

A Theoretical Study on the Photoisomerization of Stiff Stilbene: a Model of Light-Driven Rotary Molecular Motor

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Molecular rotary motors, though common in nature, were synthesized rather recently. One of the most promising categories of artificial light-driven rotary molecular motors allowing for optical control is based on helical overcrowded alkenes. For instance, light-driven rotary molecular motors (**3** in Chart 1) based on stilbene **1** have been synthesized by Feringa's group. By introducing helical substitutions into these overcrowded alkenes, the authors have successfully harnessed the nondirectional motion to achieve a unidirectional, 360° rotation around the central carbon-carbon double bond (Fig. 1). The rotational process consists of four steps, two of which occur in the electronically excited state and involve *cis*–*trans* isomerization of the central carbon-carbon bond. Though the mechanisms of these photo-initiated processes are important in rationalization of the chemical nature of the currently synthesized rotary molecular motor and to design new promising motors, they have not been well understood yet. In the present study, we carried out complete active space self-consistent field (CASSCF) calculations to explore the rotary potential-energy surface (PES) of stiff-stilbene-based molecular motor **3** in order to understand the reaction mechanism of the photoisomerization reaction and rationalize the unidirectionality of the rotation.

The *cis*-*trans* photoisomerization of stilbene has been extensively investigated. For free stilbene (**1** in Chart 1) both *trans*→*cis* and *cis*→*trans* isomerization can take place. Though their dynamics are evidently different, the wave packet from both isomers can access a conical intersection (CI) with perpendicular conformation near the minimum of the S_1 state. The ideal branching ratio of the *cis*- and *trans*- products is 50:50. The one-dimensional rotational PESs are symmetric around $\theta = 0$ and 180° for the *cis*- and *trans*-**1**, respectively.

Introducing two 5-membered rings into free stilbene produces stiff stilbene **2** (Chart 1). The 5-membered ring in **2** not only prohibits the photocyclization side reaction (which is the predominant side process in free stilbene **1**) but also more or less fixes C1–C2 bond thus makes *hula-twist* mechanism unfeasible. Therefore, the symmetry of the excited-state PESs around the Frank-Condon (FC) region of *trans*-**2** remain, while the one around *cis*-**2** has been removed by the steric compulsion between the two benzene moieties which is only significant in the *cis*-isomer. In order to avoid the high cross-plane rotational barrier, the C2–C1–C1'–C2' and C3–C2–C1–C1' dihedral angles increase

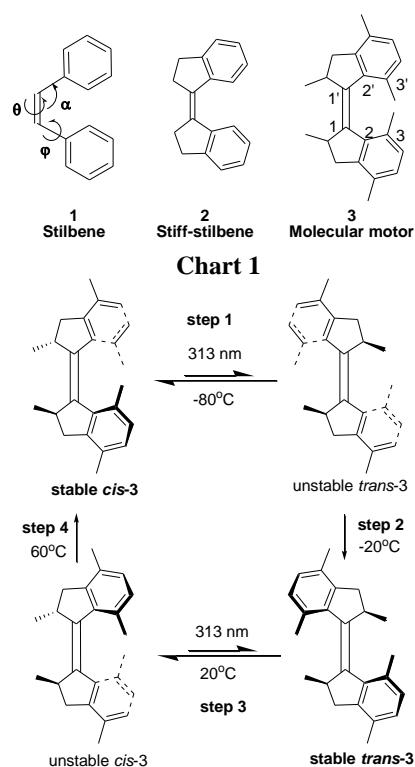


Figure 1. Four-step rotation in stiff-stilbene-based molecular motor **3**.

(or decrease) simultaneously, resulting in the helically twisted conformation and asymmetric excited-state PESs. Further introducing methyl group into stiff-stilbene **2** slightly changed the geometry of the *cis*-**3**, while put significant effects on *trans*-**3**. The strong methyl-methyl compulsions alternate both the ground- and excited-state PESs around *trans*-minimum into sloped. Tracking the geometry variation along the rotational coordinates suggests that after the photoexcitation the molecule follows the twist motion to reach the perpendicular excited-state intermediate, which represents a conformation better matching the product than the reactant. Therefore, the steric effects of 5-membered rings and the methyl groups which evidently slope the excited-state 1B surface, partially account for the unidirectionality rotation of molecular motor **3**.

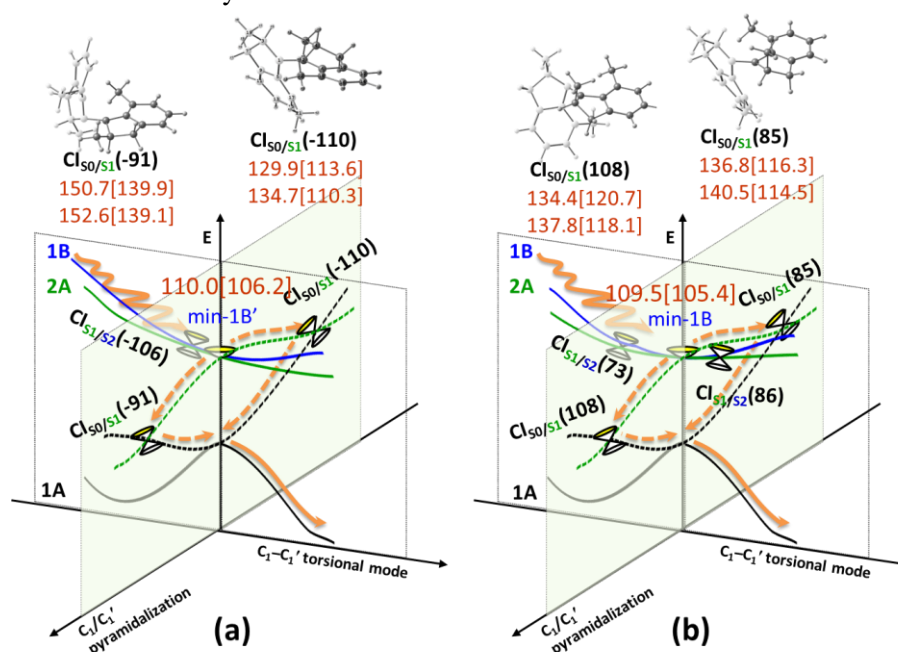


Figure 2. The reaction paths around intermediates in 1B state: (a) *min*-1B' ($\theta = -98^\circ$) in photoisomerization step 1 and (b) *min*-1B ($\theta = 85^\circ$) in photoisomerization step 3.

It is found that the photoisomerization process undergoes a 3-state, 2-coordinate mechanism: The excited molecules in 1B state first decay to 2A state through the 1B/2A seams along the primary C_1-C_1' torsional coordinate, and then follow the C_1/C_1' pyramidalization to cross the 2A/1A conical intersection and return to the ground-state PES. Along the primary reaction coordinate, several excited-state intermediates, on both the 1B and 2A states, were located. The 1B and 2A PESs approach each other from the FC region of *cis*-**3** (or *trans*-**3**) to the perpendicular intermediate region and finally intersect with each other in the vicinity of the 1B minimum (*min*-1B or *min*-1B'). The located MECPs on the 1B/2A seams have a "peak" nature and are almost identical in energy with the 1B intermediates, thus they provide opportunities for the molecules on the 1B PESs to barrierlessly access the energetically more favorable 2A surface. Moreover, with the torsional angle increasing from planar to perpendicular, the double-bond character of the central C_1-C_1' bond is weakened, correspondingly the C_1 and C_1' have high mobility along the carbon pyramidalization coordinate. Indeed, two S_0/S_1 MECPs can be found on either directions of the pyramidalization coordinate (Fig. 2). Before the excited-state molecule could cross the CI_{S₀/S₁} to reach 1A surface, they have to overcome 10~30 kcal/mol energy barriers. In short, our calculations rationalize the unidirectionality of the rotation and suggest a possible reaction mechanism for the stiff-stilbene rotary molecular motor.