

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

## Herbert Meier<sup>\*a</sup>, Michael Fetten<sup>a</sup>, Christoph Schnorpfeil<sup>a</sup>, Alexander V. Yakimansky<sup>b</sup> and Ingrid G. Voigt-Martin<sup>c</sup>

<sup>a</sup> Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany
<sup>b</sup>Institute of Macromolecular Compounds of Russian Academy of Sciences, St. Petersburg, Russia
<sup>c</sup> Institute of Physical Chemistry, University of Mainz, Welderweg 11-15, D-55099 Mainz, Germany

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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. © 1999 Elsevier Science Ltd. All rights reserved.

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

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**<sup>9</sup> were obtained. The condensation reaction with aniline led in a quantitative yield to the Schiff bases **6a,b**<sup>10</sup> which were suitable for a twofold cyclic condensation to the title compounds **7a,b**<sup>11</sup>. 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 <sup>1</sup>H NMR spectra of the pure compounds **4a,b** – **7a,b**.





## Scheme 2

3-21G *ab initio* calculations<sup>12</sup> 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 · mol<sup>-1</sup> 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**<sup>13</sup>, which corresponds to the C<sub>2h</sub> 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 ( $\lambda =$  366 nm) in chloroform, where **7a** has a  $\lambda_{max}$  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**<sup>13</sup> on irradiation ( $\lambda \ge 290$  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?



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<sup>4</sup> of the reactive singlet states S<sub>1</sub> 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 of ligomers 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.<sup>14</sup> The normally competing *E*/*Z* isomerisation is - due to steric reasons - energetically unfavorable in the annulenes **8**.

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## **References and Notes**

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- 9. Aldehydes: 5a: oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.44 (s, 3 H, CH<sub>3</sub>), 7.02/ 7.43 (AB, <sup>3</sup>J 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; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1,39 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.45 (s, 3 H, CH<sub>3</sub>), 7.04/ 7.41 (AB, <sup>3</sup>J 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).
- Schiff bases: 6a: yellow oil; CH = N: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.49 (s, 1 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 160.2; MS (70 eV): *m/e* 297 (14%, M<sup>+</sup>), 110 (100%), 6b: yellow oil; CH = N: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.56 (s, 1 H), <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 160.8.
- [18]Annulenes: 7a: mp > 250°; <sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ 7.08 (d, <sup>3</sup>J 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, <sup>3</sup>J 16.1 Hz, 4 H, 5-H), 8.29 (d, 2 H, 23-H); MS (70 eV): *m/e* 408 (100%, M<sup>+</sup>); 7b: mp > 250°; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.37 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 7.13 (d, <sup>3</sup>J 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, <sup>3</sup>J 16.1 Hz, 4 H, 5-H), 8.19 (d, 2 H, 23-H), <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 31.2 (CH<sub>3</sub>), 34.9 (C<sub>q</sub>), 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).
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- Dimers: 8a: mp > 250°, <sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ 3.51/ 4.42 (A<sub>2</sub>X<sub>2</sub>, 4 H, cyclobutane ring), 6.10/ 6.42/ 6.46 (3 d, <sup>3</sup>J 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<sup>+</sup>), 408 (100%); cyclophane 8b: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.12 (s, 36 H, CH<sub>3</sub>), 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); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 31.3 (CH<sub>3</sub>), 34.3 (C<sub>q</sub>), 43.1/ 46-3 (CH, cyclobutane rings), 123.6/ 124.8/ 125.9/ 129.1 (arom. CH), 137.3/ 138.4 (arom. C<sub>q</sub>), 150.8 (C-2).
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