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## Tetracoordinated Planar Carbon in Pentaatomic Molecules

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**Abstract:** Three pentaatomic molecules  $\text{CSi}_2\text{Al}_2$ ,  $\text{CSi}_2\text{Ga}_2$ , and  $\text{CGe}_2\text{Al}_2$  were studied at the B3LYP/6-311+G\* and MP2/6-311+G\* levels of theory (with tests also run at multiconfigurational levels) to determine whether the central carbon atom exists in a planar geometry. We found that *cis*- $\text{CSi}_2\text{Al}_2$  and *trans*- $\text{CSi}_2\text{Al}_2$  planar structures have one imaginary frequency and that distortion along this mode leads to slightly pyramidal local minima. In contrast, *cis*- and *trans*- $\text{CSi}_2\text{Ga}_2$  and *cis*- and *trans*- $\text{CGe}_2\text{Al}_2$  are true minima in their planar geometries, but their corresponding tetrahedral structures lie 25–28 kcal/mol higher in energy and are first-order saddle points on the respective energy surfaces. A molecular orbital analysis is presented to explain the preference of the planar anti-van't Hoff/Lebel structures over the corresponding tetrahedral structures. This analysis suggests that the presence of 18 valence electrons (which leads to three C–ligand  $\sigma$  bonds, one C–ligand  $\pi$  bond, and one ligand–ligand bond) is crucial for planar geometries to be stable and preferred over tetrahedral structures.

## 1. Introduction

In 1874 van't Hoff<sup>1</sup> and LeBel<sup>2</sup> independently recognized that a tetracoordinated tetravalent carbon atom prefers a tetrahedral arrangement of its substituents. This contribution to organic and general chemistry marked a milestone in understanding the structure of Carbon compounds. While X-ray structure analysis later confirmed the tetrahedral structure for tetracoordinated carbon, and the concept of  $\text{sp}^3$ -hybridization nicely explained why such structures are so profoundly stable, chemists for many years thought about how to overcome the inherent preference for tetrahedral structure and how to make chemical compounds containing *planar* tetracoordinated carbon. These efforts were accelerated by the pioneering theoretical works of Hoffmann et al.<sup>3</sup> as a result of which today's literature on tetracoordinated planar carbon is very extensive.<sup>4–6</sup>

In a large molecule, one can employ rigidly bridged fragments to “force” planarity at a carbon center. Such artificially planar sites are not the topic of the present work. We chose to search for pentaatomic molecules containing a planar central carbon atom because, for such species, only interactions between the central carbon and the ligands and the ligand–ligand interactions can be responsible for the planar arrangement. It is our belief that understanding the bonding in such molecules is important for future progress in the design molecules and compounds with tetracoordinated planar carbon.

In an earlier work, Schleyer and Boldyrev<sup>7</sup> computationally predicted that *cis*- $\text{CSi}_2\text{Al}_2$  and *trans*- $\text{CSi}_2\text{Al}_2$  were locally stable structures containing a planar tetracoordinated central carbon

atom; however, the energies of the alternative tetrahedral-like structures were not addressed in their research. In this work, we therefore first reexamine both the planar and tetrahedral-like structures of  $\text{CSi}_2\text{Al}_2$  after which we extended the search for pentaatomic molecules containing tetracoordinated planar carbon to  $\text{CSi}_2\text{Ga}_2$  and  $\text{CGe}_2\text{Al}_2$  (to explore how varying the size of the ligand atoms affects the structures' stabilities).

## 2. Computational Methods

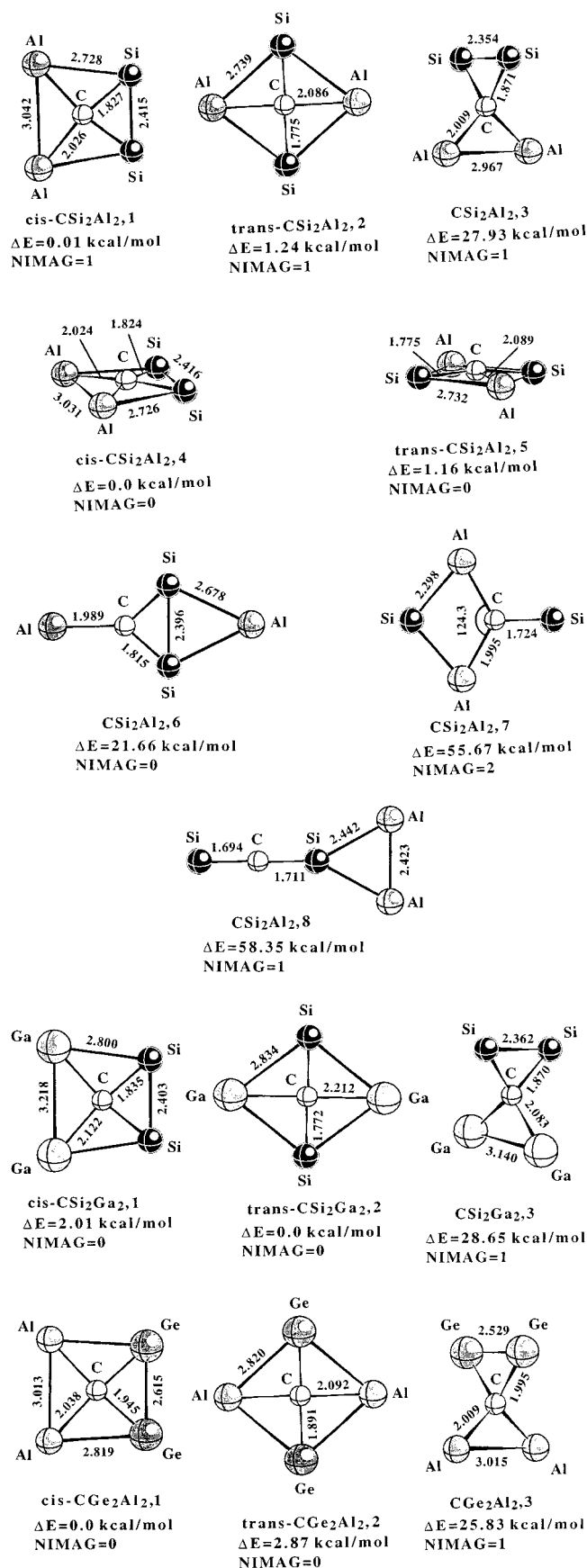
We optimized the geometries of the molecules employing analytical gradients with polarized split-valence basis sets (6-311+G\*) at the MP2 (full) level (meaning all electrons were included in the correlation calculations) for  $\text{CSi}_2\text{Al}_2$  and at the MP2(fc) level (frozen core; with only valence electrons included in the correlation calculations) for  $\text{CSi}_2\text{Ga}_2$  and  $\text{CGe}_2\text{Al}_2$ . We also carried out geometry optimization and frequency evaluation on all these molecules at the nonlocal density functional B3LYP level of theory. The fundamental vibrational frequencies, vibrational normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods. All of these calculations were carried out with the Gaussian 94 program.<sup>8</sup> In addition, as discussed below, test calculations at the MCSCF level of theory were performed to verify or refute the single-configurational nature of the electronic states.

## 3. Findings

**A.  $\text{CSi}_2\text{Al}_2$ .** The optimized geometries of a wide variety of *singlet* structures of  $\text{CSi}_2\text{Al}_2$  are presented in Figure 1. Triplet states were also examined for each of these singlet structures but were found to be substantially higher in energy and thus

(1) van't Hoff, J. H. *Arch. Neerl. Sci. Exactes Nat.* **1874**, 445.(2) LeBel, J. A. *Bull. Soc. Chim. Fr.* **1874**, 22, 337.(3) (a) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, 92, 4992. (b) Hoffmann, R. *Pure Appl. Chem.* **1971**, 28, 181.(4) Luef, W.; Keese, R. *Adv. Strain Org. Chem.* **1993**, 3, 229.(5) Sorger, K.; Schleyer, P. v. R. *J. Mol. Struct.* **1995**, 338, 317.(6) Rottger, D.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 812.(7) Schleyer, P. v. R.; Boldyrev, A. I. *J. Chem. Soc., Chem. Commun.* **1991**, 1536.

(8) GAUSSIAN 94, Revision A.1; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chem, W.; Wong, M. W.; Anders, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople J. A.; Gaussian Inc.: Pittsburgh, PA, 1995.



**Figure 1.** Optimized geometries (bond lengths are in Å and bond angles are in  $^\circ$ ), relative energies ( $\Delta E$ , in kcal/mol), and the number of imaginary vibrational frequencies (NIMAG) at the MP2(full)/6-311+G\* level for  $\text{CSi}_2\text{Al}_2$  and the MP2(fc)/6-311+G\* level for  $\text{CSi}_2\text{Ga}_2$  and  $\text{CGe}_2\text{Al}_2$ .

were not considered further (this is especially important to note because, for tetrahedral-like structures, as we discuss later, strong possibilities exist for partial occupation of degenerate (or nearly degenerate) orbitals).

Our calculations at the B3LYP/6-311+G\* level of theory on the *cis*- $\text{CSi}_2\text{Al}_2$ , 1 and *trans*- $\text{CSi}_2\text{Al}_2$ , 2 structures supported the earlier conclusion,<sup>8</sup> based on MP2/6-31G\* calculations, that both structures are minima. However, when diffuse functions were added to the basis, we found, at the MP2(full)/6-31+G\* and MP2(full)/6-311+G\* levels of theory, that both structures are saddle points rather than stable minima (see Table 1). The vibrational modes ( $\nu_6(b_1)$  for *cis*- $\text{CSi}_2\text{Al}_2$ , 1 and  $\nu_9(b_{3u})$  for *trans*- $\text{CSi}_2\text{Al}_2$ , 2) having imaginary frequencies lead, when followed "down hill", to nearly planar but pyramidal *cis*- $\text{CSi}_2\text{Al}_2$ , 4 and *trans*- $\text{CSi}_2\text{Al}_2$ , 5 structures. The corresponding inversion barriers (connecting 4 to 1 and 5 to 2) were found to be very small: 0.014 kcal/mol (*cis*- $\text{CSi}_2\text{Al}_2$ , 1) and 0.076 kcal/mol (*trans*- $\text{CSi}_2\text{Al}_2$ , 2), as a result of which one would need to use substantially higher levels of theory to make a final conclusion about the planarity of the *cis* and *trans* structures of  $\text{CSi}_2\text{Al}_2$ . To do so at this time is beyond our computational facilities. In fact, after ZPE corrections are added, the first barrier disappears and thus the global minimum structure, averaged over the ground vibrations, is effectively planar.

The tetrahedral-type structure  $\text{CSi}_2\text{Al}_2$ , 3 was found to be a first-order saddle point at the both the B3LYP/6-311+G\* and MP2(full)/6-311+G\* levels of theory and to be appreciably higher in energy (by 27–28 kcal/mol) than the pyramidal (nearly planar) structures, 4 and 5. In fact, when structure 3 is allowed to distort down hill along its imaginary frequency mode (this mode has  $a_2$  symmetry and gives rise to internal rotations of opposite sense in the SiCSi and AlAl subunits), it relaxes to structure 4 (the *cis* structure), not to structure 5 (*trans*). Therefore, the van't Hoff/LeBel tetrahedral arrangement is not only less stable than the nearly planar structure, but it is also a saddle point rather than a local minimum. As mentioned earlier, we also examined the lowest energy triplet state at this geometry and found it to be significantly higher in energy than the singlet state. We also carried out small MCSCF calculations on this singlet state to make sure it has a strongly dominant electronic configuration at this near-tetrahedral geometry, and we determined that this indeed is the case. The latter two observations are not surprising given the HOMO–LUMO energy gap (0.254 au for  $\text{CSi}_2\text{Al}_2$ , 0.250 au for  $\text{CGe}_2\text{Al}_2$ , and 0.242 au for  $\text{CSi}_2\text{Ga}_2$ ) in the species treated here.

Other structures shown in Figure 1 having one of the ligand atoms lying outside the first coordination sphere were found to be substantially less stable. Therefore, we conclude that the *cis*-quasi-planar (pyramidal) structure is indeed the global minimum on the potential energy surface of  $\text{CSi}_2\text{Al}_2$  with the *trans*-quasi-planar (pyramidal) structure lying slightly (ca. 1.2 kcal/mol) above the global minimum *cis* structure.

Why the pyramidal structures of  $\text{CSi}_2\text{Al}_2$  are somewhat more stable at the MP2(full)/6-31+G\* and MP2(full)/6-311+G\* levels of theory than their corresponding planar counterparts may lie in the small size of the cavities provided by the *cis*- $\text{Si}_2\text{Al}_2$  and *trans*- $\text{Si}_2\text{Al}_2$  fragments. Because we cannot predict with certainty that planar structures of  $\text{CSi}_2\text{Al}_2$  will be minima at higher levels of theory, in our search for pentaatomic tetracoordinated planar carbon molecules we next performed calculations on two valence isoelectronic molecules  $\text{CSi}_2\text{Ga}_2$  and  $\text{CGe}_2\text{Al}_2$ , where we expect the cavities for the central carbon atom to be larger. On the basis of our experience with the  $\text{CSi}_2\text{Al}_2$  molecule, we optimized the geometries only for the

**Table 1.** Calculated Molecular Properties of the Lowest Energy CSi<sub>2</sub>Al<sub>2</sub> Structures

<i>cis</i> -CSi <sub>2</sub> Al <sub>2</sub> , <b>1</b> ( <i>C</i> <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )	<i>trans</i> -CSi <sub>2</sub> Al <sub>2</sub> , <b>2</b> ( <i>D</i> <sub>2h</sub> , <sup>1</sup> A <sub>g</sub> )	CSi <sub>2</sub> Al <sub>2</sub> , <b>3</b> ( <i>C</i> <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )	<i>cis</i> -CSi <sub>2</sub> Al <sub>2</sub> , <b>4</b> ( <i>C</i> <sub>s</sub> , <sup>1</sup> A')	<i>trans</i> -CSi <sub>2</sub> Al <sub>2</sub> , <b>5</b> ( <i>C</i> <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )
1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3b <sub>2</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	1a <sub>g</sub> <sup>2</sup> 1b <sub>2u</sub> <sup>2</sup> 1b <sub>1u</sub> <sup>2</sup> 2a <sub>g</sub> <sup>2</sup> 3a <sub>g</sub> <sup>2</sup> 1b <sub>3u</sub> <sup>2</sup> 2b <sub>2u</sub> <sup>2</sup> 2b <sub>1u</sub> <sup>2</sup> 1b <sub>3g</sub> <sup>2</sup>	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 2b <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	1a'' <sup>2</sup> 1a'' <sup>2</sup> 2a'' <sup>2</sup> 3a'' <sup>2</sup> 4a'' <sup>2</sup> 2a'' <sup>2</sup> 5a'' <sup>2</sup> 3a'' <sup>2</sup> 6a'' <sup>2</sup>	1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 1a <sub>2</sub> <sup>2</sup> 2b <sub>1</sub> <sup>2</sup>
B3LYP/6-311+G*	B3LYP/6-311+G*	B3LYP/6-311+G*		
<i>E</i> <sub>B3LYP</sub> = -1101.986210 au	<i>E</i> <sub>B3LYP</sub> = -1101.982486 au	<i>E</i> <sub>B3LYP</sub> = -1101.952511 au		
Δ <i>E</i> <sub>B3LYP</sub> = 0.0 kcal/mol	Δ <i>E</i> <sub>B3LYP</sub> = 2.3 kcal/mol	Δ <i>E</i> <sub>B3LYP</sub> = 21.2 kcal/mol		
ν <sub>1</sub> (a <sub>1</sub> ) = 877 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>g</sub> ) = 512 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>1</sub> ) = 800 cm <sup>-1</sup>		
ν <sub>2</sub> (a <sub>1</sub> ) = 418 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>g</sub> ) = 249 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>1</sub> ) = 443 cm <sup>-1</sup>		
ν <sub>3</sub> (a <sub>1</sub> ) = 307 cm <sup>-1</sup>	ν <sub>3</sub> (b <sub>3g</sub> ) = 232 cm <sup>-1</sup>	ν <sub>3</sub> (a <sub>1</sub> ) = 323 cm <sup>-1</sup>		
ν <sub>4</sub> (a <sub>1</sub> ) = 155 cm <sup>-1</sup>	ν <sub>4</sub> (b <sub>1u</sub> ) = 571 cm <sup>-1</sup>	ν <sub>4</sub> (a <sub>1</sub> ) = 132 cm <sup>-1</sup>		
ν <sub>5</sub> (a <sub>2</sub> ) = 91 cm <sup>-1</sup>	ν <sub>5</sub> (b <sub>1u</sub> ) = 120 cm <sup>-1</sup>	ν <sub>5</sub> (a <sub>2</sub> ) = 112i cm <sup>-1</sup>		
ν <sub>6</sub> (b <sub>1</sub> ) = 174 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>2u</sub> ) = 1097 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>1</sub> ) = 537 cm <sup>-1</sup>		
ν <sub>7</sub> (b <sub>2</sub> ) = 809 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>2u</sub> ) = 165 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>1</sub> ) = 93 cm <sup>-1</sup>		
ν <sub>8</sub> (b <sub>2</sub> ) = 306 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>3u</sub> ) = 164 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>2</sub> ) = 585 cm <sup>-1</sup>		
ν <sub>9</sub> (b <sub>2</sub> ) = 157 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>3u</sub> ) = 99 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>2</sub> ) = 175 cm <sup>-1</sup>		
MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*	MP2(full)/6-311+G*
<i>E</i> <sub>MP2</sub> = -1100.447586 au	<i>E</i> <sub>MP2</sub> = -1100.445639 au	<i>E</i> <sub>MP2</sub> = -1100.403099 au	<i>E</i> <sub>MP2</sub> = -1100.447608 au	<i>E</i> <sub>MP2</sub> = -1100.445760 au
Δ <i>E</i> <sub>MP2</sub> = 0.01 kcal/mol	Δ <i>E</i> <sub>MP2</sub> = 1.24 kcal/mol	Δ <i>E</i> <sub>MP2</sub> = 27.93 kcal/mol	Δ <i>E</i> <sub>MP2</sub> = 0.00 kcal/mol	Δ <i>E</i> <sub>MP2</sub> = 1.16 kcal/mol
ν <sub>1</sub> (a <sub>1</sub> ) = 920 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>g</sub> ) = 505 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>1</sub> ) = 853 cm <sup>-1</sup>	ν <sub>1</sub> (a') = 918 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>1</sub> ) = 513 cm <sup>-1</sup>
ν <sub>2</sub> (a <sub>1</sub> ) = 422 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>g</sub> ) = 287 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>1</sub> ) = 453 cm <sup>-1</sup>	ν <sub>2</sub> (a') = 423 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>1</sub> ) = 287 cm <sup>-1</sup>
ν <sub>3</sub> (a <sub>1</sub> ) = 311 cm <sup>-1</sup>	ν <sub>3</sub> (b <sub>3g</sub> ) = 249 cm <sup>-1</sup>	ν <sub>3</sub> (a <sub>1</sub> ) = 324 cm <sup>-1</sup>	ν <sub>3</sub> (a') = 311 cm <sup>-1</sup>	ν <sub>3</sub> (a <sub>1</sub> ) = 140 cm <sup>-1</sup>
ν <sub>4</sub> (a <sub>1</sub> ) = 160 cm <sup>-1</sup>	ν <sub>4</sub> (b <sub>1u</sub> ) = 557 cm <sup>-1</sup>	ν <sub>4</sub> (a <sub>1</sub> ) = 148 cm <sup>-1</sup>	ν <sub>4</sub> (a') = 164 cm <sup>-1</sup>	ν <sub>4</sub> (a <sub>1</sub> ) = 107 cm <sup>-1</sup>
ν <sub>5</sub> (a <sub>2</sub> ) = 88 cm <sup>-1</sup>	ν <sub>5</sub> (b <sub>1u</sub> ) = 177 cm <sup>-1</sup>	ν <sub>5</sub> (a <sub>2</sub> ) = 130i cm <sup>-1</sup>	ν <sub>5</sub> (a') = 105 cm <sup>-1</sup>	ν <sub>5</sub> (a <sub>2</sub> ) = 251 cm <sup>-1</sup>
ν <sub>6</sub> (b <sub>1</sub> ) = 77i cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>2u</sub> ) = 1189 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>1</sub> ) = 577 cm <sup>-1</sup>	ν <sub>6</sub> (a'') = 886 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>1</sub> ) = 651 cm <sup>-1</sup>
ν <sub>7</sub> (b <sub>2</sub> ) = 888 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>2u</sub> ) = 201 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>1</sub> ) = 51 cm <sup>-1</sup>	ν <sub>7</sub> (a'') = 332 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>1</sub> ) = 179 cm <sup>-1</sup>
ν <sub>8</sub> (b <sub>2</sub> ) = 333 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>3u</sub> ) = 97 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>2</sub> ) = 614 cm <sup>-1</sup>	ν <sub>8</sub> (a'') = 184 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>2</sub> ) = 1186 cm <sup>-1</sup>
ν <sub>9</sub> (b <sub>2</sub> ) = 184 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>3u</sub> ) = 115i cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>2</sub> ) = 173 cm <sup>-1</sup>	ν <sub>9</sub> (a'') = 98 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>2</sub> ) = 202 cm <sup>-1</sup>
<i>Q</i> <sub>NPA</sub> (C) = -2.266 e	<i>Q</i> <sub>NPA</sub> (C) = -2.323 e	<i>Q</i> <sub>NPA</sub> (C) = -2.443 e	<i>Q</i> <sub>NPA</sub> (C) = -2.260 e	<i>Q</i> <sub>NPA</sub> (C) = -2.305 e
<i>Q</i> <sub>NPA</sub> (Si) = +0.524 e	<i>Q</i> <sub>NPA</sub> (Si) = +0.609 e	<i>Q</i> <sub>NPA</sub> (Si) = +0.441 e	<i>Q</i> <sub>NPA</sub> (Si) = +0.524 e	<i>Q</i> <sub>NPA</sub> (Si) = +0.602 e
<i>Q</i> <sub>NPA</sub> (Ga) = +0.609 e	<i>Q</i> <sub>NPA</sub> (Ga) = +0.553 e	<i>Q</i> <sub>NPA</sub> (Ga) = +0.780 e	<i>Q</i> <sub>NPA</sub> (Ga) = +0.606 e	<i>Q</i> <sub>NPA</sub> (Ga) = +0.550 e

**Table 2.** Calculated Molecular Properties of the Lowest Energy CSi<sub>2</sub>Ga<sub>2</sub> Structures

<i>cis</i> -CSi <sub>2</sub> Ga <sub>2</sub> , <b>1</b> ( <i>C</i> <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )	<i>trans</i> -CSi <sub>2</sub> Ga <sub>2</sub> , <b>2</b> ( <i>D</i> <sub>2h</sub> , <sup>1</sup> A <sub>g</sub> )	CSi <sub>2</sub> Ga <sub>2</sub> , <b>3</b> ( <i>C</i> <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )
1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3b <sub>2</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	1a <sub>g</sub> <sup>2</sup> 1b <sub>2u</sub> <sup>2</sup> 1b <sub>1u</sub> <sup>2</sup> 2a <sub>g</sub> <sup>2</sup> 3a <sub>g</sub> <sup>2</sup> 1b <sub>3u</sub> <sup>2</sup> 2b <sub>2u</sub> <sup>2</sup> 2b <sub>1u</sub> <sup>2</sup> 1b <sub>3g</sub> <sup>2</sup>	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 2b <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>
B3LYP/6-311+G*	B3LYP/6-311+G*	B3LYP/6-311+G*
<i>E</i> <sub>B3LYP</sub> = -4466.839885 au	<i>E</i> <sub>B3LYP</sub> = -4466.841958 au	<i>E</i> <sub>B3LYP</sub> = -4466.809803 au
Δ <i>E</i> <sub>B3LYP</sub> = 1.3 kcal/mol	Δ <i>E</i> <sub>B3LYP</sub> = 0.0 kcal/mol	Δ <i>E</i> <sub>B3LYP</sub> = 28.7 kcal/mol
ν <sub>1</sub> (a <sub>1</sub> ) = 842 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>g</sub> ) = 518 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>1</sub> ) = 774 cm <sup>-1</sup>
ν <sub>2</sub> (a <sub>1</sub> ) = 386 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>g</sub> ) = 153 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>1</sub> ) = 419 cm <sup>-1</sup>
ν <sub>3</sub> (a <sub>1</sub> ) = 250 cm <sup>-1</sup>	ν <sub>3</sub> (b <sub>3g</sub> ) = 181 cm <sup>-1</sup>	ν <sub>3</sub> (a <sub>1</sub> ) = 238 cm <sup>-1</sup>
ν <sub>4</sub> (a <sub>1</sub> ) = 96 cm <sup>-1</sup>	ν <sub>4</sub> (b <sub>1u</sub> ) = 477 cm <sup>-1</sup>	ν <sub>4</sub> (a <sub>1</sub> ) = 90 cm <sup>-1</sup>
ν <sub>5</sub> (a <sub>2</sub> ) = 68 cm <sup>-1</sup>	ν <sub>5</sub> (b <sub>1u</sub> ) = 133 cm <sup>-1</sup>	ν <sub>5</sub> (a <sub>2</sub> ) = 101i cm <sup>-1</sup>
ν <sub>6</sub> (b <sub>1</sub> ) = 174 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>2u</sub> ) = 111 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>1</sub> ) = 506 cm <sup>-1</sup>
ν <sub>7</sub> (b <sub>2</sub> ) = 762 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>2u</sub> ) = 109 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>1</sub> ) = 128 cm <sup>-1</sup>
ν <sub>8</sub> (b <sub>2</sub> ) = 233 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>3u</sub> ) = 167 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>2</sub> ) = 552 cm <sup>-1</sup>
ν <sub>9</sub> (b <sub>2</sub> ) = 119 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>3u</sub> ) = 70 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>2</sub> ) = 89 cm <sup>-1</sup>
MP2(fc)/6-311+G*	MP2(fc)/6-311+G*	MP2(fc)/6-311+G*
<i>E</i> <sub>MP2</sub> = -4462.517460 au	<i>E</i> <sub>MP2</sub> = -4462.520668 au	<i>E</i> <sub>MP2</sub> = -4462.475008 au
Δ <i>E</i> <sub>MP2</sub> = 2.0 kcal/mol	Δ <i>E</i> <sub>MP2</sub> = 0.0 kcal/mol	Δ <i>E</i> <sub>MP2</sub> = 28.7 kcal/mol
ν <sub>1</sub> (a <sub>1</sub> ) = 869 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>g</sub> ) = 505 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>1</sub> ) = 759 cm <sup>-1</sup>
ν <sub>2</sub> (a <sub>1</sub> ) = 374 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>g</sub> ) = 169 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>1</sub> ) = 319 cm <sup>-1</sup>
ν <sub>3</sub> (a <sub>1</sub> ) = 264 cm <sup>-1</sup>	ν <sub>3</sub> (b <sub>3g</sub> ) = 198 cm <sup>-1</sup>	ν <sub>3</sub> (a <sub>1</sub> ) = 225 cm <sup>-1</sup>
ν <sub>4</sub> (a <sub>1</sub> ) = 95 cm <sup>-1</sup>	ν <sub>4</sub> (b <sub>1u</sub> ) = 538 cm <sup>-1</sup>	ν <sub>4</sub> (a <sub>1</sub> ) = 130 cm <sup>-1</sup>
ν <sub>5</sub> (a <sub>2</sub> ) = 71 cm <sup>-1</sup>	ν <sub>5</sub> (b <sub>1u</sub> ) = 153 cm <sup>-1</sup>	ν <sub>5</sub> (a <sub>2</sub> ) = 93i cm <sup>-1</sup>
ν <sub>6</sub> (b <sub>1</sub> ) = 80 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>2u</sub> ) = 1192 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>1</sub> ) = 617 cm <sup>-1</sup>
ν <sub>7</sub> (b <sub>2</sub> ) = 832 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>2u</sub> ) = 137 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>1</sub> ) = 156 cm <sup>-1</sup>
ν <sub>8</sub> (b <sub>2</sub> ) = 255 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>3u</sub> ) = 84 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>2</sub> ) = 429 cm <sup>-1</sup>
ν <sub>9</sub> (b <sub>2</sub> ) = 136 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>3u</sub> ) = 37 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>2</sub> ) = 45 cm <sup>-1</sup>
<i>Q</i> <sub>NPA</sub> (C) = -2.135 e	<i>Q</i> <sub>NPA</sub> (C) = -2.195 e	<i>Q</i> <sub>NPA</sub> (C) = -2.333 e
<i>Q</i> <sub>NPA</sub> (Si) = +0.500 e	<i>Q</i> <sub>NPA</sub> (Si) = +0.596 e	<i>Q</i> <sub>NPA</sub> (Si) = +0.422 e
<i>Q</i> <sub>NPA</sub> (Ga) = +0.568 e	<i>Q</i> <sub>NPA</sub> (Ga) = +0.502 e	<i>Q</i> <sub>NPA</sub> (Ga) = +0.745 e

planar *cis*-CSi<sub>2</sub>Ga<sub>2</sub>, **1** *cis*-CGe<sub>2</sub>Al<sub>2</sub>, **1** and *trans*-CSi<sub>2</sub>Ga<sub>2</sub>, **2** *trans*-CGe<sub>2</sub>Al<sub>2</sub>, **2** structures, as well as for the CSi<sub>2</sub>Ga<sub>2</sub>, **3** and CGe<sub>2</sub>Al<sub>2</sub>, **3** tetrahedral type structures (see Figure 1).

**B. CSi<sub>2</sub>Ga<sub>2</sub> and CGe<sub>2</sub>Al<sub>2</sub>.** At both the B3LYP/6-311+G\* and MP2(fc)/6-311+G\* levels of theory, *all* of the planar *cis*-CSi<sub>2</sub>Ga<sub>2</sub>, **1** *cis*-CGe<sub>2</sub>Al<sub>2</sub>, **1** and *trans*-CSi<sub>2</sub>Ga<sub>2</sub>, **2**, *trans*-CGe<sub>2</sub>Al<sub>2</sub>, **2** structures were found to be minima (see Tables 2 and 3). *trans*-CSi<sub>2</sub>Ga<sub>2</sub>, **2** is more stable by 2 kcal/mol than *cis*-CSi<sub>2</sub>Ga<sub>2</sub>, **1**, while

*cis*-CGe<sub>2</sub>Al<sub>2</sub>, **1** is more stable by 3 kcal/mol than *trans*-CGe<sub>2</sub>Al<sub>2</sub>, **2**. The tetrahedral-type CSi<sub>2</sub>Ga<sub>2</sub>, **3** and CGe<sub>2</sub>Al<sub>2</sub>, **3** structures were found to be first-order saddle points and to lie 27 and 25 kcal/mol, respectively, above the most stable planar structures. Moreover, just as for CSi<sub>2</sub>Al<sub>2</sub>, these near-tetrahedral structures, when allowed to relax along their imaginary frequency mode, evolve into the corresponding *cis* structures **1**, not into the *trans* structures **2**. The extension of the cavity size

**Table 3.** Calculated Molecular Properties of the Lowest Energy CGe<sub>2</sub>Al<sub>2</sub> Structures

<i>cis</i> -CGe <sub>2</sub> Al <sub>2</sub> , <b>1</b> (C <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )	<i>trans</i> -CGe <sub>2</sub> Al <sub>2</sub> , <b>2</b> (D <sub>2h</sub> , <sup>1</sup> A <sub>g</sub> )	CGe <sub>2</sub> Al <sub>2</sub> , <b>3</b> (C <sub>2v</sub> , <sup>1</sup> A <sub>1</sub> )
1a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 3b <sub>2</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>	1a <sub>g</sub> <sup>2</sup> 1b <sub>1u</sub> <sup>2</sup> 1b <sub>2u</sub> <sup>2</sup> 2a <sub>g</sub> <sup>2</sup> 1b <sub>3u</sub> <sup>2</sup> 2b <sub>1u</sub> <sup>2</sup> 3a <sub>g</sub> <sup>2</sup> 2b <sub>2u</sub> <sup>2</sup> 1b <sub>3g</sub> <sup>2</sup>	1a <sub>1</sub> <sup>2</sup> 2a <sub>1</sub> <sup>2</sup> 1b <sub>2</sub> <sup>2</sup> 1b <sub>1</sub> <sup>2</sup> 3a <sub>1</sub> <sup>2</sup> 2b <sub>2</sub> <sup>2</sup> 4a <sub>1</sub> <sup>2</sup> 2b <sub>1</sub> <sup>2</sup> 5a <sub>1</sub> <sup>2</sup>
B3LYP/6-311+G*	B3LYP/6-311+G*	B3LYP/6-311+G*
E <sub>B3LYP</sub> = -4677.019781 au	E <sub>B3LYP</sub> = -4677.012607 au	E <sub>B3LYP</sub> = -4676.990298 au
ΔE <sub>B3LYP</sub> = 0.0 kcal/mol	ΔE <sub>B3LYP</sub> = 4.5 kcal/mol	ΔE <sub>B3LYP</sub> = 18.5 kcal/mol
ν <sub>1</sub> (a <sub>1</sub> ) = 769 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>g</sub> ) = 303 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>1</sub> ) = 715 cm <sup>-1</sup>
ν <sub>2</sub> (a <sub>1</sub> ) = 316 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>g</sub> ) = 300 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>1</sub> ) = 316 cm <sup>-1</sup>
ν <sub>3</sub> (a <sub>1</sub> ) = 198 cm <sup>-1</sup>	ν <sub>3</sub> (b <sub>3g</sub> ) = 192 cm <sup>-1</sup>	ν <sub>3</sub> (a <sub>1</sub> ) = 228 cm <sup>-1</sup>
ν <sub>4</sub> (a <sub>1</sub> ) = 150 cm <sup>-1</sup>	ν <sub>4</sub> (b <sub>1u</sub> ) = 926 cm <sup>-1</sup>	ν <sub>4</sub> (a <sub>1</sub> ) = 121 cm <sup>-1</sup>
ν <sub>5</sub> (a <sub>2</sub> ) = 69 cm <sup>-1</sup>	ν <sub>5</sub> (b <sub>1u</sub> ) = 158 cm <sup>-1</sup>	ν <sub>5</sub> (a <sub>2</sub> ) = 821 cm <sup>-1</sup>
ν <sub>6</sub> (b <sub>1</sub> ) = 180 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>2u</sub> ) = 569 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>1</sub> ) = 416 cm <sup>-1</sup>
ν <sub>7</sub> (b <sub>2</sub> ) = 724 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>2u</sub> ) = 75 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>1</sub> ) = 76 cm <sup>-1</sup>
ν <sub>8</sub> (b <sub>2</sub> ) = 238 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>3u</sub> ) = 167 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>2</sub> ) = 608 cm <sup>-1</sup>
ν <sub>9</sub> (b <sub>2</sub> ) = 131 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>3u</sub> ) = 78 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>2</sub> ) = 161 cm <sup>-1</sup>
MP2(fc)/6-311+G*	MP2(fc)/6-311+G*	MP2(fc)/6-311+G*
E <sub>MP2</sub> = -4672.743113 au	E <sub>MP2</sub> = -4672.738547 au	E <sub>MP2</sub> = -4672.701957 au
ΔE <sub>MP2</sub> = 0.0 kcal/mol	ΔE <sub>MP2</sub> = 2.9 kcal/mol	ΔE <sub>MP2</sub> = 25.8 kcal/mol
ν <sub>1</sub> (a <sub>1</sub> ) = 796 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>g</sub> ) = 306 cm <sup>-1</sup>	ν <sub>1</sub> (a <sub>1</sub> ) = 759 cm <sup>-1</sup>
ν <sub>2</sub> (a <sub>1</sub> ) = 321 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>g</sub> ) = 249 cm <sup>-1</sup>	ν <sub>2</sub> (a <sub>1</sub> ) = 319 cm <sup>-1</sup>
ν <sub>3</sub> (a <sub>1</sub> ) = 201 cm <sup>-1</sup>	ν <sub>3</sub> (b <sub>3g</sub> ) = 201 cm <sup>-1</sup>	ν <sub>3</sub> (a <sub>1</sub> ) = 225 cm <sup>-1</sup>
ν <sub>4</sub> (a <sub>1</sub> ) = 144 cm <sup>-1</sup>	ν <sub>4</sub> (b <sub>1u</sub> ) = 1026 cm <sup>-1</sup>	ν <sub>4</sub> (a <sub>1</sub> ) = 130 cm <sup>-1</sup>
ν <sub>5</sub> (a <sub>2</sub> ) = 73 cm <sup>-1</sup>	ν <sub>5</sub> (b <sub>1u</sub> ) = 182 cm <sup>-1</sup>	ν <sub>5</sub> (a <sub>2</sub> ) = 931 cm <sup>-1</sup>
ν <sub>6</sub> (b <sub>1</sub> ) = 90 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>2u</sub> ) = 626 cm <sup>-1</sup>	ν <sub>6</sub> (b <sub>1</sub> ) = 617 cm <sup>-1</sup>
ν <sub>7</sub> (b <sub>2</sub> ) = 783 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>2u</sub> ) = 119 cm <sup>-1</sup>	ν <sub>7</sub> (b <sub>1</sub> ) = 156 cm <sup>-1</sup>
ν <sub>8</sub> (b <sub>2</sub> ) = 255 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>3u</sub> ) = 83 cm <sup>-1</sup>	ν <sub>8</sub> (b <sub>2</sub> ) = 429 cm <sup>-1</sup>
ν <sub>9</sub> (b <sub>2</sub> ) = 145 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>3u</sub> ) = 75 cm <sup>-1</sup>	ν <sub>9</sub> (b <sub>2</sub> ) = 45 cm <sup>-1</sup>
Q <sub>NPA</sub> (C) = -2.228 e	Q <sub>NPA</sub> (C) = -2.264 e	Q <sub>NPA</sub> (C) = -2.418 e
Q <sub>NPA</sub> (Ge) = +0.510 e	Q <sub>NPA</sub> (Ge) = +0.591 e	Q <sub>NPA</sub> (Ge) = +0.423 e
Q <sub>NPA</sub> (Al) = +0.604 e	Q <sub>NPA</sub> (Al) = +0.541 e	Q <sub>NPA</sub> (Al) = +0.787 e

in CSi<sub>2</sub>Ga<sub>2</sub> and CGe<sub>2</sub>Al<sub>2</sub> thus seems to allow accommodation of the carbon atom within the plane of the cavity and thus to preserve the planar structure for both molecules.

#### 4. Overview

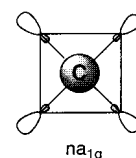
From our calculations, we conclude that pentaatomic molecules composed of a central carbon atom and two Al or Ga ligand atoms and two Si or Ge ligand atoms should have stable planar structures. We should mention that an analogous planar structure was found to be the most stable for another 18-valence electron molecule Al<sub>4</sub>O.<sup>9</sup>

To better understand when the planar or tetrahedral structure should be favored, let us examine the occupancy patterns of the valence MOs for each of these two geometries. The canonical order of the occupied valence MOs in the 32-valence electron *tetrahedral* CF<sub>4</sub> molecule is 1a<sub>1</sub><sup>2</sup>1t<sub>2</sub><sup>6</sup>2a<sub>1</sub><sup>2</sup>2t<sub>2</sub><sup>6</sup>1e<sup>4</sup>3t<sub>2</sub><sup>6</sup>1t<sub>1</sub>,<sup>6</sup> with the first four (1a<sub>1</sub><sup>2</sup> and 1t<sub>2</sub><sup>6</sup>) orbitals being the C–F σ bonds and the remaining twelve orbitals being F-atom localized lone-pair orbitals lying perpendicular and parallel to the C–F bond axes. The above orbital occupancy describes a situation with four σ bonds and no net bonding or antibonding interactions among the ligands.

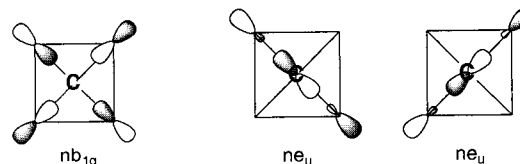
If we assume that this order of MOs remains valid for other tetrahedral molecules and (except for symmetry-imposed degeneracies) even for nearly tetrahedral molecules, then, for species with 18 valence electrons such as those treated in this paper, the tetrahedral structure would have a 1a<sub>1</sub><sup>2</sup>1t<sub>2</sub><sup>6</sup>2a<sub>1</sub><sup>2</sup>2t<sub>2</sub><sup>6</sup>1e<sup>2</sup> electronic configuration. Even though the first four electron pairs (1a<sub>1</sub><sup>2</sup>1t<sub>2</sub><sup>6</sup>) likely describe four σ bonds, this configuration would be expected to be first-order Jahn–Teller unstable (due to unbalanced bonding and antibonding interactions among its ligands) in the singlet state, and subsequent distortion should lead to a planar D<sub>4h</sub> structure, in line with our findings.

When only 16 valence electrons are present, as in CAI<sub>4</sub>, the tetrahedral geometry with a 1a<sub>1</sub><sup>2</sup>1t<sub>2</sub><sup>6</sup>2a<sub>1</sub><sup>2</sup>2t<sub>2</sub><sup>6</sup>1e<sup>0</sup> valence electronic configuration is not Jahn–Teller unstable, and, as expected, is found to be a stable minimum with four σ-bonds and four lone pairs.<sup>7</sup> Likewise for CH<sub>4</sub> with eight valence electrons, the 1a<sub>1</sub><sup>2</sup>1t<sub>2</sub><sup>6</sup> configuration (for this molecule, the lone-pair orbitals are absent because hydrogen has only 1s orbitals) is consistent with a stable structure. Therefore, the presence of 18 valence electrons is crucial for favoring tetracoordinated planar carbon over corresponding tetrahedral structures because the aufbau orbital occupancy causes unbalanced bonding and antibonding ligand–ligand interactions in the tetrahedral case

Let us now examine the orbital occupancies that arise for carbon in a *planar* tetracoordinate situation bonded to ligands that have valence s and p orbitals. The C 2s, 2p<sub>x</sub>, and 2p<sub>y</sub> orbitals lie in the plane of the molecule. The four ligand s and four ligand p<sub>σ</sub> orbitals also lie in this plane. These orbitals combine to form *four nonbonding orbitals*, localized strongly on the ligands, including na<sub>1g</sub>,



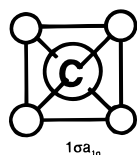
and corresponding nb<sub>1g</sub> and ne<sub>u</sub> molecular orbitals (the prefix n is used to denote nonbonding).



(9) Boldyrev, A. I.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1991**, *113*, 9045.



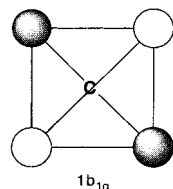
The same ligand orbitals combine with the 2s and 2p<sub>x,y</sub> orbitals of C to form a delocalized five-center bonding orbital 1σ<sub>a<sub>1g</sub></sub> (and its antibonding partner 1σ<sub>a<sub>1g</sub></sub> in which the sign of the C 2s orbital is opposite)



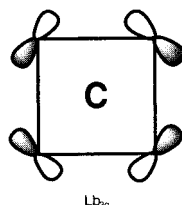
a degenerate pair of three-center bonding orbitals σ<sub>e<sub>u</sub></sub> (and their antibonding partners σ\*<sub>e<sub>u</sub></sub> in which the sign of the C 2p orbital is opposite)



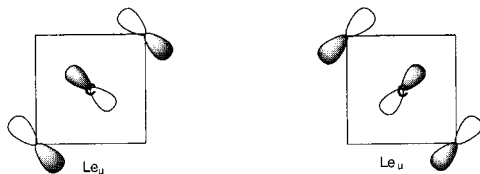
and a nonbonding ligand-centered orbital nb<sub>1</sub>.



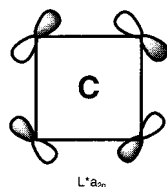
The ligand p orbitals lying perpendicular to each C–ligand axis combine to form an Lb<sub>2g</sub> orbital (the prefix L is used to denote combinations of such ligand orbitals) that is bonding among the four ligands



as well as corresponding antibonding L\*<sub>e<sub>u</sub></sub>

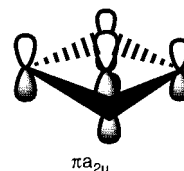


and an antibonding L\*<sub>a<sub>2g</sub></sub> orbital.



Finally, the C 2p<sub>z</sub> and ligand out-of-plane 2p orbitals combine

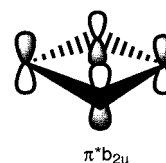
to form a five-center bonding π<sub>a<sub>2u</sub></sub> orbital



plus the antibonding counterpart π\*<sub>a<sub>2u</sub></sub> (in which the sign of the C 2p<sub>z</sub> orbital is opposite) and a degenerate set of nonbonding orbitals π<sub>e<sub>g</sub></sub>



and a ligand antibonding π\*<sub>b<sub>2u</sub></sub> orbital.



In the ground state of a molecule such as CF<sub>4</sub> with 32 valence electrons, the four nonbonding n orbitals are doubly occupied as are the three σ bonding orbitals, the 1b<sub>1g</sub> σ nonbonding orbital, and the one π bonding, two π nonbonding, and one ligand–π\* antibonding orbitals. Moreover, the two L bonding, two L\* antibonding, and one L\* antibonding orbitals are doubly occupied. The net result of such an orbital occupancy is (1) one C–ligand π bond, (2) cancellation of all ligand–ligand bonding, and (3) three C–ligand σ bonds. Compared to the tetrahedral case in which there exist four C–ligand σ bonds and no net ligand–ligand bonding, the planar structure is unfavored for this 32 valence electron case.

Likewise, for planar CH<sub>4</sub> (in which the n, L, and ligand π orbitals do not arise because H has only 1s valence orbitals), the three σ bonding orbitals and the 1b<sub>1g</sub> nonbonding orbital are doubly occupied, so only three C–H σ bonds exist, which is less favorable than the four σ bonds in tetrahedral CH<sub>4</sub>.

For a species such as AlCl<sub>4</sub> with 16 valence electrons, three of the four nonbonding n orbitals are doubly occupied as are the three σ bonding orbitals, the 1b<sub>1g</sub> nonbonding orbital, and the C–ligand π bonding orbital. Hence, one finds three net σ bonds, one π bond, and four nonbonding pairs. In tetrahedral AlCl<sub>4</sub>, as discussed earlier, one finds four σ bonds and four lone pairs. So, both planar and tetrahedral AlCl<sub>4</sub> would be expected to be locally stable species with the tetrahedral structure favored because it has four σ bonds rather than three (plus a π bond).

Finally, for species with 18 valence electrons such as we are considering in this paper, the planar structure has three of the four nonbonding n orbitals doubly occupied as are the three σ bonding orbitals, the 1b<sub>1g</sub> nonbonding orbital, the C–ligand π bonding orbital, and the ligand–ligand Lb<sub>2g</sub> bonding orbital. Thus, there are three C–ligand σ bonds, one C–ligand π bond, and one ligand–ligand bond. Recall that in the tetrahedral geometry, the 18-electron case was first-order Jahn–Teller unstable due to unbalanced ligand–ligand interactions.

In summary, planar geometries can be favored over tetrahedral when (1) Jahn–Teller instability (even if within the ligand–ligand interactions only) makes the latter locally unstable and (2) the number of valence electrons allows for maximum C–ligand and ligand–ligand bonding. The optimal case for planar structures occurs with 18 valence electrons where three  $\sigma$  and one  $\pi$  bond occur as well as one ligand–ligand bond. In molecules with more than 18 valence electrons, the  $\text{Le}_u$  orbitals, which are C–ligand antibonding and ligand–ligand nonbonding, and the  $\text{L}^*\text{a}_{2g}$  orbital, which is ligand–ligand antibonding, become occupied, each of which is destabilizing to the square-planar geometry.

In closing, it is our hope that the planar structures studied here can be verified experimentally. The  $\text{CSi}_2$  molecule has

been identified experimentally;<sup>10–12</sup> perhaps it could be used as a precursor in gas-phase reactions with aluminum or gallium atoms to prepare the  $\text{CSi}_2\text{Al}_2$  or  $\text{CSi}_2\text{Ga}_2$  molecules in the gas phase or in matrix isolation.

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