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Diels−Alder Reaction between Cyclopentadiene and C_{60}: An Analysis of the Performance of the ONIOM Method for the Study of Chemical Reactivity in Fullerenes and Nanotubes

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In this article, we theoretically analyze the Diels−Alder cycloaddition between cyclopentadiene and C_{60} for which experimental results on energy barriers and reaction energies are known. The comparison of the results obtained with the two-layered ONIOM approach using different partitions for the high- and low-level layers with those obtained employing the B3LYP/6-31G(d) method for the entire system allows us to conclude that the partition including a pyracylene unit of C_{60} in the description of the high-level layer is enough to get excellent results. Using this partition in the two-layered ONIOM approach, we have computed the energy barriers and reaction energies for this Diels−Alder reaction for different functionals, and we have compared them with experimental data. From this comparison, both the ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) and the M06-2X/6-31G(d)//ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) methods are recommended as reliable and computationally affordable approaches to be exploited for the study of the chemical reactivity of [6,6]-bonds in fullerenes and nanotubes.

1. Introduction

The most prominent representative of the fullerene family is C_{60}. Despite the ambiguous aromatic character of this molecule,[1,2] which suggests some stability, this molecule is quite reactive. Since its discovery in 1985,[3] a plethora of fullerene derivatives have been synthesized with a wide variety of chemical transformations.[4,5] Among them, exohedral cycloaddition reactions to the C_{60} cage and, in particular, Diels−Alder (DA) and 1,3-dipolar cycloadditions have been the most employed reactions for preparing fullerene derivatives.[6] The electron-withdrawing nature of C_{60} makes this molecule an ideal dienophile for DA reactions.[1,5] C_{60} readily undergoes [4 + 2] DA cycloaddition reactions with a variety of reactive dienes such as anthracene, tetracene, furan, or cyclopentadiene.[7−10] The functionalization of C_{60} through DA reaction can yield a large number of compounds including mono-, di-, and polyfunctionalized (up to six consecutive additions) products.[11] Adducts formed are sometimes thermally unstable and can undergo cycloreversion to the initial C_{60} and diene molecules upon heating.[8,9,12]

C_{60} has two types of bonds between carbon atoms, namely, the so-called [5,6]- and [6,6]-bonds, which have bond distances values of 1.458 and 1.401 Å,[13] respectively, and show different reactivity. The [6,6]-bond is shorter, has a larger π-electron density, and is more reactive than the [5,6]-bond. Then, the attack to the [6,6]-bond is preferred to the attack to the [5,6]-bond in most of the cycloadditions to C_{60},[8,14] and, in particular, the [4 + 2] DA cycloaddition exclusively involves the [6,6]-bonds without the occurrence of subsequent ring-openings.[10,15]

From a theoretical point of view, the first study of a reaction mechanism for a DA cycloaddition involving C_{60} was published in 1994 using the AM1 semiempirical method.[16] In this work, it was found that the enthalpy barrier for the [6,6]-attack of 1,3-butadiene to C_{60} is 18.4 $\text{kcal}\cdot\text{mol}^{-1}$, which is 15.8 $\text{kcal}\cdot\text{mol}^{-1}$ lower than that for the attack to the [5,6]-bond. The AM1 method was chosen in that work because it provides reasonable enthalpy barriers for DA reactions at a reduced computational cost.[17] Subsequent studies of fullerene reactivity with the location of transition states (TSs) were carried out with this methodology and also with the relatively cheap HF/STO-3G or similar methods.[18,19] Later on, the preferred method became the ONIOM approach using a combination of the B3LYP method or a similar method with a valence double-ζ basis set for the high-level layer and AM1 or the SVWN functional with a minimal basis set for the low-level calculations.[20] More recently, some studies at the density functional theory (DFT) level for the entire system employing from medium to large basis sets have been published.[21] This notwithstanding, these works require enormous amounts of computer time, and many studies are still done with a hybrid methodology such as the ONIOM method. In fact, this is the preferred method to theoretically study the chemical reactivity in nanotubes.[22] In some of our previous studies on fullerene reactivity using this method,[20] we have obtained barriers for experimental reactions that are apparently somewhat overestimated. Moreover, a recent study on the reactivity of nanotubes has show that by using AM1 as the low-level method within the ONIOM approach, the reaction energies are overestimated by ∼13 $\text{kcal}\cdot\text{mol}^{-1}$.[23]

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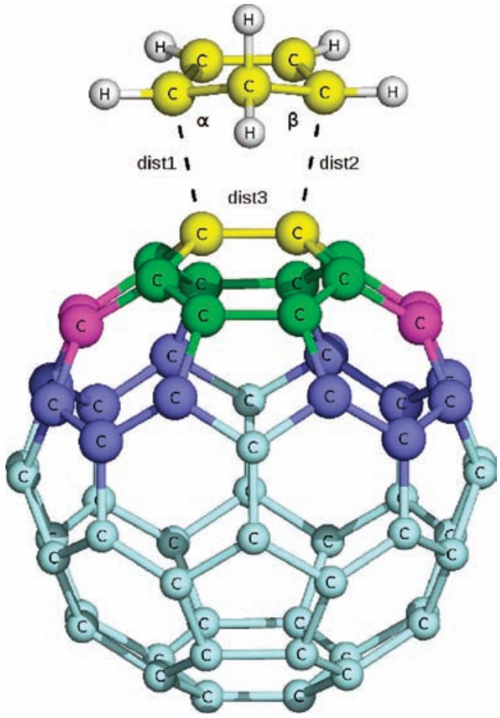

Figure 1. Scheme of the different models of C_{60} considered. Model I is the simplest model marked in yellow, and model II adds carbon atoms marked in green to the yellow ones. Model III contains the pyracylene unit (model II plus pink carbon atoms), and model IV contains the previous model plus blue carbon atoms. Moreover, the relevant distances and angles considered represented in Table 2 are shown.

The aim of this article is to analyze the DA reaction between cyclopentadiene and the [6,6]-bond of C_{60}, for which there are available experimental data on energy barriers and reaction energies to verify the reliability of methods such as ONIOM2(B3LYP/6-31G(d):AM1) or ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) to compute energy barriers and reaction energies in fullerenes and nanotubes. Pang and Wilson[8] found that the activation energy for the DA reaction of C_{60} and cyclopentadiene is 6.9 $\text{kcal}\cdot\text{mol}^{-1}$, whereas Giovane et al.[9] reported an activation energy of 26.7 ± 2.2 $\text{kcal}\cdot\text{mol}^{-1}$ for the corresponding retro-DA cycloaddition. From the combination of these two numbers, one can estimate the reaction energy in 19.8 ± 2.2 $\text{kcal}\cdot\text{mol}^{-1}$. Calculations on this DA reaction will be carried out with different ONIOM combinations and also for different partitions for the two layers treated at the low and high levels. In addition, we will carry out the study using two hybrid DFT methods for the full system. The comparison of the results obtained with the full system and the ONIOM approach will provide us with an idea of the validity of the ONIOM methodology for fullerene and nanotube reactivity studies. In addition, the comparison between theoretical and experimental results will serve as a benchmark for the different DFT methods tested. As possible partitions, we will consider for the high level the cyclopentadiene molecule in conjunction with four other fragments, namely, an ethylene molecule (model I, Figure 1), a naphthalene fragment (model II), a pyracylene molecule (model III), and a $C_{26}H_{12}$ buckybowl species[24] (model IV). A previous study by some of us[19] showed that the reaction energy and energy barrier of the DA cycloaddition of 1,3-butadiene to the central [6,6]-bond in the $C_{26}H_{12}$ polycyclic aromatic hydrocarbon are almost the same as those of C_{60}. For this reason, we expect small differences between the results of the full system and those of model IV.

2. Computational Details

Full geometry optimizations have been carried out with the hybrids MPW1K[25] and B3LYP[26] density functionals with the standard 6-31G(d) basis set[27] for the whole system. Previous studies have shown that the B3LYP/6-31G(d) method yields good energetics[28,29] for simple DA reactions and excellent geometries for curved polyarenes.[30] The two-layered ONIOM approach (ONIOM2)[31] was also employed to perform geometry optimizations using a combination of either the AM1 methodology or the SVWN method[32] together with the standard STO-3G basis set[33] for the low-level calculations and the B3LYP or the MPW1K methods with the standard 6-31G(d) basis set[27] for the high-level part. To have ample coverage, besides these functionals, others have also been tested. First, we have employed the pure exchange functional OPTX[34] combined with PBE[35] (OPBE) correlation functionals as well as the pure BP86[36,37] and BPW91[36,38] DFT methods. Second, we have employed the hybrid O3LYP.[39] Third, we have analyzed the results of single-point calculations for seven recently defined meta-hybrid functionals, the PW6B95,[40] PWB6K,[40] M05,[41] M05-2X,[42] M06,[43] and M06-2X[43] functionals. All systems have been treated with the spin-restricted formalism. Frequency calculations indicated that we got the correct stationary points, characterized by the number of negative eigenvalues of their analytic Hessian matrix (this number is zero for minima and one for any true TS). We have also checked that imaginary frequencies exhibit the expected motion. In Section 3A, we discuss electronic energies without further corrections. In Section 3B, all computed reaction and activation energies include zero-point energies (ZPEs) and thermal corrections ($C_v\Delta T - R\Delta T$) at 298 K to the electronic energies to allow direct comparison between theoretical and experimental data. However, in those cases where only single-point (SP) calculations have been performed, corrections to the electronic energy have been taken from the ONIOM(B3LYP/6-31G(d):SVWN/STO-3G) calculations. All ONIOM calculations and B3LYP and MPW1K optimizations have been performed using the Gaussian 03 program.[44] The NWChem computational package[45] has been used to perform SP calculations for the meta-hybrid functionals (PW6B95, PWB6K, M05, M05-2X, M06, and M06-2X).

3. Results and Discussion

This section is divided as follows: first, the four different models employed for ONIOM2 calculations are compared with the full B3LYP/6-31G(d) results to discuss which is the most convenient of the four ONIOM2 partitions analyzed in terms of accuracy and computational cost; second, using the most convenient ONIOM2 partition, several functionals are tested to find the ONIOM2 combination that provides better results as compared with experimental data.[8,9]

3A. ONIOM Partitions. Table 1 contains the reaction energies (ΔE_R) and energy barriers ($\Delta E^{\ddagger}$) for the ONIOM2 calculations. In Figure 2, the reaction profile with initial reactants, TS, and product has been represented. For the high-level calculations, four partitions have been analyzed (see Figure 1). For the low-level layer, either the AM1 method or the SVWN/STO-3G method have been used. Therefore, Table 1 contains the results obtained with the ONIOM2(B3LYP/6-31G(d):AM1) and ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) methods for all four partitions. These results have been compared with those obtained when treating the entire system with the B3LYP/6-31G(d) method, for which a reaction energy of $\Delta E_R = -9.1$ $\text{kcal}\cdot\text{mol}^{-1}$ and an energy barrier of $\Delta E^{\ddagger} = 17.5$ $\text{kcal}\cdot\text{mol}^{-1}$ have been obtained. The last two columns of

TABLE 1: Reaction Energies, ΔE_R, and Activation Barriers, $\Delta E^{\ddagger}$ (in kilocalories per mole), for the Different Model Systems Studied[a]

model	method for low layer	ΔE_R	$\Delta E^{\ddagger}$	$\Delta\Delta E_R$[b]	$\Delta\Delta E^{\ddagger}$[b]
real	B3LYP	−9.1	17.5		
I	AM1	−22.0	8.1	−12.9	−9.4
	SVWN/STO-3G	−3.1	16.6	6.0	−0.9
II	AM1	−8.2	16.9	0.9	−0.6
	SVWN/STO-3G	−12.4	15.8	−3.3	−1.7
III	AM1	−12.3	16.8	−3.2	−0.7
	SVWN/STO-3G	−8.7	17.9	0.4	0.4
IV	AM1	−7.8	[c]	1.3	[c]
	SVWN/STO-3G	−9.0	17.2[d]	0.1	−0.4

[a] Optimizations have been performed using the two-layered ONIOM approach, where the DFT method B3LYP together with 6-31G(d) basis set have been used to describe the so-called high layer. Two different methods have been applied for the low layer: either the semiempirical AM1 or the DFT method SVWN together with STO-3G. [b] Reaction energy as well as the reaction barrier obtained for the complete B3LYP/6-31G(d) system have been compared with the ONIOM approach. [c] We were unable to locate the transition state at this level of theory because of SCF convergence problems in the AM1 calculation. [d] Transition state close to but not fully converged (forces were converged but not displacements).

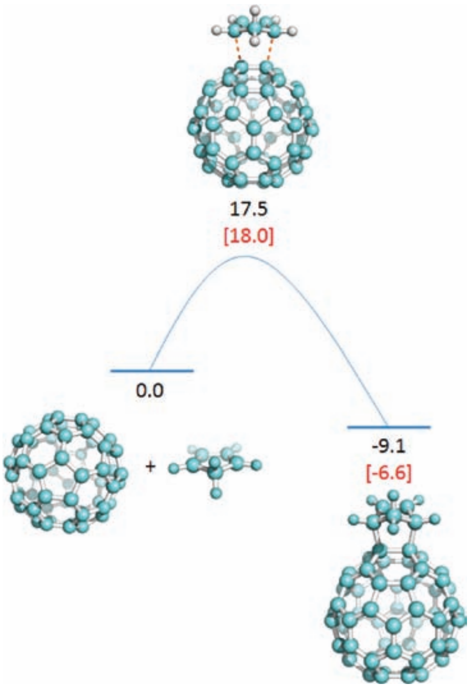

Figure 2. Reaction profile for the Diels−Alder cycloaddition reaction between cyclobutadiene and the [6,6]-bond of C_{60}. Reaction and activation energies at the B3LYP/6-31G(d) level of theory have been represented in black and expressed in kilocalories per mole. Electronic energies including thermal corrections at 298 K and ZPEs have been included between brackets and in red.

TABLE 2: Most Relevant C−C Bond Distances (in angstroms) and ∠CCC Angles (in degrees) As Depicted in Figure 1 for the Transition State of the Diels−Alder Reaction Studied and for the Different Methods and Models Considered

model	method	dist 1	dist 2	dist 3	α	β
I	AM1	2.309	2.157	1.485	88.4	92.2
	SVWN/STO-3G	2.429	1.947	1.490	84.0	96.5
II	AM1	2.092	2.503	1.474	94.9	83.7
	SVWN/STO-3G	2.211	2.225	1.455	90.2	89.9
III	AM1	2.265	2.265	1.462	89.4	89.5
	SVWN/STO-3G	2.197	2.197	1.462	90.3	90.3
IV	AM1	[a]	[a]	[a]	[a]	[a]
	SVWN/STO-3G[b]	2.203	2.190	1.461	90.1	90.2
	B3LYP	2.203	2.203	1.460	90.2	90.2

[a] We were unable to locate the transition state at this level of theory because of SCF convergence problems in the AM1 calculation. [b] Transition state close to but not fully converged (forces were converged but not displacements).

Table 1 give the difference in the reaction energies ($\Delta\Delta E_R$) and energy barriers ($\Delta\Delta E^{\ddagger}$) for the ONIOM2 calculations when compared with the B3LYP/6-31G(d) results in the complete system. In addition, Table 2 lists the C−C bond lengths and ∠CCC angles most involved in the formation of the two new bonds in the DA cycloaddition (see Figure 1).

Not surprisingly, when compared with the full B3LYP/6-31G(d) results, the largest and the smallest errors correspond to the ONIOM2(B3LYP/6-31G(d):AM1) method with model I and the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) method with model IV, respectively. Interestingly, there is a good convergence for the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) method, the overall error diminishing progressively when going from models I to IV. For the ONIOM2(B3LYP/6-31G(d):AM1) method, we do not find this behavior, and the model II approach already gives the best results, probably because of some kind of error compensation. For any of the two approaches, model I is clearly not good enough, especially for describing reaction energies. Despite having an excellent performance with the ONIOM2(B3LYP/6-31G(d):AM1) approach, model II is too small to provide good results for all kinds of cycloadditions to fullerenes. Both models III and IV when used with the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) approach yield errors less than 0.5 $\mathrm{kcal \cdot mol^{-1}}$ in both reaction and activation energies.

The results in Table 2 indicate that the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) C−C bond distances and ∠CCC angles also converge to those of the full system when going from model I to model IV. In all cases, the TS search started from a symmetric structure, and the optimization procedure led in some cases to a concerted but asynchronous TS.[46] The TS located at the B3LYP/6-31G(d) method is concerted and synchronous, and this is better reproduced by the values obtained with model III. Energy differences between the synchronous and asynchronous were minor (for instance, 0.2 $\mathrm{kcal \cdot mol^{-1}}$ in model IV).

In summary, we recommend the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) method in conjunction with the model III approach as a reliable and computationally affordable alternative to B3LYP/6-31G(d) calculations in the full system for studying the chemical reactivity of the [6,6]-bonds in other fullerenes. Both molecular structure and energetics of reactants, TS, and adduct are properly reproduced by this level of theory. In another study performed by some of us, we showed that this model also gives reaction and activation energies close to the full B3LYP description in nanotube structures.[23] Moreover, the use of the equivalent of our model III consisting of a pyrene unit of the nanotube compound within the ONIOM approach is the preferred strategy to study the chemical reactivity of nanotube compounds.[22] We therefore suggest the use of model III or equivalent for the study not only of chemical reactivity of fullerenes but also of carbon nanotube compounds provided that the curvature of the nanotube around the region of the attacked bond does not significantly differ from that of C_{60}. The ONIOM2 studies of the next section have been focused on model III.

TABLE 3: Comparison between Different Functionals[a]

functionals	ΔH_R	$\Delta\Delta H^{\ddagger}$	error ($\Delta\Delta H_R$)	error ($\Delta\Delta H^{\ddagger}$)
B3LYP/6-31G(d)	−6.6	18.0	13.2	11.1
MPW1K/6-31G(d)	−23.9	12.5	−4.1	5.6
ONIOM(BP86/6-31G(d):SVWN/STO-3G)	−10.4	11.4	9.4	4.5
ONIOM(OPBE/6-31G(d):SVWN/STO-3G)	−10.6	17.5	9.2	10.6
ONIOM(O3LYP/6-31G(d):SVWN/STO-3G)	−3.6	21.8	16.2	14.9
ONIOM(MPW1K/6-31G(d):SVWN/STO-3G)	−24.0	14.1	−4.2	7.2
ONIOM(BPW91/6-31G(d):SVWN/STO-3G)	−8.2	13.8	11.6	6.9
SP ONIOM(BP86/6-31G(d):SVWN/STO-3G)	−9.8	11.8	10.0	4.9
SP ONIOM(OPBE/6-31G(d):SVWN/STO-3G)	−10.2	17.1	9.6	10.2
SP ONIOM(O3LYP/6-31G(d):SVWN/STO-3G)	−3.7	21.7	16.1	14.8
SP ONIOM(MPW1K/6-31G(d):SVWN/STO-3G)	−23.1	14.2	−3.3	7.3
SP ONIOM(BPW91/6-31G(d):SVWN/STO-3G)	−7.7	14.1	12.1	7.2
SP ONIOM(PW6B95/6-31G(d):SVWN/STO-3G)[b]	−18.2	10.4	1.6	3.5
SP ONIOM(PWB6K/6-31G(d):SVWN/STO-3G)[b]	−23.9	10.5	−4.1	3.6
SP ONIOM(MPWB1K/6-31G(d):SVWN/STO-3G)	−23.6	13.1	−3.8	6.2
SP ONIOM(M05/6-31G(d):SVWN/STO-3G)	−17.3	14.5	2.5	7.6
SP ONIOM(M05-2X/6-31G(d):SVWN/STO-3G)	−24.7	5.6	−4.9	−1.3
SP ONIOM(M06/6-31G(d):SVWN/STO-3G)[b]	−23.8	7.4	−4.0	0.5
SP ONIOM(M06-2X/6-31G(d):SVWN/STO-3G)[b]	−24.2	6.8	−4.4	−0.1
SP PW6B95/6-31G(d)	−16.6	11.7	3.2	4.8
SP PWB6K/6-31G(d)	−23.8	11.4	−4.0	4.5
SP MPWB1K/6-31G(d)	−24.2	10.9	−4.4	4.0
SP M05/6-31G(d)	−16.2	15.4	3.6	8.5
SP M05-2X/6-31G(d)	−25.7	5.0	−5.9	−1.9
SP M06/6-31G(d)	−21.3	9.1	−1.5	2.2
SP M06-2X/6-31G(d)	−24.4	7.1	−4.6	0.2

[a] Difference between the computed energies and the experimental values is also indicated (the experimental reaction energy is −19.8 ± 2.2 kcal·mol^{-1}, and the activation barrier is 6.9 kcal·mol^{-1}). SP means single-point energy calculations performed at the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) geometry. [b] Extrapolated ONIOM energies were obtained using the NWChem computational package.[45] The ONIOM2 energies were calculated manually using the formula $E_{\mathrm{ONIOM2}} = E_{\mathrm{real,low}} - E_{\mathrm{model,low}} + E_{\mathrm{model,high}}$, where $E_{\mathrm{real,low}}$ is the energy of the real system calculated at the low level of theory, whereas $E_{\mathrm{model,low}}$ and $E_{\mathrm{model,high}}$ are the energies of the model computed at the low and high level methods, respectively.

3B. Performance of Different Functionals. As said in the Introduction, the DA reaction between cyclopentadiene and C_{60} has been studied experimentally. In particular, the activation energy for the DA reaction of C_{60} and cyclopentadiene is 6.9 kcal·mol^{-1},[8] whereas the reaction energy is estimated to be −19.8 ± 2.2 kcal·mol^{-1} from the activation energy reported for the retro-DA cycloaddition.[9] The comparison of these experimental results with the B3LYP/6-31G(d) values ($\Delta H^{\ddagger} =$ 18.0 kcal·mol^{-1} and $\Delta H_R = -6.6$ kcal·mol^{-1}) show that the B3LYP errors are larger than 10 kcal·mol^{-1} for both energy barriers and reaction energies. It is widely accepted that energy barriers computed at the B3LYP level with a medium or large size basis set are relatively good although somewhat underestimated,[47,48] notably, for the simplest DA reaction between *cis*-buta-1,3-diene and ethylene.[28,47,49] Unexpectedly, the B3LYP/6-31G(d) energy barrier for the DA reaction between cyclopentadiene and C_{60} is clearly overestimated by as much as 11.1 kcal·mol^{-1}. The reason for this overestimation, which is common to both the B3LYP/6-31G(d) and the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) methods (vide supra), has not been investigated here, but it may be related to the reduction of the HOMO−LUMO gap in curved species as compared with planar ones.[50] Previous studies have shown that the MPW1K functional with the 6-31+G(d,p) basis reduces the mean unsigned error in reaction barrier heights by a factor of three over B3LYP.[25] Therefore, we decided to check this functional for the same reaction, and the MPW1K/6-31G(d) method leads to a clear improvement over the B3LYP/6-31G(d), but the energy barriers are still overestimated with errors larger than 5 kcal·mol^{-1} (see Table 3). The result obtained using the ONIOM2(MPW1K/6-31G(d):SVWN/STO-3G) method in conjunction with model III differs by less than 1.6 kcal·mol^{-1} when compared with the MPW1K/6-31G(d) values.

As shown in Table 3, we have explored other DFT functionals with the 6-31G(d) basis set for the high level and the SVWN/STO-3G method for the low-level layer within the ONIOM2 geometry optimization and partition III. As compared with the experimental results, in all cases, the energy barrier is clearly overestimated with values that are higher than the experimental value by 4.5−14.9 kcal·mol^{-1}. Among the five functionals tested, the methods with the highest and lowest errors are, respectively, the ONIOM2(O3LYP/6-31G(d):SVWN/STO-3G) and ONIOM2(BP86/6-31G(d):SVWN/STO-3G) methods. Interestingly, for all five functionals, single-point (SP) calculations with the same methods at the ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) geometries basically yield the same results as those found when geometry optimization is allowed (differences in reaction energies and energy barriers are smaller than 1 kcal·mol^{-1} in all cases). By taking advantage of this evidence and performing only SP calculations, we have been able to test seven recently defined meta-hybrid functionals that show good performance for chemical reactivity studies.[40,43,51] Single-point calculations within the ONIOM approach have been performed for MPWB1K, M05, and M05-2X. The other meta-hybrids functionals (PW6B95, PWB6K, M06, and M06-2X) are not included in our version of Gaussian 03; however, ONIOM energies were manually calculated, applying the formula $E_{\mathrm{ONIOM2}} = E_{\mathrm{real,low}} - E_{\mathrm{model,low}} + E_{\mathrm{model,high}}$, where $E_{\mathrm{real,low}}$ is the energy of the real system calculated at the low level of theory, $E_{\mathrm{model,low}}$, and $E_{\mathrm{model,high}}$ is the energy of the model computed at the low- and high-level methods, respectively.[31] Moreover, SP calculations at the optimized ONIOM geometry have also been performed for all seven meta-hybrid functionals using the NWChem computational package. The difference in energy between the SP ONIOM and SP DFT calculations for the entire system is shown to be lower than 2.5 kcal·mol^{-1} for the reaction energy and smaller than 2.2 $\text{kcal}\cdot\text{mol}^{-1}$ for the activation barriers. Interestingly, the SP ONIOM2(PW6B95/6-31G(d):SVWN/STO-3G) and SP ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) methods yield the lowest error in the reaction and activation energies, respectively, among all SP ONIOM calculations performed (see Table 3).

The results of the SP calculations using the metahybrid functionals available in NWChem are, in general, much better than those obtained with pure and hybrid density functionals. Concretely, those obtained with the M06/6-31G(d)//(ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) and M06-2X/6-31G(d)//ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) methods yield reaction energies and energy barriers with small errors; the former method performs better for reaction energies (the error is 1.5 $\text{kcal}\cdot\text{mol}^{-1}$) and the latter method performs better for energy barriers ($\Delta H^{\ddagger}$ is overestimated by only 0.2 $\text{kcal}\cdot\text{mol}^{-1}$). The latter deviations are within the range of the accuracies for the DFT single reference methods. Because we are usually more interested in having accurate energy barriers than reaction energies, we recommend as a reliable and computationally affordable method for studying chemical reactivity of [6,6]-bonds in fullerenes and nanotubes either the ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) or the M06-2X/6-31G(d)//ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) methodology in conjunction with model III, although methods such as ONIOM2(M06/6-31G(d):SVWN/STO-3G) or ONIOM2(PW6B95/6-31G(d):SVWN/STO-3G) also perform quite satisfactorily.

4. Conclusions

In this work, we have assessed the performance of the two-layered ONIOM method to study chemical reactivity of fullerenes and nanotubes by computing the reaction energy and energy barrier of the Diels−Alder cycloaddition between C_{60} and cyclopentadiene. First, we have analyzed different partitions for the high- and low-level layers by comparing the results of the ONIOM calculations with those obtained for the entire system using the same DFT functional as that employed in the high-level layer of the ONIOM methodology. From this comparison, we have concluded that partition III involving a pyracylene unit of the C_{60} cage and the incoming diene is the one that provides the best compromise between accuracy and computational cost. Second, using this partition in the ONIOM approach, we have compared the experimental reaction and activation enthalpies of the Diels−Alder cycloaddition between C_{60} and cyclopentadiene with those obtained using a series of different DFT functionals. Our results indicate that both the ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) and the M06-2X/6-31G(d)//ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) approaches are among the most reliable and computationally efficient methods to be exploited for studying the chemical reactivity of the [6,6]-bonds in fullerenes and nanotubes.

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Supporting Information Available: Optimized Cartesian *xyz* coordinates of all analyzed species. This material is available free of charge via the Internet at http://pubs.acs.org.

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