# Theoretical and Experimental Reevaluation of the Basicity of $\lambda^3$-Phosphinine

**Nguyen-Nguyen Pham-Tran,[†,‡] Guy Bouchoux,[§] David Delaere,[†] and Minh Tho Nguyen*[,†]**

*Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium, and Laboratoire des Mécanismes Réactionnels, Département de Chimie (DCMR), Ecole Polytechnique, F-91128 Palaiseau Cedex, France*

*Received: October 12, 2004; In Final Form: January 28, 2005*

We have investigated the basicity of phosphinine ($C_5H_5P$, phosphabenzene) in reevaluating its proton affinity (PA) and gas-phase basicity (GB) and the p$K_a$ value of its protonated form. As a necessary step, we have first determined its gas-phase proton affinity. Using both mass spectrometric and quantum chemical methods, we have obtained the values PA($C_5H_5P$) = 195.8 ± 1.0 kcal mol$^{-1}$ and $GB_{298}$($C_5H_5P$) = 188.1 ± 1.0 kcal mol$^{-1}$, in good agreement with previous results. We then derived a value of p$K_a$($C_5H_6P^+$) = −16.1 ± 1.0 in aqueous solution using three different approaches: the latter markedly differs from the currently available value of −10. The reason for such a discrepancy in the p$K_a$ of protonated phosphinine in solution is discussed. In the theoretical determination of PAs, evaluation of the basis set superposition error (BSSE) showed that this effect is quite small, being 0.1−0.2 kcal mol$^{-1}$ for phosphinine, when a density functional theory (DFT) method in conjunction with a large basis set were used.

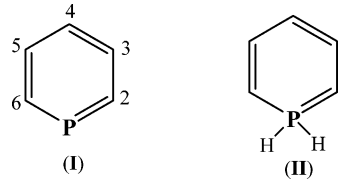
## 1. Introduction

Phosphinines are derivatives of benzenes in which a phosphorus atom is incorporated into the six-membered ring. While the $\lambda^3$-phosphinine (**I**) is the P-analogue of pyridine, $\lambda^5$-phosphinine (**II**) is a typical phosphorus compound (Scheme 1). Several reviews on the rich chemistry of phosphinines have already been available in periodicals and books.[1] For a recent comprehensive review, we would refer to the ref 1. In this present work, we have paid particular attention to the basicity of the parent $\lambda^3$-phosphinine (**I**) for which relevant quantitative parameters have not been established yet.

The basicity of a compound could usually be quantified by its intrinsic proton affinity (PA), gas-phase free energy of protonation (GB), and the p$K_a$ value of its protonated form in a solution. Gas-phase proton affinity of $\lambda^3$-phosphinine (**I**) was determined by Hodges et al.[2] to be PA($C_5H_5P$) = 195.8 kcal mol$^{-1}$, which is far smaller than the corresponding value of pyridine, namely, PA($C_5H_5N$) = 219.4 kcal mol$^{-1}$, but it is closer to that of the arsenic derivative, PA($C_5H_5As$) = 189.3 kcal mol$^{-1}$. In fact, the weak nucleophilic character of phosphinines is confirmed by the fact that they do not react with strong alkylating or protonating reagents such as ROTf (alkyl triflate) or $CF_3CO_2H$. Earlier theoretical studies[3−5] using the HF/4-31G, AM1, and PM3 levels of molecular orbital theory agreed with each other, pointing toward a preference for P-protonation over C-protonation ($C_2$ site), even though the reported results showed a rather poor quantitative agreement with the experimental PA, the difference amounting, in fact, up to 27.8 kcal mol$^{-1}$.

Another way of characterizing the basicity of a neutral molecular system is to consider the p$K_a$ of its protonated form in various solutions. This p$K_a$ value is, in such a way, a measure of the acidity of the protonated species considered and, conversely, the basicity of the neutral counterpart.

**SCHEME 1: $\lambda^3$-Phosphinine (I) and $\lambda^5$-Phosphinine (II)**




(**I**) (**II**)

In a 1971 paper,[6] Oehling and Schweig used the semiempirical complete neglect of differential overlap (CNDO/2) method to evaluate the p$K_a$ of both N-protonated pyridine and P-protonated phosphinine and obtained p$K_a$($C_5H_6P^+$) ≈ −10. The latter value was obtained on the basis of the following data: p$K_a$($C_5H_6N^+$) = 5.2, PA($C_5H_5N$) = 213 kcal mol$^{-1}$, and PA($C_5H_5P$) = 192 kcal mol$^{-1}$. According to these authors and in comparison with the differences of PA and p$K_a$ experimental values of the parent couple $NH_3/PH_3$, a difference of 21 kcal mol$^{-1}$ in the PAs of pyridine/phosphinine leads to a reduction of 15 units in going from protonated pyridine to protonated phosphinine.

A remarkable fact is that the empirical value of p$K_a$($C_5H_6P^+$) = −10 reported in ref 6 has been adopted and recorded in various books as a reference value without any further critical evaluation. In view of the surprising scarcity of accurate results on both PA and p$K_a$ values for phosphinines, we set out in the present work to reevaluate them for the parent molecule using not only mass spectroscopy for determining the PA but also the appropriate quantum chemical methods for both quantities. It turns out that there is a good agreement on PA between experimental and theoretical methods. On the contrary, our calculated results on p$K_a$ show a significant discrepancy with the value reported in ref 6. In the next sections, the determination of the gas-phase PA will first be described, then followed by the computations of the p$K_a$.

* E-mail: minh.nguyen@chem.kuleuven.ac.be.
† University of Leuven.
‡ Permanent address: Faculty of Chemistry, College of Natural Sciences, University of HoChiMinh City, Vietnam.
§ Ecole Polytechnique.

10.1021/jp045339c CCC: $30.25 
Published on Web 03/09/2005

**TABLE 1: Equilibrium Proton Transfer Thermochemical Data for Reactions $IH^+ + B \rightarrow I + BH^+$**

| B | $\Delta_1G_T°$ [a] | $GB_{298}(B)$[c,d] | $\Delta_pS°(B)$[b,d] | $GB_{298}(\mathbf{I})$[c,e] |
|---|---|---|---|---|
| methyl acetate | $-0.406 \pm 0.143$ | 189.0 | 1.195 | 188.6 |
| acetone | $+0.526 \pm 0.024$ | 186.9 | 2.079 | 187.5 |

[a] kcal mol$^{-1}$. [b] cal mol$^{-1}$ K$^{-1}$. [c] kcal mol$^{-1}$. [d] Taken from ref 8. [e] $\Delta_pS°(\mathbf{1}) = 0$, value assumed.

### 2. Evaluation of Proton Affinity and Gas-Phase Basicity of Phosphinine

For this purpose, we have employed both experimental mass spectrometric techniques and quantum chemical computations.

**2.1. Experiment.** Experimental determination of the basicity of the phosphinine molecule (**I**) has been carried out by the proton-transfer equilibrium constant method.

$$(\mathbf{I})H^+ + B \rightarrow (\mathbf{I}) + BH^+ \ (B = \text{methyl acetate and acetone}) \quad (1)$$

Proton-transfer reactions employed (eq 1) were performed on a Bruker CMS 47 X Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. The two neutrals (**I**) and B were introduced via a dual-inlet system equipped with two separate Balzers-UDV-035 valves controlling the partial pressure of each component. Experiments were done at a total indicated pressure of $(2-8) \times 10^{-8}$ mbar. The ions were produced following electron impact inside the ICR cell under the following conditions: filament current = 3.2 A and electron kinetic energy = 50 eV. After an ionization delay of ~4 s, all the ions were relaxed to thermal energies by the presence of the static pressure of the neutral reactants. This condition was checked by measuring the rate of disappearance of the reactive species $\mathbf{IH}^+$ and ensuring that it attains its upper limit. Subsequently, unwanted ions were ejected by a combination of chirp and soft radio-frequency pulses, and the remaining ions $\mathbf{IH}^+$ and/or $BH^+$ were allowed to react with the neutral molecules. Equilibrium was generally attained after a delay of 10−50 s; the reversibility of the reactions has been checked by performing three experiments where the selected ions were either $\mathbf{IH}^+$ or $BH^+$, or both. The ratio of peak intensities of $BH^+/\mathbf{IH}^+$ and the ratio of partial pressures of (**I**) and B were then used to calculate the equilibrium constant $K$ and thus to evaluate the Gibbs free energy change $\Delta_1G_T° = -RT \ln K$. The temperature of 320 K has been used in the estimation of $\Delta_1G_T°$. The partial pressure ratio was provided by the indication of an ionization gauge, Balzers IMR-132. The gauge reading has been corrected for the different ionization cross-section of the various compounds by considering their polarizabilities, as proposed earlier.[7] Polarizability values of 6.4, 7.1, and 10.0 Å$^3$ were used for acetone, methyl acetate, and phosphinine, respectively.[8]

The gas-phase basicity and proton affinity at 298 K were deduced from relationships 2 and 3:

$$GB_{298}(\mathbf{I}) = GB_{298}(B) + \Delta_1G_T° + (T - 298)[\Delta_pS°(\mathbf{I}) - \Delta_pS°(B)] \quad (2)$$

$$PA_{298}(\mathbf{I}) = GB_{298}(\mathbf{I}) + 298[S_{298}°(H^+) - \Delta_pS°(\mathbf{I})] \quad (3)$$

where $\Delta_pS°(X) = S°(XH^+) - S°(X)$ is the protonation entropy variation. The experimental results and the derived thermochemical quantities are summarized in Table 1.

A mean value of $GB_{298}(\mathbf{I}) = 188.1$ kcal mol$^{-1}$, with a probable error of ±1.0 kcal mol$^{-1}$, is thus deduced from our MS experiments. This GB leads to a proton affinity of $PA_{298}(\mathbf{I}) = 195.8 \pm 1.0$ kcal mol$^{-1}$, which is almost coincident with the value previously reported by Hodges et al.[2]

**TABLE 2: Calculated and Experimental Geometrical Parameters of $\lambda^3$-Phosphinine (I)**

| parameters[a] | HF | MP2 | B3LYP | BH & HLYP | B3PW91 | exptl[b] |
|---|---|---|---|---|---|---|
| Bond Length (Å) | | | | | | |
| R1 | 1.724 | 1.739 | 1.744 | 1.727 | 1.738 | 1.733 |
| R2 | 1.384 | 1.398 | 1.391 | 1.382 | 1.389 | 1.413 |
| R3 | 1.388 | 1.400 | 1.396 | 1.386 | 1.393 | 1.384 |
| R4 | 1.077 | 1.089 | 1.086 | 1.078 | 1.087 | |
| R5 | 1.077 | 1.089 | 1.086 | 1.079 | 1.088 | |
| R6 | 1.076 | 1.087 | 1.085 | 1.077 | 1.086 | |
| Bond Angle (deg) | | | | | | |
| A1 | 100.8 | 100.0 | 100.1 | 100.4 | 100.1 | 101.1 |
| A2 | 125.1 | 125.7 | 125.4 | 125.3 | 125.4 | 124.4 |
| A3 | 122.6 | 123.1 | 123.2 | 122.6 | 122.6 | 123.7 |
| A4 | 122.8 | 122.5 | 122.7 | 122.7 | 122.7 | 122.7 |

[a] See Figure 1 for definition of parameters. [b] Taken from ref 11.

**2.2. Quantum Chemical Calculations.** In the gas phase, the proton affinity (PA) of a molecule is defined as the negative of the enthalpy change at standard conditions (i.e., temperature and pressure) of the reaction

$$B + H^+ \leftrightarrows BH^+ \quad (4)$$

where B and $BH^+$ denote the base and its conjugate acid, respectively. Equation 5 was used to calculate the absolute proton affinity[9,10] in which $\Delta E_{el}$ represents the difference in electronic energies between the neutrals and the protonated forms at 0 K. ΔZPE corresponds to the difference in zero-point energies, whereas the last term, $^5/_2RT$, describes the thermodynamic temperature correction. The absolute PAs were calculated by means of different quantum chemical methods.

$$PA = -\Delta H = \Delta E_{el} + \Delta ZPE + \frac{5}{2}RT \quad (5)$$

Phosphinine (**I**) belongs to the $C_{2v}$ point group; its geometrical parameters determined using various levels of theory with the 6-311++G(d,p) basis set are summarized in Table 2. Compared with the available experimental results,[11] we note that the P−C bond length is shorter at both HF and BH-and-HLYP levels, but it is longer when using the hybrid B3LYP functional, and even slightly longer using the second-order perturbation theory MP2 and the B3PW91 functional. In all levels of theory used in this study, the C−C bond lengths are similar to those reported in previous calculations.[12,13] Thus, the C−C bond length alternation is calculated to be small (less than 0.5%), and it deviates by up to 2.1% with respect to the experimental values.[11] The results obtained using B3PW91/6-311++G(d,p) are in better agreement with experimental values.

Phosphinine exhibits, in principle, four positions that could be protonated, namely the P, $C_\alpha$, $C_\beta$, and $C_\gamma$ atoms (Figure 1). Table 3 summarizes the calculated values for PAs at different sites of phosphinine, making use of eq 5. The theoretical methods considered include the second-order perturbation theory (MP2), coupled-cluster theory CCSD(T), and DFT with the hybrid functional B3LYP, all in conjunction with the 6-311++G(d,p) one-electron basis set. B3LYP calculations using the larger aug-cc-pVTZ basis set are also given.

In the evaluation of PAs, the energies of the two corresponding reactants, namely the neutral substrate and the proton, are evaluated either separately or within a supermolecule. A basis set superposition error (BSSE) in the calculation of the energy

**TABLE 3: Computed Gas-Phase PAs (kcal mol$^{-1}$) at Different Sites of (I)**

| protonation site[a] | MP2[b] | B3LYP[c] | B3LYP[d] | CCSD(T)[c] | G1 | G2 | exptl. |
|---|---|---|---|---|---|---|---|
| P | 194.3 (2.0[e]) | 195.7 (0.1[e]) | 197.6 (0.1[e]) | 195.8 | 193.7 | 194.9 | 195.8[f] |
| $C_\alpha$ | 177.5 (2.0[e]) | 184.8 (0.2[e]) | 185.0 (0.1[e]) | 183.7 | 179.1 | 179.6 | |
| $C_\beta$ | 167.0 (1.7[e]) | 175.3 (0.2[e]) | 175.4 (0.1[e]) | 174.6 | 170.2 | 170.6 | |
| $C_\gamma$ | 175.0 (1.7[e]) | 182.9 (0.2[e]) | 183.4 (0.1[e]) | 182.4 | 178.1 | 178.7 | |

[a] Seeing Figure 1 for atom definition. [b] Based on MP2/6-311++G(d,p) optimized geometry. [c] Based on B3LYP/6-311++G(d,p) optimized geometry. [d] Based on B3LYP/aug-cc-pVTZ optimized geometry. [e] The values of BSSE correction in kcal mol$^{-1}$. [f] Experimental value determined in this work, see also ref 2.

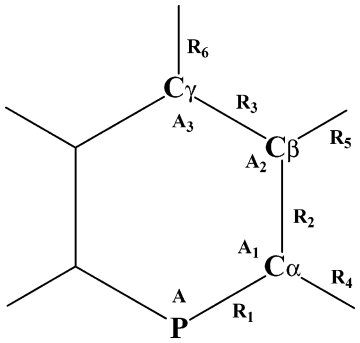



**Figure 1.** Geometric structure of $\lambda^3$-phosphinine (**I**).

of the neutral substrate could eventually be incurred in such a way that a certain correction on the calculated PA might be needed. It is usually expected that a deviation of a calculated PA value mainly arises from an inherent shortcoming of the quantum chemical method employed rather than from the lack of BSSE correction.[14] However, it has been demonstrated in previous studies[15] that the BSSE corrections on the calculated PAs could be as large as 3.3 kcal mol$^{-1}$ (13.9 kJ mol$^{-1}$). In fact, using the counterpoise method to evaluate the BSSE,[16] the resulting correction on the PA of bipyridine was evaluated to be 0.35 kcal mol$^{-1}$ at the HF/6-31G(d,p) level of MO theory and but amounting up to 3.30 kcal mol$^{-1}$ when the MP2/6-31G(d,p) level was used. In view of these results, we have evaluated the BSSE corrections on PAs, also making use of the counterpoise approach. Concretely, the BSSE value was derived from the single-point energy calculation of the neutral substrate with hydrogen ghost functions added at the position of the proton (at different sites) as found in the optimized protonated forms. To evaluate the BSSEs, we have used both the MP2 and B3LYP methods. Calculated PAs are summarized in Tables 3 and 4.

It is clear that P-protonation is consistently preferred over carbon-site protonations (Table 3). All the levels agree with each other, yielding comparable values for the PAs. When using DFT, the effect of enlarging the basis set is small for PA(C) but up to 2 kcal/mol for PA(P). The CCSD(T), G1, and G2 values for PA(P) are comparable but slightly deviate from each other. It turns out that the B3LYP/6-311++G(d,p) method provides us with the best agreement with the experimental value for PA(P). Regarding the BSSEs, our results point out that, while the corrections of 1.7−2.0 kcal mol$^{-1}$ on the MP2 PAs of phosphinine are significant and in agreement with earlier studies,[15] they are negligible at the B3LYP level (being 0.1−0.2 kcal mol$^{-1}$, Table 3). The BSSEs, calculated using the B3LYP/6-311++G(d,p) method for a series of phosphines and amines and listed in Table 4, also show that the resulting corrections are quite small. In addition, BSSE corrections do not systematically improve the agreement between calculated and experimental PAs. Overall, for the sake of uniformity and consistency with the available literature, we select the B3LYP/6-311++G(d,p) + ZPE level to calculate PAs of other compounds considered in this work (cf. Table 4).

**TABLE 4: Calculated and Experimental Protonation Thermochemistry of Considered Molecules**

| | PA (kcal mol$^{-1}$) | | | GB (kcal mol$^{-1}$) | | |
|---|---|---|---|---|---|---|
| base | calcd | exptl[a] | dev. | calcd | exptl[a] | dev. |
| $NH_3$ | 203.8 (0.9[b]) | 203.6 | 0.2 | 196.1 | 195.7 | 0.4 |
| $CH_3NH_2$ | 214.7 (0.7[b]) | 214.9 | 0.2 | 207.0 | 206.6 | 0.4 |
| $(CH_3)_2NH$ | 221.7 (0.6[b]) | 222.2 | 0.5 | 213.9 | 214.3 | 0.4 |
| $(CH_3)_3N$ | 225.9 (0.6[b]) | 226.8 | 0.9 | 218.1 | 219.4 | 1.3 |
| $(CH_3)_3P$ | 227.2 (0.5[b]) | 229.2 | 2.0 | 219.4 | 221.4 | 2.0 |
| $(CH_3)_2C_6H_5P$ | 230.1 (0.4[b]) | 231.6 | 1.5 | 222.4 | 223.9 | 1.5 |
| $C_5H_5N$ | 223.4 (0.3[b]) | 222.0 | 1.4 | 215.6 | 214.7 | 0.9 |
| 3-F−$C_5H_4N$ | 216.3 (0.3[b]) | 215.6 | 0.7 | 208.5 | 208.0 | 0.5 |
| 3-Cl−$C_5H_4N$ | 217.5 (0.3[b]) | 215.9 | 1.6 | 209.7 | 208.3 | 1.4 |
| 4-Cl−$C_5H_4N$ | 220.0 (0.3[b]) | 219.0 | 1.0 | 212.2 | 211.3 | 0.9 |
| 4-$CH_3$−$C_5H_4N$ | 228.1 (0.3[b]) | 226.4 | 1.7 | 220.3 | 218.8 | 1.5 |
| 4-$OCH_3$−$C_5H_4N$ | 231.4 (0.3[b]) | 229.9 | 1.5 | 223.6 | 222.2 | 1.4 |
| 4-CN−$C_5H_4N$ | 211.5 (0.3[b]) | 210.5 | 1.0 | 203.8 | 202.9 | 0.9 |
| $C_5H_5P$ | 195.6 (0.1[b]) | 195.8 | 0.2 | 187.9 | 187.5 | 0.4 |
| 4-F−$C_5H_4P$ | 190.7 (0.2[b]) | | | 182.9 | | |
| 4-Cl−$C_5H_4P$ | 191.5 (0.2[b]) | | | 183.8 | | |
| 4-$NO_2$−$C_5H_4P$ | 181.0 (0.3[b]) | | | 173.2 | | |
| 4-$CH_3$−$C_5H_4P$ | 199.4 (0.2[b]) | | | 191.6 | | |
| 4-$CF_3$−$C_5H_4P$ | 185.9 (0.1[b]) | | | 178.1 | | |
| 4-$OCH_3$−$C_5H_4P$ | 204.9 (0.1[b]) | | | 197.1 | | |

[a] Experimental data taken from ref 8. [b] The values of BSSE correction in kcal mol$^{-1}$.

### 3. Evaluation of p$K_a$ Value

**3.1. Methods.** In the solution phase, the basicity of a base B is usually measured by the acid dissociation equilibria (p$K_a$) of the corresponding conjugate acid ($BH^+$). Because a more strongly basic B holds a proton more tightly, its corresponding $BH^+$ ion is less acidic (higher p$K_a$), and vice versa. Equation 6 defines the p$K_a$ value of a species.

$$pK_a = -\log K_a$$

$$\Delta G^\circ = -2.303 \times RT \times \log K_a$$

$$pK_a = \frac{\Delta G^\circ}{2.303 \times RT} \tag{6}$$

Recently, there have been several papers showing the theoretical calculation of p$K_a$.[17−29] Accordingly, the p$K_a$ value of a $BH^+$ acid could be calculated in different ways. In general, this depends on the model of the proton-transfer reaction, which involves a thermodynamic cycle relevant to the solvation processes. For example, the *absolute* p$K_a$ *method*[17−24] making use of the thermodynamic cycle (cycle 1) summarized in Scheme 2. It follows that the p$K_a$ value could be calculated from the Gibbs free energy of the reverse reaction

$$BH^+ \leftrightarrows B + H^+ \tag{7}$$

whereby

$$pK_a = \frac{\Delta G^\circ}{2.303 \times RT} = \frac{\Delta G^\circ}{1.36} \tag{8}$$

**SCHEME 2: Thermodynamic Cycle 1 Used to Evaluate p$K_a$**

$$\begin{array}{ccccc} BH^+_{(gas)} & \xrightarrow{\Delta G_{gas}} & B_{(gas)} & + & H^+_{(gas)} \\ \uparrow -\Delta G_{solv}(BH^+) & & \downarrow \Delta G_{solv}(B) & & \downarrow \Delta G_{solv}(H^+) \\ BH^+_{(aq)} & \xrightarrow{\Delta G_{aq}} & B_{(aq)} & + & H^+_{(aq)} \end{array}$$

**SCHEME 3: Thermodynamic Cycle 2 Used to Evaluate p$K_a$**

$$\begin{array}{ccccccc} H_2O_{(gas)} & + & BH^+_{(gas)} & \xrightarrow{\Delta G_{gas}} & B_{(gas)} & + & H_3O^+_{(gas)} \\ \uparrow -\Delta G_{solv}(H_2O) & & \uparrow -\Delta G_{solv}(BH^+) & & \downarrow \Delta G_{solv}(B) & & \downarrow \Delta G_{solv}(H_3O^+) \\ H_2O_{(aq)} & + & BH^+_{(aq)} & \xrightarrow{\Delta G_{aq}} & B_{(aq)} & + & H_3O^+_{(aq)} \end{array}$$

where

$$\Delta G^\circ = \Delta G_{aq} = [\Delta G_{gas} - \Delta G_{solv}(BH^+) + \Delta G_{solv}(B) + \Delta G_{solv}(H^+)]$$

A different approach, called *relative* p$K_a$ *method*[24−29] employs the thermodynamic cycle outlined in Scheme 3. Accordingly, the proton exchange reaction 9 and eq 10 are used

$$BH^+ + H_2O \leftrightarrows B + H_3O^+ \quad (9)$$

$$pK_a = \frac{\Delta G^\circ}{2.303 \times RT} - \log[H_2O] = \frac{\Delta G^\circ}{1.36} - 1.74 \quad (10)$$

where

$$[H_2O] = 55.5 \text{ mol L}^{-1}$$

$$\Delta G^\circ = \Delta G_{aq} = [\Delta G_{gas} - \Delta G_{solv}(BH^+) - \Delta G_{solv}(H_2O) + \Delta G_{solv}(B) + \Delta G_{solv}(H_3O^+)]$$

$$\Delta G_{gas} = G_{gas}(B) - G_{gas}(BH^+) + G_{gas}(H_3O^+) - G_{gas}(H_2O)$$

Another way of calculating the relative p$K_a$ value consists of using the pair of a reference base[25] and its conjugate acid ($A/AH^+$) with well-known p$K_a$ values, and it features a chemical similarity to the pair ($B/BH^+$) under investigation. In this case, the proton exchange reaction 11 and eq 12 were used

$$BH^+ + A \leftrightarrows B + AH^+ \quad (11)$$

$$pK_a(BH^+) = \frac{\Delta G^\circ}{2.303 \times RT} + pK_a(AH^+) = \frac{\Delta G^\circ}{1.36} + pK_a(AH^+) \quad (12)$$

where

$$\Delta G^\circ = \Delta G_{aq} = [\Delta G_{gas} - \Delta G_{solv}(BH^+) - \Delta G_{solv}(A) + \Delta G_{solv}(B) + \Delta G_{solv}(AH^+)]$$

and

$$\Delta G_{gas} = G_{gas}(B) - G_{gas}(BH^+) + G_{gas}(AH^+) - G_{gas}(A)$$

As for the necessary calibration, we have first used all the approaches mentioned already to determine the p$K_a$ values of some compounds whose p$K_a$'s have been determined experimentally, namely the simple ammonium derivatives ($R_1R_2R_3-NH^+$), phosphonium derivatives ($R_1R_2R_3-PH^+$), and substituted protonated pyridines ($R-C_5HH_4NH^+$). Finally, we have computed the basicity for the protonated form of phosphinine and its substituted ($R-C_5HH_4PH^+$) derivatives.

**TABLE 5: Calculated and Experimental Solvation Free Energy of Neutrals (B) and Cations ($BH^+$)**

| | $\Delta G_{solv}$(B) (kcal mol$^{-1}$) | | $\Delta G_{solv}(BH^+)$ (kcal mol$^{-1}$) | |
|---|---|---|---|---|
| B | calcd | exptl[a] | calcd | exptl[a] |
| $H_2O$ | −6.18 | −6.3 | −104.95 | −104 |
| $NH_3$ | −4.37 | −4.3 | −79.91 | −79 |
| $CH_3NH_2$ | −4.49 | −4.6 | −70.46 | −70 |
| $(CH_3)_2NH$ | −3.99 | −4.3 | −64.75 | −63 |
| $(CH_3)_3N$ | −2.85 | −3.2 | −58.14 | −59 |
| $(CH_3)_3P$ | −0.43 | | −51.19 | −52 |
| $(CH_3)_2C_6H_5$ P | −0.45 | | −45.95 | |
| $C_5H_5N$ | −4.85 | −4.7 | −55.63 | −59.0 |
| 3-F−$C_5H_4N$ | −4.34 | | −59.10 | |
| 3-Cl−$C_5H_4N$ | −3.70 | | −57.96 | |
| 4-Cl−$C_5H_4N$ | −3.37 | | −56.63 | |
| 4-$CH_3$−$C_5H_4N$ | −4.54 | | −53.35 | |
| 4-$OCH_3$− | −6.12 | | −52.98 | |
| $C_5H_4N$ | −6.45 | | −62.89 | |
| 4-CN−$C_5H_4N$ | | | | |
| $C_5H_5P$ | −2.77 | | −52.31 | |
| 4-F−$C_5H_4P$ | −2.01 | | −51.83 | |
| 4-Cl−$C_5H_4P$ | −1.77 | | −51.92 | |
| 4-$NO_2$−$C_5H_4P$ | −3.85 | | −60.21 | |
| 4-$CH_3$−$C_5H_4P$ | −2.56 | | −49.03 | |
| 4-$CF_3$−$C_5H_4P$ | −1.31 | | −53.54 | |
| 4-$OCH_3$−$C_5H_4P$ | −3.34 | | −47.53 | |

[a] Experimental data taken from ref 33.

Note that, in the absolute method (thermodynamic cycle 1), we have selected the experimental values of $G_{gas}(H^+)$ and $G_{solv}(H^+)$ that amount to −6.28 and −259.5 kcal mol$^{-1}$, respectively.[30−32] In all of the methods calculating p$K_a$ values, the Gibbs free energy change of the reaction in gas phase, $\Delta G_{gas}$, was computed at the same level of theory used for the gas-phase proton affinity, namely the B3LYP/6-311++G(d,p) electronic energies along with thermal corrections tabulated using harmonic vibrational frequencies at the B3LYP/6-311G(d,p) level. The solvation Gibbs free energy difference, $\Delta G_{solv}$, was calculated using the polarizable continuum solvation model[33,34] (PCM), in which the united atom for Hartree−Fock (UAHF) definition was used for the construction of the cavities. Evaluation of the solvation energies for both neutral and protonated forms in solution were performed the HF/6-31G(d,p) level. All the structures have been determined with the *Gaussian 98* program.[35]

**3.2. Results.** The calculated results are recorded in Tables 4−7 and Figures 2−6. The p$K_a$ values of different acid $BH^+$'s were calculated by using the three equations 8, 10, and 12 and are named p$K_a^1$, p$K_a^2$, and p$K_a^3$, respectively (Table 6).

Our analysis starts with the gas-phase contributions. Figures 2 and 3 display the correlation between experimental and computed values for PAs and GBs of the series of nitrogen and phosphorus compounds for which reliable experimental results are available in the NIST database.[8] The mean absolute errors for PA and GB values on the 14 molecules selected are 1.0 and 0.9, respectively. The correlation coefficients are 0.99 in both cases. In the series of nitrogen derivatives, tertiary amines have the largest PAs. A similar trend holds true in the phosphines where the PAs amount to 187.4, 203.8, 217.1, and 227.6 kcal mol$^{-1}$ for $PH_3$, $CH_3PH_2$, $(CH_3)_2PH$, and $(CH_3)_3P$, respectively. Triethylphosphine $(C_2H_5)_3P$ also exhibits a larger PA of 235.6 kcal mol$^{-1}$.

**TABLE 6: Calculated and Experimental p$K_a$ Values**

| base | p$K_a^1$ | dev. | p$K_a^2$ | dev. | p$K_a^3$ | dev. | p$K_a$ (exptl) |
|---|---|---|---|---|---|---|---|
| $NH_3$ | 8.86 | 0.4 | 10.09 | 0.8 | 9.26 | 0.0 | 9.26[a] |
| $CH_3NH_2$ | 9.84 | 0.8 | 11.07 | 0.4 | 10.23 | 0.4 | 10.66[a] |
| $(CH_3)_2NH$ | 11.10 | 0.4 | 12.33 | 1.6 | 11.50 | 0.8 | 10.73[a] |
| $(CH_3)_3N$ | 10.19 | 0.4 | 11.42 | 1.6 | 10.59 | 0.8 | 9.81[a] |
| $(CH_3)_3P$ | 7.83 | 0.8 | 9.06 | 0.4 | 8.23 | 0.4 | 8.65[b] |
| $(CH_3)_2C_6H_5P$ | 6.11 | 0.4 | 7.34 | 0.8 | 6.51 | 0.0 | 6.50[b] |
| $C_5H_5N$ | 5.04 | 0.2 | 6.27 | 1.1 | 5.21 | 0.0 | 5.21 |
| 3-F$-C_5H_4N$ | 2.75 | 0.2 | 3.98 | 1.0 | 2.93 | 0.4 | 2.97 |
| 3-Cl$-C_5H_4N$ | 3.28 | 0.5 | 4.51 | 1.7 | 3.45 | 0.6 | 2.81 |
| 4-Cl$-C_5H_4N$ | 4.35 | 0.5 | 5.58 | 1.8 | 4.52 | 0.7 | 3.83 |
| 4-$CH_3-C_5H_4N$ | 7.03 | 1.0 | 8.26 | 2.2 | 7.21 | 1.2 | 6.03 |
| 4-$OCH_3-C_5H_4N$ | 8.02 | 1.4 | 9.25 | 2.7 | 8.19 | 1.6 | 6.58 |
| 4-CN$-C_5H_4N$ | 0.52 | 1.3 | 1.75 | 0.1 | 0.69 | 1.2 | 1.86 |
| $C_5H_5P$ | −16.21 | | −14.98 | | −16.05 | | |
| 4-F$-C_5H_4P$ | −19.60 | | −18.37 | | −19.44 | | |
| 4-Cl$-C_5H_4P$ | −18.76 | | −17.53 | | −18.60 | | |
| 4-$NO_2-C_5H_4P$ | −21.94 | | −20.71 | | −21.78 | | |
| 4-$CH_3-C_5H_4P$ | −15.69 | | −14.46 | | −15.53 | | |
| 4-$CF_3-C_5H_4P$ | −21.38 | | −20.15 | | −21.22 | | −21.22 |
| 4-$OCH_3-C_5H_4P$ | −13.33 | | −12.10 | | −13.17 | | −13.17 |

[a] Experimental data taken from ref 8. [b] Experimental data taken from ref 36.

**TABLE 7: Mean Absolute Error (MAE), Linear Regression Equation (LRE), and Correlation Coefficients of Proton Affinity (PA), Gas-Phase Basicity (GB), and p$K_a$ Value**

| *Y* | no. of samples | MAE | LRE | $R^2$ |
|---|---|---|---|---|
| PA | 14 | 1.0 | $Y = 1.01x - 1.72$ | 0.99 |
| GB | 14 | 0.9 | $Y = 1.03x - 5.54$ | 0.99 |
| p$K_a^1$ | 13 | 0.6 | $Y = 0.94x + 0.41$ | 0.94 |
| p$K_a^2$ | 13 | 1.2 | $Y = 0.94x - 0.75$ | 0.94 |
| p$K_a^3$ | 11 | 0.7 | $Y = 0.91x + 0.29$ | 0.95 |

It is worth noting that the N-site PA of 210.4 kcal mol$^{-1}$ of aniline ($C_6H_5NH_2$) is smaller than that of 215.2 kcal mol$^{-1}$ of methylamine ($CH_3NH_2$), whereas the P-site PA of 207.9 kcal mol$^{-1}$ of phenylphosphine ($C_6H_5PH_2$) is actually larger than that of 203.8 kcal mol$^{-1}$ of methylphosphine ($CH_3PH_2$). Such a larger effect of a phenyl group on PA(P) is manifested in $(CH_3)_3P$ and $(CH_3)_2(C_6H_5)P$ where the PA(P)s amount to 229.2 and 231.6 kcal mol$^{-1}$, respectively. This suggests that the hyperconjugation effect of the methyl group is operative in amines but not in phosphines.

The PA(N) of 223.9 kcal mol$^{-1}$ in pyridine is larger than that of 204.2 kcal mol$^{-1}$ in ammonia. A similar trend is observed for the PA(P) in phosphinine (195.7 kcal mol$^{-1}$) and phosphine (187.4 kcal mol$^{-1}$) but with a markedly smaller gap. Thus, to increase its basicity, nitrogen profits much more than phosphorus from the $\pi$-electron system within the six-membered ring. In fact, the sharp position of the P lone pairs does not facilitate

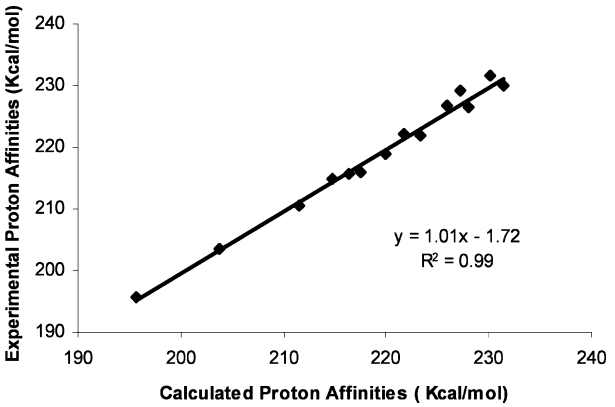



**Figure 2.** Correlation between experimental and calculated proton affinities of the nitrogen and phosphorus compounds considered.

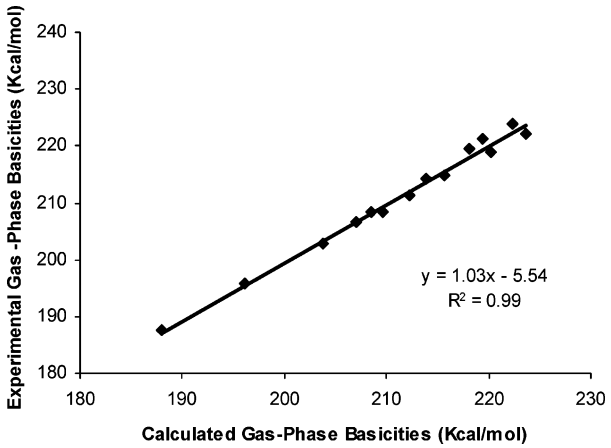



**Figure 3.** Correlation between experimental and calculated gas-phase basicities.

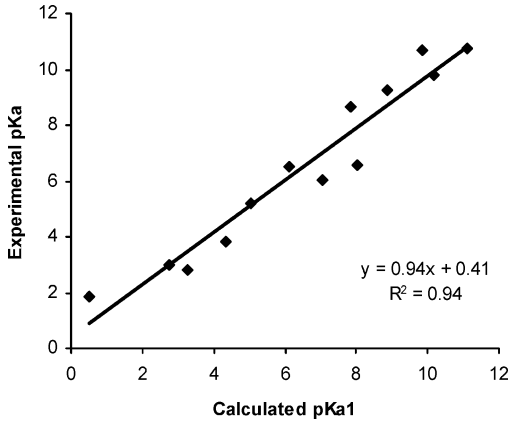



**Figure 4.** Experimental p$K_a$ versus calculated absolute p$K_a^1$ values.

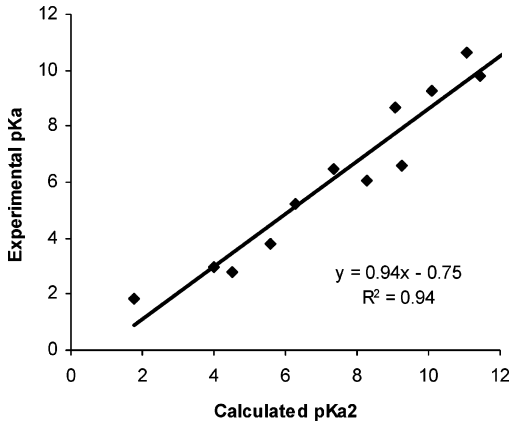



**Figure 5.** Experimental p$K_a$ versus calculated relative p$K_a^2$ values.

electron delocalization. In both series of pyridines and phosphinines, a similar trend of the effect of substituents attached at the *para* ($C_4$) position could be observed: an electron donor increases the PA, whereas electron an captor decreases it (Table 4).

The results summarized in Table 5 indicate that the solvation free energies of alkylamines could be reproduced using the method already outlined here, with a deviation of, at most, 1.0 kcal mol$^{-1}$. For the series of pyridines, we were not able to find experimental values for substituted derivatives. It is apparent that the errors of the calculated values for this series could be somewhat larger.

We now turn to the results obtained for p$K_a$ recorded in Table 6. Figures 4, 5, and 6 illustrate the correlations between the

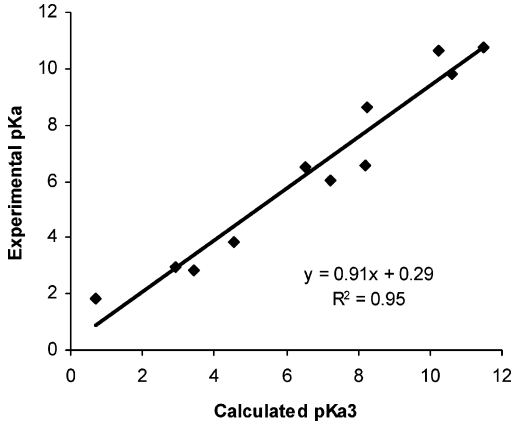



**Figure 6.** Experimental p$K_a$ versus calculated relative p$K_a^3$ values.

values calculated using the three distinct approaches outlined already. Within the limited number of available experimental values, the correlation coefficients are rather similar, around 0.94−0.95. Accordingly, the following values have been calculated for phosphinine using the three methods

$$\mathrm{p}K_a^1(\mathbf{IH}^+) = -16.21$$

$$\mathrm{p}K_a^2(\mathbf{IH}^+) = -14.98$$

$$\mathrm{p}K_a^3(\mathbf{IH}^+) = -16.05$$

The p$K_a^1$ and p$K_a^3$ values are closer to each other, whereas the p$K_a^2$ value differs from the others by more than one unit. The absolute p$K_a^1$ value has been calculated by using cycle 1 (Scheme 2). In this method, the result mainly depends on the chosen value for $\Delta G_s(H^+)$. This is, in fact, the weakness of this method, because the solvation energy of the proton is not known with high precision. We would refer to ref 19 for a detailed discussion on the determination of this value. As mentioned already, we have selected $\Delta G_s(H^+) = -259.5$ kcal mol$^{-1}$, which has also been adopted by other authors.[37] Another value is $\Delta G_s(H^+) = -264.6$ kcal mol$^{-1}$ (ref 19). If the latter value is used, the p$K_a$(**IH**$^+$) becomes −27.12, p$K_a$ ($C_5H_6N^+$) = 2.1, and p$K_a$ ($NH_4^+$) = 7.48. The former is not consistent at all with p$K_a^2$ and p$K_a^3$.

The p$K_a^2$ and p$K_a^3$ values have been calculated using cycle 2 (Scheme 3). In deriving p$K_a^2$, we need to have the solvation energies of both $H_2O$ and $H_3O^+$ species. As the errors committed on calculated values for both quantities are not mutually canceled, the resulting error on p$K_a$ is expected to be large. The difference between p$K_a^2$ and p$K_a^3$ values is that, in evaluating the latter, the $H_2O/H_3O^+$ reference is not replaced by a specific base B/BH$^+$ but rather by a series of similar bases with well-known p$K_a$'s, and the relevant data for the reference series are also well established. This is actually an interpolation in which the only unknown quantity is the p$K_a$ of the molecule under consideration. In that context, it can be expected that the errors of p$K_a^3$ could significantly be reduced thanks to a larger mutual cancellation of the systematic errors committed on the species of the same series B/BH$^+$. A limitation of the relative p$K_a^3$ method is that it is rather hard to find out accurate experimental values to be used as references for a novel compound we want to evaluate. In the case of phosphinine (**I**), we could indeed not find any experimental value for this functional group; therefore we have used instead pyridine as their reference. This is certainly a shortcoming of this approach.

Besides the effect of using thermodynamic cycles in p$K_a$ calculation, the accuracy of the calculated free energies in the gas phase and in solvent also constitutes a main factor causing errors on p$K_a$ calculation. As seen in a previous section, the error bars on calculated free energies of gas-phase neutrals and cations are not large and are usually better than the chemical accuracy. On the contrary, the errors of calculated free energies in solvent remain large and are still a challenge for computational quantum chemical methods. This is one of the reasons that the p$K_a^2$ approach provides values with poorer agreement with those obtained using other methods.

Table 7 shows a statistical analysis of the three approaches for determining p$K_a$ of (**IH**$^{+)}$ and also lists the resulting linear regression equations and correlation coefficients. The regression equations could be employed for determining the p$K_a$ of phosphinine derivatives when the PAs and/or GBs are available.

Both the number of samples used and the mean absolute errors (MAEs) given in Table 7 pledge in favor of the absolute p$K_a^1$ and relative p$K_a^3$ values. If we now consider the average value of p$K_a^1$ and p$K_a^3$ as our predicted value for the p$K_a$ of protonated phosphinine, we thus obtain p$K_a$($C_5H_6P^+$) = − 16.1 ± 1.0. This value markedly differs from the value of p$K_a$ = −10 reported in ref 6. The reason for such a discrepancy appears rather simple: In the 1971 study,[6] the authors used the semiempirical CNDO/2 method to evaluate the PA of (**I**) and other parameters. The errors committed by such a method were obviously large. As mentioned in the Introduction, to derive the p$K_a$(**IH**$^+$), the PAs of 192 and 213 kcal mol$^{-1}$ were used for pyridine and phosphinine, respectively, in a simple comparison scheme for basicities. Table 4 indicated that the absolute errors amount up to 3.8 and 9.0 kcal mol$^{-1}$ for the PAs, respectively.

## 4. Concluding Remarks

In the present investigation, we have reevaluated the basicity of phosphine (phosphabenzene) in redetermining its gas-phase proton affinity and basicity and the p$K_a$ of its protonated form. Using both mass spectrometric techniques and quantum chemical computations, we have obtained the values of PA($C_5H_5P$) = 195.8 ± 1.0 kcal mol$^{-1}$ and $GB_{298}$($C_5H_5P$) = 188.1 ± 1.0 kcal mol$^{-1}$ that are in good agreement with previous results. We then derived a value of p$K_a$($C_5H_6P^+$) = −16.1 ± 1.0 in aqueous solution, which markedly differs from the currently available value of −10 (ref 6). A reason for the discrepancy can be found in the fact that less accurate PAs tabulated using the semiempirical CNDO/2 method were employed in the earlier study. We hope that the presently reevaluated p$K_a$ value could be used as a reference in future studies on basicity of phosphinines. From a theoretical point of view, our present results point out again that the B3LYP method, when used in conjunction with a basis set from a 6-311++G(d,p) quality, provides PAs quite close to the experimental values. At this level, the corrections due to BSSEs are rather negligible (0.1−0.2 kcal mol$^{-1}$).

**Acknowledgment.** Leuven's group thanks the FWO-Vlaanderen, the KULeuven Research Council (Concerted Research Action, GOA-program), and the Council for Cooperation Development for continuing support.

## References and Notes

(1) Le Floch, P. In *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: Amsterdam, 2001.

(2) Hodges, R. V.; Beauchamp, J. L.; Ashe, A. J., III; Chan, W. T. *Organometallics* **1985**, *4*(3), 457.

(3) Lohr, L. L.; Schlegel, H. B.; Monokima, K. *J. Phys. Chem.* **1984**, *88*, 1981.
(4) Pierini, A. B.; Duca, J. S. *Int. J. Quantum Chem.* **1993**, *48*, 343.
(5) Berger, D. J.; Gaspar, P. P.; Liebman, J. F. *THEOCHEM* **1995**, *338*, 51.
(6) Oehling, H.; Schweig, A. *Phosphorus* **1971**, *1*, 203.
(7) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.
(8) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, *3*, 413. NIST Chemistry WebBook. http://webbook.nist.gov; NIST Standard Reference Database 69; National Institute of Standards and Technology: Gaitherburg, MD, March 2003.
(9) Ann, M. S.; Igor, A. T.; Christopher, J. M. *Theor. Chim. Acta* **1995**, *92*, 83.
(10) Yevgeniy, P.; Leonid, G.; Jerzy, L. *J. Phys. Chem. A* **2000**, *104*, 7346.
(11) Sorensen, G. O.; Mahler, L.; Rastrup-Anderson, N. *J. Mol. Struct.* **1974**, *20*, 119.
(12) Jonas, V.; Frenking, G. *Chem. Phys. Lett.* **1993**, *210*, 211.
(13) Nyulaszi, L. *Chem. Rev.* **2001**, *101*, 1229.
(14) (a) Deakyne, C. A. *Int. J. Mass Spectrom.* **2003**, *227*, 601. (b) Audier, H. E.; Fossey, J.; Denhez, J. P.; Jacquet, J. P.; Mourges, P. *Int. J. Mass Spectrom.* **2003**, *227*, 381. (c) Ligon, A. P. *J. Phys. Chem. A* **2000**, *104*, 8739.
(15) (a) Howard, S. T. *J. Am. Chem. Soc.* **1996**, *118*, 10269. (b) Howard, S. T.; Platts, J. A.; Alder, R. W. *J. Org. Chem.* **1996**, *60*, 6085.
(16) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(17) Lee, I.; Kim, C. K.; Han, I. S. R.; Lee, H. W.; Kim, W. K. *J. Phys. Chem. B* **1999**, *103*, 7302.
(18) Schuurmann, G.; Cossi, M.; Barone, V.; Tomasi, J. *J. Phys. Chem. A* **1998**, *102*, 6706.
(19) Mathew, D. L.; George, C. S. *J. Am. Chem. Soc.* **2001**, *123*, 7314.
(20) Jasna, J. K.; Richard, A. F.; Shi-Yi. L.; Wayne C. G. *J. Phys. Chem. A* **2002**, *106*, 1327.
(21) Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6421.
(22) Chipman, D. M. *J. Phys. Chem. A* **2002**, *106*, 7413.
(23) Saracino, G. A. A.; Improta, R.; Barone, V. *Chem. Phys. Lett.* **2003**, *373*, 411.
(24) Topol, I. A.; Tawa, G. J.; Burt, S. K. *J. Phys. Chem. A* **1997**, *101*, 10075.
(25) Tran, N. L.; Colvin, M. E. *THEOCHEM* **2000**, *532*, 127.
(26) Adam, K. R. *J. Phys. Chem. A* **2002**, *106*, 11963.
(27) Pliego, J. G.; Riveros, J. M. *J. Phys. Chem. A* **2002**, *106*, 7434.
(28) Pliego, J. G. *Chem. Phys. Lett.* **2003**, *367*, 145.
(29) Abreu, H. A. D.; Almeida, W. B. D.; Duarte, H. A. *Chem. Phys. Lett.* **2004**, *383*, 47.
(30) Reiss, H.; Heller, A. *J. Phys. Chem.* **1985**, *89*, 4207.
(31) Lim, C.; Bashford, D.; Karplus, M. *J. Phys. Chem.* **1991**, *95*, 5610.
(32) Li, J.; Fisher, C. L.; Chen, J. L.; Bashford, D.; Noodleman, L. *Inorg. Chem.* **1996**, *35*, 4694.
(33) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *225*, 327.
(34) (a) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210. (b) Cabani, S.; Mollica, G.; Lepori, V. *J. Solution Chem.* **1981**, *10*, 563.
(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.
(36) Rahman, Md. M.; Liu, H-Y.; Eriks, K.; Giering, W. P. *Organometallics* **1989**, *8*, 1.
(37) See, for example: Jaguar User's Guide, http://www.schrodinger-.com/docs/gajuar4.2/html/manual.