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On the Directionality of Double Bond Photoisomerization Dynamics Induced by a Single Stereogenic Center

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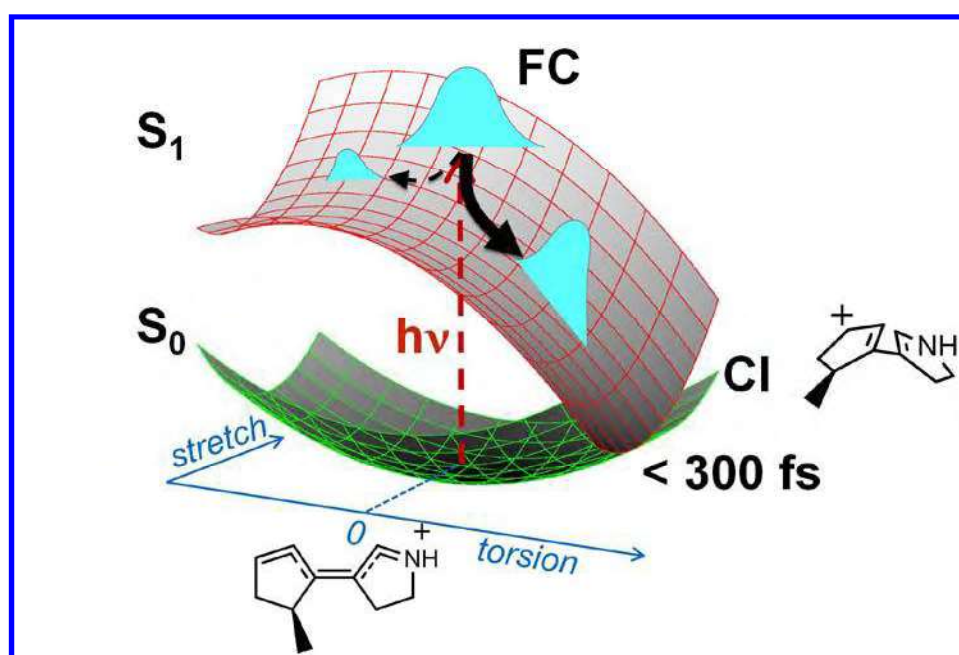
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ABSTRACT

In light-driven single-molecule rotary motors, the photoisomerization of a double bond converts light energy into the rotation of a moiety (the rotor) with respect to another (the stator). However, at the level of a molecular population, an effective rotary motion can only be achieved if a large majority of the rotors rotate in the same, specific direction. Here, we present a quantitative investigation of the directionality (clockwise vs. counterclockwise) induced by a single stereogenic center placed in allylic position with respect to the reactive double bond of a model of the biomimetic indanylidene-pyrrolinium framework. By computing ensembles of non-adiabatic trajectories at 300 K, we predict that the photoisomerization is >70% unidirectional for the $Z \rightarrow E$ and $E \rightarrow Z$ conversions. Most importantly, we show that such directionality, resulting from the asymmetry of the excited state force field, can still be observed in the presence of a small (ca. 2°) pre-twist or helicity of the reactive double bond. This questions the validity of the conjecture that a significant double bond pre-twist (e.g. $>10^\circ$) in the ground state equilibrium structure of synthetic or natural rotary motors would be required for unidirectional motion.



Keywords: Photochemistry, Isomerization, Molecular Motor, *Ab Initio* Non-adiabatic Molecular Dynamics.

The “physical” ingredients of a (molecular) motor are i) a source of energy, ii) a periodic potential energy, and iii) a structural asymmetry, as was pointed out in very simple words by Feynman.¹ At the single molecule level, the photoisomerization of a double bond provides the first two ingredients: the light energy is converted into rotary motion around the bond axis and the potential energy changes periodically along the coordinate describing the rotation. The third ingredient is provided by a chiral “environment” which has the function of breaking the local symmetry and, ultimately, prompting a unidirectional (clockwise or counterclockwise) rotary motion.

Synthetic indanylidene-pyrrolinium (IP) molecular frameworks, originally prepared² to mimic the outstanding photoisomerization properties of the visual pigment rhodopsin (Rh),³⁻⁵ could potentially yield a novel class of molecular motors. In Rh, and related microbial rhodopsins, a retinal protonated Schiff base embedded in the chiral environment provided by the protein cavity, undergoes a regiospecific, subpicosecond and *unidirectional* double bond photoisomerization with high quantum yield. IP compounds have been shown, experimentally and computationally,⁶⁻⁹ to be able to reproduce the dynamical properties of Rh, also including the vibrational coherence observed in the photoisomerization primary photoproduct⁴. On the other hand, in order to replicate the directionality of the Rh photoisomerization, the IP framework (see Chart 1, left) should be made chiral to mimic the effect of the protein cavity.¹⁰ Under these conditions, IP compounds would provide a basis for the development of *biomimetic* single-molecule rotary motors.

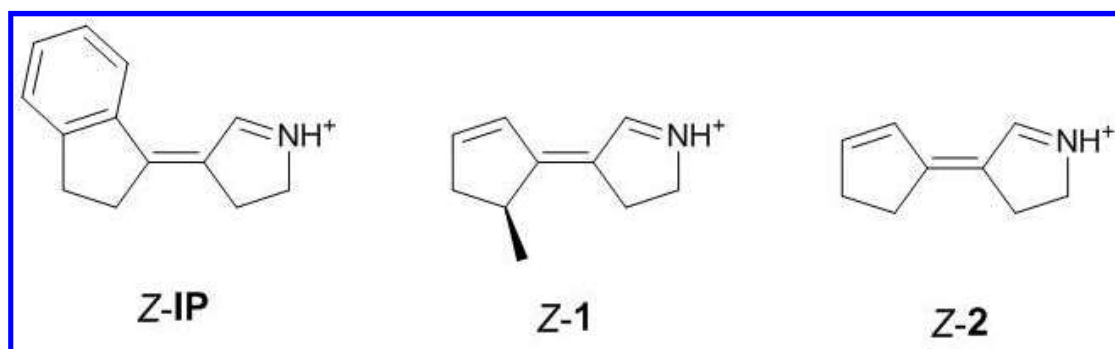


Chart 1. Z isomers of the IP framework, chiral (1) and achiral (2) model compounds.

A chiral IP framework can be obtained by insertion of one or more stereogenic centers. Indeed, unlike retinal and related model systems,^{5, 11-14} the cyclic structure of IP contains sp^3 carbons that can be made stereogenic. Synthetic single-molecule rotary motors featuring one or two stereogenic centers have been experimentally demonstrated using diarylethene frameworks.¹⁵ These frameworks feature one overcrowded C=C bond displaying a substantial (ca. 10° - 20°) pre-twist reflecting the helicity of the surrounding environment.¹⁶⁻¹⁸ Furthermore, a computationally designed protonated Schiff base system with two stereogenic centers and featuring a ca. 8° pre-twisted C=C bond imposed via hydrogen-bonding was found to display strong unidirectional motion¹⁹. These systems feature pre-twisting values not far from the ca. 5° - 10° reported for the reactive C=C bond of Rh. In the later case and in other retinal proteins, the pre-twist of the reactive double bond of the ground state chromophore is held responsible for the enhanced photoreaction speed and yield of PSBR²⁰⁻²² and also for the full directionality of the isomerization^{10, 12, 23-25}. This leads to the conjecture that significant ground state C=C bond pre-twisting is required for an effective photoisomerization directionality (i.e. this would implicitly inform on the degree of asymmetry of the excited state force field). On the other hand, it is presently not clear what would be the minimal requirements for such a unidirectional rotary motion. In other words, with the idea of uncovering rules for the design of effective single-molecule rotary motors, it appears important to find out how much the ground state planar symmetry of a C=C bond should be

perturbed to achieve a unidirectional photoisomerization. The present report addresses some of the aspects of this basic question in the context of the design of IP-based motors.

Here, we focus on the pentenylidene-pyrrolinium compounds **1** and **2** (see Chart 1) as minimal models of IPs²⁶. While **2** is planar and therefore achiral, **1** is made chiral by inserting a methyl group in an allylic position with respect to the exocyclic (central) double bond. This allows to investigate: (a) whether the inserted single stereogenic center would be sufficient to induce a unidirectional photoisomerization of the exocyclic bond and (b) what is the exact mechanism prompting the unidirectional twisting and in particular the putative role of a C=C bond pre-twist. We compute statistical ensembles of gas-phase, *ab initio* non-adiabatic molecular trajectories to show that the stereogenic center of **1**, imposing very limited symmetry breaking (i.e. a pre-twist of ca. 2°), is enough to generate a significant unidirectional motion in a room-temperature molecular population. We show that the mere *geometrical distortions* of the untwisted C=C bond of **2** or the *inertial motion of the methyl substituent* of the stereogenic center of **1** are *not* contributing to the directionality significantly.

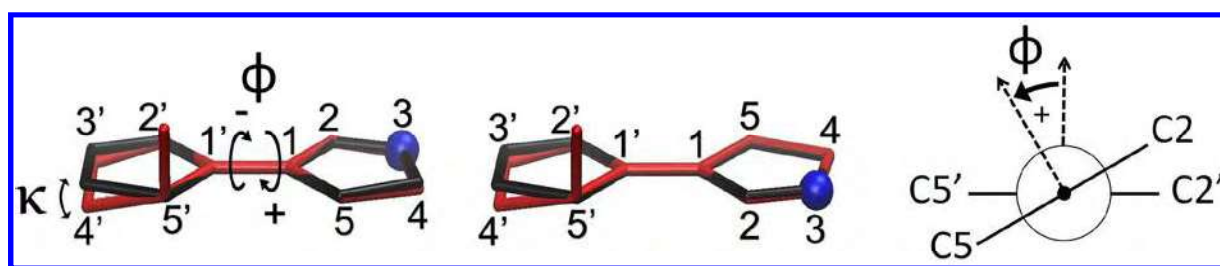


Figure 1. Superimposed structures of the chiral **1** (red) and achiral **2** (black) *Z* (left) and *E* (right) ground state equilibrium geometries. An unconventional numbering is used for facilitating the discussion. Hydrogen atoms are not shown, nitrogen atoms are represented with a blue sphere. Carbons 4, 4', 5 and 5' have sp^3 hybridization. The counterclockwise (+) direction of rotation implies an increase in the value of the twisting angle ϕ defined in the Newman projection. The largest out-of-plane deformation in **1** is along the dihedral angle κ .

All computations are performed using the *ab initio* CASSCF method²⁷ and the 6-31G* basis set with 6 electrons in 6 π -type orbitals (see SI for details). *Ab initio* non-adiabatic trajectories (see e.g.^{5, 13-14, 19, 28-29}) are computed using the recent implementation¹⁹ in Molcas 7.8³⁰ of Tully's surface hopping algorithm³¹ with quantum decoherence correction³². The computed singlet ground state (S_0) equilibrium structures of **1** and **2** are found to be very similar irrespective of the isomer (*Z* or *E*) actually compared (see Figure 1 and Table S1 in the SI). The main differences are found in the out-of-plane deformation of the pentenylidene ring, best characterized by the dihedral angle $\kappa = C1-C1'-C5'-C4'$. For compounds *Z*-**1** and *E*-**1**, $\kappa = -15.7^\circ$ and -13.9° respectively, while $\kappa = 0^\circ$ for the planar compound **2**. To characterize the twisting of the central double bond we introduce the internal coordinate $\phi = (C2'-C1'-C1-C2 + C5'-C1'-C1-C5)/2$ which approximately measures the alignment of the two p-orbital axes of the $C1'$ and $C1$ sp^2 centers defining the reactive π -bond. While $\phi = 0^\circ$ (180°) for both isomers of the planar achiral compound **2**, we note that in the chiral compound **1** the double bond is twisted by as little as $+1.3^\circ$ ($\phi = +1.3^\circ$) and $+2.2^\circ$ ($\phi = +182.2^\circ$) for the *Z* and *E* isomers respectively. Here, the (+) sign in the twist angle refers to the counterclockwise direction of rotation of the pyrrolinium moiety ("rotor") with respect to the fixed cyclopentenylidene ring ("stator") as illustrated in the Newman projection of Fig. 1 and in the movie in the SI. Since **1** and **2** have nearly untwisted $C1=C1'$ double bonds one should expect to see no difference between these two compounds and therefore little isomerization directionality, if any. We shall see that this is *not* the case.

Starting from the computed equilibrium structures of each *Z* and *E* isomer of **1** and **2**, 200 initial conditions (positions and velocities) are generated using the classical thermal sampling with a Boltzmann distribution at temperature 300 K (see details in the SI). The histograms of initial values of ϕ and κ angles (and corresponding initial velocities) are shown in Fig. 2 and 3

respectively (notice that the full width at half maximum of the ϕ distribution is ca. 5 times larger than the S_0 pre-twist). These initial conditions define an ensemble of trajectories released in the first singlet excited state (S_1), the spectroscopically allowed $\pi \rightarrow \pi^*$ transition in these systems. Among all trajectories about 10% do not react (i.e. do not decay to S_0) within 600 fs of propagation time and are disregarded in our analysis. The reactive trajectories evolve in S_1 until a conical intersection seam is approached where the trajectories hop to S_0 when ϕ is approaching a $\pm 90^\circ$ value. Hopping times are distributed between 100 and 500 fs, with a maximum probability at about 200 fs (see the SI), with no significant differences between **1** and **2**. After the decay to S_0 further twisting along the same direction leads to successful isomerization. However twisting in the reverse direction may also be observed, leading to an aborted isomerization. Irrespective of clockwise or counterclockwise twisting directions in S_1 , about 80% of the reactive trajectories lead to a successful isomerization (see the SI).

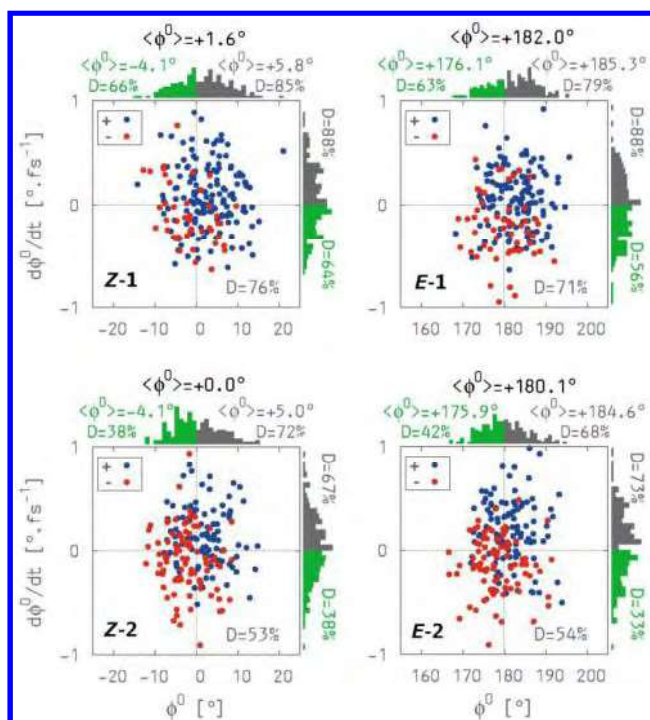


Figure 2. Correlation between the initial average twisting $\langle\phi^0\rangle$ and the photoisomerization directionality (+/-). Differences between the initial average value $\langle\phi^0\rangle$ and the ground state optimized ϕ^0 value of the twisting of the central double bond twisting angles in **2** must be due to the limited size of the populations. The differences in **1** may also be due to the anharmonicity of the potential energy well.

We now define the directionality D of a population as the percentage of the reactive trajectories travelling in the counterclockwise (+) direction. Uncertainties in D due to the finite number of trajectories are estimated to be $\sim 4\%$ (see SI). As expected for the planar, achiral compound **2**, the obtained D values of 53% and 54% for isomer Z and E , respectively, are consistent within the statistical uncertainty with a pure non-directional ($D=50\%$) behavior. Instead, and despite the very limited $C1'=C1$ pre-twist, the chiral molecule **1** displays a significant directionality with $D=76\%$ for the Z isomer and $D=71\%$ for the E isomer. This appears to be in contrast with the conjecture mentioned above that a chiral force field inducing a significant S_0 double bond pre-twist, and therefore helicity, is required for an effective unidirectional rotation, as other systems including Rh would suggest.

In order to inspect the influence of the initial pre-twist in these compounds, we analyze the ensemble of trajectories in subsets (subpopulations) corresponding to positive (gray bars in Fig. 2) and negative (green bars in Fig. 2) initial values of the pre-twist (ϕ^0) and of their corresponding velocities ($d\phi^0/dt$). The average pre-twist $\langle\phi^0\rangle$ and directionality D computed over each subpopulation are given in Fig. 2. Consistent with the pre-twist conjecture for the achiral compound **2**, positive (resp. negative) pre-twists and velocities favor the motion in the “+” (resp. “-”) direction (blue and red points in the 2D map). Indeed, with respect to the directionality D of the entire population, the directionality computed for the positively (negatively) pre-twisted subpopulations increases (decreases) nearly symmetrically, and proportionally to the average pre-twist of each sub-population as shown in Table 1. This

mirror-symmetry unidirectional dynamics is observed for both isomers of the achiral compound **2**.

In contrast, a substantial inconsistency with the pre-twist conjecture is obtained when performing the same analysis for **1**. Indeed, *in spite of a similar quasi-symmetric displacement in the $\langle\phi^0\rangle$ values of the two subpopulations*, the corresponding D values vary less than in **2**. Most importantly, the D values remain significantly above 50% for both subpopulations, thus indicating *a mirror-symmetry breaking at a dynamical level* for both isomers. Notice that the analysis of the average $d\phi^0/dt$ leads to conclusions similar to that of $\langle\phi^0\rangle$. Thus, although an initial positive or negative pre-twist may induce a significant directionality in the achiral molecule in the corresponding direction, a similar negative pre-twist of -4.1° (resp. $176.1^\circ=180-3.9$) is *not enough* to suppress the directionality in **1** which remains as large as 66% (resp. 63%) for the Z (resp. E) isomer. We conclude that a substantial geometrical pre-twist in S_0 is not, by itself, required for leading to the directionality observed in **1**.

Table 1. Analysis of the ensembles of trajectories displayed in Fig. 2 in two subpopulations. D_+-D (resp. D_-D) are the change in directionality of the subpopulations with respect to the total population and $\Delta\langle\phi^0\rangle$ the average pre-twist of the sub-populations.

	Total population	Subpopulation with >0 pre-twist		Subpopulation with <0 pre-twist	
	D	D_+-D	$\Delta\langle\phi^0\rangle$	D_-D	$\Delta\langle\phi^0\rangle$
Z-2	53	+ 19	+5.0°	– 15	-4.1°
E-2	54	+ 14	+4.6°	– 12	-4.1°
Z-1	76	+ 9	+5.8°	– 10	-4.1°
E-1	71	+ 8	+5.3°	– 8	-3.9°

As **1** exhibits large deformations in the pentenylidene ring, we also examine (see Fig. 3) the influence of κ (which represents the deformation of the ring) on the value of D . The same analysis inspecting subpopulations characterized by initial values of κ^0 or $d\kappa^0/dt$ larger or smaller than the average over the entire population, reveals that there is *no correlation* between κ and the directionality of the reaction. Therefore, also a distorted S_0 equilibrium value of κ cannot explain the directionality computed for **1**.

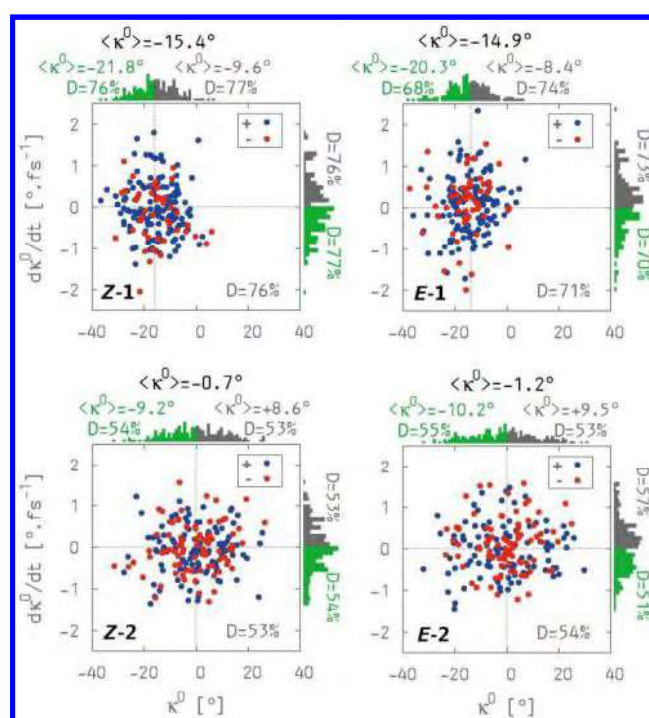


Figure 3. Correlation between the initial deformation κ^0 and the photoisomerization direction (+/-).

In order to further test the effect of the initial geometrical deformations on the directionality, we computed an additional set of 200 trajectories for the achiral compound **Z-2** forced to the initial distorted geometry of the chiral **Z-1**. The result (details in Fig. S3 and S4 of the SI) is $D=48\%$, close to the value of $D=53\%$ obtained for the non-distorted **Z-2** population. This confirms that the mere geometrical deformation generated by the stereogenic center does not determine the directionality when imposed on a system with a symmetric force field in both S_0 and S_1 .

The larger mass of the methyl substituent in **1** compared to the hydrogen in **2** may also affect the dynamics by modulating the velocity of each single atom or group, and is therefore a potential origin of directionality through an inertial effect. To investigate this effect, a new run of 200 trajectories of **Z-2** with its original set of positions and velocities is computed imposing the mass of a methyl group to the pro-S hydrogen in position C5'. Thus, such a "heavy" **Z-2** molecule evolves on the same potential energy surfaces as the original "light" compound. This ensemble (see details in Fig. S3 and S4 of the SI) yields a directionality of $D=56\%$, which is marginally different from $D=53\%$ obtained with the natural hydrogen mass, and significantly smaller than the $>70\%$ directionality computed for compound **1**. Hence, the heavier mass of the methyl substituent does not affect the directionality when imposed on a system with a symmetric force field in both S_0 and S_1 .

The results above show that neither an initial geometrical deformation nor an inertial effect are at the origin of a net directionality in the dynamics of the chiral compound **1**. Therefore, the observed large directionality (i.e. not a full directionality) must be induced by the stereogenic center imposing the asymmetry of the S_1 potential energy surface driving the dynamics. This concept is illustrated and demonstrated in Fig. 4 for the *Z* isomer of the chiral compound **1** (see the same figure for the *E* isomer in the SI). The minimum energy path, computed in terms of the intrinsic reaction coordinate starting from the Franck-Condon (FC) region of the isomer, reveals that the $C_1=C_{1'}$ immediately elongates (relaxation along the stretch coordinate), as is common to all N-protonated or N-alkylated Schiff bases. This motion "unlocks" the central double bond and initiates the twisting around the bond *in a specific direction*. Such twisting direction is imposed by the S_1 potential energy surface asymmetry along ϕ (see inset in Fig. 4). This asymmetry is present in the FC region and persists while the central bond stretches, thus triggering the twisting in the counterclockwise direction preferentially. Notice that, in our prototype system such small asymmetry goes in

the *same* direction for both isomers of **1** (see the SI). This may not occur in more complicated systems where the directionality of the potential energy surface may be opposite in the E and Z isomers²⁶ due to contrasting effects. Conversely, in **2** the S_1 potential energy surface is symmetric along ϕ and κ (see the SI) and the population is symmetrically accelerated in either the clockwise and counterclockwise directions, depending on the initial conditions, leading to a mirror-symmetry dynamics.

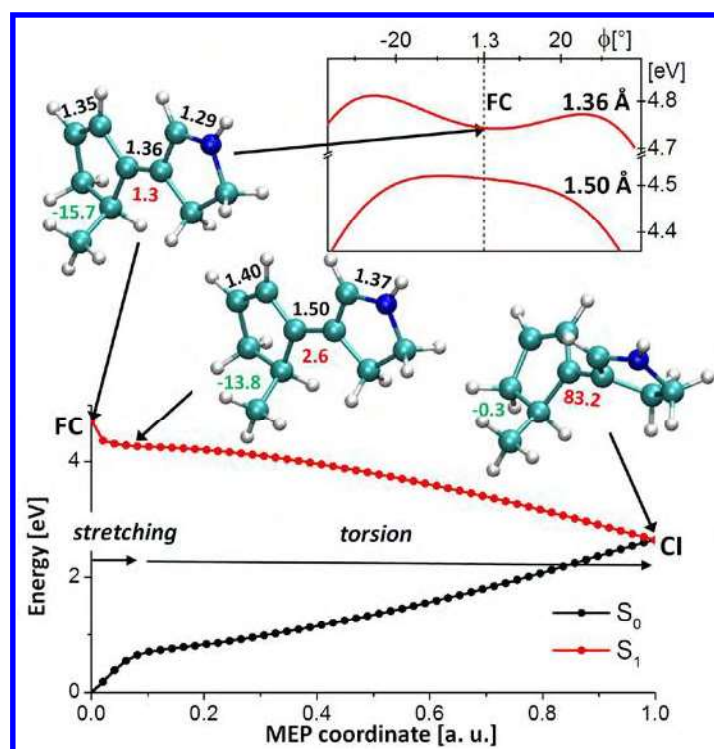


Figure 4. Excited-state reaction of Z-**1**. Minimum Energy Path (MEP) computed from the Franck-Condon (FC) state to the S_1/S_0 conical intersection (CI). Three structures are displayed along this path showing the sense of rotation. The length of the three C=C bonds is given in black, the twisting angle ϕ in red, and the dihedral κ in green. (Inset) S_1 potential energy computed as a function of the twisting angle ϕ with the central C1-C1' bond length fixed at 1.36 Å or 1.50 Å, and all other coordinates fixed at their FC values.

1
2
3 In conclusion, our comparative study reveals that a significant photoisomerization
4 directionality can be achieved by placing a stereogenic center in an allylic position with
5 respect to the isomerizing C=C bond, in spite of an almost negligible pre-twist/helicity. In
6 contrast with the conjecture that a pre-twist of the S_0 equilibrium structure is required for a
7 substantial directionality, the latter is mostly the result of the asymmetry of the S_1 force field
8 on the initial population. In other words, even a limited symmetry breaking of the S_1 potential
9 energy surface seems to have a large effect on the way the population branches between
10 clockwise and counterclockwise twisting. This is supported by the reported analysis showing
11 that the almost planar compound **1** displays a significant directionality, *even* in the
12 subpopulation showing an *opposite* average pre-twist (3-4 times larger in amplitude than the
13 equilibrium pre-twist). Furthermore, the same initial deformation of **1** imposed on **2** does not
14 yield a directionality.

15
16 The above conclusions may be important for the design of IP-based single-molecule
17 molecular motors where photoisomerization dynamics (e.g. photoreaction speed, yield,
18 vibrational coherence or directionality) is commonly rationalized or predicted by discussing
19 ground state equilibrium geometries. The presented compound **1** appears to be a borderline
20 prototype featuring a high, but not full, directionality. For such system, the documented 76%
21 and 71% directionality of **1** in the $Z \rightarrow E$ and $E \rightarrow Z$ isomerization steps respectively predict that
22 ca. 54% of the initially thermalized and reactive population (76% x 71%) will perform a full
23 $Z \rightarrow E \rightarrow Z$ rotation by absorbing two photons sequentially. In the same conditions 39% of the
24 population (24% x 71% + 76% x 29%) would have not rotated and 7% (24% x 29%) would
25 have rotated in opposite direction. This allows us to conclude that, on average 47% (= 54%-
26 7%) of the mechanical work produced by an isomerizing molecule over one full turn could be
27 exploited.

Supporting Information. Computational method; CASSCF molecular orbitals and occupation numbers; geometries of the optimized structures; trajectory movies showing photoisomerizations in the positive and negative directions; quantum yields; S₁ lifetimes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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