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# Non-Planar Oligoarylene Macrocycles from Biphenyl

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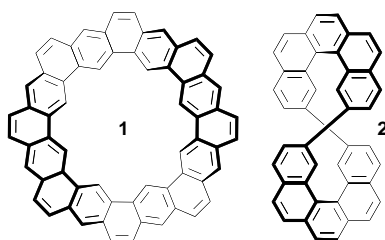
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**Abstract:** Saddle- and propeller-shaped macrocycles are obtained by fourfold Perkin condensations in transient high dilution of 4,4'-bis(phenylglyoxylic acid) with either 4,4'-bis(phenylacetic acid) or *p*-phenylenediacetic acid, followed by four-fold oxidative photocyclizations. In the saddle-shaped tetraphenanthrylene, the angle between opposite phenanthrene planes is close to the value of 90° of an ideal saddle. In the two helicene fragments of the propeller-shaped double [5]helicene, the geometry of unsubstituted [5]helicene is preserved without major macrocycle-induced distortions.

Most shape-persistent conjugated macrocycles are essentially planar, prominent examples being porphyrin, phthalocyanine, [18]-annulene,<sup>1</sup> hexa-*m*-phenylene,<sup>2</sup> kekulene,<sup>3</sup> the cyclo-*p*-phenyleneacetylenes<sup>4</sup> and the cyclo-*p*-phenylenes.<sup>5</sup> Others consist of a planar macrocycle that includes aromatic moieties that are rigidly orthogonal to the plane of the macrocycle, such as Herges's picotube,<sup>6</sup> Gleiter's [6.8]<sub>3</sub>cyclacene<sup>7</sup> and Itami's nanobelt.<sup>8</sup> Non-centrosymmetric variations of the latter type are conical macrocycles such as Stępień's chrysaoroles and chrysaorenes.<sup>9</sup>

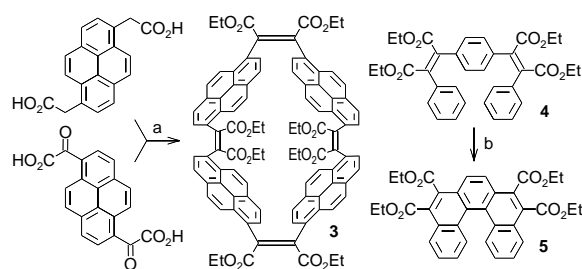
Large aromatic macrocycles where the macrocyclic thread itself is non-planar whilst still being of fixed shape are much rarer. They may be saddle-shaped such as octulene **1** (which has been obtained by Stępień and co-workers in octabutoxy-substituted form),<sup>10</sup> or consist of helicenic fragments, such as Thulin and Wennerström's propellicene **2**<sup>11</sup> (Scheme 1). Unfortunately, crystallographic structures have not been reported for either of these two archetypal examples. Related intriguing conjugated macrocycles with non-planar threads are the octaphyrins and other expanded porphyrinoids<sup>12</sup> and the first carbocyclic conjugated Möbius bands.<sup>13</sup>



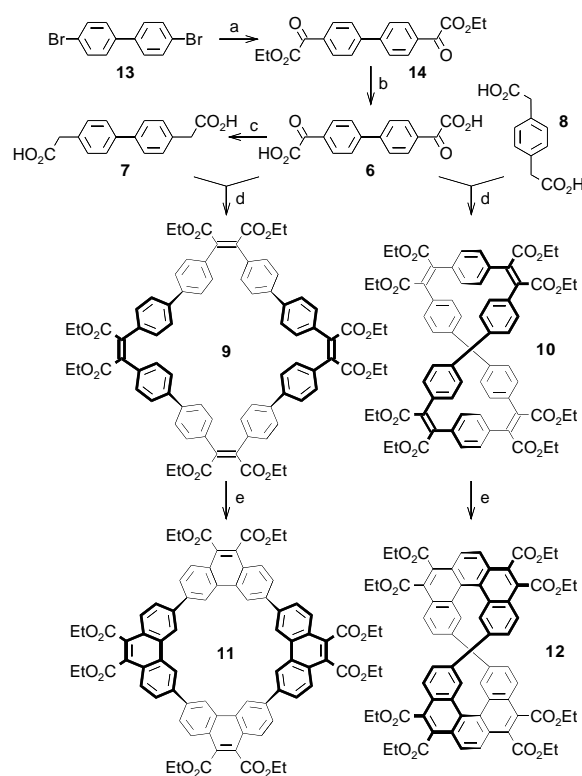
**Scheme 1.** Non-planar polycyclic aromatic macrocycles: saddle-shaped octulene **1**<sup>10</sup> and bis-helicenic propellicene **2**.<sup>11</sup>

We have recently found that the Perkin reaction of an arylenediacetic acid with an arylenediglyoxylic acid may lead selectively to the tetra-arylenevinylene macrocycle, and thus we obtained the tetrapyrenylene-tetramaleate **3** in a rather satisfying yield of 25%.<sup>14</sup> We also observed that the oxidative photocyclization of *p*-phenylene-

bis(phenylmaleate) **4** efficiently leads to [5]helicene-tetracarboxylate **5** in 77% yield<sup>15</sup> (Scheme 2). We thus wondered whether the Perkin condensation of 4,4'-bis(phenylglyoxylic acid) **6** with either 4,4'-bis(phenylacetic acid) **7** or *p*-phenylenediacetic acid **8** would give the corresponding 2+2 macrocycles **9** and **10** with similar efficiency as in the formation of **3**, and whether the resulting macrocycles could be photocyclized to the corresponding octaesters: saddle **11** and propellcene **12** (Scheme 3). The carboxylic substituents not only should ease the intramolecular photocyclization of the macrocyclic Perkin reaction products by sterically shielding the molecule against intermolecular side reactions such as cyclobutane formation,<sup>16</sup> but also could improve by their polarity the crystallization behavior of the photocyclized target macrocycles, in view of obtaining the molecular geometries from X-ray diffraction.



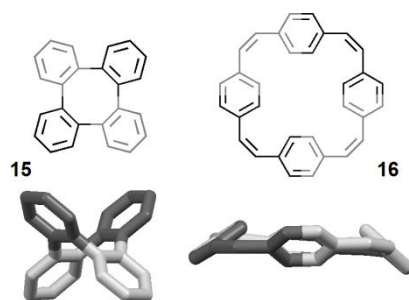
**Scheme 2.** Previous syntheses of tetrameric pyrenophane-octaester **3**<sup>14</sup> and [5]helicene-tetraester **5**.<sup>15</sup> (a) 1. NEt<sub>3</sub>, Ac<sub>2</sub>O, THF, 2. EtOH, EtBr, DBU, 25%; (b) hv, I<sub>2</sub>, O<sub>2</sub>, EtOAc, 77%.



**Scheme 3.** Synthesis of saddle-shaped tetra-3,6-phenanthrylene-octacarboxylate **11** and propellcene-octacarboxylate **12**. (a) 1. THF, *n*-BuLi, 2. EtO<sub>2</sub>CCO<sub>2</sub>Et, 62%; (b) NaHCO<sub>3</sub>, EtOH-H<sub>2</sub>O, 100%; (c) NaI, H<sub>3</sub>PO<sub>2</sub>, H<sub>2</sub>O, AcOH, 94%; (d) 1. NEt<sub>3</sub>, Ac<sub>2</sub>O, THF (high dilution), 2. EtOH, EtBr, DBU, 52% (**9**) / 21% (**10**); (e) hv, I<sub>2</sub>, O<sub>2</sub>, EtOAc-dioxane or PhMe, 47% (**11**) / 54% (**12**).

To obtain the two key biphenyl building blocks **6** and **7**, we started from 4,4'-dibromobiphenyl **13**,<sup>17</sup> in an analogous approach to the synthesis of the precursors of tetraphenophane **3** from 1,6-dibromopyrene:<sup>14</sup> **13** was dilithiated with *n*-butyllithium followed by addition of diethyl oxalate to give diglyoxylic ester **14**, which was transformed into **6** and **7** by basic hydrolysis and reduction with hypophosphorous acid and iodide. As both **6** and **7** proved to be soluble in THF at room temperature, it was possible to add an equimolar solution of these substrates from a motor-driven syringe to a refluxing solution of the Perkin reactants acetic anhydride and triethylamine over a period of 20h. Given that Perkin reactions under similar conditions are usually complete after one night,<sup>18</sup> this slow addition ensured near-ideal high dilution conditions that favor macrocycle formation over polymerization, and favor smaller macrocycles over larger ones. After in situ esterification, we thus could obtain the tetrameric (2+2) macrocycle **9** in 52% yield, which could be separated from side products of higher molecular mass by careful chromatography and precipitation. This yield is a significant improvement on the 25% cyclotetramerization yield of pyrenophane **3**, whose less soluble diacetic precursor did not allow the same high dilution procedure. Polarized light microscopy revealed that the obtained powder of **9** does not show microcrystals of straight shapes nor significant birefringence, but rather appears to be glassy, showing softening to an isotropic fluid around 190°C. It is thus not surprising that we were unable to grow single crystals of **9** for X-ray structure elucidation.

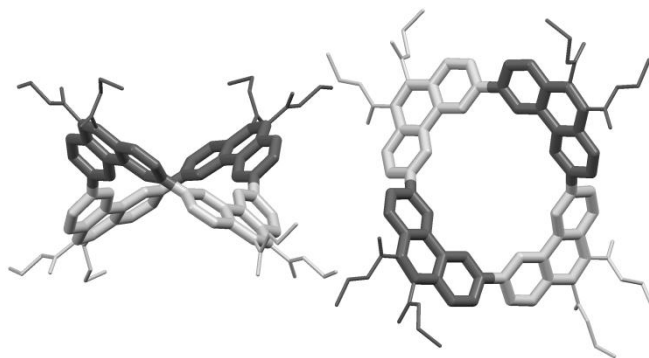
Irradiation of a 0.5 mM solution of **9** in the presence of iodine and oxygen for five days with pyrex-filtered irradiation from a medium pressure mercury lamp yielded tetraphenanthrylene **11** in 47% yield, of which we obtained crystals suitable for X-ray structure determination by slow diffusion of methanol into a chloroform solution.



**Figure 1.** Reference materials for comparison with tetraphenanthrylene **11**: Saddle-shaped tetra-*o*-phenylene **15** and essentially planar paracyclophanetetraene **16**. Bottom: lateral views of one molecule in the crystal illustrating the nonplanarity/planarity of the macrocycles;<sup>19, 20</sup> hydrogen atoms and residual solvent molecules omitted for clarity; cisoid angular units alternately colored light and dark gray.

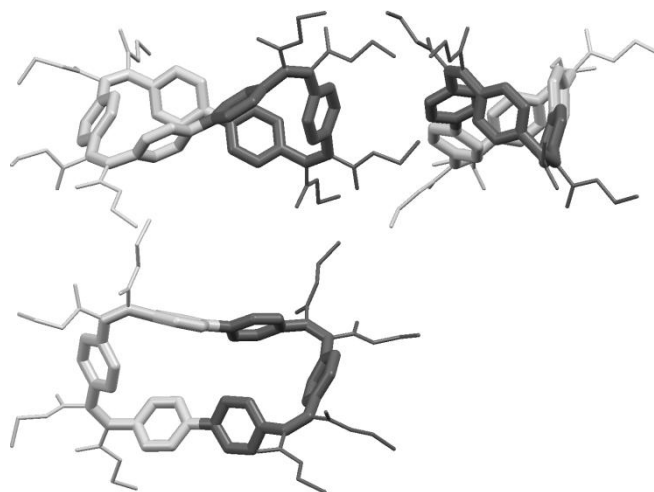
The simplest aromatic saddle-shaped molecule is *o*-tetraphenylene **15**, and a similarly simple tetrameric macrocycle with four *ortho*-bridging angular moieties is [2<sub>4</sub>]paracyclophanetetraene **16** (Figure 1). Of both, crystal structures have been reported. Whereas **16** is essentially planar,<sup>19</sup> with C-C=C bond angles at the olefinic bridges of about 132°, the angle between opposite benzene planes in **15** is 87°, <sup>20</sup> slightly sharper than the ideal value of 90° that would result from 120° bond angles and no *o*-phenylene torsion. Compared to these two antagonistic

prototype molecules, the saddle shape of tetraphenanthrylene **11** is only slightly flattened compared to **15**, with angles between opposite phenanthrene planes of around  $95^\circ$  and inner bond angles at the interphenanthrene bonds of around  $122^\circ$ , but exhibits pronounced torsion angles between interphenanthrene bonds of around  $18^\circ$ , which result from the helicenic repulsion between hydrogen atoms in the phenanthrene bay regions. These torsion angles lead to a slightly oval inner cavity of the macrocycle (Figure 2).

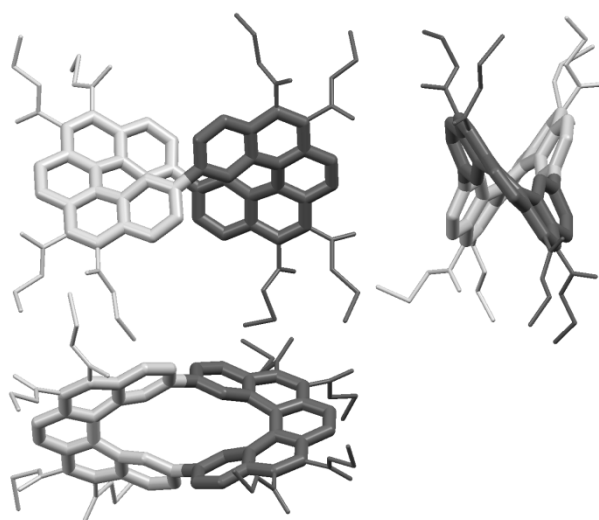


**Figure 2.** Two orthogonal views of one molecule of tetraphenanthrylene **11** in the triclinic crystal. The four substituted phenanthrene fragments are alternatingly colored light and dark gray, with ester substituents thin and aromatic moieties thick. Hydrogen atoms and residual solvent molecules omitted for clarity.

To obtain ester-substituted propellicene **12** via paracyclophane **10**, we reacted **6** with **8** following the same high dilution protocol. To our surprise, the isolated yield of **10** was with 21% significantly lower than the yield of **9**, which may indicate that the smaller and less flexible *p*-phenylene units make macrocycle **10** sterically less favored than the larger tetraphenanthrylene precursor **9** based only on biphenyl blocks. On the other hand, the greater compactness **10** eased its crystallization sufficiently to allow us to collect satisfyingly diffracting crystals by methanol-into-chloroform diffusion. In the crystal, the molecules of **10** adopt a very dissymmetric conformation (Figure 3) in which neither the two opposite biphenyl units are parallel to each other, nor the two *p*-phenylene units, with the latter adopting near-orthogonally rotated orientations with respect to each other (Figure 3, right). Thus **10** adopts a twisted conformation that is favorable for the formation of propellicene **12** (compare Figures 3 and 4, that show **10** and **12** in similar views).



**Figure 3.** Three orthogonal views of one molecule of flexible propellicene precursor **10** in the triclinic crystal. The two photocyclizable *p*-phenylene-bis(phenylmaleate) fragments are respectively colored light and dark gray, with ester groups thin and the conjugated macrocycle thick. Hydrogen atoms and residual solvent molecules omitted for clarity.

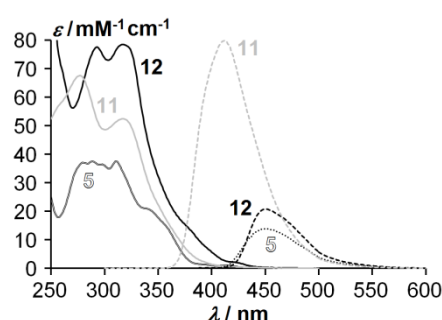


**Figure 4.** Three orthogonal views of one molecule of propellicene **12** in the monoclinic crystal. The two substituted [5]helicene fragments are respectively colored light and dark gray, with ester substituents thin and aromatic moieties thick. Hydrogen atoms and residual solvent molecules omitted for clarity, and only the predominant configuration is shown in the case of disordered ester substituents. Note that the molecule is chiral, but the crystal is not, with six molecules of each enantiomer per unit cell.

Irradiation of a dilute solution of **10** with iodine and oxygen for two days, followed by eight-fold in situ esterification, gave propellicene **12** in similar yield (54%) to the analogous fourfold photocyclization of **9** to **11**, and we obtained crystals suitable for X-ray diffraction by the same method as with **11** and **10**, albeit the crystal structure of **12** (six right- and six left-handed molecules per unit cell, disordered ester substituents) testifies of the lower propensity of chiral racemic **12** to pack periodically than nonchiral **11** or **10**. The [5]helicene fragments in the crystal of **12** are nearly undistorted with respect to unsubstituted [5]helicene<sup>21</sup> (e.g. the sums of the three inner-rim C-C-C-C torsion angles, as well as the distances between the inner carbon atoms of the terminal rings, differ by less than 3% between **12** and unsubstituted [5]helicene). This notable correspondence, together with the

relatively small configurational changes necessary to convert flexible precursor **10** into **12** (e.g. as in **10**, the central hexagons of the two helical units in **12** adopt near-orthogonally rotated orientations, see Figure 4, right) may explain why the more condensed propellicene **12** is formed by four-fold photocyclization in similarly satisfactory yield as the saddle **10**.

The absorption spectrum of **12**, with maxima at 293 and 317 nm, is similar to the corresponding monomer, the [5]helicene-tetraester **5**, with, as should be expected, roughly doubled intensity, and with only a moderate red-shift of the longest-wavelength absorption maximum (**5**: 310 nm; figure 5). The fluorescence spectra of **12** and **5** upon excitation at 280 nm are similar, and the fluorescence intensities peak at the same wavelength (450 nm) and are of similar ratio as the absorption intensities at the excitation wavelength. Optically, **12** behaves thus essentially as a dimer of **5**.



**Figure 5.** Absorption (left) and fluorescence spectra (right) of **5**, **11** and **12** in 4  $\mu$ M solution in chloroform. Fluorescence spectra are recorded upon excitation at 280 nm (where **11** and **12** absorb with the same intensity) and are in arbitrary units.

Tetraphenanthrylene **11**, with absorption maxima at 277 and 317 nm and an emission maximum at 412 nm, fluoresces about four times as intensely as bishelicylene **12** (upon excitation at 280 nm, where the absorption intensities of **11** and **12** are equal).

Both macrocycles show irreversible first oxidation and first reduction peaks by differential pulse voltammetry (DPV) at very similar values, corresponding to HOMO energies of 5.86 eV (**11** and **12**) and LUMO energies of 2.79 eV (**11**) and 2.86 eV (**12**) that yield electrochemical band gaps of 3.07 eV (**11**) and 3.00 eV (**12**) (Table 1).

**Table 1:** Physical properties of macrocycles **11** and **12**

Macrocycle	<b>11</b>	<b>12</b>
Absorption maxima (nm) [Extinction coefficients ( $M^{-1}cm^{-1}$ )] <sup>a</sup>	277 [67500], 317 [52400]	293 [77500], 317 [78400]
Fluorescence maximum (nm) <sup>a,b</sup>	412	450
Fluorescence quantum yield <sup>a,b,c</sup>	0.38	0.09
HOMO and LUMO energies (eV) <sup>d</sup>	5.86, 2.79	5.86, 2.86
Band gap (eV)	3.07	3.00

(a) 4  $\mu$ M in  $CHCl_3$ ; (b) excitation at 280 nm; (c) vs. *N*-octyl diphenylmaleimide as standard<sup>22</sup>; (d) from DPV vs. Fc<sup>+</sup>/Fc as standard, 1.5mM in DCM.

In summary, the four-fold Perkin condensation of soluble arylene-diglyoxylic acid **6** with arylene-diacetic acids **7** or **8** leads to flexible paracyclophanetetraenes **9** and **10** that undergo four-fold oxidative photocyclization in ca. 50% yield to partially condensed, fully aromatic macrocycles, saddle-shaped

tetraphenanthrylene-octacarboxylate **11** and propellicene-octacarboxylate **12**, whose crystallographic structures testify of the characteristically non-planar geometry of their macrocyclic threads.

Non-substituted [5]helicenes quickly racemize at room temperature (with a half-life of ca. 14h).<sup>23</sup> In the case of propellicene **12**, the [5]helicene moieties are not only substituted on hindering positions, but are also linked together in a way that forces them to invert simultaneously their helicity in case of racemization. We currently aim at studying this phenomenon both experimentally and theoretically.

## Acknowledgements

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## Conflicts of interest

There are no conflicts to declare.

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