Molecular transistor based on the biphenyl substituents

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We investigate the physical processes in the molecules, which have properties required in case of using as molecular switches, transistors, or other electronic elements of future computers. Studies shows that in the molecules of substituted biphenyls the angle between the planes of the phenyl rings depends on the magnitude of the applied external electric field. It significantly changes the ability of electrons to move along the long axis of the molecule. By varying the nature of the substituents, we can obtain the molecule characteristics that make these molecules promising for future using.

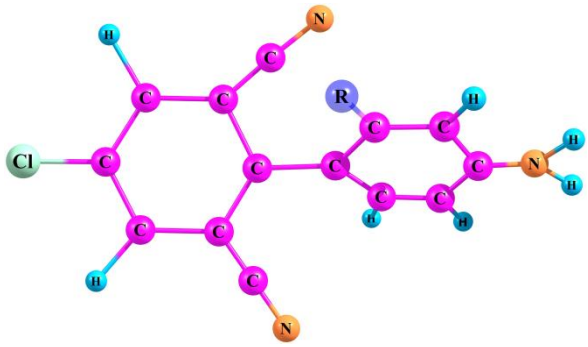
Introduction

The rapid development of modern element base of the computers poses new challenges of element base miniaturization through the producing of memory elements, switches, transistors, etc. using separate molecules.

The development of this area can lead to the ultimate miniaturization of the computer technology components. Works are mainly focused on the study of an electron transfer through a single molecule fixed between two electrodes. The flow of electrons through such a structure depends not only on the conditions at the contacts, but on the structure of molecular orbitals responsible for electron transfer.

The intensive search for the opportunities to create electronic circuits that use molecular elements as switches, transistors, etc. is carried out.[1-5] Since it is important to create stable molecular devices, only the molecules in the stable conformational transformations should be used.

The study of the geometric structure of biphenyl substituents showed, [6-8] that the angle between the planes of two phenyl groups depends essentially on the nature of the substituent (R = NO_2, CN, Cl, NH_2) in the ortho-position of the second phenyl ring:

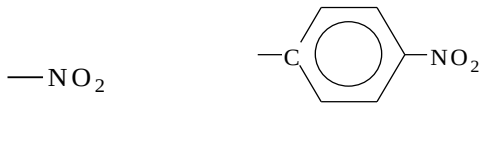


It is important that the excess charge of the substituent depends on the nature of the substituent. Substituents which have acceptor properties provide repulsion (except steric effects) of an adjacent phenyl ring cyano groups. As a consequence, the phenyl fragments of these molecules are rotated at an angle close to 90° relative to each other. In this case, the π-conjugation between the phenyl fragments are absent. Thus, the transfer of the

charge (electric current) along the molecule becomes impossible. Placing of the molecule into an electric field directed along the molecule's axis leads to a charge displacement (polarization) along the molecule's axis. This polarization leads to the change in the angle between the phenyl fragments. This effect enables the use of biphenyl derivatives as switches in electrical circuits, built on separate molecules (moletronics).

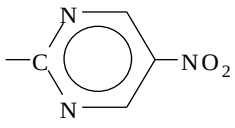
Objects of research

The study of the physical properties of substituted biphenyl led to the idea that a change in the charge state of the substituents can be carried out by a transverse electric field, i.e. these molecules can be used as field-effect transistors (FET). It is logical to use long molecular fragment, oriented parallel to the transverse direction (relative to the axis of the biphenyl molecule) of the electric field as the substituent. In all cases the electric field is chosen perpendicular to the axis of biphenyl in the plane of the phenyl ring which bears a substituent R. The direction of the field through the substituent to the axis of biphenyl was considered as positive one. Thus, the positive field pulls the electrons to the substituent, and negative one pulls them from the substituent. It can cause a rotation between the two phenyl nuclei, causing a change in conductivity of the molecule along the phenyl fragments. Thus, we will have a molecular transistor with the molecular fragment as a base**.**

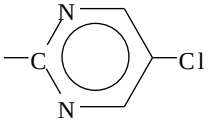


R_1

R_2



R_3



R_4

Methods of research

Quantum chemical investigations were made using the semi-empirical method AM1.[9,10] At first, the geometric structure of the molecule at the configuration interaction absence was found. Next to find the energy minimum depending on the relative orientation of the phenyl groups the calculations were performed by varying the angle in the vicinity of the found values, taking into account the configuration interaction between 12 occupied molecular orbitals (MO) and 12 free MO. The results of this research are processed by the method of least squares approximating the resulting dependence of the parabola. This allows to achieve high accuracy to find the angle between the phenyl fragments for a given value of the electric field.

Method for determining the orientation of a uniform field

First of all, we take a benzene molecule and determine the orientation of the electric field. Positive charges are displaced along the field, and negative are displaced against the field.

Next we use the buffer to place the molecule on the desktop and orient it in the space based on the data obtained for benzene. A test calculation is performed for the two molecules to make sure that the initial benzene molecule is tied to the axis. Charge displacement in the benzene molecule will indicate the direction of the field for the two molecules.

Then benzene molecule is removed from the desktop and we calculate our molecule in the electric field of given magnitude and direction.

Molecule which we examine in the FET mode is oriented so that the long axis of the molecule is perpendicular to the field lines of an external electric field. Furthermore, the electric field lines must lie in the plane of the phenyl fragment and the substituent is at the ortho-

position of this fragment and is acting as the transistor base.

The magnitude and direction of the applied electric field are set by software.

Method for calculation of the non-uniform electric field value.

A nonuniform electric field is produced by a point charge, the anion BF_4^- is a carrier. Since this anion is highly symmetrical (tetrahedral symmetry group), the center of negative charge coincides with the position of the central boron atom. To keep the orientation of the anion relative to the biphenyl molecule unchangeble during all manipulations, boron atom is bond to nitrogen atom (for substituents R1, R2 and R3) or chlorine atom (for the substituent R4) in a single molecule. The distance between these atoms can be easily set.

To determine the electric field intensity, distance r_i from the boron atom to the nitrogen atom or chlorine atom have been measured. If the magnitude of the electric field must be set in atomic units, we use the formula:

$$E_i = \left(\frac{a_0}{r_i} \right)^2 ,$$

where a_o is Bohr radius.

1 a.u. = 5,1421·10^{11} V / m.

The results of researches

Investigation of the dependence of rotation angle between the phenyl rings in the molecule mode transistor (Figure 1) shows that using of nonuniform electric field (the distance between nitrogen atoms and boron ranged from 6 to 2, 8 Å) allows rotation of the phenyl groups in biphenyl only 1 -1.2 degrees.

Quite a different result is obtained by using a uniform electric field (Figure 2b). In this case, the sensitivity of the molecules to the electric field in the FET mode is significantly greater since the uniform electric field interacts with all valence electrons of the molecule.

In particular for E = 0.02 a.u. the uniform electric field sensitivity of the molecule is an order of magnitude greater than the point charge sensitivity.

On the other hand, the relation between the rotation angle of the fragments in the case of placing the molecule in a uniform electric field is rather complicated, since the effect depends on the influence of all molecule valence electrons. This dependence leads to the fact that such a molecule even in the FET mode can be used only as a switch. However, there is a very important detail: there is the electric field strength at which the angle between the phenyl rings is 90°. And it will provide a large relative change in the amount of current which will flow along the axis of biphenyl.

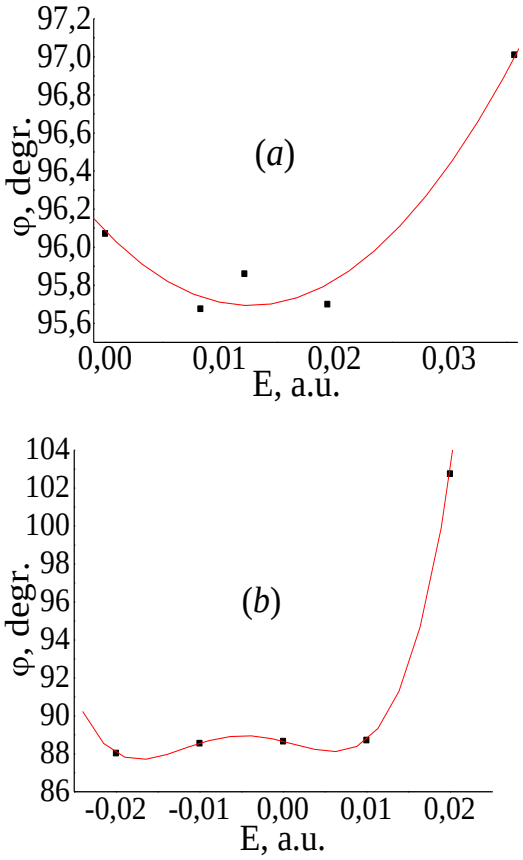


Figure 1. The dependence of the rotation angle between the phenyl rings of the biphenyl molecule with a substituent R1 on the electric field intensity of nonuniform (a) and uniform field (b).

We try to move R_1 substituent from the axis of the molecule by inserting an additional phenyl group (substituent R_2) between them and place the molecule into the uniform electric field (Figure 2).

Since the control group of atoms (nitro group) is removed from the bond between the phenyl groups, the equilibrium angle between them is reduced to 81°. It causes the second effect: the insensitivity of the molecule to the electric field directed from the long axis of the molecule to the substituent (negative direction) and a significant sensitivity to the positive direction of the field, which shifts the electron cloud to the substituent. The effect is quite significant, since the angle of rotation between the phenyl fragments changes to 20°. However, the relative change in the conductivity of the molecule, which is determined by ratio of squares of cosines of 61° and 81°, is only 9.6. Rapid increase of the dependence of the rotation angle on the electric field may cause the using of such a transistor in a mode switch.

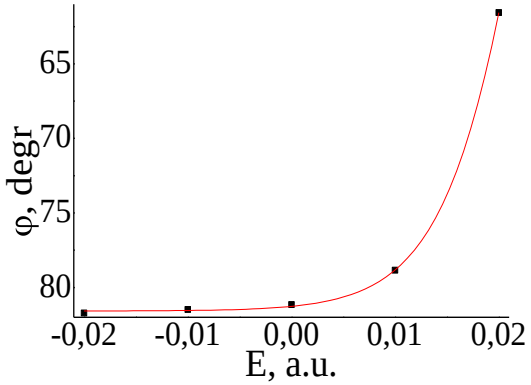


Figure 2. The dependence of the rotation angle between the phenyl rings of the biphenyl molecule with a substituent R_2 on the intensity value of the uniform electric field.

We achieve this effect because the phenyl group in the substituent R_2 does not contain active atom, which has a significant charge focused on it, the value of which could be controlled. Therefore, we have replaced the R_2 substituent with R_3.

Calculations have shown that in the absence of an external field, in the molecules at equilibrium state with a substituent R_3, the angle between the phenyl rings $\phi_{min} = 90{,}855^{\circ}$.

After that we put a molecule into an external electric field caused by the presence of the anion (Table 1). Value of the field is changed by varying distances from the CN_2 group of the substituent to anion along the axis.

Table 1. The dependence of the rotation angle between the phenyl rings of the biphenyl molecule with substituents R_3, R_4 from the intensity values of nonuniform and uniform electric fields

Substituent	Uniform electric field		Nonuniform electric field	
	E, a. u.	ϕ, degr.	E, a. u.	ϕ, degr.
R_3	0	92.5	0	90.855
	-0.01	100.5	0.015	92.25
	0.01	101	0.023	94.02
R_4	0	86	0	91.54
	0.01	87	-0.098	91.46
	-0.01	89	-0.02	91.5
	-0.028	107	-0.035	91.65

Thus, the study of biphenyl molecules with substituent R_3, chosen as a model of molecular transistor, shows that the angle between the phenyl rings can be controlled by external nonuniform electric field of the small value. Although the initial angle between the phenyl fragments are somewhat above 90°, squares of cosinuses ratio of angles between the extreme points reached 25. The molecule placed in a uniform electric field provides significantly (22° against 3,8°) better results than in the nonuniform field.

Comparing data from Figure 2 and obtained data for the substituent R_3 (Table 1) we can see improved results using the biphenyl molecule with substituent R_3 in FET mode. It is interesting that the angle is increased when an external uniform field is on regardless of the polarity of the field. Option $\phi = 90$ ° is absent. Nevertheless, squares of cosines ratio of the angles between the phenyl groups in the field is 0.01 a.u. and without field it reaches 18. We can operate in such fields as the field does not affect the stability of the molecule.

Finally, it is important to upgrade the latest option slightly by replacing only the ending nitro group to a chlorine atom (R_4).

In this molecule the substantial negative charge focuses on the nitrogen atoms of the substituent and the magnitude of this charge depends on the intensity of the uniform electric field. The dependence of the rotation angle between the phenyl rings on the applied uniform electric field is shown in Table1.

Attempts to solve the same problem using a point charge BF_4^- does not provide a good results: the displacement field gave only 0.11. This table does not illustrate the dependence ϕ (E) at increasing of the electric field in the positive direction, as it turns out, this molecule is destroyed (since the chlorine anion is separated on the long molecule axis).

Comparing this result with the data for R_3-biphenyl indicates that both molecules can be used in the transistor mode. However, the substituent R_3-biphenyl is more sensitive to the uniform electric field than the substituent R_4 (for the same values of E = 0.01 a.u.) about 6 times. However, in the case of R_4-biphenyl it is possible to set an angle of 90° between the phenyl fragments. So the application opportunities of this molecule in the FET mode are essentially expanded.

Conclusions

Thus following conclusions based on the research of the possibility of using the substituted biphenyl in FET mode may be drawn:

1. Research of nitro-substituted biphenyl molecules (R1-biphenyl) showed that at the action of the uniform electric field directed perpendicular to the axis of the molecule, the angle between the phenyl fragments sharply increase in excess of the value of the field E = 0.01 a.u., that allows the use of this molecule as a switch even in the transistor mode.

2. Placing of substituted biphenyl in a nonuniform electric field created by a point charge, reveals much (in order) smaller effect than when placing in a uniform electric field.

3. Distancing of nitro groups from the axis of biphenyl using the neutral phenyl (R2-biphenyl) insert leads to decreasing of the angle between the phenyl fragments from 90o to 82o. However, in the uniform external field E = 0.02 a.u. the additional angle of about 20o appears, ensuring opportunity of using of this molecule as in the mode of switcher and in the mode of the field effect transistor. The molecule is sensitive only to positive polarity of the electric field, which increases the magnitude of the negative charge on the nitro group.

4. Replacement of the substituent R2 by R3, which contains the active atoms that are able to control the angle between the phenyl fragments, assists to establish the initial angle close to 90^o and increase the value of this angle regardless of the polarity of a uniform electric field. Of all the tested substituents in molecule biphenyl the substituent R3 provide the greatest sensitivity of the molecule to the electric field, allowing the use of this molecule in the mode of the field effect transistor with the field values ~ 0.01 a.u.

5. Substituent R4 also contributes to the appearance of sensitivity to the electric field, but lesser than in the case of R3. However, in this case the possibility of establishing angle 90o between the phenyl fragments is realized, that significantly increases the possibility of using the molecule R4-biphenyl as a field-effect transistor.

Keywords: moletronics, biphenyl, substituents, switch, transistor.

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GRAPHICAL ABSTRACT

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Molecular transistor based on the biphenyl substituents

Elements of electric circuits of electronic devices, including computers, have a tendency to miniaturization down to molecular dimensions. This paper presents the results of research of a biphenyl molecule as a molecular model of the transistor, certain modes of its work, including the switch mode. With the use of quantum chemical methods it was investigated the affect of uniform and nonuniform, the transverse and longitudinal electric fields on the process of an electron transfer through the molecule.