J. Am. Chem. Soc. **1998,** *120,* 7967−7972

Tetracoordinated Planar Carbon in Pentaatomic Molecules

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Received April 13, 1998. Revised Manuscript Received June 2, 1998

Abstract: Three pentaatomic molecules CSi_2Al_2, CSi_2Ga_2, and CGe_2Al_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*-CSi_2Al_2 and *trans*-CSi_2Al_2 planar structures have one imaginary frequency and that distortion along this mode leads to slightly pyramidal local minima. In contrast, *cis*- and *trans*-CSi_2Ga_2 and *cis*- and *trans*-CGe_2Al_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 σ bonds, one C−ligand π 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[1] and LeBel[2] 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 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.[3] as a result of which today's literature on tetracoordinated planar carbon is very extensive.[4−6]

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[7] computationally predicted that *cis*-CSi_2Al_2 and *trans*-CSi_2Al_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 CSi_2Al_2 after which we extended the search for pentaatomic molecules containing tetracoordinated planar carbon to CSi_2Ga_2 and CGe_2Al_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 CSi_2Al_2 and at the MP2(fc) level (frozen core; with only valence electrons included in the correlation calculations) for CSi_2Ga_2 and CGe_2Al_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.[8] 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. CSi_2Al_2. The optimized geometries of a wide variety of *singlet* structures of CSi_2Al_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

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S0002-7863(98)01236-0 CCC: $15.00

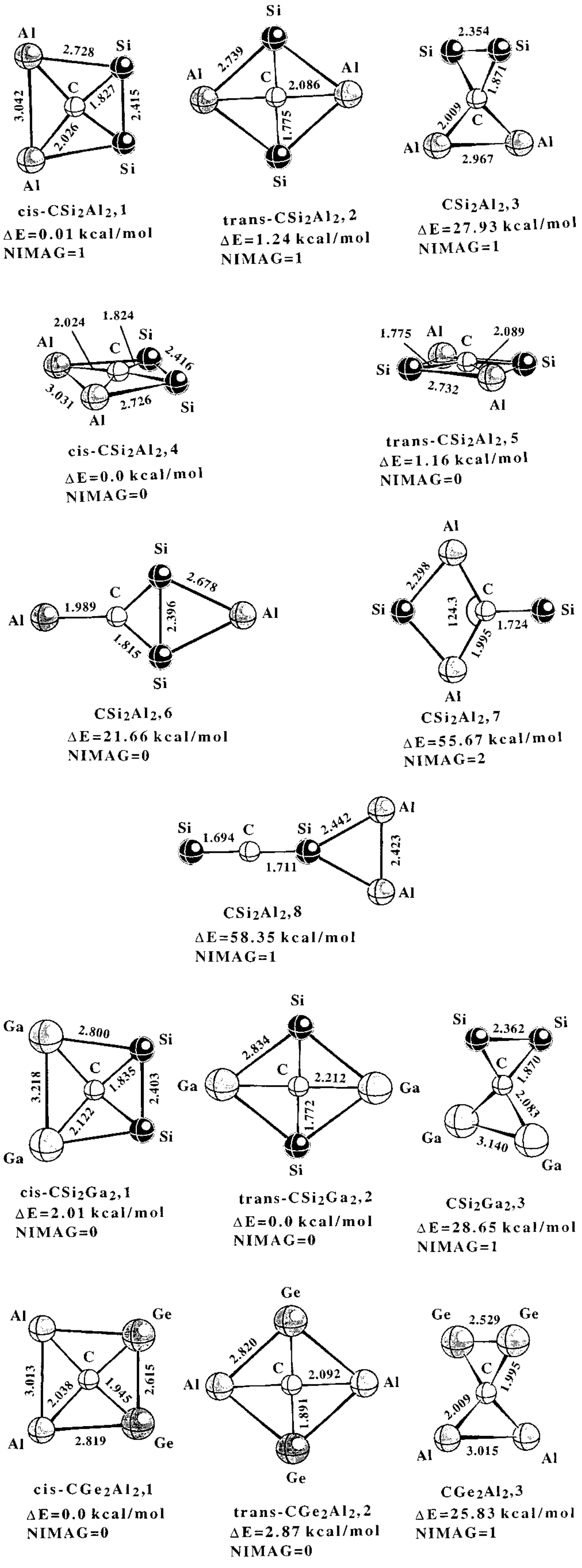


Figure 1. Optimized geometries (bond lengths are in Å and bond angles are in ^{0}), relative energies (ΔE, in kcal/mol), and the number of imaginary vibrational frequencies (NIMAG) at the MP2(full)/6-311+G* level for CSi_2Al_2 and the MP2(fc)/6-311+G* level for CSi_2Ga_2 and CGe_2Al_2.

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*-CSi_2Al_2,**1** and *trans*-CSi_2Al_2,**2** structures supported the earlier conclusion,[8] 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*-CSi_2Al_2,**1** and $\nu_9(b_{3u})$ for *trans*-CSi_2Al_2,**2**) having imaginary frequencies lead, when followed "down hill", to nearly planar but pyramidal *cis*-CSi_2Al_2,**4** and *trans*-CSi_2Al_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*-CSi_2Al_2,**1**) and 0.076 kcal/mol (*trans*-CSi_2Al_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 CSi_2Al_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 CSi_2Al_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 AlCAl 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 CSi_2Al_2, 0.250 au for CGe_2Al_2, and 0.242 au for CSi_2Ga_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 CSi_2Al_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 CSi_2Al_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*-Si_2Al_2 and *trans*-Si_2Al_2 fragments. Because we cannot predict with certainty that planar structures of CSi_2Al_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 CSi_2Ga_2 and CGe_2Al_2, where we expect the cavities for the central carbon atom to be larger. On the basis of our experience with the CSi_2Al_2 molecule, we optimized the geometries only for the

Table 1. Calculated Molecular Properties of the Lowest Energy CSi_2Al_2 Structures

cis-CSi_2Al_2, **1** (C_{2v}, $^1A_1$)	*trans*-CSi_2Al_2, **2** (D_{2h}, ^1A_g)	CSi_2Al_2, **3** (C_{2v}, $^1A_1$)	*cis*-CSi_2Al_2, **4** (C_s, $^1A'$)	*trans*-CSi_2Al_2, **5** (C_{2v}, $^1A_1$)
$1a_1^21b_2^22a_1^23a_1^22b_2^2$ $1b_1^23b_2^24a_1^25a_1^2$	$1a_g^21b_{2u}^21b_{1u}^22a_g^23a_g^2$ $1b_{3u}^22b_{2u}^22b_{1u}^21b_3g^2$	$1a_1^22a_1^21b_2^21b_1^23a_1^2$ $2b_1^24a_1^22b_2^25a_1^2$	$1a'^21a''^22a'^23a'^24a'^2$ $2a''^25a'^23a''^26a'^2$	$1a_1^21b_2^21b_1^22a_1^23a_1^22b_2^2$ $4a_1^21a_2^22b_1^2$
B3LYP/6-311+G*	B3LYP/6-311+G*	B3LYP/6-311+G*		
$E_{B3LYP} = -1101.986210$ au	$E_{B3LYP} = -1101.982486$ au	$E_{B3LYP} = -1101.952511$ au		
$\Delta E_{B3LYP} = 0.0$ kcal/mol	$\Delta E_{B3LYP} = 2.3$ kcal/mol	$\Delta E_{B3LYP} = 21.2$ kcal/mol		
$\nu_1(a_1) = 877\ cm^{-1}$	$\nu_1(a_g) = 512\ cm^{-1}$	$\nu_1(a_1) = 800\ cm^{-1}$		
$\nu_2(a_1) = 418\ cm^{-1}$	$\nu_2(a_g) = 249\ cm^{-1}$	$\nu_2(a_1) = 443\ cm^{-1}$		
$\nu_3(a_1) = 307\ cm^{-1}$	$\nu_3(b_{3g}) = 232\ cm^{-1}$	$\nu_3(a_1) = 323\ cm^{-1}$		
$\nu_4(a_1) = 155\ cm^{-1}$	$\nu_4(b_{1u}) = 571\ cm^{-1}$	$\nu_4(a_1) = 132\ cm^{-1}$		
$\nu_5(a_2) = 91\ cm^{-1}$	$\nu_5(b_{1u}) = 120\ cm^{-1}$	$\nu_5(a_2) = 112i\ cm^{-1}$		
$\nu_6(b_1) = 174\ cm^{-1}$	$\nu_6(b_{2u}) = 1097\ cm^{-1}$	$\nu_6(b_1) = 537\ cm^{-1}$		
$\nu_7(b_2) = 809\ cm^{-1}$	$\nu_7(b_{2u}) = 165\ cm^{-1}$	$\nu_7(b_1) = 93\ cm^{-1}$		
$\nu_8(b_2) = 306\ cm^{-1}$	$\nu_8(b_{3u}) = 164\ cm^{-1}$	$\nu_8(b_2) = 585\ cm^{-1}$		
$\nu_9(b_2) = 157\ cm^{-1}$	$\nu_9(b_{3u}) = 99\ cm^{-1}$	$\nu_9(b_2) = 175\ cm^{-1}$		
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*
$E_{MP2} = -1100.447586$ au	$E_{MP2} = -1100.445639$ au	$E_{MP2} = -1100.403099$ au	$E_{MP2} = -1100.447608$ au	$E_{MP2} = -1100.445760$ au
$\Delta E_{MP2} = 0.01$ kcal/mol	$\Delta E_{MP2} = 1.24$ kcal/mol	$\Delta E_{MP2} = 27.93$ kcal/mol	$\Delta E_{MP2} = 0.00$ kcal/mol	$\Delta E_{MP2} = 1.16$ kcal/mol
$\nu_1(a_1) = 920\ cm^{-1}$	$\nu_1(a_g) = 505\ cm^{-1}$	$\nu_1(a_1) = 853\ cm^{-1}$	$\nu_1(a') = 918\ cm^{-1}$	$\nu_1(a_1) = 513\ cm^{-1}$
$\nu_2(a_1) = 422\ cm^{-1}$	$\nu_2(a_g) = 287\ cm^{-1}$	$\nu_2(a_1) = 453\ cm^{-1}$	$\nu_2(a') = 423\ cm^{-1}$	$\nu_2(a_1) = 287\ cm^{-1}$
$\nu_3(a_1) = 311\ cm^{-1}$	$\nu_3(b_{3g}) = 249\ cm^{-1}$	$\nu_3(a_1) = 324\ cm^{-1}$	$\nu_3(a') = 311\ cm^{-1}$	$\nu_3(a_1) = 140\ cm^{-1}$
$\nu_4(a_1) = 160\ cm^{-1}$	$\nu_4(b_{1u}) = 557\ cm^{-1}$	$\nu_4(a_1) = 148\ cm^{-1}$	$\nu_4(a') = 164\ cm^{-1}$	$\nu_4(a_1) = 107\ cm^{-1}$
$\nu_5(a_2) = 88\ cm^{-1}$	$\nu_5(b_{1u}) = 177\ cm^{-1}$	$\nu_5(a_2) = 130i\ cm^{-1}$	$\nu_5(a') = 105\ cm^{-1}$	$\nu_5(a_2) = 251\ cm^{-1}$
$\nu_6(b_1) = 77i\ cm^{-1}$	$\nu_6(b_{2u}) = 1189\ cm^{-1}$	$\nu_6(b_1) = 577\ cm^{-1}$	$\nu_6(a'') = 886\ cm^{-1}$	$\nu_6(b_1) = 651\ cm^{-1}$
$\nu_7(b_2) = 888\ cm^{-1}$	$\nu_7(b_{2u}) = 201\ cm^{-1}$	$\nu_7(b_1) = 51\ cm^{-1}$	$\nu_7(a'') = 332\ cm^{-1}$	$\nu_7(b_1) = 179\ cm^{-1}$
$\nu_8(b_2) = 333\ cm^{-1}$	$\nu_8(b_{3u}) = 97\ cm^{-1}$	$\nu_8(b_2) = 614\ cm^{-1}$	$\nu_8(a'') = 184\ cm^{-1}$	$\nu_8(b_2) = 1186\ cm^{-1}$
$\nu_9(b_2) = 184\ cm^{-1}$	$\nu_9(b_{3u}) = 115i\ cm^{-1}$	$\nu_9(b_2) = 173\ cm^{-1}$	$\nu_9(a'') = 98\ cm^{-1}$	$\nu_9(b_2) = 202\ cm^{-1}$
$Q_{NPA}(C) = -2.266$ e	$Q_{NPA}(C) = -2.323$ e	$Q_{NPA}(C) = -2.443$ e	$Q_{NPA}(C) = -2.260$ e	$Q_{NPA}(C) = -2.305$ e
$Q_{NPA}(Si) = +0.524$ e	$Q_{NPA}(Si) = +0.609$ e	$Q_{NPA}(Si) = +0.441$ e	$Q_{NPA}(Si) = +0.524$ e	$Q_{NPA}(Si) = +0.602$ e
$Q_{NPA}(Ga) = +0.609$ e	$Q_{NPA}(Ga) = +0.553$ e	$Q_{NPA}(Ga) = +0.780$ e	$Q_{NPA}(Ga) = +0.606$ e	$Q_{NPA}(Ga) = +0.550$ e

Table 2. Calculated Molecular Properties of the Lowest Energy CSi_2Ga_2 Structures

cis-CSi_2Ga_2, **1** (C_{2v}, $^1A_1$)	*trans*-CSi_2Ga_2, **2** (D_{2h}, ^1A_g)	CSi_2Ga_2, **3** (C_{2v}, $^1A_1$)
$1a_1^21b_2^22a_1^23a_1^22b_2^2$ $1b_1^23b_2^24a_1^25a_1^2$	$1a_g^21b_{2u}^21b_{1u}^22a_g^2$ $3a_g^21b_{3u}^22b_{2u}^22b_{14}^21b_{3g}^2$	$1a_1^22a_1^21b_2^21b_1^23a_1^2$ $2b_1^24a_1^22b_2^25a_1^2$
B3LYP/6-311+G*	B3LYP/6-311+G*	B3LYP/6-311+G*
$E_{B3LYP} = -4466.839885$ au	$E_{B3LYP} = -4466.841958$ au	$E_{B3LYP} = -4466.809803$ au
$\Delta E_{B3LYP} = 1.3$ kcal/mol	$\Delta E_{B3LYP} = 0.0$ kcal/mol	$\Delta E_{B3LYP} = 28.7$ kcal/mol
$\nu_1(a_1) = 842\ cm^{-1}$	$\nu_1(a_g) = 518\ cm^{-1}$	$\nu_1(a_1) = 774\ cm^{-1}$
$\nu_2(a_1) = 386\ cm^{-1}$	$\nu_2(a_g) = 153\ cm^{-1}$	$\nu_2(a_1) = 419\ cm^{-1}$
$\nu_3(a_1) = 250\ cm^{-1}$	$\nu_3(b_{3g}) = 181\ cm^{-1}$	$\nu_3(a_1) = 238\ cm^{-1}$
$\nu_4(a_1) = 96\ cm^{-1}$	$\nu_4(b_{1u}) = 477\ cm^{-1}$	$\nu_4(a_1) = 90\ cm^{-1}$
$\nu_5(a_2) = 68\ cm^{-1}$	$\nu_5(b_{1u}) = 133\ cm^{-1}$	$\nu_5(a_2) = 101i\ cm^{-1}$
$\nu_6(b_1) = 174\ cm^{-1}$	$\nu_6(b_{2u}) = 111\ cm^{-1}$	$\nu_6(b_1) = 506\ cm^{-1}$
$\nu_7(b_2) = 762\ cm^{-1}$	$\nu_7(b_{2u}) = 109\ cm^{-1}$	$\nu_7(b_1) = 128\ cm^{-1}$
$\nu_8(b_2) = 233\ cm^{-1}$	$\nu_8(b_{3u}) = 167\ cm^{-1}$	$\nu_8(b_2) = 552\ cm^{-1}$
$\nu_9(b_2) = 119\ cm^{-1}$	$\nu_9(b_{3u}) = 70\ cm^{-1}$	$\nu_9(b_2) = 89\ cm^{-1}$
MP2(fc)/6-311+G*	MP2(fc)/6-311+G*	MP2(fc)/6-311+G*
$E_{MP2} = -4462.517460$ au	$E_{MP2} = -4462.520668$ au	$E_{MP2} = -4462.475008$ au
$\Delta E_{MP2} = 2.0$ kcal/mol	$\Delta E_{MP2} = 0.0$ kcal/mol	$\Delta E_{MP2} = 28.7$ kcal/mol
$\nu_1(a_1) = 869\ cm^{-1}$	$\nu_1(a_g) = 505\ cm^{-1}$	$\nu_1(a_1) = 759\ cm^{-1}$
$\nu_2(a_1) = 374\ cm^{-1}$	$\nu_2(a_g) = 169\ cm^{-1}$	$\nu_2(a_1) = 319\ cm^{-1}$
$\nu_3(a_1) = 264\ cm^{-1}$	$\nu_3(b_{3g}) = 198\ cm^{-1}$	$\nu_3(a_1) = 225\ cm^{-1}$
$\nu_4(a_1) = 95\ cm^{-1}$	$\nu_4(b_{1u}) = 538\ cm^{-1}$	$\nu_4(a_1) = 130\ cm^{-1}$
$\nu_5(a_2) = 71\ cm^{-1}$	$\nu_5(b_{1u}) = 153\ cm^{-1}$	$\nu_5(a_2) = 93i\ cm^{-1}$
$\nu_6(b_1) = 80\ cm^{-1}$	$\nu_6(b_{2u}) = 1192\ cm^{-1}$	$\nu_6(b_1) = 617\ cm^{-1}$
$\nu_7(b_2) = 832\ cm^{-1}$	$\nu_7(b_{2u}) = 137\ cm^{-1}$	$\nu_7(b_1) = 156\ cm^{-1}$
$\nu_8(b_2) = 255\ cm^{-1}$	$\nu_8(b_{3u}) = 84\ cm^{-1}$	$\nu_8(b_2) = 429\ cm^{-1}$
$\nu_9(b_2) = 136\ cm^{-1}$	$\nu_9(b_{3u}) = 37\ cm^{-1}$	$\nu_9(b_2) = 45\ cm^{-1}$
$Q_{NPA}(C) = -2.135$ e	$Q_{NPA}(C) = -2.195$ e	$Q_{NPA}(C) = -2.333$ e
$Q_{NPA}(Si) = +0.500$ e	$Q_{NPA}(Si) = +0.596$ e	$Q_{NPA}(Si) = +0.422$ e
$Q_{NPA}(Ga) = +0.568$ e	$Q_{NPA}(Ga) = +0.502$ e	$Q_{NPA}(Ga) = +0.745$ e

planar *cis*-CSi_2Ga_2,**1** *cis*-CGe_2Al_2,**1** and *trans*-CSi_2Ga_2,**2** *trans*-CGe_2Al_2,**2** structures, as well as for the CSi_2Ga_2,**3** and CGe_2Al_2,**3** tetrahedral type structures (see Figure 1).

B. CSi_2Ga_2 and CGe_2Al_2. At both the B3LYP/6-311+G* and MP2(fc)/6-311+G* levels of theory, *all* of the planar *cis*-CSi_2Ga_2,**1** *cis*-CGe_2Al_2,**1** and *trans*-CSi_2Ga_2,**2**, *trans*-CGe_2Al_2,**2** structures were found to be minima (see Tables 2 and 3). *trans*-CSi_2Ga_2,**2** is more stable by 2 kcal/mol than *cis*-CSi_2Ga_2,**1**, while *cis*-CGe_2Al_2,**1** is more stable by 3 kcal/mol than *trans*-CGe_2Al_2,**2**. The tetrahedral-type CSi_2Ga_2,**3** and CGe_2Al_2,**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_2Al_2, 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_2Al_2 Structures

cis-CGe_2Al_2, **1** (C_{2v}, $^1A_1$)	*trans*-CGe_2Al_2, **2** (D_{2h}, ^1A_g)	CGe_2Al_2, **3** (C_{2v}, $^1A_1$)
$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 1b_1^2 4a_1^2 3b_2^2 5a_1^2$	$1a_g^2 1b_{1u}^2 1b_{2u}^2 2a_g^2 1b_{3u}^2 2b_{1u}^2 3a_g^2 2b_{2u}^2 1b_{3g}^2$	$1a_1^2 2a_1^2 1b_2^2 1b_1^2 3a_1^2 2b_2^2 4a_1^2 2b_1^2 5a_1^2$
B3LYP/6-311+G*	B3LYP/6-311+G*	B3LYP/6-311+G*
$E_{B3LYP} = -4677.019781$ au	$E_{B3LYP} = -4677.012607$ au	$E_{B3LYP} = -4676.990298$ au
$\Delta E_{B3LYP} = 0.0$ kcal/mol	$\Delta E_{B3LYP} = 4.5$ kcal/mol	$\Delta E_{B3LYP} = 18.5$ kcal/mol
$\nu_1(a_1) = 769$ cm^{-1}	$\nu_1(a_g) = 303$ cm^{-1}	$\nu_1(a_1) = 715$ cm^{-1}
$\nu_2(a_1) = 316$ cm^{-1}	$\nu_2(a_g) = 300$ cm^{-1}	$\nu_2(a_1) = 316$ cm^{-1}
$\nu_3(a_1) = 198$ cm^{-1}	$\nu_3(b_{3g}) = 192$ cm^{-1}	$\nu_3(a_1) = 228$ cm^{-1}
$\nu_4(a_1) = 150$ cm^{-1}	$\nu_4(b_{1u}) = 926$ cm^{-1}	$\nu_4(a_1) = 121$ cm^{-1}
$\nu_5(a_2) = 69$ cm^{-1}	$\nu_5(b_{1u}) = 158$ cm^{-1}	$\nu_5(a_2) = 82i$ cm^{-1}
$\nu_6(b_1) = 180$ cm^{-1}	$\nu_6(b_{2u}) = 569$ cm^{-1}	$\nu_6(b_1) = 416$ cm^{-1}
$\nu_7(b_2) = 724$ cm^{-1}	$\nu_7(b_{2u}) = 75$ cm^{-1}	$\nu_7(b_1) = 76$ cm^{-1}
$\nu_8(b_2) = 238$ cm^{-1}	$\nu_8(b_{3u}) = 167$ cm^{-1}	$\nu_8(b_2) = 608$ cm^{-1}
$\nu_9(b_2) = 131$ cm^{-1}	$\nu_9(b_{3u}) = 78$ cm^{-1}	$\nu_9(b_2) = 161$ cm^{-1}
MP2(fc)/6-311+G*	MP2(fc)/6-311+G*	MP2(fc)/6-311+G*
$E_{MP2} = -4672.743113$ au	$E_{MP2} = -4672.738547$ au	$E_{MP2} = -4672.701957$ au
$\Delta E_{MP2} = 0.0$ kcal/mol	$\Delta E_{MP2} = 2.9$ kcal/mol	$\Delta E_{MP2} = 25.8$ kcal/mol
$\nu_1(a_1) = 796$ cm^{-1}	$\nu_1(a_g) = 306$ cm^{-1}	$\nu_1(a_1) = 759$ cm^{-1}
$\nu_2(a_1) = 321$ cm^{-1}	$\nu_2(a_g) = 249$ cm^{-1}	$\nu_2(a_1) = 319$ cm^{-1}
$\nu_3(a_1) = 201$ cm^{-1}	$\nu_3(b_{3g}) = 201$ cm^{-1}	$\nu_3(a_1) = 225$ cm^{-1}
$\nu_4(a_1) = 144$ cm^{-1}	$\nu_4(b_{1u}) = 1026$ cm^{-1}	$\nu_4(a_1) = 130$ cm^{-1}
$\nu_5(a_2) = 73$ cm^{-1}	$\nu_5(b_{1u}) = 182$ cm^{-1}	$\nu_5(a_2) = 93i$ cm^{-1}
$\nu_6(b_1) = 90$ cm^{-1}	$\nu_6(b_{2u}) = 626$ cm^{-1}	$\nu_6(b_1) = 617$ cm^{-1}
$\nu_7(b_2) = 783$ cm^{-1}	$\nu_7(b_{2u}) = 119$ cm^{-1}	$\nu_7(b_1) = 156$ cm^{-1}
$\nu_8(b_2) = 255$ cm^{-1}	$\nu_8(b_{3u}) = 83$ cm^{-1}	$\nu_8(b_2) = 429$ cm^{-1}
$\nu_9(b_2) = 145$ cm^{-1}	$\nu_9(b_{3u}) = 75$ cm^{-1}	$\nu_9(b_2) = 45$ cm^{-1}
$Q_{NPA}(C) = -2.228$ e	$Q_{NPA}(C) = -2.264$ e	$Q_{NPA}(C) = -2.418$ e
$Q_{NPA}(Ge) = +0.510$ e	$Q_{NPA}(Ge) = +0.591$ e	$Q_{NPA}(Ge) = +0.423$ e
$Q_{NPA}(Al) = +0.604$ e	$Q_{NPA}(Al) = +0.541$ e	$Q_{NPA}(Al) = +0.787$ e

in CSi_2Ga_2 and CGe_2Al_2 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

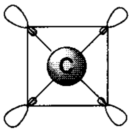
From our calculations, we conclude that pentaatomic molecules composed of a central carbon atom and two Al or Ga ligand atoms and two Si or Ge ligand atoms should have stable planar structures. We should mention that an analogous planar structure was found to be the most stable for another 18-valence electron molecule Al_4O.[9]

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_4 molecule is $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^4 3t_2^6 1t_1$,[6] with the first four ($1a_1^2$ and $1t_2^6$) 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 $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^2$ electronic configuration. Even though the first four electron pairs ($1a_1^2 1t_2^6$) 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_{4h} structure, in line with our findings.

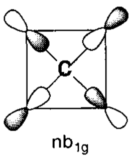
When only 16 valence electrons are present, as in CAl_4, the tetrahedral geometry with a $1a_1^2 1t_2^6 2a_1^2 2t_2^6 1e^0$ valence electronic configuration is not Jahn−Teller unstable, and, as expected, is found to be a stable minimum with four σ-bonds and four lone pairs.[7] Likewise for CH_4 with eight valence electrons, the $1a_1^2 1t_2^6$ 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, $2p_x$, and $2p_y$ orbitals lie in the plane of the molecule. The four ligand s and four ligand and p_σ orbitals also lie in this plane. These orbitals combine to form *four nonbonding orbitals*, localized strongly on the ligands, including na_{1g},

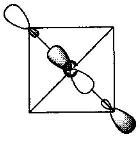


na_{1g}

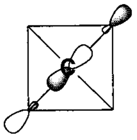
and corresponding nb_{1g} and ne_u molecular orbitals (the prefix n is used to denote nonbonding).



nb_{1g}



ne_u



ne_u

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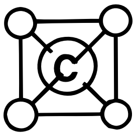
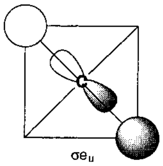
The same ligand orbitals combine with the 2s and $2p_{x,y}$ orbitals of C to form a delocalized five-center bonding orbital $1\sigma a_{1g}$ (and its antibonding partner $1\sigma a_{1g}$ in which the sign of the C 2s orbital is opposite)

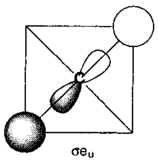


$1\sigma a_{1g}$

a degenerate pair of three-center bonding orbitals σe_u (and their antibonding partners $\sigma^* e_u$ in which the sign of the C 2p orbital is opposite)

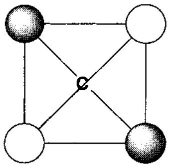


σe_u



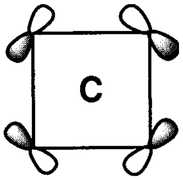
σe_u

and a nonbonding ligand-centered orbital nb_1.



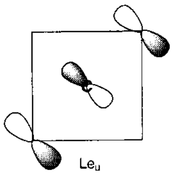
$1b_{1g}$

The ligand p orbitals lying perpendicular to each C−ligand axis combine to form an Lb_{2g} orbital (the prefix L is used to denote combinations of such ligand orbitals) that is bonding among the four ligands

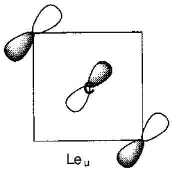


Lb_{2g}

as well as corresponding antibonding L^*e_u

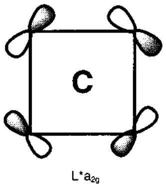


Le_u



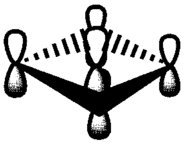
Le_u

and an antibonding L^*a_{2g} orbital.



L^*a_{2g}

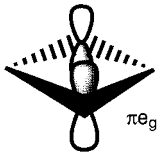
Finally, the C $2p_z$ and ligand out-of-plane 2p orbitals combine to form a five-center bonding πa_{2u} orbital



πa_{2u}

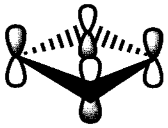
plus the antibonding counterpart $\pi^* a_{2u}$ (in which the sign of the C $2p_z$ orbital is opposite) and a degenerate set of nonbonding orbitals πe_g

πe_g



πe_g

and a ligand antibonding $\pi^* b_{2u}$ orbital.



$\pi^* b_{2u}$

In the ground state of a molecule such as CF_4 with 32 valence electrons, the four nonbonding n orbitals are doubly occupied as are the three σ bonding orbitals, the $1b_{1g}$ 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_4 (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 $1b_{1g}$ 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_4.

For a species such as CAl_4 with 16 valence electrons, three of the four nonbonding n orbitals are doubly occupied as are the three σ bonding orbitals, the $1b_{1g}$ 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 CAl_4, as discussed earlier, one finds four σ bonds and four lone pairs. So, both planar and tetrahedral CAl_4 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 $1b_{1g}$ nonbonding orbital, the C−ligand π bonding orbital, and the ligand−ligand Lb_{2g} 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 σ and one π bond occur as well as one ligand–ligand bond. In molecules with more than 18 valence electrons, the Le_u orbitals, which are C–ligand antibonding and ligand–ligand nonbonding, and the L^*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 CSi_2 molecule has been identified experimentally;[10–12] perhaps it could be used as a precursor in gas-phase reactions with aluminum or gallium atoms to prepare the CSi_2Al_2 or CSi_2Ga_2 molecules in the gas phase or in matrix isolation.

Acknowledgment. This work was supported by NSF Grant No. CHE9618904.

JA981236U

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