Computational design of linear, flat, and tubular nanomolecules using planar tetracoordinate carbon C₂Al₄ units

Yan-Bo Wu, Zong-Xiao Li, Xiao-Hua Pu, Zhi-Xiang Wang

Abstract

C₂Al₄(CH₃)₈ (1) contains two planar tetracoordinate carbons in its C₂Al₄ core. On the basis of the geometric characters of \( \text{C}_2 \text{Al}_4 \) (1), we previously used it as building blocks to design molecular chains via face-to-face (FF) condensation. In this DFT study, we show the condensation can also take place vertex-to-vertex (VV). The various VV condensations of 1 units can result in new families of molecular structures including one-dimensional molecular chains, two-dimensional sheets, and molecular tubes. They were all characterised to be energy minima by frequency calculations at the B3LYP/6-31G* level. Their HOMO–LUMO gaps larger than 3.6 eV indicate the stability of their electronic structures. Furthermore, the condensations do not destroy the C₂Al₄ pC core, as the geometric and electronic structures of the C₂Al₄ cores in these molecules are similar to those of C₂Al₄ core in the C₂Al₄(CH₃)₈ building block.

1. Introduction

The development of planar carbon (pC) chemistry [1–10] (a non-classical carbon bonding in which the central carbon atom and its four or more bound ligands/atoms are in the same plane) is currently emphasising two aspects. First, although many planar carbon species have been predicted computationally, only a few have been observed experimentally [11–14] by the photoelectron spectroscopy. While such an experiment has been proved to be powerful to characterise pC species, it tends to detect the signals of low-lying isomers for a stoichiometry, which has encouraged much effort to search for pC species that are global minima. The pC species with tetracoordination (ptC) such as CB₂⁶⁺, CAl₂Be₂⁺, C₃Al₂Be₂⁺, and LiCAl₂Be₂⁺ [16] have been found to be the global minima, and CAl₂⁺ [20], Cal₂Be, CAI₂Be₂⁺ [21], CAI₂Be₂⁺, and LiCAI₂Be⁺ [22] were identified to be the planar pentacoordinate carbon (ppC) global minima. Second, the pC species often use electron-deficient ligands/atoms to stabilize the bonding. Exposure of such ligands/atoms may result in high chemical reactivity. However, if a pC species was used as the building blocks to construct solid or nanoscale materials, the reactivity issue may be alleviated because of the protection of the surroundings. For potential experimental realisation, it is desirable that the pC units are global minima. For example, on the basis of the experimentally characterised CAI₂⁺, ptC species or its analogues, Geske and Boldyrev designed the solid which used Na as counterion [23] and Yang et al. used these ptC species to construct alkali and alkaline-earth metal sandwich molecules [24–27]. CB₂⁶ was computationally characterised to be a ptC global minimum by Pei et al., based on which Wu et al. designed B₂C grapheme and nanotubes [28]. Interestingly, Luo et al. found that the most stable structure for boron-rich 2D B–C compound has C₂₄, ptC motif [29]. On the other hand, since the pC units could be stabilized if they are embedded into solids/materials, some local minimum pC species were also attempted for such a purpose. Pancharatna et al. used all carbon ptC block C₂⁶ to construct solid [30]. The planar hexacoordinate carbon unit (CB₂⁶⁺) was used to design the ferrocene-like sandwich complex by Li et al. [31–33], the one-dimensional (1D) sandwich chains by Luo et al. [34] and the sandwich molecules by Yang et al. [35]. The C₃B₂H₄ ptC unit was used by Sun et al. and Zhang et al. to design nanoribbons and nanotubes [36,37]. Recently, Li et al. designed the silagraphe consisting of the planar tetracoordinate silicons (ptSiS) [38].

We have also been interested in designing nanomolecules, using ptC as building block. In 2007 we designed the nanoribbons and nanotubes on the basis of the CM₄H₄ (M = Ni, Pd and Pt) ptC units [39]. Recently, we found that the replacement of the six
benzene hydrogen atoms with isolobal BeH groups result in star-like $D_{6h}$ $C_6Be_6H_6$ with six ptCs. Interestingly, via intermolecular H-bridging bonding, the $C_6Be_6H_6$ star can serve as building blocks to construct the flat, tubular, and cage-like nanomolecules, which are similar in shape to graphene, carbon nanotubes, and fullerenes [40].

In this work, we report a computational design of linear, flat, and tubular molecules starting from ptC units $C_2Al_4$. The single
C2Al4 pC unit was confirmed to be a global minimum [17]. The analysis of electronic structure suggested that each Al atom in C2Al4 bears a lone pair, which may lead to the high chemical reactivity. To utilise the lone pairs and to protect the C2Al4 pC core, we designed the new pC molecules C2Al4E8 (E = H, CH3, NH2, OH, F and Cl) [41]. The attachments of these E groups to the C2Al4 core allowed us to use the C2Al4E8 (E = CH3, NH2 and OH) to construct one dimensional pC molecular chains through intermolecular face-to-face (FF) condensation [42]. Alternatively, the condensation can be vertex-to-vertex (VV). In the following, taking the C2Al4(CH3)8 (1) unit as an example, we show that the vertex-to-vertex condensation could lead to a new family of linear, flat, and tubular nanomolecules with pCs.

2. Computational details

All the molecules involved in this work were optimised and characterised to be minima at the B3LYP/6-31G(d) level. In our previous study on designing molecular chains using C2Al4E8 (E = CH3, NH2 and OH) as building blocks, the suitability of using B3LYP functional was verified by LC-BLYP [43] (i.e. BLYP functional with the long-range correction (LC) scheme of Hirao et al.) computations [42]. To calibrate the 6-31G(d) basis set, the molecules containing up to four building units of 1 were recalculated using 6-311++G(d,p) basis set. Except for the reaction energies that were slightly underestimated by B3LYP/6-31G(d) in comparison with B3LYP/6-311++G(d,p) computations, the two levels of computations predicted geometries and other properties with no essential differences. We used the B3LYP/6-31G(d) to calculate the larger molecules and the results at this level are discussed in the following. The natural bond orbital (NBO) [44,45] analysis were performed at the B3LYP/6-31G(d) level to understand their electronic structures. All calculations were carried out by using Gaussian 03 [46] and Gaussian 09 [47] packages.

3. Results and discussion

3.1. One-dimension molecules

Fig. 1 illustrates the two types of condensation, when using two 1 units as building blocks. Previously, we have employed the face-to-face (FF) condensation [42] to design molecular chains (Fig. 1A), which eliminates four methane molecules. Alternatively, two 1 units can also be connected together via vertex-to-vertex (VV) condensation, which eliminate two methane molecules to form methylene-bridged linkages (MBLs) (Fig. 1B). As depicted by Fig. 1C, depending on the positions that the eliminations occur, the VV condensation can further result in three types of chains containing two 1 units, which are shown by 2 (D2h), 3 (C2v), and 4 (D4h), respectively. They are all energy minima without imaginary frequency (see Table 1). In the first type (i.e. 2) the condensation occurs between two Al1 atoms (Al1 denotes the terminal Al atom in 1) of the two units. In the second type (i.e. 3) it occurs between the Al3 and Al4 atoms (Al4 denoting the bridging Al atom in 1) of the two units. In the third type (i.e. 4), it occurs between the two Al3's of the two units. In the following we term the three types of VV condensation as TT, TB, and BB, respectively.

Similar to the FF condensation, the VV condensation can also be extended to more than two units. By consecutive condensations, various one-dimensional molecular chains can be achieved. As shown in Fig. 1 (see 5–10), the condensation using three 1 units results in six types of 1D chains. 5 is constructed by all TT condensations, 10 by all BB condensations, and 6–9 by mixed TT/TB or BB/TB condensations. The six structures are all energy minima. For longer chains, the combinations of the three condensation patterns can result in many types of 1D structure which are unnecessary to be exhausted. As demonstrations, we only considered two scenarios which only contain TT or BB condensations for longer chains. The optimised structures of chains with four to six 1 units are included in Fig. 1. The chains 11, 13, and 15 are constructed by pure TT condensations and 12, 14, and 16 by pure BB condensations. They are all energy minima.

After the condensations, the perfect pC arrangement of C2Al4 core in 1 unit is maintained in 2–16. The bond lengths for C–C (1.335–1.340), C–Al (2.046–2.072) and C–AlT (1.897–1.918 Å) of C2Al4 core in 2–16 are comparable to the values of 1.335, 2.063, and 1.913 Å in 1, respectively, which indicate the geometric structures of C2Al4 pC cores do not change much. The HOMO–LUMO gaps of 2–16 (3.88–4.41 eV, see Table 1) are all smaller than that of 1 (4.53 eV). The gaps gradually decrease as the chains become longer. For example, the gaps for the chains 2, 5, 11, 13, and 15 (constructed by pure TT condensations) are 4.19, 4.03, 3.91, and 3.88 eV, respectively, which indicate the geometric structures of C2Al4 pC cores are close to the values of 1.335, 2.063, and 1.913 Å for 1, respectively, revealing the similar ionic bonding character of the C2Al4 ptC cores in 1D chains to that in 1.

The geometric characters of the two units, which are shown by AlB (WBICC-Al-B, 0.63–0.67) and AlT (WBICC-Al-T, 0.61–0.67), are also close to the corresponding values in 1 (0.63–0.67) and 1 (0.63–0.67), respectively, indicating the similar geometric structures of C2Al4 pC cores. The gaps gradually decrease as the chains become longer. For example, the gaps for the chains 2, 5, 11, 13, and 15 (constructed by pure TT condensations) are 4.19, 4.03, 3.91, and 3.88 eV, respectively, which indicate the geometric structures of C2Al4 pC cores are close to the values of 1.335, 2.063, and 1.913 Å for 1, respectively, revealing the similar ionic bonding character of the C2Al4 ptC cores in 1D chains to that in 1. Thus the electronic structures of C2Al4 pC cores in 2–16 are not different in essential from that in 1. The above analyses suggest the chains can be extended endlessly.

3.2. Two-dimension molecules

Table 1

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The point groups (PGs), the smallest vibrational frequencies (vmin), the HOMO–LUMO gaps (gaps), the equations for the condensation reactions (reactions), the Gibbs free energies of the reactions (RE), and the average RE per CH4 (REav) of the nanomolecules 2–26.
1 units, 17 ($D_{3h}$) and 18 ($C_{4v}$), in Fig. 2, there exist two typical condensations. 17 and 18 were confirmed to be energy minima at B3LYP/6-31G(d) level. 17 can be viewed as the BB-condensation product of the two TT-condensed 2 or the TT-condensation product of the two BB-condensed 4, thus the condensation pattern in 17 can be termed as TT/BB. 18 can be viewed as the TB condensation product of the two BB-condensed 4, so the linking pattern in 18 can be termed as TB/TB. The sheets are not limited to $2 \times 2$ in size, and the larger sheets can be constructed by further extension along the two orthogonal directions. We constructed the TT/BB- and TB/TB-condensed sheets with nine 1 units ($3 \times 3$) and sixteen 1 units ($4 \times 4$) for demonstration. At B3LYP/6-31G(d) level, these sheets 17–22 are energy minima.

The $C_{2}Al_{4}$ cores in 17–22 remain perfect ptC structures. The C–C, C–AlB and C–Al T bond lengths for $C_{2}Al_{4}$ cores range within 1.337–1.344, 2.045–2.074, and 1.899–1.919 Å, respectively, which are close to the values of 1.336–1.340, 2.046–2.07 and 1.897–1.919 Å, respectively, in 1D chains, suggesting that the
condensations between chains do not obviously influence the structure of C$_2$Al$_4$ ptC cores. The HOMO–LUMO gaps in TT/BB-condensed sheets$^{17,19,21}$ and TB/TB-condensed sheets$^{18,20,22}$ are 4.02, 3.77, and 3.66 eV, respectively, and those in TT/BB-condensed sheets$^{17}$, 19, and 21 are 4.26, 4.16, and 4.11 eV, respectively, showing a decreasing trend, but the decrease becomes smaller as the size of the sheets becomes larger. As shown in Table S1, the average values for the WBICC-Al-B, 0.65–0.66, and WBICC-Al-T, 0.59–0.61, are comparable with the corresponding values of 0.63–0.67 and 0.59–0.63 in 1D chains. Thus the covalent bonding of C$_2$Al$_4$ cores in 2D sheets is similar to that in the 1D chains. Moreover, the average values of net charges on C ($Q_C$/C$_0$ 1.11 to 1.12 |e|) are close to the values ($Q_C$ 1.11 to 1.11 |e|) in 1D chains and those on Al B ($Q_{Al-B}$ 1.62–1.64 |e|) and Al T ($Q_{Al-T}$ 1.67–1.68 |e|) are compared with the values (1.61–1.67 and 1.66–1.70 |e|, respectively) in 1D chains. So the ionic bonding of C$_2$Al$_4$ cores in 2D sheets is barely changed when the 1D chains are condensed to the 2D sheets. Furthermore, the covalent bonding in C$_2$Al$_4$ ptC cores in 2D sheets is similar to that in single 1 unit. We reason the 2D sheets can be extended infinitely.

### 3.3. Tubular molecules

Similar to graphene that can be rolled into single-walled carbon nanotubes, the 2D flat sheets can also be rolled into tubular molecules. Since the tubular molecules generally become large in size and there exist many rolling patterns, we only constructed typical tubes based on TT/BB-condensed sheets and rolled up the sheets along the direction with TT condensations for demonstration. As shown in Fig. 3, the tubes 23 and 24 have two layers with five and six 1 units in each layer, respectively. They are energy minima at the B3LYP/6-31G(d) level. The two-layered tubes 23 and 24 can be further extended, as exemplified by 25 and 26 that are also energy minima.

Due to the geometrical distortion required for forming the tubes, the C$_2$Al$_4$ cores in 23–26 are slightly bend. The bending degree can be measured by the angle AlT–C–C ($\alpha$) and the dihedral angle AlB–C–C–AlB ($\phi$) of C$_2$Al$_4$ cores. Expectedly, the C$_2$Al$_4$ core distortion in tubes 24 and 26 ($\alpha = 159.5^\circ$ and $159.4^\circ$, $\phi = 172.6^\circ$ and $177.5^\circ$) is less severe than that in tubes 23 and 25 ($\alpha = 155.6^\circ$ and $155.3^\circ$, $\phi = 170.8^\circ$ and $170.3^\circ$). The results suggest the larger the radii of tubes, the less severe the distortion of C$_2$Al$_4$ cores. Nevertheless, the C–C, C–AlB and C–AlT bond lengths (1.345–1.346, 2.057–2.071, and 1.903–1.906 Å, respectively) of C$_2$Al$_4$ cores in tubes is still comparable with that (1.337–1.344, 2.045–2.074, and 1.903–1.906 Å, respectively) in sheets. Therefore, the bonding characters of C$_2$Al$_4$ core in tubes should be similar to that in sheets. Consistently, the average WBICC-Al-B (0.64–0.65) and WBICC-Al-T (0.61–0.62) values for 23–26 (see Table S1) are close to the values of sheets (0.65–0.66 and 0.59–0.61), and the average $Q_C$ ($-1.12$ to $1.12$ |e|), $Q_{Al-B}$ (1.63–1.64 |e|) and $Q_{Al-T}$ (1.66–1.66 |e|) for tubes are within those for sheets ($-1.11$ to $-1.12$ |e|), (1.62–1.64 |e|), and (1.66–1.68 |e|), respectively. Similar to the chains and sheets, the HOMO–LUMO gaps decrease gradually as the tubes have more 1 units (the gaps for 23–26 are 3.82, 3.77, 3.72, and 3.68 eV, respectively).

### 4. Conclusions

In summary, we have designed the 1D chains, 2D flat sheets, and the nanotubes based on the C$_2$Al$_4$(CH$_3$)$_8$ units (1) with C$_2$Al$_4$ double ptC core using vertex-to-vertex (VV) linking pattern. For 1D chains and 2D flat sheets, the geometries and electronic structures of their C$_2$Al$_4$ double ptC cores are very similar to that in 1,
while for the nanotubes, the geometries of C2Al4 cores are slightly bent because of tubular structure, however, the bond lengths and the electronic structures of C2Al4 cores are not different in essential from that in I. So the structures of C2Al4 ptc core of I are maintained both geometrically and electronically in the V- and/or C2A14 nanographenes. The HOMO-LUMO gaps gradually decrease when the nanomolecules have more units, but the decrease become smaller as the size of the sheets become larger. The nanomolecules designed in this work may be another way to realize the double pTC structure and the big holes on the sheets and tubes may be useful for capturing small molecules.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.comptc.2012.05.008.

References