# Dibenzo[a,o]phenanthro[3,4-s]pycene, a Configurationally Stable Double Helicene: Synthesis and Determination of Its Conformation by NMR and GIAO Calculations[†]

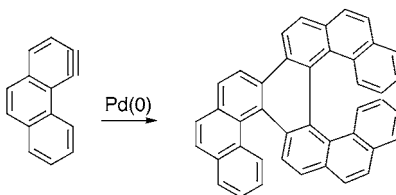**Diego Peña, Agustín Cobas,\* Dolores Pérez,\* Enrique Guitián,\* and Luis Castedo**

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ABSTRACT



A double helicene formed by a pentahelicene and a heptahelicene with two rings in common was obtained by palladium-catalyzed cyclotrimerization of 3,4-didehydrophenanthrene and was characterized conformationally by NMR and GIAO calculations.

In the past decade, interest in helicenes[1] has revived due to the use of some of these molecules as rotors,[2] ligands in asymmetric catalysis[3] and in molecular recognition research,[4] and as the self-assembling components of helical structures with high circular dichroism and specific rotation[5] or of helically twisted columnar discotic liquid crystals.[5b] Most

of the strategies developed for the synthesis of helicenes[6] involve Diels−Alder reactions[3c,5,7] or photochemical cyclizations[2,3a,b,4,8] as key steps, although a new synthesis based on the Ni(0)- or Co(I)-catalyzed intramolecular cyclotrimerization of alkynes has also been reported.[9]

In recent years, we have applied a new, palladium-catalyzed cyclotrimerization of arynes to the synthesis of a number of strained polycyclic aromatic hydrocarbons,[10] some of which contain helical fragments. In particular, compound

† Dedicated to Prof. Julio Delgado on the occasion of his 60th birthday.

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## Scheme 1



**Scheme 1**
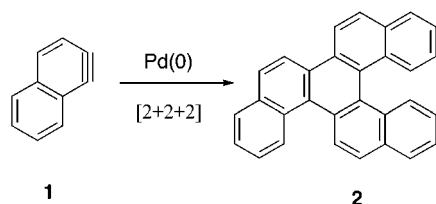
2 is the major product of the trimerization of the two-ring aryne 1,2-didehydronaphthalene (1).[10b] In this paper, we describe the cyclotrimerization of the three-ring aryne 3,4-didehydrophenanthrene (4) to form compound 5 (as far as we know, the first double helicene[11] formed by a penta-helicene and a heptahelicene with two rings in common), and we sketch the elucidation of the relative stereochemistry of the two helicenes constrained in this product.

3,4-Didehydrophenanthrene (4) was generated in the presence of $Pd_2(dba)_3$ (0.05 mol %) by treatment of compound 3 with CsF at room temperature.[12] After 12 h of stirring at room temperature, workup and chromatography afforded a single cyclotrimerization product in 26% yield.[13] Its mass spectrum shows a peak at $m/z$ 528, which corresponds to three monomer units. Its connectivity was deduced from its ^{1}H NMR spectrum: an extremely clear pattern over a range of 2.6 ppm made it possible to assign all 24 aromatic proton signals of compound 5 by COSY and NOESY correlations.[14] The poor solubility of 5 precluded ^{13}C NMR spectrometry. Consistent with the [7]helicene structure, hydrogen atoms on the terminal rings of this moiety, H2 and H23, resonate at high-field values ($\delta$ 6.69 and 6.40, respectively) as result of the anisotropic effect of the aromatic ring at the opposite end of the helix.[1c] However, whereas in unsubstituted [7]helicene these protons are magnetically equivalent, in 5 there is a difference of 0.29 ppm between their chemical shifts. Further, the chemical shifts of H1 and H24 differ by 1.03 ppm. We reasoned that these pronounced differences must be due to the presence of the fused

## Scheme 2[a]
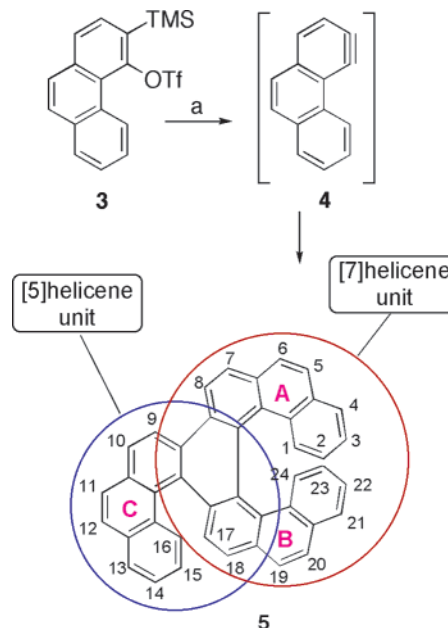


[a] Conditions: (a) CsF, $Pd_2(dba)_3$, $CH_3CN$, 26%.

phenanthrene C (see Scheme 2) and should be dependent on the conformation of the molecule.[11]

Conformational analysis of 5 using semiempirical AM1 calculations[15,16] showed, as expected, that two diastereo-merically related pairs of conformers were possible: one pair of enantiomers, which we named 5-*PP* and 5-*MM*, in which both helicenes rotate in the same sense, and another (5-*PM* and 5-*MP*), in which their senses are opposite. Here, *P* and *M* indicate right- and left-handed helices, respectively, where the first letter indicates the sense of the [7]helicene and the second that of the [5]helicene. The mixed-sense conformer 5-*PM* was the more stable by 3.1 kcal/mol. Although AM1 is known to be reliable for conformational analysis of helicenes[17] and other helically twisted polyarenes,[10c] we further optimized the obtained geometries of 5 using ab initio HF/6-31G(d) calculations and the hybrid DFT method B3LYP/6-31G(d),[18,19] which confirmed 5-*PM* as the more stable conformer by 5.0 or 4.6 kcal/mol, respectively. The barrier to interconversion of 5-*PP* into 5-*PM* via the transition state 5-TS (Figure 1) was calculated at the AM1 level to be 21.8 kcal/mol.

Even if 5-*PM* is the thermodynamically more stable conformer, this does not necessarily mean that 5 is obtained as such; indeed, we recently found that a palladium-catalyzed cyclotrimerization performed under similar conditions af-

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(13) Other possible cyclotrimerization product, the $C_3$-symmetric benzo-[c]naphtho[1,2-l]phenanthro[3,4-g]chrysene, was not detected.

(14) Data for 5: ^{1}H NMR ($C_2D_2Cl_4$, 500 MHz), $\delta$ 8.94 (d, *J* = 8.2 Hz, 1H, H16), 8.87 (d, *J* = 8.7 Hz, 1H, H8), 8.81 (d, *J* = 8.5 Hz, 1H, H9), 8.57 (d, *J* = 8.6 Hz, 1H, H17), 8.24 (d, *J* = 8.2 Hz, 1H, H7), 8.14 (d, *J* = 8.3 Hz, 1H, H10), 8.05 (d, *J* = 7.2 Hz, 1H, H13), 8.01 (s, 2H, H11 and H12), 7.83 (d, *J* = 8.6 Hz, 1H, H6), 7.72 (d, *J* = 8.7 Hz, 1H, H18), 7.67 (d, *J* = 8.7 Hz, 1H, H1), 7.66 (d, *J* = 8.7 Hz, 1H, H14), 7.62 (d, *J* = 8.4 Hz, 1H, H19), 7.56 (t, *J* = 8.4 Hz, 1H, H15), 7.55 (d, *J* = 8.4 Hz, 1H, H5), 7.45 (d, *J* = 8.3 Hz, 1H, H20), 7.40 (d, *J* = 7.6 Hz, 1H, H4), 7.28 (d, *J* = 7.5 Hz, 1H, H21), 7.06 (t, *J* = 7.1 Hz, 1H, H3), 6.91 (t, *J* = 7.0 Hz, 1H, H22), 6.69 (t, *J* = 7.1 Hz, 1H, H2), 6.64 (d, *J* = 8.5 Hz, 1H, H24), 6.40 (t, *J* = 7.3 Hz, 1H, H23); EM, *m/z* (%) 528 (M+, 100), 350 (9), 261 (40); HRMS calcd for $C_{42}H_{24}$ 528.1878, found 528.1884.

(15) Spartan from Wavefunction, Inc., Irvine, CA, 1996 (version MacSpartan Plus 1.04) was used for geometry optimizations and AM1 calculations.

(16) Enthalpies were calculated at 298 K. The nature of any stationary structure obtained at the AM1 level was evaluated by vibrational analyses, with such structures identified as minima or transition states by the presence of zero or one imaginary vibrational frequencies, respectively.

(17) (a) Janke, R. H.; Haufe, G.; Würthwein, E.-U.; Borkent, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 6031. (b) Grimme, S.; Peyerimhoff, S. D. *Chem. Phys.* **1996**, *204*, 411.
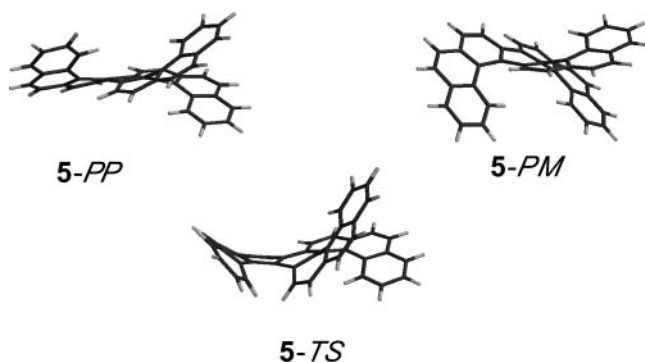
**Figure 1.** Optimized geometries for conformers *PP* and *PM* and transition state *TS* for its interconversion.

forded the product of kinetic control.[10c] An attempt to determine the actual conformation of **5** by X-ray diffraction failed because low solubility precluded its crystallization, a problem commonly encountered in the study of large polyarenes. We therefore resorted to comparison of experimental and theoretical NMR in order to solve this structural problem. The comparison of experimental and ab initio-calculated chemical shifts is a very useful tool for structural determination, particularly for $^{13}C$ and $^{15}N$ nuclei;[20] however, proton chemical shifts cannot be calculated at a level of accuracy sufficient to be useful in this context.[21] So we decided to calculate not the absolute chemical shifts but *a relative chemical shift increment* ($\Delta\delta_H$) for each proton, which we defined as the difference of calculated shielding constants ($\sigma$) for each pair of hydrogens located symmetrically in the "southern" (B) and "northern" (A) phenanthrenes of the heptahelicene unit (see Scheme 2), that is, $\Delta\delta_{H1} = \sigma_{H24} - \sigma_{H1}$, $\Delta\delta_{H2} = \sigma_{H23} - \sigma_{H2}$, etc. We reasoned that, proceeding in this way might cause the errors derived from the calculation for each pair to be canceled in some extension and that the resulting values should correlate with the experimental difference of chemical shift for the same

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(19) Differences in zero-point energies and thermal corrections were estimated at the AM1 level to be smaller than 0.1 kcal/mol and are not included in ab initio and DFT calculations.

(20) (a) Chesnut, D. B. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, p 245. (b) de Dios, A. C. J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1996**, *29*, 229.

(21) Proton chemical shifts can be obtained with ±0.1 ppm absolute accuracy if rovibrational corrections and electron correlation are included and very large basis sets are used: (a) Sundholm, D.; Gauss, J.; Schäfer, A. *J. Chem. Phys.* **1996**, *105*, 1491. (b) Chesnut, D. B. *Chem. Phys.* **1997**, *214*, 73.

pair of protons. We accordingly computed the isotropic shielding constants $\sigma$ for **5**-*PM* and **5**-*PP*, for which we used the Gauge Invariant Atomic Orbitals (GIAO)[22] method implemented in the Gaussian 98 package. These calculations were performed at the HF/6-31G* level for HF/6-31G* geometries. As Table 1 and Figure 2 show, the experimental

**Table 1.** Calculated and Experimental *Relative Chemical Shift Increment* ($\Delta\delta_H$, as Defined in the Main Text of the Manuscript) for Hydrogens H1−H8

| H | $\Delta\delta_H$ (*MM*) | $\Delta\delta_H$ (*MP*) | experimental $\Delta\delta_H$ |
|---|---|---|---|
| H1 | −0.66 | 1.04 | 1.03 |
| H2 | −0.19 | 0.27 | 0.29 |
| H3 | −0.08 | 0.14 | 0.15 |
| H4 | −0.08 | 0.12 | 0.12 |
| H5 | −0.05 | 0.10 | 0.10 |
| H6 | −0.01 | 0.20 | 0.21 |
| H7 | 0.49 | 0.54 | 0.52 |
| H8 | 0.40 | 0.28 | 0.30 |

values agreed extremely well with those calculated for **5**-*PM*, while there is a clear deviation for the values calculated for **5**-*PP*, which is particularly evident for the hydrogens of the terminal rings that are subject to strong anisotropic effects.[23] We accordingly concluded that **5** was isolated in the thermodynamically more stable conformation *PM*.
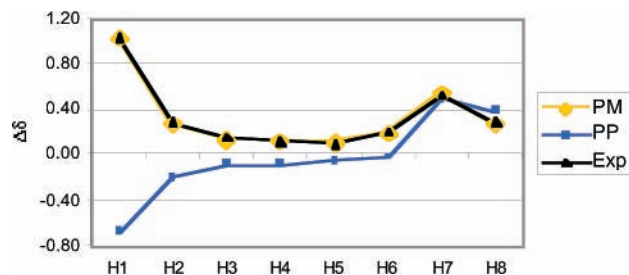


**Figure 2.** Plot of calculated and experimental *relative chemical shift increment*.

In conclusion, we have synthesized a novel, structurally unique double helicene and have established its relative stereochemistry by GIAO calculations of $^1H$ NMR data. In view of the extremely good agreement between the experimental and computed data, we believe that this procedure may be useful for determining the conformation of other large nonplanar polyarenes in solution.

(22) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(23) Similar good agreement was found for experimental and calculated $\Delta\delta_{H9} - \Delta\delta_{H16}$ (see Supporting Information). In these cases, $\Delta\delta_H$ values were also calculated taking each hydrogen atom in phenanthrene B as an internal reference for the shift of the symmetrically located hydrogen of phenanthrene C ($\Delta\delta_{H9} = \sigma_{H17} - \sigma_{H9}$, $\Delta\delta_{H10} = \sigma_{H18} - \sigma_{H10}$, etc).

**Supporting Information Available:** ^{1}H NMR, COSY, and NOESY spectra of **5**, full geometry and energy informa-tion, and a complete list with computed shielding constants, calculated $\Delta\delta_H$ for **5**-*PP* and **5**-*PM*, and experimental $\Delta\delta_H$ values. This material is available free of charge via the Internet at http://pubs.acs.org.

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