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## QUANTUM CHEMICAL STUDYING THE TRIMETHINE CYANINE DYE STRUCTURE AND RELAXATION DYNAMICS

Quantum-chemical studying polymethine dyes molecular structure and investigation of the relaxation processes of excitation have been carried out. Particularly, in the highly excited triplet state the dissociative surface exists, which corresponds to  $\sigma \rightarrow \sigma^*$ -excitation of the molecule; relaxation of excitations in the framework of this surface leads to dissociation of the molecule by lengthening the C-C bond of the molecule at the central carbon atom

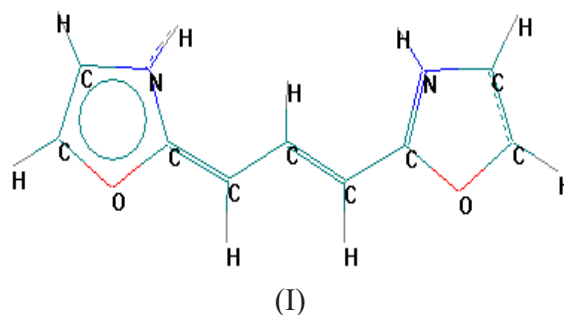
### 1. Introduction

Studying polymethine dyes is of a great importance as from fundamental pointview as applied one. Really, they have wide opportunities for application (in dye lasers, in the processes of sensitization of the sensitivity of the silver halide materials, in biology and medicine as complexing agents and fluorescent labels for dyeing etc) due to their unique properties, among which stands out the photo sustainability, intensive fluorescence and absorption in the visible or infrared range of the spectrum, depending on the structure of the dye [1-3]. Moreover, it is of a great actuality development of the new types of polymethine dyes for the needs of the photophysical, chemical and photobiological application.

It is known [4-6], that the molecules of all dyes, without exception, excited by the light of the sufficiently high energy quanta, exhibit instability, as a result tissue lose their color and saturation under the influence of solar irradiation. This work is devoted to quantum-chemical studying polymethine dyes and further investigation of the relaxation processes of excitation in the polymethine dyes.

### 2. Object of study and research methodology

In this work it is investigated one of the representatives of polymethine dyes – dioksazoltrime-tinsianin cation (I):



In the electrically neutral state, this molecule has one unpaired electron which makes it unstable. At the same time, the cationic form of the molecule exhibits stability in solution. As the anion  $CIO_4^-$  is often used. Since the molecule is dissociated in solution, we will not consider it in the calculations.

The quantum-chemical calculation methods were used for investigation, in particular AM1 method [7], which has established itself in the study of molecular relaxation of highly excited

states [4-6,8,9]. Since the polymethine dyes established itself resistant to light, we can conclude that the dissociative highly excited states are at sufficiently high energies. In that case, you need to sort several dozen of highly excited states, which is not always possible to make with a semi-empirical calculation methods. Therefore in the work as far as possible the simplest structure of the molecule was chosen to reach the selected target.

The molecule (I) has a symmetrical structure in the ground state, which is described by symmetry group  $C_{2v}$ . Its dissociation is possible only with lowering of symmetry. Therefore, we have investigated the dissociation of molecules by lengthening of the bond between the central carbon atom and the neighbouring carbon atom.

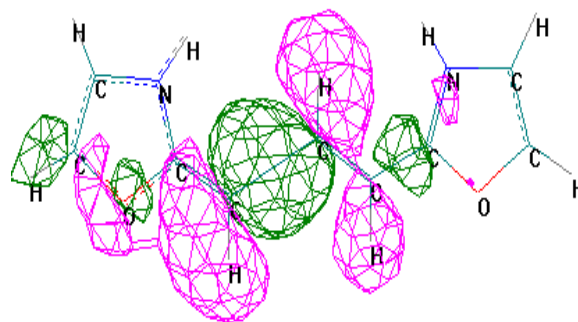
### 3. Results of the study

It is known [4-6] that each molecule has the dissociative energy surface responsible for dissociation of certain chemical bonds in the molecule. Usually the triplet state has a dissociative nature. With increasing of the bond length, which should dissociate, dissociative state becomes the lowest state of the molecule, as a result multiplicity of the molecule is changed from singlet to triplet. This principle underlies the search dissociative state in polymethine dye (I).

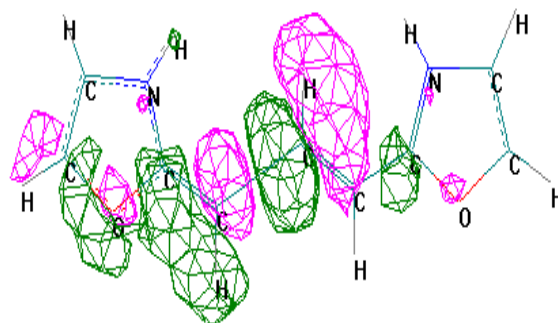
Indeed, with stretching of the bond C-C of  $1\text{Å}$  (chemical bond between central carbon atom and its neighbor) it appeared that the triplet state has become the ground state of the molecule. So the molecular orbitals (MO) which are responsible for the creation of the dissociative state were found. When the length of the bond C-C is equal to  $2,167\text{Å}$  these MO have a view:

As can be seen from these images, MO № 31 has a bonding character in relation to dissociating bond and MO № 33 – antibonding.

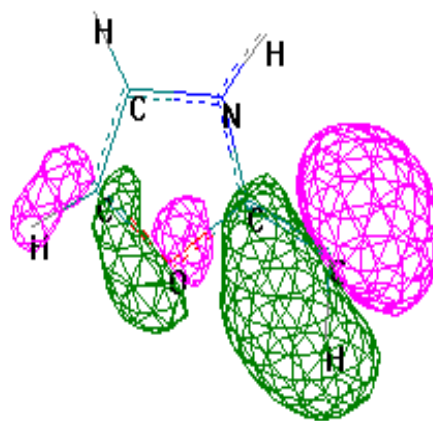
If we divide the molecule into two parts, we will see the kind of  $\sigma$ -MO, the interaction between them will lead to creating of the  $\sigma$ -MO which has been shown above :



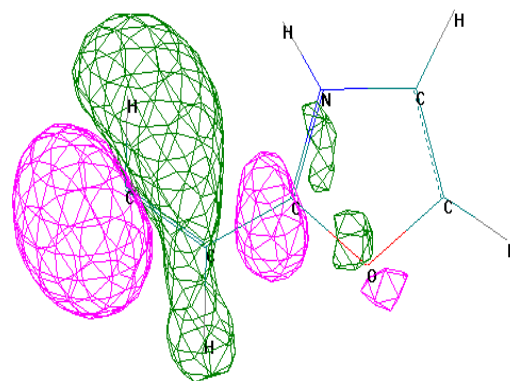
$\sigma$ -MO № 31



$\sigma^*$ -MO № 33.



$\sigma_A$ -MO



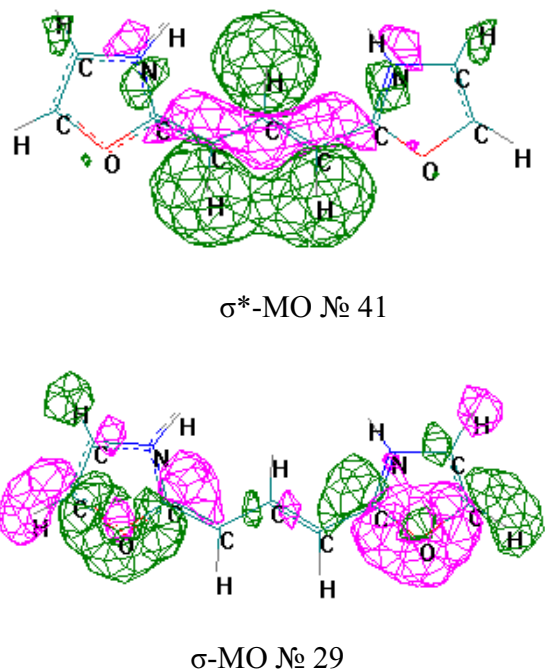
$\sigma_B$ -MO

It is easy to see that:

$$\sigma = \sigma_A + \sigma_B,$$

$$\sigma^* = \sigma_A - \sigma_B.$$

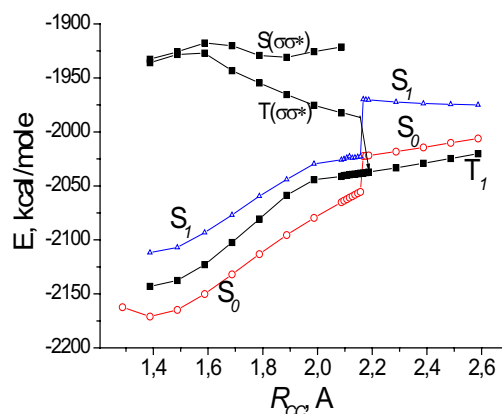
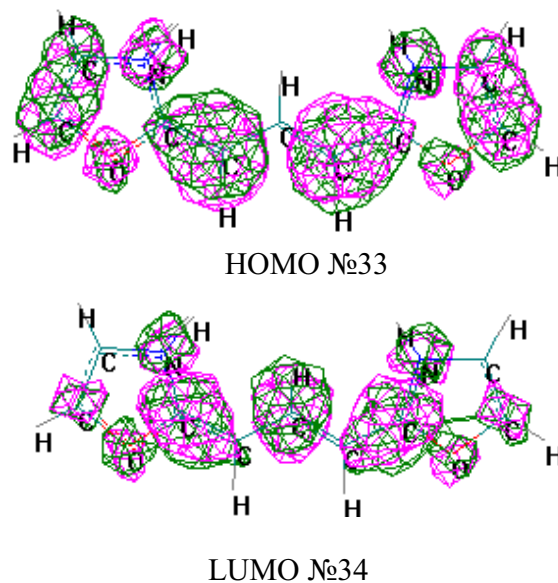
Further, by reducing the length of the C-C-bond it can be found moving both  $\sigma$ -MO of other orbitals. It was found that at the equilibrium length of the C-C-bond (1,387 Å)  $\sigma$ -MO № 31 became the 29-th, and  $\sigma^*$ -MO – № 41. Due to the interaction with other  $\sigma$ -MO their shape is essentially transformed:



First of these remains was localized at dissociating bonds, and the second was significantly modified.

If we define numbers of the selected MO for all distances, it will be easy to calculate the energy of the electronic system of the molecule in the ground and  $\sigma \rightarrow \sigma^*$ -excited state.

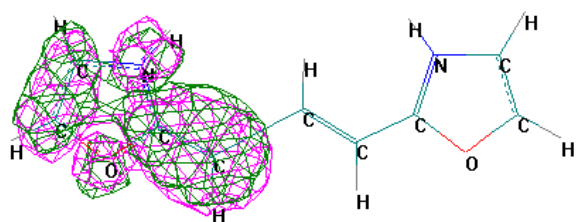
As for the equilibrium configuration the highest occupied molecular orbitals (HOMO) and lowest unoccupied (LUMO) molecular orbitals are  $\pi$ -MO and  $\pi^*$ -MO, Figure 1 shows the position of configuration curves of the singlet and triplet excited states formed by  $\pi$ -MO.



**Figure 1. The dependence of the energy of the ground and excited states of molecules (I) of the length of the dissociating bond.**

As can be seen from Figure 1,  $T(\sigma\sigma^*)$  is really a dissociative state. A new phenomenon is that with stretching of C-C-bond to 2,16Å the phase transition is observed in the electronic system of the molecule (I). As a result, the transition energy of the singlet state significantly increased, while the energy of the triplet state is almost unchanged. However, in the latter case, the nature of the triplet state has changed significantly.

Consider the sequence of occupied MOs after the phase transition. Antibonding  $\sigma^*$ -MO took place of № 33, and  $\pi$ -HOMO was transformed and took place № 34. Now this MO was localized on the smaller fragment of the molecule:



$\pi$ -MO №34

Since the molecule is in the triplet state now, one electron is localized on  $\sigma^*$ -MO, and the second – on  $\pi$ -MO №34. Consequently, we have the basic triplet  $\pi\sigma^*$ -state (electronic configuration  $(\pi)^1(\sigma^*)^1$ ).

The calculation program does not allow to attribute the quantum transitions to certain MO, if the ground state is the triplet one. However, some conclusions can be made. First of all, we can discuss what's happening with the dissociative T ( $\sigma\sigma^*$ )-state. It is easy to see that the quantum transition from the  $\sigma$ -MO № 29 to the partially occupied  $\pi$ -MO № 34 will lead to the creation of the desired T ( $\sigma\sigma^*$ )-state. Therefore, T ( $\sigma\sigma^*$ )-state remains excited state. However, since the ground state is the triplet one, too, the lifetime of this state has declined significantly. This fact does not deny the possibility of the process of dissociation of the molecule (I) to the end. Firstly, in the case of the small heat release immediately after creating T ( $\sigma\sigma^*$ )-state at the equilibrium geometry of the molecule it will be broken into fragments without changing of the energy. Secondly, if there are processes of heat release, which take away energy from dissociative T ( $\sigma\sigma^*$ )-state by discrete portions, the replacement of T( $\sigma\sigma^*$ )-excitation at the singlet ground state to the singlet  $S_1$ -state at the triplet ground state of the molecule (Fig.1) will be possible, which was not only metastable but dissociative one.

It is easy to detect the nature of  $S_0$ - and  $S_1$ -states in the triplet state by considering the electron transfer inside of the pair  $\sigma^*$ -MO № 33 and  $\pi$ -MO № 34 with forming a singlet state. In this case, the electron transfer to the  $\pi$ -MO gives the electron configuration  $(\pi)^2(\sigma^*)^0$ , which corresponds to the  $S_0$ -state. Since  $\pi$ -MO in this case has non-binding nature, increasing the length of

the C-C-bond should not significantly affect the magnitude of energy of the electron system in the molecule.

If the electron transfer occurs to  $\sigma^*$ -MO, it is formed  $S_1$ -state. The corresponding electronic configuration  $(\sigma)^2(\pi)^0(\sigma^*)^2$  resembles the electronic configuration of T ( $\sigma\sigma^*$ )-state by the same number of electrons on the  $\sigma$ -MO and  $\sigma^*$ -MO. It is clear that this situation will be dissociative, that is consistent with the curve  $S_1$  after the phase transition in Figure 1.

To find out in what state the molecule fragments are formed after the dissociation, in the work carried out calculations of the electronic system energies of both fragments depending on the number of electrons on them. The calculation results are shown in Table 1.

Table 1  
The energy of the electronic system (kcal/mol) of fragments depending on the charge state and multiplicity.

№	Smaller fragment: charge, multiplicity and energy of the electronic system	Large fragment: charge, multiplicity and the energy of the electronic system	The total energy of the electron system, E
1	charge 0, doublet, E = -968.258	charge +1, doublet, E = -1054.957	E=-2023.215, triplet
2	charge +1, triplet, E = -805.487	charge 0, singlet, E = -1187.743	E=-1993.23 triplet
3		charge 0, triplet, E = -1193.616	E=-1999.103 singlet
4	charge +1, singlet, E = -803.885	charge 0, singlet, E = -1187.743	E=-1991.628 singlet
5		charge 0, triplet, E = -1193.616	E=-1997.501 triplet



It follows from Table.1 that energetically expedient reaction should be reaction of formation of two radicals from the ground triplet state. Here-with the greater fragment of the molecule (I) must be charged. If the fragments are formed from the singlet state, then the charge will be localized on smaller fragment, and both fragments must be in the triplet state.

Surely, in order to verify the conclusions that follow from Table 1, it is necessary to the study dependence of the magnitude of the charge on the larger fragment at lengthening of dissociating bond in the singlet and triplet state of the molecule.

#### 4. Conclusions

The performed investigation allows to make the following conclusions. We have shown that in the highly excited triplet state the dissociative surface exists, which corresponds to  $\sigma \rightarrow \sigma^*$ -excitation of the molecule; relaxation of excitations in the framework of this surface leads to dissociation of the molecule by lengthening the C-C bond of the molecule at the central carbon atom. With length increasing of the dissociating bond to 2,16 Å the phase transition of the electronic system of the molecule (I) is observed, as a result the energy of the singlet state is significantly increased, while the energy of the triplet state remained practically unchanged; Besides, at dissociation of molecule from the singlet state the charge will be localized into smaller fragments, and both fragments must be in the triplet state; if dissociation will be occur from the triplet state, then energetically expedient reaction will be the formation of two radicals, and the larger fragment of molecule (I) must be charged;

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### Abstract

Quantum-chemical studying polymethine dyes molecular structure and investigation of the relaxation processes of excitation have been carried out. Particularly, in the highly excited triplet state the dissociative surface exists, which corresponds to  $\sigma \rightarrow \sigma^*$ -excitation of the molecule; relaxation of excitations in the framework of this surface leads to dissociation of the molecule by lengthening the C-C bond of the molecule at the central carbon atom

**Key words:** polymethine dyes, relaxation processes of excitation, quantum-chemical studying

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О. А. Коваленко*

## КВАНТОВО-ХИМИЧЕСКОЕ ИЗУЧЕНИЕ СТРУКТУРЫ И ДИНАМИКИ РЕЛАКСАЦИИ ТРИМЕТИН-ЦИАНИНОВОГО КРАСИТЕЛЯ

### Резюме

Приведены результаты квантово-химического изучения молекулярной структуры и процессов релаксации возбуждения полиметиновых красителей. В частности, в сильно возбужденном триплетном состоянии существует поверхность диссоциации, отвечающая возбуждению  $\sigma \rightarrow \sigma^*$  молекулы; релаксация возбуждения приводит к диссоциации молекулы за счет удлинения СС связи молекулы на центральном атоме углерода.

**Ключевые слова:** полиметиновые красители, релаксационные процессы возбуждения, квантово-химическое изучение

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## **КВАНТОВО-ХІМІЧНЕ ВИВЧЕННЯ СТРУКТУРИ І ДИНАМІКИ РЕЛАКСАЦІЇ ТРИМЕТІН-ЦІАНІНОВОГО БАРВНИКА**

### **Резюме**

Приведені результати квантово-хімічного вивчення молекулярної структури та процесів релаксації в збудженні поліметинових барвників. Зокрема, в сильно збудженому триплетному стані існує поверхня дисоціації, що відповідає збудженню  $\sigma \rightarrow \sigma^*$  молекули; релаксація збудження приводить до дисоціації молекули за рахунок подовження СС зв'язку молекули на центральному атомі вуглецю.

**Ключові слова:** поліметинові барвники, релаксаційні процеси збудження, квантово-хімічне вивчення