



N–NO₂ bond dissociation energies in acetonitrile: An assessment of contemporary computational methods



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ABSTRACT

The assessment of the N–NO₂ bond dissociation energies (BDEs) was performed by various calculating methods (B3LYP, B3PW91, B3P86, B1LYP, BMK, MPWB1K, PBE0, CBS-4M and M06-2X) at 6-311+G(2d,p) basis set. Compared with the experimental BDEs, the results show that BMK and B3P86 methods reproduce the experimental values well. The mean absolute deviations from the experimental values obtained by BMK and B3P86 methods were 0.5 and 1.5 kcal/mol, respectively. B3LYP, B3PW91, B1LYP, MPWB1K and PBE0 methods underestimated the homolytic N–NO₂ BDEs. B3LYP, B3PW91, B1LYP, M06-2X, CBS-4M methods failed to provide an accurate description of N–NO₂ BDEs for N-Nitrosulfonamide compounds and showed larger mean absolute deviations and maximum deviations. Further, substituent effect based on BMK/6-311+G(2d,p) method was analysis. Natural bond orbital analysis shows that there exist good linear correlations between $E^{(2)}$ of $\text{lpN}_1 \rightarrow \text{BD}^*(\text{O}_1-\text{N}_2)$ and Hammett constants and a better correlation between the BDEs and the second order stabilization energy $E^{(2)}$ of $\text{lpN}_1 \rightarrow \text{BD}^*(\text{O}_1-\text{N}_2)$.

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1. Introduction

Recent discoveries show that the chemistry and biochemistry of NxOy have regained tremendous research attention in the last two decades because of its significant roles in many important natural processes [1]. Nitric oxide (NO) is one of the smallest known biologically active messenger molecules among various kinds of NxOy and plays key roles in regulating many important physiological functions in living bodies [2–5]. Nitrogen dioxide has long been known in chemistry as a strong oxidant and nitrating reagent for organic synthesis, but not until very recently was it found to be associated with many destructive processes in living bodies. The research on the functions of NO₂ and NO₂[−] has started to draw increasing attention recently. Research showed that a wide spectrum of diseases was related to the exogenously and endogenously generated NO₂ [6,7].

In order to understand the mechanistic details of NO₂ or NO₂[−] in chemical or biological processes, the basic information concerning quantitative energetic changes in NO₂[−] related bond cleavage in solution should be of great value because it provides the necessary information on the thermodynamic driving forces of NO₂[−] carrier molecules to release, capture, or transfer an NO₂ (or NO₂[−])

moiety [8]. However, to our knowledge, no systematic work was reported on the theoretical predictions of Y–NO₂ bond energies in solvent system, where the NO₂-related chemical and biological activities are likely to take place. The definite and immediate need of the Y–NO₂ bond energy data bank has deepened our understanding of the board range of NO₂-related activities and stimulated us to extend our current research on NO-related bond energies [9,10] to the important Y–NO₂ bond energies. This kind of bond energy scales should also be useful for the study of stability and shock sensitivity of the Y–NO₂-type energetic materials [11] and for estimating the nitrating ability of nitro-releasing compounds in synthetic chemistry [12].

Sulfonamide is the basis of several groups of drugs, which contains sulfur–oxygen double bond and sulfur–nitrogen single bond. Sulfonamide derivatives can demonstrate synthetic applicability, such as the ability to directly introduce protected nitrogen functionality into a molecule [13]. Recently, Li et al. [8] reported the first series of experimentally determined Y–NO₂ homolytic bond energy scales of some N-Nitrosulfonamide compounds by using titration calorimetry in acetonitrile solution. Up to now, there is no related theoretical investigation for Y–NO₂ homolytic bond energy of the N-Nitrosulfonamide compounds. The ten N-Nitrosulfonamide compounds are 4-MeO-C₆H₄SO₂N(CH₃)NO₂ (C₈H₁₀SO₅N₂), 4-CH₃-C₆H₄SO₂N(CH₃)NO₂ (C₈H₁₀SO₄N₂), C₆H₅SO₂N(CH₃)NO₂ (C₇H₈SO₄N₂), 4-Cl-C₆H₄SO₂N(CH₃)NO₂ (C₇H₇SO₄N₂Cl), 4-Br-C₆H₄SO₂N(CH₃)NO₂ (C₇H₇SO₄N₂Br), 4-NO₂-C₆H₄SO₂N(CH₃)NO₂

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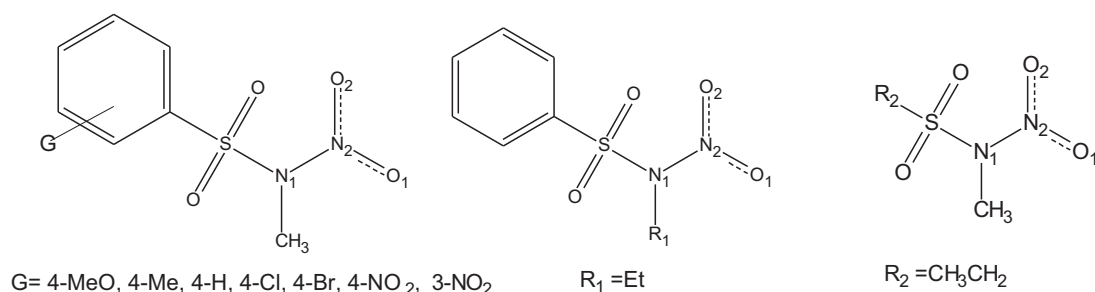


Fig. 1. The structures of the selected N-Nitrosulfonamide compounds.

($\text{C}_7\text{H}_7\text{SO}_6\text{N}_3$), $3\text{-NO}_2\text{-C}_6\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)\text{NO}_2$ ($\text{C}_7\text{H}_7\text{SO}_6\text{N}_3$), $\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{NO}_2$ ($\text{C}_8\text{H}_{10}\text{SO}_4\text{N}_2$), $\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)\text{NO}_2$ ($\text{C}_2\text{H}_6\text{SO}_4\text{N}_2$), $\text{CH}_3\text{CH}_2\text{SO}_2\text{N}(\text{CH}_3)\text{NO}_2$ ($\text{C}_3\text{H}_8\text{SO}_4\text{N}_2$), respectively. The structures of the selected N-Nitrosulfonamide compounds are showed in Fig. 1.

Density functional theory (DFT) is currently more practical for bond dissociation energy (BDE) calculations owing to their favorable scaling and reasonable CPU cost. Among these DFT methods, B3LYP, B3PW91 and B3P86 are highly popular because of their advantages in BDE calculation. The previous research shows that the C–N BDEs for imidazole derivatives computed by B3LYP/6-31G** methods are in excellent agreement with their experimental values [14]. Furthermore, B3P86 values revealed the best agreement with available experimental data in predicting C–NO BDE [9]. However, recent conducted studies from a more general perspective demonstrated that these popular DFT methods could tend to underestimate BDEs by 2–6 kcal/mol [15]. Obviously, these failures are due to deficiencies of the approximate exchange–correlation functional used for different calculating systems. So it is important to shed light on their systematic performance for a particular computational target, particularly for the N–NO₂ BDEs of the title compounds.

In the present work, performance of a variety of DFT functions, including B3LYP, B3PW91, B3P86, B1LYP, BMK, M06-2X, MPWB1K and PBE0, was examined for calculating N–N BDEs for several N-Nitrosulfonamide compounds with the available experimental data [8]. The complete basis set (CBS-4M) method was also used. The focus is to investigate their suitability and identify low-cost alternative methods so as to provide a solid basis for the rapid and accurate estimation of the properties of the N-Nitrosulfonamide compounds in the future.

2. Computational methodology

All calculations were performed with the Gaussian03 computational package [16]. Geometry optimizations and subsequent normal mode analyses at the corresponding equilibrium structures were performed for the products of the different bond scission reactions in which a single NO₂ group is removed from the parent structure. Homolytic reactions were simulated. The equilibrium geometries and bond dissociation energies were obtained at the Becke-style three-parameter Density Function Theory [17] with the Lee–Yang–Parr correlation function (LYP) [18,19], the Perdew–Wang's 91 expression (PW91) [20], Perdew's 86 (P86) [21] and PBE0 method [22]. The two meta GGA functionals (M06-2X [23], MPWB1K [24]) are also used.

The new hybrid meta DFT method MPWB1K has been developed in such a way that the functionals depend on the electron density, density gradient, Hartree–Fock exchange, and the Kohn–Sham orbitals in the form of a kinetic energy density, whereas the functionals of the hybrid DFT depend on the electron density, density

gradient, and Hartree–Fock exchange only [25]. The MPWB1K method, which was developed for kinetics calculations, has been shown to be more accurate than previously introduced MPW1K method [24].

As for the CBS-4M model [25–27], first, a geometry optimization and a zero point energy computations are carried out in Hartree–Fock theory. Then the energy is evaluated with the second order of Møller–Plesset (MP2) theory with a larger basis set and a CBS extrapolation to correct the energy through the second order. The MP4SDQ/6-31G calculation was used to approximate higher orders of contributions. There are also empirical corrections for spin contamination and a size-consistent higher-order correction. It must be noted that the new DFT method, the BMK functional, consists of modified original exchange and correlation functionals. The BMK functional is rather different from the others as it simulates a variable exact exchange by combining exact exchange (42%) and terms depending on the kinetic energy density. This allows it to be developed for various applications, ranging from accurate heat of formation prediction to calculation of rate coefficients [28].

In the PBE0 functional, there is only one coefficient, which is theoretically adjusted to 0.25, reflecting the mix of Hartree–Fock or exact exchange and the DFT exchange which is represented by the PBE density functional [29]. The correlation part is also represented by the PBE correlation functional with coefficient equal to one.

The polarized continuum model (PCM) developed by Tomasi [30–32] was employed. In this PCM model, the atomic radii of the spheres used to build the molecular cavity were adjusted by introducing chemical consideration such as hybridization, formal charge, and first neighbor inductive effect. The effect of the escaped electronic charge outside the cavity was corrected with an additional set of charges on the cavity surface distributed according to the solute electronic density in each point of the surface.

All calculations were performed at the 6-311+G(2d,p) basis set. Frequency calculations were performed at the same level of theory, to confirm the correct nature of the stationary points and to extract the zero-point vibrational energies (ZPE).

Generally, computed BDEs are reported for gas phase conditions and it is expected that these values suffer variation in different environments such as those in living organism. So, it would be interesting to know what happens to these dissociation energies in the presence of a solvent such as acetonitrile.

For N-Nitrosulfonamide compounds studied here, the BDE is defined as the difference between the zero-point-corrected energy of the parent molecule and that of the products of the unimolecular dissociation in which an NO₂ group is removed. For example, for 4-MeO-C₆H₄SO₂N(CH₃)NO₂, the BDE is

$$\text{BDE}_{\text{N-NO}_2} = E(\text{C}_8\text{H}_{10}\text{SO}_3\text{N}) + E(\text{NO}_2) - E(\text{C}_8\text{H}_{10}\text{SO}_5\text{N}_2) \quad (1)$$

Table 1
Computed BDEs (kcal/mol) in MeCN for removal of an NO₂ group in studied molecules by using various density functional theory methods with 6-311+G(2d,p) basis set.

Compound	B3LYP	B3PW91	B3P86	B1LYP	Exp. ^a
4-MeO-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	29.6(7.7)	32.2(5.1)	36.0(1.3)	30.9(6.4)	37.3
4-CH ₃ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	29.1(7.7)	31.8(5.0)	37.0(−0.2)	30.5(6.3)	36.8
C ₆ H ₅ SO ₂ N(CH ₃)NO ₂	32.5(4.1)	31.8(4.8)	35.4(1.2)	30.5(6.1)	36.6
4-Cl-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	28.8(7.5)	31.5(4.8)	35.2(1.1)	30.2(6.1)	36.3
4-Br-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	28.8(7.6)	31.5(4.9)	35.2(1.2)	30.1(6.3)	36.4
4-NO ₂ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	28.3(7.7)	31.0(5.0)	34.7(1.3)	29.6(6.4)	36.0
3-NO ₂ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	28.4(7.7)	31.1(5.0)	34.8(1.3)	29.8(6.3)	36.1
C ₆ H ₅ SO ₂ N(C ₂ H ₅)NO ₂	28.1(9.6)	30.6(7.1)	35.5(2.2)	29.4(8.3)	37.7
CH ₃ SO ₂ N(CH ₃)NO ₂	20.6(16.5)	30.9(6.2)	35.0(2.1)	29.8(7.3)	37.1
CH ₃ CH ₂ SO ₂ N(CH ₃)NO ₂	28.9(9.3)	31.4(6.8)	35.1(3.1)	30.9(7.3)	38.2
Mean absolute deviation	8.5	5.5	1.5	6.7	

The value in the parenthesis is the deviation from computed BDE for experimental one.

^a The data are from Ref.[8].

3. Results and discussion

3.1. The performance of various computational methods for the N–NO₂ BDEs of N-Nitrosulfonamide compounds in acetonitrile

The BDE results computed by using B3LYP, B1LYP, B3P86 and B3PW91 three-parameter hybrid DFT methods with 6-311+G(2d,p) basis set are presented in Table 1. The available experimental values [8] are also included. The BDEs of 10 N-Nitrosulfonamide compounds are compared with the corresponding experimental results for the system.

B1LYP has the low accuracy and performance because of the limitation in theoretical model. It is noted from Table 1 and Fig. 2 that B1LYP method failed to provide an accurate description of N–NO₂ BDEs for N-Nitrosulfonamide compounds. The method deviated from the experimental data by as much as 8.3 kcal/mol, and the mean absolute deviation was 6.7 kcal/mol for B1LYP method. Compared with B1LYP method, the mean absolute deviations of B3LYP and B3PW91 methods are 8.5 and 5.5 kcal/mol, respectively. In addition, the maximum deviations of the two methods are all larger than 7.0 kcal/mol. For B3P86 method, the mean absolute deviation was 1.5 kcal/mol and the maximum deviation was 3.1 kcal/mol, which are smaller than those of B3LYP, B3PW91 and B1LYP methods. Detailed analysis reveals that the B3LYP, B3PW91 and B1LYP methods all underestimate the BDE of the title compounds, while B3P86 method gave both negative and positive deviations.

Table 2 lists the N–NO₂ BDEs calculated by BMK, M06-2X, MPWB1K, PBE1PBE methods with 6-311+G(2d,p) basis set and CBS-4M method.

Here, the performance of M06-2X should be addressed. Zhao and Truhlar calculated the BDEs of C–H, C–C, C–O and C–F bonds by M06-2X method. They thought that M06-2X could provide the best accuracy, compared to other functionals [33]. In our paper, it is noted that M06-2X and CBS-4M methods failed to provide the accurate N–NO₂ BDE and the mean absolute deviations are 6.1 and 7.5 kcal/mol, respectively. Compared with experimental values, MPWB1K and PBE0 methods all gave the positive deviations and the mean absolute deviations were 4.3 and 2.4 kcal/mol, respectively, which is smaller than M06-2X and CBS-4M methods. BMK method generally reproduces experimental values with reasonable accuracy, and the mean absolute deviation versus the experimental values is 0.5 kcal/mol. From Table 2, it is noted that MPWB1K and PBE0 methods underestimate the N–NO₂ BDE, while BMK, M06-2X and CBS-4M methods gave the positive and negative deviations. Obviously, this agrees with previous research asserting that DFT methods usually underestimate BDE systematically.

In summary, these DFT methods and CBS-4M method exhibited different performance for calculating N–NO₂ BDE of the title compounds. BMK/6-311+G(2d,p) and B3P86/6-311+G(2d,p) methods provided accurate values and BMK/6-311+G(2d,p) method was found to be the best method because of the smaller maximum absolute deviation. Here, we must acknowledge that there are insufficient experimental data in the present work, specifically the performance attributes for the particular computational targets.

3.2. Substituent effects on the BDEs of the N–NO₂ bond

From the analysis of section 3.1, comparing the various computational methods, we know that BMK method at 6-311+G(2d,p) basis set is the best procedure to compute the dissociation energies for the N–NO₂ bond in acetonitrile. Using this method, we have studied the substituent effect on the N–NO₂ BDEs for the studied molecules, where substituted groups include both the electron donating and withdrawing groups such as 4-Cl, 4-Br, 4-NO₂, 4-CH₃, 4-CH₃O. The calculated BDEs for the selected compounds are shown in Table 3. The results show that the substituent effects on the BDEs of the selected compounds are insignificant.

Interesting point observed in the selected molecules is the change of BDEs and ΔBDE with the Hammett constants σ_p values of the substituent on the benzene. There exists the good correlation between the N–NO₂ BDE and Hammett constants. The Hammett constants σ_p [34] of OCH₃, CH₃, H, Cl, Br, NO₂ groups are −0.27, −0.17, 0.00, 0.23, 0.23 and 0.78, respectively. It is noted that BDE and ΔBDE decrease with the augment of σ_p values for Y-C₆H₄-SO₂N(CH₃)NO₂. That is to say that the electron

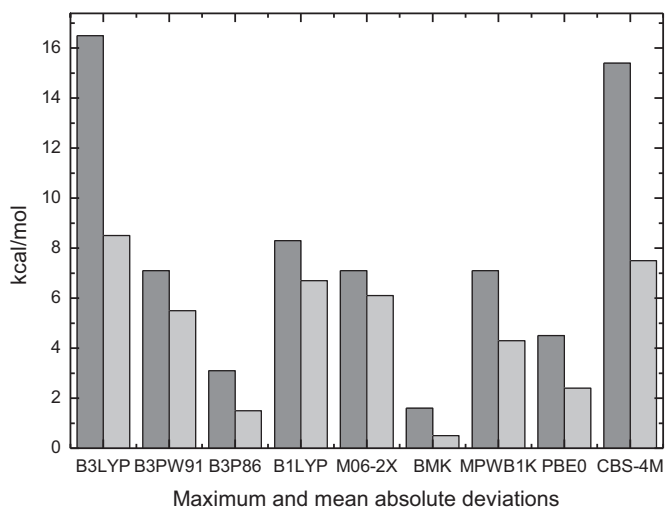


Fig. 2. Overall maximum and mean absolute deviations of various methods. Gray represents maximum deviations and light gray represents mean absolute deviations.

Table 2

Computed BDEs (kcal/mol) in MeCN for removal of an NO₂ group in studied molecules by using BMK, MPWB95, MPWB95 and PBE0 with 6-311+G(2d,p) basis set, and CBS-4M method.

Compound	BMK	M06-2X	MPWB1K	PBE0	CBS-4M	Exp. ^a
4-MeO-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	37.2(0.1)	43.1(−5.8)	33.5(3.8)	34.7(2.6)	45.9(−8.6)	37.3
4-CH ₃ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	36.9(−0.1)	42.7(−5.9)	33.3(3.5)	35.3(1.5)	44.2(−7.4)	36.8
C ₆ H ₅ SO ₂ N(CH ₃)NO ₂	36.9(−0.3)	42.8(−6.2)	33.4(3.2)	35.2(1.4)	52.0(−15.4)	36.6
4-Cl-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	36.4(−0.1)	43.0(−6.7)	32.8(3.5)	34.9(1.4)	43.1(−6.8)	36.3
4-Br-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	36.3(0.1)	42.7(−6.3)	32.1(4.3)	34.5(1.9)	43.4(−7.0)	36.4
4-NO ₂ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	36.4(−0.4)	41.8(5.8)	33.0(3.0)	33.2(2.8)	42.7(−6.7)	36.0
3-NO ₂ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	36.1(0.0)	43.2(−7.1)	32.4(3.7)	34.5(1.6)	45.6(−9.5)	36.1
C ₆ H ₅ SO ₂ N(C ₂ H ₅)NO ₂	36.2(1.5)	42.9(−5.2)	32.6(5.1)	33.7(4.0)	42.5(4.8)	37.7
CH ₃ SO ₂ N(CH ₃)NO ₂	36.4(0.7)	44.1(−7.0)	31.5(5.6)	34.6(2.5)	32.7(4.4)	37.1
CH ₃ CH ₂ SO ₂ N(CH ₃)NO ₂	36.6(1.6)	43.5(−5.3)	31.1(7.1)	33.7(4.5)	42.9(−4.7)	38.2
Mean absolute deviation	0.5	6.1	4.3	2.4	7.5	

The value in the parenthesis is the deviation from computed BDE for experimental one.

^a The data are from Ref.[8].

Table 3

Substituent effects on the BDEs of N–NO₂ homolysis (kcal/mol) by using BMK/6-311+G(2d,p) method for Y–C₆H₄–SO₂N(CH₃)NO₂, C₆H₅–SO₂N(Y)NO₂ and Y–SO₂N(CH₃)NO₂ in acetonitrile.

Y	Y–C ₆ H ₄ –SO ₂ N(CH ₃)NO ₂		Y	C ₆ H ₅ –SO ₂ N(Y)NO ₂	
	BDE	ΔBDE		BDE	ΔBDE
4-OCH ₃	37.2	0.3	Methyl	36.6	0.0
4-CH ₃	36.9	0.0	Ethyl	36.2	−0.4
4-H	36.9	0.0			
4-Cl	36.4	−0.5			
4-Br	36.3	−0.6			
4-NO ₂	36.4	−0.5			

donating group such as 4-CH₃O increases the BDE of the parent C₆H₅–SO₂N(CH₃)NO₂, while electron withdrawing group such as 4-NO₂, decreases the BDE of the parent C₆H₅–SO₂N(CH₃)NO₂, because these groups always destabilizes a radical. Fig. 3 plotted the correlation between the N–NO₂ BDE and Hammett constants for Y–C₆H₄–SO₂N(CH₃)NO₂ and the coefficient is −0.90. For C₆H₅–SO₂N(Y)NO₂, The Hammett constant [34] of methyl and Ethyl groups are −0.17 and −0.15, respectively. Obviously, the BDE decreases with the augment of Hammett constants σ_p values, which is consistent with the conclusion obtained from the analysis of Y–C₆H₄–SO₂N(CH₃)NO₂ method.

3.3. Natural bond orbital analysis

The NBO analysis provides an efficient method for studying intra- and inter-molecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron orbitals, acceptor orbitals and the interacting stabilization energy that resulted from the second-order microdisturbance theory are

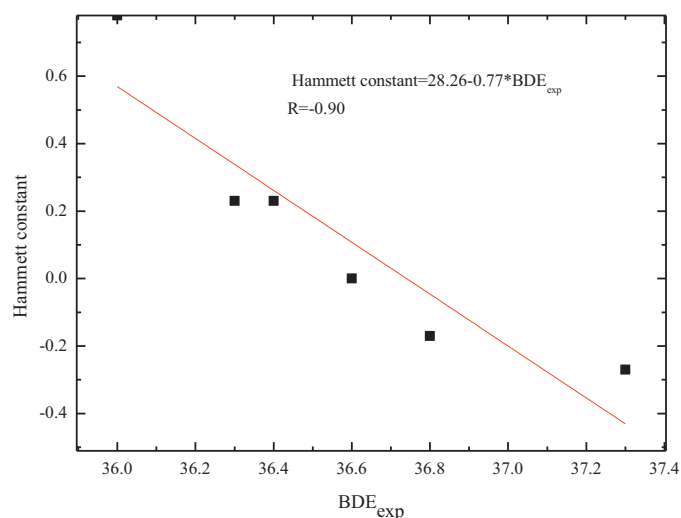


Fig. 3. The correlation between N–NO₂ BDE and Hammett constants for Y–C₆H₄–SO₂N(CH₃)NO₂.

reported [35,36]. The larger the $E^{(2)}$ value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater extent of conjugation of the whole system. Delocalization of the electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been carried out at BMK/6-311+G(2d,p) level in order to elucidate the intramolecular rehybridization and delocalization of electron density within the molecule. The important second order stabilization energies $E^{(2)}$ are reported in Table 4.

Table 4

The second-order perturbation theory analysis of Fock matrix on NBO basis at BMK/6-311+G(2d,p) method.

Entry	Compound	lpN ₁ → BD*(O ₁ –N ₂)	$E(j) - E(i)^a$ (a.u.)	$F(i,j)^b$ (a.u.)
1	4-MeO-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	51.33	0.05	0.085
2	4-CH ₃ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	40.33	0.33	0.111
3	C ₆ H ₅ SO ₂ N(CH ₃)NO ₂	38.95	0.33	0.110
4	4-Cl-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	24.01	0.46	0.097
5	4-Br-C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	24.15	0.45	0.097
6	4-NO ₂ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	11.07	3.90	0.421
7	3-NO ₂ -C ₆ H ₄ SO ₂ N(CH ₃)NO ₂	10.21	0.61	0.071
8	C ₆ H ₅ SO ₂ N(C ₂ H ₅)NO ₂	46.95	0.29	0.113
9	CH ₃ SO ₂ N(CH ₃)NO ₂	10.00	0.98	0.091
10	CH ₃ CH ₂ SO ₂ N(CH ₃)NO ₂	9.74	0.98	0.090

^a Energy difference between donor and acceptor i and j NBO orbital.

^b $F(i,j)$ is the Fock matrix element between i and j NBO orbitals.

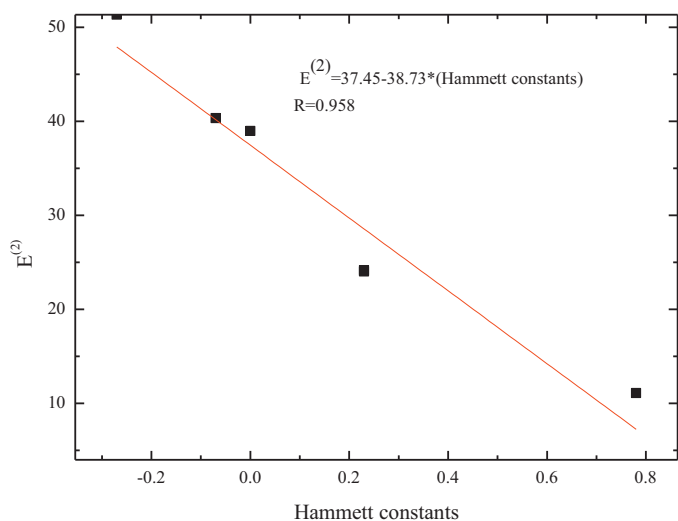


Fig. 4. Dependence of $E^{(2)}$ on Hammett constants for Y-C₆H₄-SO₂N(CH₃)NO₂ in acetonitrile solution.

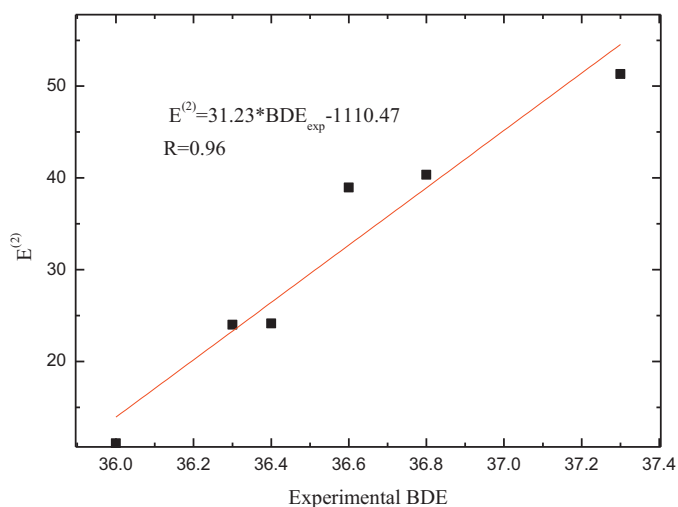


Fig. 5. Dependence of the difference of $E^{(2)}$ on experimental BDE for Y-C₆H₄-SO₂N(CH₃)NO₂ in acetonitrile solution.

From Table 4, we can see that the second order stabilization energy $E^{(2)}$ of 4-MeO-C₆H₄SO₂N(CH₃)NO₂ is the biggest among the studied compounds. This shows that the interaction between electron donors and electron acceptors, $\text{IpN}_1 \rightarrow \text{BD}^*(\text{O}_1-\text{N}_2)$, is very strong, which results in a shorter N_1-N_2 bond length. The Hammett constants [34] of OCH₃, CH₃, H, Cl, Br, NO₂ groups are -0.27, -0.07, 0.00, 0.23, 0.23, 0.78, respectively. From the data in Table 4, it is noted that the second order stabilization energy $E^{(2)}$ of $\text{IpN}_1 \rightarrow \text{BD}^*(\text{O}_1-\text{N}_2)$ is successfully correlated with Hammett constants. Fig. 4 gives the correlation between $E^{(2)}$ of $\text{IpN}_1 \rightarrow \text{BD}^*(\text{O}_1-\text{N}_2)$ and Hammett constants.

In addition, it is noted that BDEs of the title compounds have better linear correlation with the second order stabilization energy $E^{(2)}$ of $\text{IpN}_1 \rightarrow \text{BD}^*(\text{O}_1-\text{N}_2)$. The experimental BDE values of title compounds are plotted against the second order stabilization energies $E^{(2)}$ in Fig. 5. The correlation coefficient reached 0.96.

4. Conclusion

In this paper, a systematic test has been performed to study the performance of various DFT methods and CBS-4M method for N-NO₂ BDE calculation for N-Nitrosulfonamide compounds. Based

on the present computational results, some conclusions could be drawn as follows:

- (1) Upon the calculation of the homolytic BDE of the N-NO₂ bond, BMK/6-311+G(2d,p) reproduces experimental data with reasonable accuracy, and the mean absolute deviation versus the experiment is 0.5 kcal/mol.
- (2) Our calculations agree with previous research asserting that DFT methods usually underestimate BDE systematically.
- (3) The substituent effect shows that the electron donating group such as 4-CH₃O increases the BDE of the parent C₆H₅-SO₂N(CH₃)NO₂, while electron withdrawing group such as 4-NO₂, decreases the BDE of the parent C₆H₅-SO₂N(CH₃)NO₂, because these groups always destabilizes a radical.
- (4) There exist a good linear correlation between $E^{(2)}$ and Hammett constants and a better correlation between the BDEs and the second order stabilization energy $E^{(2)}$ of $\text{IpN}_1 \rightarrow \text{BD}^*(\text{O}_1-\text{N}_2)$.

We believe that such bond information should be useful in understanding the biological functions of nitrogen dioxide, especially its reactions with amino acids in vivo.

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