PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 4, 04NMEEE06(2pp) (2012)

Biphenyl Molecules as Elements of Nanoelectronics in the Electric Field

O.A. Shovkoplyas[1], Y.M. Lopatkin[1,*], P.O. Kondratenko[2]

[1] *Sumy State University, R-Korsakov 2, 40007, Sumy, Ukraine*
[2] *National Aviation University, Cosm. Komarov Ave 1, 03058, Kyiv, Ukraine*

(Received 18 June 2012; published online 22 August 2012)

This paper presents the results of investigations of the influence of the longitudinal and transverse electric field on the potential surface, the dipole moment and electronic spectra of the substituted biphenyl molecules that are offered for the role of the elements of nanoelectronics.

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

PACS numbers: 36.20.Ey, 36.40.Cg

1. INTRODUCTION

The 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 [1, 2]. The intensive searches of other possibilities are presently conducted for creation of electronic charts, in particular molecular switching elements [3,4]. Such elements are also important for the creation of element base of sensory devices.

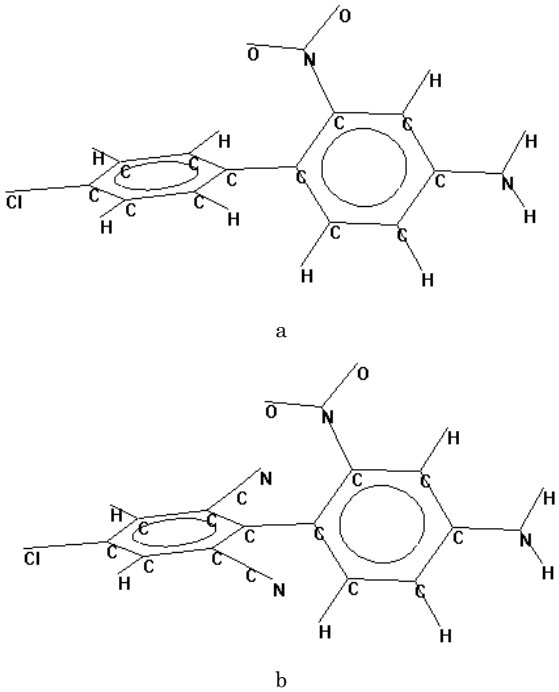
It is known that reversible changes in the state of molecules are possible at their conformation transformations. So in the works [5] with the purpose to study mechanisms of memory functioning the model of cluster of metabotropic receptors is analysed. Its conformation transitions are similar to switching of the molecular trigger, controled by chemical and electric effects. Changing the conformation states, the receptive clusters govern metabolism of cell and its «spontaneous» activity, and conformation hysteresis allows clusters to perform the functions of memory.

2. PROCEDURE, RESULTS AND DISCUSSION

This work is aimed at finding both methods and the appropriate molecule, for example, from the class of substituted biphenyl, in which a dihedral angle between phenyl rings is equal to 90º 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 on the maximal distance from a nitro-group (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 at including of the external field will lead to overlapping of the electronic π-orbitals of the phenyl rings and, as a result, large conductivity is present along the axis of molecule.

In this work it was studied the influence of the longitudinal and transversal external electrostatic field on the conformation transformations of molecules of substituted biphenyl, and also on spectroscopic properties of conformers.

Theoretical researches with the use of modern quantum-chemical methods (modeling was conducted in the software environment of HyperChem; optimization of geometrical structure of molecule was carried out by semiempiric methods of AM1 and MNDO/d [6,7] allowed in a certain measure to study the key mechanisms of switching processes in molecular elements.



a

b

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 the dihedral angle depends on correlation of contribution of two interaction: the value of energy of ππ-electronic conjugation decreases at decreasing of the angle between phenyl rings, and the value of energy of pushing away between charges on substitutes increases at the same time. If these energies are the values of one order, then the angle on which accounted the minimum energy of the electronic system of mole-

* yu.lopatkin@gmail.com

cule will significantly differ from 90°. In case of the considerable predominance one of the indicated types of interaction the configuration of molecule will correspond to extreme cases (90° or 0°).

In the continuation of works [2] the potential surface of the substituted molecules of biphenyl, whose initial geometry matches to the required condition, is investigated. Molecules placed in the homogeneous electric field with the electric field within $-0{,}025 \le E \le 0{,}025$ a.u. (the electric field 1 a.u. corresponds to $E = 5{,}1421 \cdot 1011$ V/m), directed along the long axis of molecule or normally to it. In the calculations the value of dihedral angle was varied within the limits of $20° \le \varphi \le 160°$.

It was discovered that at the critically large fields ± of 0,025 a.u. there is a potential barrier of internal rotation in the vicinity of torsion angle, equal 90°. Height of the specified potential barrier equals 1,61 kkal/mole (0,070 eV) in the field + 0,025 a.u., and 3,57 kkal/mole (0,155 eV) in the field - 0,025 a.u., that allows to switch the states of molecule (molecular trigger), by applying a voltage of the transverse field in a fraction of a volt.

The transversal electrostatic field results in some redistribution of values of charges on the atoms of molecule, resulting in displacement of position of a minimum of energy of molecule on the value by up to 50°. In their turn, the redistribution of value of charges can be explained by interaction of transversal electric-field with the transversal constituent of dipole moment of molecule, i.e. the new dipole moment of molecule consists of induced dipole moment and originally existing one in a molecule without the center of inversion.

Without regard to impressive results with the value of angle of rotation, the molecule (A) has that drawback, that potential pit in the vicinity of the minimum of energy is characterized by a small depth and very wide. The molecule (B) is deprived of this drawback.

Changing of polarity of the longitudinal field results in the redistribution of charges in the molecule.

Potential energy of interaction of the distributed over the molecule charge with the external electric field enters as the component part in Hamiltonian of the electronic system of molecule, influencing on the energy structure and the conformation structure of the molecule both in the excited and in basic state. Consequently, changing of distributing of the electronic density in the molecule, placed in the external electric field, must reflected not only on changing of energy of electronic transitions but also on probabilities of intramolecular radiative and nonradiative electronic transitions.

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

The redistribution of charges in molecules causes the change of dipole moment of molecule more than on 30 D: from + 12 to – 19 D. It should pay attention to that at changing of sign of the longitudinal field the transversal moment does not change its sign at the change of its absolute value.

The longitudinal electric field is superimposed on the longitudinal constituent of dipole moment of molecule, in results what at the external field of $E = -0{,}0054$ a.u. the longitudinal constituent of dipole moment becomes equal to the zero, i.e. depolarization of molecule comes, that can be used for control of the transfer of charge along a molecule.

The described higher influence of the electrical field on conductivity of the molecule is possible to use as a "sensor" of electric field.

Note: 0,025 a.u. − is the limiting field when the atom of chlorine is detached from molecule.

3. CONCLUSIONS

Theoretical and experimental researches of influence of the external homogeneous electrical field on the conformation of substituted molecules of biphenyl have shown that:

– at the large fields the potential barrier appears in the vicinity of 90° orientation between phenyl rings;

– it is possible to manage the value of barrier and depth of appearing potential pits by the transversal electric field, creating the effect of trigger;

– increasing of the longitudinal field to $E = 0{,}025$ a.u. results in rotation by up to $\varphi = 50°$; as conductivity will be proportional the square of integral of overlap of wave functions π-MO of phenyl nucleus, i.e. proportional $\cos 2\varphi$, it will result in appearance of conductivity along the long axis of molecule;

– the declivous potential pit in the molecule of biphenyl in the case when substitutes are atoms of hydrogen, results in fact that even at low temperatures the mutual orientation of two phenyl rings will be strongly washed out, that will not allow to get the nonconducting structure of molecule; using of cyano-groups as substitutes largely eliminate this drawback, since potential pit becomes deep;

– the longitudinal electric field not substantially influences on the value of transversal constituent of the dipole moment of the molecule;

– the external electrical field does not change the structure of molecule, that allows to utilize findings for creation of elements of moletronics.

REFERENCES

1. N. Tao, www.stormingmedia.us/52/5274/A527473.html.
2. A.V. Dmitriev, P.A. Kondratenko, A.V. Glushkov, Yu.M. Lopatkin, *Sensor Electronics and Microsystem Technologies* **2(8)**, No3, 54 (2011).
3. A.V. Glushkov, O.Yu. Khetselius, S.V. Malinovskaya, *Molecular Physics (UK)* **106**, No9, 1257 (2008).
4. P.O. Kondratenko *Fotohimichna diya svitla* (Kyiv: HNV "Kiyvsky universitet": 2005) (in Ukrainian).
5. A.N. Radchenko, *Biophysics* **38**, No2, 288 (1993) (in Russian).
6. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
7. W. Theil, A. Voityuk, *J. Phys. Chem.* **100**, No2, 616 (1996).