

Energy Structure and Stability of Merocyanine Isomers as Memory Elements or Switches

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Creation of a stable and reliable molecular device is an important task of nanotechnology. Photochromic molecules are the most promising candidates for such a purpose. One of the most prospective classes of photochromic compounds is spiropyran and its open form merocyanine. To use the spiropyran-merocyanine system it is essential to know properties of these molecules. The transformation between spiropyran and merocyanine molecules can occur in different ways. Therefore, it is important to have a complete picture of the merocyanine structures and transition routes between them. Thus, the investigation of geometric structure of the merocyanine molecule was carried out. It shows that the merocyanine molecule can be in one of the eight possible isomers taking into account the rotation around the three central bonds C(25)-C(26), C(26)-C(27), C(27)-C(28). TTT, TTC, CTT and CTC isomers have a flat geometric structure and similar absorption spectra (from 490 nm to 510 nm), thus they cannot be separated in experimental studies. All these isomers exhibit dark stability, since the energy barrier for the transition between them is more than 1 eV. The other four isomers TCT, TCC, CCT and CCC have a spiral structure, at which each of these isomers can have right-handed or left-handed structure. Transformations between neighboring isomers have been studied. The results have shown that spiral structure isomers are thermally unstable, and they turn into one of the flat isomers rapidly. That is why their contribution to the absorption spectrum of the merocyanine molecule is absent. At the same time, all flat structures are characterized by identical conductivity properties along the π -electron system and the same length of the long axis of the molecule. The obtained results are important in terms of using the spiropyran-merocyanine system as a memory element or switch in future computer systems.

Keywords: Merocyanine, Spiropyran, Molecular memory cells, Merocyanine isomers.

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1. INTRODUCTION

Nowadays, the development of multifunctional materials that can be used as sensors [1, 2], in memory elements [3], logic gates [4], intelligent and high-performance optoelectronic nanoblocks, etc. is an important task of nanotechnology. The combination of nanomaterials with photochromic molecules is of particular interest of scientists. Such combination allows to achieve reversible changes not only in the geometric structure, but also in electronic properties and nanoscale mechanics caused by the action of light. Due to the sensitivity of photochromic molecules, the light can be used as an external source of remote control of devices. The use of light as a stimulus is extremely attractive for at least two reasons: it can be transmitted over long distances with the "speed of light" and it is a source of unlimited energy. Changes at the level of one molecule, such as geometry (conformation), electronic structure, dipole moment can lead to various properties at the material level, including the form [5], conductivity [6], aggregation behavior [7], fluorescence [8], magnetism [9], etc. Thus, such photoinduced changes at the molecular level can be used to control the functions and properties of nanostructured materials.

One of the most prospective classes of photochromic compounds is spiropyran and its open form merocyanine. The action of ultraviolet radiation on colorless spiropyran (SP) leads to the breaking of the spiro-C-O bond and the subsequent rehybridization of the carbon atom from sp^3 to sp^2 . The resulting planar structure of the thus formed isomer of merocyanine (MS) provides a strong

conjugation of the π -systems of the two parts of the molecule and absorption in the visible region of the spectrum [10].

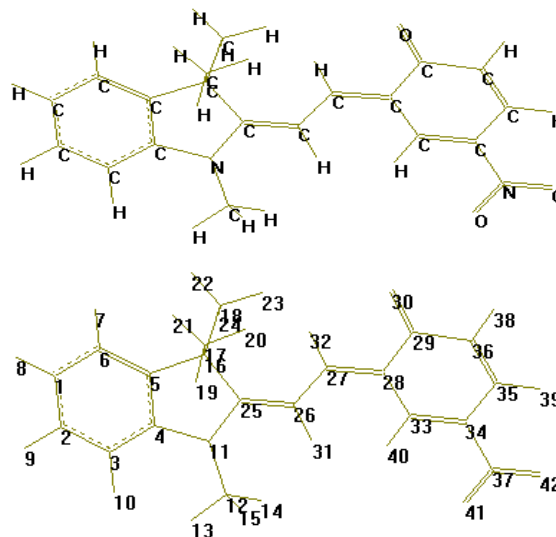


Fig. 1 – General structure of the MC molecule

The study of the properties of SP and MC molecules and the possibility of controlled transition between them is important in terms of creating electronic switches based on molecular structures. These switches have the prospect of being used in the development of new-generation computers [11-13].

The transformation between SP and MC molecules can occur in different ways [14-18]. Therefore, it is important to have a complete picture of the MC structures and transition routes between them.

2. OBJECTS AND METHODS

The standard structure of MC is presented in Fig. 1. In this work, quantum-chemical methods of investigation were used due to HyperChem-8 and MOPAC-12 software packages. The MNDO/d [19] and AM1 [20] methods were used to find the geometric structure and the energy structure of the molecules in the ground and excited states.

From Fig. 1 it can be seen that N(11)-C(25)-C(26)-C(27) fragment has a trans configuration. C(25)-C(26)-C(27)-C(28) and C(26)-C(27)-C(28)-C(29) fragments have the same configuration. These structures are called Mer-TTT, Mer-TTC, Mer-TCT, Mer-TCC, Mer-CTT, Mer-CTC,

Mer-CCT, Mer-CCC (8 structures at all); they can be obtained by changing aforesaid dihedral angles from 180° to 0°.

The aim of this work was not to find the absolute values of the coordinates of atoms in molecules, but to expose the process of transition from one state to another. Thus, semi-empirical methods were used. They allow to achieve the goal with sufficient accuracy. Some of MC isomers have such an unusual structure that it is impossible to establish it within the framework of semiempirical methods (MNDO, AM1). In view of this, methods of molecular dynamics were used with zero-order approximation methods. Only after that, the structure of the molecule was optimized using semiempirical methods. The basic calculations were carried out using the AM1 method, taking into account the configurational interaction between 10 occupied and 10 free molecular orbitals.

Table 1 – Energy characteristics of the MC isomers

Molecule	Transition	λ , nm	Oscillator strength
Mer-TTT (π -system has a flat structure)	S0 \rightarrow T1 (61-62)	975.6	0
	S0 \rightarrow T2 (60-62)	580.5	0
	S0 \rightarrow S1 (61-62)	493.5	1.0073
	Binding energy	- 4525.1842 kcal/mol - 196.231 eV	
Mer-TTC (π -system has a flat structure)	S0 \rightarrow T1 (61-62)	1020.6	0
	S0 \rightarrow T2 (60-62)	584.8	0
	S0 \rightarrow S1 (61-62)	504.4	1.0170
	Binding energy	- 4523.6136 kcal/mol - 196.163 eV	
Mer-TCT (π -system has a spiral structure)	S0 \rightarrow T1 (61-62, 60-62)	877.6	0
	S0 \rightarrow T2 (60-62, 61-63)	616.8	0
	S0 \rightarrow S1 (61-62)	493.1	0.5659
	Binding energy	- 4506.4946 kcal/mol - 195.421 eV	
Mer-TCC (π -system has a spiral structure)	S0 \rightarrow T1 (61-62)	879.8	0
	S0 \rightarrow T2 (60-62)	600.2	0
	S0 \rightarrow S1 (61-62)	504.3	0.3891
	Binding energy	- 4502.3907 kcal/mol - 195.243 eV	
Mer-CTT (π -system has a flat structure)	S0 \rightarrow T1 (61-62)	975.5	0
	S0 \rightarrow T2 (60-62)	580.4	0
	S0 \rightarrow S1 (61-62)	495.4	0.9783
	Binding energy	- 4526.2179 kcal/mol - 196.276 eV	
Mer-CTC (π -system has a flat structure)	S0 \rightarrow T1 (61-62)	1000.2	0
	S0 \rightarrow T2 (60-62)	582.9	0
	S0 \rightarrow S1 (61-62)	492.9	1.0003
	Binding energy	- 4525.1190 kcal/mol - 196.228 eV	
Mer-CCT (π -system has a spiral structure)	S0 \rightarrow T1 (61-62)	943.0	0
	S0 \rightarrow T2 (60-62)	586.6	0
	S0 \rightarrow S1 (61-62)	488.2	0.5810
	Binding energy	- 4515.7780 kcal/mol - 195.823 eV	
Mer-CCC (π -system has a spiral structure)	S0 \rightarrow T1 (61-62)	1023.9	0
	S0 \rightarrow T2 (60-62)	603.2	0
	S0 \rightarrow S1 (61-62)	539.3	0.3459
	Binding energy	- 4510.0340 kcal/mol - 195.574 eV	

3. RESULTS AND DISCUSSION

3.1 Energy Structure and Absorption Spectra of the Merocyanine Isomers

From Table 1 it can be seen that 4 isomers have a flat structure, other 4 isomers have a spiral structure. It should be pointed out that the spiral structure of the isomers makes them optically active. Moreover, each of these four isomers should have two types of spiral structures – right- and left-handed plane of light polarization.

The ground state of the molecule is characterized by the binding energy of atoms due to the overlapping of the electron shells. It is clear that different binding energies will correspond to different MC isomers. The results of the calculation of binding energy in the ground and excited states are shown in Fig. 2. From Fig. 2, it follows that plane isomers of MC are energetically favorable. At that, CTT structure is characterized by minimal energy. Energies of other flat isomers do not significantly differ from the CTT isomer. In particular, the reason for the difference in the ground-state energy of TTT and TTC isomers is the presence of interaction between the O (30) and H (31) atoms in the TTC structure. Spiral TCT and TCC structures substantially yield to flat structures, so it can be assumed that the contribution of these structures to the SP-MC transformation is insignificant.

In the last pair of spiral isomers (CCT and CCC), at-

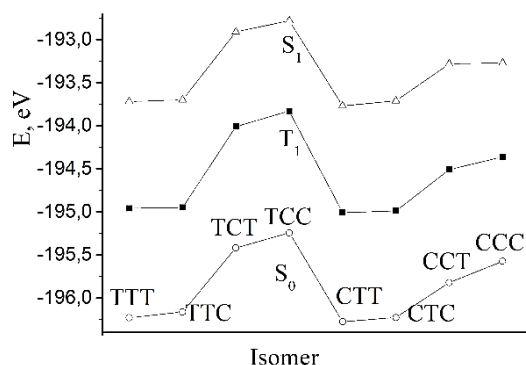


Fig. 2 – Energy structure of the MC isomers in the ground and excited states

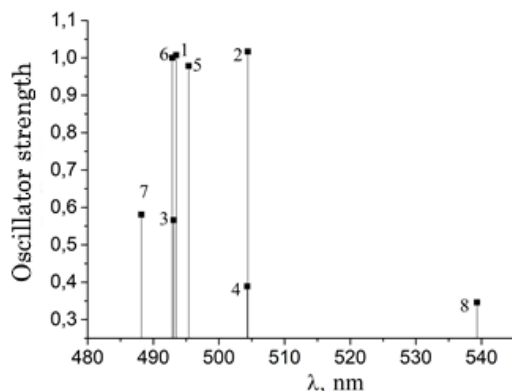


Fig. 3 – Position and oscillator strength of the long-wave band in the absorption spectrum of MC isomers (1 corresponds to Mer-TTT, 2 – Mer-TTC, 3 – Mer-TCT, 4 – Mer-TCC, 5 – Mer-CTT, 6 – Mer-CTC, 7 – Mer-CCT, 8 – Mer-CCC)

oms bind to a molecule somewhat more than the pair of TCT and TCC isomers. However, it is logical to assume that the contribution of these isomers to the general set of MC isomers is insignificant.

From Fig. 3, it can be seen that with the absence of spiral isomers of MC, the absorption band of MC will not practically feel the presence of all four isomers. Only the TTC isomer should have a band shifted to the long-wave side approximately by 10 nm. Therefore, it will expand the absorption band of MC.

3.2 Stability of the Merocyanine Isomers

Transformations between neighboring isomers will be considered below. They can be obtained by rotating a fragment of a molecule around the corresponding bond. TTT isomer was selected as the initial state and then the moiety of the molecule will be rotated around the C(27)-C(28) axis. It should be remembered that the TTT isomer has an optimized geometric structure, while the TTC isomer that will be formed in this experiment will not have an optimized geometric structure. In fact, as follows from Table 1, the binding energy in the TTC isomer is higher than in TTT by about 0.07 eV, while from Fig. 4 it can be seen that the energy difference in these states reaches 0.22 eV. Therefore, only the value of the barrier for TTT isomer can be trusted. For TTC isomer it can be calculated as $1.32 - 0.07 = 1.25$ eV.

The calculation was carried out by points taking into account the configuration interaction. Without such accounting, it is impossible to obtain reliable results.

The values of the barriers between these structures are high enough to stabilize both structures after SP-MC transformation.

Now, moieties of the TTT isomer will be rotated around C(25)-C(26) axis. In this case, the CTT isomer with an unoptimized geometry is formed. From Table 1 it follows that the energy level of the ground state of the CTT isomer is lower by 0.045 eV than the level of the TTT isomer. However, during the rotation of moieties of the TTT isomer around the C(25)-C(26) axis, steric hindrances appears due to the interaction between the H (32) atom and the methyl group. This significantly ($-195.872 + 196.276 = 0.404$ eV) raises the position of energy level (Fig. 5).

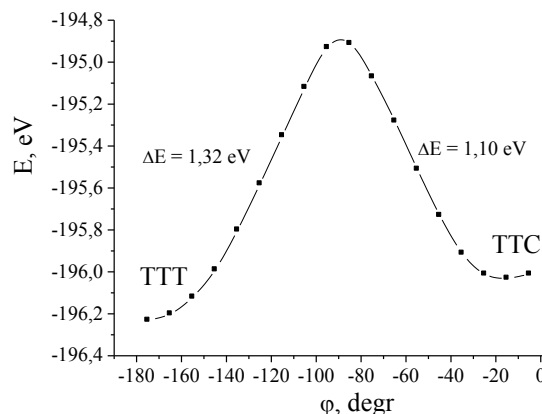


Fig. 4 – TTT → TTC transformation

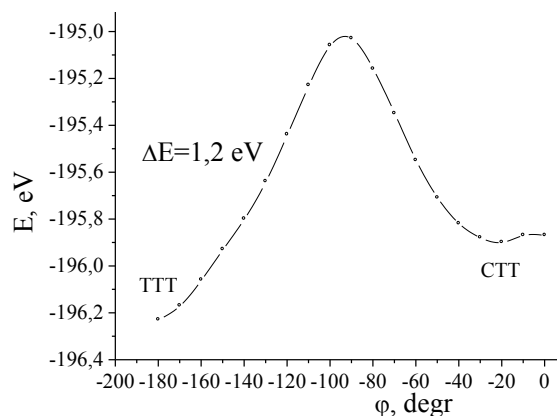


Fig. 5 – TTT → CTT transformation

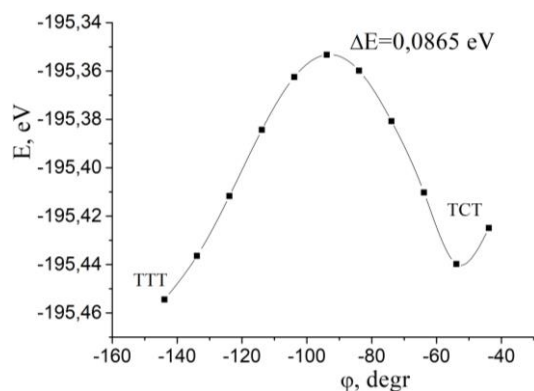


Fig. 6 – TCT → TTT transformation

The barrier height for the TTT → CTT transition is somewhat lower than for the TTT → TTC transition, but in this case, it is also insufficient to stabilize the isomers.

TTT → TCT transition will be considered.

It should be noted that the proposed above method for studying this transition by rotating molecule's moiety around the C(26)-C(27) axis does not allow to obtain reliable results. The reason is not only the presence of steric hindrances and different configurations of isomers, but also the different hybridization of the atomic orbitals of C_{spiro} . In view of this, the investigation of the TCT isomer was carried out at small rotational angles to find the value of the barrier for the TCT → TTT transition (Fig. 6). It turned out that the TCT isomer is unstable, since the value of the barrier is only 0.0865 eV.

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The next, CCT isomer, should be studied through the CCT → CTT transformation. It is possible by the rotation around C(26)-C(27) axis. In this case, only the CCT isomer has an optimal structure. Therefore, the result of this study characterizes only the value of the barrier on the way to CTT. In the CCT, atomic orbitals of C_{spiro} have a sp^2 hybridization as in flat isomers of MC. Therefore, the value of the barrier is more than 2 times higher than in the previous isomer with a spiral structure (Fig. 7).

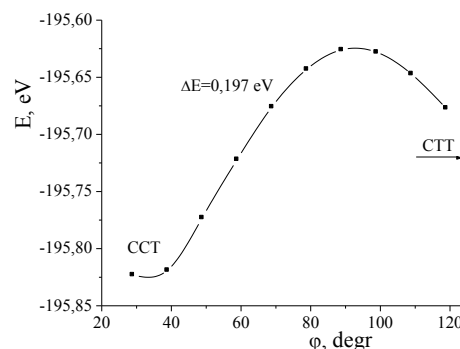


Fig. 7 – CCT → CTT transformation

4. CONCLUSIONS

In this work, it was shown that MC molecules are able to form 8 isomers. TTT, TTC, CTT, CTC isomers have a flat geometric and π -electronic structure. TCT, TCC, CCT and CCC isomers have a spiral (right-handed and left-handed for each isomer) structure. The height of the barrier on the path from one flat isomer to another flat isomer is more than 1 eV (between TTT and TTC is 1.32 eV, between TTT and CTT is 1.2 eV), and therefore these isomers are stable at room temperature. The barriers on the way from the isomer with a spiral structure to the corresponding isomer with a planar structure are: between TCT and TTT is 0.087 eV, between CCT and CTT is 0.2 eV, so that the isomers with a spiral structure reveal dark instability. The absorption spectra of four planar MC isomers are in the range from 490 nm to 510 nm and cannot be separated in experimental studies. The contribution of spiral isomers to the absorption spectrum of MC is absent due to their instability. All stable isomers have long axes of the same length. Consequently, regardless of the type of flat isomer, MC can be used to create the elemental base of future computers.

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Енергетична структура та стабільність ізомерів мероціаніну як елементів пам'яті або перемикачів

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Створення стабільних та надійних молекулярних пристроїв є важливим завданням нанотехнологій. Фотохромні молекули є найбільш перспективними кандидатами для такого завдання. Одним з найбільш перспективних класів фотохромних сполук є спіропіран та його відкрита форма – мероціанін. Для практичного застосування системи спіропіран-мероціанін важливо знати властивості цих молекул. Перетворення молекул спіропірана в мероціанін може відбуватися різними способами. Тому важливо мати повне уявлення про мероціанінові структури та шляхи переходу між ними. Таким чином, в роботі проведені дослідження геометричної структури молекули мероціаніну, які показали, що вона може перебувати у формі одного з восьми можливих ізомерів, які утворюються шляхом обертання навколо трьох центральних зв'язків: C(25)-C(26), C(26)-C(27), C(27)-C(28). Ізомери ТТТ, ТТС, СТТ та СТС мають плоску геометричну структуру та схожі спектри поглинання (від 490 нм до 510 нм), тому їх важко розрізнити експериментально. Усі ці ізомери проявляють стабільність при темних умовах, оскільки енергетичний бар'єр для переходу між ними становить понад 1 еВ. Інші чотири ізомери ТСТ, ТСС, ССТ і ССС мають спіральну структуру, і кожен з цих ізомерів може мати правообертальну або лівообертальну структуру. У роботі було досліджено трансформації між сусідніми ізомерами. Результати показали, що ізомери спіральної структури термічно нестабільні і вони швидко перетворюються на один із плоских ізомерів. Через це їх внесок у спектр поглинання молекули мероціаніну відсутній. При цьому всі плоскі структури характеризуються однаковими властивостями провідності уздовж π -електронної системи та однаковою довжиною довгої осі молекули. Отримані результати є важливими з точки зору використання системи спіропіран-мероціанін як елемента пам'яті або перемикача в комп'ютерних системах майбутнього.

Ключові слова: Мероціанін, Спіропіран, Молекулярні комірки пам'яті, Ізомери мероціаніна.