

Ab Initio Study of Low-Lying Electronic States of XP (X = Li-B, Na-Si)

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The equilibrium geometries and harmonic vibrational frequencies of the low-lying electronic states of several as yet unobserved species (LiP, BeP, BP, NaP, MgP, AlP, and SiP) were calculated at the SCF/6-31G*, MP2(full)/6-31G*, and MP2(full)/6-311+G* levels of theory. For each of these species, equilibrium structures of the ground state and lowest excited states were also optimized at the QCISD(T)/6-311+G(2df) level. For all but SiP, the bonding is found to involve high-spin ground electronic states ($^3\Sigma^-$ for LiP, $^4\Sigma^-$ for BeP, $^3\Pi$ for BP, $^3\Sigma^-$ for NaP, $^4\Sigma^-$ for MgP, $^3\Sigma^-$ for AlP) in which two electrons occupy π orbitals lying primarily on the P atom (except for BP, where three electrons are in π orbitals), and the number of valence σ electrons ranges from four to six. In each case, the number of unpaired electrons is larger than that anticipated based on covalent P-X σ -bond formation. These unusual state orderings are consistent with our earlier findings and with the bonding picture we used to explain them. SiP has two lowest electronic states $^2\Sigma^+$ and $^2\Pi$ with close energies. The bond dissociation energies were also computed and found to be 37.7 (LiP), 23.6 (BeP), 70.5 (BP), 27.4 (NaP), 12.2 (MgP), 47.2 (AlP), and 76.3 kcal/mol (SiP), with all data referring to the QCISD(T)/6-311+G(2df)+ZPE level. The corresponding calculated bond lengths are 2.342 (LiP), 2.081 (BeP), 1.758 (BP), 2.690 (NaP), 2.546 (MgP), 2.426 (AlP), and 2.007 Å (SiP).

Introduction

While diatomic molecules composed from electronegative atoms or from one electronegative and one electropositive atom are well studied experimentally, diatomics between electropositive main groups atoms are not widely studied.^{1,2} For the latter species, several unexpected features have been found.³⁻⁵ For example, Nemukhin et al.³ found that LiB has a $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^1)$ $^3\Pi$ ground electronic state instead of the expected $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2)$ $^1\Sigma^+$ state, which is the ground state of the analogous molecule BH.¹ Similarly, Mavridis and Harrison⁴ found high-spin $(\sigma^2 \sigma^1 \pi^2)$ $^4\Sigma^-$ ground states for LiC and LiSi instead of the expected $(\sigma^2 \sigma^2 \pi^1)$ $^2\Pi$ state, which is the ground state for both CH and SiH.¹ These results show that normal expectations for ground electronic states may be incorrect for molecules containing two electropositive atoms and that states with one more π electron (and hence one fewer σ electron) than anticipated are favored in LiX compounds in comparison to HX compounds. In our previous work,⁵ we studied Si-X diatomics with electropositive X atoms (X = Li-B, Na-Al) and found the unexpected high-spin states to be the ground states for all these species. We put forth a picture of the chemical bonding that is consistent with these findings.

In the present work, we extend our investigations of diatomics with electropositive atoms by examining the relative energies of high- and low-spin electronic states of several X-P diatomics, where X is a group I, II, III, or IV element. To the best of our knowledge, the ground states of none of the species, except AlP, examined here have been experimentally characterized. The AlP molecule has been studied theoretically⁶ and experimentally,⁷ and a $^3\Sigma^-$ ground electronic state has been found with several low-lying excited states. The first excited state $^3\Pi$ was only 1.8 kcal/mol above $X^3\Sigma^-$.^{6a} Experimentally, only the ground-state dissociation energy $D_0^\circ = 50.8 \pm 3.0$ kcal/mol has been obtained by mass-spectrometric technique.⁷

Other XP compounds with X from groups V and VI such as PN, PO, PF, P₂, PS, and PCl as well as CP have already been studied experimentally and theoretically (see, for example, references in refs 1 and 2). For the group IV-VII P-X diatomics, low-spin ground electronic states ($^2\Sigma^+$ for CP, $^1\Sigma^+$ for PN, $^2\Pi$ for PO, $^3\Sigma^-$ for PF, $^1\Sigma_g^+$ for P₂, $^2\Pi$ for PS, and $^3\Sigma^-$ for PCl) have

been observed. No ab initio calculations have been performed for the X-P (X = Li-B, Na-Mg,Si) molecule to the best of our knowledge.

Clearly, it seems that for P-X compounds, when the electronegativity of X is large enough, the low-spin state becomes lower in energy, while the high-spin state is favored for electropositive X species. As part of this work, we wanted to determine the "border" of electronegativity at which P-X compounds change from low- to high-spin ground states and to analyze what orbital occupancy characteristics make the high-spin electronic states more stable.

Computational Details

The geometries of low-energy electronic states of LiP, BeP, BP, NaP, MgP, AlP, and SiP were preliminarily optimized employing analytical SCF gradients⁸ with a polarized split-valence basis set (results at this level are denoted SCF/6-31G*^{9,10}) and subsequently at the correlated MP2(full) level (denoted MP2(full)/6-31G*). Even more accurate geometries were obtained by performing MP2(full) calculations with 6-311+G* basis sets¹¹⁻¹⁴ for which the fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods. Finally, our most accurately correlated total energies were evaluated in the full fourth-order frozen-core approximation both by Møller-Plesset perturbation theory¹⁵ (MP4) and the quadratic configuration interaction including singles and doubles with approximate triples QCISD(T)¹⁶ method using standard 6-311+G(2df) basis sets.

Then, for the ground and for the lowest electronic states, the geometry was reoptimized at the QCISD(T)/6-311+G(2df) level. For all open-shell species, the USCF wave functions were projected to produce pure spectroscopic states (whose results, in turn, are labeled PUSCF, PMP2, PMP3, and PMP4).¹⁷ The Gaussian 90 program suite¹⁸ was used to perform all of the results discussed here. The results of our calculations are presented in Tables I-VIII and summarized in the following section.

Results and Discussion

LiP and NaP. For these species, one might anticipate either of two valence orbital occupancies. The first is that in which two electrons occupy a nonbonding 1σ orbital on P (essentially $3s^2$),

TABLE I: Calculated Molecular Properties of the Lowest LiP States

LiP ($^3\Sigma^-$) $1\sigma^2 1\pi^2 2\sigma^2$	LiP ($^3\Pi$) $1\sigma^2 1\pi^3 2\sigma^1$	LiP ($^1\Sigma^+$) $1\sigma^2 1\pi^4$
SCF/6-31G*		
$E_{SCF} = -348.143\ 48$ $R(\text{Li-P}) = 2.378\ \text{\AA}$ $\omega_e = 479\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.016$	$E_{SCF} = -348.116\ 25$ $R(\text{Li-P}) = 2.246\ \text{\AA}$ $\omega_e = 509\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.011$	$E_{SCF} = -348.023\ 92$ $R(\text{Li-P}) = 2.171\ \text{\AA}$ $\omega_e = 486\ \text{cm}^{-1}$
MP2(full)/6-31G*		
$E_{MP2} = -348.231\ 72$ $R(\text{Li-P}) = 2.362\ \text{\AA}$ $\omega_e = 486\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.015$	$E_{MP2} = -348.205\ 49$ $R(\text{Li-P}) = 2.224\ \text{\AA}$ $\omega_e = 530\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.011$	$E_{MP2} = -348.127\ 61$ $R(\text{Li-P}) = 2.125\ \text{\AA}$ $\omega_e = 525\ \text{cm}^{-1}$
MP2(full)/6-311+G*		
$E_{MP2} = -348.384\ 53$ $R(\text{Li-P}) = 2.331\ \text{\AA}$ $\omega_e = 495\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.014$	$E_{MP2} = -348.360\ 64$ $R(\text{Li-P}) = 2.189\ \text{\AA}$ $\omega_e = 541\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.012$	$E_{MP2} = -348.284\ 75$ $R(\text{Li-P}) = 2.072\ \text{\AA}$ $\omega_e = 544\ \text{cm}^{-1}$
QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// MP2(full)6-311+G*	QCISD(T)/6-311+G(2df)// MP2(full)6-311+G*
$R(\text{Li-P}) = 2.342\ \text{\AA}$ $E_{PUSCF} = -348.171\ 96$ $E_{PMP2} = -348.279\ 16$ $E_{PMP3} = -348.297\ 79$ $E_{PMP4} = -348.304\ 09$ $E_{QCISD} = -348.299\ 35$ $E_{QCISD(T)} = -348.304\ 84$ $T_{ePMP4} = 0.0\ \text{kcal/mol}$ $T_{eQCISD(T)} = 0.0\ \text{kcal/mol}$	$R(\text{Li-P}) = 2.189\ \text{\AA}$ $E_{PUSCF} = -348.147\ 42$ $E_{PMP2} = -348.256\ 19$ $E_{PMP3} = -348.274\ 75$ $E_{PMP4} = -348.281\ 12$ $E_{QCISD} = -348.276\ 13$ $E_{QCISD(T)} = -348.281\ 82$ $T_{ePMP4} = 14.4\ \text{kcal/mol}$ $T_{eQCISD(T)} = 14.4\ \text{kcal/mol}$	$R(\text{Li-P}) = 2.072\ \text{\AA}$ $E_{SCF} = -348.052\ 01$ $E_{MP2} = -348.181\ 26$ $E_{MP3} = -348.203\ 88$ $E_{MP4} = -348.213\ 65$ $E_{QCISD} = -348.218\ 69$ $E_{QCISD(T)} = -348.235\ 48$ $T_{eMP4} = 56.8\ \text{kcal/mol}$ $T_{eQCISD(T)} = 43.5\ \text{kcal/mol}$

TABLE II: Calculated Molecular Properties of the Lowest BeP States

BeP ($^4\Sigma^-$) $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$	BeP ($^2\Pi$) $1\sigma^2 2\sigma^2 1\pi^3$	BeP ($^2\Sigma^+$) $1\sigma^2 2\sigma^1 1\pi^4$
SCF/6-31G*		
$E_{SCF} = -355.294\ 50$ $R(\text{Be-P}) = 2.084\ \text{\AA}$ $\omega_e = 629\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.764$	$E_{SCF} = -355.238\ 43$ $R(\text{Be-P}) = 1.896\ \text{\AA}$ $\omega_e = 812\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.787$	$E_{SCF} = -355.172\ 00$ $R(\text{Be-P}) = 1.769\ \text{\AA}$ $\omega_e = 936\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.767$
MP2(full)/6-31G*		
$E_{MP2} = -355.394\ 03$ $R(\text{Be-P}) = 2.063\ \text{\AA}$ $\omega_e = 641\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.763$	$E_{MP2} = -355.376\ 92$ $R(\text{Be-P}) = 1.915\ \text{\AA}$ $\omega_e = 892\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.784$	$E_{MP2} = -355.311\ 94$ $R(\text{Be-P}) = 1.764\ \text{\AA}$ $\omega_e = 1686\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.765$
MP2(full)/6-311+G*		
$E_{MP2} = -355.547\ 33$ $R(\text{Be-P}) = 2.063\ \text{\AA}$ $\omega_e = 631\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.764$	$E_{MP2} = -355.531\ 40$ $R(\text{Be-P}) = 1.924\ \text{\AA}$ $\langle S^2 \rangle = 0.795$	$E_{MP2} = -355.467\ 97$ $R(\text{Be-P}) = 1.771\ \text{\AA}$ $\omega_e = 1497\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.764$
QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)6-311+G(2df)// MP2(full)/6-311+G*
$R(\text{Be-P}) = 2.081\ \text{\AA}$ $E_{PUSCF} = -355.322\ 64$ $E_{PMP2} = -355.437\ 26$ $E_{PMP3} = -355.457\ 80$ $E_{PMP4} = -355.465\ 35$ $E_{QCISD} = -355.461\ 48$ $E_{QCISD(T)} = -355.468\ 08$ $T_{ePMP4} = 0.0\ \text{kcal/mol}$ $T_{eQCISD(T)} = 0.0\ \text{kcal/mol}$	$R(\text{Be-P}) = 1.928\ \text{\AA}$ $E_{PUSCF} = -355.270\ 02$ $E_{PMP2} = -355.428\ 16$ $E_{PMP3} = -355.446\ 76$ $E_{PMP4} = -355.460\ 34$ $E_{QCISD} = -355.449\ 73$ $E_{QCISD(T)} = -355.462\ 50$ $T_{ePMP4} = 3.1\ \text{kcal/mol}$ $T_{eQCISD(T)} = 3.5\ \text{kcal/mol}$	$R(\text{Be-P}) = 1.771\ \text{\AA}$ $E_{PUSCF} = -355.205\ 21$ $E_{PMP2} = -355.364\ 75$ $E_{PMP3} = -355.381\ 58$ $E_{PMP4} = -355.394\ 15$ $E_{QCISD} = -355.383\ 30$ $E_{QCISD(T)} = -355.395\ 18$ $T_{ePMP4} = 44.7\ \text{kcal/mol}$ $T_{eQCISD(T)} = 45.7\ \text{kcal/mol}$

three electrons occupy a 1π orbital (essentially $3p$ on P), and one electron occupies an antibonding 2σ orbital (the Li- or Na-P σ bond). In this case, a $^3\Pi$ state would be expected to be the ground state. Alternatively, the 2σ orbital was doubly occupied and the 1π orbital could be doubly occupied, and a $^3\Sigma^-$ state would then be the ground state.

Among all states with π^2 , π^3 , or π^4 occupancies, we found the following states to lie lowest for both LiP and NaP: $^3\Sigma^-$ ($1\sigma^2 1\pi^2 2\sigma^2$), $^3\Pi$ ($1\sigma^2 1\pi^3 2\sigma^1$), $^1\Sigma^+$ ($1\sigma^2 1\pi^4$), and $^5\Sigma^-$ ($1\sigma^2 2\sigma^1 1\pi^3 3\sigma^1$). The energies and physical properties of the lowest three of these states appear in Tables I and IV, respectively.

Note that a high-spin $^3\Sigma^-$ ground electronic state having $1\sigma^2 1\pi^2 2\sigma^2$ valence orbital occupancy was obtained for both

molecules. The calculated ground-state dissociation energies are 37.7 (LiP) and 27.4 kcal/mol (NaP) at the QCISD(T)/6-311+G-(2df)+ZPE level. The $^3\Pi$ state is the first excited state for both molecules and lies above the ground states by 14.4 (LiP) and 14.1 kcal/mol (NaP), respectively. The low-spin state ($^1\Sigma^+$) is 43.5 kcal/mol (LiP) and 43.1 kcal/mol (NaP) higher in energy than the $^3\Sigma^-$ triplet state.

The $^5\Sigma^-$ states do not have minima on their potential energy curves for either molecule. Vertical excitation energies for the $^3\Sigma^- \rightarrow ^5\Sigma^-$ processes are 55.3 and 33.3 kcal/mol at the MP2-(full)/6-311+G* level, respectively, for LiP and NaP. Small spin contamination was found for the $^3\Sigma^-$ and $^3\Pi$ states of both molecules, and therefore our results should be reliable.

TABLE III: Calculated Molecular Properties of the Lowest BP States

BP ($^3\Pi$) $1\sigma^2 2\sigma^2 1\pi^3 \sigma^1$	BP ($^1\Sigma^+$) $1\sigma^2 1\pi^4 2\sigma^2$	BP ($^2\Sigma^-$) $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$	BP ($^3\Pi$) $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2 2\pi^1$	BP ($^2\Sigma^-$) $1\sigma^2 2\sigma^2 1\pi^2 2\pi^2$
SCF/6-31G*				
$E_{SCF} = -365.275\ 05$ $R(\text{B-P}) = 1.730\ \text{\AA}$ $\omega_e = 1008\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.166$	$E_{SCF} = -365.200\ 24$ $R(\text{B-P}) = 1.638\ \text{\AA}$ $\omega_e = 1150\ \text{cm}^{-1}$	$E_{SCF} = -365.250\ 73$ $R(\text{B-P}) = 1.979\ \text{\AA}$ $\omega_e = 647\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.018$	$E_{SCF} = 365.231\ 99$ $R(\text{B-P}) = 1.969\ \text{\AA}$ $\omega_e = 660\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.015$	$E_{SCF} = -365.125\ 53$ $R(\text{B-P}) = 2.165\ \text{\AA}$ $\omega_e = 477\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.586$
MP2(full)/6-31G*				
$E_{MP2} = -365.423\ 81$ $R(\text{B-P}) = 1.716\ \text{\AA}$ $\omega_e = 1159\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.154$	$E_{MP2} = -365.418\ 02$ $R(\text{B-P}) = 1.694\ \text{\AA}$ $\omega_e = 1086\ \text{cm}^{-1}$	$E_{MP2} = -365.386\ 75$ $R(\text{B-P}) = 1.965\ \text{\AA}$ $\omega_e = 652\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.018$	$E_{MP2} = -365.346\ 10$ $R(\text{B-P}) = 1.967\ \text{\AA}$ $\omega_e = 636\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.015$	$E_{MP2} = -365.216\ 40$ $R(\text{B-P}) = 2.087\ \text{\AA}$ $\omega_e = 565\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.546$
MP2(full)/6-311+G*				
$E_{MP2} = -365.584\ 11$ $R(\text{B-P}) = 1.718\ \text{\AA}$ $\omega_e = 1148\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.143$	$E_{MP2} = -365.578\ 24$ $R(\text{B-P}) = 1.696\ \text{\AA}$ $\omega_e = 1072\ \text{cm}^{-1}$	$E_{MP2} = -365.551\ 71$ $R(\text{B-P}) = 1.943\ \text{\AA}$ $\omega_e = 585\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.018$	$E_{MP2} = -365.505\ 75$ $R(\text{B-P}) = 1.972\ \text{\AA}$ $\omega_e = 618\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.015$	$E_{MP2} = -365.377\ 19$ $R(\text{B-P}) = 2.101\ \text{\AA}$ $\omega_e = 514\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.547$
QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*
$R(\text{B-P}) = 1.758\ \text{\AA}$ $E_{PUSCF} = -365.313\ 46$ $E_{PMP2} = -365.481\ 37$ $E_{PMP3} = -365.503\ 54$ $E_{PMP4} = -365.517\ 15$ $E_{QCISD} = 365.510\ 20$ $E_{QCISD(T)} = -365.523\ 44$ $T_{ePMP4} = 0.0\ \text{kcal/mol}$ $T_{eQCISD(T)} = 0.0\ \text{kcal/mol}$	$R(\text{B-P}) = 1.684\ \text{\AA}$ $E_{SCF} = -365.230\ 89$ $E_{MP2} = -365.474\ 21$ $E_{MP3} = -365.480\ 11$ $E_{MP4} = -365.514\ 33$ $E_{QCISD} = -365.491\ 41$ $E_{QCISD(T)} = -365.512\ 67$ $T_{ePMP4} = 1.8\ \text{kcal/mol}$ $T_{eQCISD(T)} = 6.8\ \text{kcal/mol}$	$R(\text{B-P}) = 1.943\ \text{\AA}$ $E_{PUSCF} = -365.288\ 47$ $E_{PMP2} = -365.446\ 36$ $E_{PMP3} = -365.475\ 05$ $E_{PMP4} = -365.487\ 11$ $E_{QCISD} = -365.482\ 91$ $E_{QCISD(T)} = -365.492\ 02$ $T_{ePMP4} = 18.9\ \text{kcal/mol}$ $T_{eQCISD(T)} = 19.7\ \text{kcal/mol}$	$R(\text{B-P}) = 1.972\ \text{\AA}$ $E_{PUSCF} = -365.263\ 78$ $E_{PMP2} = -365.397\ 42$ $E_{PMP3} = -365.421\ 41$ $E_{PMP4} = -365.430\ 76$ $E_{QCISD} = -365.427\ 71$ $E_{QCISD(T)} = -365.435\ 62$ $T_{ePMP4} = 54.2\ \text{kcal/mol}$ $T_{eQCISD(T)} = 55.1\ \text{kcal/mol}$	$R(\text{B-P}) = 2.101\ \text{\AA}$ $E_{PUSCF} = -365.161\ 91$ $E_{PMP2} = -365.268\ 97$ $E_{PMP3} = -365.293\ 13$ $E_{PMP4} = -365.303\ 37$ $E_{QCISD} = -365.307\ 84$ $E_{QCISD(T)} = -365.319\ 36$ $T_{ePMP4} = 134.1\ \text{kcal/mol}$ $T_{eQCISD(T)} = 128.1\ \text{kcal/mol}$

TABLE IV: Calculated Molecular Properties of the Lowest NaP States

NaP ($^3\Sigma^-$) $1\sigma^2 2\sigma^2 1\pi^2$	NaP ($^3\Pi$) $1\sigma^2 1\pi^3 2\sigma^1$	NaP ($^1\Sigma^+$) $1\sigma^2 1\pi^4$
SCF/6-31G*		
$E_{SCF} = -502.538\ 63$ $R(\text{Na-P}) = 2.733\ \text{\AA}$ $\omega_e = 225\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.128$	$E_{SCF} = -502.513\ 08$ $R(\text{Na-P}) = 2.570\ \text{\AA}$ $\omega_e = 299\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.011$	$E_{SCF} = -502.427\ 98$ $R(\text{Na-P}) = 2.474\ \text{\AA}$ $\omega_e = 292\ \text{cm}^{-1}$
MP2(full)/6-31G*		
$E_{MP2} = -502.627\ 76$ $R(\text{Na-P}) = 2.674\ \text{\AA}$ $\omega_e = 312\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.089$	$E_{MP2} = -502.601\ 37$ $R(\text{Na-P}) = 2.547\ \text{\AA}$ $\omega_e = 332\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.011$	$E_{MP2} = -502.528\ 22$ $R(\text{Na-P}) = 2.435\ \text{\AA}$ $\omega_e = 315\ \text{cm}^{-1}$
MP2(full)/6-311+G*		
$E_{MP2} = -502.899\ 48$ $R(\text{Na-P}) = 2.666\ \text{\AA}$ $\omega_e = 298\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.070$	$E_{MP2} = -502.874\ 03$ $R(\text{Na-P}) = 2.545\ \text{\AA}$ $\omega_e = 307\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.012$	$E_{MP2} = -502.801\ 47$ $R(\text{Na-P}) = 2.435\ \text{\AA}$ $\omega_e = 304\ \text{cm}^{-1}$
QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*
$R(\text{Na-P}) = 2.690\ \text{\AA}$ $E_{PUSCF} = -502.569\ 36$ $E_{PMP2} = -502.677\ 27$ $E_{PMP3} = -502.695\ 77$ $E_{PMP4} = -502.702\ 01$ $E_{QCISD} = -502.696\ 36$ $E_{QCISD(T)} = -502.701\ 98$ $T_{ePMP4} = 0.0\ \text{kcal/mol}$ $T_{eQCISD(T)} = 0.0\ \text{kcal/mol}$	$R(\text{Na-P}) = 2.545\ \text{\AA}$ $E_{PUSCF} = -502.546\ 63$ $E_{PMP2} = -502.654\ 14$ $E_{PMP3} = -502.672\ 59$ $E_{PMP4} = -502.678\ 78$ $E_{QCISD} = -502.674\ 01$ $E_{QCISD(T)} = -502.679\ 48$ $T_{ePMP4} = 14.6\ \text{kcal/mol}$ $T_{eQCISD(T)} = 14.1\ \text{kcal/mol}$	$R(\text{Na-P}) = 2.435\ \text{\AA}$ $E_{SCF} = -502.458\ 68$ $E_{MP2} = -502.583\ 94$ $E_{MP3} = -502.606\ 37$ $E_{MP4} = -502.615\ 35$ $E_{QCISD} = -502.619\ 36$ $E_{QCISD(T)} = -502.633\ 34$ $T_{ePMP4} = 54.4\ \text{kcal/mol}$ $T_{eQCISD(T)} = 43.1\ \text{kcal/mol}$

The valence isoelectronic LiN molecule has also been studied theoretically¹⁹ and found to have a $^3\Sigma^-$ ground electronic state at the CISD/DZP(N) level. The first excited $^3\Pi$ state of LiN lies above the ground state by only 7.8 kcal/mol.

BeP and MgP. Given a total of seven valence electrons ($2s^2$ or $3s^2$ from Be or Mg and $3s^2 3p^3$ from P), the most likely candidates for low-energy configurations involve $1\sigma^2 2\sigma^2 1\pi^3 \sigma^1$, $1\sigma^2 2\sigma^2 1\pi^3$, or $1\sigma^2 1\pi^4 2\sigma^1$ occupancies. We therefore studied, for each of these two molecules, the following five low-lying electronic states: $^4\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^3 \sigma^1$), $^2\Pi$ ($1\sigma^2 1\pi^3 2\sigma^2$), and $^2\Sigma^+$ ($1\sigma^2 1\pi^4 2\sigma^1$). The results of our calculations appear in Tables II and V.

We find the high-spin $^4\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^3 \sigma^1$) state to be the ground state and the $^2\Pi$ ($1\sigma^2 2\sigma^2 1\pi^3$) state to be the lowest lying excited state for both molecules. Adiabatic X $^4\Sigma^- \rightarrow ^2\Pi$ excitation energies are 3.5 kcal/mol for BeP and 7.7 kcal/mol for MgP.

The $^2\Sigma^+$ electronic states are higher in energy and have adiabatic excitation energies of 45.7 (BeP) and 51.3 kcal/mol (MgP) (see Tables II and V).

The calculated ground-state dissociation energies are 23.6 (BeP) and 12.2 kcal/mol (MgP) at the QCISD(T)/6-311+G(2df) level. The $^2\Pi$ states are also bound for both BeSi and MgSi, but for both the $^2\Sigma^+$ excited states lie above the energy of the two atoms in their ground states.

Small spin contaminations were observed for the $^4\Sigma^-$ and $^2\Sigma^+$ states of both BeP and MgP; these states were therefore treated using the projection methods outlined above. However, for the $^2\Pi$ state, the spin contamination was very large, so our data for this state should be viewed as not very reliable.

BP and AlP. With eight valence electrons, and reflecting on the fact that π^2 and π^3 occupancies produced the lowest energy

TABLE V: Calculated Molecular Properties of the Lowest MgP States

MgP ($^4\Sigma^-$) $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$	MgP ($^2\Pi$) $1\sigma^2 2\sigma^2 1\pi^3$	MgP ($^2\Sigma^+$) $1\sigma^2 2\sigma^1 1\pi^4$
	SCF/6-31G*	
$E_{SCF} = -540.293\ 06$ $R(\text{Mg-P}) = 2.559\ \text{\AA}$ $\omega_e = 298\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.783$	$E_{SCF} = -540.259\ 66$ $R(\text{Mg-P}) = 2.407\ \text{\AA}$ $\omega_e = 382\ \text{cm}^{-1}$ $\langle S^2 \rangle = 1.546$	$E_{SCF} = -540.162\ 89$ $R(\text{Mg-P}) = 2.216\ \text{\AA}$ $\omega_e = 406\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.822$
	MP2(full)/6-31G*	
$E_{MP2} = -540.393\ 21$ $R(\text{Mg-P}) = 2.541\ \text{\AA}$ $\omega_e = 309\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.780$	$E_{MP2} = -540.365\ 74$ $R(\text{Mg-P}) = 2.356\ \text{\AA}$ $\omega_e = 411\ \text{cm}^{-1}$ $\langle S^2 \rangle = 1.542$	$E_{MP2} = -504.295\ 46$ $R(\text{Mg-P}) = 2.171\ \text{\AA}$ $\omega_e = 627\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.811$
	MP2(full)/6-311+G*	
$E_{MP2} = -540.662\ 76$ $R(\text{Mg-P}) = 2.542\ \text{\AA}$ $\omega_e = 308\ \text{cm}^{-1}$ $\langle S^2 \rangle = 3.780$	$E_{MP2} = -540.635\ 84$ $R(\text{Mg-P}) = 2.362\ \text{\AA}$ $\omega_e = 404\ \text{cm}^{-1}$ $\langle S^2 \rangle = 1.537$	$E_{MP2} = -540.566\ 63$ $R(\text{Mg-P}) = 2.175\ \text{\AA}$ $\omega_e = 539\ \text{cm}^{-1}$ $\langle S^2 \rangle = 0.802$
QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*
$R(\text{Mg-P}) = 2.546\ \text{\AA}$ $E_{PUSCF} = -540.329\ 52$ $E_{PMP2} = -540.442\ 64$ $E_{PMP3} = -540.462\ 62$ $E_{PMP4} = -540.469\ 81$ $E_{QCISD} = -540.465\ 32$ $E_{QCISD(T)} = -540.471\ 85$ $T_{ePMP4} = 0.0\ \text{kcal/mol}$ $T_{eQCISD(T)} = 0.0\ \text{kcal/mol}$	$R(\text{Mg-P}) = 2.362\ \text{\AA}$ $E_{PUSCF} = -540.305\ 42$ $E_{PMP2} = -540.426\ 42$ $E_{PMP3} = -540.446\ 32$ $E_{PMP4} = -540.454\ 96$ $E_{QCISD} = -540.449\ 63$ $E_{QCISD(T)} = -540.459\ 61$ $T_{ePMP4} = 9.3\ \text{kcal/mol}$ $T_{eQCISD(T)} = 7.7\ \text{kcal/mol}$	$R(\text{Mg-P}) = 2.175\ \text{\AA}$ $E_{PUSCF} = -540.204\ 82$ $E_{PMP2} = -540.357\ 29$ $E_{PMP3} = -540.375\ 02$ $E_{PMP4} = -540.386\ 94$ $E_{QCISD} = -540.377\ 57$ $E_{QCISD(T)} = -540.390\ 10$ $T_{ePMP4} = 52.0\ \text{kcal/mol}$ $T_{eQCISD(T)} = 51.3\ \text{kcal/mol}$

TABLE VI: Calculated Molecular Properties of the Lowest AlP States

AlP ($^3\Sigma^-$) $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2$	AlP ($^3\Pi$) $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$	AlP ($^1\Sigma^+$) $1\sigma^2 2\sigma^2 1\pi^4$	AlP ($^5\Pi$) $1\sigma^2 \sigma^2 1\pi^2 3\sigma^1 2\pi^1$	AlP ($^5\Sigma^-$) $1\sigma^2 \sigma^2 1\pi^2 2\pi^2$
		SCF/6-31G*		
$E_{SCF} = -530.585\ 43$ $R(\text{Al-P}) = 2.435\ \text{\AA}$ $\omega_e = 381\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.017$	$E_{SCF} = -582.566\ 57$ $R(\text{Al-P}) = 2.269\ \text{\AA}$ $\omega_e = 404\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.087$	$E_{SCF} = -582.497\ 54$ $R(\text{Al-P}) = 2.106\ \text{\AA}$ $\omega_e = 521\ \text{cm}^{-1}$	no minimum	$E_{SCF} = -582.437\ 92$ $R(\text{Al-P}) = 2.682\ \text{\AA}$ $\omega_e = 237\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.748$
		MP2(full)/6-31G*		
$E_{MP2} = -582.712\ 38$ $R(\text{Al-P}) = 2.412\ \text{\AA}$ $\omega_e = 388\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.016$	$E_{MP2} = -582.707\ 71$ $R(\text{Al-P}) = 2.197\ \text{\AA}$ $\omega_e = 489\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.070$	$E_{MP2} = -582.688\ 37$ $R(\text{Al-P}) = 2.050\ \text{\AA}$ $\omega_e = 672\ \text{cm}^{-1}$	$E_{MP2} = -582.652\ 52$ $R(\text{Al-P}) = 2.580\ \text{\AA}$ $\omega_e = 187\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.049$	$E_{MP2} = -582.522\ 07$ $R(\text{Al-P}) = 2.573\ \text{\AA}$ $\omega_e = 287\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.707$
		MP2(full)/6-311+G*		
$E_{MP2} = -582.981\ 75$ $R(\text{Al-P}) = 2.413\ \text{\AA}$ $\omega_e = 361\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.017$	$E_{MP2} = -582.977\ 71$ $R(\text{Al-P}) = 2.193\ \text{\AA}$ $\omega_e = 487\ \text{cm}^{-1}$ $\langle S^2 \rangle = 2.071$	$E_{MP2} = -582.958\ 93$ $R(\text{Al-P}) = 2.047\ \text{\AA}$ $\omega_e = 670\ \text{cm}^{-1}$	$E_{MP2} = -582.921\ 44$ $R(\text{Al-P}) = 2.589\ \text{\AA}$ $\omega_e = 170\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.050$	$E_{MP2} = -582.790\ 73$ $R(\text{Al-P}) = 2.567\ \text{\AA}$ $\omega_e = 282\ \text{cm}^{-1}$ $\langle S^2 \rangle = 6.703$
QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// QCISD(T)/6-311+G(2df)	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*	QCISD(T)/6-311+G(2df)// MP2(full)/6-311+G*
$R(\text{Al-P}) = 2.426\ \text{\AA}$ $E_{PUSCF} = -582.629\ 54$ $E_{PMP2} = -582.773\ 91$ $E_{PMP3} = -582.800\ 59$ $E_{PMP4} = -582.810\ 61$ $E_{QCISD} = -582.805\ 53$ $E_{QCISD(T)} = -582.813\ 29$ $T_{ePMP4} = 0.0\ \text{kcal/mol}$ $T_{eQCISD(T)} = 0.0\ \text{kcal/mol}$	$R(\text{Al-P}) = 2.230\ \text{\AA}$ $E_{PUSCF} = -582.615\ 26$ $E_{PMP2} = -582.774\ 09$ $E_{PMP3} = -582.797\ 23$ $E_{PMP4} = -582.809\ 10$ $E_{QCISD} = -582.799\ 72$ $E_{QCISD(T)} = -582.811\ 24$ $T_{ePMP4} = 0.9\ \text{kcal/mol}$ $T_{eQCISD(T)} = 1.3\ \text{kcal/mol}$	$R(\text{Al-P}) = 2.047\ \text{\AA}$ $E_{SCF} = -582.539\ 94$ $E_{MP2} = -582.753\ 04$ $E_{MP3} = -582.766\ 89$ $E_{MP4} = -582.790\ 30$ $E_{QCISD} = -582.733\ 72$ $E_{QCISD(T)} = -582.791\ 88$ $T_{ePMP4} = 12.7\ \text{kcal/mol}$ $T_{eQCISD(T)} = 13.4\ \text{kcal/mol}$	$R(\text{Al-P}) = 2.589\ \text{\AA}$ $E_{PUSCF} = -582.582\ 67$ $E_{PMP2} = -582.709\ 08$ $E_{PMP3} = -582.733\ 21$ $E_{PMP4} = -582.742\ 15$ $E_{QCISD} = -582.737\ 43$ $E_{QCISD(T)} = -582.745\ 21$ $T_{ePMP4} = 42.9\ \text{kcal/mol}$ $T_{eQCISD(T)} = 42.7\ \text{kcal/mol}$	$R(\text{Al-P}) = 2.567\ \text{\AA}$ $E_{PUSCF} = -582.481\ 13$ $E_{PMP2} = -582.574\ 80$ $E_{PMP3} = -582.597\ 69$ $E_{PMP4} = -582.607\ 44$ $E_{QCISD} = -582.613\ 75$ $E_{QCISD(T)} = -582.625\ 59$ $T_{ePMP4} = 127.5\ \text{kcal/mol}$ $T_{eQCISD(T)} = 117.8\ \text{kcal/mol}$

states for the Li-, Na-, Be-, and Mg-containing species, the following configurations seem most favorable: $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2$, $1\sigma^2 2\sigma^2 1\pi^2 2\pi^2$, $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2 2\pi^1$, $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$, and $1\sigma^2 1\pi^4 2\sigma^2$.

The following five electronic states derived from these configurations were probed for BP and AlP: $^1\Sigma^+$ ($1\sigma^2 1\pi^4 2\sigma^2$), $^3\Pi$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1$), $^3\Sigma^-$ ($1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$), $^5\Pi$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^1 2\pi^1$), and $^5\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2 2\pi^2$). For BP, a $^3\Pi$ ($1\sigma^2 2\sigma^2 3\sigma^1 1\pi^3$) ground state was obtained, while AlP has a $^3\Sigma^-$ ($1\sigma^2 2\sigma^2 3\sigma^1 1\pi^2$) ground electronic state.

The $^1\Sigma^+$ electronic state is the first excited state for BP and lies above the ground state by 6.8 kcal/mol, while the $^3\Sigma^-$, $^5\Pi$, and $^5\Sigma^-$ electronic states lie 19.7, 55.1, and 128.1 kcal/mol (all data at QCISD(T)/6-311+G(2df)) above the ground state, respectively.

The lowest excited state, $^3\Pi$, of AlP is only 1.5 kcal/mol higher than the ground state (see Table VI). An analogous low-lying $^3\Pi$ excited state (lying 11.1 kcal/mol above the ground state) is known for the isoelectronic Si_2 molecule.¹ The low-spin state $^1\Sigma^+$ is 13.4 kcal/mol higher than the ground state for AlP, and the high-spin $^5\Pi$ and $^5\Sigma^-$ states are much higher in energy (42.7 and 117.8 kcal/mol, respectively; see Table VI).

Small spin contaminations have been found for the $^3\Sigma^-$ and $^5\Pi$ states and moderate contamination appeared for the $^3\Pi$ state, while the spin contamination of the $^5\Sigma^-$ state was rather large.

These ground states are strongly bound, with calculated dissociation energies of 70.5 (BP) and 47.2 kcal/mol (AlP), both results being at the QCISD(T)/6-311+G(2df)+ZPE level. Our data for AlP agrees well with the experimental $D_0^\circ = 50.8 \pm 3.0$

TABLE VII: Calculated Molecular Properties of the Lowest SiP States

SiP ($2\Sigma^+$) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$	SiP (2Π) $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2$
SCF/6-31G*	
$E_{SCF} = -629.542\ 06$	$E_{SCF} = -629.568\ 35$
$R(\text{Si-P}) = 1.968\ \text{\AA}$	$R(\text{Si-P}) = 2.139\ \text{\AA}$
$\omega_e = 731\ \text{cm}^{-1}$	$\omega_e = 468\ \text{cm}^{-1}$
$\langle S^2 \rangle = 0.786$	$\langle S^2 \rangle = 1.255$
MP2(full)/6-31G*	
$E_{MP2} = -629.746\ 44$	$E_{MP2} = -629.731\ 85$
$R(\text{Si-P}) = 1.993\ \text{\AA}$	$R(\text{Si-P}) = 1.991\ \text{\AA}$
$\omega_e = 693\ \text{cm}^{-1}$	$\omega_e = 781\ \text{cm}^{-1}$
$\langle S^2 \rangle = 0.787$	$\langle S^2 \rangle = 0.923$
MP2(full)/6-311+G*	
$E_{MP2} = -630.018\ 07$	$E_{MP2} = -630.002\ 24$
$R(\text{Si-P}) = 1.987\ \text{\AA}$	$R(\text{Si-P}) = 1.991\ \text{\AA}$
$\omega_e = 694\ \text{cm}^{-1}$	$\omega_e = 754\ \text{cm}^{-1}$
$\langle S^2 \rangle = 0.787$	$\langle S^2 \rangle = 0.984$
QCISD(T)/6-311+G(2df)//QCISD(T)/6-311+G(2df)	
$R(\text{Si-P}) = 2.007\ \text{\AA}$	$R(\text{Si-P}) = 2.087\ \text{\AA}$
$E_{PUSCF} = -629.598\ 33$	$E_{PUSCF} = -629.628\ 28$
$E_{PMP2} = -629.825\ 74$	$E_{PMP2} = -629.816\ 19$
$E_{PMP3} = -629.840\ 98$	$E_{PMP3} = -629.843\ 74$
$E_{PMP4} = -629.863\ 75$	$E_{PMP4} = -629.858\ 52$
$E_{QCISD} = -629.842\ 90$	$E_{QCISD} = -629.848\ 80$
$E_{QCISD(T)} = -629.862\ 16$	$E_{QCISD(T)} = -629.863\ 64$
$T_{ePMP4} = 0.0\ \text{kcal/mol}$	$T_{ePMP4} = 3.3\ \text{kcal/mol}$
$T_{eQCISD(T)} = 0.9\ \text{kcal/mol}$	$T_{eQCISD(T)} = 0.0\ \text{kcal/mol}$

kcal/mol.⁷ Previously, the AlP molecule was studied and its geometry was optimized at the MRD-CI,^{6a,b} CAS-MCSCF,^{6c} and at QCISD(T)/6-311G(2df) (using SCF/6-31G* geometry) levels.^{6d} The $3\Sigma^-$ state was found to be more stable than the 3Π state by 1.2–1.8 kcal/mol at these levels. This agrees with our more sophisticated calculations, where the 3Π state is higher than the $3\Sigma^-$ ground state by 3.5 kcal/mol at the QCISD(T)/6-311+G(2df)//QCISD(T)/6-311+G(2df) level (see Table VI). The vibrational frequency of AlP ($3\Sigma^-$) calculated at the CASSCF (376 cm^{-1})^{6c} and MRSDCI (392 cm^{-1})^{6c} levels agrees with our 361- cm^{-1} MP2(full)/6-311+G* value.

SiP. With nine valence electrons ($2s^2 2p^2$ of C or $3s^2 3p^2$ of Si and $3s^2 3p^3$ of P), one may form the following electronic configurations: $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$, $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2$, $1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2 4\sigma^1$, and $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1 4\sigma^1$.

The following four electronic states derived from these electronic configurations were probed for SiP: $2\Sigma^+$ ($1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1$), 2Π ($1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2$), $4\Sigma^-$ ($1\sigma^2 2\sigma^2 1\pi^2 3\sigma^2 4\sigma^1$), and 4Π ($1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1 4\sigma^1$). At the SCF level (with 6-31G*, 6-311+G*, and 6-311+G(2df) bases), the 2Π state is the most stable. However, at PMP4/6-311+G(2df) correlated levels the $2\Sigma^+$ state is lower lying. The energy difference between the ground $2\Sigma^+$ and first excited state 2Π is only 3.3 kcal/mol at PMP4/6-311+G(2df), and at our highest QCISD(T)/6-311+G(2df)//QCISD(T)/6-311+G(2df) level the 2Π state is even lower in energy than $2\Sigma^+$ by 0.9 kcal/mol. Spin-contamination of the 2Π state is higher than for $2\Sigma^+$, and because the energy difference for these two states is very small, we are not able to predict the ground state for the SiP molecule with certainty. Both high-spin $4\Sigma^-$ and 4Π states have no minima on their potential curves, but the SiP

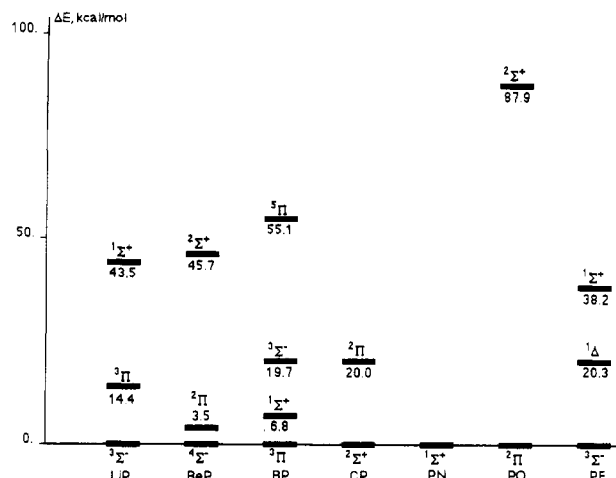


Figure 1. Energies of ground and low-lying excited states of P-X species for X ranging across the first row (at the QCISD(T)/6-311+G(2df) level).

molecule is very strongly bound in its low-spin ground state. The calculated dissociation energy is 76.3 kcal/mol at QCISD(T)/6-311+G(2df)+ZPE level. The dissociation energy $D_0^0(\text{SiP}) = 86\ \text{kcal/mol}$ obtained mass spectrometrically²⁰ is somewhat higher than our best theoretical value. Spin contamination for the $2\Sigma^+$ state is small, but for the 2Π state it is moderate. Therefore, our data are probably more accurate for the ground state.

The isovalent CN, SiN, and CP molecules have been studied experimentally.^{1,2,21-24} $2\Sigma^+$ ground and $A^2\Pi_i$ first excited states have been found for all of these diatomics. The $X^2\Sigma^+ \rightarrow A^2\Pi_i$ excitation energies are 26.4 for CN,¹ 19.7 for CP,¹ and 5.8 kcal/mol for SiN.²³ Therefore, our estimate of the $X^2\Sigma^+ \rightarrow A^2\Pi_i$ excitation energy (2 kcal/mol) of SiP agrees with the trend in the experimental data.

Overview

As summarized in Figures 1 and 2, along the first period from LiP to FP as well as within the second period from NaP to ClP, a high-spin electronic state is the ground state when X is an electropositive atom (Li, Na, Be, Mg, B, Al), and a low-spin state is the ground state when X is an electronegative atom (C, Si, N, P, O, S, F, or Cl); the border seems to occur between B and C and between Al and Si.

The excited (low-spin) $1\sigma^2 1\pi^4$ electronic configuration in LiP and NaP has three electron pairs in bonding orbitals, so formally these $1\Sigma^+$ state molecules have triple bonds. However, the bonds are very polarized in the Li^+P^- or Na^+P^- direction, and electron density concentrates mainly on P. In the $1\sigma^2 1\pi^3 2\sigma^1$ electronic configurations, one electron transfers from a bonding 1π orbital into an antibonding 2σ orbital. Longer bond lengths and lower vibrational frequencies are thus found for such states. In the $1\sigma^2 1\pi^2 2\sigma^2$ electronic configurations, two electrons are moved from 1π orbital into the 2σ orbital, and further lengthening of bonds and reductions in the vibrational frequencies are observed (see Tables I and IV).

While the bond lengths and frequencies are changed in accordance with expectations based on a simple MO picture, the

TABLE VIII: Calculated Dissociation Energies with 6-311+G(2df) Basis Set*

reaction	PUHF	PMP2	PMP3	PMP4	QCISD(T)	QCISD(T) + ZPE
$\text{LiP}(3\Sigma^-) \rightarrow \text{Li}(2S) + \text{P}(4S)$	+19.2	+35.7	+37.0	+38.2	+38.4	+37.7
$\text{BeP}(4\Sigma^-) \rightarrow \text{Be}(1S) + \text{P}(4S)$	+26.0	+29.7	+26.5	+25.8	+24.5	+23.6
$\text{BP}(3\Pi) \rightarrow \text{B}(2P) + \text{P}(4S)$	+44.4	+72.2	+68.1	+70.6	+72.2	+70.5
$\text{NaP}(3\Sigma^-) \rightarrow \text{Na}(2S) + \text{P}(4S)$	+8.8	+25.7	+27.0	+28.1	+27.8	+27.4
$\text{MgP}(4\Sigma^-) \rightarrow \text{Mg}(1S) + \text{P}(4S)$	+8.6	+14.2	+12.6	+12.8	+12.6	+12.2
$\text{AlP}(3\Sigma^-) \rightarrow \text{AlP}(2P) + \text{P}(4S)$	+27.7	+45.7	+46.1	+47.2	+47.7	+47.2
$\text{SiP}(2\Sigma^+) \rightarrow \text{Si}(3P) + \text{P}(4S)$	+22.1	+80.0	+70.7	+79.3	+77.3	+76.3

* ZPE corrections calculated at MP2(full)/6-311+G*.

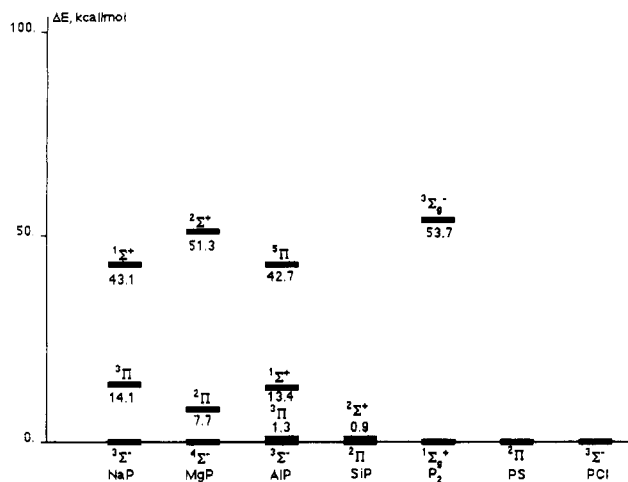


Figure 2. Energies of ground and low-lying excited states of P-X species for X ranging across the second row (at the QCISD(T)/6-311+G(2df) level).

relative total energies display the opposite trend. For both molecules, the $^3\Sigma^-$ states are the most stable, while the $^1\Sigma^+$ states with the maximal number of electrons in the bonding orbitals are the least unstable. As we discussed in our previous work on SiX diatomics,³ the reason for the higher stability of $^3\Sigma^-$ states relative to both $^3\Pi$ and $^1\Sigma^+$ states is the small nuclear electric fields in the bonding region between nuclei for diatomics containing electropositive atoms, as well as the X^+P^- charge-transfer character of the π^2 configuration.

Similar trends (Tables II and V) are found for BeP and MgP, where the bond lengths increase and vibrational frequencies decrease along the $^2\Sigma^+$ ($1\sigma^21\pi^42\sigma^1$) – $^2\Pi$ ($1\sigma^21\pi^32\sigma^2$) – $^4\Sigma^-$ ($1\sigma^21\pi^22\sigma^23\sigma^1$) series, although the electronic stability increases along this same series. For AlP, the same trend is found (see Table VI); the bond lengths increase and frequencies decrease along the series $^1\Sigma^+$ ($1\sigma^21\pi^42\sigma^2$) – $^3\Pi$ ($1\sigma^21\pi^32\sigma^23\sigma^1$) – $^3\Sigma^-$ ($1\sigma^21\pi^22\sigma^23\sigma^2$), while the total electronic stability increases.

However, BP contains the most electronegative atoms in the XP series considered here (with the exception of SiP). In this case, instead of a $^3\Sigma^-$ (π^2) ground state, the $^3\Pi$ ($1\pi^3$) is the most stable. We believe this occurs because the nuclear electric field in BP is strong enough to attract five electrons to the bonding region. When even more electronegative atoms are involved, even stronger nuclei fields occur and can lead to the stability of states with $1\pi^4$ occupancy. In fact, CP has $^2\Sigma^+$ ground states with $1\pi^4$ occupancy and in the SiP two states $^2\Sigma^+$ and $^2\Pi$ have similar energy with $1\pi^3$ and $1\pi^4$ occupancy.

Summary and Conclusions

Our primary findings on these new diatomic molecular species can be summarized as follows.

1. LiP, BeP, BP, NaP, MgP, and AlP all have high-spin ground electronic states of $^3\Sigma^-$, $^4\Sigma^-$, $^3\Pi$, $^3\Sigma^-$, $^4\Sigma^-$, and $^3\Sigma^-$ symmetry,

respectively. Except for BP, all of these states have two electrons in the π orbital. BP has a $^3\Pi$ ground state with three electrons on the bonding 1π orbital. SiP has a $^2\Sigma^+$ or a $^2\Pi$ low-spin ground state, with four or three electrons in the 1π orbital, respectively.

2. The ground states of LiP, NaP, BeP, MgP, BP, AlSi, and SiP are thermodynamically very stable with respect to dissociation.

3. Electropositive elements such as Li, Na, Be, Mg, B, and Al favor high-spin states; C, Si, N, P, O, and S favor low-spin states.

4. CP and SiP seem to form the border dividing high- and low-spin state preference.

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