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Research paper

Double helicenes

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ABSTRACT

The even double helicenes with 4–12 phenyl groups in each helix were examined at B3LYP-D3/6-311G(d). The double helicenes with 4–10 phenyl rings are less than twice as strained as their component helicenes; the strain results from twisting about the shared naphthyl moiety, with accompanying loss of aromaticity. These compounds should be reasonable synthetic targets, and computed NMR shifts are provided to aid in their characterization.

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Helicenes have fascinated organic chemist for decades [1–6]. These polycyclic aromatic systems are comprised of *ortho*-fused phenyl rings that form helices (corkscrews) to avoid steric clashing. This non-planar structure allows chemists to probe the limits of aromaticity, and their inherently chiral nature affords interesting stereochemistry and optical properties.

Over the past two years, interest has developed in double helicenes, molecules that contain two helicenes that share a common naphthyl (as in **1**) or phenyl (as in **2**) core [7–9]. An especially interesting example is the diastereomeric pair **1PP** and **1PM** prepared by Fujikawa et al. [8]. The crystal structure of the helical form **1PP** was reported, and they also estimated that **1PP** is 0.9 kcal mol^{-1} more stable than **1PM** at B3LYP/6-31G(d).

In this article we examine the simplest symmetric double helicenes, where each helicene contains four (**3**), six (**4**), eight (**5**), ten (**6**) or twelve (**7**) phenyl rings. These molecules can exist in two stereoisomeric forms: the helical *PP* form or the *meso PM* form. A number of studies of aromatic molecules involved in π-stacking point toward the necessity of including a dispersion correction in any DFT computation [10–16]. On the other hand, dispersion-corrected functionals have provided mixed results in predicting the optical activity of helicenes [17–19]. To aid is selecting an appropriate computational method, we examined **1** and **2**, whose X-ray crystal structures are known [8,9], using a number of functionals and basis sets (see Supplementary Data for details). Functionals that include a dispersion correction all provide a geometry for **1PP** and **2PP** that matches up extremely well with the experimental X-ray crystal structure, while those lacking a dispersion correction do not capture the contraction that pulls the rings together in the π-π stacking regions. While the calculated gas-phase and experimental solid phase structures may differ due to phase, a dispersion-correct functional appears to be necessary for describing these double helicene molecules. All methods, except B3LYP/6-31G(d) – the one used by Fujikawa et al. [8] – indicate that **1PM** is lower in energy than **1PP**.

The geometries of both stereoisomers of **3**–**7** were optimized using the B3LYP [20–23] functional augmented with Grimme's D3 dispersion correction [24] incorporating Becke-Johnson damping [25–28] with the 6-311G(d) basis set. Optimization of the **PP** isomers were carried out imposing D_2 symmetry while C_{2h} was imposed for the **PM** isomers. Analytical frequency analysis confirmed that all structures were local energy minima. The unscaled zero-point vibrational frequencies were utilized in computing enthalpy (reported in this article) and free energies, incorporating the quasiharmonic approximation of Truhlar and Cramer whereby low-frequency modes (less than 100 cm^{-1}) were raised to 100 cm^{-1} for the computation of the vibrational partition functions [29]. All computations were performed using *Gaussian-09* [30].

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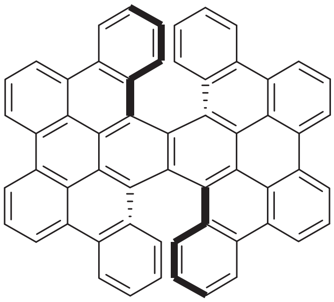
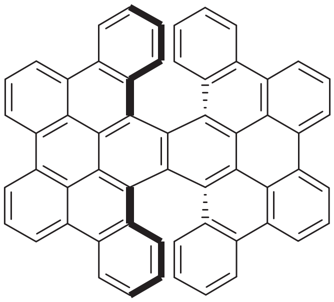
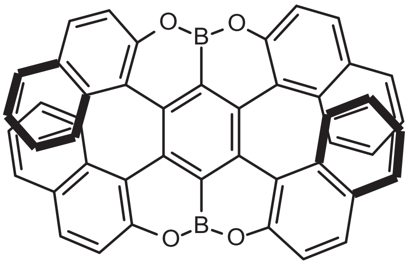


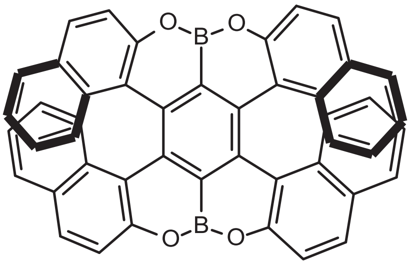
1PP



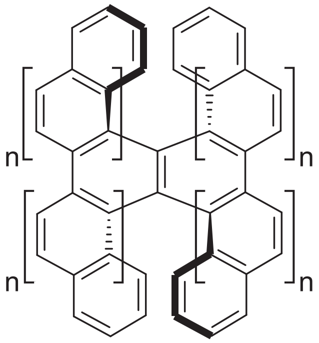
1PM



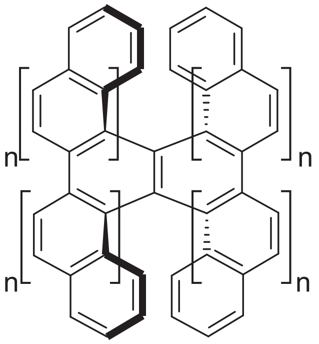
2PP



2PM



n=0: **3PP**
n=1: **4PP**
n=2: **5PP**
n=3: **6PP**



n=0: **3PM**
n=1: **4PM**
n=2: **5PM**
n=3: **6PM**

Dibenzo[*g*,*p*]chrysene **3** is the smallest hydrocarbon double helicene, containing two helicenes each with four phenyl rings. The structures of the helical and meso isomers are shown in Fig. 1. The dihedral angle C1–C2–C3–C4 (see Fig. 1) is 159.6° in **3PM** and 154.3° in **3PP**, reflecting the need of the molecule to twist out-of-plane to avoid the clashing of the C1,C1′ hydrogens. The helical **3PP** isomer is favored by 5.01 kcal mol^{-1} over the meso **3PM** isomer (Table 1).

These computations are in nice agreement with the experimental report of the X-ray crystal structure of **3PP** [31]. Only the helical isomer was identified, in agreement with it being the more stable isomer. The X-ray structure is nearly of C_2 symmetry and not far removed from D_2. The average of the C1–C2–C3–C4 dihedral angles in the crystal structure is 155.2°, just a degree different from the computed structure. These results further justify the use of the B3LYP-D3/6-311G(d) method.

The strain energy of **3** can be assessed using the group equivalent method [32] as Reaction 1, which compares the enthalpy of the helicene to unstrained, planar aromatic hydrocarbons. This reaction conserves the substitution pattern about each ring in **3**. The twisting about the central (shared) naphthalene introduces the strain, but it is relatively small in these isomers: 9.75 kcal mol^{-1} in **3PP** and 14.75 kcal mol^{-1} in **3PM**.

The next larger double helicene is **4**, having two helicenes containing six phenyl rings. The clashing at the ends of each helicene involves not just the hydrogens but C1 and C1′ themselves. This leads to significantly more strain energy in **4** (about 27 kcal mol^{-1}) than in **3** (see Table 1). (The strain energy of **4** is evaluated using Reaction 2, which again conserves the substitution pattern about each phenyl ring of **4**.) **4PP** is slightly lower in enthalpy than **4PM**.

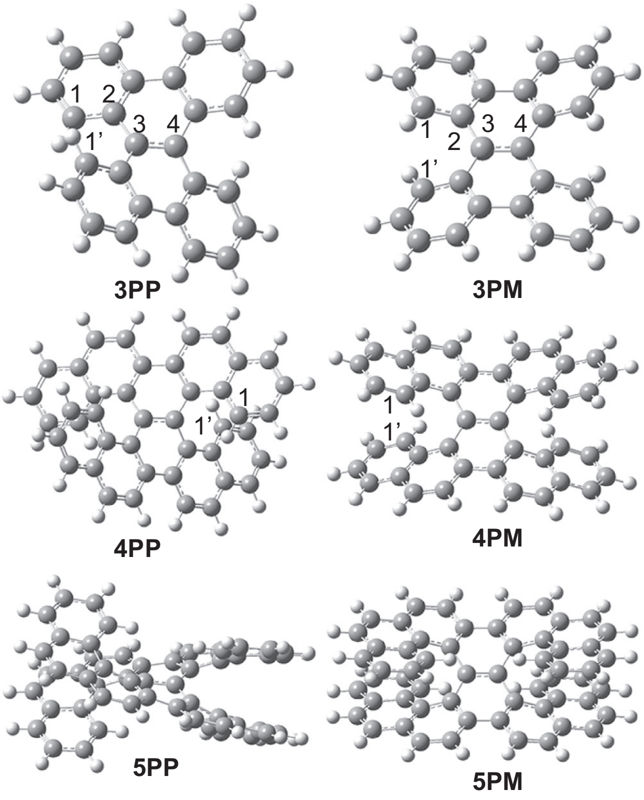


Fig. 1. Optimized structures of **3**–**5**.

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