

Invited review

Bond dissociation enthalpies in benzene derivatives and effect of substituents: an overview of density functional theory (B3LYP) based computational approach

Pham Cam Nam^{1*}, Vo Van Quan², Nguyen Minh Thong³, Pham Thi Thu Thao^{4,5}

¹Department of Chemistry, The University of Danang – University of Science and Technology

²Department of Natural Sciences, Quang Tri Teachers Training College

³The University of Danang, Campus in Kon Tum

⁴Hue University of Sciences, Hue University

⁵Le Quy Don gifted high school in Quang Tri

Received 27 October 2017; Accepted for publication 29 December 2017

Abstract

In this review, we have mainly focused on the recent computational studies on the bond dissociation enthalpies (BDE) of the X–H bonds of the *para* and *meta* substituted benzene derivatives ($3Y-C_6H_4X-H$ and $4Y-C_6H_4X-H$ with X = O, S, Se, NH, PH, CH₂, SiH₂ and Y = H, F, Cl, CH₃, OCH₃, NH₂, CF₃, CN, NO₂). In addition, the remote substituent effects on the BDE(X–H), the radical stability and parent one have also been discussed in terms of the calculated ground state effect, radical effect and total effect. Model chemistry of ROB3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p) can reproduce the BDE values with the accuracy of 1.0–2.0 kcal/mol. The good linear correlations between Hammett constants and BDE values were discovered for both *para* and *meta* substitutions in phenols, thiophenols, benzeneselenols, anilines and phenylphosphines with the R-squared larger than 0.94. In contrast, it does not occur in case of toluenes and phenylsilanes.

Keywords. Benzene derivatives, density functional theory, bond dissociation enthalpies, substituent effects, radical effect, ground state effect, total effect, Hammett constants.

1. INTRODUCTION

The chemistry of benzene derivatives, especially in phenol, thiophenol, benzeneselenol, aniline, phenylphosphine, toluene, phenylsilane and their derivatives continues to attract considerable interest [1-3]. Compounds bearing these structures ranging from synthetic compounds to the natural extracts from leaves, trees and roots have several indispensable applications in our daily life [4-6]. Among the most fundamental aspect in chemical and biochemical studies, the molecular structures, energetics, reactivity and their interrelationships are of crucial importance. For example, in a chemical reaction there are disruption and formation of chemical bonds. The making and breaking of bonds is the basis of all chemical transformation. A sound knowledge of the energies required to break bonds and the energies released upon their formation is fundamental to understanding chemical processes. The energy required to homolytic bond cleavage at

298 K and 1 atm corresponds to the enthalpy of reaction: $A-B \rightarrow A^\bullet + B^\bullet$, which is defined as the bond dissociation enthalpy of the A–B bond and symbolized by BDE(A–B) [7]. It should be noted that by definition of IUPAC, the bond dissociation energy is sometimes called the bond dissociation enthalpy (or bond enthalpy), but these terms may not be strictly equivalent [8]. Conversely, if the radicals A and B recombine to form the molecule AB, then thermal energy equivalent to the bond dissociation enthalpy is released, according to the first law of thermodynamics [9].

Hence it is essential to establish reliable data of bond dissociation enthalpies (BDEs) as direct information about the strength of the relevant chemical bond in order to understand the inherent reaction mechanism. Therefore, the BDEs already provide valuable criteria for the analysis and selection of antioxidants derived from the natural compounds extracted from plants.

The bond strength of a given bond can be

experimentally measured or computationally calculated. It exists many experiments that allow measuring the bond dissociation enthalpy [10]. Despite compilations of experimental thermochemical data for many molecules, there are numerous species for which there are no available. In addition, the data in the compilations are sometimes incorrect [11].

Experimental measurements of thermochemical processes are often expensive, difficult and need a careful manipulation, so it is highly desirable to have computational methods that can make reliable predictions and inexpensive [9]. With the recent advances in computation methods and computer capacity, this becomes more and more reality.

To the best of our knowledge, there has been no recent review on the B3LYP method for predicting the accurate BDEs in benzene derivatives and their analogues as well as the effect of substituents at the *para* and *meta* positions of the benzene ring, a short review on these topics is urgent and necessary. For the results, this review includes several sections organized in three parts. In the first part, the model chemistry of ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) was analyzed and evaluated by comparing the calculated results with the available experimental values as well as by benchmarking against the other computational methods. Conventionally, the model to the right of the double slash *i.e.* B3LYP/6-311G(d,p) is the one at which the molecular geometry was optimized and the model to the left of the double slash *i.e.* ROB3LYP/6-311++G(2df,2p) is the one at which the energy is computed. In case of radical species, specification of a restricted open shell wave function for the Becke3LYP hybrid functional requires the ROB3LYP keyword, while the unrestricted version denoted as UB3LYP is applied for geometrical optimization of the radicals. The second one, the homolytic bond dissociation enthalpies of the X–H bonds (X = O, S, Se, NH, PH, CH₂ and SiH₂) of the related benzene derivatives have been reviewed and evaluated by using ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p). In addition, the updated BDEs for a series of aniline derivatives and phenylsilane analogues were also calculated using the same procedure of computational method. The third part of this review, the effect of *para* and *meta* substituents on the BDE(X–H) have been critically analyzed considering the nature of substituent and the substituted position. The idea of a quantitative description of the substituent effect on rates and equilibria of chemical reaction ($\log(k)$ or $\log(K)$, respectively) by use of a linear regression in which the nature of the substituent (X) is described

numerically by a substituent constant was ingenious and opened a great field for further investigations [12]. Therefore in this review the correlations of Hammett's substituent constants with the BDE(X–H) values have also been explored.

2. METHODOLOGY FOR PREDICTING BDE(X–H)_s

Because of the important of bond dissociation enthalpy in many reactions, the accurate determination of BDE is an urgent task for both experimental and computational researchers and this continues to be a steady stream of work in the field from practitioners in both areas [13].

2.1. Experimental methods

Experimental determinations of BDE are still limited to simple or small molecules and are insufficient in many practical cases, in which large and complex systems have frequently to be treated [14]. In addition, experimental BDE data have large uncertainties (2.0-3.0 kcal/mol and more in some cases), making the development and comparisons of new computational technique challenges. A very concise of description of experimental methods can be found in details from Ref. [15] and references therein. For a given X–H bond in polyatomic molecules, three applicable techniques are usually proposed: *i)* The study of radical kinetics; *ii)* Photoionization mass spectrometry (PIMS) and *iii)* the acidity/electron affinity cycle. The abstraction of a hydrogen atom and creation of radical is considered in the study of radical kinetics. In this method, the concentration of atoms, free radicals, and molecules at one or several temperatures using various detecting methods [16].

Spectrometry method is used to predict the BDEs of the bond of diatomic molecules in gas phase. Mass spectrometry is a powerful tool for the study of molecular thermochemistry. There are several mass spectrometry methods used to investigate in molecular thermochemistry such as electron impact, guided ion beam, high pressure, photoionization mass spectrometry and so on [9, 15, 17]. Photoionization mass spectrometry uses a tunable light source to dissociatively ionize a target species and measures ion intensities versus photon energy and this method is widely used for the X–H bond [9].

2.2. Computational methods

In computational approach, the homolytic X–H bond dissociation enthalpies at 298.15 K and 1 atm for the

AXH molecule can be estimated from the expression.

$$\text{BDE}(X-H) = H_f(\text{AX}^\bullet) + H_f(\text{H}^\bullet) - H_f(\text{AXH}) \quad (1)$$

Where H_f 's are the enthalpies of the different species at 298.15 K and 1 atm. The enthalpy of each species was calculated from the following equation:

$$H_f = E_0 + \text{ZPE} + H_{\text{trans}} + H_{\text{vib}} + H_{\text{rot}} + RT \quad (2)$$

Where ZPE is zero point energy, H_{trans} , H_{vib} , H_{rot} are the standard temperature correction term calculated with the equilibrium statistical mechanics with harmonic oscillator and rigid rotor approximation.

In this review, the computational calculations for thiophenols, phenylphosphines, toluenes were performed using the Gaussian 03 software and the computational calculations for phenols, benzeneselenols and phenylsilanes were newly carried out using Gaussian 09 software [18].

2.3. Benchmark the computational methods for determining BDE

Based on the equations (1) and (2), a larger number of theoretical studies have been carried out over the last decade to assess the accuracy of the computational procedures for predicting the BDE [13, 14, 19-42]. Radom and coworkers [28, 43] investigated the performance of a variety of theoretical methods for the calculation of radical stabilization energies of six substituted methyl and vinyl radicals. The conclusion confirmed that UHF (unrestricted Hartree Fock) and PMP (Projected Møller-Plesset) performed poorly for radicals with significant spin contamination in the wave function. On the other hand, the calculation using RMP2/6-311+G(2df,p) single point energies were computationally inexpensive. The results for BDE using several composite methods like CBSRAD, G3(MP2)-RAD and the high level G2 [44], CBS-4 [44], W₁ showed the reasonable agreement with the experimental values. Guo and coworkers applied ONIOM-G3B3 method to predict the bond dissociation enthalpies (BDEs) of coenzyme Q, flavonoids, olives, curcumins, indolinonic hydroxylamines, phenothiazines, edaravones and antioxidants used as food additives as well as the C-H and N-H BDEs of ribonucleosides and deoxyribonucleosides [31, 34]. Especially, the DFT are now capable of providing excellent agreement with benchmark binding energies of a variety of dimers systems [45]. It also appears obligatory to use

the DFT methods which can dramatically decrease the CPU time vs. ab initio methods of similar accuracy [42]. In 1999, Dilabio and Pratt tested three DFT based procedures to evaluate the BDEs for a variety of molecules containing C-H, O-H, N-H and S-H. The results showed that ROB3LYP/6-311++G(2d,2p)/AM1; ROB3LYP/6-311++G(2d,2p)/(U)MP2(fu)/6-31G(d)/HF/6-31G(d) and ROB3LYP/6-311++G(2d,2p)/(U)B3LYP/6-31G(d)/B3LYP/6-31G(d) can generate the BDEs of these bonds with the accuracy of 1.0 to 2.0 kcal/mol [46].

The recent studied on phenol [47], thiophenol, [29] benzeneselenol [48], phenylphosphine [49] and toluene [50] and have showed that calculations with ROB3LYP/6-311++G(2df,2p)/B3LYP/6-311G(d,p) procedure using Gaussian suit of program can predict the BDEs of O-H, S-H, Se-H, P-H and C-H with the accuracy within 1-2 kcal/mol. To validate this procedure, a number of small compounds have been calculated and benchmarked. In case of S-H bond, the BDE(S-H) of two model systems namely H₂S and CH₃SH for which exact experimental results are known were calculated and compared. The calculated BDE(S-H) values for H₂S and CH₃SH are 91.5 and 86.8 kcal/mol [29], respectively, which are very close to the experimental values of 91.2±0.7 kcal/mol for the former and 87.4±0.5 kcal/mol for the latter molecule [15]. A set of small compounds in which the central atoms belong to the group VA including PH₃, NH₃, and AsH₃ were calculated using different DFT methods with a variety of basis set then being compared with the results at CCSD(T) and MP2 with a larger basis set such as aug-cc-pvTZ. The sequential results for BDE(P-H), BDE(N-H) and BDE(As-H) based on ROB3LYP/6-311++G(2df,2p) are 81.3, 107.4 and 76.1 kcal/mol, being very agreement with the experimental data of 83.9±0.5; 108.0±0.3 and 76.3±0.2 kcal/mol [15], respectively. Moreover, the calculated results for BDEs using several density functionals like B3P86, B3PW91 and O3LYP at the same basis set of 6-311++G(2df,2p) based on the optimized structures and frequency calculations at B3LYP/6-311G(d,p) have been evaluated for a variety of compounds having P-H, N-H, As-H, C-H bonds. In fact, the ROB3LYP/6-311++G(2df,2p)/B3LYP/6-311G(d,p) procedure could be used as an accurate model for determining the bond strength of various types of bonds in organic molecules [48-52].

3. THE ROB3LYP/6-311G(2DF,2P)/B3LYP/6-311G(D,P) CALCULATED FOR X-H BOND IN BENZENE DERIVATIVES

3.1. The homolytic X-H bond dissociation enthalpies of C₆H₅X-H (X = O, S, Se, NH, PH, CH₂, SiH₂)

Very recently, BDEs were computed for a variety of bonds in aromatic compounds such as C₆H₅X-H where X = O, S, Se, NH, PH, CH₂ and SiH₂. In terms of predicting the reliable values of BDEs, the computational procedure of B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) could be used as an accurate model. First, in this section, once again we reviewed the validation of this computational procedure for calculating the BDE(X-H) of phenol, thiophenol, benzeneselenol, aniline, benzenephosphine, toluene and phenylsilane. The calculated BDE(X-H) values (X = O, S, Se, NH₂, PH₂, CH₃, SiH₃) are given in Table 1 along with the available experimental values. It should be noted that there are a number of experimental values for the studied aromatic compounds and these estimated values vary in a wide range. Therefore, the analysis as well as the comparison with the available experimental values are necessary for reconfirming the efficacy of ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) procedure. First, the calculated BDE(O-H) for phenol using ROB3LYP/6-311++G(2df,2p) based on the optimized structure at B3LYP/6-311G(d,p) is 87.5 kcal/mol, being very close to the experimental

value of 87.3±1.5 kcal/mol measured using photoacoustic calorimetry (TR-PAC) [53]. Although there are several experimental values of the O-H BDE, varying within a wide range from 84.4 kcal/mol to 91.0 kcal/mol, [15, 21, 53-64] but the recommended data for BDE(O-H) of phenol is 88.0 ± 1.5 kcal/mol [15] which is larger than that in this study about 1.5 kcal/mol. It should be indicated that the ROB3LYP usually raises the BDE to be close the accurate values than the UB3LYP. The predicted value of BDE(O-H) for phenol using UB3LYP/6-311++G(2d,2p)/B3LYP/6-311G(d,p) was 82.2 kcal/mol [65] which is underestimated the experimental value. In case of thiophenol, the experimental BDE(S-H) values also vary within a wide range of 79.4 to 83.5 kcal/mol [66-70]. The most recent value (83.4 kcal/mol) was determined from the time resolved photoacoustic calorimetry (TR-PAC) experiment by dos Santos *et al.* [71]. It should be noted here the margin of error is very large up to 4 kcal/mol in this measurement. The calculated BDE(S-H) in this review is very close to that estimated by Venimadhavan *et al.* (79.4 kcal/mol) [68]. Especially for BDE(Se-H) of benzeneselenol, there is a larger deviation between the calculated value using ROB3LYP/6-311++G(2df,2p) given in Table with the experimental values. This can be explained on the basis of the existence of two lower lying electronic states of C₆H₅S radical, namely ²A' and ²A'' and the calculated BDE(Se-H) in table 1 is predicted for the latter one.

Table 1: The calculated BDE(X-H) of C₆H₅XH (X = O, S, Se, NH, PH, CH₂, SiH₂) using ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p)

X	Calculated values (in kcal/mol)	Experimental values ^a (in kcal/mol)
O	87.5	89.5±1.0; 88.3±1.5; 88.0±1.5; 87.3±1.5 [10, 53]
S	79.5	83.3±2; 79.4 [68]; 80.0; 80.8; 83.5±1.1
Se	73.5	67.0; 78.0±4.0
N	92.4 ^b	88.0±2.0; 92.3; 89.1; 89.7
P	76.3	N/A
C	89.4	87.9±1.5; 88.1±2.2; 88.6; 88.5±1.5; 89.6±1.0
Si	89.6 ^b	88.2 [17]

^aAll experimental values can be found in Ref. [15] and references therein. For specific values, references are given right behind. ^bin this work.

For aniline, our calculated BDE(N-H) is 92.4 kcal/mol, larger than those experimental values of 89.1 and 89.7 kcal/mol using pulse radiolysis and photoacoustic calorimetry, respectively [15, 72, 73]. However our predicted value is close to value of

92.3 kcal/mol determined by Bordwell *et al* using the measured *pK_a* of aniline (C₆H₅NH₂) in DMSO and oxidation potential (E_{ox}) of aniline anion (C₆H₅NH) [72, 74]. Our estimated value is 1.0 kcal/mol slightly larger than that reported by Guo

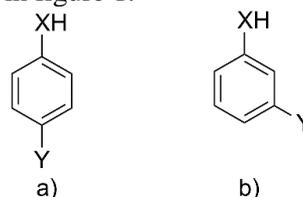
and coworker using G3 method [31] and Gomes *et al* using B3LYP methods [75]. For phenylphosphine, although no experimental value for BDE(P-H) is available, using the same procedure for calculation, the value should be 76.3 kcal/mol.

The ROB3LYP calculated BDE(C-H) in CH₃ group of toluene is reported to be 89.4 kcal/mol, which is very close to the recent experimental value of 88.5±1.5 kcal/mol [15]. The Si-H BDE of phenylsilane was calculated using ROB3LYP/6-311++G(2df,2p) method to be 89.6 kcal/mol. This value is of 1.4 kcal/mol higher than the experimental value 88.2 kcal/mol at 298.15 K [17]. However, the predicted values using unrestricted B3LYP with small basis set of 6-311G(d,p) and restricted MP2 at the 6-311++G(d,2p) are underestimated the experimental values.

Similar underestimation of BDEs was also found in number of former study not only for silane centered radicals but also for oxygen-, sulfur-, carbon-, and phosphine centered radicals. This leads to a critical conclusion that ROB3LYP appears to be the best choice for estimating the BDE of compounds containing X-H bonds.

3.2. The homolytic BDE(X-H) of a series of *para* and *meta* substituted Y-C₆H₄X-H (X = O, S, Se, NH, PH, CH₂, SiH₂ and Y = H, F, Cl, CH₃, OCH₃, NH₂, CF₃, CN and NO₂)

In fact, this procedure has been further developed and applied on various types of bonds. We subsequently presented the calculated results based on this model for a series of benzene derivatives described in figure 1.



X = O, S, Se, NH, PH, CH₂, SiH₂
Y = H, F, Cl, CH₃, OCH₃, NH₂, CF₃, CN, NO₂

Figure 1: Benzene derivatives and their related substituents

The calculated BDE(X-H) of 4Y-C₆H₄X-H and 3Y-C₆H₄X-H (X = O, S, Se, NH, PH, CH₂, SiH₂) are also given in tables 2 and 3, respectively. It is also interesting to observe how the BDE(X-H) value changes with the change of substituent at the *para* and *meta* position of the benzene ring.

Table 2: The ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) calculated BDE(X-H) of 4Y-C₆H₄X-H

Substituent Y	BDE(X-H) (kcal/mol)						
	O-H	S-H	Se-H	N-H	P-H	C-H	Si-H
H	87.5	79.5	73.5	92.4	76.3	89.8	89.6
F	85.4	77.8	73	91.0	76.3	89.8	89.7
Cl	86.1	78	73.3	91.9	76.2	89.6	89.6
CH ₃	85.1	77.5	72.7	90.8	76	89.4	89.5
OCH ₃	81.3	75.9	71.4	88.3	75.7	88.9	89.5
NH ₂	77.9	74.1	70	85.9	75	88.1	89.2
CF ₃	90.4	81.3	75.4	95	76.7	90.1	89.6
CN	89.4	81.4	75.3	95	76.5	89.4	89.4
NO ₂	91.7	82.5	76.4	96.5	76.9	89.3	89.3

Table 3: The ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) calculated BDE(X-H) of 3Y-C₆H₄X-H

Substituent Y	BDE(X-H) (kcal/mol)						
	O-H	S-H	Se-H	N-H	P-H	C-H	Si-H
H	87.5	79.5	73.5	92.4	76.3	89.8	89.6
F	88.4	80.3	74.5	93.5	76.5	90.1	89.7
Cl	88.4	80.3	74.4	93.6	76.5	90.1	89.7
CH ₃	86.9	79.3	73.5	92.0	76.2	89.7	89.0
OCH ₃	86.1	79.0	74.2	93.2	76.5	90.2	89.7
NH ₂	86.9	79.3	73.5	92.1	76.3	89.9	89.6
CF ₃	89.5	80.6	74.9	94.7	76.7	90.3	89.7
CN	90.3	81.1	74.7	94.9	76.9	90.6	89.8
NO ₂	90.7	81.4	75.2	95.2	77.1	90.6	89.8

3.2.1. X belongs to class O category

From the columns containing data for BDE of O–H, S–H, Se–H, N–H and P–H bond of Table 4, it can be observed that the effect of electron donating group (EDG) and electron withdrawing group (EWG) is opposite. Strong electronic donating substituents like OCH₃ and NH₂ at the *para* position result in sharp decrease for the BDE(X–H), except for X = P. For EWG, there is also an increase of the X–H BDE in which a larger enhancement is found for *p*-NO₂. The change of the BDEs also depends on the nature of X atom and can be placed in the order O > N > S > Se > P. A similar change of BDE values in Table 5 is also found when a substituent is at the *meta* position. A dramatically BDE(X–H) decrease with the presence of electron donating group (EDG) was found when X is N. In case of O, S and Se the difference between the parents and the corresponding *meta* substituted derivatives is within 0.0–1.5 kcal/mol. For EDG, the change is more pronounced with the increase of BDE about 1.1–4.1

kcal/mol. However, when X is P, the substituent effect is not meaningful with the change is less than 1 kcal/mol for both EDG and EWG.

3.2.2. X belongs to class S category

The change of X–H BDE of two series of aromatic compounds, Y–C₆H₄X–H with X is C or Si with that of the parent one C₆H₅X–H is presented in the two last columns of tables 4 and 5. It is clear from the BDE values in table 4 that the effect of *para* substituents on the BDE(C–H) value of toluene and BDE(Si–H) of phenylsilane are not very significant, except for the strong EDGs, like NH₂. For *meta* substitution, the effect of substituents on X–H BDE is almost trivial (table 5). It is apparent that the *para* substituents on toluenes and phenylsilanes have different effects than that observed for phenols and anilines. However, the *meta* substituent effect on the BDE(C–H) or BDE(Si–H) follows the same pattern as that is observed for phenols and anilines.

Table 4: The change of BDE(X–H) of 4Y–C₆H₄X–H upon *para* substitution (in kcal/mol)

Y	<i>para</i> substituents: 4Y–C ₆ H ₄ X–H						
	O–H ^a	S–H ^b	Se–H ^c	N–H ^d	P–H ^e	C–H ^f	Si–H ^d
H	0.0	0.0	0	0	0.0	0.0	0.0
F	-2.1	-1.7	-0.5	-1.4	0.0	0.0	0.1
Cl	-1.4	-1.5	-0.3	-0.5	-0.1	-0.2	0.0
CH ₃	-2.4	-2.0	-0.8	-1.6	-0.3	-0.4	-0.1
OCH ₃	-6.2	-3.6	-2.1	-4.1	-0.6	-0.9	-0.1
NH ₂	-9.6	-5.4	-3.5	-6.5	-1.3	-1.7	-0.4
CF ₃	2.9	1.8	1.9	2.6	0.4	0.3	0.0
CN	1.9	1.9	1.8	2.6	0.2	-0.4	-0.2
NO ₂	4.2	3.0	2.8	4.1	0.6	-0.5	-0.3

^{a,b,c,e,f}Data taken from Refs. [47], [29], [48], [49], [50], respectively; ^dIn this work

The change of $\Delta BDE_{4Y} = BDE(X-H)$ of 4Y–C₆H₄XH - BDE(X–H) of C₆H₅XH.

Table 5: The change of BDE(X–H) of 3Y–C₆H₄X–H upon *meta* substitution (in kcal/mol)

Y	<i>meta</i> substituents: 3Y–C ₆ H ₄ X–H						
	O–H ^a	S–H ^b	Se–H ^c	N–H ^d	P–H ^e	C–H ^f	Si–H ^d
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0
F	0.9	0.8	1.0	-1.2	0.2	0.3	0.1
Cl	0.9	0.8	0.9	-0.5	0.2	0.3	0.1
CH ₃	-0.6	-0.2	0.0	-0.5	-0.1	-0.1	-0.6
OCH ₃	-1.4	-0.5	0.7	-3.9	0.2	0.4	0.1
NH ₂	-0.6	-0.2	0.0	-6.0	0.0	0.1	0.0
CF ₃	2.0	1.1	1.4	1.7	0.4	0.5	0.1
CN	2.8	1.6	1.2	2.4	0.6	0.8	0.2
NO ₂	3.2	1.9	1.7	4.1	0.8	0.8	0.2

^{a,b,c,e,f}Data taken from Refs. [47], [29], [48], [49], [50], respectively; ^dIn this work

The change of $\Delta BDE_{3Y} = BDE(X-H)$ of 3Y–C₆H₄XH - BDE(X–H) of C₆H₅X.

4. SUBSTITUENT EFFECTS AND HAMMETT EQUATION

Substituent effects are among the most important structural effects influencing the chemical, physical and biological properties of a chemical species. The substituent is a small part of molecule which can be introduced by a simple chemical operation, particularly when it replaces a hydrogen atom. The substituent modified the properties of the molecule but does not alter its general character. The substituent effects are always an attractive subject for chemists [5, 12, 47].

The Hammett equation and its extended forms have been one of the most widely used means for the study and interpretation of organic reactions and their mechanisms [78, 79]. Almost every kind of organic reaction has been treated *via* Hammett equation or its modified forms, Hammett proposed that there is a relationship between the rate of a reaction and the equilibrium constant. As a result, the correlation of Hammett's substituent constant with bond dissociation enthalpies has also been found [12, 76, 78, 80].

Under this regard, the substituent constant σ at the reaction site of *para* and *meta* is usually discussed in terms of the stability of the radical which is generated from the parent molecule.

Figure 2 shows that the BDE(X-H) when substituent is placed at the *para* position of the aromatic ring depends strongly on the nature of substituent and the effect is much less in the case of *meta* site. Indeed, the correlation of original

Hammett (σ) becomes poorer when the substituents were conjugated with the reaction center. This problem was resolved by defining a new constant. Actually, depending on the hetero atom *e.g.* O, S, Se, N, P, C, Si, a suitable modified Hammett parameter has been chosen for such correlation [4, 6]. For example, in case of phenols and anilines, when a lone pair of electrons on the O and N atom could be delocalized on the substituents like *p*-CN and *p*-NO₂ a modified Hammett σ -is proposed. On the other hand, a modified Hammett σ^+ proposed by Brown and his colleagues is used when substituents conjugated with a reaction center which could effectively delocalized and since it accounts for through conjugation effects, which will be important for electron-donor groups at the *para* position. In the case of *meta* substituents, the σ_m^+ and σ_m values are found to be virtually the same [47].

4.1. Correlation between Hammett constants and BDE(X-H), in which X belongs to class O category

Figure 2 shows a Hammett's plot for the BDE(X-H) values of *para* 4Y-C₆H₄X-H (X = O, S, Se, N, P) and σ_p^+ . The σ_p^+ values were taken from the compilations of Hammett parameters by Hansch, Leo and Taft [78].

The obtained equations from such correlations between the modified Hammett constants (σ_p^+ and σ_m) and the BDE(X-H) at the *para* and *meta* of Y-C₆H₄X-H (X = O, S, Se, NH, PH) can be express as follow:

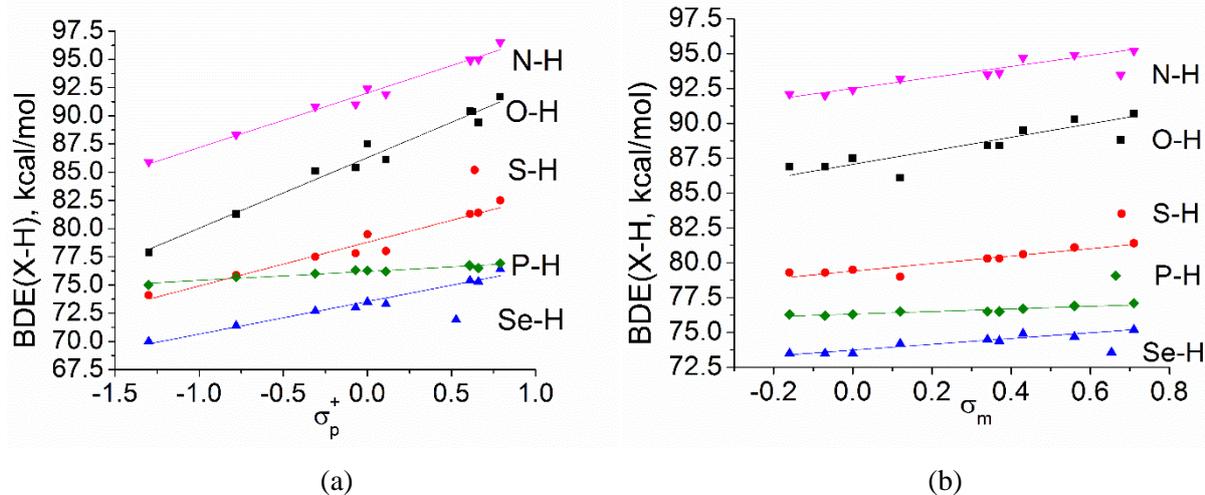


Figure 2: Plot of BDE(X-H) of the 4Y-C₆H₄X-H and 3Y-C₆H₄X-H (X = O, S, Se, NH and PH) with the Hammett constant σ_p^+ and σ_m , respectively

For 4Y-C₆H₄X-H:

Phenol:
$$\text{BDE(O-H)} = 6.2559\sigma_p^+ + 86.290 \quad R^2 = 0.9714 \quad (3)$$

$$\text{Thiophenol:} \quad \text{BDE(S-H)} = 3.8817\sigma_p^+ + 78.792 \quad R^2 = 0.9492 \quad (4)$$

$$\text{Benzeneselenol} \quad \text{BDE(Se-H)} = 2.8876\sigma_p^+ + 73.540 \quad R^2 = 0.9740 \quad (5)$$

$$\text{Aniline} \quad \text{BDE(N-H)} = 4.8444\sigma_p^+ + 92.023 \quad R^2 = 0.9823 \quad (6)$$

$$\text{Phenylphosphine} \quad \text{BDE(P-H)} = 0.7976\sigma_p^+ + 76.203 \quad R^2 = 0.9449 \quad (7)$$

For 3Y-C₆H₄X-H:

$$\text{Phenols:} \quad \text{BDE(O-H)} = 4.8707\sigma_m + 87.055 \quad R^2 = 0.8194 \quad (8)$$

$$\text{Thiophenols:} \quad \text{BDE(S-H)} = 2.6924\sigma_m + 79.401 \quad R^2 = 0.8797 \quad (9)$$

$$\text{Benzeneselenols:} \quad \text{BDE(Se-H)} = 2.0705\sigma_m + 73.738 \quad R^2 = 0.9252 \quad (10)$$

$$\text{Anilines;} \quad \text{BDE(N-H)} = 3.9474\sigma_m + 95.502 \quad R^2 = 0.9398 \quad (11)$$

$$\text{Phenylphosphines:} \quad \text{BDE(P-H)} = 0.9284\sigma_m + 76.318 \quad R^2 = 0.8742 \quad (12)$$

The R-squared is a statistical measure of how close the data are to the fitted regression line. The higher the R-squared, the better the model fits the data. Based on the equations (3) to (12), an impressive linear correlation ($R^2 > 0.97$) is observed between the BDE(X-H) and σ_p^+ for benzeneselenols ($R^2 = 0.9735$), phenols ($R^2 = 0.9714$) and thiophenols ($R^2 = 0.95$). The BDE(X-H) values of this group increase with the increasing electron withdrawing ability of the substituent (*i.e.* higher value for σ_p^+ especially with X has a lone pair of electron like O, S and Se. For example, when X = O, S and Se, the BDE(X-H)s increase with the amount of 4.20, 3.01 and 2.84 kcal/mol, respectively. The existence of an electron lone pair at the spin centered atom make the radical stabilized by EWG but destabilized by EDG [47, 77, 78]. For instance, the EDGs like CH₃, OCH₃, NH₂ reduce the BDE(O-H)s with the amount of 2.40, 6.20 and 9.60 kcal/mol, respectively due to the destabilization of the radicals generated from the parent aromatic derivatives. In the meantime, the substituents also affect in the stability the ground state. To further understand the effect of a substituent on the strength of the X-H bond, the ground state effect (GE) and radical effect (RE) can be calculated from the exchange reactions

between benzeneselenols and related species in figure 3 [48].

Figure 4 illustrates the change of BDE values based on the calculated GE and RE for Y-C₆H₄SeH. In both radicals and parents, the effect of F and Cl is insignificant and the total effect (TE = RE-GE) is very small. EWGs at *para* position tend to stabilize the parents but not the radicals. However, the latter parameter is larger thus leading to the negative TE value. For EDGs, an opposite trend is observed for the radical stability and the parent one. The RE values are found to be larger than the GE counterpart. Therefore the TE values remain considerably positive [48].

4.2. Correlation between Hammett constants and BDE(X-H), in which X belongs to class S category

Toluene and phenylsilane are the aromatic compounds with methyl (-CH₃) and silyl (-SiH₃) groups replacing one hydrogen in benzene ring which are classified as the class S category. This is due to methyl and silyl groups without any lone pair and all electrons are used in single bonds with three hydrogens and one carbon of benzene ring. Because

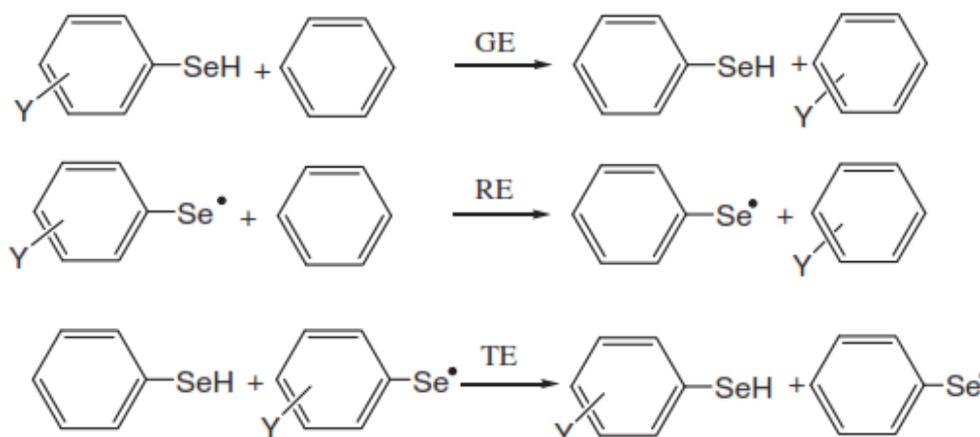


Figure 3: The exchange reactions for calculating GE and RE (Reprinted from Ref. [48])

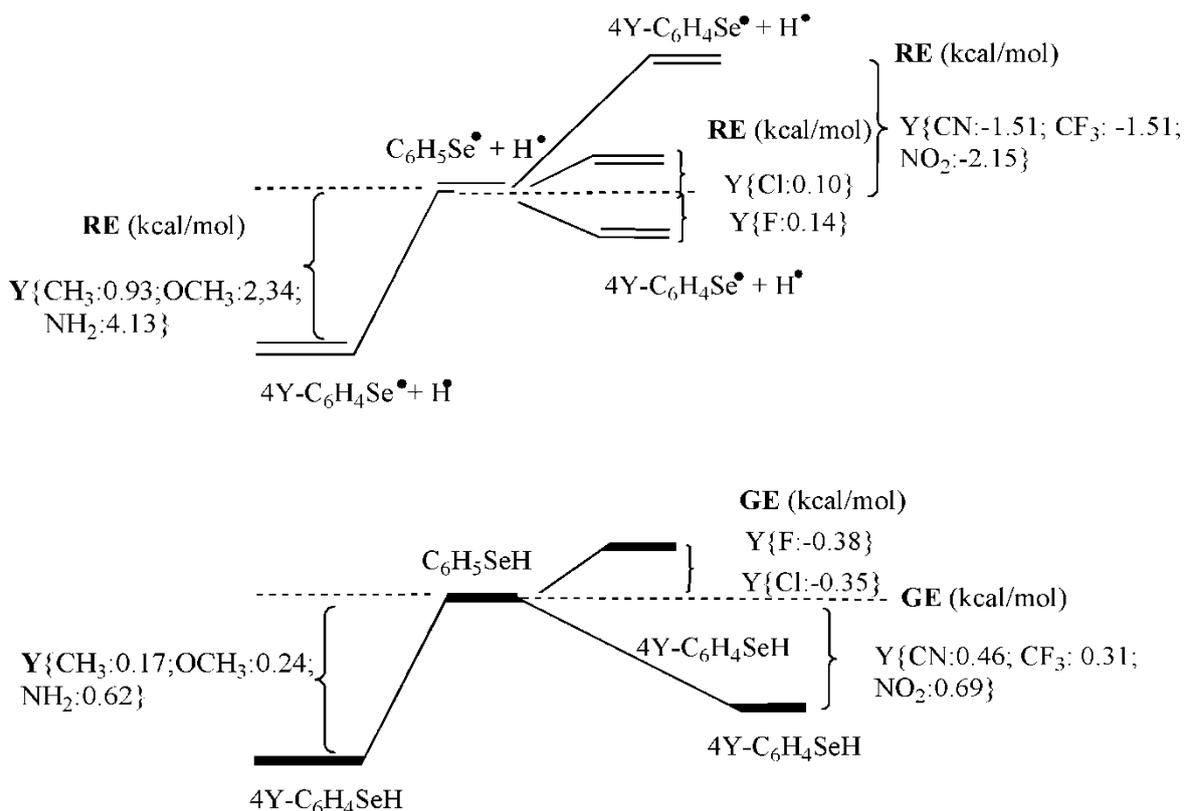


Figure 4: Calculated GE and RE for $4Y-C_6H_4Se-H$ with $Y = H, F, Cl, CH_3, OCH_3, NH_2, CF_3, CN, NO_2$. (Reprinted from Ref. [48])

of the S pattern, both toluenes and phenylsilanes do not inhibit of the good correlation between $BDE(C-H)$ or $BDE(Si-H)$ with the Hammett constants. The correlations between the Hammett σ_p^+ and σ_m constants and $BDE(C-H)$ s and $BDE(Si-H)$ s in substituted toluenes and phenylsilanes were displayed in figure 5.

For *para* substitution, in case of toluene and phenylsilane, the linear regressions between $BDE(X-H)$ s ($X = CH_2$ and SiH_2) with σ_p^+ shown in figure 5 are very poor. However, for *meta*

substitution, the correlation is slightly better for $C-H$ bond but still very poor for $Si-H$ bond. The Hammett regression result for the $BDE(C-H)$ changes *versus* σ_m constant is expressed in equation (13).

$$BDE(C-H) = 0.9699x + 89.897 R^2 = 0.8184 \quad (13)$$

This leads to a conclusion that the direction and magnitude of the effect of Y- substituents on the X-H bonds in $4Y-$ and $3Y-C_6H_4XH$ compounds have some dependence on the polarity of the X-H bond undergoing homolytic dissociation [81].

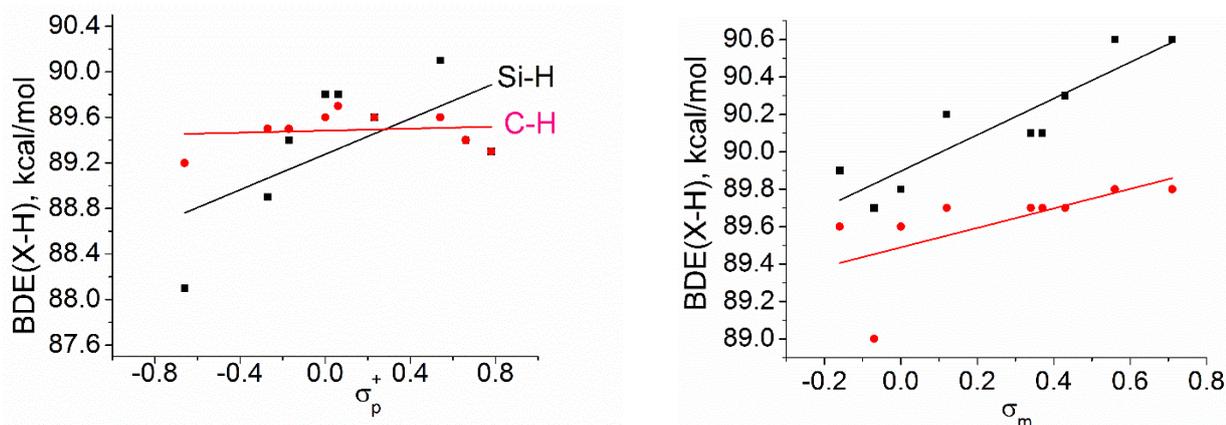


Figure 5: Plot of $BDE(X-H)$ of the $4Y-C_6H_4X-H$ and $3Y-C_6H_4X-H$ ($X = CH_2, SiH_2$) with the Hammett constant σ_p^+ and σ_m , respectively

5. CONCLUSION AND OUTLOOK

Up today, computational chemistry has evolved into a powerful tool to be used to study in many areas. In this review, the computational quantum chemical methods based on B3LYP functional have been applied to determine the bond dissociation enthalpies of a variety of substituted benzenes derivatives. In searching for suitable methods to be used in the evaluation of BDEs, the good performance of the density functional theory using restricted open-shell formalism ROB3LYP at the basis set of 6-311++G(2df,2p) in conjunction with geometries optimized at the B3LYP/6-311G(d,p) level has been demonstrated by its capacity to reproduce the BDEs of a series of X–H bond types in a range of substituted aromatic compounds YC_6H_4XH (X= O, S, Se, NH, PH, CH₂ and SiH₂; Y = H, F, Cl, CH₃, OCH₃, NH₂, CF₃, CN and NO₂). The calculated BDEs of the studied benzene derivatives have been reviewed and hence the model chemistry of ROB3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p) is defined as a convenient and economic manner, but with reliable results as compared to available experimental values with the accuracy of 1.0-2.0 kcal/mol.

Depending on the nature of centered atom X, which is polar or non-polar, the behavior of substituents at the *para* and *meta* position is quite different. The success of correlation between Hammett constants was found for substituted benzene derivatives with hetero atom X belongs to class “O” category including phenols, thiophenols, benzeneselenols, anilines and phenylphosphines. In contrast, the poor correlations are seen between BDE values of the C–H and Si–H bonds in toluenes and phenylsilanes, respectively with the Hammett substituent constants at the *para* and *meta* position of aromatic ring. Small effects of the Y-substituents have similarly observed for both C–H and Si–H bonds in substituted toluenes and phenylsilanes.

Acknowledgements. *This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number “104.06-2016.03” (3/2017/104/HĐTN).*

REFERENCES

1. Z. Rappoport. *The Chemistry of Phenols, 2 Volume Set*: John Wiley & Sons; 2004.
2. K. Ingold: *60 Years of Research on Free Radical Physical Organic Chemistry*. In: *The Foundations of Physical Organic Chemistry: Fifty Years of the James Flack Norris Award*. ACS Publications, 223-250 (2015).
3. H. Yuzawa, M. Aoki, H. Itoh, H. Yoshida. *Adsorption and photoadsorption states of benzene derivatives on titanium oxide studied by NMR*, *The Journal of Physical Chemistry Letters*, **2(15)**, 1868-1873 (2011).
4. S. P. Pogorelova, A. B. Kharitonov, I. Willner, C. N. Sukenik, H. Pizem, T. Bayer. *Development of ion-sensitive field-effect transistor-based sensors for benzylphosphonic acids and thiophenols using molecularly imprinted TiO₂ films*, *Analytica chimica acta*, **504(1)**, 113-122 (2004).
5. R. S. Sengar, V. N. Nemykin, P. Basu. *Electronic properties of para-substituted thiophenols and disulfides from ¹³C NMR spectroscopy and ab initio calculations: relations to the Hammett parameters and atomic charges*, *New Journal of Chemistry*, **27(7)**, 1115-1123 (2003).
6. I. E. H.-G. Franck, J. W. Stadelhofer. *Production and uses of benzene derivatives*. In: *Industrial Aromatic Chemistry*, Springer, 132-235 (1988).
7. S. W. Benson. *Thermochemical kinetics*, Wiley, 1976.
8. IUPAC. *Compendium of Chemical Terminology, 2nd ed.* In: Blackwell Scientific Publications, Oxford 1997.
9. S. J. Blanksby, G. B. Ellison. *Bond dissociation energies of organic molecules*, *Accounts of chemical research*, **36(4)**, 255-263 (2003).
10. J. H. Wang, D. Domin, B. Austin, D. Y. Zubarev, J. McClean, M. Frenklach, T. A. Cui, W. A. Lester. *A Diffusion Monte Carlo Study of the O-H Bond Dissociation of Phenol*, *Journal of Physical Chemistry A*, **114(36)**, 9832-9835 (2010).
11. L. A. Curtiss, J. A. Pople. *Recent Advances in Computational Thermochemistry and Challenges for the Future*. In: National Research Council (US) Chemical Sciences Roundtable. Impact of Advances in Computing and Communications Technologies on Chemical Science and Technology: Report of a Workshop. Washington (DC). National Academies Press (US), 26-34 (1999).
12. T. M. Krygowski, B. T. Stepień. *Sigma-and pi-electron delocalization: focus on substituent effects*, *Chemical reviews*, **105(10)**, 3482-3512 (2005).
13. E. R. Johnson, O. J. Clarkin, G. A. DiLabio. *Density Functional Theory Based Model Calculations for Accurate Bond Dissociation Enthalpies. 3. A Single Approach for X–H, X–X, and X–Y (X, Y = C, N, O, S, Halogen) Bonds*, *The Journal of Physical Chemistry A*, **107(46)**, 9953-9963 (2003).
14. X. -Q. Yao, X. -J. Hou, H. Jiao, H. -W. Xiang, Y. -W. Li. *Accurate calculations of bond dissociation enthalpies with density functional methods*, *The*

- Journal of Physical Chemistry A, **107(46)**, 9991-9996 (2003).
15. Y. -R. Luo. *Handbook of bond dissociation energies in organic compounds*: CRC press (2002).
 16. J. Kerr. *Bond dissociation energies by kinetic methods*, Chemical reviews, **66(5)**, 465-500 (1966).
 17. W. M. Haynes. *CRC handbook of chemistry and physics*: CRC press (2014).
 18. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson. *Gaussian 09, Revision A*, Gaussian, Inc., Wallingford CT (2009).
 19. L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, J. A. Pople. *Gaussian-1 theory of molecular energies for second-row compounds*, The Journal of Chemical Physics, **93(4)**, 2537-2545 (1990).
 20. L. R. Peebles, P. Marshall. *High-accuracy coupled-cluster computations of bond dissociation energies in SH, H₂S, and H₂O*, The Journal of Chemical Physics, **117(7)**, 3132-3138 (2002).
 21. P. Mulder, H.-G. Korth, D.A. Pratt, G.A. DiLabio, L. Valgimigli, G. Pedulli, K. Ingold. *Critical re-evaluation of the O-H bond dissociation enthalpy in phenol*, The Journal of Physical Chemistry A, **109(11)**, 2647-2655 (2005).
 22. G. da Silva, C. -C. Chen, J. W. Bozzelli. *Bond dissociation energy of the phenol OH bond from ab initio calculations*, Chemical Physics Letters, **424(1)**, 42-45 (2006).
 23. Y. Zhao, D.G. Truhlar, *How well can new-generation density functionals describe the energetics of bond-dissociation reactions producing radicals?*, The Journal of Physical Chemistry A, **112(6)**, 1095-1099 (2008).
 24. M. D. Wodrich, C. Corminboeuf, P. R. Schreiner, A.A. Fokin, P.v.R. Schleyer. *How accurate are DFT treatments of organic energies?*, Organic letters, **9(10)**, 1851-1854 (2007).
 25. V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew. *Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes*, The Journal of Chemical Physics, **119(23)**, 12129-12137 (2003).
 26. R. D. Bach, P. Y. Ayala, H. Schlegel. *A reassessment of the bond dissociation energies of peroxides. An ab initio study*, Journal of the American Chemical Society, **118(50)**, 12758-12765 (1996).
 27. C. Baciu, J. W. Gault. *An assessment of theoretical methods for the calculation of accurate structures and SN bond dissociation energies of S-nitrosothiols (RSNOs)*, The Journal of Physical Chemistry A, **107(46)**, 9946-9952 (2003).
 28. A. S. Menon, G. P. Wood, D. Moran, L. Radom. *Bond dissociation energies and radical stabilization energies: An assessment of contemporary theoretical procedures*, The Journal of Physical Chemistry A, **111(51)**, 13638-13644 (2007).
 29. A. K. Chandra, P. -C. Nam, M. T. Nguyen. *The S-H bond dissociation enthalpies and acidities of para and meta substituted thiophenols: a quantum chemical study*, The Journal of Physical Chemistry A, **107(43)**, 9182-9188 (2003).
 30. Y. Feng, L. Liu, J. -T. Wang, H. Huang, Q.-X. Guo. *Assessment of experimental bond dissociation energies using composite ab initio methods and evaluation of the performances of density functional methods in the calculation of bond dissociation energies*, Journal of chemical information and computer sciences, **43(6)**, 2005-2013 (2003).
 31. M. -J. Li, L. Liu, Y. Fu, Q. -X. Guo. *Development of an ONIOM-G3B3 Method to Accurately Predict C-H and N-H Bond Dissociation Enthalpies of Ribonucleosides and Deoxyribonucleosides*, The Journal of Physical Chemistry B, **109(28)**, 13818-13826 (2005).
 32. X. -Q. Yao, X. -J. Hou, G. -S. Wu, Y. -Y. Xu, H. -W. Xiang, H. Jiao, Y. -W. Li. *Estimation of C-C bond dissociation enthalpies of large aromatic hydrocarbon compounds using DFT methods*, The Journal of Physical Chemistry A, **106(31)**, 7184-7189 (2002).
 33. I. Y. Zhang, J. Wu, Y. Luo, X. Xu. *Accurate bond dissociation enthalpies by using doubly hybrid XYG3 functional*, Journal of computational chemistry, **32(9)**, 1824-1838 (2011).
 34. M. -J. Li, L. Liu, Y. Fu, Q. -X. Guo. *Accurate bond dissociation enthalpies of popular antioxidants predicted by the ONIOM-G3B3 method*, Journal of Molecular Structure: THEOCHEM, **815(1)**, 1-9 (2007).
 35. G. DiLabio, D. Pratt. *Density Functional Theory Based Model Calculations for Accurate Bond Dissociation Enthalpies. 2. Studies of X-X and X-Y (X, Y = C, N, O, S, Halogen) Bonds*, The Journal of Physical Chemistry A, **104(9)**, 1938-1943 (2000).
 36. S. L. Khursan. *Homodesmotic method of determining the O-H bond dissociation energies in phenols*, Kinetics and Catalysis, **57(2)**, 159-169 (2016).
 37. N. M. Khlestov, A. N. Shendrik. *Quantum-chemical DFT calculations of the energies of the O-H bond of phenols*, Theoretical and Experimental Chemistry, **46(5)**, 279-283 (2010).
 38. C. Marteau, R. Guitard, C. Penverne, D. Favier, V. Nardello-Rataj, J. M. Aubry. *Boosting effect of ortho-propenyl substituent on the antioxidant activity of natural phenols*, Food Chemistry, **196**, 418-427 (2016).
 39. M. S. Miranda, J. da Silva, J. F. Liebman. *Gas-phase thermochemical properties of some tri-substituted phenols: A density functional theory study*, Journal of Chemical Thermodynamics, **80**, 65-72 (2015).

40. C. A. McFerrin, R. W. Hall, B. Dellinger. *Ab initio study of the formation and degradation reactions of chlorinated phenols*, Journal of Molecular Structure-Theochem, **902(1-3)**, 5-14 (2009).
41. J. Shi, S. Liang, Y. S. Feng, H. J. Wang, Q. X. Guo. *Heterocyclic analogs of phenol as novel potential antioxidants*, Journal of Physical Organic Chemistry, **22(11)**, 1038-1047 (2009).
42. H. -J. Wang, Y. Fu. *Designing new free-radical reducing reagents: Theoretical study on Si-H bond dissociation energies of organic silanes*, Journal of Molecular Structure: THEOCHEM, **893(1)**, 67-72 (2009).
43. B. Chan, L. Radom. *BDE261: a comprehensive set of high-level theoretical bond dissociation enthalpies*, The Journal of Physical Chemistry A, **116(20)**, 4975-4986 (2012).
44. P. R. Rablen, J. F. Hartwig. *Accurate borane sequential bond dissociation energies by high-level ab initio computational methods*, Journal of the American Chemical Society, **118(19)**, 4648-4653 (1996).
45. J. Stewart. *Reviews in Computational Chemistry*, Reviews of Computational Chemistry (1990).
46. G. DiLabio, D. Pratt, A. LoFaro, J. Wright. *Theoretical study of X-H bond energetics (X = C, N, O, S): application to substituent effects, gas phase acidities, and redox potentials*, The Journal of Physical Chemistry A, **103(11)**, 1653-1661 (1999).
47. A. K. Chandra, T. Uchimaru. *The OH bond dissociation energies of substituted phenols and proton affinities of substituted phenoxide ions: A DFT study*, International Journal of Molecular Sciences, **3(4)**, 407-422 (2002).
48. P. C. Nam, M. T. Nguyen. *The Se-H bond of benzeneselenols (ArSe-H): Relationship between bond dissociation enthalpy and spin density of radicals*, Chemical Physics, **415**, 18-25 (2013).
49. P. -C. Nam, M. T. Nguyen, A. K. Chandra. *Effect of Substituents on the P-H Bond Dissociation Enthalpies of Phenylphosphines and Proton Affinities of Phenylphosphine Anions: A DFT Study*, The Journal of Physical Chemistry A, **108(51)**, 11362-11368 (2004).
50. P. -C. Nam, M. T. Nguyen, A. K. Chandra. *The C-H and α (C-X) Bond Dissociation Enthalpies of Toluene, C₆H₅-CH₂X (X = F, Cl), and Their Substituted Derivatives: A DFT Study*, The Journal of Physical Chemistry A, **109(45)**, 10342-10347 (2005).
51. P. C. Nam, M. T. Nguyen, A. K. Chandra. *Theoretical Study of the Substituent Effects on the S-H Bond Dissociation Energy and Ionization Energy of 3-Pyridinethiol: Prediction of Novel Antioxidant*, The Journal of Physical Chemistry A, **110(37)**, 10904-10911 (2006).
52. Pham Thi Quynh Ty, P.C. Nam. *(RO)B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p): Reliable dft methods for determining bond dissociation enthalpies*, Tạp chí Khoa học và Công nghệ đại học Đà Nẵng (2011).
53. D. Wayner, E. Lusztyk, K. Ingold, P. Mulder. *Application of Photoacoustic Calorimetry to the Measurement of the O-H Bond Strength in Vitamin E (α - and δ -Tocopherol) and Related Phenolic Antioxidants I*, The Journal of organic chemistry, **61(18)**, 6430-6433 (1996).
54. D. Wayner, E. Lusztyk, D. Pagé, K. Ingold, P. Mulder, L. Laarhoven, H. Aldrich. *Effects of solvation on the enthalpies of reaction of tert-butoxyl radicals with phenol and on the calculated OH bond strength in phenol*, Journal of the American Chemical Society, **117(34)**, 8737-8744 (1995).
55. V. F. DeTuri, K. M. Ervin. *Proton transfer between Cl⁻ and C₆H₅OH. O-H bond energy of phenol*, International Journal of Mass Spectrometry and Ion Processes, **175(1-2)**, 123-132 (1998).
56. R. M. Borges dos Santos, J. A. Martinho Simões. *Energetics of the O-H bond in phenol and substituted phenols: a critical evaluation of literature data*, Journal of Physical and Chemical Reference Data, **27(3)**, 707-739 (1998).
57. A. Colussi, F. Zabel, S. Benson. *The very low-pressure pyrolysis of phenyl ethyl ether, phenyl allyl ether, and benzyl methyl ether and the enthalpy of formation of the phenoxy radical*, International Journal of Chemical Kinetics, **9(2)**, 161-178 (1977).
58. D. J. DeFrees, R. T. McIver Jr, W. J. Hehre. *Heats of formation of gaseous free radicals via ion cyclotron double resonance spectroscopy*, Journal of the American Chemical Society, **102(10)**, 3334-3338 (1980).
59. F. Bordwell, J. P. Cheng, J. A. Harrelson. *Homolytic bond dissociation energies in solution from equilibrium acidity and electrochemical data*, Journal of the American Chemical Society, **110(4)**, 1229-1231 (1988).
60. J. A. Walker, W. Tsang. *Single-pulse shock tube studies on the thermal decomposition of n-butyl phenyl ether, n-pentylbenzene, and phenetole and the heat of formation of phenoxy and benzyl radicals*, Journal of Physical Chemistry, **94(8)**, 3324-3327 (1990).
61. M. Lucarini, P. Pedrielli, G.F. Pedulli, S. Cabiddu, C. Fattuoni. *Bond dissociation energies of O-H bonds in substituted phenols from equilibration studies*, The Journal of organic chemistry, **61(26)**, 9259-9263 (1996).
62. F. G. Bordwell, W. -Z. Liu. *Solvent effects on homolytic bond dissociation energies of hydroxylic acids*, Journal of the American Chemical Society, **118(44)**, 10819-10823 (1996).
63. H. -T. Kim, R. J. Green, J. Qian, S. L. Anderson. *Proton transfer in the [phenol-NH₃]⁺ system: An*

- experimental and ab initio study*, The Journal of Chemical Physics, **112(13)**, 5717-5721 (2000).
64. L. A. Angel, K. M. Ervin. *Competitive threshold collision-induced dissociation: Gas-phase acidity and O–H bond dissociation enthalpy of phenol*, The Journal of Physical Chemistry A, **108(40)**, 8346-8352 (2004).
 65. C. Marteau, R. Guitard, C. Penverne, D. Favier, V. Nardello-Rataj, J. -M. Aubry. *Boosting effect of ortho-propenyl substituent on the antioxidant activity of natural phenols*, Food chemistry, **196**, 418-427 (2016).
 66. D. Armstrong, Q. Sun, R. Schuler. *Reduction Potentials and Kinetics of Electron Transfer Reactions of Phenylthiyl Radicals: Comparisons with Phenoxyl Radicals 1*, The Journal of Physical Chemistry, **100(23)**, 9892-9899 (1996).
 67. D. F. McMillen, D. M. Golden. *Hydrocarbon bond dissociation energies*, Annual Review of Physical Chemistry, **33(1)**, 493-532 (1982).
 68. S. Venimadhavan, K. Amarnath, N. G. Harvey, J. P. Cheng, E. M. Arnett. *Heterolysis, homolysis, and cleavage energies for the cation radicals of some carbon-sulfur bonds*, Journal of the American Chemical Society, **114(1)**, 221-229 (1992).
 69. E. T. Denisov, T. Denisova: *Handbook of antioxidants: bond dissociation energies, rate constants, activation energies, and enthalpies of reactions*, vol. 100: CRC press; 1999.
 70. C. F. Correia, R. C. Guedes, R. M. B. dos Santos, B. J. C. Cabral, J. A. M. Simões. *O–H Bond dissociation enthalpies in hydroxyphenols. A time-resolved photoacoustic calorimetry and quantum chemistry study*, Physical Chemistry Chemical Physics, **6(9)**, 2109-2118 (2004).
 71. R. M. Borges dos Santos, V. S. Muralha, C. F. Correia, R. C. Guedes, B. J. Costa Cabral, J. A. Martinho Simões. *S–H bond dissociation enthalpies in thiophenols: a time-resolved photoacoustic calorimetry and quantum chemistry study*, The Journal of Physical Chemistry A, **106(42)**, 9883-9889 (2002).
 72. Q. Zhu, X. -M. Zhang, A. J. Fry. *Bond dissociation energies of antioxidants*, Polymer Degradation and Stability, **57(1)**, 43-50 (1997).
 73. M. Jonsson, J. Lind, T. E. Eriksen, G. Mereny. *Redox and acidity properties of 4-substituted aniline radical cations in water*, Journal of the American Chemical Society, **116(4)**, 1423-1427 (1994).
 74. F. Bordwell, X. M. Zhang, J. P. Cheng. *Bond dissociation energies of the nitrogen-hydrogen bonds in anilines and in the corresponding radical anions. Equilibrium acidities of aniline radical cations*, The Journal of Organic Chemistry, **58(23)**, 6410-6416 (1993).
 75. J. R. Gomes, M. D. Ribeiro da Silva, M. A. Ribeiro da Silva. *Solvent and Structural Effects in the N–H Bond Homolytic Dissociation Energy*, The Journal of Physical Chemistry A, **108(11)**, 2119-2130 (2004).
 76. F. G. Bordwell, J. Cheng. *Substituent effects on the stabilities of phenoxyl radicals and the acidities of phenoxyl radical cations*, Journal of the American Chemical Society, **113(5)**, 1736-1743 (1991).
 77. Z. Li, J. -P. Cheng. *A Detailed Investigation of Substituent Effects on N–H Bond Enthalpies in Aniline Derivatives and on the Stability of Corresponding N-Centered Radicals*, The Journal of organic chemistry, **68(19)**, 7350-7360 (2003).
 78. C. Hansch, A. Leo, R. Taft. *A survey of Hammett substituent constants and resonance and field parameters*, Chemical reviews, **91(2)**, 165-195 (1991).
 79. O. Exner, S. Böhm. *Background of the Hammett Equation As Observed for Isolated Molecules: Meta- and Para-Substituted Benzoic Acids*, The Journal of Organic Chemistry, **67(18)**, 6320-6327 (2002).
 80. K.-S. Song, L. Liu, Q. -X. Guo. *Remote Substituent Effects on N–X (X = H, F, Cl, CH₃, Li) Bond Dissociation Energies in P ara-Substituted Anilines*, The Journal of Organic Chemistry, **68(2)**, 262-266 (2003).
 81. Y. -H. Cheng, X. Zhao, K. -S. Song, L. Liu, Q. -X. Guo. *Remote Substituent Effects on Bond Dissociation Energies of Para-Substituted Aromatic Silanes*, The Journal of Organic Chemistry, **67(19)**, 6638-6645 (2002).

Corresponding author: **Pham Cam Nam**

Department of Chemistry, The University of Danang
 University of Science and Technology
 54, Nguyen Luong Bang, Danang City, Viet Nam
 E-mail: pcnam@dut.udn.vn; Telephone: +84 987873154.