Relaxation of the Electronic Excitation of the Molecule in the Path Spiropyran ↔ Merocyanine

P.O. Kondratenko[1,*], Yu.M. Lopatkin[2,†], T.M. Sakun[1]

[1] *Aerospace Institute, National Aviation University, 1, Lyubomyr Guzar Ave., 03058 Kyiv, Ukraine*
[2] *Sumy State University, 2, Rimsky-Korsakov st., 40007 Sumy, Ukraine*

Quantum chemical studies of the geometric and energy structure of spiropyran and merocyanine molecules, as well as intermediate states corresponding to the optimized geometry of molecules at different distances between the spiroatom and the oxygen atom are carried out. It is established that when the RCspiro-O distance increases to 2.375 Å, a phase transition occurs in the molecule structure. It is shown that the geometric structure of the spiropyran molecule is unique. As the $R_{Cspiro-O}$ distance increases, the energy of the electronic system of the molecule increases. At the same time, hybridization of AO of the spiroatom gradually changes. Excitation of the spiropyran molecule to the S_1 state, which is dissociative, causes the conversion of spiropyran to merocyanine. The energy structure of the merocyanine molecule is studied and it is shown that in this case, the relaxation of the electronic excitation includes TTT-TTS isomerization, as well as interconversion to the T_1 and T_2 states. In addition, it becomes possible to reduce the distance $R_{Cspiro-O}$ to the phase transition. The perturbation caused by the phase transition causes the conversion of the excited molecule to the ground state, resulting in the photoconversion of spiropyran to merocyanine and vice versa. The described mechanism requires that the quantum yield of the photoconversion of spiropyran to merocyanine exceeds the quantum yield of the reverse transition.

Keywords: Spiropyran, Merocyanine, Relaxation of electronic excitation, Phase transition, Mechanisms of photoconversion of spiropyran to merocyanine and vice versa.

1. INTRODUCTION

Spiropyran molecules have been of interest to researchers since their discovery in connection with the photochemical and thermochemical processes discovered in them. There has been a great deal of interest in these properties in the last 3-4 decades of the twentieth century due to the development of methods for recording optical information on media that do not contain silver halides. In this case, spiropyrans, having photochromic properties, allowed both recording and erasing of recorded information. A large scientific bibliography is devoted to these processes [1]. The description of these processes is also included in textbooks [2]. And even after the advent of electronic methods of recording, storing and transmitting information, interest in spiropyrans develops [3-5, 6]. This is due to the possibility of using spiropyrans as memory elements for different purposes and different technical implementations. Our work also focuses on the development of memory elements, switches and transistors, using the properties of individual molecules, in particular spiropyran.

For purposeful study of spiropyrans as elements of moletronics it is extremely important to know the nature of relaxation of electronic excitation of molecules, the structure of energy surfaces of the ground and excited states, ways of transformation in the spiropyran ↔ merocyanine system [6-8].

Despite the fact that thermochromic properties were discovered in 1926, which led to a rapid study of this class of compounds, the mechanisms of photochemical and thermochemical transformations in

the spiropyran-merocyanine molecular pair have not yet been unequivocally established. This prompted the authors of this study to conduct appropriate research and provide a complete description of the processes responsible for these transformations.

2. OBJECTS AND METHODS OF RESEARCH

In this work, it was conducted computational studies of spiropyran (Sp) and merocyanine (Mer) molecules, which have the structure:

Sp

Mer
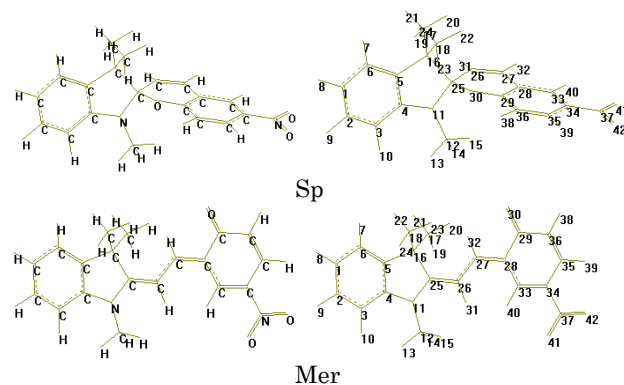
In this research, the geometric structure, energy structure and relaxation processes of electronic excitation of molecules on the way from the Sp molecule to the Mer molecule and vice versa are calculated with quantum chemical methods.

The geometric structure was studied using known quantum chemical methods: DFT [9, 10], MNDO/d and

---

* pkondrat@nau.edu.ua

† yu.lopatkin@gmail.com

AM1 [11, 12]. The latter method allows you to quickly obtain scientific results that lead to the same conclusions as when using the DFT method. Using semiempiric methods, the configurational interaction between 12 occupied MOs and 12 free MOs was set. The MO-PAC program [10] was used to establish the equilibrium geometry of intermediate states between spiropyran and merocyanine molecules.

3. RESEARCH RESULTS AND THEIR DISCUSSION

3.1 Geometric Structure and Phase Transition on the Spiropyran-Merocyanine Pathway

Spiropyran. The study of the geometric structure of the studied molecules required knowledge of the hybridization of atomic orbitals (AOs) of all atoms that form the structure of the molecule. To do this, we found the sum and magnitude of the angles between the bonds of a particular atom with its neighbors.

The sum of the angles at the atom N(11) equals $\angle(4\text{-}11\text{-}25) + \angle(25\text{-}11\text{-}12) + \angle(4\text{-}11\text{-}12) = 107.716 + 118.429° + 119.26° = 345.405°$. If there was sp^2-hybridization, we would get 360°. In the case of sp^3-hybridization, it would be $109.47122° \times 3 = 328.4137°$. Therefore, the hybridization of AOs at N(11) is intermediate between sp^2 and sp^3. In this case, the N-C(12) bond is deviated from the plane of the five-membered cycle.

In the five-membered cycle, the AOs of C(4) and C(5) atoms have sp^2-hybridization, while the AOs of C(16) and C(25) atoms have sp^3-hybridization. To maintain the high symmetry of this cycle, the AOs of N(11) atom must also have sp^3-hybridization. Probably, this is the reason for the fact that in this case the hybridization does not correspond to the planar bond configuration. And since we are dealing with an atom of another nature, the hybridization of its AOs turns out to be intermediate.

Let us check the values of the angles in the five-membered cycle: $\angle(4\text{-}16\text{-}25) = 101.867°$, $\angle(4\text{-}5\text{-}16) = 109.955°$ – instead of 120° tensed in the five-membered cycle, $\angle(5\text{-}4\text{-}11) = 111.433°$ – also tensed in the five-membered cycle. The five-membered ring is asymmetric due to the presence of the N(11) atom in the intermediate hybridization.

The sum of the angles in the pentagon is 537.953° instead of 540° for the flat configuration, and here the angle at C_{spiro} equals 106.982°. In the perpendicular plane, the angles at C_{spiro} are respectively equal: $\angle(26\text{-}25\text{-}30) = 111.595°$, $\angle(16\text{-}25\text{-}30) = 102.941°$, and $\angle(16\text{-}25\text{-}26) = 114.811°$.

Such properties of AOs of the atoms included in the five-membered ring led to the fact that the right (indoline) and left (pyran) fragments were not on the same axis. The molecule was broken at the location of the spiroatom. This, in its turn, caused asymmetry in the potential surface of the ground state. As a result, in the optimal geometry of the Sp molecule the oxygen atom can occupy only one position and cannot swap with the C(26) atom. Especially since the distance from the spiroatom to the nearby atoms C(26) and O(30) is not the same: $R(C_{Spiro} - O) = 1.49367$ Å and $R(C_{Spiro} - C(26)) =$

1.49976 Å.

Merocyanine. The sum of the angles at the atom N(11) equals to 360° (110.465° + 124.327° + 125.206°), i.e., after the Sp → Mer transformation, the pyran fragment became flat, and the hybridization of AOs of the nitrogen atom became sp^2.

The sum of the angles at the C_{spiro} atom also became equal to 360° (108.973° + 128.491° + 122.536°). The deviation of individual angles from 120° in this case is caused by the different nature of AOs of the atoms surrounding the spiroatom, as well as the decrease in the magnitude of the angles in the five-membered cycle.

The sum of the angles in the pentagon 540° (101.989° + 108.973° + 110.465° + 109.618° + 108.954°) is typical for a flat figure, although the angles are not the same due to the presence of C(16) and N(11). At the same time, AOs of C(16) remain in sp^3 hybridization and AOs of N(11) correspond to a flat structure.

Moving along a trajectory which is characterized by the minimum energy for each distance between C_{spiro} and the oxygen atom C(30), we found interesting effects. First, this applies to the two configurations of Mer (TTS and TTT). If we move from the configuration of Mer-TTS to SP, we obtain a continuous curve that characterizes the dependence of energy on the distance RC_{spiro}-O, with a small jump at $R = 2.35$ Å. If we move from Mer-TTT, the energy of the state will increase much faster than in the previous case. In addition, there is a significant jump in the magnitude of the angle and energy at a distance $R = 3.45$ Å. At the same time, the energy decreases significantly (by ~ 1.25 eV). This effect seems quite understandable, because the molecule has no symmetry with respect to the plane of the pyran ring. Thus, the channel along which we moved in this case reached the pass and the system fell into the channel along which we moved from Mer-TTS to Sp.

When we reached the distance $R = 2.375$ Å in this motion, significant changes occurred not only in the energy of the state, but also in all angles between the pyran and phenyl rings (Fig. 1). Interestingly, the sum of the three dihedral angles changes quite smoothly when moving from Sp to Mer-TTS.

As can be seen from Fig. 2, in this case the geometric structure of the molecule has changed by jump. In this case, there was a natural deviation of the indo-
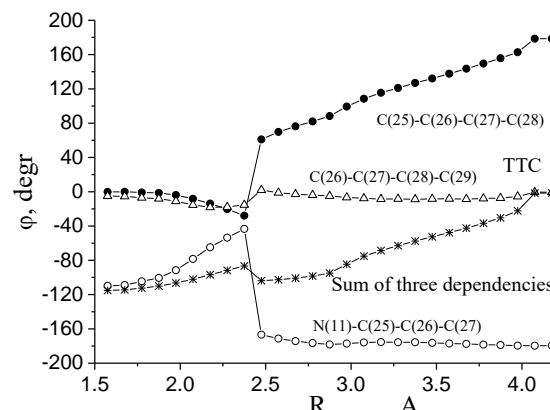
Fig. 1 – The dependence of the values of dihedral angles on the distance $R_{Cspiro\text{-}O}$. Transformation of molecule from spiropyran to merocyanine in the TTC configuration
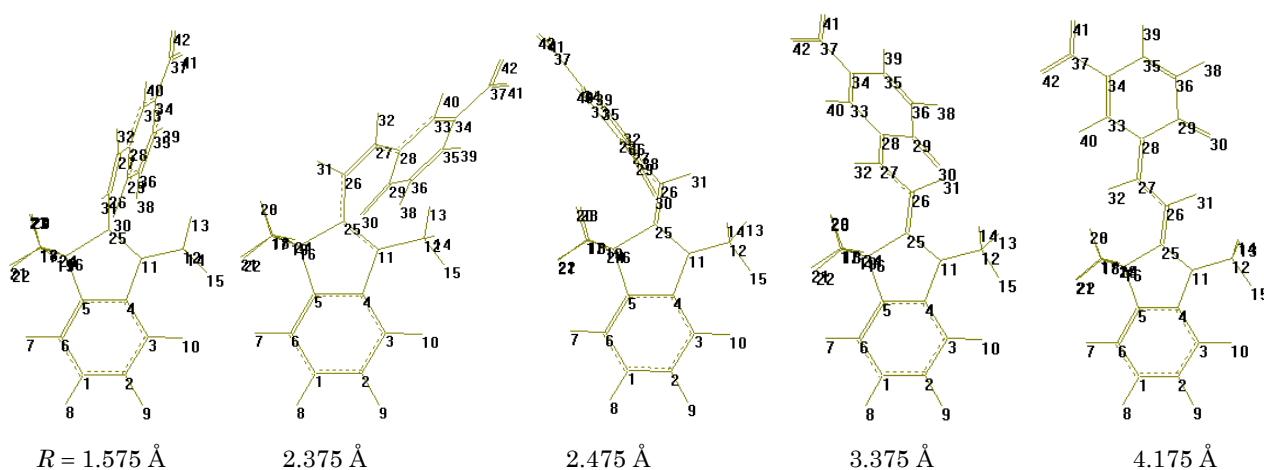
| R = 1.575 Å | 2.375 Å | 2.475 Å | 3.375 Å | 4.175 Å |

Fig. 2 – Change in the geometric structure of the Sp molecule with increasing distance Cspiro-O

line fragment from pyran in the interval $R(C_{spiro}\text{-}O) = 1.575\text{-}2.375$ Å. Further, the interaction with the methyl-amine group prevented such a change in geometry. After a further increase in the $R_{Cspiro\text{-}O}$ distance, the molecule changed its geometry and then naturally turned into the merocyanine form. What really happened?

We decided to study the change in the hybridization of AOs of the spiroatom and the N(11) atom.

To study the change in the hybridization of AOs of the spiroatom, we measured the angle of deviation of the C(25)–C(26) bond from the plane of the pyranic part of the molecule. To do this, we measured the value of the dihedral angle $\beta = \angle(5\text{-}16\text{-}25\text{-}26)$ and the value of the angle between the bonds $\alpha = \angle(16\text{-}25\text{-}26)$. The values of the angle $\angle(4\text{-}11\text{-}25\text{-}26)$ and the angle $\angle(11\text{-}25\text{-}26)$ were measured similarly. In addition, the value of the dihedral angle $\angle(12\text{-}11\text{-}25\text{-}26)$ was measured. Knowing the values of the angles α and β, we find the angle of deviation δ of the C(25)–C(26) bond from the plane:

$$\sin\delta = \sin\alpha \cdot \sin\beta.$$

By measuring the values of these angles depending on the distance $R_{Cspiro\text{-}O}$, we find the dependence of the angle δ on this distance. Thus, we learn the change law of the hybridization of the spiroatom AO. The results of the calculations are shown in Fig. 3.

From this dependence, it follows that the value of the angle δ gradually changes to zero with increasing the distance $R_{Cspiro\text{-}O}$ to 2.9 Å. Therefore, the hybridization of the AO of the spiroatom changes smoothly from sp^3 to sp^2. In the region $R_{Cspiro\text{-}O} = 2.35$ Å, there is a small jump in the found dependence. The maximum value of the studied angle reaches $\approx 40°$, while the value of the angle C(26)–C$_{spiro\text{-}O(30)}$ is 111.595°. Therefore, the C$_{spiro\text{-}O}$ axis deviates from the plane by 71.6°.

To find the nature of the observed jump, and immediately the nature of the phase transition, we separately investigated the dependence of the magnitude of mentioned above dihedral angles on the distance $R_{Cspiro\text{-}O}$. The results of this study are shown in Fig. 4.

As can be seen from this figure, the dependence of the angles between the C$_{Spiro}$–C(26) bond and C(4)–N(11) and C(5)–C(16) bonds resembles the same dependence
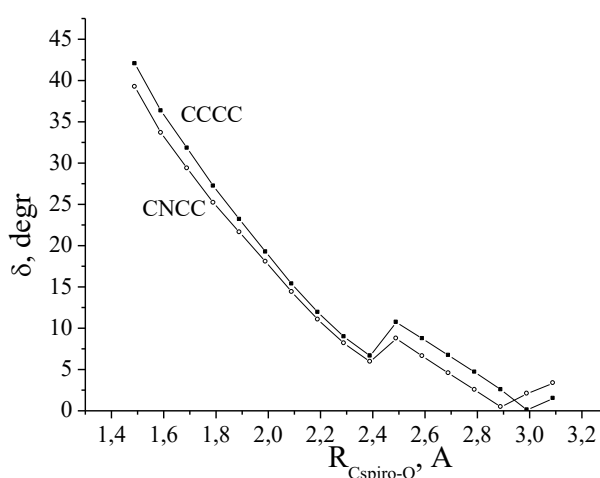

Fig. 3 – The dependence of the angle between the plane and the C$_{Spiro}$–C bond on the distance C$_{Spiro}$–O. The measurement was performed using dihedral angles C(5)–C(16)–C(25)–C(26) and C(4)–N(11)–C(25)–C(26)
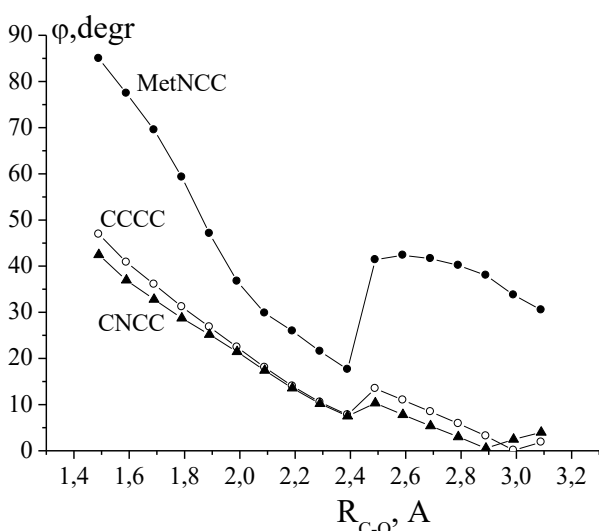

Fig. 4 – Dependence of the value of the dihedral angle between the C$_{Spiro}$–C(26) bond and N–CH$_3$, C(4)–N(11) and C(5)–C(16) bonds of the five-membered ring

for the deflection angle C_{Spiro}–C(26) from the plane of the five-membered cycle. However, it turned out that the value of the dihedral angle between the N–Met (Met = CH₃) and C_{Spiro}–C(26) bonds significantly exceeds the other two dihedral angles and, in addition, there is a sharp change in the hybridization of the nitrogen atom caused by smooth change of hybridization of AO of the C_{Spiro} atom.

While the change in the hybridization of AO of C_{spiro} resembles a phase transition of the II kind, the change in the hybridization of AO of N(11) resembles a phase transition of the I kind. This phase transition causes the rotation of the indoline fragment by almost 6° in the direction of decreasing N–C_{Spiro}–C angle (26). This fact causes a small jump in the change of the angle between the pyran plane and the C_{Spiro}–C bond.

3.2 Potential Surfaces of the Spiropyran Molecule in the Vicinity of the Phase Transition

Since we started the research by looking for the optimal route from merocyanine to spiropyran, the full potential surface was constructed by rotating the phenyl ring around the C(27)–C(28) bond. This way of finding a potential surface is natural for merocyanine. In this case, the angle $\theta = 0°$ corresponds to the TTT configuration, and the angle 180° corresponds to the TTC configuration.

To do this, we have fixated the distance $C_{Spiro-O}$ before the phase transition ($R = 1.575$ Å) and after it ($R = 2.575$ Å). The results of the study are shown in Fig. 5. As follows from this figure, for the equilibrium geometry, the minimum energy is characterized by the sp configuration with the dihedral angle $\theta = \angle(32\text{-}27\text{-}28\text{-}29) = 180°$. As this angle increases, the oxygen atom approaches the methyl group C(12)H₃, as a result of that there is a repulsion and the energy of the system increases by 8 eV. If we reduce the value of the dihedral angle, then the oxygen atom will approach the methyl group C(17)H₃; this will also cause an increase in energy (~ 3.5 eV) at an angle of 130°.

Similar studies after the phase transition have shown that the oxygen atom can cross the methyl group C(17)H₃ too strongly (increase in energy ~ 30 eV at an angle of 120°), while the distance between the oxygen atom and the methyl group C(12)H₃ always remains large enough for the interaction between them to be insignificant.

For angles of rotation that go beyond the two observed energy maxima, we have a weak dependence of the system energy on the angle of rotation, because it is due to changes in the interaction between $2pz$ AOs of neighboring atoms C(27) and C(28).

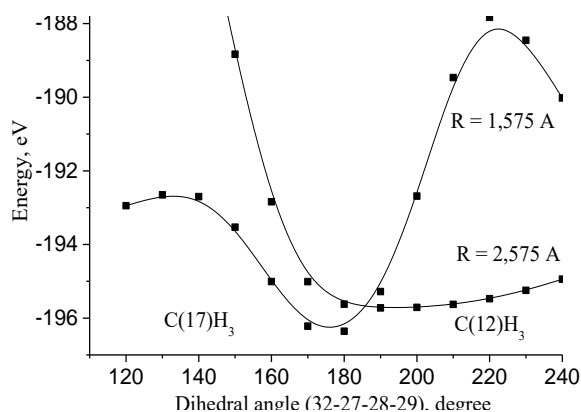**Fig. 5** – The dependence of the spiropyran ground state energy on the value of $\theta = \angle(32\text{-}27\text{-}28\text{-}29)$ for the equilibrium geometry ($R = 1.575$ Å) and after the phase transition ($R = 2.575$ Å)

3.3 Potential Surfaces of the Ground and Excited States of Spiropyran (Before the Phase Transition)

As follows from the appearance of the potential surface of the ground state (Fig. 6), the structure of the spiropyran molecule is strictly fixed and is determined by a deep energy well in the vicinity of the dihidral angle $\theta = 180°$.
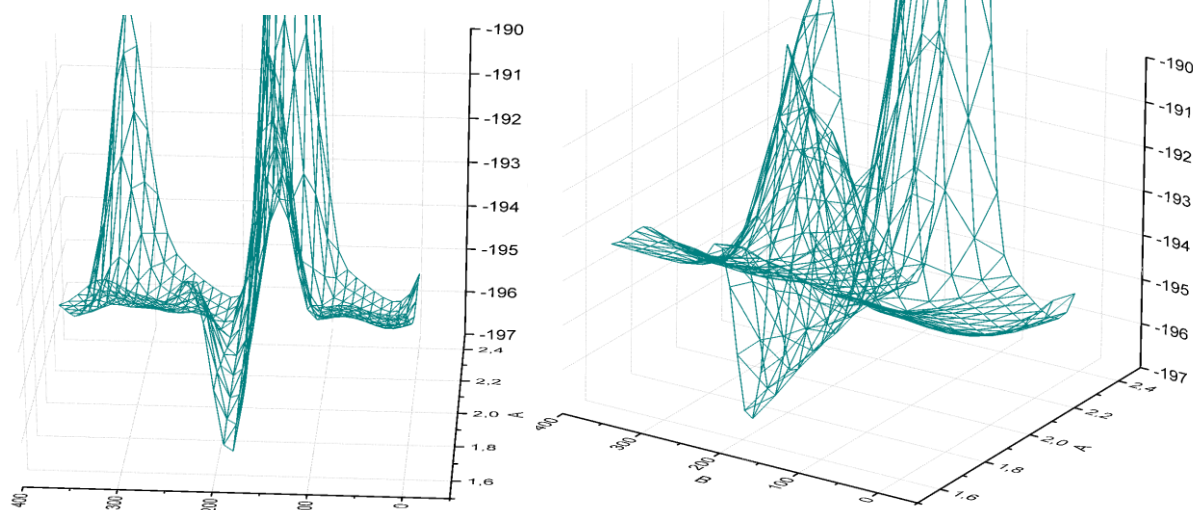
Fig. 6 – Potential surface of the ground state of the spiropyran molecule in two projections

As the distance of C$_{Spiro}$-O increases, the energy of the electronic system increases due to the change from sp^3-hybridization to sp^2-hybridization, as shown in [6]. This creates a barrier that stabilizes the molecule.

The repulsion between the oxygen atom and the two methyl groups causes two barriers. The potential surface outside these barriers turns out to be dissociative. In principle, this will not allow creating a molecule with such a configuration.

Upon excitation of the molecule to the S_1 state, it was found that the potential surface of this state at the excitation point (180°) has a dissociative character.

The energy gradient with the $R_{Cspiro-O}$ distance is so large that other relaxation processes (radiative $S_1 \rightarrow S_0$ transition, internal conversion or interconversion) will not be able to proceed in this case.

3.4 Potential Surfaces of the Ground and Excited States of Merocyanine (After the Phase Transition)

The structure of potential surfaces from the phase transition to the steady state of the merocyanine molecule is shown in Fig. 7. The curve of the steady state is shown in the foreground. The scanning of a dihedral angle from 0 to 200° is given from left to right.

The calculation of the energy surface for the S_0 state concerns the optimized geometry, while for the excited states a separate optimization was not performed, but the geometric structure of the ground state was used.

The shape of the energy surfaces of the ground and excited states of merocyanine is quite clear. Consider the energy surfaces of the S_0 and S_1 states.
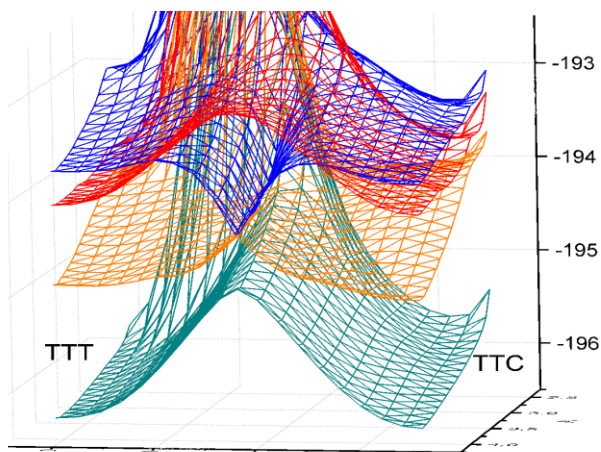
Fig. 7 – The structure of Mer energy surfaces for $R_{Cspiro-O}$ from 4.0 to 2.5 Å and for the dihedral angle $\theta = \angle(32\text{-}27\text{-}28\text{-}29)$ from 0 to 200°: S_0 – darkcyan, S_1 – blue, T_1 – orange, T_2 – red. Scanning of the angle is given from left to right

The upper occupied orbital of the merocyanine molecule is MO No 61. Accordingly, the lower free orbital is MO No 62. As follows from the structure of these MOs, the fragments of the molecule rotate around the C(27)–C(28) bond and it is a binding bond for the ground state (TTT) and a loosening one for the excited state. Therefore, the rotation of the phenyl fragment around this bond by 180° will gradually increase the energy from the lower (S_0) to the upper

(S_1) level and convert the TTT state to the TTS state. A similar picture will be for the ground state of the TTS. In this case, the rotation of the phenyl fragment will lead to the formation of Mer-TTT. The two formed energy surfaces are intersected near the angle $\theta = 90°$.

Note the fact that the merocyanine molecule is characterized by very low symmetry C$_1$. Therefore, all wave functions that describe the energy structure of the molecule have the same symmetry. And in this case, there is a rule of non-intersection of energy states due to the interaction between them [2, 13].
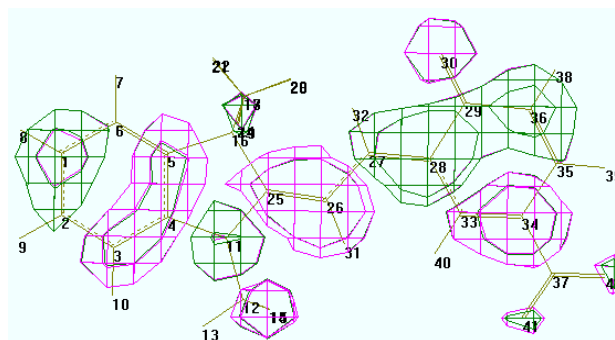
MO No 61
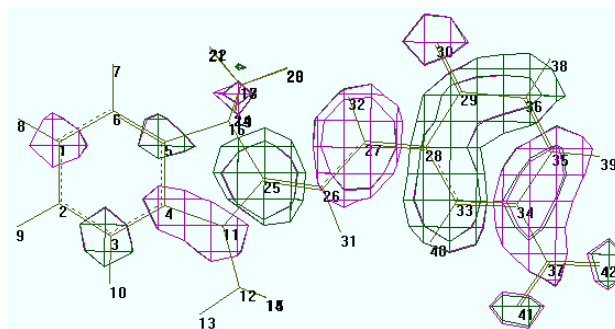
MO No 62

If the wave function of the ground state Mer-TTT is denoted by Ψ_1, and Mer-TTS – by Ψ_2, and the matrix elements are denoted, respectively, by H_{11}, H_{22}, and H_{12}, where

$$H_{ii} = \int \Psi_i \hat{H} \Psi_i dV, \quad H_{ij} = \int \Psi_i \hat{H} \Psi_j dV, \quad i, j = 1, 2,$$

then the energy of states will be described by the formula:

$$E_{1,2} = \frac{H_{11} + H_{22} \pm \sqrt{\left(H_{11} - H_{22}\right)^2 + 4H_{12}^2}}{2}.$$

To simplify the notation in the last formula, the overlap integral was set

$$S = \int \Psi_i \Psi_j dV = \delta_{ij}.$$

If the energy difference between two states is large, then the energies of the two states are found by formulas

$$E_1 = H_{11} + \frac{2H_{12}^2}{H_{11} - H_{22}}, \quad E_2 = H_{22} - \frac{2H_{12}^2}{H_{11} - H_{22}}.$$

Thus, the energy of the upper state will increase slightly, and the energy of the lower one will decrease.

If at some distance r (point of intersection) it turns out that $H_{11} = H_{22} = H_r$ and the matrix element of the interaction of states $H_{12} = H_0 \neq 0$, then

$$E_{1,2} = H_r \pm H_0.$$

It should be noted that the condition $H_0 \neq 0$ is satisfied only if the symmetry of the interacting states is the same. As we saw above, in our case this condition is satisfied.

Now we will carefully consider the form of potential surfaces S_0 and S_1 of merocyanine states. It is clearly seen that there was a splitting of energy levels by $2H_0$ due to the interaction between the states in the region of intersection of these surfaces at $\theta \approx 90°$.

Usually, the energy structure of molecules is constructed in such a way that the lower triplet state lies between the S_0 and S_1 states. The same is observed in our case. In the region of state intersection, the distance between T_1 and S_1 states is very small, which ensures efficient singlet-triplet conversion. However, the distance between S_0 and S_1 states is also small in this case. Therefore, the internal conversion channel $S_1 \rightarrow S_0$ will prevail, which ensures the flow of the cis $\leftrightarrow$ trans (TTT $\leftrightarrow$ TTS) isomerization reaction. The result will not change if a singlet-triplet conversion takes place.

As the geometric configuration approaches the states of TTT or TTS, the energy of the ground state decreases significantly due to the increase in the magnitude of the AO overlap of C(27) and C(28) atoms. For the S_1 state, this decrease in energy is significantly less, because in this case one electron is at MO No 61 and another one at MO No 62. In this case, an increase in the overlap of MO No 61 reduces the energy, and an increase in the overlap of MO No 62 increases it. As a result, the energy decrease in the S_1 state for Mer-TTT is 0.13 eV, and for Mer-TTS it is 0.21 eV. However, the presence of these potential wells determines the photochemical activity of the merocyanine molecule. Different values of potential wells in the S_1 state lead to the predominance of TTT $\rightarrow$ TTS isomerization. This is important because the photochemical transformation Mer $\rightarrow$ Sp occurs from the TTS state.

The surface of the T_2 state intersects the surface of the S_1 state at its maximum energy. In this case, the interconversion rate can be very high ($\sim 10^{11} \div 10^{13}$ s^{-1}). Thus, there are several channels of relaxation of electronic excitation of Mer from TTT or TTS configurations after excitation. The channel TTT$\leftrightarrow$TTS-isomerization through the intermediate state ($\theta = 90°$) turns on as well as $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ interconversion in addition to the radiative and nonradiative (internal conversion) $S_1 \rightarrow S_0$ transition without changing the geometry of the molecule. Also, an excitation relaxation channel has appeared, which reduces the $R_{\text{Cspiro-O}}$ distance.

Calculations show that in the S_1 state the energy increases by a height of 0.39 eV in the TTC configuration before the phase transition as the $R_{\text{Cspiro-O}}$ distance decreases. If $S_1 \rightarrow T_2$-interconversion occurs, then the energy increases by 0.41 eV in this state according to the calculations.

We noted above that the geometry was optimized only for the ground state of the molecule at different $R_{\text{Cspiro-O}}$ distances. Such optimization was not performed for excited states. Fig. 1 shows that not only the angle θ, but also other dihedral angles located between C(25) and C(28) are changed at optimization of the geometry of the molecule. Experience shows that in this case, in the presence of geometry optimization in excited states, we would obtain a decrease in energy of ~ 0.5 eV. In this case, it is sufficient that the excited Mer-TTC molecule could relax to a phase transition.

For the photochemical transformation Mer $\rightarrow$ Sp to occur, the phase transition must stimulate a nonradiative transition to the S_0 state of the Sp molecule. This will be facilitated by the fact that the value of the angle θ does not change.

It should be noted that the phase transition will contribute to the singlet-triplet conversion in the Sp $\rightarrow$ Mer transition from the S_1-state of Sp. In this case, there are significantly fewer relaxation channels for the electronic excitation of the Sp molecule compared to the discussed above relaxation of excitation of the Mer molecule from the S_1 state. Therefore, it should be expected that the quantum yield of the Sp $\rightarrow$ Mer transformation will be greater than the quantum yield of the Mer $\rightarrow$Sp transformation, which is consistent with the assumption in the work [14].

4. CONCLUSIONS

Based on the study of the processes of relaxation of electronic excitation in the spiropyran-merocyanine system, the following results were obtained.

1. It is shown that the hybridization of the atomic orbitals of the N(11) atom in the spiropyran molecule occupies an intermediate value between sp^3 and sp^2 hybridization due to the influence of the structure of the five-membered cycle of the pyran fragment. Hybridization becomes sp^2 upon transition to the merocyanine molecule.

2. The presence of a five-membered ring in the pyran fragment, as well as the presence of a nitrogen atom in it, led to the fact that the pyran and indoline fragments were not on the same axis. This, in turn, led to the fact that the oxygen atom O(30) can occupy only one position in the spiropyran molecule.

3. The merocyanine molecule turned out to be flat, and all AOs became sp^2-hybridized.

4. When the distance of $R_{\text{Cspiro-O}}$ increased to 2.375 Å, a phase transition occurred due to a slow change in the hybridization of the AO of the spiroatom and an instantaneous change in the hybridization of the AO of the N(11) atom (phase transition of the first kind). As a result, the structure of the molecule and the magnitude of all dihedral angles between the C(28) and C(28) atoms changed significantly.

5. Stabilization of the structure of the spiropyran molecule is caused by repulsion between the O(30) atom and the two methyl groups C(12)H$_3$ and C(17)H$_3$. After the phase transition, the effect of the C(12)H$_3$ group disappears, and the effect of the C(17)H$_3$ group increases. The potential surface of the Sp molecule turned out to be dissociative outside the phase transition.

6. The S_1 state of the excited Sp molecule turned out to be dissociative with a large energy gradient with the $R_{\text{Cspiro-O}}$ distance.

7. The structure of the energy surfaces of the Mer molecule in the dihedral angle $\theta - R_{Cspiro-O}$ distance coordinates resembles the structure characteristic for cis-trans isomerization of simple molecules such as stilbene. In addition, it is shown that the potential surface of the T_2 state intersects with the potential surface of the S_1 state, that provides a high rate of interconversion under conditions of low symmetry of molecules.

8. The energy surface of the S_1 state for TTT and TTS configurations of the Mer molecule has a minimum with a depth of 0.13 eV and 0.21 eV, respectively. The presence of this minimum in the structure of the potential surface provides reduction of the distance $R_{Cspiro-O}$.

9. The final reason for the Sp → Mer photoconversion is related to the conversion of singlet excitation of the Sp molecule into the ground state of the Mer molecule. The reason for the Mer → Sp photoconversion is related to the conversion of singlet and triplet excitation of the Mer molecule into the ground state of the Sp molecule. Both processes occur in the phase transition region.

REFERENCES

1. V.A. Barachevskiy, *Optika i spektroskopiya* **124** No 3, 371 (2018) [In Russian].
2. P.O. Kondratenko, *Fotokhimichna diya svitla* (Kyiv: Vydavnycho-polihrafichnyy tsentr „Kyivskyy universytet": 2005) [In Ukrainian].
3. V.I. Minkin, *Uspekhi khimii* **82** No 1, 1 (2013) [In Russian].
4. Renuka Ganesan, F. Remacle, *Theor. Chem. Acc.* **131**, 1255 (2012).
5. Rafal Klajn, *Chem. Soc. Rev.* **43** No 1, 148 (2014).
6. O.A. Kovalenko, P.O. Kondratenko, Yu.M. Lopatkin, *Int. J. Photoenergy* 161248 (2015).
7. Isabel Go´mez, Mar Reguero, Michael A. Robb, *J. Phys. Chem.* A **110**, 3986 (2006).
8. Luuk Kortekaas, Wesley R. Browne, *Chem. Soc. Rev.* 48, 3406 (2019).
9. R.G. Parr, Yang Weitao, *Density Functional Theory of Atoms and Molecules* (Oxford: Oxford University Press: 1989).
10. M.V. Malyshkina, A.S. Novikov, *Compounds* **1**, 134 (2021).
11. W. Thiel, A.A. Voityuk, *Intern. J. Quant. Chem.* **44**, 807 (1992).
12. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Amer. Chem. Soc.* **107** No 13, 3902 (1985).
13. Maurizio Persico, Giovanni Granucci, *Photochemistry: A Modern Theoretical Perspective* (Springer: 2018).
14. Mounir Maafi, *Molecules* **13**, 2260 (2008).

Релаксація електронного збудження молекули на шляху спіропіран ↔ мероціанін

П.О. Кондратенко[1], Ю.М. Лопаткін[2], Т.М. Сакун[1]

[1] *Аерокосмічний інститут, Національний авіаційний університет, проспект Любомира Гузара, 1, 03058 Київ, Україна*
[2] *Сумський державний університет, вул. Римського-Корсакова, 2, 40007 Суми, Україна*

В роботі проведені квантовохімічні дослідження геометричної та енергетичної структури молекул спіропіран та мероціаніну, а також проміжних станів, які відповідають оптимізованій геометрії молекул при різних відстанях між спіроатомом та атомом кисню. Показано, що при збільшенні відстані $R_{Cspiro-O}$ до 2,375 Å відбувається фазовий перехід в структурі молекули. Показано, що геометрична структура молекули спіропірану унікальна. При збільшення відстані $R_{Cspiro-O}$ енергія електронної системи молекули підвищується. При цьому плавно змінюється гібридизація АО спіроатома. Збудження молекули спіропірану в S_1-стан, який є дисоціативним, спричинює перетворення спіропірану в мероціанін. Вивчена енергетична структура молекули мероціаніну і показано, що в цьому випадку релаксація електронного збудження включає ТТТ-ТТС ізомеризацію, а також інтерконверсію в T_1 і T_2 стани. Крім того, з'явилась можливість зменшення відстані $R_{Cspiro-O}$ до фазового переходу. Збурення, викликане фазовим переходом, зумовлює конверсію збудженої молекули до основного стану, в результаті чого виникає фотоперетворення спіропірану в мероціанін і навпаки. Описаний механізм вимагає, щоб квантовий вихід фотоперетворення спіропірану в мероціанін перевищував квантовий вихід зворотного переходу.

Ключові слова: Спіропіран, Мероціанін, Релаксація електронного збудження, Фазовий перехід, Механізми фотоперетворення спіропірану в мероціанін і навпаки.