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New High Energy Density Small Ring Systems

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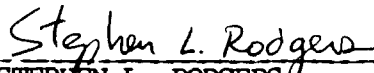
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17. ABSTRACT (Continue on reverse if necessary and identify by block number)

A theoretical research investigation of four-atom light element species has been undertaken in order to find propellants with revolutionary performance. The ab initio calculations show that the rhombic geometry is a global minima on the potential energy surface of C_4 dicarbides and diborides composed of H, Li, Be, B, C, and Si. By means of bond-stretch isomerism, bonding pattern change, these rhombic species can store significant amounts of energy - 87 kcal/mole to 122 kcal/mole. Only in the case of B_2Be_2 was the tetrahedral form stable. All of the four-atom species found stable by this investigation are estimated to provide high specific impulses.

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SUMMARY

Theoretical ab initio calculations have been carried out on tetraatomic systems in the search for advanced chemical propellants. In the approach to identify systems with revolutionary specific impulses ($I_{sp} > 500$ sec) we concentrated on molecular systems that are (a) composed of elements with high combustion energies, (b) that have a high degree of unsaturation (H-deficient), and (c) are very strained (inverted geometries of carbon and boron). The research efforts were focussed on cyclic tetraatomics to develop an understanding of their structural, energetic, and electronic properties.

The rhombic forms of C_4 , C_4H^+ , and $C_4H_2^{2+}$ were used as parent molecules. Although the linear triplet C_4 form has been observed, there are experimental indications for the existence of a rhombic isomer (the two structures are of equal stability). However, for the diprotonated species the coexistence of the linear and rhombic forms in the gas phase is unequivocal and based on charge separations that give excellent agreement with theoretical data. The estimated heat of formation of 726 kcal/mol for rhombic $C_4H_2^{2+}$ is one of the highest for a dication.

The question has been addressed whether other elemental combinations could render similar systems of high energy. Related to this question we have developed an understanding of the bonding pattern of these molecules and how their energy content may be manipulated.

A survey of light four-atom systems at the HF/6-31G* level of theory has been conducted on dicarbides and diborides with ligands ranging from Li, Be, BeH, BH, C, CH, AlH, to Si. Of the dicarbides 24 different rhombic structures are minima on the potential energy surface and 21 diborides have been characterized as are minima. While the distance between the bridgehead carbons (borons) is virtually constant throughout all dicarbides (diborides) their bonding varies significantly. To evaluate the viability of rhombic forms also tetrahedral diboride combinations have been explored. Of the 24 diborides only three light elemental combinations are minima. These are B_2Li_2 , B_2Be_2 , and $B_2Be_2H^-$.

To inspect in more detail the theoretical levels required to describe rhombic tetraatomics and to evaluate their energetic properties, full potential energy surface scans have been performed on C_2Si_2 , B_2Be_2 , and B_2Li_2 . The latter two light element systems have estimated I_{sp} values of 646 and 531 sec, respectively. These values are based on MP4/6-31G* binding energies. The calculations show that electron correlation has a large influence on

the relative stabilities and binding energies, but only marginally influences the geometrical parameters of isomeric structures. To inspect the chemical properties of such systems toward hydrogen, we have investigated the potential energy surface of $B_2Be_2H_2$.

Bonding patterns have been evaluated by analysis of the electron densities. It has been found that no transannular bond exists between the 1.523 Å separated bridgehead carbons of C_4 . However a small reduction in length results in CC bond formation, or conversely lengthening the CC distance results in further depletion of electron density in the center of the rhombic structure as is the case in C_4H^+ and $C_4H_2^{2+}$.

Because of the variation in bridgehead CC (and BB) overlap, and the notable lack of a CC bond in C_4 , we have investigated whether breaking of the transannular CC (and BB) bond can render vibrational stable species of higher energy. Such a mechanism, bond stretch isomerism, has been found in several systems. In the case of C_2Si_2 , which is isovalent with C_4 , such a rhombic structure is found 78 kcal/mol higher in energy than the global rhombic minimum. Similarly, in the case of B_2Be_2 a rhombic form is found 60.6 kcal/mol higher in energy than the global minimum. The barrier for interconversion between the two rhombic structure has not been determined but is estimated to be high because it would represent a symmetry forbidden process. This may suggest that the high energy rhombic forms have substantial kinetic stability.

Structures containing lithium atoms like B_2Li_2 have ionic bonds. Therefore the properties of B_2Li_2 and B_2Be_2 differ greatly. In collaboration with Michels we investigated how ionic complexes may render high energy materials. It was found that in the Li_3H the H^- anion is complexed to the side of triangular Li_3^+ cation unit (i.e. rendering rhombic Li_3H), thereby leaving the properties of this Li_3^+ cation unit in tact.

An investigation exploring the potential of bridging diboride units with Al atoms has been initiated. Because of the general lack of theoretical information available on Al-Al interactions, as compared with that on B-B bonds, exploratory studies have been conducted on Al_2H_6 as well as on the recently observed Ga_2H_6 and Ga_2H_4 . These studies focussed on determining binding energies and the influences governing ionic versus covalent bonding.

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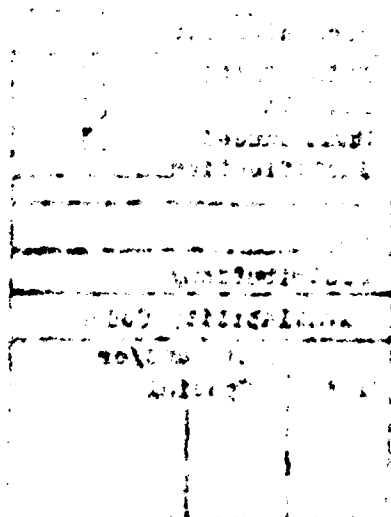
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INTRODUCTION

For decades chemists have been intrigued by small ring compounds. Many studies have been devoted to highly strained, small hydrocarbons,¹ carboranes,² and silicon derivatives.³ Although giant steps have been made in materials science and there is an increasing understanding of Li clusters, B clusters, Be clusters, C clusters and Si clusters, the information concerning bonding and energetic properties of mixed cluster compounds remains very limited. In the past three years, we systematically investigated a series of over 50 tetraatomic diborides and dicarbides by ab initio molecular orbital theory. In this report, we describe the results of this theoretical survey study on potentially high energy four-membered ring compounds composed of the elements Li, Be, B, C, Al, and Si.

The foundation for developing high energy density systems is often based on:

- (a) increasing the unsaturation by stripping molecules of all their hydrogens.
- (b) increasing the strain energy by inverting the carbon (and boron) geometries.

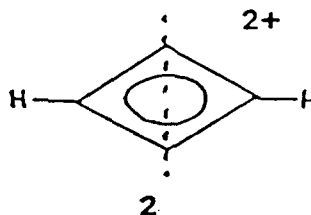
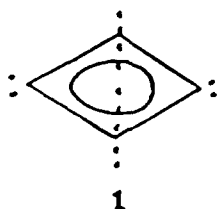
For example, there are numerous strained hydrocarbons that have either inverted tetra-coordinated (sp^3) geometries⁴ or pyramidelized olefinic bonds. In this investigation, we capitalized on the properties of inverted tricoordinated (sp^2) boron and carbon atoms.⁵ Below follows a description which uses C_4 as an example of how we developed such unsaturated systems with inverted carbon geometries, to find highly energetic, yet stable, strained ring systems.

Energetic Four-Membered Ring Structures; C_4 .

The expected increase in energy on depletion of hydrogen from the cyclic C_4 -frame is evident from the HF/6-31G* data listed in Table 1. At this level of theory, the heat of formation ΔH_f° of rhombic C_4 (D_{2h}) is 228 kcal/mol (estimated from calculated heats of hydrogenation in combination with experimental reference points—). The deduction of this value includes corrections for Δ zero point energy, hydrogenation (each 6.4 kcal/mol), $\Delta H_f^\circ(0-298^\circ)$, and for differences (7 kcal/mol) between calculated and experimental values.¹¹ The ΔH_f° value of 228 kcal/mol for rhombic C_4 (inverted sp^2) is large compared to the heat of formation of 89 kcal/mol (HF/6-31G*) for stable [1.1.1]propellane (inverted sp^3), which has a strain energy SE of 103 kcal/mol.¹⁰ The experimentally known $C_4H_2^{2+}$ dication, with the highest ΔH_f° of any cationic system (726 kcal/mol), provides further evidence of this contrast.¹² In this investigation we made use of this contrast

TABLE 1. 6-31G* energies (in a.u.), heats of formation (ΔH_f , in kcal/mol), and strain energies (SE, in kcal/mol) for C_4 structures.

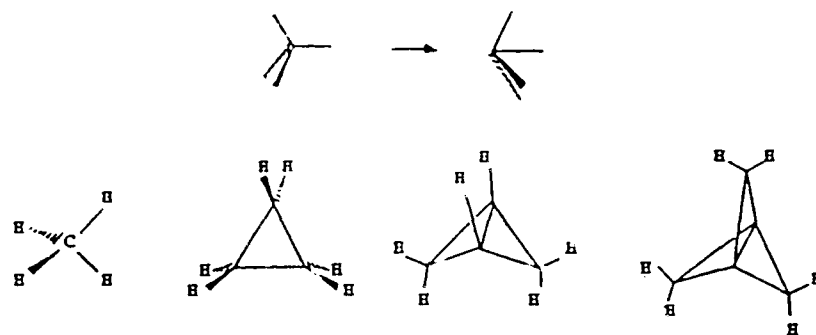
Compound	Formula	Energy	ΔH_f	SE
1 ^{4,6}	C_4	-151.14598	228	
2 ⁶	$C_4H_2^{2+}$	-151.53998	726	
Cyclobutadiene dication ⁷	$C_4H_4^{2+}$	-152.91650	623	
Bicyclo[1.1.0]butene ⁸	C_4H_4	-153.58016	142	127
1,3-Cyclobutadiene ⁹	C_4H_4	-153.64120	103	65
Bicyclo[1.1.0]butane ⁸	C_4H_6	-154.87176	51.9	65
Cyclobutene ¹⁰	C_4H_6	-154.89962	37.5	29
Cyclobutane ¹⁰	C_4H_8	-156.09703	6.8	26
Hydrogen ⁸	H_2	-1.12683		



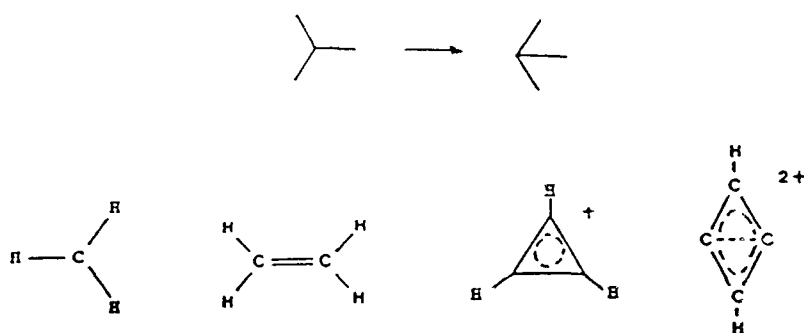
between C_4 and [1.1.1]propellane to design over forty, stable, high energy, tetraatomic species.

Rhombic Tetracarbon, C_4 .

We⁶ and others¹³ have demonstrated that rhombic C_4 (1) is of nearly the same energy as triplet linear C_4 . The unusual stability of cyclic C_4 can be explained by inspection of its molecular orbital framework.⁶ The highest occupied molecular orbital, HOMO, is a non-bonding σ -orbital between the bridgehead carbons with the electron density located outside the molecule. Hence, the HOMO does not contribute to ring strain. The stabilization of rhombic C_4 results from aromatic π bonding; a σ -bridged- π MO is also present. Besides its σ skeleton, the molecule has two lone electron pairs. In simple Lewis terms, the bonding of both bridgehead C atoms in C_4 can be described as follows: (a) two valence electrons are involved in ring C-C bonding, (b) the third electron participates in aromatic ring π bonding, while (c) the fourth electron is involved in σ nonbonding.



Scheme I. Inverted tetracoordinate geometries at carbon



Scheme II. Inverted tricoordinate geometries at carbon

Diprotonated Rhombic C_4 .

Our study on the $C_4H_2^{2+}$ dication underscores the validity of inverted planar tricoordinate carbons.⁶ Cyclic $C_4H_2^{2+}$ ($2, D_{2d}$) is only 13.3 kcal/mol (MP3/6-31G*) less stable than its triplet linear diacetylenic isomer, despite the anticipated strong electrostatic charge-charge repulsion.^{12a} Both isomers have been observed in the gas phase.^{12a} An alternative (but empirical) explanation for the stability of rhombic $C_4H_2^{2+}$ can be given along the lines shown for strain build-up in saturated hydrocarbons, now adapted for olefins (Scheme I and II). Stepwise replacement of the vicinal hydrogens from the parent ethylene by CH^+ -groups gives either the cyclopropenyl cation or cyclic $C_4H_2^{2+}$, (note that in this series the tricoordinate carbon is completely inverted, while the 2π stabilization is maintained!).

TECHNICAL DISCUSSION

The question this investigation addressed is whether the inverted tricoordinate geometry concept developed for high energy density small ring hydrocarbons can be expanded to include other elements. There are two important aspects to consider.

- (a) Do the characteristics of an inverted planar tricoordinate carbon change using bridging elements other than carbon?
- (b) Can the bridgehead carbons be replaced by other elements while maintaining the high energy density properties of the system?

To address these questions we discuss a large number of tetraatomic rhombic and tetrahedral structures and will analyze several small clusters. These latter potential energy surface studies are presented in a summarized fashion. A complete analysis for each cluster is presented in the appendices, which have appeared or are to appear in the scientific literature.

RHOMBIC STRUCTURES — Structures and Energies

Tetraatomic Dicarbides. We have examined at the 6-31G* level of theory 25 rhombic dicarbides with ligands ranging from Li, Be, BH, C, AlH, and Si, in virtually all combinations. The data are listed in Table 2. This group of planar structures includes anions, cations, and dipolar molecules. Of these 25 dicarbides, 24 are minima on the 6-31G* potential energy surface, as indicated by the zero number of imaginary frequencies. These data strongly support the viability of rhombic structures that contain inverted tricoordinate carbons irrespective of the type of bridging ligand.

Similarly impressive in these dicarbides is their rather short C-C distance which has an average value of only 1.457 Å (dianions excluded). This is unexpected because of the range of bridging elements involved. Inspection of the Mulliken overlap population indeed shows that the nature of bonding between the carbons must vary significantly. Representative values are -0.236 for $C_4H_2^{2+}$, -0.063 for C_4 , and +0.306 for C_2Be_2 . However, the Mulliken population analyses is subject to criticism, in particular for unsymmetrical bonding arrangements, and hence can not rigorously answer what types of bonding are operative in the dicarbides. We attempted Weinhold's superior Natural Bond Order approach,^{14,15} but found too many complications in using this method due to ionicity in the rhombics. The Bader electron analysis, which we will describe in the following section on bonding patterns, allowed us to characterize the bonding in these molecules.

TABLE 2. Rhombic Dicarbides RHF/6-31G* Energies, NIMAG, and Geometrical Data.

Structure X-C ₂ -Y	Energy	Nimag	Bond Distances		
			C—C	C—X	C—Y
Li-(C ₂)-Li	-90.37222	0	1.249	2.108	2.108
Li-(C ₂)-Be	-97.58752	0	1.436	1.907	1.571
Li-(C ₂)-BH	-108.30443	0	1.426	1.881	1.472
Li-(C ₂)-CH	-121.50728	0	1.470	1.968	1.348
Li-(C ₂)-C:	-120.84757	0	1.402	1.880	1.418
Li-(C ₂)-AlH	-325.48897	1	1.374	1.922	1.899
Be-(C ₂)-Be	-104.79129	0	1.459	1.565	1.565
Be-(C ₂)-BH	-115.47831	0	1.445	1.558	1.473
Be-(C ₂)-CH	-128.39388	0	1.484	1.619	1.345
Be-(C ₂)-C:	-127.98366	0	1.418	1.563	1.421
Be-(C ₂)-AlH	-332.67417	0	1.451	1.561	1.857
BeH-(C ₂)-BH	-116.13470	0	1.449	1.670	1.477
BeH-(C ₂)-CH	-129.26994	0	1.501	1.739	1.339
Beh-(C ₂)-C:	-128.66892	0	1.433	1.677	1.408
BeH-(C ₂)-AlH	-333.31024	0	1.419	1.683	1.853
BH-(C ₂)-BH	-126.15541	0	1.470	1.470	1.470
BH-(C ₂)-CH	-139.01220	0	1.529	1.526	1.345
BH-(C ₂)-C:	-138.65329	0	1.462	1.479	1.418
BH-(C ₂)-AlH	-343.35876	0	1.449	1.470	1.848
CH-(C ₂)-CH	-151.53998	0	1.593	1.386	1.386
CH-(C ₂)-C:	-151.45693	0	1.520	1.352	1.472
CH-(C ₂)-AlH	-356.27607	0	1.494	1.342	1.919
C:-(C ₂)-C:	-151.14598	0	1.457	1.425	1.425
C:-(C ₂)-AlH	-355.86570	0	1.436	1.418	1.857
AlH-(C ₂)-AlH	-560.55536	0	1.436	1.858	1.858
:Si-(C ₂)-Si:	-653.41467	0	1.415	1.818	1.818
BH-(Si ₂)-BH	-628.24903	0	2.461	1.950	1.950
:C-(Si ₂)-C:	-649.77894	-	2.292	1.863	1.863
AlH-(Si ₂)-AlH	-1057.08620	-	2.628	2.337	2.337

Tetraatomic Diborides. We have examined at the HF/6-31G* level of theory 28 rhombic diborides with ligands ranging from Li, Be, BH, C, AlH, and Si, in virtually all combinations. The 6-31G* data for these systems, that contain two valence electrons less than the discussed dicarbides, are listed in Table 3. Like the planar dicarbides this group also includes anions, cations, and dipolar molecules. Of the 28 diborides, 21 are minima on the HF/6-31G* potential energy surface, as indicated by the zero number of imaginary frequencies; the other 7 are transition structures. Similar to the dicarbides these data support the viability of rhombic structures now containing inverted tricoordinate borons with a large variety of bridging ligands.

Considering the two-electron difference with dicarbides these diborides have a relatively short average B-B distance of 1.833 Å. However, as will be shown, the bonding nature of these systems is entirely different from that in the dicarbides.

BONDING PATTERNS

An understanding of the bonding nature in the rhombic structures can be obtained by analyzing the electron density (ρ) properties of these molecules. Prof. R.F.W. Bader of McMaster University was so kind to provide us with the software that his research group has developed. A detailed description of his method and its applications can be found in the literature (also Appendix C).¹⁶ However, a synopsis of the method assists in comprehending the figures in this report.

In short, the method is concerned with the electron density ρ although connections with molecular orbitals can be made. The programs EXTREME and PROAIM were interfaced with GAUSSIAN 86 and 88 and use the same basis sets. The properties of a molecular charge distribution, based on Bader's topological analysis of density of atoms in molecules, are summarized in terms of its critical points. These are points where the charge density is a maximum, a minimum, or a saddle of the gradient path of the gradient vector field *i.e.*, $\nabla\rho = 0$. A critical point is characterized by the signs of its three principal curvatures of ρ *i.e.*, λ_1 , λ_2 , and λ_3 . A bond critical point (3,-1) has a minimum (positive curvature) in ρ on the bond path connecting two nuclei and two negative curvatures in orthogonal planes; the charge density has the appearance of a saddle. Ring critical points (3,+1) have one negative and two positive curvatures. Three positive curvatures (3,+3) define a minimum (cage critical point). The (3,-3) critical point represents atoms or nuclear attractors ("pseudo atoms") where all curvatures are positive. In the figures presented the connectivity of atoms via bond critical points are given (the molecular graphs) in both plots of the gradient vector field, (which give the separation of atoms in molecules by

TABLE 3. Rhombic Diborides RHF/6-31G* Energies, NIMAG and Geometrical Data.

Structure X-B ₂ -Y	Energy	Nimag	Bond Distances		
			B—B	B—X	B—Y
Li-(B ₂)-Li	-64.04676	0	1.540	2.197	2.197
Be-(B ₂)-Be	-78.33038	0	2.013	1.760	1.760
Be-(B ₂)-BeH	-78.95048	1	1.888	1.755	1.862
Be-(B ₂)-BH	-89.03080	0	1.809	1.753	1.598
Be-(B ₂)-CH	-102.02063	0	1.823	1.813	1.443
Be-(B ₂)-C:	-101.63581	0	1.863	1.754	1.383
Be-(B ₂)-AlH	-306.22846	1	1.997	1.756	2.040
Be-(B ₂)-Si:	-352.67586	0	1.790	1.758	1.911
BeH-(B ₂)-BH	-89.67334	1	1.742	1.870	1.594
BeH-(B ₂)-CH	-102.86362	0	1.787	1.937	1.445
BeH-(B ₂)-C:	-102.28936	0	1.765	1.906	1.39
BeH-(B ₂)-AlH	-306.86504	1	1.877	1.858	2.036
BeH-(B ₂)-Si:	-353.32652	1	1.734	1.881	1.920
BH-(B ₂)-BH	-99.72164	0	1.690	1.604	1.604
BH-(B ₂)-CH	-112.66014	0	1.719	1.658	1.444
BH-(B ₂)-C:	-112.28438	0	1.645	1.642	1.399
BH-(B ₂)-AlH	-316.93016	0	1.819	1.594	2.032
BH-(B ₂)-Si:	-363.35948	0	1.683	1.607	1.941
CH-(B ₂)-CH	-125.29859	0	1.740	1.482	1.482
CH-(B ₂)-C:	-125.15331	0	1.623	1.464	1.460
CH-(B ₂)-AlH	-329.91335	0	1.848	1.440	2.102
CH-(B ₂)-Si:	-376.30524	0	1.726	1.442	2.047
:C-(B ₂)-C:	-124.63404	1	1.752	1.420	1.420
:C-(B ₂)-Si:	-375.93214	0	1.689	1.392	2.004
:C-(B ₂)-AlH	-329.53246	0	1.813	1.382	2.037
AlH-(B ₂)-AlH	-534.12534	1	1.996	2.037	3.553
AlH-(B ₂)-Si:	-580.57306	0	1.778	2.037	1.910
:Si-(B ₂)-Si:	-627.00013	0	1.666	1.947	1.910

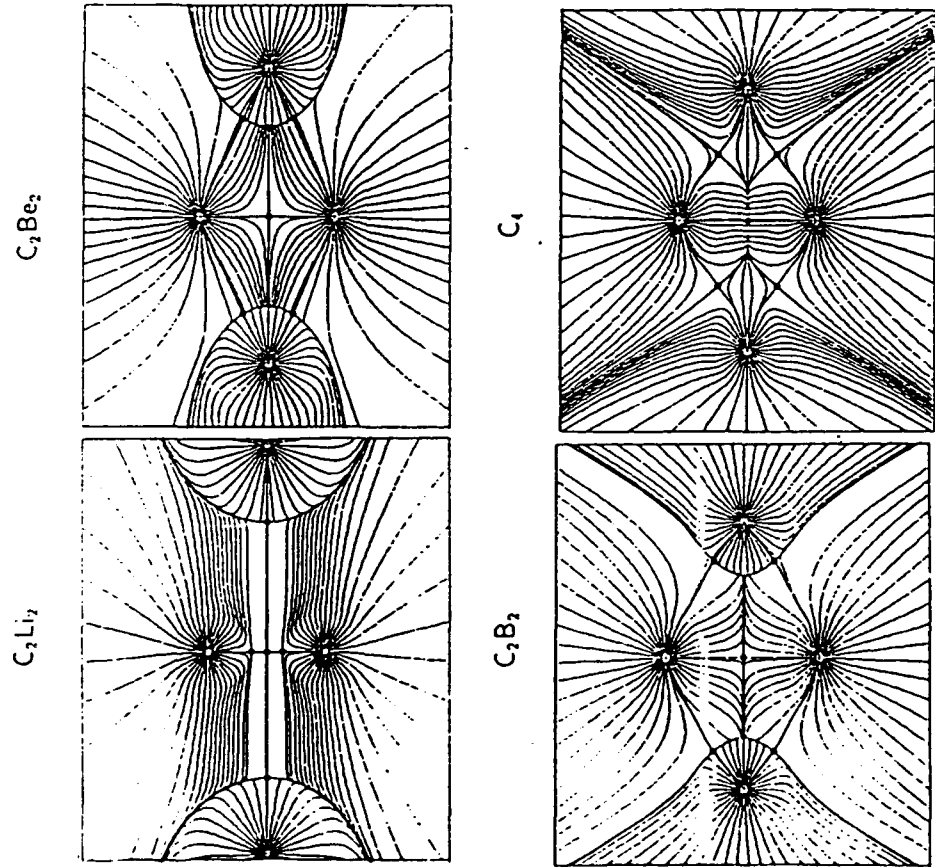
“zero flux” lines) and the Laplacian field of the charge density $\nabla^2\rho$ (the sign of which also characterizes the polarity of a bond).

Tetraatomic Dicarbides. The variation of bonding possible in planar rhombic dicarbides can be illustrated in the neutral series C_2Li_2 , C_2Be_2 , C_2B_2 , and C_4 , which shows a gradual changeover from the fully ionic C_2Li_2 system to the covalently bonded C_4 . Figure 1 gives a representation of the gradient vector field of their charge density (HF/6-31G*) in terms of the paths traced out by the vectors $\nabla\rho$ and also displays the corresponding contour maps of the Laplacian of their charge density overlaid with bond paths.

The lithiums in C_2Li_2 are bonded to the center of the C-C bond. In fact, the C-C bond path has three bond critical points and two “pseudo atoms” (nuclear attractors, (3,-3)). This unusual behavior can be interpreted as a C-C triple bond with a long path of virtually constant electron density. Recently, pseudo atoms were also found in studies by Bader and Gatti on Li and Na clusters.¹⁷ They argued tentatively that these nuclear attractors may be associated with metallic behavior. However, our observations of these (3,-3) critical points in dicarbides and diborides (*vide infra*) may indicate a more universal behavior. In replacing Li for Be to give C_2Be_2 , bond paths are found at the circumference of the rhombic structure, although there remains a high degree of ionicity. The results on C_2Be_2 agree with those reported by Cremer and Schleyer.¹⁸ The difference between C_2B_2 and C_4 reveals an interesting feature. While the zero-flux line of the bridging ligand in C_2B_2 is clearly defining the boron, in C_4 it is penetrating the rhombic structure. In fact, the two ring critical points (3,+1) and the bond critical point (3,-1) of the bridgehead-bridgehead C-C bond path in C_4 nearly coalesce, an observation also made by Ritchie.¹⁹ Evidently, the center of C_4 represents a near catastrophe point. This means that a small perturbation of C_4 can eliminate bonding between the bridgehead carbons, despite their short 1.457 Å (HF/6-31G*) separation.

The change in bonding between the bridgehead carbons becomes even more pronounced in comparing the series C_4 , C_4H^+ , and $C_4H_2^{2+}$. Their 6-31G* transannular C-C distance are 1.523 (MP2), 1.520 (HF), and 1.593 Å (HF), respectively. The Laplacian of ρ for these systems are shown in Figure 2. From this Figure it is quite clear that there is electron depletion in the center of $C_4H_2^{2+}$ and consequently this structure does not possess a transannular C-C bond.

Molecular Graphs of Dicarbides at the Molecular Plane



Laplacian plots of Dicarbides

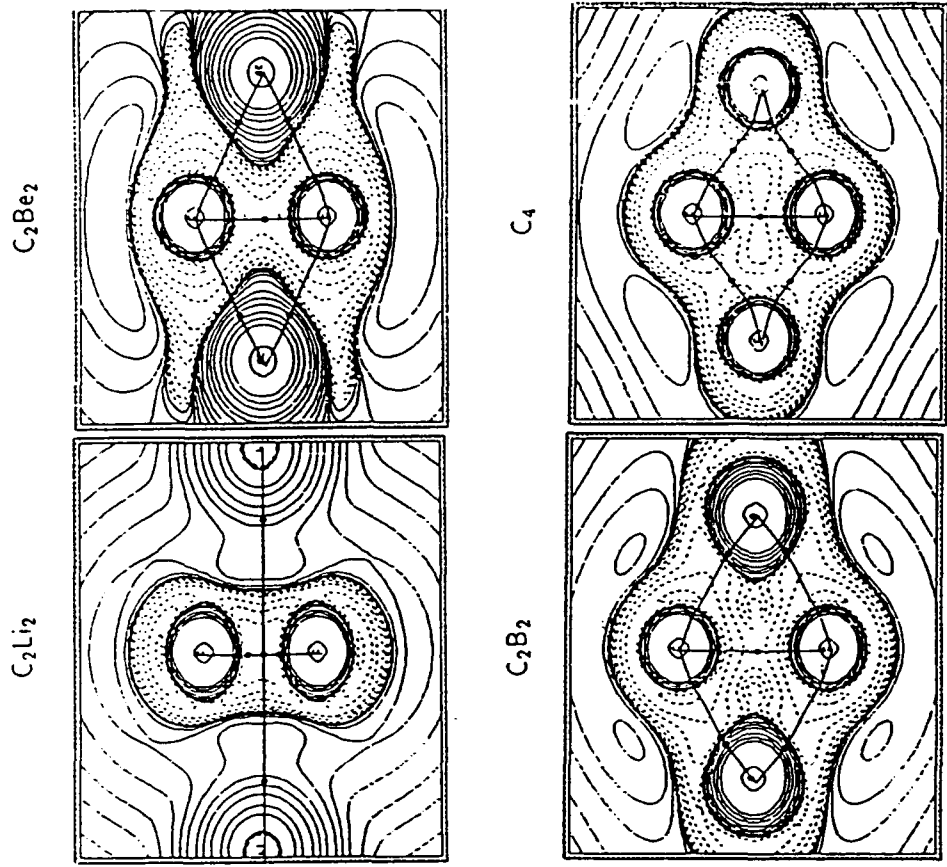


Figure 1. Gradient vector field and the Laplacian concentration of the HF/6-31G* charge density of C_2Li_2 , C_2Be_2 , C_2B_2 , and C_4 .

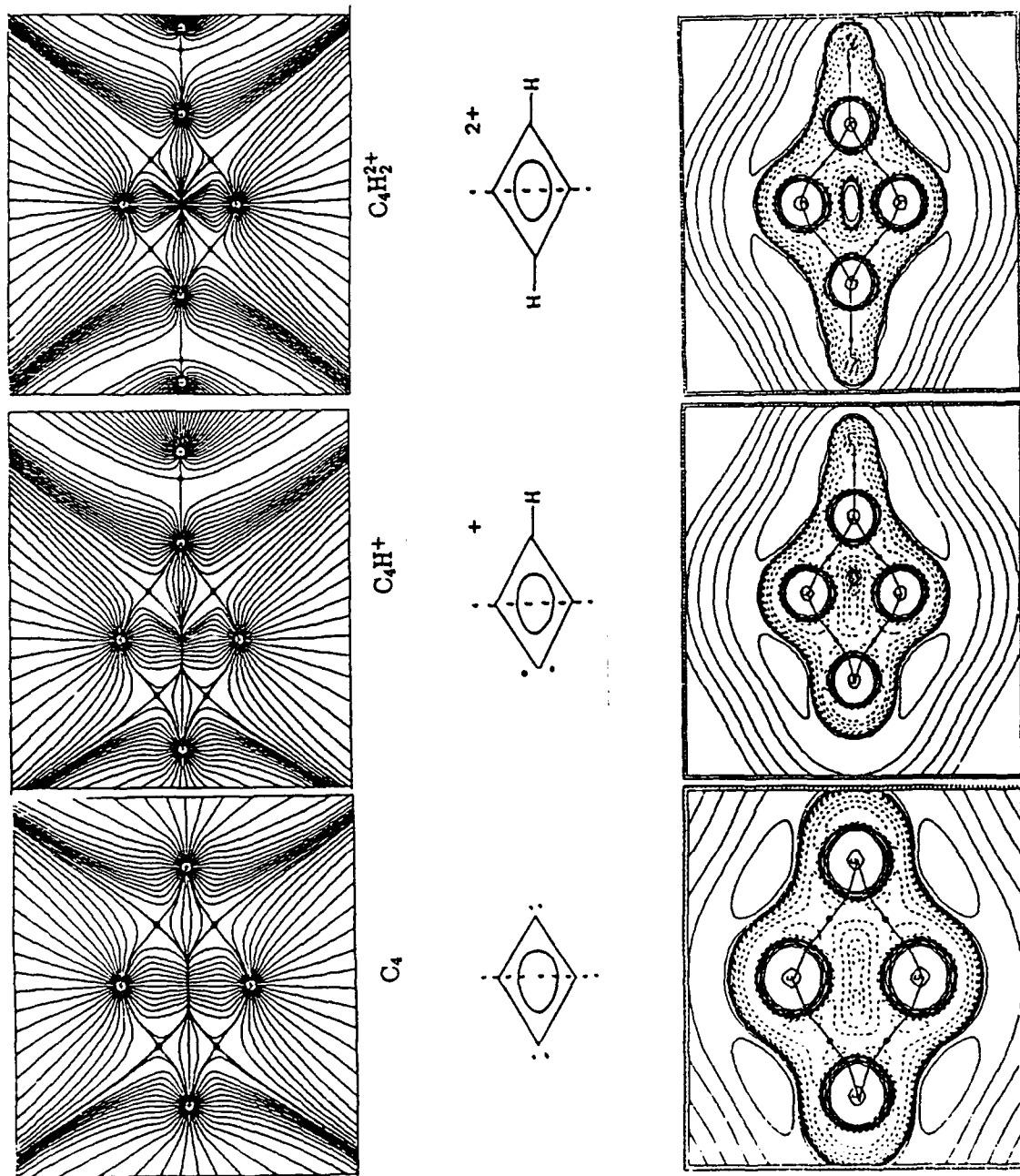


Figure 2. Gradient vector field and the Laplacian concentration of the HF/6-31G* charge density of C_4 (MP2), C_4H^+ , $C_4H_2^{2+}$

C₄ in more detail. Because of the crucial position of C₄ in the discussed series of rhombic dicarbides, we wanted to study its properties in more detail. As mentioned, it seems that at the HF/6-31G* level of theory the transannular C-C interaction changes from multiple C-C bonding in C₂Li₂ to no C-C bonding in C₄H₂²⁺. Because C₄ is the structure where this C-C bonding is lost (or formed), it seemed to us that an analysis of C₄ at higher levels of theory was desired. A brief summary of this study follows. The full analysis is given in a draft manuscript²⁰ in Appendix A.

The molecular orbital and topological electron density analysis of the MP2(Full)/6-31G* optimized rhombic C₄ structure shows that there is no transannular C-C bond despite the 1.523 Å separation between the inverted tricoordinate carbons. The peripheral bonds are short (1.451 Å, bond order = 1.15) due to strong surface (σ) and π -delocalization. This contrasts with [1.1.1]propellane, which at the same level of theory, does have bonding between the inverted tetracoordinate carbons which are separated by 1.592 Å.

Diborides. To demonstrate the difference in bonding behavior of diborides and dicarbides, we have analyzed the electron density properties of the planar rhombic forms of B₂Li₂, B₂Be₂, and B₄. Figure 3 displays the gradient vector field of their charge density in terms of the paths traced out by the vectors $\nabla\rho$ (left), while the contour maps of the Laplacian of their charge density overlaid with bond paths are given on the right hand side.

Some remarkable features are apparent. In the diborides the borons are bonded with two bond critical points (3,-1) located either on the same B-B bond path (separated by a pseudo atom) or on two separate B-B bond paths.

In the case of the covalent B₄ structure, the four ring B-B bond paths have two bond critical points each. The center of the molecule shows a depletion of charge with no bonding between the atoms (instead it is a (3,+1) ring critical point). The bonding pattern in planar B₂Be₂ is different. The two borons are bonded by two curved bond paths with an "electron density hole" (*i.e.*, a (3,+1) ring critical point) in the center. The molecule contains four conventional, although slightly polarized B-Be bonds. A combination of some of the B₄ and B₂Be₂ features is found in B₂Li₂. This cluster has two highly curved B-B bond paths, each containing two bond critical points. The center between the borons also contains a bond critical point which connects the "pseudo atoms" on the two B-B bond paths, to which also the two lithiums are bonded. This structure has no bonding at the circumference and is highly ionic.

Laplacian plots of Diborides

Molecular Graphs of Diborides at the Molecular Plane

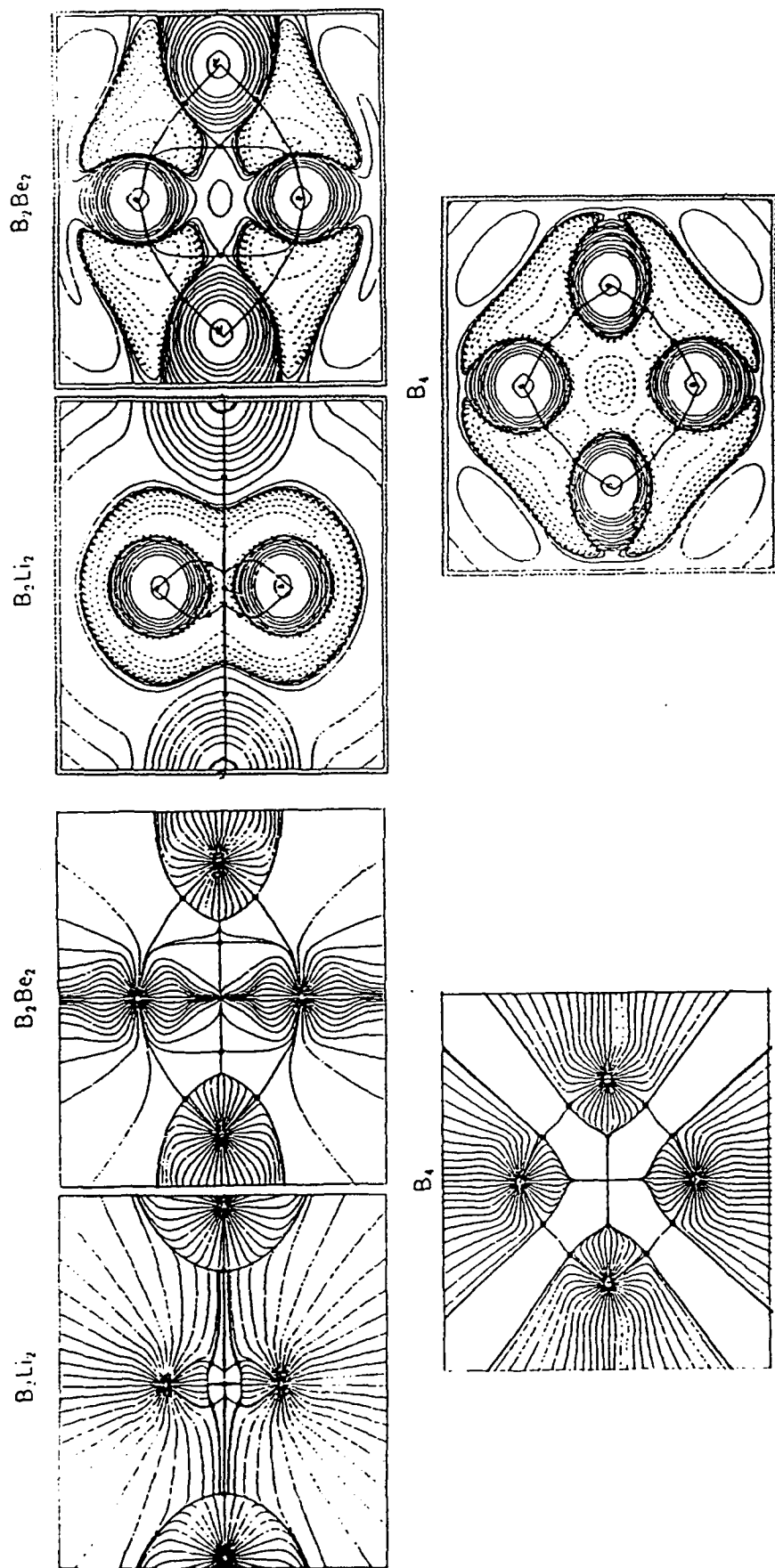


Figure 3. Gradient vector field and the Laplacian concentration of the HF/6-31G* charge density of B_2Li_2 , B_2Be_2 , and B_4 .

This analysis and the comparison with diborides makes clear that these tetraatomic diboride clusters have special bonding features, which were as of yet undiscovered. In our opinion we have just scratched the surface of the bonding features possible for boron based clusters. A more detailed study of B_2Be_2 and B_2Li_2 is given in section 2.5.2 and 2.5.3, respectively.

TETRAHEDRAL STRUCTURES

Light elemental clusters, like the tetraatomic Be_4 , may form tetrahedral structures (*vide infra*). Because several rhombic species were calculated to be transition structures we decided to evaluate tetrahedral diboride structures, which can also be considered as high density species. An incentive for this study was also provided by the fact that the above discussed rhombic structures are not necessarily the global minima. For example, linear triplets can be energetically competitive as in C_4 , C_4H^+ , and $C_4H_2^{2+}$, (all 16 valence electrons)⁶ and even be strongly preferred as in the 12 valence electron C_2Be_2 .¹⁸ The lighter 10 valence electron ionic dilithiodicarbide C_2Li_2 , however, has again a rhombic structure.²¹ Although, Li_4 is also a planar rhombic (in sharp contrast to H_4), a higher energy tetrahedral form is also feasible.

We calculated 24 tetrahedral-like diborides at the HF/6-31G* level of theory. Their geometries and energies are listed in Table 4. Of the 24 structures 9 are minima (B_2Li_2 , B_2Be_2 , and $B_2Be_2H^-$) and 16 are transition structures. This data shows that densely packed tetrahedral structures are preferred for certain light elemental combinations.

ESTIMATED SPECIFIC IMPULSES

Having established that rhombic carbon structures are of high energy, and having determined that indeed a large variety of tetraatomic rhombic and some tetrahedral clusters are minima (but not necessarily global minima) on the potential energy surface, a crude estimate of their specific impulses can be obtained with the following formula:

$$I_{sp} = 265 \times \sqrt{[(\text{heat of formation})/(\text{mol. weight})]}$$

The heat of formation is estimated from our ab initio calculated binding energy and the heats of formation of gaseous atoms from elements in their standard states. In Table 5 ab initio energies (MP4 and HF/6-31G*) of rhombic structures are used except for B_2Be_2 for which the more stable tetrahedral-like isomer was used (*vide infra*).

TABLE 4. Tetrahedral Diborides RHF/6-31G* Energies, NIMAG and Geometrical Data.

Structure X-B ₂ -Y	Energy	Nimag	Bond Distances			
			B—B	B—X	B—Y	X—Y
Li-(B ₂)-Li	-64.06043	0	1.548	2.252	2.252	3.504
Be-(B ₂)-Be	-78.37354	0	1.548	1.772	1.772	2.156
Be-(B ₂)-BeH	-79.01726	0	1.529	1.802	1.926	2.447
Be-(B ₂)-BH	-88.99520	1	1.520	1.764	1.653	2.131
Be-(B ₂)-CH	-101.87523	1	1.447	1.962	1.717	1.571
Be-(B ₂)-C:	-101.50896	1	1.484	2.102	1.511	1.557
Be-(B ₂)-AlH	-306.26094	1	1.544	1.766	2.049	2.554
Be-(B ₂)-Si:	-352.64423	1	1.524	1.763	1.993	2.569
BeH-(B ₂)-BH	-89.64323	2	1.531	1.903	1.625	2.226
BeH-(B ₂)-CH	-102.74791	2	1.525	2.173	1.480	1.852
BeH-(B ₂)-AlH	-306.90465	1	1.535	1.927	1.994	2.752
BH-(B ₂)-BH	-99.59929	2	1.567	1.656	1.656	1.908
BH-(B ₂)-CH	-112.51562	1	1.427	1.884	1.675	1.450
BH-(B ₂)-AlH	-316.87552	1	1.528	1.660	2.038	2.404
BH-(B ₂)-Si:	-363.24008	2	1.445	1.844	2.259	1.945
CH-(B ₂)-CH	-125.16082	1	1.447	1.716	1.716	1.340
CH-(B ₂)-C:	-125.00759	1	1.430	1.682	1.687	1.342
CH-(B ₂)-AlH	-329.75801	1	1.500	1.502	2.246	2.129
CH-(B ₂)-Si:	-376.15976	1	1.433	1.654	2.332	1.826
:C-(B ₂)-C:	-124.61891	2	1.407	1.750	1.750	1.383
:C-(B ₂)-AlH	-329.40172	1	1.488	1.516	2.405	1.814
AlH-(B ₂)-AlH	-534.14341	1	1.538	2.043	2.043	2.912
AlH-(B ₂)-Si:	-580.52553	1	1.526	2.040	1.997	2.823
:Si-(B ₂)-Si:	-626.90122	1	1.458	2.135	2.135	2.364

TABLE 5. Estimated I_{sp} values.^a

System	Binding Energy		Specific Impulse	
	(kcal/mol)		(sec)	
	MP4	HF	MP4	HF
B ₂ Li ₂	178.5	87.8	591	727
B ₂ Be ₂	195.4	122.7	646	738
C ₄	576.4	496.8	399	524
C ₂ Si ₂	379.0	415.5	396	354

These data confirm our supposition that rhombic structures indeed have large estimated I_{sp} values and that, as expected, they are largest for those systems that are composed of elements with the highest combustion energies. The data for B₂Li₂ and B₂Be₂ also demonstrate the significant influence of electron correlation in determining calculated binding energies. Therefore, the given I_{sp} values are only rough estimates, because of the direct relationship between the estimated magnitude of the specific impulse and the accuracy of the calculated binding energy.

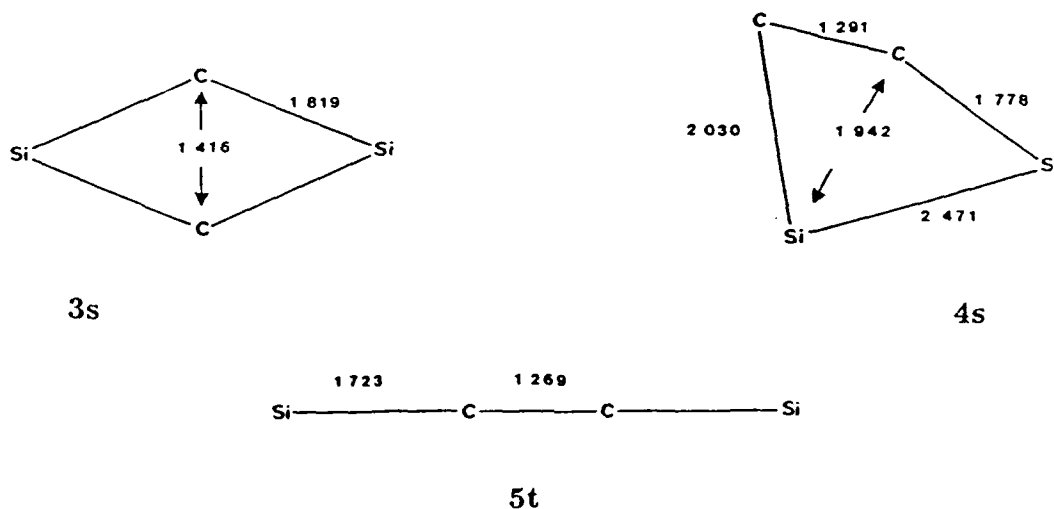
CLUSTER MOLECULES – Potential Energy Surfaces

In this section we elaborate in more detail the potential energy surfaces for a selected group of tetraatomics. Although we have demonstrated that most rhombic structure are viable species (minima), it is also apparent that they need not be the global minima. To further evaluate the potential of rhombic (or tetrahedral) species for consideration as high energy density systems, it is relevant to investigate more fully the structures of certain elemental combinations. We report here our analysis of C₂Si₂, B₂Be₂, B₂Li₂, and Li₃H, which cover a group of widely different species ranging from light to heavy elemental combinations.

Disilicondicarbide, Si₂C₂. Our first objective was to investigate a binary cluster for its structural, energetic, and electronic properties. As already noted, the 16 valence electron C₄ shows a slight preference for the rhombic over linear structure, which reverses on mono- and diprotonation to C₄H⁺ and to C₄H₂²⁺.⁶ In contrast, the related 16 electron Si₄ strongly favors a rhombic form,²² with its 20 electron tetraanion Si₄⁴⁻ fragment being tetrahedral.²³ It is well recognized that the bonding properties of silylenes differ significantly from those of the corresponding carbon compounds.³ It is then relevant to investigate the properties of a mixed cluster that contains both C and Si. We give here a very brief summary of our investigation of the potential energy surface for the C₂Si₂

system. A full description of this work has appeared in the literature²⁴ and is attached in appendix B.

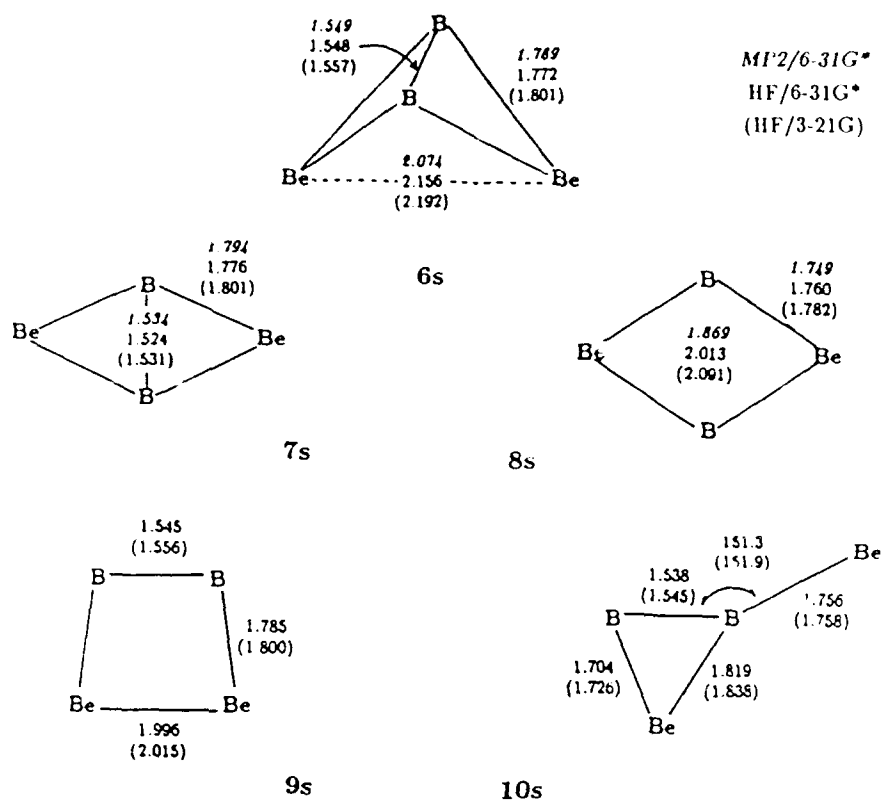
The structures and energies of the binary disilicon dicarbide C_2Si_2 in the lowest singlet (s) and triplet (t) states (14 isomers) were investigated by ab initio MO theory. Full fourth-order Møller-Plesset (MP4) perturbation theory was employed on seven HF/6-31G* optimized geometries. Rhombic dicarbide **3s** is the global minimum and 8.5 kcal/mol more stable than the rhomboidal structure **4s**, which contains an inverted tricoordinate carbon as well as an inverted tricoordinate silicon. Both cyclic structures are energetically favored over a linear triplet isomer **5t**. Whereas the relative energies are very sensitive to electron correlation effects, addition of diffuse functions (MP2 and HF/6-31+G*) has little influence.



This study shows that disilicon dicarbide has similarities with the related C_4 and Si_4 but also that it is inherently more complex; an important aspect of this will be emphasized in section 2.6. We note that there is an isoelectronic relationship between **3s** and the rhombic $Al_2Si_2^{2-}$ fragment in the $CaAl_2Si_2$ material,²⁵ which is representative for a large class of solid Zintl complexes.²⁶ The rhomboidal structure **4s**, with its mixed C/Si bonding, is also unique to binary clusters and similarly may well be an important structural type.

Diberylliumdiboride, B_2Be_2 . This 10 valence electron species is composed of the two elements with the highest combustion energies. Because of its anticipated importance as a high energy material, B_2Be_2 was subjected to a full (singlet *s* and triplet *t*) potential energy surface study to characterize its global minimum, to determine its stability, and to investigate its binding energies and properties. Because of its smaller difference in elemental electron negativities than that in the isoelectronic dilithium dicarbide (C_2Li_2 has a preferred (6°) puckered rhombic structure)²¹ and the 12 val. el. diberyllium dicarbide C_2Be_2 ,¹⁸ the properties of B_2Be_2 were expected to deviate from C_2Li_2 , C_2Be_2 , and other tetraatomics. Beryllium borides are known since the turn of the century with crystal structures (powder patterns) reported for BBe_6 , BBe_3 , BBe_2 , B_2Be , B_4Be , B_6Be , B_8Be , $B_{10}Be$, and $B_{12}Be$ with the noticable exception of B_2Be_2 .²⁷ Here we give here a very brief summary of our study of the B_2Be_2 system. A full analysis is given in Appendix C and is to appear in the literature.²⁸

The ab initio molecular orbital study of the 10 val. el. diberyllium diboride (B_2Be_2) potential energy hypersurface yields a singlet tetrahedrallike form **6s** as the global minimum at the HF and MP2/6-31G* levels of theory. At MP4/6-31G* the energy difference of **6s** with any other isomer is at least 30 kcal/mol; (high spin-contamination in triplet structures was annihilated). The topological electron density analysis, based on the theory of atoms in molecules, shows **6s** to have its Be atoms polar π -complexed to the B-B bond with an angle of 80.1° between the π planes; despite the short 2.156 Å Be-Be distance, there is no Be-Be bond. The inversion barrier ($6s \rightleftharpoons 7s \rightleftharpoons 6s$) amounts to 11.7 kcal/mol at MP4/6-31G* + ZPE and 14.6 kcal/mol at MP2/6-311G(df) + ZPE. The D_{2h} structures **7s** and **8s** are related by means of "bond-stretch" isomerism. The electron density analysis shows that the electron density is concentrated in the center of structures **7s** whereas **8s** shows a depletion of electron density in the center as compared to the periphery of this rhombic structure. The trapezoidal **9s** and the Be-substituted B_2Be ring **10s** are discussed for their structural and electronic properties. All B_2Be_2 structures show short B-B bonds (i.e., 1.549 Å for **6s**, MP2/6-31G*) with the exception of **8s** (1.869 Å, MP2/6-31G*). The effects of electron correlation on relative energies and binding energies is significant. The binding energy of the four elements in **6s** is 204 kcal/mol and that of one beryllium in **6s** is 76 kcal/mol (all MP4/6-31G*). A calculated specific impuls for **6s** is given in section 2.4.



From this study we infer that the nature of bonding (covalent and ionic complexation) is an important aspect for the formation of large clusters that may form molecular solids. This supports the finding of Dr. Brener's at the Louisiana State University that larger clusters (molecular solids) of the tetrahedral B_2Be_2 unit cell are favorable.^{2b}

Dilithiodiboride, B_2Li_2 . Both finely dispersed Li and boron compounds are known to boost the performance of rocket fuels. Therefore, our next step was to investigate the properties of the even lighter tetraatomic system, the 8 val. el dilithio diboride B_2Li_2 .

An ab initio molecular orbital study was performed on the B_2Li_2 singlet and triplet potential energy hypersurface. The singlet rhombic form 11s is the global minimum at the HF and MP4/6-31+G* levels of theory of the 10 isomers investigated. Figure 4 displays the HF/6-31G* optimized structures. At the correlated level this isomer is favored by 8.3 kcal/mol over the tetrahedral isomer and by at least 20 kcal/mol more than any other isomer. However, the data listed in Table 6 show a rather strong oscillation between the MP2, MP3, and MP4 relative energies for 11s and 12s, indicating that probably a multireference wave function is required for determination of accurate energies. The effects of electron correlation on all relative energies is very significant as graphically shown in Figure 5. A calculated specific impuls for 11s is given in section 2.4.

TABLE 6. Total (au) and Relative (kcal/mole) Energies of Li_2B_2 Isomers

Structure	HF/6-31G*	Rel. En.	NIMAG	$\langle s^2 \rangle$	MP4/6-31G*	Rel. En.
11s	-64.04676	0.0	(0)		-64.30754	0.0
11t	-64.05044	-2.3	(0)	2.03	-64.25693	31.8
12s	-64.06043	-8.6	(0)		-64.29335	8.9
12t	-64.08114	-21.6	(1)	2.25	-64.26819	24.7
13s	-64.05724	-6.6	(0)		-64.24349	40.3
13t	-64.03463	7.6	(2)	2.03	-64.23644	44.6
14s	-64.01299	21.2	(2)		-64.24051	42.1
15t	-64.07447	-17.4	(0)	2.21	-64.25147	35.2
16t	-64.08134	-21.7	(0)	2.05	-64.26682	25.6
17t	-64.06390	-10.8	(1)	2.05	-64.25268	34.4

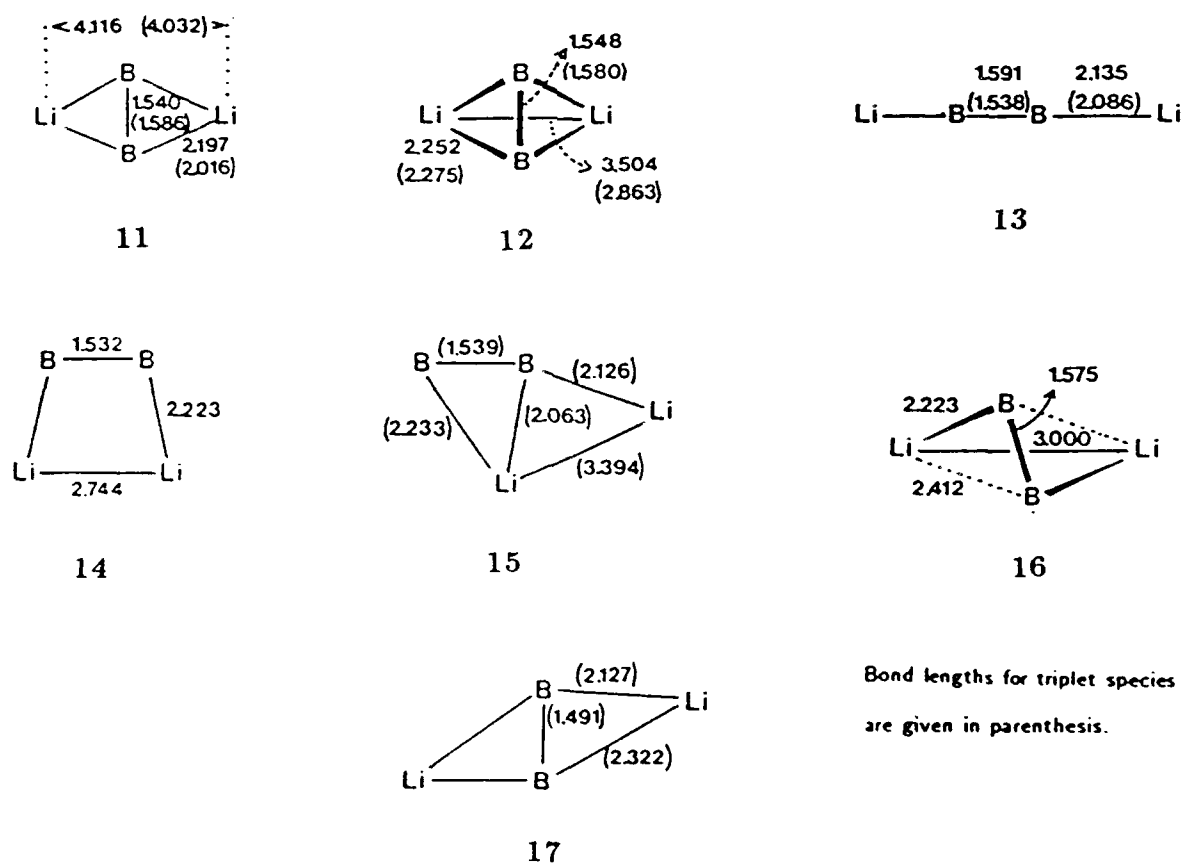


Figure 4. HF/6-31G* geometries of B_2Li_2 isomers.

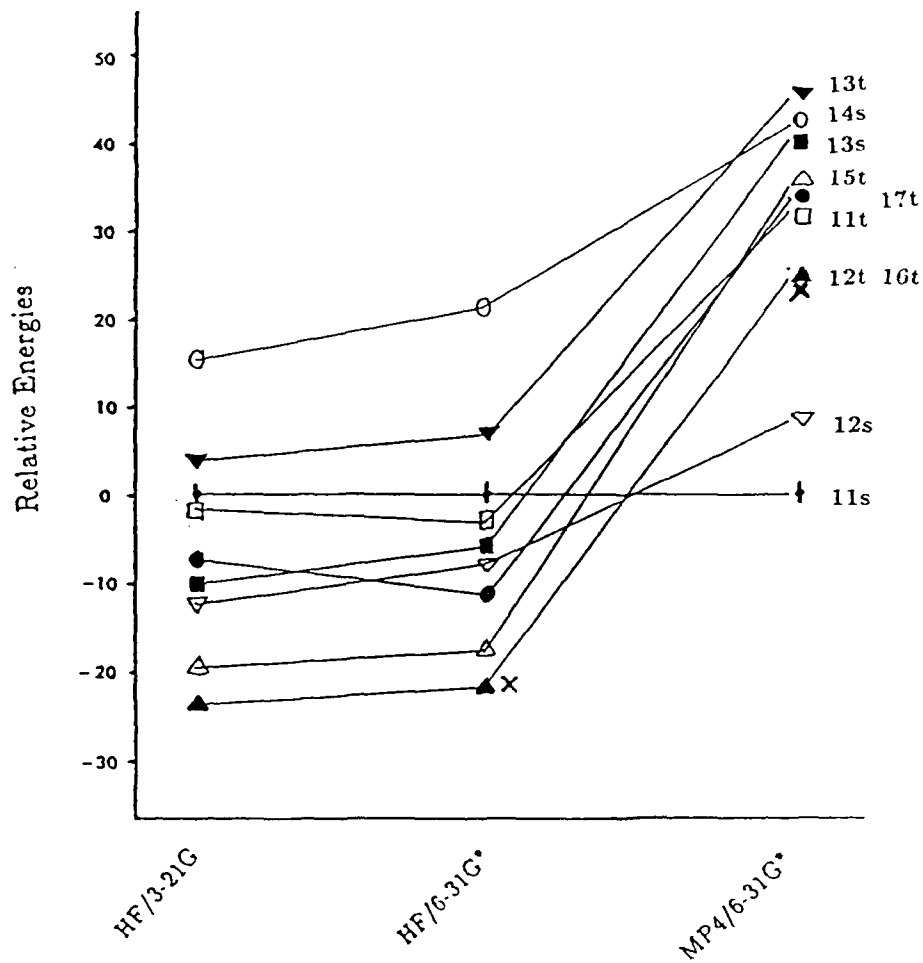


Figure 5. Plot of relative B₂Li₂ energies basis set.

The topological electron density analysis for the rhombic B_2Li_2 structure shows that the Li atoms complex ionically to the B_2 -unit. This is evident from the gradient vector field and the Laplacian of ρ , which are displayed in Figure 6. The molecular graph for **11s**, also displayed in Figure 6, shows a complex topology. This probably results from the use of a limited basis set (MP2/6-31+G*) to describe the electron density properties of the electron-rich B_2^{2-} group. The bond properties for **11s** and **12s** are listed in Table 7.

The Li_3H Ion-Pair This study was performed in collaboration with J.A. Montgomery and H.H. Michels of United Technology Research Center. Our interest in this 4 val. el. system relates to the chemistry of small clusters and ion-pair states. A full analysis of our study, which has appeared in the literature,³⁰ is given in Appendix D. A brief abstract of the work follows.

Ab initio calculations on Li_3H ion-pair states and a topological analysis of the charge density of the resulting optimized structures are reported. The global Li_3H minimum is a planar C_{2v} structure with $H-Li_3^+$ ion-pair character. The pyramidal C_{3v} structure, which is 21.5 kcal/mol higher in energy (MP2/6-311++G**), is found to have ionic H-Li bonds, but no Li-Li bonds. Although vibrational analysis indicates this structure to be a true minimum on the potential energy surface, inclusion of the vibrational zero-point energy makes the thermodynamic stability of this structure questionable.

BOND-STRETCH ISOMERISM

In the course of this work we determined that many tetraatomic systems may have the properties of bond-stretch isomerism. We resorted to the C_2Si_2 and B_2Be_2 systems to analyze this phenomenon in more detail and to establish its value in small cluster molecules. The properties of the B_2Be_2 system have been fully analyzed in the already discussed B_2Be_2 potential energy surface study that is given in Appendix C.²⁸ The study of the bond stretch isomerism in C_2Si_2 is discussed separately in full detail in Appendix E. A brief abstract of this published research³¹ follows.

The differences in bonding and electronic properties between the MP2/6-31G* optimized disilicon dicarbide structures **3** and **18** can be related to bond stretch isomerism, which occurs through a level-crossing mechanism. Their energy differences are calculated to be 78.4 at the MP4 and 91.4 kcal/mol at GVB/6-31G*. Because of the symmetry forbidden transformation no barrier for this process was calculated. Electron density analysis indicates concentration of charge in the center of rhombic structure **3** with some multiple bonding character between its transannular carbons. In contrast, the higher energy isomer

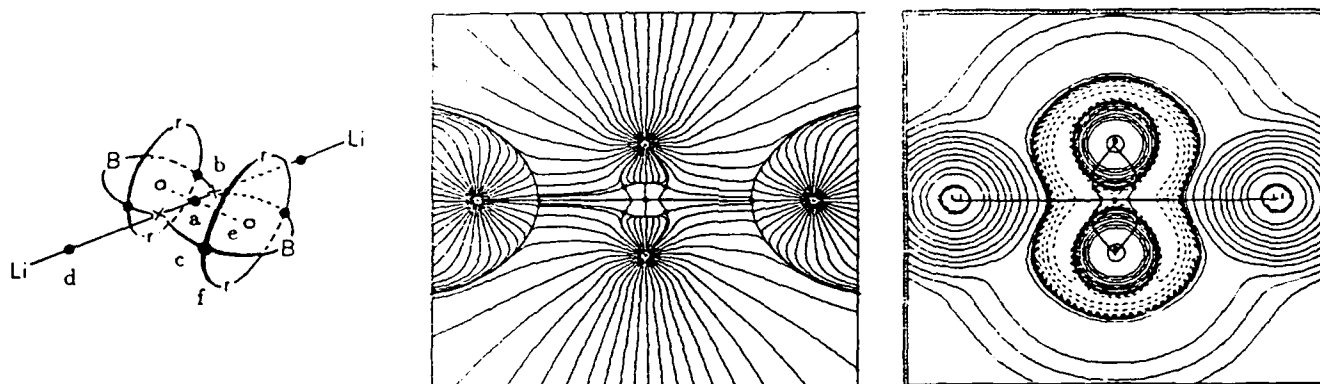
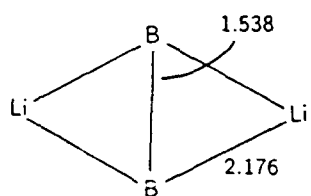
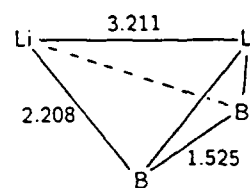


Figure 6. Molecular graph, gradient vector field, and the Laplacian concentration of the MP2/6-31+G* charge density of B₂Li₂ (11s).



11s

MP2/6-31+G* D_{2h}

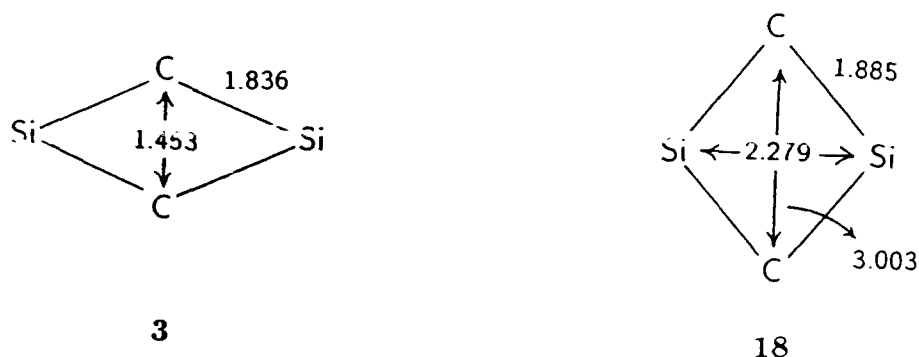


12s

MP2/6-31+G* $\angle\alpha=101.6$

TABLE 7. MP2/6-31+G* Bond Properties for 11s and 12s

Struct./Crit.Pt.	Type	λ_1	λ_2	λ_3	ϵ	dir	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$H(\mathbf{r})$	
11s	a	[3,-1]	-1.21	-0.40	0.32	2.09	\perp	0.73	-1.28	-0.60
	b	[3,-3]	-0.67	-0.64	-0.58	0.04	\parallel	0.73	-1.89	-0.57
	c	[3,-1]	-1.90	-0.65	0.67	1.94	\perp	0.73	-1.88	-0.61
	d	[3,-1]	-0.80	-0.43	4.66	0.87	\parallel	0.21	3.43	0.02
	e	[3,+3]	0.28	1.10	5.33	-	-	0.71	6.70	-0.56
	f	[3,+1]	-1.55	0.76	3.20	-	-	0.71	3.41	-0.59
12s	a	[3,-3]	-5.87	-3.10	-0.33	0.89	\perp	1.09	-9.29	-0.95
	b	[3,-1]	-6.35	-3.05	2.92	1.08	\perp	1.08	-6.48	-1.13
	c	[3,-1]	-0.65	-0.23	3.63	1.80	\perp	0.18	2.75	0.01



18 has a depletion of charge in the center relative to the circumference of the rhombic structure.

HYDROGENATED TETRAATOMICS

Another question we addressed concerns the effect of hydrogen substitution on small inorganic clusters. In contrast to the extensive literature on carbon systems, very little is known about the related inorganic systems. In light of the special bonding characteristics associated with B_2Be_2 (section 2.5.2) we decided to investigate the effect of its hydrogenation. Since boranes are energetic materials and because little is known about alanes we also explored Al_2H_6 . The latter research is a first step to a closer investigation of rhombic and tetrahedral diborides with bridging aluminum ligands.

Hydrogenated Diberyllium Diboride, $B_2Be_2H_2$. An ab initio molecular orbital study was performed on the $B_2Be_2H_2$ singlet potential energy hypersurface. Structure 19 is the global minimum of the eight isomers analyzed. These eight HF/6-31G* optimized $B_2Be_2H_2$ structures are shown under Table 8 that lists their total and relative energies at the HF and MP4/6-31G* levels. At the correlated level 19 is energetically favored by at least 14 kcal/mol over any other isomer. It is also evident that the effect of electron correlation is much less pronounced than was the case in the hydrogen-void B_2Be_2 system. However, the geometries and the data listed in Table 8 also indicate special properties related to the hydrogenation of tetrahedral/rhombic B_2Be_2 . For example, the energy difference between hydrogenation on the borons versus hydrogenation on beryllium (which formally become tricoordinate) amounts to only 15 kcal/mol.

It appears that hydrogenation of B_2Be_2 is preferred on both borons followed by hydrogenation on the two berylliums. The global minimum 19 can be regarded as a diborane(2)

complexed with two beryllium atoms. Consequently, structure **19** would also be a very energetic system. We anticipate that similar to the tetrahedral-like B_2Be_2 isomer also **19** will not contain Be-Be bonding (despite the 1.886 Å separation) but instead will have its berylliums complexed to the center of the 1.764 Å B-B bond. The 'second best' structure is ca. 15 kcal/mol less stable than **19** and contains a 1.5 Å short B-B bond with bridging Be-H groups in either a planar (**22**) or 'butterfly' (**21**) orientation; the nature of the stationary point must be determined at correlated levels. Clearly, the bonding characteristics of this system warrant further investigation.

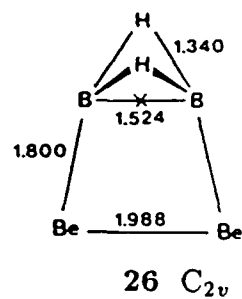
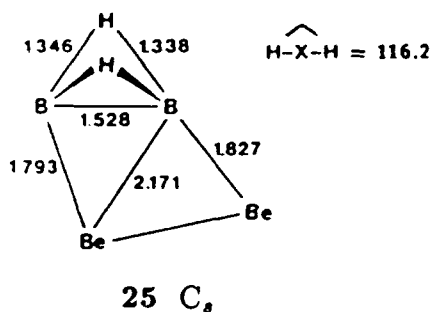
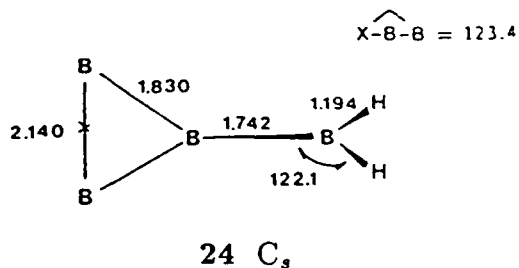
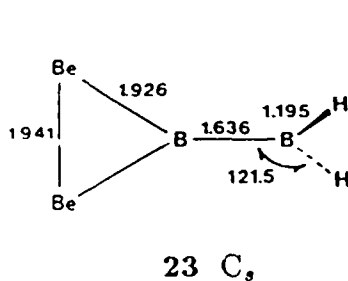
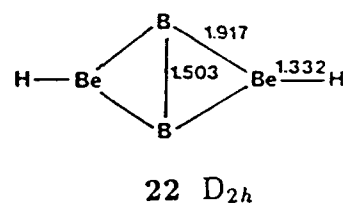
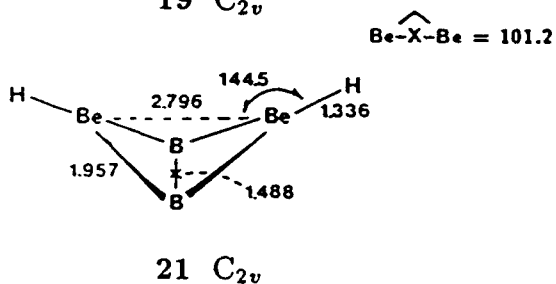
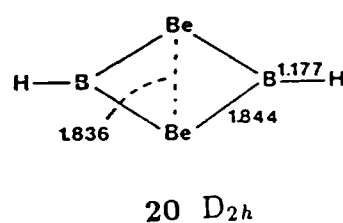
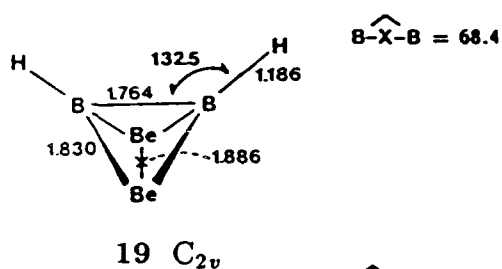
Dialane(6), Al_2H_6 , and Digallane(4), Ga_2H_4 . In contrast to the vast amount of literature on small boranes, carbon, and silicon molecules, only very little is known on small aluminum based molecules. Since aluminum, for a second row element, has a rather high combustion energy and because of its likely suitability (as boron) to form high density materials, we decided to investigate the experimentally still elusive dialane(6). An additional incentive for this study was the recent experimental observation of digallane(6).³² Therefore, a theoretical study on Al_2H_6 and Ga_2H_6 would enable us to calibrate the ab initio data against experimental Ga_2H_6 values as well as to determine the binding energy and bonding properties of Al_2H_6 . Since we recently reported on dialane(4) Al_2H_4 ,³³ it was also decided to study Ga_2H_4 with the intention to further calibrate hydrogenated group III elements. This research is considered to be a necessary first step for closer inspection of rhombic and tetrahedral systems that contain aluminum ligands. A brief summary of our studies on Al_2H_6/Ga_2H_6 ³⁴ and Ga_2H_4 ³⁵ follows. The full analysis of these systems is given in Appendix F and G, respectively, which are to appear in the literature.

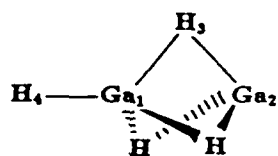
The structure, harmonic frequencies, and binding energies of dialane(6) and digallane(6) are calculated with ab initio MO theory. Excellent agreement is found with IR spectroscopic data on Ga_2H_6 . The binding energy for Al_2H_6 is 31.5 kcal/mol at MP4/6-31G** and for Ga_2H_6 a value of 23.4 kcal/mol is obtained with a Huzinaga valence triple ζ basis set after correction for ZPE and electron correlation effects at MP4.

The potential energy surface of digallane(4) Ga_2H_4 has been studied by ab initio molecular orbital theory at the MP2 level using a Huzinaga valence triply ζ basis set supplemented with d-polarization functions. Six of the eight HF/3-21G* optimized structures were characterized as minima. Their bonding properties were studied by a topological electron density analysis. Of the ionic, covalent, and μ -hydrido bridged species the tri- and bidentate $Ga^+[GaH_4]^-$ forms **27** and **28**, respectively, are the most stable isomers. However, the energy differences with the other isomers are less than 15 kcal/mol. The

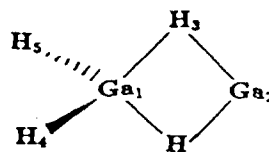
TABLE 8. Total (au) and Relative (kcal/mole) Energies of B₂Be₂H₂ Isomers.

Structure	Tot. En.	Rel. En.	NIMAG	Tot. En.	Rel. En.
19 C _{2v}	-79.62424	0.0	(0)	-79.93443	0.0
20 D _{2h}	-79.56060	39.9	(0)	-79.89878	22.4
21 C _{2v}	-79.59930	15.7	(0)	-79.91033	15.1
22 D _{2h}	-79.58958	21.8	(1)	-79.91144	14.4
23 C _s	-79.58598	24.0	(0)	-79.85155	52.0
24 C _s	-79.55500	43.5	(1)	-79.84456	56.4
25 C _s	-79.53958	53.0	(0)	-79.83565	62.0
26 C _{2v}	-79.53812	54.0	(1)	-79.83335	63.4

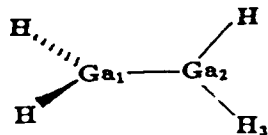




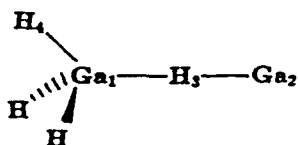
27 C_{3v}



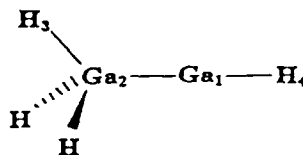
28 C_{2v}



29 D_{2d}



30 C_{3v}



31 C_{3v}

The potential energy surface of digallane(4) Ga_2H_4 has been studied by ab initio molecular orbital theory at the MP2 level using a Huzinaga valence triply ζ basis set supplemented with d-polarization functions. Six of the eight HF/3-21G* optimized structures were characterized as minima. Their bonding properties were studied by a topological electron density analysis. Of the ionic, covalent, and μ -hydrido bridged species the tri- and bidentate $Ga^+[GaH_4]^-$ forms 27 and 28, respectively, are the most stable isomers. However, the energy differences with the other isomers are less than 15 kcal/mol. The covalent D_{2d} isomer 29 is 3.5 kcal/mol less stable than 27. The head and tail complexes of $:GaH$ with GaH_3 (30 and 31), which are of similar energy, are ca. 13 kcal/mol higher in energy than 29. The potential energy surface of Ga_2H_4 is similar to that of Al_2H_4 but differences are noted.

CONCLUSIONS AND RECOMMENDATIONS

The main conclusions from our general survey on small cluster molecules (ca 60) and from our studies on seven selected systems are as follows:

The ab initio molecular orbital study on tetraatomic systems has shown that 24 of the 25 investigated rhombic dicarbides and 21 of 28 studied rhombic diborides are local or global minima on the potential energy structures. This confirms the general viability of rhombic clusters composed of the elements H, Li, Be, B, C, Al, and Si. We found that only the rhombic, tetrahedral, and (triplet) linear structures compete for the global minima. Only 3 tetrahedral (light) diboride clusters out of 24 combinations are equilibrium structures. We have also demonstrated the high energy content in these rhombic and tetrahedral clusters, which are composed of high combustion light elements. The most energetic systems investigated (MP4/6-31G**//MP2/6-31G*) are B_2Li_2 and B_2Be_2 . They have the highest estimated I_{sp} values (591 seconds and 646 seconds, resp.).

The general survey study also establishes that the bonding character between the bridgehead atoms (B or C) in rhombic and tetrahedral structures varies widely (*i.e.*, from double bonding to no bonding) and depends on the nature (electronegativity) of the bridging ligands. For example, rhombic C_4 has no transannular bonding, but C_2Be_2 has strong C-C bonding as does C_2Si_2 . Similarly B_4H_2 has no transannular bonding, but in B_2Li_2 there is a multiple B-B bond.

The potential energy surface studies on B_2Li_2 , B_2Be_2 , Li_3H , and C_2Si_2 demonstrate an extreme sensitivity of these tetraatomics to the effects of electron correlation.

Bond-stretch isomerism is a likely mechanism for energy storage and is common to the frame of rhombic tetraatomics as demonstrated in B_2Be_2 and C_2Si_2 . Such isomers have large energy differences and are separated by level crossing mechanisms, implying that the high energy isomers lie in deep potential wells.

To study the structural, energetic, and electronic properties of small clusters, composed of light elements, the total electron density of such systems must be analyzed in combination with standard ab initio molecular orbital analysis.

The main recommendations from this research toward high energy density materials are:

- (a). Higher levels of theory are required as well as a mapping of all dissociation modes for the light elemental clusters (H, Li, B, and Be) to obtain kinetic and thermodynamic data of enough accuracy to predict reliable I_{sp} values.
- (b). More work is required to predict the stabilities and properties of small clusters in conventional fuel systems.
- (c). An in-depth study of the scope of bond-stretch isomerism is needed both to evaluate its potential as an energy promoting mechanism and to find practical systems that serve as energy storage devices.

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APPENDIX A
PUBLICATIONS

The significant research results obtained under this contract have been prepared for publication in technical journals. These papers are listed below. All of these papers can be found in the open literature.

Technical Reports in Journals:

1. "Structures and Energies of Disiliciumdicarbide, C_2Si_2 ". K. Lammertsma and O.F. Guner. J. Am. Chem. Soc. 110, 5239-5245(1988).
2. "Bond Stretch Isomerism in Rhombic C_2Si_2 ". K. Lammertsma and O.F. Guner. J. Phys. Chem. 8, 7289-7292(1989).
3. "The Structure and Bonding of Li_3H Ion-Pair States". J.A. Montgomery, Jr., H.H. Michels, O.F. Guner and K. Lammertsma. Chemical Physics Letters 161, 291-295 (1989).
4. "Structural and Electronic Properties of the Tetra-atomic B_2Be_2 Cluster". K. Lammertsma and O.F. Guner. J. Am. Chem. Soc. 112, 508-516(1990).
5. Ab Initio Study on Dialane(6) and Digallane(6)". K. Lammertsma and J. Leszczynski. J. Phys. Chem. 94, 2806-2809(1990).
6. "Rhombic C_4 : Does it Contain the Shortest Non-bonding C-C Distance". K. Lammertsma, O.F. Guner, and P.V. Sudhakar. To be submitted to J. Am. Chem. Soc., 1990.