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REGULAR ARTICLE

Activation enthalpies of pericyclic reactions: the performances of some recently proposed functionals

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Abstract We have assessed the performances of three recently proposed functionals, RC (Ragot and Cortona in J Chem Phys 121:7671, 2004), TCA (Tognetti et al. in J Chem Phys 128:034101, 2008), and *Rev*TCA (Tognetti et al. in Chem Phys Lett 460:536, 2008) by calculating the activation enthalpies for ten pericyclic reactions and eighteen 1,3-dipolar cycloadditions. We have found that the local functional (RC) gives results only marginally better than the local-density approximation ones, while the two GGA functionals, TCA and *Rev*TCA, both strongly improve the results with respect to PBE. The performances of *Rev*TCA, in particular, are not far different from those of a hybrid functional such as B3LYP.

Keywords Density-functional theory · Exchange-correlation functionals · Generalized-gradient approximation · Pericyclic reactions · 1,3-Dipolar cycloadditions

1 Introduction

The predictive ability of ab initio calculations performed in the framework of the density-functional theory (DFT) [1, 2] rests on the accuracy of the available approximations for the exchange-correlation functional. Many attempts on improving the oldest one, the local-density approximation (LDA) [3, 4], have been undertaken in the past, but these attempts were not always successful. During the past two decades, however, considerable progress has been made and thus various approximate functionals, which remedy the main failures of LDA, are now available. For example, functionals such as PW91 [5], PBE [6], or BLYP [7, 8], belonging to the generalized-gradient approximation (GGA) class, are known to strongly improve the atomization energies of the molecules, but to give barrier heights for various prototypical chemical reactions which are not accurate. Better results for these barriers can be obtained by means of the so-called hybrid functionals (among which B3LYP [9, 10] is probably the most famous one), where a fraction of the exact exchange is combined with an approximate functional in order to describe the whole exchange and correlation of the system. In this case, the increased precision of the results is paid in terms of an increased computational cost and of a more difficult implementation in the computer programs. Most solid-state codes, for example, do not allow one to perform calculations using hybrid functionals.

A common practice in searching for new approximate functionals is to choose an analytical expression having some desirable features and to determine the parameters entering this expression by fitting some set of reference data (the so-called "training set"). If the training set is sufficiently large, this procedure assures good performances of the functional for a wide class of systems. A well-known functional obtained in such a way is B3LYP. The parameters which determine the mixing of exact and approximate exchange, as well as of local and nonlocal correlation, were obtained by optimizing the results

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obtained for a large set of light atoms and small molecules and for various properties, including atomization energies, heights of barriers for chemical reactions, ionization potentials, proton and electron affinities. Furthermore, the DFT contributions to the hybrid functional are parametrized on their own: the Becke exchange was optimized using the rare gas atoms as reference systems [7], while the Lee–Yang–Parr correlation [8] was derived from an expression due to Colle and Salvetti [11], which was in turn devised in order to give exact results for He.

In contrast to the "pragmatic" approach underlined above, it is possible to adopt a more "fundamental" point of view. Once more an analytical expression of the functional is chosen. This expression contains some constants which are determined by requiring the approximate functional to have some properties that the exact one is known to have. A prototype of the functionals derived in such a way is the one proposed by Perdew et al. [6].

During the past few years, adopting the fundamental approach, we have elaborated three new functionals having an increased level of sophistication. The first one is a local functional (Ragot and Cortona [12], referred to as RC hereafter), which has been tested by calculations of various atomic and molecular properties. Comparing with its natural counterpart, the LDA, we have found strong improvements for some properties (atomization energies, reaction barriers, ionization potentials, total correlation energies) and similar results for bond lengths of molecules [13, 14].

The second one is a GGA-like functional (labeled TCA in the following) devised in order to introduce density-gradient related effects into the RC approximation [15]. In this case, the natural comparison is with a typical GGA functional like PBE. Here too, we have found quite systematic improvements, with the exception of the bond lengths, for which the two approximations behave in a similar way. However, this last statement must be modulated: for hydrogen-bonded complexes the TCA errors on the hydrogen bond-lengths are almost 40% smaller than the PBE ones [15].

Finally, the third approximation is another functional of the GGA class obtained by modifying the analytical expression characterizing the TCA approximation [for this reason it will be referred to as "revised" TCA (*Rev*TCA)] in order to satisfy one more property of the exact functional. In such a way, further improvements of the TCA results have been obtained [16].

The paper is organized as follows. The main features of the three approximations mentioned above will be briefly described in the next section. Then, we will present the results we have obtained for a class of important organic chemistry reactions. Finally we will propose some conclusions of this work.

2 The functionals

2.1 The RC correlation functional [12]

The RC correlation functional is given by

$$\varepsilon_c^{\mathrm{RC}} = \frac{-0.655868\ \arctan(4.888270 + 3.177037 r_s) + 0.897889}{r_s}, \qquad (1)$$

where ε_c is the correlation energy per electron and r_s is the Seitz radius

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}. \qquad (2)$$

Written in this form, the functional is adequate for non spin-polarized systems. In order to obtain a spin-polarized version, Eq. 1 can be combined with the Wang and Perdew interpolation function [17]:

$$C(\zeta(\vec{r})) = \left(\frac{1}{2}\left[(1+\zeta(\vec{r}))^{2/3} + (1-\zeta(\vec{r}))^{2/3}\right]\right)^3, \qquad (3)$$

where ζ is the relative spin-polarization

$$\zeta = \frac{\rho_\uparrow - \rho_\downarrow}{\rho}. \qquad (4)$$

The total correlation energy of a system is then given by

$$E_c^{\mathrm{RC}} = \int A(r_s(\vec{r}))C(\zeta(\vec{r}))d^3r, \qquad (5)$$

where

$$A(r_s(\vec{r})) = \frac{3}{4\pi r_s^3}\varepsilon_c^{RC}(r_s(\vec{r})). \qquad (6)$$

The functional described above is a *local* functional which can be trivially implemented in any DFT calculation program. Furthermore, it does not contain fitted parameters. The functional dependence of ε_c from r_s was determined by a modified Colle–Salvetti approach and the values of the constants which appear in Eq. 1 were obtained by applying the resulting expression to the homogeneous electron gas in the two limit cases of high- and low densities.

2.2 The TCA correlation functional [15]

The simplest way of introducing dependence from the density gradient in the RC functional is to look for a functional having the following general expression:

$$E_c^{\mathrm{TCA}} = \int A(r_s(\vec{r}))B(s(\vec{r}))C(\zeta(\vec{r}))d^3r, \qquad (7)$$

where $A(r_s(\vec{r}))$ and $C(\zeta(\vec{r}))$ are given in Eqs. 6 and 3, respectively, s is the reduced density gradient

$$s = \left(\frac{3}{2\pi}\right)^{1/3} \left\|\vec{\nabla} r_s\right\| = \frac{\left\|\vec{\nabla}\rho\right\|}{2(3\pi^2)^{1/3}\rho^{4/3}}, \tag{8}$$

and $B(s(\vec{r}))$ is a function to be determined. As the functional is supposed to be an extension of the RC one, a natural condition on B is

$$B(0) = 1. \tag{9}$$

Furthermore, it is known that, in the large gradient limit ($s \rightarrow \infty$), the correlation energy vanishes [6]. Thus, we must have

$$\lim_{s\rightarrow\infty} B(s) = 0. \tag{10}$$

Conditions 9 and 10 are satisfied if the following simple expression of $B(s(\vec{r}))$ is assumed:

$$B(s(\vec{r})) = \frac{1}{1 + \sigma s(\vec{r})^{\alpha}}, \tag{11}$$

where σ and α are positive constants. The values of these constants have been determined by an average gradient analysis following (and extending) an approach previously developed by Zupan et al. [18, 19]: σ and α were found to have values of 1.43 and 2.30, respectively.

2.3 The *Rev*TCA correlation functional [16]

In the *Rev*TCA model, the approximate functional is required to satisfy a further exact condition. The correlation energy of a monoelectronic system must be zero. This simple and very natural condition is not verified by most of the currently used correlation energy functionals (a notable exception is LYP [8]). In other terms, they are affected by a correlation self-interaction error (cSIE). This error can be partly corrected in the TCA scheme by modifying the general expression given in Eq. 7 as follows:

$$E_c^{Rev\mathrm{TCA}} = \int A[r_s]B[s]C[\zeta](1 - D[r_s, s, \zeta])d^3r \tag{12}$$

As *Rev*TCA is conceived as an extension of TCA, the function D, which couples the three variables r_s, s, and ζ, must satisfy two natural conditions:

$$D[r_s, 0, \zeta] \equiv 0, \tag{13}$$

and

$$D[r_s, s, 0] \equiv 0. \tag{14}$$

Thanks to the first one the functional recovers the RC approximations in the homogeneous case, while the second one makes *Rev*TCA and TCA identical for non spin-polarized systems. A further condition

$$-\infty < D \leq 1 \tag{15}$$

is needed in order to be sure that the correlation energy density is negative everywhere and equal to zero when the reduced density gradient tends to infinity. But the condition which more strongly characterizes the *Rev*TCA correlation functional is the following:

$$D\left[r_s\big|_{\mathrm{Hyd}}, s\big|_{\mathrm{Hyd}}, 1\right] = 1, \tag{16}$$

which means that $E_c^{Rev\mathrm{TCA}} = 0$ for all the hydrogenoid atoms.

Conditions 13–16 are satisfied if the following expression of D is chosen:

$$D[r_s, s, \zeta] = \zeta^4\left(1 - \left\{Sinc\left(\frac{\pi s}{a r_s}\right)\right\}^2\right), \tag{17}$$

where *Sinc* is the sine cardinal function $Sinc(u) = \sin(u)/u$, and $a = (4/9\pi)^{1/3.}$ In such a way *Rev*TCA corrects the cSIE. The correction is complete for all the exact densities of the hydrogenoid atoms, and partial for all the other monoelectronic systems. Numerical tests, however, indicate that the residual correlation energy for these latter systems is indeed very small.

2.4 The exchange counterparts

The RC functional was quite naturally combined with the Slater local exchange [4] giving the SRC approximation. The TCA correlation was combined with the PBE exchange. Some arguments supporting this choice were given in [15]. On the other hand, in the *Rev*TCA case, the choice was less easy. Although the *Rev*TCA correlation could be combined with the PBE exchange on the basis of the same arguments previously used for TCA, in practice, this choice does not work; the results are definitely less accurate than those obtained by TCA. As the *Rev*TCA correlation is more accurate than the TCA one, it appears that there is some mechanism of error compensation which is more effective in one case than in the other. Fortunately, the PBE exchange can be improved in a simple way. In fact, it contains two coefficients, μ and κ [6]. The first one determines the exchange behavior at small gradients. It was determined by Perdew and coworkers in order to recover the LDA linear response regime. As it was discussed in Ref. [15], this condition is verified with excellent accuracy when the PBE exchange is combined with the TCA correlation. Thus, μ does not need to be changed. Conversely, κ deals with large values of the reduced gradient and was fixed in order to respect the local Lieb–Oxford bound [6]. As it was pointed out by Zhang and Yang [20], the original Lieb–Oxford bound is an integral condition which does not need to be respected locally. If one requires that the local Lieb–Oxford bound (as improved by Chan and Handy [21]) is verified in the so-called “physical interval” [18, 19], that is $s \in I = [0,\ 3]$, one obtains $\kappa = 1.227$. In Ref. [20], where a similar value of κ was proposed ($\kappa = 1.245$, while the original PBE value is 0.804), it was shown by numerical calculations that the integral Lieb–Oxford condition is verified in practice. In conclusion, in contrast with RC and TCA, *Rev*TCA has its own exchange contribution, which has the same expression as in the PBE case, but with the κ value modified as specified above.

3 Activation barriers for pericyclic reactions

Pericyclic reactions are of fundamental importance in organic chemistry. Many experimental and theoretical studies have been devoted to the understanding of the mechanisms underlying these transformations, so that very accurate descriptions of them are now available. Recently, Guner et al. [22] have benchmarked 11 hydrocarbon pericyclic reactions and Ess and Houk [23] 18 dipolar cycloadditions. These reference data sets have been shown to be useful for the performance assessment of density functionals (see for instance Ref. [24]). In this section, we report the results we have obtained by the functionals presented above for the activation enthalpies of these reactions.

Calculations were carried out using the development version of the Gaussian package [25]. As recommended in Refs. [22, 23], the 6-31G* basis set was used. All the geometries were fully optimized and frequency calculations were performed in order to establish if the resulting stationary points were true minima or saddle points. The activation enthalpies were evaluated by

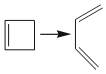
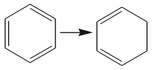
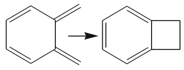
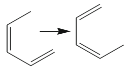
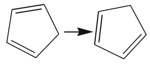
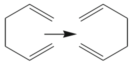
$$\Delta H_{0K}^{act} = \Delta H_{0K}^{TS} - \sum \Delta H_{0K}^{reactants}. \tag{18}$$

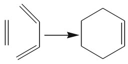
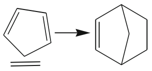
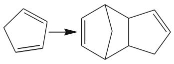
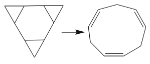
They include zero-point energies (ZPE), but no thermal corrections. Only closed-shell calculations were performed since open-shell structures have been shown to be less stable.

Statistic treatment was used in order to quantify the performances of the methods, including linear regressions and calculations of the mean signed errors (MSE) and mean absolute errors (MAE). For the hydrocarbon pericyclic reactions, the reference values are the experimental ones, whereas the multi-component CBS-QB3 values [26] define the standards for dipolar cycloadditions.

Table 1 collects the results we have obtained for ten hydrocarbon pericyclic reactions. They include three electrocyclic reactions, three sigmatropic shifts, three cycloadditions and one cycloreversion. We have not included reaction 11 of Ref. [23] in our tests because the precision of the corresponding experimental value is low

Table 1 Computed activation enthalpies ΔH_{0K}^{act} (in kcal/mol) and mean errors for three electrocyclic, three sigmatropic shifts, three cycloadditions and one cycloreversion reactions using various exchange-correlation functionals

						
Ref.^{a}	31.9	30.2	28.1	36.8	23.7	34.5
SVWN	34.8	21.1	20.5	23.7	19.7	19.7
SRC	34.4	21.1	20.5	23.8	19.7	20.0
PBE	32.7	25.2	22.7	29.5	22.7	26.2
TCA	32.2	26.5	23.5	31.0	23.6	27.8
*Rev*TCA	31.8	28.1	24.0	33.0	24.5	29.9
B3LYP^{a}	33.9	30.3	27.3	36.6	26.9	34.1

					MSE	MAE
Ref.^{a}	25.0	23.7	15.9	24.3	–	–
SVWN	0.1	1.2	−2.1	23.0	−11.2	11.8
SRC	0.6	1.7	−1.6	22.4	−11.2	11.6
PBE	12.2	13.4	11.5	19.7	−5.8	6.0
TCA	15.1	16.4	14.9	18.5	−4.5	4.5
*Rev*TCA	20.4	21.6	20.9	17.9	−2.2	3.4
B3LYP^{a}	21.4	22.3	21.2	21.5	0.1	2.0

The 6-31G* basis set is used

[a] From Refs. [22, 23]

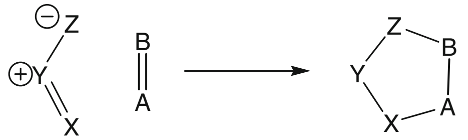


Fig. 1 The 1,3-dipolar cycloaddition

and the activation enthalpy is much greater than all the other ones.

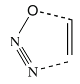
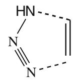
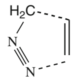
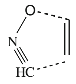
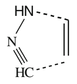
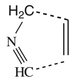
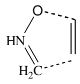
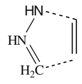
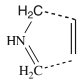
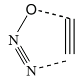
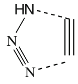
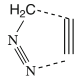
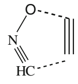
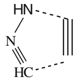
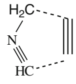
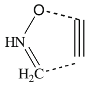
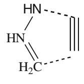
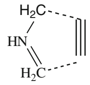
Comparing SRC with LDA (Slater exchange and Vosko–Wilk–Nusair correlation (SVWN) [27]), it appears that they give similar results, with a strong underestimation of the barriers, with the exception of the cyclobutene opening. In the cases where SRC and SVWN do not give the same results, those obtained by SRC are slightly better. However, there is one exception: it is given by the last transformation, the cycloreversion. This transformation seems to be a particular case: it is the only one for which the results obtained by the GGA functionals are worse than those given by the local ones. Considering the similarity of the SRC and SVWN results, as well as the fact that they are far from the experimental values, we have not extended the investigation of these two functionals to the second data set.

The same tendency (underestimation of the activation enthalpies except for the first reaction) is shared by PBE, but the errors are divided by 2 (MAE equal to 6.0 instead of 11.8 kcal/mol). Further improvements are obtained by TCA (MAE equal to 4.5 kcal/mol) that provides higher barriers than PBE (except for the cyclobutene opening and the cycloreversion). Similar remarks apply to the comparison between TCA and *Rev*TCA. The latter (MAE equal to 3.4 kcal/mol) gives results which compete with those obtained by B3LYP. A clear tendency can be drawn: from SRC to *Rev*TCA, via PBE and TCA, the barriers for reactions 1 and 10 decrease while all others increase.

The second set of reference data is comprised of eighteen 1,3-dipolar additions, as depicted in Fig. 1. The evolution of the barriers and consequently of the errors are similar to the first set. It can be noticed (see Table 2) that *Rev*TCA and B3LYP are the only functionals that give balanced results, in the sense that they are sometimes lower, sometimes higher, than the reference ones. It is the reason why their MSE is near to zero for the reactions involving acetylene. TCA reduces the errors for 33% with respect to PBE, whereas they are divided by 2 when going from TCA to *Rev*TCA.

A particular point deserves attention: no transition state has been found for the reaction of formoazomethine ylide with ethylene using the PBE functional. In order to get insights into this anomaly, we have investigated the relaxed potential energy surface by varying the distance *d* between the dipolarophile and the dipole. The results are plotted in Fig. 2 (where the energy origin corresponds to an infinite value of *d*). It appears that there is a maximum in the TCA and B3LYP cases, while the PBE energy monotonously increases. So, the form of the energy surface depends on the functional used for its computation.

Table 2 Computed activation enthalpies ΔH_{0K}^{act} (in kcal/mol) and mean errors for 18 1,3-dipolar cycloaddition reactions using various exchange-correlation functionals

										MSE	MAE
Ref.[a]	27.9	20.3	14.6	13.0	7.2	5.9	13.8	6.6	0.9	–	–
PBE	18.3	12.6	10.2	6.9	3.4	3.3	7.6	0.9	–	−5.9[b]	5.9[b]
TCA	20.0	14.6	12.3	8.5	5.3	5.3	9.7	3.3	1.1	−3.3	3.4
*Rev*TCA	24.9	19.3	16.3	12.0	9.2	9.2	14.3	7.9	5.2	0.9	2.0
B3LYP[a]	25.1	19.5	16.6	13.3	8.7	8.8	13.7	6.9	3.5	0.7	1.5
										MSE	MAE
Ref.[a]	27.9	20.1	15.2	14.1	8.5	7.4	14.0	8.1	1.5	–	–
PBE	17.6	11.8	10.2	7.3	3.9	4.2	6.9	2.2	−0.5	−5.9	5.9
TCA	19.2	13.7	12.1	8.8	5.6	6.1	9.7	3.3	1.1	−4.0	4.0
*Rev*TCA	23.9	18.2	15.9	12.0	9.2	9.8	13.4	9.5	5.1	0.0	1.9
B3LYP	24.5	18.6	16.4	13.7	9.1	9.5	13.0	8.5	3.6	0.0	1.4

The 6-31G* basis set is used

[a] From Ref. [23]

[b] Only for the first eight reactions

Another item which requires some discussion is the negative values obtained in the cases of the dimerization of cyclopentadiene with local approximations and of the last dipolar one with PBE. In all these cases, the transition state exists but it does not directly connect the reactants taken infinitely separated with the final product, but it connects the final product with another minimum that is an adduct formed by the reactants. Besides, this adduct is more stable that the independent reactants. For instance, for the case represented in Fig. 2, TCA finds an adduct at $d = 3.13$ Å. Such an energy profile is similar to the one found in nucleophilic substitutions where a complexation energy is defined. Following for instance Ref. [28], the $\Delta H_{0K}^{\text{act}}$ could be renamed the overall barrier (to illustrate this point, we can take the example of the last dipolar addition computed with PBE for which the overall barrier is equal to −0.5 kcal/mol and the activation barrier is equal to 1.0 kcal/mol, the adduct being characterized by a distance between both reactants equal to 3.07 Å).

Then, in the spirit of Refs. [22, 23], we plotted in Figs. 3 and 4 the DFT results against the reference values and we performed linear regressions. The ideal case is represented by the black dotted line, which corresponds to a perfect correlation. The main coefficients of the regressions are collected in Table 3 and offer a complementary way of evaluating the performances of the functionals, giving hints about the homogeneity of the performances going from one reaction to another. For the hydrocarbon reactions, the best regression coefficient R^2 for the GGAs is obtained by TCA, whereas *Rev*TCA is the most accurate for the dipolar additions. However, the best slope (B closest to 1) is obtained by PBE for the first set and by *Rev*TCA for the second one.

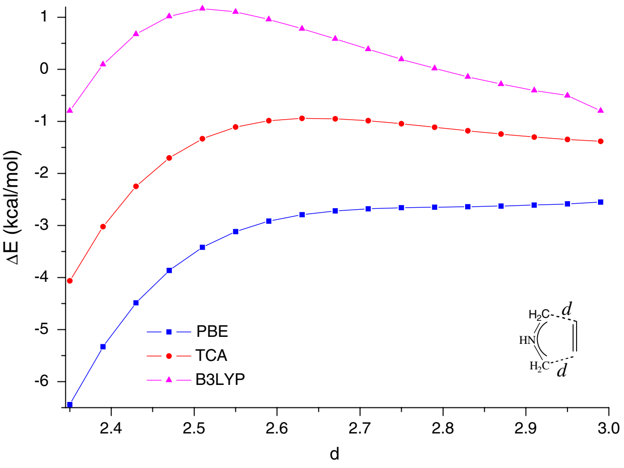


Fig. 2 Relaxed energy scan for the reaction of the formoazomethine ylide with ethylene using various density functionals and the 6-31G* basis set (d in Å)

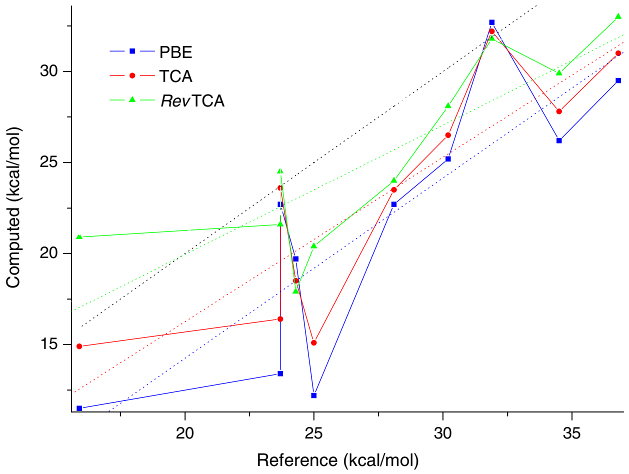


Fig. 3 Plot of computed activation enthalpies versus reference values for the ten pericyclic reactions (*full lines*) and of the corresponding linear regressions (*dotted lines*; the *black dotted line* corresponds to the perfect correlation)

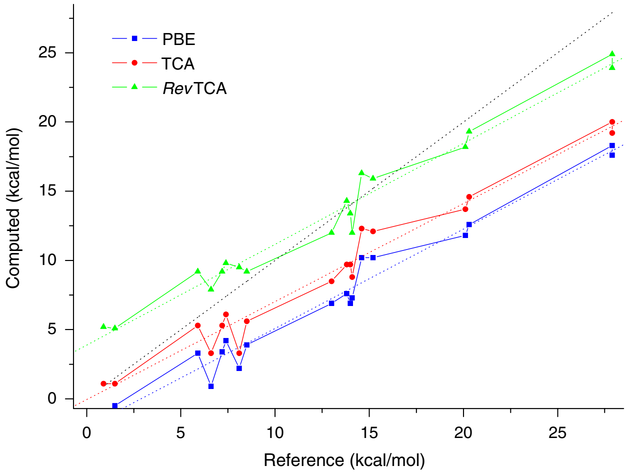


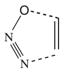
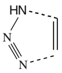
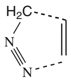
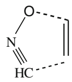
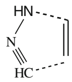
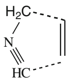
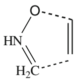
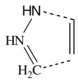
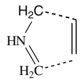
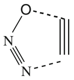
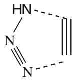
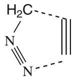
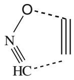
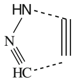
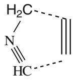
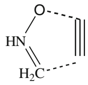
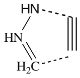
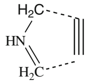
Fig. 4 Plot of computed activation enthalpies versus reference values for the 18 dipolar cycloadditions (*full lines*) and of the corresponding linear regressions (*dotted lines*; the *black dotted line* corresponds to the perfect correlation)

Finally, some remarks about our computational protocol will be made. Indeed, as already stated, the 6-31G* basis set has been chosen, following references 22 and 23. However, as stressed by Grimme et al. [29], this basis set is far from complete and the good B3LYP performances for dipolar cycloaddition reactions can be partly ascribed to the cancellation of errors stemming from the particular use of rather small double-ζ basis sets. In order to deepen this point, we test the four functionals with the corresponding Pople triple-ζ 6-311G(d,p). The results obtained from the full optimizations of the corresponding minima and transition states are gathered in Table 4. As it immediately appears, all of the activations barriers increase when

Table 3 Coefficients of the linear regressions $y = A + Bx$

$x = \Delta H^{\mathrm{act}}_{0K,\mathrm{ref}}$	Hydrocarbon reactions				Dipolar additions			
$y = \Delta H^{\mathrm{act}}_{0K,\mathrm{comp}}$	PBE	TCA	*rev*TCA	B3LYP	PBE	TCA	*rev*TCA	B3LYP
A	−5.529	−1.798	5.740	3.847	−2.073	−0.057	3.879	2.981
B	0.989	0.903	0.710	0.865	0.717	0.708	0.729	0.795
R^2	0.693	0.742	0.706	0.811	0.967	0.966	0.973	0.976

Table 4 Computed activation enthalpies $\Delta H^{\mathrm{act}}_{0K}$ (kcal/mol) and mean errors for 18 1,3-dipolar cycloaddition reactions using various exchange-correlation functionals

										MSE	MAE
Ref.[a]	27.9	20.3	14.6	13.0	7.2	5.9	13.8	6.6	0.9	–	–
PBE	21.0	14.5	11.5	8.8	4.3	4.0	9.0	2.6	−0.2	−3.8	4.3
TCA	23.0	16.7	13.7	10.7	6.3	6.2	11.3	5.1	2.1	−1.7	2.0
*Rev*TCA	27.8	21.5	17.8	14.3	10.3	10.2	16.0	9.8	6.3	2.7	2.7
B3LYP	28.6	21.9	18.5	15.7	10.2	10.1	15.6	9.1	5.0	2.7	3.1
										MSE	MAE
Ref.[a]	27.9	20.1	15.2	14.1	8.5	7.4	14.0	8.1	1.5	–	–
PBE	20.3	13.8	11.6	9.4	5.1	5.1	8.6	4.2	0.3	−4.3	4.3
TCA	22.1	15.8	13.7	11.2	7.0	7.2	10.9	6.5	2.4	−2.2	2.4
*Rev*TCA	26.8	20.4	17.5	14.6	10.8	11.0	15.4	10.9	6.3	1.9	2.1
B3LYP	28.0	21.2	18.4	16.3	10.9	11.0	15.3	10.2	5.2	2.2	2.2

The 6-311G(d,p) basis set is used

[a] From Ref. [23]

augmenting the basis set size. Accordingly, since PBE and TCA tend to underestimate the barriers at the double-ζ level, their performances improve when the basis set size is increased. Conversely, as *Rev*TCA and B3LYP provide more balanced results with the small basis set, their MAEs using the large one increase. Using the large basis set, TCA is the approximation which gives the best results. Another remarkable point is that the basis set extension enables PBE to locate a first-order saddle-point for the reaction of formoazomethine ylide with ethylene. It is not only a change for the activation barriers that a largest basis set can induce: the potential energy curve itself can be deeply modified. Nevertheless, the variations for MSE remain moderate when comparing Tables 2 and 4: for instance, they are equal to 2.1 kcal/mol (PBE), 1.6 kcal/mol (TCA) for reactions involving ethylene, and to 1.9 kcal/mol (*Rev*TCA) and 2.2 kcal/mol (B3LYP) with acetylene. These values show that the average basis shifts are not strongly functional-dependent.

4 Conclusions

In this paper, we have assessed the performances of some recently proposed functionals by calculations of the activation enthalpies of pericyclic reactions. The local RC functional gives results very close (in fact slightly better) to the LDA ones. These results complete those reported in a previous work [13], where other class of chemical reactions were studied. In that work, we found that SRC reduced significantly the MAE with respect to SVWN for Hydrogen-transfer (16%), heavy atom transfer (15%), and unimolecular and association reactions (24%), while the two approximations were found to be essentially equivalent for nucleophilic substitutions.

TCA and *Rev*TCA strongly improve the results with respect to PBE, *Rev*TCA being the most versatile among these three approximations. This is the same trend that we found in a preceding work [16], where we considered the reactions mentioned above as well as proton-transfer reactions. The performances of TCA and *Rev*TCA are not far from those of B3LYP and become even better for 1,3-dipolar cycloaddition when a large basis set is used. This is especially interesting, considering that TCA and *Rev*TCA do not contain fitted parameters, while B3LYP was optimized for systems containing light atoms such as those considered in the present work. This result does suggest that functionals belonging to the GGA class are not intrinsically less accurate than more elaborate and more time-consuming approaches.

References

1. Koch W, Holthausen MC (2000) A chemist's guide to density functional theory. Wiley-VCH, Weinheim
2. Parr RG, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, NewYork
3. Kohn W, Sham LJ (1965) Phys Rev 140:A1133. doi:10.1103/PhysRev.140.A1133
4. Slater JC (1974) Quantum theory of molecules and solids. The self-consistent field for molecules and solids, vol 4. McGraw-Hill, New York
5. Perdew JP (1991) Electronic Structure of Solids. In: Ziesche P, Eschrig H (eds) Akademie, Berlin
6. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865. doi:10.1103/PhysRevLett.77.3865
7. Becke AD (1988) Phys Rev A 38:3098. doi:10.1103/PhysRevA.38.3098
8. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785. doi:10.1103/PhysRevB.37.785
9. Becke AD (1993) J Chem Phys 98:5648. doi:10.1063/1.464913
10. Stephens PJ, Devlin JF, Chabalowski CF, Frisch MJ (1994) J Phys Chem 98:11623. doi:10.1021/j100096a001
11. Colle R, Salvetti O (1975) Theor Chim Acta 37:329. doi:10.1007/BF01028401
12. Ragot S, Cortona P (2004) J Chem Phys 121:7671. doi:10.1063/1.1792153
13. Tognetti V, Cortona P, Adamo C (2007) Chem Phys Lett 439:381. doi:10.1016/j.cplett.2007.03.081
14. Tognetti V, Adamo C, Cortona P (2007) Chem Phys 337:161. doi:10.1016/j.chemphys.2007.07.002
15. Tognetti V, Cortona P, Adamo C (2008) J Chem Phys 128:034101. doi:10.1063/1.2816137
16. Tognetti V, Cortona P, Adamo C (2008) Chem Phys Lett 460:536. doi:10.1016/j.cplett.2008.06.032
17. Wang Y, Perdew JP (1991) Phys Rev B 43:8911. doi:10.1103/PhysRevB.43.8911
18. Zupan A, Perdew JP, Burke K, Causà M (1997) Int J Quantum Chem 61:835. doi:10.1002/(SICI)1097-461X(1997)61:5<835::AID-QUA9>3.0.CO;2-X
19. Zupan A, Burke K, Ernzerhof M, Perdew JP (1997) J Chem Phys 106:10184. doi:10.1063/1.474101
20. Zhang Y, Yang W (1998) Phys Rev Lett 80:890. doi:10.1103/PhysRevLett.80.890
21. Chan KL, Handy NC (1999) Phys Rev A 59:3075. doi:10.1103/PhysRevA.59.3075
22. Guner VA, Khuong KS, Leach AG, Lee PS, Bartberger MD, Houk KN (2003) J Phys Chem A 107:11445. doi:10.1021/jp035501w
23. Ess DH, Houk KN (2005) J Phys Chem A 109:9542. doi:10.1021/jp052504v
24. Guner VA, Khuong KS, Houk KN, Chuma A, Pulay P (2004) J Phys Chem A 108:2959. doi:10.1021/jp0369286
25. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Scalmani G, Kudin KN, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Li X, Hratchian HP, Peralta JE, Izmaylov AF, Heyd JJ, Brothers E, Staroverov V, Zheng G, Kobayashi R, Normand J, Burant JC, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Chen W, Wong MW, Pople JA (2006) Gaussian Development Version, Revision F.01. Gaussian Inc., Wallingford
26. Montgomery JA, Frisch MJ, Ochterski JW, Peterson GA (1999) J Chem Phys 110:2822. doi:10.1063/1.477924
27. Vosko SH, Wilk L, Nusair M (1980) Can J Phys 58:1200
28. Joubert L, Pavone M, Barone V, Adamo C (2006) J Chem Theory Comput 2:1220. doi:10.1021/ct0600159
29. Grimme S, Mück-Lichtenfeld C, Würthwein E-U, Ehlers AW, Goumans TPM, Lammertsma K (2006) J Phys Chem A 110:2583. doi:10.1021/jp057329x