

Theoretical investigation of the structures and dynamics of synthesized molecular gyroscopes

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I. Introduction: The synthesized macrocyclic compounds with framed molecular rotators have been receiving attention as a fundamental element of nanotechnology. Crystalline molecular gyroscopes with bridged π -electronic systems have many interesting physicochemical properties. For example, the dipolar unit of a rotator in the crystal can be reoriented under the influence of external stimuli [1]. Recently, an X-ray crystallography of the novel molecular gyroscope with a phenylene rotator encased in three long siloxaalkane spokes has been reported (Fig. 1) [2] and facile rotation of the phenylene ring is observed between three stable positions. To investigate its structures and the rotational dynamics theoretically, we have performed series of quantum chemistry calculations. Notable results explored currently are reported here.

II. Methods: In order to reveal the molecular packing structure and the dynamics of this molecular gyroscope, the Non-self-Consistent Charge (NCC)-and Self-Consistent Charge (SCC)-Density Functional based Tight Binding (DFTB) methods [3] implemented in DFTB+ program package were employed [4]. In accordance with the experimental condition, a periodic boundary condition (PBC) with or without dispersion energy correction [5] was imposed in calculations. By using the force constants computed by DFTB, motions of all nuclei were evaluated based on classical mechanics with constraints on shape and volume of the unit cell.

III. Results and Discussions: The X-ray geometries of the unit cell of all three stable molecular structures are semiquantitatively reproduced by both NCC- and SCC-DFTB methods except the Si-O-Si angles of the highly flexible siloxaalkane spokes. No significant effect of dispersion energy correction is observed in optimized geometries. DFTB optimized parameters of the most stable structure are summarized in Table 1. Prior to the calculation of the rotational potential energy surface (PES)

under PBC, the qualitative agreement between DFTB and DFT (B3LYP/6-31G**) was confirmed for an isolated siloxaalkane gyroscope. We have first calculated the PES without dispersion energy and found that the rotational barrier is as high as 250 cm^{-1} . The potential is found to be asymmetric and hence expected to exhibit unidirectional rotation (Fig.2a); it also displays three stable positions of phenylene upon 1π rotation which are in reasonable agreement with the experimental observation (Table 2). Furthermore, the potential is periodic by π with respect to phenylene rotation. The SCC-DFTB method with dispersion energy correction revealed the similar appearance of the PES but the rotational height of $\sim 400\text{ cm}^{-1}$ is due to the inclusion of the van der Waals interaction (Fig.2b). These substantially low rotational barriers clearly indicate the efficiency of the encapsulating spokes to isolate the rotator from the neighboring molecules.

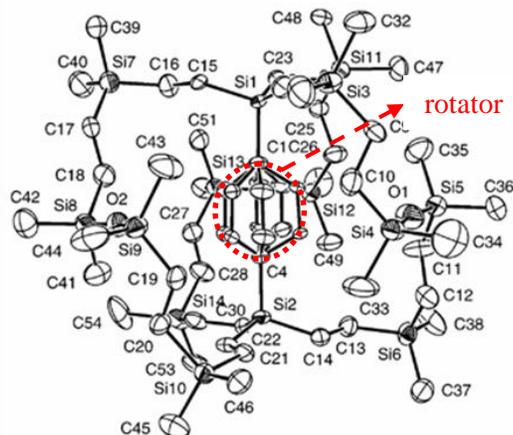


Fig.1. X-ray crystallography of a molecular gyroscope at 223 K [2]. Three stable positions of the central phenylene are shown.

Table 1: DFTB optimized parameters

| Methods | Si-O-Si angle of each arm | Distance (Å) (O & C atom of phenylene) | Dihedral angle of phenylene and Energy (E_n) |
|----------------|--|--|--|
| X-ray geometry | 0.90 π 0.96 π 0.94 π | 3.9 4.3 5.2 | 0.31 π |
| <u>DFTB</u> | | | |
| a) NCC | 0.79 π 0.78 π 0.81 π | 4.1 4.1 5.3 | 0.38 π $E = -336.52339$ |
| b) SCC | 0.80 π 0.79 π 0.83 π | 4.1 4.1 5.3 | 0.38 π $E = -336.08949$ |

Moreover, for the NCC-DFTB/MD simulations with (case II) and without (case I) dispersion correction at all temperatures (1200K, 800K, 600K, 300K), the initial angle of rotation is one of the local minima at around $\Phi=0$. In case I, the trajectory at 800K shows < 15 ps for the direct 1π phenylene flipping whereas in case II, it takes > 15 ps due to much higher barrier felt by the rotator. Similarly, at

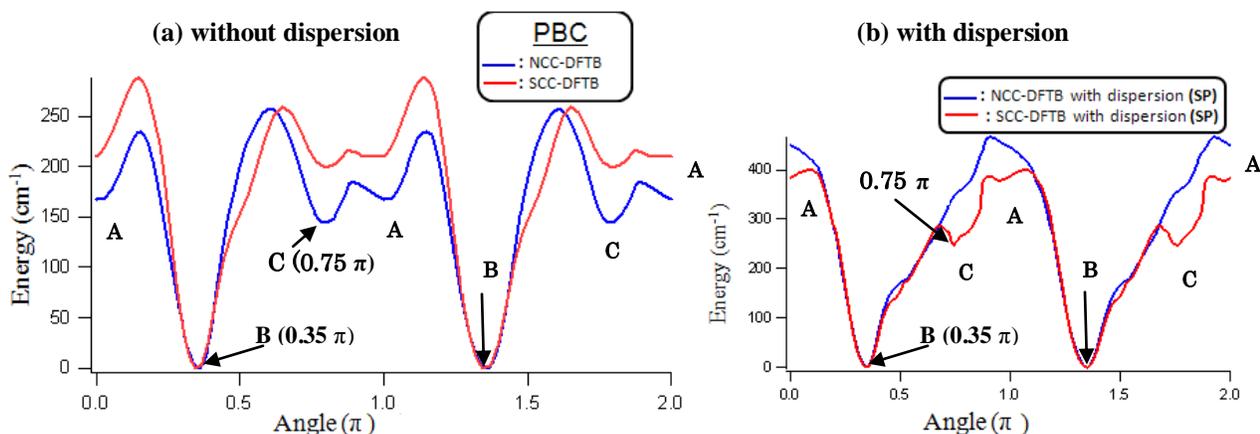


Fig.2 (a,b). Potential energy as a function of the phenylene dihedral angle

room temperature, in case I, the rotator flip-flops between the local minimum **A** and the global minimum **B** up to ~ 250 ps but in case II, it flips between three minima **A**, **B** and **C** with in 90 ps time scale. The rotational heights calculated by applying Arrhenius equation are 271 cm^{-1} and 650 cm^{-1} in case I and II respectively which are almost consistent with the heights observed at the PES (Fig.2).

Table 2: X-ray & DFTB structures

| Phenylene position | Angle Φ (π) | |
|--------------------|-------------------------|-------------|
| | Experiment ² | DFTB theory |
| First | 0.082 | 0 |
| Second | 0.31 | 0.35 |
| Third | 0.68 | 0.75 |

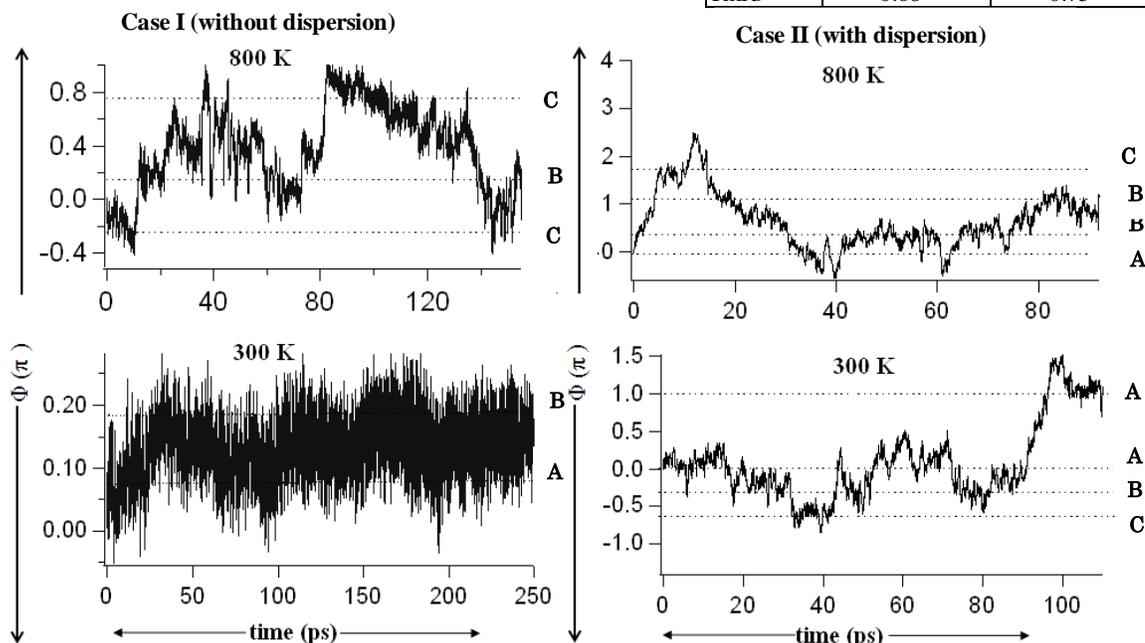


Fig.3. Rotational angle of phenylene as a function of time at 800 K and 300 K

IV. Conclusion: Inclusion of the self-charge consistency is found to be mandatory to address much weaker van der Waals interaction present in our gyroscopic system. The appearance of low rotational barriers, which is highly demandable for synthesizing crystalline free rotor, indicates a promising function as a molecular gyroscope. The facile phenylene flipping inside the cage of siloxaalkane spokes at low and high temperatures demonstrates the existence of sufficient free volume around the phenylene rotator.

References : [1] Garcia-Garibay et al. *J. Am. Chem. Soc.*, **124** (2002) 7719. [2] W. Setaka et al. *Chem. Lett.* **36** (2007) 1076. [3] D. Porezag et al. *Phys. Rev. B*, **51** (1995) 12947. [4] B. Aradi et al. *J. Phys. Chem. A*, **111** (2007) 5678 and C. Köhler et al. *Phys. Rev. B*, **64** (2001) 085333. [5] M. Elstner et al. *J. Chem. Phys.*, **114** (2001) 5149.