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STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structure of a Perfect Carbyne

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Abstract—The crystal structure of a perfect carbyne is calculated by the molecular mechanics methods. It is established that the carbyne crystals should consist of polycumulene chains arranged in hexagonal bundles. The unit cell of the perfect carbyne crystal is trigonal and contains one carbon atom. The unit cell parameters are as follows: $a = b = c = 0.3580$ nm, $\alpha = \beta = \gamma = 118.5°$, and space group $P3m1$. The perfect carbyne single crystals have a stable structure at room temperature if the length of their constituent chains is larger than 500 nm.

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INTRODUCTION

A carbon atom in chemical compounds can exist in one of the three main hybridized states, i.e., the *sp*, sp^2, and sp^3 states [1–3]. Graphite is a layered allotropic carbon modification formed by sp^2-hybridized atoms [4]. Diamond is a three-dimensional structural carbon modification composed of sp^3 atoms [5]. The third linear allotropic modification corresponding to the *sp* hybridization could not be found for a long time. In 1885, Baeyer was the first to attempt to synthesize artificially a linear carbon modification, but his attempts failed. The results of the performed investigations led the Baeyer to the conclusion that the linear carbon modification cannot exist [7, 8]. However, in 1960s, the linear carbon modification referred to as the carbyne was synthesized in the USSR [9, 10]. In 1968, the carbyne-like carbon was found in geological rocks formed in a meteorite crater [11]. Approximately two tens of various carbyne-like materials differing in structural parameters have been artificially synthesized and revealed in nature to date [12–14].

However, all these materials cannot be considered linear allotropic carbon modifications in a pure form, because they contain a large number of carbon atoms in the sp^2- or sp^3-hybridized state, as well as impurity atoms, and, moreover, the chains consisting of *sp*-hybridized atoms are not linear due to a considerable distortion [13–15]. At present, the problem associated with the three-dimensional structure of perfect carbyne crystals, the conditions for the stable existence of carbyne, and the methods for its experimental synthesis has remained unsolved. There are assumptions that the thermodynamic conditions at which the carbyne can occur in a stable state are similar to those in the vicinity of the triple point in the phase diagram of carbon [16–19].

In this respect, it is necessary to perform detailed theoretical investigations into a possible crystal structure of a perfect carbyne in order to determine the conditions for its stable existence and to design methods for the experimental synthesis of carbyne crystals. The present work was devoted to the solution of these problems.

STRUCTURAL MODEL AND CALCULATION TECHNIQUE

The model calculations were carried out for carbyne crystals composed of polycumulene (involving only double bonds) and polyyine (containing alternating single and triple bonds) infinite chains arranged parallel to each other. The perfect carbyne structure was calculated in two stages.

At the first stage, we studied the pair van der Waals interactions between the carbyne chains. The interatomic potential of the van der Waals interaction was taken from the monograph [20]. Initially, we determined the minimum lengths of the carbyne chains that can be used in the calculation. For this purpose, we calculated the specific energy E_{sp} of the pair interaction between the chains per atom. The atoms contained only in one unit cell were considered in one of the interacting chains, and the number of atoms in the second interacting chain was varied. Since a significant contribution to the interchain interaction energy is made only by the nearest neighboring atoms, the second interacting chain can have a finite length. The calculations revealed that the number of atoms in the second chain can be limited by 179 for the polycumulene chain and 138 for the polyyine chain. An increase in the number of atoms in the chains above these values leads to a change in the specific energy by less than 0.01% of the magnitude.

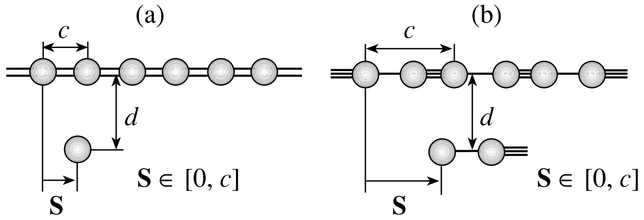


Fig. 1. Schematic diagram illustrating the relative arrangement upon translation by the vector **S** for (a) polycumulene chains and (b) polyyne chains.

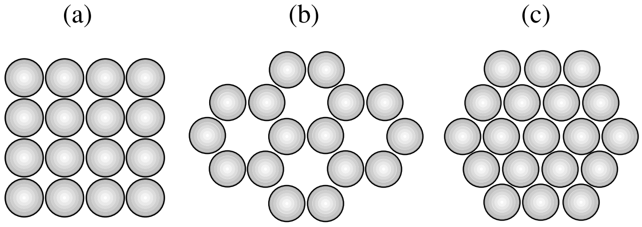


Fig. 2. Possible two-dimensional structures of carbyne bundles: (a) square structure, (b) hexagonal structure with vacancies, and (c) hexagonal structure.

The specific energy E_{sp} was calculated for different relative positions of the neighboring carbyne chains. In this case, we varied two parameters, namely, the relative translation vector **S** and the interchain distance d (Fig. 1). When calculating the pair interchain interactions, the translational vector was discretely varied from 0 to **c** with a step of 0.1**c**, where **c** is the fundamental translation vector of the carbyne chain (**c** = 0.1337 and 0.2748 nm for the polycumulene and polyyine chains, respectively). For each fixed value of the translation vector, we determined the interchain distances d_{min} at which the specific energy of the interchain interaction is minimum. The absolute minimum of the interchain interaction energy was observed for the relative translation vector equal to 0.5**c**.

In order to simplify the procedure for calculating the structure of bundles formed by carbyne chains, we constructed new potentials according to which the interaction between the carbyne chains is described not as the interaction of each atom of one carbyne chain with each atom of another carbyne chain but as the interaction of one atom of the first carbyne chain with the second carbyne chain as a whole. These potentials were represented in the form of the Lennard-Jones potentials

$$U(d, S) = -\frac{A(S)}{d^6} + \frac{B(S)}{d^{12}}, \quad (1)$$

where the coefficients A and B were calculated from the previously obtained quantities d_{min} and E_{sp} for the corresponding translation vectors with the use of the relationships

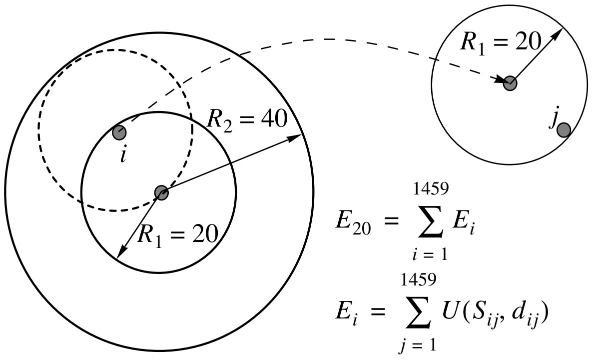
$$A(S) = \frac{2E_{sp}(S)}{d_{min}^{-6}}, \quad B(S) = \frac{E_{sp}(S)}{d_{min}^{-12}}. \quad (2)$$

The coefficients A and B depend on the translation vector **S**. The corresponding dependences are well interpolated by sixth-degree polynomials. The polynomial coefficients were calculated by the least-squares technique. As a result, the potentials describing the interchain interactions have the following form:

$$U(d, S) = -\left[A_0 + A_1S + A_2S^2 + \ldots + \frac{A_6S^6}{d^6}\right] + \left[B_0 + B_1S + B_2S^2 + \ldots + \frac{B_6S^6}{d^{12}}\right]. \quad (3)$$

At the second stage, we calculated the three-dimensional structures of the bundles of carbyne chains with a minimum specific energy of bonds per atom. The distances d between the chains and their relative translations $\mathbf{S}_{ij}$ were varied in the calculations. We considered the square and hexagonal structures of bundles and also the hexagonal structure with vacancies, because the existence of this structure was assumed in [13] (Fig. 2).

Initially, we determined the limiting size of bundles that can be used in the further calculation. For this purpose, we calculated the specific energy E_{sp} of the interaction of one atom of the central chain with all chains forming the bundle, whose radius was varied from 1 to 60 interchain distances. The analysis of the obtained dependences of the specific energy on the bundle size demonstrated that the bundle radius can be limited by 20 interchain distances (R_1 = 7.103 nm for the polycumulene bundle). This bundle contains 1459 chains. In order to simulate the conditions under which the carbyne chains should occur in infinite crystals, the calculations were performed for the bundles whose radius was two times larger than the limiting radius (R_2 = 14.206 nm). For the central part of these bundles, we calculated the sum of the specific energies of the interaction of atoms of each chain with the surrounding bundle of the limiting radius. The scheme for the calculation of the total energy of van der Waals bonds in the bundles is shown in Fig. 3. The calculated energy was divided into the number of chains in the central part of the bundle (i.e., into 1459), thus obtaining the specific energy E_{3D} of van der Waals interaction per carbon atom in the carbyne structure. The specific energy E_{3D} depends on the relative translation of the chains in the bundle and the interchain distance. In this respect, we determined the values of these parameters at which the specific energy E_{3D} is minimum. The calculations were carried out for the bundles with a random and periodic alternation of the relative translation vectors. Note that it would make no sense to calculate the specific energy E_{3D} for the bundles with the square structure and the hexagonal structure with vacancies for a random arrangement of the translation vectors, because, in these cases, there are structures with an absolute minimum of the energy E_{3D} of van der Waals bonds. In the given structures, the chains can be arranged so that the relative translation vector of each chain with respect to the nearest neighbors will be equal to half the fundamental translation vector of the carbyne chain. This arrangement corresponds to the minimum energy of the pair interactions. However, this chain arrangement is not possible for the hexagonal bundle. Therefore, the corresponding model calculations were performed for last case.



$$E_{20} = \sum_{i=1}^{1459} E_i$$

$$E_i = \sum_{j=1}^{1459} U(S_{ij}, d_{ij})$$

Fig. 3. Schematic diagram illustrating the calculation of the total energy of the van der Waals bonds in bundles of chains.

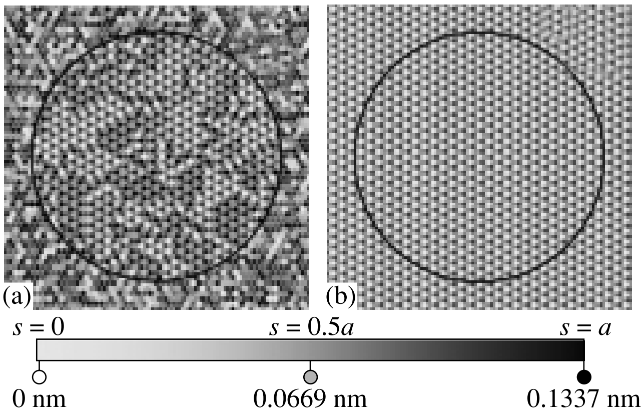


Fig. 4. Structures of the hexagonal bundles formed by polycumulene chains with (a) random arrangement and (b) periodic arrangement of the relative translation vectors and the schematic diagram illustrating the interpretation of the magnitudes of the translation vectors with respect to the origin of the coordinates. Solid lines bound the bundles with a radius equal to 20 interchain distances.

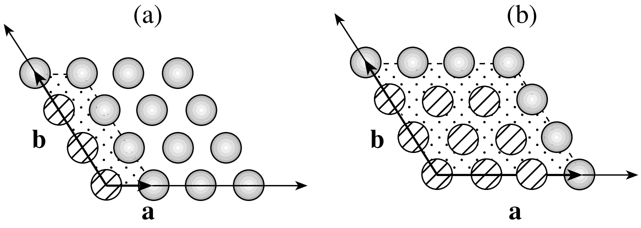


Fig. 5. Schematic drawing of (a) 1 × 3 (a = 0.3553 nm, b = 1.066 nm) and (b) 3 × 3 (a = 1.066 nm, b = 1.066 nm) unit cells in bundles of chains.

RESULTS OF CALCULATIONS

In order to simulate the random bundles, the relative translation vectors were generated by the Monte Carlo method. Among 2×10^3 structures thus generated, we chose one structure with a minimum specific energy E_{3D}. Then, an even more energetically favorable structure of the bundles was found using the following additional procedure for minimizing the energy. The chain was randomly chosen from the bundle, the translation vector of the chain was varied in a narrow range ($\Delta S \sim \pm 0.001$–$0.01c$) with respect to the initial vector, and the specific energy E_{3D} was calculated. If this energy was reduced, the new translation vector was taken for the given chain; otherwise, the translation vector remained unchanged. This procedure was carried out 10^2 times for each chain out of 1459 chains in the bundle. Figure 4a depicts the optimized structure of the hexagonal bundle formed by the polycumulene chains with a random arrangement of the relative translation vectors. The translation vector magnitude continuously varying from 0 to c is represented by gray tints (Fig. 4).

For the hexagonal bundles, we also calculated the energies of bonds for a periodic arrangement of the translation vectors obtained by translation of the unit cells with different sizes. The unit cells are designated as $a \times b$, where a and b are the fundamental translation vectors (measured in the interchain distances) for the carbyne bundles (Fig. 5). The values of a and b were varied from one to five interchain distances.

The relative translation vectors of the carbyne chains within the unit cell were constructed in two stages according to the procedure described above for the random bundles. The obtained relative arrangement of the translation vectors within the unit cell was translated over the entire bundle (the structure of the periodic hexagonal bundle with 3 × 3 unit cells is shown in Fig. 4b). Then, the specific energies E_{3D} were calculated for these bundles. The data obtained are presented in Table 1.

The results of calculations demonstrate that the minimum energy of van der Waals bonds is observed fro the bundles consisting of the polycumulene chains for which the specific energy E_{3D} is 3% lower than the specific energy E_{3D} for the bundles composed of the polyyne chains (Table 2). Therefore, the carbyne crystals should consist of polycumulene chains. The inference that the polyyne chains are energetically unfavorable as compared to the polycumulene chains also follows from a comparison of the specific energy E_k of covalent bonds per atom (this is the largest contribution to the total energy of bonds and exceeds ten times the

Table 1. Specific energies E_{3D} of the van der Waals bonds (J/mol) for bundles of polycumulene chains with $n \times m$ unit cells

m	n				
	1	2	3	4	5
1	–4481.09	–4481.91	–4481.60	–4481.91	–4481.72
2	–4481.91	–4481.91	–4481.88	–4481.89	–4481.89
3	–4481.60	–4481.88	**–4482.06**	–4481.90	–4482.02
4	–4481.91	–4481.90	–4481.90	–4481.91	–4481.94
5	–4481.72	–4481.89	–4482.02	–4481.92	–4481.96

Table 2. Minimum energies of the van der Waals bonds for different types of carbyne bundles

Type of carbyne chains	Type of two-dimensional lattice	$n \times m$	E_{3D}, J/mol
Polycumulene	periodic hexagonal	3 × 3	**–4482.06**
	random hexagonal		–4482.01
	hexagonal with vacancies	4 × 4	–2407.03
	square	2 × 2	–3539.35
Polyyne	periodic hexagonal	3 × 3	–4367.36
	random hexagonal		–4366.05
	hexagonal with vacancies	4 × 4	–2348.36
	square	2 × 2	–3453.90

energy of van der Waals bonds [1]). According to [1], the specific energies E_k for polyyne and polycumulene chains are equal to 592 and 613 J/mol, respectively. Consequently, the inference can be made that the crystals of the perfect carbyne should be composed of polycumulene chains. Furthermore, it follows from the data presented in [1, 13] that, when the length of polyyne chains becomes larger than 30–40 atoms, the difference between the lengths of ordinary and triple bonds levels off, electrons are delocalized, and polyyne chains degenerate into polycumulene chains.

A comparison between the specific energies E_{3D} of different polycumulene bundles indicates that the specific energies of bonds of atoms in the bundles with the hexagonal structure are approximately 22% lower than those in the bundles with the square structure and are 53% lower than those in the bundles with the hexagonal structure containing vacancies (Table 2). Therefore, the perfect carbyne crystals should consist of the polycumulene chains arranged in hexagonal bundles. In turn, a comparison between the specific energies E_{3D} of hexagonal bundles demonstrates that the structures with a periodic arrangement of the relative translation vectors are more preferable than random structures and the minimum specific energy E_{3D} corresponds to the periodic bundle with 3 × 3 unit cells (Table 1). In this bundle, one-third of chains have zero translation vector, the translation vector of the second third of chains is equal to $1/3c$, and the last third of chains are translated by $2/3c$. As a consequence, the relative translation vectors for each adjacent carbyne chain in the 3 × 3 bundle are equal to one-third of the fundamental translation vector c.

DISCUSSION AND CONCLUSIONS

Thus, the conclusion can be drawn that the perfect carbyne crystals should be composed of the polycumulene chains arranged in hexagonal bundles characterized by 3 × 3 unit cells. The corresponding primitive unit cell of the perfect carbyne crystals is trigonal, has a volume of 0.0146 nm^3, and contains one carbon atom. The unit cell parameters are as follows: $a = b = c = 0.3580$ nm, $\alpha = \beta = \gamma = 118.5°$, and space group $P3m1$.

However, a comparison between the bond energies for the random and periodic polycumulene hexagonal bundles demonstrates that their difference is equal to 0.1% of the magnitude. The question arises as to the stability of these structures and the possibility of transforming one structure into the other structure. In order to evaluate the stability of the structures, we calculated the height of the potential barrier that should be overcome when transforming the random structure of the carbyne bundles into their periodic structure and vice versa. For this purpose, we used the aforementioned energetically most favorable random and periodic 3 × 3 structures of the hexagonal bundles. In our calculations, the translation vector of each chain in the random structure was sequentially changed to the translation vector corresponding to the same chain in the 3 × 3 periodic structure and the specific energy E_{3D} was determined at each step (Fig. 6). As a result, the potential barrier height was estimated to be 0.207 J/mol.

The stability of the bundle structure was evaluated by comparing the potential barrier height with the energy of thermal vibrations for one degree of freedom (kT), because the relative translations of chains should occur along the z crystallographic axis. It was revealed that, at room temperature (T = 300 K), the energy of thermal vibrations in the bundles consisting of chains with a length of the order of 100 atoms is three orders of magnitudes higher than the potential barrier height. Therefore, the carbyne bundles consisting of carbyne nanochains cannot exhibit a three-dimensional order, because the chains in the bundles execute random thermal vibrations with amplitudes exceeding the distances between sites in the crystal lattice. Such a structure can be stabilized by addition of impurity atoms and formation of strong covalent bonds between chains. These carbyne-like materials have been synthesized at present [13–15]; however, they cannot be treated as perfect carbynes. The estimates show that a three-dimensionally ordered perfect structure of carbyne bundles will be stable when the environmental temperature is lower than

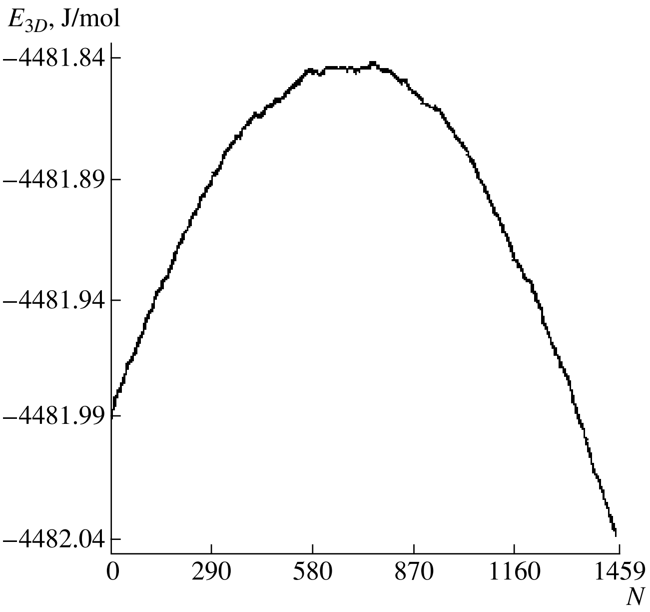


Fig. 6. Change in the bond energy of bundles formed by polycumulene chains upon transformation of a random bundle into a 3 × 3 periodic bundle.

10 K. For the ordered bundle structure to be stable at room temperature, the length of the chains forming the bundles should be more than 0.5 μm (should involve > 3000 atoms). Taking into account that the maximum length of straight-line segments of carbyne chains (without bends and interchain cross linkings) synthesized to date is less than a hundred of atoms [15], it is not surprising that three-dimensionally ordered crystals of the perfect carbyne have not been revealed in experiments. Therefore, in order to synthesize perfect carbyne single crystals stable at room temperature, it is necessary to provide the preparation of micrometer carbyne chains. It should be noted that, as follows from the data obtained in our work, it is highly improbable that the carbyne can exist at temperatures of 2800–3500 K, as was assumed in [16]. This conclusion is in good agreement with the results obtained by Basharin et al. [21], who experimentally revealed that the crystallization of liquid carbon under quasi-equilibrium conditions at temperatures of the order of 4800 K leads only to the formation of graphite without traces of any other allotropic modifications and also with the inferences made by Savvatimskii [19] that the graphite–carbyne solid phase transition cannot occur at least to a temperature of 3815 K.

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