

Hybrid Spiropyrans (Spirochromenes) with Additional Cycle in their Indoline Part

Jimsher Maisuradze*, Lali Devadze*, Shorena Akhobadze*,
Zhuzhuna Urchukhishvili*, Nino Sepashvili*

* *Laboratory of Optical Chemical Research, V. Chavchanidze Institute of Cybernetics, Georgian Technical University, Tbilisi, Georgia*

(Presented by Academy Member Shota Samsoniya)

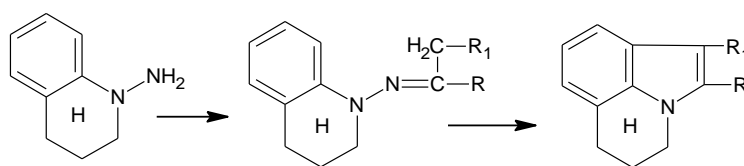
ABSTRACT. Alongside with a number of substituents in different positions, the substituents at pyrrolyn nucleus nitrogen greatly influence on the photochromic properties of spirochromenes. In this position, the growth of hydrocarbon radicals makes the presence of photochromy in a crystal state possible. We considered it purposeful to fix the nitrogen atom of pyrrole nucleus by additionally including it in a cyclic fragment. For this purpose, we used 1,2,3,4-tetrahydroquinoline as the source product. It turned out that methylisopropylketone with 1-aminotetrahydroquinol yields hydrazone, which in the diluted sulfuric acid area yields 1,7-propane-2-methylene-3,3-dimethylindoline. We treated this salt with a 5% warm KOH solution. As a result, a double-bonded base was originated, and we have obtained spiropyrans with relevant aldehydes by condensing it. The cyclic fragment gives the following properties to the spiropyrans obtained on the basis of 1,7-propane-2-methylene-3,3-dimethylindoline: the thermodynamic balance is inclined to a colored form, i.e. the compound is characterized by inverse photochromy; the life duration of photoinduced form is prolonged; the colored form has twice as much photosensitivity to visible light. By coupling such a molecule with azobenzene, we obtained a hybrid molecule having an elongated conjugate system followed by a bathochromic shift of an absorption band of a colored form. The hybrid molecule maintains the properties of both molecules: the spiropyrans and azobenzene, and therefore, the relevant absorption bands (ultraviolet and in the visible area) can be controlled with a different-frequency laser. © 2018 *Bull. Georg. Natl. Acad. Sci.*

Key words: spiropyrans, photochromy, hybrid molecule

The long practice of research in many countries demonstrated that spirochromenes obtained on the basis of indoline with their various parameters are incomparable among the photochromic compounds. Substitution of indoline with another fragment, e.g. thiazole, oxazole, selenazole, acridine, etc. leads to the total or partial deterioration of

such properties of photochromes, as light sensitivity, cyclicity, photochemical or chemical stability, solubility, etc.

Alongside with a number of substituents in different positions, the substituents at pyrroline nucleus nitrogen greatly influence on the photochromic properties of spirochromenes. In this



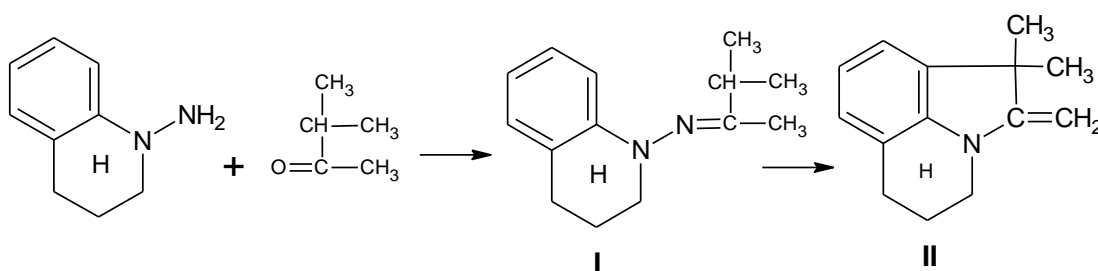
Scheme 1. Condensation of 1-aminotetrahydroquinoline with relevant aldehydes.

position, the growth of hydrocarbon radicals makes the presence of photochromy in a crystal state possible [1], while phenyl radical causes an acceleration of the speed of self-discoloration of a colored form and shift of the absorption maximum towards the long waves in the visible site of

methylbutylketone, phenylacetone and dimethylcyclohexanone [3, 4], obtained the following compounds:

Where R and R₁ are the radicals corresponding to the used ketones.

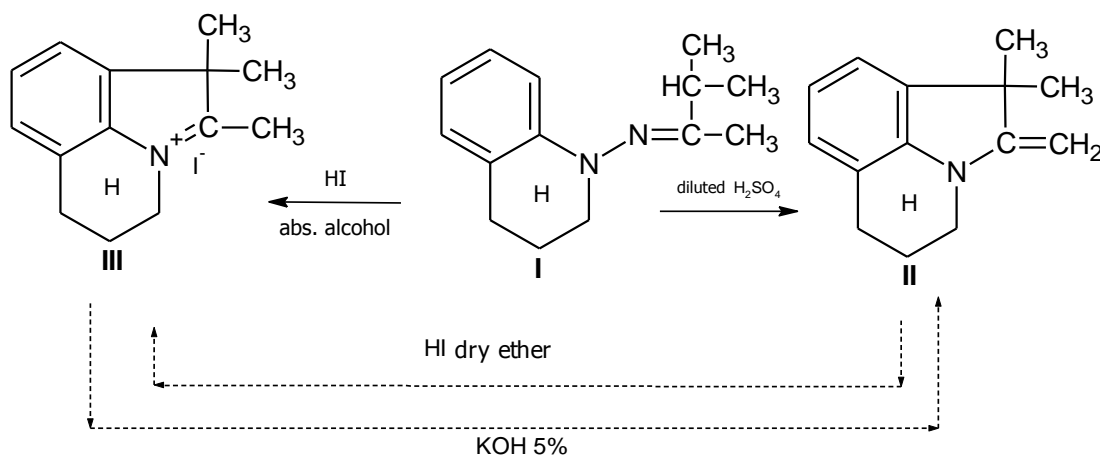
The compounds of this type would not fit our



Scheme 2. Condensation of 1-aminotetrahydroquinoline with methylisopropylketone.

spectrum [2]. We considered it purposeful to fix the nitrogen atom of pyrrole nucleus by additionally including it in a cyclic fragment. For this purpose,

purpose to obtain spirochromenes, as it is difficult or almost impossible to obtain the analogs of Fisher's base with them.



Scheme 3. Transformation of quaternary salts and double bond base.

we used 1,2,3,4-tetrahydroquinoline as the source product.

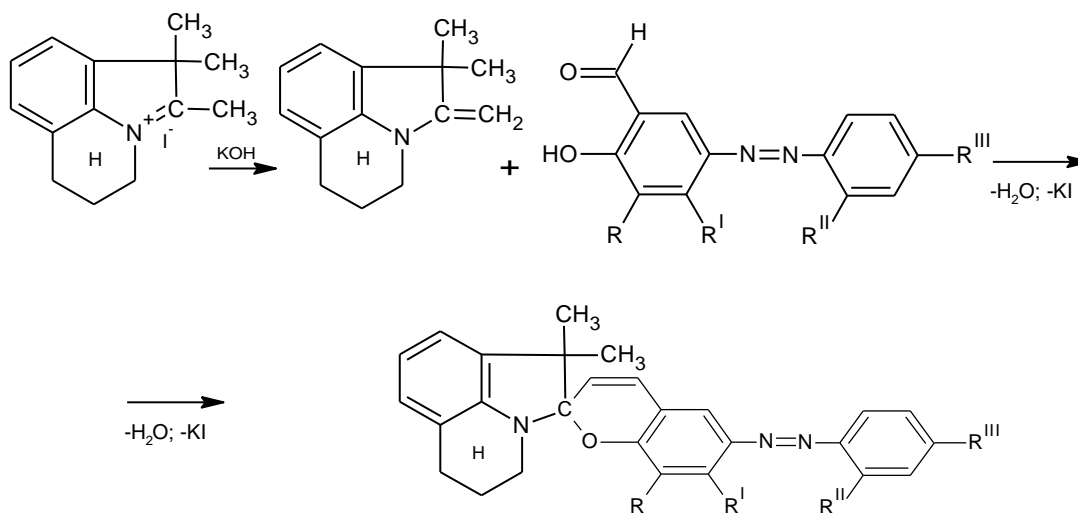
A.I. Kost and his collaborates, by using 1-aminotetrahydroquinoline and methylethylketone,

In order to achieve our aim, we used the kind of ketone having a tertiary carbon atom in α -state with a carbonyl group. It turned out that methylisopropylketone with 1-aminotetrahydroquinoline

yields hydrazone, which in the diluted sulfuric acid area yields 1,7-propane-2-methylene-3,3-dimethylindoline.

By treating the obtained compound with hydrogen iodide in dry ether, we have obtained quaternary salt. We have obtained the same salt by interacting with concentrated hydroiodic acid ($d=1.9$) on the relevant hydrazone (I) in the area of absolute alcohol. The quaternary salt obtained with this method gives the above-described base in the alkaline area, 1,7-propane-2-methylene-3,3-dimethylindoline (II). The mixture of the samples of salts does not yield depression. Graphically, these transformations can be expressed as follows:

1,7-propane-2-methylene-3,3-dimethylindoline



Scheme 4. Synthesis of targeted spiropyran.

(II), like Fisher's base, is unstable, oxidizes and gives red coloration. The intense absorption bands in an infrared zone (1650 and 3100 cm^{-1}) evidence the presence of a double bond. The electronic spectra almost coincide with the electronic spectra of Fisher's base (210 and 286 nm). Due to the base instability, we transformed it into quaternary salt (III) and isolated base from it immediately during the spiropyran synthesis.

We treated this salt (III) with a 5% warm KOH solution. As a result, a double-bonded base (II) was originated, and we have obtained spiropyrans with relevant aldehydes by condensing it.

The general plan is as follows:

IV – $R^I=R^{II}=-H$; $R=R^{III}=-NO_2$;

V – $R^I=R^{II}=-H$; $R=-OCH_3$; $R^{III}=-NO_2$;

VI – $R^I=R^{II}=-H$; $R^I=-OH$; $R^{III}=-NO_2$;

The obtained spiropyrans are dark-colored highly-melting crystal substances, which dilute well in acetone and quite fairly in benzene and alcohol. Their solutions are of different colors in different solvents.

The cyclic fragment gives the following properties to the spiropyrans obtained on the basis of 1,7-propane-2-methylene-3,3-dimethylindoline: the thermodynamic balance is inclined to a colored form, i.e. the compound is characterized by inverse photochromy; the life duration of photoinduced

form is prolonged; the colored form has twice as much photosensitivity to visible light [2].

By coupling such a molecule with azobenzene, we obtained a hybrid molecule having an elongated conjugate system followed by a bathochromic shift of an absorption band of a colored form.

The hybrid molecule maintains the properties of both molecules: the spiropyrans and azobenzene, and therefore, the relevant absorption bands (ultraviolet and in the visible area) can be controlled with a different-frequency laser.

The study of the thermodynamic and spectral properties of the above-mentioned compounds

demonstrated that thermodynamic balance in solutions, like in UV and whole range of visible area is more than photochemical one $KT > KPH$. Spectral analysis demonstrated that the common thing with the obtained spiropyrans is that conjugation occurred between two photochromic fragments and the length of the molecule conjugation increased. We observed this phenomenon in the solutions by a bathochromic shift of the relevant absorption band of a colored form. The conjugation is elongated both, in ethanol and benzene. In the first instance, it is 10 nm and it is 40 nm in the second instance as compared to the reference compounds [2]. The azobenzene fragment bonded to the chromen part is fully responsible for the bathochromic shift elongating the conjugation by additional conjugation. Insertion of NO_2 in 8-state (compound IV) results in the exposure of photochromic properties at a room temperature.

As the spectral analysis show, the peaks in the UV area correspond to the absorption of indoline fragment of spiropyran and benzene of a hybrid compound, while in the visible area, they totally correspond to the absorption of a merocyanin form. Disturbance of thermodynamic balance may occur under the impact of both, visible and UV light. In both cases, photochromic balance is below the thermodynamic balance.

Experimental part

The spectral properties of the obtained spiropyrans were studied with an optical-fiber spectrometer Avantes (AvaSpec-2048).

1,7-propane-2-methylene-3,3-dimethylindoline (II). We refluxed a mixture of 9.4 gr (0.06 moles) of 1-amino-1,2,3,4-tetrahydroquinoline and 7.3 gr (0.08 moles) of methylisopropylketone on the water bath for 3 hrs. We removed excess ketone under the reduced pressure. We added 38 ml of 12% sulfuric acid to the remained mass and heated it on a water bath for 3 hrs. After cooling, we neutralized the reaction mixture with NaOH (5 gr),

extracted with ether, dried on KOH and distilled. The main mass of oily liquid ($T_{\text{Boiling}} - 103-105^\circ\text{C}/1$ mm Hg) is crystallized after allowance. Following the recrystallization from octane: $T_{\text{Melting}} = 51-53^\circ\text{C}$. The yield is 70%. The percentage value was identified as follows: C=84.60; H=8.27, and the percentage value was calculated as follows: C=84.42; H=8.54.

1,7-propane-2,3,3-trimethylindolenine iodide (III). a) We mixed 3 ml hydroiodic acid solution ($d=1.56$) carefully with 0.008 moles of 1-amino-1,2,3,4-tetrahydroquinoline methylisopropylketone hydrazone (raw product) in 2 ml of absolute alcohol. We allowed the mixture in the darkness at 0°C . After some hours, we filtered the isolated brown crystals and crystallized them from ethanol. $T_{\text{Melting}}=284-285^\circ\text{C}$. The yield is 80%. The percentage value was identified as follows: C=51.17; H=5.93; Hal=38.27, and the percentage value was calculated as follows: C=51.37; H=5.5; Hal=38.80.

b) We passed dry hydrogen iodide in 1,7-propane-2-methylene-3,3-dimethylindoline ether solution until the crystal isolation stopped. Following the recrystallization from ethanol: $T_{\text{Melting}} = 284-285^\circ\text{C}$. The percentage value was identified as follows: C=51.17; H=5.93; Hal=38.27, and the percentage value was calculated as follows: C=51.37; H=5.5; Hal=38.80. The mixed sample does not yield depression.

6-[4''-nitrophenildiazenyl]-8-nitro-2H-chromen-2-spiro-1,7-propan-3,3-dimethylindoline (IV). We diluted 0.3 gr of 2-hydroxy-3-nitro-5[4-nitrophenyl diazenyl] benzaldehyde in 30 ml dry alcohol by refluxing. Then, we dissolved 0.52 gr of 1,7-propane-2,3,3-trimethylindolenine salt with alkali and extracted with ether. After removing the ether, we diluted the remained mass in 20 ml alcohol and added its warm solution to the warm solution of relevant aldehyde. Immediately after adding, the coloration was obvious. We continued warming for some more minutes and obtained greenish crystals. On the next day, we filtered it and

obtained 0.6 gr of target product. $T_{\text{Melting}}=240-241.5^{\circ}\text{C}$. The yield is 80%. The percentage value was identified as follows: C=65.19; H=4.63; N=14.08, and the percentage value was calculated as follows: C=64.9; H=4.60; N=14.11.

8-methoxy-6-[(4'-nitrophenyl)diazonyl]-2H-chromen-2-spiro-1,7-propan-3,3-dimethylindoline (V). Through the interaction (condensation) of 0.2 gr of 2-hydroxy-3-methoxy-5-[(4'-nitrophenyl)diazonyl] benzaldehyde and 0.22 gr of 1,7-propan-2,3,3-trimethylindoline iodine salt, we have obtained the brownish crystals like in the previous experiment. $T_{\text{Melting}}=183-184^{\circ}\text{C}$. The yield is 70%. The percentage value was identified as follows: C=69.7; H=5.39; N=11.62, and the percentage value was calculated as follows: C=69.2; H=5.35; N=11.73.

7-hydroxy-6-[(4'-nitrophenyl)diazonyl]-2H-chromen-2-spiro-1,7-propan-3,3-dimethylindoline (VI). Like in the previous experiment, by mixing the hot mixtures in equimolecular amounts of the relevant aldehyde and base, we have obtained a dark green solution, with green crystals isolated from it after one day detainment. $T_{\text{Melting}}=176-180^{\circ}\text{C}$. The yield is 75%. The percentage value was identified as follows: C=69.23; H=5.13; N=11.96, and the percentage value was calculated as follows: C=69.1; H=5.09; N=12.1.

The work was accomplished under the financing of grant project FR/395/6 – 420/13 of the Shota Rustaveli National Science Foundation.

ორგანული ქიმია

ჰიბრიდული სპიროპირანები (სპიროქრომენები) დამატებითი ციკლით ინდოლინურ ნაწილში

ჯ. მაისურაძე*, ლ. დევაძე*, შ. ახოზაძე*, ჟ. ურჩუხიშვილი*, ნ. სეფაშვილი*

**საქართველოს ტექნიკური უნივერსიტეტი, ვლადიმერ ჭავჭავაძის სახ. კიბერნეტიკის ინსტიტუტი, ოპტიკურ-ქიმიური კვლევათა ლაბორატორია, თბილისი, საქართველო*

(წარმოდგენილია აკადემიის წევრის შ. სამსონიას მიერ)

სპიროქრომენების ფოტოქრომულ თვისებებზე, გარდა მთელი რიგი ჩამნაცვლებლებისა სხვადასხვა პოზიციაში, დიდ გავლენას ახდენს აგრეთვე ჩამნაცვლებლები პიროლინის ბირთვის აზოტთან. ამ პოზიციაში ნახშირწყალბადის რადიკალების გაზრდა შესაძლებელს ხდის ფოტოქრომიის კრისტალურ მდგომარეობაში. ჩვენ მიზანშეწონილად ჩავთვალეთ პიროლის ბირთვის აზოტის ატომი დაგვეფიქსირებინა დამატებით ციკლურ ფრაგმენტში ჩართვით. ამ მიზნებისთვის ამოსავალ პროდუქტად გამოვიყენეთ 1,2,3,4-ტეტრაჰიდროქინოლინი. აღმოჩნდა, რომ მეთილიზოპროპილკეტონი 1-ამინოტეტრაჰიდროქინოლინთან იძლევა ჰიდრაზონს, რომელიც განზავებული

გოგირდმქავას არეში წარმოქმნის 1,7-პროპან-2-მეთილენ-3,3-დიმეთილინდოლინს, რომლის კონდენსაციით შესაბამის ალდეჰიდებთან ვიღებდით სპიროპირანებს. 1,7-პროპან-2-მეთილენ-3,3-დიმეთილინდოლინის ბაზაზე მიღებულ სპიროპირანებს ციკლური ფრაგმენტი ანიჭებს შემდეგ თვისებებს: თერმოდინამიკური წონასწორობა გადახრილია შეფერილი ფორმისკენ. გაზრდილია ფოტოინდუცირებული ფორმის სიცოცხლის ხანგრძლივობა; შეფერილი ფორმა ორჯერ უფრო ფოტომგრძობიარეა ხილული სინათლის მიმართ. ასეთი მოლეკულის შერწყმით აზობენზოლთან მივიღეთ ჰიბრიდული მოლეკულა, რომელსაც აქვს დაგრძელებული შეუღლებული სისტემა, რასაც თან სდევს შეფერილი ფორმის შთანთქმის ზოლის ბატოქრომული წანაცვლება. ჰიბრიდულ მოლეკულას შენარჩუნებული აქვს ორივე ფრაგმენტის – სპიროპირანის და აზობენზოლის მოლეკულების თვისებები, და აქედან გამომდინარე, შესაბამისი შთანთქმის ზოლების (ულტრაიისფერ და ხილულ უბანში) მართვა შესაძლებელია სხვადასხვა სიხშირის ლაზერით.

REFERENCES

1. Japaridze K.G., Maisuradze J. P., Gachechiladze G.G., Gomelauri E.S. (1971) Sintez i nekotorye fiziko-khimicheskie svoistva 6-nitro-2H-khromen-2-spiro-2'-N-alkil-3',3'-dimetilindolinov. *Khimiia Geterotsiklicheskikh Soedinenii*, **7**, 6: 723-724 (in Russian).
2. Makhshvili N.I., Maisuradze J. P., Japaridze K.G., Devadze L.V. (1988) Sintez 1,7-propano-2-metilen-3,3-dimetil-spiro-1'-tsiklogeksanindolinov i ikh fotokhromnykh proizvodnykh. *Izvestiia akademii nauk gruzinskoi SSR, seria khimicheskaiia*, **2**, 14: 99-104 (in Russian).
3. Kost A.N., Iudin L.G. (1957) Sintez lilolidenovykh struktur. *Khimicheskaiia nauka i promyshlennost'*, **2**, 6: 800 (in Russian).
4. Kost A.N., Iudin L.G., Terent'ev A.P. (1949) Sintez 9,10-dialkillilolidenov. *Zhurnal obshchei khimii*, **6**: 1949-1953 (in Russian).

Received January, 2018