

Negative Photochromism in Hybrid Compounds

Lali Devadze*, Gia Petriashvili*, Shorena Akhobadze*,
Tsisana Zurabishvili*, Nino Sepashvili*

* *Institute of Cybernetics, Georgian Technical University, Tbilisi, Georgia*

(Presented by Academy Member Vladimir Tsitsishvili)

Aiming at further improving properties of spiropyran (SP), sometimes spirochromenes, we considered it expedient to synthesize a new hybrid bifunctional photo-sensitive compound by introducing the second photochromic center to the SP molecule. A hybrid molecule synthesized by combining two photochromic compounds, under the theory of conjugated chromophores, is characterized by an increased photo-sensitivity and bathochromic displacement of the absorption line of a photoinduced form. The hybrid molecule synthesized by us is made up of two photochromic fragments: SP and azobenzene (AZ), with a shared benzene ring. The length of the conjugated chain created under the influence of UV light, due to the presence of an AZ fragment, is elongated and the wave length of the relevant absorption line shows a bathochromic shift. Approximation to the cheap diode laser irradiation area (780 nm) is important for the practical use of SP. A set of spectral methods, and used method of photokinetic analysis data were obtained on the photochromic properties of hybrid Compounds I, II, III and their derivatives. The synthesized compounds exhibit negative photochromism. These data represent the electronic absorption spectra of the original and photo-induced forms of kinetic and thermodynamic parameters of the dark processes, efficiency phototransformations. These parameters, along with the establishment of structural and property correlations, allow us to characterize them as photochromic effective for practical use as UV sensors and other promising technological applications in photonic (optical switches, 3D high-density optical data storage). © 2023 Bull. Georg. Natl. Acad. Sci.

negative photochromism, spiropyran, azobenzene, hybrid compounds

The concept of creating molecular machines and controlling the material at a molecular level expressed by Richard Feynman in 1959 and the chemical memory model created at the Weizmann Institute based on photochromic molecules has become a subject of study of a number of scientific centers of the world, including the Department of Optical-Chemical Studies of the Institute of

Cybernetics at the Georgian National Academy of Sciences. The scientists from this Department, on the initiative and under the leadership of Academicians Vladimir Chavchanidze and Kokhta Japaridze accomplished the synthesis and research of photochromic spiropyran. Thus, the first chemical memory model based on spiropyran in the USSR was created at the Institute of Cybernetics of the

Georgian National Academy of Sciences [1]. Vladimir Chavchanidze and Kokhta Japaridze predicted the urgency of this topic half a century earlier: indeed, in 2016, a group of researchers (James Stoddart, Bernard Feringa, Jean-Pierre Sauvage) was awarded the Nobel Prize in Chemistry for designing and synthesizing molecular machines.

Results and Discussion

A photochromic molecule is made up of two units: a photoantenna, which absorbs the light quantum, and a functional unit, which responds to the changes induced by the absorption in the photoantenna. In such systems, the light plays the role of a trigger mechanism.

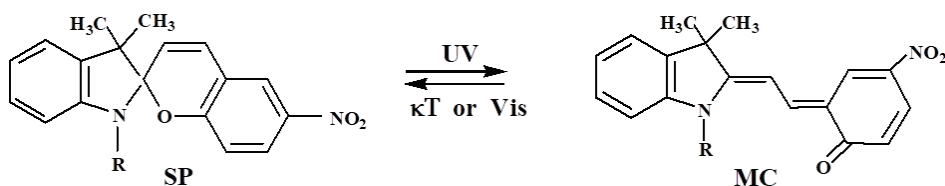
The spiropyrans (SP) among the photochromes are distinguished for preparation easiness and wide structural variations that allow obtaining the compounds with desirable thermodynamic, kinetic, spectral and photochemical properties. A photo-initiated isomerization of SP is given in Scheme 1.

The works to optimize the properties of SP were accomplished at the Department of Optical-Chemical Studies (headed by Academician Kokhta Japaridze): 1) by varying the electronic properties and positions of functional groups in a photochromic molecule, 2) by varying the molecule skeleton. As a result, synthesized compound obtained by changing indoline ring with azaindoline has higher photo-sensitivity to UV light as compared to its existing analogs; whereas the introduction of an additional fragment to the indoline part has resulted in an increased photo-sensitivity of the molecule to visible light [2,3]. Novel hybrid compounds based on these SP and AZ have also been synthesized. In order to improve the

above parameters, several hundred new compounds were synthesized. This paper presents only the results of a study of photochromic systems with negative (reverse) photochromism based on new hybrid compounds. As a rule, the majority of known photochromic compounds and systems become colored when exposed to UV or solar radiation. Therefore, they are called photochromic compounds with positive photochromism.

Less attention is focused on the synthesis and investigation of properties of photochromic compounds, systems, and materials with negative (reverse) photochromism, which consists in photoinduced bleaching or change in colour [4]. Compounds of this type and systems on their basis show negative photochromism.

In contrast to positive photochromism of spiro compounds, initial coloured MC form under the action of visible light absorbed by this form converts into photoinduced thermodynamically unstable colourless SP form. This form spontaneously transforms into initial MC form or when exposed to UV light. The process of spontaneous coloration accelerates upon heating of the system. Negative photochromism of SP is due to several reasons related to the shift of equilibrium between SP and MC forms toward the latter. The main reasons are the nature of substituents and high environmental polarity. When the environment of a SP is highly polar, or when additional substituents which stabilize the zwitterionic MC form are attached on its π -conjugation system, the coloured MC form is more stable than the colorless SP form. In these cases, irradiation of visible light causes decoloration of MC to generate SP form. When SP form is placed in the dark, it returns to the coloured



Scheme 1. Photo-initiated isomerization of spiropyran.

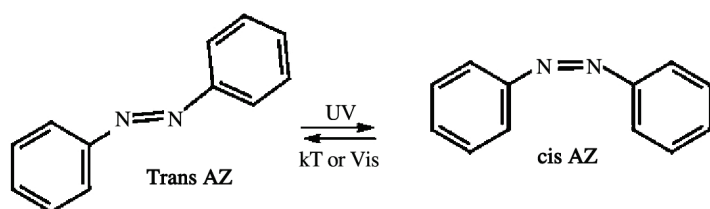
MC form. Therefore, this thermally reversible photochromic system does not need the irradiation of UV light for its photochromism which may cause degradation of the compound. For example in case of two electro-acceptor NO_2 groups, in the SP molecule with dinitro-exchanged, C-O link is disrupted right in the initial state. Therefore, the solution in the dark is coloured, i.e. the thermodynamic equilibrium is inclined to MC ($K_T > K_{PH}$). The on-off cycle in connections with negative photochromism is realized with less energy generation than with positive one, since the first stage is illuminated with visible light. The absence of ultra-violet rays in the process reduces the fatigue of photochrome and thereby increases the number of cycles. Compounds with negative photochromism are partially discoloured by ultra-violet light, since the thermodynamic equilibrium constant is larger than the photochemical one. We attempt to create such photochromic systems in connection with the increasing need for photochromic compounds with negative photochromism for improving photochromic recording media and creating products with new properties, in particular, clothes and camouflage coatings for the military, that automatically change color depending on the intensity of solar radiation, as photochromic labels in biological studies and drug delivery systems in living organism.

Photochromic Spiropyran and Azobenzene

Aiming at further improving the SP properties, we considered it expedient to synthesize a new hybrid

bifunctional photo-sensitive compound by introducing a second photochromic center to the SP molecule. A hybrid molecule synthesized by combining two photochromic compounds, under the theory of conjugated chromophores, is characterized by an increased photo-sensitivity and bathochromic displacement of the absorption line of a photo-induced form. The hybrid molecule synthesized by us is made up of two photochromic fragments SP and AZ with a shared benzene ring [5,6]. The length of the conjugated chain created under the influence of UV light, due to the presence of an AZ fragment, is elongated and the length of the wave of the relevant absorption line shows a bathochromic shift. Approximation to the cheap diode laser irradiation (780 nm) area is important for the practical use of SP.

From the Schemes 1 and 2 is seen that SP and AZ molecules undergo different types of isomerization reactions upon UV irradiation, such as ring opening (SP) and trans-cis isomerization (AZ). Hybrid compounds gained by merging SP and different photochromic compounds were synthesized and studied by a number of authors [7]. Photochromic transformations in them were mostly observed either at low temperatures, or by using femtosecond technology. Such state of affairs limits the practical use of such compounds. For improving the properties of hybrid compounds on the base of two photochromic compounds: SP and AZ, we synthesized three types of photochromic hybrid molecules by coupling AZ with: indoline SP (I); azaindoline SP with increased photosensitivity to the UV light (II) and tetrahydroquinoline SP with increased sensitivity to visible light (III).



Scheme 2. Trans-cis isomerization of azobenzene.

Hybrid Compound I gained by merging SP and AZ.

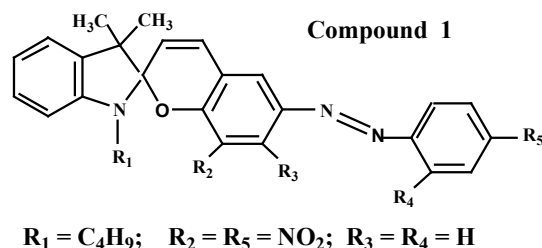
Hybrid Compound I was gained by coupling indoline SP with AZ. Absorption band of Compound I is bathochromically shifted compared to parent SP, and photochromic transformations are observed at a room temperature (the result of inserting the electroacceptor group NO₂ in the position 2). Combining two photochromes: SP and AZ in one molecule increases the length of the conjugation chain of a photoinduced form resulting in the long-wave shift of the relevant absorption band. Under the influence of the UV light, C-O bond is disturbed and the molecule transforms into a coplanar state and along conjugated chain is formed. So, it is expected that a hybrid molecule, under the influence of active light, may serve two functions: disturbance of intramolecular bond C-O in the SP fragment and geometrical changes – trans-cis isomerization in the azobenzene fragment. This can be done by varying the electrical properties of the substitute and their position in a hybrid molecule. It turned out that among the gained compounds the desirable properties were demonstrated by Compound I, where group NO₂ is substituted in the chromene part position 2 of SP and position 5 of AZ. Such positioning of electroacceptor groups weakens bond C-O and the thermal equilibrium of a compound in polar solvents shows a certain equilibrium shift to a coloured form. Until photochemical equilibrium is achieved, the solution is discoloured by UV light too.

In the dark, the thermodynamic equilibrium reinstates. Under the influence of the visible light (630 nm), the sample gets totally colourless. The process is observed at a room temperature.

We have studied the spectral properties of the sample as shown in Fig. 1. A short-wave absorption band belongs to AZ, while a long-wave absorption band is typical to the photoinduced form of SP. The absorption bands of a photoinduced form of a hybrid compound as compared to the absorption band of model compound (SP and AZ) are shifted bathochromically, that must be caused by the

origination of along conjugated chain of an open molecule form.

The absorption spectrum corresponding to the thermodynamic equilibrium established in the dark shows that the sample is coloured.

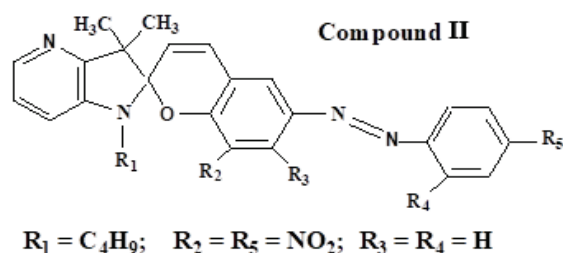


Scheme 3. Hybrid compound gained by coupling indoline spiropyran with azobenzene.

Hybrid Compound II gained by merging SP_{azaind} and AZ.

As it was noted above, as a result of replacement of indoline by azaindoline SP, the photosensitivity of SP to UV light increases. The thermodynamic equilibrium is shifted toward the closed form thereby reducing the spontaneous degradation and relaxation rate is increased.

The properties of hybrid molecules consisting of AZ and azaindoline SP are different from parent molecule. The thermodynamic equilibrium is shifted towards the coloured form. The thermodynamic equilibrium constant is greater than photochemical one $K_T > K_{PH}$, decolouration of system occurs not only by visible but by UV light too (Fig. 1).



Scheme 4. Hybrid compound gained by coupling azaindoline spiropyran and azobenzene.

As Fig. 1 shows, the visible light influenced a short-wave absorption band as well, that is a proof of a unity of the electronic cloud of the molecule

like Compound I. For Compound II (Fig. 1) the thermodynamically less stable state is the colourless form and so it exhibits negative photochromism.

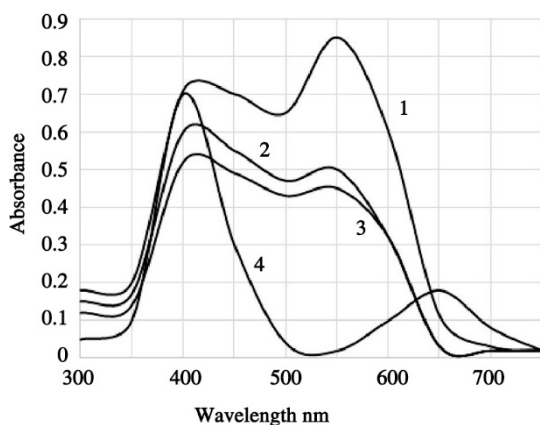
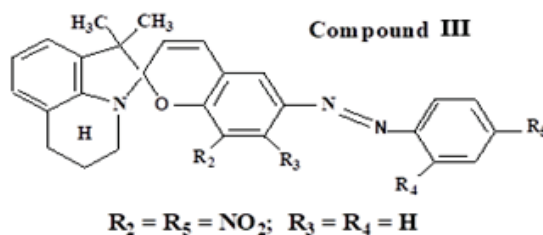


Fig. 1. Absorption bands of Compound II in ethanol: 1 – thermodynamic equilibrium; 2 – photochemical equilibrium; 3 – after radiating with visible light. 4 – Absorption bands of Compound II in toluene; thermodynamic equilibrium.

Hybrid Compound III gained by merging

SP_{THQ} and AZ. The marriage of two photochromic molecules on the base of tetrahydroquinoline SP and AZ can lead to the birth of novel hybrid compound SP_{THQ}AZ. The left fragment of hybrid molecule is indoline SP modified by us with additional cyclic moiety which makes it rigid. Such compounds exhibit negative photochromism, because the coloured MC form is more stable than the colourless SP form. The irradiation by visible light causes decolouration of MC to generate SP form. When SP form is placed in the dark, it returns to the colored MC form. Therefore, this thermally reversible photochromic system does not need the irradiation by UV light for its photochromic transformation, which may cause degradation of the compound. Studies have shown that such compounds are twice more photosensitive to visible light than their indoline analogs.



Scheme 5. Hybrid compound gained by coupling tetrahydroquinoline spirocyclic and azobenzene.

Due to the fact that thermodynamic equilibrium constant of the compounds with additional cyclic moiety in polar solvents is more than photochemical one- ($K_T > K_{PH}$) decolouration of system occurs with UV light too. The right side of the molecule SP_{THQ}AZ extends π -conjugation system and causes bathochromic shift of the absorption band of the coloured – zwitterionic form of Compound III (Fig. 2).

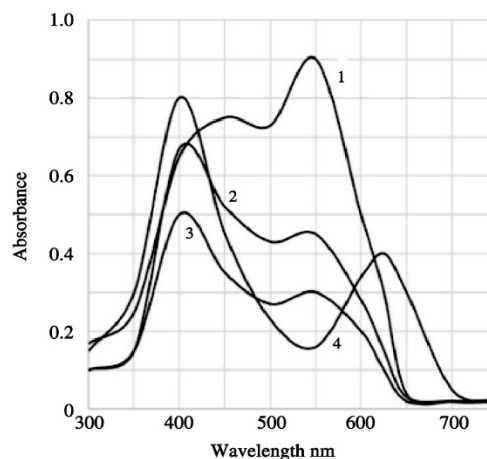


Fig. 2. Absorption band of Compound III in ethanol; 1 – thermodynamic equilibrium; 2 – photochemical equilibrium (after radiating with UV light); 3 – after radiating with visible light; 4 – Compound III in benzene, thermodynamic equilibrium.

Evidently, in the molecule conjugation is carried out, but due to steric unlike Compounds I and II the electron cloud does not become common.

A set of spectral methods, and the method of photokinetic analysis data were obtained on the photochromic properties of Compounds I, II, III

and their derivatives. These data represent the electronic absorption spectra of the original and photoinduced forms of kinetic and thermodynamic parameters of the dark processes, efficiency phototransformations. These parameters, along with the establishment of structure-property correlations, allow us to characterize them as photochromic effective for practical use. It is concluded that SPAZ has four digital codes and the potential of fabrication of multi-addressable system and molecular switching for optical memory.

Stationary electronic UVVIS absorption spectra were measured on a optical-fiber spectrometer Avantes 2048. Purity of the compounds was controlled by thin-layer chromatography and by melting points. The spectral studies were performed in solutions of organic solvents (polar ethanol and weakly polar toluene) and in PMMA- methyl methacrylate polymer films doped by SP at room temperature. The solutions were prepared at daylight or under dark conditions as needed. The photoisomerization of the hybrid molecule was induced by a illumination with 360 nm light from a 250 W high pressure lamp.

Conclusion

New hybrid photochromic compounds were investigated based on AZ and different spiropyrans: indoline SP – compound I; azaindoline SP – compound II and tetrahydroquinoline SP – compound III. Compounds II and III were first synthesized molecule and investigated by us. The photochromic transformation of the Compound I was observed at room temperature. In all the compounds conjugation and bathochromic shift of the coloured molecule were realized (see Figs. 1,2). According to the spectral data, in the Compound III, unlike Compounds I and II, the union of the electron cloud does not occur apparently due to steric hindrance (see Fig. 2). Physicalchemical studies of the synthesized new hybridcompounds will continue. The mechanism of kinetics and thermodynamics of the photochromic process of a new hybrid compounds were additionally investigated. This type of photochromic compounds will find application in future development of high-performance photochromic materials.

ფიზიკური ქიმია

უარყოფითი ფოტოქრომიზმი ჰიბრიდულ ნაერთებში

ლ. დევაძე*, გ. პეტრიაშვილი*, შ. ახოზაძე*, ც. ზურაბიშვილი*,
ნ. სეფაშვილი*

* საქართველოს ტექნიკური უნივერსიტეტი, კიბერნეტიკის ინსტიტუტი, თბილისი, საქართველო

(წარმოდგენილია აკადემიის წევრის ვ. ციციშვილის მიერ)

სპიროპირანები ფოტოქრომული ბისტაბილური ნაერთებია, რომლებიც გარე ზემოქმედებით: სინათლით, მეტალის იონებით, გათბობით, მექანიკური სტრესით და სხვ. იცვლიან ფიზიკურ-ქიმიურ თვისებებს და სტრუქტურას. ეს „ჰიკვიანი“ ნივთიერებები წარმოადგენს უნიკალურ მასალას ინფორმაციის ჩაწერისა და შენახვისთვის, ოპტიკური გადამრთველებისთვის, სხვადასხვა ტიპის სენსორებისთვის, ცოცხალ ორგანიზმში სამკურნალო პრეპარატების გადამტანი ნაწილაკებისთვის და სხვა. სპიროპირანების პარამეტრების გაუმჯობესების ერთ-ერთი გზა არის მისი მეორე ფოტოქრომულ მოლეკულასთან შეწყვილება. მიღებულ ჰიბრიდულ მოლეკულას, გაერთიანებული ქრომოფორების თეორიის თანახმად, გაუმჯობესებული ფოტომგრძობიარობა და დაგრძელებული π კონიუგირებული ჯაჭვი ექნება. ჩვენ მიერ სინთეზირებული და შესწავლილია სამი ტიპის ჰიბრიდული სტრუქტურა: ფოტოქრომული აზობენზოლის და ინდოლინის რიგის სპიროპირანების შეწყვილებით – ნაერთი I; აზობენზოლის და UV სინათლისადმი გაზრდილი ფოტომგრძობიარობის აზაინდოლინის რიგის სპიროპირანების შეწყვილებით – ნაერთი II; აზობენზოლის და ხილული სინათლისადმი გაზრდილი ფოტომგრძობიარობის ტეტრაჰიდროქინოლინის რიგის სპიროპირანების შეწყვილებით – ნაერთი III. კვლევებმა აჩვენა, რომ ჰიბრიდულ მოლეკულებში π კონიუგაციას, მოჰყვა შთანთქმის მაქსიმუმის ბატოქრომული გადანაცვლება, გარდაქმნები, ოთახის ტემპერატურაზე დაკვირვება. მიღებულ ჰიბრიდულ ნაერთებს უარყოფითი ფოტოქრომიზმი ახასიათებს. ტრიგერად ულტრაიისფერის ნაცვლად ხილული სინათლის გამოყენება ნაკლებენერგეტიკულ დანახარჯებთან ერთად, ფოტოქრომის დეგრადაციის შემცირების ხარჯზე, ზრდის პროცესის მნიშვნელოვან პარამეტრს – ციკლურობას.

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