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

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ABSTRACT

 C_2AI_4 (CH₃)₈ (1) contains two planar tetracoordinate carbons in its C_2AI_4 core. On the basis of the geometric characters of 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 C₂AI₄ pC core, as the geometric and electronic structures of the C₂AI₄ cores in these molecules are similar to those of C₂AI₄ core in the C₂AI₄(CH₃)₈ building block.

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1. Introduction

The development of planar carbon (pC) chemistry [1-10] (a nonclassical 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 CB_4^+ [15], CCu_4^{2+} , CCu_3Ag^+ , $CCu_2Ag_2^+$ [16], C_2E_4 (E = Al, Ga, In and Tl) [17], CE_4^{2-} (E = Al, Ga, In and Tl) [18] and $C_5Al_5^-$ [19] have been found to be the global minima, and CAl₅ [20], CAl₄Be, CAl₃Be₂ [21], CAl₂Be₃²⁻, and LiCAl₂Be₃⁻ [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 CAI_4^2 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]. CB₄ was computationally characterised to be a ptC global minimum by Pei et al., based on which Wu et al. designed B₂C graphene and nanotubes [28]. Interestingly, Luo et al. found that the most stable structure for boron-rich 2D B–C compound has $C_{2\nu}$ ptC motif [29]. On the other hand, since the pC units could be stabilized if they are embedded into solids/materials, some local minimum ptC species were also attempted for such a purpose. Pancharatna et al. used all carbon ptC block C_5^{2-} to construct solid [30]. The planar hexacoordinate carbon unit (CB_6^{2-}) was used to design the ferrocene-like sandwich complex by Li et al. [31-33], the onedimensional (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 silagraphene 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 CM_4H_4 (M = Ni, Pd and Pt) ptC units [39]. Recently, we found that the replacement of the six

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benzene hydrogen atoms with isolobal BeH groups result in starlike $D_{6h} C_6 Be_6 H_6$ with six ptCs. Interestingly, via intermolecular H-bridging bonding, the $C_6 Be_6 H_6$ 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



Fig. 1. Illustrations of face-to-face (FF, panel **A**) and vertex-to-vertex (VV, panel **C**) condensations. The structure of methylene-bridged linkage (MBL, panel **B**), and the definitions of terminal and bridged Al atoms (Al_T and Al_B, see panel **C**) in **1**. The B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) optimised structures of of various 1D chains, along with the key bond lengths (in Å, B3LYP/6-311++G(d,p) bond lengths are in italic). Colour codes: C: grey, H: white, Al: blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 C_2Al_4 ptC unit was confirmed to be a global minimum [17]. The analysis of electronic structure suggested that each Al atom in C_2Al_4 bears a lone pair, which may lead to the high chemical reactivity. To utilise the lone pairs and to protect the C_2Al_4 ptC core, we designed the new ptC molecules $C_2Al_4E_8$ (E = H, CH₃, NH₂, OH, F and Cl) [41]. The attachments of these E groups to the C_2Al_4 core allowed us to use the $C_2Al_4E_8$ (E = CH₃, NH₂ and OH) to construct one dimensional ptC molecular chains through intermolecular face-to-face (FF) condensation [42]. Alternatively, the condensation can be vertex-to-vertex (VV). In the following, taking the $C_2Al_4(CH_3)_8$ (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 ptCs.

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 $C_2Al_4E_8$ ($E = CH_3$, NH_2 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 faceto-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** (D_{2h}) , **3** (C_{2v}) , and **4** (D_{2h}) , respectively. They are all energy minima without imaginary frequency (see Table 1). In the first type (i.e. 2) the condensation occurs between two Al_T atoms (Al_T denotes the terminal Al atom in 1) of the two units. In the second type (i.e. 3) it occurs between the Al_T and Al_B atoms (Al_B denoting the bridging Al atom in **1**) of the two units. In the third type (i.e. 4), it occurs between the two Al_B'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

Table 1

The point groups (PGs), the smallest vibrational frequencies (ν_{min}), 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 (RE_{av}) of the nanomolecules **2–26**.

	PG	v _{min}	Gap	Reactions	RE	REav
1	D_{2h}	30	4.53			
2	D_{2h}	8	4.19	$2(1) \rightarrow 2 + 2CH_4$	9.1	4.5
3	C_{2v}	8	4.41	$2(1) \rightarrow 3 + 2CH_4$	7.3	3.7
4	D_{2h}	8	4.31	$2(1) \rightarrow 4 + 2CH_4$	6.8	3.4
5	D_{2h}	6	4.03	$3(1) \rightarrow 5 + 4CH_4$	18.5	4.6
6	C_{2v}	6	4.14	$3(1) \rightarrow 6 + 4CH_4$	16.6	4.2
7	D_{2h}	6	4.32	$3(1) \rightarrow 7 + 4CH_4$	16.2	4.1
8	D_{2h}	6	4.32	$3(1) \rightarrow 8 + 4CH_4$	15.8	3.9
9	$C_{2\nu}$	7	4.25	$3(1) \rightarrow 9 + 4CH_4$	14.9	3.7
10	D_{2h}	7	4.16	$3(1) \rightarrow 10 + 4CH_4$	14.3	3.6
11	D_{2h}	4	3.95	$4(1) \rightarrow 11 + 6CH_4$	27.9	4.7
12	D_{2h}	4	4.10	$4(1) \rightarrow 12 + 6CH_4$	21.7	3.6
13	D_{2h}	3	3.90	$5(1) \rightarrow 13 + 8CH_4$	37.4	4.7
14	D_{2h}	2	4.07	$5(1) \rightarrow 14 + 8CH_4$	29.0	3.6
15	D_{2h}	3	3.88	$6(1) \rightarrow 15 + 10 \text{CH}_4$	46.9	4.7
16	D_{2h}	1	4.05	$6(1) \rightarrow 16 + 10 \text{CH}_4$	35.8	3.6
17	D_{2h}	9	4.02	$4(1) \rightarrow 17 + 8CH_4$	28.7	3.6
18	C_{4h}	7	4.26	$4(1) \rightarrow 18 + 8CH_4$	27.0	3.4
19	D_{2h}	6	3.77	$9(1) \rightarrow 19 + 24CH_4$	82.9	3.5
20	D_{2h}	6	4.16	$9(1) \rightarrow 20 + 24CH_4$	79.1	3.3
21	D_{2h}	4	3.66	$16(1) \rightarrow 21 + 48 \text{CH}_4$	161.6	3.4
22	C_{4h}	2	4.11	$16(1) \rightarrow 22 + 48 \text{CH}_4$	150.4	3.1
23	D_{5h}	9	3.82	$10(1) \rightarrow 23 + 30CH_4$	177.6	5.9
24	D_{6h}	7	3.77	$12(1) \rightarrow 24 + 36 \text{CH}_4$	186.1	5.2
25	D_{5h}	9	3.72	$15(1) \rightarrow 25 + 50 \text{CH}_4$	276.4	5.5
26	D_{6h}	5	3.68	$18(1) \rightarrow 26 + 60 \mathrm{CH}_4$	290.7	4.8

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 ptC arrangement of C₂Al₄ core in 1 unit is maintained in 2-16. The bond lengths for C-C (1.336–1.340), C–Al_B (2.046–2.072) and C–Al_T (1.897–1.919 Å) of C_2Al_4 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 ptC 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, 3.95, 3.90, and 3.88 eV, respectively. As detailed in Table S1, the NBO analyses indicate the average values for total Wiberg bond indices of C-C moiety to Al_B (WBI_{CC-Al-B}, 0.63–0.67) and Al_T (WBI_{CC-Al-T}, 0.59–0.63) of C₂Al₄ ptC cores are close to the corresponding values of 0.65 and 0.61 for C_2Al_4 core in 1, indicating the similar covalent bonding character of the C₂Al₄ ptC cores in 1D chains **2–16** to that in **1**. On the other hand, the average values of net charges on C (Q_c , -1.11 to -1.11 |e|), Al_B (Q_{Al-T}, 1.61–1.67 |e|), and Al_T (Q_{Al-T}, 1.66– 1.70 |e|) are also close to the corresponding values in **1** (-1.11, 1.66, ad 1.70 |*e*|, respectively), revealing the similar ionic bonding character of the C_2Al_4 ptC cores in 1D chains to that in **1**. Thus the electronic structures of C₂Al₄ ptC 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

The geometric characters of **1** make it suitable to construct not only 1D chains but also two-dimensional (2D) sheets via condensations between chains. As exemplified by the 2×2 sheets with four

1 units, **17** (D_{2h}) and **18** (C_{4h}) , 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 TB-condensed **3**, so the linking pattern in **18** can be termed as TB/TB. The sheets are not limited to 2×2 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 (3×3) and sixteen **1** units (4×4) for demonstration. At B3LYP/6-31G(d) level, these sheets **17–22** are energy minima.

The C₂Al₄ cores in **17–22** remain perfect ptC structures. The C–C, C–Al_B and C–Al_T bond lengths for C₂Al₄ 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



Fig. 2. Illustration of how 1D chains are condensed together to form 2D sheets and the B3LYP/6-31G(d) optimised structures of 2D sheets with the necessary bond lengths (B3LYP/6-311++G(d,p) bond lengths are in italic).



Fig. 3. B3LYP/6-31G(d) optimised structures of tubular molecules. The H atoms are hidden for clarity and the fog is used to improve the depth perception.

condensations between chains do not obviously influence the structure of C₂Al₄ ptC cores. The HOMO-LUMO gaps in TT/BBcondensed sheets 17, 19, and 21 are 4.02, 3.77, and 3.66 eV, respectively, and those in TB/TB-condensed sheets 18, 20, and 22 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 WBI_{CC-Al-B}, 0.65–0.66, and WBI_{CC-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 C₂Al₄ cores in 2D sheets is similar to that in the 1D chains. Moreover, the average values of net charges on C (Q_C , -1.11 to -1.12 |e|) are close to the values (-1.11 to -1.11 |e|) in 1D chains and those on Al_B $(Q_{Al-B_1}$ 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 in C₂Al₄ ptC cores are barely changed when the 1D chains are condensed to the 2D sheets. The NBO results suggest that the electronic structures of C₂Al₄ core in 2D sheets remains the same as 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 C₂Al₄ cores in **23–26** are slightly bend. The bending degree can be measured by the angle Al_T –C–C (α) and the dihedral angel Al_B–C–C-Al_B (δ) of C₂Al₄ cores. Expectedly, the C₂Al₄ core distortion in tubes **24** and **26** (α = 159.5° and 155.6°/159.4°, δ = 172.6° and 172.6°/177.5°) is less severe than that in tubes 23 and 25 $(\alpha = 155.6^{\circ} \text{ and } 155.4^{\circ}/155.3^{\circ}, \delta = 170.8^{\circ} \text{ and } 170.3^{\circ}/177.5^{\circ})$. The results suggest the larger the radii of tubes, the less severe the distortion of C₂Al₄ cores. Nevertheless, the C–C, C–Al_B and C–Al_T bond lengths (1.345-1.346, 2.057-2.071, and 1.903-1.906 Å, respectively) of C₂Al₄ cores in tubes is still comparable with that (1.337–1.344, 2.045–2.074, and 1.899–1.919 Å, respectively) in sheets. Therefore, the bonding characters of C₂Al₄ core in tubes should be similar to that in sheets. Consistently, the average $\mathsf{WBI}_{\mathsf{CC-Al-B}}$ (0.64–0.65) and $\mathsf{WBI}_{\mathsf{CC-Al-T}}$ (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_{AI-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 $C_2Al_4(CH_3)_8$ units (1) with C_2Al_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_2Al_4 double ptC cores are very similar to that in 1,

while for the nanotubes, the geometries of C_2Al_4 cores are slightly bent because of tubular structure, however, the bond lengths and the electronic structures of C_2Al_4 cores are not different in essential from that in **1**. So the structures of C_2Al_4 ptC core of **1** are maintained both geometrically and electronically in the VV-condensed nanomolecules. 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 realise 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.

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