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COMPARATIVE STUDY OF THE INFLUENCE OF THE REORGANIZATION ENERGY ON THE HOLE TRANSPORT OF TWO FOUR-CYCLIC ARENES

Application of the method of quantum-mechanical calculations allowed the determination of the reorganization energy of the molecules of tetracene and p-quaterphenyl and the estimation of the transfer rate integral between neighbouring molecules present in the solid state. Comparison of the transfer rates for holes with the values of the mobility, obtained experimentally for the polycrystalline tetracene layers and p-quaterphenyl layers vaporized in the vacuum in the similar conditions indicate that the molecule's structure possess the dominate impact on the conductivity of the thin layers of these compounds.

Keywords: reorganization energy, tetracene, p-quaterphenyl, carrier mobility.

1. INTRODUCTION

Arenes have been studied for many years for potential applications in organic electronics. This perspective stimulates research on their electronic and photophysical properties [1-3]. Theoretical calculations using computational methods of quantum-mechanics can contribute to our understanding of the electronic processes decisive on charge carriers transport [4-5]. Electronic

structure of arene molecules have been studied in numerous papers. In this work we focus on finding the origin of the observed difference in the hole mobility values in the thin layers of intrinsic four cyclic arenes. This study is focused on two non-substituted arenes built from four linearly arranged benzene rings, i.e. p-quaterphenyl and tetracene.

Tetracene moiety is built of the rigid skeleton, but p-quaterphenyl moiety is built of the rings which all can rotate. The choice of these compounds is related to the fact that both studied compounds crystallize in a similar crystal lattice with identical motif of "herring bone" arrangement.

Tetracene, with chemical formula $C_{18}H_{12}$ and molecular weight 228.29 g/mol, belongs to triclinic crystal system $P\bar{1}$, $a = 6.0565 \pm 0.0009$ Å, $b = 7.8376 \pm 0.0011$ Å, $c = 13.0104 \pm 0.0018$ Å, $\alpha = 77.127 \pm 0.002°$, $\beta = 72.118 \pm 0,002°$, $\gamma = 85.792 \pm 0.002°$ [6]. The durability of the solid phase is evidenced by its thermodynamic parameters [7] such as melting point 623 K, enthalpy of fusion $\Delta_{fus}H_m(T_{fus}) = 35.9$ kJ/mol and enthalpy of vaporization $\Delta_{vap}H_m(298$ K$) = 87.4$ kJ/mol. Such durability of the layers in the conditions of electronic devices using layered structures [8] allows to treat this material as very promising for future-oriented applications in organic electronics.

P-quaterphenyl with chemical formula $C_{24}H_{18}$ and molecular weight 306.40 g/mol, belongs to monoclinic structure $P2_1/a$, $a = 8.110 \pm 0.006$ Å, $b = 5.610 \pm 0.004$ Å, $c = 17.910 \pm 0.010$ Å, $\beta = 95.80 \pm 0.06°$ [9,10]. Its thermodynamic parameters including melting point 593 - 594 K and enthalpy of fusion $\Delta_{fus}H_m(T_{fus}) = 57.6 \pm 0.9$ kJ/mol and the enthalpy of vaporization $\Delta_{vap}H_m(298$ K$) = 136.1 \pm 3,2$ kJ/mol [7], indicate its stability at room temperatures at which the layers are prepared. They do not show desorption properties up to 360 K during deposition on the Au electrode [11]. Both selected compounds have very similar crystalline characteristics such as packing density and coordination number. They differ only in the rigidity of the molecule skeleton.

2. COMPUTATIONAL PROCEDURES

2.1. Theoretical model

The real mechanism for charge transfer in solid organic materials is often difficult to determine. Generally speaking, in the high temperature limit it is assumed that in π-conjugated organic semiconductors where intermolecular interactions are formed as a result of the presence of weak bonds, the hopping transport is dominated [12]. Such a mechanism of transport is postulated in the

Marcus-Hush model. In compliance with this model the process of transfer of charge carriers through the molecule is connected with two consecutive processes. The first one, related to the internal reorganization energy λ, is relaxation to the state of dynamic equilibrium of the electronic cloud in the molecule, the second one, described by the external energy of reorganization λ_z, is readjustment of the spatial distribution of the nuclei of the atoms that built the molecule to the changed distribution of electron clouds in the molecule. However, the process of charge transfer between neighbouring molecules, related to the overlap of frontier orbitals of these molecules, is described by the transfer integral J_{ij} [2]. The weak bonds existing between molecules are weaker than the covalent bonds inside the molecule. Therefore, the calculation of the energy levels of gas molecules can be used to determine the solid phase transport of the charge carriers in the solid phase [13-14]. Such an approximation allows to conduct the quantum-mechanical calculations and leads to calculations of the values of reorganization energy for hole conductivity in the solid phase using calculations made only for a single molecule in the gas phase. Reorganization energy is a useful tool for description of the transport of both electrons and holes for majority of organic materials, where the hopping transport model can be applied. This is connected with strong localization of the charge in all of the molecules taking part in the conductivity process. Process of transferring charge in the gradient of electric field may be described from the chemical point of view as a series of successive reactions red-ox with transfer of charge [3].

Reorganization energy for hole transport λ_+ may be treated as the sum of two terms, λ_{1+} and λ_{2+}:

$$\lambda_+ = \lambda_{1+} + \lambda_{2+} = \left(E_0^+ - E_+^+\right) + \left(E_+^0 - E_0^0\right). \tag{1}$$

In the above equation, E_0^0 i E_+^+ mean the total energy of the neutral molecule and the cation in their equilibrium structures, respectively, while E_0^+ means the total energy of cation in the neutral molecule geometry, and E_+^0 means the total energy of neutral molecule in the cation geometry. The first term, λ_{1+}, corresponds to the process of cation radical formation, and the second term, λ_{2+}, corresponds to the relaxation of the charged state. The hole transfer rate, K_{el}, seen during the charge carrier transport process may be defined in the scope of the Marcus theory with use of the formula [4]:

$$K_{el} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda_+ kT}} J_{ij}^2 \exp\left(-\frac{\lambda_+}{4kT}\right), \tag{2}$$

where h is Planck constant, k - Boltzmann constant, T - temperature in kelvins, J_{ij} - electron transfer integral calculated between i and j nodes, and λ_+ is reorganization energy for hole and electron. For occurrence of good hole conductivity reorganization energy λ_+ should be low, but the value of the charge transfer energy J_{ij} should be high.

2.2. Quantum-mechanical calculations

In order to determine the internal and external energy values of the reorganization energy for p-quaterphenyl and tetracene calculation of the total energy of the molecule being in neutral or ionized state in the gas phase with use of Eq. (1) is necessary. These calculations were carried out with use of Gaussian-09 package. Since both molecules considered here contains less than 50 atoms, therefore a convenient calculation method is density functional theory (DFT) with use of the B3LYP functional. The B3LYP functional is considered to be excellent in such application and has been applied in many works to calculate the basic states of aromatic hydrocarbons molecules. It is also used in calculations of excited states [15]. Due to the complex range of calculations the functional B3LYP/6-311++G(d,p) was used, with diffusion functions for heavy atoms as well as hydrogen atoms. This approach allowed us to calculate both the distribution of electrons at given position of the nuclei of the atoms forming the molecule and the optimization of the molecule in neutral and ionized state. This level of theory gives a good agreement between the experiment and the calculated energies of orbitals for polycyclic hydrocarbons [4, 5].

3. RESULTS AND DISCUSSION

It has been obtained as a result of optimization using quantum mechanical calculations, that in the case of anthracene and p-quaterphenyl the minimum energy is achieved for plane structures. The benzene rings that form the skeleton of p-quaterphenyl molecule did not show rotation. Both tested molecules did not show a dipole moment.

3.1. Electronic properties

Both the p-quaterphenyl and the tetracene molecules are highly stable. The HOMO energy levels in p-quarterphenyl as well as in tetracene are below -5.1 eV. This low level of HOMO energy indicates the resistance of the studied molecules in respect to atmospheric factors. Resistance of this kind is revealed

during conduction of holes, i.e. using both of molecules as forming layers of a p-type semiconductor [16]. Unfortunately, the high LUMO level energy value above −3 eV, for both tested compounds shows low resistance to atmospheric factors during electron conduction. The lower LUMO level for tetracene ($E_{LUMO} = -2.401$ eV), indicates its better resistance to atmospheric factors during electron conduction than in the case of p-quaterphenyl ($E_{LUMO} = -1.951$ eV).

Table 1

Parameters of electron levels in molecules. Frontier orbitals energies: $HOMO^{(0)}$, $HOMO^{(-1)}$, $LUMO^{(0)}$, $LUMO^{(-1)}$ and the energy of forbidden states for neutral molecule, $\Delta E^{(0)} = LUMO^{(0)} - HOMO^{(0)}$, $\Delta E^{(-1)} = LUMO^{(-1)} - HOMO^{(-1)}$

	p-quaterphenyl	tetracene
$HOMO^{(0)}$ (eV)	−5,754	−5,141
$LUMO^{(0)}$ (eV)	−1,951	−2,401
$\Delta E^{(0)}$ (eV)	3,804	2,740
$HOMO^{(-1)}$ (eV)	−6,659	−6,759
$LUMO^{(-1)}$ (eV)	−1,011	−0,812
$\Delta E^{(-1)}$ (eV)	5,548	5,947

Table 2 presents calculated parameters describing the possibility of disconnecting the electron from the molecule, *IP* (ionization potential of the molecule), electron connection to the molecule, *EA* (electron affinity energy) and two components of reorganization energy: λ_{+1}, λ_{+2} calculated according to formula (1).

Table 2

The parameters describing the effect of molecular structure on hole transport

	p-quaterphenyl	tetracene
IP (eV)	13.865	13.064
EA (eV)	0.957	2.113
λ_{+1} (eV)	0.108	0.054
λ_{+2} (eV)	0.105	0.053

The values collected in Table 3 allow to calculate the charge transfer rate according to formula (3) [17]

$$J_{ij} = 0,5 \, (HOMO^{(0)} - HOMO^{(-1)}) \qquad (3)$$

Analysis of the obtained values indicates that the value of hole transfer rate, calculated with accordance of the formula (2), is significantly different for both

studied molecules. For tetracene, this value is $1{,}19 \cdot 10^{16}$ Hz and it is of order of magnitude greater than for p-quaterphenyl, for which it is equal $9{,}58 \cdot 10^{14}$ Hz. A similar difference, also of an order of magnitude, is observed for experimentally determined mobility values, for layers of these materials obtained under similar conditions and having a polycrystalline structure. For tetracene, the experimentally determined drift mobility is $\mu = 1.6 \cdot 10^{-3}$ cm^{2}Vs^{-1}[18], while for p-quaterphenyl this value is one order of magnitude lower and is equal to $\mu = 9 \cdot 10^{-5}$ cm^{2}Vs^{-1} [19].

Table 3

Comparison of the impact of the reorganization energy value and the value of the overlap integral on the hole transfer rate value K_{el}. For comparison, the table presents experimental values of mobility

	p-quaterphenyl	tetracene
$J_{ij} = 0.5(\text{HOMO}^{(0)}\text{-HOMO}^{(-1)})$ [eV]	0.453	0.809
J_{ij}^2 [eV^2]	0.205	0.654
$\lambda = \lambda_{+1} + \lambda_{+2}$ [eV]	0.212	0.107
K_{el} [Hz]	$9.58 \cdot 10^{14}$	$1.19 \cdot 10^{16}$
μ [cm^{2}Vs^{-1}]	$9.0 \cdot 10^{-5}$	$1.6 \cdot 10^{-3}$

4. CONCLUSIONS

The values obtained by calculations of reorganization energy values λ_+ for holes and values of the transfer integral J_{ij} indicate much easier conduction of holes in tetracene with respect to conduction of holes in p-quaterphenyl. The similar ratio of the speed of transferring holes K_{el}(tetracene)/K_{el}(p-quaterphenyl) $= 1.19 \cdot 10^{16}/9.58 \cdot 10^{14} = 12.4$, as well as mobility ratio μ(tetracene)/μ(p-quaterphenyl) $= 1.6 \cdot 10^{-3}/9 \cdot 10^{-5} = 17.8$ indicate a similar effect of disordered particles on the transport of holes in the polycrystalline layers of both materials.

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STUDIUM PORÓWNAWCZE WPŁYWU ENERGII REORGANIZACJI NA PRZEWODNICTWO DZIUR DWU CZTEROPIERŚCIENIOWYCH ARENÓW

Streszczenie

Zastosowanie metody obliczeń kwantowo-mechanicznych pozwoliło na wyznaczenie energii reorganizacji cząsteczek tetracenu i p-kwaterfenylu oraz oszacowanie wartości całki przenoszenia elektronu pomiędzy sąsiadującymi cząsteczkami znajdującymi się w fazie stałej. Porównanie szybkości przenoszenia dziur z wartościami ruchliwości dziur w polikrystalicznych warstwach tetracenu i p-kwaterfenylu naparowanych w próżni w identyczny sposób wskazuje na dominujący wpływ budowy cząsteczki na przewodnictwo cienkich warstw tych związków.