$[3_6]$(1,2,3,4,5,6)Cyclophane—A Molecular Pinwheel and Its Correlated Inversion: NMR and Energetic Considerations[⊥]

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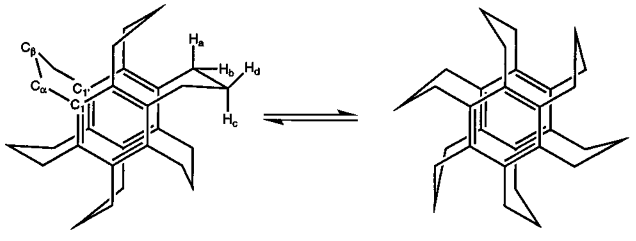
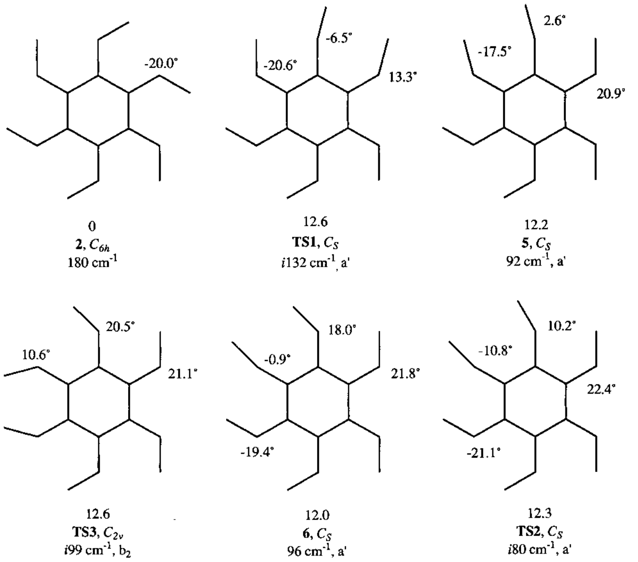
After Boekelheide's[1] achievement of "superphane" $[2_6]$-(1.2.3.4.5.6)cyclophane (**1**) in 1979, the recent synthesis of $[3_6]$-(1,2,3,4,5,6)cyclophane **2** by Sakamoto et al.[2,3] marks another milestone in cyclophane chemistry.[4−7] The fascinating structure of **2** resembles that of a "molecular pinwheel".[2] The trimethylene bridges invert rapidly at room temperature, and a 10.9 kcal mol^{-1} barrier for the degenerate **2a** ⇌ **2b** interconversion (Scheme 1) was deduced from variable temperature NMR spectroscopy.[3] Conformational NMR studies of various multibridged $[3_n]$cyclophanes suggest that the inversion process is not concerted.[8−13] However, for the inversion of a hexatuply bridged cyclophane no intermediates were characterized experimentally or even suggested. The title compound **2** has been proposed as a possible precursor for the unknown propella$[3_6]$prismane (**3**), which might be achieved by successive [2 + 2] photochemical ring closures.[2,3,14] We studied the molecular structure and the magnetic properties of **2**, its degenerate inversion, and its reaction to yield **3** using quantum chemical techniques.

Scheme 1. Flipping of the Trimethylene Bridges of **2** during Its Degenerate Rearrangement



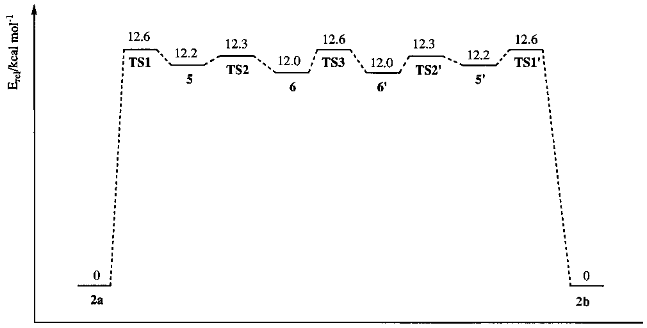
2a **2b**

Scheme 2. The Intermediates and Transition Structures (HF/6-31G*) Involved in the Flipping Process **2a** ⇌ **2b** Viewed along the 6-fold Symmetry Axis in C_{6h} **2**[a]



[a] The dihedral angles $\delta = \angle_{C\beta-C\alpha-C1-C1'}$ (as defined in Scheme 1) are given in degrees and the energies relative to **2** (HF/6-31G*) in kcal mol^{-1}. The lowest real or imaginary harmonic vibrational frequencies (HF/STO-3G) are also given.

Scheme 3. Schematic Representation of the $C_{30}H_{36}$ Potential Energy Surface for the Degenerate Interconversion between **1a** and **1b** at HF/6-31G*



Geometry optimizations of C_{6h} **2** and **3** were performed using classical mechanical force fields (MM2,[15] MM3,[16] and MM4[17]), semiempirical (MNDO,[18] AM1,[19] and PM3[20]), *ab initio* (HF), and hybrid Hartree−Fock/density functional methods, (BHLYP and B3LYP)[21−23] as implemented in Gaussian 94.[24] The basis sets employed are STO-3G, 6-31G*, and Dunning's[25] double−ζ basis set with polarization functions on both carbon and hydrogen (abbreviated as DZP). Harmonic vibrational frequencies were determined at the HF/STO-3G level. The NMR shielding tensors of **2** were calculated with the GIAO method[26,27] at the B3LYP/DZP level. We also computed the structures of **1** and of [3.3]-

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Table 1. Geometric Parameters for $[3_6](1.2.3.4.5.6)$Cyclophane **2** and Propella$[3_6]$prismane **3** (Both C_{6h} Symmetry) at Various Levels of Theory[a]

	2					**3**				
method	C1−C2	C1−Cα	Cα−Cβ	C1−C1′	δ	C1−C2	C1−Cα	Cα−Cβ	C1−C1′	δ
MM2	1.412	1.527	1.544	2.783	19.9	1.550	1.540	1.535	1.582	18.9
MM3	1.417	1.521	1.559	2.855	21.6	1.554	1.552	1.545	1.584	19.2
MM4	1.414	1.525	1.553	2.872	22.0	1.560	1.547	1.540	1.587	20.8
MNDO	1.429	1.526	1.551	2.912	13.4	1.568	1.544	1.551	1.611	4.1
AM1	1.409	1.495	1.522	2.773	20.2	1.535	1.509	1.533	1.639	15.4
PM3	1.405	1.502	1.529	2.823	22.5	1.546	1.513	1.537	1.600	7.2
HF/STO−3G	1.402	1.540	1.563	2.914	30.1	1.577	1.548	1.557	1.558	17.2
HF/6-31G*	1.399	1.529	1.555	2.989	20.0	1.572	1.538	1.549	1.549	18.2
B3LYP/6-31G*	1.411	1.528	1.560	2.985	20.1	1.581	1.539	1.556	1.567	18.2
B3LYP/DZP	1.414	1.528	1.562	2.982	20.4	1.581	1.536	1.558	1.567	18.2
BHLYP/DZP	1.402	1.519	1.549	2.965	20.5	1.551	1.510	1.531	1.542	19.6

[a] Bond lengths are in Å and angle $\delta = \angle_{C\beta-C\alpha-C1-C1'}$ (as defined in Scheme 1) is in degrees.

Table 2. Carbon−Carbon Bond Lengths (in Å) in Various Cyclophanes at B3LYP/DZP[f]

molecule	$C_{aromatic}-C_{aromatic}$	$C_{aromatic}-C_{aliphatic}$	$C_{aliphatic}-C_{aliphatic}$
1	1.417 (1.406)[a]	1.524 (1.518)[a]	1.606 (1.580)[a]
2	1.414	1.528	1.562
4		1.519 (1.512)[b]	1.554 (1.531)[b]
benzene	1.403 (1.390)[c]		
toluene	(1.396)[d]	(1.515)[d]	
ethane			(1.535)[e]

[a] X-ray; ref 28. [b] X-ray; ref 29. [c] IR; ref 31. [d] MW; ref 32. [e] MW, ref 33. [f] Experimental values are given in parentheses.

Table 3. Classical Barrier for the Degenerate Interconversion **2a** ⇌ **2b** at Various Levels of Theory (in kcal mol^{-1})

method	classical barrier[a]
AM1	9.3
HF/STO-3G	11.5
HF/6-31G*	12.6
B3LYP/DZP//HF/6-31G*	10.6
exp.	10.9[b]

[a] Zero point vibrational energy correction (HF/STO-3G) is −0.4 kcal mol^{-1}. [b] Reference 3.

paracyclophane (**4**), for which X-ray crystal structure analyses are available,[28,29] at B3LYP/DZP.

The geometries obtained for C_{6h} symmetric **2** with various theoretical methods agree well with each other (Table 1). In sharp contrast to less symmetrical cyclophanes, which are characterized by their "*bent and battered*" benzene rings,[4] **2** has planar rings with equal CC distances (Table 2). Compared to **1**, the longer trimethylene bridges in **2** result in a greater intramolecular distance between the two benzene moieties (2.9−3.0 Å in **2** vs 2.62 Å in **1**). However, the distance between graphite layers is considerably larger, 3.35 Å. Hence, the concentration of the π electrons in the space between the rings in **2** must repel the benzene rings away from each other. As a consequence, the $C_\alpha C_\beta C_{\alpha'}$ angle (see Scheme 1 for numbering) is 120°, considerably larger than the "normal" 112.4° angle observed in unstrained alkanes, e.g., propane.[30] Furthermore, the aromatic CC bonds in **2** are streched by roughly 0.01 Å with respect to benzene. Propella$[3_6]$prismane **3** is highly strained as its cyclohexane rings are severely distorted to achieve planarity. Thus, despite its six additional CC bonds, **3** is 110.8 kcal mol^{-1} (B3LYP/DZP) higher in energy than aromatic **2**.

The **2a** ⇌ **2b** isomerization is fast on the NMR time scale:[2,3] two groups of proton signals corresponding to H_a, H_b, and to H_c, H_d are observed at 20 °C. At −70 °C, these signals are resolved into four multiplets (3.09−3.32 [H_a], 2.70−2.85 [H_b], 2.41−2.68 [H_c], 1.60−1.79 [H_d]) with relative intensities of 2:2:1:1, indicating that the reversible process **2a** ⇌ **2b** is "frozen" at low temperatures.[3] The GIAO calculated chemical shifts (relative to TMS) are in reasonable agreement with both the low temperature ^1H NMR (calc.: 3.6 [H_a], 3.1 [H_b], 3.2 [H_c], 2.1 [H_d]) and room temperature ^{13}C NMR spectra (obs./calc.: 135.4/139.3 aromatic carbons, 28.5/33.4 $\boldsymbol{C}H_2CH_2\boldsymbol{C}H_2$, 20.5/26.7 $CH_2\boldsymbol{C}H_2CH_2$).[3]

The potential energy surface for degenerate conformational interconversion **2a** ⇌ **2b** is extremely flat and involves five transition structures and four minima besides **2** (Scheme 2) differing in energy by less than 0.6 kcal mol^{-1}. In the first transition structure (**TS1**), one of the methylene bridges has completely "flipped" ($\delta_1 = \angle C\beta-C\alpha-C1-C1' = 13.3°$) and pushed the adjacent bridge considerably away ($\delta_2 = -6.5°$) from its orientation in **2** ($\delta = -20.0°$). Continuing the trimethylene bending motion, which is associated with an imaginary vibrational frequency results in **5** with two bridges flipped. The structure with three flipped bridges is a C_{2v} symmetric transition state **TS3**, 12.6 kcal mol^{-1} above **2**. Due to the symmetry of the system, **2b** is reached from **TS3** via **6′**, **TS2′**, **5′**, and **TS1′**, as shown in Scheme 3. Our calculations suggest a sequential flipping process **2a** ⇌ **2b** with barriers at various levels (Table 3) which agree well with experiment (10.9 kcal mol^{-1}). A synchronous mechanism involving a D_{6h} symmetric structure is ruled out by its high energy (43.5 kcal mol^{-1} above **2**) and seven imaginary vibrational frequencies.

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Note Added in Proof. Similar results were obtained recently by Hori et al. at the HF/6-31G level.[34] Note that these authors did not completely characterize the flipping process **2a** ⇌ **2b** and only located one transition structure (**TS1**) on this PES.

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