

A Fast and Stable Photochromic Switch Based on the Opening and Closing of an Oxazine Ring

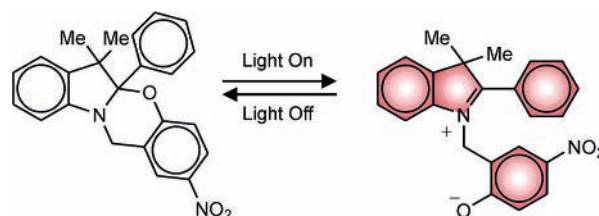
Massimiliano Tomasulo,[†] Salvatore Sortino,^{*,‡} and Francisco M. Raymo^{*,†}

Center for Supramolecular Science, Department of Chemistry, University of Miami,
1301 Memorial Drive, Coral Gables, Florida 33146-0431, and Dipartimento di
Scienze Chimiche, Università di Catania, viale Andrea Doria 8,
Catania, I-95125, Italy

ssortino@unict.it; fraymo@miami.edu

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ABSTRACT



We have designed a molecular switch based on the photoinduced opening and thermal closing of an oxazine ring. Ultraviolet excitation of this molecule induces the cleavage of a [C–O] bond to form a *p*-nitrophenolate chromophore in less than 10 ns with a quantum yield of ca. 0.1. The photogenerated isomer reverts thermally to the original oxazine within 50 ns. Our photochromic switch survives more than 3000 excitation cycles without decomposing, even in air-saturated solutions.

Photochromic compounds change their structural and electronic properties in response to optical stimulations.¹ The photogenerated state reverts to the original form either thermally or after the application of a second optical input differing in wavelength from the first. Thermally reversible photochromes offer the opportunity to alter and reset the state of an output property (e.g., color or refractive index) by simply turning on and off a light source, since they do not retain the influence of the incident radiation. The ability to restore the output level and the lack of memory effects are essential conditions for the implementation of combinational

logic functions.² As a result, these compounds have emerged as possible building blocks for the construction of molecular logic gates.³ Indeed, recent investigations have demonstrated that collections of photochromic compounds in solution^{4–10}

[†] University of Miami.

[‡] Università di Catania.

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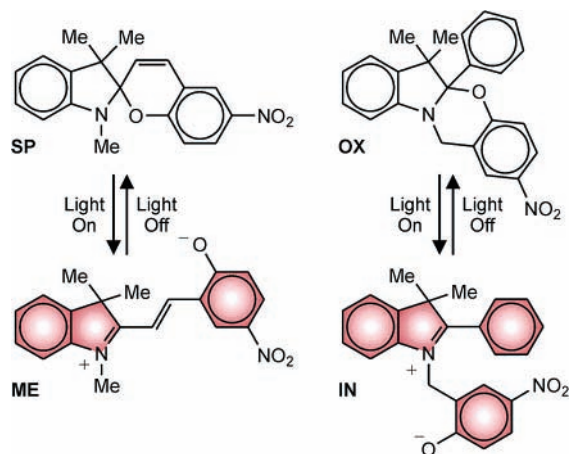


Figure 1. Reversible interconversion of a spiropyran (**SP**) and a merocyanine (**ME**) and of an oxazine (**OX**) and an indolium (**IN**).

or within rigid matrixes^{11,12} can reproduce logic functions relying on the interplay of optical signals. In particular, we have implemented molecular logic gates^{7,12} on the basis of the reversible isomerization of spiropyrans.¹³ At the present stage of their development, however, our rudimentary molecular switches suffer at least two major limitations. The thermal reisomerization of our spiropyran is relatively slow.^{7f} Thus, the output level can only be restored after a delay of several minutes, once the optical input is turned off. Furthermore, our spiropyran tolerates a limited number of switching cycles.^{12b}

The photoinduced isomerization of spiropyrans (e.g., **SP** in Figure 1) involves two consecutive steps.^{13b,c,f} Upon ultraviolet excitation, the [C–O] bond at the spirocenter cleaves in picoseconds.^{14–17} Then, the adjacent [C=C] bond switches from a cis to a trans configuration in microsec-

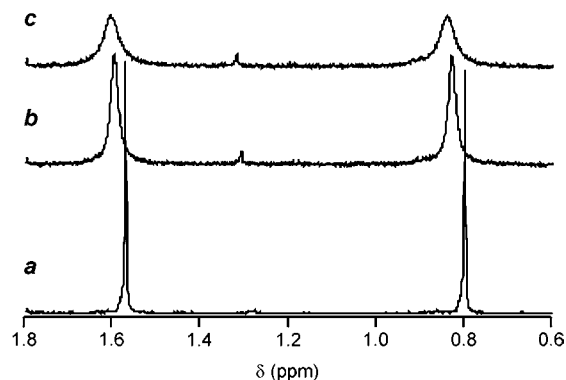


Figure 2. Partial ¹H NMR spectra (500 MHz, CD₃CN, 5 mM) of **OX** at 30 (a), 60 (b), and 70 °C (c).

onds.¹⁸ The thermal transformation of the resulting merocyanine (e.g., **ME** in Figure 1) back to the original spiropyran is slowed significantly by a necessary trans → cis reisomerization step. For example, **ME** switches back to **SP** in minutes with a rate constant of ca. $25 \times 10^{-4} \text{ s}^{-1}$ in MeCN at 25 °C.^{18f}

On the basis of these observations, we have designed the [1,3]oxazine **OX** (Figure 1). In analogy to **SP**, ultraviolet irradiation of **OX** should induce the cleavage of the [C–O] bond, involving the tertiary carbon of the indoline fragment, with the formation of a *p*-nitrophenolate chromophore. The resulting indolium **IN** (Figure 1) lacks the central double bond of **ME**. Thus, the rate of the thermal transformation of **IN** back into **OX** should not be limited by the relatively slow trans → cis reisomerization associated with **ME**.

We have synthesized **OX** in two steps (Figure S1, Supporting Information) with an overall yield of 49%. The first step involves the condensation of phenylhydrazine and *i*-propylphenyl ketone in the presence of *p*-toluenesulfonic acid. The resulting 2-phenyl-3,3'-dimethyl-3*H*-indole is then reacted with 2-chloromethyl-4-nitrophenol to produce the target compound **OX**, after treatment with aqueous potassium hydroxide.

The chiral center of **OX** imposes two distinct environments on the two methyl groups. Consistently, the ¹H NMR spectrum (spectrum **a** in Figure 2), recorded in CD₃CN at 30 °C, reveals two distinct singlets for the two sets of methyl protons. Upon warming the solution, these signals broaden

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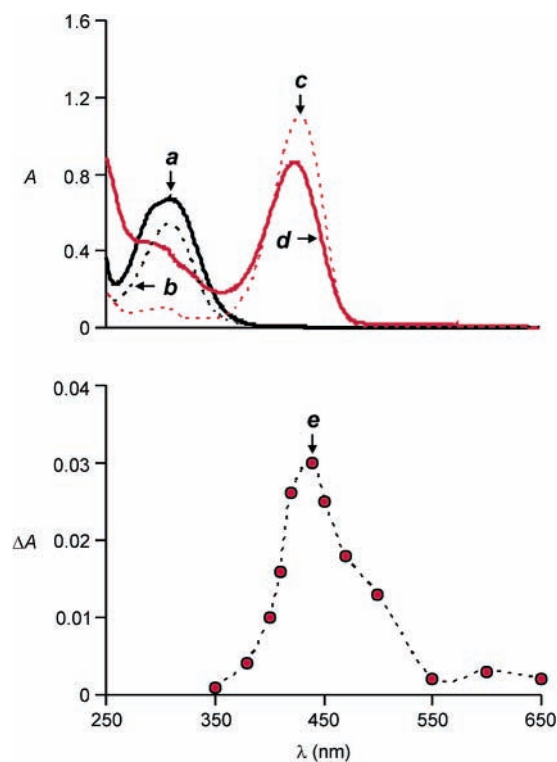


Figure 3. Steady-state absorption spectra (MeCN, 20 °C, 0.1 mM) of **OX** (*a*), *p*-nitroanisole (*b*), potassium *p*-nitrophenolate (*c*), **OX** after the addition of Bu₄NOH (10 equiv) and continuous irradiation (365 nm, 400 μW cm⁻²) for 10 min (*d*). Transient absorption spectrum (MeCN, 22 °C, 0.1 mM) of **OX** (*e*) recorded 30 ns after a laser pulse (355 nm, 6 ns, ~8 mJ).

considerably (spectra *b* and *c* in Figure 2), indicating that the two enantiomers of **OX** interconvert on the ¹H NMR time scale under these experimental conditions. The analysis of the temperature dependence of the line width¹⁹ of both singlets reveals the rate constant for the degenerate site exchange process to be $0.4 \pm 0.1 \text{ s}^{-1}$ at 25 °C.²⁰

The interconversion of the two enantiomers of **OX** demands the thermal opening of the oxazine ring with the formation of **IN**. Nonetheless, the stationary concentration of **IN** is negligible, and the steady-state absorption spectrum (spectrum *a* in Figure 3) reveals only a band at 308 nm for the *p*-nitrophenoxy chromophore of **OX**. Indeed, this absorption resembles the one observed for *p*-nitroanisole (spectrum *b* in Figure 3), under identical experimental conditions. The characteristic band at 429 nm (spectrum *c* in Figure 3) expected for the *p*-nitrophenolate component of **IN** cannot, instead, be detected (spectrum *a* in Figure 3). After the addition of Bu₄NOH and continuous irradiation, however, an intense absorption (spectrum *d* in Figure 3) for a *p*-nitrophenolate chromophore appears in the spectrum.²¹ Thus, the excitation of **OX** encourages the formation of **IN**,

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(20) The free-energy barrier is $18.0 \pm 0.2 \text{ kcal mol}^{-1}$, and the associated enthalpy and entropy of activation are $17.4 \pm 0.3 \text{ kcal mol}^{-1}$ and $-0.002 \pm 0.001 \text{ kcal mol}^{-1} \text{ K}^{-1}$, respectively.

which is “trapped” in the form of the hemiaminal **HE** (Figure 4) after the attachment of the nucleophilic hydroxide anion to the electrophilic carbon of the indolium cation. Consistently, the fast atom bombardment mass spectrum recorded at this point shows a peak at m/z 390 for **HE**.

In agreement with the formation of **HE**, the ¹H NMR spectrum of **OX** (spectrum *a* in Figure 4) changes dramatically after the addition of Bu₄NOH (spectrum *b* in Figure 4). In particular, the chemical shift of the proton H^a increases by 0.15 ppm with the transformation of **OX** into **HE**. The signals of the other aromatic protons (H^b–H^h), instead, move in the opposite direction. The largest change is observed for the resonances associated with the proton H^h, whose chemical shift decreases by 0.85 ppm. Furthermore, the AB system associated with the diastereotopic pair of methylene protons Hⁱ and H^m is maintained, confirming the presence of a chiral center also in **HE**.

Laser flash photolysis measurements confirm the photo-induced opening of the oxazine ring with the formation of **IN**. Indeed, the transient absorption spectrum of **OX** (spectrum *e* in Figure 3), recorded 30 ns after laser excitation, shows a band at 440 nm, which can be assigned to a *p*-nitrophenolate chromophore (spectra *c* and *d* in Figure 3). In agreement with this assignment, control experiments with *p*-nitroanisole exclude a possible association of this transient absorption with the triplet state of the *p*-nitrophenoxy fragment of **OX**. In fact, no transient absorptions are observed for *p*-nitroanisole under identical experimental conditions.²² Furthermore, the quantum yield of singlet oxygen is less than 0.02 when the photoinduced conversion of **OX** into **IN** is performed in air-saturated MeCN.

The evolution of the absorbance at 440 nm (Figure 5) indicates that the formation of **IN** occurs within the laser pulse (ca. 6 ns). The quantum yield for the photoinduced conversion of **OX** into **IN** is ca. 0.1. A kinetic analysis of the absorbance decay at 440 nm shows that the photogenerated isomer **IN** reverts thermally to **OX** with a first-order rate constant of $(46 \pm 1) \times 10^6 \text{ s}^{-1}$.²³ Therefore, the original state is fully restored within ca. 50 ns. Furthermore, the reversible interconversion of **OX** and **IN** is not accompanied by any photodegradation, even in air-saturated solutions. Indeed, the steady-state and transient absorption spectra of **OX** recorded before (spectra *a* and *e* in Figure 3) and after more than 3000 laser pulses are identical. Thus, virtually all **OX** is recovered in full after thousands of excitation cycles. The remarkable photochemical stability of **OX** agrees with the inability of this compound to sensitize efficiently the formation of singlet oxygen, which is responsible in part for the degradation of spiropyrans.^{18e,f,24–26}

The trace in Figure 5 demonstrates that the absorbance at 440 nm can be altered and reset with nanosecond switching

(21) The band for the *p*-nitrophenolate chromophore develops also if the solution of **OX** and Bu₄NOH is not irradiated. However, the thermal process is significantly slower than the photoinduced transformation.

(22) The triplet state of *p*-nitroanisole has a subnanosecond lifetime in MeCN: Mir, M.; Jansen, L. M. G.; Wilkinson, F.; Bourdelande, J. L.; Marquet, J. J. *Photochem. Photobiol. A* **1998**, *113*, 113–117.

(23) Kinetic analyses at different wavelengths within the transient absorption (*e* in Figure 3) gave essentially the same value for the rate constant.

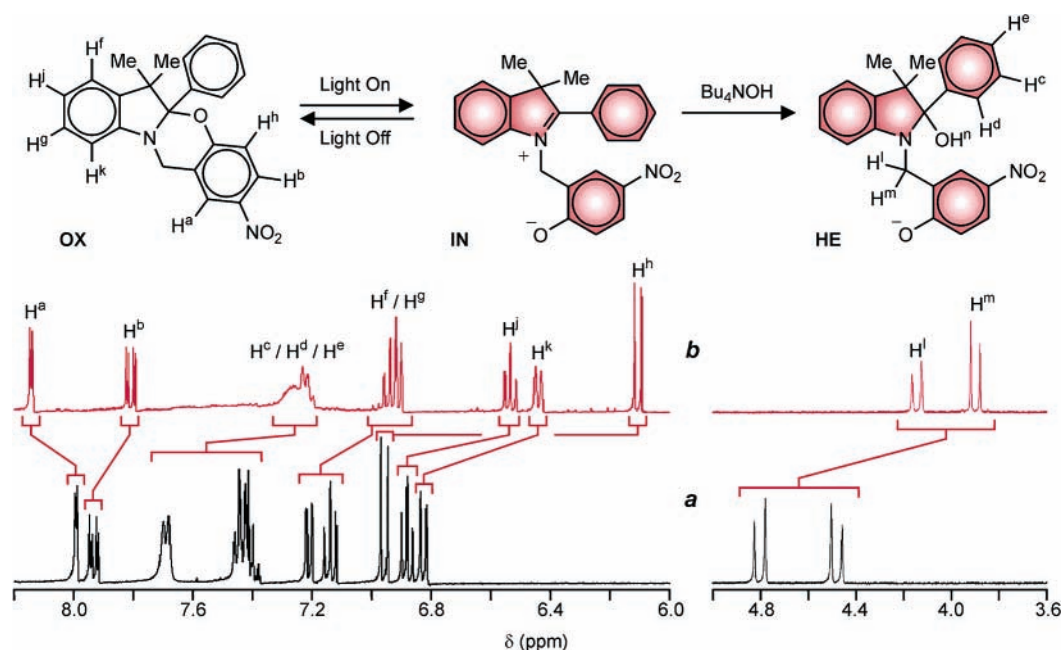


Figure 4. Partial ^1H NMR spectra (400 MHz, CD_3CN , 10 mM) of **OX** before (a) and after (b) the addition of Bu_4NOH (2 equiv) and thermal equilibration.

speeds by turning a laser on and off. The short time scales of these processes correspond to an improvement of 10 orders of magnitude over any of our earlier all-optical processing schemes.^{7,12} The elimination of the sluggish *trans* \rightarrow *cis* step, limiting the thermal reisomerization of spiropyrans, has

translated into this dramatic decrease in switching times. In addition, this structural modification has conferred remarkable stability on the photoresponsive molecular skeleton. Furthermore, the significant changes in dipole moment and molecular polarizability accompanying the photoisomerization can, in principle, be exploited to photoregulate a diversity of material properties with unprecedented switching speeds.^{1e} Thus, our molecular design for the realization of fast and stable photochromic compounds can evolve into the development of a new family of photoresponsive materials.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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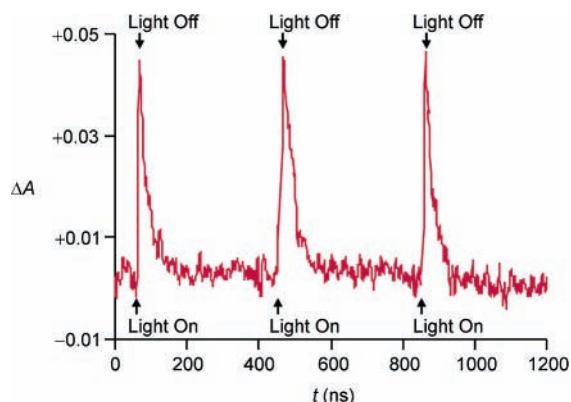


Figure 5. Three consecutive switching cycles of **OX** (MeCN, 22 °C, 0.1 mM) performed by laser excitation (355 nm, 6 ns, ~8 mJ) and followed by monitoring the absorbance of **IN** at 440 nm.

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