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SYNTHESIS OF [2.0.2.0]METACYCLOPHANEDIENE AND BI-4,5-PHENANTHRYLENE

Bengt Thulin and Olof Wennerström
Department of Organic Chemistry, Chalmers University of Technology
and University of Göteborg, S-402 20 Göteborg, Sweden

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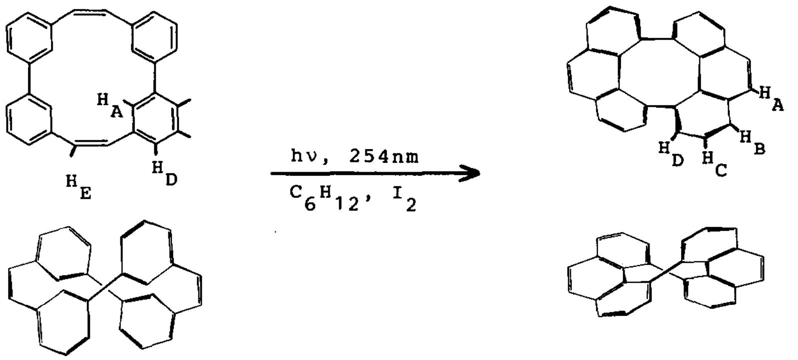
Non-planar aromatic molecules are now well-known. Many examples can be found among the cyclophanes[1] and helicenes,[2] and the circulenes[3] are especially interesting. [n]Circulenes with n ≥ 7 have too long a periphery and too short an inner ring and should be saddle-shaped. So far only hetero [7] and [8]circulenes are known.[3,4] They are all planar or nearly planar. A "hexa[7]circulene" with two hydrogens instead of one unsaturated bridge, 3, has recently been reported.[5]

In this paper we report the facile synthesis of [2.0.2.0]metacyclophanediene, 1, and bi-4,5-phenanthrylene, 2, (Scheme 1) a non-planar analogue of [8]circulene lacking two unsaturated bridges.

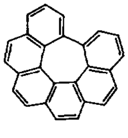


Scheme 1

Bromination of 3,3′-dimethylbiphenyl with two and four equivalents of NBS yielded 3,3′-bis-(bromomethyl)biphenyl and 3,3′-bis(dibromomethyl)biphenyl, respectively. Treatment of the former with triphenylphosphine and hydrolysis of the latter gave the starting materials for a bis-Wittig reaction. Equivalent amounts (2 mmol) of the 3,3′-biphenyldicarbaldehyde and the triphenylphosphonium salt of 3,3′-bis(bromomethyl)biphenyl were suspended in dry DMF at -40 °C. Lithium ethoxide in ethanol was added dropwise during 24 h. The usual isolation and separation[6,7] gave [2.0.2.0]metacyclophanediene, 1 (4 %, m.p. 113-115 °C). ^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.61 (4, t, H_A), 7.31 (4, t, H_C), 7.18 (4, d of t, H_B or H_D), 7.11 (4, d of t, H_B or H_D), 6.60 (4, s, H_E), $J_{AB} = J_{AD}$ = 1.5 Hz, $J_{BC} = J_{CD}$ = 7.5 Hz. MS (70 eV): m/e 356 (100 %, M^+), 355 (6), 354 (5), 353 (6), 352 (6), 351 (5), 350 (6), 340 (8), 339 (15), 182 (11), 178 (9), 176 (10), 175 (9), 169.5 (12), 168.5 (13), 163 (13) and 156.5 (10). Abs. mass: Found 356.156 ± 0.003; calc. for $C_{28}H_{20}$ 356.156. UV (cyclohexane): 282 nm, ε = 19 500.

The metacyclophane (13 mg) was dissolved in cyclohexane with iodine as oxidant and was irradiated with a low-pressure mercury lamp (Rayonet reactor) for 15 h. The reaction mixture was separated by chromatography on silica gel with tetrachloromethane as eluant, to give bi-4,5-phenanthrylene, 2 (8.3 mg, 65 %, m.p. 262-263 °C). ^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.80 (4, d of d, H_B), 7.66 (4, s, H_A), 7.40 (4, t, H_C), 6.63 (4, d of d, H_D), J_{BC} = J_{CD} = 7.5 Hz, J_{BD} = 1.4 Hz. MS (70 eV): m/e 352 (67 %, M^+), 351 (80), 350 (100), 349 (13), 348 (27), 176 (7), 175.5 (13), 175 (47), 174.5 (7), 174 (27). Abs. mass: Found 352.126 ± 0.003; calc. for $C_{28}H_{16}$ 352.125. UV (cyclohexane): 253 nm, ε = 100 000.

Bi-4,5-phenanthrylene can not be a planar molecule. The two phenanthrene units must be considerably twisted to give the molecule the shape of a two-bladed propeller with three perpendicular C_2 axes, symmetry point group D_2. We have previously reported the synthesis of another propeller-shaped compound, propellicene or bi-2,13-helicenylene, 4.[8] A comparison of the chemical shifts for the protons H_D in 2 and 4 reveals that in 2, H_D is shifted 1.25 ppm upfield relative to phenanthrene, whereas H_D in 4 is only shifted 0.35 ppm relative to [5]helicene. In compound 2, H_D must be forced over the face of the adjacent phenanthrene unit. The effect is of the same magnitude as in hexahelicene.[9]



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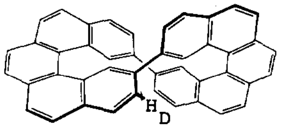

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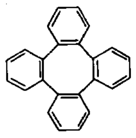

5

The barrier of inversion of tetrabenzocyclooctatetraene, 5, is larger than 26 kcal.[10] An analogous barrier is expected for bi-4,5-phenanthrylene. The height of this barrier and the rather intriguing mechanism for inversion of 2 can now be studied by both a theoretical and an experimental approach.

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