Estimation of C−C Bond Dissociation Enthalpies of Large Aromatic Hydrocarbon Compounds Using DFT Methods

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Four density-functional methods (B3LYP, B3PW91, MPW1PW91, and B3P86) are employed to compute the C−C homolytic bond dissociation enthalpies (BDE) of a set of aromatic hydrocarbons related to coal structures with aliphatic linkages. In comparison with the available experimental data, the B3P86 method can provide reasonably reliable BDE values for these model compounds. The BDE values for large aromatic hydrocarbon systems of interest are computed, and the substituent effects are discussed.

Introduction

With increasing demands of clean coal processes, environment protection and effective usage of natural resources, conventional technologies in combustion, pyrolysis, gasification and liquefaction processes are facing great challenges. The organic portion of coal predominantly consists of polycyclic aromatics, as well as other hydrocarbons and heterocyclic clusters, which join together into a cross-linked three-dimensional network by either short aliphatic or ether linkages. All these clean coal processes are directly associated with homolytic bond dissociations of the organic structures of coal into smaller molecules.[1] Therefore, the knowledge of thermochemical mechanisms, for which the thermal behaviors of bond dissociation steps are particularly important, is clearly desired as a basis for manipulating process conditions. However, the mechanistic understanding of these thermal reactions at the molecular level is very difficult due to the complexity of coal structures.

Apart from the mechanistic aspect, thermo-chemical studies of coal model compounds have been proven to be a useful research tool, and the relative conversion rates of the model structures are predictable from the bond dissociation energies.[2] Therefore, a systematic understanding on the stability of a relevant bond within the coal structures is of practical and theoretical importance.[1,3,4] Because very critical and varied conditions had to be used so as to experimentally obtained the stability data of model compounds related to coal, it is very difficult to compare all the available experimental data in a consistent way. However, modern computational methods might provide an alternative tool for studying coal chemistry more systematically.

As part of our current investigations on the thermal reactivity of coal structures, we are interested in the energetic aspects of the bond dissociation reactions in coal conversion processes. The bond dissociation enthalpies for a limited number of model compounds used in coal chemistry have been determined

experimentally,[5−9] and these data could fortunately serve as reference for theoretical computations.[10−23] However, theoretical calculations of bond dissociation enthalpies are very demanded for more complicated model compounds (more representative to coal structures), for which experimental data are not available. Theoretical methods such as high-level G2[11,14,15] and CCSD,[14,16,17] which can give accurate results, are very expensive to apply and only limited to very small systems. For relatively large systems, the IMOMO[14,18−21] scheme has been proven to reproduce experimental values. However, the IMOMO (G2MSr: ROMP2/6-31G(d)) method for hydrocarbons of as many as fifteen carbon atoms seems also very expensive to apply for reproducing the experimental results in a reasonable way. Therefore, it is desired to have other alternative ways to combine low computational cost and high accuracy in thermochemical computations for larger coal systems because previous studies in similar topics were incomplete in selecting DFT functionals.[10−23]

Here, we present estimations of the dissociation enthalpies (BDE) of C−C bonds bridging aromatic fragments by using different density functional (DFT) approaches,[24] which are found to be effective and accurate for energetic calculations, including ionization potentials and BDE's.[25] Chart 1 shows the compounds, which were chosen to model the aliphatic linkages in coal structures. Our study shows that the B3P86 method reproduces the experimental BDE's of large systems very well in an inexpensive way.
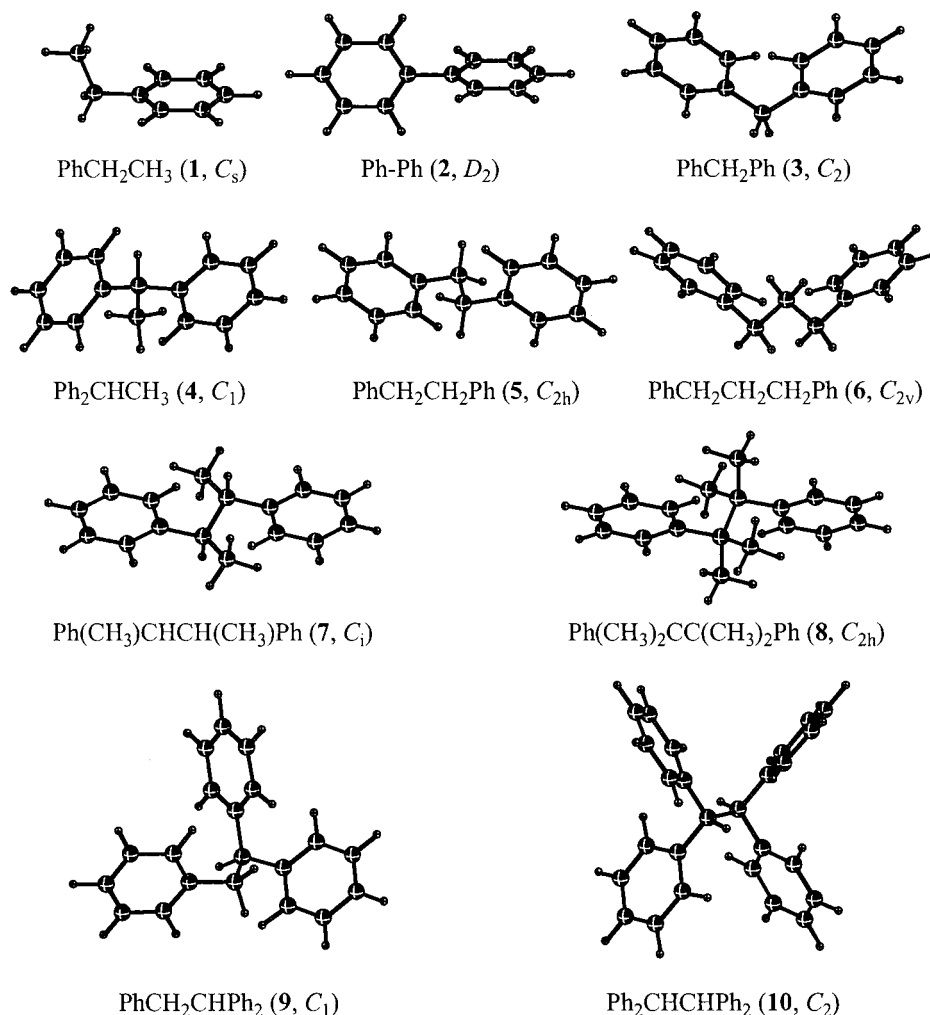
Computational Details

All the calculations were carried out using the Gaussian 98[26] program. Geometries in Chart 1 and the related radical species were optimized at the (U)B3LYP/6-31G(d) level. The B3LYP/6-31G(d) method has been used for structure optimizations in many works with high accuracy and moderate computational cost.[22−24,27] Subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag = 0) and provide thermal (E_{th}, 298 K) and zero-point energies (ZPEs).[28] Single-point energies on the optimized structures were computed with four different functionals (B3LYP,[24] B3PW91,[29] MPW1PW91,[30] and B3P86[31])

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CHART 1: B3LYP/6-31G(d) Optimized Coal Models (1−10) with Aliphatic Linkages

PhCH$_2$CH$_3$ (**1**, C_s)   Ph-Ph (**2**, D_2)   PhCH$_2$Ph (**3**, C_2)

Ph$_2$CHCH$_3$ (**4**, C_1)   PhCH$_2$CH$_2$Ph (**5**, C_{2h})   PhCH$_2$CH$_2$CH$_2$Ph (**6**, C_{2v})

Ph(CH$_3$)CHCH(CH$_3$)Ph (**7**, C_i)   Ph(CH$_3$)$_2$CC(CH$_3$)$_2$Ph (**8**, C_{2h})

PhCH$_2$CHPh$_2$ (**9**, C_1)   Ph$_2$CHCHPh$_2$ (**10**, C_2)

and the flexible 6-311+G(d,p) basis set. These DFT methods were chosen because the B3LYP had been proven to be very accurate in geometry computation, B3PW91 and MPW1PW91 were considered to be an advanced scheme in considering long-range interactions, and B3P86 had been reported to be promising in energetic calculations. The calculated energetic data are summarized in Table 1. All energetic calculations are based on ground state structures. Since several conformations (staggered, gauche, and eclipsed) exist for substituted alkanes, only staggered conformations were chosen as global minima because gauche and ecliptic conformations are higher in energy. The BDE's at 298 K were calculated by using the thermo-chemical scheme supplied by Gaussian[32] and used by Morokuma[21] as in the following equation: BDE$_{298}$(R_1 − R_2) = [$\Delta_f H_{298}$(R_1) + $\Delta_f H_{298}$(R_2)] − $\Delta_f H_{298}$(R_1 − R_2), in which R_1 − R_2 is the neutral hydrocarbon, and R_1 and R_2 are the corresponding radicals.

Results and Discussion

A benchmark calculation was carried out for eight alkane and alkyl benzene molecules. Table 2 summarizes the computed BDE values, which are compared with the available experimental data and the best computational data of Morokuma.[21] All the DFT methods tested reproduce the bond dissociation enthalpy patterns observed in the experimental findings. For example, (i) C(sp^3)−C(sp^3) bonds have lower BDE values than those of C(sp^2)−C(sp^3); (ii) the more substituted, the lower the

BDE; and (iii) benzyl radicals can be formed more easily than alkyl radicals. This reflects the C−C bond strengths and the stability of the formed radicals. The stability of radicals can be explained by the hyper-conjugative resonance between the single-occupied radical center and the C−H bonds of the methyl groups in alkyl radicals and the conjugative resonance between the radical center and the phenyl groups in benzyl radicals.[33]

In addition to these results, more details into the quality of individual methods can be obtained from Table 2. It is shown that the B3LYP underestimates the BDE values by 4.4−8.2 kcal/mol with an average deviation of 6.2 kcal/mol as compared to the experimental data, while B3P86 performs best with an average deviation of 1.7 kcal/mol. Figure 1 shows the good linear relationship between the B3P86 calculated and experimental BDE values (R^2 = 0.983). It is found that MPW1PW91 has slightly larger deviation than B3P86, but both perform better than the G2MSr method.[21] The worst performance of the hybrid B3LYP functional is surprising, as also reported previously.[34] The benchmark calculations show that B3P86 performs well. However, it should be noted that there is apparently a monotonic trend: B3LYP < B3PW91 < MPW1PW91 < B8P86, and that a constant shift of 4.5 kcal/mol would bring the B3LYP values to overlap the B3P86 ones. On this basis, we might expect good agreement between the calculated and experimental values of large molecules.

Most coal model compounds studied here are aromatic hydrocarbon compounds with aliphatic linkages. Since there are

TABLE 1: Computed Zero-Point Energies (ZPE, scaled by 0.9806), Thermal Energies (E_{th}), and Total Electronic Energies

species	ZPE[a]	E_{th} (298 K)[a]	B3LYP[b]	B3PW91[b]	MPW1PW91[b]	B3P86[b]
PhC_2H_5 (**1**)	98.8	103.9	−310.96273	−310.83839	−310.87806	−312.00621
Ph-Ph (**2**)	114.3	120.4	−463.42261	−463.23442	−463.29979	−464.89179
$PhCH_2Ph$ (**3**)	132.0	139.1	−502.74338	−502.54084	−502.61099	−504.35873
$(Ph)_2CHCH_3$ (**4**)	149.9	157.7	−542.06512	−541.84839	−541.92364	−543.82744
$PhCH_2CH_2Ph$ (**5**)	150.0	157.9	−542.06921	−541.85182	−541.92661	−543.83030
$PhCH_2CH_2CH_2Ph$ (**6**)	167.9	176.7	−581.39345	−581.16151	−581.24101	−583.30062
$Ph(CH_3)CHCH(CH_3)Ph$ (**7**)	185.4	195.1	−620.71328	−620.46780	−620.55299	−622.76878
$Ph(CH_3)_2CC(CH_3)_2Ph$ (**8**)	221.4	232.4	−699.34025	−699.06761	−699.16402	−701.69254
$(Ph)_2CHCH_2Ph$ (**9**)	200.9	211.7	−773.16863	−772.85886	−772.96942	−775.64883
$(Ph)_2CHCH(Ph)_2$ (**10**)	251.7	265.4	−1004.26808	−1003.86661	−1004.01323	−1007.46814
$CH_3\cdot$	18.7	21.3	−39.85516	−39.83824	−39.84015	−40.01472
$CH_3CH_2\cdot$	37.4	40.5	−79.18499	−79.15353	−79.15972	−79.49055
$Ph\cdot$	55.0	58.3	−231.62227	−231.52696	−231.55860	−232.35299
$PhCH_2\cdot$	72.1	76.3	−270.98719	−270.87614	−270.91239	−271.86349
$PhCH_2CH_2\cdot$	89.1	94.5	−310.29046	−310.16598	−310.20724	−311.31369
$Ph(CH_3)CH\cdot$	89.9	95.1	−310.31545	−310.19030	−310.23117	−311.33843
$Ph(CH_3)_2C\cdot$	107.6	113.9	−349.64107	−349.50191	−349.54766	−350.81111
$PhCH_2CH_2CH_2\cdot$	107.1	113.4	−349.61557	−349.47641	−349.52237	−350.78471
$Ph(CH_3)CH(CH_3)CH\cdot$	125.0	132.2	−388.94443	−388.79114	−388.84193	−390.26048
$Ph(CH_3)_2C(CH_3)_2C\cdot$	160.6	169.4	−467.58922	−467.40800	−467.46918	−469.20006
$(Ph)_2CH\cdot$	123.9	130.8	−502.10499	−501.90094	−501.97197	−503.69944
$Ph(CH_3)CH(Ph)CH\cdot$	159.1	167.9	−580.74295	−580.51033	−580.59126	−582.63014
$Ph(CH_3)_2CC(CH_3)Ph\cdot$	195.1	205.3	−659.37543	−659.11582	−659.20750	−661.55879
$PhCH_2CHPh\cdot$	141.3	149.2	−541.420450	−541.20234	−541.27824	−543.16115
$(Ph)_2CHCH_2\cdot$	140.2	148.3	−541.39322	−541.17616	−541.25286	−543.13496
$(Ph)_2CHCHPh\cdot$	192.2	202.9	−772.52245	−772.21202	−772.32356	−774.98199

[a] At (U)B3LYP/6-31G(d) (kcal/mol). [b] Single-point calculations with the 6-311+G** basis set and the (U)B3LYP/6-31G(d) geometries (hartree).

TABLE 2: Computed Bond Dissociation Enthalpies (BDE, kcal/mol, 298 K), Compared with the Available Experimental Values

models	B3LYP	B3PW91	MPW1PW91	B3P86	CCSD(T)[a]	G2MSr[a]	exptl[b]
CH_3-CH_3	84.3	85.9	86.4	88.6	88.1	87.4	90.4 ± 0.3
$C_2H_5-CH_3$	81.4	83.0	83.8	85.7	87.4	87.0	85.8 ± 1
$Ph-CH_3$	96.5	97.9	98.8	100.8			101.8 ± 2
$(CH_3)_2CH-CH_3$	78.7	80.3	81.3	83.2	86.5	86.6	85.7 ± 1
$(CH_3)_3C-CH_3$	76.0	77.6	78.8	80.7	85.4	86.0	84.1 ± 1
$PhCH(CH_3)-CH_3$	66.4	68.5	69.7	71.2		78.1	74.6 ± 1.5
$PhCH_2-C_2H_5$	66.3	68.6	69.8	71.2			71.8 ± 1
$PhCH_2-CH_2CH_2CH_3$	66.9	69.2	70.5	71.9			72.1 ± 1

Deviations from Experimental BDEs (BDE$_{exptl}$ − BDE$_{calcd}$)

models	B3LYP	B3PW91	MPW1PW91	B3P86	CCSD(T)[a]	G2MSr[a]
CH_3-CH_3	6.1	4.5	4.0	1.8	2.3	3.0
$C_2H_5-CH_3$	4.4	2.8	2.0	0.1	1.6	1.2
$Ph-CH_3$	5.3	3.9	2.0	1.0		
$(CH_3)_2CH-CH_3$	7.0	5.4	4.4	2.5	0.8	0.9
$(CH_3)_3C-CH_3$	8.1	6.5	5.3	3.4	1.3	1.9
$PhCH(CH_3)-CH_3$	8.2	6.1	4.9	3.4		3.5
$PhCH_2-C_2H$	5.5	3.2	2.0	0.6		
$PhCH_2-CH_2CH_2CH_3$	5.2	2.9	1.6	0.2		
av	6.2	4.4	3.3	1.7	1.5	2.1

[a] Reference 22. [b] Reference 8.

more than one ground state structures for large molecules on the potential energy surface, only the most stable states with staggered conformations were selected. In the case of 1,3-diphenyl propane ($PhCH_2CH_2CH_2Ph$), which has two conformations with the same energy, only the one with lower frontier orbital energy was chosen. The calculated BDE values for molecules shown in Chart 1 are given in Table 3 including the available experimental data.[6−9]

On the basis of the benchmark qualities in Table 2, one might expect that B3P86 should also reproduce the experimental data relatively well. Indeed, among the eight data in Table 3, five of them are only slightly underestimated with a largest deviation of 2.4 kcal/mol. The B3P86 BDE's for $PhCH_2-CH_3$ (**1**, 73.9 kcal/mol) and $(Ph)_2CH-CH_3$ (**4**, 65.4 kcal/mol) are closer to the experimental values (75.8 ± 1.5, 67.6 kcal/mol) than those of GeMSr (79.0, 72.9 kcal/mol[21]). However, it is also necessary to point out that the computed data for $PhCH_2-Ph$ (**3**), $(Ph)_2-$

$CH-CH(Ph)_2$ (**10**), and $(Ph)_2CH-CH_2Ph$ (**9**) are much lower than the experimental values (with deviations of 4.8, 7.8 and 8.5 kcal/mol, respectively), and this might be mainly due to
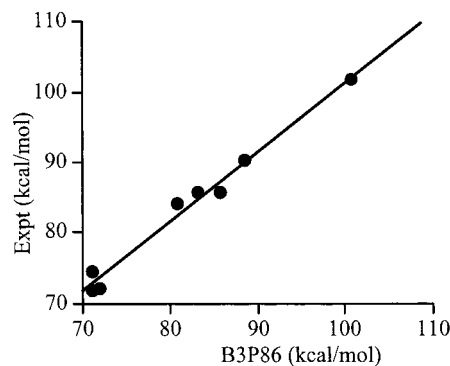

Figure 1. Comparison of calculated and experimental BDE values.

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TABLE 3: Computed Bond Dissociation Enthalpies (kcal/mol, 298 K) and Bond Lengths (Å), Compared with the Available BDE Experimental Data

bonds	B3LYP	B3PW91	MPW1PW91	B3P86	exptl	difference [f]	R_{C-C}
			X−CH₃ bond				
PhCH₂−CH₃ (**1**)	69.1	71.4	72.3	73.9	75.8 ± 1.5[a]	−1.9	1.539
(Ph)₂CH−CH₃ (**4**)							
Ph(CH₃)CHCH(Ph)−CH₃ (**7**)	60.2	62.9	64.3	65.4	67.6[b,c]	−2.2	1.541
Ph(CH₃)₂CC(CH₃)(Ph)−CH₃ (**8**)	66.3	68.9	70.3	71.8			1.541
	63.0	65.5	67.2	68.9			1.549
			X−Ph bond				
CH₃CH₂−Ph (**1**)	92.4	93.9	95.1	96.9			1.515
Ph−Ph (**2**)	108.0	109.5	110.8	112.9	113.7[b]	−0.8	1.486
PhCH₂−Ph (**3**)	79.6	82.0	83.4	84.8	89.6[b]	−4.8	1.521
PhCH₂CH₂−Ph (**5**)	93.1	94.6	95.8	97.6			1.513
PhCH₂CH₂CH₂−Ph (**6**)	92.6	94.2	95.4	97.2			1.514
Ph(CH₃)CHCH(CH₃)−Ph (**7**)	87.4	89.4	91.1	92.9			1.524
Ph(CH₃)₂CC(CH₃)₂−Ph (**8**)	76.2	78.6	80.9	82.9			1.547
(Ph)₂CHCH₂−Ph (**9**)	91.0	92.7	94.1	95.9			1.515
PhCH2CH(Ph)−Ph (**9**)	74.8	77.1	79.0	80.3			1.526
(Ph)₂CHCH(Ph)−Ph (**10**)	73.3	76.0	78.2	79.5			1.530
			X−X and X−Y Bond				
PhCH₂−CH₂Ph (**5**)	54.1	57.1	58.5	59.5	61.4[b,d]	−1.9	1.552
Ph(CH₃)CH−CH(CH₃)Ph (**7**)	46.9	49.9	52.1	52.9			1.563
(Ph)₂CH−CH(Ph)₂ (**10**)	32.7	36.9	39.7	39.8	47.5[b,e]	−7.8	1.565
Ph−CH(CH₃)Ph (**4**)	75.7	78.0	79.7	79.7			1.529
PhCH₂CH₂−CH₂Ph (**6**)	66.8	69.0	70.3	71.6	73.9[b]	−2.4	1.542
Ph(CH₃)₂C−C(CH₃)₂Ph (**8**)	31.8	35.4	38.5	39.5			1.617
(Ph)₂CH−CH₂Ph (**9**)	43.4	46.7	48.8	49.3	57.8[b,e]	−8.5	1.560

[a] Reference 8. [b] Reference 3. [c] Reference 5. [d] Reference 6. [e] In liquid tetralin; ref 7. [f] Difference between the B3P86 computed and the experimental values.
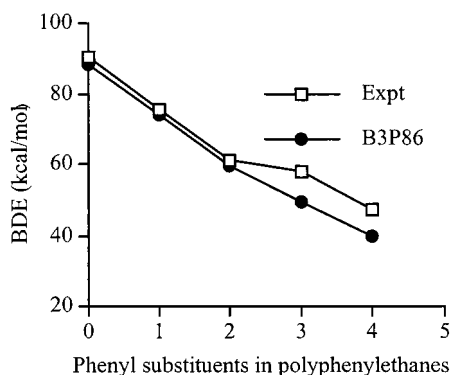

Figure 2. Computed and experimental phenyl substitution effects on BDE.

Figure 3. Computed methyl substitution effects on BDE.

the experimental inconsistency resulting from different experimental conditions used.[35] For example, some were obtained in solvents,[7] on which the BDE data of Poutsma[4] were based. Whatever the reasons for this discrepancy may be, it is not the first time for the correction of experimental data through systematic computations.[36]

Table 3 lists the calculated C−C bond lengths with the expected trend that the shorter the bond length, the larger the BDE within the group, from which one of the formed radical is the same. In the case of the formation of different radicals, no correlation between bond length and BDE can be found, and this is mainly due to the relative stabilities of the radicals formed. In addition, the steric effect in the neutral hydrocarbons and the different stabilizing factors in the formed radicals may also result in small BDE, but it is very difficult to separate them quantitatively.

The substitution effects are shown in Figures 2 and 3, the central C(sp³)−C(sp³) BDEs of the ethane derivatives decrease as the number of phenyl or methyl substituents increases, and phenyl groups have much larger substitution effect than methyl groups. As shown in Figure 2, the first two phenyl groups have
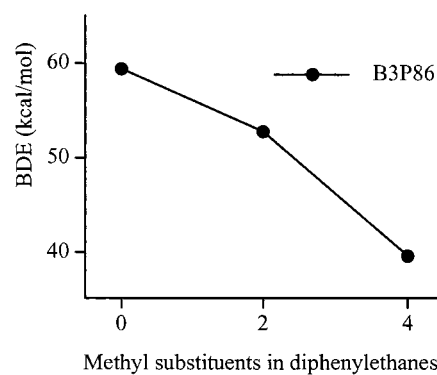
larger effects (about 14 kcal/mol) than the third and fourth (about 10 kcal/mol), and this difference is reflected by their structures. For example, PhCH₂• has a planar C_{2v} structure, which can result in perfect conjugative resonance (electronic effect), while Ph₂CH• has a nonplanar (twisted) C_2 structure due to the steric interaction of the two phenyl groups, and the steric and electronic effects compensate to some extent. As shown in Figure 3, the opposite trend is found for the alkyl substitution; the first two methyl substituents have a smaller effect (3.3 kcal/mol per CH₃) than the additional two (6.7 kcal/mol per CH₃). This can also be explained by electronic effects caused by their structural differences, since all three radicals have planar carbon frameworks, and this results in the conjugative interaction and increased methyl hyperconjugation.

To test the radical substitution effects discussed above, homodesmotic exchange equations[37] were employed. The exothermicity indicates stabilizing effect, while endothermicity indicate destabilizing effect. For the phenyl substitution, exchange eqs 1−3 were used. Equation 1 shows the considerable conjugative interaction (−32.9 kcal/mol) between the radical center and benzene ring in PhCH₂•. Equation 2 also shows large effect of two phenyl groups in Ph₂CH•. However, the stabilizing

energy of -25.4 kcal/mol is smaller than in $PhCH_2^\bullet$. Their difference in eq 3 shows clearly that the second phenyl has a destabilizing effect, as compared to the first one.

$$PhCH_3 + CH_3^\bullet = PhCH_2^\bullet + CH_4 \qquad (1)$$

$$\Delta H = -32.9 \text{ kcal/mol}$$

$$Ph_2CH_2 + CH_3^\bullet = Ph_2CH^\bullet + CH_4 \qquad (2)$$

$$\Delta H = -25.4 \text{ kcal/mol}$$

$$Ph_2CH_2 + PhCH_2^\bullet = Ph_2CH^\bullet + PhCH_3 \qquad (3)$$

$$\Delta H = +7.5 \text{ kcal/mol}$$

For abstracting methyl substitution, eqs 4−6 are used. As shown in eq 4, methyl has a stabilizing effect (-3.1 kcal/mol) in $Ph(CH_3)CH^\bullet$, and the effect of two methyl groups in $Ph(CH_3)_2C^\bullet$ (-6.8 kcal/mol, eq 5) is larger. Their difference in eq 6 shows that the second methyl group has an enhanced stabilization effect compared to the first one. These results agree well with our analysis from Figures 2 and 3.

$$PhCH_2^\bullet + PhCH_2CH_3 = Ph(CH_3)CH^\bullet + PhCH_3 \quad (4)$$

$$\Delta H = -3.1 \text{ kcal/mol}$$

$$PhCH_2^\bullet + PhCH(CH_3)_2 = Ph(CH_3)_2C^\bullet + PhCH_3 \quad (5)$$

$$\Delta H = -6.8 \text{ kcal/mol}$$

$$Ph(CH_3)CH^\bullet + PhCH(CH_3)_2 = Ph(CH_3)_2C^\bullet + PhCH_2CH_3 \qquad (6)$$
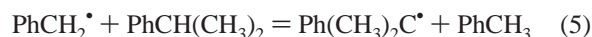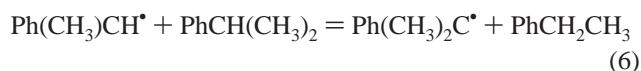
$$\Delta H = -3.7 \text{ kcal/mol}$$

Now the question raises if the better performance of the B3P86 scheme comes from the better geometry optimization. Thus, test calculations were carried out for a set of molecules. For 1,1-diphenylethane (**4**), a representative example, the B3P86/6-311+G(d,p) BDE with the B3LYP/6-31G(d) geometry (65.4 kcal/mol) is nearly the same as that with the B3P86/6-31G(d) geometry (65.5 kcal/mol), and both are very close to the experimental value (67.6 kcal/mol). On the other hand, the B3LYP/6-311+(d,p) BDE with B3LYP/6-31(d) geometry (60.2 kcal/mol) is the same as that with B3P86/6-31G(d) geometry (60.2 kcal/mol), and both are smaller than the experimental value. This indicates that the functional rather the geometry is responsible for the quality of BDE calculations. Therefore, all geometries were obtained from B3LYP/6-31G(d) calculation.

Since B3P86 and B3LYP have the same exchange (B3) functional, the difference in correlation functionals should be responsible for the unsatisfactory performance of the B3LYP method. Thus, more sophisticated exchange and correlation functionals are needed for accurate calculations of C−C bond dissociation enthalpies. A detailed discussion on these different functionals is beyond the scope of this paper, but can be found in the literature.[38]

Conclusions

The bond dissociation enthalpies (BDE) of a set of aromatic hydrocarbon compounds were computed with four different density functionals. It was found that B3P86 method gives reasonable agreement with the experimental values, while B3LYP functional does not match the expected performance

and has the largest deviations. Additionally, the errors of two data sets were found to be too high and therefore further experimental validation work is needed.

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(35) Regarding to the discrepancy between experiment and theory, the referees suggested the analysis of (a) the basis set superposition error (BSSE), (b) the solvent effect, and (c) the intramolecular dispersion effects. Using $PhCH_2PH$ as model, we found that all three factors are not large enough for such a big discrepancy. Indeed, the BSSE for the 6-311+G(d, p) basis set is about 0.5 kcal/mol, and the solvent effects using the isodensity surface polarized continuum model (IPCM, Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Soonoan, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098) and cyclohexane as solvent contributes with less than 0.1 kcal/mol, which is not very surprising since all the bonds in hydrocarbon are not highly polarized. The intramolecular dispersion effect (Fortunelli, A.; Selmi, M. *Chem. Phys. Lett.* **1994**, *223*, 390, the biggest effect found in norborane for each C−C bond is ca. 0.2 kcal/mol) is also not large enough for the observed discrepancy. Therefore, we used the uncorrected data for discussion.

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