, **6a,b**);

separation of mixtures **6a**(**7a**)/**6b**(**7b**) on neutral silica gel was unproblematical; acids catalyze the cycloreversion. The UV absorption spectra of pure **7a,b** reveal effective σ-conjugation between the two dienic chromophors (e.g. λ_{max} = 274 nm for **6a**, 304 nm for **7a**).[16]



	a	b
R	C_6H_5	CF_3

In analogy to the standard route to pagodanes[7], the synthesis of diazapagodanes **C** requires the (*exo*-)addition of an acetylene equivalent to the heterodiene part of **7** and of the newly created N=N double bond to the opposite butadiene part - with the latter step hopefully enjoying enough entropic assistance to overcome N_2 elimination. Whilst experiments with electron rich reactants[10,17] are in progress, an explorative study with **7a**, maleic anhydride (**9**), and N-phenyl-triazolinedione (**10**) points to analogies and discrepancies with the dibenzo-photoproduct.[18] The major product (30%, ca. 60% on recovered **6a**) arising from the expectedly slow reaction with **9** (2.5 equiv., 80°C, 9.5 kbar, toluene, 19 h) was identified as [2.2.1.1]diazapagodane **15** - in the not observed intermediate **11** the intramolecular addition of the somewhat strained C=C double bond to the diazabutadiene part is relatively rapid. From the "titration" of **7a** with the red **10** at room temperature quantitatively a ca. 1:1 mixture of two isomeric adducts (MS) resulted - **16**, the tetraza-analogue of **15** (**12** not being detectable), and **13** (X-ray); this latter cycloaddition mode ("pincer"-type) had not been observed in the prior studies for **10**.[18] To be noted, after standard degradation **13** → **14** no pagodane **17** but only **6a** was found. Dimethyl acetylenedicarboxylate, dicyanoacetylene and TCE did not undergo cycloaddition but yielded highly colored products arising from nucleophilic addition of **7a** through one of its nitrogen-ring atoms.[17]



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9) The new compounds are characterized by elemental analyses and spectral data (IR, UV, ^{1}H-, ^{13}C-NMR, MS). E.g. ^{1}H-NMR ($CDCl_3$): **6a** (**6b**): $\delta_{3''(6'')\text{-H}} = 6.72$ (6.7), $\delta_{4''(5'')\text{-H}} = 6.50$ (6.6); **7a** (**7b**): $\delta_{9(12)\text{-H}} = 5.51$ (5.80), $\delta_{10(11)\text{-H}} = 5.34$ (5.38). - UV (CH_3CN): **6a**: $\lambda_{max}(\varepsilon) = 338$ nm (sh, 390), 274 (19800), 214 (sh, 25100); **7a**: $\lambda_{max}(\varepsilon) = 392$ nm (sh, 2680), 368 (sh, 5460), 312 (sh, 6420), 304 (12000), 232 (sh, 6500).
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13) Crystal data for **6a**: $C_{30}H_{24}N_2$, $\lambda = 1.54184$, crystal system: monoclinic, space group $P2_1/c$, No. 14, $a = 11.5591(7)$, $b = 14.2661(3)$, $c = 15.1306(9)$ Å, $\beta = 98.440(2)°$, $V = 2468.1(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.110$ gcm^{-3}. - Enraf-Nonius CAD4 diffractometer, graphite monochromator, crystal size [mm]: 0.40 x 0.30 x 0.15, data collection mode: ω-2Θ-scan, collected reflections: 5295, independent reflections: 5115 ($R_{int} = 0.017$), reflections observed [$I > 2\sigma(I)$]: 4218, $\mu = 0.465$ mm^{-1}, empirical absorption correction. - Solution by direct phase determination (SIR88), method of refinement: full-matrix least-squares on F. Hydrogen positions werde refined isotropically, data-to-parameter ratio: 9.6, $R = 0.046$, $R_w = 0.053$, EoF = 4.036, extinction coefficient: 1.56 x 10^{-6}, largest diff. peak: 0.307 eÅ^{-3}, final average shift/error: 0.01, program used: MOLEN (Enraf-Nonius, 1990). Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the deposition number CSD 405092, the names of the authors, and the journal citation.
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