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ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JANUARY 2015

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# Directionality of Double-Bond Photoisomerization Dynamics Induced by a Single Stereogenic Center

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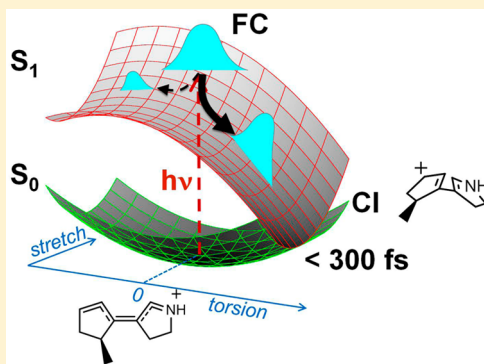
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## Supporting Information

**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 → E and E → 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°) pretwist or helicity of the reactive double bond. This questions the validity of the conjecture that a significant double-bond pretwist (e.g., >10°) in the ground state equilibrium structure of synthetic or natural rotary motors would be required for unidirectional motion.

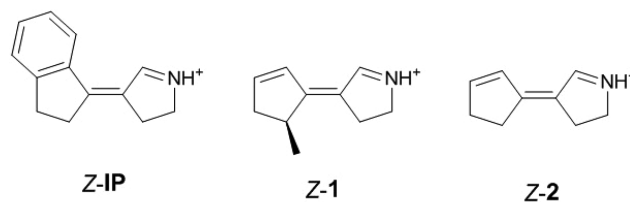


The “physical” ingredients of a (molecular) motor are (i) a source of energy, (ii) a periodic potential energy, and (iii) a structural asymmetry, as was pointed out in very simple words by Feynman.<sup>1</sup> At the single-molecule level, the photoisomerization of a double bond provides the first two 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 prepared<sup>2</sup> to mimic the outstanding photoisomerization properties of the visual pigment rhodopsin (Rh),<sup>3–5</sup> 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,<sup>6–9</sup> to be able to

reproduce the dynamical properties of Rh, also including the vibrational coherence observed in the photoisomerization primary photoproduct.<sup>4</sup> Besides, the IP framework (see Chart 1, left) should be made chiral to mimic the effect of the protein cavity to replicate the directionality of the Rh photoisomerization.<sup>10</sup> Under these conditions, IP compounds would provide a

**Chart 1. Z Isomers of the IP Framework, Chiral (1) and Achiral (2) Model Compounds**



**Received:** December 15, 2014

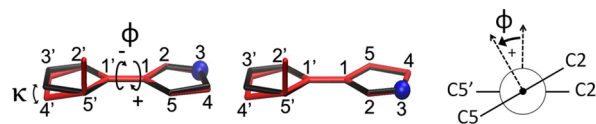
**Accepted:** January 23, 2015

basis for the development of biomimetic single-molecule rotary motors.

A chiral IP framework can be obtained by insertion of one or more stereogenic centers. Indeed, unlike retinal and related model systems,<sup>5,11–14</sup> 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.<sup>15</sup> These frameworks feature one overcrowded  $C=C$  bond displaying a substantial (ca.  $10$ – $20^\circ$ ) pretwist reflecting the helicity of the surrounding environment.<sup>16–18</sup> Furthermore, a computationally designed protonated Schiff base system with two stereogenic centers and featuring a ca.  $8^\circ$  pretwisted  $C=C$  bond imposed via hydrogen bonding was found to display strong unidirectional motion.<sup>19</sup> These systems feature pretwisting values not far from the ca.  $5$ – $10^\circ$  reported for the reactive  $C=C$  bond of Rh. In the later case and in other retinal proteins, the pretwist of the reactive double bond of the ground-state chromophore is held responsible for the enhanced photoreaction speed and yield of PSBR<sup>20–22</sup> and also for the full directionality of the isomerization.<sup>10,12,23–26</sup> This leads to the conjecture that significant ground-state  $C=C$  bond pretwisting is required for an effective photoisomerization directionality (i.e., this would implicitly inform on the degree of asymmetry of the excited state force field). 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 to be 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 IPs.<sup>27</sup> 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 us 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 pretwist. We compute statistical ensembles of gas-phase, ab initio nonadiabatic molecular trajectories to show that the stereogenic center of **1**, imposing very limited symmetry breaking (i.e., a pretwist of ca.  $2^\circ$ ), 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.

All computations are performed using the ab initio CASSCF method<sup>28</sup> and the 6-31G\* basis set with six electrons in six  $\pi$ -type orbitals. (See the SI for details.) Ab initio nonadiabatic trajectories (see, e.g., refs 5,13,14,19,29,30) are computed here using the recent implementation<sup>19</sup> in Molcas 7.8<sup>31</sup> of Tully's surface hopping algorithm<sup>32</sup> with quantum decoherence correction.<sup>33</sup> 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

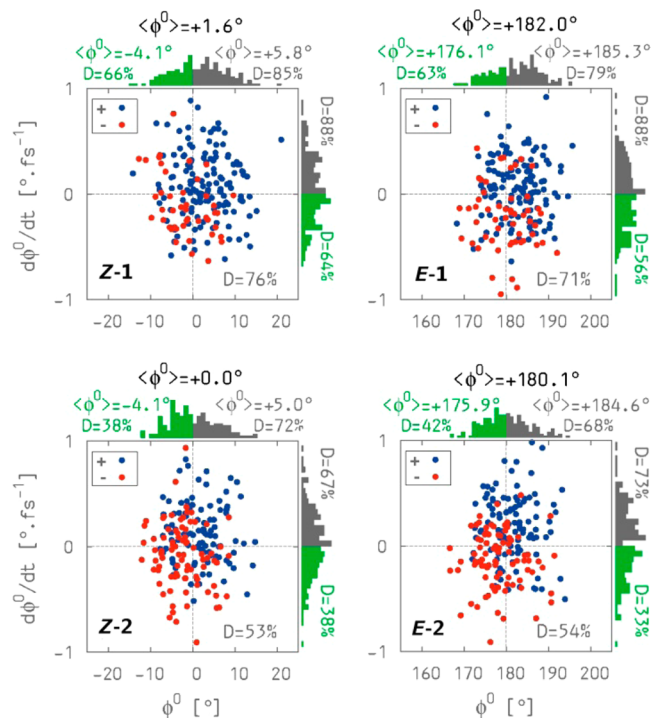


**Figure 1.** Superimposed structures of the chiral **1** (red) and achiral **2** (black) Z (left) and E (right) ground-state equilibrium geometries. An unconventional numbering is used for facilitating the discussion. Hydrogen atoms are not shown; nitrogen atoms are represented with a blue sphere. Carbons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

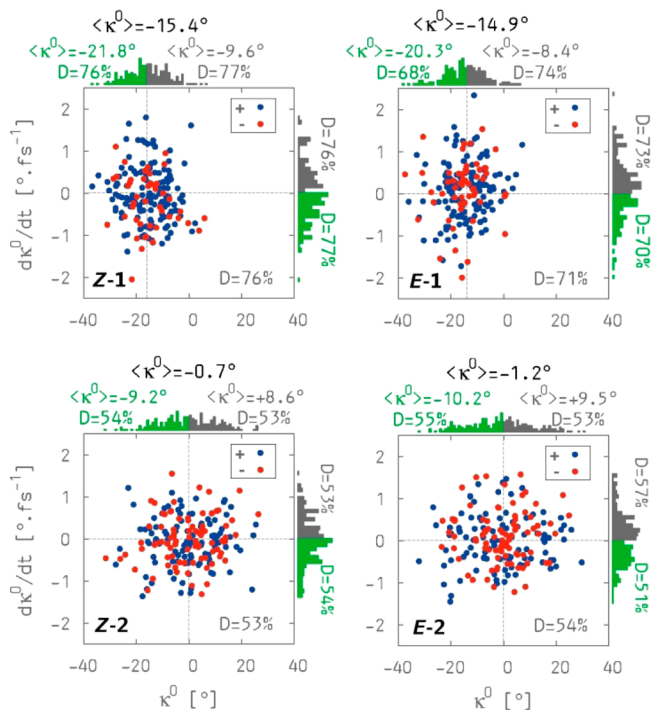
found in the out-of-plane deformation of the pentenylidene ring, best characterized by the dihedral angle  $\kappa = C1-C1'-C5'-C4'$ . For compounds Z-**1** and E-**1**,  $\kappa = -15.7$  and  $-13.9^\circ$  respectively, while  $\kappa = 0^\circ$  for the planar compound **2**. To characterize the 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  $\pi$  bond. While  $\phi = 0^\circ$  ( $180^\circ$ ) 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 Figure 1 and in the movie in the SI. Because **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 the details in the SI.) The histograms of initial values of  $\phi$  and  $\kappa$  angles (and corresponding initial velocities) are shown in Figures 2 and 3 respectively. (Notice that the full width at half-maximum of the  $\phi$  distribution is ca. five times larger than the  $S_0$  pretwist.) 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  $\sim 10\%$  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  $\phi$  is approaching a  $\pm 90^\circ$  value. Hopping times are distributed between 100 and 500 fs, with a maximum probability at  $\sim 200$  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  $S_1$ ,  $\sim 80\%$  of the reactive trajectories lead to a successful isomerization. (See the SI.)

We now define the directionality  $D$  of a population as the percentage of the reactive trajectories traveling in the counterclockwise (+) direction. Uncertainties in  $D$  due to the finite number of trajectories are estimated to be  $\sim 4\%$ . (See the



**Figure 2.** Correlation between the initial average twisting  $\langle \phi^0 \rangle$  and the photoisomerization directionality ( $\pm$ ). Differences between the initial average value  $\langle \phi^0 \rangle$  and the ground-state optimized  $\phi^0$  value 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.



**Figure 3.** Correlation between the initial deformation  $\kappa^0$  and the photoisomerization direction ( $\pm$ ).

SI.) As expected for the planar, achiral compound **2**, the obtained  $D$  values of 53 and 54% for isomers Z and E, respectively, are consistent within the statistical uncertainty with a pure nondirectional ( $D = 50\%$ ) behavior. Instead, and

despite the very limited  $C1'=C1$  pretwist, 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 previously mentioned that a chiral force field inducing a significant  $S_0$  double-bond pretwist and therefore helicity is required for an effective unidirectional rotation, as other systems including Rh would suggest.

To inspect the influence of the initial pretwist in these compounds, we analyze the ensemble of trajectories in subsets (subpopulations) corresponding to positive (gray bars in Figure 2) and negative (green bars in Figure 2) initial values of the pretwist ( $\phi^0$ ) and of their corresponding velocities ( $d\phi^0/dt$ ). The average pretwist  $\langle \phi^0 \rangle$  and directionality  $D$  computed over each subpopulation are given in Figure 2. Consistent with the pretwist conjecture for the achiral compound **2**, positive (respectively negative) pretwists and velocities favor the motion in the “+” (respectively “−”) 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) pretwisted subpopulations increases (decreases) nearly symmetrically and proportionally to the average pretwist of each subpopulation, as shown in Table 1. This mirror-symmetry unidirectional dynamics is observed for both isomers of the achiral compound **2**.

**Table 1.** Analysis of the Ensembles of Trajectories Displayed in Figure 2 in Two Subpopulations<sup>a</sup>

	total population	subpopulation with $>0$ pretwist		subpopulation with $<0$ pretwist	
		$D$	$D_+ - D$	$D_- - D$	$\Delta \langle \phi^0 \rangle$
Z-2	53		+19	−15	−4.1°
E-2	54		+14	−12	−4.1°
Z-1	76		+9	−10	−4.1°
E-1	71		+8	−8	−3.9°

<sup>a</sup> $D_+ - D$  (resp.  $D_- - D$ ) is the change in directionality of the positively (resp. negatively) pretwisted subpopulation with respect to the total population and  $\Delta \langle \phi^0 \rangle$  the average pretwist of the subpopulations.

In contrast, a substantial inconsistency with the pretwist conjecture is obtained when performing the same analysis for **1**. Indeed, despite 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 pretwist may induce a significant directionality in the achiral molecule in the corresponding direction, a similar negative pretwist of  $-4.1^\circ$  (respectively,  $176.1^\circ = 180 - 3.9$ ) is not enough to suppress the directionality in **1**, which remains as large as 66% (respectively, 63%) for the Z (respectively E) isomer. We conclude that a substantial geometrical pretwist in  $S_0$  is not, by itself, required for leading to the directionality observed in **1**.

As **1** exhibits large deformations in the pentenylidene ring, we also examine (see Figure 3) the influence of  $\kappa$  (which represents the deformation of the ring) on the value of  $D$ . The same analysis inspecting subpopulations characterized by initial values of  $\kappa^0$  or  $d\kappa^0/dt$  larger or smaller than the average over the entire population reveals that there is no correlation



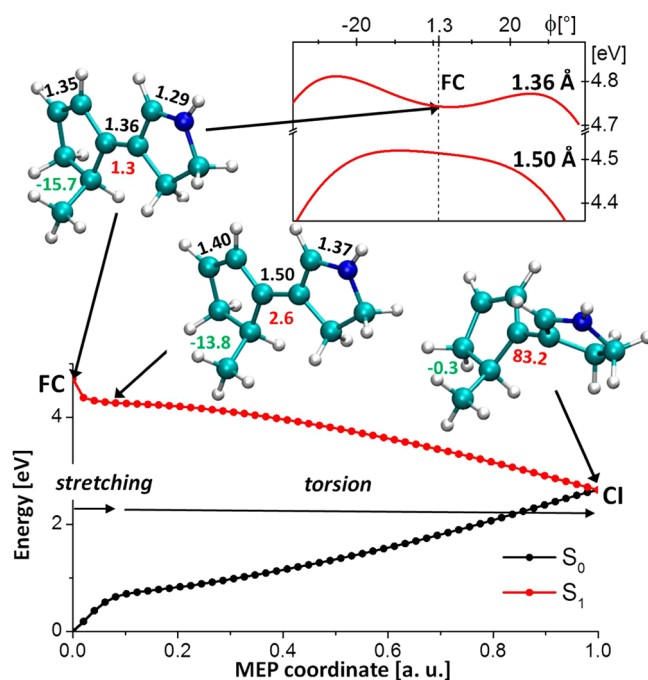
between  $\kappa$  and the directionality of the reaction. Therefore, also a distorted  $S_0$  equilibrium value of  $\kappa$  cannot explain the directionality computed for **1**.

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 Figures S3 and S4 of the SI) is  $D = 48\%$ , close to the value of  $D = 53\%$  obtained for the nondistorted 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 with 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 Figures 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 Figure 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  $\phi$ . (See the inset in Figure 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 isomers<sup>27</sup> due to contrasting effects. Conversely, in **2** the  $S_1$  potential energy surface is symmetric along  $\phi$  and  $\kappa$  (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.

In conclusion, our comparative study reveals that a significant photoisomerization directionality can be achieved by placing a stereogenic center in an allylic position with respect to the



**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 direction of rotation. The lengths of the three C=C bonds are given in black, the twisting angle  $\phi$  in red, and the dihedral  $\kappa$  in green. (Inset)  $S_1$  potential energy computed as a function of the twisting angle  $\phi$  with the central C1–C1' bond length fixed at 1.36 or 1.50 Å, and all other coordinates fixed at their FC values.

isomerizing C=C bond, despite an almost negligible pretwist/helicity. In contrast with the conjecture that a pretwist of the  $S_0$  equilibrium structure is required for a substantial directionality, the latter is mostly the result of the asymmetry of the  $S_1$  force field on the initial population. In other words, even a limited symmetry breaking of the  $S_1$  potential energy surface seems to have a large effect on the way the population branches between clockwise and counterclockwise twisting. This is supported by the reported analysis showing that the almost planar compound **1** displays a significant directionality, even in the subpopulation showing an opposite average pretwist (three to four times larger in amplitude than the equilibrium pretwist). Furthermore, the same initial deformation of **1** imposed on **2** does not yield a directionality.

The above conclusions may be important for the design of IP-based single-molecule molecular motors, since in these and other retinal-related compounds photoisomerization dynamics (e.g., photoreaction speed, yield, vibrational coherence, or directionality) are commonly rationalized or predicted by discussing ground-state equilibrium geometries. The presented compound **1** appears to be a borderline prototype featuring a high, but not full, directionality. For this IP-model system, the documented 76 and 71% directionalities of **1** in the Z → E and E → Z isomerization steps, respectively, predict that ca. 54% of the initially thermalized and reactive population ( $76\% \times 71\%$ ) will perform a full Z → E → Z rotation by absorbing two photons sequentially. In the same conditions 39% of the population ( $24\% \times 71\% + 76\% \times 29\%$ ) would have not rotated and 7% ( $24\% \times 29\%$ ) would have rotated in opposite direction. This allows us to conclude that on average 47% ( $= 54 - 7\%$ ) of

the mechanical work produced by an isomerizing molecule over one full turn could be exploited.

## ■ ASSOCIATED CONTENT

### ■ 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;  $S_1$  lifetimes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Lutz Greb for sharing unpublished information. This work was supported by the French Agence Nationale de la Recherche (ANR) through the grant ANR-11-JS04-0010 and the High-Performance Computing center (pôle HPC) at Université de Strasbourg. L.M.F. and A.V. acknowledge support from grants CTQ-2012-36966 of the Spanish Secretaría de Estado de Investigación Desarrollo e Innovación, and CCG2013/EXP-089 of the University of Alcalá. M.O. acknowledges funding from the Italian MIUR (PRIN 2012-2014) and partial funding from the EU-FP7 (Marie-Curie POF-GA-2012-332233), the National Science Foundation under grant no. CHE-1152070 and the Human Frontier Science Program Organization under grant RGP0049/2012CHE09-56776.

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