Supporting information

Phototransformation of Tetrazoline oxime ethers: Photoisomerization vs photodegradation

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1. Irradiations

1.1 Emission spectrum of polychromatic tubes

![Figure SI-1: Emission spectrum of polychromatic tubes](image)

1.2 Polychromatic quantum yields

Polychromatic quantum yields were obtained using the following expression,

\[
\Phi = \frac{R_{1-Z}}{R_{ia}} \tag{eq.1}
\]

where \( R_{1-Z} \) is the rate of photolysis of 1-Z, \( R_{ia} \) is the rate of light absorption,

\[
R_{ia} = \sum_{280}^{350} (1 - 10^{-A_{\lambda}}) I_{\lambda} l^{-1} \Delta\lambda \tag{eq.2}
\]

In equation 2, \( A_{\lambda} \) is the absorption of the sample and \( I_{\lambda} \) is the photon fluence rate at wavelength \( \lambda \) at the front face of the reactor, as measured with an Ocean Optics spectroradiometer. \( \Delta\lambda \) was set at 5 nm and \( A_{\lambda} \) and \( I_{\lambda} \) were averaged within the 5-nm wavelength ranges. \( l \) is the averaged path length. \( R_{ia} \) was found to be 2.25x10^{-6} Einstein/L/s.
2. Formation and identification of 1-E

2.1 UPLC analysis of irradiated 1-Z at very low conversion extent

Figure SI-2: Evolution of the chromatogram of 1-Z during its polychromatic irradiation in acetonitrile. a) Only the Z isomer is present initially. b) After 60 s, 1-E is the only photoproduct.
2.2 HPLC-MS of 1-E

The HPLC-MS data below confirmed that 1-Z and 1-E show the same m/z.

Figure SI-3: HPLC-MS data of a mixture of 1-Z (retention time 2.01 min) and 1-E (retention time 1.98 min) obtained after irradiation of 1-Z.
2.3 UV spectra of 1-Z and 1-E

Figure SI-4: UV spectra of isomers 1-Z (a) and 1-E (b). Comparison of spectra obtained by HPLC (dotted line) with those obtained by conventional UV spectrophotometry (solid line) for 1-Z and after subtraction for 1-E.
**Figure SI-5:** Theoretical absorption spectra of 1-Z and 1-E
3. Irradiation of 1-Z in polychromatic light

Figure SI-6: Consumption profile of 1-Z (□) and formation profile of 1-E (△), and degradation photoproducts (○) upon polychromatic irradiation. The irreversible photodegradation is obtained by subtracting the amounts of 1-Z and 1-E from the initial concentration of 1-Z. Solid lines were obtained by the fitting procedure.
4. Irradiation of 2-Z in polychromatic light

**Figure SI-7:** Consumption profile of 2-Z (□) and formation profile of 2-E (△), and degradation photoproducts (○) upon polychromatic irradiation. The irreversible photodegradation is obtained by subtracting the amounts of 2-Z and 2-E from the initial concentration of 1-Z. Solid lines were obtained by the fitting procedure.
5. UV spectra of 4 and 5

![UV spectra of 4 and 5](image)

**Figure SI-8:** UV spectra of 4 and 5 in acidic water -acetonitrile mixture (55:45, v/v)

6. Calculation of the electronic absorption spectra of species 4 and 6

Time-Dependent Density Functional Theory (TD-DFT) calculations were performed at the B3LYP/6-31(d,p) level to obtain the electronic absorption spectra of species 4 and 6. These are shown below in the most stable conformation.

![Structures of 4 and 6](image)

The theoretical UV absorption spectra are shown below. This Figure shows that both species 4 and 6 absorb in the same regions at ~230 nm and ~280 nm. However, the carbonyl species 4 is a stronger UV absorbant (x3) than the imine 6 at 280 nm.
Figure SI-9: Theoretical absorption spectra of 4 (solid line) and 6 (dotted line)

Figure SI-10: Changes of the absorption spectrum of an irradiated solution of 1-Z upon acidification. Solid line: pure acetonitrile; dashed line: addition of pure water; dotted line: addition of acidified water with orthophosphoric acid (0.1%)
6. Data on 3-Z and 3-E

6.1 Photoisomerization of 3-Z into 3-E

Figure SI-11: Concentrations evolution of isomers 3-Z and 3-E during the polychromatic irradiation of 3-Z. After establishment of the photostationary state, [3-E]/[3-Z] = 6.2.
6.2 Absorption spectra of 3-Z and 3-E

Figure SI-12: Experimental absorption spectra of isomers 3-Z (solid line) and 3-E (dotted line), determined by spectrum subtraction.
7. MS data on 7 and 8

a)

b)

Figure SI-13: MS data of 7 (a) and 8 (b)
**Figure SI-14:** Experimental UV spectra of 7 (solid line) and 8 (dotted line)

**Figure SI-15:** Theoretical UV spectra of 8 (dotted line) and M8 (solid line)
8. Phototransformation of 4 in polychromatic irradiation

![Graph showing concentration profile of 4 during polychromatic irradiation. Only one photoproduct is detected by HPLC.](image)

**Figure SI-16:** Concentration profile of 4 (○) during its polychromatic irradiation. Only one photoproduct (●) is detected by HPLC.

![MS data of photoproduct 9 in ES⁻, m/z=173.](image)

**Figure SI-17:** MS data of photoproduct 9 in ES⁻, m/z=173.
9. Phototransformation of M8 in polychromatic irradiation

Figure SI-18: Absorbance evolution of a solution of M8 in acetonitrile during its polychromatic irradiation. Irradiation times: 0, 5, 10, 15, 25, 40, 60 min