Angewandte Chemie

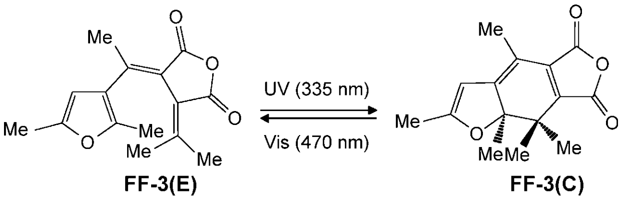
DOI: 10.1002/ange.200907250

Photochromic Systems

Significance of a Zwitterionic State for Fulgide Photochromism: Implications for the Design of Mimics**

Gaia Tomasello, Michael J. Bearpark, Michael A. Robb, Giorgio Orlandi, and Marco Garavelli**

The design of efficient, thermally stable, fatigue-resistant, two-way (i.e., optically bistable) photochromic systems was pursued by Heller and Oliver with 2,5-dimethyl-3-furylfulgide (**FF-3**),[1] a molecule that undergoes a fully reversible photoinduced six-electron ring-closing/ring-opening electrocyclic reaction (Scheme 1).[2] The replacement of the hydrogen atoms on the ring-closing carbon atoms has the two-fold effect of eliminating fatigue (hydrogen-shift side reactions are now prevented) and creating thermal irreversibility (thermal disrotatory ring opening is frustrated for steric reasons), and the use of a heteroaromatic ring enables high conversion efficiency owing to clearly separated absorption bands with high extinction coefficients and high reaction quantum yields (QYs).[3] These properties, added to the minor dependency on the environment and temperature, make fulgides highly attractive for potential applications as optical recording media (for example, fulgide-based nanodots were recently presented as a promising nanotechnological approach to the fabrication of organic memory devices)[4] and molecular photoswitches. In the last two decades, extensive research has been devoted to the improvement of these compounds and the development of related derivatives.



Scheme 1. Light-driven ring-closing (**E**→**C**)/ring-opening (**C**→**E**) electrocyclic reaction of 2,5-dimethylfurylfulgide (**FF-3**).

Femtosecond time-resolved spectroscopy[5–7] has invariably revealed that the **FF-3** open form, **E**, undergoes an efficient and ultrafast internal conversion (IC) that causes a subpicosecond decay of its transient absorption/fluorescence and leads to the direct formation of the closed-ring isomer **C**. Together with this path, a slower (> 10 ps) indirect route involving a bottleneck intermediate, **I**, was also reported for the formation of **C**,[5] although more recent spectroscopic data[6,7] challenge this view. Because of these differing interpretations, and to assess the factors responsible for furyl fulgide photochromism, we mapped the relaxation paths and energies for this process, from the Franck–Condon (FC) region on S_1 to the photoproduct wells on S_0, by advanced CASPT2//CASSCF[8] computations of the minimum-energy path (MEP), to unveil the intrinsic (i.e., in vacuo) electrocyclization ability of **FF-3**. Although a recent time-dependent DFT (TDDFT) study[6] presented clues for an efficient (i.e., barrierless) **E***→**C** electrocyclization path that possibly involves an S_1/S_0 conical intersection (CI), the computational level employed in that study is known to describe charge-transfer states poorly,[9] and is unable to locate CIs, describe their electronic properties, and provide a reliable charge analysis of the photochemically relevant states. We have now overcome these problems and present a scenario herein that is in agreement with the experimental observations. We disclose the principles behind and the chemical/physical basis for the efficient photochromism of **FF-3** and suggest new guidelines for the de novo design of fulgide mimics.

Relevant information and energetic data are collected in Table 1. The bright state S_1 (a single π(HOMO)→π^*(LUMO) excitation) has a dipole moment higher than that of S_0; thus, a significant charge translocation occurs upon excitation from the heteroaromatic ring to the anhydride moiety (see charge analysis in Table 1). This result is consistent with the nature and the polar character of the state that initiates photocyclization, as suggested by previous theoretical[10] studies and by the dependence of the spectroscopic properties of this state on the polarity of the solvent.[11] Both CASPT2 and TDDFT consistently predict a bright S_1 state. Thus, although CASPT2 overestimates the energy of S_1, we can trust (at least qualitatively) the mechanistic scenario presented below, as the order of photorelevant states is correct. Finally, the similarity with the, albeit incomplete, reactive scheme previously found at the TDDFT level[6] adds further support to this conviction (see the Supporting Information for further details and discussions).

Figure 1 displays the MEPs for the photochemical electrocyclic process: following **FF-3**(**E**) excitation, molecules are funneled along a barrierless path that develops entirely along the ionic state S_1 and drives the system towards an S_1/S_0 crossing, **CI**, in which the C1–C6 bond is highly shortened (2.19 Å) with respect to that of the FC structure (3.64 Å). The

---

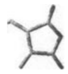
[*] Dr. G. Tomasello, Prof. G. Orlandi, Dr. M. Garavelli
Dipartimento di Chimica "G. Ciamician"
Università degli Studi di Bologna
Via Selmi 2, 40126 Bologna (Italy)
E-mail: marco.garavelli@unibo.it

Dr. M. J. Bearpark, Prof. M. A. Robb
Department of Chemistry, Imperial College London
London SW7 2AZ (UK)
E-mail: m.bearpark@imperial.ac.uk

[**] M.G., G.O., and G.T. thank E4 Computer Engineering Spa for computational time granted and technical assistance.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200907250.

Table 1: Computed relative (E) and vertical energies (ΔE), $S_0 \rightarrow S_1$ oscillator strength (f), wavefunction (Ψ) characterization (relevant configuration and its weight), dipole moment (μ), and charge analysis for the structures discussed in the text.[a]

Structure		E	ΔE[b]	f	Ψ	μ	Charges[c]	
		[kcal mol^{-1}]	[kcal mol^{-1}]			[D]		
E	S_0	0.0	–	–	$(4a)^2\,(5a)^0$ 0.91	6.5	−0.09	0.09
	S_1	100.6	100.6 *81.8* (85.4)	0.12 *0.10*	$(4a)^1\,(5a)^1$ 0.92/*0.64*	14.0	0.63	−0.63
C	S_0	−29.3	–	–	$(4a)^2\,(5a)^0$ 0.89	6.1	0.04	−0.04
	S_1	48.6	77.9 *58.6* (60.9)	0.22 *0.16*	$(4a)^1\,(5a)^1$ 0.88/*0.62*	11.7	0.16	−0.16
CI	S_0	26.4	–	–	$(4a)^2\,(5a)^0$ 0.68	6.5	0.03	−0.03
	S_1	30.4	3.9 *2.0*	0.00 *0.00*	$(4a)^1\,(5a)^1$ 0.82	10.9	0.21	−0.21
C*$_{Min}$	S_0	−2.87	–	–	$(4a)^2\,(5a)^0$ 0.72	7.2	−0.05	0.05
	S_1	25.6	28.5	0.10	$(4a)^1\,(5a)^1$ 0.76	12.9	0.36	−0.36

[a] TDDFT values are also reported in italics for comparison. See the Experimental Section and the Supporting Information for further details. [b] The experimental values for the reaction in toluene are given in brackets.[6] [c] Mulliken charges are summed up on each displayed fragment.

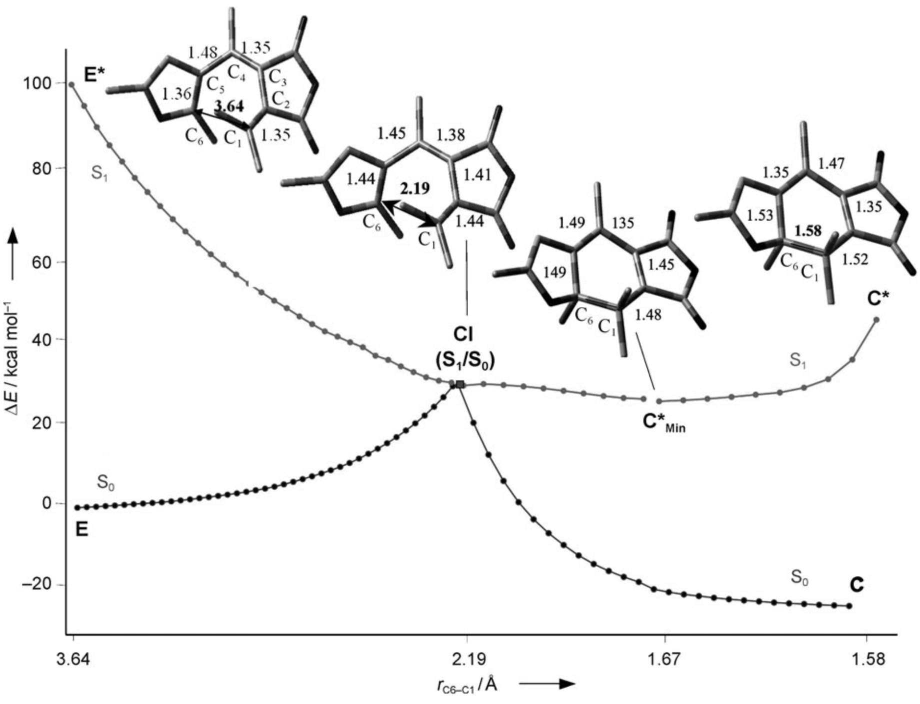


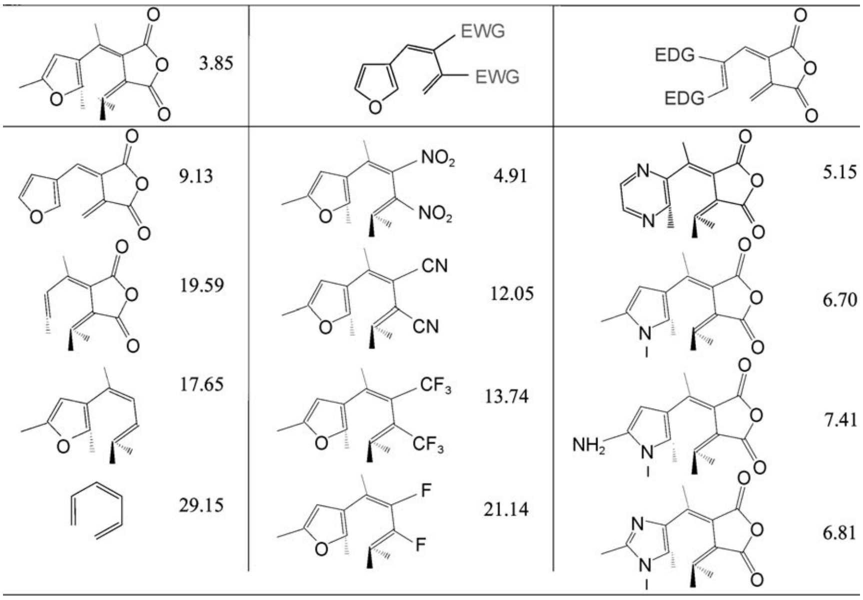
Figure 1. CASPT2//CASSCF/6-31G* MEPs computed on S_1 and S_0 to explain **FF-3** ring-closing/ring-opening photoreactivity (bond lengths in Å).

mechanistic (shortening of the bond formed upon ring closing) and energetic features (lack of excited-state barriers on the path to **CI**) indicate a photoinitiated (yet not finalized on S_1) cyclization process that involves an ultrafast IC and account nicely for the 100 fs fluorescence lifetime of **E***.[6] Upon decay, the photochemical path branches into two routes, one of which leads to **E**, the other to **C**. Notably, other possible processes (e.g., C2−C6 bond formation, which is seen in many other less efficient photocyclization systems) are prevented in this case. Thus, unwanted side reactions that would cause intrinsic fatigue can be ruled out. This reasoning is again in nice agreement with the high photochromic performance and fatigue resistance found for **FF-3**.

Somewhat different behavior is found for the cycloreversion process. In this case, the S_1 MEP drives the system initially to an excited-state intermediate, **C***$_{\mathbf{Min}}$, for which the S_1–S_0 energy gap is still large (ca. 30 kcal mol^{-1}) and which displays a stretched (although not yet broken) C1−C6 bond (1.67 Å). By proceeding along the C1−C6 bond-elongation coordinate and overcoming a small 5 kcal mol^{-1} barrier, the system reaches the same S_1/S_0 crossing **CI** described before. Notably, the existence of **C***$_{\mathbf{Min}}$ and the S_1 barrier to the crossing region account for the larger fluorescence, the slower reaction rate, and the smaller QY (ca. 8%) observed from **C***.[5] We tentatively assign **C***$_{\mathbf{Min}}$ as the intermediate **I** invoked for the slower indirect **E***→**I**→**C** route for the formation of **C**:[5] photoexcited **E*** molecules that escape the **CI** funnel may be trapped in the excited well of **C***$_{\mathbf{Min}}$, and thus follow the fate of **C*** (which is indeed involved in a slower IC process).[5] In any case, this path belongs to the dynamical domain, and its population cannot be assessed at this level. The potential impact of environmental effects, which may disrupt the stability of the shallow excited intermediate **C***$_{\mathbf{Min}}$, ultimately explains the lack of evidence found previously for this route in different environments.[6,7]

The reversibility of the photocyclization, the high ring-closing rate and high QY, the lack of unwanted photoproducts, and, more generally, the remarkable properties that characterize the two-way photochromism of furyl fulgides, depend on the electronic nature of the photochemically relevant state S_1 and, in turn, of the conical intersection involved in the reaction. Specifically, the ionic character of S_1 distinguishes the photoreactivity of furyl fulgides from that of other (often less efficient) systems (e.g., cyclohexadiene,[12,13] 1,2-dihydronaphthalene[14]), whose photochemistry is driven by a covalent S_1 state. Whereas the latter triggers the formation of a biradical minimum, and a barrier is typically necessary to access a tetraradical S_1/S_0 conical intersection for the photocyclization,[13–15] the former leads to a zwitterionic CI along a direct barrierless path from **E***. Remarkable differences in the geometric/electronic properties of the crossings involved account for the very different photochemical outcomes. The prototype covalent/covalent tetraradical conical intersection found in the hexatriene/cyclohexadiene couple[12] is compared with the ionic/covalent CI found in **FF-3** in Figure 2. It is apparent that, whereas the former may simultaneously lead to different, and competitive, electron-recoupling patterns and products (e.g., electron recombinations at positions C1–C6, C2–C6),[12] the latter is biased to a unique outcome, namely, the C1–C6 ring-closing/ring-opening process.

The reason for the intrinsic high stability of the ionic state in furyl fulgides lies in the strong electron-withdrawing (EW) and electron-donating (ED) ability of the anhydride and heteroaromatic groups, respectively, which stabilize this state and its underlying charge transfer. This understanding opens unprecedented scenarios for the de novo design of related photochromes. In fact, it may be assumed that other substituents that act as good EW/ED groups can stabilize this state and promote similar photochromism. The S_1–S_0 energy gap was computed at the position of the **CI** structure found in **FF-3** for differently substituted molecules without the anhydride–furyl functionality (Scheme 2). Remarkably, when the stabilization effect on the ionic state was removed, S_1 became a covalent state (i.e., the ionic state was above S_1), and the degeneracy disappeared (see the large S_1–S_0 energy gaps reported in the first column). Inversely, when strong EW/ED groups were present, the ionic character of S_1 (and, in turn, the ionic/covalent S_1/S_0 CI) was recovered (see the small S_1–S_0 energy gaps in the second and third columns). For example, EW groups, such as nitro, cyano, and trifluoromethyl groups, and ED groups, such as pyrazyl, pyrryl, and imidazyl groups, seem to be good replacements for the anhydride and furyl moieties, respectively, as they return a zwitterionic S_1 state and a conical intersection of similar stability to that of **CI** (Figure 1; note that pyrryl fulgides are already a well-known family of photochromes).[2]



Scheme 2. Effect of alternative EW/ED groups on the S_1–S_0 energy gap (in kcal mol^{-1}) computed for the **CI**-like structure. See text for details.

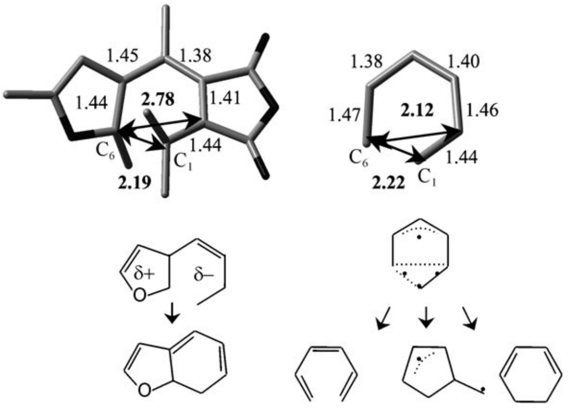


Figure 2. Geometric/electronic structure of the photochemically relevant conical intersections computed for **FF-3** (left) and cyclohexadiene[12] (right; bond lengths in Å).

In conclusion, we have shown that a zwitterionic excited state and its conical intersection with S_0 control the photodynamics of furyl fulgides and determine their remarkable photochromic properties. A rationale was suggested for chemical modifications that preserve the stability of photoinduced charge transfer and would probably lead to compounds that mimic fulgide photochromism. This promising approach should enable the fabrication of novel efficient photochromes.

Experimental Section

A CASPT2//CASSCF/6-31G* approach was adopted; that is, geometry optimizations and fully unconstrained MEP[16] computations were carried out (by using Gaussian03[17]) at the CASSCF level on the ground (single-state wavefunction) and photochemically relevant S_1 states (equally weighted two-root state-average wavefunction), and all the energies and oscillator strengths were reevaluated (by using MOLCAS6)[18] at the CASPT2 level[8] (equally weighted two-root state-average wavefunction, imaginary level shift 0.2 au; see the Supporting Information for results from the use of an equally weighted five-root state-average wavefunction). A reduced active space of eight π electrons in eight π orbitals was always employed. It was selected on the basis of a RASSCF computation of a preliminary full active space (16 π electrons in 14 π orbitals) by excluding all those (mostly empty/doubly occupied) orbitals that are not important for the description of the photochemically relevant states. Oscillator strengths (f) were computed by using correlated (CASPT2) energies within the RASSI approach.[19] TDDFT/B3LYP/6-31G* calculations were also used for comparative purposes when required. See the Supporting Information for further details.

Received: December 23, 2009

Keywords: computational chemistry · conical intersections · electrocyclic reactions · fulgides · photochromism

---

[1] H. G. Heller, S. Oliver, *J. Chem. Soc. Perkin Trans. 1* **1981**, 197.
[2] Y. Yokoyama, *Chem. Rev.* **2000**, *100*, 1717.
[3] H. G. Heller in *CRC Handbook of Organic Photochemistry and Photobiology* (Eds.: W. M. Horspool, P.-S. Song), CRC, Boca Raton, FL, **1995**, p. 173.
[4] S. Rath, M. Heiling, H. Port, J. Wrachtrup, *Nano Lett.* **2007**, *7*, 3845.
[5] M. Handschuh, M. Seibold, H. Port, H. C. Wolf, *J. Phys. Chem. A* **1997**, *101*, 502.
[6] R. Siewertsen, F. Renth, F. Temps, F. Sonnichsen, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5952.
[7] H. Port, P. Gartner, M. Hennrich, I. Ramsteiner, T. Schock, *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 15.
[8] K. Andersson, P. Å. Malmqvist, B. O. Roos, *J. Chem. Phys.* **1992**, *96*, 1218.
[9] A. Dreuw, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, *126*, 4007; A. W. Lange, M. A. Rohrdanz, J. M. Herbert, *J. Phys. Chem. B* **2008**, *112*, 6304.
[10] Y. Yoshioka, T. Tanaka, M. Sawada, M. Irie, *Chem. Lett.* **1989**, *18*, 19.
[11] C. Lenoble, R. S. Becker, *J. Phys. Chem.* **1986**, *90*, 2651.
[12] M. A. Robb, M. Garavelli, M. Olivucci, F. Bernardi, *Rev. Comput. Chem.* **2000**, *15*, 87.
[13] M. Garavelli, P. Celani, M. Fato, M. J. Bearpark, B. R. Smith, M. Olivucci, M. A. Robb, *J. Phys. Chem. A* **1997**, *101*, 2023; A. Nenov, P. Kolle, M. A. Robb, R. de Vivie-Riedle, *J. Org. Chem.* **2010**, *75*, 123.
[14] G. Tomasello, F. Ogliaro, M. J. Bearpark, M. A. Robb, M. Garavelli, *J. Phys. Chem. A* **2008**, *112*, 10096.
[15] M. Boggio-Pasqua, M. Ravaglia, M. J. Bearpark, M. Garavelli, M. A. Robb, *J. Phys. Chem. A* **2003**, *107*, 11139.
[16] M. J. Bearpark, M. A. Robb, H. B. Schlegel, *Chem. Phys. Lett.* **1994**, *223*, 269; P. Celani, M. A. Robb, M. Garavelli, F. Bernardi, M. Olivucci, *Chem. Phys. Lett.* **1995**, *243*, 1.
[17] M. J. Frisch et al., Gaussian, Inc., Wallingford CT, **2004**.
[18] G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, *Comput. Mater. Sci.* **2003**, *28*, 222.
[19] P.-Å. Malmqvist, B. O. Roos, *Chem. Phys. Lett.* **1989**, *155*, 189.