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A Theoretical Study of the Substituent Effects on the P–X (X = H, F, Cl) Bond Dissociation Energies in *para*- and *meta*-Substituted Aromatic Phosphines

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The P–X (X = H, F, and Cl) bond dissociation energies (BDEs) for a number of *para*- and *meta*-substituted aromatic phosphines were calculated using R(O)MP2/6-311++g(d, 2p)//(U)B3LYP/6-31g(d) method. The results showed the importance of the radical effect as well as the ground effect on the BDEs. For X = H case, because the substituent affected the neutral phosphine to the same extent as it affected the radical, substituent effects on the P–H BDE were small ($\rho^+ = 0.28$ kJ/mol). In comparison, for X = F or Cl case, because the substituent affected the neutral phosphine much more strongly than it affected the radical, substituent effects on the P–F ($\rho^+ = -3.25$ kJ/mol) or P–Cl ($\rho^+ = -1.31$ kJ/mol) BDEs were significant. Therefore, the substituent effects on BDEs of the Z–X bonds in compounds of the general formula 4-YC_6H_4Z–X varied when X changed, which meant that a recent proposal (*J. Am. Chem. Soc.*, **123**, 5518 (2001)) was unfortunately not supported.

Bond dissociation energies (BDEs) are defined as the enthalpy changes of the following reaction in the gas phase:

$$X\text{–}Y \rightarrow X^\bullet + Y^\bullet \qquad (1)$$

They are fundamentally important in chemistry and therefore, have been interesting for several decades.[1] So far, although considerable efforts have been devoted to the development of experimental methods to measure BDEs, the BDE values for many important chemical species still remain unknown.[2]

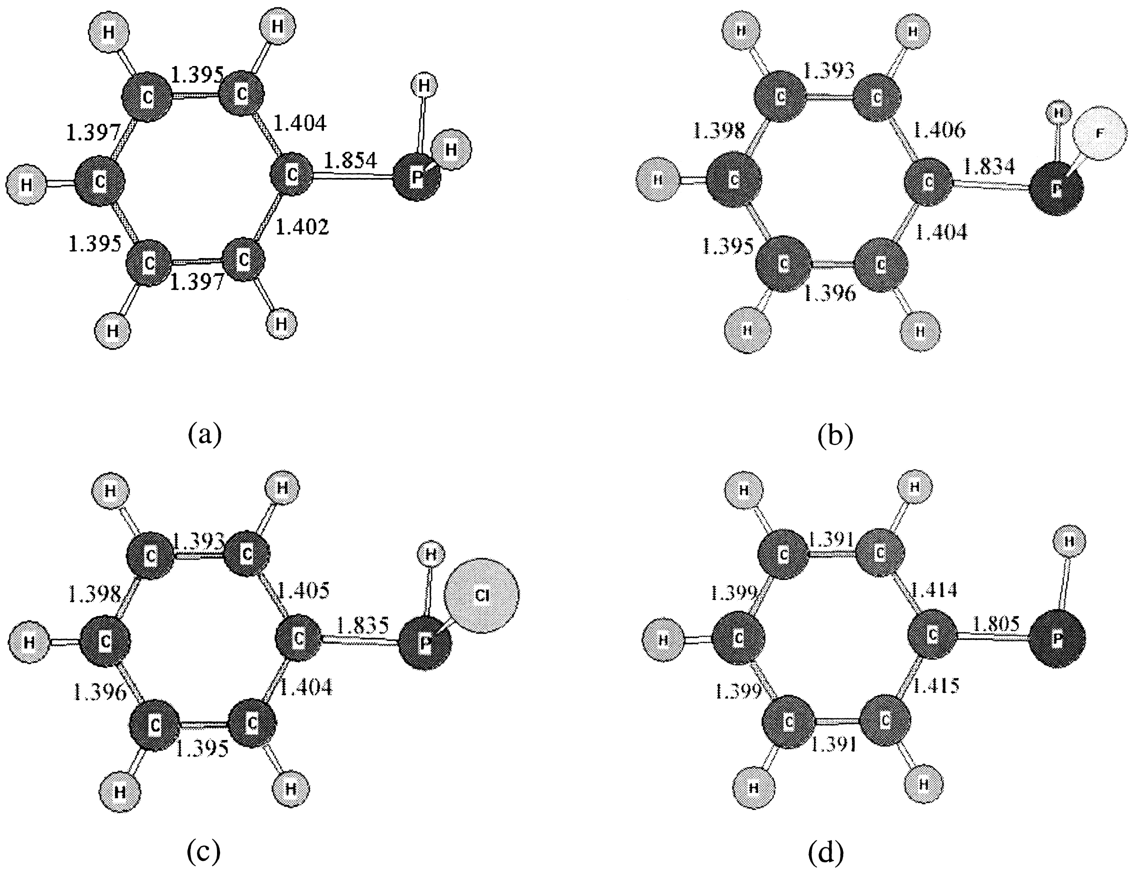
Substituent effect is another interesting issue in the study of BDEs, an issue which has not yet been completely settled. For example, for some time it has been assumed that the direction and magnitude of the effects of Y-substituents on the Z–X BDEs in compounds of the general formula 4-YC_6H_4Z–X could be correlated with the polarity of the Z-X bond undergoing homolysis.[3] However, in the very recent studies it was proposed that when Y have significant effects on Z–X BDEs it must be due to their stabilization or destabilization of the radical instead of the neutral compound regardless of the nature of X, Y, and Z.[4] This argument was thought to be evidenced by the fact that the effects of Y on C–X BDEs in 4-$YC_6H_4CH_2$–X (X = H, F, Cl, Br) are roughly equal for each X, despite large changes in C–X bond polarity. The same argument was also thought to be supported by the fact that changes in O–X BDEs induced by changing Y in 4-YC_6H_4O–X (X = H, CH_3, CH_2Ph) are large and essentially identical for each X ($\rho^+ = 6.7$–6.9 kcal/mol).[5] In addition, it was predicted that the effects of Y on N-X BDEs in 4-YC_6H_4NH–X were not only independent of X but were also of a magnitude intermediate between that of the 4-YC_6H_4O–X and 4-$YC_6H_4CH_2$–X families of compounds, namely, $\rho^+ \approx 3.0$ kcal/mol.[4]

Herein, we studied the P–X BDEs of a number of 4-YC_6H_4–PH–X and 3-YC_6H_4–PH–X (X = H, F, Cl) molecules. The questions which interested us include the substituent effects on the structures of the aromatic phosphines and their corresponding radicals, the substituent effects on the BDEs of the P–X bonds, and the relative importance of the ground effects and radical effects (See later discussion of this paper for definitions of ground and radical effects) on the P–X BDEs. With such information available, we could then examine if the aforementioned proposal about the BDEs of 4-YC_6H_4Z–X molecules was also correct for Z = P case. It should be mentioned that so far little has been known about the P–X BDEs, and no study has ever been performed on the substituent effects on phosphine radicals.

Methods

All the calculations were performed with GAUSSIAN 98.[6] A series of fifteen *para*- and *meta*-substituted aromatic phosphines (Y-$C_6H_4PH_2$), and their fluorinated and chlorinated derivatives (YC_6H_4PH–F and YC_6H_4PH–Cl) were studied. As these fifteen substituents represented the most popular ones used for physical organic chemistry and their $\sigma_p{}^+$ (or σ_m) constants spanned a large range, we were confident that the linear energy relationship analyses on the basis of our calculation results were meaningful and reliable in term of statistics.

The geometries of the phosphine molecules and their corresponding radicals were fully optimized with (U)B3LYP/6-31g(d) method without any constraints. It should be mentioned that such a level of geometry optimization represented a good compromise between the CPU cost and the accuracy of the calculations for neutral molecules as well as radicals. In fact, the same method was used by Radom et al. very recently



(a) (b) (c) (d)

Fig. 1. The (U)B3LYP/6-31g(d) optimized structures of (a) H–$C_6H_4PH_2$, (b) H–C_6H_4PHF, (c) H–C_6H_4PHCl, and (d) H–C_6H_4–$PH^{\bullet}$ species.

in their comprehensive study of the BDEs of even smaller substituted methyl radicals.[7]

After geometry optimization, frequency calculations were done on all the optimized species at (U)B3LYP/6-31g(d) level to verify that the optimized geometries were real minima on the potential surface (no imaginary frequencies). The total energy of every species was calculated at R(O)MP2/6-311++g(d,2p) level, and these results were corrected with zero point energies obtained at (U)B3LYP/6-31g(d) level scaled by a factor of 0.9806. It should be mentioned that the use of R(O)MP2 instead of UMP2 or PMP2 method was to minimize the spin contamination, which had been previously shown to badly affect the accuracy of BDE calculations.[8] Moreover, use of R(O)MP2 was found to be better than use of the DFT methods in the calculations of the radical stabilization energies (RSEs).[7]

The BDEs were calculated as the enthalpy changes of the reactions shown by Eq. 2 at 0 K. The RSEs were calculated as the enthalpy changes of the reactions shown by Eq. 3 at 0 K. The ground effects (GEs) of the bond dissociation, which could reveal the interaction between the substituent and neutral PHX group, were calculated as the enthalpy change of the isodesmic reaction shown in Eq. 4 at 0 K. Finally, the radical effects (REs), which could reveal any influence of the substituent on the stability of the R–PH• radical, were calculated as the enthalpy changes of the isodesmic reaction shown in Eq. 5 at 0 K.

$$\mathrm{Y{-}C_6H_4{-}PH{-}X \rightarrow Y{-}C_6H_4{-}PH^{\bullet} + X^{\bullet}} \tag{2}$$

$$\begin{aligned}&\mathrm{C_6H_5{-}PH{-}X + Y{-}C_6H_4{-}PH^{\bullet}}\\&\quad\rightarrow \mathrm{C_6H_5{-}PH^{\bullet} + Y{-}C_6H_4{-}PH{-}X}\end{aligned} \tag{3}$$

$$\mathrm{C_6H_6 + Y{-}C_6H_4{-}PHX \rightarrow C_6H_5{-}PHX + Y{-}C_6H_5} \tag{4}$$

$$\mathrm{C_6H_6 + Y{-}C_6H_4{-}PH^{\bullet} \rightarrow C_6H_5{-}PH^{\bullet} + Y{-}C_6H_5} \tag{5}$$

Results and Discussion

1. Geometry. In Fig. 1 are shown the optimized geometries of H–$C_6H_4PH_2$, H–C_6H_4PHF, H–C_6H_4PHCl, and H–C_6H_4–$PH^{\bullet}$ species. From Fig. 1, it can be seen that from the neutral phosphines to their corresponding radicals the most significant change occurs in the C–P bond length. In detail, in H–$C_6H_4PH_2$ the C–P bond length is 1.854 Å, in H–C_6H_4PHF it is 1.834 Å, in H–C_6H_4PHCl it is 1.835 Å, and in H–C_6H_4–$PH^{\bullet}$ it is 1.805 Å. Presumably, the significant decrease in the C–P bond length is caused by the conjugation between the radical and the phenyl group.

Thus, we list the C–P bond lengths of all the *para*-phosphines and their corresponding radicals in Table 1. Using the Brown's $\sigma_p{}^{+}$ [9] and Jiang's σ_{JJ} [10] substituent constants (Table 1), we also conducted the multi-variable linear regression analyses on the C–P bond lengths. The corresponding results are summarized in Table 2. Herein, it should be mentioned that

Table 1. C–P Bond Lengths (Å) of *para*-Substituted Aromatic Phosphines (4-$YC_6H_4PH_2$, 4-YC_6H_4PH–F and 4-YC_6H_4PH–Cl) and of Their Corresponding Radicals Obtained at (U)B3LYP/6-31g(d) Level

Y	Y–C_6H_4–PH_2	Y–C_6H_4–PHF	Y–C_6H_4–PHCl	Y–C_6H_4–$PH^\bullet$	$\sigma_p{}^+$	σ_{JJ}
H	1.8540	1.8349	1.8341	1.8054	0.00	0.00
CH_3	1.8523	1.8314	1.8307	1.8029	−0.31	0.15
$N(CH_3)_2$	1.8439	1.8160	1.8176	1.7950	−1.70	1.00
NH_2	1.8455	1.8193	1.8201	1.7968	−1.30	—
OCH_3	1.8482	1.8248	1.8248	1.8003	−0.78	0.23
OH	1.8487	1.8255	1.8254	1.8008	−0.92	—
SCH_3	1.8504	1.8280	1.8281	1.7994	−0.60	0.62
F	1.8530	1.8327	1.8318	1.8049	−0.07	−0.02
Cl	1.8540	1.8356	1.8350	1.8044	0.11	0.22
CN	1.8528	1.8422	1.8443	1.8040	0.66	0.42
$COCH_3$	1.8522	1.8390	1.8418	1.8023	0.50	0.54
$CONH_2$	1.8532	1.8382	1.8409	1.8039	0.36	0.38
COOH	1.8514	1.8400	1.8427	1.8037	0.42	0.38
NO_2	1.8498	1.8441	1.8448	1.8048	0.79	0.36
CF_3	1.8536	1.8404	1.8430	1.8067	0.61	−0.01

Table 2. Results of Multi-Variable Regression Analyses of the C–P Bond Lengths against the Brown's $\sigma_p{}^+$ and Jiang's σ_{JJ} Substituent Constants[a)]

System	Y–C_6H_4–PH_2	Y–C_6H_4–PHF	Y–C_6H_4–PHCl	Y–C_6H_4–$PH^\bullet$
A	1.85308	1.83409	1.83379	1.80486
Error in A	0.00074	0.00034	0.00050	0.00025
B	0.00203	0.01130	0.01280	0.00264
Error in B	0.00074	0.00033	0.00050	0.00025
t value of B	2.74	33.64	25.69	10.45
C	−0.00497	0.00100	0.00483	−0.00593
Error in C	0.00182	0.00082	0.00122	0.00062
t value of C	−2.73	1.21	3.95	−9.57
Correlation coefficient *r*	0.860	0.996	0.993	0.987

a) The regression was done using the equation $R_{C\text{–}P} = A + B\cdot\sigma_p{}^+ + C\cdot\sigma_{JJ}$

the multiple-variable linear regression can show the dependence of a parameter y on a set of variables x_1, x_2, ..., and x_n on the basis of the following equation

$$y = a_0 + a_1x_1 + a_2x_2 + \dots + a_nx_n \qquad (6)$$

The coefficients a_0 to a_n can be optimized so that the difference between the expectation y values and actual y values is minimized. Under this condition, the sign and magnitude of each coefficient a_i could indicate the dependence of y on x_i.

It should also be mentioned that the Brown's $\sigma_p{}^+$ substituent constant reflects the polar induction/resonance effects of a substituent. Thus a positive $\sigma_p{}^+$ value means that a substituent is electron-withdrawing while otherwise it is electron-donating. In comparison, Jiang's σ_{JJ} constants were established on the basis of the ability of a *para*-substituent to stabilize the 4-Y–$C_6H_4CH_2{}^\bullet$ radical via the so-called spin-delocalization effect. Recently we found that such a spin-delocalization effect actually reflects the ability of a substituent to stabilize any non-polarized π electrons (even in closed-shell molecules) in addition to the radicals.[11] Thus, we refer to the corresponding effect as the nonpolar π electron delocalization effect. It should be mentioned that the polar induction/resonance effect and the nonpolar π electron delocalization effect are orthogonal to each other.

From Table 2, it can be seen that there is a decent correlation between the C–P bond length and the Brown's $\sigma_p{}^+$ and Jiang's σ_{JJ} substituent constants for 4-Y–$C_6H_4PH_2$ as indicated by the fair correlation coefficient ($r = 0.860$). The errors in the coefficients *A*, *B*, and *C* are smaller than the absolute values of *A*, *B*, and *C*. Therefore, qualitatively it can be concluded from the positive coefficient ahead of $\sigma_p{}^+$ ($B = 0.00203 \pm 0.00074$) that electron-withdrawing substituents should increase the C–P bond length whereas electron-donating groups should decrease it. The reason for such an effect may be the polarization of the C–P bond, namely, C being the positive end of the bond whereas P being the negative end. As such, an electron-withdrawing *para*-substituent should remove some negative charge from P and thereby increase the C–P bond length. By contrast, the coefficient ahead of σ_{JJ} is negative ($C = -0.00497 \pm 0.00182$). This means that for the substituent that can better stabilize non-polarized π electrons (here presumably the lone pair electrons on P), the C–P bond is shorter. The reason for it apparently is the increase of the covalent bond order of C–P by the nonpolar π electron delocalization. Finally, it should be mentioned that the *t*-values[12] for *B* and *C* (2.74 vs −2.73) are both large and almost equal to each other for the 4-Y–$C_6H_4PH_2$ system. Therefore, both the polar induction/resonance and the nonpolar π electron delocalization effects are important for the C–P bond length in this system.

Table 3. Bond Dissociation Energies, Radical Stabilization Energies, Ground Effects, and Radical Effects Calculated for the *para*-Substituted Aromatic Phosphines (kJ/mol)

Y	RE	$4\text{-}YC_6H_4PH\text{–}\mathbf{H}$			$4\text{-}YC_6H_4PH\text{–}\mathbf{F}$			$4\text{-}YC_6H_4PH\text{–}\mathbf{Cl}$		
		BDE	GE	RSE	BDE	GE	RSE	BDE	GE	RSE
H	0.00	299.03	0.00	0.00	421.94	0.00	0.00	282.27	0.00	0.00
CH_3	1.86	298.26	1.09	0.77	422.16	2.08	−0.22	282.94	2.53	−0.67
$N(CH_3)_2$	13.16	296.59	10.72	2.44	423.92	15.14	−1.98	283.67	14.55	−1.39
NH_2	3.72	297.73	2.42	1.30	423.45	5.22	−1.51	282.98	4.42	−0.70
OCH_3	3.22	298.09	2.28	0.94	423.42	4.70	−1.48	283.43	4.37	−1.15
OH	1.92	298.88	1.77	0.15	423.22	3.20	−1.28	283.04	2.69	−0.77
SCH_3	3.43	298.35	2.75	0.68	422.09	3.58	−0.15	282.58	3.74	−0.30
F	−0.60	299.44	−0.20	−0.41	422.26	−0.28	−0.32	282.24	−0.64	0.03
Cl	0.45	298.78	0.21	0.25	421.36	−0.13	0.58	281.88	0.06	0.40
CN	−1.14	297.96	−2.22	1.08	416.71	−6.37	5.22	280.13	−3.29	2.14
$COCH_3$	0.97	296.94	−1.12	2.09	417.52	−3.44	4.42	281.43	0.13	0.84
$CONH_2$	0.78	297.92	−0.33	1.11	417.93	−3.23	4.01	281.44	−0.05	0.83
COOH	0.36	297.70	−0.98	1.34	417.44	−4.14	4.50	281.09	−0.82	1.18
NO_2	−1.73	299.43	−1.33	−0.40	416.74	−6.93	5.19	280.48	−3.53	1.79
CF_3	−0.44	297.77	−1.70	1.26	417.99	−4.38	3.95	281.02	−1.69	1.25

From Table 2 it can be seen that the *para* substituent effects on the C–P bond lengths in the 4-Y–C_6H_4PHF and 4-Y–C_6H_4PHCl systems are also significant, as indicated by the high correlation coefficients (0.996 and 0.993). Here, the positive regression coefficients ahead of σ_p^+ (0.01130 ± 0.00033 and 0.01280 ± 0.00050) again indicate that the polar induction/resonance effects are important to the C–P bond length in the way that an electron-withdrawing substituent elongates this bond. However, the errors for the coefficients ahead of σ_{JJ} are almost as large as the coefficient themselves. This means that the dependence of the C–P bond length on the nonpolar π electron delocalization effect is not significant in the two systems, presumably because the F and Cl atoms greatly alter the energy level of the lone pair electrons on P, so that their conjugation with the *para*-substituents is not effective. Thus, only the polar induction/resonance effects are important to the C–P lengths in the 4-Y–C_6H_4PHF and 4-Y–C_6H_4PHCl systems. The same conclusion can also be drawn from the *t*-value analyses of the regressions (33.64 vs 1.21, and 25.69 vs 3.95).

Interestingly, the situation is different again when we consider the C–P bond lengths in the Y–C_6H_4–$PH^\bullet$ systems. Here, the correlation coefficient is high (0.987), indicating strong dependence on the substituent effects. As the *t*-values for both the σ_p^+ and σ_{JJ} constants are large (10.45 vs −9.57) and they are almost equal to each other, it can be concluded that both the polar induction/resonance effects and nonpolar π electron delocalization effects are important for the C–P bond length. The same conclusion can also be drawn from the fact that the errors for regression coefficients B and C are much smaller than the absolute values of B and C themselves. Since B is positive, an electron-withdrawing substituent will increase the C–P bond length while an electron-donating one should shorten it. Since C is negative, a stronger nonpolar π electron delocalization between the substituent and the single (π) electron on P radical should shorten the C–P bond.

2. Bond Dissociation Energies. Before talking about the BDEs of aromatic phosphines, we need to mention that the only P-H BDE we have found in literature is that for PH_3. This value was measured to be 345.0 ± 1.9 kJ/mol at 0 K.[1] In comparison, our calculated value for the same bond dissociation is 317.4 kJ/mol at R(O)MP2/6-311++g(d,2p)//(U)B3LYP/6-31g(d) level. Thus, our calculated value is 27.6 kJ/mol lower than the experimental value, which is true for most current theoretical calculations on BDEs.[7,8] We believe that similar underestimation should apply for our calculated P–X BDEs values for aromatic phosphines listed in Table 3. In other words, the experimental P–H BDE for a compound like H–C_6H_4–PH_2 should be about 326.6 kJ/mol. This value is about 18.4 kJ/mol lower than that found for PH_3, indicating the radical stabilization effect of the aromatic ring. Nevertheless, because of the error cancellation in the calculation of a series of substituted compounds, the calculated RSEs should be much more accurate.[4,7,8,13] The large number of substituents (fifteen) being used should also establish the statistical reliability of the following analyses.

From Table 3, it can be seen that P–F bond is the strongest, followed by P–H bond, and then P–Cl bond. The polar induction/resonance substituent effects on the BDEs can be reflected by a Hammett-type regression, as shown in the following equations:

$$\mathrm{BDE}_{\mathrm{P\text{–}H}} = 298.23\ (\pm 0.22) + 0.28\ (\pm 0.29)\ \sigma_p^+\ (r = 0.26) \tag{7}$$

$$\mathrm{BDE}_{\mathrm{P\text{–}F}} = 420.06\ (\pm 0.33) - 3.25\ (\pm 0.44)\ \sigma_p^+\ (r = 0.90) \tag{8}$$

$$\mathrm{BDE}_{\mathrm{P\text{–}Cl}} = 281.85\ (\pm 0.12) - 1.31\ (\pm 0.15)\ \sigma_p^+\ (r = 0.92) \tag{9}$$

From the above equations, it can be seen that the polar induction/resonance substituent effects on the P–H BDEs are small. This fact is not only reflected by the small ρ^+ value (0.28 kJ/mol) or its large error (0.29 kJ/mol), but also indicated by the poor correlation coefficient (r = 0.26). Interestingly, it should be mentioned that the ρ^+ value for P–H BDEs is actual-

Table 4. Results of Dual-Parameter Regression Analyses of the P–X BDEs against the Brown's $\sigma_p{}^+$ and Jiang's σ_{JJ} Substituent Constants[a)]

System	Y–C_6H_4–PH_2	Y–C_6H_4–PHF	Y–C_6H_4–PHCl
U	298.81	421.58	282.28
Error in U	0.33	0.32	0.15
V	0.01	−4.26	−1.66
Error in V	0.33	0.32	0.15
t value of V	0.03	−13.51	−11.12
W	−1.95	−4.46	−1.17
Error in W	0.81	0.77	0.36
t value of W	−2.42	−5.77	−3.20
Correlation coefficient *r*	0.658	0.974	0.963

a) The regression was done using the equation $BDE_{P\text{–}X} = U + V\cdot\sigma_p{}^+ + W\cdot\sigma_{JJ}$

ly smaller than that previously reported for C–H BDEs in toluenes ($\rho^+ = 0.5$ kcal/mol).[4]

By contrast, the polar induction/resonance effects of *para* substituents on the P–F BDEs of 4-YC_6H_4PH-F are much more significant ($\rho^+ = -3.25$ kJ/mol). Compared to the values of ρ^+ for O–H BDEs in phenols ($\rho^+ = 6.9$ kcal/mol)[4] and for N–H BDEs in anilines ($\rho^+ = 3.0$ kcal/mol),[4] the above value is very interesting because it is negative. This means that unlike what happens to the O–H BDEs in phenols or N–H BDEs in anilines, the electron-withdrawing substituents reduce the P–F BDEs whereas the electron-donating ones increase the P–F BDEs. The relatively high correlation coefficient (0.90) and the small error for ρ^+ (0.44 kJ/mol) also indicate that the ρ^+ value is real.

Similarly, the effect of *para* substituents on the P–Cl BDEs of 4-YC_6H_4PH–Cl is also significant ($\rho^+ = -1.31$ kJ/mol). This value is located between that of P–H and of P–F. It is also statistically reliable because of the good correlation coefficient (0.92) and the small error found for ρ^+ (0.15 kJ/mol).

Thus, the fact that the ρ^+ values for H, F, and Cl are significantly different means that the previous hypothesis[4] is unfortunately not justified. In other words, the effects of Y on P–X BDEs in 4-YC_6H_4PH–X (X = H, F, Cl) are not equal for each X, which is different from the substituent effects observed for C–X BDEs in 4-$YC_6H_4CH_2$–X (X = H, F, Cl, Br) and O–X BDEs in 4-YC_6H_4O–X (X = H, CH_3, CH_2Ph).[4]

The above discrepancy can be explained if the stabilization/destabilization effects of the substituents on the neutral compounds before bond cleavage are considered. Thus, we perform Hammett-type regressions on the calculated GEs and REs for the three groups of phosphines, as shown in the following equations:

$$RE = 1.15\,(\pm 0.54) - 3.88\,(\pm 0.72)\,\sigma_p{}^+ \ (r = 0.83) \quad (10)$$

$$GE_{P\text{–}H} = 0.36\,(\pm 0.41) - 3.60\,(\pm 0.55)\,\sigma_p{}^+ \ (r = 0.88) \quad (11)$$

$$GE_{P\text{–}F} = -0.72\,(\pm 0.45) - 7.12\,(\pm 0.59)\,\sigma_p{}^+ \ (r = 0.96) \quad (12)$$

$$GE_{P\text{–}Cl} = 0.73\,(\pm 0.53) - 5.18\,(\pm 0.70)\,\sigma_p{}^+ \ (r = 0.90) \quad (13)$$

From the above equations it can be seen that the RE, which is the same for all the P–X systems, has a modestly strong dependence ($\rho^+ = -3.88$ kJ/mol) on the substituents. In comparison, $GE_{P\text{–}H}$ has a ρ^+ value of −3.60 kJ/mol. As such a value is not very different from that for RE, it is immediately clear that the remote substituent effect on the P–H BDEs should be very small. By contrast, the ρ^+ value for $GE_{P\text{–}F}$ is −7.12 kJ/mol, and −5.18 kJ/mol for $GE_{P\text{–}Cl}$. Since these two values are both significantly more negative than that for RE, it can be expected that the *para* substituent effects on P–F and P–Cl BDEs should be significant. Thus, the different substituent effects exhibited by different P–X systems are caused by the different ground effects, or in other words, the different abilities of the substituents to stabilize/destabilize the neutral molecules before bond homolysis.

The above opinion is in agreement with many former studies,[14] where it was suggested that the ground effects could not be ignored in the consideration of BDEs. Thus, the negligible ground effects observed for the C–X BDEs in 4-$YC_6H_4CH_2$–X (X = H, F, Cl, Br) and O–X BDEs in 4-YC_6H_4O–X (X = H, CH_3, CH_2Ph)[4] may be caused by the fact that in these systems the substituent stabilization/destabilization effects on the neutral compounds are fortuitously too small.

3. Nonpolar π Electron Delocalization Effects on P–X BDEs. From the above discussions it is clear that the polar induction/resonance effects cannot account for all the substituent effects observed for P–X BDEs. Thus, we need to look into the role of the other type of substituent effect, spin delocalization or more generally, nonpolar π electron delocalization effect.[10] For that purpose, we conducted dual-parameter regressions[15] on the BDEs of P–X bonds against $\sigma_p{}^+$ and σ_{JJ} constants, whose results are summarized in Table 4.

From Table 4, it can be seen that the P–H BDEs do not have significant (if any) dependence on the polar induction/resonance effect, which is shown by the large error in the estimation of the coefficient before $\sigma_p{}^+$ as well as the small *t*-value found for the coefficient. In comparison, the dependence of the P–H BDEs on the nonpolar π electron delocalization effect is significant. This is not only indicated by the fact that the error for the coefficient before σ_{JJ} is smaller than the coefficient itself, but also suggested by the relatively large *t*-value found for the coefficient. Nevertheless, it can be noticed that the total regression for P–H BDEs is poor (r = 0.658). This suggests that the nonpolar π electron delocalization substituent constants obtained from the carbon radicals are not adequate for other elements. The detailed reason for this remains to be clar-

Table 5. The Mulliken Charge and Spin Density at the Phosphorous Atom in 4-$YC_6H_4PH^\bullet$ Radicals Calculated from the R(O)MP2/6-311++g(d,2p) Populations (a.u.)

Y	Charge	Spin
H	−0.313637	0.926498
CH_3	−0.318155	0.925513
$N(CH_3)_2$	−0.350577	0.914662
NH_2	−0.335189	0.917119
OCH_3	−0.326822	0.921730
OH	−0.320057	0.921949
SCH_3	−0.317667	0.921215
F	−0.298904	0.926286
Cl	−0.298615	0.926221
CN	−0.267148	0.922655
$COCH_3$	−0.293254	0.922967
$CONH_2$	−0.289023	0.924904
COOH	−0.283958	0.923784
NO_2	−0.256749	0.923186
CF_3	−0.278784	0.927301

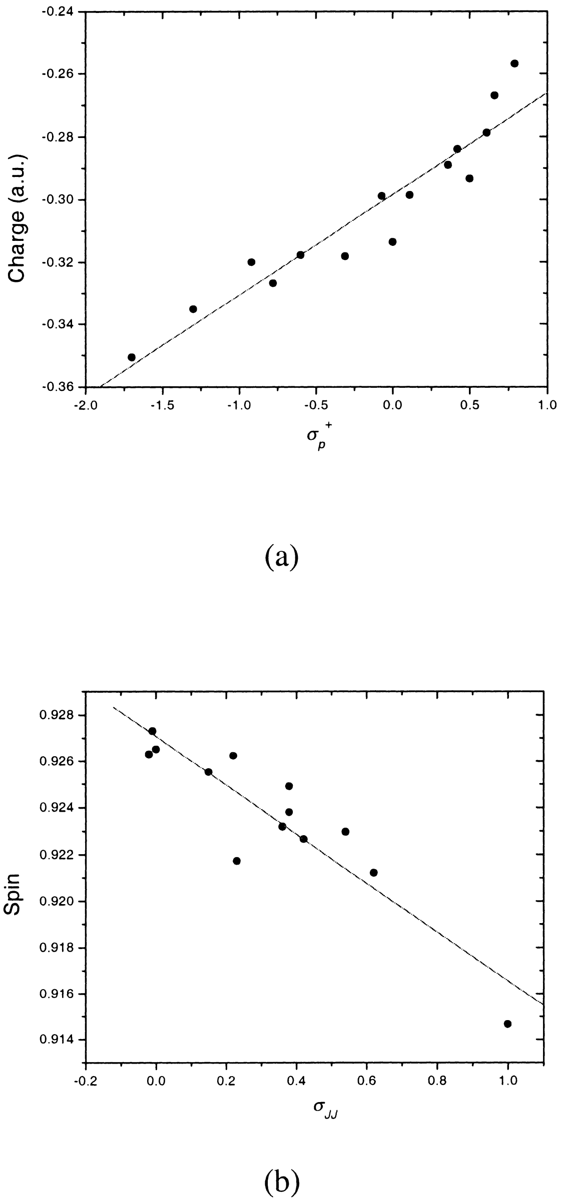


Fig. 2. The correlations of the Mulliken charge and spin density of the phosphine radicals with the Brown's $\sigma_p{}^+$ and Jiang's σ_{JJ} substituent constants.

ified.

In contrast to the P–H BDEs, P–F, and P–Cl BDEs show good correlations with the two types of substituent constants. In particular, they show very strong dependence on the polar induction/resonance effect, which is indicated by the large *t*-values found for the coefficients before $\sigma_p{}^+$. In comparison, the nonpolar π electron delocalization effect plays a less important role for P–F and P–Cl BDEs.

Thus, the above analyses show that the polar induction/resonance effect and the nonpolar π electron delocalization effect both affect the P–X BDEs. However, it is known that the former effect can easily outweigh the latter one.[16] Therefore, for P–F and P–Cl BDEs where the starting material 4-Y–C_6H_4–PHX (X = F or Cl) and product 4-Y–C_6H_4–$PH^\bullet$ are quite different in term of the polarity, the former effect is more important. On the other hand, for P–H BDEs where the starting material 4-Y–C_6H_4–PH_2 and product 4-Y–C_6H_4–$PH^\bullet$ are not expected to be very different in term of the polarity, the role of the second effect becomes clear.

4. Charge and Spin Delocalization. For the radicals, it is found that the Mulliken charge (Table 5) on the phosphorus atom is in good linear correlation with the substituent $\sigma_p{}^+$ constants (r = 0.95) (Fig. 2a). However, correlation of the charge with the substituent σ_{JJ} constants is very poor (r = −0.33). Clearly, the charge distribution mainly relies on the polar resonance effect.

By contrast, the spin on the phosphorus atom does not correlate with the $\sigma_p{}^+$ constants well (r = 0.74). Use of σ_{JJ} constants (Fig. 2b) results in a significantly better correlation (r = 0.91), indicating the importance of the nonpolar π electron delocalization effect on the spin delocalization.

Thus, the charge and spin densities again show the different effects of the polar resonance effect and nonpolar π electron delocalization effect on the P–X BDEs.

5. *meta*-Substitution Effect. In Table 6 are listed the calculated BDEs for *meta*-substituted aromatic phosphines. On the basis of these BDEs, the *meta*-substituent effects on the P–H, P–F, and P–Cl BDEs can be revealed from the following linear regressions against the substituent σ_m constants:

$$\begin{aligned} BDE_{P\text{–}H} &= 299.24\ (\pm 0.24) \\ &\quad + 1.63\ (\pm 0.69)\ \sigma_m\ (r = 0.54) \end{aligned} \tag{14}$$

$$\begin{aligned} BDE_{P\text{–}F} &= 422.81\ (\pm 0.42) \\ &\quad - 5.42\ (\pm 1.23)\ \sigma_m\ (r = -0.77) \end{aligned} \tag{15}$$

$$\begin{aligned} BDE_{P\text{–}H} &= 283.73\ (\pm 0.40) \\ &\quad - 3.42\ (\pm 1.19)\ \sigma_m\ (r = -0.62) \end{aligned} \tag{16}$$

Comparing the above equations with Eqs. 7-9 we can see that correlations of the *meta*-substituent effects on the P–X BDEs with the substituent constants are not as good as they are in the *para*-substitution case. Not only are the correlation co-

Table 6. Bond Dissociation Energies Calculated for the *meta*-Substituted Aromatic Phosphines (kJ/mol)

Y	σ_m	BDE		
		$3\text{-YC}_6\text{H}_4\text{PH}$–**H**	$3\text{-YC}_6\text{H}_4\text{PH}$–**F**	$3\text{-YC}_6\text{H}_4\text{PH}$–**Cl**
H	0.00	299.03	421.94	282.27
CH_3	−0.07	298.54	422.02	283.39
$N(CH_3)_2$	−0.16	298.90	423.95	285.56
NH_2	−0.16	298.74	422.54	283.40
OCH_3	0.12	300.09	424.03	283.52
OH	0.12	298.91	422.42	283.00
SCH_3	0.15	300.50	423.77	285.32
F	0.34	299.02	421.08	281.23
Cl	0.37	299.72	419.89	282.30
CN	0.56	300.07	418.80	281.36
$COCH_3$	0.38	301.14	422.56	284.40
$CONH_2$	0.28	300.64	422.06	283.23
COOH	0.37	299.47	420.68	282.90
NO_2	0.71	299.90	418.85	281.26
CF_3	0.43	299.58	418.89	281.09

efficients lower for the *meta*-substitution case, but also the errors in the estimated slopes of regressions are larger.

Nevertheless, the *meta*-substituent effects are consistent with what we observe for the *para*-substitution case. First, the P–H BDEs have a positive correlation with the substituent σ_m constants. Therefore, an electron-withdrawing group would increase the P–H BDE, whereas an electron-donating one would decrease the P–H BDE.

In comparison, the P–F and P–Cl BDEs have negative correlations with the substituent σ_m constants. The absolute slope of the regression for the P–F BDEs is larger than that for the P–Cl ones. These negative correlations mean that an electron-donating substituent should increase the P–F or P–Cl BDE, while an electron-withdrawing one should reduce it. Explanations for all these effects are presumably the same as those for the *para*-substitution case as discussed above.

Conclusion

We have studied the P–X (X = H, F, and Cl) bond dissociation energies for a number of *para*- and *meta*-substituted aromatic phosphines. The results showed the importance of the radical effect as well the ground effect on the BDEs. For X = H case, because the substituent affected the neutral phosphine to the same extent as it affected the radical, substituent effects on the P–H BDE were small. In comparison, for X = F or Cl case, because the substituent affected the neutral phosphine much more strongly than it affected the radical, substituent effects on the P–F or P–Cl BDEs were significant. Therefore, the substituent effects on BDEs of the Z–X BDEs in compounds of the general formula $4\text{-YC}_6\text{H}_4\text{Z–X}$ varied when X changed, which was in contrast to a recent proposal.

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