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# $[O^{9,24}][2.1.2.1]$METACYCLOPHANE-9-ENE, A "TWIN CYCLOPHANE", AND ITS DEHYDROGENATION PRODUCTS - SYNTHESIS, STRUCTURE DETERMINATION AND $^1$H-NMR-SPECTROSCOPY

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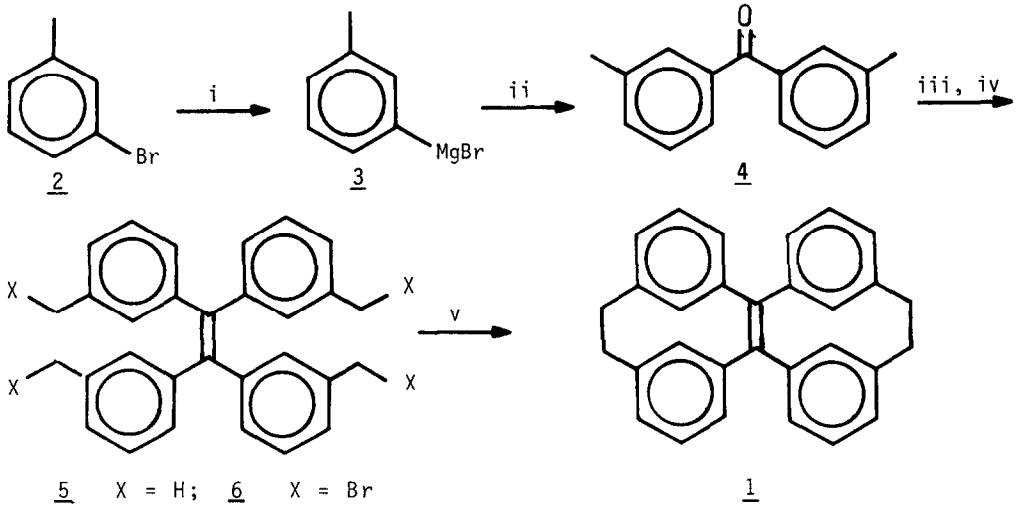
Summary: The synthesis of $[O^{9,24}][2.1.2.1]$metacyclophane-9-ene and of its dehydrogenation products, the new pyrenocyclophanes 8, 10, 11, and 12, is described; their structures are discussed in connection with their $^1$H-NMR-spectra.

Cyclophanes have found increasing interest during the last two decades because of their unusual structures and the resulting surprising physical, chemical and spectroscopic properties.[1,2] One interesting subclass of cyclophanes are the multilayered compounds, which contain two or more cyclophane units connected by short bridges between the stacked aromatic rings. However, there are other interesting possibilities to combine different cyclophane units in one molecule. Our aim was the synthesis of $[O^{9,24}][2.1.2.1]$metacyclophane-9-ene (1). This new cyclophane has the structural characteristic of two identical cyclophane units connected by a bridge of two common carbon atoms. We suggest that this type of cyclophane-annelated cyclophanes could be denoted "twin-cyclophanes" ("Zwillingscyclophane") as the two cyclophane units are fused in a manner reminding of siamese twins. 1 was synthesized in a four step synthesis:



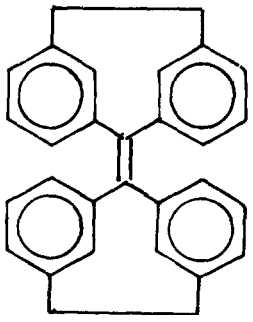

2 3 4

5 X = H; 6 X = Br 1

i) Mg, THF; ii) m-$CH_3C_6H_4COCl$/THF, -78°C; iii) $TiCl_3/LiAlH_4$ or $TiCl_4$/Zn in THF; iv) NBS/$CCl_4$, h·ν; v) $C_6H_5Li$/Ether/r.t.;

Synthesis of 3-methylphenylmagnesiumbromide (3) from 3-bromotoluene (2) and its reaction with 3-methylbenzoic acid chloride at low temperature in THF solution yielded 3,3'-dimethylbenzophenone (4) (b.p. 125°C/0.03 torr; 70 %). Reductive coupling[3,4,5] of 4 with either $TiCl_3/LiAlH_4$ (a) or $TiCl_4/Zn$ (b) yielded tetra(p-tolyl)ethene (5) (m.p. 115°C; (a) 70%, (b) 55%; $^1$H-NMR: -Ar-$CH_3$ δ = 6,7-7 ppm, m, 16H; -Ar-$CH_3$ δ = 2,17 ppm, s, 12H). Selective fourfold monobromination of the four methyl groups of 5 was accomplished with NBS in tetrachloromethane to give tetrakis[3-(bromomethyl)-phenyl]ethene 6 (pale yellow, viscous oil; 35% after column chromatography on silica gel with a 9:1 mixture of petroleum/ethylacetate; ($^1$H-NMR: -Ar$CH_2$Br δ = 7-7,4 ppm, m, 16H; -Ar-$CH_2$Br δ = 4,17 ppm, s, 8H). Reaction of 6 with phenyllithium in ether gave 21% of crude 1 after column chromatography (petroleum/ethylacetate 9:1) (m.p. 93°C after preparative HPLC with acetonitrile as solvent; $^1$H-NMR see below).

UV-irradiation of 1 yielded a deep red photoproduct. This agrees with a similar observation of Boekelheide et al.[6,7] made with [2.2]metacyclophane--1-ene. However, ring closure reaction of 6 could not only give 1 but also 7. For this reason a reliable structure determination of 1 needs chemical transformation of the ring closure product to the known pyreno[4,5-4',5'] pyrene (8)[8] or bis[4,5-phenanthrylen]ethene (9)[9]. Dehydrogenation of the ring closure product with palladium/Charcoal yielded two main products which were purified by preparative HPLC and identified by their 300 MHz- H-NMR spectra. The product with the longer retention time was 8 (MS : $M^{+\cdot}$ m/z 376 (100%); $^1$H-NMR: δ = 9,26 ppm, d, 4H; δ = 8,27 ppm, d, 4H; δ = 8,26 ppm, s, 4H;) being identical in all respects with data published by Clar et al.[8]. The other possible oxidation product 9 was not found. Hence, 1 is the correct structure for this new cyclophane.



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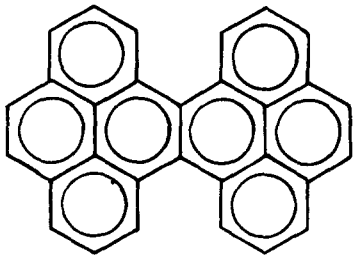

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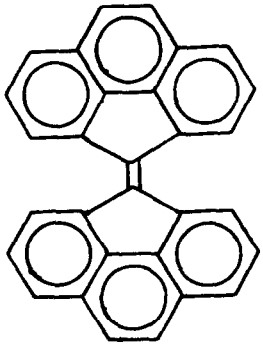

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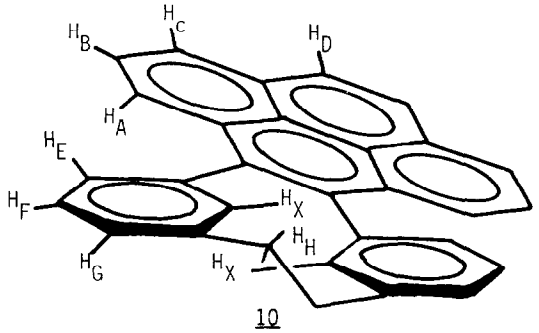
The second reaction product was identified as anti-pyreno[4,5-1',2']-[2.2]metacyclophane (10) (MS : $M^{+\cdot}$ m/z 380 (100%); $^1$H-NMR : [$H_H$] ( AA'BB') δ = 3,30-3,34 ppm and 2,10-2,60 ppm, 4H; [$H_A$] δ = 8,72 ppm, d, 2H; [$H_B$] δ = 8,15 ppm, t, 2H; [$H_C$] δ = 8,25 ppm, d, 2H; [$H_D$] δ = 8,25 ppm, s, 2H; [$H_F$] δ = 7,32 ppm, t, 2H; [$H_E$, $H_G$] δ = 7,22-7,44 ppm, 4H;).

Dehydrogenation of 1 with sulfur yielded another product besides 8 and 10 which was identified as 4,5-dihydropyreno[9,10-1',2'] pyrene by its mass spectrum and $^1$H-NMR. Oxidation of 1 with oxygen during irradiation ($CHCl_3$, r.t., 500 W photolamp, 30 minutes) yielded two new products. After purification by HPLC about equal amounts of the new cyclophanes 11 and 12 could be isolated. 11 was identified as syn-4,5-dihydropyreno[9,10-1',2'][2.2]metacyclophane (MS: m/z 382 (100%); $^1$H-NMR: [$H_A$] δ = 7.98 ppm, d, 2H; [$H_B$] δ = 3,42 ppm, s, 4H; [$H_X$] δ = 7,10 ppm, s, 2H; [$H_D$] δ = 6,68 ppm, d, 2H; [$H_E$] δ = 6,76 ppm, t, 2H; [$H_F$] δ = 6,61 ppm, d, 2H; [$H_H$] δ = 3-3,4 ppm, m, 4H; 12 was anti-4,5--dihydropyreno [9,10-1',2'][2.2]metacyclophane (12) : (MS : $M^{+\cdot}$ m/z 382 (100%), $^1$H-NMR : [$H_A$] δ = 8,25 ppm, d, 2H; [$H_B$, $H_C$] δ = 7,51-7,47 ppm, m, 4H; [$H_G$] δ = 3,37 ppm, s, 4H; [$H_D$, $H_E$, $H_F$] δ = 7,34-7,39 ppm, t, 2H, and δ = 7,14-7,18 ppm, t, 4H; [$H_X$] δ = 5,41 ppm, s, 2H).

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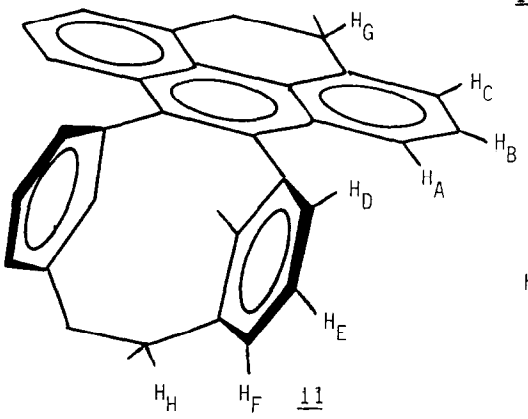


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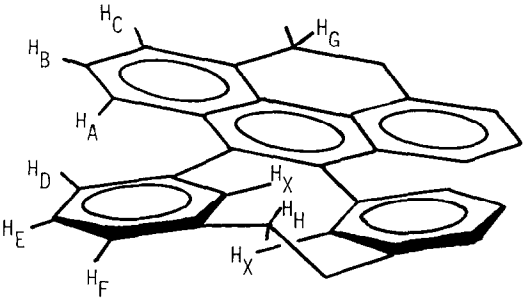


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The complicated 300 MHz $^1$H-NMR spectrum of 1 indicates a structure of low symmetry. Two signals at 6,07 ppm and 6,15 ppm (1H each) are typical of the "internal" protons of the cyclophanes, and indicate different conformations of the two cyclophane units of 1. Obviously, one half of the molecule has a syn-, the other an anti-conformation.

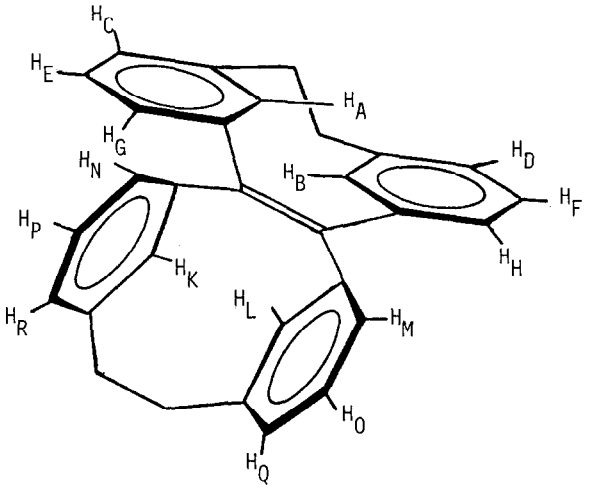
With the help of 2D-$^1$H-NMR-experiments nearly all signals of the aromatic protons could be identified in the spectrum (Table 1). However, a complete interpretation of the signals of the protons at the bridges could not be achieved. The $CH_2$-protons of the anti-cyclophane unit appear as a AA'XX' spin

system at $\delta \approx 2{,}1$ ppm and $\delta \approx 3{,}2$ ppm, respectively, and the $CH_2$-protons of the syn-cyclophane unit probably as a complicated ABCM-system centered at $\delta \approx 3{,}1$ ppm. The $^1$H-NMR-spectrum of 1 showed no temperature dependence in the range of -20°C to +50°C. This shows, that the molecule of 1 possesses no conformative mobility in spite of its rather twisted structure.

Table 1

| anti-unit | δ[ppm] |
|---|---|
| $H_A$ | 6,04 |
| $H_C$, $H_D$ | 7,07 and 7,10 |
| $H_E$, $H_F$ | 7,24 - 7,33 |
| $H_G$ | 7,50 |
| $H_B$ | 6,12 |
| $H_H$ | not detected |

| syn-unit | δ[ppm] |
|---|---|
| $H_K$, $H_L$ | 7,03 and 7,07 |
| $H_M$ | 6,66 |
| $H_O$ | 7,05 |
| $H_Q$ | 6,48 |
| $H_N$ | 6,76 |
| $H_P$ | 7,05 |
| $H_R$ | 6,46 |

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