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Energy of Pair Interaction of Molecular Systems: Excited State – Ground State of Molecules Pentyl – and Pentyloxy – Cyanobiphenyls

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The energies of pair interaction of molecular systems: first excited state and ground state of molecules pentyl – and pentyloxy – cyanobiphenyls was calculated and equilibrium configuration of these molecular systems was determinate. Pair orientated destabilization energies evaluation is given at the absorbtion and emission processes.

INTRODUCTION

The excited electronic state of molecules takes part in many processes, including absorbtion and emission energy processes, formation of excimers and others. There are evidences in the literature[1,2] received on the base of absorbtion and emission spectrums about, that the molecules of cyanobiphenyls form excimer state. That is why the evaluation task was put for the energy of pair energies interaction for two molecular systems: pentyl and pentyloxy - cyanobiphenyls (5CB and 5OCB) their dimer structure and excimer structure, if one of the molecules is first excited state. Basing on these data we want to determine equilibrium mutual configurations of molecules and to estimate energies of pair orientated destabilization at the condition of transfer from non equilibrium excited state of molecular system $(M–M^*)^{non}$, which follows absorbing energy into the excimer equilibrium state $(M–M^*)^{eq}$.

Earlier[3] was investigated pair intermolecular interaction of dimer state of molecular systems 1CB and 3CB, and intermolecular interaction energies was calculated, also were determined mutual conformations of these molecules, which correspond to antyparallel disposition of the dipole moments of molecules. Dimmer structure of cyanobiphenyls is confirmed by experimental data[4].

METHOD OF CALCULATION

At the intermolecular interaction calculations of the excimer state of the molecular systems the method was used, which we used earlier for dimer state calculations. The intermolecular interaction energies are calculated by the method based on the Rayleigh-Shrodinqer perturbation theory. The interaction energy E_{tot} is approximated by sum of the terms: electrostatic - E_{es}, induction - E_{ind}, dispersion – E_{dis} and valence repulsive E_r energies. The electron net charges, atomic dipoles and ionization potential of ground and excited states used in the calculation of the first three terms have been approximated by the CNDO/2 molecular orbital method. The valence repulsive energy, which is not included in the perturbation theory, was estimated from the repulsive part of the Lennard–Jones potential in which the coefficients of the repulsive terms were taken from literature[5] for ground state of molecules. For the excited states of molecules we used the same parameters, because that information is not existing in the scientific literature and as we think, the repulsive parameters for the ground and excited states of molecules are slightly distinguished.

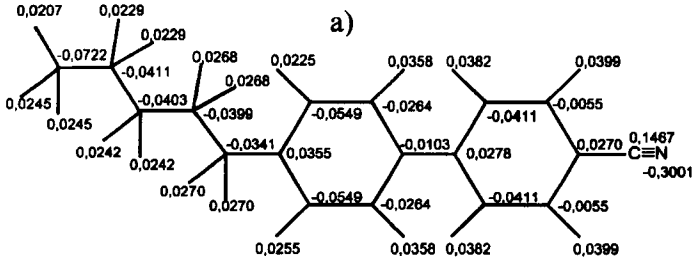
Polarizability of interatomic bonds necessary for the E_{ind} and E_{dis} calculations for the ground states of molecules are taken from[6]. For excited states of molecules the determination of polarizability interatomic bonds is the problem we face, and the data we have for now is the polarizability of a certain number of molecules, and also the method of experimental determination of polarizability of molecules in excited state is worked out. At the determination of polarizability α_e and dipole moment μ_e of excited molecules the spectral shift method was used, which is based on the theory of the universal intermolecular interactions in mixtures[7]. Polarizability and dipole moment of 5CB and 5OCB excited state of molecules was determined from the relations

$$\alpha_g - \alpha_e = \frac{C_3^a a^3}{\frac{3}{2}\frac{II'}{I+I'}}, \quad \mu_e = \mu_g - \frac{C_1 hca^3}{2\mu_g} \tag{1}$$

where C_1^a, C_3^a is the parameters of the theory of the universal interactions, a – Onzaqer radius of molecule, I, I' – ionization potentials. The values of the polarizabilities α_g and dipole moments μ_g of the ground state of molecules are taken from the literature[8] and from our calculations molecular orbital theory. On the basis of received data α_e of molecules 5CB and 5OCB and also known data α_e series of compounds additive scheme was constructed alike the calculations of polarizabilities of interatomic bonds of ground state of molecules.[6]

CALCULATION AND EXSPERIMENT RESULTS AND DISCUSSION

The calculated distributions of electron density over the atoms of 5CB and 5OCB ground and state are given in Figure 1.2. As it can be seen from Figure 1.2 the dipole moments of ground state S_0 there molecules is determined by polar group – $C \equiv N$. Absolute electric charge on these atoms is equal 0,1467 and – 0,3001, respectively for 5CB and 0,1468 and – 0,3002 for 5OCB.



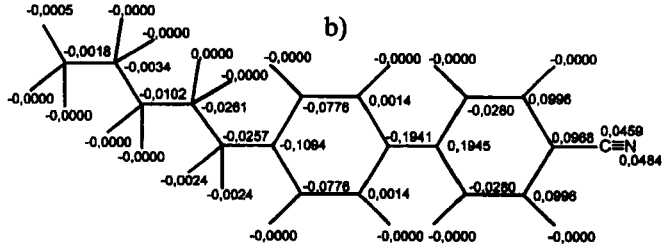


FIGURE 1 Absolute electric charge on the atoms of the 5CB molecule, a) – ground state, b) – excited state

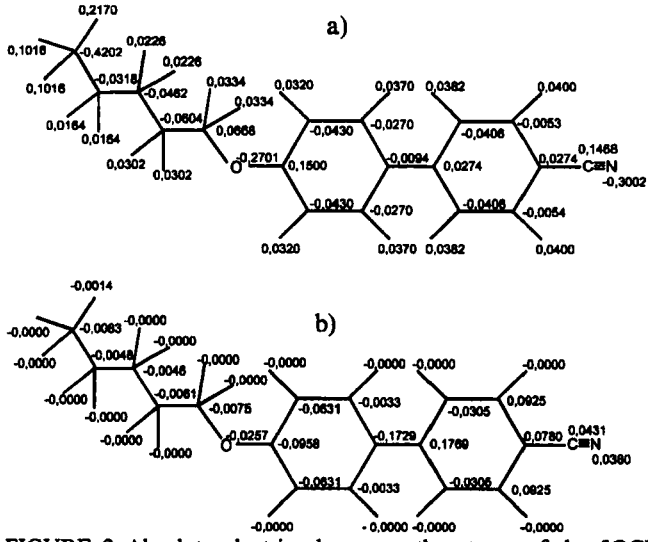


FIGURE 2 Absolute electric charge on the atoms of the 5OCB molecule, a) – ground state, b) – excited state

The presence of the great negative electric on the atom of oxygen of the 5OCB molecule is lowing down the dipole moment up to the value 3,5D. Electric charges on the atom of the nitrogen of the excited state S_1 of the 5CB and 5OCB are equal to 0,0484 and 0,0380 respectively and electrons shift to the atoms of the pentyl and pentylphenyl of molecular groups. In excited state vector of the dipole moment vary inversely and its value are equal $\mu_e \approx 10D$ for 5CB and $\mu_e \approx 8D$ for 5OCB molecules. The obtained electron distributions over atoms were then used calculations of the intermolecular interaction energies.

On the Figure 3 is shown the dependence of the frequency of the maximum longwave band of absorbtion of the molecule 5CB from the function of the universal interaction, wich is determined by refractive indices of solvents.

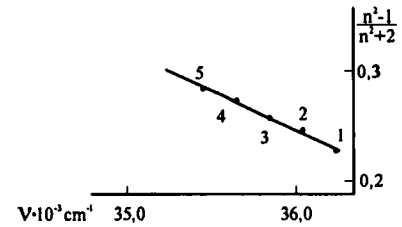


FIGURE 3 Dependence of the frequency of the maximum absorbtion from the function universal interaction. Solvents: 1 – C_2H_5OH; 2 - C_6H_{14}; 3 – C_4H_9OH; 4- CCl_4; 5 – $CHCl_3$;

From this dependence experimental values of polarizability α_e and dipole moment μ_e of 5CB were determined with the usage of the formulas (1). Such results for excited molecule of 5CB were obtained: polarizability is equal $\alpha_e \approx 77\overset{o}{A}^3$, dipole moment is $\mu_e \approx 10D$ and its vector is changing for the reverse as compared to the ground state, which is prooved by the calculated data.

Below we present some resultes of calculation intermolecular total energies and their components (E_{es}, E_{ind}, E_{dis}, E_τ) at different mutual pair orientations of the molecular systems of the 5CB and 5OCB.

In Table 1,2,3,4 are given this dependencies from the angle of the rotation respective of oz –axis (Figure 4) and different distances between the molecular centers for dimer state (M-M) and excimer state (M-M*).

TABLE 1 The angle dependencies of the interaction energies from distances between molecular centers of the dimer 5CB

angle rotation respective OZ axis	$E_{es}, \frac{kJ}{mol}$	$E_r, \frac{kJ}{mol}$	$E_{ind}, \frac{kJ}{mol}$	$E_{dis}, \frac{kJ}{mol}$	$E_{tot}, \frac{kJ}{mol}$
1	2	3	4	5	6
	$\Delta x = 2\,\mathring{A}, \Delta y = 0, \Delta z = 5\,\mathring{A},$				
0°	9,982	1,877	-1,739	-13,213	-3,093
180°	0,589	4,552	-1,705	-17,828	-14,388
	$\Delta x = 4{,}5\,\mathring{A}, \Delta y = 0, \Delta z = 5\,\mathring{A},$				
0°	7,633	1,041	-1,300	-10,045	-2,671
180°	-1,981	2,391	-1,538	-14,317	-15,449
	$\Delta x = 5\,\mathring{A}, \Delta y = 0, \Delta z = 5\,\mathring{A},$				
0°	7,257	0,953	-1,225	-2,264	-2,473
180°	-2,257	2,065	-14,797	-13,740	-15,412

TABLE 2 The angle dependencies of the interaction energies from distances between molecular centers of the excimer 5CB

1	2	3	4	5	6
	$\Delta x = 4{,}5\,\mathring{A}\ \ \Delta y = 0, \Delta z = 5\,\mathring{A},$				
0°	-7,975	4,041	-3,452	-20,089	-30,480
180°	6,851	2,265	-4,928	-28,637	-24,327
	$\Delta x = -0{,}5\,\mathring{A}, \Delta y = 0, \Delta z = 5\,\mathring{A},$				
0°	-6,249	3,344	-5,263	-31,643	-39,815
180°	5,108	5,622	-4,866	-35,714	-29,849
	$\Delta x = -1\,\mathring{A}, \Delta y = 0, \Delta z = 5\,\mathring{A},$				
0°	-6,136	3,465	-5,350	-31,618	-39,639
180°	4,301	5,530	-4,765	-34,732	-29,670

TABLE 3 The angle dependencies of the interaction energies from distances between molecular centers of the dimer 5OCB

1	2	3	4	5	6
	$\Delta x = 0{,}3\,\text{Å}$, , $\Delta y = 0$, $\Delta z = 5{,}5\,\text{Å}$, .				
0°	5,631	1,618	-1,338	-24,884	-18,978
180°	-1,697	0,619	-0,794	-22,229	-24,102
	$\Delta x = 1{,}2\,\text{Å}$, $\Delta y = 0$, $\Delta z = 5{,}5\,\text{Å}$,				
0°	4,631	1,446	-1,467	-24,286	-19,675
180°	-1,827	0,723	-0,928	-22,601	-24,637
	$\Delta x = 1{,}8\,\text{Å}$, $\Delta y = 0$, $\Delta z = 5{,}5\,\text{Å}$,				
0°	3,561	1,304	-1,542	-23,546	-20,219
180°	-1,756	0,798	-1,041	-22,534	-24,532

TABLE 4 The angle dependencies of the interaction energies from distances between molecular centers of the excimer 5CB

1	2	3	4	5	6
	$\Delta x = 1{,}2\,\text{Å}$, $\Delta y = 0$, $\Delta z = 5{,}5\,\text{Å}$,				
0°	-1,977	1.446	-4,230	-47,600	-48,413
180°	-1,659	0,723	-3,499	-44,596	-49,035
	$\Delta x = -1\,\text{Å}$, $\Delta y = 0$, $\Delta z = 5{,}5\,\text{Å}$,				
0°	-2,224	1,492	-4,703	-48,204	-53,638
180°	0,364	0,485	-2,496	-40,784	-42,431
	$\Delta x = -1{,}5\,\text{Å}$, $\Delta y = 0$, $\Delta z = 5{,}5\,\text{Å}$,				
0°	-3,294	1,375	-4,677	-46,925	-53,525
180°	0,702	0,439	-2,307	-38,962	-40,128

As it's shown in the Table 1,2 minimum of energy for dimer of 5CB is equal to E_{tot}= -15,46$\frac{kJ}{mol}$ and values of the distances between the molecular centers are $\Delta x = 4{,}5\,\text{Å}$, $\Delta z = 6\,\text{Å}$, $\Delta y = 0$. In this case molecules are placed antyparallel to each other. For excimer state of 5CB the total energy of nonequilibrium state which follows absorbing energy

is equal to $E_{tot}^{non} = -24{,}33\,\frac{kJ}{mol}$. Reoriented relaxation leads to equilibrium excited state of the molecular system the energy of which is equal to $E_{tot}^{eq} = -39{,}82\,\frac{kJ}{mol}$. In this state the orientation of both molecules is parallel and their dipole moments are antyparallel in contrast to the configuration of the dimer, their molecules as well as dipole moments are antyparallel. In Figure 4 is shown schemes of mutual orientation of molecules of dimer and axcimer states.

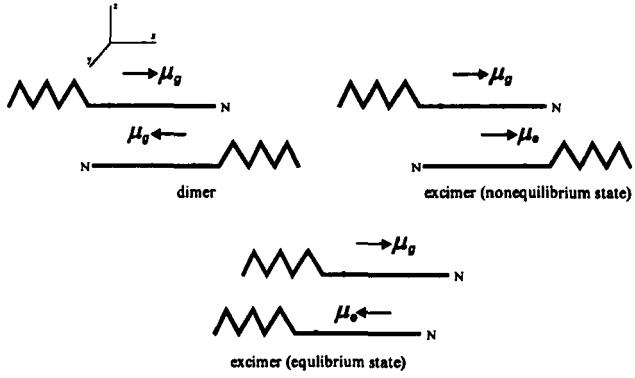


FIGURE 4. Schemes of mutual orientation of molecules of dimer and excimer.

For molecular pair system 5OCB the total energy of dimer in equilibrium state is equal to $-24{,}64\,\frac{kJ}{mol}$, nonequilibrium excimer state $-49{,}03\,\frac{kJ}{mol}$, and equilibrium excimer__state $-53{,}63\,\frac{kJ}{mol}$ (Table 3,4). Mutual orientation of molecules of excimer 5OCB is alike to the orientation of molecules of 5CB. Let's call the difference of the energy between nonequilibrium state that appeared immediately after intramolecular vibrational relaxation and equilibrium state energy of the pair orientated destabilization ($E_{tot}^{non} - E_{tot}^{eq}$). This value for molecular system 5CB turned

out to be equal to $15{,}49\frac{kJ}{mol}$, and for molecular system of 5OCB – $4{,}6\frac{kJ}{mol}$, which is pointing at the relatively big value of relaxation shift in kinetically emission spectrum for 5CB. The experiment is showing this shift for 5CB is equal to 500 $см^{-1}$, for 5OCB it is smaller.

CONCLUSION

The results obtained during the research is one of the first attempts to evaluate the energy of pair interaction between the excited state of molecule and its ground state and also to establish their mutual orientation in equilibrium state. Of course, the results might not be absolute, because some data used in calculation such as polarizability of interatomic bonds and parameters of the repulsive of excited state of molecule are taken approximately. However in general the obtained results are quite convincing.

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