

A New, General Strategy for Achieving Planar Tetracoordinate Geometries for Carbon and other Second Row Periodic Elements

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Highly stable structures with planar tetracoordinate central atoms, Al_4O , Al_4N^- , Al_3SiN , *cis*- $\text{Al}_2\text{Si}_2\text{C}$, *trans*- $\text{Al}_2\text{Si}_2\text{C}$ and AlSi_3B , are predicted computationally at the *ab initio* MP4SDTQ/6-311 + G*/MP2(full)/6-31G* level.

Planar arrangements of four substituents coordinated to second row atoms initially predicted theoretically¹⁻³ are still rare, but experimental examples are slowly accumulating.⁴ This paper discloses a new way to achieve such exceptional geometries. A number of molecules, *e.g.* **1-6**, calculated at reasonably high *ab initio* levels [geometries optimized at MP2(full)/6-31G* and final total energies calculated at MP4SDTQ/6-311 + G*/MP2(full)/6-31G* + ZPE], illustrate the strategy employed.

The basic idea, to surround a central atom by a planar perimeter, has been explored in the past, but no good possibilities have been revealed. For example, the central carbon arrangements in [4.4.4.4]fenestrane **7** and in an aromatic analogue, **8**, are expected to distort strongly from planarity.³

The simplest perimeter possible would be comprised of only four atoms, but these must offer the correct set of bond length relationships. In other words, the four-membered ring must be large enough not only to enclose a first row atom comfortably, but also to provide strong binding. Bonds involving second row elements are longer than those of the second Li-Ne period. There is another important requirement: the combination of atoms chosen must offer the appropriate number of valence electrons consistent with the symmetry desired. We suspected that the isoelectronic species, **1-6**, might fulfil both these prerequisites.

The 'hyperaluminium oxide' candidate Al_4O , in various geometries and states, was examined extensively first.⁵ Indeed, computations at the MP4SDTQ/6-311 + G*/MP2(full)/6-31G* + ZPE *ab initio* level not only showed singlet **1** in square planar D_{4h} symmetry to be the global Al_4O minimum, but also to be highly stable energetically towards all

possible dissociation pathways. Thus, the decomposition of **1** into Al_3O and an Al atom was calculated to be endothermic by 45.5 kcal mol⁻¹ (1 cal = 4.184 J) and the atomization energy $D_0^0(\text{Al}_4\text{O})$ was 301.2 kcal mol⁻¹ at the PMP4/6-311 + G* + ZPE//MP2(full)/6-31G* + ZPE *ab initio* level. This computational discovery and characterization of Al_4O , a species which does not appear to have been mentioned in the literature before, demonstrates that many similar species with planar tetracoordinate central atoms should be possible. We have explored a few of these and report the results.

The bonding in **1** is partly ionic and partly covalent. As the central oxygen atom has nearly its maximum negative charge, O^{2-} , the Al-O interactions are largely electrostatic. However,

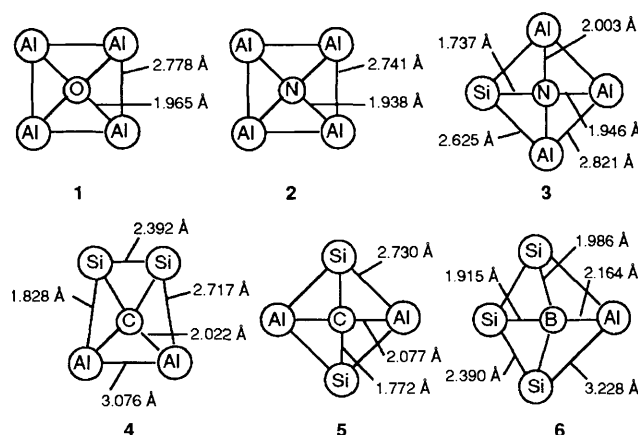
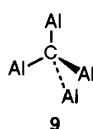
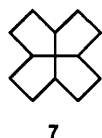


Table 1 Calculated total energies (a.u.) and harmonic frequencies (cm⁻¹) of BSi₃Al, CSi₂Al₂, NSi₃Al, NAl₄⁻ and OAl₄ species^a

	HF/6-31G*	MP2(full)/6-31G*	HF/6-31G*	MP2(full)/6-31G*
1			2	
<i>E</i> _{tot}	-1042.51725	-1042.96855	<i>E</i> _{tot}	-1022.12916
<i>v</i> ₁ (a _{1g})	390 (0)	384	<i>v</i> ₁ (a _{1g})	434 (0)
<i>v</i> ₂ (a _{2u})	207 (13)	157	<i>v</i> ₂ (a _{2u})	262 (26)
<i>v</i> ₃ (b _{1g})	171 (0)	204	<i>v</i> ₃ (b _{1g})	275 (0)
<i>v</i> ₄ (b _{2g})	287 (0)	268	<i>v</i> ₄ (b _{2g})	306 (0)
<i>v</i> ₅ (b _{2u})	88 (0)	90	<i>v</i> ₅ (b _{2u})	80 (0)
<i>v</i> ₆ (e _u)	451 (234)	538	<i>v</i> ₆ (e _u)	686 (201)
<i>v</i> ₇ (e _u)	173 (29)	246	<i>v</i> ₇ (e _u)	218 (11)
3			4	
<i>E</i> _{tot}	-1069.08025	-1069.53977	<i>E</i> _{tot}	-1099.43026
<i>v</i> ₁ (a ₁)	880 (225)	902 (216)	<i>v</i> ₁ (a ₁)	935 (311)
<i>v</i> ₂ (a ₁)	450 (48)	420 (56)	<i>v</i> ₂ (a ₁)	477 (31)
<i>v</i> ₃ (a ₁)	258 (0)	266 (2)	<i>v</i> ₃ (a ₁)	935 (311)
<i>v</i> ₄ (a ₁)	207 (4)	210 (4)	<i>v</i> ₄ (a ₁)	183 (0)
<i>v</i> ₅ (b ₁)	253 (11)	167 (11)	<i>v</i> ₅ (a ₂)	94 (0)
<i>v</i> ₆ (b ₁)	89 (0)	107 (0)	<i>v</i> ₆ (b ₁)	249 (13)
<i>v</i> ₇ (b ₂)	548 (396)	632 (394)	<i>v</i> ₇ (b ₂)	831 (273)
<i>v</i> ₈ (b ₂)	310 (0)	296 (7)	<i>v</i> ₈ (b ₂)	323 (43)
<i>v</i> ₉ (b ₂)	181 (7)	210 (2)	<i>v</i> ₉ (b ₂)	165 (1)
5			6	
<i>E</i> _{tot}	-1099.42218	-1099.87506	<i>E</i> _{tot}	-1133.22328
<i>v</i> ₁ (a _g)	560 (0)	512 (0)	<i>v</i> ₁ (a ₁)	810 (295)
<i>v</i> ₂ (a _g)	262 (0)	295 (0)	<i>v</i> ₂ (a ₁)	479 (5)
<i>v</i> ₃ (b _{3g})	267 (0)	248 (0)	<i>v</i> ₃ (a ₁)	344 (73)
<i>v</i> ₄ (b _{1u})	603 (501)	679 (453)	<i>v</i> ₄ (a ₁)	200 (18)
<i>v</i> ₅ (b _{1u})	116 (1)	165 (0)	<i>v</i> ₅ (b ₁)	174 (4)
<i>v</i> ₆ (b _{2u})	1105 (52)	1197 (281)	<i>v</i> ₆ (b ₁)	96 (0)
<i>v</i> ₇ (b _{2u})	162 (1)	196 (0)	<i>v</i> ₇ (b ₂)	974 (167)
<i>v</i> ₈ (b _{3u})	235 (10)	128 (5)	<i>v</i> ₈ (b ₂)	394 (5)
<i>v</i> ₉ (b _{3u})	103 (1)	93 (10)	<i>v</i> ₉ (b ₂)	92 (1)

^a IR intensities (km mol⁻¹) are given in parentheses.



natural population analysis⁵ indicates the Al-Al overlap to be considerable. The geometry of **1** also is favourable. The calculated Al-O (1.954 Å) and Al-Al (2.763 Å) distances are both quite close to the 'single bond' values: R(Al-O) = 1.72 Å in Al₂O,^{6a} R(Al-O) = 1.71 Å in H₂AlOH,^{6b} R(Al-O) = 1.69 Å in H₂AlOCH₃,^{6b} R(Al-O) = 1.67 Å and R(Al=O) = 1.57 Å in Al₃O₂,^{6c} and R(Al-Al) = 2.610 Å in H₂Al-AlH₂,^{7a} R(Al-Al) = 2.727 Å in Al₂(³Π_u),^{7b} R(Al-Al) = 2.863 Å in the metal.^{7c} The 18 valence electrons in Al₄O fully occupy all degenerate orbitals in the ¹A₁ ground state [valence orbital occupancy: (1a_{1g})²(1e_u)⁴(1a_{2u})²(2a_{1g})²(2e_u)⁴(1b_{1g})²(1b_{2g})²(2a_{2u})⁰].

In the obvious isoelectronic analogue, **2** (Al₄N⁻), nitrogen replaces the oxygen in **1**. The lower electronegativity of the central atom, N, results in an increase in the covalent character of both the N-Al and the Al-Al bonds, even though the charge on N remains high (N = -2.24 in **2**). **2** is the global energy minimum; the predicted frequencies (which might facilitate experimental verification) are given in Table 1. The vectors corresponding to the lowest frequencies lead to *D*_{2d}

distortion. As with Al₄O,⁵ an alternative geometry for Al₄N⁻ with *D*_{2d} symmetry was calculated, but was found to be higher in energy. [Another isoelectronic analogue, CAl₄²⁻ (¹A_{1g}) not only is unstable towards electron loss in the isolated state, but also has three imaginary frequencies in *D*_{4h} symmetry.]

When two fewer valence electrons are present, as in the neutral CAl₄ molecule, tetrahedral symmetry **9** [¹A₁ state with the (1a₁)²(1t₂)⁶(2a₁)²(2t₂)⁶(1e)⁰ valence electron configuration] is calculated to be favoured. However, the aluminium ligands in **9** are too far apart [R(Al-Al) = 3.249 Å] to permit effective overlap.

The mixed silicon-aluminium species **3** (*C*_{2v}, ¹A₁), **4** (*C*_{2v}, ¹A₁), **5** (*D*_{2h}, ¹A_g) and **6** (*C*_{2v}, ¹A₁) are intriguing as neutral planar tetracoordinate nitrogen, carbon and boron candidates, respectively. All these structures are minima (no imaginary frequencies, see Table 1) and all have large atomization energies (kcal mol⁻¹): *D*₀⁰ (**3**) = 309.9, *D*₀⁰ (**4**) = 354.6, *D*₀⁰ (**5**) = 354.6, and *D*₀⁰ (**6**) = 334.3 [all at MP4SDTQ/6-311 + G*/MP2(full)/6-31G* + ZPE]. This atomization energy for **4** differs from that calculated at MP4SDTQ/6-31G* and at QCISD(T)/6-31G* only by 5 kcal mol⁻¹. These atomization energies are comparable to those of CH₄, *D*₀⁰ = 392.1 and CCl₄, *D*₀⁰ = 306.1 kcal mol⁻¹.⁸ Therefore, **3-6** should be stable in isolated states in the gas phase or in matrixes, although they may well aggregate and disproportionate otherwise. The electronic structures of these species are quite similar. The M-X bonds are essentially ionic and the central atoms have nearly the same charge, -2.2 to -2.4, but all species have appreciable central atom-ligand and ligand-ligand overlap populations (Table 2). The covalent contribution to the M-X bonding decreases but that to the M-M bonding increases along the BSi₃Al, CSi₂Al₂, NSi₃Al₃ series. The central atom-ligand overlap population dominates

Table 2 NBO charges and non-orthogonal natural atomic overlap populations of 1–6 species (HF/6-31G*)

	1	2	3	4	5	6
Q(X)	-1.67	-2.24	-2.20	-2.39	-2.42	-2.21
Q(Si)	—	—	+0.43	+0.51	+0.62	+0.58 ^a +0.27 ^b
Q(Al)	+0.42	+0.31	+0.57 ^c +0.62 ^d	+0.69	+0.59	+0.77
Q(X–Si)	—	—	0.67	0.82	0.97	1.10 ^a 1.03 ^b
Q(X–Al)	0.21	0.36	0.25 ^c 0.31 ^d	0.40	0.30	0.26
Q(Si–Al)	—	—	0.54	0.39	0.43	0.07
Q(Si–Si)	—	—	—	0.75	—	0.77
Q(Al–Al)	0.59	0.61	0.44	0.28	—	—

^a Atom Si in the *trans*-position with respect to the Al atom. ^b Atom Si in the *cis*-position with respect to the Al atom. ^c Atom Al in the *trans*-position with respect to the Si atom. ^d Atom Al in the *cis*-position with respect to the Si atom.

in BSi_3Al , while in NSiAl_3 the ligand–ligand overlap populations are larger. Perimeter bonding is highly important to achieve planar structures and to stabilize these molecules. Eighteen valence electrons are necessary to fill the bonding orbitals completely (see above), and thus are the ‘magic number’ for planar species of this type.

Clearly, many other combinations of chemical elements might also prefer planar tetracoordinate arrangements involving central main group atoms. Complexation of the outer atom with appropriate ligands, or their elaboration with substituents, might facilitate preparation and isolation. We are exploring such possibilities computationally. Complexes of transition metals provide examples. The crystal structure of $[\text{Re}_4\text{C}(\text{CO})_{15}\text{I}]^-$ shows a carbon in the centre of a nearly planar, D_{2d} among the complexed Re moieties.^{4c} Cotton has found planar rectangular oxygen tetracoordination in $[\{\text{Nb}_4\text{OCl}_8(\text{PhC})_4\}_2]^{2-}$ dianions and calls attention to the square planar oxygen environment in NbO .^{4g}

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