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THE ORIGIN OF THE INTERACTION RESPONSIBLE FOR THE DIFFERENCE OF HOLE MOBILITY OF TWO DERIVATIVES OF ANTHRACENE

Hole mobility of the layers built from two anthracene derivatives differing in the substitution of the central benzene ring, i.e. anthrone substituted with only one keto group and anthraquinone substituted with two keto groups differs by one order of magnitude despite the fact that both have almost identical crystal structure. We ascribe this difference to existence of an additional intermolecular interaction arising in the layer of anthrone.

Keywords: anthrone, anthraquinone, DFT calculations, mobility.

1. INTRODUCTION

The process of generation and transfer of charge in solid organic materials cannot be described by just one theoretical model. This is due to the diversity of organic molecules and to the differences in their packing in the solid layer. In particular, among organic materials, active materials such as organic semiconductors built from the polycyclic molecules can be distinguished. They have an effect of aromaticity and constitute a quantum system, where the areas showing the effects of charge carriers localization and delocalization are bordering each other. The theory of hopping transport well describes charge carrier transport at room temperature for such an organic semiconductors.

Experimental determination of the microscopic properties of charge carrier transport needs the research on the electric transport in the layers of materials creating similar crystal structure, but differring in only one element of structure of the molecules which compose the layer. Therefore this distinguished element of the structure of the molecule should be associated with this property of molecule which can significantly change the type of intermolecular interactions.

Potential of intermolecular electrostatic interactions is formed by sum of contributions derived from atomic charges, dipoles and the higher multipole moments which vanished by symmetry [1]. If the molecular crystal is formed only by the van der Waals interactions, the shortest intermolecular distances should be in the range as follows: C...H of 2.8 – 2.9 Å and C...C of 3.3 – 3.4 Å [2-3]. Therefore, at the distances of this range between adequate elements of the molecule, the contributions from atomic quadrupole moments can be neglected and for calculations of the crystalline electrostatic potential only atomic point charges and point dipoles should be used. In some molecular crystals the effect of the crystal structure exceeds the effect of presence of hydrogen bonding and is directed oppositely to it. In this case the total effect of crystalline electrostatic potential reduces the molecular dipole moment [2].

An interesting problem is the possibility of examination the properties of materials made of similar molecules but differentiating with one specific element of structure of molecule and simultaneously creating almost identical crystalline structures. Such experiment allows us to put the hypothesis that the variation of properties of such materials can be attributed to the element which dfferentiate the structure of molecules. Anthrone and anthraquinone are such a pair of molecules appropriate for comparison of properties in host solid state. Both of the mentioned above compouds crystallize in a similar crystal structure.

The parameters of nearly the same structures of anthraquinone, $C_{14}H_8O_2$ [4] and anthrone, $C_{14}H_{10}O$ [5] are presented in Table 1.

Table 1.

The parameters of the crystal structures of anthraquinone [4] and anthrone [5] and their molecule dipole moment [6]

Compound	Space group	Lattice constant, [Å]	Lattice angle β [degree]	Dipole moment, [D]
Antraquinone ($C_{14}H_8O_2$)	C_{2h}^5($P2_1/c$)	$a_0 = 7.8684(5)$, $b_0 = 3.9634(3)$ $c_0 = 15.7839(13)$	102.687(6)	0.6 (in benzene)
Anthrone ($C_{14}H_{10}O$)	C_{2h}^5($P2_1/c$)	$a_0 = 7.8647(7)$ $b_0 = 3.9816(2)$, $c_0 = 15.813(1))$	101.786(4)	3.66 (in benzene)

Our previous experiments have shown that there is a difference between mobility of anthraquinone and anthrone. Mobility of anthrone is of one order of magnitude greater than for anthraquinone layers. This difference is valid for polycrystalline, quasi-amorphous and amorphous layers for both considered compounds [7].

2. CALCULATIONS

The calculations were carried out with use of TD-DFT (time dependent – density functional theory) with GAUSSIAN 09 program [8]. The structures of anthraquinone and anthrone were optimized at B3LYP (Becke three parameter (exchange), Lee Yang, and Parr) method using 6-311+g(d,p) basis set. The structure was considered completely optimized when stationary point was located and was confirmed by absence of imaginary frequencies. Based on the optimized geometric structure, the HOMO, LUMO and band gap calculations were performed with the same level of theory at the ground state.

The optimized geometric structures with electrostatic potential map of the anthraquinone and anthrone molecules in the ground state are shown in Fig. 1. The distribution of the atom charges in the anthrone molecule indicates the presence of dipole moment marked in the Fig. 1a by an arrow.

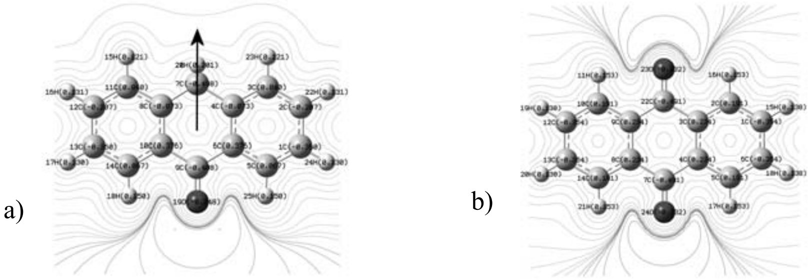
a)
b)

Fig. 1 The ground state of molecules of: a) anthrone (the arrow indicates the dipole moment) and b) anthraquinone. The electrostatic potential map is visualized and all of the atoms are signed with their symbols and their charge.

The bonds of the central ring of anthrone are single, i.e. 7C-8C, 7C-4C and 9C-10C, 9C-6C but all the others between carbons and carbon – oxygen are double. It is similar for the anthraquinone molecule, i.e. 22C-9C, 22C-3C and 7C-8C, 7C-4C are single but all the others between carbons and carbon – oxygen are double. The symmetry of molecules causes that for anthrone the bonds lengths 7C-8C and 9C-10C are equal to bond lengths of 7C-4C and 9C-6C, respectively. For anhraquinone molecule we observe the same behaviour for bond lengths 22C-9C and 7C-8C in comparison to 22C-3C and 7C-4C.

Table 1

Bond lengths for anthrone and anthraquinone molecules in gas phase in comparison to the solid state.

anthrone			anthraquinone		
bond	gas phase	X-ray in solid phase [5]	bond	gas phase	X-ray in solid phase [4]
	[Å]	[Å]		[Å]	[Å]
19O – 9C	1.223	1.109	24O – 7C	1.220	1.224
9C – 6C	**1.489**	**1.475**	**7C – 4C**	**1.492**	**1.478**
6C – 4C	1.402	1.391	4C – 3C	1.406	1.372
4C – 7C	**1.507**	**1.488**	**3C – 22C**	**1.492**	**1.478**
7C – 20H	1.097		22C – 23O	1.220	1.224
6C – 5C	1.404	1.389	4C – 5C	1.398	1.391
5C – 1C	1.385	1.376	5C – 6C	1.390	1.372
1C – 2C	1.399	1.364	6C – 1C	1.398	1.410
2C – 3C	1.389	1.360	1C – 2C	1.,390	1.372
3C – 4C	1.401	1.412	2C – 3C	1.398	1.391

3. DISCUSSION

The great difference about 6.4% in the length of the bonds among single bonds and double bounds existing between carbons in tetracene skeleton is observed for anthrone and anthraquinone. This difference takes place for molecules in gas phase and for molecules in solid phase.

The question arises if such a change of the single bond length between carbons in the midle rings for both considered molecules may be reflected in the different change of electronic properties of both molecules. The aromatic stabilization energy is the measure of aromaticity of the molecule and is correlated with the number of electrons contributing to aroamaticity. Theory [9] suggests that interatomic exchange - correlation potential $V_{xc}(\Omega_A,\Omega_B)$, where Ω_A and Ω_B the interacting Quantum Atoms partitioning the energy of molecule into atomic (self) and interatomic (bond) parts of different topological subspaces, is to the first order approximation inversely proportional to the inter-nuclear distance R_{AB} between the nuclei of interacting atoms:

$$\frac{\delta(\Omega_A,\Omega_B)}{R_{AB}} = m \cdot V_{xc}(\Omega_A,\Omega_B) \tag{1}$$

m is an universal constant for any type of atom, and $\delta(\Omega_A,\Omega_B)$ is delocalization index used in the quantum theory of atoms in molecules (QTAM) equivalent to a covalent bond order [10]. The charges of carbon atoms are similar so $\delta(\Omega_A,\Omega_B)$ can be in analysis of single bonds considered as constant. The differences of R_{AB} for single bonds of anthrone and anthracene is less than 1%. Therefore we can assume that the change of aromatic stabilization energy for both examined molecules is nearly the same. This phenomenon is associated with a similar reduction of aromaticity of the central ring of both considered compounds. Therefore differences in charge transport properties between these compounds should not be sought in reduction of aromaticity of the molecule.

Therefore, we must look for another factor that has the potential to change the charge carrier transport which is observed in the solid layers.

The non-symmetrical substitution of anthracene molecule is realized with the origin of a large natural dipole moment of anthrone compared to the value of small dipole moment obtained while the symmetrical substitution is realized for anthraquinone. The increased mobility of charge carriers in anthrone layers should be related to the presence of the considerable value of dipole moment. The low mobility of charge carriers in anthraquinone is caused by a low value of dipole moment. This hypothesis could be built based on the obtained results described above.

To understand the role of dipole-dipole interactions occurring during charge transfer phenomena, it is necessary to analyze what are the sources of interactions. For this purpose it is convenient to analyse Hamiltonian describing such interactions.

The choice of the Hamiltonian in the situation described in this article is connected with the fact that nuclear dynamics is much slower than the dynamics of charge carriers and the fact that electronic coupling is weak. Hamiltonian for charge transport should be connected with static disorder, based on the assumption on the electronic density of states and on the hopping rates between localized states.

For low electron density materials one-electron Hamiltonian is convenient for presentation of the different kinds of charge carriers motion [11]:

$$H = H_0 + H_1 + H_2 + H_3 + H_4 \tag{2}$$

where:

$$\begin{aligned}
H_0 &= \sum_n \varepsilon \cdot a_n^+ a_n + \sum_\lambda \hbar \cdot \omega_\lambda \cdot \left(b_\lambda^+ b_\lambda + \frac{1}{2} \right), \\
H_1 &= \sum_n \sum_m J_{nm} \cdot a_n^+ a_m , \\
H_2 &= \sum_\lambda \sum_m g_{n\lambda}^2 \cdot \hbar \cdot \omega_\lambda \cdot a_n^+ a_m \left(b_\lambda + b_{-\lambda}^+ \right), \\
H_3 &= \sum_n \sum_{\substack{m \\ n \neq m}} \sum_\lambda f_{nm\lambda}^2 \cdot \hbar \cdot \omega_\lambda \cdot a_n^+ a_m \left(b_\lambda + b_{-\lambda}^+ \right), \\
H_4 &= \sum_n \delta\varepsilon_n \cdot a_n^+ a_n + \sum_n \sum_{\substack{m \\ n \neq m}} \delta J_{nm} \cdot a_n^+ a_n .
\end{aligned}$$

Hamiltonian H_0 represents the total energy of the system. It is assumed that the molecules and the lattice built by these molecules are in the excited state but without inter-interactions. Energy of the excited state of a molecule in the defined lattice node is described with node energy ε, its variations are described with $\delta\varepsilon_n$. The variation of ε is connected with non-phonon dispersion of energy states (diagonal elements H_{nn} of the Hamiltonian matrix). Non-diagonal elements δJ_{nm} (n ≠ m, n, m – elements in the Hamiltonian matrix), represent the non-diagonal disorder of the force of interactions between two lattice nodes, but without presence of phonons (for example connected with disorder due to dipole-dipole orientation). a_n^+, a_n are respectively the operators of creation and annihilation of excited electron with energy ε in the node n, and b_n^+, b_n are respectively the operators of normal oscillations with energy $\hbar\omega_\lambda$ interact with electron in the state n and $g_{n\lambda}$ is non-dimensional coupling constant for this interaction. Transfer Hamiltonian H_1 describes electron transfer from node (n) to node (m) with overlapping energy J_{nm}. Terms H_2 and H_3 describe the impact of the lattice vibrations on the electron flow. The last H_4 is divided into two disorder terms, first one is responsible for statistic diagonal disorder and the second one for statistic non-diagonal disorder.

Dipole-dipole interactions energy between the dipole $d\vec{s}_1$ 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 is shown below in the form of the sum of interactions with all other dipoles [12]:

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

where r_{1n} is a position of n-th dipole, α-sign a manifold of the network of point dipoles.

This energy of dipole-dipole interaction may be an element for the second term in the Hamiltonian H_4. In the case of anthraquinone, with the molecules with natural dipole moment measured in benzene of 0.6 D ($2.00 \cdot 10^{-30}$ Cm) [6], this energy is of the order of 10^{-5} - 10^{-6} eV, that is of three orders of magnitude less than the van der Waals potential energy (estimated in the range of $10^{-3} \div 7 \cdot 10^{-2}$ eV), but anthrone molecules possess a significant natural dipole moment, when measured in benzene is of 3.66 D ($1.22 \cdot 10^{-29}$ Cm) [6] and in this case the energy of dipole-dipole interaction can be in the order of 10^{-2} - 10^{-3} eV. It means the value comparable to the van der Waals potential. These additional dipole-dipole energies present for anthrone structures can lead to broadening of the bands in the condensed form and to the enhanced overlapping of the wave functions for the charge carriers conducting via localized states.

3. CONCLUSIONS

In this article, we explicitly stated that for both described derivatives of anthracene, i.e. anthrone and anthraquinone, obtained as a substitution of the middle ring of tethracene skeleton with one or two ketone groups leads to the low almost identical (within 1% range) changes of the aromatic stabilization energy. At the same time, the determined change of bonds lengths between carbon atoms in the midle ring relative to analogous bond lengths for atoms in the side rings is of the value near 6.4%. This value is almost the same for both studied molecules. The above analysis of possible phenomena affecting the energy of interactions described by Hamiltonian terms indicated that the basic source of the difference in energy of interactions are dipol-dipol interactions. Therefore, the fact that mobility for polycrystalline, quasi-amorphous and amorphous layers of anthrone is of one order of magnitude greater than for anthraquinone layers can be attributed to the magnitude of the constant dipole moment of individual molecules. We believe that the only source of such of differences of the mobility value of charge carriers for both considered compounds is the presence of the significant natural dipole moment in anthrone molecules in comparison to the anthraquinone molecules.

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REFERENCES

[1] Buckingham A.D., Fowler P.W. 1984. A model for the geometries of van der Waals complexes. Can. J. Chem. 63, 2018-2025.

[2] Yatsenko A.V. 2003. Molecular crystals: the crystal field effect on molecular electronic structure. J. Mol. Model. 9, 207-216.

[3] Weber G. 1981. The structure of a 2:1 host guest complex between p-nitroaniline and 18-crown-6. Z. Naturforsch. B 36, 896-897.

[4] Fu Y. 1998. Temperature dependence of the rigid-body motion of anthraquinone. B54, 308-315.

[5] Yap G.P.A., Wisner J.A. 1997. CSD Communication (Private Communication).

[6] Landolt-Börnstein. 1971. Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Berlin: Springer Verlag.

[7] Kania S. 2014. Hole drift mobility of anthrone and anthrachinone layers with different structures. Sci. Bull. Techn. Univ. Lodz, Physics, 35: 17-24.

[8] 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., M. Ehara, 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., and Fox D.J., Wallingford CT: Gaussian, Inc.

[9] Badri Z., Foroutan-Nejad C. 2016. Unification of ground-state aromaticity criteria – structure, electron delocalization, and energy – in light of the quantum chemical topology Phys. Chem. Chem. Phys. 18: 11693-11699.
[10] Pendás A.M., Blanco M.A., Francisco E. 2006. Chemical fragments in real space: definitions, properties, and energetic decompositions. J. Comput. Chem., 28, 161-184.
[11] Pope M., Swenberg C.E. 1982. Electronic processes in organic crystals, New York: Clarendon Press.
[12] Kitaigorodskii A.J. 1973. Molecular Crystals and Molecules, New York: Acad. Press.

ŹRÓDŁO POWSTANIA ODDZIAŁYWAŃ ODPOWIEDZIALNYCH ZA RÓŻNICE RUCHLIWOŚCI DWU POCHODNYCH ANTRACENU

Streszczenie

Wykazano, w przypadku antronu i antrachinonu będących pochodnymi antracenu podstawionego w środkowym pierścieniu jedną lub dwiema grupami ketonowymi obserwuje się jedynie małe i prawie identyczne zmiany aromatycznej energii stabilizacji (w zakresie 1%). Oba rozpatrywane związki mają prawie identyczną strukturę krystaliczną. Jednakże ruchliwość dziur w antronie jest o jeden rząd wyższa niż w antrachinonie, niezależnie, czy jest badana w warstwach amorficznych, quasi-amorficznych czy też krystalicznych. Dlatego też jedynym źródłem obserwowanej doświadczalnie różnicy ruchliwości nośników ładunku może być obecność dużego momentu dipolowego cząsteczki antronu w porównaniu do małej wartości momentu dipolowego cząsteczki antrachinonu.