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Non-Planar Oligoarylene Macrocycles from Biphenyl

Antoine Robert, Pierre Dechambenoit, Elisabeth A. Hillard, Harald Bock and Fabien Durola

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 90º 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, hexa-m-phenylene, kekulene, the cyclo-p-phenyleneacetylenes and the cyclo-p-phenylenes. 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, Gleiter’s [6.8]cyclacene and Itami’s nanobelt. Non-centrosymmetric variations of the latter type are conical macrocycles such as Stępień’s chrysaoroles and chrysaorenes.

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), or consist of helicenic fragments, such as Thulin and Wennerström’s propellicene 2 (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 and the first carbocyclic conjugated Möbius bands.

Scheme 1. Non-planar polycyclic aromatic macrocycles: saddle-shaped octulene 1 and bis-helicenic propellicene 2.

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%. We also observed that the oxidative photocyclization of p-phenylene-
bis(phenylmaleate) 4 efficiently leads to [5]helicene-tetracarboxylate 5 in 77% yield (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 propellicene 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, 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 and [5]helicene-tetraester 5. (a) 1. NEt₃, Ac₂O, THF, 2. EtOH, EtBr, DBU, 25%; (b) hν, I₂, O₂, EtOAc, 77%.

Scheme 3. Synthesis of saddle-shaped tetra-3,6-phenanthrylene-octacarboxylate 11 and propellicene-octacarboxylate 12. (a) 1. THF, n-BuLi, 2. EtO₂CCO₂Et, 62%; (b) NaHCO₃, EtOH-H₂O, 100%; (c) NaI, H₃PO₄, H₂O, AcOH, 94%; (d) 1. NEt₃, Ac₂O, THF (high dilution), 2. EtOH, EtBr, DBU, 52% (9) / 21% (10); (e) hν, I₂, O₂, 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 13,17 in an analogous approach to the synthesis of the precursors of tetrapyrenophane 3 from 1,6-dibromopyrene:14 13 was dilitiated 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,18 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 190ºC. 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 tetraphenantrylene 11 in 47% yield, of which we obtained crystals suitable for X-ray structure determination by slow diffusion of methanol into a chloroform solution.

The simplest aromatic saddle-shaped molecule is o-tetraphenylene 15, and a similarly simple tetrameric macrocycle with four ortho-bridging angular moieties is [2,4]paracyclophanetetraene 16 (Figure 1). Of both, crystal structures have been reported. Whereas 16 is essentially planar,19 with C-C=C bond angles at the olefinic bridges of about 132º, the angle between opposite benzene planes in 15 is 87º,20 slightly sharper than the ideal value of 90º that would result from 120º bond angles and no o-phenylene torsion. Compared to these two antagonistic
prototype molecules, the saddle shape of tetr phenanthrylene 11 is only slightly flattened compared to 15, with angles between opposite phenanthrene planes of around 95° and inner bond angles at the interphenanthrene bonds of around 122°, but exhibits pronounced torsion angles between interphenanthrene bonds of around 18°, 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 tetr phenanthrylene 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 tetr phenanthrylene 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).
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\textsuperscript{21} (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.

Tetraphenanthrylene 11, with absorption maxima at 277 and 317 nm and an emission maximum at 412 nm, fluoresces about four times as intensely as bishelicenylene 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>
<thead>
<tr>
<th>Macrocycle</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maxima (nm) [Extinction coefficients (M⁻¹ cm⁻¹)]</td>
<td>277 [67500], 317 [52400]</td>
<td>293 [77500], 317 [78400]</td>
</tr>
<tr>
<td>Fluorescence maximum (nm)</td>
<td>412</td>
<td>450</td>
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<tr>
<td>Fluorescence quantum yield</td>
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<td>0.09</td>
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<tr>
<td>HOMO and LUMO energies (eV)</td>
<td>5.86, 2.79</td>
<td>5.86, 2.86</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>3.07</td>
<td>3.00</td>
</tr>
</tbody>
</table>

(a) 4 µM in CHCl₃; (b) excitation at 280 nm; (c) vs. N-octyl diphenylmaleimide as standard; (d) from DPV vs. Fc+/Fc as standard, 1.5mM in DCM.

In summary, the four-fold Perkin condensation of soluble arylene-diglyoxycylic acid 6 with arylene-diacetic acids 7 or 8 leads to flexible paracyclophane-tetraenes 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 propellocene-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). In the case of propellocene 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.

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Conflicts of interest

There are no conflicts to declare.

Notes and references


