



Temperature induced rotation in a [4.4]cyclophane

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ABSTRACT

The synthesis, the X-ray, NMR and molecular modeling structure determination of a new ortho-para[4.4]cyclophane are reported. The similarity of the $\pi(\text{CO})-\pi(\text{Ar})$ driven conformational equilibrium of this compound to the work of an amusement ride machinery is also revealed.

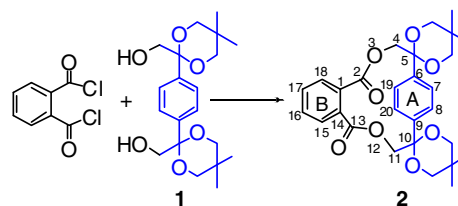
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Although their importance beyond chemical curiosities is yet to be demonstrated, the design (at molecular or supramolecular level) of architectures and machineries that can reproduce the work of motors,^{1,2} muscles,^{3–6} or (home) devices^{7,8} is a well-represented field of chemical research.^{9–16} Recent papers reveal the building of molecular shuttles,^{17–20} giant gyroscope,^{21–25} hinges,²⁶ tweezers,²⁷ and scissors.^{28,29} In a previous work,^{30,31} we obtained [7.7]cyclophane-based molecular rudders, wringer and rocking chair. Herein, we describe and investigate the unusual conformational behavior of more hindered [4.4]cyclophanes that could be used for building new molecular devices.

Orthopara[4.4]cyclophane **2** was obtained in fair yields starting from 1,3-dioxane diol **1** and phthaloyldichloride (Scheme 1).

The solid state molecular structure of **2** (Fig. 1) reveals as its most salient feature the proximity of the 1,4-phenylene ring to one of the CO groups (C^2O^4 in Fig. 1) and indicates $\pi-\pi$ interactions between these units.

According to the literature data,³² the short distance from O^4 to the center of ring A (3.12 Å) and the slightly tilted orientation of the planes of the ester group ($\text{O}^3\text{C}^2\text{O}^4$) and the opposite aromatic ring A (the dihedral angle between the two planes is $\omega = 28.53^\circ$) suggest the important overall stabilization of the structure by the



Scheme 1. Synthesis of cyclophane **2**.

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CO-aromatic interactions. These $\pi-\pi$ interactions are brought about by the *anti-anti* conformation of one of the chains $-\text{C}^{14}-\text{C}^{13}(\text{O})-\text{O}^{12}-\text{C}^{11}\text{H}_2-\text{C}^{10}-$ [torsion angles for the bonds $-\text{C}^{13}(\text{O})-\text{O}^{12}-$ and $-\text{O}^{12}-\text{C}^{11}\text{H}_2-$ are -176.63 and 167.46], the twisting of the other bridge to the *anti-anticlinal* conformation [the torsion angles for the bonds $-\text{C}^2(\text{O})-\text{O}^3-$ and $-\text{O}^3-\text{C}^4\text{H}_2-$ of the similar $-\text{C}^1-\text{C}^2(\text{O})-\text{O}^3-\text{C}^4\text{H}_2-\text{C}^5-$ moiety are -173.82 and -101.17], the deformation of the *para*-phenylene ring (the angle between the bonds C^5-C^6 and C^9-C^{10} is 31.86°) and the *face-tilted-to-face* arrangement of rings A and B ($\alpha_{A/B} = 36.35^\circ$). Additionally, $\text{C}-\text{H}-\pi$ and $\pi-\pi$ interactions of rings A and B are found in the lattice (shown in SI).

To investigate the molecular motions characteristic to this cyclophane, we took into account several conformational equilibria (Scheme 2). The dioxacyclohexane parts of the cyclophane are anancomeric (rigid) with axial disposition of the *para*-phenylene

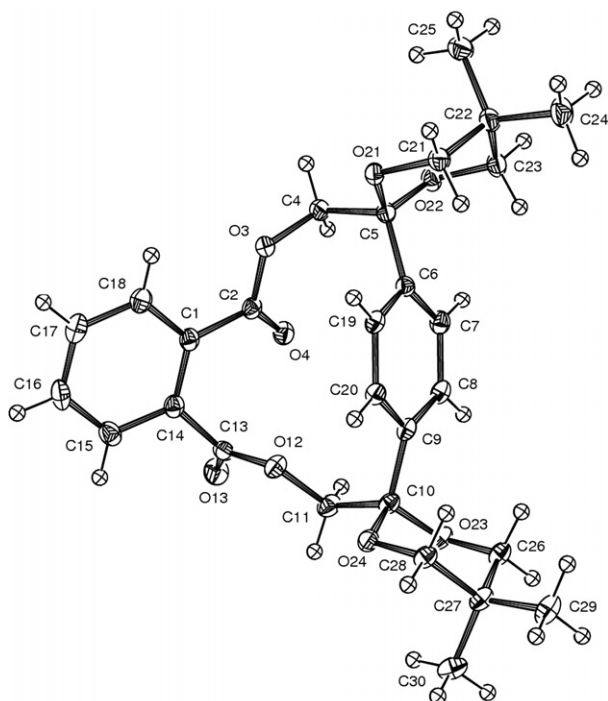
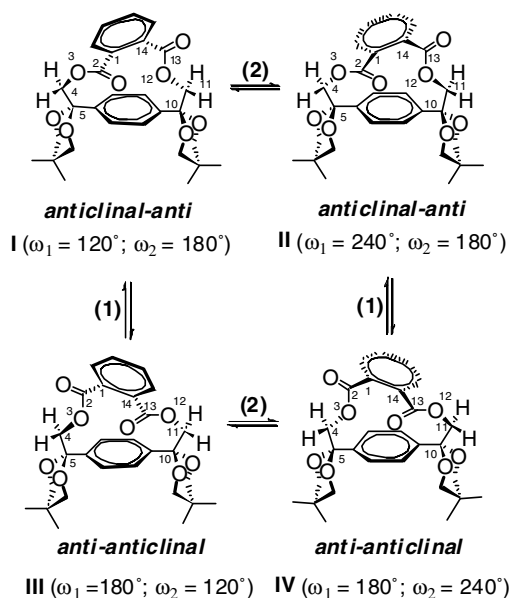


Figure 1. ORTEP diagram of compound 2.



Scheme 2. Flipping of the bridges and *outside-inside* movement of the CO groups in [4.4]cyclophane 2.

ring for both dioxacyclohexane units. The ester parts of the cyclophane (the bridges) are flexible and, therefore, allow the molecular motions of interest to take place. The conformational behavior of the bridges is complex and involves both the common (for [4.4]cyclophanes)³³ flipping of the *ortho*-phenylene ring (Scheme 2; equilibrium 2) and the *outside-inside* movement of the CO groups (Scheme 2, equilibrium 1, I \rightleftharpoons III; II \rightleftharpoons IV). This last conformational process requests the interchange of the *anti-anti* and *anti-anticlinal* conformations of the C(ar)-CO-O-CH₂-C(-O-CH₂)₂- parts of the bridges. This conformational change amounts

to $+60^\circ$ torsion around the O³-C⁴H₂ (ω_1) bond and -60° torsion around the O¹²-C¹¹H₂ (ω_2) bond. The flipping of the bridges requests the modification of the *anticlinal* conformer (I) to its enantiomeric structure (II) [rotation of $+120^\circ$ or -120° around O³-C⁴H₂ (ω_1) for I \rightleftharpoons II and around O¹²-C¹¹H₂ (ω_2) for III \rightleftharpoons IV]. We calculated the energies associated to these conformational changes (SI). The *inside-outside* movement of the CO groups (equilibrium denoted with 1 in Scheme 2) was found to have a small barrier (the value found by molecular modeling is $\Delta G^\ddagger = 6.6$ kcal/mol), while for the flipping of the bridges (denoted with 2) the calculated barrier is considerably higher ($\Delta G^\ddagger = 23.4$ kcal/mol).

These movements that push and pull at the same time in front and behind and shake the *ortho*-substituted phenylene ring can be compared with the work of a 'molecular amusement ride' (the support of the machine is represented by the *para*-phenylene moiety, the chair is the *ortho*-phenylene ring and the mechanism is formed by the -CO-O-CH₂- parts of the bridges, Fig. 2).

In order to experimentally observe the conformational changes in cyclophane 2, variable temperature ¹H and ¹³C NMR experiments were carried out (Figs. 3 and 4 and SI). The temperatures were increased or decreased and ¹H NMR spectra were recorded after each 10 °C temperature modification. We also compared the conformational behavior of molecule 2 in CDCl₃ (non competing

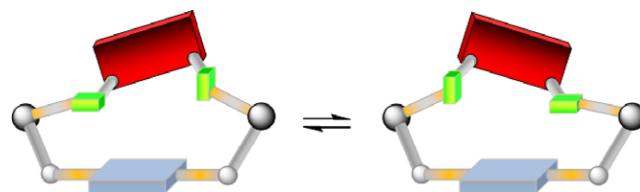


Figure 2. Macroscopic representation of the amusement ride machine.

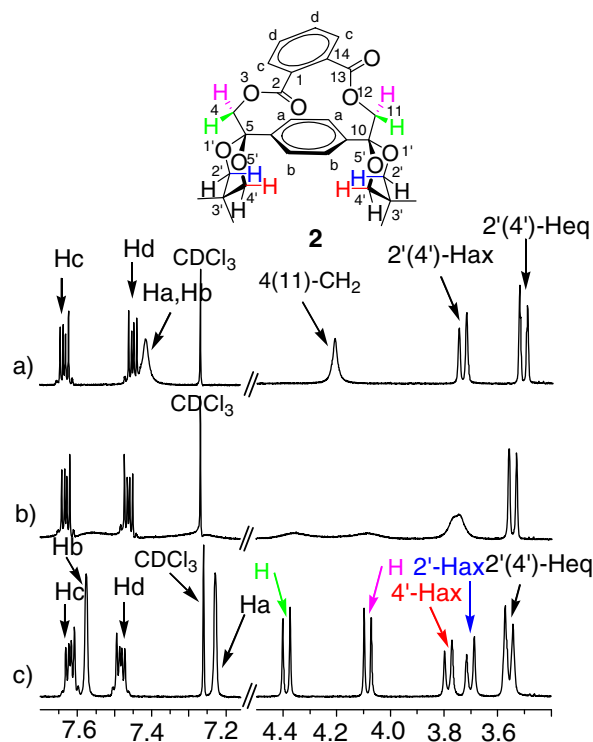


Figure 3. Variable temperature NMR experiments (CDCl₃) run with compound 2 (a: 330 K; b: 290 K; c: 220 K).

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