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# Inverse versus Normal Dithienylethenes: Computational Investigation of the Photocyclization Reaction

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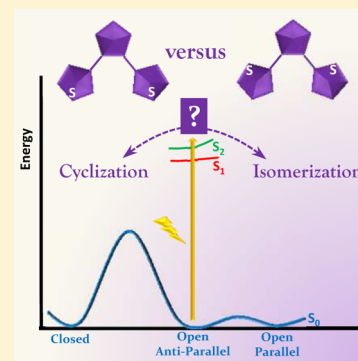
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## Supporting Information

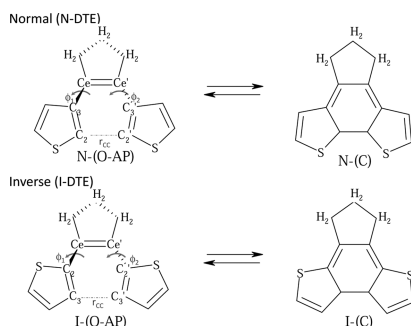
**ABSTRACT:** The understanding of the intimate electronic processes in photochromes is essential to optimize the properties of light-controllable devices. For one of the most studied classes of molecular switches, namely, dithienylethenes, the relative efficiencies of the normal and inverse structures remained puzzling. Indeed, despite a larger ratio of the active antiparallel conformers for the latter, the quantum yields of cyclization of inverse dithienylethenes do not exceed those of its normal counterpart. In the present contribution, we provide the first explanation of this experimental outcome using multireference ab initio quantum chemistry. We demonstrate the existence of a fluorescent intermediate on the  $S_1$  state of the inverse system that generates a photochemically unreactive conformation in the ground state. This study paves the way toward a rational development of efficient molecular photochromes presenting a photon-quantitative response.

**SECTION:** Molecular Structure, Quantum Chemistry, and General Theory



In the course of developing molecular optoelectronic and optobioelectronic devices, dithienylethenes<sup>1</sup> (DTE) have

**Scheme 1. Representation of the Two DTE under Study, With Numbering of the Key Atomic Positions and Dihedral Angles**



**Table 1.** Selected CASSCF Geometrical Parameters and Relative CASPT2 Energy of the Stationary Points and the CIs of N-DTE<sup>a</sup>

state	structure	$r_{CC}$	$\phi_1$	$\phi_2$	relative energy
N-S <sub>0</sub>	O-AP	3.530	53.0	42.8	0.0
	C	1.546	3.9	3.7	2.0
	O-P	4.377	−143.1	46.8	−0.8
	TS1 <sup>b</sup>	1.989	20.7	19.3	46.2
	TS2 <sup>c</sup>	4.767	111.1	79.9	2.7
N-S <sub>1</sub>	O-AP	2.241	11.1	12.0	72.6
	C	1.560	10.5	11.8	72.9
	O-P	4.692	−177.1	8.7	103.8
	TS <sup>d</sup>	1.929	14.7	15.9	68.0
N-S <sub>2</sub>	O-AP	3.325	−0.6	0.5	120.6
	C	1.569	12.6	13.2	105.8
	O-P	4.752	177.0	−0.4	120.0
N-CI(S <sub>2</sub> /S <sub>1</sub> )		2.554	31.2	16.9	122.5 (2.0)
N-CI(S <sub>1</sub> /S <sub>0</sub> )		2.011	49.7	10.8	102.9 (9.1)

<sup>a</sup>Distances are in Å, and torsion angles are in degrees. The relative energies with respect to N-S<sub>0</sub>(O-AP) are in kcal·mol<sup>−1</sup>. For CIs, the value of the upper state is given, whereas the values in brackets correspond to the energy differences between the upper and lower states. <sup>b</sup>Connects N-S<sub>0</sub>(O-AP) and N-S<sub>0</sub>(C). <sup>c</sup>Connects N-S<sub>0</sub>(O-AP) and N-S<sub>0</sub>(O-P). <sup>d</sup>Connects N-S<sub>1</sub>(O-AP) and N-S<sub>1</sub>(C).

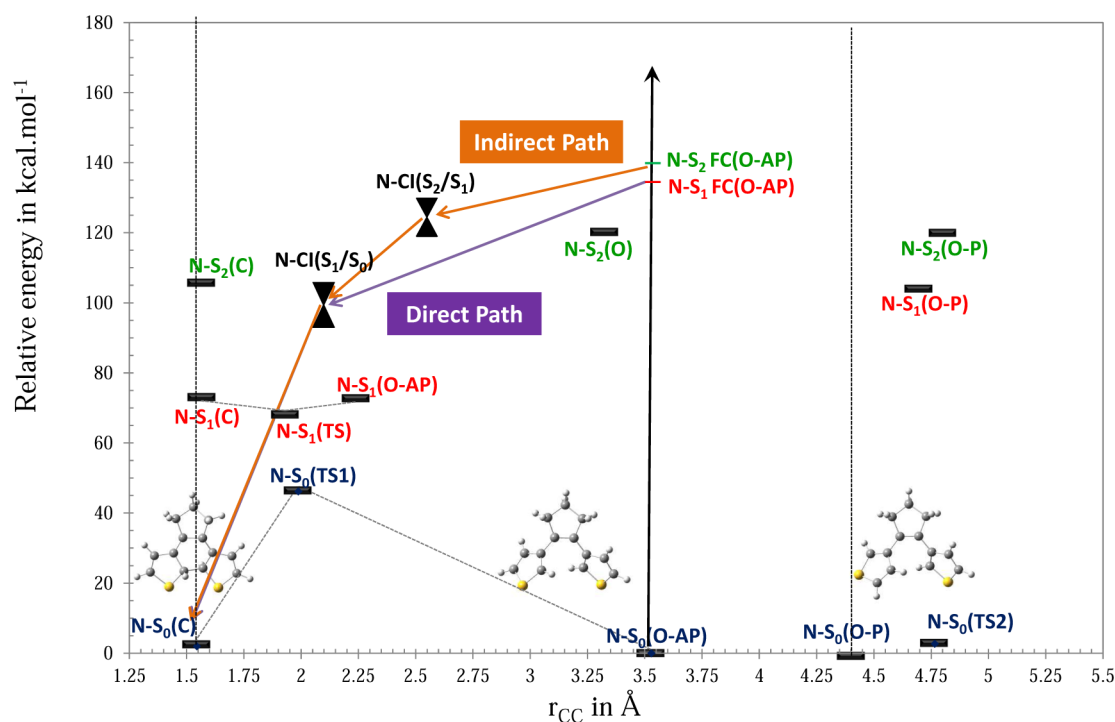
(S<sub>1</sub>) includes a barrier in N-DTE but a more favorable downhill profile in I-DTE.<sup>15</sup> These theoretical studies also pointed out the existence of a conical intersection (CI) between S<sub>0</sub> and S<sub>1</sub> for N-DTE, involved in both cyclization and cycloreversion processes.

With regards to the photocyclization reaction, it is well-known that the QY is limited by the existence of (at least) two OF conformers, a photoactive antiparallel (AP) and nonreactive parallel (P) compounds. For N-type DTE, the AP/P ratio is close to 1:1, limiting the cyclization QY to 0.5,<sup>12,20,21</sup> whereas in I-

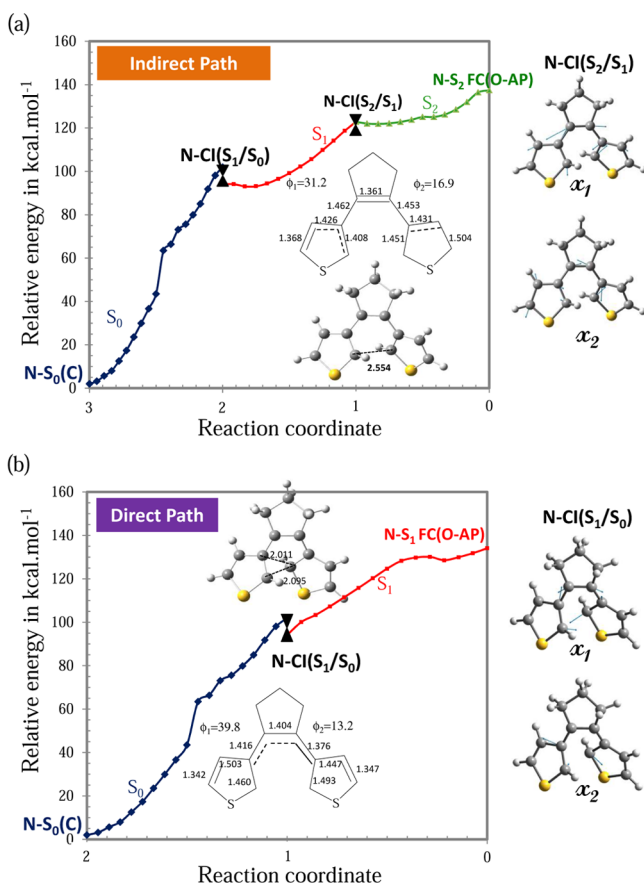
DTE, we have recently demonstrated in a joint theoretical/experimental investigation that the AP conformer is present in large excess (3:1),<sup>22</sup> which would suggest a more effective open-to-closed conversion than that in N-DTE. However, the measured cyclization QY of I-DTE is smaller than that of the corresponding N-type.<sup>16</sup> Indeed, the ring-closure QY of perfluorocyclopentene I-DTE ranges from 0.17 to 0.25,<sup>16</sup> whereas N-DTE, with similar substituents, present QYs in the 0.21–0.50 range.<sup>15,23</sup> To the best of our knowledge, this counterintuitive behavior has never been rationalized before.

Aiming to increase the cyclization QY, Fukumoto et al.<sup>24,25</sup> have recently proposed a N-type dithiazolylazaindole derivative where an intramolecular hydrogen bond stabilizes the DTE in its AP photoactive conformation. This strategy successfully yields to a quasi photon-quantitative reaction, while in the case of I-DTE derivatives stabilized in the AP conformation thanks to the introduction of an alkyl or methoxy bridge between the two thiophene moieties, the photocyclization QY could not exceed 0.7.<sup>26</sup> To respond to the challenging conception of photon-quantitative responsive systems, N-type structures seem to constitute a better candidate than I-DTE, but once again, the underlying photoreactivity remains unexplored.

In this Letter, we have therefore investigated the OF → CF cyclization process for the two DTE of Scheme 1.<sup>27</sup> To this end, the PESs of the ground and low-lying excited states have been obtained at the CASSCF level, and subsequent multiconfigurational second-order perturbation theory (CASPT2) calculations have been carried out to account for the dynamic correlation energy.<sup>28</sup> We must emphasize that CIs are crucial to understand the DTE photoactivity<sup>19</sup> and that the cyclization QY shall depend on different factors.<sup>29</sup> On the one hand, one has to check the existence and accessibility of CI driving such a specific reaction by mapping the relevant PES and locating chemically meaningful CI points.<sup>30</sup> On the other hand, the branching at a



**Figure 1.** PESs of N-DTE. The CASPT2//CASSCF(10,10)/6-31G(d) relative energies of the ground S<sub>0</sub> and two lowest-lying excited states (S<sub>1</sub> and S<sub>2</sub>) are plotted as a function of the distance between the two reactive carbon atoms  $r_{CC}$ .



**Figure 2.** PESs of N-DTE along the (a) indirect and (b) direct cyclization paths. The CASPT2/6-31G(d) relative energies of the ground  $S_0$  and two lowest-lying excited states ( $S_1$  and  $S_2$ ) are plotted as a function of the reaction coordinate. For the former, the reaction coordinates of 0, 1, 2, and 3, respectively, correspond to  $N-S_0(O-AP)$ ,  $N-CI(S_2/S_1)$ ,  $N-CI(S_1/S_0)$ , and  $N-S_0(C)$ , while for the latter, the reaction coordinates of 0, 1, and 2, respectively, correspond to  $N-S_0(O-AP)$ ,  $N-CI(S_1/S_0)$ , and  $N-S_0(C)$ . The variation of the main geometrical parameters along the reaction coordinate can be found in the SI.

**Table 2. Selected CASSCF Geometrical Parameters and CASPT2 Relative Energy of the Stationary Points and the CIs of I-DTE<sup>a</sup>**

state	structure	$r_{CC}$	$\phi_1$	$\phi_2$	relative energy
I- $S_0$	O-AP	3.598	48.2	51.1	0.0
	C	1.560	1.7	1.7	10.0
	O-P	5.016	71.9	-169.1	0.8
	TS1 <sup>b</sup>	2.309	4.3	4.6	56.4
	TS2 <sup>c</sup>	5.075	106.0	109.7	2.6
I- $S_1$	O-AP	3.156	9.6	11.9	88.2
	C	2.352	9.5	10.7	78.3
	O-P	4.782	9.8	-177.0	89.7
I- $S_2$	O-AP	3.345	-1.0	-1.1	111.3
	O-P	4.822	-1.5	177.7	112.9
I- $CI(S_2/S_1)$		2.125	44.5	2.7	136.8 (8.6)
I- $CI(S_1/S_0)$		1.459	114.9	2.0	94.8 (0.2)

<sup>a</sup>The energies are relative to the value of  $S_0(O-AP)$  in kcal·mol<sup>-1</sup>. See the title and footnotes of Table 1 for more details. <sup>b</sup>Connects I- $S_0(O-AP)$  and I- $S_0(C)$ . <sup>c</sup>Connects I- $S_0(O-AP)$  and I- $S_0(O-P)$ .

particular CI point can limit the QY value, and competitive photochemical reaction paths must be considered using

structural and dynamical information. In this work, we explore the possibility that the first factor can rationalize the observed QY. We stress that (i) while the PESs of N-type DTE belonging to the  $C_2$  point group were previously mapped,<sup>15,17–19</sup> these studies focused on the cycloreversion process only; (ii) for I-DTE, no CI between the ground and low-lying excited states was located before;<sup>15</sup> (iii) previous PES mapping did not consider the parallel conformation. These three limitations are overcome in this Letter where we successively examine both N- and I-type PESs.

For the N-DTE, the main structural and energetic properties of the stationary points (minima, transition states (TSs), and CI) are listed in Table 1, whereas detailed structures can be found in the Supporting Information (SI). Figure 1 displays the adiabatic PES [CASPT2//CASSCF(10,10)/6-31G(d) level with no symmetry constraints ( $C_1$ )] for the ground ( $S_0$ ) and the two lowest excited states ( $S_1$  and  $S_2$ ) as a function of the distance between the two reactive carbon atoms  $r_{CC}$ .

Using 6-31G(d), we recover all key features obtained with previous 6-31G calculations.<sup>19</sup> Indeed, the O-AP isomer is more stable than its closed counterpart. The ground-state photocyclization barrier,  $N-S_0(TS1)$ , is large, preventing a thermal reaction, whereas the potential energy barrier on  $S_1$  is much smaller and even disappears at the CASPT2 level. To properly check the existence of such a barrier, one should ideally carry out a geometry optimization at the CASPT2 level.<sup>31</sup> Unfortunately, this computational strategy is still out of reach for DTE structures. As shown in Table 1, on  $S_0$ , the O-P conformer<sup>32</sup> presents the same energy as the AP structure, the difference of less than 1 kcal·mol<sup>-1</sup> in favor of the P structure being within the typical error bar of CASPT2. This is consistent with a 1:1 ratio. In addition, the relatively small P/AP isomerization barrier (less than 3 kcal·mol<sup>-1</sup>),  $N-S_0(TS2)$ , allows for an easy interconversion between the two open conformers. In  $N-S_0(O-P)$ , the distance between the two reactive carbon atoms is larger than 4.2 Å, which was shown to prevent photocyclization.<sup>33</sup> Besides, after excitation, the relaxation on both  $S_1$  or  $S_2$  does not directly go toward the cyclization direction but to further torsional motions, implying stretching of the reactive carbon bond (Figure 1). Hence, as expected, we conclude that the P isomer cannot directly participate to the ring-closure process.

Starting from the only photoactive isomer,  $N-S_0(O-AP)$ , the  $C_1$  photochrome can reach either  $S_1$  or  $S_2$  because the corresponding oscillator strengths are similar (respectively, 0.011 and 0.015, as indicated in Table S.I in the SI, where the vertical energy transitions are analyzed). For N-DTE, recent experimental works<sup>34,35</sup> supported by previous theoretical studies<sup>18,19</sup> have demonstrated that the rapid cyclization reaction (subpicosecond to picosecond time domain) are mediated by CIs. We have identified two CIs,  $N-CI(S_2/S_1)$  and  $N-CI(S_1/S_0)$ , involved in the ring-closure process (see Table 1, Figure 2, and the SI). The structures of the CI as well as the two branching vectors, namely, the gradient difference  $\mathbf{x}_1$  and the derivative coupling  $\mathbf{x}_2$  vectors, are represented in Figure 2. A careful analysis of these data indicates that for each CI, one mode is consistent with the photocyclization process. Indeed, for  $N-CI(S_2/S_1)$  [ $N-CI(S_1/S_0)$ ], a displacement along  $-\mathbf{x}_1$  [ $+\mathbf{x}_1$ ] leads to the formation of a  $\sigma$  bond between the two thiophene rings and to the stretching of the central ethene bond. In short, for N-DTE, we can consider both an indirect or direct cyclization paths (Figure 1):

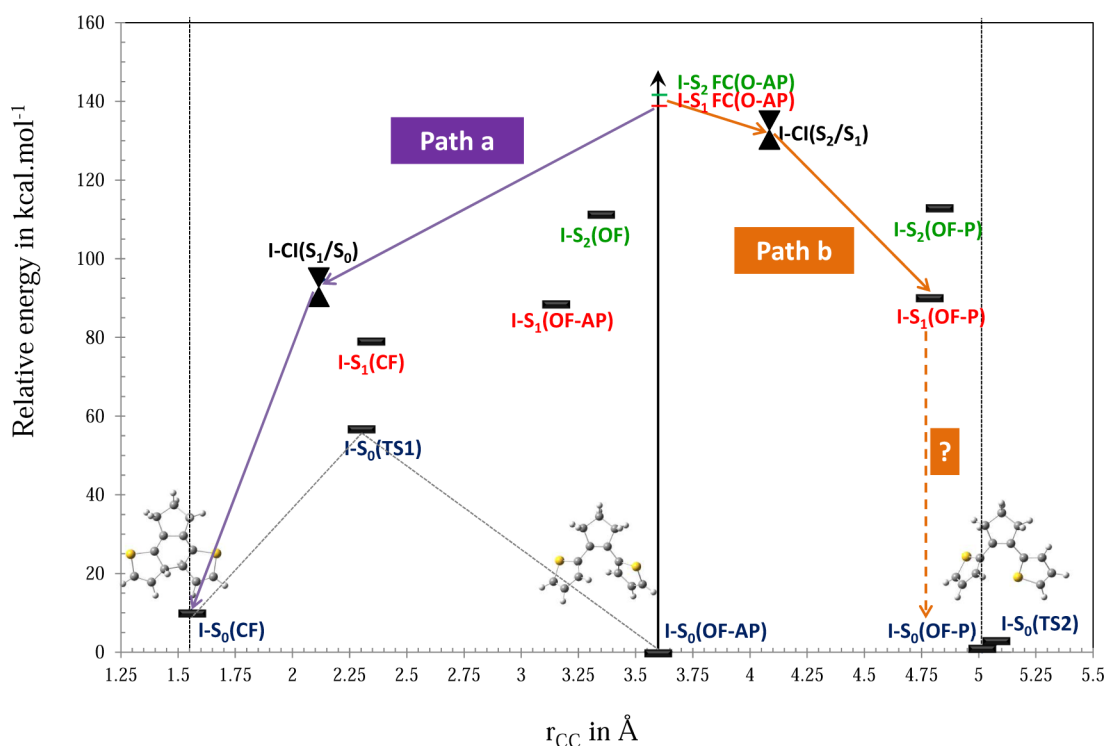
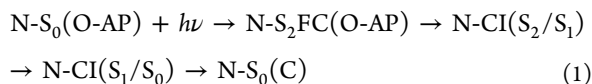
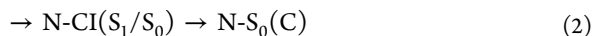


Figure 3. PESs of I-DTE. See the caption of Figure 1 for more details.

Indirect ( $S_2/S_1$  relaxation prior to cyclization):



Direct:  $\text{N-S}_0(\text{O-AP}) + h\nu \rightarrow \text{N-S}_1\text{FC}(\text{O-AP})$

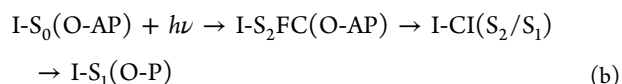
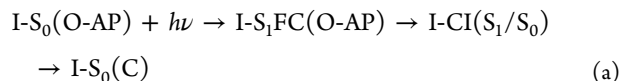


where FC stands for Franck–Condon. The common feature defining the ring-closure path is the relaxation from  $S_1$  to  $S_0$  via  $\text{N-CI}(S_1/S_0)$ , which is in accordance with Kasha's rule.<sup>36</sup> To confirm the existence of these pathways, we have calculated the linear synchronous transit (LST) path,<sup>37</sup> varying linearly all geometrical parameters from one critical point to the following one. Figure 2 shows that the PES along both LST paths systematically goes downhill without a significant potential barrier. We thus conclude that both direct and indirect cyclization paths are energetically possible.

For I-DTE, Table 2 and Figure 3 provide the key structural and energetic information (see also the SI). As in N-DTE, the photocyclization barrier is large on the ground-state PES, whereas the corresponding  $S_1$  PES is rather smooth, which is in perfect accordance with previous calculations.<sup>15</sup> In agreement with DFT calculations,<sup>13,22</sup> Table 2 shows that, contrary to N-DTE, the  $S_0(\text{O-AP})$  conformer is slightly more stable than its P counterpart (though the differences are again small) and that the  $\text{O-AP} \leftrightarrow \text{O-P}$  isomerization barrier  $\text{I-S}_0(\text{TS2})$  is small. The P form  $\text{I-S}_0(\text{O-P})$ , which presents a  $r_{\text{CC}}$  distance larger than the photochromic bond threshold (4.2 Å) displays strongly different photochemical properties compared to the N-type compound; after excitation, the relaxation on either  $S_1$  or  $S_2$  slightly goes toward the decrease of the  $r_{\text{CC}}$  bond distance.

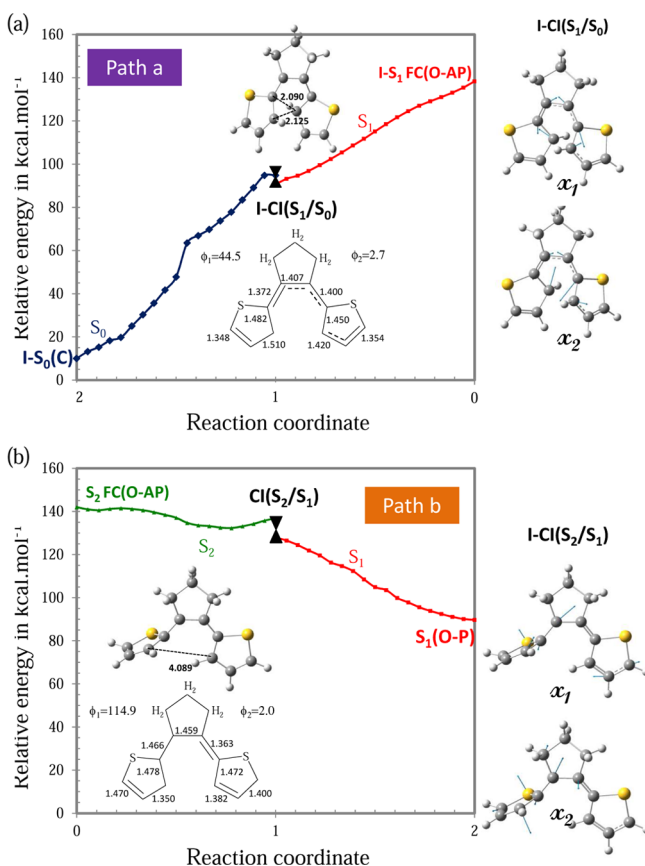
Using the photoactive isomer  $\text{I-S}_0(\text{AP-O})$  as a starting point,  $S_2$  is the brightest state, but  $S_1$  is not completely forbidden, their

respective oscillator strength values being 0.009 and 0.002 (vertical excitation properties are described in the SI). We have identified two CIs,  $\text{I-CI}(S_2/S_1)$  and  $\text{I-CI}(S_1/S_0)$ , and the structure and branching features for these two CI can be found in Figure 4. This figure clearly suggests that  $\text{I-CI}(S_1/S_0)$  is the only CI involved in the ring-closure process. For this CI, the structural parameters are similar to those of the corresponding  $\text{N-CI}(S_1/S_0)$  as well as to the CI mediating the photochemistry of the hexatriene/cyclohexadiene couple (the smallest possible DTE model).<sup>29,38</sup> In this CI, there is a triangular arrangement with a three-electron coupling between  $C_2$ ,  $C_3$ , and  $C_3'$  (see Scheme 1). A displacement along the  $\alpha_1$  vector leads to the formation of the closed-ring structure, whereas  $\alpha_2$  describes the formation of a five-carbon ring leading to a well-known (nonreactive) byproduct.<sup>39–42</sup> The second CI  $\text{I-CI}(S_2/S_1)$  presents a very distinct topology; one of the two thienyl group has a fairly large dihedral angle  $\phi_1$ , leading to a nearly perpendicular orientation of the two thienyl rings. Displacements along the  $\alpha_1$  or  $\alpha_2$  vectors lead to torsional motions, and by following  $\alpha_1$ , a geometry optimization of the  $S_1$  PES actually yields  $\text{I-S}_1(\text{O-P})$ . Two possible reaction pathways can therefore be considered after photoexcitation of  $\text{I-S}_0(\text{AP-O})$  (Figure 3):



The analysis of the LST paths in Figure 4 actually shows that both reaction pathways are energetically possible. For the second path, after reaching  $\text{I-S}_1(\text{O-P})$ , one can reasonably assume that the system will relax radiatively to a ground-state structure presenting a P orientation of the two thiophene rings. Recently,





**Figure 4.** PESs of the I-DTE molecule along paths a and b. For the former, the reaction coordinates 0, 1, and 2, respectively, correspond to I-S<sub>0</sub>(O-AP), I-CI(S<sub>1</sub>/S<sub>0</sub>), and I-S<sub>0</sub>(C) structures. For the latter, the reaction coordinates 0, 1, and 2, respectively, correspond to I-S<sub>0</sub>(O-AP), I-CI(S<sub>2</sub>/S<sub>1</sub>), and I-S<sub>1</sub>(O-P) structures. See Figure 2 and the SI for more details.

using TD-DFT calculations,<sup>22</sup> we have shown that for I-DTE, the P structure is the only isomer responsible for the emission properties (the AP I-DTE displays no luminescence), which is consistent with the present results (see the data of Figure 4). Our results also correlate with recent experimental findings of Uchida et al.,<sup>16</sup> who have found an inverse relationship between the cyclization and fluorescence QYs; the cyclization QY gradually decreases when the fluorescence QY increases. Our simulations hint that this outcome is due to the branching of two pathways after photoexcitation of the AP isomer.

In summary, we have used a CASPT2//CASSCF approach to investigate the cyclization process of one inverse and one normal DTE. It turns out that a CI driving the photocyclization of the population promoted to the S<sub>2</sub> state exists for the N species but not for I-DTE (while both systems are reactive on S<sub>1</sub>). Actually, the unexpected smaller cyclization QY of I-DTE is probably related to the existence of two competitive reaction paths after photoexcitation of the most stable AP open-ring isomer, one efficiently mediating the ring-closure process and the other yielding to an AP ↔ P photoisomerization after S<sub>2</sub> excitation, which is counterproductive for photochromism.<sup>43</sup> In the course of setting up photon-quantitative responsive systems, this study thus shows the following: (1) Without specific care regarding the irradiation wavelength (see 3), the I-DTE family does not constitute the best candidates to conceive efficient photo-switches. (2) The existence of P conformers cannot be

overlooked when studying DTE- photoactive properties; because the Boltzmann population is generally in disfavor of the P structure, its existence is usually neglected, and only few theoretical and/or experimental studies actually consider the evolution of P structures upon light irradiation.<sup>20,34</sup> For the first time, we show that a photochemical reaction path connects the AP and P structures through the existence of a CI. It is thus crucial to consider both the ground-state and excited-state PES features before neglecting the role of the P conformation. (3) The cyclization of inverse DTE could show wavelength dependence; populating exclusively S<sub>1</sub> should increase the cyclization QY, while populating exclusively S<sub>2</sub> should enhance fluorescence. Therefore, by using a lower-energy irradiation wavelength and/or by modifying the DTE skeleton in a way to lift the S<sub>1</sub>–S<sub>2</sub> near-degeneracy, one should increase the I-DTE cyclization QY. We have already proved the existence of such a wavelength effect for the *meta*-cyclophan-1-ene family where the S<sub>1</sub> excitation leads to a cyclization QY value close to unity, whereas for excitation above the S<sub>2</sub> energy threshold, the photocyclization is less efficient, with QYs ranging in the 0.4–0.7 region.<sup>44</sup> We are currently investigating this aspect for DTE in light of the present study.

## METHOD

Stationary points on the ground and low-lying singlet states were determined at the CASSCF(10,10)/6-31G(d) level. The active space includes 10 orbitals occupied by 10 electrons, 10 ( $\pi, \pi^*$ ) orbitals for the open isomers and 8 ( $\pi, \pi^*$ ) plus the 2 ( $\sigma, \sigma^*$ ) orbitals of the C–C reactive bond for the closed isomers. It has been previously shown that a larger active space, including the lone pairs of the sulfur atoms, does not lead to significant differences for the lowest-energy structures as the considered excited states do not involve excitations from lone pair electrons.<sup>17,19,45</sup> The 6-31G(d) atomic basis set represents a compromise between cost and accuracy, and it yields a typical excitation energy error smaller than 3 kcal·mol<sup>−1</sup>.<sup>46</sup> CASSCF/6-31G(d) geometry optimizations were carried out with the Gaussian 09 code.<sup>47</sup> The TS searches have been performed using the synchronous transit-guided quasi-Newton (STQN)<sup>48</sup> implemented in Gaussian 09. For all of the optimized structures, vibrational frequencies have been computed to confirm the nature of the resulting geometry (minimum or a saddle point). To account for dynamical electronic correlation, CASPT2 calculations were carried out by using the MOLCAS 7.8 software.<sup>49</sup> For each optimized geometry, three-root state-averaged calculations with equal weight were performed at the CASSCF/6-31G(d) level of theory and were followed by single-root CASPT2/6-31G(d) calculations relying on the SA-CASSCF wave functions.<sup>50,51</sup> During the CASPT2 calculations, an imaginary shift of 0.1 au was applied to avoid the effects of intruder states while loosing only a minimal amount of dynamical correlation energy.

## ASSOCIATED CONTENT

### Supporting Information

Structures of the main critical points of N-DTE and I-DTE; description of the lowest excited states in the Franck–Condon region; CASSCF potential energy surfaces; variation of the coordinates along the reaction paths; representation of the initial forces in the Franck–Condon region. 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.

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