Formation of carboxylic acid complexes with polyaromatic hydrocarbons of the coronene series. Quantum chemical modelling

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Abstract. The paper presents the results of molecular modelling of the carboxylic acid interaction with polyaromatic hydrocarbons (PAH) of a coronene series in the framework of the semi-empirical PM6-DH2 method. It has been shown that the orientation of the acid molecule when all its atoms are in the plane parallel to the PAH one is the most preferable. Using the results of the thermodynamic parameters assessment, it was shown that for complexes of acetic acid with considered PAH the binding enthalpy and Gibbs free energy increase in the series from coronene to dicircumcoronene. An acid hydrocarbon radical elongation leads to an increase in the binding enthalpy and Gibbs free energy of carboxylic acids of the series CnH2n+1-COOH (n = 0 ÷ 5) with dicircumcoronene. Complexes of carboxylic acids with PAH are stabilized by nonvalent CH...C_PAH interactions. It was found that the thermodynamic parameters of the complexes formation linearly correlate with the number of stabilizing CH...C_PAH interactions for considered complexes of carboxylic acids CnH2n+1-COOH (n = 1 ÷ 5) with dicircumcoronene.

1. Introduction

Among the promising methods for graphene production exfoliation of graphite and its intercalation compounds in liquid media using ultrasound is actively studied and developed, as well as the preparation and subsequent reduction of graphite oxide [1, 2]. Graphene and its related structures modification ensuring the presence of acid groups on the surface gives rise to new useful properties and the expansion of the scope of application of graphene and its derivatives [3, 4]. Preparation of acceptor-type graphite intercalation compounds involves the adsorption of acids (HNO₃, H₂SO₄) on its surface as the first stage of the reaction [5, 6]. Carboxylic acids and their derivatives are actively used to stabilize graphite nitrate by producing cointercalation compounds (GNCC) [5]. Such binary or triple GNCCs, as well as the initial graphite and graphite nitrate, can act as precursors of carbon nanoparticles of various morphologies – graphenes, few-layered graphenes, nanoscrolls in the process of graphite matrix exfoliation in liquid media [7–9]. In this case, the interaction of organic cointercalants with the graphite and nanoparticle surface will take place both at the stage of formation of cointercalation compounds and in the process of deintercalation. When preparing dispersions of carbon nanoparticles by GNCCs liquid phase exfoliation and studying their properties and possible applications, it is also necessary to take into account the processes of adsorption and desorption of organic cointercalants in the system. Thus, the need to assess the thermodynamic parameters of interaction of graphite, graphene, and related structures with carboxylic acids, as well as the structural reorganization of components in such systems during the
complexation, stimulates interest in studying graphene-carboxylic acid systems by quantum chemical modelling.

Often, studies on modelling the adsorption of small molecules on graphene by density functional methods have been carried out with aromatic hydrocarbons of the coronene series as a model of the graphene plane [10–13]. The success of using semi-empirical methods for studying associative interactions with the graphene surface [14, 15] and self-association of carboxylic acids [16, 17] determines their choice for complex systematic studies of the interaction of carboxylic acids with the surface of graphene.

All of the above determined the aim of this work – to calculate the thermodynamic and structural parameters of the interaction of carboxylic acids C$_{9n}$H$_{2n+1}$-COOH (n=0÷5) with polyaromatic hydrocarbons of the coronene series (PAHs) as a model system of the graphene and related structures surfaces within the framework of the semi-empirical quantum chemical method PM6-DH2.

2. Calculation methodology

In the study of the molecular adsorption of carboxylic acids at the graphene plane the next polyaromatic hydrocarbons were selected as a model: coronene C$_{24}$H$_{12}$, circumcoronene C$_{54}$H$_{18}$, and dicircumcoronene C$_{96}$H$_{34}$, since these systems are successfully used for the quantum chemical description of the interaction of small molecules with a carbon surface [10]. For considered systems all calculations were performed in the supermolecule approximation without taking into account the solvent effect.

To optimize molecular geometry, calculate the parameters of the electronic structure and thermodynamic characteristics of hydrocarbons, acids and their complexes, we used the dispersion-corrected semi-empirical method PM6-DH2 [18, 19], implemented in the MOPAC2016 software package [20]. This method includes corrections for taking into account both dispersion interactions and hydrogen bonds. It is excellent for graphene plane optimization up to 1006 carbon atoms [14, 15]. At the first stage molecular geometry was optimized (the value of the parameter controlling the final gradient norm was GNORM=0.01) for all objects. Then the frequencies of harmonic oscillations and thermodynamic parameters were calculated. The stationary points obtained after optimization were determined as minima, because there were no negative values of the analytic harmonic vibrational frequencies for them.

The binding enthalpy, entropy and Gibbs free energy were used to analyze obtained models of the carboxylic acids complexes with PAHs. The binding enthalpy was calculated using the equation:

\[
\Delta H_{\text{binding}} = \Delta_f H_0^{\text{complex}} - \Delta_f H_0^{\text{PAH}} - \Delta_f H_0^{\text{acid}},
\]

where \(\Delta_f H_0^{\text{complex}}, \Delta_f H_0^{\text{PAH}}, \) and \(\Delta_f H_0^{\text{acid}}\) are the formation enthalpies of the intermolecular complex, hydrocarbon, and acid correspondingly. In a similar manner the change in binding entropy was calculated. The binding Gibbs free energy was calculated according to the equation:

\[
\Delta G_{\text{binding}} = \Delta_f G_0^{\text{complex}} - \Delta_f G_0^{\text{PAH}} - \Delta_f G_0^{\text{acid}},
\]

and \(\Delta_f G_0^{\text{acid}}\) are the formation Gibbs energies of the intermolecular complex, hydrocarbon, and acid respectively.

The ChemCraft program [21] was used to visualize the structural models.

3. Results and discussion

In this work polyaromatic hydrocarbons of the coronene series (figure 1) and carboxylic acids C$_{9n}$H$_{2n+1}$- COOH (n=0÷5) are used as model systems for studying the adsorption of carboxylic acids on graphene. Note, that in this paper we consider carboxylic acids of normal structure in an all-trans conformation, since such acid molecules will subsequently form monolayers on the graphite or graphene surface with the most dense and ordered structure [22–24]. Table 1 lists the experimental [25] and calculated by the PM6-DH2 method thermodynamic parameters for the formation of the studied carboxylic acids and PAHs. The calculated values of the formation enthalpy and entropy for acid are in good agreement with the corresponding available experimental data for the gas phase.
coronene $C_{24}H_{12}$

circumcoronene $C_{54}H_{18}$

dicircumcoronene $C_{96}H_{24}$

**Figure 1.** Aromatic hydrocarbons used as model systems to represent the graphene plane.

Often, when studying the adsorption of small molecules on graphene, when PAHs act as a model of the carbon plane, researchers assess the thermodynamic characteristics and limit oneself to calculating the adsorption energy as the difference between the corresponding enthalpies or the total energies of complexes and free molecules [14, 26–28]. We consider not only a change in the enthalpy of the system, which characterizes the thermal effect of the reaction, but also a change in the Gibbs free energy, which allows us to estimate the stability of the complexes formed.

**Table 1.** Experimental and calculated thermodynamic parameters of formation of the studied carboxylic acids and PAHs.

| Compound      | $\Delta_f H^0_{\text{gas}}$, kcal/mol | $S^0_{\text{gas}}$, cal/(mol·K) |
|---------------|--------------------------------------|----------------------------------|
|               | Calculated                           | Experimental [25]                | Calculated                           | Experimental [25] |
| H-COOH        | -87.95                               | -90.46                           | 59.73                                | 59.44              |
| CH$_3$-COOH   | -101.31                              | -103.49                          | 69.85                                | 67.59              |
| C$_2$H$_5$-COOH | -105.56                            | -108.94                          | 78.99                                | -                  |
| C$_3$H$_7$-COOH | -111.14                            | -113.74                          | 86.14                                | 84.43              |
| C$_4$H$_9$-COOH | -116.53                            | -117.35                          | 90.45                                | 105.11             |
| C$_5$H$_{11}$-COOH | -120.82                           | -122.37                          | 99.30                                | -                  |
| C$_2$H$_{12}$  | 74.10                                | 70.53                            | 113.33                               | -                  |
| C$_{24}$H$_{12}$ | 155.15                             | -                                | 177.22                               | -                  |
| C$_{54}$H$_{18}$ | 264.62                             | -                                | 256.24                               | -                  |

3.1. Interaction of acetic acid with aromatic hydrocarbons of the coronene series

At the first stage of studying the interaction of PAHs with carboxylic acids various models of acetic acid and coronene complexes were obtained, in which the carbon atom of the carboxyl group is located above the center of the central ring in PAH molecule (cf. figure 2, model M1) and one of the carbon atoms of the central ring of the PAH molecule (cf. figure 2, models M2 – M4). Various orientations of the acid molecule relative to the plane of the PAH molecule are considered in order to conduct comparative analysis. In the case of models M1 and M2, the C1–C2 bond in the acid molecule is oriented perpendicular to the plane of the PAH molecule and methyl group is directed towards PAH. In M3 and M4 complexes a parallel orientation of the C1–C2 bond in the acid molecule to the plane of the aromatic molecule is realized. In this case the plane in which the atoms of the carboxyl group lie is perpendicular (model M3) or parallel (model M4) to the PAH plane. Optimization of the molecular geometry for such complexes and calculation of formation thermodynamic parameters show that formation of complexes of types M3 and M4 is more preferable from the viewpoint of the Gibbs free energy (table 2). It should
be noted that a complex of acetic acid with coronene oriented according to M2 model type cannot be obtained with full optimization of all structural parameters of the system, which, in our opinion, is associated with a fairly strong influence of the edge atoms of PAH. Only partial freezing of some structural parameters of the complex (fixing a perpendicular orientation of the acid C1-C2 bond relative to the PAH plane) makes it possible to obtain a complex of this type and calculate its thermodynamic characteristics. Therefore, coronene is not a reliable model for the study of complexes of this type. Also, an attempt to obtain complexes of types M1 and M2 in which the carboxyl group is directed toward the plane of the aromatic molecule was unsuccessful for the given series of PAHs.

**Table 2.** Binding enthalpies and Gibbs free energies (in kcal/mol) for complexes of acetic acid with polyaromatic hydrocarbons

| PAH     | M1  | M2  | M3  | M4  |
|---------|-----|-----|-----|-----|
|         | ΔH<sub>binding</sub> | ΔG<sub>binding</sub> | ΔH<sub>binding</sub> | ΔG<sub>binding</sub> | ΔH<sub>binding</sub> | ΔG<sub>binding</sub> |
| C<sub>24</sub>H<sub>12</sub> | -5.16 | 2.92 | -4.80 | 4.62 | -5.72 | -0.48 | -5.72 | 0.34 |
| C<sub>34</sub>H<sub>18</sub> | -5.04 | 8.79 | -4.97 | 8.64 | -4.30 | 0.74 | -6.69 | -1.21 |
| C<sub>66</sub>H<sub>24</sub> | -4.97 | 9.85 | -4.83 | 10.38 | -5.47 | -0.90 | -7.04 | -0.46 |

The formation of acetic acid complexes with the studied PAHs according to the type of models M1–M4 is characterized by heat release (the values of the change in the enthalpy of the complex formation reaction are negative). However, complexes of types M1 and M2, in which the methyl group of the acid is directed towards the plane of the PAH molecule, are unstable, since positive values of the binding Gibbs free energy are obtained for them (table 2). The considered complexes of acetic acid with PAH are characterized by distances between molecules of the order of 2.67–3.91 Å (table 3), which is consistent with the results of *ab initio* and DFT calculations in the studies of C-H/π interactions for model systems based on aromatic hydrocarbons and molecules containing C-H bonds [29–32]. The intermolecular distances calculated for benzene complexes with methane were within 2.3–4.0 Å [29–33] for various methods. In this work the smallest distance between the carbon atom of the carboxyl group and the nearest carbon atom of the PAH molecule (d(C...C), Å) is obtained for complexes of type M4, but the smallest distances between nearest carbon atoms in acid and PAH (3.22 Å) are observed for the M1 and M2 complexes. The smallest distance between the hydrogen atom of the methyl group and the nearest carbon atom of the PAH (d(H...C), Å) is also observed for M4 model (table 2). All values of d(C...C) and d(H...C) are in the range 2.67–4.70 Å, which exceeds the sum of the Van der Waals radii of corresponding atoms (3.06 and 2.61 Å) and excludes the possibility of covalent bond formation between the acid molecule and PAH.

**Table 3.** Structural characteristics (in Å) of acetic acid complexes with polyaromatic hydrocarbons.

| PAH     | M1  | M2  | M3  | M4  |
|---------|-----|-----|-----|-----|
|         | d(C...C) | d(H...C) | d(C...C) | d(H...C) | d(C...C) | d(H...C) |
| C<sub>24</sub>H<sub>12</sub> | 4.70 | 2.78 | 4.69 | 2.77 | 3.33 | 3.03 | 3.33 | 2.77 |
| C<sub>34</sub>H<sub>18</sub> | 4.73 | 2.81 | 4.70 | 2.73 | 3.91 | 2.90 | 3.46 | 2.78 |
| C<sub>66</sub>H<sub>24</sub> | 4.70 | 2.73 | 4.70 | 2.78 | 3.62 | 3.17 | 3.35 | 2.67 |

A slight change in the reaction enthalpy and an increase in Gibbs free energy are observed (table 2) in the series from coronene to dicircumcoronene for the formation of complexes acetic acid – PAHs (figure 2) according to the type of models M1 and M2. It is obvious that coronene and circumcoronene will be incorrect to use as a model of a graphene system in adsorption studies of other representatives of the homologous series of normal carboxylic acids. Therefore, further calculations for the adsorption of a number of C1-C6 acids are performed using dicircumcoronene as a model of the graphene plane. During calculation of the thermodynamic parameters of formation of PAH complexes with acetic acid...
accounting for dispersion interactions using the PM6-DH2 method negative values of Gibbs free energies are obtained for models of complexes of types M3 and M4, which indicates their stability.

Figure 2. The investigated variants of the mutual orientation of acetic acid and PAH in which the carbon atom of the acid carboxyl group is located above the center of PAH ring (model M1) and above the carbon atom of the central PAH ring (models M2 – 4).

3.2. Interaction of carboxylic acids $C_nH_{2n+1}$-COOH ($n = 0 \div 5$) with dicircumcoronene

The interaction of carboxylic acids $C_nH_{2n+1}$-COOH ($n = 0 \div 5$) with dicircumcoronene is studied in terms of model complex formation of M3 and M4 type, since negative values of $\Delta G_{\text{binding}}$ are obtained for
such complexes in the case of acetic acid. A change in the orientation of the carboxylic acid group relative to the PAH plane leads to a change in the binding enthalpy and Gibbs free energy (table 4). The most preferable orientation of acid turns out to be the one when the carboxylic group and all carbon atoms of the hydrocarbon radical lie in the same plane parallel to the PAH plane (figure 3, model M4). Complexes in which the indicated acid groups are oriented perpendicular to the PAH plane (figure 3, model M3) are characterized by lower binding Gibbs free energy. Note that the orientation of the acid molecule according to the model M4 corresponds to arrangement of other surfactant molecules when modelling their behavior on graphene. Here [34], parallel orientation of ethoxylated alcohol molecules with respect to the graphene plane along the so-called “zig-zag” is recorded, when the surfactant chain is oriented at an angle of 30° to the graphene plane. Such behavior, according to the authors of ref. [34], is stipulated by the match between the hydrocarbon tail and the graphene carbon atoms, which is consistent with our approach to the description of such systems.

**Figure 3.** Optimized structures of dicircumcoronene complexes with pentanoic acid (side view) with different acid orientations relative to the PAH plane.

As it is shown above for acetic acid, dicircumcoronene is used as a model of the graphene plane for further investigation the adsorption of a number of carboxylic acids on graphene. When constructing models of intermolecular complexes, the acid molecule is located at a distance of about 3.5 Å from the PAH plane. Its orientation corresponds to the model M4 (figure 4).

**Figure 4.** Optimized structure of the complex of dicircumcoronene with hexanoic acid (model M4).

It is interesting to note that during the formation of complexes according to the type of model M4 with various acid chain lengths, the distance between the acid molecules and the polyaromatic hydrocarbon in the complex practically does not change (table 4). The lengths of acid C-H bonds taking part in nonvalent interactions with PAH elongated marginally in the complex with respect to the free acid molecules: $\Delta l_{C-H}$ values are only 0.001 Å. Also the change in the electron density on the hydrogen
atoms of these bonds is insignificant: the difference in partial charges on these hydrogen atoms in the free and complexed acids lies in the range $\Delta q_{H} = (0.003-0.006)$ e. The observed $\Delta l_{C-H}$ and $\Delta q_{H}$ values are in good agreement with the characteristics obtained for benzene complexes with various C-H bond donors [32] using the DFT methods.

Table 4. Binding enthalpies, entropies and Gibbs free energies, as well as structural characteristics of molecular complexes of dicircumcoronene with carboxylic acids $C_nH_{2n+1}$COOH ($n = 0 \div 5$).

| R-COOH, R: | $\Delta H_{binding}$, kcal/mol | $\Delta S_{binding}$, cal/(mol·K) | $\Delta G_{binding}$, kcal/mol | d(C…C), Å | d(H…C), Å |
|-----------|-------------------|-----------------|-------------------|----------|----------|
| H         | -2.96             | -5.28           | 0.02              | 3.77     | 3.19     |
| CH₃       | -5.46             | -7.04           | -0.89             | 3.62     | 3.35     |
| C₂H₅      | -6.57             | -8.57           | -2.19             | 3.69     | 3.37     |
| C₃H₇      | -8.06             | -10.16          | -1.37             | 3.72     | 3.39     |
| C₄H₉      | -7.60             | -11.52          | -1.56             | 3.81     | 3.39     |
| C₅H₁₁     | -10.24            | -13.69          | -3.99             | 3.99     | 3.39     |

For complexes of types M3 and M4 for dicircumcoronene with the studied acids a monotonic decrease of the binding enthalpy is observed (table 4). Negative values of $\Delta H_{binding}$ indicate the exothermal process. The obtained values of $\Delta G_{binding}$ for the studied systems according to the type of model M3 are negative except for the complex with formic acid, and are quite low (the absolute values of $\Delta H_{binding}$ and $\Delta G_{binding}$ are discussed hereinafter). The stability of the complexes increases for acids in the range from formic to hexanoic.

The obtained complexes of carboxylic acids with dicircumcoronene are apparently stabilized due to nonvalent interactions of the C-H…CₚAᵣ type. An analysis of the data in table 4 reveals the presence of linear correlations between the thermodynamic parameters of complex formation and the number ($K$) of such stabilizing interactions (figure 5 and eqs. (1) – (3)) for model M4. For the studied series of acids $K$ is determined by the length of the hydrocarbon radical of the acid and corresponds to the number of carbon atoms in it. In figure 6 the lines correspond to predicted values of thermodynamic parameters according to correlation eqs. (1) – (3), and the points correspond to the directly calculated ones. Formic acid was excluded from the considered correlation due to the absences of nonvalent interactions of the indicated C-H…CₚAᵣ type.

$$\Delta H_{binding} = (-1.63 \pm 0.07)K + (-5.32 \pm 0.24) \text{ kcal/mol}$$
$$R = 0.997, \ N = 5 \quad (1)$$

$$\Delta S_{binding} = (-1.44 \pm 0.42)K + (-21.7 \pm 1.4) \text{ cal/(mol·K)}$$
$$R = 0.894, \ N = 5 \quad (2)$$

$$\Delta G_{binding} = (-1.20 \pm 0.13)K + (1.14 \pm 0.42) \text{ kcal/mol}$$
$$R = 0.983, \ N = 5 \quad (3)$$

The obtained dependences (1) – (3) are characterized by a rather high correlation coefficients and are of prognostic value when assessing the interaction energy of larger PAHs with carboxylic acids.
Figure 5. Dependences of binding enthalpy, entropy, and Gibbs free energy on the number (K) of complex stabilizing C-H...C\textsubscript{PAH} interactions (a) and visualization of C-H...C\textsubscript{PAH} interactions by the example of a complex of pentanoic acid with dicircumcoronene (b)

4. Conclusion

In the framework of the semi-empirical PM6-DH2 method the interaction of carboxylic acids \( \text{C}_n\text{H}_{2n+1}\text{COOH} \) (n=0÷5) with polyaromatic hydrocarbons of coronene series is studied. It is shown that for the associates of acetic acid with regarded PAHs the binding enthalpy and Gibbs free energy increase by absolute value during the transition from coronene to dicircumcoronene. This comes out in favor to use the latter PAH for modelling the behavior of longer-chained carboxylic acids at its surface. In this case an increase of the hydrocarbon chain length leads to an increase in the binding enthalpy and Gibbs free energy for carboxylic acids with dicircumcoronene. It has been shown that the most preferable alignment of the acid in the complex is when the carboxyl group and all the carbon atoms of the acid lie in a plane parallel to the PAH plane. It was found that the thermodynamic parameters of complex formation between carboxylic acid \( \text{C}_n\text{H}_{2n+1}\text{COOH} \) (n=1÷5) with dicircumcoronene linearly correlate with the number of nonvalent stabilizing C-H...C\textsubscript{PAH} interactions. It is reasonable to study further the interaction of carboxylic acids and PAHs with a large number of carbon atoms in order to extrapolate the results and assess the formation thermodynamic parameters of acid complexes with graphene.

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