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Physical Chemistry

Pyridoxal-Based Spiropyrans

Kokhta Japaridze*, Lali Devadze, Jimsher Maisuradze**,
Izolda Mzhavanadze**, Nino Sepashvili****

* *Academy Member, V. Chavchanidze Institute of Cybernetics, Tbilisi*
** *V. Chavchanidze Institute of Cybernetics, Tbilisi*

ABSTRACT. The spectral-kinetic characteristics of spiropyrans synthesized on the basis of pyridoxal in amorphous (glassy) layers were studied and compared with the properties of 2H-chromene-2-spiro-2'-1'-3'-3'-dimethylindoline. In pyridoxal-based spiropyrans an increase in resolution of the absorption spectrum and in the dipole moment of a molecule is observed. *© 2010 Bull. Georg. Natl. Acad. Sci.*

Key words: *photochromism, spiropyrans, indoline and chromene fragments, pyridoxal, nanostructures.*

Bistable molecules and molecular ensembles, i.e. systems existing in two thermodynamically stable conditions separated by a definite energy barrier, can be used as base elements of nanotechnology facilities.

Transitions between these two conditions are carried out by light, temperature, mechanical effect, electric and magnetic fields, etc. The effective and most convenient technique is the induction of molecular regrouping under the effect of light associated with the phenomenon of photochromism. On the basis of photochromic compounds, representing double-bit systems, molecular switches, transistors, elements of optical memory, including three-dimensional memory, are created. Spiropyrans constitute the most important class of organic photochromes, revealing photochromic properties in solutions, polymeric matrices, crystals, as well as in amorphous (glassy) layers. Today, spiropyrans are the most actively studied photochromic organic compounds. Upon photoinduction by ultraviolet light (UV), the bulk, non-colored molecule of spiropyran, as a result of photoisomerization, transforms into a colored, coplanar merocyaninic form with the absorption line in the visible region of spectrum. In comparison with other classes of organic photochromic materials, spiropyrans are distinguished for high photosensivity, maximum values of two-photon absorption coefficient. The first memory device with the two-photon information record was realized precisely on spiropyran [1].

Specific practical applications of photochromic materials should meet various requirements: to protect the organs of vision, strong absorption in the visible and UV regions is necessary, whilst for information processing systems – absorption in the laser radiation region. In order to create an elemental base for optical computers, photochromes should be compatible with polymeric matrices; light-switchable systems need photochromes with high thermal stability; information processing requires rapid-relaxing photochromes; whereas information storage needs compounds capable of preserving the photoinduced dying for a long time. Photochrome-sensors should be selectively sensitive to the selected parameters (pH, metals, availability of charged particles, etc.). For systems storing solar energy in the form of energy of voltage of metastable but kinetically stable structures, photochrome maximally using the solar spectrum, the photoinduced form of which is colorless, is required.

Time of retention of information being recorded on

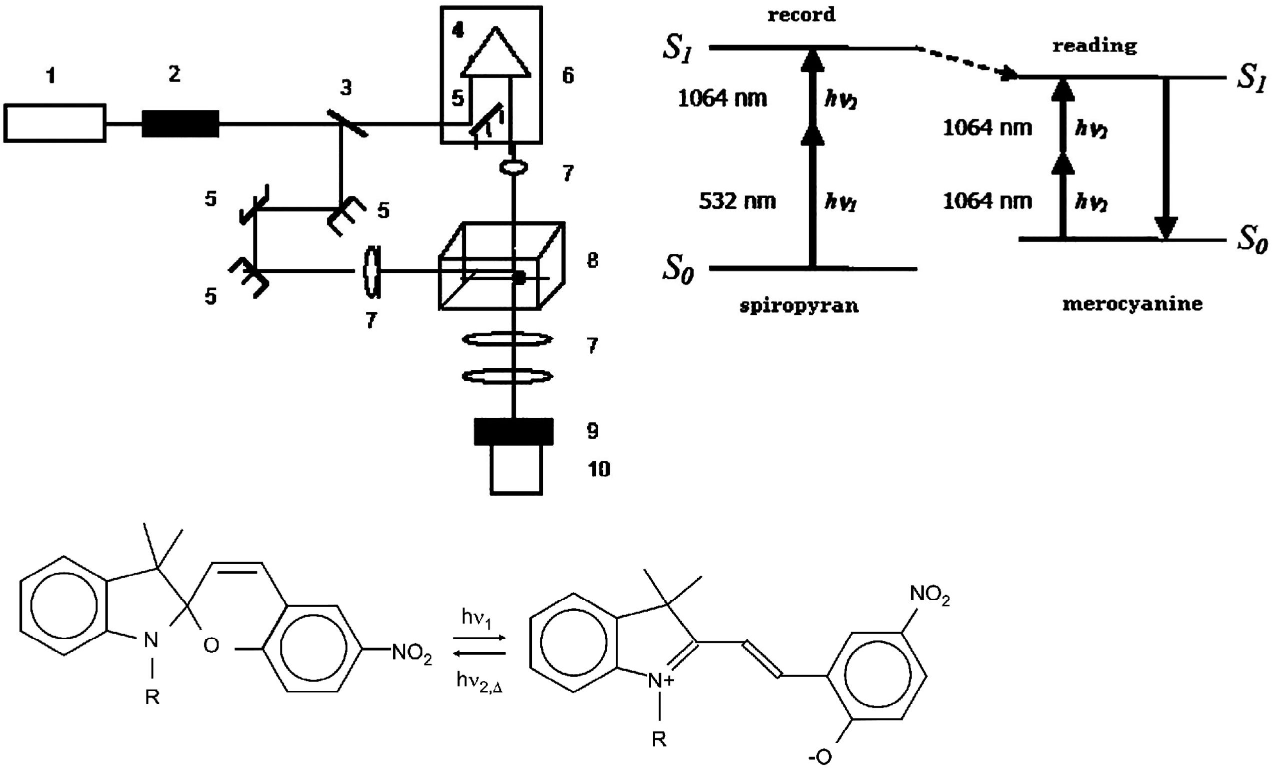

Fig. 1. Diagram of information record by means of two-photon absorption. **1** - laser; **2** - frequency converter; 3 - beam splitter; 4 - prism; 5 - mirrors; 6 - delay line; 7 - lenses; 8 - photochromic recording media; 9 - polychromator; 10 - irradiation detector.

spiropyrans can be regulated within a wide range; the image changeover for a new one or its real-time correction is possible, as well as multiple rerecording on the same specimen with resolution on the molecular level, also a relatively easy synthesis and structural modification of the molecule enabling the possibility of effective management of photocharacteristics. Methods of regulation of the photochemical properties of spiropyrans include the variation of substituents both in the chromene fragment and the indoline part of the molecule or the simultaneous modification of both parts. In addition to information technologies, spiropyrans are also applied in the development of various fields of nanotechnologies (in engineering, medicine, materials science, physics, chemistry, biology, ecology), that is in tasks of making functional materials, devices and systems on the basis of objects sized 1-100nm, taking into account their physical, chemical and biological regularities and characteristics. The work [2] demonstrates that colorless methylacrylate films containing photochromic molecules of spiropyran in the polymer chain are colored upon mechanical loads. In the constructions covered with such films the emerging defects are easily detectable by sight. Studies demonstrated that the coloring mechanism consists in the C-O bond breaking, as in the case of photochromism. Also reported [3] is the metallochromism of spiropyrans on the basis of which developed are chemosensors capable of photochromic transformations and cation-induced isomerizations at the expense of complexation of merocyaninic isomers with metal cations.

Proceeding from the above, a synthesis of new photochromic materials with improved parameters (photosensitivity, stability of the photoinduced form, big dipole moment originating upon photoinduction, absence of destruction upon radiation of the specimen and reading of information, etc.) and investigation of the physical and chemical processes going in them is an important stage of scientific and technological research. The use of nanostructures revealing properties different from those of the substance from which they are formed makes it possible to widely vary the material properties using intermolecular interactions. Consequently, the achievements in photonics and chemistry of novel photoactive materials play a decisive role at the level of nanosystems. Using the processes of self-organization of spiropyran molecules – the ability of creating various aggregates (nanoparticles), it is possible to form pre-organized supramolecular, optically and photochemically active centers and to make, on their basis, new materials of various designations. Realized in supramolecular systems is such principle of organization and functioning of matter as molecular discrimination, i.e. chemical informatics; also implemented are self-organization and

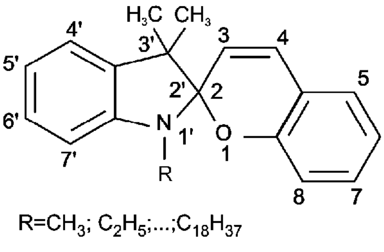

Fig. 2. Schematic representation of 2H-chromene-2-spiro-2'-1'-3'-3'-dimethylindoline (**1**).

programmed self-assembly of supramolecular systems. For molecular coloring solutions, the active center is the dye molecule surrounded by the solvent molecules. Interaction of the dye molecule with the surrounding molecules leads to their optical spectra in solutions often found to be unstructured. In ordinary matrices, heterogeneous broadening reduces the optical spectrum resolution and, in contrast to homogeneous broadening conditioned by interaction of the electron-excited molecule with intramolecular vibrations, is not reduced at the substance temperature decrease. Heterogeneous broadening associated with different molecular environments leading to the scattering of frequencies of the electronic transition of molecules can be reduced on condition that the homogeneous environment around the optically active molecule is formed, for example if an amorphous (glassy) layer of the substance is formed.

As noted, the regulation of photochemical properties of spiropyrans can be carried out by varying different substituents – from electron-donors to electron-acceptors, in both fragments of the molecule.

By insertion of the nitrogen atom in the indoline fragment of the spiropyran molecule in the position 4', compounds were obtained with increased photosensitivity to ultraviolet rays and thermal equilibrium being shifted towards the closed form, which contributes to photochrome stability, for the merocyaninic molecule of the compound undergoes autodestruction [4, 5]. A priori it can be assumed that the substitution of the CH group with the nitrogen atom, in position 7 of the chromene part, will make its corrections to the molecule properties (solubility, formation of complexes, aggregates, etc.).

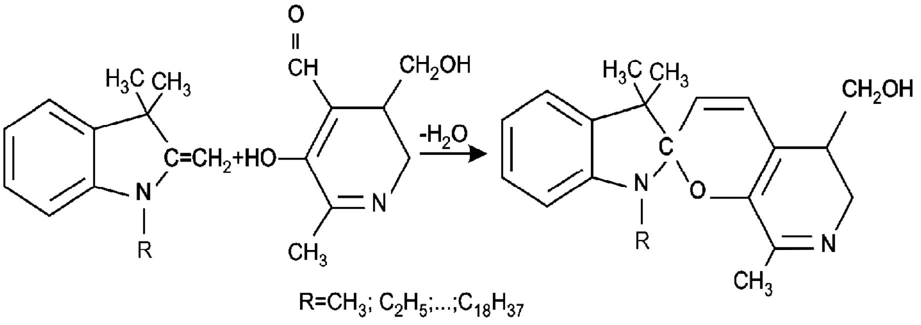

Fig. 3. Schematic representation of synthesis of pyridoxal -based spiropyrans (2)

Spiropyrans were synthesized on the basis of pyridoxal (compounds (**2**)) [6]. Fig.3 is a schematic representation of the synthesis of pyridoxal-based spiropyrans.

The spectral and kinetic characteristics of the synthesized compounds (**2**) in the amorphous layers were studied by means of the fiber-optic spectrometer Avantes and compared with the properties of 2H-chromene-2-spiro-2'–1'-3'-3'-dimethylindoline (compound **1**). Amorphous layers, in contrast to solutions, consist exclusively of the

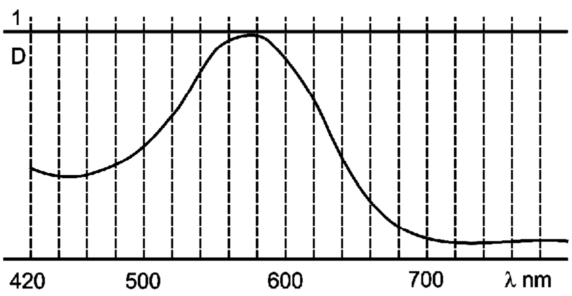

Fig. 4. Absorption spectrum of compound **2** in amorphous condition after photoinduction by UV light (λ= 365 nm) at t = 0^0C.

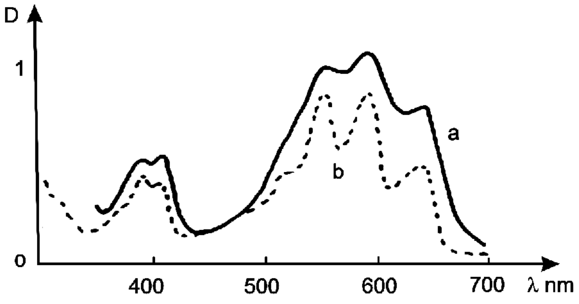

Fig. 5. Absorption spectrum of a) compound **1** in the amorphous condition, at t = 0^0C; b) the same compound in the mixture of methyl cyclohexane and decalin, at t = -160^0C

photoinducible centers; therefore, the photochromic transformations can be observable at higher temperatures. In fact, the photochromic transformations of compound **1** in the mixture of methylcyclohexane and decalin are observable at t = -160^0C (at the given temperature the mixture transforms into transparent glass); at the same time, the absorption spectrum of the photoinduced amorphous layer of the same compound **1** was observable at the temperature t = 0^0C [7]. For compound **2**, the situation was similar. The photochromic properties in the amorphous layers of spiropyran **2** reveal themselves at t = 0^0C; the absorption spectrum given in Fig. 4 has a band in the visible region with the maximum at λ=575 nm.

Under the same conditions, the absorption spectrum of compound **1** is structured (has several peaks) and broadened, Fig. 5 [6].

As a result of irradiation, the C-O bond is broken and intramolecular reorganization takes places, i.e. the molecules where the indoline and chromene parts were located in mutually orthogonal planes become coplanar. We treat the formed colored merocyaninic nanoparticles as a "guest" in the environment of non-induced spiropyran molecules – the "host". Thanks to the environment rigidity and the conformity of the "guest" form to that of the "host", it was possible to reduce the heterogeneous broadening in the amorphous layers, increasing thus the resolution of the spectrum. Reduction of heterogeneous broadening and a hypsochromic shift of the band give grounds to assume that upon photoinduction by UV rays, the originated coplanar merocyaninic molecules would form dimers of nanosizes. The identity of the spectra of compound **1** in the indifferent solution and amorphous state is indicative of the commensurability of the dipole moments of methyl cyclohexane and spiropyran molecules. According to the unstructured spectrum of compound **2**, it is concluded that the value of its dipole moment is more than that of compound **1**. The spectrum of amorphous layers of benzothiazole spiropyrans, whose dipole moment exceeds the indoline analogs, also consists of one absorption band [7].

New spiropyrans have been synthesized on the basis of pirydoxal (constituent part of vitamin B$_6$) and their physical and chemical characteristics in amorphous layers have been studied. Differences of the pirydoxal-based spiropyrans from indoline analogs: reduction of heterogeneous broadening, i.e. increase of the spectrum resolution and rise of the dipole moment of the molecule are demonstrated.

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ფიზიკური ქიმია

სპიროპირანები პირიდოქსალის ბაზაზე

კ. ჯაფარიძე*, ლ. დევაძე, ჯ. მაისურაძე**, ი. მჟავანაძე**, ნ. სეფაშვილი****

* *აკადემიკოსი, ვ. ჭავჭანიძის კიბერნეტიკის ინსტიტუტი, თბილისი*
** *ვ. ჭავჭანიძის კიბერნეტიკის ინსტიტუტი, თბილისი*

პირიდოქსალის ბაზაზე სინთეზირებულია სპიროპირანები. ამორფულ (მინისებრ) ფენებში შესწავლილია მათი სპექტრულ-კინეტიკური მახასიათებლები და შედარებულია 2H-ქრომენ-2-სპირო-2'-1'-3'-3'-დიმეთილინდოლინის თვისებებთან. პირიდოქსალის ბაზაზე მიღებულ სპიროპირანებში დაიკვირვება შთანთქმის სპექტრის გარჩევის უნარიანობის და მოლეკულის დიპოლური მომენტის გაზრდა.

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