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## INTERMOLECULAR INTERACTIONS FOR TWO CHOSEN ANTHRACENE DERIVATIVES

*The nature of intermolecular interactions for anthrone and anthraquinone differs due to the symmetry of substitution of the central benzene ring, i.e. anthrone substituted with only one keto group and anthraquinone substituted with two keto groups. In order to interpret the interactions among the molecules, the interaction energies between molecules in crystals were calculated using DFT B3LYP calculations. The results reveal the consistency between calculated “lattice energies” and theirs terms and thermodynamical properties as density, boiling point and melting point of examined compounds.*

**Keywords:** intermolecular interactions, anthrone, anthraquinone, DFT calculations, organic semiconductors.

### 1. INTRODUCTION

The common interest in the recognizing the nature of influence of the molecule structure on the intermolecular interactions is seen not only in the scope of basic sciences but emerges from a strictly specified demands of the electronic industry. Anthracene derivatives are in the range of materials which may be used to produce solar cells, organic electroluminescence diodes (OLEDs) and organic field effect transistors (OFETs) or to produce devices such as gas sensors and specific chemical field-effect transistors [1,2]. Understanding the microscopic processes determining the charge carrier mobility in organic materials is essential for improvement of the quality of existing devices made of organic semiconductors. This article is continuation of our previous studies on different aspects of anthrone and anthraquinone as the derivatives of anthracene [3-6]. This

study is an attempt to describe the character of the intermolecular interaction energies in the solid-state phase of two above mentioned anthracene derivatives i.e. anthrone and anthraquinone. The property of the unsubstituted anthracene is also considered in this paper for separation the effect of the substitution.

Both compounds mentioned above crystallize in the nearly identical crystal lattices [7], monoclinic system with point group  $C_{2h5}$  and space group (P21/a) with bimolecular unit of the dimensions (at 20°C):  $a_0 = (15.83 \pm 0.04) \text{ \AA}$ ,  $b_0 = (3.97 \pm 0.01) \text{ \AA}$ ,  $c_0 = (7.89 \pm 0.01) \text{ \AA}$ ,  $\beta = 102.5^\circ$  for anthraquinone [8], and  $a_0 = (15.80 \pm 0.03) \text{ \AA}$ ,  $b_0 = (3.998 \pm 0.005) \text{ \AA}$ ,  $c_0 = (7.860 \pm 0.016) \text{ \AA}$ ,  $\beta = (101^\circ 40' \pm 10')$ ,  $Z=2$  for anthrone [9]. The main difference, essential for our studies, is the fact that the anthraquinone molecules being centrosymmetric possess nearly zero dipole moment [7], opposite to the non-centrosymmetric anthrone molecules which are characterized by large dipole moment of 3.5 D [7].

Anthrone is monoclinic and belongs statistically to the space group  $C_{2h5} - P21/a$  [8], but the molecules are non-centrosymmetrical, there are only two molecules per unit cell; these are arranged statistically in orientations so that, anthrone possesses higher symmetry than would be normally expected from two asymmetric molecules. The crystal structure of anthrone at 20 and  $-90^\circ \text{ C}$  has been refined and is found to possess long-range disorder, with a statistical distribution of anthrone molecules among two centrosymmetrically-related orientations [7].

### 1.1. Properties connected with lattice interactions

The expression “lattice energy” as used in this paper describes the energy of interaction of a single reference molecule having a structure as it occurs in the solid state with all other molecules of the crystal lattice.

The energy of interaction between two molecules is commonly expressed in terms of four key components: electrostatic, polarization, dispersion, and exchange-repulsion terms [10]:

$$E_{tot} = E_{ele} + E_{pol} + E_{dis} + E_{rep} \quad (1)$$

The first term is due to Coulombic interaction between two unperturbed molecular charge distributions (formed by electrons and nuclei), and it can be positive when it is de-stabilizing factor or negative when it is stabilizing factor. Second term is always negative, from electrostatic interactions due to the energy lowering associated with the perturbation (polarization) of the electron density of

each molecule by the other. The third term, dispersion term, is Grimme's dispersion correction [11]. The last term,  $E_{rep}$  is the exchange-repulsion energy calculated between unperturbed quantum-mechanical charge distributions of the monomers according to the exclusion principle, this term is always positive, destabilizing.

The proportions of each of above mentioned energy terms (Eq.1) directly affects the crystal packing. Distribution of observed interatomic distances in crystals indicates that the distances between the molecules are greater than would result from the molecular dimensions determined by the van der Waals radii [12]. This proves a significant impact of the repulsion energy term (positive value) on the resultant energy,  $E_{tot}$ . This phenomenon should be referenced in the materials density values (see Table 1 for density values,  $d$ ). On the contrary, the values of melting point (Mp) and boiling point (Bp) should be justified by the value of those energy terms that have negative values (see Table 1).

**Table 1**

Basic properties of anthrone and anthraquinone in comparison to anthracene [7,8,14]. (MW – molecular weight, Mp – melting point, Bp – boiling point,  $d$  – density).

	anthrone (C <sub>14</sub> H <sub>10</sub> O)	anthraquinone (C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> )	anthracene (C <sub>14</sub> H <sub>10</sub> )
CAS number	90-44-8	84-65-1	120-12-7
MW [g/mol]	194.228	208.212	178.229
Mp [K]	428	559	483
Bp [K]	994	653	613
$d$ [g/cm <sup>3</sup> ]	1.33	1.44	1.28

## 2. DFT CALCULATIONS

The DFT calculations were made with use CrystalExplorer 17, with Gaussian 09 package [13]. B3LYP lattice energies have been computed by direct summation of interaction energies over molecules in cluster interacting with a central molecule. For each calculation of the "lattice energy" the seven dimers were used (Table 2). Two levels of theory, i.e. B3LYP/6-31G(d,p) and B3LYP/6-311G(d,p) were used for calculations.

**Table 2**

Calculation details.

Compound	number of dimers used for calculations	symbol of molecule position	$R$ , separation of molecular centroids, [Å]
anthrone (C <sub>14</sub> H <sub>10</sub> O)	2	-x, y+1/2, -z+1/2	8.15
	2	-x, y+1/2, -z+1/3	10.15
	1	x, y, z	7.86
	1	x, y, z	3.98
	1	x, y, z	8.82
anthraquinone (C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> )	2	-x, y+1/2, -z+1/2	8.14
	2	-x, y+1/2, -z+1/3	10.04
	1	x, y, z	7.87
	1	x, y, z	3.96
	1	x, y, z	8.81
anthracene (C <sub>14</sub> H <sub>10</sub> )	2	-x+1/2, y+1/2, -z	5.23
	2	-x+1/2, y+1/2, -z	9.89
	1	x, y, z	11.17
	1	x, y, z	6.02
	1	x, y, z	12.69

The calculations were made in the cluster using a cutoff based on separation of molecular centroids  $R$ . The computations were made for molecules separated by no more than 12 Å.

### 3. RESULTS AND DISCUSSION

The results of DFT calculations are presented in Table 3 and Table 4. The values of total energy  $E_{tot}$  calculated in two levels of theory, i.e. B3LYP/6-31G(d,p) and B3LYP/6-311G(d,p) are slightly different. The  $E_{tot}$  values calculated for anthracene and anthraquinone vary below 5%. However in the case of anthrone, it is a change of 8%. This is due the large change in calculated values of  $E_{ele}$  and  $E_{rep}$  terms. The minimum of the total energy for anthraquinone is deeper than for anthrone. This difference is consistent with the observed density difference between anthraquinone and anthrone (see Table 1), where  $d = 1.44$  g/cm<sup>3</sup> for anthraquinone and  $d = 1.33$  g/cm<sup>3</sup> for anthrone. The values of total “lattice energy” calculated in similar manner via DFT B3LYP theory calculations (cutoff of separated centroids  $R = 12$  Å.) by Thomas et. al. [15] were  $-0.98$  eV for anthracene and  $-1.185$  eV for anthraquinone.

**Table 3**

“Lattice energy” terms calculated in the. B3LYP/6-31G(d,p) levels of theory (the error of estimations 10%).

Compound	$E_{ele}$	$E_{pol}$	$E_{dis}$	$E_{rep}$	$E_{tot}$
	[eV]	[eV]	[eV]	[eV]	[eV]
anthrone (C <sub>14</sub> H <sub>10</sub> O)	-0.059	-0.097	-1.488	0.796	-0.848
anthraquinone (C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> )	-0.309	-0.087	-1.323	0.775	-0.944
anthracene (C <sub>14</sub> H <sub>10</sub> )	-0.241	-0.044	-1.224	0.712	-0.797

**Table 4**

“Lattice energy” terms calculated in the. B3LYP/6-311G(d,p) levels of theory (the error of estimations 10%).

Compound	$E_{ele}$	$E_{pol}$	$E_{dis}$	$E_{rep}$	$E_{tot}$
	[eV]	[eV]	[eV]	[eV]	[eV]
anthrone (C <sub>14</sub> H <sub>10</sub> O)	-0.196	-0.102	-1.488	1.000	-0.785
anthraquinone (C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> )	-0.413	-0.093	-1.389	0.961	-0.934
anthracene (C <sub>14</sub> H <sub>10</sub> )	-0.355	-0.052	-1.224	0.868	-0.762

#### 4. CONCLUSION

For anthraquinone “lattice energy” term calculated in DFT B3LYP theory (Table 2 and Table 4) has a greater absolute value. The difference between “lattice energies” energies for both studied compounds is  $(0,15 \pm 0.02)$  eV what does mean a value of about 19% of anthrone “lattice energy” term. This difference is reflected in the values of melting points experimentally measured for both compounds. A deeper “total lattice energy” energy minimum for anthraquinone is associated with its higher melting point. The ratio of the total energy of  $E_{tot}$  for anthraquinone and for anthrone is 1,30 what is very close to the value of the ratio of the corresponding melting points (see Table 1) for both compounds being at 1,19.

This comparability of those ratio coefficients proves that the melting process is a statistical process in which the instantaneous individual interactions of dimers do not affect the nature of the phase change. Therefore this process is not related to a specific type of component interactions which are listed in the equation (1).

The different situation emerges when the substance boils. The molecules from liquid are separated into a gaseous state, which is characterized by the presence of free molecules that are not bound with each other. This transition requires breaking the shortest bonds. Such a phase transition is therefore connected with breaking a two-body interaction. Table 5 shows the components of the network energy at the moment of breaking the last bond. It seems that the higher level of boiling point of anthrone is caused by two components of the "lattice energy", i.e. the polarization and dispersion component.

**Table 5**

"Lattice energy" terms calculated in the B3LYP/6-311G(d,p) levels of theory for minimal separation of molecules (the error of estimations 10%).

Compound	$R$ [Å]	$E_{ele}$ [eV]	$E_{pol}$ [eV]	$E_{dis}$ [eV]	$E_{rep}$ [eV]	$E_{tot}$ [eV]
anthrone (C <sub>14</sub> H <sub>10</sub> O)	3,98	-0.033	-0.086	-0,752	0,439	-0.432
anthraquinone (C <sub>14</sub> H <sub>8</sub> O <sub>2</sub> )	3,96	-0.083	-0.073	-0,642	0.432	-0.366
anthracene (C <sub>14</sub> H <sub>10</sub> )	5,23	-0.104	-0.017	-0,360	0.218	-0.209

On the basis of the above results, we can assume that the DFT analysis of dipole interactions is a convenient tool for determining the trend of thermodynamic parameter variability for a selected group of polycyclic derivatives.

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## ODDZIAŁYWANIA MIĘDZYCZĄSTECZKOWE DLA DWU WYBRANYCH POCHODNYCH ANTRACENU

### Streszczenie

Przeprowadzono obliczenia oddziaływań międzycząsteczkowych wykorzystując program CrystalExplorer17 z wykorzystaniem pakietu oprogramowania Gaussian09. Obliczenia DFT wykazały zgodność pomiędzy uzyskanymi wartościami energii „siecisk krystalicznych” badanych związków i jej składowych z osobna a wybranymi do analizy doświadczanymi właściwościami termodynamicznymi jak gęstość materiału, temperatura wrzenia i temperatura topnienia badanych związków. Badania wykazały inny charakter oddziaływań zachodzących podczas procesu topnienia i podczas procesu wrzenia. Proces topnienia związany jest z całkowitą energią sieci. Temperatura wrzenia związana jest z zerwaniem oddziaływań pomiędzy pojedynczymi cząsteczkami. Decydujące jest tu zerwanie oddziaływania dipolowego i dyspersyjnego.