Cycloaddition Reactions of Butadiene and 1,3-Dipoles to Curved Arenes, Fullerenes, and Nanotubes: Theoretical Evaluation of the Role of Distortion Energies on Activation Barriers

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Abstract: Diels–Alder cycloadditions of butadiene and 1,3-dipolar cycloadditions of azomethine ylide, fulminic acid, and the parent nitrone to polyacenes, fullerenes, and nanotubes have been investigated with density functional theory and ONIOM methods. Activation barriers obtained for cycloaddition reactions on planar and curved systems have been shown to be highly correlated to the energy needed to distort the reactants to the geometry of the transition state (TS).

Keywords: cycloaddition · density functional calculations · Diels–Alder reactions · distortion/interaction theory · Marcus theory · ONIOM

Introduction

Diels–Alder and 1,3-dipolar cycloadditions are among the most important methods to obtain six- and heterocyclic five-membered rings. These reactions involve additions to alkenes, arenes, and even fullerenes, and related carbon nanostructures. Cycloaddition reactions are among the most straightforward procedures for fullerene- and nanotube-functionalization.[1–5]

The routine preparation of fullerene derivatives from 1,3-dipolar cycloadditions[6,7] makes this functionalization a suitable procedure for the preparation of a wide variety of fullerene derivatives of interest in chemical biology and in materials science.[4] While some fullerene derivatives such as Diels–Alder cycloadducts[8] or Bingel methanofullerenes (Figure 1)[9,10] undergo retro-cycloadditions, except under special conditions, cycloadducts of azomethine ylides are stable and do not undergo the corresponding retro-cycloaddition reaction easily.[1,11,12] The 1,3-dipolar cycloadditions to C60 were also studied theoretically for alkyl azides and azomethine ylides (Figure 1).[13–15]

C60 reacts with different nitrile oxides forming [6,6]fullerene-isoxazolines, where in this case the retro-cycloaddition was also possible.[16–18] There are no experimental results for the addition of simple nitrones to fullerenes as they are very unstable; however, the addition of N-silyloxynitrones to C60 has been investigated.[19] The 1,3-dipolar cycloadditions of diazomethane, nitrite oxide, and nitrone to C60 were studied
at the B3LYP/6-31G(d)//AM1 level, where the closed [6,6] adducts were predicted as the most stable ones and a concerted mechanism was followed.[20]

The 1,3-dipolar cycloadditions of azomethine ylides to other carbon nanostructures, such as carbon nanotubes (CNTs),[21–25] nanofibers,[26] nanohorns,[27] nanoonions,[28,29] and nanorods,[30] have been reported. Although most studies of the functionalization of carbon nanotubes through 1,3-dipolar cycloaddition reactions involve the addition of azomethine ylides, the reactions with other 1,3-dipoles such as nitrile imines and ozone have also been achieved.[5,21,31,32]

The [4+2] Diels–Alder reaction involving fullerenes takes place readily due to the electron-deficient nature (low LUMO) of C_{60}. A wide variety of dienes were found to react with C_{60}+[33–38] but some of the final cycloaddition adducts were shown to undergo the retro-Diels–Alder reaction.[39] Success was also achieved for the addition of dienes such as ortho-quinodimethane due to the final gain in aromaticity of the cycloaddition product.[39–41]

This reaction was also performed on the sidewalls of CNTs.[42] The active diene was ortho-quinodimethane (generated in situ from 4,5-benzo-1,2-oxathiin-2-oxide) and the reaction was accomplished by using microwave irradiation. Lu and co-workers studied the Diels–Alder reaction theoretically by means of the ONIOM approach.[43] They observed that the 1,3-butadiene addition to (5,5) carbon nanotubes was disfavored, but the cycloaddition of o-quinodimethane was feasible due to the aromatic stabilization of the adducts.

During the last few decades, much theoretical and experimental research has been focused on the understanding of the mechanisms of these reactions. Although there was controversy about the concerted or stepwise nature of these mechanisms,[44,45] it is now widely accepted that a concerted \([4,4,2]\) mechanism is followed in most of the cases; the stepwise mechanism is higher in energy than the corresponding concerted one.[46–47]

The prediction of reactivity and regioselectivity of cycloaddition reactions, and in general of pericyclic reactions, is usually based on the Frontier Molecular Orbital (FMO) theory developed by Fukui in the 1960s.[46–53] Although the FMO theory has been successfully applied to a wide variety of organic reactions,[50] it fails in predicting, for example, the reactivity of polycyclic aromatic hydrocarbons (PAHs).[54]

Thermodynamic models such as those developed by Bell, Evans, and Polanyi,[55] Brønsted,[56] and Marcus[57] have also been used to describe relative rates of chemical reactions. The applications of these thermodynamic models to cycloadditions has been considered by our group.[58] Recently, Ess and Houk have shown that the energy to distort the 1,3-dipole and dipolarophile to the transition state geometry, rather than FMO interactions or reaction thermodynamics, controls the reactivity for cycloadditions of 1,3-dipoles with alkenes or alkynes.[59,60]

Up to now, the distortion/interaction model has been applied mainly to the cycloadditions of different dipoles to ethylene and acetylene[50] or to hydrogenations and Diels–Alder reactions of planar arenes and nitrogen heterocycles.[60] Here, we have tested the distortion/interaction model for the cycloaddition reactions of curved arenes, fullerenes, and single-walled carbon nanotubes (SWCNTs).

**Computational methodology:** Full geometry optimizations were performed with the hybrid density functional B3LYP method[61–63] with the 6-31G(d) basis set[64,65] by using the Gaussian 03 suite of programs.[66] In the case of the nanotube compounds, full geometry optimizations were carried out with the two-layered ONIOM approach.[67,68] The density functional theory (DFT) Xα exchange (α = 2/3) functional[69] in conjunction with the electron gas correlation functional (in Vosko–Wilk–Nusair parameterization)[70] that is, the so-called SVWN method with the STO-3G basis set[71] was used for the low level calculations and the hybrid density functional B3LYP method[61–63] with the 6-31G(d) basis set[64,65] was employed for the high level system. The use of the SVWN method for the low level calculations within the ONIOM approach was recently found to give reaction and activation energies close to the full B3LYP calculations for fullerene compounds.[72] However, single point calculations with B3LYP/6-31G(d) on the ONIOM geometry (i.e., B3LYP/6-31G(d)//ONIOM(B3LYP/6-31G(d):SVWN/STO-3G) for these large systems were also performed. The choice of DFT methods was based on previous studies, which showed that DFT (and, in particular, the relatively inexpensive B3LYP method combined with the 6-31G(d) basis set) provides a reliable description of reaction mechanisms of pericyclic reactions.[14,73–77] Recently, the activation barriers for 1,4-dihydration and Diels–Alder reactions of PAHs obtained at B3LYP/6-31G(d) were shown to be linearly correlated (with a slope of approximately 1) to the activation energies at MPWB1K/6-311G+(3df,2p)//B3LYP/6-31G+(d).[60] All systems were treated with the spin-restricted formalism; for highly asymmetric transition states (TSs) spin-unrestricted calculations were also performed, but the closed shell results are stable with respect to the unrestricted ones. All TSs were optimized by calculating the force constants at the first optimization point, and by using the Hessian update as introduced by Bohill.[78] Each TS was characterized through analytical vibrational frequencies to have one (and only one) imaginary frequency, corresponding to the approach of the two reacting molecules.

We tested the performance of the semiempirical method AM1 for the less accurate method within the ONIOM approach. Single-point calculations at the optimized ONIOM geometry by using SVWN method and STO-3G for the low level (i.e., ONIOM(B3LYP/6-31G(d):AM1)/ONIOM-(B3LYP/6-31G(d):SVWN/STO-3G) showed a dramatical change on the reaction and activation energies (see the following section).
Results and Discussion

The effect of pyramidalization on the reactivity of distorted ethylene and naphthalene: The 1,3-dipolar cycloadditions of formazomethine ylide and the Diels–Alder reactions of s-cis-1,3-buta diene with ethylene were investigated. Throughout the paper, we use s-cis-1,3-buta diene as the reactant. The energy required to convert s-trans-1,3-buta diene to the cis conformation (3.9 kcal mol\(^{-1}\)) should be included in the total activation energy when comparing to experiment. The sp\(^2\) carbon atoms of ethylene were pyramidalized by constraining the dihedral angles (H-C-C-H) during the optimization of the reactant and the transition state (see Table 1). This dihedral (dih) constraint was not included in calculations of the final adduct.

Table 1. Reaction energies (\(\Delta E_r\) in kcal mol\(^{-1}\)), activation barriers (\(\Delta E^*\) in kcal mol\(^{-1}\)), distortion energies (\(\Delta E^d\) in kcal mol\(^{-1}\)), and length (\(R_{CC}\) in Å) of the bonds being formed at the TS for the 1,3-dipolar cycloaddition of azomethine ylide and the Diels–Alder reaction of s-cis-1,3-buta diene with distorted ethylene. Both dihedral angles (H-C-C-H, marked in gray) were fixed in the reactant and in the TS, but not in the product.

Table 1 summarizes the energetics of the cycloadditions of formazomethine ylide and s-cis-buta diene to ethylene and various pyramidalized ethylenes. The cycloaddition to non-distorted ethylene is highly exothermic (−68.4 kcal mol\(^{-1}\)) and has a very low activation barrier of 1.2 kcal mol\(^{-1}\). The distances between the atoms that will form the new bonds

are quite long (2.535 Å) in the TS and the dihedral angle (H-C-C-H) is 166.5°. When ethylene is constrained and distorted, the reaction energies become more exothermic, and the activation barriers decrease. The difference between re-action energies for the distorted and undistorted systems is defined as the energy required to distort the reactant. As distortion increases, the forming C–C bond becomes longer in the TS. This is in agreement with the Hammond–Leffler postulate as the more exothermic the reaction is, the more reactant-like is the geometry of the TS. If the dihedral angle is lower than 160° no transition state can be found for the 1,3-dipolar cycloaddition.

The distortion energies measure the energies to achieve the transition state geometries without allowing interactions between the cycloaddends. When the alkene is distorted beyond the 167° dihedral of the fully optimized transition state, the barrier becomes small and then zero.

Borden and co-workers performed theoretical studies of reactions of some pyramidalized polycyclic alkenes. They observed that as the pyramidalization angle increases, there is a dramatic decrease of the energy of the LUMO and a much smaller increase of the HOMO energy. This difference was rationalized on the basis of hybridization and overlap of the atomic orbitals that comprise these MOs. This reduction of the energy of the LUMO was also observed by Houk and co-workers upon bonding acetylene and pyramidalizing ethylene. We also observe a large decrease of the LUMO energies of pyramidalized ethylenes (ethylene has a B3LYP LUMO energy of +0.49 eV, whereas, in pyramidalized ethylene (dih=100°) the LUMO energy is −2.15 eV). The HOMO energies remain approximately the same.

For the Diels–Alder reaction in the absence of constraints, the reaction and activation energies are −41.3 and 18.5 kcal mol\(^{-1}\), respectively (Table 1). The distances between the C atoms forming the new bonds at the synchronous TS are 2.273 Å, and the dihedral angle (H-C-C-H) is 154.3°. However in the Diels–Alder case, all TSs could be optimized, except for the highly pyramidalized structure (dih=100°) where no barrier was found.

The same types of calculations were performed for cycloadditions to the central C–C bond (called 1 in the next section, and in Figure 2) of naphthalene. Table 2 summarizes the results of the 1,3-dipolar cycloaddition with formazomethine ylide and the Diels–Alder reaction with s-cis-1,3-buta diene. The dihedral angle at the TS geometry of the unconstrained naphthalene is approximately 150.9°, and the distances between the atoms forming the new bonds are significantly different (1.905 and 2.527 Å). The addition of formazomethine ylide to distorted naphthalene is an endothermic reaction for dih=160°, whereas in the other cases the reaction becomes more favorable (from −5.4 to −116.3 kcal mol\(^{-1}\) for dih=150–100°). When the dihedral angle (C-C-C-C) is less than 120° no TS could be located, and there is no barrier. The Diels–Alder reaction for the unconstrained naphthalene is clearly endothermic (\(\Delta E_r = 39.4\) kcal mol\(^{-1}\)) with an extremely high activation barrier.
The reaction becomes exothermic and there is a significant drop in the activation barrier when the dihedral angle (C-C-C-C) is lower than 130° and there is a significant drop in the activation barrier when bond length (R_{CC}) in (A) in the TS for the 1,3-dipolar cycloaddition of azomethine ylide and the Diels–Alder reaction of \textit{s-cis}-1,3-butadiene to naphthalene. Both dihedral angles (C-C-C-C) marked in gray are fixed in the reactant and TS, but not in the product.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
Dihedral angle & Distorted naphthalene & D$_{\text{cis}}$ methine ylide & 1,3-butadiene$^{[b]}$ reaction & & & & \\
[\textdegree] & & & & & & & \\
\hline
\text{unconstrained} & 9.2 & 28.7 & 35.8 & 1.905$^{[a]}$ & 130.4 & 60.7 & 66.1 & 2.038 \\
\hline
160 & 2.8 & 28.3 & 61 & 1.848 & - & - & - \\
150 & -5.4 & 14.1 & 20.9 & 1.932 & 20.6 & 46.2 & 58.6 & 2.038 \\
140 & -17.3 & 5.2 & 11.3 & 2.501 & 13.0 & 34.2 & 39.6 & 2.134 \\
130 & -33.4 & -1.3$^{[a]}$ & 0.1 & 3.253 & -11.0 & 14.4 & 19.0 & 2.239 \\
120 & -54.6 & - & - & - & -24.3 & 13.3 & 16.4 & 2.359 \\
110 & -81.8 & - & - & - & -51.6 & 6.8 & 9.6 & 2.513 \\
100 & -116.3 & - & - & - & -86.1 & 2.0 & 4.8 & - \\
\hline
\end{tabular}
\caption{Reaction energies ($\Delta E_g$ in kcal mol$^{-1}$), activation barriers ($\Delta E^\ast$ in kcal mol$^{-1}$), distortion energies ($\Delta E_d$ in kcal mol$^{-1}$), and forming C–C bond length ($R_{CC}$ in A) in the TS for the 1,3-dipolar cycloaddition of azomethine ylide and the Diels–Alder reaction of \textit{s-cis}-1,3-butadiene to naphthalene. Both dihedral angles (C-C-C-C) marked in gray are fixed in the reactant and TS, but not in the product.}
\end{table}

The 1,3-dipolar cycloaddition and Diels–Alder reactions to PAHs, curved arenes, and fullerene derivatives: The cycloadditions were studied with different molecules ranging from planar aromatic hydrocarbons (benzene, naphthalene, anthracene, hexacene, and coronene) to curved arenes such as cycloheptacene. Several model systems for fullerenes, nanotubes, and graphene were included, such as coronene and corannulene, and derivatives involving a set of five-membered rings added to the peripheries of coronene and corannulene (see Table 2). As in any fullerene structure, the introduction of pentagonal rings induces curvature. Curved corannulene (Figure 2i) is a model for fullerenes, and curved coronene (Figure 2g) is a model for nanotubes. The cycloadditions of formalomethine ylide and butadiene to C$_{24}$ and (5,5) and (6,6) nanotubes have also been studied. The lengths of the molecular tube segments used consists of six rows of benzenoid units, namely C$_{12}$H$_{20}$ and C$_{15}$H$_{24}$ for (5,5) and (6,6), respectively. These two nanotube systems have different diameters, 7.02 and 8.34 Å for (5,5) and (6,6), respectively. Therefore, the reactivity of (5,5) is expected to be higher than for (6,6) due to the differences in curvature.

The bonds to which cycloadditions were studied are represented in Figure 2. Bond 1 (dark gray) corresponds to an addition to the center bond, bond 2 (light gray), bond 3 (gray), and bond 4 (black) involve additions to the periphery. In the case of anthracene, another bond called 5 was also studied in order to include all possible additions.

The most exothermic additions to naphthalene, anthracene, and hexacene involve bond 3 (−37.6, −41.4, −45.3 kcal mol$^{-1}$ for the 1,3-dipolar cycloaddition, and −13.5, −18.0, and −21.5 kcal mol$^{-1}$ for the Diels–Alder reaction, see Table 3 and Figure 2). This reaction has the lowest activation energy for all cases studied, except in hexacene where bond 2 has a somewhat smaller activation barrier. The addition to bond 3 is the most favorable reaction as it only disrupts the aromaticity of a single benzene ring. The second reaction at the most preferred bond, 2, involves disruption of the aromaticity of half of the system, while the rest of the cycloaditions interrupt the aromaticity of the whole molecule.

Another example of this higher reactivity is found for cycloheptacene (see Table 3). In this case, the reaction energies found are generally exothermic (−83.5 and −60.2 kcal mol$^{-1}$ for the 1,3-dipolar cycloadditions, and 5.0 and −30.9 kcal mol$^{-1}$ for the Diels–Alder reactions). The activation barrier for the Diels–Alder reaction to bond 2, and no barrier at all is found for the 1,3-dipolar cycloaddition. The C-C-C-C dihedral angle for this system is 155°, and as ob-
Coronene can be considered a small model system for graphene. The cycloadditions to bond 4 of coronene have the highest exothermicities (−37.6 and −13.2 kcal mol\(^{-1}\)) for the 1,3-dipolar cycloaddition and the Diels–Alder reaction, respectively, and the lowest activation barriers (8.9 and 32.6 kcal mol\(^{-1}\), see Figure 2, and Table 3). The favorable cycloaddition reaction to bond 4 is due to its location on the periphery of the molecule. Additions to other bonds are endothermic.

For coronene, the most favorable addition is the reaction to bond 4 (exothermic by −49.9 kcal mol\(^{-1}\)) when reacting with the 1,3-dipole and by −19.7 kcal mol\(^{-1}\) when reacting with s-cis-1,3-butaadiene, see Table 3). As pointed out in a previous paper by Kavitha et al., this preference for bond 4 is mainly attributed to the location of bond 4 on the periphery of the molecule where pyramidalization in the transition state is easiest to accommodate.\(^{[4]}\)

When an outer layer of five-membered rings is fused onto coronene, the preferred addition is still to bond 4 (reaction energies of −27.3 and 6.3 kcal mol\(^{-1}\) for CH\(_2\)N(H)CH\(_2\) and C\(_2\)H\(_4\), respectively). However, the addition to bond 2 is also favorable and close in energy to reaction at bond 4 (reaction energies of −26.9 and 8.2 kcal mol\(^{-1}\)). The activation energies are somewhat higher (2.6 and 31.5 kcal mol\(^{-1}\) for bond 4 in the 1,3-dipolar cycloaddition and the Diels–Alder reaction, respectively, as compared to 5.1 and 34.2 kcal mol\(^{-1}\) for the reactions at bond 2, see Table 3). The curved coronene used as a model for the nanotube structures presents a difference between the addition to bond 1 and bond 2 of approximately 20 kcal mol\(^{-1}\) for the reaction energies and from 5 to 10 kcal mol\(^{-1}\) for the activation barriers. This difference between these additions is not observed for the case of a (5,5) nanotube model, where both reactions present similar exothermicities (−26.3 and −26.1 kcal mol\(^{-1}\) for the 1,3-dipolar cycloaddition and 10.5 and 8.8 kcal mol\(^{-1}\) for the Diels–Alder reaction), but it is indeed the case for (6,6) nanotubes where a difference of approximately 10 kcal mol\(^{-1}\) for the reaction energy is found (see Table 3). The reactivity of (5,5) and (6,6) nanotubes is significantly different. The reactions of the more curved (5,5) structure are more exothermic. The 1,3-dipolar cycloaddition to bond 1 presents the most favorable reaction in both cases. The reaction energies are −26.3 and −17.2 kcal mol\(^{-1}\), and the activation barriers are 4.3 and 9.7 kcal mol\(^{-1}\) for the additions to (5,5) and (6,6) SWCNTs, respectively (Table 3). Figure 3 shows the TS geometries corresponding to the cycloaddition reaction to bond 1 of (5,5) and (6,6) SWCNTs. In all cases, concerted but asynchronous TSs were found.

Lu and co-workers studied the 1,3-dipolar cycloadditions to different (n,n) armchair nanotube structures at the ONIOM(B3LYP/6-31G(d):AM1) level of theory.\(^{[43]}\) They found that the addition of formoazomethine ylide to (5,5) SWCNT has a reaction energy of −39.3 kcal mol\(^{-1}\) and an activation barrier of 3.4 kcal mol\(^{-1}\). These values are clearly different from the ones that we obtained (−26.3 and 4.3 kcal mol\(^{-1}\)) for ΔE\(_R\) and ΔE\(_A\), respectively, with B3LYP/6-31G(d)/ONIOM(B3LYP/6-31G(d):SVWN/STO-3G).

Single point (SP) calculations performed at B3LYP/6-31G(d) at the optimized geometry by using ONIOM-(B3LYP/6-31G(d):SVWN/STO-3G) give reaction energies and activation barriers that differ by only 1–5 kcal mol\(^{-1}\). In order to test the validity of our results, we performed an SP calculation by using the semi-empirical method AM1 for the low level at the ONIOM(B3LYP/6-31G(d):SVWN/STO-3G):
3G) optimized geometry, that is, ONIOM(B3LYP/6-31G(d):AM1)/ONIOM(B3LYP/6-31G(d):SVWN/STO-3G), and the reaction and activation energies differed by 20 and 3 kcal mol\(^{-1}\), respectively (as compared to the B3LYP energies). This indicates that the use of the AM1 method as the low level method within the ONIOM approach leads to an underestimation of reaction and activation energies in comparison with the values obtained for the treatment of all atoms at the high level of theory.

The Diels–Alder reaction is not exothermic for any of the nanotubes considered (see Table 3). This is in agreement with a previous study in which the Diels–Alder reactions involving different dienes were assessed by using the two-layered ONIOM approach ONIOM(B3LYP/6-31G(d):AM1).\(^{[85]}\) Again, the reaction and activation energies found by using AM1 for the low level (1.6 and 32.4 kcal mol\(^{-1}\), respectively) are not in line with our B3LYP/6-31G(d)//ONIOM-(B3LYP/6-31G(d):SVWN/STO-3G) calculations (10.5 and 33.4 kcal mol\(^{-1}\), respectively), providing strong evidence that AM1 should not be used for the low level of theory within the ONIOM approach for the study of these systems.

Interesting results were obtained for the curved corannulene. The most favorable addition is to bond 2 (\(\Delta E_R = -48.4\) and \(-15.8\) kcal mol\(^{-1}\), and \(\Delta E^* = -2.6\) and 19.8 kcal mol\(^{-1}\) for the 1,3-dipolar cycloaddition and Diels–Alder reaction, respectively, see Table 3 and Figure 2). In the case of the 1,3-dipolar cycloaddition, a reaction intermediate was found. Although the TS and the latter complex present substantially different geometries, the activation barrier referred to the reactant intermediate is 0.0 kcal mol\(^{-1}\). This fact together with the low imaginary frequency found corresponding to the approach of both reacting molecules at the TS (64.1i) give strong evidence of an extremely flat potential energy surface.

In fullerene structures, there are different bond types. An initial classification can be made based upon the bonds that are situated between two hexagonal rings (called [6,6]), and those located between an hexagonal and a pentagonal ring (called [5,6]) (see Figure 4).

Bond 2 in corannulene or in the model system for fullerene (curved corannulene) is actually a [6,6] bond type, whereas bond 1 is a [5,6] bond. Therefore, the results of the addition to 1 and 2 can be directly compared to the addition to [6,6] and [5,6] bonds in \(C_{60}\). In the case of the 1,3-dipolar cycloaddition, the reaction and activation energies for the addition to the [6,6] bond (2) in the model system are \(\Delta E_R = -48.4\) and \(\Delta E^* = -2.6\) kcal mol\(^{-1}\), whereas in \(C_{60}\) these values are \(\Delta E_R = -53.5\) and \(\Delta E^* = -4.1\) kcal mol\(^{-1}\). Again, a negative activation barrier is found, and due to the extremely flat potential energy surface no reaction inter-
medium was localized. The reaction energies and barriers for the addition to the [5,6] bond (1) are \( \Delta E_R = -34.3 \) and \( \Delta E^* = 2.1 \text{ kcal mol}^{-1} \) in the model compound, and in the case of \( C_{60} \) fullerene \( \Delta E_R = -34.4 \) and \( \Delta E^* = 1.5 \text{ kcal mol}^{-1} \) (Table 3). Therefore, the study of the cycloaddition reaction in what we have called curved corannulene gives reaction energies as well as activation barriers which are very close to the ones obtained in the final fullerene structure. This is not unexpected in view of previous studies. This is mainly attributed to the introduction of pentagonal rings that induce curvature to the structure. The pyramidalization angle as defined by Haddon, for bonds \( 1(12.4^\circ) \) and \( 2(10.46^\circ) \) in curved corannulene are similar to the ones found for \([6,6]\) and \([5,6]\) bonds \((11.64^\circ \text{ for both}) \) in \( C_{60} \). This model also works well for the Diels–Alder reaction, where the addition to the \([6,6]\) bond gives \( \Delta E_R = -15.8 \) and \( \Delta E^* = 19.8 \text{ kcal mol}^{-1} \) for the model system, whereas in the case of \( C_{60} \) these values are \( \Delta E_R = -21.7 \) and \( \Delta E^* = 17.8 \text{ kcal mol}^{-1} \). The addition of 1,3-butadiene to the \([5,6]\) bond has reaction and activation energies of \( \Delta E_R = -3.0 \) and \( \Delta E^* = 28.2 \text{ kcal mol}^{-1} \) for curved corannulene, and \( \Delta E_R = -3.0 \) and \( \Delta E^* = 29.2 \text{ kcal mol}^{-1} \) for \( C_{60} \). Figure 5 shows the TS geometries for the cycloadditions of azomethine ylide and butadiene to the \([6,6]\) and \([5,6]\) bonds of \( C_{60} \). The cycloadditions to the \([6,6]\) bonds are always synchronous. However, concerted but asynchronous TSs are found for the additions to \([5,6]\) bonds.

**Reactions of nitrone and nitrile oxide 1,3-dipoles:** We have expanded the study of 1,3-dipolar cycloadditions to include other 1,3-dipoles, the parent nitride oxide and nitrite.

Cycloadditions were explored for the most favorable positions found in the case of azomethine ylide and 1,3-butadiene. These more favorable positions include bond 3 for naphthalene, anthracene, and hexacene; bond 4 for corannulene; bonds 2 and 4 for curved corannulene; bonds 1, 2, and 4 for corannulene; and all positions in the case of curved corannulene (1–4), \( C_{60} \) fullerene (1 and 2), and (5,5) and (6,6) nanotubes (1 and 2) (see Table 4).

In addition to calculations on formoazomethine ylide (CH\(_2\)N(H)CH\(_2\)), we studied the reactions of the parent methylene nitrite (CH\(_2\)=N(H)O\(^-\)) and fulminic acid (HC\(_2\)=N–O\(^-\)), the parent nitride oxide. Methylene nitrite and fulminic acid are unsymmetrical and can give two regioisomer products. We studied both orientations in all relevant cases. In most of the cases studied, the difference between the two approaches was less than 2 kcal mol\(^{-1}\).

Reactivities of the 1,3-dipoles decrease in the series: formoazomethine ylide > fulminic acid > methylene nitrite. In general, all reaction energies increase by 20–30 kcal mol\(^{-1}\) between each pair in the series. Activation energies are 11–14 kcal mol\(^{-1}\) higher on going from azomethine ylide to fulminic acid and then to methylene nitrite. This is not surprising as formoazomethine ylide is the most reactive 1,3-dipole due to its small HOMO–LUMO gap (3.62 eV as compared to 5.52 and 6.80 eV for nitrite and nitrile oxide, respectively). Although the difference in reaction energies for fulminic acid and methylene nitrite is 10 kcal mol\(^{-1}\), the variation of activation barriers is only about 3 kcal mol\(^{-1}\). This is in agreement with the earlier funding that nitrium and azomethine ylides have the same activation barriers in reactions with ethylene and acetylene, in spite of very different reaction energies.

As noted earlier, the reaction energies and activation barriers for the curved corannulene are very close to those obtained for the fullerene case. The 1,3-dipolar cycloadditions of methylene nitrite and fulminic acid to the \([5,6]\) bond of curved corannulene (bond 1) and the \([5,6]\) addition to \( C_{60} \) are unfavorable compared to additions to the \([6,6]\) bonds of corannulene and \( C_{60} \). The 1,3-dipolar cycloadditions to the \([6,6]\) bond (bond 2) of curved corannulene and \( C_{60} \) have re-
The addition of the nitrile oxide and the nitrone to the 1,3-dipolar cycloaddition and the Diels–Alder reaction with distorted ethylene and naphthalene are plotted. Although the points could be fitted to a line, in all cases a curvature is still observable. The theoretical Marcus curve [Eq. (2)]:

$$\Delta G^+ = \Delta G_0^+ + \frac{1}{2} \Delta G_{\text{rxn}}^+ + \Delta G_{\text{rxn}}^2 / 16 \Delta G_0^+$$

can be simplified to the Dimroth equation (Eq. (1)). However, this linear relationship introduced by Marcus was obtained for nearly thermoneutral reactions. In these cases,

$$\Delta G = \Delta G_0^+ + \frac{1}{2} \Delta G_{\text{rxn}}^+ + \Delta G_{\text{rxn}}^2 / 16 \Delta G_0^+$$

Table 4. Reaction energies ($\Delta E_R$, $\Delta E^*$), activation barriers ($\Delta E_R$), and distortion energies ($\Delta E_D$) for the different 1,3-dipolar cycloadditions considered.

<table>
<thead>
<tr>
<th>Methylene nitrene</th>
<th>Fulminic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_R$</td>
<td>$\Delta E^*$</td>
</tr>
<tr>
<td>benzene exo</td>
<td>7.9</td>
</tr>
<tr>
<td>naphthalene 3</td>
<td>–2.6</td>
</tr>
<tr>
<td>naphthalene 3, 2(a)</td>
<td>–3.0</td>
</tr>
<tr>
<td>anthracene 3</td>
<td>–6.8</td>
</tr>
<tr>
<td>anthracene 3, 2</td>
<td>–7.1</td>
</tr>
<tr>
<td>hexacene 3</td>
<td>–12.2</td>
</tr>
<tr>
<td>hexacene 3, 2</td>
<td>–12.0</td>
</tr>
<tr>
<td>coronene 4</td>
<td>–4.9</td>
</tr>
<tr>
<td>curved coronene 2</td>
<td>5.7</td>
</tr>
<tr>
<td>curved coronene 2, 2</td>
<td>6.6</td>
</tr>
<tr>
<td>curved coronene 4</td>
<td>6.6</td>
</tr>
<tr>
<td>coronulene 1</td>
<td>9.5</td>
</tr>
<tr>
<td>coronulene 2</td>
<td>6.0</td>
</tr>
<tr>
<td>coronulene 2, 2</td>
<td>9.3</td>
</tr>
<tr>
<td>coronulene 4</td>
<td>–16.0</td>
</tr>
<tr>
<td>curved coronulene 1</td>
<td>–0.5</td>
</tr>
<tr>
<td>curved coronulene 2</td>
<td>–14.3</td>
</tr>
<tr>
<td>curved coronulene 2, 2</td>
<td>–14.7</td>
</tr>
<tr>
<td>curved coronulene 3</td>
<td>5.6</td>
</tr>
<tr>
<td>curved coronulene 3, 2</td>
<td>3.5</td>
</tr>
<tr>
<td>curved coronulene 4</td>
<td>–14.3</td>
</tr>
<tr>
<td>C_{60} [6,6]</td>
<td>–15.8</td>
</tr>
<tr>
<td>C_{60} [5,6]</td>
<td>0.0</td>
</tr>
<tr>
<td>(5,5) SWCNT 1</td>
<td>6.1</td>
</tr>
<tr>
<td>(5,5) SWCNT 2</td>
<td>5.4</td>
</tr>
<tr>
<td>(6,6) SWCNT 1</td>
<td>14.8</td>
</tr>
<tr>
<td>(6,6) SWCNT 2</td>
<td>24.5</td>
</tr>
</tbody>
</table>

[a] For those addition sites where two possible regioisomers can be formed, both possible orientations of the dipoles have been studied (and have been marked in the Table using the nomenclature X and X_2).

Figure 6. TS geometries for the addition of azomethine ylide, methylene nitrene and fulminic acid to bond 1 of (5,5) and (6,6) SWCNTs.

Discussion

Thermodynamic models such as those developed by Bell, Evans, and Polanyi (BEP),[55] Brønsted[56] and Marcus[57] relate the reaction energy ($\Delta G_R$, $\Delta H_R$, or $\Delta E_R$) of a reaction to the activation barrier ($\Delta G^*$, $\Delta H^*$, or $\Delta E^*$), and have been satisfactorily applied to describe chemical reactivity. The BEP relationship or the Marcus relationship for nearly thermoneutral reactions can be simplified to the Dimroth relationship [Eq. (1)]

$$\Delta \Delta E^* = \frac{1}{2} \Delta \Delta E_R$$

In Figure 8a, activation energies versus reaction energies for the 1,3-dipolar cycloaddition and the Diels–Alder reaction with distorted ethylene and naphthalene are plotted. The points could be fitted to a line, in all cases a curvature is still observable. The theoretical Marcus curve [Eq. (2)]:

$$\Delta G^+ = \Delta G_0^+ + \frac{1}{2} \Delta G_{\text{rxn}}^+ + \Delta G_{\text{rxn}}^2 / 16 \Delta G_0^+$$

can be simplified to the Dimroth equation (Eq. (1)). However, this linear relationship introduced by Marcus was obtained for nearly thermoneutral reactions. In these cases,
Cycloadditions to distorted ethylene and naphthalene are very exothermic, and the linear approximation is no longer appropriate.

The same correlation was studied for the 1,3-dipolar cycloadditions of formoazomethine ylide and the Diels–Alder reactions of 1,3-butadiene with PAHs, curved arenes, C_{60}, and (5,5) and (6,6) nanotubes (see Figure 8b). In both reactions, activation barriers and reaction energies seem to be correlated, although the correlation coefficient ($R^2$) is lower than 0.90 in all cases ($R^2$ is 0.807 and 0.880 in the Diels–Alder and 1,3-dipolar cycloaddition reactions, respectively). The least-square lines give slopes close to the expected $1/2$ (0.441 and 0.624 for the Diels–Alder reactions and 1,3-dipolar cycloaddition reactions, respectively). However, poorer results are obtained in the case of the 1,3-dipolar cycloadditions of different dipoles: formoazomethine ylide, fulminic acid, and methylene nitrone (see Figure 8c). In these cases, there are large deviations from linearity. The use of the Dimroth approximation of the Marcus curve should only be applied for strongly exothermic reactions. However, the fit to a second order polynomial curve do not improve the correlation factors obtained for the lineal approximation (see Figure 8d). The correlation factor found in all cases is lower than 0.9. Moreover, the fitted curves present a second order term close to 0, which clearly indicates that the lineal Dimroth approximation used remains valid. Although there are some cases where the BEP relationship between activation barriers and reaction energies is fulfilled,[89] it cannot be considered a general rule for describing chemical reactivity for cycloaddition reactions.

Recently, Ess and Houk have shown that the energy to distort the 1,3-dipole and dipolarophile to the transition state geometry, rather than FMO interactions or reaction thermodynamics, controls reactivity for cycloadditions of 1,3-dipoles with alkenes or alkynes.[58,59] Although the reaction barrier is not a simple function of the reaction energy, it is clearly correlated to the distortion energy. The distortion energy,[83,90,91] also called deformation energy[92] or activation strain,[93] is defined as the energy required to distort the dipole and dipolarophile into the geometry they possess in the transition state, without allowing interaction between the fragments. Thus, the activation energy of a reaction can

Figure 7. TS geometries for the cycloadditions of methylene nitrone to bond 1 of a) (5,5) and c) (6,6) SWCNTs, and the cycloaddition of fulminic acid to bond 1 of b) (5,5) and d) (6,6) SWCNTs. Relevant distances and angles are represented in Å and degrees, respectively. All structures have been optimized at the ONIOM(B3LYP/6-31G(d):SVWN/STO-3G) level of theory. Those atoms that have not been included in the high layer are transparent.
be expressed as the sum of the distortion energy ($\Delta E_d$) and
the interaction energy ($\Delta E_i$) between addends involved in
the transition state.

In a unimolecular reaction, the activation barrier is equal
to the distortion energy of the molecule to achieve the ge-
ometry of the TS. For bimolecular reactions, a good correla-
tion has been found between activation barriers and distor-
tion energies, showing that a higher reaction barrier implies
a higher deformation of dipole and dipolarophile in the
transition state.

Figure 9 shows the representation of activation barriers ($\Delta E^*$) versus the total distortion energies ($\Delta E_d^*$) found for all considered systems.

Interestingly, although the BEP principle was not fol-
lowed in the case of the 1,3-dipolar cycloaddition of formo-
azomethine ylide and the Diels–Alder reaction of $x$-cis-1,3-
butadiene with distorted ethylene and naphthalene, the acti-
vation energies do correlate well with to distortion energies.
A good correlation is found for all cases as indicated by the $R^2$ value.

Because of the spherical shape of fullerenes, strain occurs
as a consequence of the pyramidalization of carbon atoms.
The pyramidalization of the carbon atoms leads to a trans-
formation of the p orbitals to hybrid orbitals, and $\pi$ bonding
is weakened leading to larger C–C bond lengths. The curved
$\pi$ conjugation present in any fullerene or carbon nanotube
makes them remarkably different from planar $\pi$-conjugated
compounds such as graphite or planar PAHs. Cycloaddition
reactions of fullerene and its derivatives have been analyzed
by considerations of bond lengths and orbital coeffi-
cients.$^{[94,95]}$ Short bond distances together with high pyrami-
dalization angles are usually considered to be the most impor-
tant structural parameters related to fullerene reactivity. On
the other hand, low-lying unoccupied orbitals that present
suitable energy and shape to interact are also required. Al-
though the chemistry of free fullerene is considered to be
quite well-understood, there are still some cases of fullerene
derivatives such as the endohedral metallofullerenes where
the exohedral reactivity is just beginning to be studied.
There are some cases where the previously mentioned pa-
rameters to understand cycloaddition reactions give contra-
dictory predictions. The most pyramidalized bonds do not
always lead to the most favorable addition;$^{[96]}$ those bonds
with extremely long carbon distances can also be reactive.$^{[93]}$
Moreover, the predictions of reactivity from the LUMOs
are qualitatively correct, but they are much too imprecise
in the sense that one finds many bonds with suitable orbitals
for the interaction with a diene or a 1,3-dipole.$^{[94]}$ Although
the distortion/interaction model requires to know the TS ge-

Figure 8. Plot of the B3LYP/6-31G(d) activation energies ($\Delta E^*$) versus the reaction energy ($\Delta E_R$) for a) the Diels–Alder reaction of 1,3-butadiene with distorted naphthalene (gray triangles) and ethylene (dark gray triangles) and the 1,3-dipolar cycloaddition of azomethine ylide to dis-
torted naphthalene (gray circles) and ethylene (dark gray circles); b) the
Diels–Alder reaction of 1,3-butadiene with all considered PAHs, arenes,
fullerenes and carbon nanotubes (black triangles, $\Delta E^* = 0.441\Delta E_R + 20.02, R^2 = 0.807$) and the 1,3-dipolar cycloaddition of azomethine ylide
(gray circles, $\Delta E^* = 0.624\Delta E_R + 32.26, R^2 = 0.880$); c) the 1,3-dipolar cy-
claddition with formoazomethine ylide (gray circles), fulminic acid
(black squares), and methylene nitronate (white diamond) ($\Delta E^* = 0.241\Delta E_R + 21.30, R^2 = 0.431$); d) the Diels–Alder reaction (black trian-
gles) fitted to a second order polynomial curve ($\Delta E^* = 0.003\Delta E_R^2 + 0.551\Delta E_R + 31.46, R^2 = 0.892$) and the 1,3-dipolar cycloaddition with azo-
methine ylide (gray circles, $\Delta E^* = -0.004\Delta E_R^2 + 0.557\Delta E_R + 19.44, R^2 = 0.840$).
Interestingly, the activation energy ($\Delta E^*$) correlates well with the distortion energy ($\Delta E_d$) even in real curved systems (see Figure 9b and c). Although some points deviate from the line by a considerable amount (up to 15 kcal mol$^{-1}$), the overall correlation is very good, as indicated by the $R^2$ value. The reaction series for either the Diels–Alder reaction with 1,3-butadiene or the 1,3-dipolar cycloaddition with formozomethine ylide give a linear relationship ($\Delta E^* = 0.794\Delta E_d - 2.388$, $R^2 = 0.926$). Good correlations are also obtained when the other 1,3-dipoles are included ($\Delta E^* = 0.759\Delta E_d - 2.249$, $R^2 = 0.902$).

Reaction energies, activation barriers, and distortion energies found for curved systems are always more favorable than for flat compounds. Curvature makes the reaction easier, since the system has to be deformed to a lesser extent to react. The opposite effect could also be expected in those curved systems where curvature makes the reaction more difficult. Higher distortion energies are also found for the cycloaddition to bonds that disrupt the aromaticity of the whole system.

Our results show that the energy required to distort the dipole and dipolarophile to the TS geometry is well correlated with the activation barrier of the reaction. In those cases where the BEP principle is followed, good correlations between distortion energies and activation barriers are also found. Of considerable interest is that in those systems where the BEP principle was not obeyed, the distortion/interaction model was followed.

Conclusions

The 1,3-dipolar cycloaddition with three dipoles, formozomethine ylide, fulminic acid, and methylene nitrone and the Diels–Alder reaction with 1,3-butadiene have been studied for reactions with PAHS, curved arenes, $C_{60}$ fullerene, and (5,5) and (6,6) SWCNTs. The most favorable addition has been found to be to bond 3 for naphthalene, anthracene, and hexacene; and bond 4 for coronene and corannulene. In the case of the model systems, curved coronene still reacts preferentially at bond 4, but reactions of bond 2 are more favorable for curved corannulene. These model systems give reaction and activation energies similar to the ones obtained in the real fullerene and nanotube systems. The [6,6] bond in $C_{60}$ is the preferred addition site for all dipoles and butadiene. Although the 1,3-dipolar cycloadditions of formozomethine ylide and fulminic acid to (5,5) SWCNTs are exothermic, in the rest of the cases considered, these reactions are unfavorable. The ONIOM approach used (ONIOM-B3LYP/6-31G(d)/SVWN/STO-3G) to describe SWCNT systems give relative energies very similar to the single point (SP) calculation treating all atoms at the high level of theory (i.e., B3LYP/6-31G(d)). The use of AM1 for the low level within the ONIOM approach gives underestimated values of the reaction and the activation energies, and this method is not recommended for the study of nanotube systems.
The distortion/interaction model is a good way to analyze and describe the chemical reactivity found in PAHs, curved arenes, C60 fullerene, and (5,5) and (6,6) SWCNTs. Activation barriers obtained for two different types of cycloaddition reactions on planar and curved systems have been shown to be highly correlated to the energy needed to distort the reactants to the geometry of the TS.

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