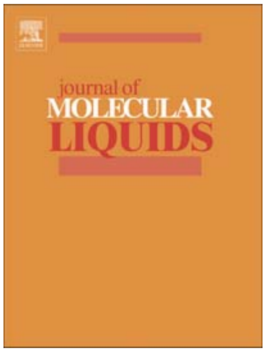

4-(4′-Alkyloxyphenylazo)benzoyl chlorides not only intermediates but photosensitive mesogens for optical switching

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4-(4’-alkyloxyphenylazo)benzoyl chlorides not only intermediates butphotosensitive mesogens for optical switching

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Abstract

This paper presents results of our studies of a full homologous series of 4-(4’-alkyloxyphenylazo)benzoyl chlorides. Until now these compounds have been used only as intermediates for more complex materials and their properties were not investigated as acid chlorides are considered unstable and hence useless for applications. We show that they are in fact quite durable and posses liquid-crystalline properties in a broad temperature range. In addition fast switching times of cis-trans isomerization with less than an hour relaxation time are demonstrated for the series, which makes these compounds promising materials for optical switching.

Keywords: liquid crystals, azobenzene, chloride, photoisomerization, optical switching, new materials.

1. Introduction

Liquid crystals are unique materials with properties placing them between conventional liquids and solid crystals[1-3]. Long-range order combined with flow ability allow to apply them in many branches of modern technology. They have contributed to considerable development of optoelectronics, photovoltaics, diagnostics, sensorics and obviously LC display technologies[4-10]. Special properties of these materials are strictly related to molecules arrangement which can be modified by different factors such as temperature, light, concentration etc[11-14]. Among liquid crystalline materials, azobenzene derivatives[15-20] are of special interest due to theirintriguing ability of cis-trans isomerization[21-23] upon irradiation by light of suitable wavelength. This process causes a change in material properties, like for example absorption spectra, yet is fully reversible. Cis isomer is unstable and after certain time it returns to trans form. It had to be the reason why these materials have gained popularity as components for optical storage[24-26], photomechanical actuators[27-28], photoresponsive surface[29-32]. Furthermore, isomerisation changes the geometry of molecule - isomer cis is a bent version of isomer trans which must affect the arrangement of molecules in the system. This leads to the conclusion that the appearance of the cis-isomer in the system affects the mesomorphism of the compound[33].

Nowadays, great emphasis is placed on finding new liquid-crystalline phases[34-37]. By certain modifications of chemical structure completely different properties can be obtained[38-39]. Still, our knowledge related to properties-structure dependence is insufficient to enable us to precisely design and synthesize the compounds with desired properties. The syntheses of whole homologous series of liquid-crystallinecompounds allow to contribute to this knowledge and examine the impact of some aspects of chemical structure on material properties, especially mesomorphism[40-42].

This paper describes our studies of a full homologous series of 4-(4’-alkyloxyphenylazo)benzoyl chlorides. Although, these compounds are well known in the literature, they are rather obtained as intermediates, which are used in further steps of syntheses, for example of very popular bent-core molecules. Based on the published papers, in which 4-(4’-alkyloxyphenylazo)benzoyl chlorides are mentioned,it can be concluded that these compounds were considered, together with other acid chlorides, unstable and hence useless from applications point of view. Their properties were not studied. This paper demonstrates that 4-(4'-alkyloxyphenylazo)benzoyl chlorides are in fact quite stable for a considerable period of time. They possess as well liquid-crystalline properties in a relatively wide temperature range. The kinetics studies of their cis-trans isomerisation are also presented here. Finally, the influence of the molecule length on selected physical properties such as mesoporphism and photoisomerization rate is described.

2. Experimental

2.1. Synthesis

4-(4’-alkyloxyphenylazo)benzoic acids were prepared according to the procedure which is described elsewhere[43]. Oxalyl chloride, triethylamine and all used solvents were purchased and used without additional purification. For the purpose of this study a full homologous series of 4-(4’-alkyloxyphenylazo)benzoyl chlorides has been synthesized [Fig. 1], from methyl to octadecyl one. Further in this work acronyms X-Cl for 4-(4’-alkyloxyphenylazo)benzoyl chlorides will be used, where X represents the length of the alkoxy chain.

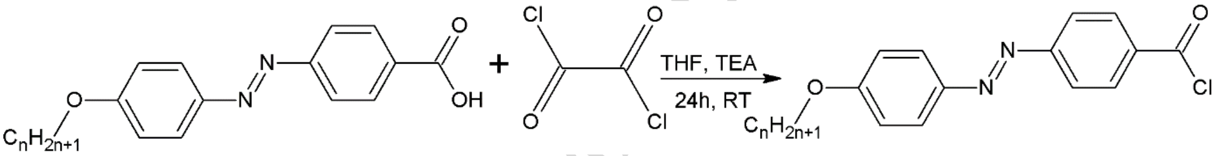

Figure 1. The synthesis route of 4-(4’-alkyloxyphenylazo)benzoyl chlorides.

A mixture of appropriate 4-(4’-alkyloxyphenylazo)benzoic acid (1.25 mmol), oxalyl chloride (0.16 g, 1.25 mmol) and triethylamine (0.13 g, 1.25 mmol) in dry tetrahydrofuran was stirred at room temperature for 24 hours. After that time the solvent was removed. The crude precipitate was purified by column gel chromatography (dichloromethane- silica gel mobile phase- stationary phase). Subsequently the product was recrystallized from hexane. Yield: 40-75%. ^{1}H NMR and EA measurements details of all synthesized compounds are available in supplementary data.

2.2. Measurements Setup

Elemental analysis measurements ere conducted with the Vario EL III elemental analyzer while the NMR spectra were measured in deuterated chloroform with the Bruker Avance III 500 MHz high resolution spectrometer. These methods confirmed structure and purity of all studied molecules.

Liquid-crystalline mesophases were investigated by polarized optical microscopy (POM), thermo-optical analysis (TOA) and differential scanning calorimetry (DSC). Characteristic liquid-crystalline textures were observed under Olymp1us polarized light microscope BX61-P (TRF) and captured with Bresser camera 9 Mpix. The thermo-optical analyser used in experiment is described in details in different paper[44.] Calorimetric measurements were carried out by Perkin Elmer 8500 calorimeter under nitrogen atmosphere with the scan rate of 10 K min^{-1}. Thermograms were recorded by the use of thermogravimeter TG-DTA Setaram SETSYS 16/18.

X-Ray studies were conducted by the use of Xcalibur diffractometer with a Ruby CCD detector, MoK_α radiation, $\lambda = 0.71073$ Å, T = 100(2) K; 5736 reflections collected (CrysAlisPro, Agilent Technologies, Version 1.171.35.19, 2011), 3140 unique ($R_{int} = 0.0433$); refinement: 3140 reflections, 182 parameters, R_1 [$I > 2\sigma(I)$] = 0.0616, wR_2 (all data) = 0.1431, GOF on F^2 = 0.942; max./min. residual electron density: 0.549/−0.313 e $Å^{-3}$; min/max absorption coefficients 0.789/0.356. The crystal structure was solved by direct methods in SHELXS and refined in SHELXL software (G. M. Sheldrick, SHELXTL 5.1, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA 1997).

2.3. UV-Vis studies

Optical properties of all 14 synthesized compounds were studied by UV-Vis spectroscopy. The measurements were conducted for dichloromethane solutions of average concentration of $1,72 \cdot 10^{-5}$mol/dm^3. First the wavelength corresponding to the maximum absorbance has been determined. In further studies all compounds were irradiated by the suitable wavelength to cause the isomerization process. The kinetics of both isomerization and relaxation processeswere evaluated. All measurements were performed on UV-Visible Spectrophotometer Varian Carry500 in the room temperature. Moreover the mercury lamp was used as a source of the UV light causing isomerization (λ=365nm). As the influence of the alkyl chain length on isomerization kinetics is minor the results are presented for one selected derivative 18-Cl.

3. Results and Discussion

3.1. Thermal properties and crystal structure

Thermal stability of synthesized compounds was examined by thermogravimetry. The obtained results are shown in Figure 2. All materials are stable in the temperature range from 0 to 150 °C.The least stable is the shortest homologue 1-Cl, which starts to decompose above 200°C. Other compounds decompose on average between 300 and 350°C.

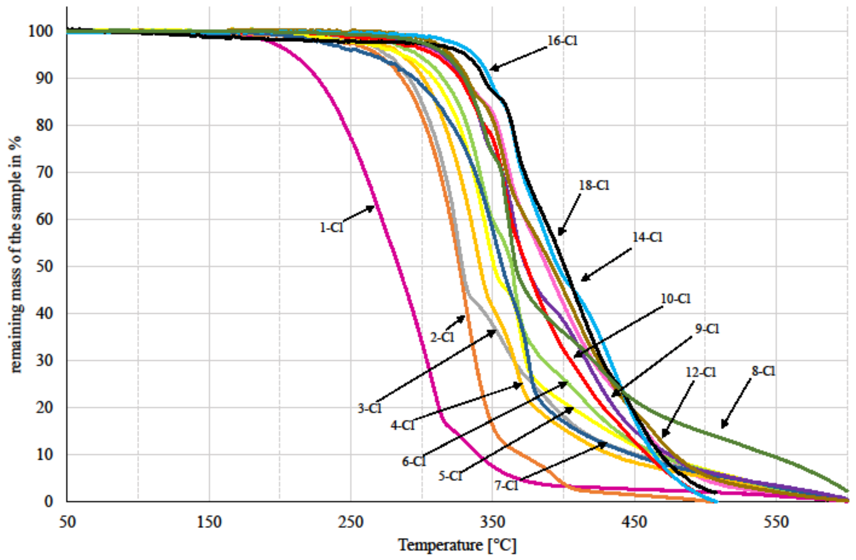

Figure 2. The thermogravimetric results for the homologues series of 4-(4’-alkyloxyphenylazo)benzoyl chlorides.

For homologue 2-Cl XRD measurements were carried out and crystal structure was solved. Resulting crystal structure is shown in Figure 3. 2-Cl crystallizes in triclinic crystallography system and $P\bar{1}$ group. In one cell there are two molecules of 2-Cl. The dimensions and angles of the cell are as follows: a = 6.9100(4), b = 9.4973(6), c = 10.7025(6) Å, α = 82.013(5)°, β = 74.561(5)^{o}, γ = 81.894(5)°. Moreover, two hydrogen bonds were identified. Their parameters are shown in Table 1. Full XRD results are available in CIF file in supplementary data.

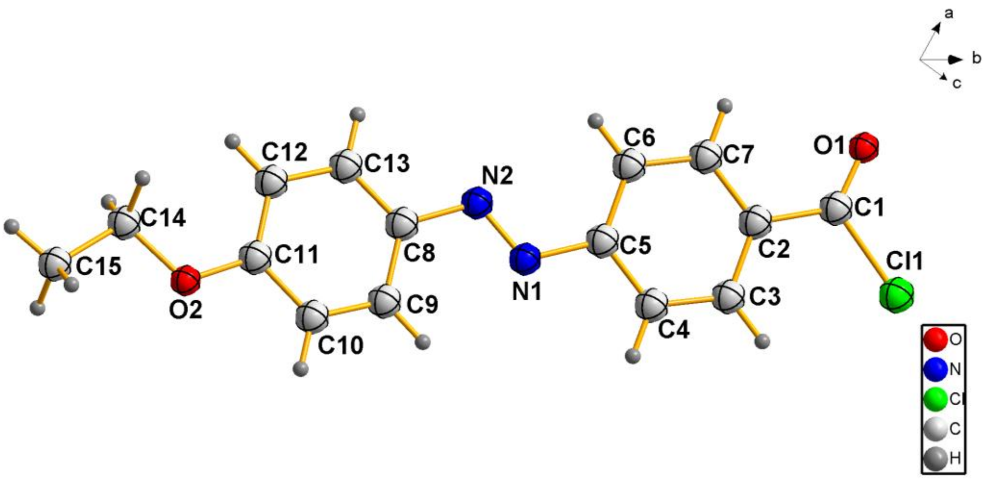

Figure 3. Molecular structure of 2-Cl. Thermal ellipsoids are drown at 50% probability.

Table 1. Hydrogen bonds for 2-Cl [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3)···Cl(1)	0.95	2.58	3.019(3)	108
C(4)-H(4)···O(1)^i	0.95	2.49	3.196(4)	131

Symmetry code: [i] -1+x,y,z

3.2. Mesomorphic Behaviour

Among 14 synthesised compounds 12 exhibit liquid-crystalline properties [Fig. 4.]. Phase transition temperatures and enthalpies are shown in Table 2. In the presented series only 1-Cl and 2-Cl do not undergo mesomorphic phase transitions. This fact can be explained by significantly higher (more than 20 Celsius degree) melting temperatures than in case of the other homologues. All other homologues display one enantiotropic mesophase, which has been identified as smectic A basing on the well described in literature characteristic focal-conic texture observed under polarised microscope A sample photograph representative of observed textures is presented in Figure 5. For the first homologue with liquid-crystalline behaviour - 3-Cl, smectic A has 30 Celsius degrees width. For compounds with middle-length alkyloxy chain, from 4-Cl to 12-Cl, smectic A is much wider and ranges from 40 to even 75 degrees.With the increase of alkyloxy chain length to 14 and above, range of smectic phase is narrowing However, in each material the liquid-crystalline range can be regarded as broad compared to quite low phase transitions temperatures. Except first three homologues melting points of presented materials do not exceed 100°C.

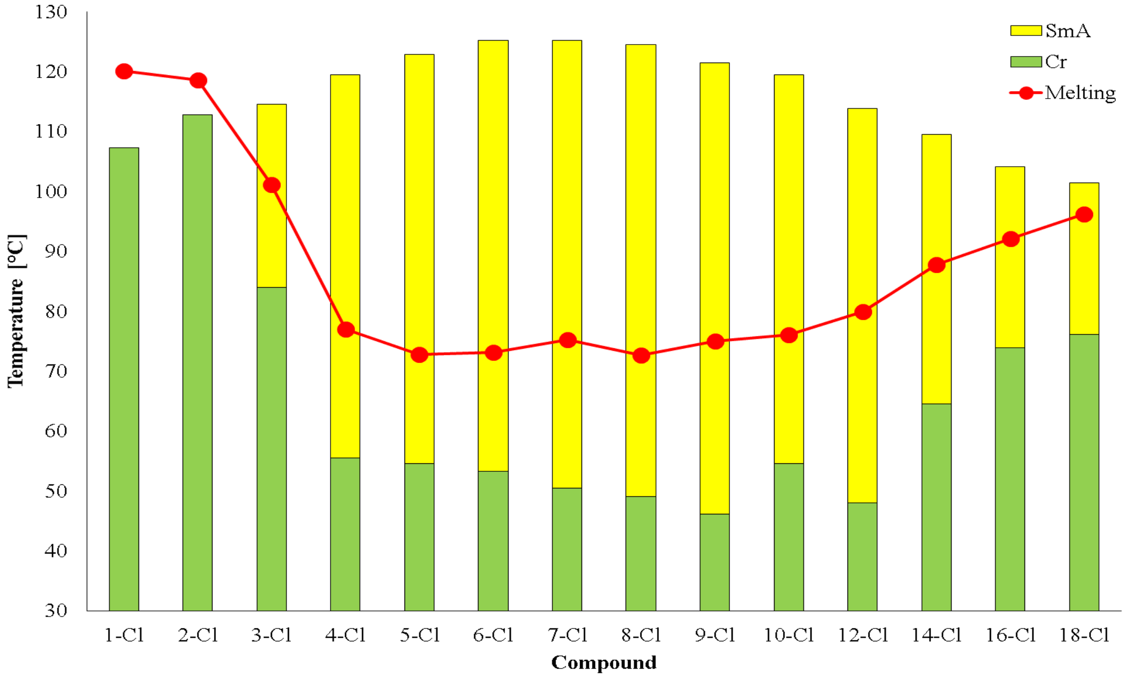

Figure 4. The diagram of liquid-crystalline properties of presented materials.

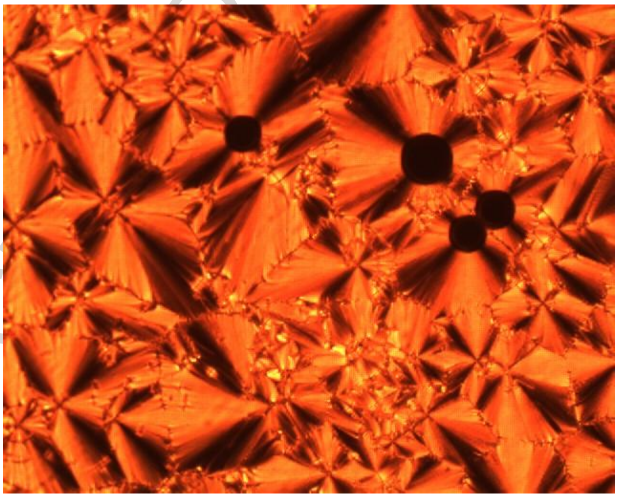

Figure 5. Focal-conic texture of smectic A mesophase.

Allphase transitions entropy values are presented in Figure 6. The average value of crystallization entropy amounts to 87.83 J mol^{-1}K^{-1} and is shown as a green line in the Figure 6. Melting entropy is on average 109.75 J mol^{-1}K^{-1} and is shown with the red line. In the homologous series both parameters increase with the length of the alkyloxy chain. Moreover for isotropic-smectic transition the entropy was calculated. Results are shown in Figure 7. The average value of this phase transition is significantly lower. It amounts to 17,26 J mol^{-1}K^{-1} on average. Values for all homologues are mostly congruous.

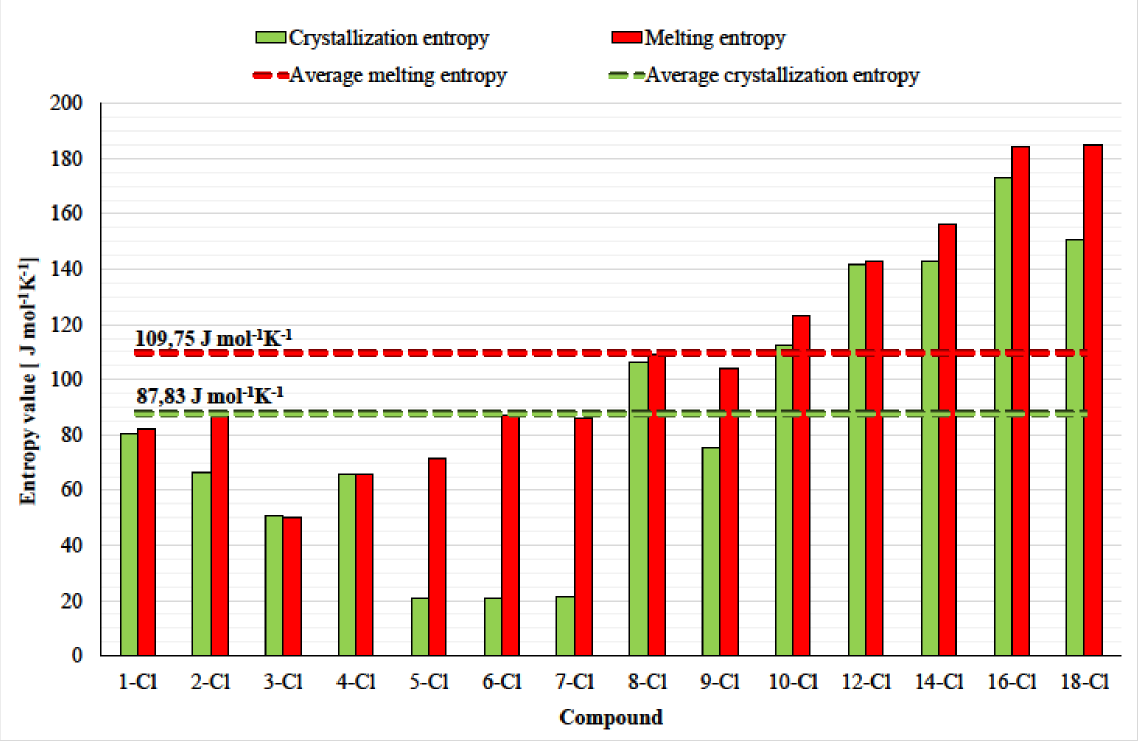

Figure 6. Entropies of crystallisation and melting of full homologues series of X-Cl.

Table 2. Temperatures (in °C) and enthalpies (in kJ mol^{-1}) of observed phase transitions in 4-(4'-alkyloxyphenylazo)benzoyl chlorides.

Acronym	Melting	Crystallization	SmA		Iso
1-Cl	120.1 [32.3]	107.3 [30.7]			•
2-Cl	118.6 [34.3]	112.8 [25.6]			•
3-Cl	101.1 [18.8]	84.0 [18.0]	•	114.6 [6.65]	•
4-Cl	77.0 [23.1]	55.5 [21.7]	•	119.5 [6.21]	•
5-Cl	72.8 [24.7]	54.6 [6.91]*	•	122.9 [6.48]	•

6-Cl	73.2 [30.2]	53.3 [6.86]*	●	125.2 [6.58]	●
7-Cl	75.3 [30.1]	50.5 [6.96]*	●	125.2 [6.77]	●
8-Cl	72.7 [37.8]	49.1 [34.26]	●	124.5 [6.93]	●
9-Cl	75.0 [36.3]	46.2 [24.0]	●	121.5 [6.97]	●
10-Cl	76.1 [43.0]	54.6 [36.9]	●	119.5 [6.99]	●
12-Cl	79.9 [50.36]	48.0 [45.51]	●	113.8 [6.97]	●
14-Cl	87.8 [56.5]	64.5 [48.3]	●	109.5 [6.46]	●
16-Cl	92.1 [67.4]	73.9 [60.1]	●	104.1 [6.99]	●
18-Cl	96.2 [68.4]	76.1 [52.6]	●	101.4 [6.73]	●

*- only partial crystallisation was observed.

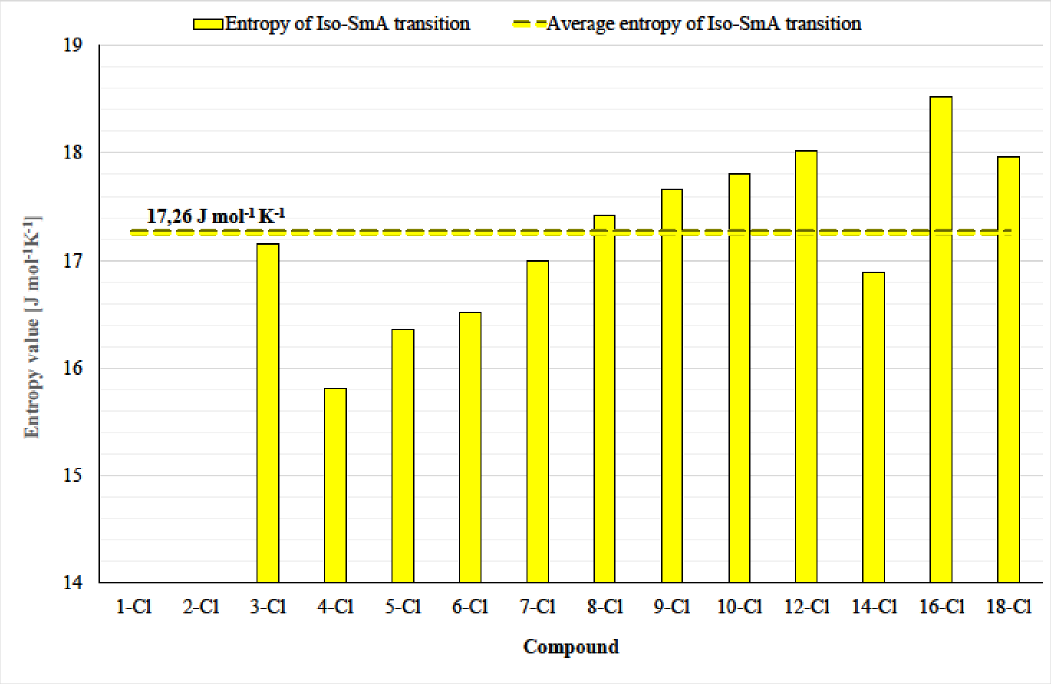

Figure 7. Entropies for Isotropic-SmA phase transitions of 4-(4'-alkyloxyphenylazo)benzoyl chlorides.

3.3. Photoisomerization Studies

At the beginning of spectroscopic studies all compounds were in pure trans form. The adequate spectrum is marked with a black line [A, Fig.8.]. Two local maximums can be seen, characteristic of azobenzen derivatives, low intensity n-π* absorption band in the visible region around 450 nm and high intensity π-π* absorption band in the UV region at 371nm Subsequently the wavelength corresponding to maximum absorbance value was denoted. For most synthesized compounds this wavelength was 371nm. The mercury lamp with filter (365nm) was used to irradiate the materials. This light corresponds to the π-π* transition energy gapand is suitable for converting trans isomer into cis one. This geometry change is reflected in the shape of the UV-Vis spectrum. With irradiation the cis isomer population is growing in the system. That can be observed as a decrease of absorption band in the UV region and simultaneous increase of band in the visible region [A, Fig.8.]. This process continues until the equilibrium between trans and cis isomers is reached. The photoisomerization phenomenon in azobenzene derivatives is fully reversible. After certain time the thermal relaxation process can be observed [C, Fig.8.]. Normally it is much slower than isomerization and it defines the usefulness of the material for optical applications. Kinetic constants of isomerization and relaxation processes were calculated for all members of the series, an example of 18-Cl is shown in Figure 8. [B, D, Fig.8.]. For most of the analysed compounds these values were around $1{,}20\cdot10^{-1}\,\frac{1}{s}$ for isomerization and $2{,}15\cdot10^{-3}\,\frac{1}{s}$ for relaxation. Especially the second value is quite surprisingbe cause typically similar compounds are characterized by the values of 10^{-5} order.

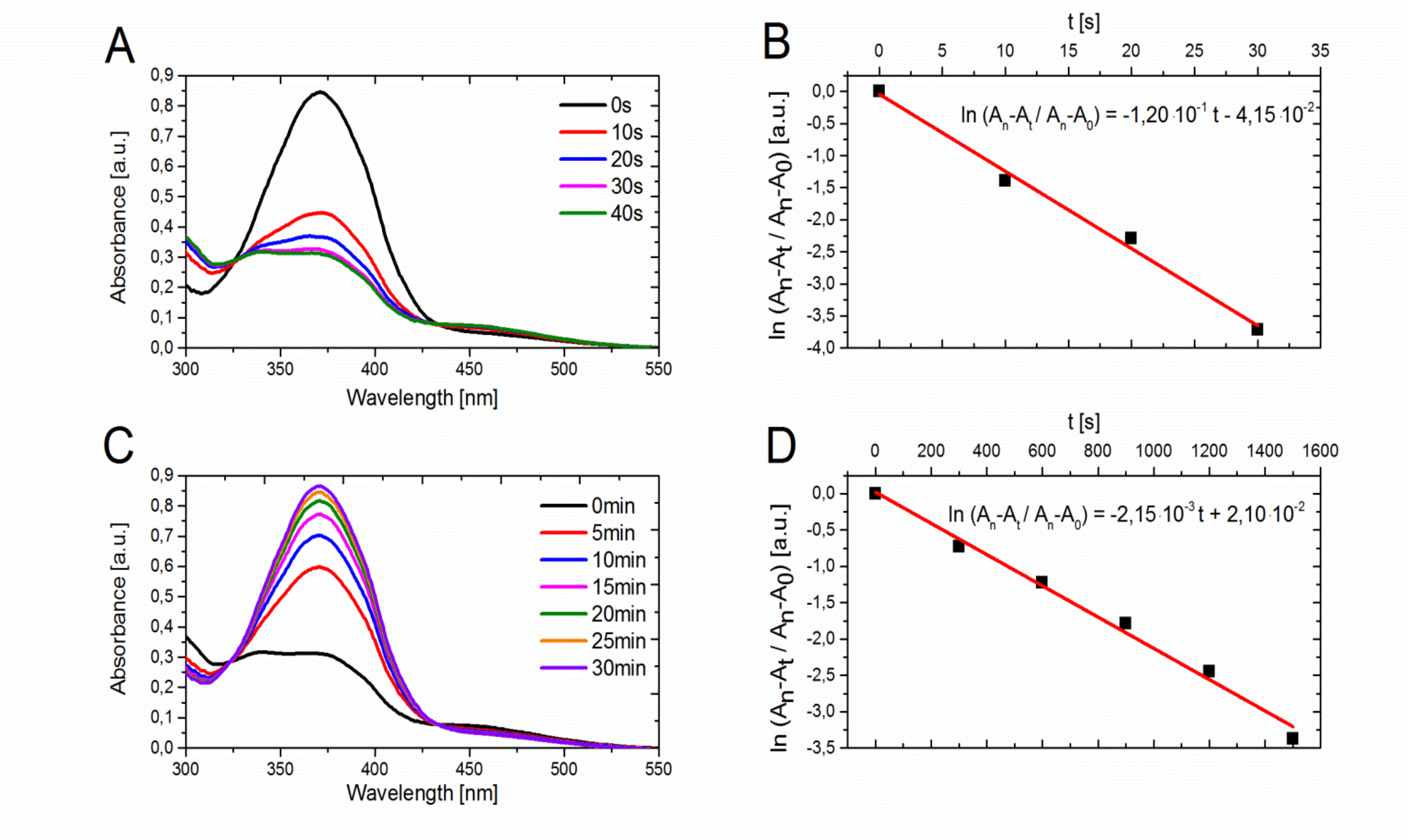

Figure 8. UV-Vis spectra of 18-Cl compound in dichloromethane solution and corresponding kinetics plots:

A UV-Vis spectra captured after different irradiation times, B – the plot of $\ln(A_n\text{-}A_t / A_n\text{-}A_0)$ vs irradiation time , C – UV-Vis spectra captured in different intervals after the irradiation was switched off, D - the plot of $\ln(A_n\text{-}A_t / A_n\text{-}A_0)$ vs relaxation time

4. Conclusions

In this paper properties of 14 new azobenzene derivatives from homologous series of 4-(4’-alkyloxyphenylazo)benzoyl chlorides have been described . Until now these compounds were considered unsuitable for any applications due to suspected instability common for acid chlorides and therefore mentioned only as intermediates towards more complex compounds and never studied in detail. Our studies demonstrate that they are in fact stable in time and when heated up to 150 degrees Celsius. 12 of 14 members of the series are also liquid-crystalline with single smectic A mesophase appearing in a range of 30 or more degrees. As is expected of azo compounds, they display cis-trans isomerization. What is however surprising is the very short time of relaxation back to trans state, which is 1 hour while similar known compounds need at least 24 hours. This last parameter makes the analysed materials worth considering as optical switches.

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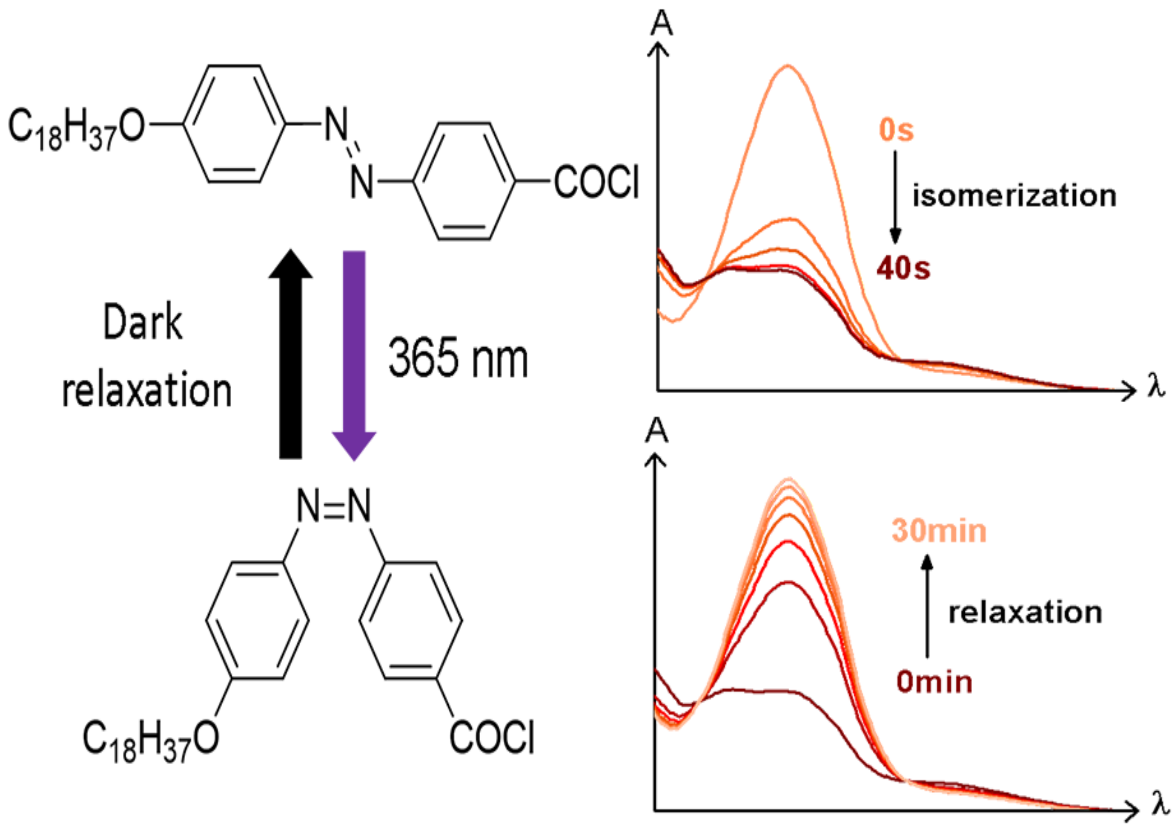

Graphical Abstract

Highlights

- Full homologues series of 4-alkoxyazobenzene chlorides was synthesized
- Unexpected liquid-crystalline properties were discovered and investigated
- Kinetic constants of photoisomerization process were calculated
- Influence of the molecule length on mesomorphism and photoisomerization rate were defined