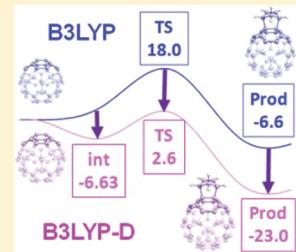


# Dispersion Corrections Essential for the Study of Chemical Reactivity in Fullerenes

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Supporting Information

**ABSTRACT:** In a previous paper (*J. Phys. Chem. A* 2009, 113, 9721), we analyzed theoretically the Diels–Alder cycloaddition between cyclopentadiene and C<sub>60</sub> for which experimental results on energy barriers and reaction energies are known. One of the main conclusions reached was that the two-layered ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) method provides results very close to the full B3LYP/6-31G(d) ones. Unfortunately, however, both the exothermicity of the reaction and the energy barrier were clearly overestimated by these two methods. In the present work, we analyze the effect of the inclusion of Grimme's dispersion corrections in the energy profile of this reaction. Our results show that these corrections are essential to get results close to the experimental values. In addition, we have performed calculations both with and without dispersion corrections for the Diels–Alder reaction of C<sub>60</sub> and several dienes and for the Diels–Alder cycloaddition of a (5,5) single-walled carbon nanotube and 1,3-cis-butadiene. The results obtained indicate that inclusion of dispersion corrections is compulsory for the study of the chemical reactivity of fullerenes and nanotubes.



## INTRODUCTION

Diels–Alder (DA) and 1,3-dipolar cycloadditions are among the most employed reactions for the functionalization of fullerenes.<sup>1</sup> The electron-withdrawing nature of fullerenes makes these molecules ideal dienophiles for DA and 1,3-dipolar reactions.<sup>2</sup> C<sub>60</sub> readily undergoes [4 + 2] DA cycloaddition reactions with a variety of reactive dienes, such as anthracene, tetracene, furan, or cyclopentadiene.<sup>3</sup> The [4 + 2] DA cycloaddition involves exclusively the [6,6]-bonds without the occurrence of subsequent ring openings.<sup>3f,4</sup> Adducts formed are sometimes thermally unstable and can undergo cycloreversion to the initial C<sub>60</sub> and diene molecules upon heating.<sup>3b,c,5</sup> One of the first reported DA reactions to C<sub>60</sub> was that of cyclopentadiene.<sup>3d,f</sup> In subsequent works, Pang and Wilson<sup>3b</sup> found that the activation energy for the DA reaction of C<sub>60</sub> and cyclopentadiene is 6.9 kcal·mol<sup>-1</sup>, whereas Giovane et al.<sup>3c</sup> reported an activation energy of 26.7 ± 2.2 kcal·mol<sup>-1</sup> for the corresponding retro-DA cycloaddition. From the combination of these two numbers, one can estimate the reaction energy to be -19.8 ± 2.2 kcal·mol<sup>-1</sup>.

In a recent paper,<sup>6</sup> some of us theoretically analyzed the DA reaction between cyclopentadiene and the [6,6]-bond of C<sub>60</sub> to verify the reliability of two-layered methods such as ONIOM2-(B3LYP/6-31G(d):SVWN/STO-3G) to compute energy barriers and reaction energies in fullerenes and nanotubes. Calculations on this DA reaction showed that the partition involving a pyracylene unit of the C<sub>60</sub> cage and the incoming diene provided reaction energies and energy barriers that are very close to those obtained by the full B3LYP/6-31G(d) calculations.

The energy barrier predicted by the B3LYP/6-31G(d) method was overestimated by ~11 kcal·mol<sup>-1</sup>. This is quite surprising, since it is usually said that energy barriers obtained with B3LYP in combination with a medium or large size basis sets are relatively good (especially in comparison with other functionals<sup>7</sup>), although somewhat underestimated,<sup>8</sup> notably, for the simplest DA reaction between *cis*-buta-1,3-diene and ethylene, in which it underestimates the barrier by ~5 kcal·mol<sup>-1</sup>.<sup>8a,e,g</sup> The error found in the reaction energy estimate was even larger.<sup>6</sup> At that time, we were unable to provide a reasonable explanation for the huge difference between the theoretical and experimental values.

On the July 6, 2010, the authors assisted at an inspiring conference on the dispersion effects by Prof. Grimme at the IX Girona Seminar.<sup>10</sup> After the talk, we decided to investigate whether the dispersion effects can be responsible for the large errors in our theoretical estimation of the reaction energy and energy barrier for the DA cycloaddition between cyclopentadiene and C<sub>60</sub>. We anticipate here that we have found that inclusion of London dispersion effects is mandatory to get accurate description of the energy profile in the DA cycloaddition studied here. Preceding work by Goerigk and Grimme<sup>11</sup> showed that the B3LYP mean absolute deviation for an extensive benchmark including thermochemistry, kinetic, and noncovalent interactions was reduced by about 2 kcal·mol<sup>-1</sup> when dispersion corrections were taken into account

**Received:** September 25, 2010

**Revised:** February 2, 2011

**Published:** March 25, 2011

**Table 1.** Comparison between the Reaction Energies,  $\Delta H_R$ , and Activation Barriers,  $\Delta H^\ddagger$  (in  $\text{kcal}\cdot\text{mol}^{-1}$ ), Corresponding to the [4 + 2] Diels–Alder Cycloaddition Reaction between  $C_{60}$  and Cyclopentadiene<sup>a</sup>

	$\Delta H_R$	$\Delta H^\ddagger$	$\Delta H_I^\ddagger$	error ( $\Delta \Delta H_R$ )	error ( $\Delta \Delta H^\ddagger$ )	error ( $\Delta \Delta H_I^\ddagger$ )
B3LYP/6-31G(d) <sup>b,c</sup>	-6.6 (-6.4)	18.0 (17.9)		13.2 (13.4)	11.1 (11.0)	
B3LYP-D/6-31G(d)	-23.3	2.3	9.1	-3.5	-4.6	2.2
ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) <sup>b,c</sup>	-5.9 (-5.8)	18.5 (18.3)		13.9 (14.0)	11.6 (11.4)	
ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G)	-22.6	2.7	9.4	-2.8	-4.2	2.5
ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G)	-22.0	8.2	12.1	-2.2	1.3	5.2

<sup>a</sup>  $\Delta H^\ddagger$  corresponds to the activation barrier calculated with respect to isolated reactants (i.e.,  $H^{\text{TS}} - (H^{C_{60}} + H^{\text{cyclopentadiene}})$ ), whereas  $\Delta H_I^\ddagger$  refers to the optimized reactant complex (i.e.,  $H^{\text{TS}} - H^{\text{int}}$ ). The difference between the computed energies and the experimental values is also indicated (the experimental reaction energy is  $-19.8 \pm 2.2 \text{ kcal}\cdot\text{mol}^{-1}$  and the activation barrier is  $6.9 \text{ kcal}\cdot\text{mol}^{-1}$ ). <sup>b</sup> From ref 6. <sup>c</sup> In parentheses, the relative enthalpies including solvent effects.

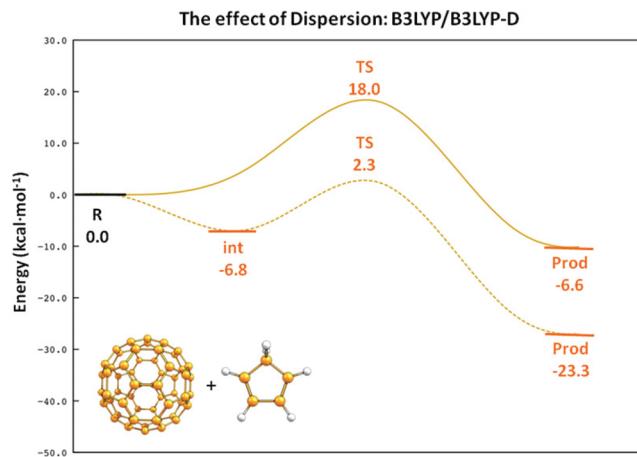
(B3LYP-D). In addition, previous works by Kruse and Grimme<sup>12</sup> and Korona et al.<sup>13</sup> already pointed out the importance of including the London dispersion corrections to obtain good estimates of the interaction energy of  $C_{60}$  and  $C_{70}$  with encapsulated  $H_2$  molecules. Moreover, Hesselmann and Korona reported that dispersion corrections are necessary to accurately compute the interaction energy of  $C_{60}$  with an encapsulated noble gas molecule.<sup>14</sup> However, in these works, the authors did not analyze the reactivity of these endohedral fullerenes.

## COMPUTATIONAL DETAILS

Full geometry optimizations have been carried out with the hybrid B3LYP<sup>15</sup> density functional with the standard 6-31G(d) basis set.<sup>16</sup> The two-layered ONIOM approach (ONIOM2)<sup>17</sup> has also been employed to perform geometry optimizations using a combination of the SVWN method<sup>18</sup> together with the standard STO-3G basis set<sup>19</sup> for the low-level calculations and the B3LYP methods with the standard 6-31G(d) basis set<sup>16</sup> for the high-level part. In both cases, we also performed the study including dispersion corrections following Grimme's approach (B3LYP-D and ONIOM2-D).<sup>20</sup>

In selected cases, we have also carried out calculations with the M06-2X functional.<sup>21</sup> 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 0 for minima and 1 for any true transition state). We have also checked that imaginary frequencies exhibit the expected motion. All reported 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. Solvent effects have been estimated in some particular cases with single-point calculations on the gas phase optimized structures using the polarizable continuous solvation model (PCM) and considering toluene as the solvent.<sup>22</sup>

All calculations including Grimme's dispersion corrections<sup>20a,b</sup> were performed using a locally modified version of the Gaussian 09 program (the “IOP(3/124=3)”) because including the dispersion correction was not yet correctly implemented in Gaussian 09, revision A.02; the  $S_6$  value for B3LYP was incorrectly set to 1.0 instead of 1.05, as recommended by Grimme;<sup>20b</sup> this has been corrected in the B.01 revision).<sup>23</sup> Apart from that, we have adapted the program to allow the inclusion of dispersion effects within the ONIOM approach with the  $S_6$  value set to 1.05 for the high-level B3LYP-D and to 1.0 for the low-level SVWN-D. The

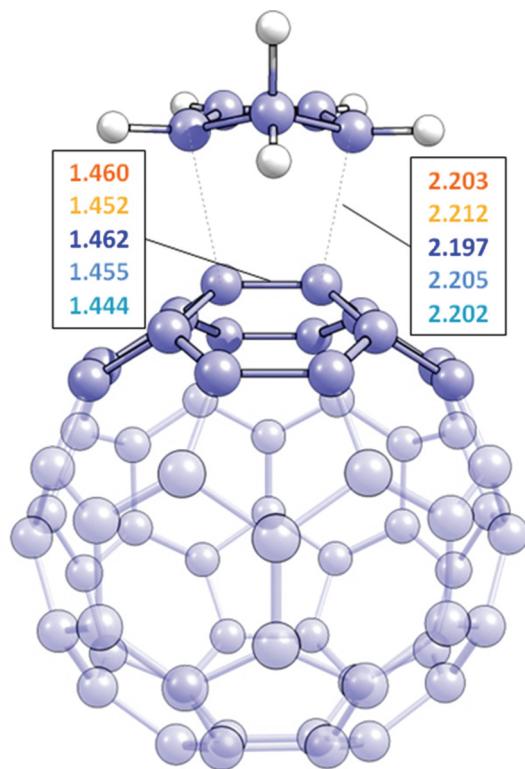


**Figure 1.** Comparison between the energy profile (in  $\text{kcal}\cdot\text{mol}^{-1}$ ) for the reaction between  $C_{60}$  and cyclopentadiene computed at B3LYP/6-31G(d) (represented in orange and using a straight line) and at B3LYP-D/6-31G(d) taking into account Grimme's dispersion corrections (in orange and discontinuous line).

SVWN functional was not considered in Grimme's study,<sup>20b</sup> and in the case of functionals that do not have a fitted  $S_6$  value, the standard procedure is to assign a  $S_6$  value of 1.0.

## RESULTS AND DISCUSSION

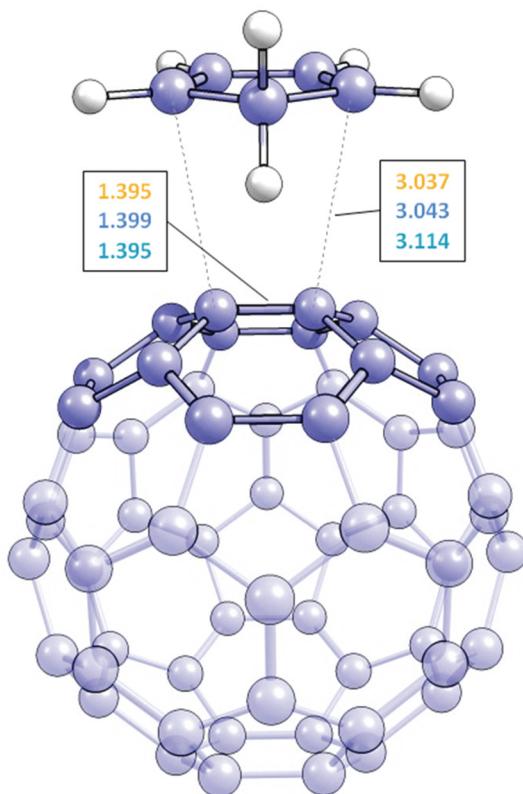
Table 1 contains the reaction energies ( $\Delta H_R$ ) and energy barriers ( $\Delta H^\ddagger$ ) for all calculations performed.  $\Delta H^\ddagger$  corresponds to the activation barrier calculated with respect to isolated reactants (i.e.,  $H^{\text{TS}} - (H^{C_{60}} + H^{\text{cyclopentadiene}})$ ), whereas  $\Delta H_I^\ddagger$  is relative to the optimized reactant complex (i.e.,  $H^{\text{TS}} - H^{\text{int}}$ ) for those methods that find such an intermediate. In Figure 1, the reaction profiles obtained with the B3LYP and B3LYP-D methods with initial reactants, intermediate, transition state (TS), and product have been represented. As can be seen in Figure 1, there is an important effect of the dispersion correction on the energy profile. This correction increases from the reactants to products and leads to an intermediate species (reactant complex) that is not found in the absence of dispersion corrections. The presence of this intermediate is not unexpected, given the predictable van der Waals interactions between polarizable  $C_{60}$  and cyclopentadiene molecules. Stabilization of this intermediate with respect to separated reactants is as large as  $6.8 \text{ kcal}\cdot\text{mol}^{-1}$ . The TS is



**Figure 2.** Representation of the optimized transition state structure with the most relevant distances (in Å). The different colors used to denote the C–C bond distances indicate the level of theory used. B3LYP/6-31G(d) values are depicted using dark orange; B3LYP-D/6-31G(d), in light orange; ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G), in dark blue; ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G), in light blue; and ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G), in cyan. H atoms and dark-blue C atoms constitute the layer treated at a high level in the ONIOM2 approach.

stabilized by dispersion by as much as  $15.7 \text{ kcal} \cdot \text{mol}^{-1}$ , as compared with free  $\text{C}_{60}$  and cyclopentadiene. Finally, the stabilization of the products is even larger ( $16.7 \text{ kcal} \cdot \text{mol}^{-1}$ ). The three last columns of Table 1 give the error in the theoretical estimates of reaction energies ( $\Delta\Delta H_R$ ) and energy barriers ( $\Delta\Delta H^\ddagger$  and  $\Delta\Delta H_{\text{I}}^\ddagger$ ) when compared with the experimental values. In solution of tetrachloroethane, benzene, or toluene, which are the solvents used experimentally,<sup>3b,c,f</sup> the molecular collisions are efficient enough to cool the otherwise rovibrationally hot reactant complex, causing it to be in thermal equilibrium with the environment. In this situation, the energy barrier measured experimentally corresponds to the energy difference between the TS and the reactant complex. Therefore, the experimental barrier of  $6.9 \text{ kcal} \cdot \text{mol}^{-1}$  must be compared with the  $\Delta H_{\text{I}}^\ddagger$  for the methods that yield a reactant complex and with  $\Delta H^\ddagger$  otherwise.

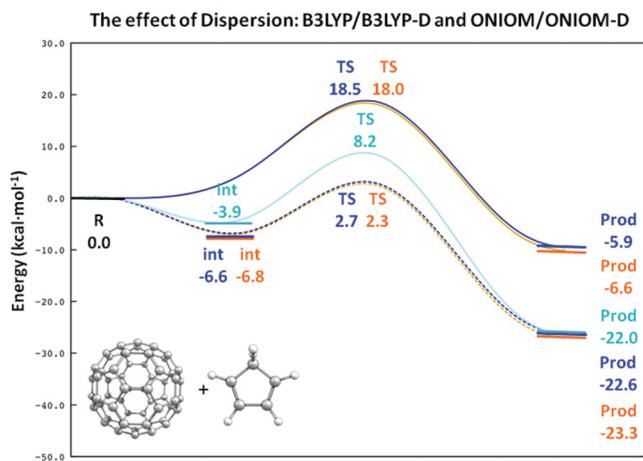
Table 1 shows that the B3LYP/6-31G(d) method underestimates the absolute value of the reaction energy by  $13.2 \text{ kcal} \cdot \text{mol}^{-1}$  and overestimates the energy barrier by  $11.1 \text{ kcal} \cdot \text{mol}^{-1}$ . These errors remain almost the same ( $13.4$  and  $11.0 \text{ kcal} \cdot \text{mol}^{-1}$ , respectively) when the effect of the solvent is considered. Due to the absence of charged or polarized intermediates and TSs in the reaction mechanism, inclusion of solvent effects almost does not change the energy profile obtained in the gas-phase, especially in the presence of solvents with low dielectric constants, such as those used experimentally for this reaction. For this reason, except otherwise



**Figure 3.** Representation of the optimized reactant complex structure with the most relevant distances (in Å). The different colors used to denote the C–C bond distances indicate the level of theory used: B3LYP-D/6-31G(d), in light orange; ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G), in light blue; and ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G), in cyan. H atoms and dark-blue C atoms constitute the layer treated at a high level in the ONIOM2 approach.

noted, throughout the manuscript, the discussed results will be referred to the gas-phase. When dispersion corrections are included, the exothermicity of the reaction is overestimated by  $3.5 \text{ kcal} \cdot \text{mol}^{-1}$ , and the energy barrier, by  $2.2 \text{ kcal} \cdot \text{mol}^{-1}$ . As compared with B3LYP/6-31G(d), B3LYP-D/6-31G(d) calculations increase the exothermicity by a huge factor of  $\sim 3.5$  and reduce the energy barrier by half. Although the difference between the B3LYP-D/6-31G(d) theoretical estimates and the experimental results is far from being negligible, the B3LYP-D/6-31G(d) method clearly improves the B3LYP/6-31G(d) results.

It is clear from our results that the dispersion corrections are essential to make theoretical predictions of the reactivity of fullerenes. There are some examples of experimentally relatively facile reactions of fullerenes<sup>24</sup> for which relatively high barriers have been computed. We think that most of these barriers are likely to be overestimated because of the lack of dispersion interactions in the theoretical approaches used. It is worth noting that Siegbahn, Blomberg, and Chen<sup>25</sup> have shown in a recent paper that for some mechanisms of enzymatic reactions, van der Waals interactions are significant along the whole reaction profile and have to be included to get good agreement with experiments. Some of us have also recently reported that the inclusion of dispersion correction (i.e., B3LYP-D) is, indeed, needed for getting good results for weak interactions with the B3LYP functional.<sup>26</sup> Finally, two years ago, Rakow and co-workers showed that including



**Figure 4.** Energy profile (in  $\text{kcal}\cdot\text{mol}^{-1}$ ) corresponding to the Diels–Alder reaction of  $\text{C}_{60}$  with cyclopentadiene computed at B3LYP/6-31G(d) (represented in orange and continuous line), B3LYP-D/6-31G(d) (in orange, discontinuous line), ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) (in blue, continuous line), ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G) (in blue, discontinuous line) and ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) (in cyan, continuous line).

dispersion corrections in B3LYP calculations is crucial to correctly compute the reaction barrier of the exchange in  $\text{BBr}_3$  by  $\text{HSiR}_3$ .<sup>27</sup> The effects reported in these works are, however, not as large as those observed in the present work.

Figure 2 shows the molecular structure of the concerted and synchronous TS. As can be seen, differences in the most important distances (the attacked [6,6] C–C bond of  $\text{C}_{60}$  and the two forming bonds) calculated at the B3LYP/6-31G(d) and B3LYP-D/6-31G(d) levels are less than 0.01 Å, the B3LYP-D/6-31G(d) TS being somewhat earlier as expected from the fact that the reaction is more exothermic at this level of theory.<sup>28</sup> The geometry of the reactant complex found with the B3LYP-D/6-31G(d) method drawn in Figure 3 shows that the distance between cyclopentadiene and  $\text{C}_{60}$  in this intermediate is  $\sim 3$  Å.

As said in the Introduction, in our previous contribution,<sup>6</sup> it was found that the two-layered ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) method provides geometries and energies very close to the full B3LYP/6-31G(d) results. As shown in Table 1 and Figure 4, energy differences in reaction energies and energy barriers for these two methods are  $< 0.7 \text{ kcal}\cdot\text{mol}^{-1}$ . Figure 3 shows that the differences in the two most important distances of the TS are of only few thousandths of an angstrom. In this figure, the pyracylene unit of the  $\text{C}_{60}$  and the cyclopentadiene molecule taken as the high level layer is depicted. We have checked here that the same behavior is found when going from the B3LYP-D/6-31G(d) to the ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G) method. Table 1 and Figures 2 to 4 indicate that this is, indeed, the case. Differences in energies between these two methods are again less than  $0.7 \text{ kcal}\cdot\text{mol}^{-1}$ , and differences in the distances of the TS and the reactant complex are of few thousandths of an angstrom.

We have also tested the performance of the hybrid meta exchange-correlation DFT functional M06-2X,<sup>21</sup> which includes medium-range correlation. It was found that M06-2X correctly accounts for  $\pi-\pi$  stacking interactions and nonbonded interactions;<sup>21</sup> however, it was observed that B3LYP (with double- $\zeta$  basis sets) gives values that are closer to CBS-QB3 estimates than

**Table 2.** Comparison between the Reaction Energies  $\Delta H_r$  and Activation Barriers  $\Delta H^\ddagger$  (in  $\text{kcal}\cdot\text{mol}^{-1}$ ) Corresponding to the [4 + 2] Diels–Alder Cycloaddition Reaction between  $\text{C}_{60}$  and Several Dienes, And between (5,5) SWCNT and 1,3-cis-Butadiene Computed at ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) and ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G) Taking into Account Grimme’s Dispersion Correction<sup>a</sup>

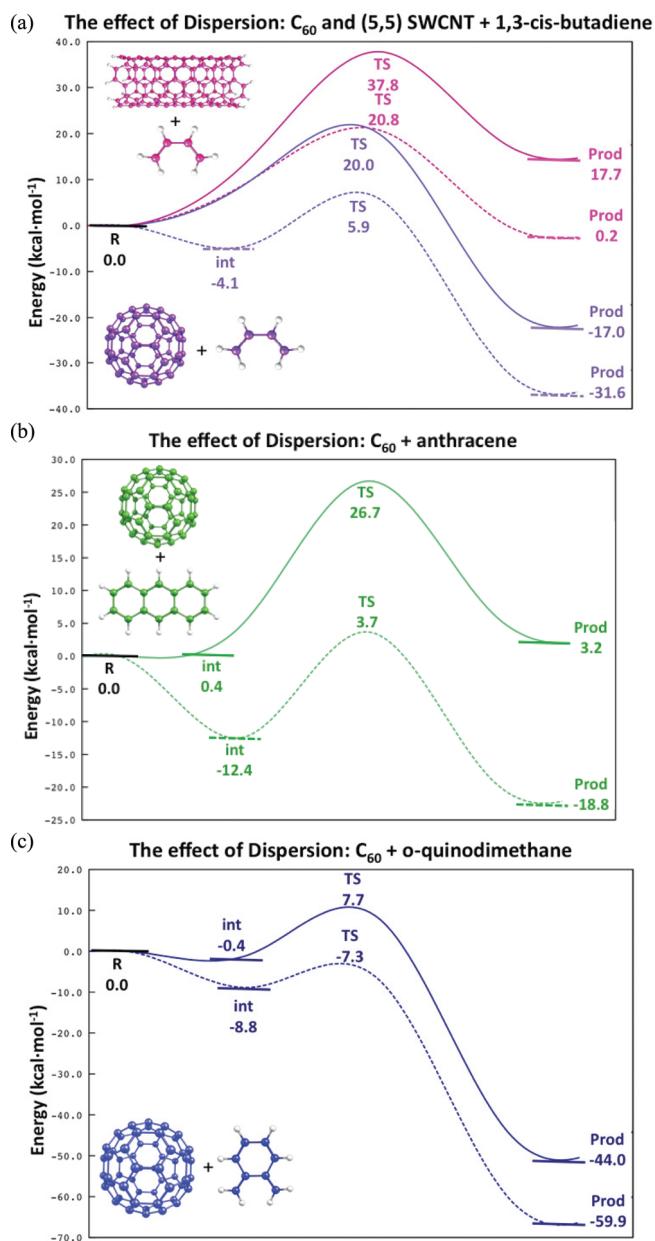
	ONIOM			ONIOM-D		
	$\Delta H_r$	$\Delta H^\ddagger$	$\Delta H_I^\ddagger$	$\Delta H_r$	$\Delta H^\ddagger$	$\Delta H_I^\ddagger$
(5,5) SWCNT + 1,3-cis-butadiene	17.7	37.8		0.2	20.8	
$\text{C}_{60}$ + 1,3-cis-butadiene	-17.0	20.0		-31.6	5.9	10.0
$\text{C}_{60}$ + anthracene		3.2	26.7	26.4	-18.8	3.7
$\text{C}_{60}$ + <i>o</i> -quinodimethane		-44.0	7.7	8.2	-59.9	-7.3
						1.4

<sup>a</sup>  $\Delta H^\ddagger$  corresponds to the activation barrier calculated with respect to isolated reactants (i.e.,  $H^{\text{TS}} - (H^{\text{C}_{60}} + H^{\text{diene}})$ ), whereas  $\Delta H_I^\ddagger$  refers to the optimized reactant complex (i.e.,  $H^{\text{TS}} - H^{\text{int}}$ ).

M06-2X for estimating the conversion of  $\pi$  to  $\sigma$  bonds in cycloaddition reactions.<sup>29</sup> Our calculations performed at ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) for the cycloaddition reaction of  $\text{C}_{60}$  with cyclopentadiene indicate that ONIOM2(M06-2X:SVWN) gives accurate reaction energies (the reaction energy is overestimated by 2.2  $\text{kcal}\cdot\text{mol}^{-1}$ ; see Table 1 and Figure 4), but somewhat less accurate activation barriers.

As already mentioned, the experimental barrier of 6.9  $\text{kcal}\cdot\text{mol}^{-1}$  should be compared with the difference in energy between the TS and the reactant complex. The ONIOM2(M06-2X:SVWN) computed activation barrier ( $\Delta H_I^\ddagger$ ) is 5.2  $\text{kcal}\cdot\text{mol}^{-1}$  higher than the experimental value. As compared with the ONIOM2-D(B3LYP:SVWN) results, the overestimation of the ONIOM2(M06-2X:SVWN) energy barrier is due to a destabilization of the transition state relative to separated reactants. This effect is already seen in the formation of a less stable reactant complex (the reactant complex at B3LYP or ONIOM2(B3LYP:SVWN) is  $\sim -6.7 \text{ kcal}\cdot\text{mol}^{-1}$  more stable than isolated reactants, whereas it is only  $-3.9 \text{ kcal}\cdot\text{mol}^{-1}$  at ONIOM2(M06-2X:SVWN)). This lower stability of the reactant complex located at ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G) is consistent with the longer C–C bond distance between the reacting carbons of the cyclopentadiene and  $\text{C}_{60}$  on the optimized structure (at ONIOM2(M06-2X:SVWN) the distance is 3.114 Å, whereas it is 3.037 and 3.043 Å for full B3LYP-D and ONIOM2-D(B3LYP:SVWN), respectively, see Figure 3). Although both B3LYP-D and M06-2X provide an accurate description of the cycloaddition reaction studied here, the use of B3LYP-D is preferred because it provides a better estimate of the activation barrier of the process.

We have finally extended our study considering other dienes reacting with  $\text{C}_{60}$  and also a single-wall carbon nanotube (SWCNT) (an armchair (5,5) SWCNT consisting of six rows of benzenoid units; namely,  $\text{C}_{140}\text{H}_{20}$ ) to investigate whether the effect of dispersion is only important for the particular reaction  $\text{C}_{60}$  + cyclopentadiene or if it is rather general. In Table 2 and Figure 5, the energy profiles for the reaction of  $\text{C}_{60}$  and the (5,5)-SWCNT with 1,3-cis-butadiene and the reaction of  $\text{C}_{60}$  with either anthracene or *o*-quinodimethane are represented. For the cycloaddition reaction between  $\text{C}_{60}$  and cyclopentadiene, we observed that the introduction of dispersion effects leads to an overall stabilization of 16.7  $\text{kcal}\cdot\text{mol}^{-1}$  for the reaction energy and 15.7  $\text{kcal}\cdot\text{mol}^{-1}$  for the



**Figure 5.** Energy profile (in  $\text{kcal}\cdot\text{mol}^{-1}$ ) corresponding to the Diels–Alder reaction of (a)  $C_{60}$  (represented in lilac) and a (5,5) SWCNT (represented in pink) with 1,3-cis-butadiene computed at ONIOM2-B3LYP/6-31G(d):SVWN/STO-3G (continuous line) and ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G) (discontinuous line); (b)  $C_{60}$  with anthracene computed at ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) (green continuous line) and ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G) (green discontinuous line); (c)  $C_{60}$  with o-quinodimethane computed at ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) (dark blue continuous line) and ONIOM2-D(B3LYP/6-31G(d):SVWN/STO-3G) (dark blue discontinuous line).

activation barrier (calculated with respect to separated reactants). Similar results are obtained when 1,3-cis-butadiene is considered (i.e., both the reaction and the activation energies are stabilized by  $\sim 15 \text{ kcal}\cdot\text{mol}^{-1}$ ) and when a (5,5) SWCNT is used instead of  $C_{60}$  as the dienophile (there is an overall stabilization of approximately  $17 \text{ kcal}\cdot\text{mol}^{-1}$ ).<sup>30</sup> Therefore, the incorporation of dispersion effects

remains extremely relevant to accurately compute the activation and reaction energies of cycloaddition reactions involving fullerene and related carbon nanostructures.

It is not surprising that the energetics of the DA reaction between  $C_{60}$  and anthracene are even more affected by the consideration of dispersion corrections. The reaction and the activation energy of the process including dispersion are  $\sim 22 \text{ kcal}\cdot\text{mol}^{-1}$  more stable than the uncorrected values, which convert the reaction from highly unfavorable (the reaction energy is endothermic by  $3.2 \text{ kcal}\cdot\text{mol}^{-1}$  and the activation barrier is  $\sim 27 \text{ kcal}\cdot\text{mol}^{-1}$ ) to substantially favorable (the reaction energy is exothermic by  $\sim -18 \text{ kcal}\cdot\text{mol}^{-1}$ , and the barrier with respect to separated reactants is reduced to  $3.7 \text{ kcal}\cdot\text{mol}^{-1}$ ). Finally, dispersion effects are also important for the study of the cycloaddition reaction between o-quinodimethane and  $C_{60}$  (corrected values are  $\sim 15 \text{ kcal}\cdot\text{mol}^{-1}$  more stable than the dispersion-free reaction and activation barriers).

In summary, we have shown in this paper that dispersion corrections change dramatically the energy profile of the DA reactions between  $C_{60}$  and several dienes. Large stabilizations are found in all cases studied, which range from  $\sim 15 \text{ kcal}\cdot\text{mol}^{-1}$  for relatively small dienes, such as 1,3-cis-butadiene, cyclopentadiene, or o-quinodimethane, up to  $22 \text{ kcal}\cdot\text{mol}^{-1}$  for those larger dienes presenting aromatic rings, such as anthracene. The reactivity profile of a (5,5) SWCNT is also dramatically modified after the incorporation of dispersion corrections. Effects in the molecular structure of reactants, TS, and adducts are minor. However, they are very important in the energy profile, and the present work indicates that proper inclusion of London dispersion interactions is needed to obtain accurate energies. Therefore, we conclude that inclusion of dispersion corrections is mandatory for the study of the chemical reactivity of fullerenes and nanotubes.

## ASSOCIATED CONTENT

**S Supporting Information.** Table S1 with the optimized Cartesian xyz coordinates (in angstroms) of all analyzed species. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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## ACKNOWLEDGMENT

The following organizations are thanked for financial support: the Ministerio de Ciencia e Innovación (MICINN, Project nos. CTQ2008-03077/BQU and CTQ2008-06532/BQU), the DIUE of the Generalitat de Catalunya (Project nos. 2009SGR637 and 2009SGR28), and the European Community (postdoctoral fellowship PIOF-GA-2009-252856). Excellent service by the Centre de Supercomputació de Catalunya (CESCA) is gratefully acknowledged. The authors also are grateful for the computer resources, technical expertise, and assistance provided by the Barcelona Supercomputing Center—Centro Nacional de Supercomputación. Support for the research of M. Solà was received through the ICREA Academia 2009 prize for excellence in research funded by the DIUE of the Generalitat de Catalunya. We thank Dr. Carles Curutchet for locally adapting the Gaussian 09, revision A.02 program and Prof. Dr. Per E. M. Siegbahn for providing us with a copy of ref 25.

## ■ REFERENCES

- (1) (a) Śliwa, W. *Fullerene Sci. Technol.* **1997**, *5*, 1133–1175. (b) Mayollo, J.; Krautler, B. *Fullerene Sci. Technol.* **1996**, *4*, 213–226. (c) Krautler, B.; Puchberger, M. *Helv. Chim. Acta* **1993**, *76*, 1626–1631. (d) Krautler, B.; Mayollo, J. *Tetrahedron* **1996**, *52*, 5033–5042. (e) Hirsch, A. *Synthesis* **1995**, 895–913. (f) Hirsch, A. *Top. Curr. Chem.* **1999**, *199*, 1–65. (g) Martín, N. *Chem. Commun.* **2006**, 2093–2104. (h) Hirsch, A. *The Chemistry of Fullerenes*; Thieme: Stuttgart, 1994.
- (2) (a) Haddon, R. C. *Science* **1993**, *261*, 1545–1550. (b) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157–161.
- (3) (a) Sarova, G. H.; Berberan-Santos, M. N. *Chem. Phys. Lett.* **2004**, *397*, 402–407. (b) Pang, L. S. K.; Wilson, M. A. *J. Phys. Chem.* **1993**, *97*, 6761–6763. (c) Giovane, L. M.; Barco, J. W.; Yadav, T.; Lafleur, A. L.; Marr, J. A.; Howard, J. B.; Rotello, V. M. *J. Phys. Chem.* **1993**, *97*, 8560–8561. (d) Tsuda, T.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296–1298. (e) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344–345. (f) Rotello, V. M.; Howard, J. B.; Yadav, T.; Conn, M. M.; Viani, E.; Giovane, L. M.; Lafleur, A. L. *Tetrahedron Lett.* **1993**, *34*, 1561–1562.
- (4) (a) Gügel, A.; Kraus, A.; Spickermann, J.; Belik, P.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 559–561. (b) Solà, M.; Duran, M.; Mestres, J. *J. Am. Chem. Soc.* **1996**, *118*, 8920–8924. (c) Solà, M.; Mestres, J.; Martí, J.; Duran, M. *Chem. Phys. Lett.* **1994**, *231*, 325–330.
- (5) Wang, G.-W.; Saunders, M.; Cross, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 256–259.
- (6) Osuna, S.; Morera, J.; Cases, M.; Morokuma, K.; Solà, M. *J. Phys. Chem. A* **2009**, *113*, 9721–9726.
- (7) Simón, L.; Goodman, J. M. *Org. Biomol. Chem.* **2011**, *9*, 689–700.
- (8) (a) Poater, J.; Solà, M.; Duran, M.; Robles, J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 722–731. (b) Bento, P.; Solà, M.; Bickelhaupt, F. M. *J. Comput. Chem.* **2005**, *26*, 1497–1504. (c) Kang, J. K.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *115*, 11040–11051. (d) Bento, A. P.; Solà, M.; Bickelhaupt, F. M. *J. Chem. Theory Comput.* **2008**, *4*, 929–940. (e) Barone, V.; Arnaud, R. *Chem. Phys. Lett.* **1996**, *251*, 393–399. (f) Rice, B. M.; Pai, S. V.; Chabalowski, C. F. *J. Phys. Chem. A* **1998**, *102*, 6950–6956. (g) Tucker, J. M.; Standard, J. M. *J. Mol. Struct. (Theochem)* **1998**, *431*, 193–203. (h) Jursic, B. S. *J. Mol. Struct. (Theochem)* **1998**, *430*, 17–22. (i) Thummel, H. T.; Bauschlicher, C. W. *J. Phys. Chem.* **1997**, *101*, 1188–1192. (j) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936–2941. (k) Durant, J. L. *Chem. Phys. Lett.* **1996**, *256*, 595–602. (l) Kormos, B. L.; Cramer, C. J. *J. Phys. Org. Chem.* **2002**, *15*, 712–720.
- (9) (a) Jursic, B. S. In *Recent Developments and Applications of Modern Density Functional Theory*; Seminario, J. M., Ed.; Elsevier Science: Amsterdam, 1996; Vol. 4, p 709–741; (b) Bertrán, J. *Theor. Chem. Acc.* **1998**, *99*, 143–150. (c) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036–6043. (d) Jursic, B.; Zdravkovski, Z. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1223–1227.
- (10) *Girona Seminar on Electron Density, Density Matrices and Density Functionals*, Girona, 2010; <http://iqc.udg.edu/gs2010>; accessed February 1, 2011.
- (11) Goerigk, L.; Grimme, S. *J. Chem. Theory Comput.* **2010**, *6*, 107–126.
- (12) Kruse, H.; Grimme, S. *J. Phys. Chem. C* **2009**, *113*, 17006–17010.
- (13) Korona, T.; Hesselmann, A.; Dodziuk, H. *J. Chem. Theory Comput.* **2009**, *5*, 1585–1596.
- (14) Hesselmann, A.; Korona, T. *Phys. Chem. Chem. Phys.* **2011**, *13*, 732–743.
- (15) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (16) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.
- (17) (a) Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 19357–19363. (b) Dapprich, S.; Komáromi, I.; Byu, K. S.; Morokuma, K.; Frisch, M. J. *Mol. Struct. (Theochem)* **1999**, *461*–462, 1–21. (c) Vreven, T.; Byu, K. S.; Komáromi, I.; Dapprich, S.; Montgomery, J. A., Jr.; Morokuma, K.; Frisch, M. J. *J. Chem. Theory Comput.* **2006**, *2*, 815–826.
- (18) (a) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4. (b) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- (19) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657–2664.
- (20) (a) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463–1473. (b) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799. (c) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
- (21) (a) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167. (b) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (22) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117–129. (b) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027–2094.
- (23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.02 ed.; Gaussian, Inc.: Pittsburgh, PA, 2009.
- (24) (a) Martín, N.; Altable, M.; Filippone, S.; Martín-Domenech, A.; Güell, M.; Solà, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1439–1442. (b) Altable, M.; Filippone, S.; Martín-Domenech, A.; Güell, M.; Solà, M.; Martín, N. *Org. Lett.* **2006**, *8*, 5959–5962. (c) Güell, M.; Martín, N.; Altable, M.; Filippone, S.; Martín-Domenech, A.; Solà, M. *J. Phys. Chem. A* **2007**, *111*, 5253–5258. (d) Filippone, S.; Barroso, M. I.; Martín-Domenech, A.; Osuna, S.; Solà, M.; Martín, N. *Chem.—Eur. J.* **2008**, *14*, 5198–5206. (e) Filippone, S.; Barroso, M. I.; Martín-Domenech, A.; Osuna, S.; Solà, M.; Martín, N. *Chem.—Eur. J.* **2008**, *14*, 5709–5709. (f) Izquierdo, M.; Osuna, S.; Filippone, S.; Martín-Domenech, A.; Solà, M.; Martín, N. *J. Org. Chem.* **2009**, *74*, 1480–1487. (g) Izquierdo, M.; Osuna, S.; Filippone, S.; Martín-Domenech, A.; Solà, M.; Martín, N. *J. Org. Chem.* **2009**, *74*, 6253–6259. (h) Delgado, J. L.; Osuna, S.; Bouit, P.-A.; Martínez-Alvarez, R.; Espíldora, E.; Solà, M.; Martín, N. *J. Org. Chem.* **2009**, *74*, 8174–8180. (i) Izquierdo, M.; Osuna, S.; Filippone, S.; Martín-Domenech, A.; Solà, M.; Martín, N. *Eur. J. Org. Chem.* **2009**, 6231–6238.
- (25) Siegbahn, P. E. M.; Blomberg, M. R. A.; Chen, S.-L. *J. Chem. Theory Comput.* **2010**, *6*, 2040–2044.
- (26) Swart, M.; Solà, M.; Bickelhaupt, M. *F. J. Comput. Chem.* **2011**, *32*, 1117–1127.
- (27) Rakow, J. R.; Tüllmann, S.; Holthausen, M. C. *J. Phys. Chem. A* **2009**, *113*, 12035–12043.
- (28) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.
- (29) Pieniazek, S. N.; Clemente, F. R.; Houk, K. N. *Angew. Chem., Int. Ed.* **2008**, *47*, 7746–7749.
- (30) Osuna, S.; Houk, K. N. *Chem.—Eur. J.* **2009**, *15*, 13219–13231.