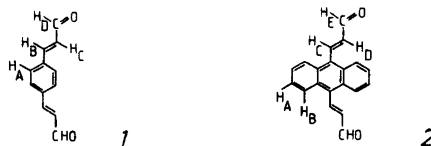
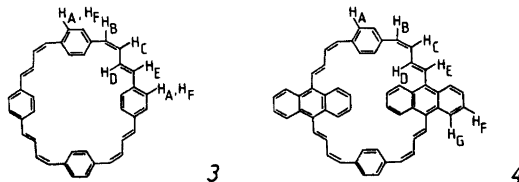


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The structure of 3, [4.4.4.4]paracyclophane-*cis,trans,trans,cis,cis,trans,trans,cis*-octaene or, according to IUPAC nomenclature; pentacyclo-[28.2.2.2.2<sup>6-9</sup>.2<sup>14-17</sup>.2<sup>22-25</sup>]tetraconta-2,4,6,8,10,-12,14,16,18,20,22,24,26,28,30,32,33,35,37,39-eicosane, follows from its mass and NMR spectra. The mass spectrum shows the molecular ion as parent peak and little fragmentation.



The <sup>1</sup>H NMR spectrum showed two sharp singlets for the two types of benzene rings and an ABMX-pattern for the olefinic protons. Spin decoupling and simulation gave the shifts and coupling constants. The large coupling constant  $J_{CD} = 12$  Hz indicates that the molecule is relatively planar with *S-trans* orientation of the butadiene bridges. *S-cis* orientation would lead to a more compact, but less planar, structure due to steric interaction between the inner protons. The benzene rings rotate fast on the NMR time scale. No coalescence of the signals was observed on cooling the sample down to  $-110$  °C.

[4.4.4.4]Paracyclophaneoctane, 3, can be regarded as a [16]annulene with four benzene rings inserted into four single bonds in a symmetrical way. The corresponding isomer of [16]annulene with *cis,cis,trans,trans,cis,cis,trans,trans* orientation of the double bonds is not the one observed in the crystalline state<sup>4</sup> nor one of the major isomers in solution.<sup>5</sup> It is noteworthy that 3 (and 4) which contains eight double bonds, four *cis* and four *trans*, is, in contrast to the annulenes, rather stable and can be isolated as one single isomer.

The UV spectrum of 3 is much simpler than that of the annulenes.<sup>6</sup> It shows two absorption bands at 345 nm ( $\epsilon$  74 000) and 360 nm ( $\epsilon$  75 000 in cyclohexane).

The  $\pi$  electron system of 3 contains 40 electrons of which 32 can be considered as conjugated in a macrocyclic ring, and therefore the compound is formally an anti-Hückel system. Ring current effects on the chemical shifts are small. Although the shift difference between the internal and external protons H<sub>C</sub> and H<sub>D</sub> is 1.54 ppm which is *ca.* 1/3 of the value for [16] annulene at  $-110$  °C, the corresponding difference in the closely related open chain

## Synthesis of [4.4.4.4]Cyclophanes

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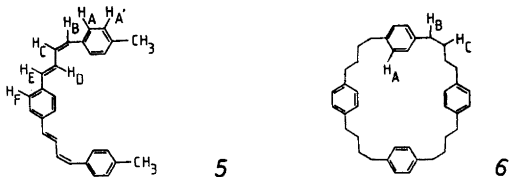
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We have previously reported that multiple Wittig reactions provide an efficient synthetic route to cyclophanes with ethylene bridges between the aromatic rings.<sup>1,2</sup> Although the overall yields are often low (< 15 %), the simple starting materials and procedure for separation and isolation of the products make this one-step synthesis an easy route to a large number of cyclophanes and bicyclophanes<sup>3</sup> and their derivatives.

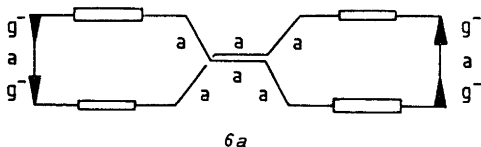
We now report the synthesis, by four-fold Wittig reactions, of cyclophanes in which four aromatic rings are bridged by butadienes of known conformations.

1,4-Benzenedicarbaldehyde and 9,10-anthracenedicarbaldehyde were converted to the vinylous dialdehydes 1, 1,4-benzenedipropenal, and 2, 9,10-anthracenedipropenal. The dialdehydes 1 and 2 were reacted with the bis-triphenylphosphonium salt from 1,4-bis(bromomethyl)benzene in *N,N*-dimethylformamide at  $-40$  °C in the presence of lithium ethoxide to give *ca.* 2 % yield of the [4.4.4.4]cyclophane-octaenes 3 and 4, respectively.

product **5** is p.98 ppm. The latter compound was isolated as a by-product from the Wittig reaction.



The unsaturated cyclophane **3** is easily hydrogenated to [4.4.4.4]paracyclophane, **6**, which has four butane bridges with three  $sp^3$ - $sp^3$  C-C bonds each of which may have *anti* or *gauche* orientations. The minimum number of *gauche* bonds is four. Several conformations are possible, many of which should be of similar energy with only small energy barriers in between. The size of the cavity in the centre of the molecule varies with the conformation. A particularly compact one is **6a**. The NMR spectrum of **6** shows an upfield shift of the aromatic protons ( $\delta$  6.49) from mutual shielding of the benzene rings which should be oriented pairwise parallel as in **6a**.



The structure of **4**, [4](9,10)anthraceno-[4]para[4](9,10)anthraceno[4]paracyclophane-*cis-trans,trans,cis,cis,trans,trans,cis*-octaene is slightly different from that of **3**. The butadiene bridges have the same *S-trans* conformation ( $J_{CD}$  11 Hz) but the molecule is less planar than **3** due to the anthracene rings. The interactions between the hydrogens  $H_D$  and  $H_E$  in the bridges and the hydrogens  $H_C$  in the anthracene rings force the molecule to adopt a non-planar conformation. The weak delocalisation of the  $\pi$ -electrons over the whole molecule is apparent from the small shift difference between  $H_C$  and  $H_D$ , which is 0.51 ppm, as well as from the UV spectrum (cyclohexane, 260 nm,  $\epsilon$  145 000). The less planar structure of **4** as compared to **3** gives it a more cage-like structure and thus makes it more interesting as a potential molecular "host" for small acceptor molecules.

**Experimental.** Mass spectra were recorded on an AEI MS 902, UV spectra on a Beckman DK2, and NMR spectra on a Bruker WH 270.

**1,4-Benzenedipropenal**, **1**, and **9,10-anthracenedipropenal**, **2**, were prepared by Wittig reactions between 1,4-benzenedialdehyde or 9,10-anthracenedialdehyde, respectively, and the triphenylphosphonium salt from 2(bromomethyl)-1,3-dioxolane<sup>7</sup> followed by acid hydrolysis which gave **1** [53%, m.p. 158–160 °C, NMR (CDCl<sub>3</sub>):  $\delta$  9.47 ( $H_D$ , d,  $J_{CD}$  7.4 Hz),

7.63 ( $H_A$ , s), 7.48 ( $H_B$ , d,  $J_{BC}$  16 Hz), and 6.77 ( $H_C$ , dd)] and **2**, [44%, m.p. 238 °C, NMR (CDCl<sub>3</sub>):  $\delta$  10.1 ( $H_E$ , d,  $J_{DE}$  8 Hz), 8.51 ( $H_C$ , d,  $J_{CD}$  16 Hz), 8.25 and 7.63 ( $H_A$  and  $H_B$ , m), and 6.74 ( $H_D$ , dd)].

**Cyclophanes 3 and 4** were prepared by Wittig reactions from the dialdehydes **1** and **2**, respectively, and the bistrisphenylphosphonium salt from 1,4-bis(bromomethyl)benzene in dry dimethylformamide at -40 °C with lithium ethoxide as base, giving ca. 2% yield of **3** [m.p. 245 °C, decomp, NMR (CDCl<sub>3</sub>):  $\delta$  7.58 and 7.54 ( $H_A$  and  $H_F$ , two s), 7.89 ( $H_D$ , m,  $J_{DE}$  16 and  $J_{CD}$  12 Hz), 6.60 ( $H_E$ , d) and 6.35 ( $H_B$  and  $H_C$ , m,  $J_{BC}$  11 and  $J_{BD}$  -1.5 Hz)]. MS (70 eV):  $m/e$  512 ( $M^+$ , 100%), 256 (13), 255 (14), 217 (14), 215 (13), 179 (12), 165 (17), 141 (20), 129 (15), 128 (11), and 115 (11). Abs. mass 512.246  $\pm$  0.005; calc. for C<sub>46</sub>H<sub>32</sub> 512.250], and **4** [m.p. >350 °C, NMR (CDCl<sub>3</sub>):  $\delta$  7.96 and 7.10 ( $H_F$  and  $H_C$ , m), 7.19 ( $H_E$ , d,  $J_{DE}$  16 Hz), 7.06 ( $H_A$ , s), 6.91 ( $H_D$ , dd,  $J_{CD}$  11 Hz), 6.40 ( $H_C$ , dd,  $J_{BC}$  12 Hz), 6.29 ( $H_B$ , d)]. MS (70 eV):  $m/e$  712 ( $M^+$ , 100%), 676 (29), 365 (20), 253 (26), 252 (52), 228 (20), 215 (46), and 207 (29). Abs. mass 712.308  $\pm$  0.006; calc. for C<sub>56</sub>H<sub>40</sub> 712.313]. The detailed reaction conditions and the separation and isolation of the products by column chromatography were the same as previously reported for other fourfold Wittig reactions.<sup>8</sup>

**Compound 5** was isolated in trace amounts from the Wittig reaction that gave cyclophane **3** and characterized by its NMR spectrum (CDCl<sub>3</sub>) only:  $\delta$  7.35 ( $H_S$ , m), 7.33 ( $H_F$ , s), 7.27 and 7.18 ( $H_A$  and  $H_A'$ , m), 6.65 ( $H_E$ , d,  $J_{DE}$  16 Hz), 6.49 ( $H_B$ , d,  $J_{BC}$  12 Hz), 6.37 ( $H_C$ , t,  $J_{CD}$  12 Hz), and 2.38 ( $H_{methyl}$ , s).

**Cyclophane 6**, was prepared in a quantitative yield from **3** by hydrogenation over palladium on charcoal in benzene [m.p. 139–141 °C. NMR (CDCl<sub>3</sub>):  $\delta$  6.49 ( $H_A$ , s), 2.51 ( $H_B$ , m) and 1.53 ( $H_C$ , m)].

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