ORIGINAL RESEARCH

On molecular dynamics of the diamond D$_5$ seeds

Beata Szefler · Mircea V. Diudea

Abstract Diamond D$_5$ is a hyperdiamond with the rings being mostly pentagonal and built up on the frame of *mtn* structure, appearing in clathrate hydrates of type II. As the seed of D$_5$, the centrohexaquinane C$_{17}$ was proposed (Diudea, Stud Univ Babes-Bolyai Chem 55(4):11–17, 2010). In this article, we study the molecular dynamics MD of four structures based on C$_{17}$ skeleton, as all carbon or partly oxygenated derivatives. The results are discussed in terms of structural stability as given by DFT calculations as well as by the stable fluctuations of root mean square deviations and total, potential and kinetic energies provided by MD calculations.

Keywords Diamond D$_5$ · Centrohexaquinane · HF · DFT · Molecular dynamics

Introduction

In the Nano-era, a period starting with the discovery of C$_{60}$, in 1985, the carbon allotropes played a dominant role. Among the carbon structures, fullerenes (zero-dimensional), nanotubes (one dimensional), graphene (two dimensional), diamond, and spongy carbon (three dimensional) were the most studied [1–3], both from theoretical reasons and applications perspective.

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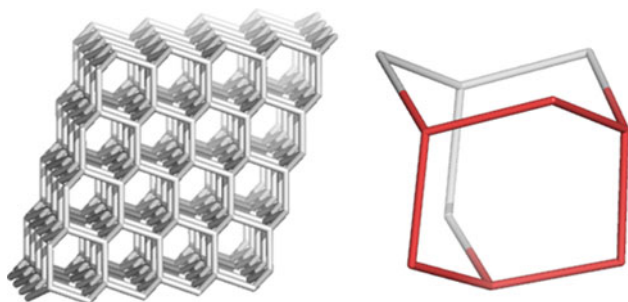Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, A. Janos 11, 400028 Cluj-Napoca, Romania

Diamond D$_6$, the beautiful classical diamond, with all-hexagonal rings of sp^3 carbon atoms (Fig. 1), crystallized in a face-centered cubic *fcc* network (space group *Fd3m*), has kept its leading interest among the carbon allotropes, even as the "nano" varieties [4–9]. Its aesthetical appeal and mechanical characteristics are of great importance in jewelry and technique. Synthetic diamonds are currently produced by a variety of methods, including high pressure–high temperature, chemical vapor deposition, ultrasound cavitation [10], etc.

However, the diamond D$_6$ is not unique: a hexagonal network called lonsdaleite (space group *P6$_3$/mmc*) [11], was discovered in a meteorite in the Canyon Diablo, Arizona, in 1967. Several diamond-like networks have also been proposed [2, 12, 13].

In a previous study, Diudea and Ilić [14] described some multi-tori (i.e., structures showing multiple hollows—see Ref. [15]), one of them illustrated in Fig. 2, left.

The reduced graph of this multi-torus provided the structure for the seed of diamond D$_5$: C$_{17}$, (Fig. 2, right) consisting of a tetravalent atom surrounded by six pentagons, the maximum possible number of pentagons around a sp^3 carbon atom. According to the chemical nomenclature, C$_{17}$ is a centrohexaquinane, a class of structures previously studied by Gund [16], Paquette [17], and more recently by Kuck [18–20].

Diamond D$_5$ is the name given by Diudea to diamondoids consisting mostly of pentagonal rings [14, 21]. D$_5$ is a hyperdiamond built up as a trinodal net in the frame of *mtn* structure; it belongs to the space group Fd-3m [22] while its seed is eventually the centrohexaquinane C$_{17}$. However, D$_5$ belongs to the family of Clathrates; it is precisely the type II clathrate C$_{34}$ [23], of which Si$_{34}$-analogue was already synthesized.

C$_{17}$ can dimerize to $2 \times$ C$_{17}$ = C$_{34}$ (Fig. 3), the repeating unit, in crystallographic terms, of the diamond D$_5$ network. In crystallochemical terms, an adamantane-like

Fig. 1 Diamond D$_6$ (*left*) and its repeating unit, adamantane (*right*)

Fig. 3 A joint of two C$_{17}$ units (*left*) to give a dimer C$_{34}$ (*right*), the repeating unit (in crystallographic terms) of the diamond D$_5$ network
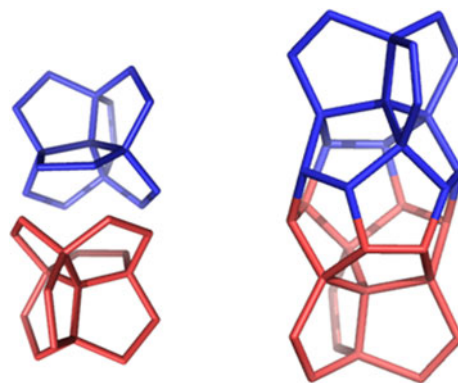

Fig. 2 A multi-torus (*left*) and its reduced graph C$_{17}$ (*right*), the seed of diamond D$_5$
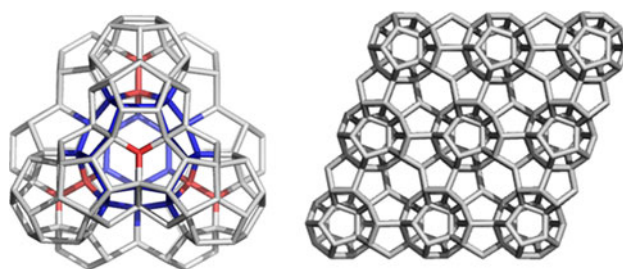

Fig. 4 Adamantane-like structure (*left*) of the diamond D$_5$ network (*right*)

Table 1 The single point energies of the optimized structures at DFT (B3LYP/6-311+G**) level of theory

B3LYP	C$_{17}$	D$_1$	D$_2$	P$_1$
B3LYP (a.u.)	−655.058	**−766.491**	−766.480	−766.479
B3LYP_Gap (eV)	5.868	**6.461**	6.264	6.274

structure, as ada_20_158 (Fig. 4, left) is the monomer which will probably condense to form the diamond D$_5$ network (Fig. 4, right).

In the above symbols, "20" refers to C$_{20}$, which is the main unit of the hyper-diamond D$_5$, while the last number counts the carbon atoms in structures.

The ratio C-sp^3/C-total trends to 1 in a large enough network. As the content of pentagons R [5] per total rings trends to 90% in this yet hypothetical carbon allotrope, the net was called the diamond D$_5$ [21].

Method

The optimized structures, at Hartree–Fock HF (HF/6-31G**) and DFT (B3LYP/6-311+G**) levels of theory, were submitted to molecular dynamics MD procedure. All calculations were performed in gas phase by Gaussian 09 [24] while MD calculations were done in vacuum, using Amber 10.0 software [25]. The single point energy minima
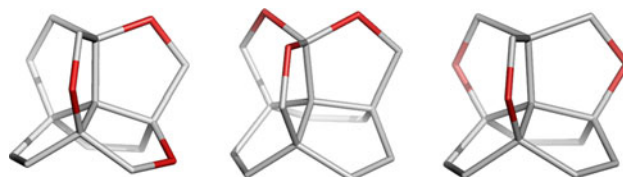

Fig. 5 C$_{17}$_hexaquinane trioxo-derivatives: Paquette P$_1$ (*left*) and Diudea, D$_1$ (*middle*) and D$_2$ (*right*)

obtained for the investigated structures are shown in Table 1. Before the MD was run, the atomic charges were calculated according to Merz-Kollmann scheme via the RESP [26] procedure at HF/6-31G** level. The AMBER force field [27] was used for dynamic trajectory generation. There were several steps of molecular dynamics. After stabilization of energies and root mean square deviation (RMSD) values during run, the actual molecular dynamics were performed, in a cascade way. Each tested system was heated by 20 ps while MD simulations were 100 ns long. The visualizations were prepared in the GaussView program. After MD run, the values of RMSD and energies of analyzed structures were

Table 2 The averages total energy (E_{tot}) values estimated, by MD, on geometries in the gas phase

C_{17}

Temp (K)	300	600	900	1200	1400	1600	1800
E_{tot} (kcal/mol)	127.405	180.379	233.358	286.460	322.227	357.665	393.123
δ	5.789	11.585	17.373	23.121	27.070	30.932	34.938

D_1

Temp (K)	300	600	900	1200	1400	1600
E_{tot} (kcal/mol)	144.996	197.907	250.689	303.114	337.947	373.136
δ	5.782	11.593	17.273	23.106	26.739	30.745

D_2

Temp (K)		300		600		900
E_{tot} (kcal/mol)		116.45		169.266		222.049
δ		5.783		11.542		17.363

P_1

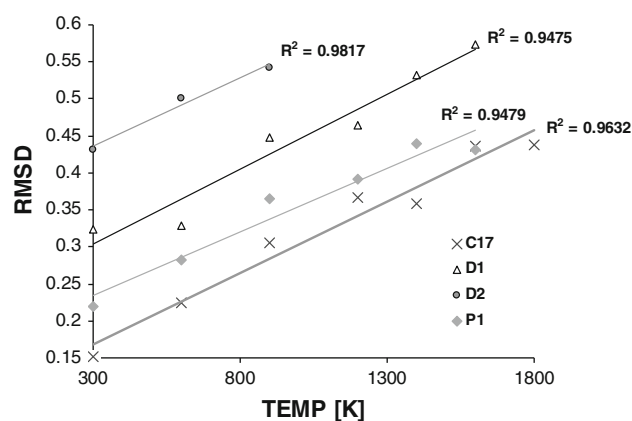| Temp (K)	300	600	900	1200	1400	1600
E_{tot} (kcal/mol)	142.574	195.448	247.889	300.329	335.524	370.602
δ	5.798	11.535	17.300	23.076	26.931	30.678

The averaged values were calculated on all the generated points of energies in every 1 ps of molecular dynamics. Symbol δ means the standard deviation
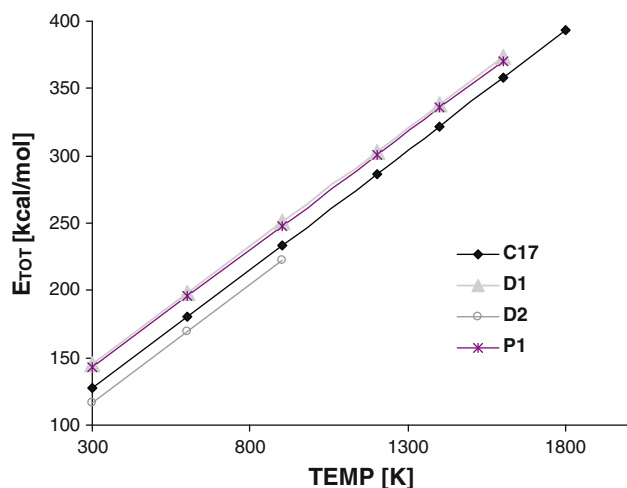
Fig. 6 The plot of total energy (E_{tot}) versus temperature (Temp)

Fig. 7 The plot of RMSD versus temperature (Temp)

recorded: total energy (E_{tot}), kinetic energy (E_{kin}), and potential energy (E_{pot}). In the analysis, averaged values of all generated points of energies and values of RMSD in every 1 ps of MD were used.

Results and discussion

Stability evaluation was performed on four hypothetical seeds of D_5, the all-carbon structure C_{17} (Fig. 2, right) and

three trioxa-derivatives of C_{17}. The isomer in Fig. 5, left was synthesized by Paquette and Vazeux [17], and is hereafter denoted P_1. The other two structures, denoted D_1 and D_2 (Fig. 5, middle and right) were proposed, by Diudea, as possibly appearing in rearrangements of the Paquette's P_1 structure. The last two structures would be the appropriate ones in the next step of dimerization to C_{34}, in fact the repeating unit [23] of the structure we call here D_5.

The stability of molecules was evaluated both in static and dynamic temperature conditions. The isomer D_1 seems the most stable among all studied structures, as given by

Table 3 The values of standard deviations of E_{tot} at a given temperature (see the center of each slide), for the four investigated structures
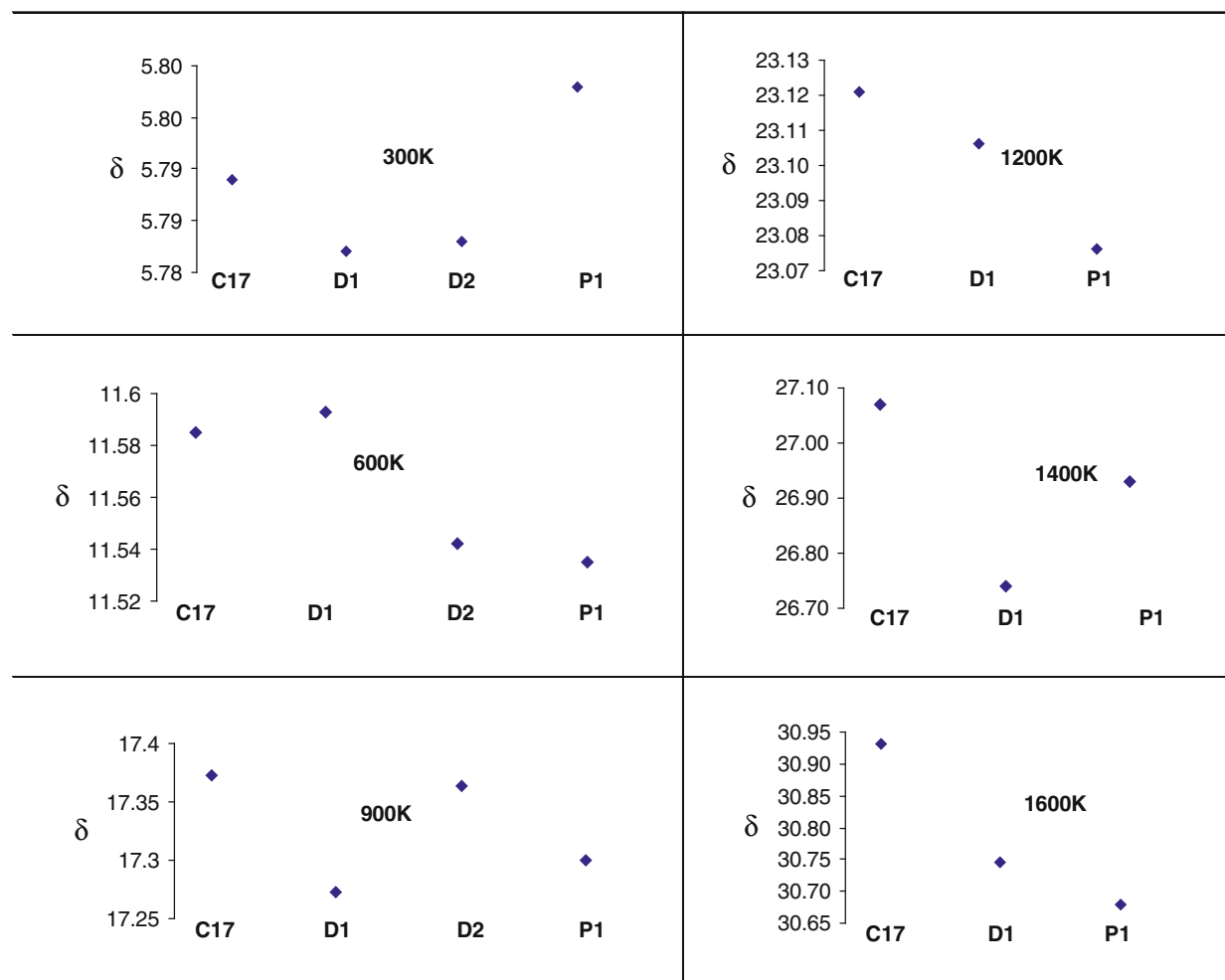
Table 4 The averaged RMSD values estimated by molecular dynamics MD on the geometries in the gas phase

C_{17}

Temp (K)	300	600	900	1200	1400	1600	1800
RMSD	0.151	0.224	0.305	0.366	0.358	0.437	0.438
δ	0.024	0.032	0.045	0.056	0.054	0.054	0.062

D_1

Temp (K)	300	600	900	1200	1400	1600
RMSD	0.324	0.328	0.448	0.465	0.532	0.574
δ	0.134	0.088	0.079	0.086	0.091	0.118

D_2

Temp (K)	300	600	900
RMSD	0.432	0.500	0.542
δ	0.257	0.245	0.208

P_1

Temp (K)	300	600	900	1200	1400	1600
RMSD	0.220	0.283	0.365	0.392	0.440	0.431
δ	0.062	0.069	0.092	0.070	0.093	0.070

The averaged values were calculated on all the generated points of RMSD in every 1 ps of MD. Symbol δ represents the standard deviation

C$_{17}$ (300K-1800K)   C$_{17}$ (2000K)

D$_1$ (300K-1600K)   D$_1$ (1800K)

D$_2$ (300K-900K)   D$_2$ (1200K)
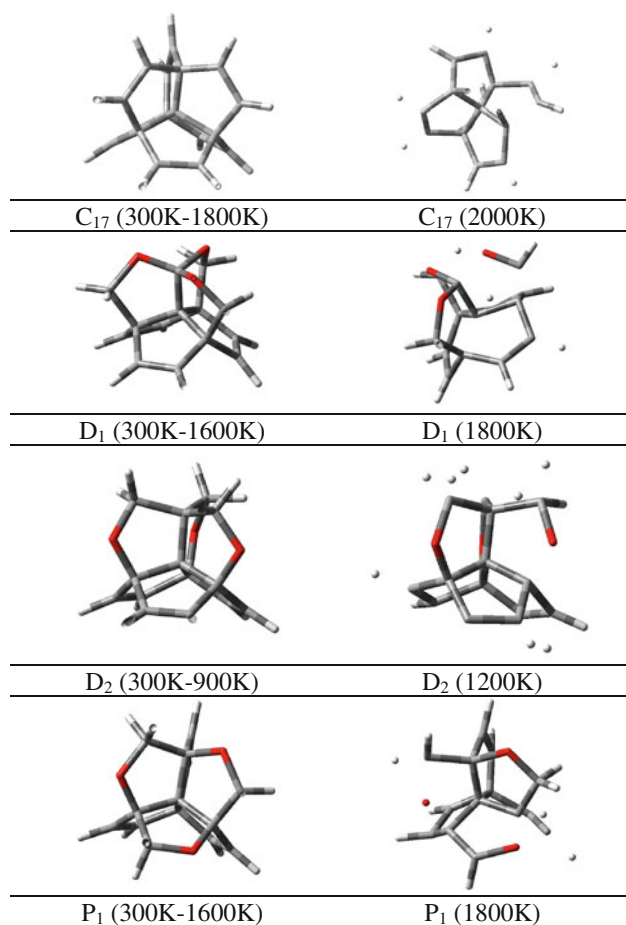
P$_1$ (300K-1600K)   P$_1$ (1800K)

Fig. 8 The structure of the tested hypothetical seeds of the diamond D$_5$ during molecular dynamics

optimization in gas phase at DFT level (Table 1). In decreasing the stability, it follows P$_1$ and D$_2$. However, the all-carbon C$_{17}$ appears the most stable at MD treatment, even at DFT level is the last one. This is probably because the C–C bond is more stable at temperature variations (see Fig. 8).

In MD, C$_{17}$ keeps its structure up to about 1800 K, while its destruction starts at 2,000 K (Tables 2, 4; Figs. 6, 7). Kuck has reported a centrohexaindane, as the most symmetric structure in this series but also a benzo-centrohexaquinane [19, 20] as the last step structure in the synthesis of a non-planar 3D structure, designed according to mathematical rules. However, in the synthesis of centrohexaquinane-derivatives, C$_{17}$ remained yet elusive.

Very close to C$_{17}$ behaves the oxygen-containing isomer D$_1$, as expected from its highest stability at DFT level (Table 1-the values in bold).

Despite a very long time of molecular dynamics (100 ns) was leaded, it is believed that prolonged annealing at 1,800 K for both P$_1$ and D$_1$ isomers finally resulted in the destruction of these molecules. Thus, P$_1$ and D$_1$ isomers

behave similarly in MD conditions. The isomer D$_2$ was the least stable one, as the largest RMSD values were recorded for this isomer.

According to molecular dynamics, it is clear that by increasing temperature resulted in higher values of energy and RMSD (and their standard deviations) of all the analyzed structures, with high values of correlation. The plots of E_{tot} versus temperature for all tested systems are given in (Fig. 6), while for RMSD the plots are given in Fig. 7. As expected, the correlations in the RMSD plot are a little lower than those for E_{tot}. The MD calculations, listed in Tables 2, 3, and 4 show the followings.

As can be seen from Tables 2 and 3, the values of standard deviations of the averaged values of E_{tot} are closely correlated with the values of temperature, in the range the molecular dynamics simulations were done. The values of these standard deviations at a given temperature are similar for all four studied structures (Tables 2, 3), due to their structural relatedness.

The smallest values of the RMS deviation are observed for C$_{17}$, with the lowest values of standard deviation (δ) at all the studied values of temperature (Table 4).

In the case of P$_1$, one can see a similar behavior but somewhat with larger values of RMSD (as well as values of the standard deviation), compared to the all-carbon structure C$_{17}$ (Table 4). It confirms the structural stability of the above structures. The largest values of the RMS deviation were recorded for D$_2$ isomer (Table 4; Fig. 7).

Visualization of the structural changes (first step destruction, the right column) is presented in Fig. 8.

Conclusions

Structural stability of several hypothetical seeds of the diamond D$_5$ was investigated. It was evaluated both in static and dynamic temperature conditions by molecular dynamics MD. During MD, the all-carbon C$_{17}$ appeared the most resistant to changes of temperature. Structural and energetic stability of the other three seeds of D$_5$ vary both with the values of temperature and evolution time in molecular dynamics and the arrangement of oxygen atoms in the molecules. Among all the studied structures, the D$_2$ isomer is the most sensitive to changes in temperature. After optimization by B3LYP, D$_1$ isomer seemed to be the most stable one. The structure stability of D$_1$ and P$_1$ isomers in MD are similar. These two isomers are only slightly more sensitive to temperature as compared with the all-carbon C$_{17}$. These results could be useful in guiding further reactions, e.g., the dimerization to C$_{34}$ and condensation to adamantane-like structures, finally leading to the diamond D$_5$.

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