Effect of Substituents on the P–H Bond Dissociation Enthalpies of Phenylphosphines and Proton Affinities of Phenylphosphine Anions: A DFT Study

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The homolytic bond dissociation enthalpies (BDEs) for the P–H bonds in substituted phenylphosphines (X–C₆H₄–PH₂) have been estimated using the (RO)B3LYP procedure with the 6–311++G(2df,2p) basis set. The BDEs for the P–H bond in PH₃, N–H bond in NH₃ and X–C₆H₄–NH₂ (X = H, CH₃, and NO₂), and the As–H bond in AsH₃ have also been determined by the same computational procedure and compared with the experimental results to assess the reliability of our method. The proton affinities (PAs) of the arylphosphine anions (X–C₆H₄–PH⁻) have also been determined at the same level of theory. The effect of substituents on the BDE(P–H) and the PA values have been analyzed in terms of the substituent effects on the stability of the phenylphosphines, radicals, and anions. Additionally, accurate estimations for the electron affinity values of phenylphosphine radicals have been performed. We also explore the correlations of Hammett’s substituent constants with the BDEs of the P–H bonds of phenylphosphines and the PA values of arylphosphine anions.

Introduction

The determination of accurate bond dissociation enthalpies (BDEs) has been an interesting computational task for years. Recently, there is a growing interest in the computed BDEs for many types of bonds. Bordwell et al. observed that electron-withdrawing substituents at the meta and para position of the phenyl ring interact with the S–H, N–H, and O–H dipoles resulting in the lowering of ground-state energies and leading to an increase in BDEs in the order S–H < N–H < O–H. Our present study can reveal the effect of such interaction for the P–H bond and ascertain where the P–H bond stands in that order.

The determination of the strength of the P–H bonds in phenylphosphine (C₆H₅–PH₂) and its substituted derivatives (X–C₆H₄–PH₂) is the main purpose of this paper. The energy required for homolytic bond cleavage corresponds to the enthalpy change for the reaction

X–C₆H₄–PH⁺ + H⁻ (1)

Conversely, if the radicals X–C₆H₄–PH⁺ and H⁻ recombine to form the molecule X–C₆H₄–PH₂, the energy equivalent to the bond dissociation enthalpy is released.

method to reproduce bond strength for many types of organic compounds. The properties of phenylphosphine and its derivatives have recently been investigated by Nam et al. It is predicted that the proton affinities of these compounds is in the range of 863 ± 10 kJ mol⁻¹. Recently, Cheng et al. determined the BDE values for a number of substituted phenylphosphines by applying the (RO)MP2/6-311++G(d,2p) method. However, their calculated result for PH₃ was found to be 27.6 kJ mol⁻¹ lower than the experimental value (345.0 ± 1.9 kJ mol⁻¹) at 0 K. They expected similar underestimation for phenylphosphines as well. Thus, better estimation for the BDE(P–H) of phenylphosphines is required. Moreover, our BDE values for the P–H bonds of phenylphosphines can be compared to the N–H bonds of the corresponding aniline compounds to understand the effect of substituents on different types of bonds. Bordwell et al. observed that electron-withdrawing substituents at the meta and para position of the phenyl ring interact with the S–H, N–H, and O–H dipoles resulting in the lowering of ground-state energies and leading to an increase in BDEs in the order S–H < N–H < O–H.

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The gas-phase acidity of a phenylphosphine molecule and its substituted derivatives can approximately be calculated from

Footnotes:

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TABLE 1: BDE Values [in kJ mol$^{-1}$] of the X–H Bonds of PH$_3$, NH$_3$, and AsH$_3$ as Obtained from Different Methods and Basis Sets

<table>
<thead>
<tr>
<th>model chemistry</th>
<th>PH$_3$ (351.0 ± 2.0)$^a$</th>
<th>NH$_3$ (452.7 ± 1.3)$^a$</th>
<th>AsH$_3$ (319.2 ± 1.3)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB3P86/6-311G(d,p) // B3P86/6-311G(d,p)</td>
<td>396.17</td>
<td>498.24</td>
<td>367.76</td>
</tr>
<tr>
<td>UB3P86/6-311+++(2df,2p) // B3P86/6-311G(d,p)</td>
<td>396.65</td>
<td>501.96</td>
<td>368.57</td>
</tr>
<tr>
<td>ROB3LYP/6-311+++(2df,2p) // B3P86/6-311G(d,p)</td>
<td>401.26</td>
<td>507.04</td>
<td>371.93</td>
</tr>
<tr>
<td>UB3LYP/6-311G(d,p) // B3LYP/6-311G(d,p)</td>
<td>342.79</td>
<td>440.68</td>
<td>314.56</td>
</tr>
<tr>
<td>UB3LYP/6-311+++(2df,2p) // B3LYP/6-311G(d,p)</td>
<td>343.62</td>
<td>444.71</td>
<td>315.37</td>
</tr>
<tr>
<td>ROB3LYP/6-311+++(2df,2p) // B3LYP/6-311G(d,p)</td>
<td>347.54</td>
<td>449.39</td>
<td>318.05</td>
</tr>
<tr>
<td>UB3LYP/6-311+++(2df,2p) // B3LYP/6-311G(d,p)</td>
<td>332.55</td>
<td>444.42</td>
<td>314.33</td>
</tr>
<tr>
<td>UB3LYP/6-311+++(2df,2p) // B3LYP/6-311G(d,p)</td>
<td>343.54</td>
<td>444.92</td>
<td>315.42</td>
</tr>
<tr>
<td>ROB3LYP/6-311+++(2df,2p) // B3LYP/6-311G(d,p)</td>
<td>347.51</td>
<td>449.64</td>
<td>318.21</td>
</tr>
<tr>
<td>UB3LYP/Aug-cc-pVDZ// B3LYP/Aug-cc-pVDZ</td>
<td>334.48</td>
<td>438.19</td>
<td>309.63</td>
</tr>
<tr>
<td>UMP2/Aug-cc-pVDZ// B3LYP/Aug-cc-pVDZ</td>
<td>331.11</td>
<td>420.5</td>
<td>286.55</td>
</tr>
<tr>
<td>UMP2P/Aug-cc-pVTZ// B3LYP/Aug-cc-pVDZ</td>
<td>329.89</td>
<td>449.42</td>
<td>307.03</td>
</tr>
<tr>
<td>CCSD/Aug-cc-pVDZ// B3LYP/Aug-cc-pVDZ</td>
<td>317.35</td>
<td>417.48</td>
<td>294.60</td>
</tr>
<tr>
<td>CCSD/Aug-cc-pVTZ// B3LYP/Aug-cc-pVDZ</td>
<td>333.43</td>
<td>435.23</td>
<td>312.18</td>
</tr>
<tr>
<td>CCSD(T)/Aug-cc-pVDZ// B3LYP/Aug-cc-pVDZ</td>
<td>319.96</td>
<td>421.85</td>
<td>297.28</td>
</tr>
<tr>
<td>CCSD(T)/Aug-cc-pVTZ// B3LYP/Aug-cc-pVDZ</td>
<td>336.67</td>
<td>440.82</td>
<td>315.65</td>
</tr>
</tbody>
</table>

$^a$ From ref 13.

The PA value of the corresponding phenylphosphine anions (X–C$_6$H$_4$–PH$^-$) is well correlated with gas-phase acidities and Hammett’s reactivity parameters derived for the solution-phase acidities for substituted phenols$^{2,15,16}$ and thioanisoles.$^4$ A good linear correlation is, therefore, expected between the gas- and solution-phase acidities. Thus, it will be interesting to find out whether such correlation also holds for the phenylphosphines. Moreover, a reaction constant can also be derived from these correlations.

Computational Details

All calculations were performed using the GAUSSIAN 98 suite of programs.$^{17}$ The geometries of para- and meta-substituted phenylphosphines (X–C$_6$H$_4$–PH$_2$, X = H, F, Cl, CH$_3$, NH$_2$, OCH$_3$, CN, CF$_3$, and NO$_2$) were fully optimized by using the DFT with hybrid B3LYP functional in conjunction with the 6-311G(d,p) basis set. We used the UB3LYP procedure for the geometry optimization of the aryphosphine radicals (X–C$_6$H$_4$–PH). The harmonic vibrational frequencies were then computed at the optimized geometry using the same level of theory. Thermal correction to enthalpy was obtained at this level. Single-point calculations were also carried out with an extended basis set of 6-311+++(2df,2p). The restricted open-shell formalism (ROB3LYP) with the large basis set was applied for the open-shell radicals at the UB3LYP/6-311G(d,p) optimized geometry.

The homolitic P–H bond dissociation enthalpy [BDE(P–H)] value at 298 K for the molecule X–C$_6$H$_5$–PH$_2$ was estimated from the expression

\[
\text{BDE(P–H)} = H(f(X–C_6H_4–PH)) - H(f(X–C_6H_4–PH_2))
\]

where $H(f)$'s are the enthalpies of different species at 298 K. The enthalpies were estimated from the usual expression: $H(f)$ = E$_o$ + ZPE + H$_{trans}$ + H$_{rot}$ + H$_{vib}$ + RT. The H$_{trans}$, H$_{rot}$, and H$_{vib}$ are the translational, rotational, and vibrational contributions to enthalpy, respectively. The energy of the H atom was taken as the exact energy of −0.5 Hartree. Because there is a problem of self-interaction in the DFT procedure,$^{18}$ for this reason, the DFT does not give the exact energy [−0.5 Hartree] for this simplest system. The same approach was adopted before by DiLabio et al.$^8$ This procedure has been shown to be sufficient for getting reliable results and reproduces data to be in good agreement with experimental values.$^{2,4,8,9}$ (We are going to analyze the methodology further in this work).

The PA of X–C$_6$H$_5$–PH$^-$ was calculated from the following expression

\[
\text{PA}(X–C_6H_5–PH^-) = H(f(X–C_6H_5–PH^-)) + H(f(H^+)) - H(f(X–C_6H_5–PH_2))
\]

Results and Discussion

Earlier works show that the (RO)B3LYP procedure adopted here reproduces BDE values quite accurately and also very close to the experimental data. However, the basis set and the methodology applied for accurate BDE calculation generally varies from one type of bond to the other. Thus, it is important to evaluate first whether the (RO)B3LYP procedure can estimate the BDE values accurately for some model systems with different types of bonds for which experimental results are known. This is more important because experimental BDE(P–H) data for X–C$_6$H$_5$–PH$_2$ systems are not available.

In this context, we first examine three simple systems PH$_3$, NH$_3$, and AsH$_3$ in which the central atoms belong in the group VA. BDE parameters for PH$_3$, NH$_3$, and AsH$_3$ were calculated by using different DFT methods with a variety of basis set. In addition, CCSD(T) and MP2 calculations are also carried out. The results obtained from these calculations are given in Table 1. Table 1 shows that in comparison to the available experimental BDE results,$^{13}$ the B3P86 overestimates the BDEs for the P–H, N–H, and As–H bonds by 45–50 kJ mol$^{-1}$. On the other hand, MP2 calculations even with a large double-$\xi$ basis set underestimate the BDE values by an amount of 28–30 kJ mol$^{-1}$. MP2 calculations with a triple-$\xi$ basis functions give slightly better results. Even the CCSD(T) with a larger basis set such as Aug-cc-pVTZ fails to produce the desired results. Moreover, ab initio methods such as MP2 and CCSD(T) with a large basis set are computationally too expensive to apply finally to the X–C$_6$H$_5$–PH$_2$ molecules. Under these circumstances, the (RO)B3LYP/6-311+++(2df,2p)//B3LYP/6-311G(d,p) model chemistry [henceforth referred simply as the (RO)B3LYP] appears to be the best choice for estimating the BDE of compounds containing X–H bonds. Table 1 shows that in all of the three cases the present DFT method produces BDE values, which are as good as the corresponding experimental results. Because geometry optimizations with a larger basis set
TABLE 2: Calculated and Experimental BDE(N–H) Values [in kJ mol$^{-1}$] for Meta and Para-Substituted Anilines

<table>
<thead>
<tr>
<th></th>
<th>meta</th>
<th>experimental</th>
<th>para</th>
<th>experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO$_2$NH$_2$</td>
<td>375.9</td>
<td>375.3$^{a}$, 372.8$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHO$_2$NH$_2$</td>
<td>385.3</td>
<td>370.2, 371.1$^c$, 366.1$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_2$CHO$_2$NH$_2$</td>
<td>398.7</td>
<td>404.9, 404.6$^d$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$From ref 19. $^b$From ref 13. $^c$Measured in water, from ref 26. $^d$Measured in DMSO, from ref 27.

TABLE 3: (RO)B3LYP Calculated P–H Bond Dissociation Enthalpies [BDE(P–H) in kJ mol$^{-1}$] for Meta- and Para-Substituted Phenylphosphines

<table>
<thead>
<tr>
<th>X</th>
<th>meta calculated $\Delta$BDE$^a$</th>
<th>calculated $\Delta$BDE$^a$</th>
<th>para calculated $\Delta$BDE$^a$</th>
<th>$\Delta$BDE$_{P-m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>319.34</td>
<td>0.0</td>
<td>319.34</td>
<td>0.0</td>
</tr>
<tr>
<td>F</td>
<td>320.21</td>
<td>0.87</td>
<td>319.37</td>
<td>-0.84</td>
</tr>
<tr>
<td>Cl</td>
<td>319.98</td>
<td>0.64</td>
<td>318.86</td>
<td>-0.48</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>318.85</td>
<td>-0.49</td>
<td>318.16</td>
<td>-1.18</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>319.96</td>
<td>0.62</td>
<td>316.88</td>
<td>-2.46</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>319.28</td>
<td>-0.06</td>
<td>313.96</td>
<td>-5.38</td>
</tr>
<tr>
<td>CN</td>
<td>321.68</td>
<td>2.34</td>
<td>320.70</td>
<td>-1.41</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>320.80</td>
<td>1.46</td>
<td>321.04</td>
<td>1.70</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>322.46</td>
<td>3.12</td>
<td>321.62</td>
<td>2.28</td>
</tr>
</tbody>
</table>

$^a$BDE = BDE(X=C$_6$H$_5$PH–H) – BDE(C$_6$H$_5$PH–H)

[6-311++G(d,p)] do not make any significant change in the Bond Dissociation Enthalpies of Phenylphosphines. Optimization geometries can be carried out at the B3LYP/6-311G(d,p) level. As stated earlier, the method was found to be very good for estimating the BDE for the O–H and S–H bonds as well. To test the (RO)B3LYP method further, we also calculated BDE(N–H) values in aniline and substituted anilines. The calculated BDE(N–H) values are listed in Table 2. Our calculated value of 375.9 kJ mol$^{-1}$ for aniline is found to be very close to the recent experimental value of 375.3 kJ mol$^{-1}$ (and 372.8 kJ mol$^{-1}$). The BDE(N–H) value estimated by using the high-level G3 method was reported to be 379.12 kJ mol$^{-1}$, which is quite close to our value. Our calculated BDE(N–H) values for –CH$_3$ and –NO$_2$-substituted anilines are also found to be very close to the experimental values. In fact, in all of the cases, the differences between our calculated BDE values and the corresponding experimental results never exceed 4 kJ mol$^{-1}$. We, therefore, believe that the (RO)B3LYP method can be applied for the calculation of accurate BDE(P–H) values of substituted phenylphosphines. This model is expected to achieve a target accuracy of around 6 kJ mol$^{-1}$.

**Bond Dissociation Enthalpies of Phenylphosphines.** Our calculated BDE(P–H) values for para- and meta-substituted phenylphosphines are given in Table 3. Recently, Cheng et al. have estimated the BDE(P–H) values substituted with phenylphosphine systems by using the ROMP2/6-311++G(d,p)//UB3LYP/6-31+G(d) procedure. However, according to their estimate, the calculated values are more than 25 kJ mol$^{-1}$ lower than the corresponding experimental values. For example, in the case of PH$_3$, their calculated BDE(P–H) value at 0 K amounts to 317.4 kJ mol$^{-1}$, whereas the corresponding experimental value is 345.0 ± 1.9 kJ mol$^{-1}$. They expected similar underestimation for the phenylphosphine systems as well. In fact, our (RO)B3LYP calculated BDE(P–H) value (315.06 kJ mol$^{-1}$) at 0 K for the parent phenylphosphine molecule is nearly 16 kJ mol$^{-1}$ higher than the value (299.03 kJ mol$^{-1}$) obtained by Cheng et al. Similar differences in BDE(P–H) values can be observed for all of the para- and meta-substituted phenylphosphine compounds as well. As an example, Figure 1 displays the differences between our calculated BDE(P–H) values and those obtained by Cheng et al. for the para-substituted phenylphosphines. Our results are, therefore, the first accurate information about the BDE(P–H) values of phenylphosphines. It may be worthwhile here to observe how the phenyl group substitution changes the strength of the P–H bond in the XH$_3$ (X = N and P) molecule. The experimental BDE(N–H) values for NH$_3$ and PH–NH$_2$ amounts to 447.7 and 375.3 kJ mol$^{-1}$, respectively. Thus, phenyl substitution for a hydrogen atom in NH$_3$ reduces the bond strength by nearly 72 kJ mol$^{-1}$. In the case of PH$_3$, our calculated results show that phenyl substitution lowers the BDE(P–H) value by around 28 kJ mol$^{-1}$, which is almost half that observed for NH$_3$. Strength of the P–H bond is significantly lower than the N–H bond in both XH$_3$ and C$_6$H$_5$–XH$_3$ (X = N and P) molecules. Of course, the difference in BDE is much higher for the XH$_3$ molecule. It is interesting to observe how the BDE(P–H) values change with the change in the substituent at the meta and para position of phenylphosphines. The $\Delta$BDE(P–H) values [$\Delta$BDE(P–H) = BDE(X–C$_6$H$_5$PH–H) – BDE(C$_6$H$_5$PH–H)] are presented in Table 3. The effect of electron-donating (EDG) and electron-withdrawing groups (EWG) on the BDE(P–H) values of the para-substituted phenylphosphines is the opposite. The EDG group (like CH$_3$, OCH$_3$, and NH$_2$) at the para position increases the strength of the P–H bond, whereas the EWG group (CN, CF$_3$, and NO$_2$) at the same position increases the strength of the P–H bond. For example, the BDE(P–H) value of para-amino phenylphosphine is more than 5 kJ mol$^{-1}$ lower than that for the parent phenylphosphine molecule. The CI substituion at the para position lowers the BDE(P–H) value by almost 0.5 kJ mol$^{-1}$, and thus, it behaves like an EDG. However, the effect of substituents on the P–H bond strength is found to be much lower than that observed for the N–H bond in aniline. O–H bond in substituted phenols, and S–H bond in substituted thiophenols. As an example, the NH$_2$ group at the para position of phenol, aniline, thiophenol, and phenylphosphine reduces the O–H, N–H, S–H, and P–H bond strength from the corresponding parent molecule by an amount of 40.2, 26.3, 22.6, and 5.4 kJ mol$^{-1}$, respectively. In all of the cases, the effect of substituents on the N–H bond of aniline is higher than that on the P–H bond of phenylphosphine. The methyl group at the para position of aniline weakens the N–H bond by an amount of 1.7 kJ mol$^{-1}$, whereas the same group reduces the BDE(P–H) value in phenylphosphine by an amount of 1.2 kJ mol$^{-1}$. It was demonstrated before that the substituent effect on the strength of a bond could not be explained in terms of the changes in the bond properties (such as the force constant and electron density around the bond) themselves. It is generally believed that electron-donating substituents at the para position stabilize the radical and raise the ground-state energies of the molecule.
to some extent. In fact, Brinck et al. showed that the ΔBDEs for phenols with EDGs as substituents were mainly determined by the stabilization of the radical because of spin delocalization.23 As a result, the BDE value decreases from that for the parent molecule. On the other hand, EWGs at the para position interact with the P–H dipoles causing a lowering of the ground-state energies and thereby increasing the BDE(P–H) values.

Substituent effect at the meta position is found to be strikingly different from that at the para position. EDG (such as CH3, NH2, and OCH3) at the meta position has a very mild effect on the BDE(P–H) value in comparison to the parent phenylphosphine molecule. Thus, in the case of EDGs, there is a substantial difference (see the ΔBDEp–m values in Table 2) between the BDE(P–H) values for meta- and para-substituted phenylphosphines. On the contrary, EWGs (like CH3 and NO2) at the meta position increases the BDE(P–H) values significantly, and the difference in the BDE(P–H) values for the meta and para substituent is less significant. The F− and Cl− substituents at the meta position behave like an EWG, which is opposite to that observed when they are at the para position. This contrasting behavior can be explained from the well-known field and resonance effects of the F− and Cl− substituents.23 At the meta position, these two substituents manifest only the −I field effect, whereas at the para position, the field effect diminishes (because of a longer distance from the reactive site), but they act as an electron donor by the resonance effect (+M groups).23

To understand clearly the reason behind the variation of BDE(P–H) with the change in position of the substituent, we have calculated the enthalpy differences [ΔHp–m] between para- and meta-substituted phenylphosphines and the phosphine radicals. Figure 2 displays the graphical representation of the same. As can be seen from the figure, the para-substituted phenylphosphine molecule and radical are always more stable than the corresponding meta products. Of course, the effect is more pronounced for phenylphosphine radicals (except for −CF3 substitution). As a result, in general, the BDE(P–H) value for the para-substituted phenylphosphine is lower than the corresponding meta-substituted phenylphosphine. In the case of strong EDGs (OCH3 and NH3), the ΔHp–m value for the phenylphosphine radical is much greater than the ΔHp–m value for the phenylphosphine molecule, and therefore, the BDE(P–H) value for the para-substituted product is much lower than the corresponding meta counterpart. In general, the change in the stability of the phosphine radical with the change in the substituent position (from meta to para or vice versa) is the dominant factor that controls the dependence of the BDE(P–H) value on the substituent position.

**Acidity of Substituted Phenylphosphine.** The gas-phase proton affinities for the phosphorus atom of meta- and para-substituted arylphosphine anions (X–C6H4–PH−) are determined from the enthalpy values of the substituted phenylphosphine molecules and the corresponding phenylphosphine anions at the B3LYP/6-311++G(2df,2p) level as described in eq 3. The gas-phase acidity of the phenylphosphine molecule should be correlated with the PA value of the phenylphosphine anion, and the greater the PA value, the lower the acidity should be. The calculated PA values for a set of meta- and para-substituted phenylphosphine anions are given in Table 4. The quality of our results cannot be judged directly by comparing with the experimental results, because such data are not available. However, our previous works on phenol2 and thiophenol4 systems show that the present B3LYP procedure is capable of producing quite accurate PA values. For example, in the case of phenoxide ion, the calculated value was 1455.2 kJ mol−1, which is very close to the experimental value of 1451.4 kJ mol−1.15 For the thiophenoxide ion, the calculated and experimental PA values were found to differ by only 4 kJ mol−1.4 During the present study, we have evaluated the PA value of C6H5NH−, and our calculated value (1534.0 kJ mol−1)4 is very close to the experimental value of 1533 ± 8.8 kJ mol−1.24 We, therefore, believe that our calculated PA values for substituted phenylphosphine systems should be very close to the exact values.

Our calculated PA value for the phenylphosphine anion is 1484.0 kJ mol−1. This is substantially lower than the PA value of C6H4NH− (1534.0 kJ mol−1) but higher than the PA values of phenoxide ion (1455.2 kJ mol−1)2 and thiophenoxide ion (1420.0 kJ mol−1)4 obtained at the same level of theory. Thus, acidity of phenylphosphine should be greater than phenylamine but it is much less acidic than phenol and thiophenol. An electron-donating substituent at the para position tends to increase the PA values for phenylphosphine anions, whereas an electron-withdrawing substituent at the same position reduces the PA values significantly. Among the EDGs, the highest effect was observed for the NH2 group, where the PA value increases by almost 28 kJ mol−1 from the parent phenylphosphine anion. EDGs are likely to destabilize the anion and thereby increase the PA value. On the other hand, EWGs stabilize the anion by delocalizing the negative charge on the phosphorus atom over the ring, and as a result, the PA value decreases. The most dramatic effect can be observed (see Table 4) for the strong EWG NO2, which reduces the PA value from the parent anion by more than 100 kJ mol−1. The C−P bond length can give an indication for the delocalization of the negative charge, because this bond length should become shorter because of inductive and resonance stabilization. Indeed, we observed that for the EWGs at both the positions the C−P bond length becomes shorter from the C−P bond length (1.814 Å) in the parent phenylphosphine anion. For example, the C−P bond lengths for the para NO2–C6H4–PH− and CN–C6H4–PH− amount to 1.777 and 1.785 Å, respectively. The same values for the meta NO2–C6H4–PH− and CN–C6H4–PH− are calculated to be 1.803 and 1.804 Å, respectively. The presence of resonance stabilization when EWG is at the para position makes the C−P bond length shorter than that of the meta position.

**TABLE 4: Calculated Proton Affinities [PA in kJ mol−1] for the Para and Meta-Substituted Phenylphosphine Anions [PA(XC6H4PH−)] Using the B3LYP-6-311++G(2df,2p)//B3LYP/6-311G(d,p) Method**

<table>
<thead>
<tr>
<th>X</th>
<th>meta para</th>
<th>ΔPAmetapara</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1484.0</td>
<td>1484.0</td>
</tr>
<tr>
<td>F</td>
<td>1463.7</td>
<td>1478.3</td>
</tr>
<tr>
<td>Cl</td>
<td>1457.0</td>
<td>1457.6</td>
</tr>
<tr>
<td>CH3</td>
<td>1486.2</td>
<td>1491.0</td>
</tr>
<tr>
<td>OCH3</td>
<td>1486.0</td>
<td>1500.3</td>
</tr>
</tbody>
</table>

Figure 2. Enthalpy differences between the para- and meta-substituted phenylphosphines and between para- and meta-substituted phenylphosphine radicals.
bond shorter than the corresponding meta product. A strong
EDG at the para position, like NH$_2$, tends to increase the C–P
bond from the parent phenylphosphine anion, while it has no
effect at the meta position. The influence of EDGs on PA is
found to be also insignificant in most of the cases when they
are at the meta position. EWGs at the meta position decrease
the PA values but to a much lesser extent than that observed
when they are at the para position. For example, the PA value
of the p-nitrophenylphosphine anion is found to be 45.8 kJ mol$^{-1}$
lower than that for the corresponding m-nitro counterpart.
Phenylphosphine, therefore, becomes more acidic when EWG
is at the para position. In general, electron-withdrawing substituents make phenylphosphine more acidic, whereas
electron-donating substituents at the para position reduce the acidity
of phenylphosphine. In both the positions, F and Cl behave like
electron-withdrawing substituents and increase the acidity of
phenylphosphine, although the effect is greater at the meta
position. Substituent effect is found to be much more pro-
nounced on PA values than that observed on the BDE(P–H)
values. For para-substituted phenylphosphine derivatives, the
BDE(P–H) values change within a range of 0.03 (F) to −5.4
(NH$_2$) kJ mol$^{-1}$ from the parent phenylphosphine molecule,
whereas upon substitution, the PA values change from 5.7 (F)
to 102.5 (NH$_2$) kJ mol$^{-1}$ with respect to the phenylphosphine
anion.

Correlation of Hammett’s Parameter with BDE(P–H)
and PA. The substituent effects on the BDE(P–H) and PA
values have been discussed in the previous section. The BDE-
(P–H) values for the para-substituted phenylphosphines are
found to vary within a range of 5.4 kJ mol$^{-1}$, whereas those
for the meta-substituted products vary within a narrow range
of 3.1 kJ mol$^{-1}$. Hammett’s parameters have been used for a
long time to estimate the substituent effects on various prop-
ties. Thus, it is interesting to observe the substituent effects on
BDE(P–H) of phenylphosphine in terms of Hammett’s reactiv-
ity parameters ($\sigma$). To account for the through conjugation
effects, especially for the electron-donor groups at the para
position, a modified set of parameters ($\sigma^+$) is generally used
for such correlation studies. Through conjugation effect is in-
significant when the substituent is at the meta position, and
as a result, $\sigma_m^+$ and $\sigma_m$ values are nearly the same. The modified
$\sigma_p^+$ and $\sigma_m$ parameters were taken from the compilations
of Hammett parameters by Hansch, Leo, and Taft. Figures 3
and 4 show the correlation between the BDE(P–H) values and
the modified Hammett’s parameters for the para- and meta-
substituted phenylphosphines, respectively. A good linear cor-
relation is observed between the BDE(P–H) and $\sigma_p^+$ values.
The BDE(P–H) value increases with the increase in the
electron-withdrawing ability of the substituent. For meta
substituents, the correlation between BDE(P–H) and $\sigma_m$ parameters
is less impressive. The correlation equations obtained for para
and meta phenylphosphines are given below

$$\text{BDE}(P-H) = 3.268\sigma_p^+ + 318.94 \quad (R = 0.97)$$  \hspace{1cm} (4)

$$\text{BDE}(P-H) = 3.696\sigma_m + 319.34 \quad (R = 0.94)$$  \hspace{1cm} (5)

The positive slope of both equations tells us that a substituent
with a positive $\sigma_p^+$ or $\sigma_m$ increases the BDE(P–H), otherwise
decrease the BDE(P–H) values. The larger the absolute value
of $\sigma_p^+$ or $\sigma_m$, the stronger is the effect on BDE. The slopes
of these lines can be compared with those obtained for the
substituted phenols and thiophenols. For the para-substituted
products, the slopes of the correlation lines are 25.3, 16.2, and
3.3 for phenols, thiophenols, and phenylphosphines, respec-
tively. These values clearly show that the substituent effect on
BDE is strongest for the O–H bonds in phenols. This is in
conformity with the para-substituent effect order (S–H < N–H
< O–H) predicted by Bordwell and co-workers. Including
our present results on para-substituted phenylphosphine systems,
the substituent effect order on BDEs can be written as P–H <
S–H < N–H < O–H. A similar trend can also be observed from
the slopes of the correlation lines of the meta-substituted
derivatives of phenols, thiophenols, and phenylphosphines. We
should mention here that in contrast to our results, Cheng et
al. obtained a very poor correlation between their calculated
BDE(P–H) values and $\sigma_p^+$ parameters, and the slope of the
correlation line was only 0.28. Our estimated slope value is
almost 12 times higher than their value. We believe this is due
to their poor estimation of the BDE(P–H) values by the ROMP2
method as discussed before.

It has been demonstrated that the substituent effects in
phenoxide ions in the solution and gas phases are linearly
related. Thus, Hammett’s substituent constants can be used
in the correlation study with the gas-phase PA values of
phenylphosphine ions. However, it is argued that the regular
substituent constants ($\sigma$) are not generally applicable to systems
with a direct conjugation between the substituent and the
reaction center. Thus, a different set of parameters ($\sigma^r$) has
been proposed for systems where a permanent negative charge on
the reaction center can be resonance-stabilized by a substituent.
The $\sigma^r$ parameters have been determined mainly from the
aqueous acidities of phenols and from the aqueous basicities of
anilines. For substitution at the meta position, such direct
conjugation does not occur and $\sigma_m^-$ can be taken as the same
as $\sigma_m$. We have used the PA values of the substituted

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Correlation between BDE(P–H) values (kJ mol$^{-1}$) for the
para-substituted phenylphosphines and modified Hammett’s parameters.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Hammett plot of BDE(P–H) values (kJ mol$^{-1}$) for meta-
substituted phenylphosphines and Hammett’s substituent constants.}
\end{figure}
TABLE 5: Electron Affinities [EA in kJ mol\(^{-1}\)] of Meta- and Para-Substituted Phenylphosphine Radicals [X-C\(_6\)H\(_4\)-PH] with B3LYP/6-311+++(2df,2p)/B3LYP/6-311G(d,p) Model Chemistry

<table>
<thead>
<tr>
<th>X</th>
<th>meta EA</th>
<th>para EA</th>
<th>(\Delta\text{EA}_{\text{para}})</th>
<th>X</th>
<th>meta EA</th>
<th>para EA</th>
<th>(\Delta\text{EA}_{\text{para}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>147.7</td>
<td>147.7</td>
<td>0.00</td>
<td>NH(_2)</td>
<td>140.2</td>
<td>112.9</td>
<td>–27.3</td>
</tr>
<tr>
<td>F</td>
<td>169.3</td>
<td>153.9</td>
<td>–15.4</td>
<td>CN</td>
<td>202.0</td>
<td>218.4</td>
<td>16.4</td>
</tr>
<tr>
<td>Cl</td>
<td>175.7</td>
<td>174.1</td>
<td>–1.6</td>
<td>CF(_3)</td>
<td>186.8</td>
<td>199.9</td>
<td>13.1</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>145.4</td>
<td>140.0</td>
<td>–5.4</td>
<td>NO(_2)</td>
<td>206.8</td>
<td>254.5</td>
<td>47.7</td>
</tr>
<tr>
<td>OCH(_3)</td>
<td>146.7</td>
<td>129.3</td>
<td>–17.4</td>
<td>Cl(_2)</td>
<td>202.0</td>
<td>218.4</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Phenylphosphine as the theoretical descriptor to correlate with \(\sigma_p\) and \(\sigma_m\). The correlation equations obtained for para- and meta-substituted arylphosphate radicals as follows:

\[
\text{PA} = 1482.9 - 76.062\sigma_p^- \quad (R = 0.98) \quad (6)
\]

\[
\text{PA} = 1484.3 - 79.280\sigma_m^- \quad (R = 0.97) \quad (7)
\]

As evidenced from the two equations, the PA values have a good linear correlation with the Hammett’s substituent constants.

The negative slope of these two equations indicate that the larger the value of \(\sigma_p^-\) or \(\sigma_m^-\), the lower is the PA value. It also indicates that the substituent effect on the homolytic and heterolytic bond dissociation enthalpies are opposite to each other. When the slope value (–76.06) in eq 6 is compared with the similar values for phenoxy group (–72.2\(^2\)) and thiophenoxy group (60.6), it can be concluded that the para-substituent effect is larger on the acidity of phenylphosphine. On the contrary, the effect of meta substitution on acidity is highest for phenol.

**Electron Affinity of Phenylphosphine Radicals.**

The calculated electron affinities (EAs) of phenylphosphine radicals [X-C\(_6\)H\(_4\)-PH] are given in Table 5. No experimental result for these systems is available, and thus, the present EA values are the first accurate reported data. The EA of parent phenylphosphine C\(_6\)H\(_5\)-PH radical is evaluated to be 147.7 kJ mol\(^{-1}\). In general, our results are larger by about 12 kJ mol\(^{-1}\) than the calculated values of Cheng et al.\(^{12}\) Substituent effects, especially at the para position, are found to be much stronger on EA values of phenylphosphine than that observed for the BDE(P-H) values of phenylphosphine and the PA values of phenylphosphine anion. All EWG substituents increase the EA values in both the para and meta position, but the effect is much stronger at the para position. This is clear from the \(\Delta\text{EA}_{\text{para}}\) values given in Table 5. This is because of the fact that EWGs stabilize the anion more than the radical, and the effect is more when they are at the para position. At the para position, the –NO\(_2\) group can induce both inductive and resonance stabilization to the phenylphosphine anion, and as a result, the EA value is greater by 48 kJ mol\(^{-1}\) from the EA value when the same group is at the meta position. On the other hand, EDGs (like CH\(_3\) and NH\(_2\)) reduce the EA values because of the greater stabilizing effect on the radical. The effect is more pronounced when these groups are at the para position. As observed before for BDE(P-H) and PA values, EDGs have very little effect on EA while at the meta position.

Like Hammett’s correlation for the BDE(P-H) and PA values, we tried to find similar correlation for the EA values of phenylphosphine radicals. The EA values for the meta-substituted radicals were found to be well-correlated with the corresponding \(\sigma_p^-\) values. For the para-substituted radicals, the EA values were best correlated with the \(\sigma_p^-\) values, although the EA value (112.9 kJ mol\(^{-1}\)) for the –NH\(_2\)-substituted phenylphosphine radical was found to be much lower than that expected from the \(\sigma_p^-\) value (–0.15). In fact, the correlation coefficient becomes 0.99 when this value is removed from the analysis. The following correlation equations were obtained for para- and meta-substituted arylphosphate radicals:

\[
\text{EA} = 147.8 + 80.28\sigma_p^- \quad (R = 0.97) \quad (8)
\]

\[
\text{EA} = 147.7 + 83.17\sigma_m^- \quad (R = 0.97) \quad (9)
\]

**Conclusions**

In this study, we have reported the accurate BDE(P-H) values for meta- and para-substituted phenylphosphines obtained from (RO)B3LYP model DFT calculations. It has been demonstrated first that the method is capable of producing results within ±6 kJ mol\(^{-1}\) of the exact results. Although no experimental value for BDE(P-H) in phenylphosphine is available, our results show that this value should be 319.34 ± 6 kJ mol\(^{-1}\). EDG at the para position of phenylphosphine reduces the P-H bond strength from the parent molecule, while the effect is insignificant at the meta position. On the contrary, EWG increases the P-H bond strength at both positions. This is because of the difference in the stabilizing effect of a substituent on the phenylphosphine molecule and radical. EDGs stabilize the radical more, and as a result, the BDE(P-H) value decreases, whereas EWGs lower the ground-state energy of phenylphosphine and increase the BDE(P-H) values. The accurate PA values for the substituted phenylphosphine anions are also reported for the first time. The PA value of phenylphosphine anion amounts to 1484.0 kJ mol\(^{-1}\), and thus, phenylphosphine should be more acidic than phenylamine. The substituent effect is the opposite on the PA value of the phenylphosphine anion. Here, EDGs enhance the PA value from the parent phenylphosphine molecule and EWGs reduce it. The effect is especially stronger for the EWGs, and this is because of the strong stabilizing effect of an EWG on the phenylphosphine anion. The BDE(P-H), PA, and EA values have a strong linear correlation with Hammett’s parameters. Such correlation equations can be used for generating new data. When our results for para-substituted phenylphosphines are compared with the previous results on phenol, thiophenol, and aniline, the substituent effect order on BDEs can be written as P-H < S-H < N-H < O-H. As a byproduct, the accurate electron affinities of substituted arylphosphate radicals are also reported.

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**References and Notes**
