

Theoretical investigation of the structures and dynamics of molecular gyroscopes encapsulating halogen-substituted phenylene rotators

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I. Introduction: The crystalline molecular gyroscopes encapsulating phenylene rotators have received much attention in terms of their unique structures, dynamics and functions. Especially halogen-substituted phenylene-bridged molecular gyroscopes are expected to have dipolar units that can be reoriented under the influence of electric fields [1]. Recently, Setaka et al. have reported the synthesis and structure of the novel molecular gyroscopes having halogen-substituted phenylene rotators encased in three long siloxaalkane spokes (Stator) [2]. They observed two different stable positions for the difluorophenylene rotator at 273 K (Fig. 1) and only one position for the dichlorophenylene rotator at 153 K. Similarly, a

strong deformation of the siloxaalkane spokes caused by the steric interaction with the halogen atoms on the central phenylene ring has also been reported. During the course of theoretically investigating crystal structures and rotational dynamics of experimentally synthesized crystalline molecular gyroscopes, we are interested in a crystalline molecular gyroscope having a difluorophenylene rotator (ROT-F). The notable results explored currently are reported here.

II. Method: Recently, we applied the Density Functional based Tight Binding (DFTB) method [3] to investigate the molecular packing structure and rotary dynamics of the crystalline siloxaalkane molecular gyroscope having a phenylene rotator (ROT-H) [4]. We achieved good agreements with the experimental results. Therefore, in our present study, we have also applied the same theoretical method for characterizing crystalline ROT-F. In accordance with the experimental condition, a periodic boundary condition (PBC) is imposed in the calculations. By using the force constants computed by DFTB, the motions of all nuclei are evaluated based on the classical mechanics with constraints on the lattice constants of the unit cell.

III. Results and Discussions: The X-ray geometries of the unit cells of two degenerate molecular structures of ROT-F are semiquantitatively reproduced by the DFTB method except the Si-O-Si angles of the highly flexible siloxaalkane spokes (see Table 1). These angles are more acute in ROT-F than in ROT-H derivative. It indicates that the siloxaalkane-cage of the ROT-F expands outward with respect to the oxygen atom for accommodating more bulky rotator. In order to confirm it, we measured the intervening space that exists between an oxygen atom of each siloxaalkane arm and the nearest carbon atom of the phenylene ring (O-C distances: d_1 , d_2 and d_3 in Fig. 2) for ROT-F and ROT-H and found that ROT-F possesses

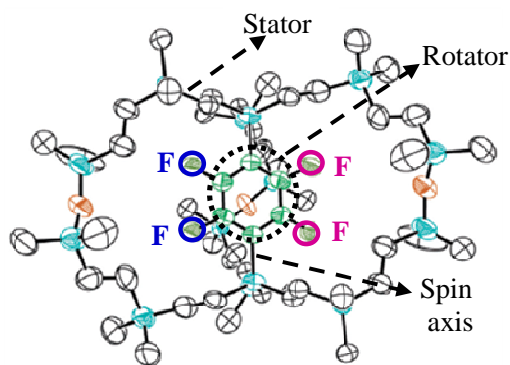


Fig.1. An X-ray crystallography of the siloxaalkane molecular gyroscope having a difluorophenylene rotator at 273 K. Two stable positions of the rotator differ by π flipping are shown.

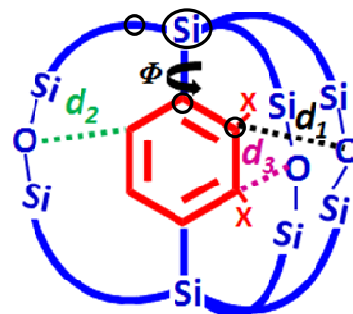


Fig.2. A schematic representation of the siloxaalkane molecular gyroscope. The encircled atoms define the dihedral angle. X = H for ROT-H and X = F for ROT-F.

comparatively large amount of clearance around the rotating unit (see Table 1). It assures that the shape of the siloxaalkane-cage in ROT-F deforms from that of the ROT-H derivative to avoid steric effects with the fluorine on phenylene. To estimate a rotational energy barrier (E_a) of the ROT-F, we scanned the potential energy surface (PES) under PBC (Fig. 3) and found that the difluorophenylene rotator experiences as high as 1700 cm^{-1} energy barrier (E_a of the phenylene rotator in ROT-H $\cong 250\text{ cm}^{-1}$ [4]). The PES clearly displays two stable degenerate molecular structures, α and α' and their relation by π difluorophenylene flipping. It confirms the two-fold rotational axis of the ROT-F molecule with respect to the difluorophenylene rotator. These theoretical findings are in reasonable agreements with the experimental observations. Moreover, we performed DFTB / molecular dynamics (MD) simulations of the ROT-F at 1200 K and 300 K, and calculated the concerned dihedral angle that designates the difluorophenylene orientation at each MD step. At each kinetic temperature, the initial angle of the difluorophenylene ($\sim 0.44\pi$) corresponds to its equilibrium position α as shown in Fig. 4 and from this position; difluorophenylene ring is observed to flip by π and reaches to its degenerate position α' ($\sim 1.44\pi$). The timescale of the π flipping at high temperature is found to be shorter than at moderate temperature, as expected.

Table 1. X-ray vs. DFTB optimized parameters

Molecular gyroscopes	Si-O-Si angle (π)		O-C distance (\AA)			Phenylene dihedral angle (π)	
	X-ray	DFTB	X-ray	DFTB	DFTB	X-ray	DFTB
ROT-F	0.96	0.78	d_1	8.4	7.7	0.56	0.44
	0.84	0.75	d_2	5.9	5.5		
	0.84	0.74	d_3	5.9	5.8		
ROT-H	0.96	0.81	d_1	5.2	5.3	0.55	0.35
	0.90	0.77	d_2	4.3	4.1		
	0.96	0.81	d_3	3.9	4.1		

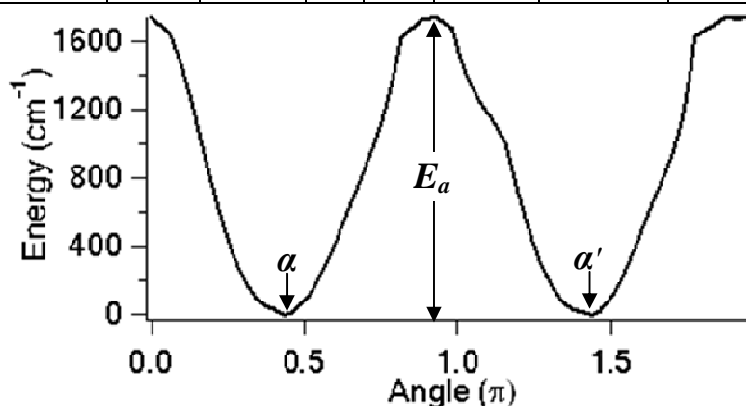


Fig.3. Potential energy as a function of the difluorophenylene angle obtained by DFTB under PBC.

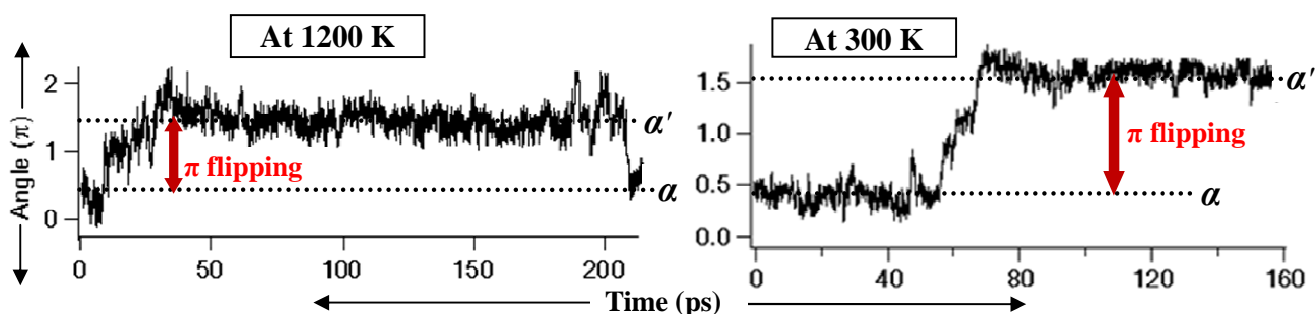


Fig.4. Rotational angle of difluorophenylene as a function of time at 1200 K and 300 K.

IV. Conclusion: We successfully located two degenerate molecular structures of the ROT-F under crystal condition. They are found to be related to each other by π difluorophenylene flipping and have to cross $\sim 1700\text{ cm}^{-1}$ energy barrier to undergo structural exchange between them. The flipping motion of the difluorophenylene inside a cage of the siloxaalkane spokes at high and moderate temperatures indicates a promising function as a molecular gyroscope.

References : [1] Garcia-Garibay et al. *J. Am. Chem. Soc.*, **124** (2002) 7719. [2] W. Setaka et al. *Chem. Lett.* **39** (2010) 468. [3] D. Porezag et al. *Phys. Rev. B*, **51** (1995) 12947. [4] A. B. Marahatta et al. (to be submitted).