SCIENTIFIC BULLETIN OF THE LODZ UNIVERSITY OF TECHNOLOGY
No. 1219 Physics, Vol. 38 2017

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THE EFFECT OF THE DIPOLE MOMENT ON HOLE CONDUCTIVITY OF POLYCRYSTALLINE FILMS OF TWO ANTHRACENE DERIVATIVES

Hole mobility in the polycrystalline layers of anthrone and anthraquinone differs in one order of magnitude in spite of nearly the same crystalline structure. The origin of this difference was determined with use of the quantum-mechanical calculations carried out at the density functional theory level using the B3lYP functional in conjunction with the 6-311++G(d,p) basis set. Based on theses calculations, we suppose that these difference can result from the presence of the dipol moment in the anthrone molecules.

Keywords: charge carrier mobility, reorganization energy, transfer integral, anthrone, anthraquinone, TD-DFT, hole drift mobility, carrier transport, dipole moment, polycrystalline films.

1. INTRODUCTION

Anthracene derivatives can be used in organic electronics as the essential active materials for functional devices such as organic light emitting diodes (OLEDs) [1,2] or organic field-effect transistors (OFETs) [2]. Therefore, the proper understanding of the governing charge transport mechanisms in these materials is interesting from both practical and theoretical points of view. The quantity which properly explains the properties of the material in the scope of the charge transport is the electric charge mobility. Information about mobility allows to determine the macroscopic parameters of the device built with use of the certain material. Simultaneously, the range of mobility value is dependent on the microscopic parameters such as the geometrical structure of the molecules, spatial and energetic distribution of the electrons in the molecule and the interactions between neighbouring molecules. The magnitude of the charge carrier mobility is first of all a resultant of such factors as the reorganization energy λ, charge carrier transfer integrals J_{ij} between neighbouring molecules in the lattice points i, j described as the Dexter transfer [3] and the molecules packing in the layer. However, if the molecules that built the layer have a dipole moment then the charge transfer is affected by long range interaction *i.e.* Förster transfer [4].

The Förster coupling understood as the interactions of pairs of permanent dipoles, *i.e.* between the dipole $\mathrm{d}\vec{s}_1$ in the centre of the coordinate system having direction s_1 in the field originated from the network of point dipoles with directions s_n may be described in the form of the sum of interactions with all other dipoles [5]:

$$\delta J_{1\alpha} = \frac{d^2}{2} \sum_{n=2}^{\infty} \left[\frac{\vec{s}_1 \vec{s}_n}{\left|\vec{r}_{1n}\right|^3} - \frac{3\left(\vec{s}_1 \vec{r}_{1n}\right)\left(\vec{s}_n \vec{r}_{1n}\right)}{\left|\vec{r}_{1n}\right|^5} \right], \tag{1}$$

where r_{1n} is a position of n-th dipole and α denotes a manifold of the network of point dipoles. This type of interaction may increase the dispersion of distribution of localized energy levels, what should influence a change in mobility value.

Problems presented in this paper are related to the different values of mobility in two anthracene derivatives almost identical in the crystallographic sense. The presented discussion concerns the results of quantum-mechanical calculations carried out for molecules of two compounds with significant difference in value of permanent dipole moment. Microscopic picture of phenomena occurring during transfer of charge carriers is described in the scope of Marcus-Hush theory. We treat the presence of long range Förster coupling as a modification of the model mentioned above.

Two similarly substituted aromatic hydrocarbons derived from anthracene, *i.e.* anthrone and anthraquinone were chosen as the basis of our studies. Both compounds crystallize in the nearly identical crystal lattices [6], *i.e.* monoclinic with space group $C_{2h}^5(P2_1/a)$ with bimolecular unit cell of the dimensions a_0 = 15,8 Å, b_0 = 3,94 - 3,99 Å, c_0 = 7,865(10) Å, β = 102°43(2)' for anthraquinone and a_0 = (15.80±0.03) Å, b_0 = (3.998±0.005) Å, c_0 = (7.86±0.16) Å, β = 101°40' for anthrone (at room temperature) [7]. The main essential difference due to the considerations discussed here is that the anthraquinone molecules, being centrosymmetric, possess dipole moment equal nearly zero, opposite to the non-centrosymmetric anthrone molecules which are characterised by large dipole moment of 3.5 D (1.19·10^{-29} Cm) (measured in benzene) [8].

2. THEORETICAL DESCRIPTIONS

2.1. Application of the Marcus-Hush theory

Intermolecular hole transfer rate, K_{el}, during charge transport can be described on the basis of Marcus-Hush theory [9, 10] by:

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

where h is the Planck constant, k - Boltzmann constant, T – absolute temperature in Kelvin scale, J_{ij} – charge transfer integral for the hole transfer between the molecules i and j, and λ_+ refers to the reorganization energy for holes. Higher values of the hole mobility are possible when the reorganization energy λ_+ is small and the transfer integrals J_{ij} for holes are high. The reorganization energy for the hole conductivity λ_+ is calculated as the sum of two terms: λ_c for the energy needed for reorganization of the neutral molecule geometry to the cation geometry upon removal an electron and λ_n for the energy needed for reorganization to obtain cation geometry back to a neutral state upon re-accepting an electron. Therefore, in order to be able to determine the energy of reorganization for hole conductivity, it is necessary to calculate the total energy values of the molecule in the following states: optimized neutral state, E_{nn}, optimized cation state, E_{kk}, cation in the neutral geometry, E_{kn}, and the neutral molecule in the cation geometry, E_{nk}:

$$\lambda_+ = \lambda_c + \lambda_n = \left(E_{kn} - E_{kk}\right) + \left(E_{nk} + E_{nn}\right). \tag{3}$$

The transfer integral for hole conductivity, J_{ij}, can be calculated using Koopmann theorem working well independently of the distance between neighbouring molecules [11]. Its value is calculated to be equal to half of the difference between the energies of the HOMO (high occupied molecular orbital) and the next -highest occupied molecular orbital, the $\mathrm{HOMO}^{(-1)}$ [12,13] which can be written by the following formula:

$$J_{ij} = 0.5 \cdot \left(HOMO - HOMO^{(-1)}\right). \tag{4}$$

This approach is based on tight binding formalism, assuming that the HOMO states at the ground state of neutral molecule is similar to the HOMO of the cationic species. We analyse two materials with molecules differ only by substitution group, and the presence of dipole moment, therefore the approach presented in this article (eqs. (2), (3) and (4)) should allow us to relate transport properties to chemical structure at least qualitatively.

2.2. Computational methodology

The gas phase anthrone and anthraquinone molecules are optimized separately in the neutral and cation states using density functional theory (DFT). The calculations are conducted by means of B3LYP functional, in which Becke's three-parameter hybrid exchange functional [14] is combined with the Lee-Yang-Parr correlation functional [15]. We use a basis set with diffuse functions, namely the basis 6-311++G(d,p) as was implemented in the Gaussian 09 quantum-mechanical package [16]. Basis set with diffuse functions is important for molecular system where electrons are relatively far from nucleus, *i.e*. systems in their excited states, systems with low ionization potential. The calculations on the cationic species were performed with use of the unrestricted B3LYP formalism. The basis set with diffuse functions 6-311++G(d,p) allows theoretical determination of all parameters appearing in the Marcus-Hush equation (2), including the four energies of molecules that appear in the equation (3) and the transfer integral defined by the equation (4).

3. RESULTS AND DISCUSSION

The calculated differences of the bond lengths for anthrone and anthraquinone molecules in the gas phase in comparison to the solid state are published in [17]. We are currently presenting the visualization of the electronic clouds of the frontier orbitals of both molecules under study and of anthracene molecule properties taken as a reference. Figures 1-3 represent the occupied HOMO and HOMO$^{(-1)}$ orbitals and unoccupied LUMO orbitals. The visualization of frontier orbitals presented in Figs. 1-3 indicates that the electron clouds of these orbitals are concentrated on the anthracene skeleton. The anthracene molecules retain the shape of frontier orbitals in all of the considered states *i.e*. optimized neutral molecule, optimized cation, neutral molecule in cation geometry and cation in neutral molecule geometry (Fig. 3).

The shape of frontier orbitals of two derivatives of anthracene under study do not show such behaviour (Figs. 1 and 2). We note that the shape of corresponding frontier orbitals for considered two anthracene derivatives are different from that which has the unsubstituted anthracene. Such a situation is observed either for neutral molecules as for cations.

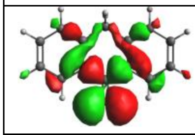
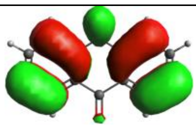
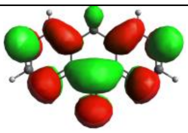
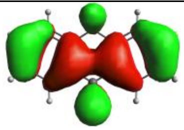
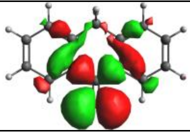
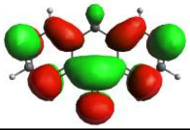
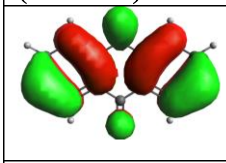
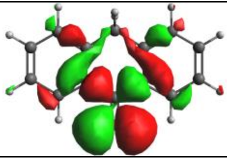
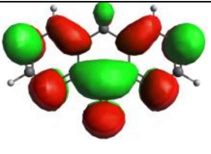
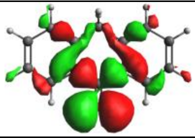
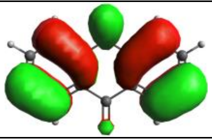
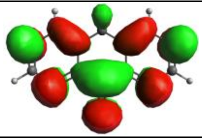
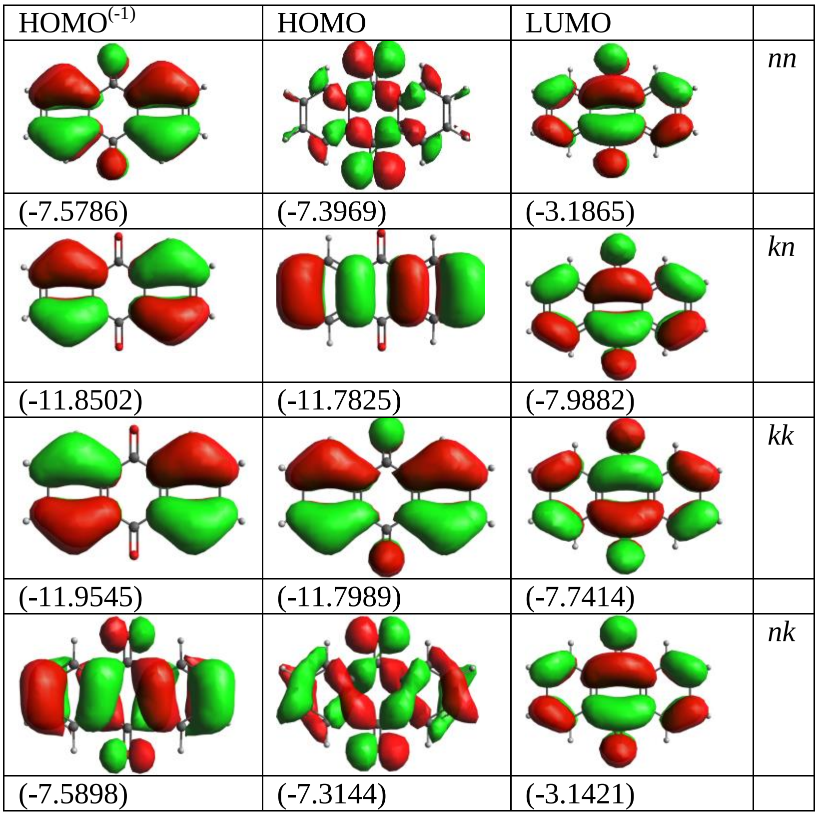
HOMO$^{(-1)}$	HOMO	LUMO	
			*nn*
(-7.0425)	(-6.9928)	(-2.1437)	
			*kn*
(-11.5403)	(-11.0816)	(-6.3318)	
			*kk*
(-11.4842)	(-11.1246)	(-6.2807)	
			*nk*
(-7.0818)	(-6.8230)	(-2.1004)	

Fig. 1. Frontier orbitals having direct participation in electron transitions in anthrone, calculated orbitals energies are given in eV (*nn* - optimized geometry of neutral molecule, *kk* - optimized cation, *kn* - cation in the geometry of neutral state, *nk* - neutral molecule in geometry of cation)

The asymmetry of substitution in the anthrone molecule is clearly manifested in the asymmetry of the spatial distribution of its frontier orbitals. The presence of this asymmetry is seen in the greater increase in the number of nodal points in the space distribution of frontier orbitals for anthraquinone in neutral forms than for the cation forms. The removal of the electron from a molecule has a considerable effect on the energy of all orbitals, strongly reducing this energy. All cation orbitals are binding, what means the stability of both the molecule in a neutral state and being a cation. However, the energy differences between them are maintained, *i.e.* between the energy levels of HOMO and HOMO$^{(-1)}$ and between the energy levels of LUMO and HOMO for all calculated structures of a given molecule.



HOMO$^{(-1)}$	HOMO	LUMO	
			nn
(-7.5786)	(-7.3969)	(-3.1865)	
			kn
(-11.8502)	(-11.7825)	(-7.9882)	
			kk
(-11.9545)	(-11.7989)	(-7.7414)	
			nk
(-7.5898)	(-7.3144)	(-3.1421)	

Fig. 2. Frontier orbitals having direct participation in electron transitions in anthraquinone. Calculated orbitals energies are given in eV (*nn* - optimized geometry of neutral molecule, *kk* - optimized cation, *kn* - cation in the geometry of neutral state, *nk* - neutral molecule in geometry of cation)

Reorganization energies for hole conductivity calculated for the molecules of anthrone, anthraquinone and anthracene are presented in Table 1, whereas in Table 2 the values of the hole transfer rate for above mentioned compounds, calculated with use of the procedure exploits the formulas (1) and (2), are presented.

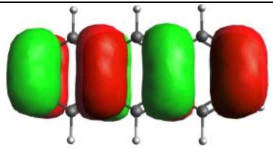
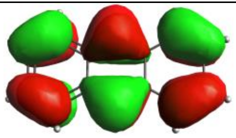
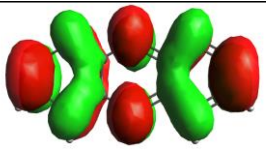
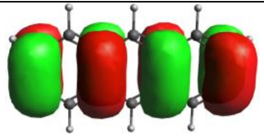
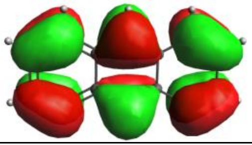
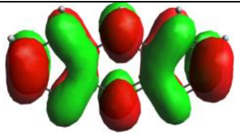
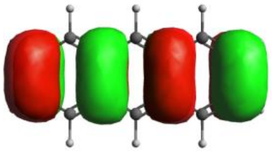
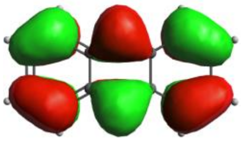
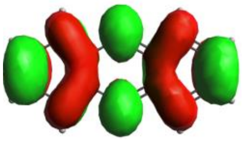
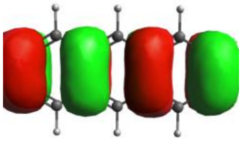
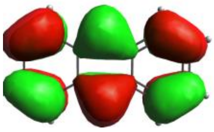
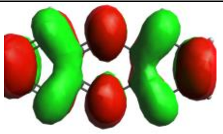
HOMO$^{(-1)}$	HOMO	LUMO	
			*nn*
(-6.7503)	(-5.5538)	(-1.9355)	
			*kn*
(-11.1330)	(-10.2922)	(-6.6254))	
			*kk*
(--11.836)	(-10.1681)	(-6.777)	
			*nk*
(6.8678)	(-5.4415)	(-2.1568)	

Fig. 3. Frontier orbitals having direct participation in electron transitions in anthracene, calculated orbitals energies are given in eV (*nn* - optimized geometry of neutral molecule, *kk* - optimized cation, *kn* - cation in the geometry of neutral state, *nk* - neutral molecule in geometry of cation)

On the basis of the results presented in the tables we can conclude that the reorganization energy for anthrone is higher by 0.040 eV than that for anthraquinone. The transfer rate for holes is higher by one order of magnitude for anthraquinone $K_{el} = 1.020 \cdot 10^{14}$ Hz, than for anthrone, $K_{el} = 4.659 \cdot 10^{12}$ Hz. The above would suggest that the hole transfer under unit electric field in anthraquinone should be easier. Experimental results presented in Table 3 suggest that the hole mobility in anthrone is much greater than in anthraquinone. The hole mobility for anthrone $\mu = (7 \pm 2) \cdot 10^{-3}$ cm^2(Vs)$^{-1}$ is almost one order of magnitude higher than for anthraquinone, $\mu = (8 \pm 2) \cdot 10^{-4}$ cm^2(Vs)$^{-1}$. The anthrone molecule in comparison to the molecule of anthraquinone possess strong dipole moment, whose value measured in benzene is $\mu_d = 3.5$ D in comparison to the almost zero value of the dipole moment for anthraquinone. Taking into account the above consideration, it can be assumed that the correction of the Förster transfer in the formula for the transfer integral for charge carrier transfer can't be neglected and it can be assumed that magnitude of the mobility value is strongly influenced by the dipole moment.

Table 1

The results of quantum-mechanical calculations (functional B3LYP/6-311++(G(d,p)): orbitals energy levels of HOMO and LUMO as well as the reorganization energy for hole conductivity, vertical ionization energy IP_v and vertical electron affinity EA_v.

compound	HOMO	LUMO	Reorganization energy for hole conductivity, λ+	IP_v	EA_v
	[eV]	[eV]	[eV]	[eV]	[eV]
anthrone	-6.992	-2.144	0.173	-8.59	-0.57
anthraquinone	-7.396	-3.186	0.135	-9.09	-1.60
anthracene	-5.553	-1.936	0.139 (0.136 [11])	-7.16	-0.49

Table 2

Calculation of the hole transfer rate with use the formulas (1) and (2)

compound	J_{ij} [eV]	J_{ij}^2 [eV^2]	λ [eV]	$\exp(-\lambda/(4kT))$	K_{el} [Hz]
anthrone	0.0249	$6.199 \cdot 10^{-4}$	0.173	0.1873	$4.659 \cdot 10^{12}$
anthraquinone	0.0909	$8.260 \cdot 10^{-3}$	0.135	0.2715	$1.020 \cdot 10^{14}$
anthracene	0.5982	$3.579 \cdot 10^{-1}$	0.139	0.2611	$4.187 \cdot 10^{15}$

Table 3

Experimentally obtained hole mobility values in the polycrystalline layers of anthrone and anthraquinone [18])

compound	μ [cm^2(Vs)$^{-1}$]
anthrone	$(7 \pm 2) \cdot 10^{-3}$
anthraquinone	$(8 \pm 2)\ 10^{-4}$

ACKNOWLEDGEMENTS

We would like to express gratitude to prof. B. Marciniak and dr Ewa Różycka-Sokołowska for valuable discussions and to prof. Wieczorek for preparation of the spectral grade anthraquinone and anthrone and for enabling the X-ray analysis.

The calculations presented in this paper are performed using the PLATON project's infrastructure at the Computer Center of Lodz University of Technology.

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WPŁYW MOMENTU DIPOLOWEGO NA PRZEWODNICTWO DZIUR W WARSTWACH POLIKRYSTALICZNYCH DWU POCHODNYCH ANTRACENU

Streszczenie

Ruchliwości dziur w polikrystalicznych warstwach antronu i antrachinonu różnią się prawie o jeden rząd wielkości, pomimo niemal tej samej struktury krystalicznej. Źródło tej różnicy próbowano określić przy użyciu obliczeń kwantowo-mechanicznych przeprowadzonych na poziomie teorii funkcjonału gęstości (DFT) z wykorzystaniem funkcjonału B3LYP, stosując funkcje bazy 6-311++G(d,p). Na podstawie tych obliczeń przypuszczamy, że ta różnica jest wynikiem obecności momentu dipolowego w cząsteczkach antronu.