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Quantum-chemical studies of the interaction of partially oxidized graphene-like planes with each other

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Using the methods of quantum chemistry, the energy effects of the interaction of partially oxidized graphene-like planes with each other and the effect on this characteristic of the nature of the functional groups present in the oxidized graphene-like planes, as well as the dimensions of the graphene-like planes themselves, were clarified. It was established that the reaction between the hydroxyl and aldehyde groups of two interacting graphene-like planes is the most thermodynamically probable, regardless of the dimensions of the graphene-like planes. The reaction between two carboxyl groups of different graphene-like planes is the least thermodynamically probable. To create nanocomposites by interacting graphene-like planes with each other, it is necessary that the graphene-like planes contain hydroxyl and aldehyde groups.

Keywords: oxidized graphene-like planes, chemical reaction, pyrene, coronene, density functional theory method, cluster approximation.

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Introduction

Creation of sp²-hybridized carbon-carbon composite nanomaterials is a promising direction of modern science [1–4]. Nanocomposites with the specified properties, as evidenced by the literature, can be created in a wide variety of ways, in particular, in the interaction of sp²-hybridized carbon materials with inorganic compounds and metals [5, 6], with polymers [7, 8], as well as with low molecular weight organic substances [9, 10]. Also, when obtaining new sp²-hybridized carbon-carbon composite materials with unique properties, it was recently possible to obtain functionalized carbon materials [11–14], in particular, partially oxidized forms of graphene [15, 16]. One of the promising ways of creating carbon nanocomposites presented in [17] is its result in the production of large-scale graphene sheets by dispersing graphene particles with certain functional groups in organic solvents.

Another approach to the experimental creation of carbon nanocomposites is based on the so-called

crosslinking of graphene sheets [18–20], that is, on the covalent interaction of different graphene-like planes (GLP). In particular, work [21] even proposed the concept of so-called conformational engineering, which consists in the construction of new composites from sheets of oxidized graphene. It was reported in [22] that dehydration, for example, by vacuum drying an aqueous solution of graphene oxide (GO), causes irreversible spontaneous cross-linking of its sheets. Dehydrated GO films retain their structural integrity in water, and they can no longer re-disintegrate into individual layers after stirring. At the bilayer level, after dehydration, folded GO sheets are fixed, which do not dissociate together even after sonication. Spectroscopic studies confirm the formation of new chemical bonds, suggesting a condensation-esterification reaction between GO sheets.

To find out the features of the creation of new carbon nanocomposites, computer modeling methods are successfully used, in particular, calculation schemes of quantum chemistry [23–26], as well as molecular dynamics [27–29].

It is known that the process of creating a composite material based on thermally expanded graphite (TRG) and carbon nanotubes (CNTs) consists in simultaneous deagglomeration of CNTs and intercalation of natural graphite [30]. This procedure can be carried out in two ways: electrochemical (anodic) or chemical oxidation. In our previous works [31–33], it was shown that the process of creating a carbon nanocomposite TRG-CNT occurs as follows: graphite oxidized to the first stage was hydrolyzed, washed to neutral pH, dried and heat-treated at a temperature of $\sim 1000^\circ\text{C}$ in a gas horizontal industrial furnace. Next, the obtained TRG nanocomposite powder was rolled on horizontal rolls. It was assumed that the formation of sp^2 -hybridized carbon-carbon composites is related not only to the effect of physical factors (pressure, temperature) on the starting material, but also to the chemical interaction of individual partially oxidized GLPs with each other. Since there are various oxygen-containing functional groups on the surface of partially oxidized carbon graphene materials, which are capable of exhibiting significant chemical activity [34]. But it remains unknown how covalent bonding of GLPs is possible during the formation of sp^2 -hybridized carbon-carbon composite materials. Therefore, the goal of the work was to find out the interaction energy of partially oxidized graphene-like planes with each other and the effect on this characteristic of the nature of functional groups that are present in oxidized GLPs using quantum chemistry methods.

I. Objects and calculation methods

Polyaromatic pyrene molecules with different functional groups on their periphery were considered as models of partially oxidized GLPs, while the functional groups were chosen so that the carbon atom near them had a different degree of oxidation, the lowest near the hydroxyl group (Fig. 1, *a,d,g*), higher - in carbonyl (Fig. 1, *b,e,h*), and the largest - in carboxyl (Fig. 1, *c,f,i*).

In addition, in order to take into account the size effect of GLP on the energy parameters of the studied reactions, graphene-like planes with a gross composition of $\text{C}_{24}\text{H}_{12}$ (coronene) were used (Fig. 1, *d–e*), and $\text{C}_{42}\text{H}_{16}$ (Fig. 1, *e–g*).

Calculations were performed using the GAMESS program (US) [35] within the framework of the density functional theory (DFT) with the B3LYP functional [36, 37] and the 6-31G(d,p) basis set, taking into account the Grimme D3 dispersion correction [38, 39]. This calculation method has proven itself well in modeling graphene-like clusters [40].

II. Results and their discussion

The first of the considered reactions consists in the interaction of GLP with a hydroxyl group on the periphery with the same graphene-like plane (Fig. 2). At the same time, there is an interaction of two hydroxyl groups of different GLPs with the release of a water molecule and the formation of a reaction product in which the GLPs are

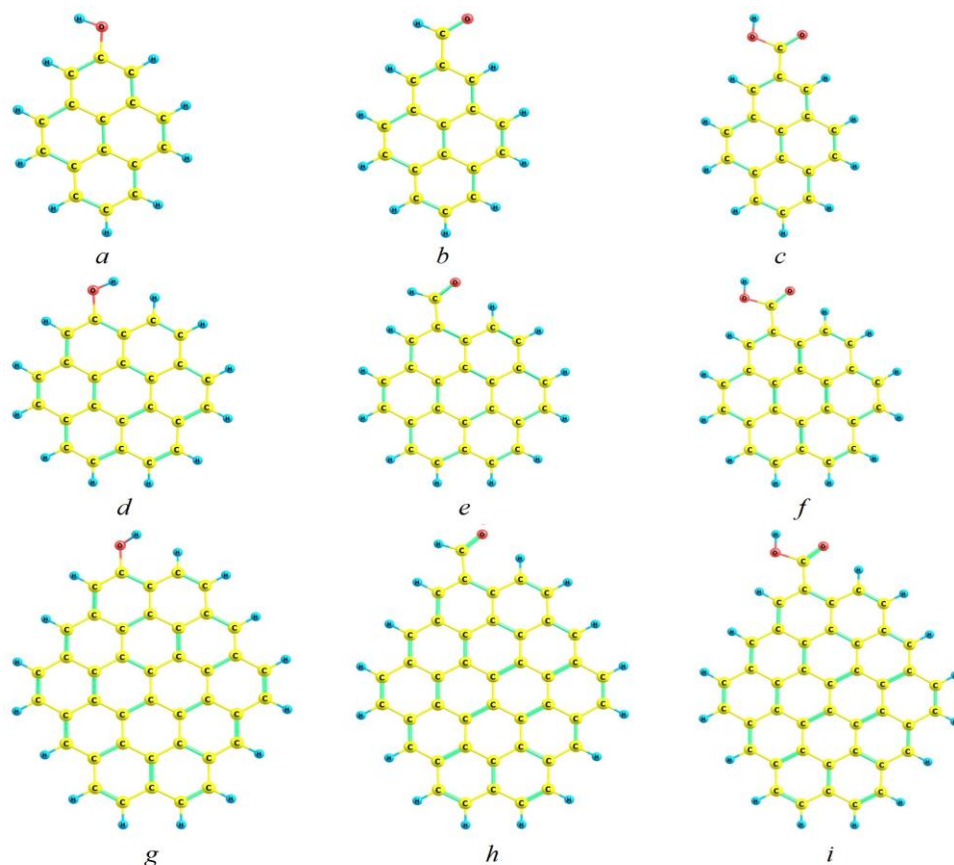
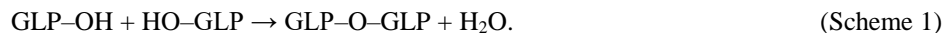


Fig. 1. Equilibrium geometry of partially oxidized GLPs of different sizes, with hydroxyl (*a, d, g*), aldehyde (*b, e, h*), and carboxyl (*c, f, i*) groups.

covalently connected to each other by an oxygen bridge.

This reaction can be represented by scheme 1:



According to (Scheme 1), a hydrogen atom of one hydroxyl group (Fig. 2, *a*) interacts with an oxygen atom of another hydroxyl group (Fig. 2, *b*), as a result of which the bond between C–O atoms of the last group is broken and a water molecule is formed (Fig. 2, *d*), and the oxygen atom of the other hydroxyl group forms a covalent bond

with the carbon atom of the second GLP. In this way, a product is formed (Fig. 2, *c*), which consists of two chemically bonded GLP planes with the help of an oxygen bridge.

The energy effect of reactions was calculated according to formula (1):

$$\Delta E_{\text{react}} = [E_{\text{tot}}(\text{GLP-O-GLP}) + E_{\text{tot}}(\text{H}_2\text{O})] - 2 E_{\text{tot}}(\text{GLP-OH}), \quad (1)$$

where $E_{\text{tot}}(\text{GLP-O-GLP})$ is the total energy of the interaction product of two GLPs with hydroxyl groups, $E_{\text{tot}}(\text{H}_2\text{O})$ is the total energy of the reaction product – H_2O , $E_{\text{tot}}(\text{GLP-OH})$ is the total energy of the GLP with a hydroxyl group.

The energy effect of this reaction (Scheme 1), calculated by formula (1), has a positive value and is +22.2 kJ/mol (see Table).

When using larger GLP models, the reaction products are localized (Fig. 3), similar in structure to the previous case (Fig. 2, *c*).

As can be seen from Figures 3, *a* and 3, *b*, despite the different sizes of the GLP, the reaction products obtained are similar to each other. It should be noted that the two GLPs in the reaction products are not located in a common plane, but placed at a small angle. For the smallest model (Fig. 2, *c*), the angle between the planes is 64.4° , for the product consisting of two coronene planes (Fig. 3, *a*), this angle is much larger and reaches 90.2° , and for the largest by the size of the reaction product (Fig. 3, *b*), the angle between the GLPs is similar to the previous one and is

equal to 90.3° . This may indicate that the further increase in the size of GLPs with hydroxyl groups will have almost no effect on the angle between the planes. Therefore, in the reaction products (Scheme 1), the GLPs are located almost perpendicular to each other, regardless of the size of the initial GLPs. This non-coplanarity of the two GLPs is apparently caused by a significant repulsion of a pair of closely spaced hydrogen atoms of neighboring graphene-like planes, one from each of them (see Figs. 2 and 3). As the size of the graphene-like planes in the reaction product increases, their mutual repulsion increases, as can be seen from the distances between the hydrogen atoms of different GLPs (2.8 Å for pyrene, 3.3 Å for coronene, and 3.5 Å for the maximum size GLP).

The energy effect of the reaction during product formation (Fig. 3, *a*), calculated according to formula (1), also has a positive, but much smaller value, as in the previous case, and is +1.3 kJ/mol. A similar value of the energy of the formation of the product of the reaction involving the maximum-sized GLP among those considered in the work is even closer to 0, but it is slightly

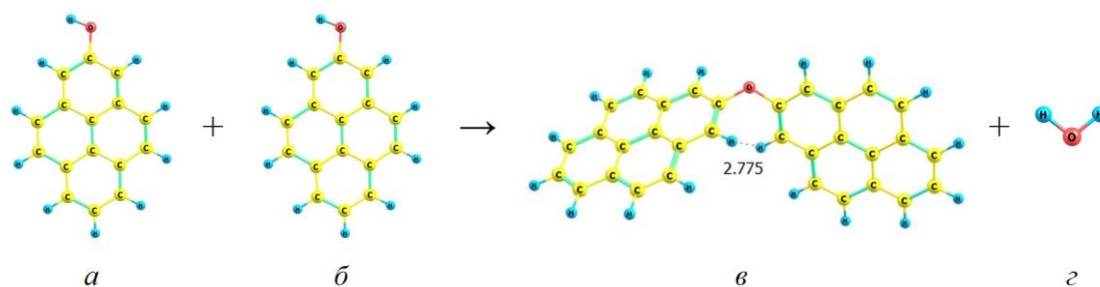


Fig. 2. Equilibrium geometry of the molecules of the starting substances (*a*, *b*) and reaction products (*c*, *d*) of the interaction of two GLPs with a hydroxyl group on the periphery, (here and further the distances between atoms are given in Å).

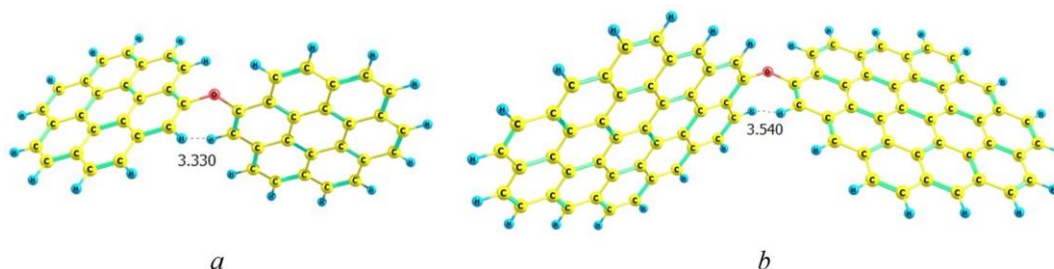
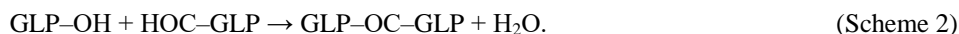


Fig. 3. Equilibrium geometry of the molecules of the reaction products of two graphene-like planes ($\text{C}_{24}\text{H}_{12}$ – (*a*), $\text{C}_{42}\text{H}_{16}$ – (*b*)) with hydroxyl groups.

smaller than the previous one and is only +0.1 kJ/mol (see the Table).

Next, the reaction between GLP with a hydroxyl group on the periphery and a graphene-like plane

containing an aldehyde group was considered (Fig. 4). In this reaction, the hydroxyl group of one GLP interacts with the aldehyde group of another GLP according to scheme 2:



According to this scheme, the oxygen atom of the hydroxyl group (Fig. 4, *a*) interacts with the hydrogen atom of the aldehyde group (Fig. 4, *b*). As a result, the C–O bond between the hydroxyl group and GLP is broken, and, in turn, the H–C bond in the aldehyde group is broken with the formation of a water molecule. At the same time, the carbon atom of the first GLP (Fig. 4, *a*) interacts with

the carbon atom of the aldehyde group of the second graphene-like plane (Fig. 4, *b*) with the formation of a reaction product (Fig. 4, *c*), in which the two GLPs are covalently linked between themselves through the carbonyl group (>C=O).

The energy effect of reactions was calculated according to formula (2):

$$\Delta E_{\text{react}} = [E_{\text{tot}}(\text{GLP-OC-GLP}) + E_{\text{tot}}(\text{H}_2\text{O})] - [E_{\text{tot}}(\text{GLP-OH}) + E_{\text{tot}}(\text{HOC-GLP})], \quad (2)$$

where $E_{\text{tot}}(\text{GLP-OC-GLP})$ is the total energy of the interaction product of the hydroxyl group of one GLP with the aldehyde group of another GLP, $E_{\text{tot}}(\text{H}_2\text{O})$ is the total energy of the H₂O molecule, $E_{\text{tot}}(\text{GLP-OH})$ is the total energy of the GLP with a hydroxyl group, $E_{\text{tot}}(\text{HOC-GLP})$ is the total energy of GLP with an aldehyde group.

As the results of the calculation according to formula (2) show, the energy effect of the reaction (Scheme 2), in contrast to similar values for the reaction (Scheme 1), has a negative value, for the product of the reaction, in which the graphene-like planes are the smallest, is -17.1 kJ/mol (see Table).

When using the coronene molecule (Fig. 1, *d, e*) and the molecule with the composition C₄₂H₁₆ (Fig. 1, *e, c*) as starting GLPs for the reaction (Scheme 2), reaction products are formed (Fig. 5), the molecules of which are

similar in structure to those considered above (Fig. 4, *c*). In the molecules of the reaction products (Scheme 2), as can be seen from these figures, the GLPs are located relative to each other not perpendicularly, as in the reaction products (Scheme 1), and not parallel, but at an acute angle. In particular, for the structure depicted in fig. 4, *c*, this angle is 47.8°, for the product from coronene derivatives (Fig. 5, *a*) it is slightly larger and has a value of 53.3°, and for the product of the reaction with GLP of the maximum size (Fig. 5, *b*), is 54.2°.

The energy effect of the reaction (Scheme 2), calculated according to formula 2, during the formation of a product from coronene derivatives (Fig. 5, *a*), in contrast to the similar value (-17.1 kJ/mol), where in the molecule of the reaction product (Scheme 2) graphene-like planes are the smallest, has a value close to 0 and is +0.5 kJ/mol.

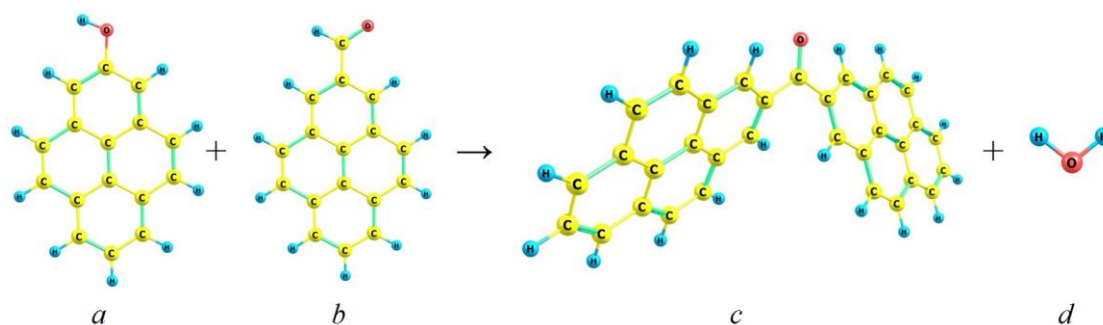


Fig. 4. Equilibrium geometry of the molecules of the starting substances and reaction products of the interaction of two GLPs that contain hydroxyl and aldehyde groups.

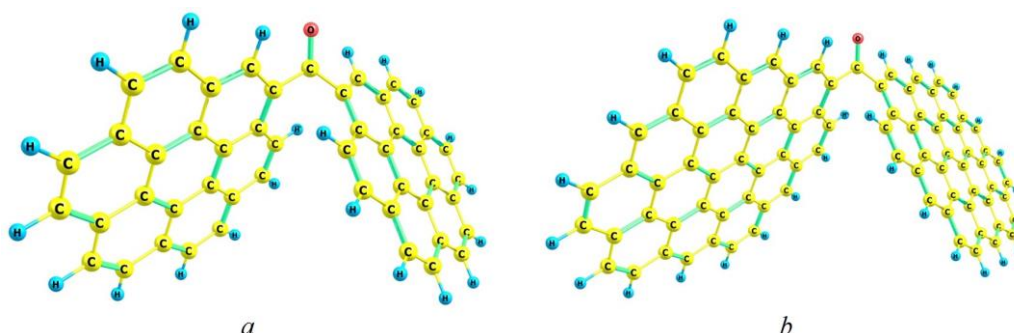


Fig. 5. Equilibrium geometry of the molecules of the reaction products of two graphene-like planes (C₂₄H₁₂ – (*a*), C₄₂H₁₆ – (*b*)) with hydroxyl and aldehyde groups.

With a further increase in the size of the GLP during product formation (Fig. 5, *b*), the energy effect slightly decreases in absolute value to -0.9 kJ/mol.

Subsequently, the reaction between GLP with a

hydroxyl group on the periphery and GLP with a carboxyl group on the periphery was investigated. In it, the hydroxyl group of one GLP interacts with the carboxyl group of another GLP according to Scheme 3:



According to this scheme, similar to the reaction discussed above (Scheme 2), the oxygen atom of the hydroxyl group (Fig. 6, *a*) interacts with the hydrogen atom of the carboxyl group (Fig. 6, *b*), as a result of which the C–O bond between the hydroxyl group and GLP in the molecule of the starting substance (Fig. 6, *a*), while the H–O bond in the carboxyl group breaks with the formation of a water molecule. At the same time, the carbon atom of

the first GLP (Fig. 6, *a*) interacts with the oxygen atom of the carboxyl group of the second graphene-like plane (Fig. 6, *b*) with the formation of a reaction product (Fig. 6, *c*), in which the two GLPs are covalently linked between themselves through the ester group (–O–C(=O)–).

The energy effect of reactions was calculated according to the formula:

$$\Delta E_{\text{react}} = [E_{\text{tot}}(\text{GLP-O-OC-GLP}) + E_{\text{tot}}(\text{H}_2\text{O})] - [E_{\text{tot}}(\text{GLP-OH}) + E_{\text{tot}}(\text{HOOC-GLP})], \quad (3)$$

where $E_{\text{tot}}(\text{GLP-O-OC-GLP})$ is the total energy of the interaction product of the hydroxyl group of one GLP with the carboxyl group of another GLP, $E_{\text{tot}}(\text{H}_2\text{O})$ is the total energy of the H_2O molecule, $E_{\text{tot}}(\text{HOOC-GLP})$ is the total energy of the GLP with the carboxyl group.

As the results of the calculation according to formula (3) show, the energy effect of the reaction (Scheme 3), similar to the analogous reaction values (Scheme 1), has a positive value, which is for the product of the reaction, in which the GLP is the smallest (Fig. 6, *c*), +26.0 kJ/mol (see Table).

When using larger GLP models ($\text{C}_{24}\text{H}_{12}$ and $\text{C}_{42}\text{H}_{16}$), molecules of the reaction products are formed (Fig. 7), similar in structure to the previous one (Fig. 6, *c*).

An interesting feature of the molecular geometry of

these reaction products is that the GLPs are located in one plane, regardless of the size of the graphene-like planes used, which is due to the occurrence of a hydrogen bond between the hydrogen atom of one GLP and the carbonyl oxygen atom of the other. The length of this bond is 2.152 Å, which is characteristic of the case when the hydrogen atom of the C–H bond takes part in the hydrogen bond. This approximately O•••H distance is also preserved when using larger GLPs, in particular, in the product where coronane is used as the GLP, this distance is 2.118 Å (Fig. 7, *a*), and for the product in which the GLPs are of the maximum size - 2.110 Å (Fig. 7, *b*).

The energy effect of the reaction (Scheme 3) when a coronene molecule is used as a GLP is also positive and is 4.1 kJ/mol smaller than the similar value for the same

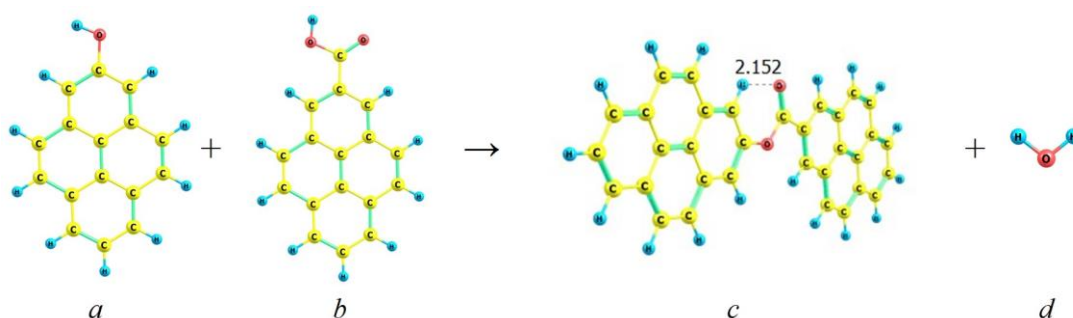


Fig. 6. Equilibrium geometry of molecules of starting substances and reaction products of the interaction of two graphene-like planes containing hydroxyl and carboxyl groups.

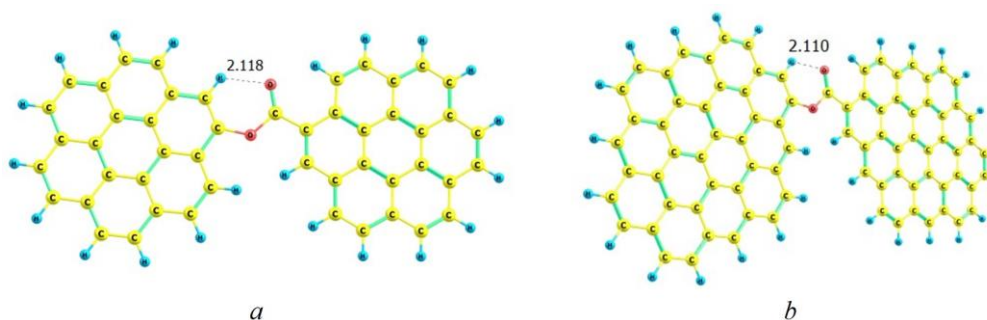
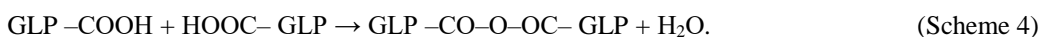


Fig. 7. Equilibrium geometry of the molecules of the reaction products of two graphene-like planes ($\text{C}_{24}\text{H}_{12}$ - (*a*), $\text{C}_{42}\text{H}_{16}$ - (*b*)) with hydroxyl and carboxyl groups.

reaction, in which a pyrene molecule was used as graphene-like planes, and is +21.9 kJ/mol. If the GLP is dominated by a larger molecule, in particular C₄₂H₁₆ (Fig. 7, *b*), then the energy effect is also a positive value, which has a value of +19.9 kJ/mol (see Table).

And finally, for comparison, the interaction of two GLPs with carboxyl groups on the periphery of each of them is considered. This reaction can be represented by scheme 4:



According to this scheme, the hydrogen atom of the carboxyl group of the molecule of the first starting substance (Fig. 8, *a*) interacts with the oxygen atom of the acid center of the carboxyl group of the molecule of the second starting substance (Fig. 8, *b*). As a result, the C–O bond between the hydroxyl group and the carbon atom in the carboxyl group of the molecule of the second starting substance is broken, while the H–O bond in the carboxyl group of the molecule of the first starting substance is broken (Fig. 8, *a*) with the formation of a water molecule.

At the same time, the oxygen atom of the acid center of the carboxyl group of the molecule of the first starting substance interacts with the carbon atom of the carboxyl group of the molecule of the second starting substance (Fig. 8, *b*) with the formation of a molecule of the reaction product (Fig. 8, *c*), in which two GLPs are covalently connected to each other through a symmetric group (–C(=O)–O–C(=O)–).

The energy effect of reactions was calculated according to formula (4):

$$\Delta E_{\text{react}} = [E_{\text{tot}}(\text{GLP-CO-O-OC-GLP}) + E_{\text{tot}}(\text{H}_2\text{O})] - 2 E_{\text{tot}}(\text{GLP-COOH}), \quad (4)$$

where $E_{\text{tot}}(\text{GLP-CO-O-OC-GLP})$ is the total energy of the interaction product of two GLP s with carboxyl groups, $E_{\text{tot}}(\text{H}_2\text{O})$ is the total energy of the reaction product – H₂O, $E_{\text{tot}}(\text{GLP-COOH})$ is the total energy of the GLP with a carboxyl group.

The energetic effect of the GLP reaction with two carboxyl groups (Scheme 4) when using pyrene molecules as graphene-like planes, calculated according to formula (4), is the maximum of all previously considered and amounts to +74.5 kJ/mol.

When the size of these graphene planes increases, molecules of the reaction products are formed (Scheme 4), which are also similar in spatial structure to each other

(Fig. 9, *a* and 9, *b*) and the reaction product molecule with carboxylatedpyrene molecules (Fig. 8).

As can be seen from these figures, in contrast to the molecules of the products of the HP reaction with hydroxyl and carboxyl groups (Scheme 3), in all these molecules of the reaction products (Scheme 4), the graphene-like planes are not parallel to each other, but form some angle between them, like and in the molecules of products of the reaction of HP with hydroxyl and aldehyde groups (Scheme 2) (Fig. 4, *c* and Fig. 5). In particular, the angle between graphene-like planes in the smallest pyrene-containing reaction product (Fig. 8, *c*) is 77.2°. In the larger product, in which the GLP was

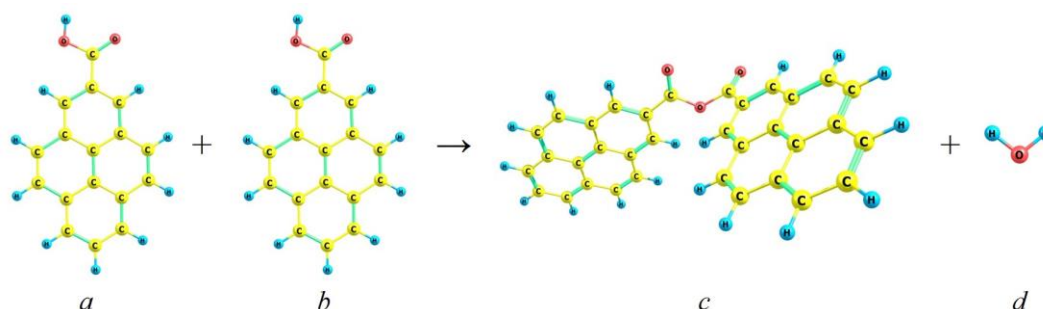


Fig. 8. Equilibrium geometry of molecules of starting substances and reaction products of the interaction of two graphene-like planes with a carboxyl group on the periphery.

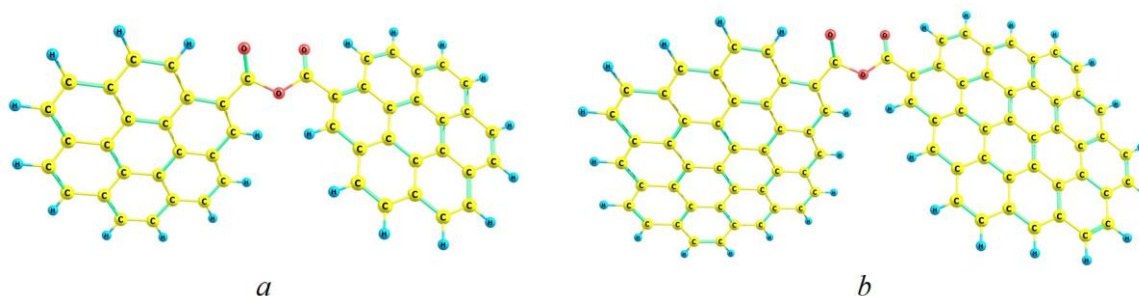


Fig. 9. Equilibrium geometry of the molecules of the reaction products of two graphene-like planes (C₂₄H₁₂ – (*a*), C₄₂H₁₆ – (*b*)) with two carboxyl groups.

Table

Energy effects of the interaction of partially oxidized graphene-like planes with each other.

No. reaction scheme	Interaction scheme	ΔE_{react} (kJ/mol)		
		C ₁₆ H ₁₀	C ₂₄ H ₁₂	C ₄₂ H ₁₆
1	GLP-OH + HO-GLP → GLP-O-GLP + H ₂ O	+22.2	+1.3	+0.1
2	GLP-OH + HOC-GLP → GLP-OC-GLP + H ₂ O	-17.1	+0.5	-0.9
3	GLP-OH + HOOC-GLP → GLP-O-OC-GLP + H ₂ O	+26.0	+21.9	+19.9
4	GLP-COOH + HOOC-GLP → GLP-CO-O-OC-GLP + H ₂ O	+74.5	+70.6	+69.3

dominated by coronene molecules, the corresponding angle is slightly smaller and has a value of 54.7°. For the reaction product of the maximum size, this angle is almost the same as the previous one and is 55.9°. Such non-coplanarity is caused by the presence of closely spaced oxygen atoms with a significant negative charge on each of them in the considered molecules.

The energy effect of the reaction (Scheme 4) for the crown-containing product also has a positive value, which is +70.6 kJ/mol, and for the reaction product of an even larger size, this value is even smaller and its value is +69.3 kJ/mol (see Fig. Table).

It can be seen from the table that, regardless of the size of the GLP, the lowest absolute value of the energy effect with the participation of the same oxygen-containing group is characteristic of the reaction of the interaction of the GLP with hydroxyl and aldehyde groups (Scheme 2). It should also be noted that for all the considered reactions except the reaction (Scheme 2), with an increase in the size of the GLP, the magnitude of the energy effect decreases. The greatest dependence of the energy effect on the size of the graphene-like planes is observed for the reaction (Scheme 1) of the interaction of the GLP with hydroxyl groups. In this case, the values of ΔE_{react} decrease from 22.2 for pyrene-containing GLPs to 0.1 kJ/mol for C₄₂H₁₆ GLPs. For the reaction (Scheme 2), with an increase in the size of the graphene-like planes, on the contrary, the energy effect increases by 16.2 kJ/mol, from -17.1 to -0.9 kJ/mol. For the reaction of the interaction of a hydroxyl group with a carboxyl group in graphene-like planes, ΔE_{react} differ by 6.1 kJ/mol when the size of the GLP changes from the minimum to the maximum. And with the interaction between two carboxyl groups (Scheme 4), similar values change by only 5.2 kJ/mol.

Conclusions

Therefore, as evidenced by the analysis of the results of quantum chemical calculations, the reaction between the hydroxyl and aldehyde groups of two interacting GLPs is the most thermodynamically probable, regardless of the dimensions of the graphene-like planes.

The reaction of the interaction of hydroxyl groups of two adjacent graphene-like planes is slightly less thermodynamically probable.

The reaction between two carboxyl groups of different graphene-like planes is the least thermodynamically probable.

To create nanocomposites by interacting graphene-like planes with each other, it is necessary that the graphene-like planes contain hydroxyl and aldehyde groups.

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Квантовохімічні дослідження взаємодії частково окиснених графеноподібних площин між собою

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Методами квантової хімії з'ясовані енергетичні ефекти взаємодії частково окиснених графеноподібних площин між собою і їхня залежність від природи оксигенвмісних функціональних груп, які наявні в них, а також від розмірів самих графеноподібних площин. Встановлено, що найбільш термодинамічно ймовірною є реакція між гідроксильною і альдегідною групами двох взаємодіючих графеноподібних площин незалежно від їхніх розмірів. Найменш термодинамічно ймовірною є реакція між двома карбоксильними групами різних графеноподібних площин. Для створення нанокомпозитів при взаємодії графеноподібних площин між собою, необхідно щоб у складі графеноподібних площин були наявні гідроксильні і альдегідні групи.

Ключові слова: окиснені графеноподібні площини, хімічна реакція, пірен, коронен, метод теорії функціонала густини, кластерне наближення.