Influence of the Electric Field on the Electronic Properties of the Substituted Biphenyl Molecules

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This paper presents the results of investigations into the influence of the longitudinal and transverse electric field on the potential surface, the dipole moments and electronic spectra of the substituted biphenyl molecules that can be regarded as the elements of nanoelectronics.

Keywords: Nanoelectronics, Molecule, Biphenyl, Conformation, Potential surface, Dipole moment, Electronic spectrum.

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1. INTRODUCTION

The long-term purpose of moletronics consists in the development of the electronic keys that are central components in every electronic card on the basis of one molecule. Works in this field can result in the final miniaturization of analog and digital charts. They are directed, mainly, at the study of transfer of electrons through one molecule between two electrodes. The stream of electrons through such a construction is controlled by the bias voltage between electrodes, the distance between a molecule and electrodes, and also by the third electrode ("breech-block") [1].

The intensive searches for other possibilities to create electronic charts, in particular, molecular switching elements are being conducted [2-9]. To project such elements is also important for creating the element base of sensory devices.

It is known that reversible changes in the state of molecules are possible at their conformational transformations. So in the works [10-12] the model of metabotropic receptors cluster is analyzed to study the mechanisms of memory functioning. Its conformation transitions are similar to switching of the molecular trigger controlled by chemical and electric influences. Changing the conformation states, the receptive clusters operate the metabolism of a cell and its "spontaneous" activity, and conformational hysteresis allows clusters to perform the functions of memory.

2. EXPERIMENTAL

The task of this work is to find not only methods but also an appropriate molecule, for example, from the class of substituted biphenyl ones in which a dihedral angle between phenyl rings is equal to 90 degrees in a ground state that corresponds to a minimum of energy of the inhibited conformation at which substitutes in ortho-position (atoms of hydrogen or cyano-groups) of phenyl rings are in the maximal distance from a nitrogroup (Fig. 1). In this case the conjugation between the π-systems of phenyl rings and, as a result, the conductivity along the axis of molecule are absent. The turn of phenyl rings while switching the external field will

lead to overlapping the electronic π-orbitals of the phenyl rings and, as a result, higher conductivity is provided along the axis of molecule.
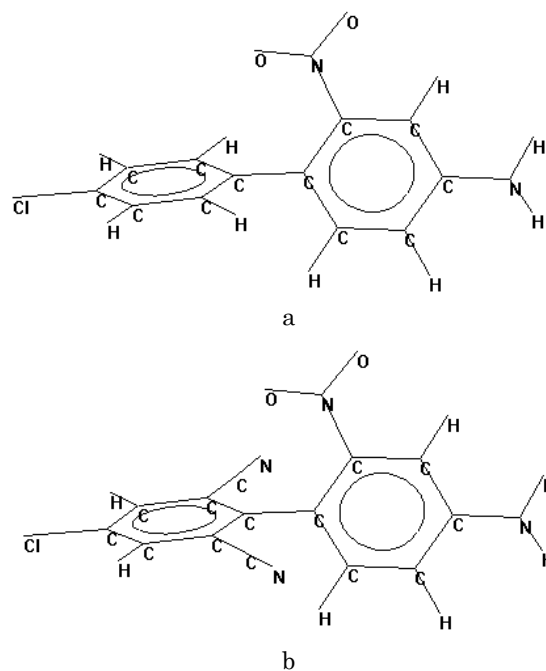

Fig. 1 – The investigated molecules of substituted biphenyl. In ortho-position of phenyl ring: a – substitutes are atoms of hydrogen, b – substitutes are cyano-groups

The value of a dihedral angle depends on the correlation between contributions of two interactions: the value of π-electronic conjugation energy is falling when the angle between phenyl rings is decreasing, and the value of energy of pushing between charges on substitutes is increasing at the same time. If these energies are the values of the same order, then the minimum of the molecule electronic system energy will differ significantly from the energy which the system has at 90°. In case one of the indicated interaction types predominates considerably the configuration of a molecule will

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correspond to extreme cases (90° or 0°).

This work studies the influence of the longitudinal and transversal external electrostatic field on the conformational transformations of substituted biphenyl molecules (Fig. 1), and also on spectroscopy properties of conformers.

Theoretical researches using modern quantum-chemical methods (modeling was conducted in the software environment of HyperChem; optimization of the geometrical structure of a molecule was carried out by semiempiric methods of AM1 and MNDO/d [13-14]) allowed in a certain measure to study the key mechanisms of switching processes in molecular elements.

In the course of works [9] the potential surface of the substituted molecules of biphenyl (Fig. 1) was investigated which initial geometry corresponds the required condition. Molecules were placed into the homogeneous electric field within $-0.025 \leq E \leq 0.025$ a.u. (the electric field of 1 a.u. corresponds to $E = 5.1421 \cdot 10^{11}$ V/m) that was directed along the long axis of a molecule or normal to it. In the calculations the value of the dihedral angle varied within the limits of $20° \leq \varphi \leq 60°$ (Fig. 2).

It was discovered that there was a potential barrier of internal rotation at the critically high strength of ± 0.025 a.u. in the vicinity of the torsion angle, equal to 90°. Its height is 1.61 kkal/mole (0.070 eV) in the field of $+ 0.025$ a.u., and 3.57 kkal/mole (0.155 eV) in the field of $- 0.025$ a.u. that allows to controll the states of a molecule (a molecular trigger) changing the voltage of the transversal field in a fraction of a volt.
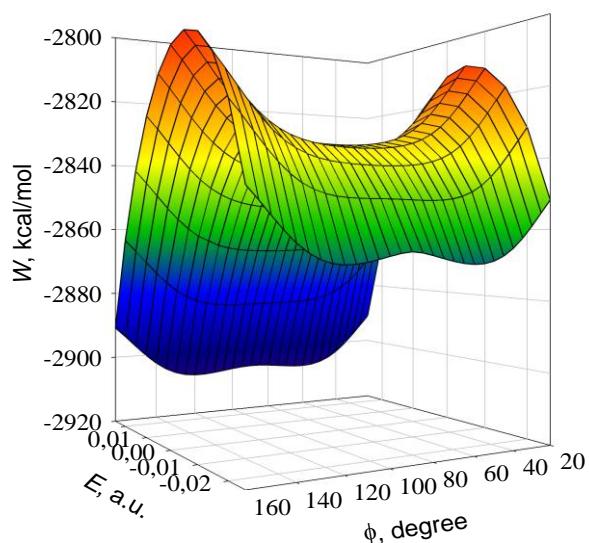

Fig. 2 – Influence of the electric field on the potential surface at the different values of the dihedral angle

The transversal electrostatic field results in some redistribution of values of charges on the atoms of a molecule displacing the position of the minimum of molecule energy by the angle up to 50° degrees (Fig. 1). In its turn, the redistribution of charges can be explained by the interaction of the transversal electric field with the transversal constituent of the molecule dipole moment, i.e. the new dipole moment of a molecule consists of the induced and initially present dipole moment in the molecule without the center of inversion.

Table 1 – Influence of the transversal field on the value of the dihedral angle in equilibrium configuration of the molecule (a)

E, a.u.	α, degrees	W, kkal / mole
0	89.3	$- 2837.8344$
$E_X = 0.025$	120	$- 2835.4687$
$E_X = 0.025$	70	$- 2888.4619$
$E_Z = 0.025$	40	$- 2855.7678$
$E_Z = - 0.025$	125	$- 2886.0254$

Despite the impressive results of the rotation angle value, the molecule (a) has that drawback that the potential pit in the vicinity of the energy minimum has the small depth and large width (Fig. 3). The molecule (b) is devoid of this drawback.
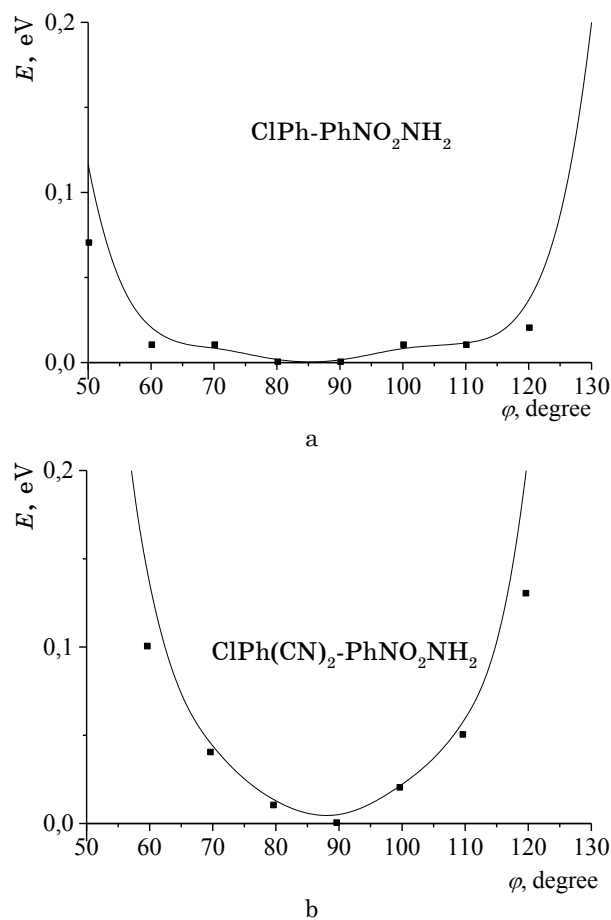

a

b

Fig. 3 – Curves of potential energy for molecules (a) and (b)

Figure 3 illustrates the redistribution of charges in a molecule as a result of changing the longitudinal field polarity.

Potential energy of interaction of the charge distributed over the molecule with the external electric field enters as the component part in Hamiltonian of the electronic system of molecule, influencing the energy and conformation structure of the molecule both in the excited and basic states. Consequently, the change of the electronic density distribution in a molecule placed in the external electric field must affect not only the changes of electronic transitions but also probabilities of intramolecular radiative and nonradiative electronic transitions.
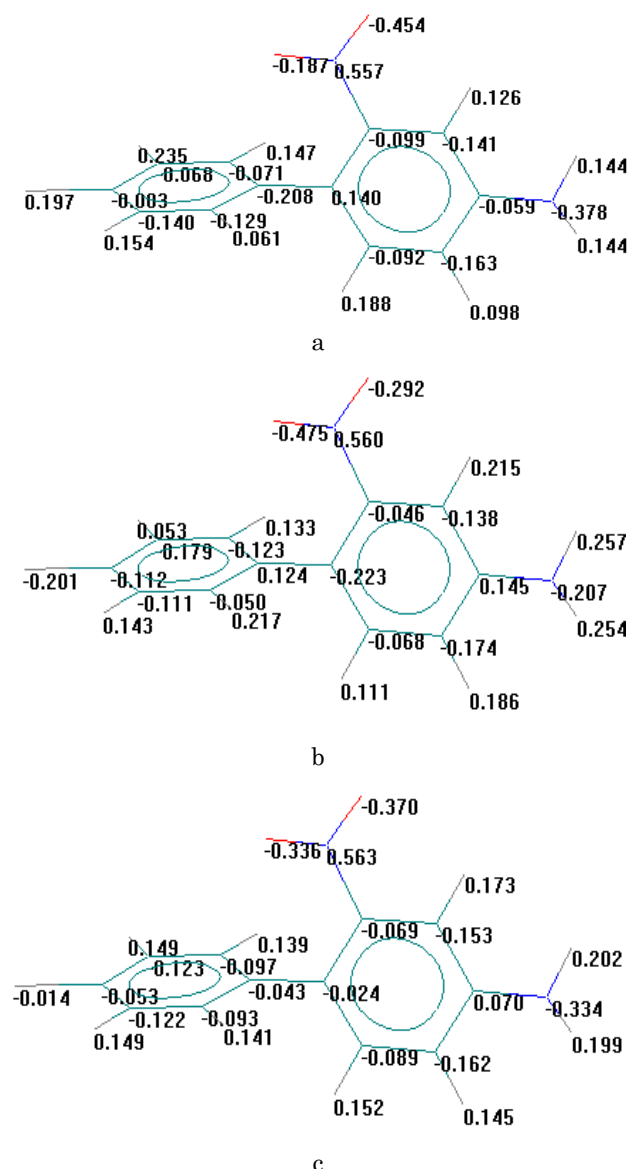
Fig. 4 – Redistribution of charges in the biphenyl molecule at application of the longitudinal electrostatic field of different directions: $E_y = + 0.025$ a.u. (a), $E_y = - 0.025$ a.u. (b), $E_y = 0$ (c)

After switching off the electric field the spectrum of absorption is restored.

Spectral positions and forces of oscillators (a) in the different conformation states are presented in Table 2.

Spectral effects are interpreted by changing probability of quantum transitions because of the electronic density redistribution in chromophore in basic and excited states of the dye in the external electric field [15].

Anisotropic changes in the spectra of absorption and luminescence of organic dyes placed in the electric field can be recommended as a very sensible method both for the analysis of the field value and orientation of a molecule in this field.

3. DISCUSSION OF RESULTS

The redistribution of charges in molecules (Fig. 4) causes the change of a molecule dipole moment more than by 30 D: from + 12 to – 19 D (Table 3).

Table 2 – Wavelengths and oscillator force in light-spectrum of a biphenyl molecule absorption at different fields and rotation angles of phenylic rings in relation to each other

$E = 0$		$E = - 0.025$ a.u.					
$\varphi = 90$ °		$\varphi = 90$ °		$\varphi = 60$ °		$\varphi = 120$ °	
λ, nm	f	λ, nm	f	λ, nm	f	λ, nm	f
344.45	0.156	698.27	0.001	781.04	0.833	767.14	0.869
245.22	1.901	474.34	0.003	329.43	0.025	328.23	0.027
226.95	0.824	301.24	0.001	320.05	0.051	319.54	0.072
225.44	0.317	262.30	0.183	263.12	0.188	262.82	0.166
201.89	1.192	252.52	0.051	242.88	0.160	242.42	0.158

It should paid attention that at the change of sign of the longitudinal field the transversal moment changes its absolute value saving its sign.

The longitudinal electric field is applied on the longitudinal constituent of the dipole moment of the molecule, as a result, the longitudinal constituent of the dipole moment becomes equal to zero when the external field of $E = - 0.0054$ a.u., i.e. depolarization of the molecule takes place that enables to control the transfer of charge along the molecule.

The above-described influence of the electric-field on the conductivity of a molecule can be applied as "an electric field sensor".

Table 3 – The dipole moment at the different values of the longitudinal (along the main axis of the molecule) electrostatic field

E, a.u.	X, D	Y, D	Z, D	Total, D
+ 0.025	5.563	– 19.305	3.182	20.341
0	4.399	– 3.258	2.638	6.076
– 0.025	3.320	12.973	1.961	13.534

Note: 0.025 a.u. – is the limiting field when the atom of chlorine is detached from the molecule.

4. CONCLUSIONS

Theoretical and experimental researches of influence of the external homogeneous electric field on conformation of substituted biphenyl molecules have shown that:
– in the large fields a potential barrier appears in the vicinity of 90-degree orientation between phenyl rings;
– it is possible to control the value of barrier and depth of appearing potential pits by the transversal electric field creating the effect of a trigger;
– increasing of the longitudinal field to $E = 0.025$ a.u. results in rotation of the phenyl ring up to $\Delta\varphi = 50$ °; as conductivity will be proportional to the square of the overlap integral of the π-MO phenyl nuclei wave functions, i.e. proportional to $\cos^2\varphi$ that will result in appearance of conductivity along the long axis of the molecule;
– when substitutes are atoms of hydrogen the declivous potential pit in the molecule of biphenyl makes the mutual orientation of two phenyl rings be very fuzzy even at low temperatures that will not allow to get the non-conducting structure of a molecule; the use of cyano-groups as substitutes largely removes this drawback as a potential pit becomes deep;
– the longitudinal electric field does not influence the

value of the transversal constituent of the dipole moment of the molecule significantly;

– substantial influence of the external electric field on the position and force of oscillator of bands in the absorption spectra of the investigated molecules is found out;

– the external electric field does not change the structure of the molecule that allows the application of the obtained data to create elements of moletronics.

Влияние электрического поля на электронные свойства замещенных молекул дифенила

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В работе представлены результаты исследований влияния продольных и поперечных электрических полей на потенциальную поверхность, дипольные моменты и электронные спектры молекул замещенных дифенила, которые можно рассматривать как элементы наноэлектроники.

Ключевые слова: Наноэлектроника, Молекула, Дифенил, Конформация, Потенциальная поверхность, Дипольный момент, Электронный спектр.

Вплив електричного поля на електронні властивості заміщених молекул дифенілу

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У роботі представлені результати досліджень впливу поздовжніх та поперечних електричних полів на потенціальну поверхню, дипольні моменти й електронні спектри молекул заміщених дифенілу, які можна розглядати як елементи наноелектроніки.

Ключові слова: Наноелектроніка, Молекула, Дифеніл, Конформація, Потенціальна поверхня, Дипольный момент, Електронний спектр.

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