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DOUBLE-LAYER SILICENE-BASED CARCERANDS: MOLECULAR CONTAINERS FOR UNSTABLE COMPOUNDS

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We have studied the formation of a "host-guest" type carcerand with a double-layer silicene (DL-S) as a host and an unstable antiaromatic cyclobutadiene as a guest.

By employing the methods of MM+, PM3 and Monte-Carlo, there has been studied the positioning of molecules of cyclobutadiene in a DL-S depending on intercalate concentration and intercalation temperature. At that the deformation vibrations of the DL-S crystal grate do not exceed 0.017 nm, and the vibrations of the intercalate molecules do not exceed 0.025 nm which provides for configuration and conformation stability of the system. The silicene planes do not move relatively each other and the order of the silicon atoms between the planes remains the same – AB… (similar to the silicene single crystal). When initially heated from 0 to ~273 K, the systems energy grows gradually, then rises sharply between 273–300 K and 350–400 K, then, with the temperature growth, it reaches a plateau which proves its high stability up to ~420 K.

In the temperature range 0–273 K there appears physical sorption while chemisorption is observed at higher temperature (~300 K) which is peculiar of π-π interactions of classical aromatic and quasiaromatic cyclic and heterocyclic systems.

There have been calculated the UV-spectra of the DL-S depending on the intercalate concentration in terms of the modified Benes-Hilderbrand method. There has been shown that the association constant of the system studied is 380 l·mol^{-1}, with computation accuracy ≥ 0.977.

***Keywords:** double-layer silicene, cyclobutadiene, intercalation, modelling, association constant*

INTRODUCTION

Carcerands are relatively young and extremely interesting compounds. The first carcerands were synthesized in 1985 by a group of scientists headed by Donald J. Cram [1]. The authors suggested as a "host" various large organic molecules that grasped a "guest" thus implementing in a future complex new and interesting physical and chemical properties. Among carcerands, as inclusion compounds the most deeply studied and most widely spread are carcerands based on various derivatives of calix[n]arenes, cyclodextrins, *etc.* [2–4]. They are known under the general name – "host-guest" complexes. "Guests" in such complexes can be metal ions, organic molecules (including biologically active molecules), coordination compounds or metal chelates, with aromatic or heteroaromatic ligands. On the other hand, "hosts" can be single/multi-walled carbon nanotubes, multi-layer graphene or silicene structures. Unique physical properties of multi-walled nanosystems (especially of silicene-based ones) have been the subject of keen interest lately [4–9].

Silicene is a newly discovered material which is monoatomic layer thin. It is a two-dimensional (2D) nanomaterial classified as a nanosheet which has large lateral dimensions up to micrometers, but thickness of several nanometers or less [4]. The unique properties and morphology of such material make it ideal for a variety of applications, including electronic devices, batteries and sensors. A 2D silicene nanosheet can be considered an analogue of graphene. The specific surface area of nanomaterials can play one of the key roles in their application [4, 5, 10–12]. Anomalous transportation and field effects open a wide prospect of their applying in nanoelectronics

[2, 6, 13–15]. Such nanostructures are assumed to be promising spintronics materials due to the long electron free path, weak spin-orbital interaction and long spin scattering [16, 17]. What is more, chemical and physical modification of multi-walled nanosystems enables to reveal their new extraordinary features. Thus, intercalation with atoms (molecules) allows us to change the Fermi level position, relative electron and hole concentration, without considerable changes in energy-band structure of source nanomaterials [7, 18].

On the other hand, unique optical, electrical and magnetic [19], and also biological properties of complexes [8] stimulate creation of intercalates on their base with multi-layer silicene, since the capability of these complexes to coordinate with multi-layer silicene [9] allows us to obtain new materials as effective elements for photo- and magnetosensitive devices, drug delivery, imaging and therapy, as well as to use these materials as an antidetonant in motor and aviation fuels.

As identification of structure-to-property relations is an important task of chemistry and materials physics, the aim of this work was to study theoretically the structure of double-layer silicene (DL-S) intercalated with cyclobutadiene molecules when heated by the methods of MM+, PM3 and Monte-Carlo. In this work our goal was also to calculate the UV-spectra of a DL-S depending on intercalate concentration as well as to determine the association constant of the "DL-S intercalate" system.

MODEL AND METHODS

Our main object of interest – a DL-S [4] – was modelled with 32 silicon (Si) atoms in each plane. The distance between the planes was chosen to be 0.3855 nm (we selected the AB… order of Si atoms between the planes). DL-S intercalation is produced via introduction of the intercalate molecules into the inter-layer space. As stated above, our goal was to study the system of two silicene planes, with cyclobutadiene molecules intercalated between them. Of particular interest are the positions of the cyclobutadiene relatively each other and the Si atoms, mutual positioning of the silicene planes in the presence of the cyclobutadiene intercalates (with or without keeping the AB…

order of Si atoms between the planes), as well as the stability of the system under heat treatment.

In the model considered the interaction potential (Leonard-Jones potential) between Si atoms (see Eq. (1)) and carbon (C) atoms directly mated the pair potential of high energy of atomic excitation [20]. It was described by the Born-Mayer equation within 0–0.91 nm of effective interaction radius (see Eq. (2)):

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \qquad (1)$$

where r – distance between particle centres, ε – depth of potential pit, σ – distance at which the interaction energy is equal to zero (parameters ε and σ characterise atoms of corresponding substances);

$$U(r) = A \exp(-r/b), \qquad (2)$$

where A, b – constant, for every pair of colliding particles.

To describe the interatomic interaction at a distance smaller than 0.2 nm, we have used the Tersoff-Brenner potential [21]. Total potential energy of system U is expressed as a sum of bonding energies for all pairs of atoms forming this system

$$U = \sum_{i} \sum_{j>i} \left[V_R\left(r_{ij} \right) - B_{ij}^{*} V_R\left(r_{ij} \right) \right], \qquad (3)$$

where r_{ij} – distance between i and j atoms; $V_R(r)$ – exponential function included into the Morse type potential which corresponds to the energies of attraction and repulsion between the atoms; B_{ij}^{*} – the function expressing the dependence of binding energy of the i and j atoms on the angles θ_{ijk} between the bond i-j and close bonds i-k and j-k.

To describe the interatomic interaction at a distance greater than 0.21 nm we have employed the Tersoff-Brenner potential [21] along with the Ziegler-Biersack-Litmark pair potential [20]. The length of Si–Si bonds in a silicene was 0.222 nm (Si-Si-Si angle is 109.5°; Si sp^3-hybridization), the C–Si interaction was described by the Lennard-Jones pair potential [22] with potential interaction energy 0.11 eV. The modelled period of one excitation cascade was 2 ps, and the energy conservation law in every calculation cycle was correlated within 0.15 %. The initial coordinates of

the intercalate were selected in conformity with the law of random numbers.

To perform the task above the following numerical modelling scheme was used:

1) the first calculation stage was based on the MM+ molecular mechanics method;

2) the second stage was based on the semi-empirical PM3 method. It should be noted that the main distinction of this method from the others is their different parameterisation. In our case the PM3 method was parameterised to the best match of calculated and experimental molecule formation heats;

3) the third stage was based on the Monte-Carlo method.

To calculate the association constant of the "DL-S intercalate" complex formed, there was employed the modified Benes-Hilderbrand method that accounts the data on maximum DL-S absorption values at various intercalate concentrations in the UV-spectra.

RESULTS AND DISCUSSION

The studied system (see Fig. 1) proved to be rather heat-resistant in a wide temperature range (up to ~400 K). At that the deformation vibrations of the DL-S crystal grate do not exceed 0.017 nm, and the vibrations of the

intercalate molecules do not exceed 0.025 nm that provides for configuration and conformation stability of the system. The silicene planes do not move relatively each other and the order of the Si atoms between the planes remains the same – AB… (similar to the silicene single crystal). Temperature dependence of the model system energy is shown in Fig. 2. As it is seen, when initially heated from 0 to ~273 K the energy of the systems grows gradually, then rises sharply between 273–300 K and 350–400 K, then, with the temperature growth, it reaches a plateau which proves its high stability up to ~420 K. At the temperature over 420 K all cyclobutadiene molecules are extruded from the field of active interaction with silicene planes which results in cyclobutadiene further impossible free state existence.

It should be noted that this variant of the model suggested allows us to demonstrate thermodynamic selectivity of physical and chemical sorption-desorption. In the temperature range 0–273 K there appears physical sorption while chemisorption is observed at higher temperature value (~300 K) which is peculiar of π-π interactions of classical aromatic and quasiaromatic cyclic and heterocyclic systems.
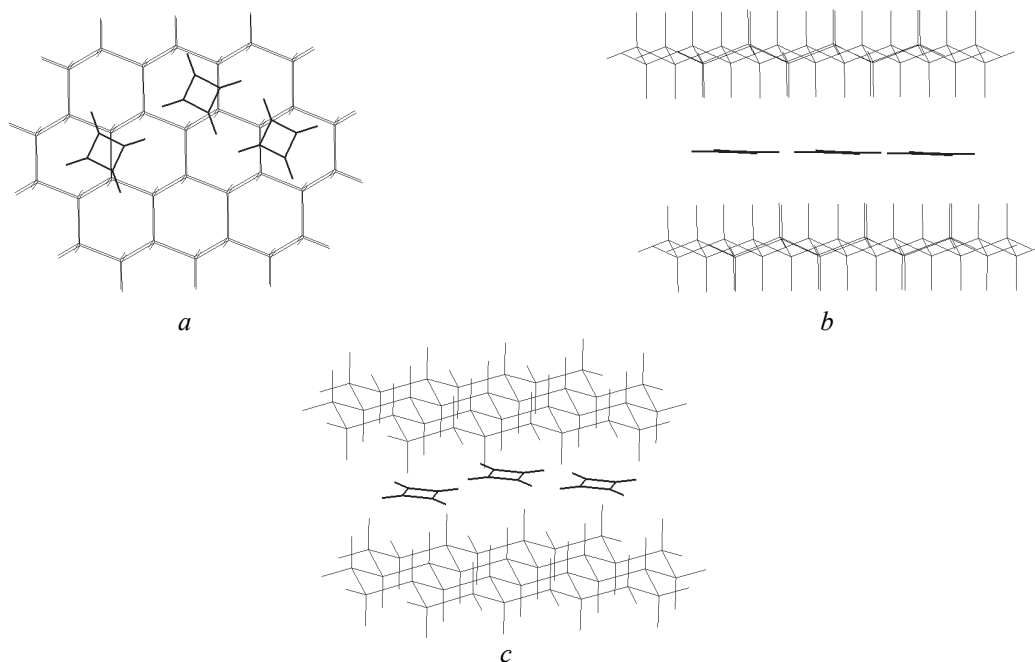

Fig. 1. A starting geometric model of the "DL-Silicene-intercalate" system: (*a*), (*b*) –orthogonal projections; (*c*) – side view
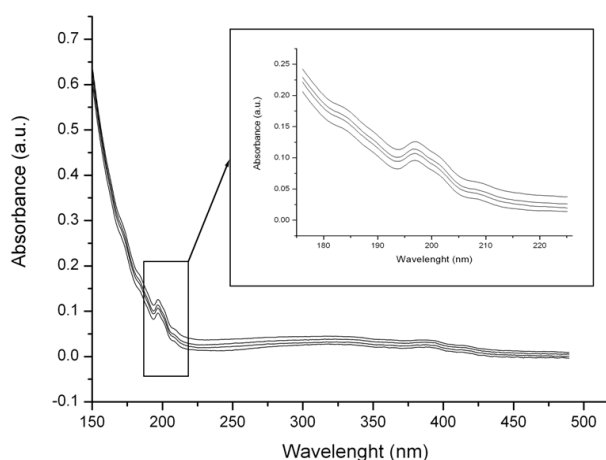
Finally, theoretical calculations of UV-absorption spectra (Fig. 3) of the DL-S depending on the intercalate concentration in terms of the modified Benes-Hilderbrand method (Eq. (4)) show that the association constant (K_{ass}) of the system studied is 380 l·mol^{-1} with computation accuracy ≥ 0.977,

$$C_{quest}(A_0 - A) = \frac{1}{K_{ass} \cdot \Delta\varepsilon} \cdot \frac{1}{C_{host}} + \frac{1}{\Delta\varepsilon}, \qquad (4)$$

where C_{quest} and C_{host} – "quest" and "host" concentration, respectively; A_0 – silicene absorption and A – silicene-cyclobutadiene absorption, respectively; $\Delta\varepsilon$ – change of molar extinction coefficient.
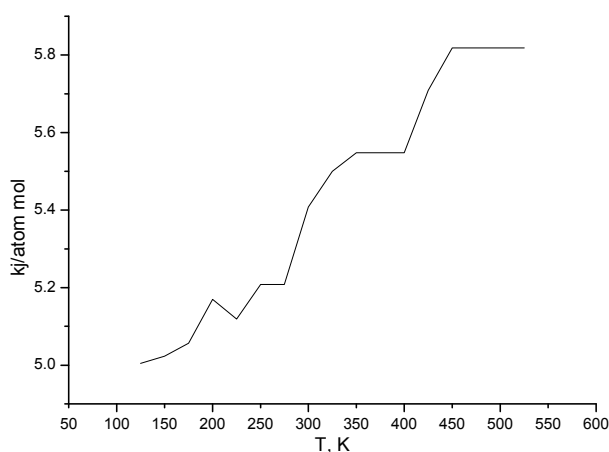
Fig. 2. Temperature dependence of the "DL-Silicene-intercalate" model systems

Fig. 3. Theoretical UV-absorption spectrum of the DL-Silicene system

CONCLUSION

There has been found the type of cyclobutadiene molecules arrangement in the interlayer space of the DL-S. The calculations allow us to prove that the "DL-S intercalate" system is rather stable at the temperature up to ~273 K which provides reliability and stability of the process of intercalate synthesis under conditions regular for this procedure. However,

under further heating there is observed gradual intercalate extrusion outside the inter-layer space. At 350–400 K silicene is left without the intercalate. The association constant of the "DL-S intercalate" system has been theoretically calculated and it is equal to 380 l·mol^{-1}, that means possible existence of an antiaromatic molecule under room conditions.

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Карцеранди на основі двошарового силіцену: молекулярні контейнери для нестабільних сполук

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Використовуючи методи молекулярної механіки ММ+, напівемпіричного квантовохімічного РМ3 і Monte-Carlo, досліджено характер розміщення молекул циклобутадієну у двошаровому силіцені залежно від концентрації інтеркаляту та температури інтеркаляції. Зі збільшенням температури (вище ~273–300 К) відбувається послідовне руйнування утворених зв'язків з екструзією міжплощинного інтеркаляту. Подальше збільшення температури до 350 К характеризується десорбцією інтеркаляту та стабілізує досліджувану систему загалом, зберігаючи при цьому лише одну молекулу інтеркаляту. За температури 400 К циклобутадієн повністю екструдує силіцен, руйнуючись при цьому. Розраховано УФ-спектр силіцену залежно від концентрації інтеркаляту та знайдено константу асоціації досліджуваної системи, яка становить 380 л·моль$^{-1}$.

Ключові слова: двошаровий силіцен, циклобутадієн, інтеркалювання, моделювання, константа асоціації

Карцеранды на основе двухслойного силицена: молекулярные контейнеры для нестабильных соединений

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Используя методы молекулярной механики ММ+, полуэмпирического квантово-химического РМ3 и Monte-Carlo, исследован характер размещения молекул циклобутадиена в двухслойном силицене в зависимости от концентрации интеркалята и температуры интеркалирования. Показано, что с увеличением температуры (выше ~273–300 К) происходит последовательное разрушение образованных связей с экструзией межплоскостного интеркалята. Последующее увеличение температуры до 350 К характеризуется десорбцией интеркалята и стабилизирует исследуемую систему в целом, сохраняя при этом только одну молекулу интеркалята. При температуре 400 К циклобутадиен полностью экструдирует силицен, разрушаясь при этом. Рассчитан УФ-спектр силицена в зависимости от концентрации интеркалята и найдена константа ассоциации исследуемой системы, которая составляет 380 л·моль$^{-1}$.

Ключевые слова: двухслойный силицен, циклобутадиен, интеркалирование, моделирование, константа ассоциации

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