

**SYLWESTER KANIA<sup>1,2</sup>, BARBARA KOŚCIELNIAK-MUCHA<sup>2</sup>  
JANUSZ KULIŃSKI<sup>2</sup>, PIOTR SŁOMA<sup>2</sup>  
KRZYSZTOF WOJCIECHOWSKI<sup>2</sup>**

<sup>1</sup> Institute of Physics, Lodz University of Technology, ul. Wólczańska 219, 90-924 Łódź, Poland, e-mail: if@p.lodz.pl

<sup>2</sup> Centre of Mathematics and Physics, Lodz University of Technology, al. Politechniki 11, 90-924 Łódź, Poland, e-mail cmf.adm@p.lodz.pl

## **POLARIZATION OF ORGANIC AROMATIC MOLECULE IN ANIONIC AND CATIONIC STATE**

*The modification of electron states and the change in the geometry of the structure of molecule during hopping transport of charge carriers depends on the symmetry of the molecule. During electric transport the molecule reversibly transforms from neutral state to cation when hole conductivity occurs or to anion when electron conductivity occurs. The energies of orbitals HOMO and HOMO-1 of anthrone and anthraquinone are always negative, what allows for holes transport. Positive energies of LUMO and LUMO+1 orbitals of anion of anthrone and anthraquinone in structure of anion or neutral molecule make electron transport difficult.*

**Keywords:** DFT, anthraquinone, anthrone, charge transport.

### **1. INTRODUCTION**

The results of quantum-chemical calculations allow to specify the hopping conduction parameters at the molecular level [1, 2, 3]. Conduction in a high-resistance material occurs in two stages. The first stage is the takeover of a charge carrier by the molecule in the form of the entire electron or entire hole. The second stage is transferring a single electron between neighbouring molecules [4, 5, 6]. This process should be independent of the existence of bonds between molecules of organic material and it cannot be carried out in such a way that solid phase damage would occur. Maintaining stability of solid phase in the organic semiconductor under equilibrium conditions is possible due to the

existence of van der Waals or London dispersion forces [7] appearing when the electron density fluctuations of neighbouring molecules occur. The lack of charge transfer of the value of the charge of the whole electron from one molecule to another is a special feature of such binding interactions. Even if the above-mentioned interactions are strong, they are not accompanied by the transfer of charge equal or greater than the charge of one electron from one molecule to another. There is also no strong localization of an electron pair between neighbouring molecules what is a special property of covalent bond. The strength of intermolecular interactions is significantly determined by the distance between the centers of mass (centroids) of the molecules, but the twisting of the planes of molecules relative to each other also plays an important role. Possibility of occurrence of favourable  $\pi$ -stacking interactions between molecules for electric conduction depends on the orientation of molecules. At equilibrium, the distance between centroids of the organic molecules forming the crystalline solid phase is quite significant, and in the case of anthracene and its derivatives is of the order of 4 Å. When the distance between the centers of the molecules is above about 8 Å then the molecules practically do not interact and the molecular orbitals do not contribute to conductivity [5]. The lack of charge transfer between molecules in dispersion interactions allows treating these interactions almost as a kind of physical adsorption or chemisorption. There is no spontaneous unilateral flow of electrons between adjacent molecules under equilibrium conditions therefore, an effective equilibrium for red-ox reactions connected with electron taking over by molecules is observed. However, polarization by an external electric field causes current flow through layers made of organic molecules which involves the molecules to uptake the electrons. Thus, there must be a step when the next molecule takes over the entire electron previously released from the preceding molecule during the charge carrier transfer process.

This electron exchange between neighbouring molecules can be considered as a chemical reaction. Marcus-Hush theory [4] enables to understand the process of conduction as a red-ox reaction string to which organic matter molecules are subjected while transferring charge carriers occurs. This theory was used to describe hopping conduction in organic materials in the 1990s. Total charge of a molecule changes during the process of charge transfer. Molecule transferring an electron as a negative charge carrier becomes an anion for a short time, while a molecule carrying a positive charge carrier (hole) becomes a cation for a short time. The molecule returns to the neutral state after completing such a red-ox reaction which is the special feature of this process. The molecule does not dissociate into fragments and has the same properties as before the process of taking charge and transferring the charge carrier. The energy effect associated with such a process can be calculated as reorganization energy [1, 5].

The value of the reorganization energy for conduction of holes is  $\lambda_+$

$$\lambda_+ = \lambda_c + \lambda_n = (E_{kn} - E_{kk}) + (E_{nk} + E_{nn}), \quad (1)$$

where  $\lambda_c$  is the energy necessary for the reorganization of the neutral geometry of molecule to the cation geometry during electron removal. The symbol  $\lambda_n$  denotes the energy necessary for the reorganization to change the cation geometry again to the neutral geometry when attached electron from the neighbouring molecule.

Therefore, to determine the reorganization energy for hole conductivity, the total energy for the molecule in the following states should be determined:

- $E_{nn}$  is optimized state of the neutral molecule,
- $E_{kk}$  is optimized state of the molecule being a cationic radical,
- $E_{kn}$  is optimized state of the molecule being a cation in the structure of a neutral molecule,
- $E_{nk}$  is optimized state of the neutral molecule in the cation structure.

Similar calculations are carried out in the case of reorganization energy calculation,  $\lambda_-$  for electron transport

$$\lambda_- = \lambda_c + \lambda_n = (E_{an} - E_{aa}) + (E_{na} + E_{nn}), \quad (2)$$

Here,  $\lambda_-$  is calculated as the sum of  $\lambda_c$  for the energy necessary to reorganize the geometry of the neutral molecule to the anion geometry when attaching the electron, and  $\lambda_n$  for the energy necessary for the reorganization to change the geometry of the anion again to the geometry of the neutral molecule when the electron is donated to the neighbouring molecule.

Therefore, to determine the reorganization energy for electron transport, the total energy for a molecule in the following states should be determined as follows:

- $E_{nn}$  is optimized state of the neutral molecule,
- $E_{aa}$  is optimized state of the molecule being an anionic radical,
- $E_{an}$  is optimized state of the molecule being anion in the structure of the neutral molecule,
- $E_{na}$  is optimized state of the neutral molecule in the anion structure.

Experimental results revealed that the mobilities of charge carriers are different in the case of conduction of layers of two anthracene derivatives. This difference is observed for both crystalline and amorphous samples [8]. It was shown in our previous work [1] that this difference has its origin in the existence of a constant dipole moment in anthron molecules and lack of it in anthraquinone molecules. Analysis of solid phase X-ray studies [4, 7] and our quantum mechanical calculations carried out for both considered molecules [9]

proved that the change in aromatic stabilization energy, calculated relative to unsubstituted anthracene, is practically the same and amounts to approx. 1%. This feature is observed despite of the fact that the central benzene ring of anthrone molecule is substituted with one ketone group and for anthraquinone molecule central benzene ring is substituted symmetrically with two ketone groups. This is accompanied by an almost equal change in the length of bonds between carbon atoms in the side and the middle rings, which is about 6.4% for both molecules under study. Thus, there is no noticeable steric effect associated with symmetrical or asymmetrical substitution of the middle anthracene ring with one or two ketone groups on reorganization energy.

The question arises here whether the polarity of the molecule has an impact on the stability of the excited states of the cation and anion and enables hole or electron transport.

We want to find answer to this question calculating the states of external orbitals (FMO) of the two molecules under consideration. We carry out analysis of the states of molecules that are used to define the reorganization energy defined by formula (1) for transport of holes and formula (2) for electron transport.

## 2. CALCULATION RESULTS AND DISCUSSION

The "four-point" [1, 5] method (Eqs. (1) and (2)) was used to calculate the reorganization energy. DFT calculations were carried out using the Gaussian 09 program [10] at the level of theory B3LYP/6-311+G(d, p). The calculations in the scope of the "four-point" method required the calculation of the structure of the molecule in the cation, anion and in the neutral state. They were performed for molecules in the gas phase. The choice of calculations in the gas phase is associated with the observation that the strong localization of charge carriers on molecules in oligoacene derivatives causes that the electronic states of the molecule are similar in the gas phase and in the solid phase [11]. The shift caused by the presence of the crystal field is almost constant for all external orbitals given molecule [12]. The differences in the energy of external orbitals and not their absolute values are important for our considerations.

An interesting problem is the possibility of realizing a stable molecule in the cation or anion state. In order to answer this question, the calculation of the energy value of the levels HOMO, HOMO-1, LUMO and LUMO+1 is required. LUMO levels are important for electron conduction while HOMO levels are important for conduction of holes. The molecule is not stable in the gas phase when the obtained energy values of the orbital are non-negative. The additional

multi-body interactions that counteract the destruction of the solid phase caused by the flow of the charge carrier through the molecule appear in the presence of particles in the solid phase.

The results of quantum-chemical calculations obtained by us allow for preliminary determination of cation and anion stability. Tables 1 and 2 show the results of calculations for the anthraquinone and the anthron molecules, respectively. Both molecules are derivatives of anthracene, and they crystallize in almost the same crystal structure with similar lattice constants [13, 14]. The results for the unsubstituted anthracene molecule are shown in Table 3 for comparison.

Table 1  
Calculated electronic properties of molecule of anthraquinone during transfer of charge carrier

	1	2	3	4	5	6	7	8
			[D]	[eV]	[eV]	[eV]	[eV]	[eV]
cation in cation structure	+1	doublet	0.0033	-11.9545	-11.9376	-7.7414	-6.2945	4.196
cation in neutral structure	+1	doublet	0.0003	-11.8503	-11.7825	-7.9882	-6.3789	3.794
neutral in cation structure	0	singlet	0.0003	-7.5898	-7.3144	-3.1421	-2.0180	4.172
<b>neutral in neutral structure</b>	<b>0</b>	<b>singlet</b>	<b>0.0003</b>	<b>-7.5786</b>	<b>-7.3969</b>	<b>-3.1865</b>	<b>-2.0583</b>	<b>4.210</b>
neutral in anion structure	0	singlet	0.0002	-7.5814	-7.4741	-3.5329	-2.1062	3.941
anion in neutral structure	-1	doublet	0.0003	-2.7900	-0.0185	1.9124	2.2757	1.930
anion in anion structure	-1	doublet	0,0001	-2.8806	-0.3777	1.8607	2.2640	2.238

1 - charge, 2 - spin, 3 - dipole moment, 4 - HOMO-1, 5 - HOMO, 6 - LUMO, 7 - LUMO+1, 8 -  $E_g$ .

Table 2  
Calculated electronic properties of molecule of anthrone during transfer of charge carrier

	1	2	3	4	5	6	7	8
			[D]	[eV]	[eV]	[eV]	[eV]	[eV]
cation in cation structure	1	doublet	4.7756	-11.4843	-11.1246	-6.2806	-5.5054	4.843
cation in neutral structure	1	doublet	4.7156	-11.5403	-11.0816	-6.3318	-5.3854	4.750
neutral in cation structure	0	singlet	3.8761	-7.0818	-7.0042	-2.1004	-1.0653	4.904
<b>neutral in neutral structure</b>	<b>0</b>	<b>singlet</b>	<b>3.8667</b>	<b>-7.0426</b>	<b>-7.2649</b>	<b>-2.1437</b>	<b>-0.9442</b>	<b>5.121</b>
neutral in anion structure	0	singlet	4.0854	-7.1332	-7.0290	-2.5007	-0.8898	4.528
anion in neutral structure	-1	doublet	4.6776	-2.2101	0.9891	2.2601	2.3587	1.271
anion in anion structure	-1	doublet	4.8151	-2.2422	0.6059	2.2490	2.3467	1.643

1 - charge, 2 - spin, 3 - dipole moment, 4 - HOMO-1, 5 - HOMO, 6 - LUMO, 7 - LUMO+1, 8 -  $E_g$ .

In the case of hole conductivity, both HOMO and HOMO-1 levels for anthraquinone, anthron and anthracene are significantly below the vacuum level. Thus, we can conclude that conduction of holes is always possible both for anthraquinone and for anthrone. The energy values of the LUMO and LUMO+1 levels are decisive for electron conduction. For the molecule in the neutral state in the neutral structure as well neutral in the anion structure for both

anthraquinone and anthrone molecules the energies of the LUMO and LUMO+1 levels are negative. However, the transition of the molecule to the anion structure (in the  $-1$  charge state) leads to positive high energy values (above 1.8 eV) of the LUMO and LUMO+1 orbitals. Even if the energy shift caused by the presence of a crystal field is taken into account, which according to some estimates for anthracene derivatives may have a value of even 1.7 eV [12], the energy values of LUMO orbitals do not allow maintaining anion stability in solid state. This means that the implementation of effective transport of negative carriers in anthraquinone and anthrone is difficult. Moreover, in the case of anthrone, the positive energy of its HOMO level in the anion state indicates that obtaining a stable anion of the anthrone is difficult.

Table 3  
Calculated electronic properties of molecule of anthracene during transfer of charge carrier

	1	2	3	4	5	6	7	8
			[D]	[eV]	[eV]	[eV]	[eV]	[eV]
cation in cation structure	1	doublet	0	-11.1836	-10.1681	-6.7775	-4.9838	3.390
cation in neutral structure	1	doublet	0	-11.1330	-9.4758	-6.6254	-5.0630	2.850
neutral in cation structure	0	singlet	0	-6.8676	-5.4415	-2.1568	-0.6900	3.284
<b>neutral in neutral structure</b>	<b>0</b>	<b>singlet</b>	<b>0</b>	<b>-6.7988</b>	<b>-5.5764</b>	<b>-2.0240</b>	<b>-0.7483</b>	<b>3.552</b>
neutral in anion structure	0	singlet	0	-6.8856	-5.4564	-2.2120	-0.7581	3.236
anion in neutral structure	-1	doublet	0	-1.5913	1.0294	2.4330	2.4751	1.403
anion in anion structure	-1	doublet	0	-1.4909	0.8297	2.4251	2.4624	1.595

1 - charge, 2 - spin, 3 - dipole moment, 4 - HOMO-1, 5 - HOMO, 6 - LUMO, 7 - LUMO+1, 8 -  $E_g$

Despite the similarity of the molecules and the structures in which they crystallize, there is a significant difference in the value of the energy gap  $E_g$  between molecules under consideration. Anthrone having a permanent dipole moment has the value of the energy gap clearly higher than anthraquinone and anthracene.

### 3. CONCLUSIONS

The results of calculation clearly indicate the high stability of the anthraquinone and the anthrone cations. The conductivity of holes in solid phase is possible for both materials in this situation.

A high positive value of LUMO and LUMO+1 levels for anthraquinone above 1.8 eV does not allow for stable electron conduction in anthraquinone solid phase. However, the negative value of the HOMO level for the anion

allows the molecule to move through the solid phase to the basic level of the anion, in the ionization state +1. This allows application of anthraquinone in the form of a solid phase for the needs of technology used in electrochemical environment.

The high positive value of HOMO, LUMO and LUMO+1 levels for the anthrone does not allow the anthrone to be obtained in a stable anion state. This makes effective electron transport for applications in organic electronics more difficult to accomplish. It should be noted, however, that the properties of anthrone anion are more favourable for applications than the properties of unsubstituted anthracene anion.

Despite the similarity of the molecules and structures in which they crystallize, there is a significant difference in the value of the energy gap  $E_g$  between anthrone, anthraquinone and anthracene.

The obtained results indicate other areas of possible applications of anthraquinone and anthrone in organic electronics.

The high value of the forbidden gap can be beneficial for the use of both materials for the production of active layers in solar cells, where high resistance is required due to the need to separate generated charges.

## REFERENCES

- [1] Oberhofer H., Reuter K., Blumberger J. 2017. Charge transport in molecular materials: an assessment of computational methods. *Chem. Rev.* 117: 10319-10357. <https://doi.org/10.1021/acs.chemrev.7b00086>
- [2] Kukhta A.V., Kukhta I.N., Kukhta N.A., Neyra O.L., Meza E. 2008. DFT study of the electronic structure of anthracene derivatives in their neutral, anion and cation forms. *J. Phys. B: At. Mol. Opt. Phys.* 41: 20, 205701. <https://doi.org/10.1088/0953-4075/41/20/205701>
- [3] Wen S.-H., Li A., Song J., Deng W.-Q., Han K.-L., Goddard III W.A. 2009. First-principles investigation of anisotropic hole mobilities in organic semiconductors. *J. Phys. Chem. B* 113: 8813-8819. <https://pubs.acs.org/doi/10.1021/jp900512s>
- [4] Marcus R.A. 2000. Tutorial on rate constants and reorganization energies. *J. Electroanal. Chem.* 483: 1-2, 2-6. [https://doi.org/10.1016/S0022-0728\(00\)00011-5](https://doi.org/10.1016/S0022-0728(00)00011-5)
- [5] Datta A., Mohakud S., Pati S.K. 2007. Electron and hole mobilities in polymorphs of benzene and naphthalene: role of intermolecular interactions. *J. Chem. Phys.* 126: 144710-1-144710-6. <https://doi.org/10.1063/1.2721530>
- [6] Marcus R.J. 1993. Electron transfer reactions in chemistry. Theory and experiment. *Rev. mod. phys.* 65: 3, 599-610. <https://doi.org/10.1103/RevModPhys.65.599>
- [7] Ehrlich S., Moellmann J., Grimme S. 2012. Dispersion-corrected density functional theory for aromatic interactions in complex systems. *Accounts Chem. Res.* 46: 4, 916-926. <https://www.pubs.acs.org/accounts/10.1021/ar3000844>

- [8] Kania S. 2014. Hole drift mobility of anthrone and anthracinone layers with different structures. *Sci. Bull. Techn. Univ. Lodz, Physics*, 35: 17-24. <http://cybra.lodz.pl/dlibra/publication/15667/edition/12516/content>
- [9] Kania S., Kuliński J., Sikorski D. 2018. The origin of the interaction responsible for the difference of hole mobility of two derivatives of anthracene. *Sci. Bull. Techn. Univ. Lodz, Physics*, 39: 27-35. <https://doi.org/10.34658/physics.2018.39.27-35>
- [10] Gaussian 09, Revision A.02. 2009. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Peralta Jr., J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas O., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J., Wallingford CT: Gaussian, Inc.
- [11] Skobel'tsyn D.V. 1966. Chapter III The oriented gas model and its application to molecular crystals polarization diagrams of luminescence. in: *Physical optics. The Lebedev Physics Institute series*. 25: 44-66. [https://doi.org/10.1007/978-1-4684-7206-6\\_3](https://doi.org/10.1007/978-1-4684-7206-6_3)
- [12] Choi S.-I., Jortner J., Rice S.A., Silbey R. 1964. Charge transfer exciton states in aromatic molecular crystals. *J. chem. phys.* 41: 3294-3306. <http://dx.doi.org/10.1063/1.1725728>
- [13] Fu Y. 1998. Temperature dependence of the rigid-body motion of anthraquinone. *Acta Cryst. B54*, 308-315. <https://doi.org/10.1107/S0108768197013414>
- [14] Srivastava S.N. 1962. Crystal structure of anthrone. *Z. Krist.* 117: 5-6, 386-398. <https://doi.org/10.1524/zkri.1962.117.5-6.386>

## POLARYZACJA CZĄSTECZKI AROMATYCZNEJ W STANIE ANIONU I KATIONU

### Streszczenie

Wyniki obliczeń jednoznacznie wskazują na dużą stabilność kationów antrachinonu i antronu. Realizacja przewodnictwa dziur jest w tej sytuacji możliwa dla obu materiałów. Wysoka dodatnia wartość poziomów LUMO



i LUMO+1 dla antrachinonu powyżej 1,8 eV nie pozwala na uzyskanie stabilnego przewodzenia elektronów w fazie stałej antrachinonu. Jednak ujemna wartość poziomu HOMO dla anionu pozwala na przejście cząsteczki w fazie stałej do podstawowego poziomu anionu w stanie jonizacji +1. Pozwala to na wykorzystanie antrachinonu w postaci fazy stałej dla potrzeb technologii wykorzystującej środowisko elektrochemiczne. Wysoka wartość dodatnia poziomów HOMO oraz LUMO i LUMO +1 dla anionu antronu utrudnia uzyskanie efektywnego przewodzenia elektronów dla zastosowań w technologii elektroniki organicznej. Jednak dzięki posiadaniu podstawnika, własności anionu antronu są korzystniejsze dla zastosowań niż własności anionu niepodstawionego antracenu. Pomimo podobieństwa cząsteczek i struktur, w jakich krystalizują, występuje znacząca różnica w wartości przerwy energetycznej  $E_g$  pomiędzy antronem i antrachinonem. Uzyskane wyniki wskazują na inne obszary możliwych zastosowań antrachinonu i antronu w elektronice organicznej. Wysoka wartość energii przerwy zabronionej może być korzystna dla zastosowań obu materiałów do wytwarzania warstw aktywnych w komórkach słonecznych, gdzie wymagana jest wysoka rezystywność ze względu na konieczność rozdziału generowanych ładunków.