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ELECTRICAL AND THERMAL PROPERTIES OF ANTHRAQUINONE LAYERS

Quantum-chemical calculations indicate that the bond lengths in the anthraquinone anthracene backbone are shorter than the corresponding bonds in unsubstituted anthracene. The shape of the frontier molecular orbitals (FMO) indicates the possibility of more efficient electron capture by the anthraquinone molecule than by the anthracene molecule while maintaining stability in the conditions prevailing in electrochemical cells. Differential scanning calorimetry (DSC) studies indicate the temperature stability of anthraquinone above the melting point up to 300°C. The glass transition is determined at about 100°C.

Keywords: anthraquinone, differential scanning calorimetry (DSC), DFT calculations.

1. INTRODUCTION

Transport of electric charge through molecular materials is connected with the polarization of the frontier molecular orbitals (FMO). In a crystalline non-organic semiconductor, a high dielectric constant value of about 9 - 13, is connected with strong and effective screening of the charge carrier by a easy and fast readjustment of the distribution of the surrounding space electron density. In organic semiconductor a much smaller value of dielectric constant of about 3 - 4, enable to create the bonded electron–hole pair named exciton [1]. Charge transport in the organic material can be treated as an addition of the extra electron to the lowest unoccupied molecular orbital (LUMO) or the hole to the highest occupied molecular orbital (HOMO). The hole is used in the meaning of the presence of one electron in the HOMO level instead the two electrons [2]. Charge transport understood in this way requires the appearance of the excited electronic states different from the ground state. Therefore, the conduction process cannot be considered only as a thermal process, or associated only with diffusion or only with electron transport in an electric field, but as a complex physico-chemical process. A characteristic feature of this process is that after the charge transfer process occurs, the molecule is recovered in the ground state. For applications in organic electronics, the thermal resistance of the organic semiconductor layer to Joule-Lenz heat generated during electric conduction is also desirable. For applications, therefore, it is important that the molecule does not undergo dissociation into fragments during the transfer of charge carrier. Therefore, studies on the electrical properties of the material should be associated with studies on thermal properties. An interesting organic compound exhibiting semiconductor properties is anthraquinone. The anthracene skeleton of this molecule is not sensitive to red-ox processes [3]. The only places where the red-ox reaction can occur more easily are oxygen atoms substituted at the position 9 and 10. This fact was used in modern battery design where Al is the metallic anode and anthraquinone is the organic cathode [4]. In such an electrochemical environment, the addition of one electron to each of the oxygen atoms being substituents in the anthraquinone molecule is a reversible reaction.

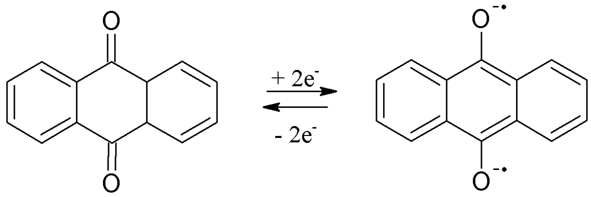


Fig. 1. Addition reaction of two electrons in anthraquinone, under electrochemical stabilization conditions, is a reversible reaction [4].

The problem of chemical resistance to environmental conditions is one of the basic restrictions for practical applications of organic material. However, the above example indicates that the material to be used in the field of electrochemistry and organic electronics additionally should be capable of reversibly subject to red-ox reactions even when excited to higher ionization level.

2. MATERIAL

Anthraquinone represents a low-weight molecular material, which does not crystallize very well [5] *i.e.* in the needle shape from 2-butanone or usually twinned crystals from benzene and toluene [6]. Empirical formula of the molecule is $C_{14}H_8O_2$, molecular weight 208.22. The molecule is planar, all of the hydrogen atoms are placed in the anthracene skeleton plane [7]. The earlier X-ray diffraction studies on anthraquinone [7] assigned the monoclinic crystal system with space group $P2_1/a$ and lattice constants $a = 15.810 \pm 0.015$ Å, $b = 3.942 \pm 0.005$ Å, $c = 7.865 \pm 0.010$ Å and $\beta = 102°43' \pm 2'$ and unit cell volume 477.8 Å^3. More recent studies [5,6] have indicated space group $P2_1/c$ with the lattice parameters shown in Table 1 [6]. The unit cell volume determined from this measurements is 480.21(7) Å^3 [6] in temperature of 296 K. To determine the effect of the presence of two substituents in Table 1, in addition to the properties of two described anthraquinone crystal structures, the properties of two anthracene crystal structures are also given [8,9]. Anthracene crystallizing in the monoclinic crystal system has the unit cell volume equal to 473.66(16) Å^3 [9] close to that of anthraquinone unit cell. However the lattice constants of the two compounds are significantly different.

Table 1

The parameters of the monoclinic crystal structures of anthraquinone [6] at 296 K and anthracene [8, 9] at 293 K and their molecular dipole moments [10]

Compound	**Space group**	**Lattice constant, [Å]**	**Lattice angle, *β* [degrees]**	**Dipole moment, [D]**
Antraquinone ($C_{14}H_8O_2$) [6]	$C_{2h}^5(P2_1/c)$	$a_0 = 7.8684$ (5). $b_0 = 3.9634(3)$ $c_0 = 15.7839(13)$	102.687(6)	0,6 (in benzene)
Anthracene ($C_{14}H_{10}$) [9]	$C_{2h}^5(P2_1/c)$	$a_0 = 11.166$ (2). $b_0 = 6.021(1)$ $c_0 = 8.553(2)$	124.54(3)	
Anthracene ($C_{14}H_{10}$) [8]	$C_{2h}^5(P2_1/c)$	$a_0 = 8.553$ $b_0 = 6.021$ $c_0 = 18.849$	102.59(3)	

The values given in the Table 1 and cited in the text above from [7] indicate significant difficulties in determining the actual crystal structure of both anthracene and its anhraquinone derivative. Therefore, for a more accurate analysis of the properties the solid state and the properties of the molecule itself, it is beneficial to use quantum-chemical calculations [5]. The best consistency of the calculation results with the X-ray structural characterization in the case of anthraquinone is obtained when density functional theory (DFT) calculations on the B3LYP/6-311 level of theory are performed [5]. Also our previous calculations [11,12] indicated that DFT calculations can be used to determine the energy distribution and the spatial distribution of both the molecule itself and the electrical properties associated with the anthraquinone crystal lattice cell.

3. QUANTUM-CHEMICAL CALCULATION

The calculations in the gas phase were carried out with use GAUSSIAN 09 program [13] with use of DFT calculations in the 6-311+g(d,p) level of theory. The structure parameters of anthraquinone molecule being in the neutral, kation and anion state were determined. Optimization of the molecule structure of anthraquinone allowed us to determine the values of bond length in the anthraquinone molecule. The electrical properties in the volume of the anthraquinone are associated with both the crystal packing of the molecules and the structure itself and only with the structure of the molecule itself. The question therefore arises whether the properties of the material are determined by the skeleton properties itself, or whether two oxygen substitution in the positons 9 and 10 has a significant impact.

3.1. Calculations of anthraquinone molecule

The anthraquinone molecule consists of a rigid skeleton of anthracene, which is a linear system of three benzene rings substituted in the middle ring symmetrically with two oxygen atoms.

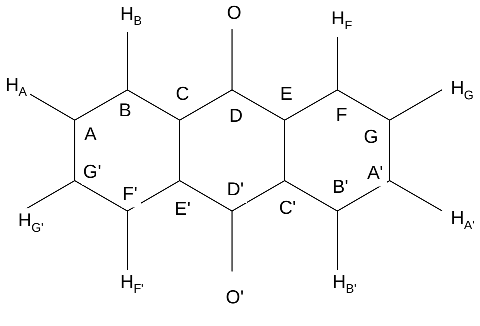


Fig. 2. Anthraquinone molecule. The marking of atoms takes into account the symmetry of the molecule.

Quantum-chemical calculations indicate that substitution of the anthracene skeleton with two oxygen atoms significantly changes the length of corresponding bonds in both the anthracene and anthraquinone molecules (Fig. 2). The calculated differences of bond lengths in gas phase for antracene and anthraquinone in the case of chemically equivalent bonds DE and D´C´, EF and C´B´ as well as FG and B´A´ are +0,094 Å (6.7%), –0.031 Å (2.1%) and +0.022 Å (1,6%), respectively (Table 2). There is observed that the length of pair of bonds DE and D´C´ in anthracene are nearly equal to the pair of bonds FG and B´A´ of anthraquinone, and the length of pair of bonds DE and D´C´ in anthraquinone are nearly equal to the pair of bonds FG and B´A´ of anthracene. It is well known that the bond energy in organic chemistry depends on the bond length: the shorter the bond, the more energetic it is. This is associated with the trend for stabilization energy in the manner that when the shorter bond is in the benzene ring then the greater stabilization energy is and consecutively the more aromatic benzene ring will be [14]. In general, the local aromaticity of the oligoacene molecule increases steadily from the peripheral to the central ring [15]. This tendency is clearly seen for anthracene. For anthraquinone the greater aromaticity can be connected with peripheral ring and the lower one with central ring.

Table 2

Equivalence of bonds in the structure of molecule anthracene and molecule anthraquinone (calculation made with DFT B3LYP/6-311++G(d,p)). Identification of bonds as in Fig. 2, and length in Å

	Bond	**Bond length gas phase anthracene**	**Bond length gas phase anthraquinone**	**Bond length solid phase anthraquinone, from X-ray diffraction crystallography [5]**	**Difference of bond length, 4-3**
1	2	3	4	5	6
bonds chemically equivalent	DE and D´C´	1.3989	1.4924	1.487(2) and 1.481(2)	+0.094
	EF and C´B´	1.4293	1.3984	1.393(2) and 1.395(2)	-0.031
	FG and B´A´	1.3674	1.3897	1.381(2) and 1.379(2)	+0.022
bonds chemically different	FG and A´G	1.3674 and 1.4250	1.3897 and 1.3978	1.381(2) and 1.377(3)	
	EF and EC´	1.4293 and 1.4427	1.3984 and 1.4064	1.393(2) and 1.398(2)	
	EC´ and GA´	1.4427 and 1.4250	1.4064 and 1.3978	1.398(2) and 1.377(3)	

When examining the case of pairs of chemically different bonds, *i.e.* FG and A′G, EF and EC′ as well as EC′ and GA′, the greater differentiation in the case of anthracene than for anthraquinone molecules is seen.

The data given in Table 2, Table 3 and Table 4 indicate that changes in the length of bonds in the molecule are reflected in the image of the electron density distribution of the molecule. It is clearly visible a different picture of external frontier molecular orbitals (FMO), *i.e.* HOMO and LUMO orbitals for both anthracene and anthraquinone molecules.

Table 3

Comparison of the shape of anthracene and anthraquinone frontier molecular orbitals (FMO) important for conduction of holes

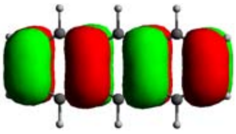
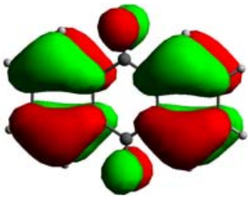
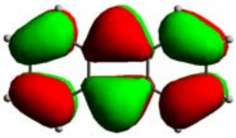
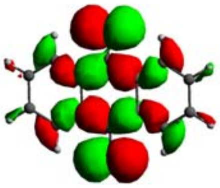
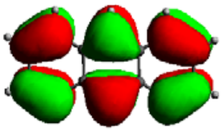
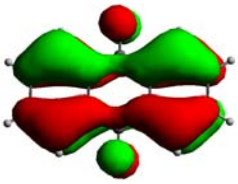
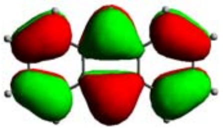
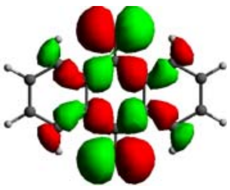
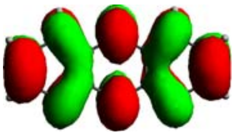
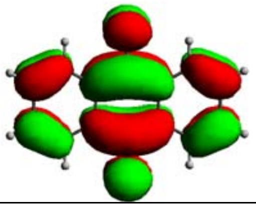
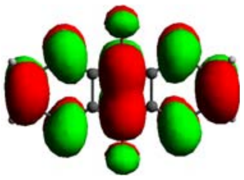
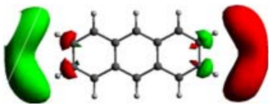
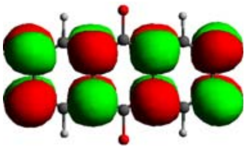
FMO	**Charge of the molecule**	**Anthracene**	**Anthraquinone**
HOMO-1	0 neutral		
HOMO	0 neutral		
HOMO	+1 cation		

Table 4

Comparison of the shape of anthracene and anthraquinone frontier molecular orbitals (FMO) important for electrochemical stabilization in the conditions when is need to connect one or two extra electrons to the molecule

FMO	**Charge of the molecule**	**Anthracene**	**Anthraquinone**
HOMO-1	–1 anion		
HOMO	–1 anion		
LUMO	–1 anion		
LUMO+1	–1 anion		

3.2. Discussion

The results of calculations for hole conductivity (Table 3) indicate that hole conductivity associated with the transfer of electrons between external FMO orbitals, *i.e*. HOMO, HOMO–1 is possible for both anthraquinone and anthracene. The anthraquinone molecule has a spatial distribution of HOMO orbitals such that conduction of holes can occur even when ionising this molecule to the charge state of +1. This would allow the use of anthrachinone for active layers under conditions of positive ionization of molecules, *e.g.* under conditions existing in electrochemical cells.

When anthraquinone molecule is an anion, it has such a spatial distribution of FMO orbitals (Table 4) that allows conduction of electrons.

Comparison of the shape of the outer orbitals (FMO) of both anthraquinone and anthracene molecules in the anion state, important for electrochemical stability, *i.e.* under the conditions when of one or two electron must be connected to the molecule (Table 2), indicates that under these conditions anthraquinone is stable. Molecule of anthracene in this conditions has no possibility to hold the electron in the benzene rings of the skeleton.

4. MEASUREMENTS AND DISCUSSION

4.1. DSC measurements

To determine the stability of the compound at melting temperature we used the measurement method of scanning calorimetry – differential scanning calorimetry (DSC). The DSC method allows to made simultaneous measurement of both the temperature and heat flow. They are recorded as a function of time and temperature. The difference in the amount of heat required to increase the temperature of the sample crucible and reference crucible is recorded. DSC measurement allows qualitative and quantitative determination of physical and chemical changes that are associated with endothermic and exothermic processes, as well as changes in heat capacity.

The measurement was made using a TA Instruments Universal Analysis Q2000 computer controlled research-grade DSC device for temperature and heat flow regulation. The measuring system diagram is presented in Fig. 3.

The DSC technique, due to the automation of its precision measurement, does not require the use of a large number of samples to perform the measurement. Thermal analysis is performed automatically on small samples. The measurements were made with anthraquinone with purity grade > 99% (HPLC) from Fluka with flash point 185°C and melting point in the range of 283-287°C.

DSC curve is presented in Fig. 4. The sample mass was 11.260 mg, and the measurement was made in the ambient of nitrogen gas. Heating rate was 0.35°C/min, start temperature was 25°C and final temperature 300°C.

Melting temperature of anthraquinone was determined to be $T_c = 284.56°\text{C}$ (Fig. 4b). Glass transition point was observed in the region where the inflection point of thermal curve was registered, *i.e.* at $T_g \approx 100°\text{C}$ (Fig. 4a). The examined material did not decompose after passing through the melting point.

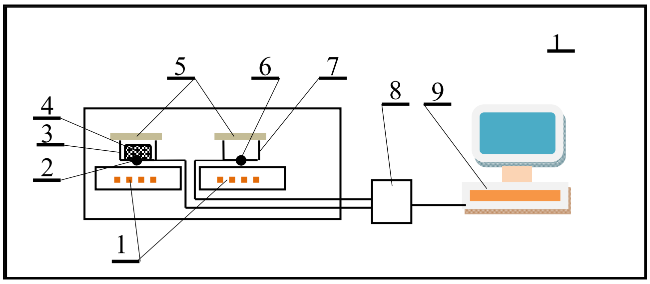


Fig. 3. Experimental scheme of DSC apparatus, 1 – heaters, 2 – measuring thermocouple, 3 – cruisible with a sample, 4 – sample, 5 – covers, 6 – reference thermocouple, 7 – reference cruisible, 8 – interface, 9 – computer reading the temperature and regulating heat flow.

4.2. Discussion

The obtained melting temperature of anthraquinone $T_c = 284.56°\text{C}$. is consistent with the results of Fu *et al.* [5], where this value was set at $T_c = 284.8°\text{C}$. During melting, anthraquinone does not decompose. The fact Interesting from the point of view of organic electronics applications is that the glass transition temperature for anthraquinone appears about 100°C, *i.e.* above the operating temperatures of electronic devices used in commercial applications at room temperatures.

5. CONCLUSIONS

During transport of charge carriers through the material, the charge transfer through the molecule must occur. This charge transfer through molecule can be interpreted as occurrence of red-ox processes. Therefore, it is important that the molecule does not dissociate and the electron transfer reactions should be reversible. These requirements are met by the anthraquinone molecule. The stability of the anthraquinone molecule for applications of organic electronics is a compromise between the required stability of the molecule and the required electron transfer reactions. These conditions are forced by the need to meet specific requirements resulting from the use of an electronic device using

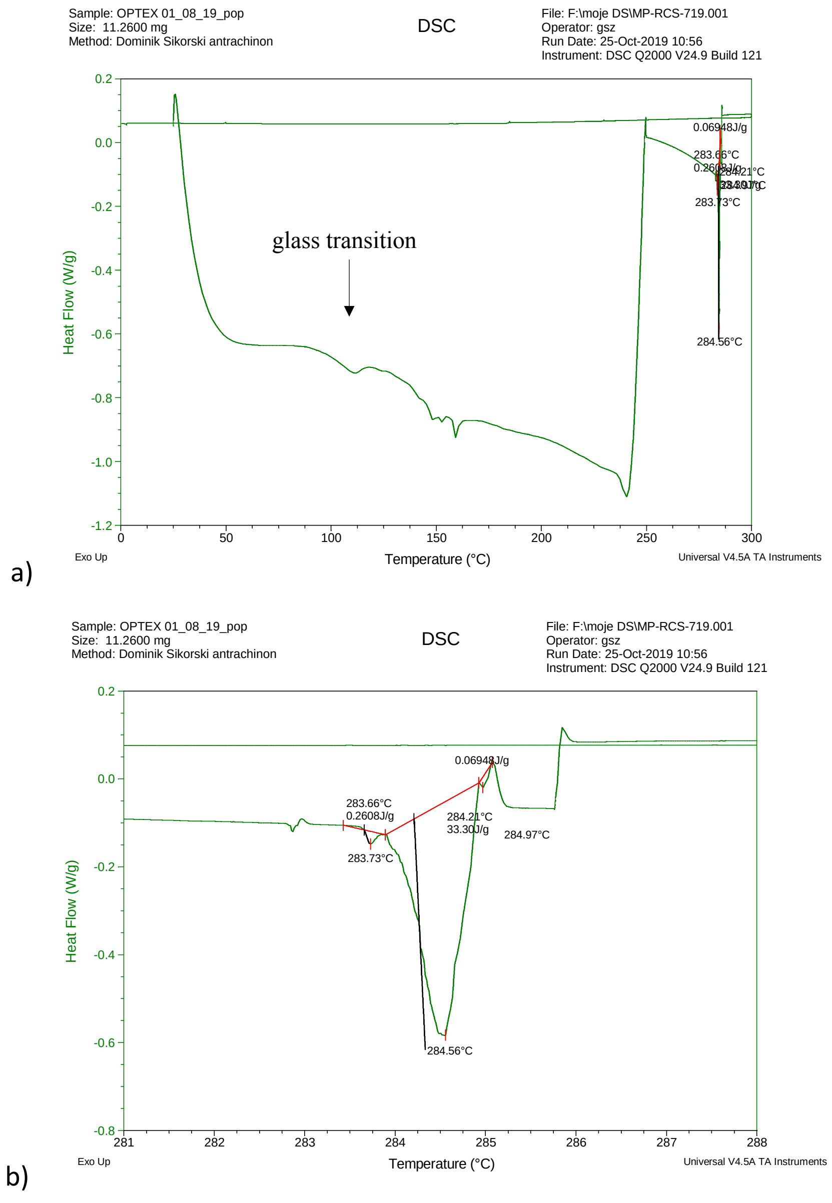


Fig. 4. Determination of antrachinone melting point by DSC method, a) thermogram for the entire measuring range (visible transition associated with the transition of glass transition at a temperature of about 100°C), b) enlarged area near the melting point.

anthraquinone as an active material. Anthraquinone can be used as an active substance working in solid state electronics devices because it is not subject to thermodynamic changes of the structure up to about 100°C, where it is subject to glass transition. In the DSC measurement range, *i.e.* up to 300°C, it is not dissociated into fragments.

Quantum-chemical calculations indicate that the bond lengths in the anthracene skeleton of anthraquinone molecule are shorter than the corresponding bonds in non-substituted anthracene. The shape of external orbitals (FMO) indicates the possibility of effective electron capture by the anthraquinone molecule while maintaining stability in the conditions existing in electrochemical cells. Anthracene molecule does not meet such conditions. DSC studies indicate the chemical stability of anthraquinone above the melting point. Electronic properties including the shape of FMO orbitals and temperature resistance of anthraquinone molecules allow to treat this material as having potential for use as active material in electronics.

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WŁASNOŚCI ELEKTRYCZNE I TERMICZNE WARSTW ANTRACHINONU

Streszczenie

Obliczenia kwantowo-chemiczne wskazują, że długości wiązań w szkielecie antracenowym antrachinonu w zewnętrznym pierścieniu benzenowym są krótsze niż odpowiadające im wiązania w niepodstawionym antracenie. Świadczy to o zwiększeniu energii rezonansu w zewnętrznych pierścieniach benzenowych cząsteczki antrachinonu. Kształt orbitali zewnętrznych (FMO) wskazuje na możliwość bardziej efektywnego przejmowania elektronów przez cząsteczkę antrachinonu niż przez cząsteczkę antracenu z zachowaniem stabilności w warunkach panujących w komórkach elektrochemicznych. Badania DSC wskazują na stabilność chemiczną antrachinonu powyżej temperatury topnienia aż do 300°C. Antrachinon w pobliżu temperatury 100°C wykazuje przemianę zeszklenia, poniżej tej temperatury nie wykazuje przemian fazowych. Własności elektryczne i termiczne antrachinonu wskazują na duży potencjał tego związku dla zastosowań w elektronice organicznej.