5152 *J. Phys. Chem. A* **1999,** *103,* 5152−5160

Theoretical Study of H_mGaPH_n. Characteristics of Gallium−Phosphorus Multiple Bonds

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Received: January 4, 1999

Equilibrium structures, harmonic vibrational frequencies, and relative energies of 12 neutral or ionic gallium phosphorus hydrides are reported and analyzed. Hartree−Fock (HF), Becke's three-parameter exchange with Lee, Yang, and Parr correlation DFT (B3LYP), and second-order Møller−Plesset (MP2) calculations using the 6-311++G(d,p) basis set were performed on all molecules. Gallium−phosphorus bond energies were determined based on the MP2/6-311++G(d,p) calculations of the equilibrium structures and of their decomposition products. We find that the gallium−phosphorus double bond is, perhaps, surprisingly strong (i.e., 93 ± 2 kcal/mol) and short (2.128 ± 0.018 Å); CCSD(T)/6-311++G(3df,3dp) single-point calculations on HGaPH corroborate the prediction of a strong double bond. Bond order analysis of some of the neutral species revealed that these compounds satisfy a Pauling relation between bond length and bond order, and also bond energy and bond order. CASSCF(8|8) calculations on H_2PGa show that the surprising weakness of the phosphorus−gallium bond in this compound can be understood in terms of an occupied antibonding σ orbital. Comparisons of the B3LYP method to HF and MP2 methods reveal that the B3LYP DFT method, in most cases, gives relative energies and equilibrium structures in substantial agreement with the MP2 method for these types of compounds.

I. Introduction

Gallium phosphide has proven to be a valuable alternative to other more toxic and/or more costly compounds as a semiconductor.[1] As commercial interest in this compound has increased, so too has interest in its preparation.[2] Impurities in gallium phosphide crystals are usually due to the current methods of synthesizing this compound, which involve removal of hydrocarbons from the gallium phosphide precursor at high temperatures, 150−200 °C,[3] or by laser irradiation. Therefore, characterizing possible synthetic targets that provide fewer chances for introducing impurities into gallium phosphide crystals is becoming increasingly important. Monomeric gallium−phosphorus compounds are scarce,[4,5] and Ga−P bonds have not been thoroughly characterized experimentally. Moreover, they also have not been the subject of extensive ab initio calculations.[3−6] Thus, theoretical investigation over a wide range of possible gallium phosphorus hydrides is warranted and timely.

Gallium−phosphorus double bonds have been hypothesized to exist, but determining the characteristics of this bond has not been pursued aggressively until recently. It has been noted that in many gallium−phosphorus compounds, whether monomeric or not, the phosphorus has a pyramidal coordination with its substituents.[7] This lack of planarity does not allow for significant donation of the lone pair on phosphorus to the gallium adduct. It is therefore believed[7] that for the gallium−phosphorus double bond to exist, two criteria must be satisfied: First, there must be planarity at the phosphorus atom, or at least a flattened pyramidal geometry; second, the Ga−P bond length must be significantly lower than the sum of the covalent radii (2.33 Å), after electrostatic corrections have been introduced. Using these arguments, and NMR techniques, it has been shown that a few compounds exhibit weak π-bonding character.[7]

Ab initio calculations are excellent tools for the elucidation of the bonding structure of compounds. They have been used extensively in the investigation of molecules containing multiple bonds, including those composed of one or more heavier main group elements (see, e.g., refs 8−13). Few ab initio calculations have been performed on monomeric gallium−phosphorus compounds,[4] while even fewer calculations have been performed on gallium−phosphorus hydrides, such as H_3GaPH_3.[3,6] With the exception of the work by Marsden and co-workers,[6] these calculations were primarily used to supplement experimental data and were not analyzed to great extent.

Twelve gallium phosphorus hydrides were studied in this work. Figure 1 shows compounds **1**−**6**, where **1** is H_3GaPH_3, and **2**−**6** result from a series of H_2 eliminations of **1**. Compounds **9** and **10** are depicted in Figure 2. These structures result from the hydrogen ion and hydride ion abstractions, respectively, at the phosphorus atom in HGaPH (**3**). Compounds **11** and **12** are shown in Figure 3. These structures resemble structures **9** and **10**, except these compounds are a result of hydrogen abstractions at the gallium atom in **3**. Alternatively, compounds **9**−**12** may be viewed as hydrogen ion or hydride ion additions to the monomeric GaP. Compounds **7** and **8** may be involved in further reactions of **4** and **2** and have been included in this study; they are shown in Figure 4.

In this study, equilibrium structures for each molecule were determined using three different methods: Hartree−Fock (HF), second-order Møller−Plesset perturbation theory (MP2), and Becke's three-parameter exchange with Lee, Yang, and Parr correlation density functional theory (B3LYP).[14] A triple-split valence basis set was used in all calculations, with polarization and diffuse functions added to all atoms; the common designation of this basis set is 6-311++G(d,p).[15−18] Use of this relatively large basis set for the geometry optimizations was thought necessary because preliminary calculations showed that many of the compounds exhibited bond angles characteristic of conventional orbital hybridization, while others did not.

10.1021/jp9900133 CCC: $18.00

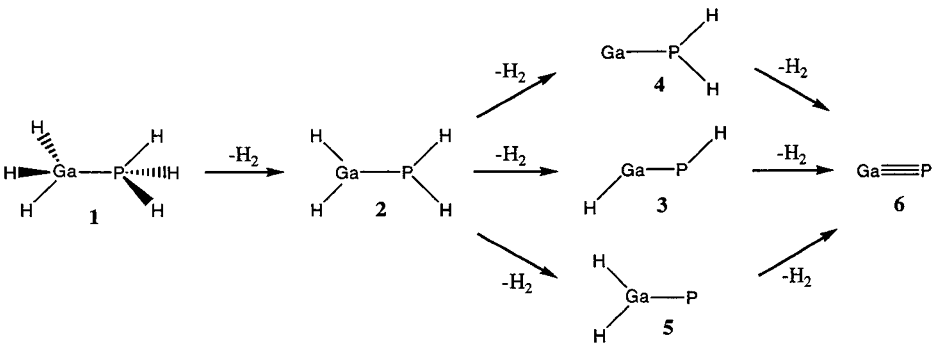


Figure 1. Series of hydrogen elimination products of H_3GaPH_3 to form gallium phosphide.

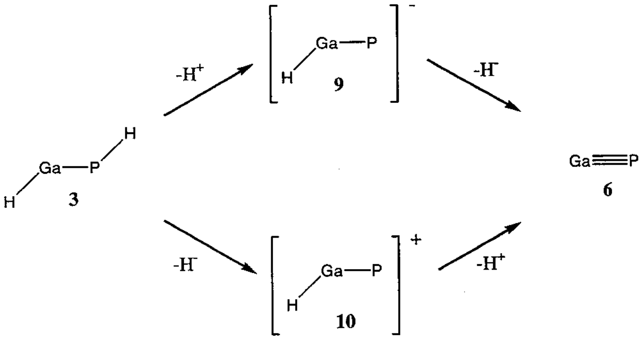


Figure 2. Products of proton and hydride abstractions from the phosphorus of HGaPH.

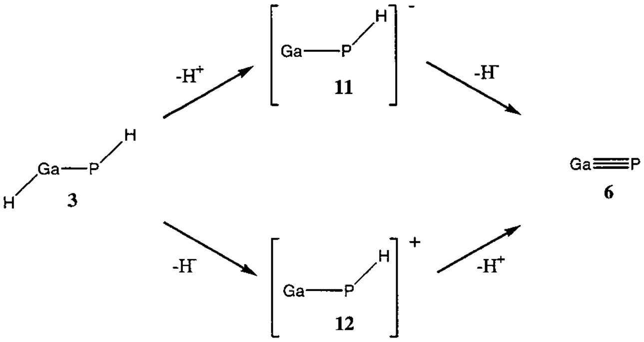


Figure 3. Products of proton and hydride abstractions from the gallium of HGaPH.

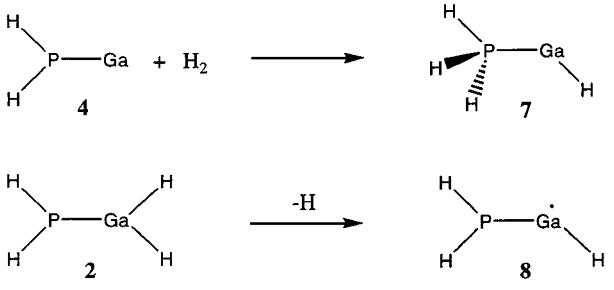


Figure 4. Other gallium phosphorus hydrides related to **2** and **4**.

Therefore, the polarization functions gave the basis set the flexibility to accommodate these differences. Several of the anionic species showed considerable localization of the negative charge, so that the addition of the diffuse functions enabled the negative charges to be characterized more reliably. Vibrational frequencies were also obtained at the MP2/6-311++G(d,p) level for all reported molecules.

Unless noted otherwise, single-reference calculations were performed on a DEC Alpha 3000 300X workstation, using the Gaussian94 Revision B.2 suite of programs.[19] The exponents and coefficients of the 6-311++G(d,p) basis set used in this study were the default values for Gaussian94; the geometric convergence criterion was determined by including the keyword "Tight" in the optimization specifications. When the keyword "Tight" is used, the four criteria for convergence, viz., the maximum force, the rms force, the maximum displacement, and the rms displacement, are a factor of 30 smaller than the default values used in Gaussian94. Bond orders for the molecular compounds were obtained at the MP2/6-311++G(d,p) level using the method developed by Mayer,[20] implemented in the GAMESS suite of programs.[21] The GAMESS suite of programs was also used for the CASSCF calculations reported herein. GAMESS calculations were run on the University of North Dakota Computer Center IBM SP2.

Previous calculations[22,23] on a large number of systems have shown that for calculating atomization energies, electron affinities, and ionization potentials, the methods used in this study are not expected to be accurate to within 2 kcal/mol of experimental quantities. Systematic studies of basis set superposition error (BSSE) corrections have recently been shown to be comparable to this value for similar basis sets.[6,24] Moreover, our calculation of the BSSE correction for compound **7** found that the bond energy was overestimated by 2.2 kcal/mol at the MP2/6-311++G(d,p) level. Therefore, the added expense of BSSE corrections does not seem to be warranted for the reported level of calculations.

Similarly, exploratory studies of relativistic effects on the geometries of **3** and **4** were also performed. The geometries of **3** and **4** were calculated using the Stephens/Basch/Krauss[25] ECP implemented in Gaussian98W under the keyword CEP-31. It was found that at the HF level, the Ga−P and Ga−H bond lengths changed by less than 0.01 Å when relativistic effects are taken into account for both **3** and **4**. However, the Ga−P bond length at the MP2 level in **3** was shortened by 0.034 Å, while this bond length in **4** was shortened by 0.023 Å. Although these differences are not negligible for definitive studies of specific molecules, they appear to be relatively uniform and thus further discussion of relativistic effects will not be included in this work. It may also be noted that differences in the 0.02−0.03 Å range compare to differences between (nonrelativistic) MP2 and B3LYP results, as reported in section V. Relativistic calculations were run on a Dell XPS500.

The effects of a possible multireference nature for these types of molecules were also considered. CASSCF(8|8) calculations were performed on structures **3** and **4** using GAMESS and the 6-311++G(d,p) basis set. These calculations show that the differences between the MP2-optimized geometries and the MCSCF-optimized geometries, including the Ga−P bond length, are comparable (e.g. <0.02 Å) to the differences between results using the MP2 and DFT methods. Although the differences between MCSCF and MP2 are not negligible, which suggests that definitive studies will produce additional small changes to

TABLE 1: Energies (au) of 1−6 at the HF, B3LYP, and MP2 Levels of Theory, and the 6-311++G(d,p) Basis Set

	HF	B3LYP	MP2
1	−2267.411 560	−2269.830 216	−2267.634 267
2	−2266.268 498	−2268.643 216	−2266.464 979
3	−2265.076 081	−2267.417 796	−2265.257 124
4	−2265.108 453	−2267.445 216	−2265.279 826
5	−2265.025 057	−2267.351 320	−2265.180 798
6	−2263.833 372	−2266.144 468	−2264.005 216

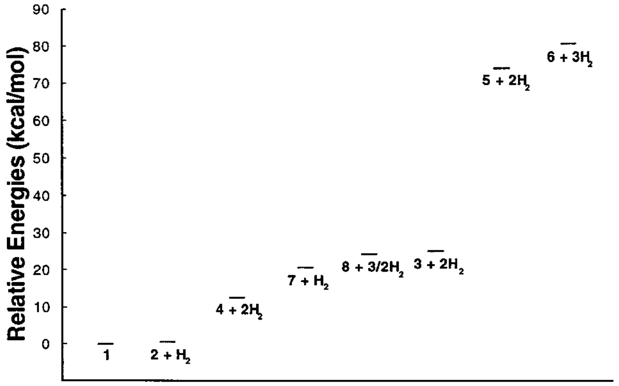


Figure 5. Energy of formation of **2**−**8** relative to **1** at the MP2/6-311++G(d,p) level.

geometries, the differences in the results for the methods are sufficiently small and uniform that comparative studies at the MP2 level may be expected to be useful.

Section II focuses on the relative energies of the compounds included in this study and attempts to develop an understanding of the bond energies of the various gallium−phosphorus bonds. Results of geometry optimizations and calculations of vibrational frequencies are presented and discussed in section III. The results of calculations on the ionic species are given in section IV. A more detailed comparison of predictions at the HF, B3LYP and MP2 levels is presented in section V. We summarize our results in a concluding section.

II. Thermochemistry

The energies of compounds **1**−**6** at the HF, B3LYP, and MP2 levels, and using the 6-311++G(d,p) basis set, are given in Table 1. A comparison of the relative energies of these compounds, including zero-point vibrational energy corrections, is shown in Figure 5. These relative energies include H_2 as necessary, also computed at the MP2/6-311++G(d,p) level, in order to preserve stoichiometry. The energy difference between **1** and **2** is only about 1.5 kcal/mol and, so, should be considered to be isenergetic to within accepted accuracies of the computational method. Previously reported experiments[26] on the synthesis of Me_2HPGaH_3 showed that if the product was left at room temperature, gas was evolved, and the original product was believed to decompose to Me_2PGaH_2. However, this compound was not stable enough to be detected by gas-phase spectroscopic methods. Our calculations of the very small energy separation between **1** and **2** support that such decomposition would be thermodynamically feasible, even at room temperature.

Compounds **3**−**6** are considerably higher in energy than **1** and **2**. **3** is approximately 27 kcal/mol higher in energy than **1**, while **4** is only about 14 kcal/mol higher in energy. These compounds are much closer in energy to **1** and **2** than are **5** and **6**, but are nonetheless too high in energy to be thermodynamically accessible.

One of the primary goals of this work was to determine characteristics of various gallium phosphorus bonds. The change in internal energy in reaction 1 is seen to equal the (negative of the) energy of the dative bond formed between phosphine and gallane.

TABLE 2: Ga−P Bond Energies (kcal/mol) of 1−6 (See Text for More Detail)[a]

	energy (kcal/mol)		energy (kcal/mol)
1	11.5	**4**	38
2	62	**5**	74
3	89	**6**	101

[a] Energies are based on MP2/6-311++G(d,p) calculations.

$$H_3Ga + PH_3 \rightarrow H_3GaPH_3 \qquad -E_{Ga-P(1)} \tag{1}$$

The MP2/6-311++G(d,p) energies, in atomic units, of GaH_3 and PH_3 are −1924.999 910 and −342.613 216, respectively. Hence, ΔU for this reaction is −13.3 kcal/mol, which is altered to −11.5 kcal/mol with the inclusion of the zero-point energy. This calculation essentially agrees with previous calculations of the Ga−P bond energy by Marsden and co-workers:[6] their calculations at the MP2 level using a double-ζ basis set, in conjunction with pseudopotentials, showed that the binding energy of this compound is 48 kJ/mol, i.e., 11.5 kcal/mol. They calculate the BSSE to lower the bond energy by 13 kJ/mol, or 3.1 kcal/mol, at the MP2/DZ level.

In order to determine the Ga−P bond strength in **2**, the same method that was used to find the Ga−P bond energy in **1** was again used, i.e.,

$$H_2Ga + H_2P \rightarrow H_2GaPH_2 \qquad -E_{Ga-P(2)} \tag{2}$$

In this instance, the lowest doublet state of each reactant was used in the calculation. The energies, in atomic units, calculated for H_2Ga and H_2P at the MP2/6-311++G(d,p) level were −1924.375 634 and −341.984 418, respectively. This method was extended straightforwardly to compounds **3**−**6** for determining the Ga−P bond strengths. Table 2 lists the Ga−P bond energies for compounds **1**−**6**, based on the MP2/6-311++G(d,p) energies. While geometries predicted at the MP2/6-311++G(d,p) level are usually quite accurate for closed-shell systems, energies and energy differences are often not yet converged. Higher levels of electron correlation, along with larger basis sets, must be used to accurately predict energy differences. In order to determine the reliability of the energy trends predicted by the MP2/6-311++G(d,p) calculations, the Ga−P bond energy of **3** was calculated at the CCSD(T)/6-311++G(3df,3pd)[17,27−29] level, using the optimized geometries at the MP2/6-311++G(d,p) level. The Ga−P bond energy predicted at the higher level was found to be 96 kcal/mol, which corresponds to a relative difference of about 8%. Even though this difference is not negligible, errors of this magnitude should not affect trends predicted by the MP2 calculations, especially for the strongly bonded compounds.

Many elements that are capable of forming bonds of different order with each other are known to obey a relationship between bond strength and bond order that was originally given by Pauling in 1946.[30] The Pauling relationship postulates that a linear relationship exists between the bond length and the natural logarithm of the bond order,

$$R = R_s - C_R \ln(n) \tag{3}$$

where R_s is the single bond length, C_R is a constant, and n is the bond order. Since bond length and bond strength are also supposed to be linearly related, it should hold that the bond

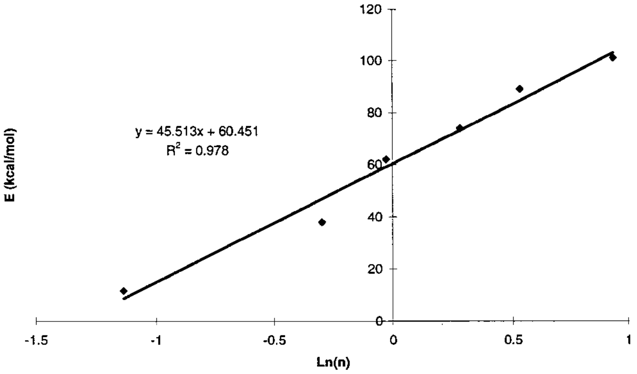


Figure 6. Plot of bond energy vs natural log of bond order for compounds **1**−**6**.

energy is also linearly related to the natural log of the bond order.[30] Equation 4 is a Pauling relation involving bond energies

$$E = E_s + C_E \ln(n) \tag{4}$$

where E is the bond energy, E_s is the bond energy of a single bond, C_E is a constant, and n is the bond order. Of course, it is simplistic to assume a priori that a set of bonds between two arbitrary elements will obey a Pauling relationship. We investigate the veracity of such a relationship for the Ga−P compounds under study.

Bond orders for **1**−**6** were obtained using Mayer's method[20] as implemented in GAMESS,[21] for the MP2/6-311++G(d,p) level optimized structures. The Ga−P bond orders calculated for compounds **2**, **3**, and **6** were 0.973, 1.699, and 2.546, respectively. Allowing for recognized deviations between predictions from Mayer's method and traditional integer value bonds,[20] these values suggest that these compounds contain a single, double, and triple Ga−P bond, respectively. This observation is corroborated by the Ga−P bond length of **2**, which is very near 2.33 Å, i.e., the sum of the covalent radii of gallium and phosphorus; and **6** is accepted as having a gallium−phosphorus triple bond. The Ga−P bond order for **1** was calculated to be 0.320, which would suggest that this is a weak dative-type bond. Compound **5** has a calculated Ga−P bond order of 1.322, while that of **4** is 0.744.

Figure 6 is a plot of the bond energies of **1**−**6** versus the natural log of the bond orders of these compounds. The correlation constant for this linear fit is 0.978, nicely supporting the original hypothesis of a linear relationship. There is a data point, however, that has substantially larger deviation from the fit as do all other points. This point corresponds to compound **4**, which shows a considerable *weakening* of the Ga−P bond upon elimination of hydrogen at the gallium atom. This behavior is somewhat counterintuitive and further analysis of this molecule was deemed necessary.

Upon examination of orbitals of compound **4**, it was determined that a σ antibonding orbital between the gallium and the phosphorus was occupied. The appearance of an antibonding occupied orbital was surprising and suggested that this molecule required an MCSCF calculation to better understand the electronic structure and, specifically, to determine the contributions of various electron configurations to the ground state structure. The MCSCF calculation was performed using GAMESS, with the same basis set that was used in the Gaussian94 calculations. The GAMESS calculation was run using six orbitals for each set of d orbitals, while the Gaussian94 calculation used five orbitals for each set of d orbitals. For the MCSCF calculation, the four highest-lying occupied orbitals were correlated with four unoccupied orbitals. All $^1A'$ CSFs consistent with distributing eight electrons among the eight orbitals were included in the calculation; hence the designation CASSCF(8|8). The MCSCF active space was 6a″ 16a′ 17a′ 18a′ 7a″ 19a′ 20a′ 8a″. Table 3 lists the coefficients and orbital occupation numbers of the CSFs with the largest contributions from the CASSCF(8|8) calculation, in the natural orbital basis.

TABLE 3: Largest Coefficients and Orbital Occupation Numbers of CSFs from CASSCF(8|8) Calculation of 4 in the Natural Orbital Basis

coeff	6a″	16a′	17a′	18a′	7a″	19a′	20a′	8a″
0.960 761	2	2	2	2	0	0	0	0
−0.073 433	2	1	2	1	1	0	0	1
−0.083 350	2	1	2	1	0	0	2	0
−0.088 566	2	0	2	2	0	0	2	0

The molecule was positioned such that the *xy*-plane is the symmetry plane, with the gallium having a positive *x*-component, the phosphorus having a negative *x*-component, and both the gallium and phosphorus lying on the *y*-axis. The hydrogens have a negative *x*-component and a positive *y*-component, and have equal but opposite *z*-components. In the natural orbital representation, the 6a″ orbital appears to be a H−P−H bonding orbital (P: 3p_z: 0.332 649, $H_\pm$: 1s: ±0.258 079). The 16a′ orbital has Ga−P antibonding character (Ga: 4s: −0.642 615, 4s': −0.503 004, 4p_x: −0.203 491, P: 3p_x: 0.139 453, 4s: 0.126 017). The 17a′ orbital appears to be another H−P−H bonding orbital (P: 3p_y: 0.371 337, 3p_y': 0.198 982, $H_\pm$: 1s: 0.222 242). The 18a′ orbital appears to be a localized phosphorus orbital (3s: 0.599 925, 3s′: 0.505 511). Now considering the weakly occupied orbitals, the 7a″ orbital is that of a localized gallium orbital (4p_z: −0.497 153, 4p_z': −0.518 952). The 19a′ orbital has H−P−H antibonding character (P: 3p_y: −0.634 923, 3p_y': −0.244 467, $H_\pm$: 1s: 0.577 782), while the 20a′ orbital is another localized gallium orbital (4p_y: −0.503 041, 4p_y': −0.515 646). And finally, the 8a″ orbital corresponds to another H−P−H antibonding orbital (P: 3p_z: 0.738 070, $H_\pm$: 1s: ∓0.489 404).

Since compound **4** possesses an occupied Ga−P σ antibond, the ability to predict the bond order based on standard methods is suspect. A similar plot as Figure 6, excluding the point corresponding to **4**, shows much stronger agreement (correlation constant of 0.9961) to a Pauling type relationship (E_s = 62.423, C_E = 44.013). According to this plot, the Ga−P single bond energy is about 62 ± 1 kcal/mol, which is almost identical to the Ga−P bond energy calculated for **2**. Based on this plot, the bond order of compound **4** would be 0.574 (which ought to be compared with the value of 0.744 from Mayer bond order analysis of the single reference description of **4**).

Previous experiments on compounds similar to those presented in this study report the surprising finding that upon formation of Me_2PGaH_2 from Me_2HPGaH_3, via hydrogen elimination (reaction 5), this compound decomposes readily to form gallium metal and Me_2HP, with further loss of hydrogen gas.[26]

$$\mathrm{Me_2HPGaH_3} \xrightarrow{-\mathrm{H_2}} \mathrm{Me_2PGaH_2} \rightarrow \mathrm{Me_2PH} + \mathrm{Ga} + {}^1\!/_2\mathrm{H_2} \tag{5}$$

Compound **2** is similar to the product formed experimentally by Greenwood et al., Me_2PGaH_2. Compound **4** of this study is the product of a hydrogen elimination at the gallium atom of H_2PGaH_2 (**2**). In order to help elucidate the unusual experimental result, two other compounds that are related to compound **4** were considered. Compound **7** is the product of hydrogenation of **4** across the Ga−P bond, while compound **8** corresponds to

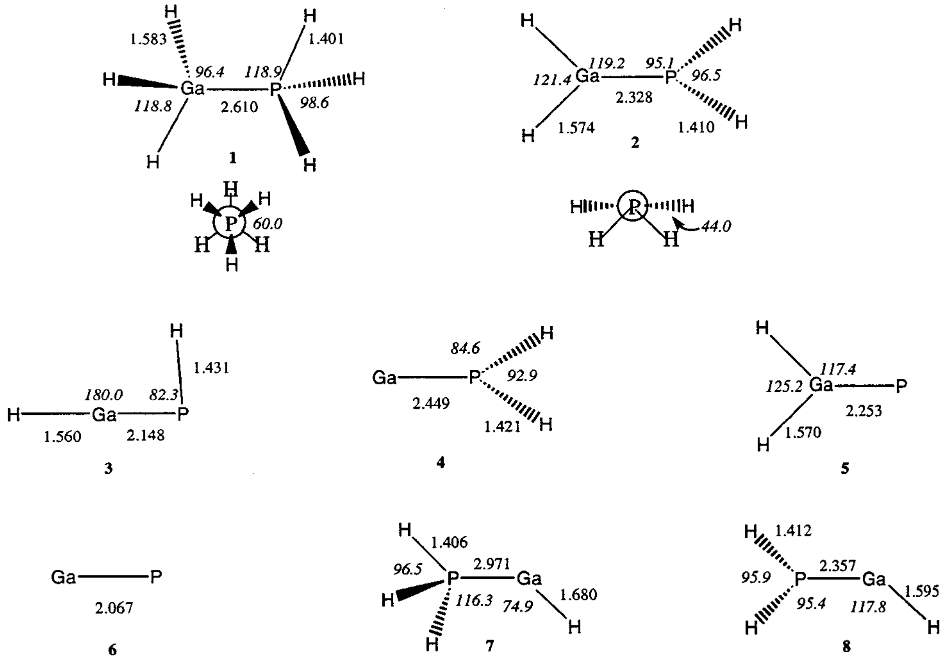


Figure 7. MP2/6-311++G(d,p) geometries of compounds **1**−**8**. Bond lengths in angstroms, bond angles in degrees.

TABLE 4: Geometrical Parameters of 1−8 at the HF/ and B3LYP/6-311++G(d,p) Levels[a]

	Ga−P	Ga−H	P−H	∠H−Ga−P	∠Ga−P−H
1	2.699 (2.608)	1.582 (1.573)	1.399 (1.413)	96.6 (96.3)	118.3 (119.3)
2	2.343 (2.331)	1.571 (1.567)	1.408 (1.422)	119.2 (119.0)	98.0 (96.1)
3	2.146 (2.145)	1.552 (1.554)	1.422 (1.438)	178.3 (177.7)	88.1 (85.1)
4	2.475 (2.479)		1.414 (1.431)		93.7 (88.2)
5	2.278 (2.222)	1.566 (1.564)		117.7 (118.9)	
6	2.143 (2.103)				
7	3.398 (2.942)	1.673 (1.696)	1.405 (1.418)	74.8 (73.4)	115.2 (115.4)
8	2.371 (2.391)	1.590 (1.608)	1.408 (1.425)	117.8 (115.9)	96.6 (94.5)

[a] Bond lengths are in angstroms, bond angles are in degrees. B3LYP values in parentheses.

a homolytic cleavage of a Ga−H bond in **2**. The energies of **7** at the HF, B3LYP, and MP2 levels were found to be −2266.237 524, −2268.616 621, and −2266.431 036 hartrees, respectively. After zero-point vibrational energies were included, the energy of **7** was found to be 22.9 kcal/mol higher than that of **1** at the MP2/6-311++G(d,p) level. For compound **8**, the energies at the HF, B3LYP, and MP2 levels were calculated to be −2265.667 761, −2268.014 112, and −2265.843 178 hartrees, respectively. The energy of **8** is 26.0 kcal/mol higher than that of **1** at the MP2/6-311++G(d,p) level. The relative energies of these compounds are shown in Figure 5. The Ga−P bond energies in **7** and **8** were calculated using the Hess's law argument described earlier that was used to calculate the bond energies for **1**−**6**. These energies were found to be only 4 kcal/mol for **7** and 71 kcal/mol for **8**. Hence, the energy of the Ga−P bond in **7** is even weaker than in compound **1**, whereas compound **8** has a Ga−P bond which is comparable in strength to a single bond. Thus, our calculations suggest that structures similar to **7** may be involved in the experimentally observed reaction of substituted **2**.

III. Geometries

The optimized geometries of compounds **1**−**8** at the MP2/6-311++G(d,p) level are shown in Figure 7. The geometrical parameters of the corresponding minima at the HF and DFT levels are given in Table 4. Calculation of the harmonic vibrational frequencies at the MP2/6-311++G(d,p) level showed the absence of imaginary frequencies and so confirmed that these structures are, at least, local minima. Compound **2** has C_s symmetry, where the Ga−P bond axis is normal to the plane formed by the phosphorus and its two hydrogens. The Ga−P bond length in this structure is within 0.02 Å of the experimental Ga−P bond length found in a gallium−phosphorus monomer which has alkyl and aryl groups substituted for the hydrogens, $Mes_2GaP(tBu)_2$.[5] Moreover, both of these structures have Ga−P bond lengths that are within 0.02 Å of the sum of the covalent radii: 2.33 Å. One can see from Figure 7 that **1** has a staggered conformation, giving this molecule C_{3v} symmetry. The long Ga−P bond length corroborates the energy argument given in the preceding section that this structure possesses a weak dative-type bond between the gallane and phosphine moieties. **3** is a planar structure, but only has C_s symmetry. Compound **4** is not a planar structure, but nonetheless has C_s symmetry, with the Ga−P bond axis normal to the H−P−H plane (i.e., similar to the structure found for **2**). Compound **5** is a planar structure possessing C_{2v} symmetry. **6** is gallium phosphide, which obviously has $C_{\infty v}$ symmetry. Compound **7** is found to have C_s symmetry, while compound **8** has no symmetry elements beyond the identity.

As may be expected, as one eliminates hydrogen across the gallium−phosphorus bond, the Ga−P bond length shortens; this shortening may be drastic, e.g., from **1** to **2** and from **2** to **3**, or less so as in going from **3** to gallium phosphide (**6**). However, it is at first surprising that upon dehydrogenation at the gallium atom in **2** to form **4**, the Ga−P bond length actually increases (by almost 0.12 Å); in light of the discussion in the previous

TABLE 5: Harmonic Vibrational Frequencies (cm^{-1}) of 1−8 at the MP2/6-311++G(d,p) Level

mode	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Ga−P stretch	179	360	475	287	390	526	101	336
H−Ga−H bend	724, 756(2)[a]	747			697			
H−P−H bend	1044, 1165(2)	1139		1075			1150	1128
Ga−H stretch	1957(2), 1980	2008, 2009	2037		2007, 2012		1612	1897
P−H stretch	2559, 2576(2)	2498, 2511	2381	2429, 2438			2541	2509

[a] Values in parentheses denote number of degenerate modes.

section, this geometrical change may be understood as occurring as a result of population of a Ga−P antibonding orbital. The dehydrogenation at the phosphorus atom in **2**, to form **5**, shortens the Ga−P bond by about 0.075 Å. Compound **7** shows nearly a 0.4 Å increase in the Ga−P bond length upon removal of a hydrogen molecule from the gallium atom of **1**. It is interesting to note that removal of one hydrogen atom from the gallium in **2** (i.e., to form **8**), also increases the bond length (i.e., by about 0.050 Å), and the resulting bond length is intermediate between that in **2** and **4** (where two hydrogens have been lost). In general, the Ga−H and P−H bond lengths only change on the order of 0.010−0.015 Å upon each hydrogen molecule elimination. However, there are significant exceptions: the Ga−H bond length in **7** is over 0.1 Å longer than the Ga−H bond lengths reported for the other compounds, while the Ga−H bond length in **8** is between 0.030 and 0.050 Å longer than that for the other compounds. The P−H bonds of **7** and **8** are not significantly different than those of the other compounds.

Vibrational frequencies of **1**−**8** are listed in Table 5. The frequency of the normal mode dominated by the Ga−P bond stretch increases from **1** to **2** and from **2** to **3**, as we would expect from the above consideration of geometrical changes and the usual assumption that bond length is inversely proportional to bond strength. The large increase in the Ga−P stretching frequency between **1** and **2** (i.e., a 101% increase) and between **2** and **3** (i.e., an additional 64% increase) suggests that the multiple bonds in these structures behave similar to multiple bonds composed of lighter atoms. However, there is a significant decrease, about 20%, in the vibrational frequency in going from **2** to **4**, which is coincident with the bond lengthening already noted. The Ga−P frequency for **7** is the lowest reported Ga−P stretching frequency for these compounds, and is only a little over half as large as that reported for compound **1**. It may be recalled that compound **7** was calculated to be essentially nonbonding (i.e., Ga−P "bond energy" of only 4 kcal/mol). All of these compounds follow the qualitative expectation that an increase in the length of the gallium−phosphorus bond is accompanied by a decrease in the vibrational frequency of that bond.

Bond lengths (of compounds **1**−**3**, **5**, and **6**) are plotted versus natural logarithms of bond orders (cf. eq 3) in Figure 8. The bond orders of Figure 8 are again the results from the Mayer analysis that were used for the energy plot. As with the energy analysis, compound **4** was excluded on the basis of the presence of an occupied σ antibonding orbital. For this plot, the y-intercept corresponds to the Ga−P single bond length, which is calculated to be 2.312 ± 0.01 Å. This value is about 0.016 Å shorter than the Ga−P bond length calculated for **2**. The correlation constant for this plot is 0.995, which strongly supports the validity of the linear Pauling relation for these molecules. It is interesting to note that, based on the data obtained from Figure 8, the bond order of **4** is calculated to be 0.597, which is within 5% of that calculated using energy arguments, i.e., the energy plot similar to Figure 6 after removal of **4** from the data set. Using Figure 8, the bond order predicted for compound **8** is 0.845, which is as we would expect: between that of **2** and that of **4**. The nonbonding compound **7** has a calculated bond order of only 0.084. As mentioned above, the Ga−P vibrational frequency in **7** is significantly less than in any other compound. ν(Ga−P) in **8** is slightly less than halfway between the corresponding frequency in **2** and **4** and so corroborates the bond order calculation.

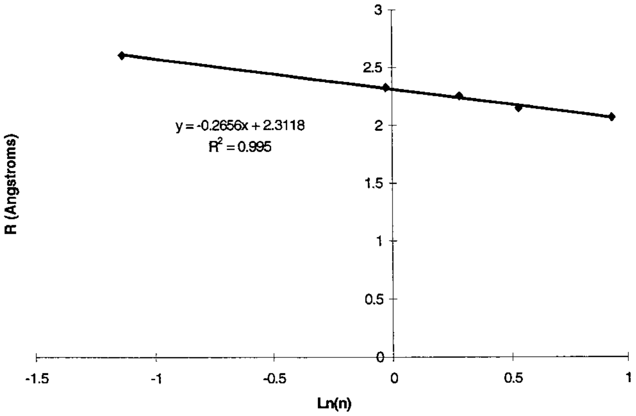
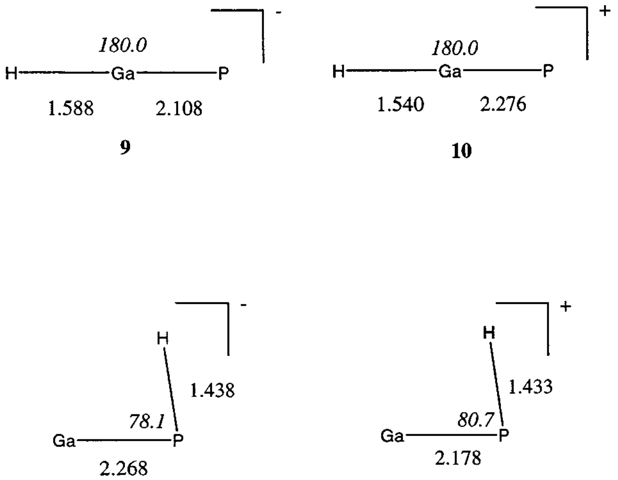


Figure 8. Plot of bond length vs natural log of bond order for compounds **1**−**3**, **5**, and **6**.



9 **10** **11** **12**

Figure 9. MP2/6-311++G(d,p) geometries of compounds **9**−**12**. Bond lengths in angstroms, bond angles in degrees.

IV. Ionic Compounds

Figure 9 shows the MP2/6-311++G(d,p) level optimized geometries of molecular ions (**9**−**12**) formed from the addition of a proton or hydride to gallium phosphide (**6**). Table 6 lists the geometrical parameters of these various ions at the HF and B3LYP levels of theory. Structures **9** and **10** can also be characterized as resulting from the cleaving of the P−H bond in **3** heterolytically. Comparison of **9** and **10** shows that the removal of electron density from the gallium−phosphorus compound, i.e., going from a negative ion to a positive ion, is accompanied by an increase in the Ga−P bond length and a

TABLE 6: Geometrical Parameters of 9−12 at the HF/ and B3LYP/6-311++G(d,p) Levels[a]

	Ga−P	Ga−H	P−H	∠H−Ga−P	∠Ga−P−H
9	2.072 (2.085)	1.576 (1.576)		180.0 (180.0)	
10	2.276 (2.282)	1.532 (1.537)		180.0 (180.0)	
11	2.270 (2.286)		1.431 (1.446)		89.0 (83.9)
12	1.943 (2.245)		1.390 (1.437)		180.0 (86.1)

[a] Bond lengths are in angstroms, bond angles are in degrees. B3LYP values in parentheses.

TABLE 7: Harmonic Vibrational Frequencies (cm^{-1}) of 9−12 at the MP2/6-311++G(d,p) Level

mode	9	10	11	12
Ga−P stretch	506.3	403.0	358.3	374.1
H−Ga−P bend	340.2, 340.3	368.4, 388.2		
Ga−P−H bend			427.5	524.3
Ga−H stretch	1879.0	2137.2		
P−H stretch			2319.9	2383.7

decrease in the Ga−H bond length. Structures **11** and **12** can be characterized as resulting from cleaving of the Ga−H bond in **3** heterolytically. In contrast to the situation with ions **9** and **10**, comparison of **11** and **12** shows that the Ga−P bond length decreases as electron density is removed from the gallium−phosphorus compounds. The P−H bond lengths behave similar to the Ga−H bond lengths in **9** and **10**: a removal of electron density decreases the bond length.

At the Hartree−Fock level, **12** is predicted to be a linear molecule, whereas the DFT and MP2 methods predict a bent structure. Attempts to obtain a linear isomer of **12** at the DFT and MP2 levels of theory produced structures with imaginary frequencies, which were not further investigated.

Table 7 lists the vibrational frequencies, at the MP2/6-311++G(d,p) level, of compounds **9**−**12**. The vibrational frequency of the Ga−P stretch in **9** is within 10% of that for **6**, i.e., a triple bond. The Ga−P stretch in **10** is about 10% higher than that of **2**, i.e., a single bond. It should be noted that for compound **10**, our calculations did not produce exact degeneracy in the bending modes; presumably, a multideterminant zero-order wave function would be necessary. The Ga−P stretches for **11** and **12** are within 10% of the Ga−P stretch in **2**.

Using the data obtained from the plot of the bond lengths versus the bond orders for compounds **1**−**3**, **5**, and **6** (cf. Figure 8), the Ga−P bond orders were predicted for compounds **9**−**12**. The bond order for **9** was calculated to be 2.154. The vibrational frequency of the Ga−P stretch is between the frequency calculated for a double and triple bond, so this value of the bond order appears to be at least qualitatively correct. The Ga−P bond order for **10** was calculated to be 1.144, which is supported by a vibrational frequency that was calculated to be about 10% larger than that of a single bond. Compound **11** was calculated to have a bond order of 1.179; however, its Ga−P harmonic vibrational frequency is lower than expected and is virtually the same as that for a singly bonded structure. Compound **12** was calculated as having a bond order of 1.655; as with compound **11**, the Ga−P vibrational frequency is lower than expected; in this case the deviation is more pronounced, and is only about 5% larger than that of the singly bonded **2**. So, the agreement between the Pauling relation and vibrational data for ionic compounds is not as strong as it is for neutral species. Based on these bond orders, and using eq 4 with constants obtained from the energy plot, the Ga−P bond energies for **9**−**12** were calculated and are reported in Table 8.

The energies of compounds **9**−**12** at the HF, B3LYP, and MP2 levels are given in Table 9. Compounds **9** and **11** correspond to products of hydride ion addition to gallium phosphide, while compounds **10** and **12** correspond to proton addition to gallium phosphide. Table 10 lists the internal energy changes associated with these various reactions, based on the MP2/6-311++G(d,p) calculations of the species involved. It would appear that proton addition is considerably more thermodynamically favorable than hydride ion addition; but in either case, coordination at the phosphorus is more favorable than at the gallium atom.

TABLE 8: Bond Energies of 9−12 Based on Pauling Relationship (See Text for More Detail)

	energy (kcal/mol)		energy (kcal/mol)
9	96	**11**	70
10	68	**12**	85

TABLE 9: Energies (au) of 9−12 at the HF, B3LYP, and MP2 Levels of Theory, and the 6-311++G(d,p) Basis Set

	HF	B3LYP	MP2
9	−2264.515 206	−2266.868 913	−2264.706 783
10	−2264.179 127	−2266.452 159	−2264.308 268
11	−2264.542 090	−2266.884 872	−2264.721 449
12	−2264.042 559	−2266.482 981	−2264.340 065

TABLE 10: Internal Energy Changes of Given Reactions at the HF, B3LYP, and MP2/6-311++G(d,p) Levels

	HF (kcal/mol)	B3LYP (kcal/mol)	MP2 (kcal/mol)
$H^- + GaP \rightarrow$ **9**	−119	−114	−119
$H^+ + GaP \rightarrow$ **10**	−213	−189	−186
$GaP + H^- \rightarrow$ **11**	−135	−126	−128
$GaP + H^+ \rightarrow$ **12**	−127	−208	−206

V. Comparison of Methods

It is generally accepted that the MP2 method gives geometries and energies that are essentially more accurate than the Hartree−Fock method (see, e.g., ref 31). However, there is considerable debate on the relative accuracies of the various DFT methods with respect to more traditional correlation methods, such as MP2. Driving this comparison is the fact that DFT methods are less computationally expensive, sometimes considerably, than correlated methods such as MP2. Because (approximate) DFT methods are not directly related to a variational principle or convergent perturbation series, their accuracy must be established through numerical experiment. In this section, we report such comparisons for the molecules and molecular ions studied.

The Ga−P bond lengths calculated at the B3LYP level for compounds **1**−**3** were all within 0.005 Å of that calculated at the MP2 level. However, for compounds **4**−**6**, the Ga−P bond length was calculated to be longer, by anywhere from 0.030 to nearly 0.100 Å (i.e., for **6**), using the B3LYP method. In every instance, except for **4**, the Ga−P bond lengths at the B3LYP level were closer to those calculated at the MP2 level than were the HF calculations. The Ga−H bond lengths calculated at the B3LYP level were all within 0.010 Å of those at the MP2 level. The P−H bonds of both **1** and **2** were calculated to be about 0.012 Å longer at the B3LYP level, while for the rest of the compounds they were calculated to within 0.010 Å of those from the MP2 calculations. All H−Ga−P bond angles were calculated at the B3LYP level to be within 2.5° of those calculated by the MP2 method, while the Ga−P−H bond angles were calculated to be anywhere from 0.4° to 3.6° larger at the B3LYP level than at the MP2 level.

B3LYP calculations underestimated the Ga−P bond length in **9** by 0.023 Å, while the bond length in **10** was overestimated by only 0.006 Å. All Ga−H and P−H bond lengths in these compounds were calculated to be within 0.010 Å of each other at the B3LYP and MP2 levels. The H−Ga−P bond angles for **9** and **10** were calculated by both MP2 and B3LYP to be 180.0°; the Ga−P−H bond angles for **11** and **12** were calculated to be between 5° and 6° larger at the B3LYP level than at the MP2 level. The calculations using the HF method predicted the bond angles in **11** to be over 10° larger than those from the MP2 calculations, and for **12**, the HF calculation produced a linear structure instead of a bent one.

The HF method overestimated the dehydrogenation reaction energies, relative to the MP2 results (cf. Figure 5), of compounds **2**−**6** in every case except for **5**. The errors were anywhere from 1 to 20 kcal/mol. The B3LYP method was in closer agreement with MP2 in all cases except for **4** and **5**, where it underestimated the reaction energies by 5.0 and 8.2 kcal/mol, respectively, while the HF method overestimated **4** by 2.6 kcal/mol and underestimated the reaction energy producing **5** by 7.1 kcal/mol. For **9**−**11**, the difference between the HF and MP2 reaction energies (cf. Table 10) ranged from overestimation by 27 kcal/mol to exact agreement. In the case of **12**, where the HF method was unable to optimize to the bent structure, the error was 79 kcal/mol! The B3LYP method was in considerably better agreement with MP2 than was the HF method for compounds **9**−**12**: the B3LYP differences from the MP2 calculations only ranged from 5 kcal/mol lower to 3 kcal/mol higher.

VI. Conclusions

The equilibrium geometries and energies of various gallium−phosphorus hydrides have been determined using Hartree−Fock, B3LYP density functional method, and second-order Møller−Plesset perturbation theory with a 6-311++G(d,p) basis set. It is apparent from these structures that gallium and phosphorus can form, perhaps surprisingly, strong double bonds, although unsaturation at gallium leads to forming weaker than expected bonds. It is also found that dative bonds are notably weak; geometrical evidence suggests that the cause of this weak interaction is a poor overlap of the unhybridized gallium p- and phosphorus s-orbitals. It was found that the energies of **1** and **2** are virtually indistinguishable, while the other compounds lie considerably higher in energy than **1**. It was shown that compounds containing Ga−P bonds conform to a Pauling relationship between bond length and bond order and between bond energy and bond order.

From the fitted Pauling relationship, our predicted Ga−P single bond length of about 2.312 ± 0.010 Å is in essential agreement with earlier theoretical and experimental studies. We predict a double bond length of 2.128 ± 0.018 Å, and our predicted triple bond length of 2.020 ± 0.025 Å is in agreement with the accepted value. The Ga−P single bond energy was calculated to be 62 ± 1 kcal/mol, while the double and triple bond energies were calculated to be 93 ± 2 and 111 ± 2 kcal/mol, respectively. The P−H bond in all compounds studied appears to be composed of an unhybridized p-orbital from the phosphorus and the s-orbital of the hydrogen. The Ga−H bond, however, appears to have contribution from sp^2- and sp-hybridized orbitals of the gallium.

Single-reference calculations of **4** showed that one of the occupied orbitals of this molecule is a Ga−P antibonding σ orbital. A CASSCF (8|8) calculation confirmed the nature of this orbital. Consequently, compound **4** has a very weak Ga−P bond (38 kcal/mol). Observed experimental reactivity of Me_2HPGaH_3 (scheme 5) may be interpreted as consistent with our calculation of **4**. Moreover, compounds **7** and **8** may be intermediates in such reactions; with compound **7** showing even further weakening of the Ga−P bond. Scheme 5, as written or with hydrogens replacing the methyl groups, should be examined with higher-level calculations and with determination of appropriate transition states.

Comparisons of the methods used in this study show that the B3LYP variant of DFT can give reaction energies of neutral gallium−phosphorus compounds in substantial agreement with the MP2 method (average deviation based on **1**−**6**: 4.4 kcal/mol). The HF method gives an average difference of 10.5 kcal/mol. B3LYP predicted reaction energies of gallium phosphide with H^+ or H^- deviate from MP2 results by an average of 3.2 kcal/mol. The HF average energy difference for these types of reactions was 16.1 kcal/mol, excluding **12** for which the HF method had qualitative failure.

The DFT method, in most cases, is in closer agreement with MP2 in calculating Ga−P bond lengths of neutral species (average distance, based on **1**−**8**: 0.025 Å) than is the HF method (0.157 Å, reduced to 0.045 Å with exclusion of **7**). B3LYP is in reasonably good agreement in calculating the Ga−H bond lengths (0.010 Å), and the P−H bond lengths (0.011 Å). B3LYP is also in better agreement with MP2 than is HF for calculating bond angles for these compounds. The average deviation of the Ga−P bond length in the ionic compounds (**9**−**12**) at the DFT level from the MP2 level was 0.037 Å, which is comparable, although larger, than the difference for the neutral compounds. In summary, B3LYP and MP2 are in semiquantitative agreement on the equilibrium molecular geometries of both the neutral and ionic compounds studied.

Acknowledgment. The authors gratefully acknowledge the Office of Naval Research (Grant No. N00014-96-1-1049) for financial support of the research presented herein. The authors also thank the University of North Dakota Computer Center for generously allowing the use of the UND IBM SP2.

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