

Advances in understanding the photoresponsive behavior of azobenzenes substituted with strong electron withdrawing groups



Valentin Victor Jerca^{a,b}, Florica Adriana Jerca^{a,*}, Ileana Rau^c, Ana Maria Manea^c, Dumitru Mircea Vuluga^a, Francois Kajzar^{c,d}

^a Centre for Organic Chemistry "Costin D. Nenitescu", Romanian Academy, 202B Spl. Independentei CP 35-108, Bucharest 060023, Romania

^b University "POLITEHNICA" of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of Bioresources and Polymer Science, 1-5 Gh. Polizu Street, Bucharest 011061, Romania

^c University "POLITEHNICA" of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of General Chemistry, 1-7 Polizu Street, Bucharest 011061, Romania

^d Université d'Angers, Institut des Sciences et Technologies Moléculaires d'Angers, Bd Lavoisier, 49045 Angers cedex, France

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ABSTRACT

In this paper, a detailed isomerization study of a series of 2,4-nitro/cyan substituted azobenzenes is conducted by UV–Vis spectroscopy. The experiments, carried out in both toluene and N,N'-dimethylformamide, reveal an intriguing behavior. Interestingly, the disubstituted azo-derivatives display stable Z isomers in DMF, while in toluene they exhibit very fast relaxation. In addition, the azo-derivatives thermally isomerize from the metastable Z form to the thermodynamically stable E isomer through either inversion route or rotational mechanism, depending on the chemical nature of the substituents and on the solvent polarity.

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1. Introduction

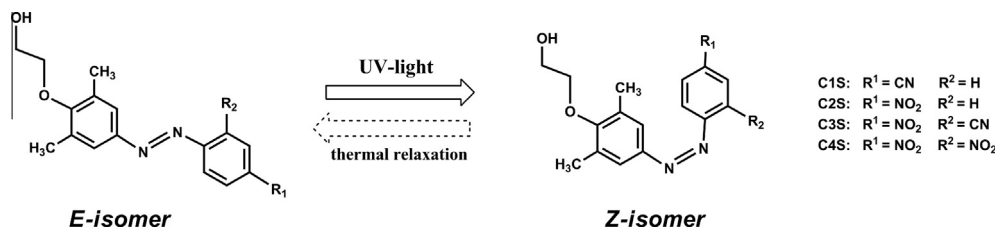
Azobenzene and its derivatives are fascinating molecules that have numerous applications in the field of nonlinear optics [1–5], surface relief gratings [1,6], photoswitching [7], optical data storage [8], photoprobes [9] and liquid crystals alignment [10]. The key to the interesting applications of azobenzenes is the facile and reversible isomerization of the azo bond, between the more thermally stable E configuration and the meta-stable Z form [11–15]. This photo-isomerization of azobenzenes with ultraviolet irradiation or laser has been used to influence conformational, optical or surface properties of polymeric materials that incorporate them [16,17]. An azo solution under illumination will achieve a photostationary state, with a steady-state E–Z composition based on the competing effects of photoisomerization and thermal relaxation back into the E state. The steady-state composition depends on the quantum yields for the two isomerization processes and the thermal relaxation rate constant (k_r), which is particular to each system. The composition also depends on irradiation intensity, wavelength, temperature, and solvent–solute interactions. It

is generally accepted that the Z–E thermal relaxation may take place either by rotation, or by flip–flop inversion of one of the nitrogen atoms [18,19]. The rotation and inversion pathways are competitive, but one may be favored over the other, depending on the electronic nature of the substituents covalently bonded to one or both phenyl rings, and on the polarity of the reaction medium [20].

The parent azobenzene molecule can bond very different chemical groups in order to adjust the optical properties and response time of a target material [21]. These substitutions will also dramatically change the spectroscopic properties, affecting the relative position and intensity of the absorption bands in UV–Vis spectra. Consequently, the azobenzenes were divided into three spectroscopic classes, as described by Rau [22]: azobenzene-type molecules, aminoazobenzene-type molecules, and pseudo-stilbenes, respectively. The pseudo-stilbenes give rise to the most efficient photo-response due to the fact that the two absorption spectra overlap significantly, allowing a single wavelength of light to effectuate both the forward and as well as the reverse photo-isomerization. This leads to a mixed photo-stationary state, where the two isomers are being constantly interconverted between themselves. Nevertheless, in some cases, where the azo molecule is being used as a switch or where a two-state system is desired, this overlap of the spectra becomes obviously

* Corresponding author.

E-mail address: adriana_jerca@yahoo.com (F.A. Jerca).



Scheme 1. Chemical structures of the photoresponsive azo-derivatives.

undesirable. The azobenzene-type molecules can isomerize from Z configuration back into E configuration very slow when bulky substituents are introduced to hinder the thermal relaxation [23,24]. Moreover, recent studies conducted by our group revealed that it is even possible to yield stable Z-isomers, when a proper solvent is used [25]. In addition, the nature and position of substituents on the aromatic rings had a great contribution to this behavior. This last feature of the azobenzene-type molecules is a very promising tool that allows fine-tuning of the optical response for holographic memories [26,27], and optical storage data [28].

Understanding the isomerization kinetics of different substituted azo-derivatives in solution is of great importance in order to gain control over the response time and to design good photoresponsive materials for specific applications. With this goal in mind, we extended the study and investigated the E–Z–E isomerization kinetics of four related azo-derivatives (illustrated in Scheme 1). We investigate the factors, like substitution pattern, substituent nature and chromophore-solvent interactions, which controlled the photoresponsive behavior of these azo-derivatives compared to the previous reported ones.

2. Experimental

2.1. Materials

The isomerization studies were carried out on cyano-, nitro-substituted azobenzene archetype molecules, having different substitution pattern, that have been characterized by us elsewhere [29]. Toluene and N,N'-dimethylformamide (DMF), spectrophotometric grade were purchase from Merck and used as such.

2.2. Spectroscopic measurements

The kinetics of photoisomerization and thermal relaxation were followed by UV–Vis spectrophotometry, on an Ocean Optics High-Resolution Fiber Optic Spectrometer HR 4000, equipped with a Peltier thermostat sample holder. After maintaining the azo dye solution in the dark overnight, the isomerization was induced by irradiation with a UV laser (Hamamatsu) producing monochromatic radiation at 365 nm wavelength. The output of the laser was coupled to deliver light directly into the UV sample holder, orthogonal to spectral observation axis. In all experiments, the power density of the UV incident light was adjusted to 30 mW/cm². Experiments were carried out with diluted solutions (5 × 10⁻⁵ M) in N, N'-dimethylformamide and toluene (spectrophotometric grade). The Z–E thermal relaxation of solutions was studied in the dark over a temperature range. For C1S and C2S the temperature range was 20, 40, 60, 80 °C, while C3S and C4S solutions were investigated at 0, 10, 20, and 40 °C.

2.3. Theory/calculations

The photoisomerization experimental data were analyzed according to Eq. (1).

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = k_i t, \quad (1)$$

where t is the irradiation time, A_0 , A_t and A_∞ are the E form absorbances corresponding to the time 0, t and photostationary state (PSS), respectively, and k_i is the rate constant of E–Z photoisomerization.

In the case of thermal relaxation, the kinetics follow Eq. (2), where k_r is the rate constant of the Z–E relaxation, A_0 , A_t and A_∞ are the Z form absorbances corresponding to the time 0, t and photostationary state and t is the relaxation time.

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = k_r t \quad (2)$$

The content of the Z-isomer at the PSS was determined using relation (3).

$$\alpha_Z = \frac{A_0 - A_{PSS}}{A_0}, \quad (3)$$

where A_0 and A_{PSS} represent the absorbances at λ_{max} for E isomer before and after irradiation with UV light, respectively. This formula assumes negligible absorption of the Z-isomer at E absorption maximum.

Activation parameters were determined by measuring the temperature dependence of the rate constant and fitting the data with the Arrhenius equation (Eq. (4)) or the Eyring equation (Eq. (5)) to obtain the activation energy, E_a , the enthalpy of activation, ΔH^\ddagger , and the entropy of activation, ΔS^\ddagger .

$$\ln k = \ln A - \frac{E_a}{RT}, \quad (4)$$

where k is the thermal rate constant, R is the universal gas constant, T is the temperature in Kelvin, A is the steric factor and E_a is the activation energy.

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{RT} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R}, \quad (5)$$

where ΔH^\ddagger , is the enthalpy of activation, ΔS^\ddagger the entropy of activation, k_B is the Boltzmann constant, h is Planck's constant.

3. Results and discussions

3.1. UV discussion

For reason of simplicity, although CxS azobenzenes are 4, 4'- and 2, 4, 4'-substituted compounds, we will name monosubstituted the ones that have one acceptor group and disubstituted the ones that have two acceptors groups. The UV–Vis absorption spectra of CxS azo-derivatives exhibit two characteristic absorption bands related to the strong π – π^* transitions of E azobenzene around 350–380 nm (depending on the substitution pattern and substituent nature) and weak absorption around 450–470 nm originating from the forbidden symmetry of n– π^* transitions.

The absorption maxima of the CxS azo-derivatives varied function of the substitution pattern, as showed in Table 1. Comparing

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