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Pyrolysis of a Tubular Aromatic Compound

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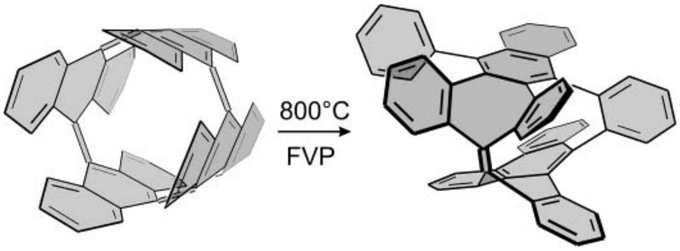
ABSTRACT



In the attempt to close the walls of a small tubular system that is a substructure of a [4,4] armchair nanotube a very unusual rearrangement reaction was observed.

After the recent achievement of the rational synthesis of C_{60}[1] the conventional synthesis of carbon nanotubes or short pieces thereof remains as one of the most interesting targets in nonnatural product synthesis. Aiming at this target we pursue a strategy of ring-enlargement metathesis and subsequent dehydrocyclization.[2] The first step of this strategy was realized by metathetic dimerization of tetradehydrodianthracene to the cyclic tetraanthraceneylidene (picotube) **1**, which is the first rationally synthesized fully conjugated tubular aromatic compound. Eightfold cyclodehydration at the ortho positions of the benzene rings should lead to the complete closure of the tube walls and to the formation of a short piece of a [4,4] armchair carbon nanotube.

Semiempirical (AM1) calculations predicted the overall elimination of eight hydrogen molecules to be endothermic by 205.9 kcal mol^{-1}, on average 25.7 kcal mol^{-1} for each dehydrocyclization step. However, since there is a stepwise increase of the strain energy the first step is endothermic by only 8.5 kcal mol^{-1} and the enthalpy of formation of the most stable isomers of the following steps is predicted to be only 3.2, 3.4, and 1.4 kcal mol^{-1}. After the fourth step yielding a D_{2h} symmetric compound the strain energy increases dramatically to 60.2. The subsequent steps are endothermic with 48.2, 43.0, and 38.2 kcal mol^{-1}.

In preliminary studies we applied the frequently used oxidation procedures for the condensation of aromatic compounds[3] in solution such as Scholl[4] or Kovacic[5] conditions or irradiation in the presence of iodine,[6] however, we only obtained polymeric material. Flash vaccum pyrolysis (FVP) induced dehydrocyclizations which are known to be able to build up a considerable amount of strain, e.g. in the synthesis of buckybowls,[7] also did not lead to the expected

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(1) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500−1503.

(2) (a) Kammermeier, S.; Herges, R. *Angew. Chem.* **1996**, *108*, 470−472; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 417−419. (b) Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem.* **1996**, *108*, 2834−2836; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2669−2671. (c) Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem.* **1997**, *109*, 2317; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2200−2202. (d) Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem.* **1997**, *109*, 1825−1828; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1757−1760.

(3) Review: (a) Hagen, S.; Hopf, H. *Top. Curr. Chem.* **1998**, *196*, 47−82. (b) Balaban, A. T.; Nenitzescu In *Friedel−Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; p 979.

(4) Scholl, R.; Meyer, K. *Chem. Ber.* **1934**, *67*, 1229−1238.

(5) (a) Kovacic, P.; Koch, F. W. *J. Org. Chem.* **1965**, *30*, 3176−3181. (b) Vivekanantan, S. I.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem.* **1997**, *109*, 1676−1679.

(6) Mallory, F. B.; Butler, K. E.; Evans, A. C.; Brondyke, E. J.; Mallory, C. W.; Yang, C.; Ellenstein, A. *J. Am. Chem. Soc.* **1997**, *119*, 2119−2124.

(7) E.g.: Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744 (AM1: 47.0 kcal mol^{-1} per dehydrocyclization step).

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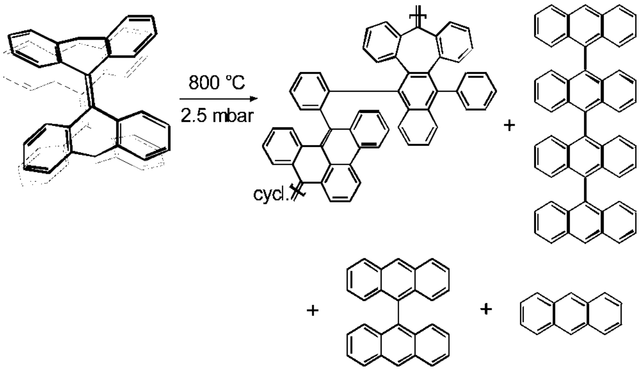
dehydrocyclization but yielded an interesting and completely unexpected compound.

The FVP experiments were performed at 800 °C (quartz tube, diameter 20 mm, heated length 30 cm, 15 mL Argon min^{-1}, 2.5 mbar). The overall conversion of the starting material was 40%. At higher temperatures the material decomposed to amorphous carbon at the hot quartz surface and a large number of isomers were formed which were difficult to separate. At 800 °C anthracene, bianthryl,[8] tetraanthryl,[9] and an unsymmetrical main product[10] were isolated (Scheme 1).[11] Mass spectrometry proved that the latter was an isomer of the starting material. The structural assigment finally was achieved by X-ray analysis (Figure 1).

Scheme 1. Reaction Products of the Flash Pyrolysis of the Picotube



There is still a beltlike 16-electron periphery as in the starting compound and all carbon atoms are still sp^2 hybridized, but at least 4 bonds must have been made and broken to form the complicated polycyclic ring system including the seven-membered ring. According to DFT calculations (B3LYP/6-31G*) the pyrolysis product is 52 kcal/mol (!) more stable than the picotube. We propose the following mechanism for the radical isomerization (Scheme 2).

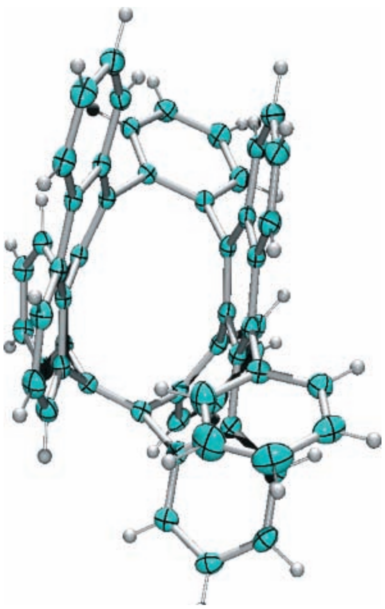
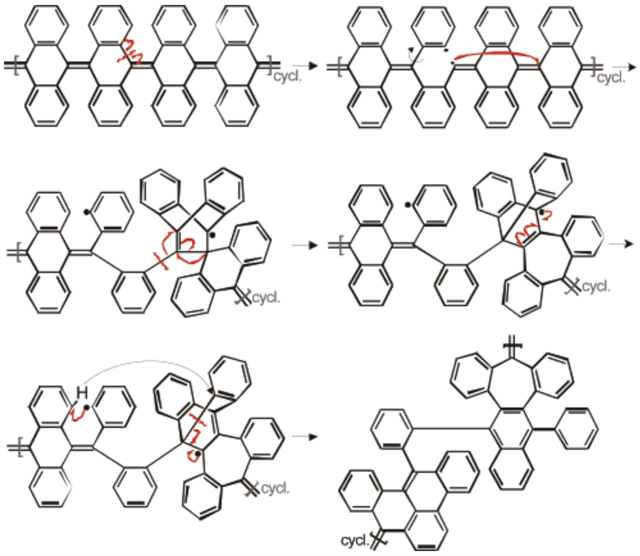


Figure 1. Ortep plot of the crystal structure of the cyclic pyrolysis product.

Scheme 2. Proposed Mechanism of the Isomerization



A remarkable feature in the ^{1}H NMR spectrum is the signal at 4.65 ppm. According to an analysis of the NMR spectrum the signal can be assigned to an ortho proton of the phenyl group, which is located within the shielding region above the center of a benzene ring on the opposite side of the beltlike structure (Figure 2). The phenyl ring is forced to

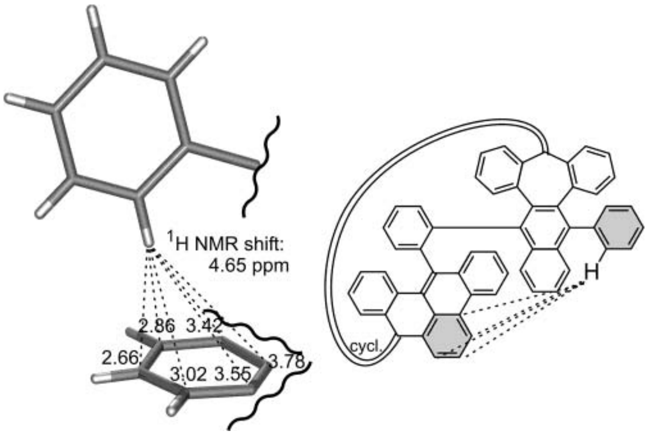


Figure 2. Distances of the *o*-hydrogen atom of the phenyl group from the carbon atoms of the opposing benzene ring (in Å).

rotate to this sterically and electronically unfavorable position by the steric interaction with the neighboring suberene unit.

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Supporting Information Available: X-ray structure data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Anthracene and bianthryl were identified by comparison of ^{1}H and ^{13}C spectra with commercially available and independently synthesized samples: Liebermann, C.; Gimbel A., *Chem. Ber.* **1887**, *20*, 1855.

(9) Tetranthryl was independently synthesized from bromoanthracene, dibromobianthryl, and butyllithium: M. Deichmann, R. Herges, unpublished. Because of the low solubility tetraanthryl could only be identified by UV and MS. The identity with the pyrolysis product was checked by UV, MS, and co-injection to the HPLC.

(10) Elementary analysis: calcd C 95.5, H 4.5; exptl C 95.4, H 4.6.

(11) 250-mg (355 μmol) picotubes were used for pyrolysis in each run. The recovery was 90%. 40% (142 μmol) thereof was starting material, 5% (12 mg, 17 μmol) cyclic pyrolysis product, 8 mg of anthracene, 12 mg of bianthryl, and about 3 mg of tetraanthryl were isolated.