

[2<sub>4</sub>]Naphthalenophanes

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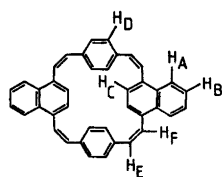
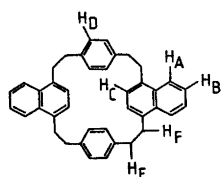
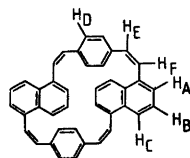
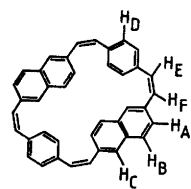
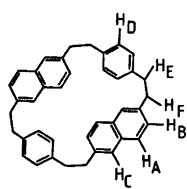
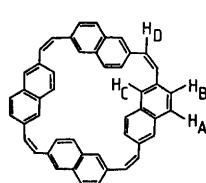
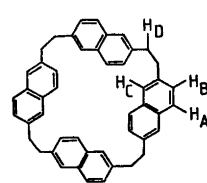
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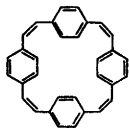
Cyclophanetetraenes with two or four naphthalene units, compounds *1a–4a*, have been prepared by fourfold Wittig reactions from aromatic dialdehydes and bisphosphonium salts. Hydrogenation of the unsaturated cyclophanes gave the corresponding saturated compounds *1b*, *3b* and *4b*. The planarity of the cyclophanes, the delocalization of the  $\pi$  electrons and dynamic processes in some of the cyclophanes are discussed on the basis of their UV and NMR spectra and cyclic voltammograms.

The use of four- or sixfold Wittig reactions for the synthesis of cyclophanetetraenes and bicyclophanehexaenes has recently been developed in this laboratory.<sup>1,2</sup> Some of the cyclophanes are possible precursors for topologically interesting compounds such as propellicenes and circulenes.<sup>3,4</sup> Others are of stereochemical

interest as models for the study of planarity,  $\pi$  electron delocalization and aromaticity. Some of the cyclophanes show temperature-dependent NMR spectra which allow the study of dynamic processes. Electrochemical and theoretical studies have also been made.<sup>5,6</sup>

Inspection of molecular models (CPK) of the cyclophanes indicates that, in certain conformations, the central cavities may be large enough to allow host-guest inclusion complexes to form with small substrates. However, the UV and NMR spectra of the cyclophanes studied so far indicate that the favoured conformations are either as planar as possible to maximize the  $\pi$  electron overlap, or compact to minimize the volume. The incorporation of naphthalene into the cyclophanes enlarges the  $\pi$  system and may also lead to increased deviation from pla-

*1 a**1 b**2 a**3 a**3 b**4 a**4 b*



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rarity for steric reasons. With these points in mind, and as an extension of the previous work, some cyclophanes containing 1,4-, 1,5-, or 2,6-naphthalene units have been prepared (compounds 1–4).

## RESULTS AND DISCUSSION

The cyclophanes *1a*, *2a*, and *3a* were prepared by Wittig reaction of 1,4-benzenedicarbaldehyde and an equimolar amount of the bisphosphonium salt from 1,4-, 1,5-, or 2,6-bis(bromomethyl)naphthalene, respectively.<sup>7</sup> Cyclophane *4a* was prepared analogously from 2,6-naphthalenedicarbaldehyde<sup>8</sup> and the bisphosphonium salt from 2,6-bis(bromomethyl)naphthalene. The yields of the cyclophanes were low even in comparison with the yields of the corresponding cyclophanes with benzene, thiophene, or furan rings.<sup>9</sup> However, the simplicity of the synthesis and the starting materials makes this route attractive in comparison with alternative routes.<sup>9</sup> The cyclophanes *1b*, *3b*, and *4b* with saturated bridges were obtained by hydrogenation of the unsaturated cyclophanes over palladium on charcoal, whereas *2a* was only partially reduced under the same conditions.

All the cyclophanetetraenes reported here are coloured, ranging from very pale (*2a*) to bright yellow (*3a*). The UV spectra (Table 1) imply that some of the compounds can be rather planar which minimizes their central cavity. Inspection of space-filling models (CPK) of the tetraenes *1a*, *2a*, *3a*, and *4a* shows that *3a* and *4a* can attain relatively planar conformations with extensive  $\pi$  electron overlap. There is little steric hindrance for the fast rotation of the benzene and naphthalene rings in such conformations. The <sup>1</sup>H NMR spectra of compounds *1a*–*4a* (see Table 1) can be used in conjunction with their UV spectra to determine the extent and effects of planarity, conjugation, and aromaticity in these compounds. Near-planarity of some of the cyclophanetetraenes may render them able to sustain a ring current which should be reflected by the chemical shifts of the protons on the ring perimeter. All the naphthalenophanetetraenes *1a*–*4a* are formally anti-Hückel systems (*i.e.* they have  $4n$   $\pi$  electrons around the perimeter), and any shift effect should therefore be paratropic.<sup>10</sup> If so, the inner protons should be shifted to lower field than normal while the outer protons should be shifted to higher field. Rotation of the benzene and naphthalene rings interconverts the outer and inner protons. The induced field is stronger inside the ring than outside, and the observed shifts correspond to the net effect which should be a downfield shift. The NMR spectra show that the paratropic effect, if it is present at all, is very small. This is in agreement with the effect in [2<sub>4</sub>]paracyclophane-

Table 1. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) and UV (ethanol or cyclohexane) spectra and reduction potentials (V vs. SCE in DMF) from cyclic voltammetry of the [2<sub>4</sub>]naphthalenophanetetraenes and some reference compounds.

Compound	Chemical shifts			Double bonds	UV spectra; longest wavelength absorption		Cyclic voltammetry V
	Naphthalene $\alpha$ -positions	$\beta$ -positions	Benzene		$\lambda_{\max}$ nm	log $\epsilon$	
<i>1a</i>	8.05	7.40, 7.33	6.90	6.85	295	4.04	
<i>2a</i>	7.85	7.23, 7.16	6.59	6.82	287	4.13	
<i>3a</i>	7.94, 7.63	7.45	7.39	6.57	315	4.78	– 1.71
<i>4a</i>	7.88, 7.57	7.42		6.73	335	4.13	– 2.17
<i>5</i>			7.32	6.45	303	4.76	– 1.70
<i>cis</i> -Stilbene			7.21	6.53 <sup>14</sup>	276	4.02 <sup>15</sup>	– 2.18 <sup>16</sup>
Naphthalene	7.81	7.46 <sup>14</sup>			285	3.62 <sup>17</sup>	– 2.57 <sup>18</sup>

tetraene, **5**, which is rather planar but not considered paratropic.<sup>11</sup> However, there might be a small downfield shift of the benzene protons in **3a** and **5** ( $\delta$  7.39 and 7.32, respectively) which correlates with the large extinction coefficient for the longer wavelength absorption in the UV spectra. By analogy with **5**, the structure of which is known,<sup>12</sup> it seems as if the naphthalenophane **3a** has a similar, relatively planar, structure whereas the naphthalenophane **4a** is less planar. The naphthalenophanes **1a** and **2a** seem to be non-planar.

To gain further information on the planarity and the delocalization of the  $\pi$  electrons in the naphthalenophanetetraenes, we have studied their electrochemical reduction using cyclic voltammetry. In dry DMF, the cyclophane **5** undergoes a completely reversible two-electron reduction to the dianion which converts the formally anti-Hückel  $\pi$  electron system to a Hückel system.<sup>5</sup> As might be expected, the naphthalenophane **3a** shows the same behaviour on reduction at the same potential (see Table 1), whereas the naphthalenophane **4a** is reversibly reduced at 0.46 V more negative potential. The naphthalenophanes **1a** and **2a** are not reversibly reduced under the same experimental conditions.

The exchange of two benzene rings in cyclophane **5** for 2,6-naphthalene units does not, therefore, seem to affect the geometry or the spectroscopic characteristics to any great extent. However, the exchange of the remaining two benzene rings does change the geometry to a less planar structure. The steric interactions between protons H<sub>A</sub> and H<sub>B</sub> (Fig. 1) in 1,4- or 1,5-naphthalenophanetetraenes also cause the compounds **1a** and **2a** to prefer less planar conformations. Apparently, small changes have considerable effects on the structures of these cyclophanes which seem to be governed by the balance between steric factors and the delocalization of  $\pi$  electrons.

As already mentioned, rotation of the benzene and naphthalene rings in the cyclophanes

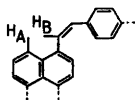
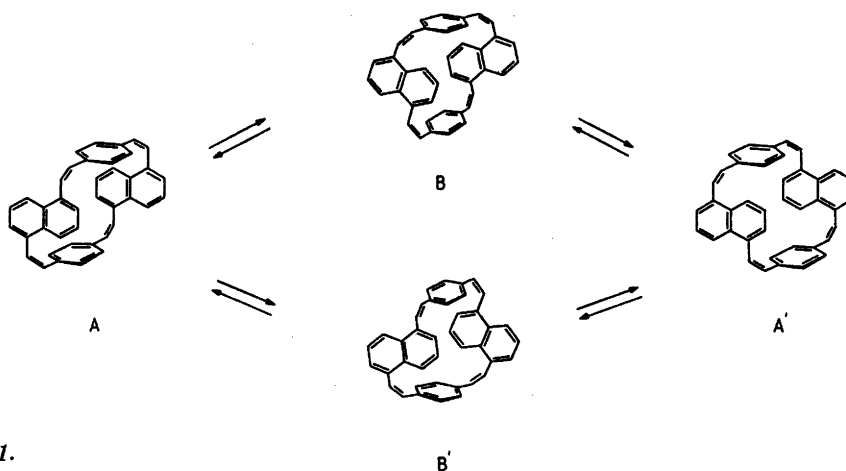


Fig. 1.

**1a**–**4a** is fast on the NMR time scale, and the NMR spectra usually show the average chemical shift. In the naphthalenophanetetraene **2a**, the flexibility of the molecule is reduced and the NMR spectrum is temperature dependent. At 30 °C some of the peaks are broad. Warming the sample to 60 °C led to a sharpening of the peaks and to the spectrum shown in Table 1 with the expected coupling constants. On cooling the sample, the peaks broadened and sharpened again at –10 °C to two sets of peaks with the same pattern as at 60 °C. The two sets had unequal intensities (ratio 3/1 from integration) and slightly different shifts. The presence of two similar sets of peaks indicates an equilibrium between two conformations *A* and *B* resulting from a slow rotation of the naphthalene units as shown in Scheme 1. The highest symmetry obtainable by the conformers is *C*<sub>2h</sub> for *A* and *D*<sub>2</sub> for *B*. It is difficult to decide which one is of lower energy. The rotation of the benzene rings is fast on the NMR time scale in both conformations at low temperatures. However, at –100 °C (CD<sub>2</sub>Cl<sub>2</sub>–toluene-*d*<sub>6</sub>) the sample gives an NMR spectrum with broadened singlets for the benzene rings. It has not been possible to freeze out this rotation.

Of the naphthalenophanes with saturated bridges, compound **1b** shows an interesting temperature dependent NMR spectrum. At 30 °C the cyclophane has a normal spectrum with two multiplets ( $\delta$  3.32 and 2.98, AA'BB'-pattern) for the methylene protons. On cooling the sample (CD<sub>2</sub>Cl<sub>2</sub>–toluene-*d*<sub>6</sub>) the multiplets from the methylene protons are shifted upfield, broaden, and then at –100 °C, separate to three broad peaks at  $\delta$  3.64 (4 H), 3.01 (4 H), and 2.59 (8 H). Simultaneously, the low-field AA'BB'-pattern from the unsubstituted halves of the naphthalene units changes to an ABCD-pattern. The multiplet originally at 3.32 coalesces at ca. –60 °C, while the multiplet originally at 2.98 coalesces at ca. –70 °C. It is assumed that, at –100 °C, the former multiplet appears at 3.64 and 2.59 and the latter multiplet at 3.01 and 2.59. These data have been used in a simple calculation of the barrier to rotation, assuming exchange of two sites. This gives a value of 40 kJ mol<sup>-1</sup> which is similar to the calculated barrier for [2<sub>4</sub>]paracyclophane (38 kJ mol<sup>-1</sup>).<sup>13</sup> Although these results do not allow any definite assignment of the most



Scheme 1.

stable conformation(s), the loss of the symmetry of the naphthalene AA'BB'-pattern indicates an unsymmetrical arrangement of the two naphthalene units. A conformation in which the two benzene rings are sandwiched between the naphthalenes (see Fig. 2) fits the results. In such a conformation, all bridges have *gauche* orientation of the same sign. This conformation is also consistent with the observed upfield shift of the benzene protons ( $\delta$  6.64) and the protons in the disubstituted halves of the naphthalene units ( $\delta$  6.69). The benzene rings still rotate quickly on the NMR time scale and the observed upfield shift is an average value. In the conformation shown in Fig. 2, the cavity is minimized and this seems to be a general phenomenon among these types of cyclophanes.

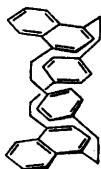


Fig. 2.

## EXPERIMENTAL

NMR spectra were obtained on a Bruker WH 270 instrument using  $\text{CDCl}_3$  as solvent unless otherwise stated. IR spectra were obtained on a Beckman IR9, UV spectra on a Beckman DK-2A, and MS on an AEI MS902

instrument. Melting points were determined on a Reichert hot stage apparatus.

The apparatus, reaction conditions, and work-up for the Wittig reactions have been described earlier.<sup>1</sup> All the bisphosphonium salts from bis(bromomethyl)naphthalenes were prepared in near-quantitative yields by reflux (overnight) of the appropriate bis(bromomethyl)naphthalene with two equivalents of triphenylphosphine in dry dimethylformamide. The salts were dried (12 h) *in vacuo* before use. The bis(bromomethyl)naphthalenes were prepared from the corresponding dimethylnaphthalenes according to the literature.<sup>7</sup> Naphthalene-2,6-dicarbaldehyde was prepared from 2,6-dimethylnaphthalene.<sup>8</sup> Commercial benzene-1,4-dicarbaldehyde was recrystallized before use.

[2](1,4)Naphthaleno[2]paracyclo[2](1,4)-naphthaleno[2]paracyclophanetetraene, 1a. The Wittig reaction of the bistrisphenylphosphonium salt from 1,4-bis(bromomethyl)naphthalene (3.9 g, 4.7 mmol) and benzene-1,4-dicarbaldehyde (0.63 g, 4.7 mmol) followed by usual isolation and separation yielded the cyclophane 1a which was recrystallized as yellow needles from dichloromethane-methanol (36 mg, 1.5%, m.p. 200 °C). IR (KBr): 2940 (m), 1610 (m), 1520 (m), 1450 (m), 1220 (m), 1130 (m), and 760 (s)  $\text{cm}^{-1}$ . For UV data see Table 1. NMR:  $\delta$  8.05 (4H, m,  $\text{H}_A$  or  $\text{H}_B$ ), 7.40 (4H, m,  $\text{H}_A$  or  $\text{H}_B$ ), 7.33 (4H, s,  $\text{H}_C$ ), 6.90 (8H, s,  $\text{H}_D$ ), 6.91 (4H, d,  $\text{H}_E$  or  $\text{H}_F$ ), and 6.80 (4H, d,  $\text{H}_E$  or  $\text{H}_F$ ,  $J_{\text{EF}}$  12 Hz). MS (70 eV):  $m/e$  508 ( $\text{M}^+$ , 100%), 507 (5), 254 ( $\text{M}^{2+}$ , 7), 253 (7), and 252 (7). Abs. mass 508.218  $\pm$  0.003; calc. for  $\text{C}_{40}\text{H}_{28}$  508.218.

[2](1,4)Naphthaleno[2]paracyclo[2](1,4)-naphthaleno[2]paracyclophane, 1b. Hydrogenation of 1a in benzene at room temperature over a Pd/charcoal catalyst yielded 1b (yield 96%, m.p. 185–186 °C, white cryst. from dichloromethane/methanol). NMR:  $\delta$  7.98 (4H, m,  $\text{H}_A$

or H<sub>B</sub>), 7.65 (4H, m, H<sub>A</sub> or H<sub>B</sub>), 6.69 (4H, s, H<sub>C</sub>), 6.64 (8H, s, H<sub>D</sub>), 3.32 (8H, m, H<sub>F</sub> or H<sub>E</sub>), 2.98 (8H, m, H<sub>E</sub> or H<sub>F</sub>). MS (70 eV): *m/e* 516 (M<sup>+</sup>, 41 %), 257 (16), 155 (23), 154 (100), 105 (11), and 104 (57). Abs. mass 516.280 ± 0.003; calc. for C<sub>40</sub>H<sub>36</sub> 516.281.

[2](1,5)Naphthaleno[2]paracyclo[2](1,5)-naphthaleno[2]paracyclophanetetraene, 2a. The Wittig reaction of the bistrisphenylphosphonium salt from 1,5-bis(bromomethyl)naphthalene (2.93 g, 3.5 mmol) and benzene-1,4-dicarbaldehyde (0.47 g, 3.5 mmol) followed by the usual isolation and separation yielded the cyclophane 2a (32 mg, 2 %, m.p. 285–286 °C, pale yellow needles from dichloromethane–methanol). IR (KBr): 3020 (m), 2940 (m), 1600 (m), 1505 (m), 1410 (m), 850 (s), and 800 (s) cm<sup>-1</sup>. UV see Table 1. NMR: δ 7.85 (4H, d, H<sub>C</sub>), 7.23 (4H, dd, H<sub>B</sub>, J<sub>BC</sub> 8.4 Hz), 7.16 (4H, d, H<sub>A</sub>, J<sub>AB</sub> 7.2 Hz), 6.92 (4H, d, H<sub>F</sub> or H<sub>E</sub>), 6.72 (4H, d, H<sub>E</sub> or H<sub>F</sub>, J<sub>EF</sub> 12 Hz), and 6.59 (8H, s, H<sub>D</sub>). MS (70 eV): *m/e* 508 (M<sup>+</sup>, 100 %), 507 (15), 506 (9), 253 (11), and 165 (11). Abs. mass 508.218 ± 0.003; calc. for C<sub>40</sub>H<sub>28</sub> 508.218.

[2](2,6)Naphthaleno[2]paracyclo[2](2,6)-naphthaleno[2]paracyclophanetetraene, 3a. The Wittig reaction of the bistrisphenylphosphonium salt from 2,6-bis(bromomethyl)naphthalene (5.0 g, 6 mmol) and benzene-1,4-dicarbaldehyde (0.81 g, 6 mmol) followed by the usual isolation and separation yielded the cyclophane 3a (80 mg, 2.6 %, m.p. 284–285 °C, yellow needles from dichloromethane–methanol). IR (KBr): 3020 (m), 1605 (m), 1415 (m), 910 (s), 880 (s), and 820 (s) cm<sup>-1</sup>. UV see Table 1. NMR: δ 7.94 (4H, d, H<sub>C</sub>), 7.63 (4H, d, H<sub>A</sub>), 7.45 (4H, dd, H<sub>B</sub>, J<sub>AB</sub> 8 Hz, J<sub>BC</sub> 2 Hz), 7.39 (8H, s, H<sub>D</sub>), 6.60 (4H, d, H<sub>E</sub> or H<sub>F</sub>), 6.57 (4H, d, H<sub>E</sub> or H<sub>F</sub>, J<sub>EF</sub> 12 Hz). MS (70 eV): *m/e* 508 (M<sup>+</sup>, 100 %), and 254 (M<sup>+</sup>, 8.5). Abs. mass 508.217 ± 0.003; calc. for C<sub>40</sub>H<sub>28</sub> 508.218.

[2](2,6)Naphthaleno[2]paracyclo[2](2,6)-naphthaleno[2]paracyclophane, 3b. Hydrogenation of 3a in benzene at room temperature over a Pd/charcoal catalyst yielded 3b (95 %, m.p. 257 °C, white prisms from dichloromethane–methanol). NMR: δ 7.26 (4H, d, H<sub>A</sub>), 7.20 (4H, broad s, H<sub>C</sub>), 6.86 (4H, dd, H<sub>B</sub>, J<sub>AB</sub> 8.5 Hz, J<sub>BC</sub> 1.5 Hz), 6.83 (8H, s, H<sub>D</sub>), 3.06 (8H, m, H<sub>E</sub> or H<sub>F</sub>), 2.97 (8H, m, H<sub>E</sub> or H<sub>F</sub>). MS (70 eV): *m/e* 516 (M<sup>+</sup>, 82 %), 258 (14), 257 (38), 155 (26), and 154 (100). Abs. mass 516.281 ± 0.005; calc. for C<sub>40</sub>H<sub>36</sub> 516.281.

[2<sub>4</sub>](2,6)Naphthalenophanetetraene, 4a. The Wittig reaction of the bistrisphenylphosphonium salt from 2,6-bis(bromomethyl)naphthalene (5.82 g, 6.95 mmol) and naphthalene-2,6-dicarbaldehyde (1.28 g, 6.95 mmol) followed by the usual isolation and separation yielded the cyclophane 4a (84 mg, 2 %, m.p. > 350 °C, pale yellow prisms from dichloromethane–methanol). IR (KBr): 2960 (m), 1470 (m), 910 (s), 830 (s), 760 (s) cm<sup>-1</sup>. UV see Table 1. NMR: δ 7.88 (8H, broad s, H<sub>C</sub>), 7.57 (8H, d, H<sub>A</sub>), 7.42 (8H, dd, H<sub>B</sub>, J<sub>AB</sub> 8 Hz, J<sub>BC</sub> 1 Hz), and

6.73 (8H, s, H<sub>D</sub>). MS (70 eV): *m/e* 608 (M<sup>+</sup>, 100 %, and 304 (M<sup>2+</sup>, 16). Abs. mass 608.250 ± 0.003; calc. for C<sub>48</sub>H<sub>32</sub> 608.251.

[2<sub>4</sub>](2,6)Naphthalenophane, 4b. Hydrogenation of 4a in benzene at room temperature over a Pd/charcoal catalyst yielded after 72 h, 4b (90 %, m.p. 235–236 °C). NMR: δ 7.38 (8H, d, H<sub>A</sub>), 7.26 (8H, broad s, H<sub>C</sub>), 6.99 (8H, dd, H<sub>B</sub>, J<sub>AB</sub> 8 Hz, J<sub>BC</sub> 2 Hz), and 3.15 (16H, s, H<sub>D</sub>). MS (70 eV): *m/e* 616 (M<sup>+</sup>, 80 %, 308 (14), 307 (37), 155 (32), 154 (100), and 153 (10). Abs. mass 616.307 ± 0.010; calc. for C<sub>48</sub>H<sub>40</sub> 616.313.

The cyclic voltammograms were obtained at a hanging mercury drop electrode in dry dimethylformamide containing tetraethylammonium perchlorate (0.1 M) at scan rates of 25 mV s<sup>-1</sup>. The reduction potentials were measured against a standard Ag/AgNO<sub>3</sub> electrode and converted to the SCE-scale by adding 0.43 V, which is the difference for cyclophane 5 under the experimental conditions.

*Acknowledgements.* We are indebted to Prof. B. Lamm for help and advice with the cyclic voltammetry, and to Dr. T. Olsson for discussions regarding the temperature dependent NMR spectra. Financial support from the Swedish Natural Science Research Council is appreciated.

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Received March 23, 1979.