DFT and Proton Transfer Reactions: A Benchmark Study on Structure and Kinetics

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S *Supporting Information*

ABSTRACT: A significant number of different exchange correlation functionals, ranging from generalized gradient approximations to double hybrids, has been tested on a difficult playground represented by proton transfer reactions. In order to have a complete picture of their performances, both energetics and structural features have been compared and the obtained ranking compared with those issued from the standard test for kinetics (i.e., the DBH24/08 set). Among all of the functionals, the ωB97X, BMK, B1LYP, and PBE0-DH approaches are those providing a good error balance on all four trials. Beyond these figures, the obtained results allow for some general considerations, such as those on the role of Hartree–Fock exchange in reaction barriers or the relation between structure and energetics.

1. INTRODUCTION

Proton transfer (PT) reactions play a pivotal role in so many chemical processes that it could be difficult to make an exhaustive list. As an example, acid–base neutralization, tautomeric interconversion in DNA basis, enzymatic reactions, and charge transport can be cited.[1–6] It is not surprising that PT has been defined as "the most general and important reaction in chemistry,"[7] and therefore, it is still attracting a great deal of attention from both the experimental and theoretical points of view.

Focusing on the theoretical aspects and, in particular, on the energetics of this reaction, it has been clearly shown in the past that the inclusion of electronic correlation is mandatory for an accurate determination of the thermodynamics and, more important, of the kinetics of the PT reactions (see, for instance, ref 8). Indeed, post-Hartree–Fock (HF) methods including correlation effects, at a level well beyond second order perturbation theory, are necessary for an accurate estimate of PT barriers.[9] As matter of fact, methods like coupled cluster (CC) are among the few that provide precise global potential energy surfaces (PES) and barriers for any kind of proton transfer. However, these approaches can be rarely applicable to molecules containing more than a dozen atoms, thus excluding most of the systems of chemical relevance. As for many other properties, methods rooted in density functional theory (DFT) represent a viable alternative, due to their competitive accuracy/cost ratio. However, before being routinely applicable, DFT methods need to go through an assessment step, where the performances of each exchange-correlation functional are assessed by a comparison with higher-level theoretical approaches (e.g., CC) or, if available, accurate experimental results.[10] In this sense many test sets have been set up to estimate their performances on, for instance, reactivity,[11,12] giving an estimate of the error expected for almost all known functionals. Sometimes, it is also possible, and desirable, to associate the performances of a functional with the physics

behind it. For instance, improved atomization energies can be obtained by modifying the behavior of the functional in the low range of the reduced density.[13]

PT was among the first reactions to be systematically studied at the dawn of modern DFT approaches, about 20 years ago. These works, carried out on a limited number of exchange-correlation functionals, clearly pointed out the underestimation of PT barriers by gradient-generalized approximations (GGAs) and how the inclusion of HF exchange can (partially) correct this problem.[14–19] This effect was later related to the self-interaction error (SIE),[20,21] which induces an artificial stabilization of delocalized states[22] such as the transition state (TS) in PT reactions. The inclusion of HF exchange enhances the electron localization and it has, therefore, some beneficial effects on the estimates of activation energies.[23]

Such conclusions, underestimation of activation energies using GGAs and the relation with the percentage of HF exchange in hybrid functionals, have been confirmed over the years. Surprisingly, to the best of our knowledge, no systematic benchmarks have been carried out since these pioneering works, if one excludes a very recent paper by Truhlar and collaborators on three small dimers[24] and some studies on very specific systems (see, for instance, refs 25–27). On the other hand, hydrogen transfer (HT) reactions have been included in the DBH24/08 set, a standard benchmark for reactivity.[28,29]

Nevertheless, PT reactions of interest in chemistry could be significantly different from HT reactions, including both intra- and intermolecular reactions with low (few kcal/mol) and high (tens of kcal/mol) barriers. A strong modification of the electronic systems, like in the π-conjugated molecules, could further tune the energetic of the reaction.[30,31] In this context, we have recently studied protonated imizadole dimers, as a model system for charge transport in membranes, in which the

PT reaction is assisted by a strong rearrangement of the electronic structure.[27] Such systems were revealed to be very challenging for many DFT approaches, including those characterized by good numerical results on reaction kinetics. Starting from this study and with the aim to (partially) fulfill the lack of information about PT reactions, a detailed analysis of the numerical performances of a large number of functionals is presented. In particular, and in contrast with respect to common trends, both energetics and structural features are here analyzed for 27 exchange-correlation functionals, and their results are compared with CC results. The benchmark is carried out on a set of nine systems, chosen as representative of different PT reactions (high and low barriers, intra- and inter-PTs, electronic structure rearrangements). Finally, a comparison with the results obtained for the standard benchmark for reaction barriers, the so-called DBH24/08 set, is done. The aim of the paper is double: on one hand, it is to find the best functional(s) for PT reactions, and on the other hand, it is to verify that modern DFT functionals really represent an improvement with respect to older (and widely used) approaches.

2. COMPUTATIONAL DETAILS

All calculations were carried out with a locally modified version of the Gaussian 09 package.[32] Among the large number of exchange correlation functionals present in the literature, 27 were chosen in order to cover different rungs of Perdew's ladder,[33] including GGAs, meta-GGAs, global and range separated hybrids (GHs and RSHs), and up to the recently introduced double hybrids (DHs). The whole list of functionals is reported in Table 1. This list, albeit nonexhaustive, contains some of the most used and best performing DFT approaches for chemical applications.

DFT structures have been obtained using the 6-311+G(2d,p) basis, and subsequent 6-311+G(3df,3pd) single point calculations have been carried out in order to obtain improved PT barriers. For the M06 family, an "ultrafine" grid corresponding to 96 radial shells around each atom, and a spherical product grid having 32 θ points and 64 ϕ points in each shell, has been used.[59,60]

In order to obtain accurate reference values, molecular structures were optimized at the CCSD/cc-pVTZ level, and then energies were evaluated at the CCSD(T)/aug-cc-pvVTZ level.

3. RESULTS AND DISCUSSION

The nine systems analyzed are sketched in Figure 1 and labeled from A to I. They represent a wide range of H-bonded systems undergoing either to intra- or intermolecular PT reactions. For some of them, namely, systems C, D, F, and I, PT is coupled with a significant rearrangement of the π-electron systems, an effect which has been suggested to be problematic to be described at the DFT level.[16,61] Both symmetric (A−F) and nonsymmetric (G−I) PT reactions were chosen, so that 12 energy barriers have been considered in total.

Four different benchmarks were then carried out. The first consists of the evaluation of PT energy barriers (hereafter PTEB) at the B3LYP/6-311+G(2d,p) optimized structures. The second is the standard energy barrier evaluations on the DBH24/08 database for kinetics. The last two involve the comparison of the PTEBs and the optimized H-bond structural parameters for each considered functional with the reference

Table 1. List of the Considered Exchange-Correlation Functionals

functional	%HF exchange[a]	reference
	GGA	
GRAC	0	34
BLYP	0	35
TCA	0	36
PBEPBE	0	37
	meta-GGA	
VSXC	0	38
B97D	0	39
	global hybrids	
B972	21	40
B1LYP	25	41
BMK	42	42
X3LYP	21	43
B3LYP	20	44
B3LYP-D	20	44, 45
BHandHLYP	50	46
mPW1PW91	25	47
mPW1K	42.8	48
PBE0	25	49
M06-HF	100	50
M06	27	51
M06-2X	54	51
	range-separated hybrids	
CAM-B3LYP	19/65	52
LC-PBEPBE	0/100	53
LC-ωPBE	0/100	54
ωB97XD	22/100	55
ωB97X	16/100	56
ωB97	0/100	56
	double hybrids	
PBE0-DH	50	57
B2PLYP	53	58

[a]The min/max for range separated hybrids.

CCSD(T) and CCSD values, respectively. In such a way, energy (first and third benchmarks) and structural (forth benchmark) effects are separated, while the second set will show how PT reactions are peculiar with respect to more traditional organic reactions as those contained in the DBH24/08 set. The results obtained in the three benchmarks will be discussed separately, and some comments on the final "ranking" of the functionals will be then given.

B3LYP and CCSD values, with the corresponding CCSD(T) energies, are reported in Table 2, in order to supply the reference values used in the following discussions. The Cartesian coordinates of the molecules computed at the CCSD level are reported in the Supporting Information.

3.1. Proton Transfer Barriers at Given Structures. In recent years, it has become a common practice to compare functional performances on different physicochemical properties at given geometries. Following this line, the results obtained with all 27 exchange-correlation functionals using the B3LYP/6-311+G(2d,p) structures are collected in Table 3. For the sake of simplicity, only mean signed deviations (MSDs), mean absolute deviations (MAEs), and root mean square deviations (RMSDs) are reported, while details are given in Table S1, Supporting Information.

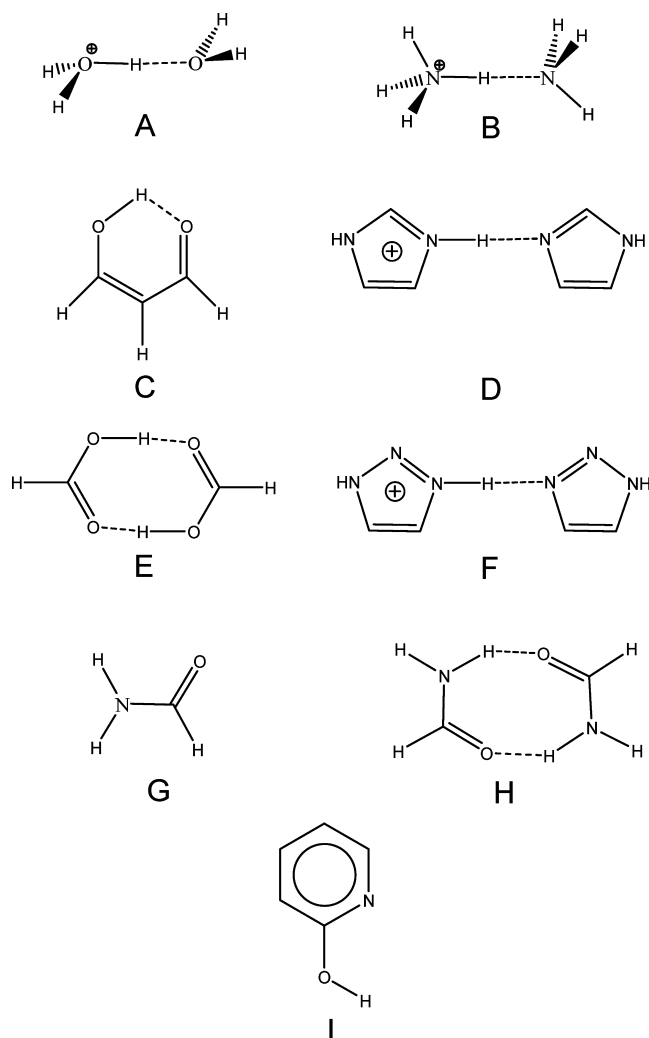The first three places in the list are occupied by three RSHs, namely, ωB97X and its version corrected for dispersion,

Figure 1. Sketch of the considered systems in their minimum energy isomer, undergoing proton transfer reactions: (A) protonated water dimer, (B) protonated ammonia dimer, (C) malonaldehyde, (D) protonated imidazole dimer, (E) formic acid dimer, (F) protonated triazole dimer, (H) formamide, (G) formamide dimer, (I) pyridine.

Table 2. Reference CCSD/cc-pVTZ Values for the H-Bond Structural Parameters (Å; A = H Acceptor, D = H Donor) and Proton Transfer Barriers ($\Delta E^{\#}$, kcal/mol) Obtained at CCSD(T)/aug-cc-pVTZ//CCSD/cc-pVTZ Level[a]

system	d(AD)	d(AH)	d(HD)	$\Delta E^{\#}$
A[b]	2.750	1.700	1.051	6.71
B	2.719(2.695)	1.620(1.553)	1.100(1.142)	1.02(0.93)
C	2.611(2.571)	1.737(1.674)	0.982(1.001)	3.87(3.85)
D	2.681(2.668)	1.603(1.561)	1.079(1.107)	1.05(1.06)
E	2.689(2.666)	1.702(1.663)	0.988(1.004)	7.90(7.90)
F	2.673(2.655)	1.611(1.543)	1.075(1.114)	1.14(1.03)
G	2.276(2.278)	2.542(2.546)	1.003(1.009)	46.77(46.75)
H	2.888(2.924)	1.874(1.901)	1.018(1.027)	19.10(18.86)
I	2.282(2.290)	2.233(2.255)	0.963(0.969)	38.05(37.96)

[a]Only the values for the lowest energy minima are reported, while in parentheses are reported the structural parameters obtained with the B3LYP/6-311+G(2d,p) approach and the energies computed at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(2d,p) level. [b]Fixed geometry.

Table 3. Mean Signed Deviations (MSD), Mean Absolute Deviations (MAD), and Root-Mean Square Deviations (RMSD) for Proton Transfer Barriers[a]

	functional	MSD	RMSD	MAD
1	ωB97XD	−0.02	0.85	0.71
2	ωB97X	0.55	1.15	0.75
3	CAM-B3LYP	−0.34	0.95	0.77
4	B1LYP	0.17	1.03	0.78
5	PBE0-DH	−0.66	1.00	0.81
6	BMK	0.46	1.26	0.84
7	X3LYP	−0.47	0.98	0.86
8	B3LYP	−0.52	1.02	0.90
9	M06	−0.69	1.12	0.94
10	B3LYP-D	−0.66	1.17	0.97
11	B972	−0.82	1.14	0.99
12	LC-ωPBE	−0.77	1.19	1.01
13	ωB97	0.88	1.49	1.01
14	mPW1K	0.24	1.27	1.02
15	M06-2X	−0.68	1.33	1.12
16	VSXC	−0.03	1.96	1.30
17	mPW1PW91	−1.32	1.53	1.33
18	PBE0	−1.59	1.77	1.59
19	M06-HF	−1.01	2.71	1.91
20	LC-PBEPBE	−2.16	2.51	2.16
21	BLYP	−2.20	2.65	2.20
22	BHandHLYP	2.32	3.13	2.32
23	B97D	−2.40	2.74	2.40
24	GRAC	−2.52	2.99	2.52
25	B2PLYP	3.05	3.86	3.05
26	TCA	−3.23	3.69	3.23
27	PBEPBE	−3.95	4.42	3.95

[a]All of the values are in kcal/mol.

ωB97XD, and CAM-B3LYP. These functionals contain about 20% HF exchange at short-range, and a similar percentage (25%) is also present in the following, B1LYP, a GH. Not far behind follows the PBE0-DH functional, the first double hybrid built on a rigorous theoretical basis,[62] and a functional specifically built for reaction kinetics, BMK. Concerning the bottom of the ranking, most of the GGA functionals, like PBEPBE, can be found here, as expected. More surprisingly, B2PLYP and BHandHLYP are among the lowest in the rank, both containing a high ratio of HF exchange (see Table 3). Looking in detail at the single activation energies (Table S1), it appears that these two functionals significantly overestimate all of the values, a peculiar behavior that they (partially) share only with ωB97 (a middle-ranked functional). It is also interesting to note that for some functionals the TSs seem to be more stable than the corresponding minima; i.e., these functionals provide negative energies (Table S1). While for GGA and meta-GGA models (PBE, TCA, B97D) this can be ascribed to SIE,[22] the interpretation for M06-HF (two negative energies) and LC-PBE (one negative energy) appears more difficult, both having a relevant percent of HF exchange, which should compensate for SIE. From our results, the negligible effect of dispersion on the PTEBs is also clearly evident. Indeed, the ωB97X and B3LYP functionals provide results very close to those obtained with the respective counterparts including empirical dispersion corrections (i.e., ωB97XD and B3LYP-D).

Finally, the low spreading of the obtained results must be noted, as it appears from the close RMSD and MAE values computed for almost all of the functionals.

3.2. The DBH24/08 Data Set. The DBH24/08 database can be considered as the *de facto* reference for testing functional performances on reactivity barriers. It is composed by 24 barriers for 12 reactions, including hydrogen transfer (HT), heavy atom transfer (HAT), nucleophilic substitution (NS), and unimolecular and association (UA) reactions. The obtained results are reported in Table 4. Among all of the considered

Table 4. Mean Signed Deviations (MSD), Mean Absolute Deviations (MAD), and Root-Mean Square Deviations (RMSD) for the DBH24/08 Benchmark for Kinetics[a]

	functional	MSD	RMSD	MAD
1	M06-2X	0.13	1.45	1.03
2	BMK	0.34	1.82	1.53
3	PBE0-DH	0.84	2.13	1.60
4	mPW1K	0.13	2.10	1.61
5	ωB97XD	0.80	2.41	1.89
6	B2PLYP	1.87	2.42	2.04
7	BHandHLYP	−0.65	2.75	2.10
8	ωB97X	−0.33	2.49	2.10
9	LC-ωPBE	−0.81	2.74	2.18
10	M06	1.80	3.50	2.42
11	M06-HF	−1.41	3.56	2.50
12	ωB97	−1.30	3.19	2.59
13	B972	1.92	3.69	2.74
14	CAM-B3LYP	2.42	3.32	2.78
15	LC-PBEPBE	−0.36	4.40	3.40
16	B1LYP	3.28	3.98	3.43
17	mPW1PW91	3.12	4.19	3.45
18	PBE0	3.53	4.76	3.83
19	B3LYP	4.31	5.14	4.39
20	X3LYP	4.34	5.16	4.44
21	B3LYP-D	4.77	5.62	4.84
22	VSXC	4.25	6.19	4.56
23	B97D	5.97	7.64	6.09
24	GRAC	7.37	8.88	7.38
25	TCA	7.56	9.38	7.56
26	BLYP	7.93	9.23	7.93
27	PBEPBE	8.46	10.45	8.46

[a]All of the value are in kcal/mol.

functionals, those expressly designed for kinetics are the best performing. Indeed, at the top of the list, M06-2X and BMK are found, showing significantly better performances than those for PTBEs. This is also true for other functionals like B2PLYP and BHandHLYP, thus further confirming the role of HF exchange in determining reaction barriers.[23,63,64] At the same time, B1LYP and B3LYP provide significantly high deviations, in contrast with the results obtained for the PT reaction database. Stable in the ranking are the PBE0-DH and ωB97D functionals, both providing comparable deviations (see Table 4). Looking more in detail at the HT reactions (Table S2), it appears that B2PLYP, BHandHLYP, and PBE0-DH give similar errors, whereas larger deviations are obtained with the ωB97D functional. It is noteworthy that also LC-ωPBE gives comparably good results on HT reactions.

In summary, our results clearly show how the performances of most of the functionals differ when considering the DBH24/08 (specify designed for kinetics) or PT data sets, with only few functionals having comparable relative positions in the two rankings.

3.3. Optimized Structures: PT Barriers and H-Bond Structural Parameters. As previously mentioned, most of the recent benchmarks are based on the assumption that structural parameters are less sensible in the choice of the functional than other properties, including thermochemistry. With few notable exceptions,[65,66] it is custom nowadays to test a DFT approach using given (fixed) structures, sometimes optimized at the post-HF level, as, for instance, is the case of the G2 set for thermochemistry.[67] However, not only could such a practice introduce some spurious effects but also it is far from what is in use for (real) chemical applications, where often the same method is used for both structural optimization and energy evaluation. In order to investigate the structural effect on PTBEs, eight systems (B−I in Figure 1) and 16 functionals, selected among the most representative of the 27 in the set, have been considered. $H_5O_2^+$ has not been optimized since, as is well-know, it has only a stable structure.

The obtained H-bond parameters have been compared with those computed at the CCSD level (see Table 2 for the reference values), and the results are collected in Table 5. Two

Table 5. Mean Signed Deviations (MSD), Mean Absolute Deviations (MAD), and Root-Mean Square Deviations for H-Bond Parameters[a]

	functional	MSD	RMSD	MAD
1	M06	0.001	0.016	0.012
2	BMK	−0.002	0.017	0.013
3	ωB97X	−0.008	0.019	0.014
4	ωB97	−0.003	0.028	0.017
5	B1LYP	−0.006	0.024	0.018
6	B2PLYP	−0.010	0.032	0.024
7	X3LYP	−0.010	0.035	0.026
8	B3LYP	−0.007	0.035	0.026
9	CAM-B3LYP	−0.018	0.042	0.031
10	LC-ωPBE	−0.023	0.051	0.037
11	PBE0-DH	−0.030	0.057	0.040
12	M06-2X	−0.024	0.057	0.041
13	mPW1PW91	−0.031	0.065	0.047
14	PBE0	−0.028	0.071	0.051
15	LC-PBEPBE	−0.037	0.088	0.066
16	M06-HF	−0.051	0.110	0.079

[a]In the case of asymmetric systems, only the values for the lowest energy structure (reported in Figure 1) have been considered, and the protonated water dimer has not been included. All of the values are in Å.

global hybrids, namely, M06 and BMK, containing 27 and 42% of HF exchange, respectively, give the most accurate structures. They are followed by two RSHs, ωB97X and ωB97, and by another GH, B1LYP. The largest deviations have been obtained with PBE0, LC-PBE, and M06-HF, their MAEs ranging from 0.051 to 0.079 Å.

The situation becomes more involved when the computed energies are compared with the reference CCSD(T) values. Indeed, functionals providing accurate geometries, like BMK, M06, or ωB97, give larger errors on energies. The opposite holds for PBE0-DH and B3LYP, with smaller deviations on energies and significant inaccuracy on structures. In contrast, B1LYP and ωB97X are not only those giving the lowest deviations on PTBEs but they seem to provide balanced results on the two distinct properties.

From these data, it is difficult to extract any trends linking, for instance, H-bond lengths to HF exchange contribution or to the corresponding activation energy. This absence of any correlation clearly appears from the plot in Figure 2, where the
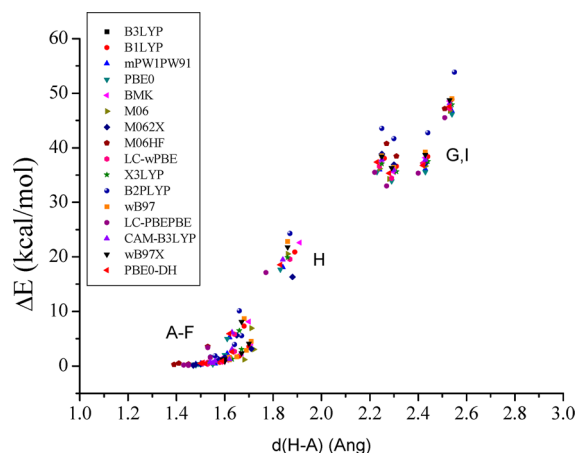

Figure 2. Plot of the energy barriers as a function of the hydrogen-acceptor (H-A) distances for all of the considered systems and functionals.

distance between the hydrogen involved in the H-bond and the acceptor atoms are reported against the associated activation energy. While a linear relation, independent of the type of functional considered, has been recently evidenced for protonated N-cycles,[27] this is no longer the case when different types of PT reactions are considered. Indeed, the data of Figure 2 are basically grouped by energy values, and also within each subgroup the values are scattered.

3.4. Some Comments. All of the functionals have been ranked with respect to their performances on the four considered trials, namely PTBEs at a given geometry, the DBH24/08 set for kinetics, and PTBEs at optimized geometries and related H-bond geometrical parameters. The total score (as the sum of the four positions) is reported in Figure 3. Starting from this final ranking, several comments can then be made. The first one concerns the change of the relative functional ranking in going from one benchmark to another. Let us start with the variations in going from PTEBs computed at fixed
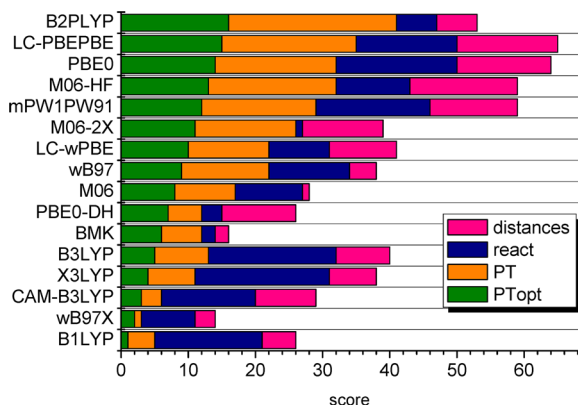

Figure 3. Summary of the functional score for the four benchmarks: proton transfer barriers at B3LYP geometry (PT), proton transfer barriers at respective optimized geometry (PTopt), standard NBH24/08 test (react), and H-bond structural parameters (distances).

geometries with respect to those obtained with the relaxed structures. For most of the functionals, the ranking is very similar. For instance, ωB97X is classed second in the two sets, while PBE0-DH is fifth in the first (fixed geometry) and seventh in the second (optimized geometry) sets. Remarkable exceptions are the M06-2X (15th and 11th) and M06-HF (19th and 13th), which are clearly penalized by the use of the fixed geometry (see Table 6). Albeit few functionals change their

Table 6. Mean Signed Deviations (MSD), Mean Absolute Deviations (MAD), and Root-Mean Square Deviations (RMSD) for Proton Transfer Barriers Obtained Using the Optimized Structures for Each Functional[a]

	functional	MSD	RMSD	MAD
1	B1LYP	0.25	1.04	0.76
2	ωB97X	0.60	1.17	0.77
3	CAM-B3LYP	−0.33	0.98	0.80
4	X3LYP	−0.42	0.97	0.86
5	B3LYP	−0.51	0.99	0.86
6	BMK	0.50	1.33	0.94
7	PBE0-DH	−0.81	1.12	0.95
8	M06	−0.63	1.23	1.00
9	ωB97	1.01	1.54	1.05
10	LC-ωPBE	−0.88	1.30	1.07
11	M06-2X	−0.70	1.31	1.07
12	mPW1PW91	−1.39	1.62	1.39
13	M06-HF	−0.69	2.50	1.64
14	PBE0	−1.65	1.85	1.65
15	LC-PBEPBE	−0.58	4.79	3.13
16	B2PLYP	3.20	4.02	3.20

[a]All of the values are in kcal/mol.

positions in going from one to another test, this result could raise some warnings for a correct functional benchmarking, which should consider both energy and structural parameters at the same time. It is noteworthy that similar conclusions (a functional minimizing errors on energy does not necessarily give optimal structures) were reached many years ago (see, for instance, ref 41) and more recently have been evidenced for molecules and solids.[66]

This fact is even more evident when comparing the ranking on the energy (at fixed geometry) with that on structural parameters. Indeed, almost all of the functionals perform in a very different way on the two properties. For instance, the most accurate functional on the structure is M06, ranked eighth in energy, while B2PLYP is in the sixth position in the structure and last (16th) in energy. X3LYP, B3LYP, B1LYP, and ωB97X provide, instead, very equivalent performances.

The situation gets more involved in the case of the results for the DBH24/08 set. Here, the mismatch between the two rankings is clear. As an example, B2LYP is the sixth best performing functional on the DBH24/08, and it is only in 25th position on the PTEB (at fixed geometry), while B1LYP shows the opposite behavior, 16th in the first set and fourth in the second. PBE0-DH is, instead, characterized by more regular performances, being third and fifth in the two lists, respectively. The bottom of the list, however, is quite similar between the two rankings, grouping all of the GGA functionals.

These results underline that functionals performing well for energy do not necessarily do the same for structure and that the DBH24/08 set cannot be considered a representative for PT reactions.

A second general comment concerns the position of each functional in the final ranking. This latter is based, of course, on the assumption that each trial has the same weight. As is clearly apparent from the data in Figure 3, the best classified functional is the recent ωB97X model, which provides high ranking in all four trials. It is followed by BMK, B1LYP, and PBE0-DH. Even if the total score is similar for the three functionals, the first (BMK) is accurate on both reaction barriers for the DBH24/08 set and H-bond distances, while the second (B1LYP) is particularly inaccurate on the first set (DBH24/08 set) and the third (PBE0-DH) on the second trial (H-bond distance). Notably, these three functionals represent two different rungs on Perdew's ladder (GH and DH), thus confirming, as already found for other functionals,[36,51,68] that for some properties the performances of different families could be very close. Indeed, it becomes more and more difficult to relate some physical features of a functional (e.g., respect of the uniform gas limit, asymptotical behavior) to its performances. Analogously, it is not possible to correlate the fraction of the HF exchange to the accuracy on PTBEs or on the corresponding H-bond distances. While these effects could be evidence for functionals belonging to the same family (e.g., BLYP, B3LYP, B1LYP), this is no more the case when a more complex functional form (that is going from B1LYP to CAM-B3LYP) or different families of functionals are considered. For instance, the BMK (42% HF exchange) and M06 (0% HF echange) both perform well on distances. The use of a complex analytical form for functionals, often also not based on strong physical constraints, prevents a straightforward analysis of their performances. Finally, the systematic improvement found for all of the considered properties in going from PBEPBE to PBE0 to PBE0-DH should be noted. Such behavior is not found for the BLYP family (BLYP, B3LYP, and B2PLYP), thus well underlining the robustness of these parameter-free approaches, including the PBE functional in a formally consistent fashion.

4. CONCLUSION

A number of different exchange correlation functionals have been tested on the difficult playground represented by proton transfer reactions. In particular, four different benchmarks have been considered: (1) energy barriers at a given structure, (2) energy barriers at the optimized structure, (3) structural parameters of the H-bond involved in the PT reaction, and (4) the DHB24/08 set for kinetics. The set of molecules chosen contains different kinds of proton transfers, characterized by intra- and inter-reactions, low and high barriers, and PTs involving a significant rearrangement of the electronic system. The results obtained not only indicate the functionals providing the most equilibrated results for the four trials, namely, ωB97X, B1LYP, BMK, and PBE0-DH, but also evidence some points which deserve general consideration. In particular, PT reactions present peculiar characteristics so that benchmarks used for kinetics could be not representative of the functional performances on such a class of reactions.

All the same, the great effort observed in recent years in defining better performing functionals produced approaches with remarkable accuracy, sometimes independent from their nature (GH, RSH, or DH). Unfortunately, this progress is sometimes made at the expense of simplicity, and the use of complex analytical form impedes a direct and informative connection between the physical basis on which functionals are (or could be) built and a specific property. Finally, as remarked many years ago for PT reactions[41] and recently evidenced,[66]

energy and structure represent two disconnected features, and both should be considered in fully meaningful benchmarks.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Details on the proton transfer barriers and related H-bond parameters as well as information on the DHB24/08 statistics are given in Tables S1−S6. Optimized CCSD structures are also reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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