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The C−H and α(C−X) Bond Dissociation Enthalpies of Toluene, $C_6H_5{-}CH_2X$ (X = F, Cl), and Their Substituted Derivatives: A DFT Study

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The homolytic C−H bond dissociation enthalpies (BDEs) of toluene and its para- and meta-substituted derivatives have been estimated by using the (RO)B3LYP/6-311++G(2df,2p)//(U)B3LYP/6-311G(d,p) procedure. The performance of two other hybrid functionals of DFT, namely, B3PWP91 and O3LYP, has also been evaluated using the same basis sets and molecules. Our computed results are compared with the available experimental values and are found to be in good agreement. The (RO)B3LYP and (RO)O3LYP procedures are found to produce reliable BDEs for the C−H bonds in toluene and the C−X (X = F, Cl) bond in α-substituted toluene ($C_6H_5{-}CH_2X$) and their substituted derivatives. The substituent effect on the BDE values has been analyzed in terms of the ground-state effect and the radical effect. The effect of polarization of the C−H bond on the substituent effect is also analyzed. The BDE(C−H) and BDE(C−X) values for α-substituted (X = F and Cl) toluenes with a set of para substituents are presented for the first time.

1. Introduction

The bond dissociation enthalpy (BDE) is known to be a good indicator of chemical reactivity and also an important thermodynamic quantity to describe the energetics of chemical reaction. Hence, there is a growing interest in the evaluation of BDEs for various kinds of bonds. Computational methods, especially the density functional theory (DFT)-based methods, have been found to be an efficient and useful tool for estimating BDE values and can be used as an alternative to carrying out expensive and tedious experiments for determining BDE values.[1−7] Very recently, BDEs were computed for a variety of bonds in compounds such as $Y{-}C_6H_4{-}X$, where X = O−H,[7,8] S−H,[9−11] N−H,[12] Si−H,[13] P−H,[14] etc. We observed from our earlier studies[8,10,14] that the (RO)B3LYP/6-311++G(2df,2p)//(U)B3LYP/6-311G(d,p) DFT procedure could be used as an accurate model for determining the bond strength of various types of bonds in organic molecules. In fact, DiLabio and coworkers first pointed out the efficacy of this (RO)B3LYP procedure in connection with their effort to develop DFT-based model chemistries to obtain reliable BDE values even in large molecules.[5,15,16] Subsequent studies in our group established and enlarged the scope of this model further.[10,14] The suitability of this procedure for the estimation of BDEs for various types of bonds has been evaluated further here. In this work, our main focus is to study the BDE values for the C−H bonds in the methyl group of toluene and its α- and remotely substituted derivatives.

Toluene has an important role in organic chemistry. Knowledge of the BDE values of the C−H bonds in toluene and its substituted derivatives can be useful for understanding the chemistry of toluene-like compounds. Toluene is also the most abundant aromatic hydrocarbon, and in the atmosphere the toluene−OH reaction can go through by H-atom abstraction from the methyl group. The rate of this abstraction reaction should be directly related with the strength of the C−H bond in the methyl group. Moreover, we take this opportunity to evaluate the para- and meta-substituent effect on the C−H bond strength of toluene and compare it with the same on the O−H, N−H, S−H, and P−H bond strengths of phenol, aniline, thiophenol, and phenylphosphine, respectively. It is known that para substituents have different effects on the BDEs of toluenes and phenols.[17] In fact, the substituent effect in carbon-centered radicals is quite different than what is observed on heteroatmic radicals.[17,18] Generally, electron-donating groups (EDGs) stabilize the radical more and reduce the BDE value, whereas electron-withdrawing groups (EWGs) stabilize the ground state due to dipolar interaction and have an opposite effect on the BDE. On the other hand, carbon-centered radicals ($Y{-}C_6H_4{-}CH_2{\bullet}$) can be stabilized by both EDGs and EWGs.[19] Interestingly, the para-substituent effect of EWG on α-substituted toluene follows a pattern observed for phenols, thiophenols, and anilines.[20,21] It is thus interesting to analyze the effect of different types of substituents on the BDE value for the C−H bond of toluene, especially for meta-substituted compounds, because it is not known whether the meta-substituent effect on toluene follows the same pattern as that of phenol and aniline. We compute the BDE values by using three different functionals, B3LYP, B3PW91, and O3LYP. Among these, the former one is already known to produce reliable BDE values. It will be interesting to evaluate the performance of the latter two, especially O3LYP. This functional has been proposed recently by Handy and Cohen.[22] Its so-called “left−right” correlation strategy is supposed to rectify the incorrect dissociation limits of the Hartree−Fock wave function and can thus describe bond dissociation better. In fact, before zeroing in to the above-

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mentioned three functionals for the present study, we have evaluated the C−X bond strength for a small set of CH_3X (X = H, F, Cl) molecules by using these three combinations of exchange and correlation functionals. We have observed from these results that B3LYP, B3PW91, and O3LYP can produce BDE values as good as those obtained from the expensive ab initio methods such as CCSD(T)/aug-cc-pVTZ, G2, etc. and produce BDE values within the limit of chemical accuracy.

To the best of our knowledge, there have been very few theoretical works on the BDEs of the benzylic C−H of toluene and α-substituted toluene. Wen et al.[21] used the B3LYP functional with a small basis set of 6-31G(d) to investigate the substituent effects on the BDEs of the C−H bond of toluene. They emphasize the importance of the radical effect (RE) on BDE and highlighted the role of the apparent electronegativity of the radical center in controlling the directions of radical substituent effects. Their B3LYP-calculated BDEs were found to be 4−5 kcal/mol lower than the experimental values. Later, Bean analyzed the substituent effect on the C−H bond strength of toluene in detail by using the semiempirical AM1 method.[23] He pointed out the role of the captodative and anticaptodative effects depending upon the electronegativity of the radical center. The AM1-calculated BDE values were lower by almost 55 kJ/mol than the corresponding experimental values, but the relative trend was reproduced at this level.[23] Our aim in this context is to standardize the DFT procedure and calculate BDE values as good as any experimental data. The calculated BDE values will then be useful for thermochemical analysis when experimental results are not available.

The energy required for homolytic bond cleavage of the benzylic C−H bond in toluene and its substituted derivatives corresponds to the enthalpy change for the reaction:

$$\mathrm{Y{-}C_6H_5{-}CH_2X \rightarrow Y{-}C_6H_4{-}CHX^{\bullet} + H^{\bullet}} \qquad (1)$$

In the present work, BDE values are evaluated directly from the enthalpy change of this reaction.

2. Computational Methods

All calculations were performed by using the GAUSSIAN-03 suite of programs.[24] A cluster of PCs with pentium-4 processors was used for the computations. Geometries of toluene, α-substituted toluene, and their para- and meta-substituted derivatives ($Y-C_6H_4-CH_2X$, Y = H, F, Cl, CH_3, OCH_3, NH_2, CN, CF_3, and NO_2; X = H, F, Cl) were optimized by using three methods of DFT (B3LYP, B3PW91, and O3LYP) with the 6-311G(d,p) basis set, and the harmonic vibrational frequencies were computed at these optimized geometries. We used the corresponding unrestricted method for the geometry optimization of radicals ($Y-C_6H_4-CHX^\bullet$). The spin contamination is generally low for DFT methods, and in our case it never exceeds 0.785. The enthalpy values were evaluated from the single-point energy obtained from each DFT method with an extended basis set of 6-311++G(2df,2p) and taking thermal corrections to enthalpy from the respective 6-311G(d,p) results. The restricted open-shell formalism (ROB3LYP, ROB3PW91, and ROO3LYP) with the large basis set was used for estimating enthalpy values of the open-shell radicals. It should be pointed out here that geometry optimizations and frequency calculations with the larger 6-311++G(2df,2p) basis set increase the computational cost by almost 6 times but do not have any significant effect (~0.1 kJ/mol) on our calculated BDE values at the (RO)B3LYP/6-311++G(2df,2p)//(U)B3LYP/6-311G(d,p) level. This justifies our strategy of using the smaller 6-311G(d,p) basis set for geometry optimizations and frequency calculations. The DFT procedures adopted here are henceforth simply referred as (RO)B3LYP, (RO)B3PW91, and (RO)O3LYP. The homolytic BDE(C−H) value at 298.15 K for the molecule $Y-C_6H_4-CH_2X$ was calculated from the expression:

$$\mathrm{BDE(C{-}H)} = H(\mathrm{Y{-}C_6H_4{-}CHX^{\bullet}}) + H(\mathrm{H^{\bullet}}) - H(\mathrm{Y{-}C_6H_4{-}CH_2X}) \qquad (2)$$

where H's are the enthalpies of different species at 298.15 K. The enthalpies were estimated from usual expression: $H(298.15\ \mathrm{K}) = E_0 + \mathrm{ZPE} + H_{\mathrm{trans}} + H_{\mathrm{rot}} + H_{\mathrm{vib}} + RT$. The H_{trans}, H_{rot}, and H_{vib} are the translational, rotational, and vibrational contributions to enthalpy, respectively. The ZPE and H_{vib} were estimated from the unscaled vibrational frequencies, because the scaling factor for the B3LYP/6-311G(d,p) method is close to unity (0.9877 for ZPE and 0.9679 for frequencies)[25] and also it does not change the BDE value significantly (~ 1 kJ/mol). Low-frequency vibrational modes are generally better represented by hindered rotational motion, and this treatment may be very important for kinetic studies. However, we treated these low-frequency vibrations also as vibrational modes to keep the procedure simple, and also it was unlikely to change the BDE values significantly. The enthalpy value for the H-atom was estimated by taking its exact energy of −0.5 hartree. The same approach was adopted before by DiLabio et al.[5] and also by us[8,10] and was found to give better agreement with experimental results.

3. Results and Discussion

As we mentioned before, we first calculated the BDEs of C−H, C−F, and C−Cl bonds in these three simple systems CH_4, CH_3F, and CH_3Cl with the B3LYP, B3PW91, and O3LYP functionals of DFT with an extended 6-311++G(2df,2p) basis set. The geometries were optimized with the 6-311G(d,p) basis set for each functional, and then, the BDE value was calculated following the procedure mentioned above. Our aim was to find out whether these functionals could produce consistent and reliable BDE values for different types of bonds. We observed that (RO)B3LYP, (RO)B3PW91, and (RO)O3LYP were capable of producing BDE values within an accuracy limit of ±8 kJ/mol. This agrees with the conclusion made by Chandra and coworkers[8,10] that (RO)B3LYP with the 6-311++(2df,2p) basis set reduces the error under 6 kJ/mol and also to the others.[26]

3.A. BDE(C−H) Values of Substituted Toluenes. We have then used the above-mentioned three DFT methods for calculating the BDE(C−H) values of toluene and its substituted derivatives. This gives an opportunity for further evaluation of the B3PW91 and O3LYP methods. It may be worthwhile to mention here that the ring C−H bonds are much stronger than the C−H bond in the methyl group of toluene and may not be important from a reactivity point of view. Our (RO)B3LYP-calculated BDE(C−H) value for the ring C−H bond amounts to 473.5 kJ/mol, which is almost 100 kJ/mol higher than the BDE(C−H) value of the methyl C−H bond in toluene. Our calculated BDE(C−H) value for the ring carbon in toluene is found to be very close to the experimental BDE(C−H) value for benzene (472.2 ± 2.2 kJ/mol).[27] The most recent experimental BDE value for the benzylic C−H bond is reported to be 375.0 ± 8.4 kJ/mol.[27,28] This value is very close to our B3LYP- and O3LYP-calculated BDE values. The calculated BDE(C−H) values for para-substituted toluenes are given in Table 1 along with the available experimental results. In general, the (RO)B3LYP and (RO)O3LYP BDE(C−H) values are in

TABLE 1: Calculated BDE(C−H) Values for para-Substituted Toluene ($Y-C_6H_4-CH_3$) Using the (RO)B3LYP, (RO)B3PW91, and (RO)O3LYP Methods with the 6-311++G(2df,2p) Basis Set[a]

	BDE(C−H) in kJ/mol				ΔBDE[b]	
Y	B3LYP	B3PW91	O3LYP	exptl[c]	B3LYP	exptl
H	375.87	380.03	372.97	370.3[d](375.0)[e]	0.00	0.00
F	375.80	379.86	372.63	375.1	−0.07	4.8 (0.1)
Cl	374.96	379.06	371.68	371.3	−0.91	1.0 (−3.7)
CH_3	374.26	378.45	371.23	369.7	−1.61	−0.6 (−5.3)
OCH_3	372.18	376.44	368.81	362.5	−3.69	−7.8 (−12.5)
NH_2	368.59	372.94	365.19		−7.28	
CN	374.10	376.18	370.70	368.0	−1.77	−2.3 (−7.0)
CF_3	376.93	381.14	373.85		1.06	
NO_2	373.62	378.17	370.27	373.4	−2.25	3.1 (−1.6)

[a] The 6-311G(d,p) basis set is used for geometry optimization and frequency calculations (see text for details). Available experimental results are also included. [b] ΔBDE = BDE(*para*-$Y-C_6H_4CH_2-H$) − BDE($C_6H_5CH_2-H$). [c] Most recommended experimental value, taken from ref 27. [d] Experimental value 370.3 ± 6.3 kJ/mol, ref 34. [e] Experimental value 375.0 ± 8.4 kJ/mol, ref 28.

TABLE 2: Calculated BDE(C−H) Values for meta-Substituted Toluene ($Y-C_6H_4-CH_3$) Using the (RO)B3LYP, (RO)B3PW91, and (RO)O3LYP Methods with the 6-311++G(2df,2p) Basis Set[a]

	BDE(C−H) in kJ/mol				ΔBDE[b]	
Y	B3LYP	B3PW91	O3LYP	exptl[c]	B3LYP	exptl
H	375.87	380.03	372.97	370.3 (375.0)	0.00	0.0
F	376.92	381.11	373.99	373.6	1.05	3.3(−1.4)
Cl	377.15	381.32	374.28	373.0	1.28	2.7(−2.0)
CH_3	375.21	379.43	372.27	371.4	−0.66	1.1(−3.6)
OCH_3	377.53	381.63	374.66	378.8	1.66	8.5(3.5)
NH_2	376.15	380.29	373.11		0.28	
CN	379.07	383.12	376.2	371.0	3.2	0.7(−4.0)
CF_3	377.71	381.03	374.77		1.84	
NO_2	379.18	383.20	376.28	375.0	3.31	4.7(0.0)

[a] The 6-311G(d,p) basis set is used for geometry optimization and frequency calculations (see text for details). Available experimental results are also included. [b] ΔBDE = BDE(*meta*-$Y-C_6H_4CH_2-H$) − BDE($C_6H_5CH_2-H$). [c] Most recommended experimental value, taken from ref 27.

very good agreement to the corresponding experimental values. The (RO)B3PW91-calculated BDE values are found to be 4−5 kJ/mol higher than the corresponding B3LYP results. In most of the cases, these BDE values also differ by more than 8 kJ/mol from the corresponding experimental values. Thus the B3PW91 results are not within the limit of chemical accuracy. Our (RO)B3LYP-calculated BDE(C−H) value (375.9 kJ/mol) for toluene is found to be the same as the BDE(N−H) value of aniline[14] estimated at the same level of theory. Meanwhile, this value is much lower than the BDE(C−H) value of CH_4 (441.7 kJ/mol), which must be due to the stabilizing effect of the phenyl group on the benzyl radical. The calculated BDE(C−H) values for meta-substituted toluenes are presented in Table 2. Once again, the B3PW91 results for the BDE(C−H) values are found to be higher than those obtained from the B3LYP and O3LYP methods. The results obtained from the latter two methods are found to be quite close to the corresponding experimental values. The (RO)B3LYP- and (RO)O3LYP-calculated BDE(C−H) values can, therefore, be safely used where experimental results are not available (such as NH_2- and CH_3-substituted toluenes).

It is clear from the ΔBDE values in Table 1 that the effect of para substituents on the BDE(C−H) value of toluene is not very significant, except for the strong EDGs, like NH_2. Our calculated ΔBDE values for para-substituted toluenes follow almost the same pattern as that observed from experiment. In the case of NO_2, our calculated ΔBDE value is −2.25 kJ/mol, whereas two experimental results for toluene suggest two possible values of 3.1 and −1.6 kJ/mol. Due to the large uncertainty (~ ±8 kJ/mol)[28] in the experimental results, it is difficult to confirm any particular ΔBDE value. However, a negative ΔBDE value for $-NO_2$ is expected from the known substituent effect (discussed later) of an EWG on C−H bond strength and also from the fact that all the three DFT methods consistently show weakening of the C−H bond upon NO_2 substitution. The BDE(C−H) values obtained from the (U)B3LYP method for toluene, *para*-amino toluene, and *para*-nitro toluene are 367.72, 360.83, and 365.5 kJ/mol, respectively. Although these BDE values are almost 8 kJ/mol lower from the corresponding (RO)B3LYP results, the (U)B3LYP method produced similar ΔBDE values as those obtained from the (RO)B3LYP calculations. For example, the ΔBDE values amount to −6.9 and −2.2 kJ/mol for para $-NH_2$- and $-NO_2$-substituted toluenes, respectively, at the (U)B3LYP level. The substituent effect is known to be much stronger on the BDE(O−H) value of phenol and the BDE(N−H) value of aniline.[7,17] Most interestingly, both EDGs and EWGs tend to reduce the C−H bond strength from that observed for the parent toluene molecule. The effect of EWGs on the BDE(C−H) of toluene is, therefore, opposite to what is observed for the BDE(O−H) of phenol,[7,8] the BDE(N−H) of aniline,[17] and the BDE(P−H) of phenylphosphine.[14] It is apparent that para substituents on toluenes have different effects on the ground and radical state stabilities than that observed for phenols or anilines. In fact, it was demonstrated before that in the case of phenol and aniline, the radical effect (RE) is more important for EDGs, whereas the ground-state effect (GE) plays a crucial role for EWGs.[8,17,29] As a result EDGs reduce the X−H bond strength, whereas EWGs enhance it. A similar trend (known as the *O*-pattern[30]) can be observed for all heteroatomic radical systems (e.g., O•, S•, N•, P•). In contrast, the RE is believed to be the most important factor for para-substituted toluene systems, and both EDGs and EWGs tend to reduce the C−H bond strength (known as the *S*-pattern[29]).[20,21,31] One reason behind it must be the low polarity of the C−H bond; as a result dipolar interaction between this bond and the para substituent is very small and the GE becomes negligible. To analyze it further, we have calculated the enthalpy changes for the ground state and radical while going from the parent toluene molecule ($C_6H_5-CH_3$) and radical ($C_6H_5-CH_2$•) to the corresponding substituted molecule ($Y-C_6H_4-CH_3$) and radical ($Y-C_6H_5-CH_2$•), respectively. These values are given in Table 3. The relative magnitude of these two quantities should give a clear indication of the factor that controls the substituent effect. As can be seen from Table 3, in almost all cases (except $-CF_3$) the para-substituent effect is greater for the radical than in the ground state, especially for the strong electron-donating groups, like $-NH_2$. *As the RE is pronounced for both EDGs and EWGs at the para position,* BDE(C−H) values become lower from the parent toluene

TABLE 3: Enthalpy Differences (in au) between Substituted Toluene and Toluene and Also between Substituted and Parent Radicals Estimated at the (RO)B3LYP/6-311++G(2df,2p)//6-311G(d,p) Level

	$H(\mathrm{YC_6H_4CH_3}) - H(\mathrm{C_6H_5CH_3})$		$H(\mathrm{YC_6H_4CH_2}\cdot) - H(\mathrm{C_6H_5CH_2}\cdot)$	
substituent	meta	para	meta	para
H	0.0000000	0.0000000	0.0000000	0.0000000
F	−99.2814664	−99.2807046	−99.2810648	−99.2808314
Cl	−459.6357235	−459.6354468	−459.6352368	−459.6357931
CH_3	−39.3008632	−39.3007219	−39.301114	−39.3013337
OCH_3	−114.5294252	−114.5285480	−114.5287944	−114.5299540
NH_2	−55.3620188	−55.3610061	−55.3619113	−55.3637778
CN	−92.2719177	−92.2723725	−92.2707003	−92.2730468
CF_3	−337.1588231	−337.1591671	−337.1581235	−337.1587616
NO_2	−204.5715535	−204.5722258	−204.5702909	−204.5730814

molecule upon substitution of both types. A further signature of radical stabilization can be obtained from the $C-CH_2\cdot$ bond length between the methyl carbon and ring carbon in the radical. This bond length is seen to reduce considerably and gain more double bond character for both EDG and EWG. For example, this bond length amounts to 1.3998, 1.3976, and 1.3979 Å for $-NH_2$, $-CN$, and $-NO_2$ para substituents, whereas it amounts to 1.4039 Å in the $C_6H_5-CH_2\cdot$ radical.

Interestingly, the meta-substituent effect on the BDE(C−H) of toluene follows almost a similar pattern as that observed for phenol and aniline. Here EDGs have a mild increasing effect on the C−H bond strength, whereas, contrary to the para position, EWGs enhance the C−H bond strength in comparison to the parent molecule. Experimental ΔBDE values for meta substituents show two different trends depending upon the two different experimental BDE values (370.3 and 375.0 kJ/mol) for toluene. Our calculated ΔBDE values do not follow strictly either of these trends. But both calculated and experimental results suggest a weak meta-substituent effect on BDE(C−H) values. Once again, we look at the enthalpy changes given in Table 3 for the ground and radical state upon substitution. It is clear that for meta substituents, the ground-state enthalpy changes more than that for the radical. As a result the BDE(C−H) value increases upon substitution at the meta position of toluene. The GE, therefore, determines the substituent effect on BDE(C−H) in the case of meta substituents, whereas RE is the key factor for para substituents. This contrasting behavior becomes apparent when we look at the correlation between BDE(C−H) values and Hammett's parameters for para- and meta-substituted toluenes. Because of the *S*-pattern, the BDE(C−H) values for para-substituted toluenes do not exhibit any linear correlation with the polar Brown σ_p^+ constants.[32] On the other hand, there exists a reasonably good correlation (see Figure 1) between the BDE(C−H) values and σ_m values[32] for meta-substituted toluenes.

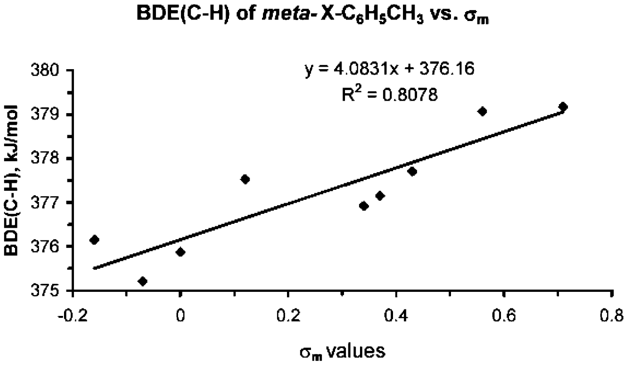

Figure 1. Plot of BDE(C−H) values for meta-substituted toluene against Hammett's parameters (σ_m).

TABLE 4: Enthalpy Differences (in kJ/mol) between para- and meta-Substituted Toluenes ($Y-C_6H_4-CH_3$) and Radicals ($Y-C_6H_4-CH_2\cdot$) Calculated at the (RO)B3LYP/6-311++G(2df,2p)//6-311G(d,p) Level[a]

	ΔH_{p-m}(calcd)		ΔBDE_{p-m}	
Y	toluene	radical	calcd	exptl[b]
H	0.00	0.00	0.00	0.00
F	2.00	0.88	−1.12	1.50
Cl	0.73	−1.46	−2.19	−1.70
CH_3	0.37	−0.58	−0.95	−1.70
OCH_3	2.30	−3.04	−5.35	−16.3
NH_2	2.66	−4.90	−7.56	
CN	−1.19	−6.16	−4.97	−3.00
CF_3	−0.9	−1.68	−0.78	
NO_2	−1.77	−7.33	−5.56	−1.6

[a] The differences in BDE(C−H) values are also given. [b] Most recommended experimental value, taken from ref 27.

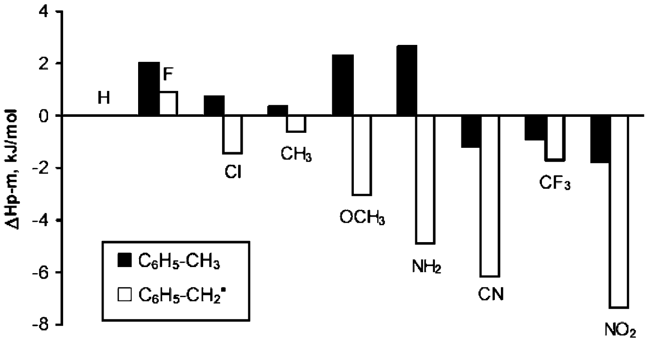

Figure 2. Enthalpy differences (ΔH_{p-m}) between the para- and meta-substituted toluenes ($Y-C_6H_4CH_3$) and radicals ($Y-C_6H_4CH_2\cdot$).

Due to the contrasting role of meta and para substituents on the stability of the ground-state molecule and radical, the BDE(C−H) value of toluene differs with the change in substituent position. The effect is more pronounced for strong EDGs (e.g., OCH_3, NH_2) and EWGs (e.g., CN, NO_2). For example, the difference of BDE(C−H) values between para- and meta-substituted toluene amounts to 7.6 and 5.6 kJ/mol for $-NH_2$ and NO_2 group, respectively. The change of BDE(C−H) values (ΔBDE_{p-m}), ground−state, and radical enthalpies (ΔH_{p-m}) of toluene upon changing substitution position are given in Table 4 and also shown graphically in Figure 2. The EDGs impart more stability on toluene when they are at the meta position. On the contrary, for EWGs, the stability of para-substituted toluene is more than that of the corresponding meta counterpart. Meanwhile, it can be seen from Table 4 (also Figure 2) that the para-substituted radical ($Y-C_6H_4-CH_2\cdot$) is always more stable in comparison to its meta counterpart for both EDGs and EWGs. Since EDGs at the meta position stabilize the ground state more than the corresponding para product and the reverse is true for the radical, the BDE(C−H) value increases from the para-substituted product and even becomes greater than the parent molecule. It is also clear from the magnitude of ΔH_{p-m} values

TABLE 5: Calculated BDE(C−H) Values (in kJ/mol) of α-Substituted Toluene and Its para-Substituted Derivatives ($Y-C_6H_4-CH_2X$, X = F, Cl) Using the (RO)B3LYP/6-311++G(2df,2p)//6-311G(d,p) Method

	X = F		X = Cl	
Y	calcd	ΔBDE	calcd	ΔBDE
H	362.55	0	363.00	0.00
F	363.39	0.84	363.72	0.72
Cl	361.49	−1.06	361.73	−1.27
CH_3	360.80	−0.75	362.70	−0.30
OCH_3	364.95	2.40	362.40	−0.60
NH_2	364.60	2.05	361.36	−1.64
CN	358.12	−4.43	357.56	−5.44
CF_3	361.55	−0.90	361.00	−2.00
NO_2	356.44	−6.11	356.02	−6.98

for substituted toluene and radical that the stability of the radical is a more important factor and controls the change in BDE(C−H) values with the change in substituent position. This is especially true for EWGs, where the para-substituted product is more stable than the meta counterpart for the molecule and radical. Thus, the RE primarily determines the effect of change in substituent position on the BDE(C−H) of toluene, whereas the GE only changes the extent of such an effect.

3.B. BDE(C−H) of α-Substituted ($Y-C_6H_4-CH_2X$) Toluene. We have estimated the BDE(C−H) values for α-substituted toluene ($Y-C_6H_4-CH_2X$, X = F, Cl) with the same set of para substituents as that used for toluene. This can help us to understand how α-substitution affects the BDE(C−H) value. As we already observed from this study and previous studies that the (RO)B3LYP method gives consistent and accurate results for BDEs of several types of bonds, this procedure is only used for the present set of systems. Our calculated values are given in Table 5. No experimental results are available for comparison with our calculated values. However, observing the accuracy of the (RO)B3LYP procedure, these BDE(C−H) values should be close to the exact values and can be taken for any thermochemical analysis.

The results in Table 5 show that F- or Cl-substution at the α-position of toluene weakens the C−H bond considerably in comparison to the respective toluene molecule. The results are most significant when an EWG is present at the para position of toluene. Owing to its electronegative nature, F (and Cl also) pulls electrons toward itself, and as a result, the C−H bond becomes weaker. This change in BDE values for α-substitution can be compared to the same observed for halogen substitution in methane. The calculated BDE(C−H) values for CH_4, CH_3F, and CH_3Cl amount to 441.7, 423.2, and 417 kJ/mol (experimental values are 439.3, 423.8, and 419 kJ/mol, respectively).[27] Thus F-substitution reduces the BDE(C−H) value by nearly 18 kJ/mol, and the effect is slightly more for Cl-substitution. In toluene, F-substitution at the α-position reduces the bond strength by 13 kJ/mol and almost the same value is obtained for Cl-substitution. Thus, the presence of the phenyl group reduces the effect of halogen substitution at the carbon-center. Now, the remote substituent effect on α-substituted toluene shows a similar pattern as that observed for toluene and discussed before. The EWGs at the para position tend to reduce the C−H bond strength from the parent molecule for both α-F- and α-Cl-substituted toluenes. Cheng et al.[20] observed that the presence of an EWG at the α-position of toluene ($Y-C_6H_4-CH_2X$, X = EWG) change the pattern (from *S*- to *O*-pattern) of the para-substituent effect and most of the strong para-EWGs strengthen the C−H bond rather than weakening it. In the case of F- and Cl-substitution at the α-position, however, we cannot notice any change in the pattern of the substituent effect on BDE(C−H) and it follows the same trend (*S*-pattern) as that observed for toluene. Much stronger EWG at the α-position may be required to induce any change in the substituent effect pattern. In this context, it will be interesting to study further at what level of polarized toluene this switch over from one pattern to the other begins. The electronegativity of X may be a good index to judge the polarized nature of toluene.

TABLE 6: BDE(C−X) Values (in kJ/mol) for para-Substituted $Y-C_6H_4-CH_2X$ (X = F, Cl) Using (RO)B3LYP/6-311++G(2df,2p)//6-311G(d,p) Model Chemistry

	X = F		X = Cl	
Y	calcd	exptl[a]	calcd	exptl[a]
H	410.43	408.4	285.87	299.6
F	409.86		285.68	289.0
Cl	408.33		283.52	
CH_3	409.46		285.87	292.5
OCH_3	411.79		285.66	
NH_2	410.86		284.72	
CN	405.39		278.41	280.3
CF_3	409.11		282.52	
NO_2	404.29		277.66	

[a] Most recommended experimental value, taken from ref 27.

3.C. BDE(C−X) Values of α-Substituted ($Y-C_6H_4-CH_2X$, X = F, Cl) Toluene. We have also extended our work for calculating the C−F and C−Cl bond strength and studying the remote para-substituent effect on it in $Y-C_6H_4-CH_2F$ and $Y-C_6H_4-CH_2Cl$ for a set of EDGs and EWGs as Y. The calculations were performed by using the (RO)B3LYP method only. The calculated results are presented in Table 6. Very few experimental results are available for these systems. Our calculated BDE(C−F) value of 410.4 kJ/mol for $C_6H_5-CH_2F$ agrees very well with the experimental value of 408.4 kJ/mol.[26] Similarly, the calculated BDE(C−Cl) values for *para*-Me-$C_6H_4-CH_2Cl$ and *para*-NC−$C_6H_4-CH_2Cl$ are very close to the corresponding experimental values. Only for $C_6H_5-CH_2Cl$, our calculated BDE(C−Cl) value is found to be somewhat lower than the experimental value. Since the (RO)B3LYP method provides consistent and accurate BDE values for almost all types of bonds, we could not find any reason to suspect our calculated value. In fact, high experimental uncertainties on BDE values are well-known in many cases.[33] In any case, our results in general show that the (RO)B3LYP method can also be used for determining the BDE(C−X) (X = F, Cl) values within chemical accuracy. The remote para-EDGs have hardly any effect on the C−F and C−Cl bond strengths, whereas para-EWGs reduce the C−F and C−Cl bond strength from that observed for the parent molecule ($C_6H_5-CH_2F/Cl$). *Thus for para-EWGs, the substituent effect on C−H, C−F, and C−Cl bonds follows the same pattern and in all the cases the bond becomes weaker upon substitution.*

4. Conclusions

The accurate BDE(C−H) values have been calculated for the C−H bond in the methyl group of toluene and its meta- and para-substituted derivatives. The (RO)B3LYP and (RO)O3LYP results are seen to be in close agreement with the experimental values. The (RO)B3PW91-calculated BDE(C−H) values for toluenes are found to be slightly higher than the experimental results. It might be better to use the unrestricted formalism (UHF) for the radical rather than the restricted one (ROHF) if one prefers to use the B3PW91 method. But certainly, (RO)B3LYP and (RO)O3LYP can be the methods of choice for estimating BDE(C−H) values. The para-substituent effect, especially for EWGs, on the BDE(C−H) of toluene is found to be different from that observed for the O−H bond in phenol and the N−H bond in aniline. The RE is found to be more important than the GE for both EDGs and EWGs at the para position of toluene, and it causes the reversal in trend between toluene and phenol. Interestingly, the meta-substituent effect on BDE(C−H) is found to follow almost the same trend as that observed for phenol[8] and phenylphosphine.[14] Here, the GE dominates over the RE for EWGs, and as a result, the BDE(C−H) value increases from that of the parent molecule. The BDE(C−H) values for meta-substituted toluene correlate reasonably well with the Hammett's parameters. We have also found that the effect of change in substitution position on the BDE(C−H) value mainly depends on the RE factor. Accurate BDE(C−H), BDE(C−F), and BDE(C−Cl) values for the α-substituted (with F and Cl) toluene and its remote para-substituted derivatives have also been given for the first time. The substituent effect on the strength of these bonds is seen to follow the same trend as that observed for toluene.

Supporting Information Available: B3LYP/6-311G(d,p)-optimized Cartesian coordinates for substituted toluenes ($Y-C_6H_4-CH_3$) and radicals ($Y-C_6H_4-CH_2^\bullet$). This material is available free of charge via the Internet at http://pubs.acs.org.

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