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SPECTROSCOPICAL INVESTIGATIONS OF THERMAL AND PHOTO INDUCED *CIS→TRANS* ISOMERISATIONS IN SOME CHLORO-AZOMONOETHERS

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Photo and thermal cis→trans isomerization kinetics were investigated for a class of chloro-azomonoethers. We found that in the particular case of this class the photo induced isomerization overlaps with the thermal isomerization. For thermal isomerization (dark conditions) we have remarked multiple mechanisms that overlap revelated by multiexponential behavior. Our experimental constant rates for the photo and thermal cis→trans isomerization was in the same range with values reported in literature. Activation energies for major thermal mechanism shows a dependence with molecule charge distribution.

Keywords: *cis-trans* transition, azo dye.

1. Introduction

One of the most important characteristics of molecular systems is the ability to be reversibly switched between two different states [1]. These materials, called switching materials at the molecular level, are indispensable for data storage, for optoelectronic and optical devices, holographic systems and display devices. The increase in the physical needs of data storage as well as the optical density of information leads to the use of storage, processing and recording materials with good packaging [2]. A possible solution is the range of photochromic materials which includes azobenzene polymers [3]. The two molecular states, *cis* and *trans* isomers, being both optically and thermally convertible, are able of a significant geometrical change and therefore the generation of molecular movements is possible. Molecular drivers with azobenzenes as the power source are applications

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for various molecular fields such as medicine (intelligent enzymes [4], “host–guest” recognition [5]), non-linear optics [6] and molecular machines [7-9].

This class of polymers contains azo molecules in the central structure [10]. Usually, the substances were used as pigments, dyes or pH indicators with the isomerization process considered a handicap, but now it is becoming a very interesting scientific territory to investigate.

The two isomeric forms, *cis* and *trans*, are transformed forward *trans→cis* under UV light irradiation and reverse *cis→trans* with photo excitation (by appropriate visible light with wavelength of 400-450 nm) or thermally activation [11,12]. First, it requires the absorption of a high energy photon, usually from UV range, by the more energetically stable *trans* form to obtains a less stable *cis* form [13,14]. The return to the stable state by non-radiative decay is more complicated, it occurs both under light excitation and thermal activation [15].

The process involves a series of stages: (i) nuclear coordinate relaxation, (ii) de-excitation and (iii) other relaxation with possible mechanisms such as: inversion, rotation, concerted inversion, spin-assisted inversion and inversion-assisted rotation [16]. The modification of conventional azo group (–N=N–) for the thermal process involves the two N–N–C angles and the C–N–N–C dihedral angle. Therefore, the thermal *cis→trans* isomerization can be easily controlled. Isomerization mechanisms [17] and thermal-dark *cis→trans* feedback kinetics were investigated [1,18].

The two mechanisms, photoexcitation and thermal activation, differ fundamentally in their relaxation time. The photoinduced *trans→cis* isomerization process is quite fast (milliseconds), depending on the power of the light source. The photo-reconversion is fast (seconds / minutes) and the thermal reconversion in the *trans* isomer is much slower (minutes / days).

The steric factor plays an important role in the energetics of the molecule, so that in the *trans* stable state, the two bonds connecting the azo group to the aromatic rings are parallel, resulting in an elongated, flat shape of the molecule. In the less stable *cis* state, this angle becomes ~ 120^0, and the molecules adopts a non-flat V-type conformation with a dipole moment of 3.0 D [19].

In addition to the dipole moment, the $n - \pi^*$ and $\pi - \pi^*$ absorption bands of the electronic spectra also differ [20]. Typically, azocompounds are characterized by a very intense $\pi - \pi^*$ transition band corresponding to the UV spectral region (320 nm) and a much less intense band corresponding to the $n - \pi^*$ transition in the visible spectral region (450 nm) [14, 21]. For the *cis* isomer, the $\pi - \pi^*$ transition band moves to shorter wavelengths, simultaneously with the increase in the intensity of the $n - \pi^*$.

The aim of this work is to provide a systematic approach to better understand the thermal effects and the photo induced ones on the *cis→trans* isomerization phenomenon in a specific class of azo compounds. Important characteristics for the process such as the absorption band (width and intensity), photo and thermal isomerization kinetics depends on the various residues attached to azobenzene, so the study of some classes of azo compounds becomes important.

Thus, the absorption spectra of the back-process to the *trans* isomer form by exposing the *cis* isomer to visible light and by spontaneous thermal regeneration in the dark are analyzed; rate constants and the activation parameters are determined.

2. Experimental sections

Materials and their structural formulas

We studied five compounds (see Figure 1): 1. 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-phenyldiazene (COBPD); 2. 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-(2-chlorophenyl)diazene (COB2CD); 3. 1-(4'-((4-chlorobenzyl) oxy)-[1,1'-biphenyl]-4-yl)-2-(p-tolyl)diazene (COBTD);4. 1-(4'-((4-chlorobenzyl) oxy)-[1,1'-biphenyl]-4-yl)-2-(4-chlorophenyl)diazene (COB4CD); 5. 1-(4'-((4-chlorobenzyl)oxy)-[1,1'-biphenyl]-4-yl)-2-(3,4-dichlorophenyl)diazene (COBD CD). These substances were synthesized and characterized in the previous work [22] from the point of view of the UV-Vis, mass spectrometry, IR and ^{1}H-NMR.

UV–Vis absorption spectra of studied substances

The UV–Vis absorption spectra (see examples from Figure 2) of the azo compounds in UV transparent solvent 1,4–dioxane were obtained with an Ocean Optics Spectrometer HR4000. Each solution's concentration was in range 10^{-6} M -10^{-5} M.

For all five compounds we note the three absorption bands; two in UV range and one in visible range. The first band consists an overlap of two B-bands ($\pi - \pi^*$ transition) in the range of λ_1~271-272 nm and λ_2 ~ 315-323 nm, is due to the aromatic rings (see examples for COBTD and COB4CD in Figure 2). The second band, K-bands, is situated near λ_3 ~ 375-393 nm range, is also due to the $\pi - \pi^*$ electronic transitions generated by the conjugation between –N=N– bridge and rings that occurred from the change of the geometry of molecules. We use these bands for the further investigation of *cis*→*trans* transitions. The thirds band, R-band, observed in visible range at the λ_4 ~ 418-472 nm is due to azogroup and corresponds to the lowest transition assigned to the partial forbidden ($n - \pi^*$) electronic transition. This band is generated by lone pair in N=N bridge can be assumed to intramolecular charge transfer [23, 24]. We obtain for COBPD λ_1=271.76 nm, λ_2 = 315.58 nm, λ_3 =378.86 nm, λ_4 = 435.01 nm; for COB2CD λ_1=271.89 nm, λ_2 = 319.8 nm, λ_3 =387.71 nm, λ_4 = 472.97 nm and for COBDCD λ_1=273.42 nm, λ_2 = 323.77 nm, λ_3 =383.02 nm, λ_4 = 425.21 nm.

Experimental investigations of the isomerization cycle, *trans→cis→trans*

A population of *cis*-isomers was generated by irradiating the solutions in the *trans* form with UV light from a 500W quartz lamp with 350 nm UV filter for at least 30 min.

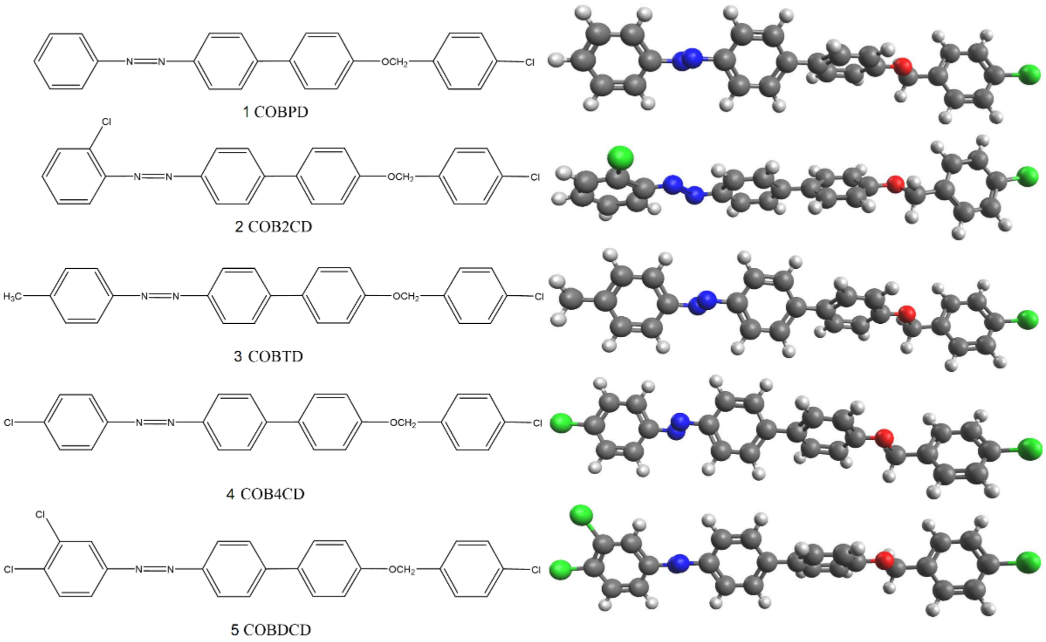


Fig. 1. Chemical structures, numbering, abbreviation of the studied class of chloro-azomonoethers and optimized geometries only for trans isomer (energy minimization, force field MMFF94, Avogadro 1.2.0 software)

Solutions of chloro-azomonoethers for UV–Vis spectra measurements were prepared by dissolving substances in high purity acetone solvent to obtain concentrations in range of 10^{-6}-10^{-5} M. We use acetone instead of 1,4-dioxan because dioxan is hydroscopic, more toxic than acetone and give less time stable solutions. The study of kinetics of the isomerization cycle is possible due to the concentration change of *trans* and *cis* isomers that generate differences in the positions and intensities of the characteristic bands in the UV–Vis absorption spectra. In order to do this, we recorded a large series of UV–Vis spectra before, during and after UV irradiation. The UV-Vis spectra during UV irradiation are useful only for establish that the process *trans* → *cis* occur and the maximum concentration of *cis* isomer is obtained at the end of UV irradiation.

We set that *trans* form spectra recorded before UV irradiation (named $A(\lambda,\infty,T)$, equivalent with hypothetical spectra recorded at time=∞, steady conditions), *Cis* form spectra $A(\lambda,0,T)$, represents first spectra recorded immediately after UV irradiation, (time=0, steady conditions) and intermediate spectra at some process times t ($A(\lambda,t,T)$) (see examples from Figure 3A,B). Increase with time of second band ($\pi - \pi^*$ transition band at 380 nm) associated with the changes of the geometry of molecules was observed. It strongly indicates the reversible isomerization of the *cis* to *trans* form.

The kinetics of reverse *cis*→*trans* photoisomerization cycle was studied by irradiated the *cis* sample solutions (in 1 cm optical path quartz cuvette) with filtered light from an incandescent lamp (using 440 nm narrow visible filter) in thermostatic conditions (25°C) (see examples from Figure 3A,B).

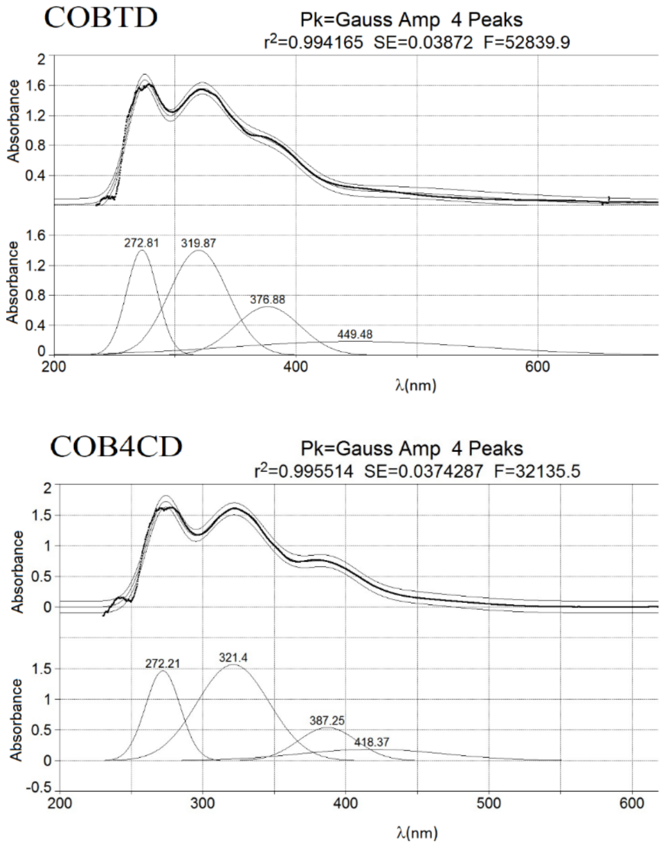


Fig. 2. UV–Vis absorption spectra of COBTD and COB4CD. Spectra of COBPD, COB2CD and COBDCD are very similar (see the informations in text).

The absorption spectra in the case of the *cis*→*trans* thermal activated process (in the dark conditions) was recorded for all five substances using also 1 cm optical path quartz cuvette in thermostatic conditions (data not presented). The measurements were performed at different temperatures (30, 32, 33, 40, 42 and 50°C).

Process kinetics

According to the Lambert-Beer law, in our case absorbance $A(\lambda,t,T)$ must depends on wavelength of light λ, time *t*, temperature *T*, ε - molar absorption coefficient, c – concentration and x – optical path:

$$A(\lambda,t,T) = \varepsilon(\lambda,t,T)\, c(t)x \ .$$

In order to study the reverse process kinetics (thermal or photo) we consider that at time zero, entire population of *trans*-isomer was zero $c_{trans}(0) = 0$, only *cis* isomer suffers isomerization process $c_{cis}(0) = c_{prep}$.

We can remark that $c_{cis}(0) = c_{trans}(\infty) = c_{cis}(t) + c_{trans}(t) = c_{prep}$, where c_{prep} is the solute concentration.

At *t* moment : $A(\lambda,\infty) - A(\lambda,t) = (\varepsilon_{trans}(\lambda) - \varepsilon_{cis}(\lambda))c_{cis}(t)x$, and for *t=0*, $A(\lambda,\infty) - A(\lambda,0) = (\varepsilon_{trans}(\lambda) - \varepsilon_{cis}(\lambda))c_{cis}(0)x$, thus

$$\frac{A(\lambda,\infty)-A(\lambda,t)}{A(\lambda,\infty)-A(\lambda,0)} = \frac{c_{cis}(t)}{c_{cis}(0)} = e^{-kt} = f(t), \qquad (1)$$

where k - rate constant, in the assumption of mono-exponential behavior (see case of COBTD from Figure 3A').

The bi-exponential (*i=2*) (see case of COB4CD from Figure 3B') or multi-exponential behavior (*i>2*) assumes that two or more isomerization processes occur simultaneously. Thus:

$$\frac{c_{cis}(t)}{c_{cis}(0)} = \frac{A(\lambda,\infty)-A(\lambda,t)}{A(\lambda,\infty)-A(\lambda,0)} = \sum_{i=1}^{n} p_i\, e^{-k_i t} = f(t), \qquad (2)$$

where curves are fitted better to a multi-exponential equation taking into account the components p_i (percents) with different kinetics rates k_i.

Using Eq. 1 or 2 in the set of curves $A(\lambda,t,T)$ the isomerization constant rates can be determined.

In Figure 3A,B we chose to display as examples the time dependency of spectra $A(\lambda,t,T)$ only for COBTD and COB4CD at five selected time moments. In Figure 3A',B' are shown examples of the exponential behavior of isomerisation *cis→trans* process. Only compound 3 (COBTD) show a mono-exponential behavior, the others four substances have multiexponential behavior, probably bi-exponential. Phenomenologically, is possible to have multiexponential behavior if two of more processes overlap. In this particular case, photo induced and thermal activated processes overlap. Since the real constant rates (or relaxation time) are close to each other (differ by at most one order of magnitude), over the entire experimental time, the signal's changes (Eq. 2) arise from the above-mentioned nonlinear effect.

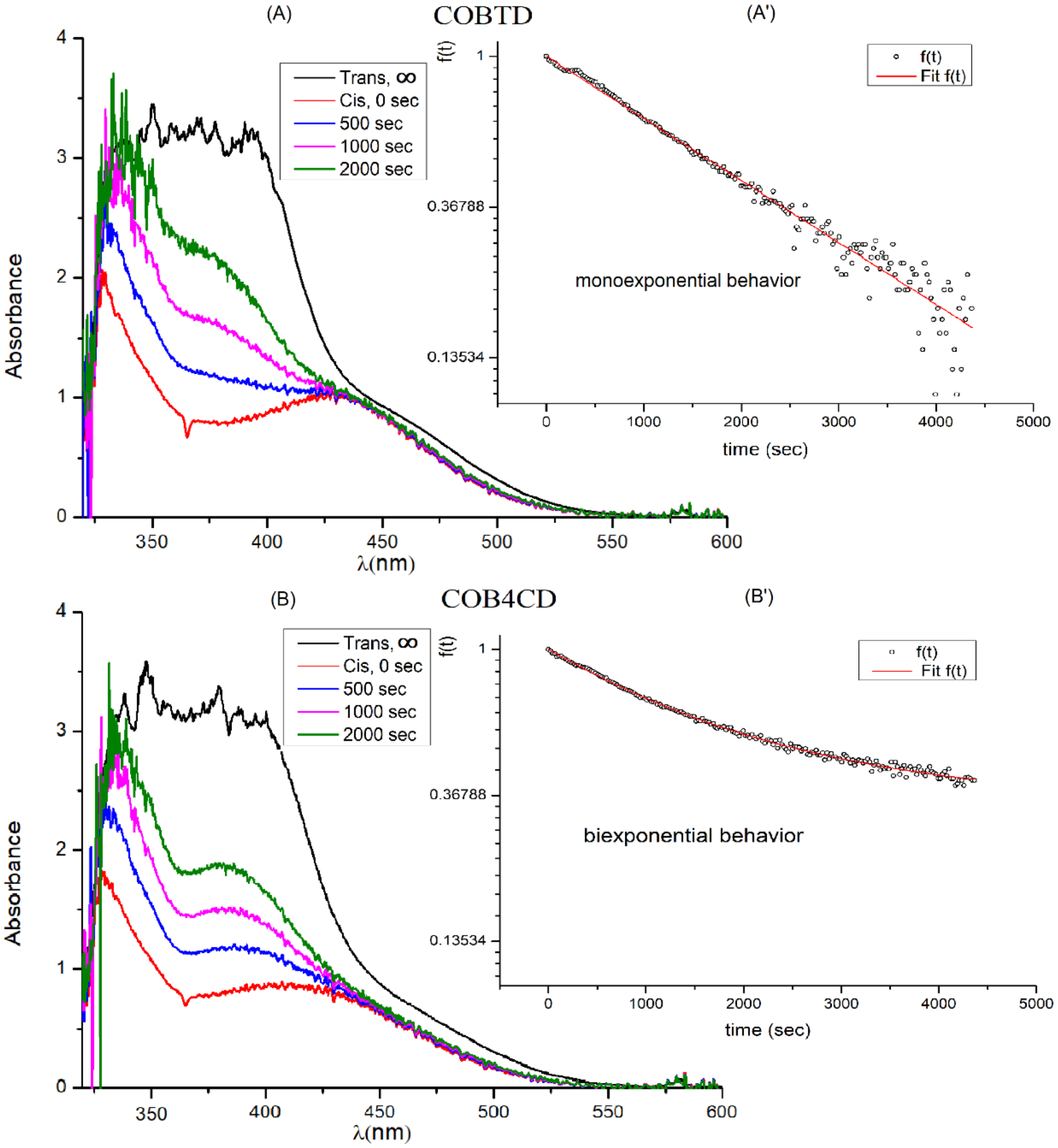


Fig. 3. UV–Vis absorbtion spectra (panels A,B) at different time points and kinetics f(t) (photo & thermal) of cis→trans process (panels A',B') of COBTD and COB4CD in acetone.

Solving this problem is not trivial from the mathematical point of view. In an earlier work [25], we estimated some important values for exponential curves. Thus, if we consider an equivalent form for Eq. 2, $\sum_{i=1}^{n} p_i\, e^{-k_i t} = \sum_{i=1}^{n} p_i\, e^{-\frac{t}{T_i}} = s(t)$, we can compute easily the important statistical test objects for distribution of relaxation times T_i:

1) the mean value of relaxation times $\langle T \rangle = \int_0^{\infty} s(t)dt \cong \int_0^{\Lambda} s(t)dt$;

2) the dispersion $\sigma^2 = (\langle T^2\rangle - \langle T\rangle^2)$, using $\langle T^2\rangle = \int_0^\infty t \cdot s(t)dt$;

3) the asymmetry $a_s = \frac{\langle T-\langle T\rangle\rangle^3}{\sigma^3}$, using $\langle T^3\rangle = \frac{1}{2}\int_0^\infty t^2 s(t)dt$;

4) the kurtosis $k = \frac{\langle T-\langle T\rangle\rangle^4}{3\sigma^4}$, using $\langle T^4\rangle = \frac{1}{3!}\int_0^\infty t^3 s(t)dt$.

All these objects give a strong indication that there is an overlap of the exponential terms. Despite this, the mathematical problem is only half-solved, we need to estimate relaxation rates and corresponding populations (or distribution function). In our experimental conditions when signal is affected by the presence of noise, estimations of number of exponentials or distribution function is quite difficult [25]. For a particular case, two major component of relaxation times distribution (two relaxation times in case of discrete values) the methods presented in papers [25,26] give very good results. But, for three of more components the results are strongly affected by noise. We conclude that, in our experimental condition, noise and insufficiently relaxed signal, two values for relaxation time can be considered.

Table 1.

Exponential parameters extracted from exponential behavior of chloro-azomonoethers (see examples from Figure 3A',B'). $p_2 = 1 - p_1$.

Compound	p_1		k_1 (s^{-1})		k_2 (s^{-1})		
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Adj. R-Square
COBPD	0.32988	0.07678	5.05E-05	3.78E-05	5.30E-04	4.29E-05	0.9966
COB2CD	0.50972	0.0506	<1E-05	1.65E-05	5.05E-04	4.22E-05	0.99428
COBTD	0	-	-	-	4.11E-04	-	0.99012
COB4CD	0.40933	0.03121	2.16E-05	1.43E-05	6.28E-04	2.83E-05	0.99729
COBDCD	0.35663	0.07632	<1E-05	3.70E-05	5.35E-04	5.28E-05	0.9902

The value of photo induced mechanism suggests that k_2 constant rate is characteristic for photo transition population p_1 and therefore k_1 represent thermal constant rate associated with population p_2. All these values are very similar with values reported in literature [14,16].

Figure 4A,B shows kinetics of thermal activated processes of chloro-azomonoethers COBTD and COB4CD in acetone (steady and dark conditions). From the analysis of these five substances, we remark that only compound 3 (COBTD) has monoexponential behavior (reveleated by statistical test objects). Thus, we conclude that thermal activated process is non common, consist in overlap of different relaxations mechanisms (at least two).

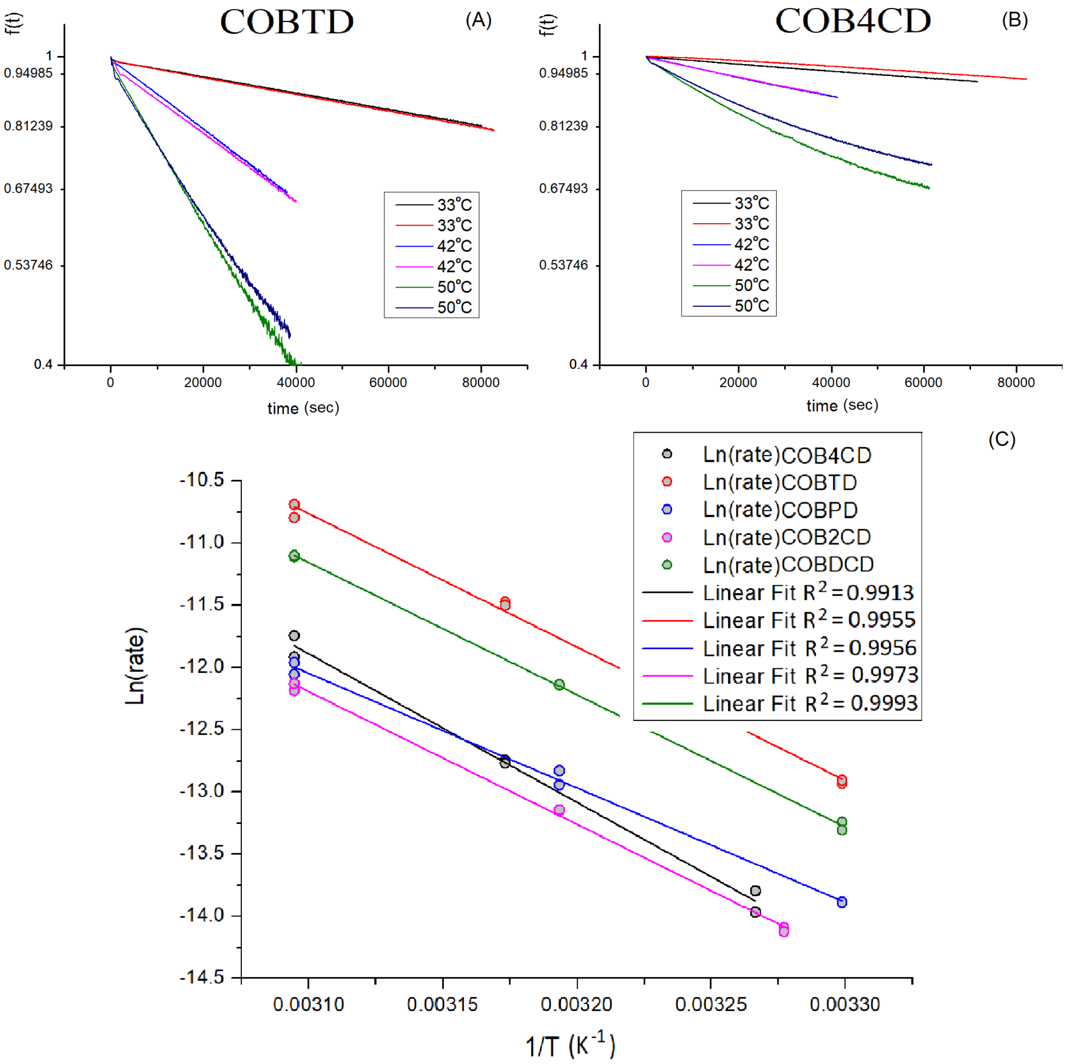


Fig. 4. The duplicate measurements of kinetics of thermal cis→trans process (dark return) (panels A,B) of COBTD and COB4CD in acetone. Panel C represent Arrhenius plot for all five chloro-azomonoethers.

The reason of these particular behaviour is due to existence of different pathways for *cis→trans* processes (explained by the existence of different transition states) [16]. We display in Figure 5 a model with two pathways for the thermal *cis→trans* isomerization of compound 4 (COB4CD). We show two intermediar transition states: "*in*" based on inversion mechanism that consist from an inversion inplane of angle between azogroup and adiacent carbon –N=N–C and "*ro*", based on rotation mechanism azo group axis –N=N– coupled with outplane torsion of dihedral angle C–N=N–C.

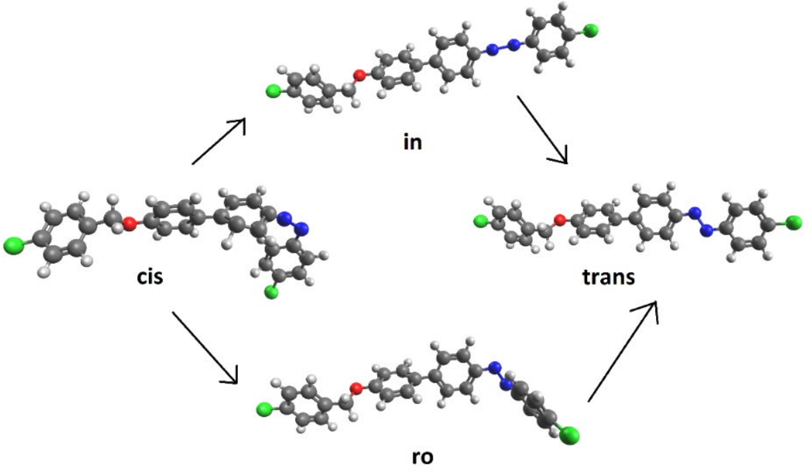


Fig. 5. Proposed mechanisms for the thermal cis→trans isomerization of substance 4, COB4CD. In the middle present transition states “in” and “ro”.

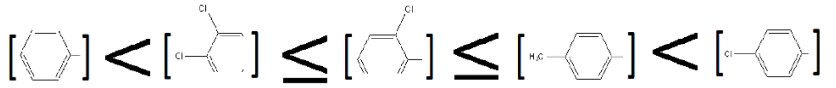
We estimate relaxation rates and used only fast relaxation rate (the values are more accurate) for evaluation of the activation energies (Table 2) that came from Arrhenius plot (see Figure 4C).

The value of activation energies for the thermal activated of isomerization process probably depend on charges around of the residues attached to the molecule in opposition with amino group.

In Table 2 we summarize these energies in decrease order:

Table 2.

Scale of activation energies E_a calculated from linear dependence of Ln(k)=f(1/T) from Figure 4C.

					
Compound	1 COBPD	5 COBDCD	2 COB2CD	3 COBTD	4 COB4CD
E_a(kJ/mol)	76.49	88.38	88.71	89.24	99.30

Energy reported in Table 2 are in same range reported in literature [16].

3. Conclusions

In this study, we have analyzed the absorption spectra, photo and the thermal *cis→trans* isomerization of some class of chloro-azomonoethers.

The principal results can be summarized as: UV–Vis spectra of these compounds consist on superposition of three bands thus is difficult to assign band specific only *cis* or *trans* form. The photo induced isomerization process is accompanied by thermal induced process for the most of substances. Also, multiexponential decreasing of *cis* concentration reveals the overlaps of multiple thermal activated mechanisms for isomerization process. We develop a model with two possible mechanisms for thermal isomerization. For more accurate calculations of activation energies corresponding to each thermal isomerization pathways are need to conduct very long-time experiments for ensure the good estimation of relaxation rates.

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