

Quantum-chemical study of C—H bond dissociation enthalpies of various small non-aromatic organic molecules

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Abstract: In this work, C—H bond dissociation enthalpies (BDE) and vertical ionization potentials (IP) for various hydrocarbons and ketones were calculated using four density functional approaches. Calculated BDEs and IPs were correlated with experimental data. The linearity of the corresponding dependences can be considered very good. Comparing two used functionals, B3LYP C—H BDE values are closer to experimental results than PBE0 values for both used basis sets. The 6-31G* basis set employed with both functionals, gives the C—H BDEs closer to the experimental values than the 6-311++G** basis set. Using the obtained linear dependences $BDE_{\text{exp}} = f(BDE_{\text{calc}})$, the experimental values of C—H BDEs for some structurally related compounds can be estimated solely from calculations. As a descriptor of the C—H BDE, the IPs and ^{13}C NMR chemical shifts have been investigated using data obtained from the B3LYP/6-31G* calculations. There is a slight indication of linear correlation between IPs and C—H BDEs in the sets of simple alkanes and alkenes/cycloalkenes. However, for cycloalkanes and aliphatic carbonyl compounds, no linear correlation was found. In the case of the ^{13}C NMR chemical shifts, the correlation with C—H BDEs can be found for the sets of alkanes and cycloalkanes, but for the other studied molecules, no trends were detected.

Keywords: BDE, NMR chemical shift, alkanes, alkenes, descriptor, radical scavenging

Introduction

The formation and cleavage of bonds is the basis of all chemical transformations. A sound knowledge of the energies required to break bonds and the energies released upon their formation is fundamental for understanding chemical processes (Benson 1976). The energy required for the homolytic R—H bond cleavage is called the bond dissociation enthalpy (BDE) and it corresponds to the reaction enthalpy of the following chemical process



It is given by Eq. 2

$$\text{BDE} = H(\text{R}^{\bullet}) + H(\text{H}^{\bullet}) - H(\text{RH}) \quad (2)$$

where the $H(\text{R}^{\bullet})$ stands for the total enthalpy of the radical, the $H(\text{H}^{\bullet})$ for the total enthalpy of the abstracted hydrogen atom and the $H(\text{RH})$ is the total enthalpy of the molecule. In many types of natural compounds, the BDE of specific bond is one of the most important parameters characterizing their biological effects, e.g. antioxidant or radical scavenging action (Bordwell et al. 1994, Pratt et al. 2004).

The values of BDE can be determined by various experimental methods in gas or solution phase utilizing different physico-chemical principles. Ruscic et al. (Ruscic et al. 1989) employed photoionization mass spectrometry. Target species were dissociatively ionized in the spectrometer and the gas-phase

BDE was obtained as the sum of the energies of two individual reactions. Next, Ervin applied acidity/electron affinity cycle to extract gas-phase BDEs. This method is based on heterolytic bond cleavage. BDE is then calculated by summation of energies for three reactions (Ervin 2001). Radical kinetics uses the forward and reverse rate constants measured to determine BDEs (Seakins et al. 1992). Bordwell's et al. electrochemical approach (Bordwell et al. 1993) applies the equilibrium acidity and oxidation potential values of the conjugated anion for BDE determination. Jonsson et al. carried out pulse radiolysis experiments in water (Jonsson et al. 1994). McFaul et al. employed photoacoustic calorimetry (McFaul et al. 1997) to determine gas-phase BDEs. Thermodynamic cycle method (Zhu et al. 1997) gives almost identical results as Bordwell's et al. electrochemical approach, because this method uses the equilibrium acidities and oxidation potentials of the conjugated anions measured in DMSO, too. The quantum chemistry combined with the computational chemistry becomes a suitable tool for research of wide range of molecular properties. It can serve for calculation of quantities, which are hardly measurable, as well as for predictions of trends between them. However, calculations of larger molecules (more than 50 non-hydrogen atoms) often call for a large computational time. Therefore, it is necessary to choose an appropriate treatment which represents a reasonable compro-

mise between the computational time and the accuracy of results. In this context, the systematic calculations performed for the set of model compounds are of importance. These calculations are directly connected with the choice of the suitable quantum chemical approach (*ab initio* or density functional theory) and basis set selection. Then, the comparison of obtained theoretical results with available experimental data enables to assess the reliability of chosen quantum chemical method. In addition, appropriately chosen set of model molecules allows to find relationships between molecular structure and the molecular reactivity or physical properties. In the case of the model antioxidant compounds, the theoretical calculations allowed to extract some descriptors linearly correlating with BDEs. In the work of Klein et al. (Klein et al. 2006) it was clearly shown that N—H BDEs of substituted anilines, O—H BDEs of substituted phenols and S—H BDEs of substituted thiophenols correlate with vertical ionization potential (IP) satisfactorily. The work of Klein and Lukeš (Klein and Lukeš 2006) revealed good linearity of O—H BDE = $f(R(C—O))$ dependence, where $R(C—O)$ is phenolic C—O bond length in substituted phenols. Linearity of N—H BDE = $f(R(C—N))$ dependence, where $R(C—N)$ is C—N bond length in substituted anilines, has been also assessed as satisfactory by Vagánek et al. (Vagánek et al. 2013).

Although the literature clearly shows that number of theoretical and experimental studies focused on the homolytic C—H bond cleavage is low in comparison to reports on the N—H or O—H bond dissociation, importance of this process in biological systems is indisputable. The energetics of the homolytic C—H bond dissociation is crucial in many biomolecules (e.g. carotenoids, sterols) consisting of linear or cyclic hydrocarbons. With respect to the above mentioned facts, the main goal of this work is to assess the suitability of two commonly used density functional approaches for C—H BDE calculations in the set of selected simple alkanes, alkenes, cycloalkanes, cycloalkenes, ketones, cyclic ketones and acetaldehyde. Calculated gas-phase BDEs will be compared with available experimental or theoretical results. We will also investigate the correlation between the C—H BDEs and ^{13}C NMR chemical shifts for the carbon atom, where the hydrogen atom will be abstracted. To our knowledge, there are not available studies trying to correlate BDEs with NMR chemical shifts.

Computational details

All calculations were performed using Gaussian 03 program package (Frisch et al. 2003).

The geometry of each compound and radical structure was optimized in the gas phase using density functional theory (DFT) method with B3LYP (Becke's three parameter Lee-Yang-Parr) (Lee et al. 1988) and PBE0 (Perdew-Burke-Ernzerhof) (Adamo and Barone 1999) functionals without any constraints (energy cut-off of 10^{-5} kJ mol $^{-1}$, final RMS energy gradient under 0.01 kJ mol $^{-1}$ Å $^{-1}$). For the species having more conformers, all conformers were investigated. B3LYP and PBE0 functionals represent widely applied approaches for the theoretical study of reaction enthalpies. For mono-substituted phenols, thiophenols and anilines, it has been found that B3LYP functional provided BDEs in very good accordance with available experimental and/or theoretical results (Klein et al. 2006, Klein and Lukeš 2006, Rimarčík et al. 2011, Vagánek et al. 2013). PBE0 functional is able to provide bond cleavage energetics and physico-chemical properties of small and medium-size molecules in very good agreement with experimental data and computationally more demanding methods (Adamo et al. 1999, Adamo and Barone 1999, Rimarčík et al. 2008, Saracino et al. 2003, Vagánek et al. 2013), too. Calculations were performed in the 6-31G* (Rassolov et al. 2001) and 6-311++G** (Binkley et al. 1980) basis sets. B3LYP/6-311++G** and PBE0/6-311++G** results serve as the benchmark calculations in this work. The optimized structures were confirmed to be real minima by frequency analysis (no imaginary frequency). All enthalpies were calculated for 298.15 K. Total enthalpies of the hydrogen atom, $H(\text{H}^{\bullet})$, used in BDEs calculation from Eq. 2, are -1314.96 (B3LYP/6-311++G**), -1312.04 (PBE0/6-311++G**), -1309.75 (B3LYP/6-31G*) and -1306.69 (PBE0/6-31G*) in kJ mol $^{-1}$. For gas-phase ^{13}C NMR chemical shifts calculation the GIAO (McWeeny 1962, Ditchfield 1974, Dodds et al. 1980, Wolinsky et al. 1990) method at the B3LYP/6-31G* level was employed.

Results and discussion

Calculation of BDEs

Some molecules from selected set contain two or more different C—H bonds, therefore their BDEs are different too. In each molecule, we have focused on the bond with the lowest BDE (see Fig. 1), for which experimental values are available. The BDE value is tightly associated with the stability of formed radical. The more stable radical is formed, the lower BDE value of given bond is. In general, if two or more different C—H bonds are present in a molecule, then the one on the carbon with the larg-

est number of alkyl groups attached has the lowest BDE. It is caused by the stabilization of formed radical by inductive effects of alkyl groups. In the case of a double bond presence in a molecule, the C—H bond in α -position to double bond has the lowest BDE because of unpaired electron conjugation with π -electrons of the double bond (Clayden et al. 2001, Lengyel et al. 2012).

Experimental and calculated C—H BDE values are summarized in Tab. 1. While almost all calculated values are underestimated in comparison to the experiment, B3LYP/6-31G* values are closest to the experimental ones. On the other hand, values obtained by PBE0/6-311++G** approach are the mostly underestimated ones in average. For this set of molecules, B3LYP functional gives results which are closer to experimental data in comparison to PBE0 results. Tab. 1 shows that the differences between B3LYP and PBE0 C—H BDE values are in the 2.5–7.2 kJ mol⁻¹ range for both applied basis sets. Vagánek et al. (Vagánek et al. 2013) found that the differences between PBE0/6-311++G** N—H BDEs and B3LYP/6-311++G** N—H BDE values for the set of 42 *para*- and *meta*-substituted anilines are not larger than 2 kJ mol⁻¹. Comparing the basis sets, it is evident that 6-31G* results are closer to experimental values for both functionals. From the Tab. 1 it can be seen that the differences between 6-31G*

and the 6-311++G** C—H BDEs are up to 8 kJ mol⁻¹. Lengyel et al. found that in the case of sterols the differences between B3LYP/6-31G* C—H BDEs and B3LYP/6-311++G** results are within 2 kJ mol⁻¹ (Lengyel et al. 2012). Because of the structural similarity between sterols and molecules from our set, we tried to compare BDEs of certain C—H bonds in sterols with C—H BDEs obtained in this work. For example C7—H BDEs of all Δ^5 -sterols studied by Lengyel et al. are in range of 328–329 kJ mol⁻¹. This bond is analogous to cyclohexene, for which our calculated C—H BDE value is 335 kJ mol⁻¹. C24—H bond of cholesterol is similar to butane, their BDEs are 398 kJ mol⁻¹ and 401 kJ mol⁻¹ respectively. BDEs of C25—H in cholesterol and of C—H bond studied in 2-methylpropane reached 383 and 387 kJ mol⁻¹, C24²—H BDE in avenasterol and BDE in Z-but-2-ene have values of 341 kJ mol⁻¹ and 349 kJ mol⁻¹. Finally, similar bonds in desmosterol (C26—H) and Z-but-2-ene reached BDEs of 353 kJ mol⁻¹ and 349 kJ mol⁻¹. The lower values in sterols may be caused by additional inductive effects, that help to stabilize formed radicals. In the case of C26—H of desmosterol and Z-but-2-ene, the inductive effect of geminal alkyl group diminishes the stabilizing mesomeric effect of double bond and results in the higher BDE value of the sterol.

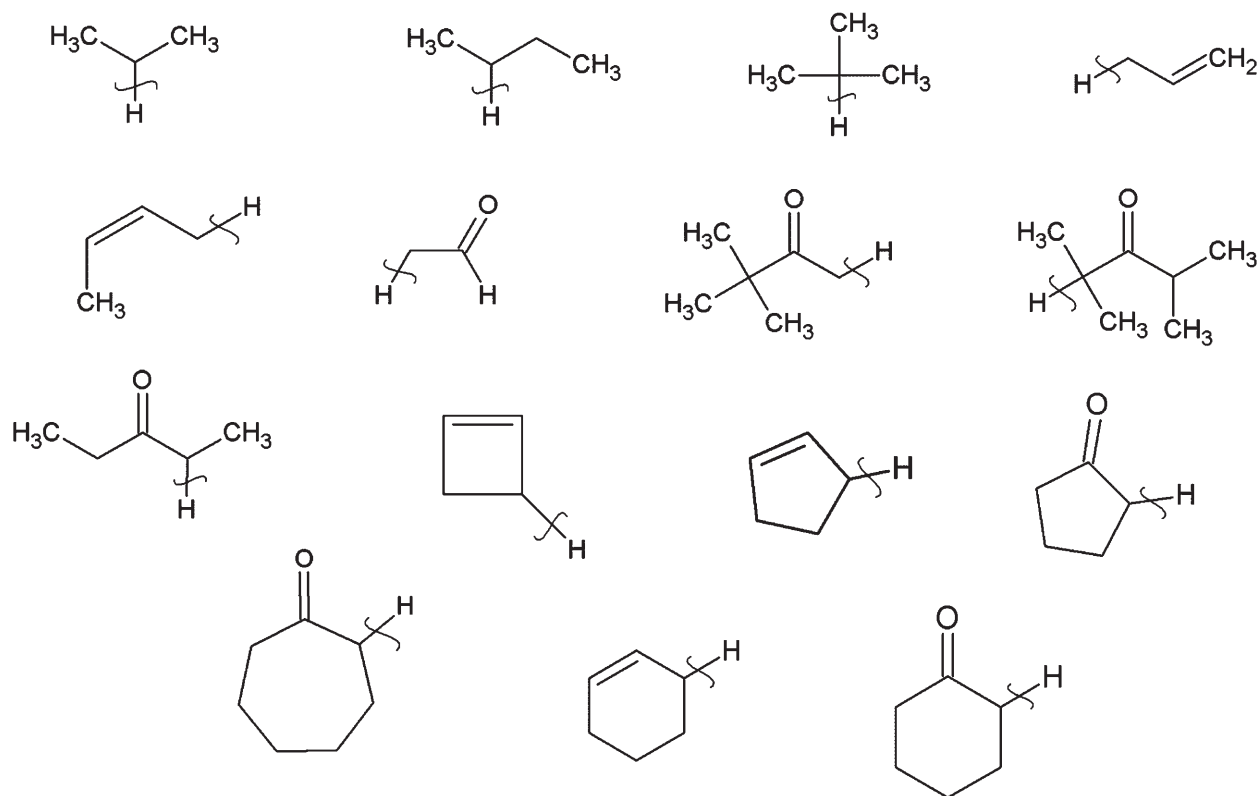


Fig. 1. Studied molecules containing different C—H bonds. BDEs were calculated for depicted C—H bonds. Molecules with all bonds equivalent are not shown.

Tab. 1. Calculated and experimental gas-phase C—H BDEs and experimental errors of C—H BDE measurements in kJ mol^{-1} .

	Experimental		B3LYP		PBE0	
	Value	Error	6-31G*	6-311++G**	6-31G*	6-311++G**
Methane	439.3 ^a	0.1 ^a	436.2	428.5	429.3	422.0
Ethane	423.0 ^a	1.7 ^a	416.6	409.2	410.0	402.9
Propane	412.5 ^a	1.7 ^a	400.3	393.8	394.2	387.9
Butane	410.9 ^a	2.1 ^a	401.2	394.7	395.4	388.9
2-Methylpropane	403.8 ^a	1.7 ^a	386.9	382.6	381.9	377.2
Cyclopropane	444.8 ^b	1.3 ^b	442.4	438.6	436.7	432.7
Cyclobutane	404.4 ^b	4.2 ^b	404.2	399.3	398.8	393.5
Cyclopentane	403.3 ^b	2.5 ^b	389.9	384.8	383.7	378.3
Cyclohexane	399.6 ^b	4.2 ^b	402.3	395.8	397.1	390.8
Ethene	463.2 ^a	2.5 ^a	454.4	449.7	447.2	442.6
Propene	371.5 ^a	1.7 ^a	352.9	348.7	348.1	344.2
Z-But-2-ene	358.2 ^b	6.3 ^b	349.4	344.2	344.8	340.0
Cyclobutene	381.6 ^b	9.6 ^b	368.6	364.1	362.1	357.7
Cyclopentene	344.3 ^b	4.6 ^b	336.4	332.5	331.3	327.4
Cyclohexene	355.6 ^b	4.2 ^b	334.5	330.7	330.0	326.4
Acetaldehyd	393.3 ^a	8.4 ^a	384.1	381.8	380.3	378.2
Acetone	393.3 ^c	4.2 ^c	388.9	386.7	385.1	382.9
Pentan-3-one	368.2 ^c	4.2 ^c	349.6	349.7	344.8	344.6
2,4-Dimethylpentan-3-one	355.6 ^c	4.2 ^c	346.3	345.3	341.9	340.3
3,3-Dimethylbutan-2-one	393.3 ^c	4.2 ^c	386.3	384.6	382.8	381.0
Cyclopentanone	368.2 ^c	4.2 ^c	365.1	363.2	362.0	359.8
Cyclohexanone	368.2 ^c	4.2 ^c	362.3	360.1	358.7	356.4
Cycloheptanone	368.2 ^c	4.2 ^c	361.5	359.9	359.0	357.4

^a(Blanksby and Ellison 2003), ^b(Bachrach 2007), ^c(Bordwell 1990).

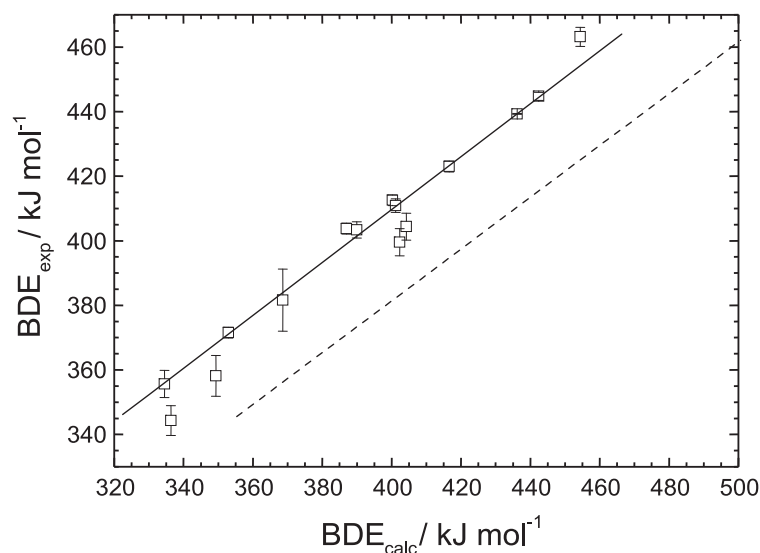


Fig. 2. Dependence of the experimental C—H BDEs on the B3LYP/6-31G* C—H BDE values (open squares, solid line) and on the B3LYP/6-31G* C—H BDEs approximated from the B3LYP/6-31G* total electronic energies (dashed line).

We also tried to correlate the available experimental results with obtained BDE values. Since experimental BDEs of ketones were estimated in DMSO, they

were not taken into least squares method, although solvent causes shift in BDE usually not exceeding few units of kJ mol^{-1} (Klein et al. 2007, Klein

and Lukeš 2006, Rimarčík et al. 2011). Because of acetaldehyde is chemically different from the remaining molecules, we have excluded it from the data evaluation, too. Weighted least square method involving measurement errors of the experimental gas-phase BDEs gives correlation coefficients of 0.994 for B3LYP/6-31G* and PBE0/6-311++G** and 0.995 for B3LYP/6-311++G** and PBE0/6-31G*. Equations of regression lines are as follows (values of BDE_{exp} and BDE_{calc} are in kJ mol^{-1}):

$$BDE_{\text{exp}} = 82.0 + 0.82 BDE_{\text{calc}} \quad (3)$$

B3LYP/6-311++G**

$$BDE_{\text{exp}} = 74.0 + 0.85 BDE_{\text{calc}} \quad (4)$$

PBE0/6-31G*

$$BDE_{\text{exp}} = 78.6 + 0.84 BDE_{\text{calc}} \quad (5)$$

PBE0/6-311++G**

$$BDE_{\text{exp}} = 72.3 + 0.87 BDE_{\text{calc}} \quad (6)$$

From the correlation coefficients of Eqs. 3–6, it can be clearly seen that the linearity of all four depend-

ences can be considered very good. Therefore, if experimental gas-phase BDEs are not available for some structurally related compounds (for example terpenoids, carotenoids, waxes, oils and fatty acids), these equations enable prediction of experimental values solely from calculations. Dependence of experimental BDEs on B3LYP/6-31G* values is shown in Fig. 2. The dashed line represents the correlation between the experimental BDEs and the BDEs approximated from the total electronic energies, which were calculated using Eq. 2, but the B3LYP/6-31G* total electronic energies were used instead of total enthalpies. It is evident that the depicted regression lines are parallel. Therefore, it can be assumed that zero point energy, translational, vibrational, and rotational contributions to BDE are almost uniform for all studied molecules and radicals. Similar results were obtained using the remaining approaches. As a result, the diversities between BDEs of various molecules come mainly from the electronic energies, while other contributions to BDE are nearly constant. BDEs approximated from total electronic energies are larger than gas-phase ones. It can be concluded, that calculations of C–H BDEs using chosen approaches

Tab. 2. Calculated and experimental gas-phase IPs and experimental errors of IP measurements in eV.

	Experimental ^a		B3LYP		PBE	
	Value	Error	6-31G*	6-311++G**	6-31G*	6-311++G**
Methane	12.61	0.01	14.12	14.21	14.18	14.14
Ethane	11.52	0.04	12.19	12.27	12.19	12.21
Propane	10.90	0.10	11.46	11.54	11.46	11.49
Butane	10.53	0.10	11.10	11.19	11.11	11.15
2-Methylpropane	10.74	0.05	11.12	11.21	11.13	11.18
Cyclopropane	9.80	0.10	10.63	10.82	10.67	10.80
Cyclobutane	9.82	0.05	10.89	10.99	10.92	10.95
Cyclopentane	10.33	0.15	10.79	10.89	10.80	10.86
Cyclohexane	10.00	0.03	10.11	10.25	10.16	10.65
Ethene	10.51	0.02	10.36	10.59	10.34	10.51
Propene	9.69	0.09	9.57	9.78	9.56	9.77
Z-But-2-ene	9.11	0.02	8.93	9.09	8.92	9.07
Cyclobutene	9.43	0.02	9.26	9.47	9.26	9.41
Cyclopentene	9.01	0.02	8.80	8.98	8.80	8.95
Cyclohexene	8.94	0.02	8.77	8.97	8.77	8.91
Acetaldehyde	10.14	0.02	10.00	10.22	9.96	10.11
Acetone	9.69	0.01	9.45	9.68	9.43	9.60
Pentan-3-one	9.22	0.02	8.98	9.22	8.98	9.16
2,4-Dimethylpentan-3-one	8.95	0.01	8.75	8.96	8.77	8.92
3,3-Dimethylbutan-2-one	9.12	0.01	8.93	9.15	8.93	9.09
Cyclopentanone	9.28	0.01	9.00	9.25	9.01	9.19
Cyclohexanone	9.16	0.01	8.87	9.11	8.87	9.05
Cycloheptanone	9.17	0.02	8.82	9.06	8.82	9.00

^a(NIST WebBook 2013).

in these and other similar natural or synthetic compounds are relevant and lead to reliable results.

Correlation of IPs and ^{13}C NMR shifts with BDEs

Gas-phase vertical ionization potentials were calculated using the same quantum chemical approaches as BDEs. Calculated and experimental values of IP are listed in Tab. 2.

Data in Tab. 2 clearly show that all employed computational approaches provide practically the same results. All calculated data were correlated with available experimental values using weighted least square method.

Equations obtained from the linear regression are as follows (IP_{exp} and IP_{calc} are in eV):

B3LYP/6-31G*

$$\text{IP}_{\text{exp}} = 3.06 + 0.684 \text{IP}_{\text{calc}} \quad (7)$$

B3LYP/6-311++G**

$$\text{IP}_{\text{exp}} = 2.74 + 0.702 \text{IP}_{\text{calc}} \quad (8)$$

PBE0/6-31G*

$$\text{IP}_{\text{exp}} = 3.13 + 0.677 \text{IP}_{\text{calc}} \quad (9)$$

PBE0/6-311++G**

$$\text{IP}_{\text{exp}} = 2.77 + 0.703 \text{IP}_{\text{calc}} \quad (10)$$

Correlation coefficients reached the values: 0.990 for the B3LYP/6-31G*, 0.992 for the B3LYP/6-311++G**, 0.989 for the PBE0/6-31G*

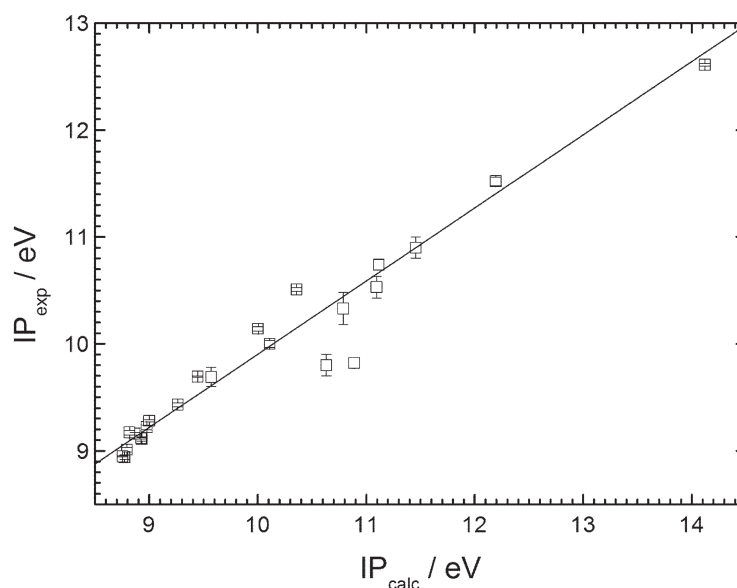


Fig. 3. Dependence of the experimental IPs on the B3LYP/6-31G* IP values.

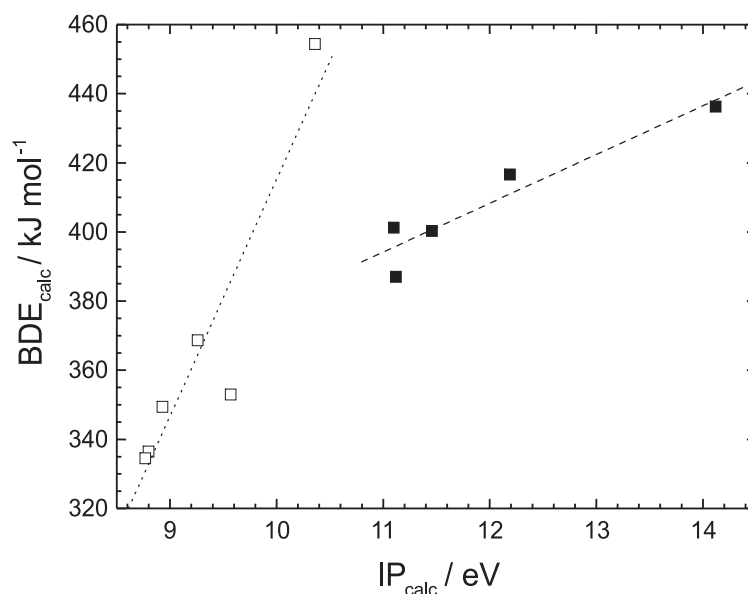


Fig. 4. Dependence of the B3LYP/6-31G* C—H BDEs on the B3LYP/6-31G* IP values for alkanes (solid squares, dashed line) and for alkenes/cycloalkenes (open squares, dotted line).

and 0.990 for the PBE0/6-311++G**. Therefore, the linearity of Eqs. 7–10 can be also considered very good. Correlation between the B3LYP/6-31G* IPs and experimental values is depicted in Fig. 3. As the potential descriptors of the C—H BDEs, IPs and ^{13}C NMR chemical shifts have been employed for B3LYP/6-31G* results.

As shown in Fig. 4, there is a correlation between IPs and C—H BDEs in the sets of simple alkanes and alkenes/cycloalkenes. However, for cycloalkanes and aliphatic carbonyl compounds no useful correlation was found. Using linear regression, we have obtained these equations for alkanes (Eq. 11) and for alkenes/cycloalkenes (Eq. 12)

$$\text{BDE}_{\text{calc}}/\text{kJ mol}^{-1} = 239.1 + 14.100 \text{ IP}_{\text{calc}}/\text{eV} \quad (11)$$

$$\text{BDE}_{\text{calc}}/\text{kJ mol}^{-1} = -270.0 + 68.522 \text{ IP}_{\text{calc}}/\text{eV} \quad (12)$$

with correlation coefficients of 0.947 and 0.929 respectively. For cyclic ketones, correlation coefficient reached 0.9994, but only for 3 available points. Thus, further investigation is required to confirm the existence of the expected trend for large set of molecules.

We have also tried to correlate the ^{13}C NMR chemical shifts with the C—H BDEs. The chemical shift of carbon atom participating in studied C—H bond cleavage was used. At first, we compared the calculated chemical shifts with available experimental values. We found, that gas-phase B3LYP/6-31G* ^{13}C NMR chemical shifts are in good agreement with the experimental results (see Tab. 3). Although experimental chemical shifts were measured in CDCl_3 , they correlate satisfactorily with correlation coefficient of 0.964. Using least square method, the

Eq. 13 was obtained.

$$\delta_{\text{exp}}/\text{ppm} = -2.0 + 1.066 \delta_{\text{calc}}/\text{ppm} \quad (13)$$

Tab. 3. Calculated (gas-phase, B3LYP/6-31G*) and experimental (CDCl_3 solvent) ^{13}C NMR chemical shifts in ppm.

	Experimental ^a	Calculated
Methane		-3.2
Ethane		9.4
Propane		19.5
Butane		27.6
Isobutane		26.2
Cyclopropane		0.5
Cyclobutane		24.6
Cyclopentane	26.1	28.1
Cyclohexane	27.1	27.5
Ethene		116.1
Propene		20.7
Z-But-2-ene		13.9
Cyclobutene		31.9
Cyclopentene	32.6	34.2
Cyclohexene	25.3	27.0
Acetaldehyde	30.9	29.8
Acetone	30.8	28.3
Pentan-3-one	35.5	35.5
2,4-Dimethylpentan-3-one	38.9	40.8
3,3-Dimethylbutan-2-one	24.6	24.4
Cyclopentanone	38.3	37.7
Cyclohexanone	42.0	41.1
Cycloheptanone	43.9	40.1

^a(SDBSWeb 2013).

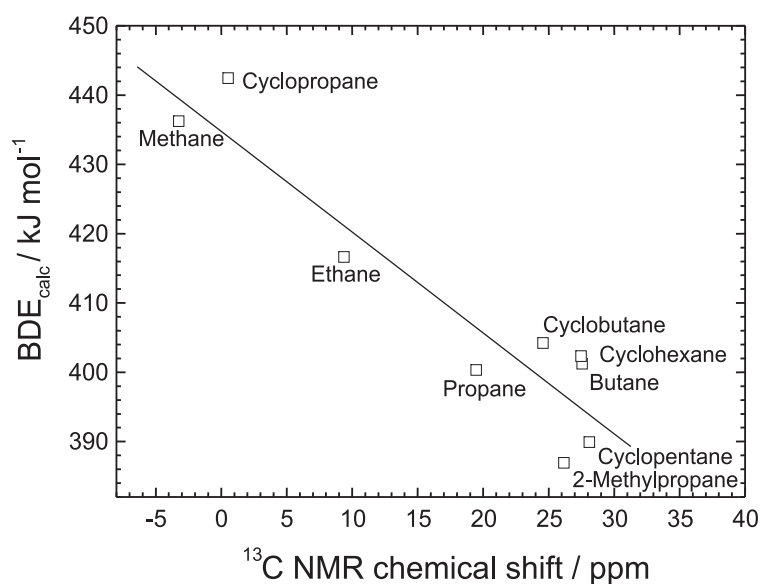


Fig. 5. Dependence of the B3LYP/6-31G* C—H BDE values on the B3LYP/6-31G* ^{13}C NMR chemical shifts of alkanes and cycloalkanes.

Subsequently, we correlated the calculated chemical shifts with B3LYP/6-31G* BDEs. In the set of alkanes and cycloalkanes, a correlation can be found, but for the other studied molecules, there is no apparent trend between ^{13}C NMR chemical shifts and C—H BDE values. The following equation was obtained using least squares method (alkanes, cycloalkanes):

$$\text{BDE}_{\text{calc}}/\text{kJ mol}^{-1} = 434.8 - 1.455 \delta_{\text{calc}}/\text{ppm} \quad (14)$$

The correlation coefficient reached the value of 0.9344. Dependence of the alkanes and cycloalkanes C—H BDEs on ^{13}C NMR chemical shifts is presented in Fig. 5. It can be seen that the linearity of this dependence is rather poor. Since the NMR chemical shift is much more sensitive to chemical surroundings of examined atom than BDE value, the structurally different molecules must be evaluated separately. Investigation of correlation between BDEs and NMR parameters for other types and larger sets of molecules is the objective for the future studies.

Conclusion

As for N—H and O—H bonds in anilines and phenols (Klein et al. 2006), IPs can be used as C—H BDE descriptor for alkanes, alkenes, cycloalkenes, too. However, one should evaluate the chemically different sets of molecules separately. In the case of NMR chemical shifts, our results indicate the correlation for alkanes and cycloalkanes. Unfortunately, in other molecules, there is no evidence of correlation. The presence of heteroatom or double bond significantly affects the local magnetic field. Thus, chemical shift can be used as a BDE descriptor only for a set of chemically similar molecules. Furthermore, we have proved, that C—H BDE calculations in large molecules using smaller 6-31G* basis set provide reliable results in adequate time. The Eqs. 3–6 can be used to correct the calculated values and predict experimental values more precisely. Presented results confirm that B3LYP/6-31G* approach can be applied for the theoretical study of C—H BDEs in large group of natural hydrocarbon compounds including terpenoids, carotenoids, waxes, oils and fatty acids. In the future, it is necessary to investigate the influence of the environment on the studied quantities.

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