Intramolecular Torque Study of a Molecular Rotation Stimulated by Electron Injection and Extraction

Chen Lei
Department of Physics, City University of Hong Kong

Fei Qi
Institute of Computational and Theoretical Studies & Department of Physics, Hong Kong Baptist University

Kulpavee Jitapunkul
Department of Physics, City University of Hong Kong

Yanling Zhao
Department of Physics, City University of Hong Kong

Ruiqin Zhang
Department of Physics, City University of Hong Kong

See next page for additional authors

This document is the authors' final version of the published article.
Link to published article: https://doi.org/10.1021/acs.jpca.8b04368

APA Citation
An Intramolecular Torque Study of a Molecular Rotation
Stimulated by Electron Injection and Extraction

Lei Chen,¹,³ Fei Qi,² Kulpavee Jitapunkul,¹ Yanling Zhao,¹,⁴ Ruiqin Zhang,¹,⁴,* Michel A. Van Hove²,*

¹Department of Physics, City University of Hong Kong, Hong Kong SAR, China
²Institute of Computational and Theoretical Studies & Department of Physics, Hong Kong Baptist University, Hong Kong SAR, China
³School of Medicine, Yangzhou University, Yangzhou, Jiangsu 225001, China
⁴Shenzhen Research Institute, City University of Hong Kong, Shenzhen 518057, China

*Corresponding author e-mail: aprqz@cityu.edu.hk
*Corresponding author e-mail: vanhove@hkbu.edu.hk

ABSTRACT:

Rotation-inducing torque based on interatomic forces is a true indicator of internal molecular rotations. We use the induced intramolecular torque to study the underlying rotational mechanism stimulated by an electron injection or extraction for the rotor molecule 9-(2,4,7-trimethyl-2,3-dihydro-1H-inden-1-ylidene)-9H-fluorene, which consists of a “rotator” fragment and a “stator” fragment. The results show that the charged molecule in a quartet spin state can rotate internally, while that in the doublet state cannot. The torque on the rotator in the quartet state always maintains unidirectional rotation. In addition, the attachment/extraction of an electron leads to the reduction of the rotational energy barrier by about 18 kcal/mol, facilitating a more favorable molecular rotation than in the neutral singlet state. Our finding provides a molecular-level understanding of various transformation pathways for experimental designs and further demonstrates the effectiveness of the torque approach.
Introduction

Rotation-inducing torque, which is ubiquitous in many molecular motors, is an efficient indicator of the molecular rotation.\textsuperscript{1-3} It can provide insights into the possibilities of internal rotations in all kinds of molecules and facilitate their modification through computational design in advance of experiments, along with an efficient guidance from a detailed analysis of their rotational behavior. In the past decade, the Feringa group has experimentally obtained a series of molecular motors with unidirectional rotation characteristics.\textsuperscript{4-6} One of them is the light-driven molecular rotary motor 9-(2,4,7-trimethyl-2,3-dihydro-1H-inden-1-ylidene)-9H-fluorene, which we call TDHY-fluorene in this paper and present in Figure 1. This molecule is well known for its continuously unidirectional 360° rotation around the central C=C bond axis. The rotational cycle consists of four steps, two of which occur in the electronic excited states (steps 1 and 3), while the other two are thermal helix inversions from meta-stable to stable isomers at ground states (steps 2 and 4). To reveal its underlying mechanism, theoretical studies have been performed by extensively mapping the rotational configuration trajectories in multidimensional space, which require high-quality and time-consuming calculations because of an exhausting search through a high-dimensional structural space.\textsuperscript{7-8} In our previous work,\textsuperscript{9} we proposed a convenient “torque” estimation method to qualitatively track its light-driven unidirectional rotation based on density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations.
Figure 1. Four-step rotation scheme in a light-driven molecular rotary motor, here called TDHY-fluorene. Two photochemical and two thermal steps are involved in a complete 360° rotary cycle. The different dihedral angles are given for each state and marked as 1-2-3-4 to track the rotation of the rotator (red) along the C=C axis linking it to the “stator” (black). (In reality, the “stator” can also rotate, if only for conservation of angular momentum.)

Lowering the activation energy is an effective way to promote a chemical reaction. Since the early days of electrochemistry, it has been widely known that the creation of radicals by injecting/extracting a single electron into/from the reactants may facilitate reactions.\(^{10-11}\) The study of the prominent role of the electron in chemical reactions has been restricted to the electron-induced dissociation mechanism. Through the use of high-level \textit{ab initio} methods, Cederbaum’s group demonstrated that the barrierless cis–trans isomerization can be realized by attaching a single electron to the dicyanoethylene molecule.\(^{12}\) Analysis of the electronic structure indicated that both electron affinity (formation of anionic radicals) in the π* orbitals of neutral olefins and electron ionization (generation of cationic radicals) in the π orbitals can significantly weaken the C=C double bond of the neutral molecule and
make the cis-trans isomerization occur more easily. In the past decade, electron injection or removal has been performed in many tip-induced isomerization experiments using a scanning tunneling microscope (STM) which can transfer electrons between the tip and the substrate.\textsuperscript{13-17} These experiments demonstrated that complicated reactions occur when they are accompanied by the electron transfer, for example, multiple bond-breaking,\textsuperscript{16} tautomerization,\textsuperscript{17} and complex fragmentations.\textsuperscript{18} However, the underlying microscopic mechanism of the electron-driven chemical reactions is not fully understood and requires further detailed study in order to achieve reasonable designs for experiments.

Herein, we present a detailed theoretical study concerning the molecular rotation behavior of TDHY-fluorene induced by an electron injection / extraction. Since TDHY-fluorene is a successful light-driven molecular rotary motor\textsuperscript{4-6} which tends to rotate after photo-excitation, another way to observe its intramolecular rotation by electron injection and extraction is conceived. Because many research groups investigate the rotation of molecules undergoing electron gain and loss, by means of theoretical calculations and STM experiments,\textsuperscript{12-17} we propose to investigate whether the electronic configuration variation in this molecule would be also helpful to start a more efficient rotation. The evaluation of its rotational ability is obtained by employing the torque approach based on atomic forces calculated at the density functional theory level of CAM-B3LYP/6-31+G(d,p). We confirm its rotational tendency by describing the anionic or cationic potential energy surface (PES) towards isomerization. Thus, from the microscopic mechanism analysis of this useful
characteristic, we gain a new understanding of the electron-driven chemistry that has not been well explored yet.
Computational Details

All calculations were performed using density function theory (DFT) methods implemented in the Gaussian 09 package,\textsuperscript{19} with the hybrid functional CAM-B3LYP\textsuperscript{20-21} and the basis set 6-31+G(d,p).\textsuperscript{22-23} The reliability of this functional has been validated in our prior study\textsuperscript{9} by comparing the excitation energies of two equilibrium states of the TDHY-fluorene molecule with reported higher levels of calculation using TD-BH&HLYP/6-31G(d) and SA-REBH&HLYP/6-31G(d) functionals.

The torque approach which we introduced in earlier work allows rapidly and qualitatively predicting the rotational possibility of a rotary motor using atomic forces and coordinates, after choosing a suitable rotational center, via single-point total-energy calculations of unequilibrated configurations.\textsuperscript{9} To study either initial or subsequent rotation, the torque referred to a selected rotation center can be simply calculated from the forces acting on each individual atom and may be projected accordingly if an obvious axis of rotation is available, such as a single strong C=C bond acting as an "axle" between the stator and the rotator in TDHY-fluorene. Once the initial direction of rotation is obtained, one may follow the rotation by turning the rotator rigidly through a few steps in that direction, repeating the foregoing at each step. It is assumed that the rotator’s rigidity is particularly valid in ultrafast light driven processes, as observed experimentally for another similar rotor molecule where rotation happens on a timescale of tens of femtoseconds after the photo-excitation,\textsuperscript{24} much faster than the relaxation of the functional groups in the excited state.
Afterwards, on the longer timescale, the radiationless transition back to the ground state conformer should be studied with a local optimization by constraining a suitable dihedral angle for updating the direction of rotation due to shape and state changes in this rotor molecule. Thus, this approach includes regular cases of flexible molecules, which can change their shape and electronic structure during rotation. Single point calculations of DFT can generate atomic force vectors, i.e., the analytical gradients of total energies with atomic coordinates, which can be used to further calculate the needed torques for rotation predictions according to the following scheme. The total torque on a rotator is obtained as the vector $\vec{T} = \sum_i \vec{r}_i \times \vec{F}_i$, where $i$ runs over all atoms of the rotator, $\vec{F}_i$ is the total force acting on atom $i$ from all other atoms in the molecule, and $\vec{r}_i$ is the position of atom $i$ relative to a reference point. The direction of rotation (counterclockwise as seen from the rotator to the stator in Figure 1) will simply be given by the approximate direction in which $\vec{T}$ points ("up" vs. "down"). For simplicity, a flexible axis along the C=C bond of the TDHY-fluorene rotor molecule is chosen for studying the rotation around it. The total calculated torque is projected onto the C=C axis.
Results and Discussion

Figure 2. Schemes of different electronic states in cationic / neutral / anionic TDHY-fluorene.

In order to clearly understand the different electronic states of cationic / neutral /anionic systems, the schematic diagram of electron distribution in frontier molecular orbitals (FMOs) of each system is plotted, as presented in Figure 2. The electrons are arranged in pairs in the FMOs for the neutral molecule in the ground state ($S_0$), while for its first excited state ($S_1$), one electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) resulting in two single electrons with opposite spin direction occupying two different energy levels in molecular orbitals (MOs). The unidirectional rotation in the TDHY-fluorene rotor molecule can be experimentally light-driven by photoisomerization between $S_0$ and $S_1$ states. The anionic/cationic TDHY-fluorene can be formed by injecting/extracting a single electron at its ground state. Two low-energy spin states are listed in Figure 2 for cationic and anionic systems, respectively. There is one unpaired electron in the doublet spin state ($D_0$) and three unpaired electron in the quartet spin state ($Q_0$) of anionic and cationic TDHY-fluorene.
We aim to investigate whether the charged molecule at the ground state can have a similar rotation as the neutral molecule.

Figure 3. Relative energy profiles of neutral and charged molecules. (a) Neutral molecules in ground state ($S_0$) and excited state ($S_1$) for excitation process are presented for torsion angles from 15 to 85°; the relative energy for the relaxation process is presented for torsion angles from 90 to 155°. (b) Charged molecules in doublet spin state ($D_0$) and quartet spin state ($Q_0$) are presented for torsion angles from 15 to 85° for the excitation process and torsion angles from 90 to 155° for the relaxation process.

The conversion process from Isomer 1 to Isomer 2 (cf. Figure 1) is composed of two steps: the excitation step (corresponding to a torsion angle from 15° to 85°) and the relaxation step (corresponding to a torsion angle from 90° to 155°). As introduced in Computational Details earlier, we successively use rigid models to simulate the excited model (torsion angle from 15° to 85°) due to ultrafast light-driven processes on a timescale of hundreds of femtoseconds after the photo-excitation, and relaxed models (torsion angle from 90° to 155°) with a local optimization by constraining a suitable dihedral angle for updating the direction of rotation to simulate the relaxation step of the radiationless decay to the ground state conformer. This is consistent with the experimental process.
We have calculated each configuration for every 5° of torsion angle as shown in Figure 3a-b by relatively rapid electronic optimization without time-consuming geometric optimization, corresponding to torsion angles from 15° to 85°. From 90° to 155°, due to the much longer de-excitation timescale, we allow the rotator (and stator) to be non-rigid in the ground state $S_0$. This requires structural optimization at fixed torsion angles, which is achieved by fixing to the same values the aforementioned dihedral angle 1-2-3-4 (cf. Figure 3) involving the C=C bond. We also used the non-rigid structure of the cationic and anionic $D_0$ (corresponding to torsion angles from 90° to 155°) to describe the relaxed process. However, the numbers of electrons in cationic and anionic TDHY-fluorene are different from the neutral one. Since there are different numbers of electrons in cationic systems, neutral systems, and anionic systems, in order to discuss the potential energy surface (PES) at the level of the same number of electrons, the adjustment energy with equal number of electrons is calculated for the cationic system and the anionic system as described in the following equations.

**Anion system:** $E_{\text{Adjustment energy}} = E_{\text{Total energy}} - E_{\text{Energy of electron in HOMO}}$

**Cationic system:** $E_{\text{Adjustment energy}} = E_{\text{Total energy}} + E_{\text{Energy level of LUMO}}$

The result of energy adjustment calculation is presented in Figure 3. In order to facilitate comparison, we repeated the calculation of the unidirectional rotation from the $S_1$ state to the $S_0$ state as illustrated in Figure 3a. The results shown in Figure 3b
indicate that the energy of both cationic and anionic systems with quartet spin multiplicity decreases with the torsion angle from 15° to 85° which is similar to the energy curve of the neutral molecule in the S₁ state shown in Figure 3a. Thus, the high spin state of charged molecules can produce a rotational behavior along the cation Q₀ and anion Q₀ PESs from 15° to 85°. However, the energy of charged systems with low spin state increases gradually with the torsion angle in the range of 15° to 85°. This energy variation trend is contrary to the S₁ state curve of the neutral molecule, so the positively and negatively charged systems with low spin state cannot cause the motor molecules to rotate. In addition, we note that, for Neutral_S₀ PES, the molecule must overcome an energy barrier with the value of 65 kcal/mol when the torsion angle increases from 15° to 154°, while for the cationic and anionic systems, the energy barriers for twisting the C=C double bond are 55 kcal/mol for Cation_D₀ and 47 kcal/mol for Anion_D₀, respectively. It is clear that the energy barrier is reduced by 18 kcal/mol for Anion_D₀ and 10 kcal/mol for Cation_D₀ as compared with the neutral case near the torsion angle of 85°. The introduction of the charge in the isomerization significantly reduces the energy barrier, which is consistent with an earlier report.¹²

To further validate the reliability of the calculated results by the CAM-B3LYP functional, we additionally calculated PES profiles by two other well-known DFT functionals, M062X and ωB97XD, with the same basis set 6-31+G(d,p). As shown in Figures 3b and S1, the PES profiles from these three DFT functionals are in good agreement with each other, with acceptable data differences (see Table S1). This
implies that the torque profiles by CAM-B3LYP functional are also consistent with those from the M062X and ωB97XD functionals. The CAM-B3LYP functional is thus reliable for the purposes of this work.

Figure 4. Total torque $T_{C=C}$ (in units of piconewton × nanometer $= 10^{-21}$ N.m) of the rotator of cationic and anionic TDHY-fluorene projected onto the C=C double bond axis as a function of the torsion angle from Isomer 1 to Isomer 2, assuming rigid rotation of the rotator until 85°, then optimized rotation beyond 85°.

For further discussion of the rotational behavior of the charged molecule, the torque method is used to simulate a simple rigid rotation of the rotator to qualitatively explore whether or not there is a tendency to rotate continuously in the counterclockwise direction for cationic and anionic systems. In order to facilitate comparison, we repeated the calculation of the unidirectional rotation from the $S_1$ state to the $S_0$ state as illustrated in Figure 4a, which confidently predicts the counterclockwise rotational evolution from the $S_1$ state to the $S_0$ state as indicated by the arrows, due to the continuity of the torque change. The total torque on the rotators in the cationic and anionic systems is illustrated in Figure 4b. We note that there are no net forces on any atom in the equilibrated lowest-energy Isomer 1. Therefore,
total torque on the rotator in Isomer 1 is zero. As the atomic geometry has not changed but the electron occupation is changed, non-zero net forces on most atoms occurs resulting in a significant positive total torque on the rotator, as projected onto the C=C bond axis (see Figure 4a near the ground state's torsion angle of 15°). The positive sign implies a counterclockwise rotation, looking from the rotator toward the stator. This counterclockwise rotation is reflected by a negative slope of the PES surface (seen as a downward slope in Figure 3a), driving the rotor molecule to rotate in the counterclockwise direction. For the cation Q\(_0\) and anion Q\(_0\) states, we note that the total torque on the rotator remains positive or close to zero as the torsion angle increases from 15° to 85°. Hence, the rotation can still continue in the counterclockwise direction, and the cation Q\(_0\) and anion Q\(_0\) PESs in Figure 3b with the torsion angle increasing from 15° to 85° also confirm a continuous downward slope in the counterclockwise direction. On the other hand, for the cation D\(_0\) and anion D\(_0\) states, the total torque on the rotator changes from positive to negative as the dihedral angle goes from 15° to 85°, which means that the rotator initially rotates in the counterclockwise direction corresponding to the positive torque values and then rotates in the clockwise direction when the total torque on the rotator become negative. Thus, the rotation cannot continue in the counterclockwise direction and the twisting angle cannot reach 85°. The cation D\(_0\) and anion D\(_0\) PESs in Figure 3b indicate that the potential energy increases with the torsion angle increasing from 15° to 85° so that the rotation of the molecule is prevented.

For the relative energy versus the torsion angle curves of high spin states as
shown in Figure 3, we found that the cation $Q_0$ and anion $Q_0$ PES curves intersect with the cation $D_0$ and anion $D_0$ PES curves in the torsion angle range of 60° to 80°. The motor molecules will not jump down from the high spin state to low spin state because the rotator torque of the high spin state is positive and the torque on the low spin state rotor is negative. Considering the continuity of the torque change in the high spin state, the motor molecules should therefore keep rotating in the counterclockwise direction as the torsion angle increases.

**Conclusions**

In this work, we used the intramolecular torque method to study the photo-isomerization mechanism of cationic and anionic TDHY-fluorene with different spin multiplicities induced by an electron injection / extraction. The results show that the quartet spin multiplicity can effectively induce the internal rotation of motor molecules. The change in the properties of charged molecules does not have such an effect. The energy analysis shows that the higher spin state of the anionic and cationic molecules can drive the motor molecules to rotate in order to achieve molecular isomerization. When the torsion angle is close to 85°, the energy is close to the minimum value of the high spin state, while the low spin state cannot drive the rotor to rotate due to the rising energy as the torsion angle increases. Intramolecular torque calculations show that the torque in the high spin state remains positive, ensuring that the rotor can continue to rotate in the counterclockwise direction. In addition, we also find that the introduction of charge significantly reduces the energy
barrier by about 18 kcal/mol in the isomerization process. Therefore, our finding provides information to facilitate probing different transformation pathways for better experimental design of molecular motors.

Acknowledgements

This work was supported by the Collaborative Research Fund of Hong Kong Research Grants Council (Project No. C2014-15G), and the National Natural Science Foundation of China (Project No. 21703190). The Institute of Computational and Theoretical Studies (ICTS) at HKBU is supported by the Institute of Creativity, which is sponsored by Hung Hin Shiu Charitable Foundation (孔憲紹慈善基金贊助). We acknowledge the High Performance Cluster Computing Centre in Hong Kong Baptist University, which receives funding from the RGC and UGC of Hong Kong and Hong Kong Baptist University, for providing the computational resource.
References


(8) Kazaryan, A.; Lan, Z.; Schafer, L. V.; Thiel, W.; Filatov, M. Surface Hopping


(20) Rostov, I. V.; Amos, R. D.; Kobayashi, R.; Scalmani, G.; Frisch, M. J. Studies of the Ground and Excited-State Surfaces of the Retinal Chromophore using


TOC Graphic