Reliability of hybrid density theory—semiempirical approach for evaluation of bond dissociation energies

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The various bond dissociation energies for organic molecules are computed with the hybrid B3LYP/6-31G(d) theory model on AM1 energies. This approach computes bond dissociation energies that are very similar to full B3LYP/6-31G(d) computed values, which are, on the other hand, 5–10 kcal mol^{-1} away from the experimental values. If correction factors are applied, very good agreement with the experiment can be obtained. This approach is designed to evaluate bond dissociation energies on large molecular systems with a modest computational requirement.

Introduction

One of the great advantages of theoretical computational chemistry is that it can reproduce and predict physical properties of organic molecules with reasonable accuracy.[1–5] Therefore, experimental chemists can rely on the computed values for planning, or even adjusting their experimental procedures and data. Although geometries and energies of various molecular systems can be reproduced reasonably well with semiempirical and *ab initio* methods, for small polar molecular systems, neither semiempirical nor *ab initio* methods with a basis set of modest size can generate accurate values.[6] Broad applications of density functional theory (DFT) methods have widened the applicability of the computational methods, and suggest that a combination of theory and experiment should be a part of the majority of the research efforts.[7–10] In this respect, we have demonstrated that some density functional theory methods represent a reliable approach for computing geometries,[11–21] reaction activation barriers,[22–46] relative energies (complexation energies),[47–51] vibrational spectra,[52,53] and bond dissociation energies (BDE).[54–59]

It is well known that computing the activation barrier for a chemical transformation is a particularly difficult computational task, because bond breaking and bond making processes are involved for which computational methods are not clear-cut. The same is true for the determination of bond dissociation energies. In addition, organic chemists are usually interested in large molecules. If computational chemistry were to become a research tool in experimental organic chemistry, the evaluation of the energy for large chemical systems should be obtained in reasonably short computational time. Accurate *ab initio* computational methods, such as complete basis set *ab initio* methods, can be applied to molecular systems with only a few heavy atoms.[60–63] The situation is slightly better in the case of density functional theory methods, but again there is a practical limit between the size of the molecule and the time necessary to obtain trustworthy computational data.

Recently, we have successfully studied the hybrid DFT energy evaluation on the AM1 (semiempirical) computed energies for the evaluation of activation barriers.[64–68] The results obtained on organic molecules are almost the same as the full density functional calculations, as well as the experimental results. That is not surprising, because the AM1[69] semiempirical method is well parametrized and AM1 and B3LYP[70,71] computed geometries for all stationary points on the potential energy surface are very similar.[72] In this way fast and reliable results can be obtained for large molecular systems. It is very important to mention that the accuracy of this approach strongly depends on how well the semiempirical method is parametrized. If the molecule contains some elements that are not included in AM1 parameterization, or geometries are not well defined, such as in the case of sulfur and phosphorus compounds, the generated energy might substantially deviate from experimental values.

Computation of bond dissociation energies is very valuable for experimental organic chemists, because many chemical transformations are occurring through the formation of free radicals as a rate-determining step.[73] Therefore, evaluation of the bond dissociation energy before the actual experiment can help an experimental organic chemist to plan the experiment better, as well as explain the reaction outcome. Because the majority of organic chemists have an interest in large molecular systems, we wish to present our evaluation of the bond dissociation energies with the B3LYP/6-31G(d)//AM1 computational approach for a wide variety of organic molecules.

Computational methods

All geometries were optimized with the AM1[69] semiempirical method as a part of the MOPAC[74] computational package. Energies were evaluated by B3LYP[70,71] a hybrid density functional method by using a 6-31G(d)[75] basis set as implemented in the GAUSSIAN[76] 94 computational package.

Results and discussion

Although computational methods are becoming very accurate it is very common to use various correction factors to obtain even better agreement between experiment and theory. One of the most frequently used ones is the scaling factor for the Hartree–Fock (HF) molecular frequencies.[77] Recently, we have applied scaling factors for C–H and C–halogen dissociation energies computed at the B3LYP/6-311+G(2d,2p) theory level.[59] We have demonstrated that this approach is reliable for computing the C–H bond dissociation energies. Let us now explore if this is also true when DFT-AM1 (B3LYP/6-31G(d)//AM1) theory level is applied. The C–H bond dissociation energies for various organic systems are presented in Table 1. Due to the nature of the computed energies, they cannot be corrected by zero point energy, or brought to the standard energies; therefore, the correction factor should reflect that as well. The DFT-AM1 model performs well. For instance, the uncorrected B3LYP computed C–H bond dissociation energy in methane is 111.1 kcal mol^{-1}, while the DFT-AM1 computed energy is 112.3 kcal mol^{-1}. The DFT-AM1 computed energies are about 10% higher than the experimental values.[78] It should be pointed out that many experimental bond dissociation energies have very high experimental errors (some ±3 kcal mol^{-1}) and that some of the values are approximate. Nevertheless, if we use

Table 1 The DFT-AM1 calculated C–H bond dissociation energies (kcal mol^{-1}) obtained from total energies for H–R→H + R reaction

				BDE$_{exp}$	
H–R	E_{HR}/BDE$_{corr}$	E_R	BDE		
H–CH_3	−40.517564	−39.838268	112.3	102.0	102.2
H–C_2H_5	−79.828209	−79.155828	108.0	98.0	98.3
H–$CH(CH_3)_2$	−119.141124	−118.473160	105.2	95.0	95.7
H–$C(CH_3)_3$	−158.455130	−157.791797	102.3	92.0	93.1
H–CCH	−77.325410	−76.603581	139.0	125.0	126.4
H–$CH{=}CH_2$	−78.587018	−77.894663	120.0	108.0	109.2
H–CH_2–$CH{=}CH_2$	−117.905729	−117.259901	91.3	86.6	83.1
H–$CH_2C_6H_5$	−271.564428	−270.914116	94.1	87.9	85.6
H–CH_2CN	−132.753467	−132.094458	99.6	89.0	90.6
H–cyclopropyl	−117.893781	−117.209087	115.7	106.3	105.2
H–cyclobutyl	−157.209820	−156.543614	104.1	96.5	94.7
H–cyclopentyl	−196.546474	−195.885824	100.6	94.5	91.5
H–cyclohexyl	−235.875152	−235.207230	105.2	95.5	95.7
H–cycloheptyl	−275.173339	−274.508155	103.5	92.5	94.2
H–cyclopentadienyl	−194.099729	−193.461699	86.4	81.2	78.6
H–C_6H_5	−232.248079	−231.560181	117.7	110.2	107.1
H–CN	−93.422603	−92.710416	133.0	120.0	121.0
H–CHO	−114.499813	−113.841794	99.0	87.0	90.1
H–$COCH_3$	−153.828299	−153.170554	98.8	86.0	89.9
H–CH_2OCH_3	−155.022746	−154.359214	102.4	93.0	93.2

$E_H = -0.500273$; correction factor 0.91; BDE = computed bond dissociation; BDE$_{exp}$ = experimental bond dissociation energy; BDE$_{corr}$ = corrected bond dissociation energy (correction factor 0.91).

Table 2 The DFT-AM1 X–H bond dissociation energy (kcal mol^{-1}) computed from total energies for H–X→H + X reaction

Compound	$E_{H\text{–}X}$	E_X	BDE$_{cal}$	BDE$_{exp}$
H–NH_2	−56.546585	−55.870006	110.6	110.0
H–NO	−130.461412	−128.883837	48.5	49.5
H–NF_2	−254.876346	−254.258943	73.5	75.7
H–N_3	−164.781721	−164.138472	89.7	87.0
H–OH	−76.408843	−75.722373	116.8	119.0
H–OCH_3	−115.713001	−115.049034	102.7	104.4
H–OC_6H_5	−307.464152	−306.826936	85.9	88.0
H–OOH	−151.515975	−150.873123	89.5	87.2
H–OCOH	−189.750124	−189.074485	110.0	110.0
H–$OCOCH_3$	−229.076191	−228.405336	107.0	106.0
H–ONO	−205.687933	−205.065337	76.8	78.3
H–ONO_2	−280.872666	−280.213524	100.0	101.2
H–SH	−399.384561	−398.739290	90.9	90.5
H–SCH_3	−438.694574	−438.054418	87.8	88.0

$E_H = -0.500273$; BDE$_{cal}$ = computed bond dissociation energy; BDE$_{exp}$ = experimental bond dissociation energy.

a correction factor of 0.91, an excellent agreement between corrected (Table 1) and experimental values at 298 K will be attained.[78] We believe this is a general procedure for fast evaluation of the C–H bond dissociation energies in various organic molecular systems.

As we have mentioned in the introductory part of this paper, the hybrid DFT methods compute the geometries and energies of small polar molecular systems exceptionally well. Naturally, these molecular systems contain many heteroatoms, and some of them have hydrogen–heteroatom bonds. Nevertheless, it is interesting that the DFT-AM1 computed hydrogen–heteroatom bond dissociation energies are in exceptionally good agreement with experimental values (Table 2). The computed values deviate at most by ~2 kcal mol^{-1} from the experimental values. Indeed this is accurate computing, considering that many experimental data have an experimental error higher than 2 kcal mol^{-1}.

Let us now explore the inexpensiveness of the DFT-AM1 hybrid in computing carbon–carbon dissociation energies (Table 3). The same correction factor as in the evaluation of the C–H bond dissociation energies was used. In this case, the corrected bond dissociation energies vary substantially from the experimental values. For hydrocarbons, ketones, and carboxylic acids the agreement is as good as it is in the case of the C–H bond energy evaluation. For instance, the H_3C–CH_3 bond dissociation energy is estimated to be 86.6 kcal mol^{-1}, while the experimental value is 88.0 kcal mol^{-1}. For an acid, *e.g.*, $C_6H_5CH_2$–COOH, the bond dissociation energy was estimated to be 69.6 kcal mol^{-1}, which is in good agreement with a value of 68.1 kcal mol^{-1}, which was determined experimentally (Table 3). The same is true for ketones. For instance, the C–C bond dissociation energy in $C_6H_5CH_2CO$–$CH_2C_6H_5$ was evaluated to be 65.7 kcal mol^{-1}, in excellent agreement with the experimental value of 65.4 kcal mol^{-1} (Table 3). The computed values are not as close to the experimental values if strongly polar, or if multiple bonds are close to the C–C bond being broken. This deviation is due to the fact that the AM1 computed geometries for these molecular systems, and of course the corresponding radicals are not correct because of inappropriate parameterization. This is especially true for molecular systems with carbon–nitrogen triple bonds close to the C–C bond breaking, and in the presence of elements that require d-orbitals, such as fluorine. The AM1 geometries for these molecular systems are far from the experimental values, and in this case the DFT energies are also quite different than the experimental values. That was clearly demonstrated in the example of H_3C–CN, NC–CN, and C_6H_5CO–CF_3 bond dissociation energies (Table 3). For those molecular systems, the DFT-AM1 approach was not appropriate for evaluating C–C bond dissociation energies, except when the relative energies of similar molecular systems are compared (such as the various structural isomers with the same empirical formula).

The correction factors that were used to adjust the H–C, and C–C DFT-AM1 computed energies are not suitable for correction of the C–N calculated energies. Better agreement can be obtained by using a 0.95 correction factor, as it is demonstrated in Table 4. In this way, the computed C–N bond dissociation energy deviates 2 kcal mol^{-1} from the experimental values. It is interesting to point out that on all four different groups of nitrogen organic compounds (amines, azo, nitro, and nitroso compounds), the computed BDE are in relatively good agreement with the experimental values. If we now explore the accuracy of the DFT-AM1 approach for computing C–O bond dissociation energies (Table 5), then 0.95 as a correction factor is too high, and the best agreement is obtained with a 0.85 correction factor. This certainly demonstrates that almost every type of bond requires a different correction factor.

This statement is further supported by the fact that if N–N or O–O bond dissociation energies are computed, the estimated

Table 3 The DFT-AM1 C–C bond dissociation energies (kcal mol^{-1}) computed from total energies for R^1–R^2→R^1 + R^2 reaction

R^1–R^2	$E_{R^1–R^2}$	E_{R^1}	E_{R^2}	BDE$_{cal}$	BDE$_{exp}$	BDE$_{corr}$
$H_3C–CH_3$	−79.828209	−39.838268	−39.838268	95.2	88.0	86.6
$CH_3–CF_3$	−377.550116	−39.838268	−337.547915	102.3	101.2	93.1
$CF_3–CF_3$	−675.244576	−337.547915	−337.547915	93.3	96.9	84.9
$H_3C–CN$	−132.753440	−39.838268	−92.710416	128.5	123.9	116.9
NC–CN	−185.654606	−92.710416	−92.710416	146.7	128.0	133.5
$C_6H_5CH_2–CH_2CH_3$	−350.187541	−270.914116	−79.155828	73.8	69.0	67.2
$CH_3–CH_2CN$	−172.066031	−39.838268	−132.094458	83.6	72.7	76.0
$C_6H_5CH_2–CH_2NH_2$	−366.215320	−270.914116	−95.191610	68.8	65.7	62.6
$CH_3CO–COCH_3$	−306.467146	−153.170554	−153.170554	79.1	67.4	72.0
$C_6H_5CH_2–COOH$	−460.120284	−270.914116	−189.084229	76.5	68.1	69.6
$C_6H_5CH_2CO–CH_2C_6H_5$	−655.248085	−384.218953	−270.914116	72.2	65.4	65.7
$C_6H_5CO–CF_3$	−682.598451	−344.912722	−337.547915	86.5	73.8	78.7

BDE$_{cal}$ = computed bond dissociation energy; BDE$_{exp}$ = experimental bond dissociation energy; BDE$_{corr}$ = corrected bond dissociation energy (correction factor 0.91).

Table 4 The DFT-AM1 C–N bond dissociation energies (kcal mol^{-1}) computed from total energies for R^1–R^2→R^1 + R^2 reaction

R^1–R^2	$E_{R^1–R^2}$	E_{R^1}	E_{R^2}	BDE$_{cal}$	BDE$_{exp}$	BDE$_{corr}$
$CH_3–NH_2$	−95.850747	−39.838268	−55.870006	89.4	84.9	84.9
$C_6H_5CH_2–NH_2$	−326.901971	−270.914116	−55.870006	74.0	71.9	70.3
$C_6H_5NH–CH_3$	−326.906916	−286.951735	−39.838268	73.3	67.7	69.6
$CH_3NN–CH_3$	−189.266946	−149.338789	−39.838268	56.4	52.5	53.6
$C_2H_5NN–C_2H_5$	−267.893828	−188.654381	−79.155828	52.5	50.0	49.9
$(CH_3)CHNN–CH(CH_3)_2$	−346.521530	−227.971218	−118.473160	48.4	47.5	46.0
$(CH_3)_3CNN–C(CH_3)_3$	−425.153860	−267.287280	−157.791797	46.9	43.5	44.6
$CH_3CH_2–NO_2$	−284.322234	−79.155828	−205.065337	63.4	62.0	60.2
$C_6H_5–NO$	−361.531309	−231.560181	−129.883837	54.8	51.5	52.1
$C_6F_5–NO$	−857.644354	−727.678152	−129.883837	51.7	50.5	49.1

BDE$_{cal}$ = computed bond dissociation energy; BDE$_{exp}$ = experimental bond dissociation energy; BDE$_{corr}$ = corrected bond dissociation energy (correction factor 0.95).

Table 5 The DFT-AM1 C–O bond dissociation energies (kcal mol^{-1}) computed from total energies for R^1–R^2→R^1 + R^2 reaction

R^1–R^2	$E_{R^1–R^2}$	E_{R^1}	E_{R^2}	BDE$_{cal}$	BDE$_{exp}$	BDE$_{corr}$
$CH_3–OC(CH_3)_3$	−272.920923	−39.838268	−233.002453	80.9	66.3	68.8
$CH_3–OC_6H_5$	−346.769020	−39.838268	−306.826931	65.1	57.0	55.3
$CH_3–OCH_2C_6H_5$	−386.074997	−39.838268	−346.104155	83.2	67.0	70.7
$CH_3–O_2SCH_3$	−628.358075	−39.838268	−588.404086	72.6	66.8	61.7
$CH_2CHCH_2–O_2SCH_3$	−705.753684	−117.259901	−588.404086	56.3	49.6	47.9
$C_6H_5CH_2–O_2SCH_3$	−859.419696	−270.914116	−588.404086	63.7	52.9	54.1

BDE$_{cal}$ = computed bond dissociation energy; BDE$_{exp}$ = experimental bond dissociation energy; BDE$_{corr}$ = corrected bond dissociation energy (correction factor 0.85).

Table 6 The DFT-AM1 C–O bond dissociation energies (kcal mol^{-1}) computed from total energies for R^1–R^2→R^1 + R^2 reaction

R^1–R^2	$E_{R^1–R^2}$	E_{R^1}	E_{R^2}	BDE$_{cal}$	BDE$_{exp}$
$CH_3O–OCH_3$	−230.141343	−115.049036	−115.049036	27.2	37.6
$HO–OC(CH_3)_3$	−308.780633	−75.722378	−233.002453	35.0	46.3
$CH_3CH_2O–OCH_2CH_3$	−308.777670	−154.363817	−154.363817	31.0	37.9
$(CH_3)_2CHO–OCH(CH_3)_2$	−387.409865	−193.681290	−193.681290	29.7	37.7
$(CH_3)_3CO–OC(CH_3)_3$	−466.043577	−233.002453	−233.002453	24.3	38.0
$(CF_3)_3CO–OC(CF_3)_3$	−2252.273694	−1126.120057	−1126.120057	21.1	35.5
$CH_3COO–OOCCH_3$	−456.845861	−228.405719	−228.405719	21.6	30.4
$H_2N–NH_2$	−111.845955	−55.870017	−55.870017	66.5	70.8
$CH_3NH–NH_2$	−151.157579	−95.186211	−55.870017	63.6	64.8
$(CH_3)_2N–NH_2$	−190.469193	−134.504408	−55.870017	59.5	62.7

BDE$_{cal}$ = computed bond dissociation energy; BDE$_{exp}$ = experimental bond dissociation energy.

values are substantially lower than the experimental values (Table 6). There is no one correction factor with which excellent agreement between computed and experimental values for both N–N and O–O bond dissociation energies can be obtained. However, it is possible to obtain a relatively good agreement with experimental data if a 1.2 correction factor for O–O bond dissociation energy for some peroxides is used, but there is no general correction factor. Therefore, this approach should not be used for the evaluation of O–O and N–N bond dissociation energies.

Conclusion

Computing bond dissociation energies by DFT-AM1 (B3LYP/6-31G(d)//AM1) methods has advantages as well as disadvantages. The C–H, C–C, and C–heteroatom bond dissociation energies can be accurately computed using this approach for a majority of organic compounds. Unfortunately, there is no unique correction factor that could be used to obtain a better agreement between theory and experiment. On the other hand, the H–heteroatom bond dissociation energies are very close to the experimental data and corrections are not required. Also, the heteroatom–heteroatom bond dissociation energies are substantially underestimated and there is not a general correction factor for these computed energies. Therefore, for computing these energies, the DFT-AM1 approach should not be used.

It should be pointed out that the computed energies are compared with bond experimental values at 298 K, and the scaling factor should reflect that effect as well. The accuracy of the DFT-AM1 computing is strongly influenced by the accuracy of the AM1 semiempirical method to compute geometries of organic molecules. AM1 is well parametrized for organic molecules in general, but not for molecular systems with heteroatom–heteroatom bonds. Even high-level *ab initio* methods are not satisfactory when reproducing experimental geometries for such systems. Therefore, as expected, the DFT-AM1 approach fails to generate accurate heteroatom–heteroatom bond dissociation energies.

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