rically equivalent. On this basis we would predict barriers of 5 kcal/mol for both the cyclohexyl and 1-hydroxycyclohexyl radicals, if the inversion pathway does not involve higher energy conformers, and at least 6.4 kcal/mol if the boat is an intermediate between chair and twist-boat. In either case we do not agree with the proposal that the 1-hydroxycyclohexyl radical has the twist-boat form as the most stable conformation.[3]

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Molecular Orbital Study of Tetrahedral, Planar, and Pyramidal Structures of the Isoelectronic Series BH_4^-, CH_4, NH_4^+, AlH_4^-, SiH_4, and PH_4^+

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Abstract: Eight valence electron ZH_4 systems strongly prefer tetrahedral geometry. Alternative geometries, square planar (D_{4h}) and pyramidal (C_{4v}), were investigated in detail theoretically; electronic structures reveal how substituents might stabilize these forms preferentially. With the possible exception of BH_4^-, all ZH_4 planar (D_{4h}) and pyramidal (C_{4v}) species studied prefer singlet to triplet states. For the planar forms, two alternative singlet lumomers compete. CH_4 and NH_4^+ (both D_{4h}) prefer HOMOs of $\pi(a_{2u})$ symmetry because of the greater electronegativity of the central atom. σ-Donor, π-acceptor substituents should stabilize these forms. Planar BH_4^-, AlH_4^-, SiH_4, and PH_4^+ prefer HOMOs with $\delta(b_{1g})$ symmetry because of the lower central atom electronegativity, the longer Z-H bonds, and, for the second-row species, the participation of d orbitals. π-Acceptor, σ-donor substituents should stabilize these forms. Pyramidal (C_{4v}) singlet ($^1A_1$) structures are preferred over planar singlets for CH_4, NH_4^+, and PH_4^+. The electron density is more evenly distributed upon pyramidalization; this is favored when Z is less electronegative. AlH_4^-, of all the species investigated, is indicated to require the least amount of energy to achieve planarity; SiH_4 is next best. Planarity is least favorable for CH_4. These results indicate how much inherent energetic opposition must be overcome in order to achieve planar or pyramidal structures.

Introduction

Eight valence electron ZH_4 molecules prefer to be tetrahedral.[2] Alternative geometries are very unstable. Planar methane, for example, not only is calculated to be more than 150 kcal/mol higher in energy than the tetrahedral form,[3a] but also to be unstable toward dissociation. Planar NH_4^+ [3a,4a] and nontetrahedral D_{4h} and C_{4v} forms of SiH_4[4b,c] are similarly indicated to be only somewhat more favorable in these respects. The energy difference between planar and tetrahedral tetracoordinate carbon and silicon compounds can, however, be reduced significantly through substitution.[3,4c,d] Molecules which prefer planar geometries have been demonstrated,[3c] claimed,[4c] or suggested.[3a,b,4d]

In this paper we extend our investigation to include the entire set of isoelectronic ZH_4 species: BH_4^-, CH_4, NH_4^+, AlH_4^-, SiH_4, and PH_4^+. Using ab initio molecular orbital theory,[5] the structures and energies of tetrahedral (T_d), planar (D_{4h}), and pyramidal (C_{4v}) forms have been studied at uniform levels of approximation. The results reveal significant quantitative and qualitative differences among these species. Variations in the electronic structure have important implications for choice of substituents which might be used to help attain unusual geometries.

Computational Method

The structure of the first-row hydrides, BH_4^-, CH_4, and NH_4^+, were optimized using the 6-31G* basis set[6] (a split-valence basis including d-type polarization functions on the heavy atom). For the second-row hydrides, AlH_4^-, SiH_4, and PH_4^+, geometry optimizations were carried out with the STO-3G* basis set,[7] a minimal basis augmented by a set of d orbitals on the second-row atom. Singlets were calculated using the restricted Hartree-Fock method.[8a] The unrestricted Hartree-Fock (UHF) method[8b] was used for triplets. Estimates of correlation energy were made using second-order Møller-Plesset theory (MP2).[9] Results are designated thus: MP2/6-31G*//6-31G* (this indicates a single-point MP2/6-31G* calculation carried out on the 6-31G* optimized geometry). Mulliken population analyses[10] employed STO-3G[11] wave functions with STO-3G optimum geometries.

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Table I. Calculated Total Energies, *E* (hartrees), and Relative Energies, Δ*E* (kcal/mol), for the First-Row ZH_4 molecules

molecule	symmetry	valence electronic configuration	state	STO-3G//STO-3G		6-31G*//6-31G*		MP2/6-31G*//6-31G*	
				E	Δ*E*	*E*	Δ*E*	*E*	Δ*E*
BH_4^-	T_d	$2a_1^2 1t_2^6$	$^1A_1$	−26.553 47	0.0	−26.965 10	0.0	−27.071 30	0.0
	C_{4v}	$2a_1^2 1e^4 1b_1^1 3a_1^1$	$^3B_1$	−26.247 25	192.1	−26.768 84	123.2	−26.868 78	127.1
	D_{4h}	$2a_{1g}^2 1e_u^4 1b_{1g}^1 1a_{2u}^1$	$^3B_{2u}$	−26.240 57	196.3	−26.765 53	125.2	−26.867 97	127.6
	C_{4v}	$2a_1^2 1e^4 3a_1^2$	$^1A_1$	−26.145 41	256.1	−26.726 99	149.4	−26.853 34	136.8
	D_{4h}	$2a_{1g}^2 1e_u^4 1b_{1g}^2$	$^1A_{1g}(\delta)$	−26.215 10	212.3	−26.752 63	133.3	−26.848 06	140.1
	D_{4h}	$2a_{1g}^2 1e_u^4 3a_{2u}^2$	$^1A_{1g}(\pi)$	−26.038 94	322.9	−26.646 65	199.8	−26.784 99	179.7
CH_4	T_d	$2a_1^2 1t_2^6$	$^1A_1$	−39.726 86	0.0	−40.195 17	0.0	−40.336 95	0.0
	C_{4v}	$2a_1^2 1e^4 3a_1^2$	$^1A_1$	−39.398 46	206.1	−39.962 77	145.8	−40.118 68	137.0
	D_{4h}	$2a_{1g}^2 1e_u^4 3a_{2u}^2$	$^1A_{1g}(\pi)$	−39.344 41	240.0	−39.922 45	171.1	−40.082 37	159.7
	D_{4h}	$2a_{1g}^2 1e_u^4 1b_{1g}^1 3a_{2u}^1$	$^3B_{2u}$	−39.399 90	205.2	−39.938 17	161.3	−40.067 52	169.1
	D_{4h}	$2a_{1g}^2 1e_u^4 1b_{1g}^2$	$^1A_{1g}(\delta)$	−39.194 75	333.9	−39.781 54	259.6	−39.911 76	266.8
NH_4^+	T_d	$2a_1^2 1t_2^6$	$^1A_1$	−55.868 85	0.0	−56.530 77	0.0	−56.702 80	0.0
	C_{4v}	$2a_1^2 1e^4 3a_1^2$	$^1A_1$	−55.613 07	160.5	−56.331 84	124.8	−56.512 98	119.1
	D_{4h}	$2a_{1g}^2 1e_u^4 3a_{2u}^2$	$^1A_{1g}(\pi)$	−55.605 35	165.3	−56.319 24	132.7	−56.502 02	126.0
	D_{4h}	$2a_{1g}^2 1e_u^4 3a_{2u}^1 1b_{1g}^1$	$^3B_{2u}$	−55.493 63	235.4	−56.190 52	213.5	−56.344 04	225.1

Table II. Calculated Total Energies, *E* (hartress), and Relative Energies, Δ*E* (kcal/mol), for the Second-Row ZH_4 Molecules

molecule	symmetry	valence electronic configuration	state	STO-3G//STO-3G		STO-3G*//STO-3G*	
				E	Δ*E*	*E*	Δ*E*
AlH_4^-	T_d	$3a_1^2 2t_2^6$	$^1A_1$	−241.167 32	0.0	−241.208 58	0.0
	D_{4h}	$3a_{1g}^2 2e_u^4 1b_{1g}^2$	$^1A_{1g}(\delta)$	−241.015 98	95.0	−241.087 00	76.3
	C_{4v}	$3a_1^2 2e^4 1b_1^1 4a_1^1$	$^3B_1$	−240.894 93	170.9	−240.937 13	170.3
	D_{4h}	$3a_{1g}^2 2e_u^4 1b_{1g}^1 2a_{2u}^1$	$^3B_{2u}$	−240.828 81	212.4	−240.853 75	222.7
	C_{4v}	$3a_1^2 2e^4 4a_1^2$	$^1A_1$	−240.783 06	241.1	−240.825 73	240.2
SiH_4	T_d	$3a_1^2 2t_2^6$	$^1A_1$	−287.917 38	0.0	−287.971 86	0.0
	D_{4h}	$3a_{1g}^2 2e_u^4 1b_{1g}^2$	$^1A_{1g}(\delta)$	−287.674 72	152.2	−287.789 99	114.1
	C_{4v}	$3a_1^2 2e^4 1b_1^1 4a_1^1$	$^3B_1$	−287.679 05	149.6	−287.740 28	145.3
	C_{4v}	$3a_1^2 2e^4 1a_1^2$	$^1A_1$	−287.634 25	177.6	−287.703 63	168.3
	D_{4h}	$3a_{1g}^2 2e_u^4 1b_{1g}^1 4a_{2u}^1$	$^3B_{2u}$	−287.649 59	168.0	−287.695 08	193.1
PH_4^+	T_d	$3a_1^2 2t_2^6$	$^1A_1$	−339.025 02	0.0	−339.084 64	0.0
	C_{4v}	$3a_1^2 2e^4 4a_1^2$	$^1A_1$	−338.793 81	145.1	−338.886 55	124.3
	C_{4v}	$3a_1^2 2e^4 4a_1^1 1b_1^1$	$^3B_1$	−338.786 33	149.8	−338.866 68	136.8
	D_{4h}	$3a_{1g}^2 2e_u^4 1b_{1g}^1 4a_{2u}^1$	$^3B_{2u}$	−338.775 99	156.3	−338.845 41	150.1
	D_{4h}	$3a_{1g}^2 2e_u^4 1b_{1g}^2$	$^1A_{1g}(\delta)$	−338.657 15	230.8	−338.824 55	163.2
	D_{4h}	$3a_{1g}^2 2e_u^4 4a_{2u}^2$	$^1A_{1g}(\pi)$	−338.634 74	244.9	−338.644 66	276.1

Results and Discussion

As expected, the tetrahedral forms are considerably lower in energy than all other structures considered (Tables I and II). Indeed, with the exception of planar AlH_4^-, all the higher energy ZH_4 structures are calculated to be unstable toward dissociation into smaller fragments, e.g., $ZH_3^{\cdot}$ and $H^{\cdot}$ (vide infra). The relative energies of the different geometries and electronic states, however, show interesting and complex variations (Figures 1 and 2).

Planar–Tetrahedral Energy Differences. The planar-tetrahedral energy differences for singlet CH_4 is calculated to be 159.7 kcal/mol (MP2/6-31G*//6-31G*). The energy difference is high for many of the others as well. However, comparatively small values are obtained for SiH_4 and for AlH_4^-, e.g., only 76.3 kcal/mol (STO-3G*) for the latter. The basis set dependence found for the first-row hydrides indicates that the true energy differences for the second-row hydrides should be lower at more sophisticated theoretical levels. Tetracoordinate aluminum and silicon are thus the most promising candidates for planarity which might be induced by appropriate substitution.

The higher energy of the planar forms as well as the calculated variations in the planar-tetrahedral energy differences can be attributed to the electronic structures of ZH_4 molecules (Figure 3). In the tetrahedral forms, there are four bonding combinations of the central atom valence s and p orbitals with the hydrogen s orbitals. These give rise to optimal Z-H bonding in eight valence electron ZH_4 molecules. In the planar structures, however, only the three lowest MOs, a_{1g} and e_u, are stabilized, bonding combinations. The next two MOs, a_{2u} and b_{1g}, are nonbonding and lie considerably higher in energy. Therefore, such eight-electron systems are unfavorable in the planar forms. Since only six electrons are Z-H binding, the planar forms tend to dissociate. Another interesting consequence is that the planar-tetrahedral energy difference can be considered to be due to Z-H bond weakening. This difference should be inversely related to Z-H bond strength (in the tetrahedral form). Unfortunately, all the calculated results cannot be compared directly since the quality of the basis sets used is different for the first- and second-row hydrides. However, the planar-tetrahedral energy difference order of $CH_4 > NH_4^+ > BH_4^-$ and $PH_4^+ > SiH_4 > AlH_4^-$ within each row provides confirmation; the Z-H bond strengths show the opposite variation.

Electronic Structures of the Planar Forms. There are only three stabilized bonding orbitals, a_{1g} and e_u, in planar ZH_4 systems. When eight valence electrons are present, the HOMO can either be the a_{2u} or the b_{1g} orbital. The a_{2u} orbital is a purely nonbonding p(π) orbital localized on the central atom. The b_{1g} orbital, of d(δ)-type symmetry, has a node at the center and is localized on the hydrogens (Figure 3). This orbital can either be antibonding (if the hydrogens approach too closely), nonbonding (if the hydrogen overlap is essentially zero), or bonding (if the central atom has a low-lying d orbital). Two

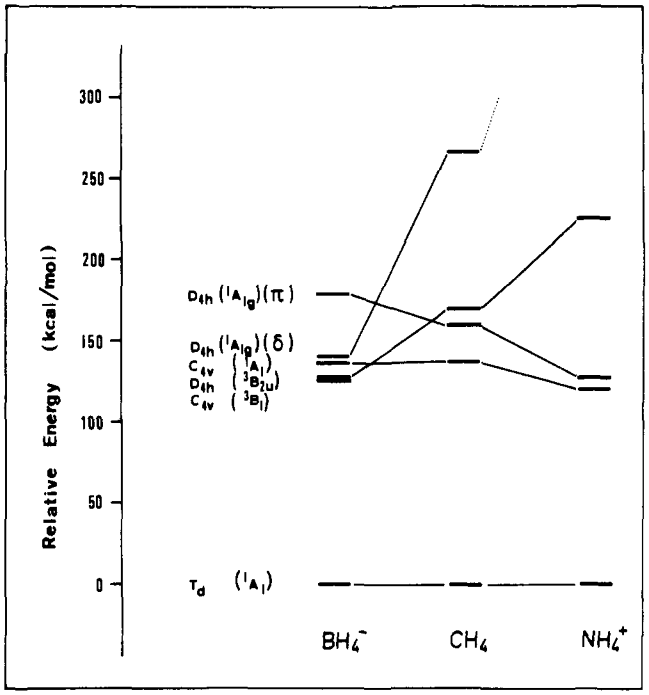


Figure 1. The calculated (MP2/6-31G*//6-31G*) relative energies for the first-row ZH_4 molecules. C_{4v} ($^3B_1$) states for CH_4 and NH_4^+ were not energy minima (see text).

lumomers[12] are thus possible. We shall refer to them as the π and the δ lumomers, the designations reflecting the symmetry of the HOMO in each case.

The electron density in the π lumomer is concentrated on the central atom. The hydrogens carry the bulk of the electronic charge in the δ lumomer (Table V). The lumomer preference is therefore strongly influenced by the electronegativity of the central atom. Thus, CH_4 and NH_4^+ have an $a_{2u}(\pi)$ HOMO, while BH_4^-, SiH_4, AlH_4^-, and PH_4^+, with more electropositive central atoms, have a b_{1g} HOMO in their most stable singlet planar forms. The preferences dictated by electronegativity are so strong that we were unable to calculate the energies of the alternative lumomers of AlH_4^-, SiH_4, and NH_4^+: the electronic configuration always reverted to that of the most stable lumomer during SCF iterations with the procedures we employed. The energy difference between the lumomers is very large (>100 kcal/mol) for CH_4 and for PH_4^+. Only in BH_4^- are the two forms relatively close in energy. The δ lumomer is preferred by 39.6 kcal/mol at the MP2/6-31G*//6-31G* level.

The hydrogen repulsion effects should operate similarly. The Z-H bond lengths (Tables III and IV), N-H < C-H < B-H < P-H < Si—H < Al-H, vary in a parallel way to central atom electronegativity. As already noted, closer approach of the hydrogen atoms should result in destabilization of the b_{1g} orbital, although the presence of d orbitals on the central atom will influence the result.

The differing electronic structures of the most stable ZH_4 forms have interesting consequences with regard to the tendency of a given planar species to pyramidalize. The nature of the HOMO and the LUMO also determines the type of substituents needed to stabilize a planar form preferentially. Finally, the likelihood of stable triplet states is indicated by the magnitude of the energy differences between the a_{2u} and b_{1g} orbitals. These effects will now be analyzed in detail.

Pyramidal C_{4v} Structures. Interestingly, all six isoelectronic ZH_4 species do not behave similarly with regard to pyramidal C_{4v} distortion. The lowest energy singlet planar D_{4h} forms of CH_4 and NH_4^+ become more stable on pyramidalization by 22.7 and 6.9 kcal/mol, respectively (MP2/6-31G*//6-31G*). The lowest energy D_{4h} forms of the other ZH_4 molecules resist C_{4v} distortion. The electronic structures are responsible for this differing behavior. The a_{2u} orbital of a planar lumomer can be significantly stabilized through relaxation to the pyramidal structure. The resulting a_1 MO acquires considerable s hybridization and HH attractive character (Figure 3). The b_{1g} orbital of a δ lumomer, however, becomes destabilized on distortion to C_{4v} symmetry owing to increased H-H repulsion. Therefore, only the π lumomers prefer C_{4v} geometry. The

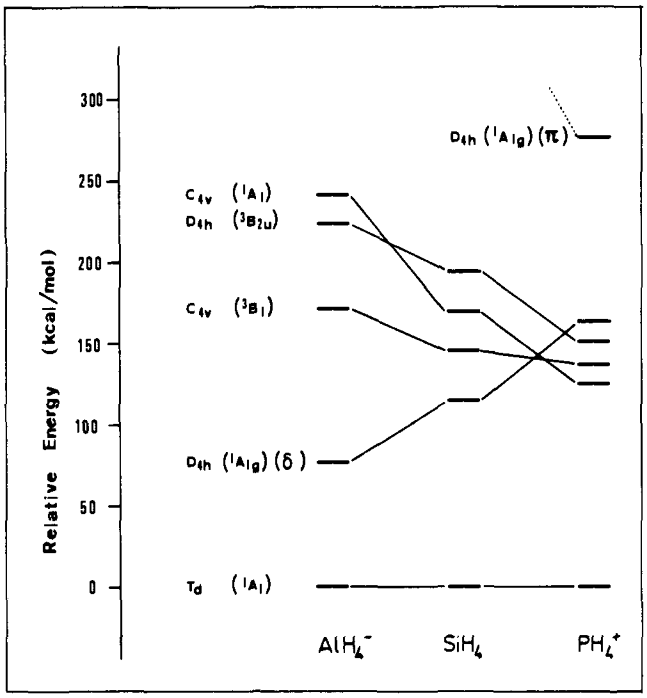


Figure 2. The calculated (STO-3G*//STO-3G*) relative energies for the second-row ZH_4 molecules.

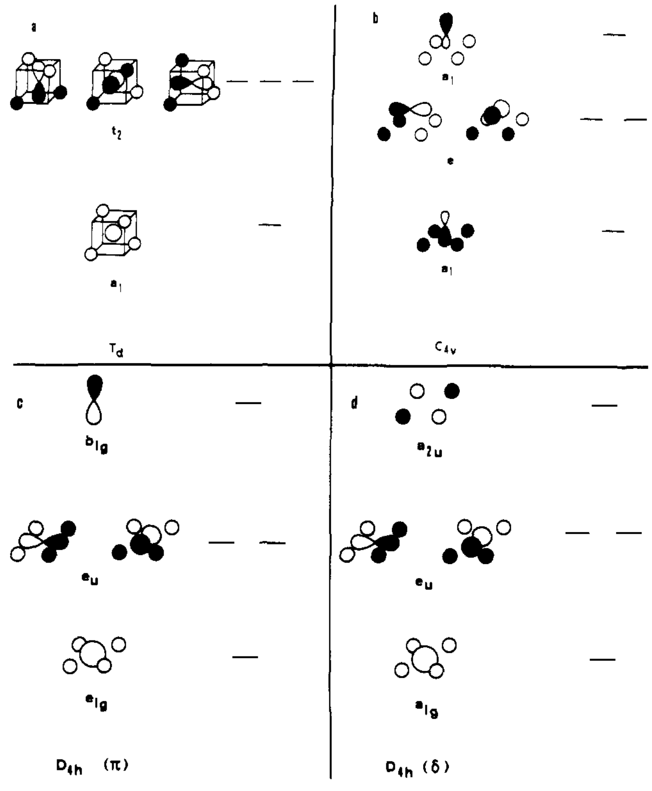


Figure 3. The occupied molecular orbitals of (a) tetrahedral, T_d, (b) pyramidal, C_{4v}, (c) planar, D_{4h}(π lumomer), and (d) planar, D_{4h}(δ lumomer) forms of eight valence electron ZH_4 molecules.

Table III. Optimized Geometries[a] of the First-Row ZH_4 Molecules

			STO-3G		6-31G*	
molecule	symmetry	state	r_{ZH}	∠HZH[b]	r_{ZH}	∠HZH[b]
BH_4^-	T_d	${}^1A_1$	1.176		1.243	
	C_{4v}	${}^3B_1$	1.266	87.3	1.314	87.2
	D_{4h}	${}^3B_{2u}$	1.246		1.293	
	C_{4v}	${}^1A_1$	1.258	47.6	1.297	62.6
	D_{4h}	${}^1A_{1g}(\delta)$	1.325		1.376	
	D_{4h}	${}^1A_{1g}(\pi)$	1.122		1.189	
CH_4	T_d	${}^1A_1$	1.083		1.084	
	C_{4v}	${}^1A_1$	1.165	69.5	1.127	72.5
	D_{4h}	${}^3B_{2u}$	1.171		1.165	
	D_{4h}	${}^1A_{1g}(\pi)$	1.074		1.082	
	D_{4h}	${}^1A_{1g}(\delta)$	1.249		1.237	
NH_4^+	T_d	${}^1A_1$	1.044		1.013	
	C_{4v}	${}^1A_1$	1.095	80.6	1.048	81.1
	D_{4h}	${}^1A_{1g}(\pi)$	1.057		1.036	
	D_{4h}	${}^3B_{2u}$	1.161		1.130	

[a] Bond lengths in Å, angles in deg. [b] ∠HZH is given only when it is not determined by symmetry.

Table IV. Optimized Geometries[a] of the Second-Row ZH_4 Molecules

			STO-3G		STO-3G*	
molecule	symmetry	state	r_{ZH}	∠HZH[b]	r_{ZH}	∠HZH[b]
AlH_4^-	T_d	${}^1A_1$	1.512		1.523	
	D_{4h}	${}^1A_{1g}(\delta)$	1.559		1.564	
	C_{4v}	${}^3B_1$	1.606	81.5	1.604	81.3
	D_{4h}	${}^3B_{2u}$	1.550		1.550	
	C_{4v}	${}^1A_1$	1.163	51.3	1.620	50.5
SiH_4	T_d	${}^1A_1$	1.421		1.424	
	D_{4h}	${}^1A_{1g}(\delta)$	1.466		1.466	
	C_{4v}	${}^3B_1$	1.500	87.1	1.493	83.3
	C_{4v}	${}^1A_1$	1.518	55.9	1.498	54.8
	D_{4h}	${}^3B_{2u}$	1.468		1.461	
PH_4^+	T_d	${}^1A_1$	1.382		1.380	
	C_{4v}	${}^1A_1$	1.469	62.3	1.443	59.2
	C_{4v}	${}^3B_1$	1.459	86.3	1.445	85.3
	D_{4h}	${}^3B_{2u}$	1.443		1.428	
	D_{4h}	${}^1A_{1g}(\delta)$	1.443		1.423	
	D_{4h}	${}^1A_{1g}(\pi)$	1.423		1.417	

[a] Bond lengths in Å, angles in deg. [b] ∠HZH is given only when it is not determined by symmetry.

Table V. Mulliken Population Analyses (STO-3G)

molecule	symmetry	state	Z–H overlap population	charge on Z	charge on H
BH_4^-	T_d	${}^1A_1$	0.754	−0.140	−0.215
	C_{4v}	${}^3B_1$	0.547	−0.235	−0.191
	D_{4h}	${}^3B_{2u}$	0.577	−0.273	−0.182
	C_{4v}	${}^1A_1$	0.370	−0.622	−0.094
	D_{4h}	${}^1A_{1g}(\delta)$	0.584	0.336	−0.334
	D_{4h}	${}^1A_{1g}(\pi)$	0.571	−1.000	0.000
CH_4	T_d	${}^1A_1$	0.772	−0.263	0.066
	C_{4v}	${}^1A_1$	0.448	−0.459	0.115
	D_{4h}	${}^1A_{1g}(\pi)$	0.624	−0.799	0.200
	D_{4h}	${}^3B_{2u}$	0.589	−0.164	0.041
	D_{4h}	${}^1A_{1g}(\delta)$	0.544	0.372	−0.093
NH_4^+	T_d	${}^1A_1$	0.653	−0.407	0.352
	C_{4v}	${}^1A_1$	0.498	−0.524	0.381
	D_{4h}	${}^1A_{1g}(\pi)$	0.557	−0.700	0.425
	D_{4h}	${}^3B_{2u}$	0.474	−0.111	0.278
AlH_4^-	T_d	${}^1A_1$	0.582	0.684	−0.421
	D_{4h}	${}^1A_{1g}(\delta)$	0.504	0.896	−0.474
	C_{4v}	${}^3B_1$	0.378	0.325	−0.331
	D_{4h}	${}^3B_{2u}$	0.463	0.192	−0.298
	C_{4v}	${}^1A_1$	0.188	−0.029	−0.243
SiH_4	T_d	${}^1A_1$	0.703	0.640	−0.160
	D_{4h}	${}^1A_{1g}(\delta)$	0.571	1.030	−0.258
	C_{4v}	${}^3B_1$	0.491	0.458	−0.114
	C_{4v}	${}^1A_1$	0.314	0.238	−0.060
	D_{4h}	${}^3B_{2u}$	0.558	0.338	−0.084
PH_4^+	T_d	${}^1A_1$	0.699	0.673	0.018
	C_{4v}	${}^1A_1$	0.389	0.494	0.127
	C_{4v}	${}^3B_1$	0.501	0.668	0.083
	D_{4h}	${}^3B_{2u}$	0.538	0.581	0.105
	D_{4h}	${}^1A_{1g}(\delta)$	0.524	0.239	−0.060
	D_{4h}	${}^1A_{1g}(\pi)$	0.558	−0.065	0.226

degree of pyramidalization and the associated stabilization are determined by the electronegativity of the central atom. In the C_{4v} form, the a_1 HOMO is no longer entirely localized on the central atom and the electron density is more evenly distributed over the whole molecule than in the D_{4h} structure (Table V). Pyramidalization effectively reduces the negative charge on the central atom. Thus, electronegative central atoms inhibit pyramidalization. The calculated results confirm this analysis. The π D_{4h} lumomers of BH_4^-, PH_4^+, CH_4, and NH_4^+ readily distort to C_{4v} geometries. The energy lowering at the MP2/6-31G*//6-31G* level is inversely related to the electronegativity of the central atom (kcal/mol): NH_4^+ (6.9), CH_4 (22.7), BH_4^- (42.9) (Table I). The degree of pyramidality, as indicated by the values of the optimized HZH angles, exhibits the same trend: 81.1, 72.5, and 62.6°, respectively (Table III). The reduction in the negative charge at the central atom on going from π D_{4h} to the corresponding C_{4v} form is evident from Table V for these three cases.

Triplet States. With the exception of BH_4^-, the most stable D_{4h} or C_{4v} structure is calculated to be a singlet for all ZH_4 species. Even for BH_4^-, the triplet D_{4h} and C_{4v} forms are favored by only 9 kcal/mol relative to the singlet pyramidal geometry (MP2/6-31G*//6-31G*, Table I). Since this level of theory is known to overestimate the stability of triplets relative to singlets,[13] the most stable nontetrahedral structure is likely to be a singlet for this case as well.

The HOMO and the LUMO of the planar forms are well separated in energy, although both MOs are essentially nonbonding orbitals. The separation is particularly large for AlH_4^- and for NH_4^+; the small and the large electronegativity of the central atom, respectively, induces a strong preference for one of the nonbonding MOs relative to the other. Filling both MOs with one electron each therefore costs considerable energy for these two ions. The ZH_4 singlet–triplet energy difference is gradually reduced as the electronegativity difference between Z and H becomes smaller. The π and δ lumomers of planar BH_4^- have comparable energy. Therefore, the triplet state is calculated to be relatively stable for this ion. The tendency of molecules in triplet states to adopt C_{4v} geometries is restricted by the partial occupation of both a_{2u} and b_{1g} orbitals. As with the D_{4h} singlets, the degree of pyramidalization is inversely related to the electronegativity of the central atom. As a result, NH_4^+ and CH_4 triplets prefer planarity. Triplet BH_4^- prefers the C_{4v} over the planar geometry by only 0.5 kcal/mol (MP2/6-31G*//6-31G*). A modest preference of 13.3 kcal/mol is calculated for triplet PH_4^+ with the STO-3G* basis. This value is probably overestimated by this small basis set (compare STO-3G and 6-31G* results of the first-row hydrides, Table I). The much larger C_{4v}–D_{4h} energy differences calculated for triplet SiH_4 (47.8) and for triplet AlH_4^- (52.4) cannot entirely be due to the inadequacy of the basis set, and reflect the effect of electronegativity on pyramidalization.

Substituent Effects. Although all planar and pyramidal ZH_4 arrangements are calculated to be very unstable relative to the tetrahedral forms, suitable substituents can reduce the energy difference. The substituents stabilizing planar tetracoordinate carbon have been investigated in detail.[3a] Even reversal of the

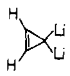
Table VI. Calculated (6-31G*//6-31G*) Energies of Reactions 1-4 for the First-Row ZH_4 Molecules (kcal/mol)

molecule	reaction 1	reaction 2	reaction 3	reaction 4
BH_4^-		85.0	96.6	85.1
CH_4	457.0	86.6	340.2	92.1
NH_4^+	217.4	100.0		122.6

normal tetrahedral preference may be possible. Interestingly, of the six species considered here, the largest planar-tetrahedral energy difference is calculated for CH_4. It should be easier to realize unusual geometries through substitution in the other systems. AlX_4^- and SiX_4 are particularly attractive in this respect.

As a direct consequence of the alternating electronic structure of the most stable planar lumomer, there can be a fundamental difference in substituent effects. The lower energy planar forms of CH_4 and NH_4^+ have π-type HOMOs. Therefore, π-acceptor, σ-donor groups with vacant p orbitals (e.g., Li, BeR, BR_2) stabilize this arrangement.[3a] Electropositive substituents are ideally suited for this purpose. Several compounds e.g., **1–3,** are indicated to prefer planar over tetrahedral structures.[3] The X-ray structure of **4** reveals the presence of a planar tetracoordinate carbon,[3c] although the reasons may be more complex. Substituent effects on NH_4^+ are likely to be of a similar kind and magnitude.[14]

1



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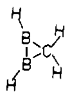

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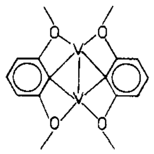
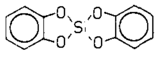


4
(PARTIAL STRUCTURE)

In the planar forms of AlH_4^-, SiH_4, BH_4^-, and PH_4^+, the δ lumomer is more stable. In these systems, the π a_{2u} orbital is the LUMO and the δ b_{1g} orbital is the HOMO. To have a stabilizing effect π-donor, σ-acceptor substituents are needed. Electronegative groups like OH, NH_2, and F are therefore expected to reduce the planar-tetrahedral energy difference in these systems. The prospect of drastically influencing the geometrical preferences, e.g., of AlX_4^- and SiX_4, with such "normal" substituents is exciting. Only recently has this possibility been considered. The space group of the orthosilicic acid ester, **5**, has been taken to imply the planarity of the molecule.[4c]



5

Semiempirical MNDO calculations indicate a low barrier to planarization.[4d] Additional coordination and/or intermolecular interaction in the crystal have been suggested as factors which would alter the usual structural preference in this molecule.[4c,d] Racemization studies in solution involving appropriately substituted orthosilicates and orthoaluminates deserve experimental attention. Further calculational results on δ-lumomer systems will be presented subsequently.[15]

Basis Set and Electron Correlation Effects. Certain clear trends in basis set and electron correlation effects are seen in the present study. In going from the minimal to the split-valence basis sets, a large energetic effect in favor of the planar and pyramidal forms results. The stabilization of the planar form is particularly large. The effect of the inclusion of d orbitals in the basis set may be anticipated on symmetry grounds: the δ D_{4h} lumomers are preferentially stabilized. The d orbitals have practically no effect on the relative stability of the π D_{4h} forms. Although electron correlation has been treated only to second order in the Möller-Plesset scheme, an intuitively understandable trend is seen. Inclusion of electron correlation results in a pronounced stabilization of the π lumomer and in somewhat less destabilization of the δ D_{4h} lumomer relative to the tetrahedral form. There is a greater concentration of electron density in one region of the molecule in the π lumomer, while it is distributed over more centers in the δ lumomer. Singlets become more stable relative to triplets with the inclusion of the electron correlation. This effect is well documented.[13]

Table VII. Calculated (STO-3G*//STO-3G*) Energies of Reactions 1-4 for the Second-Row ZH_4 Molecules (kcal/mol)

molecule	reaction 1	reaction 2	reaction 3	reaction 4
AlH_4^-		146.2	182.5	188.5
SiH_4	520.6	115.1	428.5	115.2
PH_4^+	250.2	108.9		98.8

Dissociation Energies. Four possible dissociation reactions, (1)-(4), have been considered, involving loss of H^+, H^-, and H_2. The energies of the dissociation products relative to the tetrahedral ZH_4 species are given in Tables VI and VII.

$$ZH_4 \rightarrow ZH_3^- + H^+ \qquad (1)$$

$$ZH_4 \rightarrow ZH_3^\cdot + H^\cdot \qquad (2)$$

$$ZH_4 \rightarrow ZH_3^+ + H^- \qquad (3)$$

$$ZH_4 \rightarrow {}^3ZH_2 + H_2 \qquad (4)$$

Since the products of reactions 2 and 4 involve open-shell systems, the corresponding energy differences are underestimated at the levels of theory used in the present work.[13] For example, the calculated CH bond strength of 86.7 kcal/mol can be compared with the experimental value of 105 kcal/mol. Furthermore, the reaction energies for the second-row hydrides are calculated to be too large owing to the small basis set employed. However, the *trends* in these energies are likely to be correctly reproduced, since a series of isoelectronic species are compared.

Comparing the results of Tables I and II with those of Tables VI and VII, nontetrahedral ZH_4 molecules are found to be unstable with respect to homolytic bond dissociation. AlH_4^- is the only exception. In fact, planar singlet AlH_4^- is stable with respect to all the four dissociation modes considered.

An interesting trend is seen in the calculated energies of reactions 2 and 4. While the reaction energies increase along the series $BH_4^- < CH_4 < NH_4^+$, the second-row hydrides show the opposite variation: $AlH_4^- > SiH_4 > PH_4^+$. What is the origin of this differing behavior within an isoelectronic series? In the tetrahedral form of the ZH_4 species, AlH_4^-, BH_4^-, PH_4^+, and NH_4^+, the charge is mainly localized on the hydrogens. Loss of H_2 or $H^\cdot$ leads to products in which increased charge is borne by the central atom. For example, the negative charge on Al is larger in $AlH_3^{\cdot-}$ and in AlH_2^- relative to AlH_4^-. Similarly, greater positive charge resides on N in $NH_3^{+\cdot}$ and in NH_2^+ relative to NH_4^+. The charge buildup is resisted by the electronegativity demands of the central atom. Therefore, the dissociation energies are large when the electronegativity difference between Z and H is large, as in AlH_4^- and NH_4^+. The energies are smaller in BH_4^- and in PH_4^+. The opposing trends in the dissociation energies in the first- and second-row hydrides result.

Conclusions

The preference of eight valence electron ZH_4 molecules to adopt tetrahedral geometries is confirmed by quantitative MO calculations. Alternative planar and pyramidal structures may be realized by incorporation in a rigid framework or by suitable substitution. The energetic cost of deformation and the choice of the substituents are indicated by the present ab initio calculations. Of the six ZH_4 molecules studied, CH_4 requires the largest energy for planarization; the corresponding energy for NH_4^+, BH_4^-, and PH_4^+ is also considerable. Planarization is indicated to be relatively easy for AlH_4^- and, to a lesser extent, for SiH_4. The planar–tetrahedral energy difference is inversely related to the Z–H bond strength.

An orbital isomerism is exhibited by the planar forms. The species with more electronegative central atoms, CH_4 and NH_4^+, have π-type HOMOs. The other ZH_4 molecules prefer δ-type HOMOs. The choice of the electronic configuration is determined by the central atom electronegativity. As a result, triplet states lie considerably higher in energy, with the possible exception of planar BH_4^-. The electronic structural dichotomy has interesting consequences. The lumomer with the π-type HOMO pyramidalizes readily without activation. The δ lumomer resists this distortion. The symmetry of the HOMO also determines the kind of substituents needed for stabilization. The π lumomers are stabilized by π-acceptor, σ-donor groups, for example, electropositive substituents. The δ lumomers require π-donor, σ-acceptor groups like OR, NR_2, and F for stabilization. Silanes and alanes with this substitution pattern are more easily studied experimentally. Structural investigations to test our conclusions would be of interest.

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An MO Study on the Structure and the Stability of the $CH_5^+(CH_4)_n$ Cluster (n = 0, 1, 2, and 3)

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Abstract: An ab initio MO calculation is made for the $CH_5^+(CH_4)_n$ (n = 0, 1, 2, and 3) system with the 4-31G basis set. As a result of the geometry optimization, the first and the second CH_4's attack two elongated C–H bonds successively and the third CH_4 attacks the C–H bond of the methyl group of CH_5^+. The secondary attack of CH_4 ($CH_5^+\cdots CH_4\cdots CH_4$) is found to be energetically unfavorable. The process of clustering, which is influenced by the mutual steric effect of CH_4's, results in the formation of five "satellites" around CH_5^+. The pattern of the electronic interaction involved in the $CH_5^+(CH_4)$ cluster is analyzed by the energy decomposition scheme and configuration analysis. The role of some charge-transfer and polarization interactions on the cluster formation is discussed.

I. Introduction

It is well known that in the gas phase protonated species of nonpolar molecules exist as cluster ions. For H_3^+, the temperature dependence of the equilibria $H_{n-2}^+ + H_2 = H_n^+$ (n = 5, 7, 9, and 11) is measured with the pulsed electron beam mass spectrometer and the structure of the H_n^+ cluster is proposed on the basis of the observed enthalpy changes.[2] According to a recent theoretical calculation, it is affirmed that the process of this clustering is described as the successive attachment of H_2's to three corners of the triangle of H_3^+.[3] Protonated methane, CH_5^+, has also attracted much attention as a "superacid" and some gas-phase experiments have been

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