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−C_6H_4−PH_2) 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 PH_3, N−H bond in NH_3 and X−C_6H_4−NH_2 (X = H, CH_3, and NO_2), and the As−H bond in AsH_3 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−C_6H_4−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 a variety of bonds in compounds like X−C_6H_4−Y, such as O−H,[1,2] S−H,[3−5] N−H,[6] Si−H[7], etc. The density functional theory (DFT) with B3LYP functional turns out to be an effective tool for accurate estimation of BDEs in many organic compounds.[8,9] Our previous studies[2,4] were focused on BDEs of the O−H and S−H bonds in substituted phenols and thiophenols, respectively, where we analyzed the effect of substituents in the *meta* and *para* positions on the ring. It was observed that the BDEs of the O−H and S−H bonds can be estimated accurately (with an error bar of ±6 kJ/mol) by applying DFT at the level of (RO)B3LYP/6-311++G(2df,2p).

Organic molecules containing phosphorus offer fascinating possibilities for structural, synthetic, and mechanistic study. Besides being crucial biomolecules in metabolic processes, they find important practical applications, e.g., as anticancer and antiviral drugs, immunosuppressives, insecticides, and fuel and lubricant additives.[10] Knowledge of the BDE values for the P−H bonds can be very useful for understanding the chemistry of organophosphorus compounds. Unfortunately, the experimental as well as theoretical BDE data for the compounds containing P−H bond are very limited. This is especially true for the phenylphosphine systems. This leads us to calculate and predict these values using quantum chemical methods. In this work, we have determined the BDE values for the P−H bonds [BDE(P−H)] of phenylphosphine and its *meta*- and *para*-substituted derivatives. Another purpose of our present work is to show that the (RO)B3LYP procedure can be used as an accurate 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.[11] It is predicted that the proton affinities of these compounds is in the range of 863 ± 10 kJ mol^{-1}. Recently, Cheng et al.[12] determined the BDE values for a number of substituted phenylphosphines by applying the R(O)MP2/6-311++G(d,2p) method. However, their calculated result for PH_3 was found to be 27.6 kJ mol^{-1} lower than the experimental value (345.0 ± 1.9 kJ mol^{-1})[13] 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.[14] 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 (C_6H_5−PH_2) and its substituted derivatives (X−C_6H_4−PH_2) is the main purpose of this paper. The energy required for *homolytic* bond cleavage corresponds to the enthalpy change for the reaction

$$\mathrm{X{-}C_6H_4{-}PH^{\cdot} + H^{\cdot}} \qquad (1)$$

Conversely, if the radicals X−C_6H_4−$PH^{\cdot}$ and $H^{\cdot}$ recombine to form the molecule X−C_6H_4−PH_2, the energy equivalent to the bond dissociation enthalpy is released.

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

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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

model chemistry	PH$_3$ (351.0 ± 2.0)[a]	NH$_3$ (452.7 ± 1.3)[a]	AsH$_3$ (319.2 ± 1.3)[a]
UB3P86/6-311G(d,p) // B3P86/6-311G(d,p)	396.17	498.24	367.76
UB3P86/6-311++G(2df,2p) // B3P86/6-311G(d,p)	396.65	501.96	368.57
ROB3P86/6-311++G(2df,2p) // B3P86/6-311G(d,p)	401.26	507.04	371.93
UB3LYP/6-311G(d,p) // B3LYP/6-311G(d,p)	342.79	440.68	314.56
UB3LYP/6-311++G(2df,2p) // B3LYP/6-311G(d,p)	343.62	444.71	315.37
ROB3LYP/6-311++G(2df,2p) // B3LYP/6-311G(d,p)	**347.54**	**449.39**	**318.05**
UB3LYP/6-311++G(d,p) // B3LYP/6-311++G(d,p)	332.55	444.42	314.33
UB3LYP/6-311++G(2df,2p) // B3LYP/6-311G(d,p)	343.54	444.92	315.42
ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311++G(d,p)	**347.51**	**449.64**	**318.21**
UB3LYP/Aug-cc-pVDZ // B3LYP/Aug-cc-pVDZ	334.48	438.19	309.63
UMP2/Aug-cc-pVDZ// B3LYP/Aug-cc-pVDZ	311.11	429.5	286.55
UMP2YP/Aug-cc-pVTZ //B3LYP/Aug-cc-pVDZ	329.89	449.42	307.03
CCSD/Aug-cc-pVDZ// B3LYP/ Aug-cc-pVDZ	317.35	417.48	294.60
CCSD/Aug-cc-pVTZ // B3LYP/Aug-cc-pVDZ	333.43	435.23	312.18
CCSD(T)/Aug-cc-pVDZ // B3LYP/Aug-cc-pVDZ	319.96	421.85	297.28
CCSD(T)/Aug-cc-pVTZ // B3LYP/Aug-cc-pVDZ	336.67	440.82	315.65

[a] From ref 13.

the PA value of the corresponding phenylphosphine anions (X−C$_6$H$_4$−PH$^-$). Good linear correlation has been observed between gas-phase acidities and Hammett's reactivity parameters derived for the solution-phase acidities for substituted phenols[2,15,16] and thiophenols.[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 by 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 arylphosphine 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 homolytic P−H bond dissociation enthalpy [BDE(P−H)] value at 298 K for the molecule X−C$_6$H$_4$−PH$_2$ was estimated from the expression

$$\mathrm{BDE(P{-}H)} = H_f(\mathrm{X{-}C_6H_4{-}PH^{\bullet}}) + H_f(\mathrm{H^{\bullet}}) - H_f(\mathrm{X{-}C_6H_4{-}PH_2}) \quad (2)$$

where H_f's are the enthalpies of different species at 298 K. The enthalpies were estimated from the usual expression: $H_f(298\ \mathrm{K}) = E_0 + \mathrm{ZPE} + H_{\mathrm{trans}} + H_{\mathrm{rot}} + H_{\mathrm{vib}} + RT$. 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$_4$−PH$^-$ was calculated from the following expression

$$\mathrm{PA(X{-}C_6H_4{-}PH^-)} = H_f(\mathrm{X{-}C_6H_4{-}PH^-}) + H_f(\mathrm{H^+}) - H_f(\mathrm{X{-}C_6H_4{-}PH_2}) \quad (3)$$

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$_4$−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-ζ basis set underestimate the BDE values by an amount of 28−30 kJ mol^{-1}. MP2 calculations with a triple-ζ 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$_4$−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

	meta	experimental	para	experimental
$HC_6H_4NH_2$	375.9	375.3[a], 372.8[b]		
$CH_3C_6H_4NH_2$	385.3		370.2	371.1,[c] 366.1[a]
$NO_2C_6H_4NH_2$	398.7		404.9	404.6[d]

[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

	meta		*para*		
X	calculated	ΔBDE[a]	calculated	ΔBDE[a]	ΔBDE_{p-m}
H	319.34	0.0	319.34	0.0	0.00
F	320.21	0.87	319.37	0.03	−0.84
Cl	319.98	0.64	318.86	−0.48	−1.12
CH_3	318.85	−0.49	318.16	−1.18	−0.69
OCH_3	319.96	0.62	316.88	−2.46	−3.08
NH_2	319.28	−0.06	313.96	−5.38	−5.33
CN	321.68	2.34	320.27	0.93	−1.41
CF_3	320.80	1.46	321.04	1.70	0.16
NO_2	322.46	3.12	321.62	2.28	−0.84

[a] $\Delta BDE = BDE(X-C_6H_4PH-H) - BDE(C_6H_5PH-H)$

[6-311++G(d,p)] do not make any significant change in the BDE values, geometry optimizations 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.[2,4] 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} [19] (and 372.8 kJ mol^{-1}).[14] 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.[6] 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.[12] 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}.[12] 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.[12] 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.[12] 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 X−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 [20] and 375.3 kJ mol^{-1},[19] 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 $C_6H_5-XH_2$ (X = N and P) molecules. Of course, the difference in BDE is much higher for the XH_3 molecule.

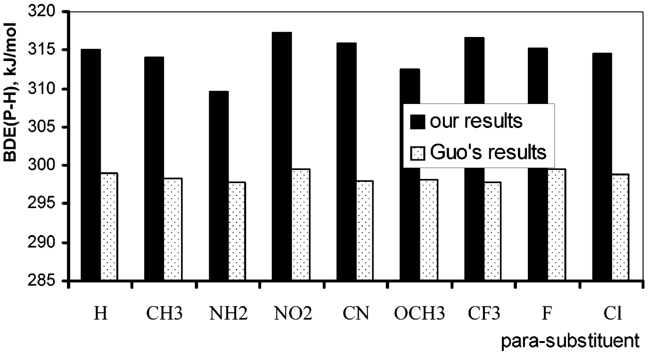

Figure 1. Differences between our calculated BDE(P−H) values and those obtained by Guo and co-workers[12] for the *para*-substituted phenylphosphines.

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 ΔBDE(P−H) values [ΔBDE(P−H) = $BDE(X-C_6H_4PH-H) - BDE(C_6H_5PH-H)$] 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 reduces the P−H bond strength, 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 Cl substitution 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,[21] O−H bond in substituted phenols,[2] and S−H bond in substituted thiophenols.[4] 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,[21] 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.[22] It is generally believed that electron-donating substituents at the *para* position stabilize the radical and raise the ground-state energies of the molecule

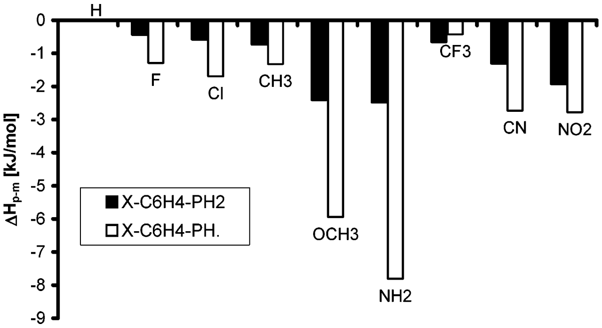

Figure 2. Enthalpy differences between the *para*- and *meta*-substituted phenylphosphines and between *para*- and *meta*-substituted phenylphosphine radicals.

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.[22] 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 CH_3, NH_2, and OCH_3) 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 ΔBDE_{p-m} values in Table 2) between the BDE(P−H) values for *meta*- and *para*-substituted phenylphosphines. On the contrary, EWGs (like CN and NO_2) 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 [ΔH_{p-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 $-CF_3$ 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 (OCH_3 and NH_2), the ΔH_{p-m} value for the phenylphosphine radical is much greater than the ΔH_{p-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.

Acidities of Substituted Phenylphosphine. The gas-phase proton affinities for the phosphorus atom of *meta*- and *para*-substituted arylphosphine anions ($X-C_6H_4-PH^-$) 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 phenol[2] and thiophenol[4] 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 anion, 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 $C_6H_5NH^-$, and our calculated value (1534.0 kJ mol^{-1}) 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.

TABLE 4: Calculated Proton Affinities [PA in kJ mol^{-1}] for the *Para* and *Meta*-Substituted Phenylphosphine Anions [PA($XC_6H_4PH^-$)] Using the B3LYP6-311++(2df,2p)//B3LYP/6-311G(d,p) Method

X	*meta*	*para*	ΔPA_{p-m}	X	*meta*	*para*	ΔPA_{p-m}
H	1484.0	1484.0	0.0	NH_2	1491.8	1513.8	22.0
F	1463.7	1478.3	14.6	CN	1432.5	1414.7	−17.8
Cl	1457.0	1457.6	0.6	CF_3	1446.8	1433.8	−13.0
CH_3	1486.2	1491.0	4.8	NO_2	1428.4	1382.6	−45.8
OCH_3	1486.0	1500.3	14.3				

Our calculated PA value for the phenylphosphine anion is 1484.0 kJ mol^{-1}. This is substantially lower than the PA value of $C_6H_5NH^-$ (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 NH_2 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 NO_2, 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* $NO_2-C_6H_4-PH^-$ and $CN-C_6H_4-PH^-$ amount to 1.777 and 1.785 Å, respectively. The same values for the *meta* $NO_2-C_6H_4-PH^-$ and $CN-C_6H_4-PH^-$ 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

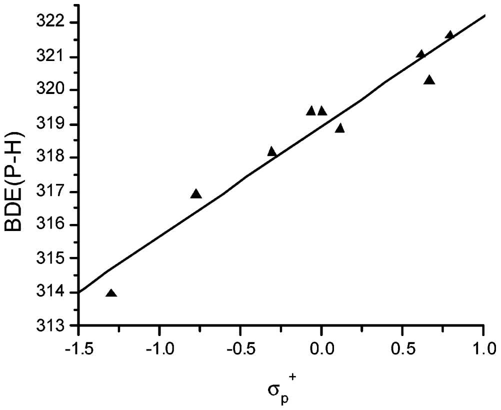

Figure 3. Correlation between BDE(P−H) values (kJ mol^{-1}) for the *para*-substituted phenylphosphines and modified Hammett's parameters.

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 pronounced 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 properties. Thus, It is interesting to observe the substituent effects on BDE(P−H) of phenylphosphine in terms of Hammett's reactivity parameters (σ). To account for the through conjugation effects, especially for the electron-donor groups at the *para* position, a modified set of parameters (σ^+) is generally used for such correlation studies. Through conjugation effect is insignificant when the substituent is at the *meta* position, and as a result, $\sigma_m{}^+$ and σ_m values are nearly the same. The modified $\sigma_p{}^+$ and σ_m parameters were taken from the compilations of Hammett parameters by Hansch, Leo, and Taft.[25] 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 correlation 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 σ_m parameters is less impressive. The correlation equations obtained for *para* and *meta* phenylphosphines are given below

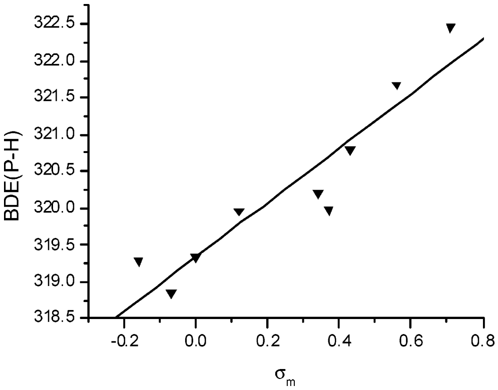

Figure 4. Hammett plot of BDE(P−H) values (kJ mol^{-1}) for *meta*-substituted phenylphosphines and Hammett's substituent constants.

$$\mathrm{BDE(P-H)} = 3.268\sigma_p{}^+ + 318.94 \quad (R = 0.97) \qquad (4)$$

$$\mathrm{BDE(P-H)} = 3.696\sigma_m + 319.34 \quad (R = 0.94) \qquad (5)$$

The positive slope of both equations tells us that a substituent with a positive $\sigma_p{}^+$ or σ_m increases the BDE(P−H), otherwise they decrease the BDE(P−H) values. The larger the absolute value of $\sigma_p{}^+$ or σ_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,[2] thiophenols,[4] and phenylphosphines, respectively. 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.[14] 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.[12] 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.[16] 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 (σ) are not generally applicable to systems with a direct conjugation between the substituent and the reaction center. Thus, a different set of parameters (σ^-) has been proposed for systems where a permanent negative charge on the reaction center can be resonance-stabilized by a substituent.[25] The $\sigma_p{}^-$ parameters have been determined mainly from the aqueous acidities of phenols and from the aqueous basicities of anilines.[25] For substitution at the *meta* position, such direct conjugation does not occur and $\sigma_m{}^-$ can be taken as the same as σ_m. We have used the PA values of the substituted

TABLE 5: Electron Affinities [EA in kJ mol^{-1}] of *Meta*- and *Para*-Substituted Phenylphosphine Radicals [$X-C_6H_4-PH^{\cdot}$] with B3LYP/6-311++(2df,2p)/B3LYP/6-311G(d,p) Model Chemistry

	EA				EA		
X	*meta*	*para*	ΔEA_{p-m}	X	*meta*	*para*	ΔEA_{p-m}
H	147.7	147.7	0.00	NH_2	140.2	112.9	−27.3
F	169.3	153.9	−15.4	CN	202.0	218.4	16.4
Cl	175.7	174.1	−1.6	CF_3	186.8	199.9	13.1
CH_3	145.4	140.0	−5.4	NO_2	206.8	254.5	47.7
OCH_3	146.7	129.3	−17.4				

phenylphosphine ions as the theoretical descriptors to correlate with σ_p^- and σ_m. The correlation equations obtained for *para*- and *meta*-substituted arylphosphine ions as follows:

$$PA = 1482.9 - 76.062\sigma_p^- \quad (R = 0.98) \tag{6}$$

$$PA = 1484.3 - 79.280\sigma_m \quad (R = 0.97) \tag{7}$$

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 σ_p^- or σ_m, the lower is the PA value. It also indicates that the substituent effect on the homolytic and heterolytic bond dissociation enthalpy is opposite to each other. When the slope value (−76.06) in eq 6 is compared with the similar values for phenoxide ion (−72.2)[2] and thiophenoxide ion (60.6),[4] it can be concluded that the *para*-substituent effect is largest 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 [$X-C_6H_4-PH^{\cdot}$] 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 $C_6H_5-PH^{\cdot}$ 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 radicals 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 ΔEA_{p-m} 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 σ_m values. For the *para*-substituted radicals, the EA values were best correlated with the σ_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 σ_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 arylphosphine radicals:

$$EA = 147.8 + 80.28\sigma_p^- \quad (R = 0.97) \tag{8}$$

$$EA = 147.7 + 83.17\sigma_m \quad (R = 0.97) \tag{9}$$

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 affinites of substituted arylphosphine radicals are also reported.

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