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## Kinetic Control in the Palladium-Catalyzed Synthesis of *C*<sub>2</sub>-Symmetric Hexabenzotriphenylene. A Conformational Study

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

Departamento de Química Orgánica, Universidad de Santiago de Compostela y Unidad Asociada al CSIC, 15706 Santiago de Compostela, Spain

qoenrgui@uscmail.usc.es

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## ABSTRACT



The hitherto unisolated, thermodynamically unstable  $C_2$ -symmetric conformer of hexabenzotriphenylene (1) has been efficiently synthesized by palladium-catalyzed cyclotrimerization of 9,10-didehydrophenanthrene (4). The barriers to conformational interconversion of 1 are examined experimentally and by computational studies.

The chemistry of overcrowded PAHs has become a field of increasing interest in recent years. This kind of molecule usually displays some grade of distortion from planarity to minimize steric strain,<sup>1</sup> giving rise to interesting structures such as helicenes,<sup>2</sup> twists, or propeller-like geometries.<sup>3</sup> The study of the structure and conformational stability of these molecules is important not only from the theoretical point of view but also for their potential applications in catalysis, material science, or supramolecular chemistry. A particular subclass of overcrowded PAHs is formed by molecules with

"ideal"  $D_{3h}$  symmetry, such as polysubstituted triphenylenes, which are forced to adopt conformations of lower symmetry to relieve steric congestion. Studies on the geometries of these compounds have shown that for most of them  $C_2$ symmetric conformations are preferred to the intuitively more predictable  $D_3$ -symmetric ones.<sup>4</sup> In general, the experimentally determined geometries are in accordance with the calculated lowest energy conformations.<sup>5,6</sup>

An interesting example of a nominally  $D_{3h}$ -symmetric PAH is hexabenzotriphenylene (dibenzo[ $f_{,j}$ ]phenanthro[9,10-s]-picene 1), a highly strained molecule whose synthesis has

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been shown to be difficult so far.<sup>7</sup> Recently Pascal and coworkers reported the preparation of 1 in 5% yield by FVP



of phenanthrene-9,10-dicarboxylic anhydride and its structural characterization as a  $D_3$ -symmetric molecular propeller.<sup>6</sup> Afterward, we reported a more convenient synthesis of **1** based on the palladium-catalyzed cyclotrimerization of 9,10-didehydrophenanthrene (9,10-phenanthryne, **4**) (Scheme 1).<sup>8,9</sup>



Further work carried out after our preliminary communication revealed two important new observations: (1) optimization of the procedure followed for the isolation of 1 from the reaction mixture led to an improvement in the yield from 39% to a remarkable 68%;<sup>10</sup> (2) heating of our compound in solution, or storage at room temperature for

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(10) **Experimental procedure:** To a solution of triflate **3** (106 mg, 0.27 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (14 mg, 0.013 mmol) in CH<sub>3</sub>CN (5 mL) was added finely powdered anhydrous CsF (122 mg, 0.8 mmol), and the mixture was stirred at room temperature for 12 h. The resulting suspension was filtered under vacuum. The solid obtained was washed with CH<sub>3</sub>CN (2 × 1 mL) and Et<sub>2</sub>O (0.5 mL) and dissolved in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O 9:1 (40 mL) The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through a short pad of SiO<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> as eluant), and concentrated under reduced pressure to afford **1** (32 mg, 68%) as a yellow solid, only slightly soluble in common organic solvents: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.63 (d, *J* = 8.0 Hz, 6H), 8.18 (d, *J* = 8.2 Hz, 6H), 7.59 (dt, *J* = 7.5, 1.2 Hz, 6H), 7.25 (dt, *J* = 7.6, 1.0 Hz, 6H); MS, *m*/*z* (%) 528 (M<sup>+</sup>, 29), 264 (16), 261 (66), 254 (100); HRMS for C4<sub>2</sub>P<sub>4</sub>, caled 528.1878, found 528.1869.

long periods of time (several months), led to the gradual disappeareance of the original signals and the emergence of new peaks in the <sup>1</sup>H NMR spectrum. Careful revision of the spectral data showed that the product, as originally isolated from our reaction, presented an <sup>1</sup>H NMR spectrum (Figure 1b) in which each signal was shifted 0.03–0.09 ppm



**Figure 1.** (a) <sup>1</sup>H NMR spectra (250 MHz) of  $1-C_2$  in CDCl<sub>3</sub> at 298 K; (b)  $1-D_3$  in CDCl<sub>3</sub> at 298 K (250 MHz); (c)  $1-C_2$  in 3:1 CS<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> at 200 K (500 MHz); (d)  $1-C_2$  in 3:1 CS<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> at 298 K (500 MHz).

downfield with respect to the data reported in the literature,<sup>11</sup> while the new emerging peaks were coincidental with these previously reported data (Figure 1a).

We attributed this unexpected observation to a conformational change in **1**. Taking into account that the compound obtained by Pascal had  $D_3$  symmetry, as determined by an X-ray analysis, we reasoned that the product obtained by us should be the thermodinamically less stable and hitherto unisolated  $C_2$ -symmetric conformer. The appearance of only four signals in the <sup>1</sup>H NMR spectrum (Figure 1b,d) could be due to rapid interconversion of the two possible  $C_2$ enantiomeric conformers (I and II) at room temperature. Note that in this case enantiomerization is achieved by slippage of two of the outer benzo groups (A and B in I and II, Figure 2) and that in this conversion the  $C_2$  axis is rotated by 120°. Subsequent conversions of this type eventually result in scrambling of the six benzo groups. Satisfyingly, when we carried out low-temperature NMR experiments, we observed at 200 K the splitting of each signal into three signals of equal intensity (Figure 1c), in accordance with the expected spectrum for a  $C_2$ -symmetric conformer. This result was rather surprising since semiempirical and ab initio calculations had shown a strong preference (by 5-9 kcal/mol) for the  $D_3$  geometry of 1.<sup>6</sup> Intrigued by our finding, we decided to carry out experimental and computational studies on the conformational stability of 1. Here we report the results of these studies.

The kinetics for the conversion of  $C_2$  to  $D_3$  conformations (II to III) were determined by <sup>1</sup>H NMR in 1,1,2,2tetrachloroethane- $d_2$ , at constant temperatures 55, 60, 65, 71, and 82 °C. The rate constants k for each temperature were determined from the first-order plots shown in Figure 3. From these data, the Arrhenius plot gave the activation energy  $E_a$ of 22.8 kcal/mol, while the activation parameters  $\Delta H^{\ddagger}$  (22.0

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<sup>(11)</sup> The data that we initially gave for the spectrum in CDCl<sub>3</sub>, identical to those previously reported,<sup>6,7</sup> were obtained from a sample that had been heated in solution for extended periods of time in an attempt to obtain a satisfactory <sup>13</sup>C NMR spectrum.



Figure 2. Schematic drawings of the  $C_2$  and  $D_3$  conformations and the transition states of hexabenzotriphenylene (1).

kcal/mol),  $\Delta S^{\ddagger}$  (-12.3 cal/(mol K)), and  $\Delta G^{\ddagger}$  (26.2 kcal/mol) could be calculated by application of the Eyring equation. This moderately high barrier to conversion reflects the relative kinetic stability that we observed for the  $C_2$  conformations at room temperature or below. The barrier to the much faster interconversion of the  $C_2$  enantiomers was estimated by dynamic NMR.<sup>12</sup> We registered the <sup>1</sup>H NMR spectrum of 1- $C_2$  in CS<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> (3:1) at different temperatures between 25 and -73 °C (200 K) and found that the spectrum displays coalescence of the signals marked with an asterisk in Figure 1c, at  $T_c = 247 \pm 2$  K, with  $\Delta \nu = 102$  Hz (at 500 MHz). From these observed values, the rate constant  $k_c$  ( $k_{247} = 226$  s<sup>-1</sup>) and the free energy of activation  $\Delta G^{\ddagger}$  (11.7 kcal/mol) for the racemization were determined.

The barriers to interconversion of the conformers of hexabenzotriphenylene (1) were also estimated by using



**Figure 3.** Rates of conversion of  $1-C_2$  to  $1-D_3$  in 1,1,2,2-tetrachloroethane- $d_2$  at constant temperatures 55, 60, 65, 71, and 82 °C.

computational methods. The ground states and the transition states for the interconversion processes were located at the semiempirical AM1<sup>13</sup> level using the SPARTAN program.<sup>14</sup>

The nature of any stationary structure was evaluated by way of vibrational analyses, with such structures identified as minima or transition states by the presence of zero or one imaginary vibrational frequencies, respectively. The geometries initially obtained were fully optimized at the ab initio Hartree—Fock level using the basis sets 3-21G and 6-31G-(d) of the GAUSSIAN program.<sup>15</sup> These fully optimized geometries for the  $C_2$  (II) and  $D_3$  (III) conformations, and for the transition states proposed for the racemization  $C_2$ —  $C_2$  (TS-I) and for the conversion  $C_2$ — $D_3$  (TS-II), are represented in Figure 2, together with schematic drawings which illustrate these geometries by showing the relative disposition of the six outer benzene rings of the molecule.

The structures of the transition states **TS-I** and **TS-II** resemble somehow the geometries of the transition states proposed for the racemization of [n]helicenes (n = 5-8),<sup>16,17</sup>

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with two outer benzo groups oriented face-to-face. The transition state for the racemization  $C_2-C_2$  (**TS-I**) presents  $C_s$  symmetry, while the transition state for the conversion  $C_2-D_3$  (**TS-II**) shows a highly distorted structure with  $C_1$  symmetry. This greater distortion accounts for the experimentally observed (and theoretically predictable) higher barrier to interconversion of  $C_2$  to  $D_3$  conformation than to racemization of  $C_2$  conformers.<sup>18</sup>

The results of the computations for the interconversion barriers are given in Table 1. All calculations showed that

Table 1.	Experimental and Calculated Barriers to			
Conformational Interconversions in Hexabenzotriphenylene				
(kcal/mol)	a			

	$C_2 - C_2$		$C_2 - D_3$
method	$\Delta H^{\sharp}$	$\Delta G^{\ddagger}$	$\Delta H^{\sharp}$
experimental		11.7 <sup>b</sup>	22.0
AM1	10.6 <sup>b</sup>	$11.5^{b}$	22.2 <sup>c</sup>
RHF/3-21G	14.2		31.2
RHF/6-31G(d)	12.5		30.2
B3LYP/6-31G(d)	10.6		26.5
B3LYP/6-311G(d,p)	11.4		26.7
BLYP/6-31G(d)	10.4		25.5
BLYP/6-311G(d,p)	10.1		24.5

<sup>*a*</sup> Differences in zero-point energies and thermal corrections were estimated at AM1 level to be smaller than 1 kcal/mol and are not included in ab initio and DFT calculations. <sup>*b*</sup> Determined for T = 247 K. <sup>*c*</sup> Determined for T = 341 K.

the barrier to interconversion of  $C_2$  to  $D_3$  is substantially higher than the one to  $C_2-C_2$  conversion. However, the quantitative results varied notably depending on the theoretical level used. Semiempirical AM1 calculated energies match the experimental results fairly well while, as expected, the ab initio Hartree–Fock calculations considerably overestimate the barriers of both processes, particularly for the  $C_2 D_3$  transformation, and the performance is not improved significantly by increasing the size of the basis set. An analogous trend has previously been reported for studies on the racemization of [5]helicene,<sup>17</sup> which demonstrates the usefulness of AM1 calculations for this kind of system. The large deviations of the ab initio Hartree–Fock barriers could be attributed to the neglect of electron correlation effects, which are expected to be important for the conformational changes that proceed through highly distorted transition states.

Single-point calculations at B3LYP<sup>19</sup> and BLYP<sup>20</sup> levels with several basis sets using RHF/6-31G(d) optimized geometries were also performed. The density functional methods (DFT), which include to some extent electron correlation effects, gave also barriers in good agreement with the experimental value for the racemization of the  $C_2$ conformers and only 2.5–3.5 kcal/mol above the experimental barrier for the  $C_2$ – $D_3$  process. The BLYP method gave slightly better values than the popular hybrid B3LYP method.<sup>21</sup>

In conclusion, we have shown that the palladium-catalyzed cyclotrimerization of 9,10-didehydrophenanthrene is an efficient, high-yielding method for the synthesis of hexabenzotriphenylene (1) and that the structure of the product obtained by this mild procedure has  $C_2$  symmetry, in contrast with previous results by other authors who isolated the thermodynamically more stable  $D_3$  conformer. Our studies on the conformational stability of 1 have demonstrated that the racemization of the  $C_2$ -symmetric conformers is a rapid process, while the conversion to  $1-D_3$  has a much higher barrier, which makes the  $C_2$  conformers relatively persistent at room temperature or below. The computational calculations performed, especially the semiempirical AM1 and DFT methods, are in good agreement with the experimental results and also with reports on mechanistically related processes such as the racemization of helicenes.

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**Supporting Information Available:** Variable temperature <sup>1</sup>H NMR spectra of **1**, details of the kinetic experiments, and full geometry and energy information. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(18)</sup> This proposal parallels in every respect the analysis of the conformational interconversion of perchlorotriphenylene (ref 4b), except for the symmetry of the  $C_2-D_3$  transition state.

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<sup>(21)</sup> For the racemization of [5]helicenes, the BLYP method has also been shown to be superior than the hybrid B3LYP (ref 17).