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Computational design of linear, flat, and tubular nanomolecules using planar tetracoordinate carbon C_2Al_4 units

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ABSTRACT

$C_2Al_4(CH_3)_8$ (**1**) contains two planar tetracoordinate carbons in its C_2Al_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 C_2Al_4 ptC core, as the geometric and electronic structures of the C_2Al_4 cores in these molecules are similar to those of C_2Al_4 core in the $C_2Al_4(CH_3)_8$ building block.

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 CAl_5^+ [20], CAl_4Be, $CAl_3Be_2^-$ [21], $CAl_2Be_3^{2-}$, and $LiCAl_2Be_3^-$ [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 CAl_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]. CB_4 was computationally characterised to be a ptC global minimum by Pei et al., based on which Wu et al. designed B_2C graphene and nanotubes [28]. Interestingly, Luo et al. found that the most stable structure for boron-rich 2D B–C compound has C_{2v} 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 one-dimensional (1D) sandwich chains by Luo et al. [34] and the sandwich molecules by Yang et al. [35]. The $C_3B_2H_4$ 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 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

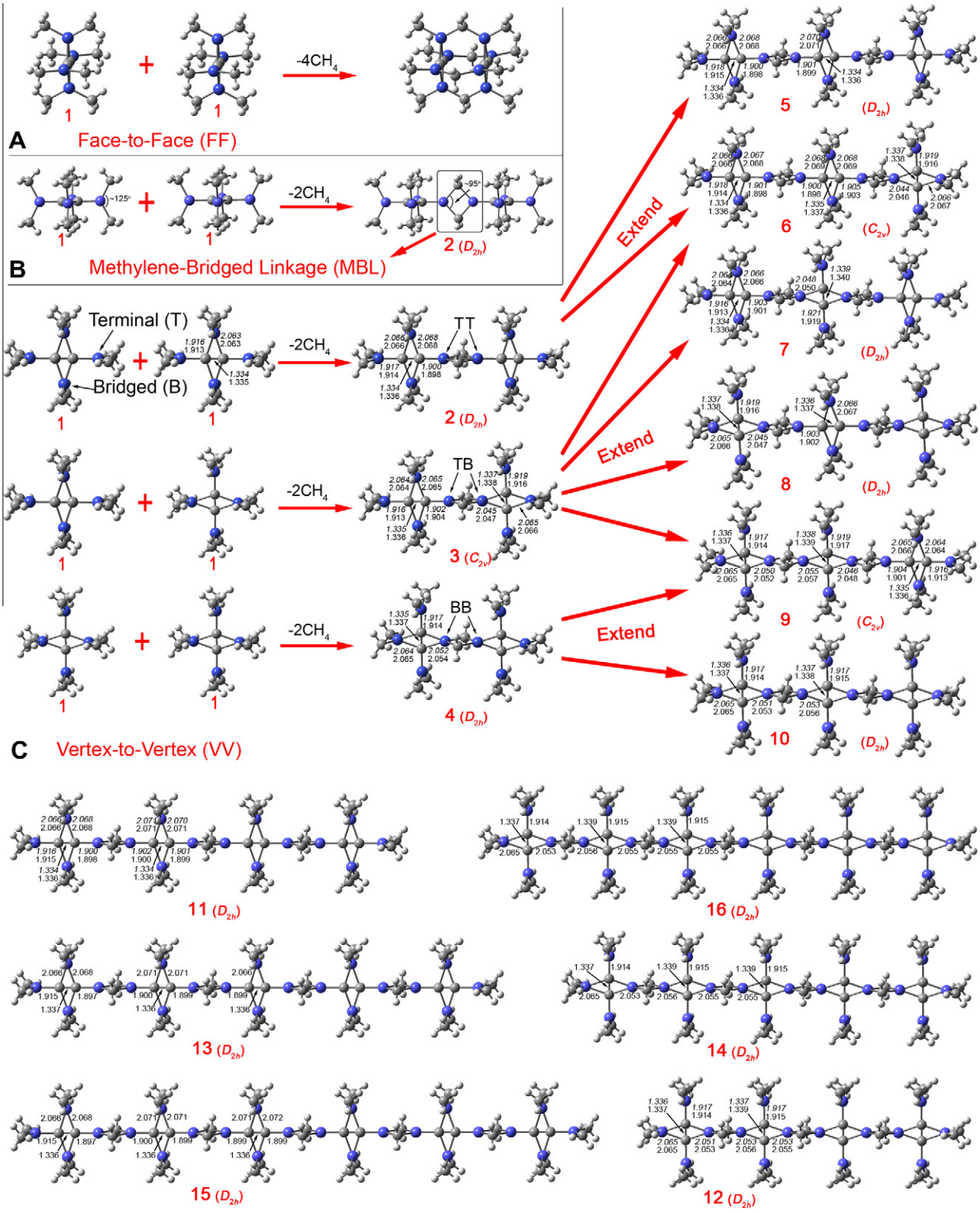

Fig. 1. Illustrations of face-to-face (FF, panel **A**) and vertex-to-vertex (VV, panel **C**) condensations. The structure of methylene-bridged linkage (MBL, panel **B**), and the definitions of terminal and bridged Al atoms (Al_T and Al_B, see panel **C**) in **1**. The B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) 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.)