



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

This is the peer reviewed version of the following article:

Original:

Marchand, G., Eng, J., Schapiro, I., Valentini, A., Frutos, L.M., Pieri, E., et al. (2015). Directionality of Double-Bond Photoisomerization Dynamics Induced by a Single Stereogenic Center. THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS, 6(4), 599-604 [10.1021/jz502644h].

Availability:

This version is available <http://hdl.handle.net/11365/977032> since 2017-09-15T22:07:21Z

Published:

DOI:10.1021/jz502644h

Terms of use:

Open Access

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. Works made available under a Creative Commons license can be used according to the terms and conditions of said license.

For all terms of use and more information see the publisher's website.

(Article begins on next page)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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

Gabriel Marchand,^{‡,†,¶} Julien Eng,[†] Igor Schapiro,[‡] Alessio Valentini,^{‡,††} Luis Manuel

Frutos,^{††} Elisa Pieri,[‡] Massimo Olivucci,^{,‡,§} Jérémie Léonard^{*,‡} and Etienne*

Gindensperger^{,†}*

[‡] Institut de Physique et Chimie des Matériaux de Strasbourg & Labex NIE, Université de
Strasbourg, CNRS UMR 7504, Strasbourg, France

[†] Institut de Chimie, Université de Strasbourg, CNRS UMR 7177, Strasbourg, France

[‡] Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Italy

[§] Chemistry Department, University of Bowling Green, USA

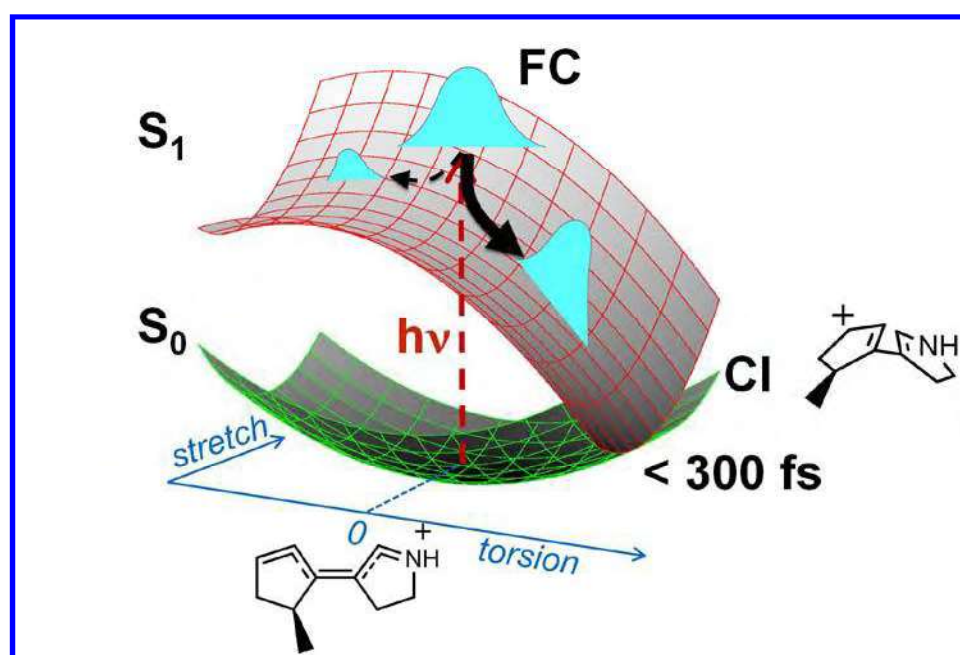
^{††} Unidad Docente de Química Física, Universidad de Alcala, Spain

Corresponding Authors

egindensperger@unistra.fr, leonard@ipcms.unistra.fr, molivuc@bgsu.edu

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.



1
2
3 Keywords: Photochemistry, Isomerization, Molecular Motor, *Ab Initio* Non-adiabatic
4
5 Molecular Dynamics.
6
7
8
9
10

11
12 The “physical” ingredients of a (molecular) motor are i) a source of energy, ii) a periodic
13 potential energy, and iii) a structural asymmetry, as was pointed out in very simple words by
14 Feynman.¹ At the single molecule level, the photoisomerization of a double bond provides
15 the first two ingredients: the light energy is converted into rotary motion around the bond axis
16 and the potential energy changes periodically along the coordinate describing the rotation.
17
18 The third ingredient is provided by a chiral “environment” which has the function of breaking
19 the local symmetry and, ultimately, prompting a unidirectional (clockwise or
20 counterclockwise) rotary motion.
21
22
23
24
25
26
27
28
29
30

31 Synthetic indanylidene-pyrrolinium (IP) molecular frameworks, originally prepared² to
32 mimic the outstanding photoisomerization properties of the visual pigment rhodopsin (Rh),³⁻⁵
33 could potentially yield a novel class of molecular motors. In Rh, and related microbial
34 rhodopsins, a retinal protonated Schiff base embedded in the chiral environment provided by
35 the protein cavity, undergoes a regiospecific, subpicosecond and *unidirectional* double bond
36 photoisomerization with high quantum yield. IP compounds have been shown, experimentally
37 and computationally,⁶⁻⁹ to be able to reproduce the dynamical properties of Rh, also including
38 the vibrational coherence observed in the photoisomerization primary photoproduct⁴. On the
39 other hand, in order to replicate the directionality of the Rh photoisomerization, the IP
40 framework (see Chart 1, left) should be made chiral to mimic the effect of the protein cavity.¹⁰
41
42 Under these conditions, IP compounds would provide a basis for the development of
43 *biomimetic* single-molecule rotary motors.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

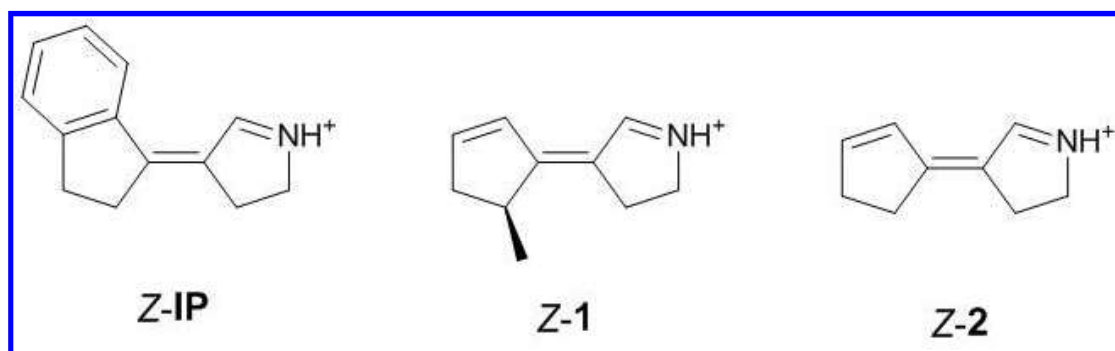
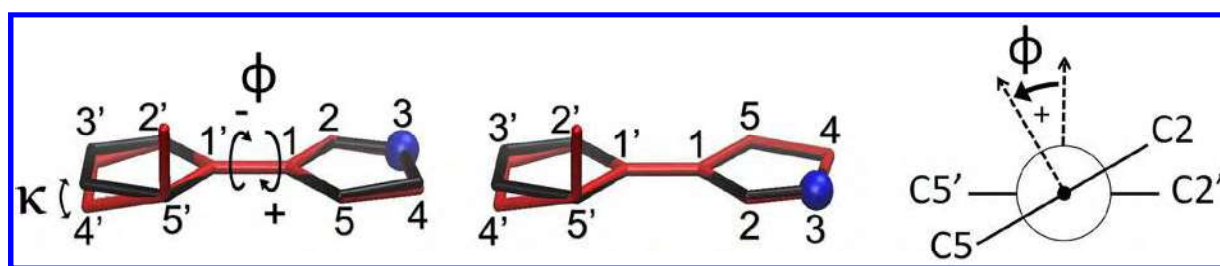


Chart 1. Z isomers of the IP framework, chiral (1) and achiral (2) model compounds.

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

1
2
3 perturbed to achieve a unidirectional photoisomerization. The present report addresses some
4
5 of the aspects of this basic question in the context of the design of IP-based motors.
6
7

8 Here, we focus on the pentenylidene-pyrrolinium compounds **1** and **2** (see Chart 1) as
9
10 minimal models of IPs²⁶. While **2** is planar and therefore achiral, **1** is made chiral by inserting
11
12 a methyl group in an allylic position with respect to the exocyclic (central) double bond. This
13
14 allows to investigate: (a) whether the inserted single stereogenic center would be sufficient to
15
16 induce a unidirectional photoisomerization of the exocyclic bond and (b) what is the exact
17
18 mechanism prompting the unidirectional twisting and in particular the putative role of a C=C
19
20 bond pre-twist. We compute statistical ensembles of gas-phase, *ab initio* non-adiabatic
21
22 molecular trajectories to show that the stereogenic center of **1**, imposing very limited
23
24 symmetry breaking (i.e. a pre-twist of ca. 2°), is enough to generate a significant
25
26 unidirectional motion in a room-temperature molecular population. We show that the mere
27
28 *geometrical distortions* of the untwisted C=C bond of **2** or the *inertial motion of the methyl*
29
30 *substituent* of the stereogenic center of **1** are *not* contributing to the directionality
31
32 significantly.
33
34
35
36
37

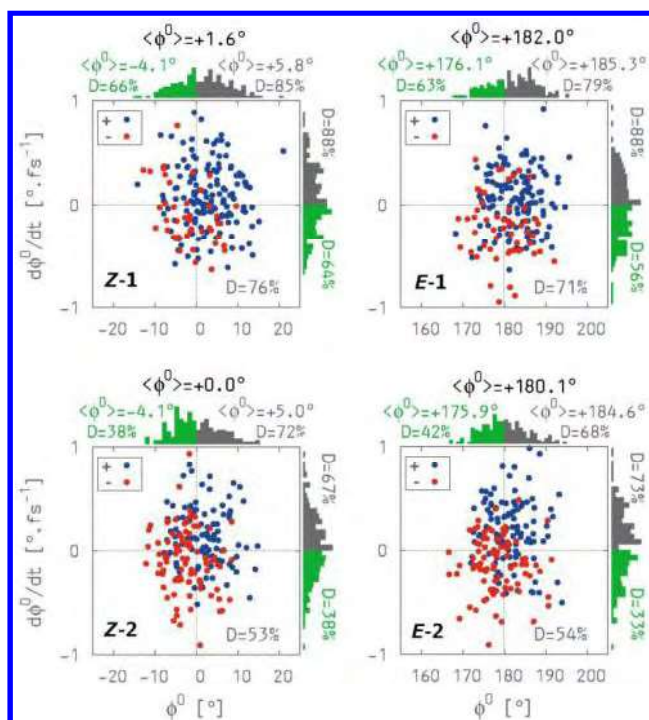


48 **Figure 1.** Superimposed structures of the chiral **1** (red) and achiral **2** (black) *Z* (left) and *E*
49
50 (right) ground state equilibrium geometries. An unconventional numbering is used for
51
52 facilitating the discussion. Hydrogen atoms are not shown, nitrogen atoms are represented
53
54 with a blue sphere. Carbons 4, 4', 5 and 5' have sp^3 hybridization. The counterclockwise (+)
55
56 direction of rotation implies an increase in the value of the twisting angle ϕ defined in the
57
58 Newman projection. The largest out-of-plane deformation in **1** is along the dihedral angle κ .
59
60

1
2
3
4
5 All computations are performed using the *ab initio* CASSCF method²⁷ and the 6-31G* basis
6 set with 6 electrons in 6 π -type orbitals (see SI for details). *Ab initio* non-adiabatic trajectories
7 (see e.g.^{5, 13-14, 19, 28-29}) are computed using the recent implementation¹⁹ in Molcas 7.8³⁰ of
8 Tully's surface hopping algorithm³¹ with quantum decoherence correction³². The computed
9 singlet ground state (S_0) equilibrium structures of **1** and **2** are found to be very similar
10 irrespective of the isomer (*Z* or *E*) actually compared (see Figure 1 and Table S1 in the SI).
11
12 The main differences are found in the out-of-plane deformation of the pentenylidene ring, best
13 characterized by the dihedral angle $\kappa = C1-C1'-C5'-C4'$. For compounds *Z*-**1** and *E*-**1**, $\kappa = -$
14 15.7° and -13.9° respectively, while $\kappa = 0^\circ$ for the planar compound **2**. To characterize the
15 twisting of the central double bond we introduce the internal coordinate $\phi = (C2'-C1'-C1-C2$
16 $+ C5'-C1'-C1-C5)/2$ which approximately measures the alignment of the two p-orbital axes of
17 the $C1'$ and $C1$ sp^2 centers defining the reactive π -bond. While $\phi = 0^\circ$ (180°) for both isomers
18 of the planar achiral compound **2**, we note that in the chiral compound **1** the double bond is
19 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
20 respectively. Here, the (+) sign in the twist angle refers to the counterclockwise direction of
21 rotation of the pyrrolinium moiety ("rotor") with respect to the fixed cyclopentenylidene ring
22 ("stator") as illustrated in the Newman projection of Fig. 1 and in the movie in the SI. Since **1**
23 and **2** have nearly untwisted $C1=C1'$ double bonds one should expect to see no difference
24 between these two compounds and therefore little isomerization directionality, if any. We
25 shall see that this is *not* the case.
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52

53 Starting from the computed equilibrium structures of each *Z* and *E* isomer of **1** and **2**, 200
54 initial conditions (positions and velocities) are generated using the classical thermal sampling
55 with a Boltzmann distribution at temperature 300 K (see details in the SI). The histograms of
56 initial values of ϕ and κ angles (and corresponding initial velocities) are shown in Fig. 2 and 3
57
58
59
60

1
2
3 respectively (notice that the full width at half maximum of the ϕ distribution is ca. 5 times
4 larger than the S_0 pre-twist). These initial conditions define an ensemble of trajectories
5 larger than the S_0 pre-twist). These initial conditions define an ensemble of trajectories
6 released in the first singlet excited state (S_1), the spectroscopically allowed $\pi \rightarrow \pi^*$ transition in
7 these systems. Among all trajectories about 10% do not react (i.e. do not decay to S_0) within
8 600 fs of propagation time and are disregarded in our analysis. The reactive trajectories
9 evolve in S_1 until a conical intersection seam is approached where the trajectories hop to S_0
10 when ϕ is approaching a $\pm 90^\circ$ value. Hopping times are distributed between 100 and 500 fs,
11 with a maximum probability at about 200 fs (see the SI), with no significant differences
12 between **1** and **2**. After the decay to S_0 further twisting along the same direction leads to
13 successful isomerization. However twisting in the reverse direction may also be observed,
14 leading to an aborted isomerization. Irrespective of clockwise or counterclockwise twisting
15 directions in S_1 , about 80% of the reactive trajectories lead to a successful isomerization (see
16 the SI).
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



1
2
3 **Figure 2.** Correlation between the initial average twisting $\langle\phi^0\rangle$ and the photoisomerization
4 directionality (+/-). Differences between the initial average value $\langle\phi^0\rangle$ and the ground state
5 optimized ϕ^0 value of the twisting of the central double bond twisting angles in **2** must be due
6 to the limited size of the populations. The differences in **1** may also be due to the
7 anharmonicity of the potential energy well.
8
9

10
11
12
13
14
15
16 We now define the directionality D of a population as the percentage of the reactive
17 trajectories travelling in the counterclockwise (+) direction. Uncertainties in D due to the
18 finite number of trajectories are estimated to be $\sim 4\%$ (see SI). As expected for the planar,
19 achiral compound **2**, the obtained D values of 53% and 54% for isomer Z and E , respectively,
20 are consistent within the statistical uncertainty with a pure non-directional ($D=50\%$) behavior.
21
22 Instead, and despite the very limited $C1'=C1$ pre-twist, the chiral molecule **1** displays a
23 significant directionality with $D=76\%$ for the Z isomer and $D=71\%$ for the E isomer. This
24 appears to be in contrast with the conjecture mentioned above that a chiral force field
25 inducing a significant S_0 double bond pre-twist, and therefore helicity, is required for an
26 effective unidirectional rotation, as other systems including Rh would suggest.
27
28
29
30
31
32
33
34
35
36
37
38

39
40 In order to inspect the influence of the initial pre-twist in these compounds, we analyze the
41 ensemble of trajectories in subsets (subpopulations) corresponding to positive (gray bars in
42 Fig. 2) and negative (green bars in Fig. 2) initial values of the pre-twist (ϕ^0) and of their
43 corresponding velocities ($d\phi^0/dt$). The average pre-twist $\langle\phi^0\rangle$ and directionality D computed
44 over each subpopulation are given in Fig. 2. Consistent with the pre-twist conjecture for the
45 achiral compound **2**, positive (resp. negative) pre-twists and velocities favor the motion in the
46 “+” (resp. “-“) direction (blue and red points in the 2D map). Indeed, with respect to the
47 directionality D of the entire population, the directionality computed for the positively
48 (negatively) pre-twisted subpopulations increases (decreases) nearly symmetrically, and
49 proportionally to the average pre-twist of each sub-population as shown in Table 1. This
50
51
52
53
54
55
56
57
58
59
60

1
2
3 mirror-symmetry unidirectional dynamics is observed for both isomers of the achiral
4
5 compound **2**.
6

7
8 In contrast, a substantial inconsistency with the pre-twist conjecture is obtained when
9
10 performing the same analysis for **1**. Indeed, *in spite of a similar quasi-symmetric displacement*
11 *in the $\langle\phi^0\rangle$ values of the two subpopulations*, the corresponding D values vary less than in **2**.
12
13 Most importantly, the D values remain significantly above 50% for both subpopulations, thus
14
15 indicating *a mirror-symmetry breaking at a dynamical level* for both isomers. Notice that the
16
17 analysis of the average $d\phi^0/dt$ leads to conclusions similar to that of $\langle\phi^0\rangle$. Thus, although an
18
19 initial positive or negative pre-twist may induce a significant directionality in the achiral
20
21 molecule in the corresponding direction, a similar negative pre-twist of -4.1° (resp.
22
23 $176.1^\circ=180-3.9$) is *not enough* to suppress the directionality in **1** which remains as large as
24
25 66% (resp. 63%) for the Z (resp. E) isomer. We conclude that a substantial geometrical pre-
26
27 twist in S_0 is not, by itself, required for leading to the directionality observed in **1**.
28
29
30
31
32
33
34
35
36

37 **Table 1.** Analysis of the ensembles of trajectories displayed in Fig. 2 in two subpopulations.
38
39 D_+-D (resp. D_-D) are the change in directionality of the subpopulations with respect to the
40
41 total population and $\Delta\langle\phi^0\rangle$ the average pre-twist of the sub-populations.
42
43
44

	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**.

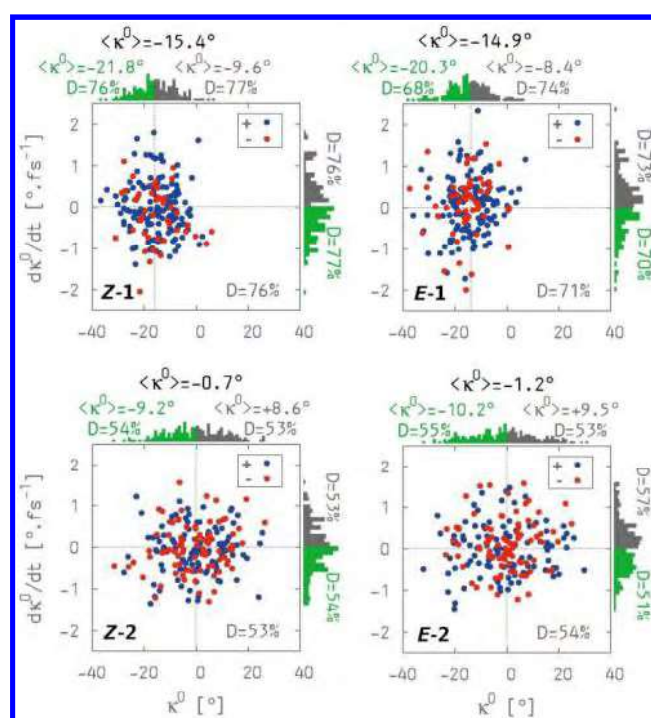


Figure 3. Correlation between the initial deformation κ^0 and the photoisomerization direction (+/-).

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 .

1
2
3 The larger mass of the methyl substituent in **1** compared to the hydrogen in **2** may also
4 affect the dynamics by modulating the velocity of each single atom or group, and is therefore
5 a potential origin of directionality through an inertial effect. To investigate this effect, a new
6 run of 200 trajectories of *Z-2* with its original set of positions and velocities is computed
7 imposing the mass of a methyl group to the pro-S hydrogen in position C5'. Thus, such a
8 "heavy" *Z-2* molecule evolves on the same potential energy surfaces as the original "light"
9 compound. This ensemble (see details in Fig. S3 and S4 of the SI) yields a directionality of
10 $D=56%$, which is marginally different from $D=53%$ obtained with the natural hydrogen mass,
11 and significantly smaller than the $>70%$ directionality computed for compound **1**. Hence, the
12 heavier mass of the methyl substituent does not affect the directionality when imposed on a
13 system with a symmetric force field in both S_0 and S_1 .
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28

29 The results above show that neither an initial geometrical deformation nor an inertial effect
30 are at the origin of a net directionality in the dynamics of the chiral compound **1**. Therefore,
31 the observed large directionality (i.e. not a full directionality) must be induced by the
32 stereogenic center imposing the asymmetry of the S_1 potential energy surface driving the
33 dynamics. This concept is illustrated and demonstrated in Fig. 4 for the *Z* isomer of the chiral
34 compound **1** (see the same figure for the *E* isomer in the SI). The minimum energy path,
35 computed in terms of the intrinsic reaction coordinate starting from the Franck-Condon (FC)
36 region of the isomer, reveals that the $C_1=C_1'$ immediately elongates (relaxation along the
37 stretch coordinate), as is common to all N-protonated or N-alkylated Schiff bases. This
38 motion "unlocks" the central double bond and initiates the twisting around the bond *in a*
39 *specific direction*. Such twisting direction is imposed by the S_1 potential energy surface
40 asymmetry along ϕ (see inset in Fig. 4). This asymmetry is present in the FC region and
41 persists while the central bond stretches, thus triggering the twisting in the counterclockwise
42 direction preferentially. Notice that, in our prototype system such small asymmetry goes in
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32 The above conclusions may be important for the design of IP-based single-molecule
33 molecular motors where photoisomerization dynamics (e.g. photoreaction speed, yield,
34 vibrational coherence or directionality) is commonly rationalized or predicted by discussing
35 ground state equilibrium geometries. The presented compound **1** appears to be a borderline
36 prototype featuring a high, but not full, directionality. For such system, the documented 76%
37 and 71% directionality of **1** in the $Z \rightarrow E$ and $E \rightarrow Z$ isomerization steps respectively predict that
38 ca. 54% of the initially thermalized and reactive population (76% x 71%) will perform a full
39 $Z \rightarrow E \rightarrow Z$ rotation by absorbing two photons sequentially. In the same conditions 39% of the
40 population (24% x 71% + 76% x 29%) would have not rotated and 7% (24% x 29%) would
41 have rotated in opposite direction. This allows us to conclude that, on average 47% (= 54%-
42 7%) of the mechanical work produced by an isomerizing molecule over one full turn could be
43 exploited.

1
2
3 **Supporting Information.** Computational method; CASSCF molecular orbitals and
4 occupation numbers; geometries of the optimized structures; trajectory movies showing
5 photoisomerizations in the positive and negative directions; quantum yields; S₁ lifetimes. This
6 material is available free of charge via the Internet at <http://pubs.acs.org>.
7
8
9
10
11

12 **Present Addresses**

13
14
15
16
17 || Present Address: Chemistry Department, UMR 6230, CNRS-University of Nantes,
18 France.
19
20
21

22 **ACKNOWLEDGMENT**

23
24
25
26 We thank Lutz Greb for sharing unpublished information. This work was supported by the
27 French Agence Nationale de la Recherche (ANR) through the grant ANR-11-JS04-0010 and
28 the High-Performance Computing center (pôle HPC) at Université de Strasbourg. L.M.F. and
29 A.V. acknowledge support from grants CTQ-2012-36966 of the Spanish Secretaría de Estado
30 de Investigación Desarrollo e Innovación, and CCG2013/EXP-089 of the University of
31 Alcalá.
32
33
34
35
36
37
38
39
40

41 **References**

- 42
43
44
45 (1) Feynman, R. P. L., R.; Sands, M. *The Feynman Lectures on Physics*. 1963; Vol. 1.
46 (2) Lumento, F.; Zanirato, V.; Fusi, S.; Busi, E.; Latterini, L.; Elisei, F.; Sinicropi, A.;
47 Andruniów, T.; Ferré, N.; Basosi, R., *et al.* Quantum Chemical Modeling and Preparation of a
48 Biomimetic Photochemical Switch. *Angew. Chem. Int. Ed.* **2007**, *46*, 414-420.
49 (3) Kandori, H.; Shichida, Y.; Yoshizawa, T. Photoisomerization in Rhodopsin.
50 *Biochemistry-Moscow* **2001**, *66*, 1197-1209.
51 (4) Wang, Q.; Schoenlein, R. W.; Peteanu, L. A.; Mathies, R. A.; Shank, C. V. Vibrationally
52 Coherent Photochemistry in the Femtosecond Primary Event of Vision. *Science* **1994**, *266*,
53 422-424.
54 (5) Polli, D.; Altoe, P.; Weingart, O.; Spillane, K. M.; Manzoni, C.; Brida, D.; Tomasello,
55 G.; Orlandi, G.; Kukura, P.; Mathies, R. A., *et al.* Conical Intersection Dynamics of the
56 Primary Photoisomerization Event in Vision. *Nature* **2010**, *467*, 440-U88.
57 (6) Briand, J.; Braem, O.; Rehault, J.; Leonard, J.; Cannizzo, A.; Chergui, M.; Zanirato, V.;
58 Olivucci, M.; Helbing, J.; Haacke, S. Coherent Ultrafast Torsional Motion and Isomerization
59 of a Biomimetic Dipolar Photoswitch. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3178-3187.
60

- (7) Léonard, J.; Schapiro, I.; Briand, J.; Fusi, S.; Paccani, R. R.; Olivucci, M.; Haacke, S. Mechanistic Origin of the Vibrational Coherence Accompanying the Photoreaction of Biomimetic Molecular Switches. *Chem. Eur. J.* **2012**, *18*, 15296-15304.
- (8) Léonard, J.; Briand, J.; Fusi, S.; Zanirato, V.; Olivucci, M.; Haacke, S. Isomer-Dependent Vibrational Coherence in Ultrafast Photoisomerization. *New J. Phys.* **2013**, *15*, 105022.
- (9) Sinicropi, A.; Martin, E.; Ryazantsev, M.; Helbing, J.; Briand, J.; Sharma, D.; Léonard, J.; Haacke, S.; Cannizzo, A.; Chergui, M., *et al.* An Artificial Molecular Switch That Mimics the Visual Pigment and Completes Its Photocycle in Picoseconds. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 17642-17647.
- (10) Strambi, A.; Durbeej, B.; Ferré, N.; Olivucci, M. Anabaena Sensory Rhodopsin Is a Light-Driven Unidirectional Rotor. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 21322-21326.
- (11) Garavelli, M.; Celani, P.; Bernardi, F.; Robb, M. A.; Olivucci, M. The C5h6nh2+ Protonated Schiff Base: An Ab Initio Minimal Model for Retinal Photoisomerization. *J. Am. Chem. Soc.* **1997**, *119*, 6891-6901.
- (12) Weingart, O.; Schapiro, I.; Buss, V. Photochemistry of Visual Pigment Chromophore Models by Ab Initio Molecular Dynamics. *J. Phys. Chem. B* **2007**, *111*, 3782-3788.
- (13) Klaffki, N.; Weingart, O.; Garavelli, M.; Spohr, E. Sampling Excited State Dynamics: Influence of Hoop Mode Excitations in a Retinal Model. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14299-14305.
- (14) Ruckenbauer, M.; Barbatti, M.; Müller, T.; Lischka, H. Nonadiabatic Photodynamics of a Retinal Model in Polar and Nonpolar Environment. *J. Phys. Chem. A* **2013**, *117*, 2790-2799.
- (15) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. Light-Driven Monodirectional Molecular Rotor. *Nature* **1999**, *401*, 152-155.
- (16) Kazaryan, A.; Kistemaker, J. C. M.; Schäfer, L. V.; Browne, W. R.; Feringa, B. L.; Filatov, M. Understanding the Dynamics Behind the Photoisomerization of a Light-Driven Fluorene Molecular Rotary Motor. *J. Phys. Chem. A* **2010**, *114*, 5058-5067.
- (17) Unidirectional motion has also been recently demonstrated to occur in an imine featuring an overcrowded N=C bond.¹⁸
- (18) Greb, L.; Lehn, J.-M. Light-Driven Molecular Motors: Imines as Four-Step or Two-Step Unidirectional Rotors. *J. Am. Chem. Soc.* **2014**, *136*, 13114-13117.
- (19) García-Iriepa, C.; Marazzi, M.; Zapata, F.; Valentini, A.; Sampedro, D.; Frutos, L. M. Chiral Hydrogen Bond Environment Providing Unidirectional Rotation in Photoactive Molecular Motors. *J. Phys. Chem. Lett.* **2013**, *4*, 1389-1396.
- (20) Schoenlein, R. W.; Peteanu, L. A.; Wang, Q.; Mathies, R. A.; Shank, C. V. Femtosecond Dynamics of *Cis-Trans* Isomerization in a Visual Pigment Analog: Isorhodopsin. *J. Phys. Chem.* **1993**, *97*, 12087-12092.
- (21) Kochendoerfer, G. G.; Mathies, R. A. Spontaneous Emission Study of the Femtosecond Isomerization Dynamics of Rhodopsin. *J. Phys. Chem.* **1996**, *100*, 14526-14532.
- (22) Kukura, P.; McCamant, D. W.; Yoon, S.; Wandschneider, D. B.; Mathies, R. A. Structural Observation of the Primary Isomerization in Vision with Femtosecond-Stimulated Raman. *Science* **2005**, *310*, 1006-1009.
- (23) Altoè, P.; Cembran, A.; Olivucci, M.; Garavelli, M. Aborted Double Bicycle-Pedal Isomerization with Hydrogen Bond Breaking Is the Primary Event of Bacteriorhodopsin Proton Pumping. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 20172-20177.
- (24) Okada, T.; Sugihara, M.; Bondar, A.-N.; Elstner, M.; Entel, P.; Buss, V. The Retinal Conformation and Its Environment in Rhodopsin in Light of a New 2.2 Å Crystal Structure. *J. Mol. Biol.* **2004**, *342*, 571-583.

1
2
3 (25) Struts, A. V.; Salgado, G. F. J.; Tanaka, K.; Krane, S.; Nakanishi, K.; Brown, M. F.
4 Structural Analysis and Dynamics of Retinal Chromophore in Dark and Meta I States of
5 Rhodopsin from 2h Nmr of Aligned Membranes. *J. Mol. Biol.* **2007**, *372*, 50-66.

6
7 (26) Sampedro, D.; Migani, A.; Pepi, A.; Busi, E.; Basosi, R.; Latterini, L.; Elisei, F.; Fusi,
8 S.; Ponticelli, F.; Zanirato, V., *et al.* Design and Photochemical Characterization of a
9 Biomimetic Light-Driven Z/E Switcher. *J. Am. Chem. Soc.* **2004**, *126*, 9349-9359.

10 (27) Roos, B. O. The Complete Active Space Self-Consistent Field Method and Its
11 Applications in Electronic Structure Calculations. In *Advances in Chemical Physics*, John
12 Wiley & Sons, Inc.: 2007; pp 399-445.

13 (28) Groenhof, G.; Bouxin-Cademartory, M.; Hess, B.; de Visser, S. P.; Berendsen, H. J. C.;
14 Olivucci, M.; Mark, A. E.; Robb, M. A. Photoactivation of the Photoactive Yellow Protein:
15 Why Photon Absorption Triggers a Trans-to-Cis Isomerization of the Chromophore in the
16 Protein. *J. Am. Chem. Soc.* **2004**, *126*, 4228-4233.

17 (29) Barbatti, M. Nonadiabatic Dynamics with Trajectory Surface Hopping Method. *Wiley*
18 *Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 620-633.

19 (30) Aquilante, F.; De Vico, L.; Ferré, N.; Ghigo, G.; Malmqvist, P.-å.; Neogrady, P.;
20 Pedersen, T. B.; Pitoňák, M.; Reiher, M.; Roos, B. O., *et al.* Molcas 7: The Next Generation.
21 *J. Comput. Chem.* **2010**, *31*, 224-247.

22 (31) Tully, J. C. Molecular Dynamics with Electronic Transitions. *J. Chem. Phys.* **1990**, *93*,
23 1061-1071.

24 (32) Granucci, G.; Persico, M.; Zocante, A. Including Quantum Decoherence in Surface
25 Hopping. *J. Chem. Phys.* **2010**, *133*, 134111.
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60