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Synthesis and Photodimerisation of Tetrabenzo[*ab,f,jk,o*]-[18]annulenes

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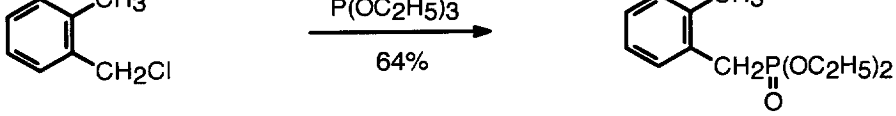
Abstract: The tetrabenzo[*ab,f,jk,o*][18]annulenes **7a,b**, generated in a 5-step synthesis, show photodimerisation and –oligomerisation reactions in the solid state and in solution. The state of aggregation determines the reaction route. Whereas the cyclodimer **8a** has a simple cyclobutane structure, the dimer **8b** is a highly symmetrical cyclophane.

Keywords: Annulenes; Aggregation; Dimerisation; Cyclophanes.

Areno-condensed annulenes represent discotic molecules which attract attention in materials science because of their applications as liquid crystals and photoconductors.[1-6] Moreover they show interesting photochemical properties.[3,4,7,8]

We synthesised the tetrabenzo-condensed [18]annulenes **7a,b** on the route described below. 1-Chloromethyl-2-methylbenzene (**1**) was transformed to the phosponate **2**, which yielded in a Wittig-Horner reaction with the aldehydes **3a,b** the (*E*)-stilbenes **4a,b**. The acetal group of **4a** was hydrolyzed and the bromine atom of **4b** substituted by a formyl group so that the aldehydes **5a,b**[9] were obtained. The condensation reaction with aniline led in a quantitative yield to the Schiff bases **6a,b**[10] which were suitable for a twofold cyclic condensation to the title compounds **7a,b**[11]. The *anti*-elimination of aniline in a strongly alkaline medium generated selectively (*E*)-configurated double bonds. There were no hints for (*Z*)-configurated CC double bonds in the ^{1}H NMR spectra of the pure compounds **4a,b** – **7a,b**.



Scheme 1 1 2

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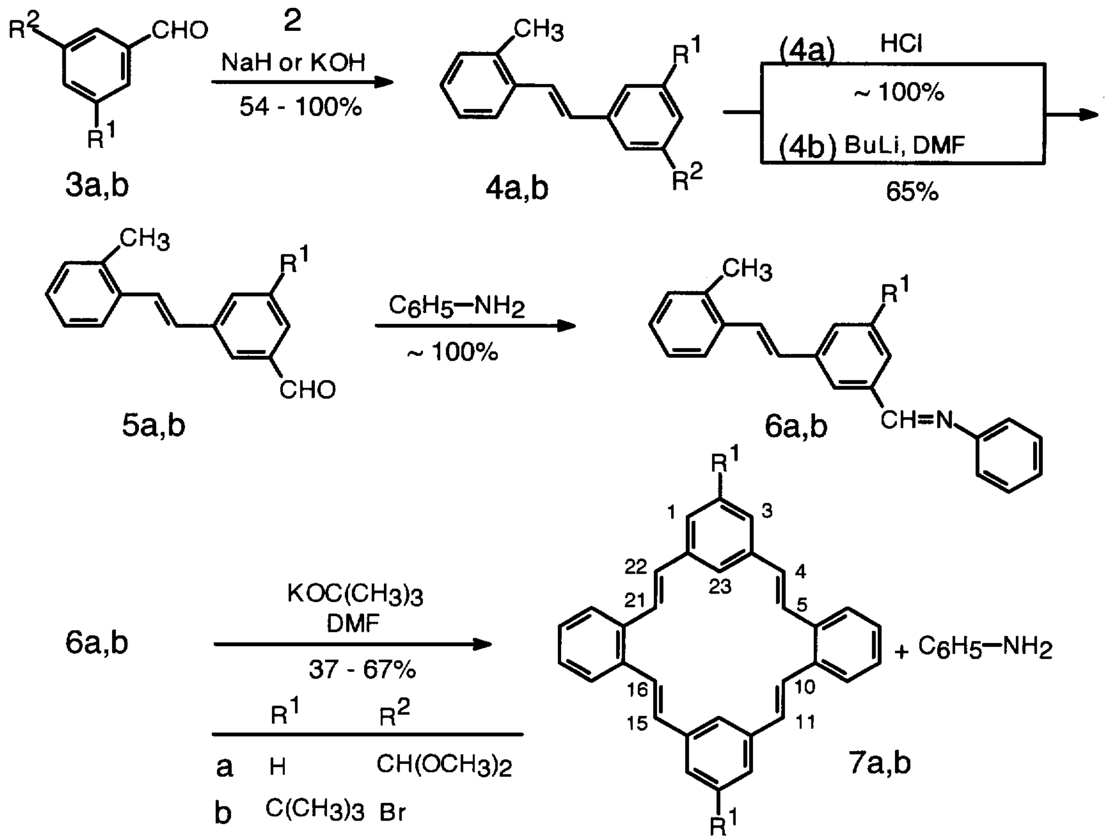
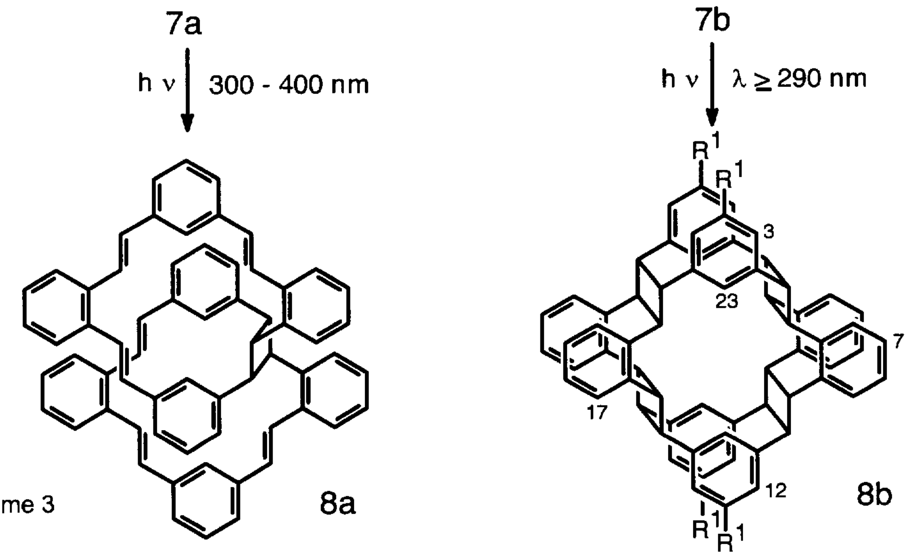


Scheme 2

3-21G *ab initio* calculations[12] predict different possible aggregations of **7a** to molecular pairs. The C_{2h} species, in which the double bond between C-10 and C-11 of one molecule lies over the double bond between C-4 and C-5 of the other molecule, and a C_i species, in which the double bond between C-4 and C-5 of one molecule lies over the double bond between C-21 and C-22 of the other molecule, are most favorable. Both species are stabilized by $-$ 4.67 kcal $\cdot$ mol^{-1} related to the monomer. The average distances of the olefinic centers amount to 397 pm in the C_{2h} case and to 392 pm in the C_i arrangement. These distances are close enough for a $\pi\pi$ interaction and a photochemical dimerisation to 4-membered rings.

Irradiation (300 nm $\leq \lambda \leq$ 400 nm) of **7a** in the solid state led to the dimer **8a**[13], which corresponds to the C_{2h} molecular pair. After a conversion of 30% the portion of oligomers increased strongly. Prolonged irradiation gave a quantitative yield of oligomers. It is reasonable, that **8a** can form further CC single bonds by irradiation. The monochromatic irradiation (λ = 366 nm) in chloroform, where **7a** has a λ_{max} value of 292 nm, resulted in a complete disappearance of the long wavelength absorption and yielded quantitatively oligomers. Thus, we were surprised that the compound **7b** showed an opposite behavior; it gave a highly symmetrical cyclophane **8b**[13] on irradiation ($\lambda \geq 290$ nm) in benzene. The corresponding molecular pair of **8a** does not represent an energetically favorable aggregate in the ground state. The 18-membered rings form in **8b** a belt structure with eight condensed benzene rings at the edges of the belt. Irradiation of **7b** in the solid state generated oligomers. How can these results be explained?



Scheme 3

In the crystalline state, obviously the *topochemistry* governs the photoreaction. In solution, the *aggregation tendency* and the *concentration* play the decisive role. Due to the short average lifetime[4] of the reactive singlet states S_1 of areno-condensed annulenes concerted $[2\pi + 2\pi]$ cyclodimerisation processes require high concentrations of the monomer or high aggregation tendencies. The irradiation of **7b** was performed in a $0.4 \cdot 10^{-3}$ M solution; **7a** is much less soluble than **7b** so that only highly diluted solutions in benzene, chloroform or other organic solvents can be obtained. One can assume that the aggregation tendencies of **7a** and **7b** do not differ significantly; thus, the higher concentration of **7b** seems to be responsible for the photodimerisation reaction in solution. The formation of oligomers on the other hand can be rationalized in the stilbene series via relatively long-lived benzylic radicals – a process which can be already observed for (*E*)-stilbene in highly diluted solutions.[14] The normally competing *E/Z* isomerisation is - due to steric reasons - energetically unfavorable in the annulenes **8**.

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9. Aldehydes: **5a**: oil; ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3 H, CH_3), 7.02/ 7.43 (AB, ^3J 16.2 Hz, 2 H, olefin. H), 7.20 (m, 3 H, arom. H), 7.51 (m, 2 H, arom. H), 7.75 (m, 2 H, arom. H), 8.01 (m, 1 H, 2-H), 10.04 (s, 1 H, CHO); **5b**: oil; ^{1}H NMR ($CDCl_3$): δ 1,39 (s, 9 H, $C(CH_3)_3$), 2.45 (s, 3 H, CH_3), 7.04/ 7.41 (AB, ^3J 16.2 Hz, 2 H, olefin. H), 7.20 (m, 3 H, arom. H), 7.59 (m, 1 H, arom. H), 7.72/ 7.79/ 7.88 (m, 3 H, arom. H), 10.04 (s, 1 H, CHO).
10. Schiff bases: **6a**: yellow oil; CH = N: ^{1}H NMR ($CDCl_3$): δ 8.49 (s, 1 H), ^{13}C NMR ($CDCl_3$): δ 160.2; MS (70 eV): *m/e* 297 (14%, $M^{+\cdot}$), 110 (100%), **6b**: yellow oil; CH = N: ^{1}H NMR ($CDCl_3$): δ 8.56 (s, 1 H), ^{13}C NMR ($CDCl_3$): δ 160.8.
11. [18]Annulenes: **7a**: mp > 250°; ^{1}H NMR ($C_2D_2Cl_4$): δ 7.08 (d, ^3J 16.1 Hz, 4 H, 4-H), 7.20 (m, 4 H, 1-H), 7.27 (m, 4 H, 7-H), 7.32 (t, 2 H, 2-H), 7.70 (m, 4 H, 6-H), 7.83 (d, ^3J 16.1 Hz, 4 H, 5-H), 8.29 (d, 2 H, 23-H); MS (70 eV): *m/e* 408 (100%, $M^{+\cdot}$); **7b**: mp > 250°; ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 18 H, $C(CH_3)_3$), 7.13 (d, ^3J 16.1 Hz, 4 H, 4-H), 7.26 (d, 4 H, 1-H), 7.29 (m, 4 H, 7-H), 7.75 (m, 4 H, 6-H), 7.88 (d, ^3J 16.1 Hz, 4 H, 5-H), 8.19 (d, 2 H, 23-H), ^{13}C NMR ($CDCl_3$): δ 31.2 (CH_3), 34.9 (C_q), 116.9 (C-23), 125.3 (C-6), 125.8 (C-1), 126.0 (C-5), 127.8 (C-7), 130.0 (C-4), 135.0/ 138.0 (C-3a, C-5a), 152.3 (C-2).
12. R. Yu, A. V. Yakimansky, I. G. Voigt-Martin, M. Fetten, C. Schnorpfeil, D. Schollmeyer, H. Meier, publication in preparation.
13. Dimers: **8a**: mp > 250°, ^{1}H NMR ($C_2D_2Cl_4$): δ 3.51/ 4.42 (A_2X_2, 4 H, cyclobutane ring), 6.10/ 6.42/ 6.46 (3 d, ^3J 16.0 Hz, 6 H, A parts of three olefin. AB systems), 6.70 – 7.80 (m, 34 H, arom. H and B parts of AB systems), 7.89 ("s", 2 H, arom. H), 8.22 ("s", 2 H, arom. H); MS (FD): *m/z* 816 (31%, $M^{+\cdot}$), 408 (100%); cyclophane **8b**: ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 36 H, CH_3), 4.83/ 5.39 (AA'MM, 8 H, cyclobutane rings), 6.68 ("s", 8 H, 1-H), 7.14 (m, 8 H, 7-H), 7.48 (m, 8 H, 6-H), 8.11 ("s", 4 H, 23-H); ^{13}C NMR ($CDCl_3$): δ 31.3 (CH_3), 34.3 (C_q), 43.1/ 46-3 (CH, cyclobutane rings), 123.6/ 124.8/ 125.9/ 129.1 (arom. CH), 137.3/ 138.4 (arom. C_q), 150.8 (C-2).
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