Stability of $C_{20}$ fullerene chains

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ABSTRACT

The stability of $(C_{20})_N$ chains, where $C_{20}$ fullerenes are covalently coupled is analyzed by numerical simulation using a tight-binding potential. Various channels of losing the chaincluster structure of the $(C_{20})_N$ complexes have been determined including the decay of the $C_{20}$ clusters, their coalescence, and the separation of one $C_{20}$ fullerene from a chain. The lifetimes of the $(C_{20})_N$ chains with $N = 3 - 7$ for $T = (2000 - 3500)$ K are directly calculated by the molecular dynamics method. It has been shown that although the stability of the chains decreases with an increase in $N$, it remains sufficiently high even for $N \gg 1$. An interesting lateral result is the observation of new $(C_{20})_N$ isomers with the combination of various intercluster bonds and the maximum binding energy of fullerenes in the chain.
Since the experimental detection of the smallest possible fullerene \((C_{20})_N\) [1] in 2000 (see Fig. 1a), a problem of existing a solid phase (fullerite) based on this fullerene attracts considerable interest (by analogue with the known fullerite consisting of \(C_{60}\) fullerenes [2,3]). Theoretical calculations [4-7] indicate the possibility of forming a condensed state of \(C_{20}\) fullerenes, although there is yet no commonly accepted opinion about the crystal structure of this hypothetical cluster substance [5-7]. In experiments, in addition to the \(C_{20}\) fullerene, only charged dimers \((C_{20})_2^+\), as well as complexes \((C_{20})_N^+\) with \(N = 3 - 13\), were observed [8]. Reports [9,10] on synthesizing \(C_{20}\) crystals have not yet been corroborated. In contrast to the \(C_{60}\) fullerite, where single clusters are bounded due to weak van der Waals attraction, the intercluster bonds in the \(C_{20}\) fullerite must be covalent according to the theory developed in [4-7]; therefore, they must be very rigid. On the one hand, this can promote the stability of the solid phase. On the other hand, the strong coupling between clusters can lead to transformation into another atomic configuration,

Previously, we showed [11] that a single \(C_{20}\) fullerene loses its spheroidal shape at high temperatures through decay into various energetically unfavorable quasi-one-dimensional or quasi-two-dimensional configurations rather than through a transition to a ”bowl” isomer with minimum total energy \(E\). The \((C_{20})_2\) dimer can lose its molecular structure (see Fig.1b) due both to the decay of one of the \(C_{20}\) fullerenes and to the coalescence of two \(C_{20}\) fullerenes into a \(C_{40}\) cluster [12,13]. In this case, the height \(U\) of the lowest energy barrier bounding the initial metastable configuration decreases from \(\approx 5\) eV to \(\approx 2.5\) eV [12]. This decrease leads to a decrease in the activation energies of the corresponding processes and, as a consequence, a decrease in the lifetime at a given temperature [13]. With increasing the number of fullerenes in the \((C_{20})_N\) complexes with \(N > 2\), the stabilization of the metastable state due to an increase in the number of nearest neighbors, as well as appearance of new mechanisms of stability loss,
can be expected.

In this work, we theoretically analyze the thermal stability of the quasi-one-dimensional \((C_{20})_N\) chains as a first step of analysis of the stability of macroscopic three-dimensional cluster structures based on \(C_{20}\) fullerenes. Such metastable chains with various bonds between fullerenes (see Figs. 2a-c) were previously considered using the density functional theory (DFT) and the combination of the tight-binding approximation with the DFT (DFTB method) [4,7]. It was shown that the binding energy of fullerenes \(\Delta E = E(C_{20}) - E[(C_{20})_N]/N\) for a given \(N\) is minimal (the total energy \(E[(C_{20})_N]\) is maximal) in chains with open-[2+2] intercluster bonds, as in the isomer \((C_{20})_2\) with the minimum total energy \(E[(C_{20})_2]\) (see Fig. 1b).

We use the tight-binding method [14], which was successfully applied to simulate both small clusters and macroscopic carbon structures (previously, we successfully used it to investigate various characteristics of the \(C_{20}\) and \(C_{60}\) fullerenes, as well as other carbon systems [11-13,15,16]). First, we verify that this method gives the same sequence of the \((C_{20})_N\) chains in their energies (i.e., in \(\Delta E\)) as that obtained in more accurate DFT calculations [4,7]. In agreement with [4,7], we found that \(\Delta E\) is maximal in the chains with open-[2+2] bonds and is smaller in the chains with "twisted" bonds (in terminology accepted in [7]). The extrapolation of data obtained for \(N = 3 - 12\) to \(N \to \infty\) gives \(\Delta E = 4.341, 4.338, \) and 2.744 eV/\(C_{20}\) for open-[2+2], twisted, and [2+2] bonds, respectively, see Fig. 3.

Moreover, we found that combinations of various intercluster bonds are possible, see Figs. 2d and 2e. In this case, the binding energies \(\Delta E\) are usually between the corresponding \(\Delta E\) values for the chains with one type of bonds (see Fig. 2d). However, there is an interesting exception. For \(N \geq 4\), the presence of one or several twisted bonds in the chain with open-[2+2] bonds can increase \(\Delta E\), i.e., reduce the total energy. Thus, the combination of open-[2+2] and twisted bonds are most energetically favorable. However, the energy gain is so small (cf. Figs.
2a and 2e) that the configurations with pure open-[2+2] bonds and with the combination of open-[2+2] and twisted bonds are almost degenerate.

To analyze the thermal stability of the \((C_{20})_N\) chains, we use the molecular dynamics method. Configurations with open-[2+2] bonds are taken as initial configurations. At the initial time, each atom is given a random velocity and displacement so that the total momentum and angular momentum of the entire system are equal to zero. Then, forces acting on atoms are calculated and classical Newtonian equations of motion are solved with a time step of \(t_0 = 2.72 \cdot 10^{-16} \text{ s}\). The total energy of the system (the sum of the potential and kinetic energies) remains unchanged in the simulation process, which corresponds to the case, where the system is not in the thermal equilibrium with the environment [15]. In this case, the dynamic temperature \(T\) is a measure of the relative motion energy of atoms and is calculated as \([17,18]\) \(\langle E_{\text{kin}} \rangle = \frac{1}{2} k_B T (3n - 6)\), where \(\langle E_{\text{kin}} \rangle\) is the time-average kinetic energy of the entire system, \(k_B\) is the Boltzmann constant, and \(n = 20N\) is the number of atoms in a \((C_{20})_N\) chain. Since the lifetimes \(\tau\) of the \((C_{20})_N\) complexes to the time of loss of their cluster-chain structure increase exponentially as \(T\) decreases and, moreover, the time necessary for numerical calculations for a given \(T\) value increases with \(N\) as \(N^3\), we perform simulation for the chains with \(N \leq 7\) for temperatures \(T = (2000-3500) \text{ K}\). Nevertheless, we trace the evolution of these chains for \(t > 1 \text{ ns}\) (and even for \(t > 10 \text{ ns}\) for \(N = 3\)), whereas \(ab \ initio\) calculations are usually restricted to \(t < 0.1 \text{ ns}\).

First, in the process of evolution of the \((C_{20})_N\) chains for \(t < \tau\), we observed very frequent (in time 0.1-1 ps) changes of one or several open-[2+2] bonds between the \(C_{20}\) fullerenes to twisted bonds and vise versa. These changes occur due, first, to the closeness of the energies of the corresponding configurations (see Fig. 2) and, second, to a low height of the potential barrier separating these configurations \((U \approx 0.6 \text{ eV for } N = 2 [12])\), which is easily overcome.
at temperatures $T > 2000$ K. Such changes in the intercluster bonds lead neither to the loss of the spheroidal shape of the $C_{20}$ fullerenes in the chain nor to the breakdown of the chain.

We surprisingly observed one more way for reorganizing bonds between the $C_{20}$ clusters, in which the overall chain shape of the $(C_{20})_N$ complexes also remains unchanged. In this case, one of the open-$[2+2]$ bonds is first broken and, then, is recovered in a very short time ($\sim 0.1$ ps), but between other atoms, being rotated at an angle of about $70^\circ$ with respect to the other open-$[2+2]$ bonds in the chain, see Fig. 4a. Such changes in the intercluster bonds occur quite rarely (likely because the corresponding energy barrier is comparatively high); nevertheless, we repeatedly observe them in the chains with various $N$ values. It is interesting that the binding energies $\Delta E$ of the $(C_{20})_N$ isomers appearing in this case are slightly higher than the corresponding $\Delta E$ values in the isomers with open-$[2+2]$ bonds or combinations of open-$[2+2]$ and twisted bonds (e.g., $\Delta E$ increases by 0.017 and 0.015 eV/$C_{20}$ for $N = 3$ and 5, respectively, if the open-$[2+2]$ bond between the first and second $C_{20}$ fullerenes in the chain is turned). We also observe the formation of isomers in which one of the open-$[2+2]$ bonds is not only turned, but also twisted, see Fig. 4b. Their binding energies are as a rule higher by a very small value of $\sim 0.01$ eV/$C_{20}$. Therefore, these isomers correspond to energetically favorable configurations for the corresponding $N$ values. We do not know works reported about such $(C_{20})_N$ isomers.

The problem of the optimal (for the minimum total energy) number of turned and twisted bonds and the order of their alternation with each other and with the open-$[2+2]$ bonds requires a separate consideration, which is beyond the scope of this paper. This problem is insignificant for the main aim of this work, i.e., analysis of the thermal stability of $(C_{20})_N$ chains, because all found isomers are almost degenerate and hold the chain structure. Nevertheless, note that the results obtained in this work illustrate how the simulation of the dynamics of a complex many-particle system allows one to automatically find new metastable configurations the existence
of which is not a priori obvious and which can be missed when they are sought on the basis of other (e.g., symmetry) considerations. *Ab initio* calculations of the binding energies of the new \((C_{20})_N\) isomers found in this work would be of interest.

Similar to the simulation of the thermal stability of the \((C_{20})_2\) cluster dimers [12,13], we observe the decays of one of the fullerenes in the chain, see Fig. 5. In this case, the binding energy \(\Delta E\) decreases by 1.5 - 2.5 eV; i.e., the system transits to an energetically less favorable configuration; this is accompanied by a decrease in its temperature, because the total energy is a constant. When the end fullerene decays (see Fig. 5a), the fullerenes remaining in the chain hold their individualities for a longer time than in the case of the decay of one of the central fullerenes (Fig. 5b). This is explained partially by a more significant decrease in \(\Delta E\) (i.e., by a stronger cooling of the system) and partially by a smaller number of stressed covalent bonds in the remaining fullerenes. In any case, soon after the decay of one fullerene, the \((C_{20})_N\) complex completely loses its chain structure and transits to various (usually, quasi-two-dimensional) configurations with lower binding energies.

Similar to the \((C_{20})_2\) dimer [12,13], in addition to decay, there is a fundamentally different mechanism of losing the individuality of the \(C_{20}\) fullerenes in the chain: coalescence of two neighboring \(C_{20}\) fullerenes into a \(C_{40}\) cluster, see Fig. 6. In this case, the binding energy \(\Delta E\) increases by 0.5 - 1.5 eV (the larger increase corresponds to the \(C_{40}\) cluster whose structure is closer to the ideal \(C_{40}\) fullerene). An increase in \(\Delta E\) is accompanied by an increase in the temperature of the system, which leads to a fast decay of both the \(C_{40}\) cluster and the \(C_{20}\) fullerenes remaining in the chain. As a result, some quasi-two-dimensional configuration is usually formed.

The separation of one \(C_{20}\) fullerene from the \((C_{20})_N\) chain (see Fig. 7) is a new channel of the breakdown of this chain that is absent for the \((C_{20})_2\) dimer. We emphasize that such separation
was observed only once for the chain with \( N = 3 \). This likely is explained by a small frequency factor \( A \) of the corresponding process. It is interesting that the separation of the \( C_{20} \) fullerene from the chain occurs after its transition to an isomer with the turned \( \textit{open}-[2+2] \) bond, cf. Figs. 4a and 7.

In order to determine the activation energies \( E_a \) for decay and coalescence by the Arrhenius formula for \( \tau(T) \) from the numerical experiment, it is necessary to collect a sufficiently large statistical sample for each \( N \) value, as was previously done for the \( C_{60} \) fullerene [15] and \((C_{20})_2\) dimers [13]. Since the corresponding calculations require very large computation time, we compare \( \tau \) values obtained for certain temperatures in the range \( T = (2000 - 3500) \) K to the dependences \( \tau(T) \) found previously [13] for the decay and coalescence of the \( C_{20} \) fullerenes in the \((C_{20})_2\) dimer, see Fig. 8. In this case, similar to [13], the finite-heat-bath correction [19,20] is taken into account by setting \( \tau^{-1}(T) = A \exp(-E_a/k_BT^*) \), where \( T^* = T - E_a/2C \) [the microcanonical heat capacity is assumed to be \( C = (3n - 6)k_B \), where \( n = 20N \)]. As seen in Fig. 8, the loss of the stability of the chains for \( T < 2500 \) K is caused only by the coalescence of the \( C_{20} \) fullerenes, whereas this loss for \( T > 2500 \) K is caused by both coalescence and decay, although the decay events occur much rarely. Although an increase in \( N \) leads to a decrease in \( \tau \), the \((C_{20})_N\) chains remain sufficiently stable for \( N \gg 1 \). The average coalescence activation energy for the \((C_{20})_2\) dimer is equal to \( E_a = 2.7 \) eV [13], this energy for the \((C_{20})_N\) chains with \( N > 2 \) is only halved according to analysis of the “computer experiment” data. Then, a macroscopically large lifetime \( \tau \sim 10^7 \) s is obtained for temperature \( T = 300 \) K with the parameter \( A \sim 10^{16} \) s\(^{-1}\) [13].

Our next aim is to analyze the stability of two-dimensional and three-dimensional systems based on the \( C_{20} \) fullerenes, which will be done in a future work.
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Fig. 1. (a) Fullerene $C_{20}$; (b) *open-[2+2]* isomer of the $(C_{20})_2$ cluster dimer. The binding energy of fullerenes in the dimer is $\Delta E = 2.470 \text{ eV}/C_{20}$. 
Fig. 2. Chains (C_{20})_5 with the (a) open-[2+2], (b) [2+2], and (c) twisted bonds, as well as chains with the combination of (d) open-[2+2] bonds and [2+2] bonds and (e) open-[2+2] bonds and twisted bonds. The binding energies ΔE of fullerenes in the chains are (a) 3.598, (b) 2.298, (c) 3.511, (d) 2.973, and (e) 3.630 eV/C_{20}. 
Fig. 3. Binding energies $\Delta E$ of $C_{20}$ fullerenes in $(20)_N$ chains vs. $1/N$ for the chains with the intercluster (triangles) [2+2] bonds, (squares) open-[2+2] bonds, and (circles) twisted bonds, see Figs. 2a-c. The solid lines are the rms approximation.
Fig. 4. (a) \((\text{C}_20)_3\) isomer with \textit{open}-[2+2] bonds rotated with respect to each other. (b) \((\text{C}_20)_5\) isomer appearing due to the rotation and subsequent twisting of the \textit{open}-[2+2] bond between the second and third \text{C}_{20} fullerenes. The binding energies \(\Delta E\) of fullerenes in the chains are (a) 3.122 and (b) 3.624 eV/\text{C}_{20}. 
Fig. 5. Metastable configurations formed after the decay of one of the C\textsubscript{20} fullerenes in the (a) (C\textsubscript{20})\textsubscript{3} and (b) (C\textsubscript{20})\textsubscript{4} chains. The initial temperature $T =$ (a) 3070 and (b) 3280 K, the lifetime before decay $\tau =$ (a) 11.6 and (b) 0.8 ps, and the binding energy after relaxation $\Delta E =$ (a) 0.790 and (b) 1.772 eV/C\textsubscript{20}. 
Fig. 6. Various configurations of the \((C_{20})_4\) chain that are formed after the coalescence of two \(C_{20}\) fullerenes into a \(C_{40}\) cluster. The initial temperature \(T = (a) 2720\) and \((b) 2460\) K, the lifetime before coalescence \(\tau = (a) 0.17\) and \((b) 26.9\) ps, and the binding energy after relaxation \(\Delta E = (a) 5.059\) and \((b) 3.880\) eV/\(C_{20}\).
Fig. 7. Snapshots of the \((20)_3\) chain (a) before the separation of the C\(_{20}\) fullerene, (b) at the intermediate stage, and (c) after the separation. The initial temperature is \(T = 2200\) K, the lifetime before the separation is \(\tau = 1.76\) ns, and the time interval between the first and third snapshots is \(\Delta t = 3.8\) ps.
Fig. 8. Logarithm of the lifetime $\tau$ (second) of the $(C_{20})_N$ chains to the time of (closed points) the decay of one of the $C_{20}$ fullerenes or (open points) coalescence of two $C_{20}$ fullerenes into a $C_{40}$ cluster vs. the inverse initial temperature (Kelvins) with the inclusion of the finite-heat-bath correction, see the main text, for $N =$ (circles) 3, (squares) 4, (triangles) 5, (diamonds) 6, and (stars) 7. The cross corresponds to the separation of one $C_{20}$ fullerene for $N = 3$. The solid and dashed lines correspond to the decay and coalescence, respectively, of the $C_{20}$ fullerenes into the $(C_{20})_2$ dimer (from [13]).