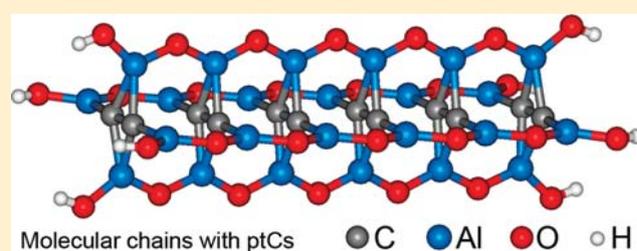


# Design of Molecular Chains Based on the Planar Tetracoordinate Carbon Unit $C_2Al_4$

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**ABSTRACT:** B3LYP DFT study revealed that the planar tetracoordinate carbon (ptC) molecules,  $C_2Al_4E_8$  ( $E = CH_3, NH_2,$  and  $OH$ ), could be condensed to one-dimensional molecular chains containing planar or quasi-planar  $C_2Al_4$  units by eliminating  $CH_4, NH_3,$  and  $H_2O$  molecules. Natural bond orbital analyses indicate that the electronic structures of  $C_2Al_4$  moieties in the chains, including ionic and covalent bonding, do not change significantly in comparison with those of the free  $C_2Al_4E_8$  ( $E = CH_3, NH_2,$  and  $OH$ ) ptC species. The reason for the structural evolution from ptC units to the molecular chains is discussed. Because of the eliminations of stable hydride molecules ( $CH_4, NH_3,$  and  $H_2O$ ), the condensations are thermodynamically favorable, which implies the promise to synthesize the materials experimentally.



## 1. INTRODUCTION

Strategies to reduce the very large energy difference between planar and tetrahedral tetracoordinate carbon arrangements were first proposed by Hoffmann, Alder, and Wilcox in 1970.<sup>1</sup> The first computational discovery of a molecule with a planar tetracoordinate carbon (ptC), 1,1-dilithiocyclopropane in 1976,<sup>2</sup> has been followed by numerous further examples, both experimental and theoretical.<sup>3–34</sup> The major strategies to stabilize molecules or species featured with ptC arrangement include the electronic induction,<sup>1,2,18,19</sup> mechanic confinement,<sup>1,5,20</sup> or the combination of both.<sup>21,22</sup> Recently, the advances in the ptC chemistry has triggered interests to utilize such a nonclassical carbon bonding to design solid or nanoscale molecules.

On the basis of the experimentally characterized  $CaAl_4^{2-}$  ptC species or its analogues,<sup>13–16</sup> Geske et al. designed  $CaAl_4^{2-}$ -based solid which uses Na as counterion<sup>35</sup> and Yang et al. used these ptC species to construct alkali and alkaline-earth metal sandwich molecules.<sup>36–39</sup>  $CB_4$  was computationally characterized to be a ptC global minimum by Pei et al.,<sup>40</sup> based on which Wu et al. designed  $B_2C$  graphene and nanotubes.<sup>41</sup> Because the ptC units in the bulky solids/molecules are generally more stable than the isolated single ptC species due to geometric confinement, some ptC local minima were also attempted for this purpose. Pancharatna et al. used the all-carbon ptC block  $C_5^{2-}$ <sup>18,19</sup> to construct the solid.<sup>42</sup> The planar hexacoordinate

carbon unit ( $CB_6^{2-}$ )<sup>8</sup> was used to design the ferrocene-like sandwich complexes by Li et al.,<sup>43</sup> the one-dimensional (1D) sandwich chains by Luo et al.,<sup>44</sup> and the sandwich materials by Yang et al.<sup>45</sup> The  $C_3B_2H_4$  ptC unit<sup>46</sup> was used by Sun et al. and Zhang et al. to design nanoribbons and nanotubes.<sup>47,48</sup> Recently, Li et al.<sup>49</sup> designed the silagraphene consisting of the planar tetracoordinate silicons (ptSi).

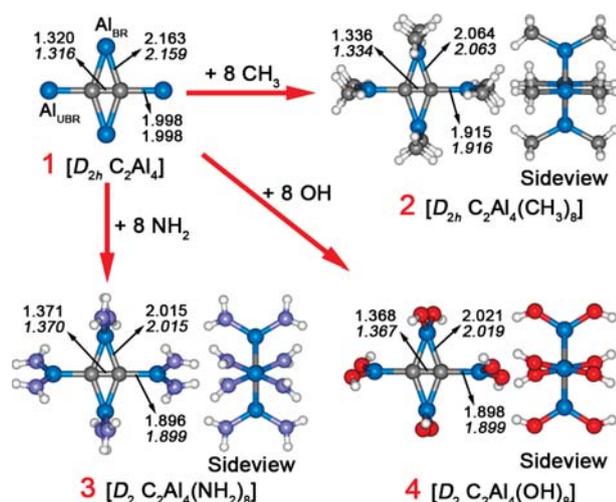
We were interested in using the ptC bonding to design materials. On the basis of the  $CM_4H_4$  ( $M = Ni, Pd,$  and  $Pt$ ) units, we reported the design of nanoribbons and nanotubes in 2007.<sup>50</sup> Recently, we found the replacement of hydrogen in benzene with BeH group results in  $D_{6h}$   $C_6Be_6H_6$  with all ptCs. The replacement of BeH group with Al atom led to the binary starlike aromatic C–Al species  $C_nAl_n$  ( $n = 4–6$ ), of which the  $D_{5h}$   $C_5Al_5^-$  was verified to be the global minimum with five ptCs.<sup>34</sup> Interestingly,  $C_6Be_6H_6$  can be assembled via H-bridging bonding into flat, tubular, and cage-like nanomolecules, which are in shape similar to the graphene, carbon nanotubes, and fullerenes.<sup>51</sup>

In this work, we report the computational design of one-dimensional (1D) ptC molecular chains. Previously, we found the rhombic  $D_{2h}$   $C_2Al_4$  species (1 in Figure 1) with double

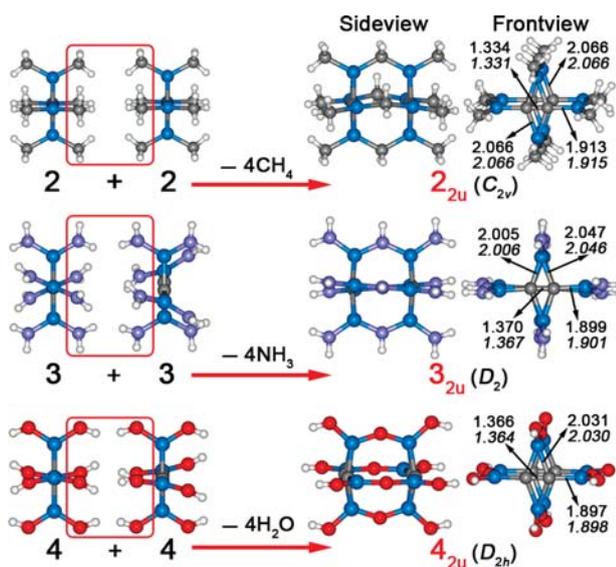
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**Figure 1.** B3LYP/6-31+G(d)-optimized structures of 1–4, along with the key bond lengths (the B3LYP/6-31++G(d,p) values are in italics). Color code, Al, blue; C, gray; N, purple; O, red; H, white.



**Figure 2.** Illustration of how ptC units are condensed together. The key bond lengths are given in angstroms (the B3LYP/6-31++G(d,p) values are in italics).

ptCs to be the global minimum.<sup>52</sup> The Al atoms in this species only use one of three valence electrons to form chemical bonding with its neighbors and the other two electrons exist as a lone pair. Because the lone pairs could be reactive, we proposed to use substituents to elaborate the  $C_2Al_4$  species, which led to a new type of ptC molecules,  $C_2Al_4E_8$  ( $E = H, CH_3, NH_2, OH, F,$  and  $Cl,$  etc.).<sup>53</sup> Among them, we conceived that  $C_2Al_4E_8$  [ $E = CH_3$  (2),  $NH_2$  (3), and  $OH$  (4), see Figure 1] could be condensed to give 1D ptC molecular chains. As we will show, the condensations only slightly affect the geometries and the electronic structures of  $C_2Al_4$  moieties and are all thermodynamically favorable.

**Table 1.** Calculated Properties of the Species Studied in This Work, Including Point Groups (PG), Lowest Vibrational Frequencies ( $\nu_{\min}$ ), the HOMO–LUMO Gaps (gap), and the Dihedral Angle  $Al_{BR}-C=C-Al_{BR}$  ( $\delta$ )

	BS	PG	$\nu_{\min}$	gap	$\delta$
2	BS1 <sup>a</sup>	$D_{2h}$	27	4.48	180.0
2	BS2 <sup>b</sup>	$D_{2h}$	30	4.49	180.0
2 <sub>2u</sub>	BS1	$C_{2v}$	31	3.95	177.2
2 <sub>2u</sub>	BS2	$C_{2v}$	31	3.95	177.5
2 <sub>3u</sub>	BS1	$C_{2h}$	25	3.69	180.0/177.3
2 <sub>3u</sub>	BS2	$C_{2h}$	26	3.67	180.0/177.7
2 <sub>4u</sub>	BS2	$C_{2v}$	23	3.54	179.6/178.2
2 <sub>5u</sub>	BS2	$C_{2h}$	17	3.47	180.0/179.3/178.4
2 <sub>6u</sub>	BS2	$C_{2v}$	18	3.42	179.7/179.0/178.7
3	BS1	$D_2$	27	3.46	180.0
3	BS2	$D_2$	32	3.46	180.0
3 <sub>2u</sub>	BS1	$D_2$	15	2.85	171.6
3 <sub>2u</sub>	BS2	$D_2$	16	2.82	171.6
3 <sub>3u</sub>	BS1	$D_{2h}$	10	2.55	180.0/172.2
3 <sub>3u</sub>	BS2	$D_{2h}$	3	2.52	180.0/172.2
3 <sub>4u</sub>	BS2	$D_{2h}$	7	2.40	179.6/172.1
3 <sub>5u</sub>	BS2	$D_{2h}$	8	2.33	180.0/179.5/172.0
3 <sub>6u</sub>	BS2	$D_{2h}$	7	2.29	179.9/179.5/172.0
4	BS1	$D_2$	22	3.83	180.0
4	BS2	$D_2$	27	3.82	180.0
4 <sub>2u</sub>	BS1	$D_{2h}$	26	3.51	161.2
4 <sub>2u</sub>	BS2	$D_{2h}$	27	3.46	162.4
4 <sub>3u</sub>	BS1	$D_{2h}$	27	3.09	180.0/167.4
4 <sub>3u</sub>	BS2	$D_{2h}$	26	3.07	180.0/167.6
4 <sub>4u</sub>	BS2	$D_{2h}$	24	2.99	179.7/167.3
4 <sub>5u</sub>	BS2	$D_{2h}$	22	2.92	180.0/179.5/167.2
4 <sub>6u</sub>	BS2	$D_{2h}$	19	2.87	179.8/179.3/167.1

<sup>a</sup> BS1: 6-31++G(d,p) (values are in italics). <sup>b</sup> BS2: 6-31+G(d).

## 2. METHODS

All the structures reported in this paper were optimized and characterized to be minima at the B3LYP/6-31+G(d) level. To calibrate the quality of 6-31+G(d) basis set used in this study, the short chains were recalculated with larger 6-311+G(d) basis set, which essentially gave very close results (see the tables below and in the Supporting Information). To calibrate the reliability of B3LYP functional on the large molecules, all chains were recalculated at BLYP/6-31+G(d) level considering the general long-range correction scheme (LC) of Hirao and co-workers<sup>54</sup> (i.e., at LC-BLYP/6-31+G(d) level). It has been found the LC-BLYP/6-31+G(d) predicted geometries and condensation energies close to those predicted by B3LYP/6-31+G(d); the differences of bond length were less than 0.04 Å and that of condensation energies were less than 4.2 kcal/mol (see Supporting Information). The B3LYP/6-31+G(d) results were used in the following discussion. The unscaled B3LYP/6-31+G(d) harmonic frequencies were used for thermal and entropic corrections at 298 K and 1 atm. The natural bond orbital (NBO)<sup>55,56</sup> analyses were performed at the B3LYP/6-31+G(d) level to understand their electronic structures. The LC-BLYP calculations were performed by using the Gaussian 09 package,<sup>57</sup> and all other

**Table 2.** Enthalpy and Gibbs Free Energy Changes ( $\Delta H$  and  $\Delta G$ ) of the Condensations at the B3LYP/6-31+G(d) Level

eq	$\Delta H$	$\Delta G$
$2 + 2 \rightarrow 2_{2u} + 4\text{CH}_4$ (1)	-14.2	-28.4
$3 + 3 \rightarrow 3_{2u} + 4\text{NH}_3$ (2)	-5.3	-25.0
$4 + 4 \rightarrow 4_{2u} + 4\text{H}_2\text{O}$ (3)	-23.2	-40.1
$2_{2u} + 2 \rightarrow 2_{3u} + 4\text{CH}_4$ (4)	-14.5	-29.4
$3_{2u} + 3 \rightarrow 3_{3u} + 4\text{NH}_3$ (5)	-4.6	-23.8
$4_{2u} + 4 \rightarrow 4_{3u} + 4\text{H}_2\text{O}$ (6)	-8.7	-26.8
$2_{3u} + 2 \rightarrow 2_{4u} + 4\text{CH}_4$ (7)	-14.4	-27.7
$2_{4u} + 2 \rightarrow 2_{5u} + 4\text{CH}_4$ (8)	-14.3	-29.3
$2_{5u} + 2 \rightarrow 2_{6u} + 4\text{CH}_4$ (9)	-14.4	-27.7
$3_{3u} + 3 \rightarrow 3_{4u} + 4\text{NH}_3$ (10)	-4.7	-22.4
$3_{4u} + 3 \rightarrow 3_{5u} + 4\text{NH}_3$ (11)	-4.7	-22.1
$3_{5u} + 3 \rightarrow 3_{6u} + 4\text{NH}_3$ (12)	-4.2	-22.3
$4_{3u} + 4 \rightarrow 4_{4u} + 4\text{H}_2\text{O}$ (13)	-11.3	-29.4
$4_{4u} + 4 \rightarrow 4_{5u} + 4\text{H}_2\text{O}$ (14)	-11.0	-28.6
$4_{5u} + 4 \rightarrow 4_{6u} + 4\text{H}_2\text{O}$ (15)	-11.0	-29.0

DFT calculations were carried out by using the Gaussian 03 package.<sup>58</sup>

### 3. RESULTS AND DISCUSSION

Figure 2 illustrates the condensations of two units of  $\text{C}_2\text{Al}_4\text{E}_8$  ( $\text{E} = \text{CH}_3$  (2),  $\text{NH}_2$  (3), and  $\text{OH}$  (4)) molecules. By eliminating four  $\text{CH}_4$ ,  $\text{NH}_3$ , or  $\text{H}_2\text{O}$  molecules, two units of 2, 3, and 4 can be condensed to give the drumlike molecules  $2_{2u}$ ,  $3_{2u}$ , and  $4_{2u}$ , respectively. Note that the subscript “nu” ( $n = 2-6$ ) here and hereafter represents the number of ptC units in a chain. The harmonic frequency analyses indicate  $2_{2u}$ – $4_{2u}$  to be energy minima (the lowest vibrational frequencies ( $\nu_{\text{min}}$ ) are listed in Table 1). The HOMO–LUMO gaps of  $2_{2u}$ – $4_{2u}$  are 3.95, 2.82, and 3.46 eV, respectively, are slightly smaller (ca. 0.4 eV) than those in 2–4, 4.49, 3.46, and 3.82 eV, respectively. The equations, eqs 1–3 in Table 2, estimate the thermodynamics of the condensations. The negative  $\Delta H$  and  $\Delta G$  values tell that the condensations are thermodynamically favorable. Because the condensations are entropically favorable, the thermodynamic favorability of the condensations is more pronounced in terms of  $\Delta G$  than  $\Delta H$ .

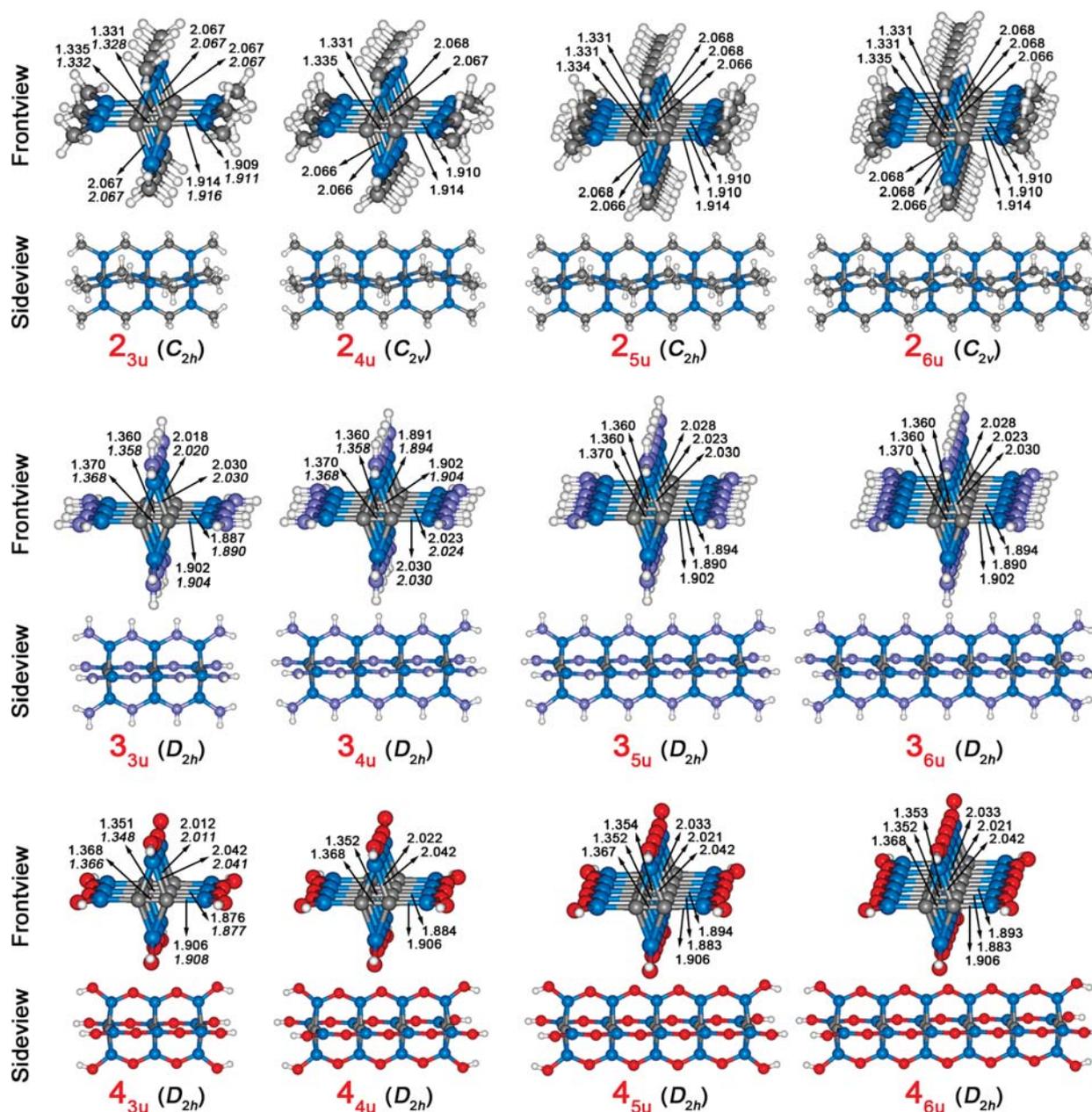
The symmetries of  $2_{2u}$  ( $C_{2v}$ ) and  $4_{2u}$  ( $D_{2h}$ ) are different from those of 2 ( $D_{2h}$ ) and 4 ( $D_2$ ).  $3_{2u}$  and 3 have the same point group ( $D_2$ ), but  $3_{2u}$  tends to have  $D_{2h}$  symmetry. In comparison with the perfect planar  $\text{C}_2\text{Al}_4$  cores in 2–4, those in  $2_{2u}$ – $4_{2u}$  are slightly bent, implying that the condensations cause strains. Interestingly, while the gradually decreased  $\angle \text{Al}_{\text{BR}}-\text{C}=\text{C}-\text{Al}_{\text{BR}}$  (subscript BR means the bridging atoms) dihedral angles ( $\delta$ ),  $177.1^\circ$  ( $2_{2u}$ ),  $171.6^\circ$  ( $3_{2u}$ ), and  $161.2^\circ$  ( $4_{2u}$ ) and the increased  $\text{Al}-\text{X}_{\text{BR}}-\text{Al}$  ( $\text{X} = \text{C}, \text{N}, \text{and O}$ ) bond angles,  $122.8^\circ/123.2^\circ$  ( $2_{2u}$ ),  $131.0^\circ/132.0^\circ$  ( $3_{2u}$ ), and  $146.1^\circ/150.5^\circ$  ( $4_{2u}$ ), imply that the strains could increase from  $2_{2u}$  to  $4_{2u}$  the condensation to give  $4_{2u}$  is most favorable. This disagreement can be attributed to the stronger affinity of H to O in eliminated

$\text{H}_2\text{O}$  molecule than H to N and C in eliminated  $\text{NH}_3$  and  $\text{CH}_4$  molecules, respectively.

The NBO analyses reveal that the condensations do not affect the electronic structures of the  $\text{C}_2\text{Al}_4$  core significantly. As compared in Table S1 in the Supporting Information, the atoms in  $\text{C}_2\text{Al}_4$  cores of  $2_{2u}$ – $4_{2u}$  bear atomic charges close to those in 2–4, respectively. The total Wiberg bond indices on C and Al ( $\text{WBI}_{\text{C}}$  and  $\text{WBI}_{\text{Al}}$ ) and the total Wiberg bond orders between Al and the two central C atoms ( $\text{WBI}_{\text{CC-Al}}$ ) for  $\text{C}_2\text{Al}_4$  moieties of  $2_{2u}$ – $4_{2u}$  are comparable to those of 2–4. The similar electronic structures signify that both covalent and ionic interactions in the ptC fragments are well maintained, which, together with the thermodynamically favorable condensation, implies the promise to use more units to build even longer 1D molecular chains.

The molecular chains with three to six ptC units were optimized and the minimum structures are displayed in Figure 3. The symmetries of  $2_{nu}$  ( $n = 2-6$ ) chains have the pattern of  $C_{2v}$  ( $2_{2u}$ )  $\rightarrow$   $C_{2h}$  ( $2_{3u}$ )  $\rightarrow$   $C_{2v}$  ( $2_{4u}$ )  $\rightarrow$   $C_{2h}$  ( $2_{5u}$ )  $\rightarrow$   $C_{2v}$  ( $2_{6u}$ ), while  $3_{nu}$  ( $n = 3-6$ ) and  $4_{nu}$  ( $n = 2-6$ ) chains have unchanged symmetry ( $D_{2h}$ ). The difference in symmetry change could be attributed to the steric repulsions among the groups attached to Al when the units are condensed into chains. As shown in Figure 4, when the units are condensed to form chains, the ideal interlayer distance between the neighboring  $\text{C}_2\text{Al}_4$  moieties (having an out-of-plane  $\pi$  MO) should be close to the general value (i.e., about 3.4 Å) in the  $\pi$  stacked system. To adopt such a distance, the bridging  $-\text{CH}_2-$  groups in the  $2_{nu}$  chains move outward compared to the  $-\text{CH}_3$  groups in single 2 and thus the C–Al–C angle (shown as a1 and a2 angles in Figure 4) becomes smaller, causing the increased repulsion between the bridging  $-\text{CH}_2-$  and the terminal  $-\text{CH}_3$  groups. Thus, the  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups are arranged zigzag to release the strains, leading to the structural evolution from  $D_{2h}$  to alternate  $C_{2v}$ – $C_{2h}$ – $C_{2v}$ – $C_{2h}$ –... structures. Consistently, the interlayer distances between  $\text{C}_2\text{Al}_4$  cores in  $2_{nu}$  ( $n = 2-3$ ) chains are slightly larger than 3.4 Å. On the contrary, the sizes of N and O are too small to match the distance requirement. Compared to the  $-\text{NH}_2$  and  $-\text{OH}$  groups in 3 and 4, the  $-\text{NH}-$  and  $-\text{O}-$  groups in  $3_{nu}$  and  $4_{nu}$  ( $n = 2-3$ ) chains move inward and the N–Al–N and O–Al–O angles (see angle b1, b2, c1, and c2 angles in Figure 4) become larger, resulting in the decreased repulsions between the bridged  $-\text{NH}-$  and terminal  $-\text{NH}_2$  groups or between the bridged  $-\text{O}-$  and terminal  $-\text{OH}$  groups. Thus, the  $-\text{NH}-$  and  $-\text{NH}_2$  as well as  $-\text{O}-$  and  $-\text{OH}$  groups can arrange linearly to promote the structural evolution from  $D_2$  to  $D_{2h}$ . Indeed, the interlayer distances between  $\text{C}_2\text{Al}_4$  cores of  $3_{nu}$  or  $4_{nu}$  ( $n = 2-3$ ) chains are all slightly smaller than 3.4 Å.

Due to the geometric confinement, the middle  $\text{C}_2\text{Al}_4$  moieties in  $2_{3u}$ – $4_{3u}$  are perfectly planar. Understandably, those in the terminal units are still convex: the  $\delta$  values are  $177.7^\circ$ ,  $172.2^\circ$ , and  $167.6^\circ$  in  $2_{3u}$ – $4_{3u}$ , respectively, which are larger than those in their corresponding 2u species, indicating the less distorted  $\text{C}_2\text{Al}_4$  moieties. Note that the  $\delta$  value of  $167.4^\circ$  in  $4_{3u}$  is substantially larger than the  $161.2^\circ$  in  $4_{2u}$ . This suggests that the strains in  $4_{3u}$  are not released as much as that in  $4_{2u}$ . Consistently, the condensations of 4 into 2u to give 3u (eq 6) release less heat than that of eq 3 ( $-8.7$  vs  $-23.2$  kcal/mol in  $\Delta H$  and  $-26.8$  vs  $-40.1$  kcal/mol in  $\Delta G$ , see Table 2 for details). As tabulated in Table S1 in the Supporting

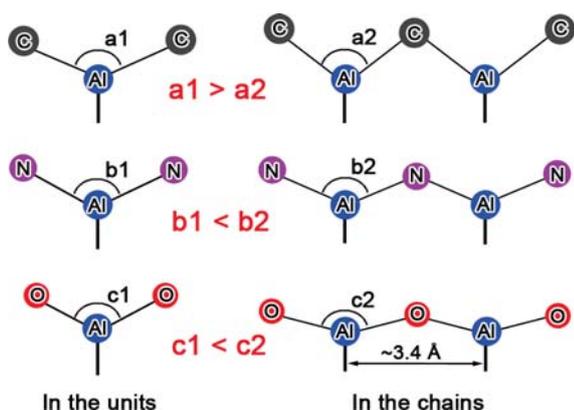


**Figure 3.** Optimized structures of 3u–6u species with key bond lengths for the  $C_2Al_4$  moieties. The normal and italic bond lengths are the B3LYP/6-31+G(d) and B3LYP/6-311++G(d,p) values, respectively.

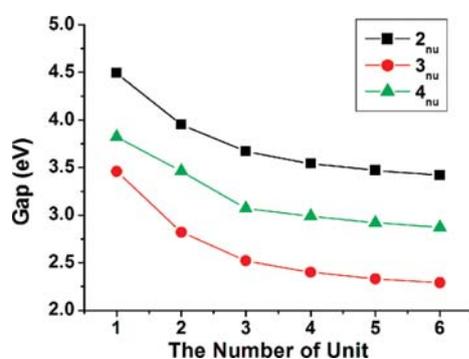
Information, the NBO analysis on the 3u species shows that both the natural charges on C and Al atoms  $C_2Al_4$  moieties and the  $WBI_C/WBI_{Al}/WBI_{CC-Al}$  values are similar to those in building block 2–4. This indicates that both electrostatic and covalent interactions in the  $C_2Al_4$  moieties do not change significantly when the new units are added, which resembles the situation in 2u species.

Similar to the situation in 3u species, the nonterminal  $C_2Al_4$  moieties in 4u–6u species are planar or almost planar ( $\delta > 179.0^\circ$ , see Table 1) and those in terminal units are convex, i.e., from 3u- to 6u-condensed species, the structures of the non-terminal  $C_2Al_4$  moieties in these longer chains are very similar. Correspondingly, the heats of formations (eqs 7–15 in Table 2)

are relatively close (averagely  $-15.7$ ,  $-1.9$ , and  $-11.1$  kcal/mol in  $\Delta H$  and  $-29.9$ ,  $-21.5$ , and  $-29.0$  kcal/mol in  $\Delta G$  for the chains condensed by 2–4, respectively). The negative heats of formations indicate that the formations of molecular chains are thermodynamically favorable. As expected, the NBO analysis (see Table S1 in the Supporting Information) reveals that the natural charge distribution and the  $WBI_{Al}/WBI_C/WBI_{CC-Al}$  values are close to the 2u and 3u species, which suggests that the elongation of molecular chains does not affect the electronic structures of  $C_2Al_4$  ptC cores. As shown in Figure 5, the HOMO–LUMO gaps decrease as the chain becomes longer but the decreasing extent becomes smaller and smaller. The variation pattern of HOMO–LUMO gaps suggests the gaps of long chains



**Figure 4.** Variation of the angles concerning the repulsions of anchored groups.



**Figure 5.** Changes of HOMO–LUMO gaps vs the lengths of the chains.

will converge to a certain value, which implies the insulator property for the infinite chains.

#### 4. CONCLUSION

In summary, we have shown the ptC molecules ( $C_2Al_4E_8$ ,  $E = CH_3, NH_2,$  and  $OH$ ) can be condensed to form the one-dimensional molecular chains. The  $C_2Al_4$  cores in these chains are planar or nearly planar and maintain electronic structures (including both ionic and covalent bonding interaction) similar to those in the individual molecules. Because of the elimination of the stable hydride ( $CH_4, NH_3,$  and  $H_2O$ ), the condensations are thermodynamically favorable in terms of both enthalpies and Gibbs free energies.

#### ■ ASSOCIATED CONTENT

**S** **Supporting Information.** Tables summarizing the LC-BLYP/6-31+G(d) predicted condensation thermodynamics and the B3LYP/6-31+G(d) NBO analysis results, and the full form of refs 57 and 58. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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