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Merocyanine–spiropyran relaxation processes

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Abstract. In the paper mechanisms of merocyanine–spiropyran transformation were investigated. It was shown that in dark conditions for such transformation it is necessary to overcome the potential barrier with height of ∼0.6 eV. A barrierless transformation into the spiropyran molecule is possible due to the rotation of the phenyl moiety of the merocyanine molecule by 90° relative to the plane of the molecule. It was proved that a 90° orientation of moieties in the merocyanine molecule is achievable only in a photochemical way because in S_1 state of the molecule energy of the potential surface is lowered by rotation the phenyl moiety relative to its plane.

1 Introduction

Among the dynamic materials much attention is paid to the systems which are capable of reversible transformations. One of the classes of such dynamic materials are photochromic materials [1–11]. Spiropyran as one of the representatives of photochromic compounds has become an object of many scientific researches [12–21]. Its photochromic properties are conditioned on the transition to the planar merocyanine form under the influence of UV radiation and backwards under the influence of visible radiation.

During many decades a great deal of attention of physicists and chemists is paid to the investigation of the photochemical transformation from the spiropyran to the merocyanine molecule and also to the photochemical and dark transformation from the merocyanine to the spiropyran molecule. This happens due to the fact that photochromic materials for optical data recording have been created on the basis of the spiropyran molecule [22].

Great interest of researchers is attracted to the spiropyran as a material for creating sensors [23–28], data storage devices [29–33], optical switches [34–37] and cell imagining [38,39]. Alongside spiropyrans find their application as part of photoswitchable ligands of biomolecules [40], in drug delivery, particularly for cancer treatment [41,42].

An important feature of the spiropyran molecule and its conversion product – merocyanine is that the spiropyran absorbs light in the near ultraviolet region of spectrum, and the merocyanine – in the visible region [22]. The irradiation of the polymer layer which contains spiropyran causes a spiropyran–merocyanine transformation with a high quantum yield. As a result a negative visible image appears. If the film with the recorded data is irradiated in the visible region of spectrum or is placed in the dark conditions for a long time, the reverse transformation will occur and the image (recorded data) will disappear. The process of data recording–erasing can be repeated many times.

Despite the great efforts of scientists, the mechanisms of photochemical and dark transformations in the spiropyran–merocyanine system have not been studied completely.

It is not known for sure why and in what way the spiropyran–merocyanine and vice versa transformation takes place. Without the complete understanding of this process it is not possible to design a device which is suitable for use out of laboratory conditions. Some investigations explain the mechanism of photochromism of the spiropyran molecule through the excited states [43–49], while others describe it as a chain of the conformational transformations [50–52].

With the development of computer technologies necessity in development of photographic information recording with using the photochemical processes in the recording medium has significantly decreased. However, some new problems have appeared. These problems are associated with the miniaturization of memory elements in computers of the future which will be built on the separate molecules. The authors of this study observed that the
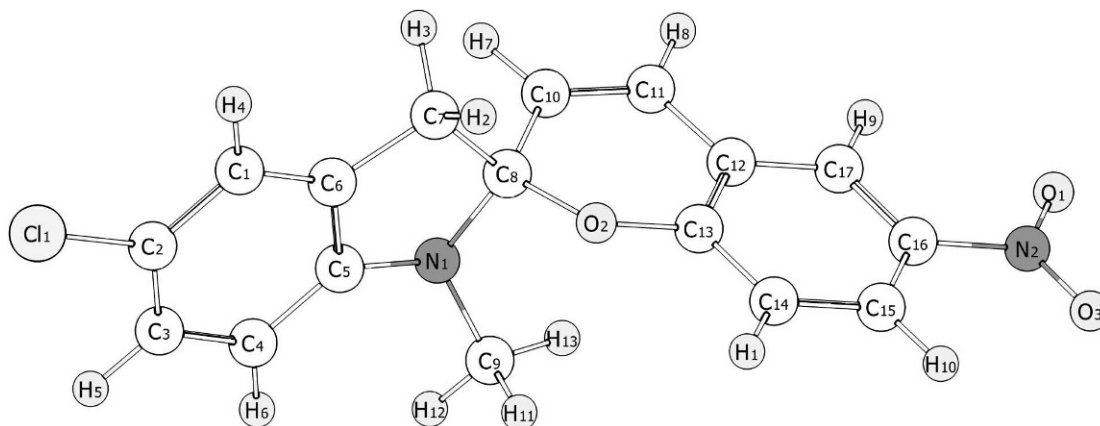
[a] e-mail: olha.kovalenko@ssu.edu.ua

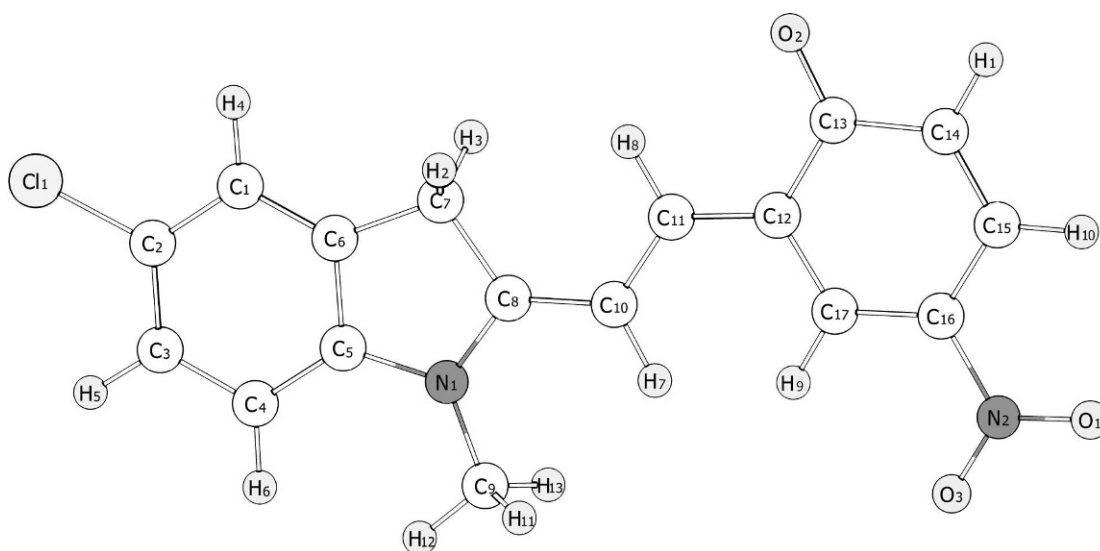**Fig. 1.** General structure of the spiropyran molecule.

Fig. 2. General structure of the merocyanine molecule.

spiropyran–merocyanine system could be used as a controlling element in computers of the future [53,54]. This is due to the fact that the structure of the π-orbitals of the spiropyran molecule does not contribute to a charge transfer along the long axis of the molecule, whereas the π-orbitals of the merocyanine are delocalized all along the molecule. The last is a pledge of the possibility of an electron transfer along the long axis of the molecule, i.e. the conductivity of the molecule. Thereby, the investigation of transformation mechanisms from the spiropyran to the merocyanine and vice versa has become relevant again.

This work is devoted to the study of data erasing mechanisms, in other words transformation from the merocyanine to the spiropyran molecule.

2 Objects and methods

In this work for doing a research a substituted spiropyran and merocyanine molecules of the following formulas were chosen (Figs. 1 and 2).

Such type of substituents has been chosen in order to provide localization of the molecule between two electrodes. Geometry structure of the spiropyran and merocyanine molecules has been optimized at camb3lyp/6-31g(d) level. In order to verify that the molecules which were obtained after geometry optimization are stable minima, frequency calculations at the same level of theory were performed for these structures.

From the structure of the spiropyran molecule it can be seen that it contains a central carbon atom with sp^3 hybridization of atomic orbitals that prevents coupling of the π-electron systems of the right and left moieties of the molecule. During the transformation from the spiropyran to the merocyanine $sp^3 \rightarrow sp^2$ rehybridization takes place. As a result, the merocyanine molecule has a planar structure and a united π-electron system.

For the detection of the mechanisms of the merocyanine–spiropyran transformation $(\mathrm{MC} \rightarrow \mathrm{SP})$ the quantum-chemical methods have been used.

Our investigation was performed using density functional theory which is implemented in the quantum-chemical package Gaussian 09 and a semi-empirical
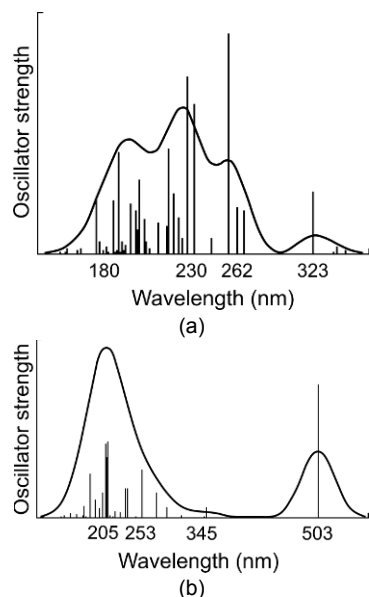
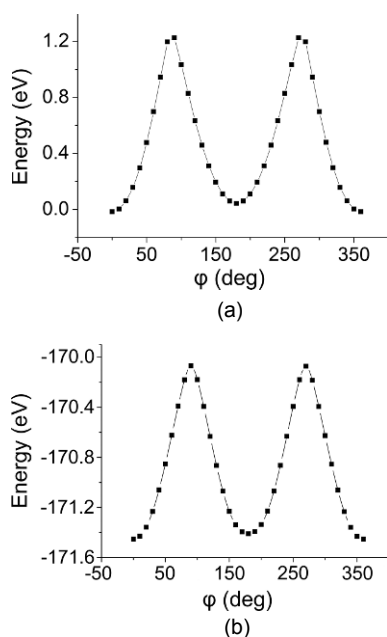**Fig. 3.** (a) The absorption spectrum of the spiropyran. (b) The absorption spectrum of the merocyanine.

Fig. 4. (a) The potential barrier of the rotamer relative to C_{11}–C_{12} bond calculated at camb3lyp/6-31g(d) level of theory. Energies are presented relative to energy of merocyanine. (b) The potential barrier of the rotamer relative to C_{11}–C_{12} bond calculated with AM1 method.

method AM1 which is implemented in MOPAC-12. AM1 is the method of valence approximation, i.e. it takes into account the valence electrons and atomic orbitals of the valence shells [55]. For the class of organic molecules the use of semi-empirical methods can be justified inspite of the fact that this method yields to ab initio or DFT methods. Their advantage is that their parameterization was carried out with taking into account experimental values

of the characteristics of real substances. Therefore these values are reproduced precisely enough and adequately reflect the experimental results [56]. Fundamentally semi-empirical and non-empirical methods do not differ in their approaches to the solution of the Schrödinger equation. Moreover, semi-empirical methods and ab initio methods have the same general scheme of calculations, but nevertheless in the semi-empirical methods each stage of the calculations is greatly simplified [57].

In this work we were interested in qualitative information about our molecule, such as its molecular orbitals and energy trends (not absolute values). Due to the fact that DFT is a time-consuming method some laborious calculations have been done using AM1 method. To ensure that results will not differ much, the potential barrier of the rotamer relative to C_{11}–C_{12} bond was calculated using both methods. Results showed insignificant difference.

To find an energetic structure of the molecules a configuration interaction between 10 occupied and 10 unoccupied molecular orbitals have been taken into account. The calculated absorption spectra of the spiropyran and the merocyanine molecules are shown in Figure 3. Comparison of the calculated absorption spectra with the experimental results showed their full consistency.

In Figures 3a and 3b vertical lines show the calculated positions of quantum transitions, the solid curve – the calculated absorption spectra.

3 Results and discussion

The structural difference between the observed molecules consists in the fact that the merocyanine molecule has a planar structure while in the spiropyran molecule the indoline and phenyl (benzopyran) moieties are orthogonal. It follows that during the transformation from the merocyanine molecule to the spiropyran molecule, one moiety must to be rotated by 90° relative to the other. In addition, the chain of atoms –CH–CH– connecting the phenyl moiety with the carbon spiro atom, must change its configuration from trans-configuration to cis-configuration during the merocyanine–spiropyran transition.

Calculations showed that potential barriers appear under the conformational transformations. Shape of the potential barriers calculated with DFT method are shown in Figure 4a. Geometry optimization has been held with every change of the dihedral angle. Thus, we have steady states and optimal positions of nuclei that corresponds to the adiabatic process. Camb3lyp/6-31g(d) level of theory was used to calculate molecule's energy on every step. In Figure 4b the same barriers calculated using AM1 method are shown. It can be seen that rotation of the phenyl moiety by 90° requires energy about 1.23 eV calculated with DFT and 1.38 eV calculated with AM1.

In carrying out calculations using MOPAC-12 the perpendicular orientation of the phenyl moiety was fixed and the O atom has been moved closer to the spiroatom. At the same time, all other distances and angles have been optimized. The result is presented in Figure 5.

As it follows from Figure 5, the dark transformation from the merocyanine to the spiropyran on the optimized
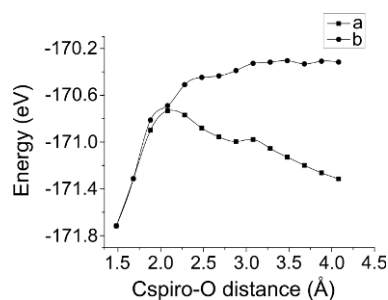
Fig. 5. The dependence of the electron system's energy of the molecule from the Cspiro–O distance in a case of an ordinary MC → SP transition (a) and MC → SP transition with fixed 90° angle between indoline and phenyl (b).
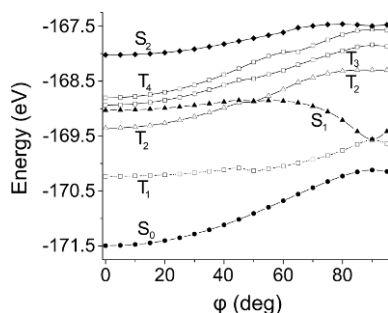

Fig. 6. The energetic structure of the merocyanine molecule depending on the angle φ – an angle of rotation of the phenyl moiety relative to the plane of the molecule.

route (curve a) requires overcoming of the activation energy about 0.6 eV. With such value of the barrier the merocyanine molecule shows instability, however the reaction proceeds slowly enough. If the phenyl moiety is rotated by 90°, there will be no energetic barriers on the way to the spiropyran. Therefore, the reverse MC → SP transformation happens quickly.

At the end of the route atoms of the molecule proved to be strictly in positions as in the spiropyran molecule. This can be explained by configuration of the potential surface with "narrow path" which was described in the paper [54].

These results initiated the investigation of the energetic structure of the merocyanine molecule depending on the angle of rotation of the phenyl moiety. Figure 6 shows the results of energetic structure calculation of the ground, excited singlet and excited triplet states of the merocyanine molecule.

From this investigation it can be seen that during such a rotation of the phenyl moiety the energy of the ground state of the molecule has increased by 1.38 eV. It greatly exceeds the barrier on the optimal route of the MC → SP transformation. The energy of the T_1 state has increased by 0.6 eV. For others triplet states an increase of energy is significantly greater.

Special attention should be paid to the energetic surface of the S_1-state. When the rotation angle increases from 0° to 50°, the energy of the S_1 state increases by 0.18 eV and then it significantly decreases reaching its minimum at 90°. The observed value of the barrier in the excited

state is absolutely inessential for the rotation process of the phenyl moiety by 90°.

The reason for energy decrease of the molecule in the S_1 state is the fact that the HOMO fragment on the HC–Ph bond has bonding character and LUMO on the same bond-antibonding character. Corresponding molecular orbitals (MO) are described in Figure 7.

The calculated value of excitation energy of the merocyanine molecule in S_1 state is 2.465 eV, while at 90° orientation of moieties an energy distance ΔE ($S_0 \rightarrow S_1$) decreases to 0.58 eV. Such decrease of the energy distance greatly accelerates the nonradiative transition to the ground state. Since the energy of the molecule in this state (1.38 eV) is considerably higher than the value of the energetic barrier ($\sim$0.6 eV) for SP → MC transformation, the photochemical conversion process from the merocyanine to the spiropyran molecule proceeds with high efficiency.

From the form of molecular orbitals of the ground and excited states of the merocyanine follows that not only C–Ph bond has antibonding character (that is why a rotation of the phenyl moiety around C–Ph axis takes place) but Cspiro–C bond has the same character (but contribution of the C atom on the formation of the molecular orbital of the S_1 state is significantly decreased).

Therefore, possible effects related to the rotation of the indoline moiety around the Cspiro–C bond were calculated. The result of this calculation is shown in Figure 8.

According to Figure 8 the rotation of both moieties by 90° increases energy of S_1 state and does not make the structure of the molecule closer to the spiropyran molecule. The only indoline moiety rotation around the Cspiro–C axis will prevent the merocyanine–spiropyran transformation due to steric hindrance on the way of reduction the Cspiro–O distance. The value of the barrier during the rotation of the indoline moiety is 0.22 eV. Due to this fact the rotation of the indoline moiety relative to the phenyl moiety will be slower (a probabilities ratio of rotation of the indoline and phenyl moieties is 0.2). As a result the quantum yield of the MC → SP phototransformation is still high ($\sim$80%).

Thus, only rotation of the phenyl moiety around C–Ph axis by 90° ensures the return of the merocyanine molecule to the spiropyran. This will be facilitated by the fact that at 90° orientation the structure of the –CH–CH– chain will be changed from trans to cis configuration (which is peculiar to the spiropyran molecule). Such a change will be almost barrierless.

4 Conclusions

The following conclusions have been made on the basis of carried out quantum-chemical researches and comparing results of theoretical researches with experiments:

- the merocyanine molecule can transform to the spiropyran molecule in dark conditions, overcoming the potential barrier with the height of $\sim$0.6 eV;
- rotation of the phenyl moiety of the merocyanine molecule by 90° relative to the plane of the molecule without a simultaneous change of the rest molecule
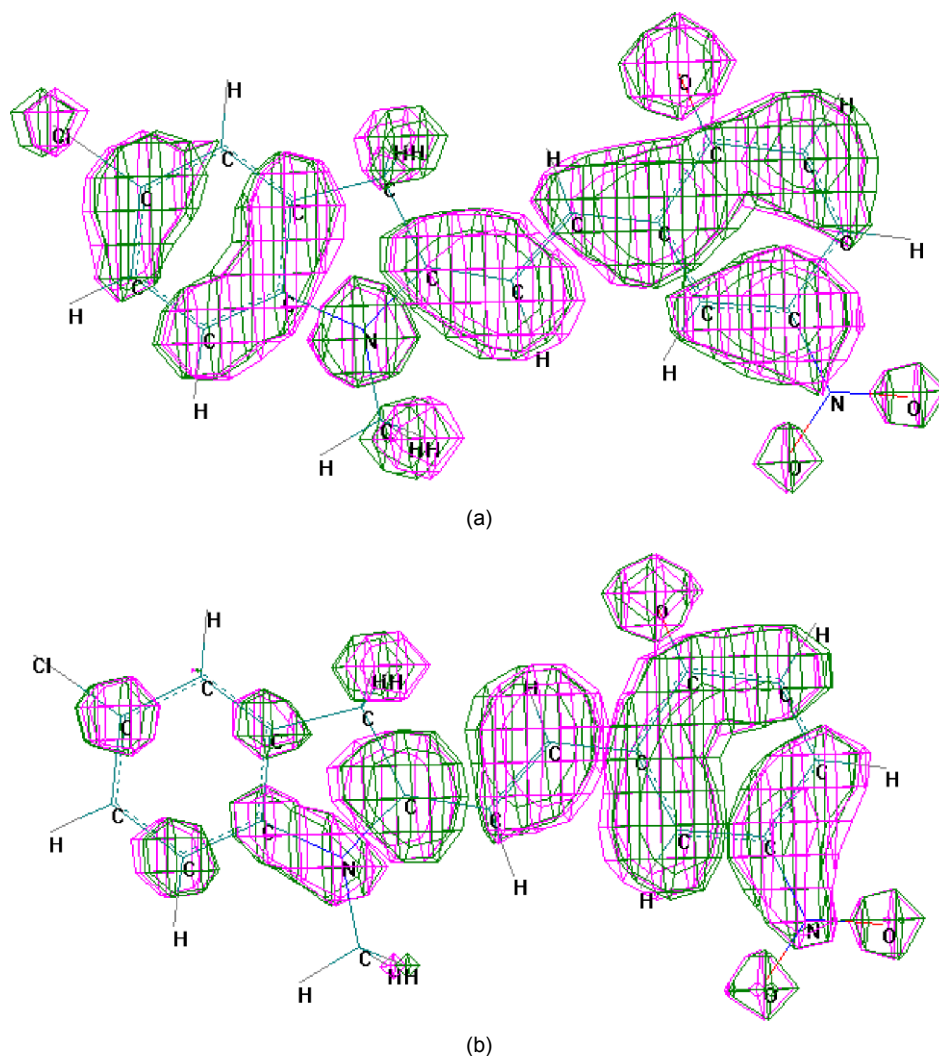
Fig. 7. (a) The molecular orbital no. 58 – HOMO. (b) The molecular orbital no. 59 – LUMO.
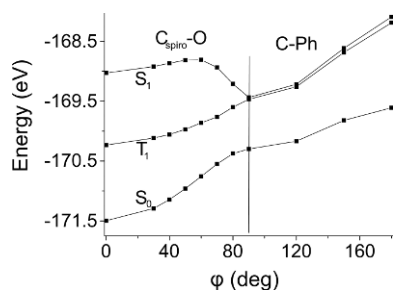

Fig. 8. The dependence of energy of ground and excited states of the molecule from the angle φ – an angle of rotation of the indoline moiety around the Cspiro–C axis (from $0°$ to $90°$) and then further rotation of the phenyl moiety from $0°$ to $90°$ (on the graph from $90°$ to $180°$).

parameters (no optimization of the molecular structure) increases the energy of the molecule by 1.38 eV;

– optimization of the molecular structure of the merocyanine molecule with $90°$ orientation of the phenyl moiety decreases energy of the system insignificantly;

– excitation of the merocyanine molecule to S_1 state makes the rotation of the phenyl moiety by $90°$ energetically favorable. At the same time the energy distance ΔE $(S_0 \rightarrow S_1)$ decreases to 0.58 eV. This fact ensures a fast non-radiative relaxation of the molecule's excitation;

– it is expected that the photochemical erasing of the recorded data in the spiropyran–merocyanine system will occur with a quantum yield which is close to unity. For dark erasing of the recorded data it is necessary to raise the temperature of the memory element;

– a rotation of the indoline moiety around the Cspiro–C axis is a competing process to a rotation of the phenyl moiety by $90°$ relative to the plane of the molecule. The rotation of the indoline moiety does not cause the transformation from the merocyanine molecule to the spiropyran molecule. It only decreases a value of the quantum yield of the MC $\rightarrow$ SP phototransformation by 20%;

– the transformation from the spiropyran to the mero-
cyanine molecule under the influence of light and
the reverse transformation can be used as a conduc-
tivity switch of a cell which is built on a separate
spiropyran molecule.

The authors declare that there is no conflict of interests
regarding the publication of this paper.

Author contribution statement

The authors contributed equally to the paper
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