# Is corannulene a better diene or dienophile? A DFT analysis

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Diels Alder reactivity of corannulene has been probed using density functional theory (DFT) at B3LYP/6-31G* level by employing it both as a diene and a dienophile in cycloaddition with ethylene and 1,3-butadiene as typical partners. Computations reveal that corannulene acts better as a dienophile than as a diene and as a dienophile it undergoes normal electron demand type addition with 1,3-butadiene, and as a diene corannulene undergoes inverse electron demand type addition with ethylene. When employed as a dienophile the addition takes place preferentially in the rim position than in the spoke position due to strong steric and electronic reasons. Further in the rim addition rim exo approach is favored kinetically and thermodynamically. As a diene, corannulene shows regioselectivity for rim–spoke addition over spoke–spoke addition. Concerted type cycloadditions have been studied and the reactions are seen to take place preferentially on the convex face. The effect of substituents in butadiene on the reactivity and the reaction of butadiene–pentaindenocorannulene (an extended corannulene) system has been investigated for the most favorable rim exo positions. Copyright © 2007 John Wiley & Sons, Ltd.

**Keywords:** Diels Alder reaction; corannulene; pentaindenocorannulene; density functional theory; regioselectivity

## INTRODUCTION

Fullerenes are classified as the third allotrope of carbon and they became much popular after the discovery of $C_{60}$ in 1985. The remarkable stability and football like structure of $C_{60}$ stimulated the interests of many workers worldwide.[1,2] This has led to several reports on the synthesis, structure and reactivity,[3,4] stability, spectra of the molecule, and its possible applications in various fields.[5–9] This molecule which was once thought to exist in interstellar clouds was soon found to have immense technological relevance and was declared the wonder molecule of the last decade. Corannulene, another curved π system and described as a polar cap of $C_{60}$,[5–11] was synthesized much earlier but relatively less investigated until recently. In fact, fullerene research has significantly contributed to the increasing importance of corannulene chemistry.

Recently corannulene has been subjected to detailed computational and theoretical investigations.[12–17] Corannulene is an equally interesting molecule with a bowl geometry, an open ended structure unlike fullerenes. The bowl structure leads to two π faces, concave and convex, with different electron density distributions and it introduces differing preferences for complexation and reactivity[3,10,11] that has led to many investigations. Corannulene has 10 double bonds delocalized and distributed over 5 hexagonal rings around the pentagon hole and has 11 Kekulé structures. The $C_{5v}$ symmetry of the molecule partitions the 25 carbon–carbon bonds into four bond types indicated as rim (a), spoke (b), flank (c), and hub (d) bonds in Fig. 1 and their double bond character decreases in the order rim > spoke > flank > hub. Table 1 lists bond orders and bond lengths of selected bonds of corannulene, 1,3-butadiene, and ethylene. Rim and spoke bonds have higher double bond character and

have been observed to undergo reactions characteristic of double bonds though they are the part of aromatic sextets.[14–16] Various types of bonds, Mulliken charges on corannulene, butadiene, and ethylene and the picture of HOMO–LUMO of corannulene are presented in Fig. 1.

Further these double bonds can organize themselves as *cis* fixed dienes and can show Diels Alder reactivity as a diene. This raises a question as to whether corannulene is a better diene or dienophile and this question is mainly addressed in this work. Further its relative reactivity as a dienophile (with dienes like butadiene, isoprene, and chloroprene), the mechanism and regioselectivity of Diels Alder additions of corannulene are also discussed here through density functional theory (DFT) modeling of these reactions. The effect of bowl depth on reactivity has been investigated by reacting another deeper bowl pentaindenocorannulune (PEC) an extended corannulene system with butadiene.

## COMPUTATIONAL DETAILS

DFT calculations have been performed using GAUSSIAN 03 suite of programs[18] using Becke's three-parameter non-local

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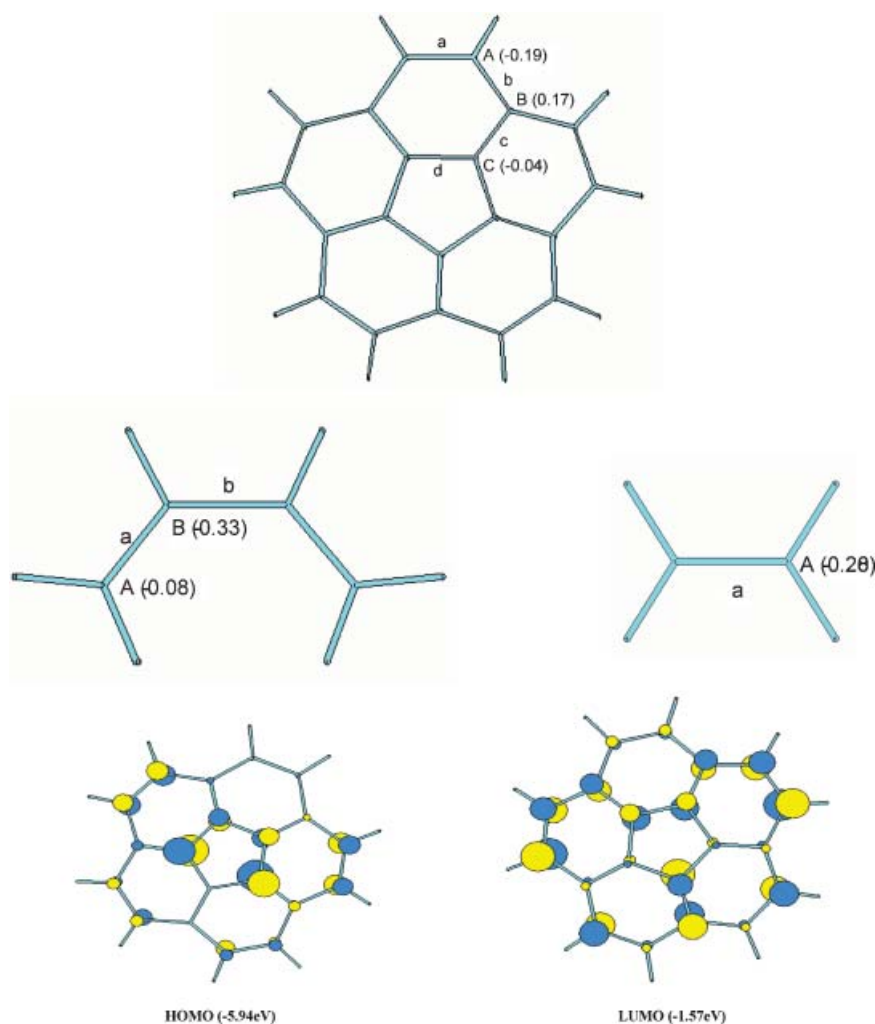    Department of Chemistry, University of Pune, Pune—411 007, India

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**Figure 1.** Various bond types (a–d) and atom types (A–C) of corannulene, 1,3-butadiene (a–b) and ethylene (a) and Mulliken charges on carbon atoms of corannulene, butadiene, and ethylene. HOMO and LUMO of corannulene are also depicted

exchange functional[19,20] and the non-local correlation functional of Lee et al. [21] with 6–31G* basis set. This combination (B3LYP/6–31G*) is chosen based on its performance reported in the literature and also considering the computational cost.[22,23] All equilibrium geometries have been fully optimized to better than 0.001 Å for bond distances and 0.1° for bond angles. The stationary points have been characterized by frequency calculations and the transition states [TSs] have single imaginary frequency and the minima have real frequencies. TSs have been further confirmed by examining their transition vectors and by animating the imaginary frequency using a visualization program MOLEKEL[24] and by performing IRC calculations. The reaction progress has been verified by the Wiberg bond order analysis (The percent of bond formation and cleavage is defined as [BO-(TS)i–BO(R)i]/[BO(P)i–BO(R)i] X 100 where 'i' can be either a forming or a cleaving bond. See also the References [25–27] for detailed information) and the deformation energies have been calculated for the TSs as reported earlier.[25–28] All energies have been corrected for zero point effects. Energy decomposition analyses[29] were performed for TSs to explain the significance of quantities influence the bonding in the reaction pathways. Energy decomposition analysis program were interfaced in Gaussian 03.

## RESULTS AND DISCUSSION

Among the above four bond types, rim and spoke bonds are seen to have higher bond orders (Table 1) and this makes the rim and spoke bonds have greater chance for addition. Jemmis and coworkers[30] have shown that the rim bonds in corannulene are predicted to be more susceptible to electrophilic attack in comparison to spoke bonds. Theoretically corannulene can act both as a diene and a dienophile; as a dienophile, it can undergo Diels Alder cycloaddition with 1,3-butadiene in the rim and spoke position. Alternatively as a diene, corannulene can react with ethylene in the rim–spoke and spoke–spoke fashion. It should be noted that rim–spoke and spoke–spoke positions offer a 'cis fixed diene' motif.

In all these additions with corannulene, concerted paths have been traced; stepwise mechanisms have not been considered in view of the fact that they are all carbon neutral addition and corannulene is known to pass through concerted TSs in dipolar addition.[13] Initially, 1,3-butadiene and ethylene have been approached in the convex and concave side of corannulene but computations show that TSs and adducts are stabilized only on the convex side. The fact that convex side is more reactive than concave side has also been discussed by Sygula and Rabideau.[31]

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**Table 1.** Computed bond lengths (Å) and bond orders at B3LYP/6–31G* level of theory along with experimental bond lengths of various C–C bond types of corannulene (a–d), 1, 3-butadiene (a and b) and ethylene (a)

| Bond type | Bond length | | Bond order |
|---|---|---|---|
| | Expt[a,b] | Theory[#] | |
| Corannulene[a] | | | |
|   Rim (a) | 1.374 | 1.390 | 1.627 |
|   Spoke (b) | 1.408 | 1.385 | 1.335 |
|   Flank (c) | 1.441 | 1.448 | 1.214 |
|   Hub (d) | 1.410 | 1.417 | 1.184 |
| Butadiene[b] | | | |
|   (a) | 1.349 | 1.339 | I.884 |
|   (b) | 1.467 | 1.457 | 1.125 |
| Ethylene[b] | | | |
|   (a) | 1.339 | 1.331 | 2.039 |

[a] Reference [39].
[b] Reference [40].
[#] Bond types are indicated in Fig. 1.

Steric and electronic requirements favor the addition on the convex side rather than on the concave side and therefore convex-addition alone are considered here. The diene and dienophile units in corannulene are the part of local aromatic sextet and this impedes the reactivity. This fact is discussed by comparing these reactions with that of the Diels Alder addition with typical diene and dienophile, (1,3-butadiene–ethylene). Schemes 1 and 2 represent the reaction of corannulene with 1,3-butadiene and corannulene with ethylene. The optimized geometries are given in Fig. 2 and the free energy profiles of the additions are shown in Fig. 3. Activation and reaction energies, deformation energies, frontier orbital energy (FOE) gaps, thermodynamic parameters at 298.15 K are presented in Tables 2 and 3 lists all bond order data.

Finally, reactions of isoprene and chloroprene with corannulene have been studied to examine the effect of substituents on the Diels Alder reactivity and the reaction of butadiene with PEC has been studied for understanding the effect of bowl depth on the Diels Alder reactivity.

**Corannulene as dienophile**

Corannulene can undergo addition across its rim and spoke bonds with 1,3-butadiene and in the rim addition there are endo and exo approaches. In the endo and exo addition the reacting butadiene moiety orients respectively exo and endo to the reacting benzenoid ring of corannulene. In the spoke addition, there is only one possibility of approach which is shown in Scheme 1. FOE gap values listed in Table 2 show that the reaction is normal electron demand type and this is further confirmed by quantum of charge transfer ($q_{CT}$) values for the Rim exo TS (+0.036) for the 1,3-butadiene–corannulene reaction. $Q_{CT}$ values for Rim endo TS and Spoke TS also show the same trend.

*Rim addition*

Optimized geometries presented in Fig. 2 show that rim addition passes through synchronous TSs and the rim exo and rim endo addition involves an activation free energy of 42.8 and 43.9 kcal mol$^{-1}$, respectively (Table 2) and the computed reaction energies show that rim addition is exothermic. Deformation energy analysis indicates that the major part of the activation energy is spent for distorting 1,3-butadiene. Bond indices presented in Table 3 show that the TSs are reactant like with the BFC$_{ave}$ value falling in the range of 42 to 43.

*Spoke addition*

Spoke addition passes through an asynchronous TS (Fig. 2) with hub carbon interacting more closely than the spoke carbon. Hub
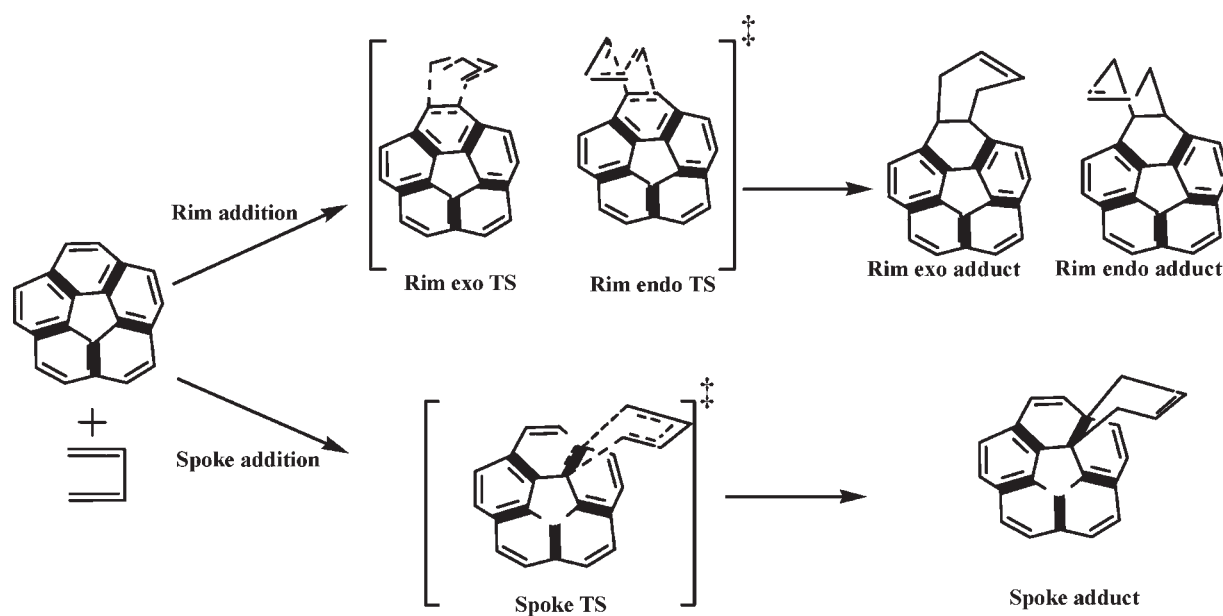


**Scheme 1.** Reaction of 1,3-butadiene with corannulene
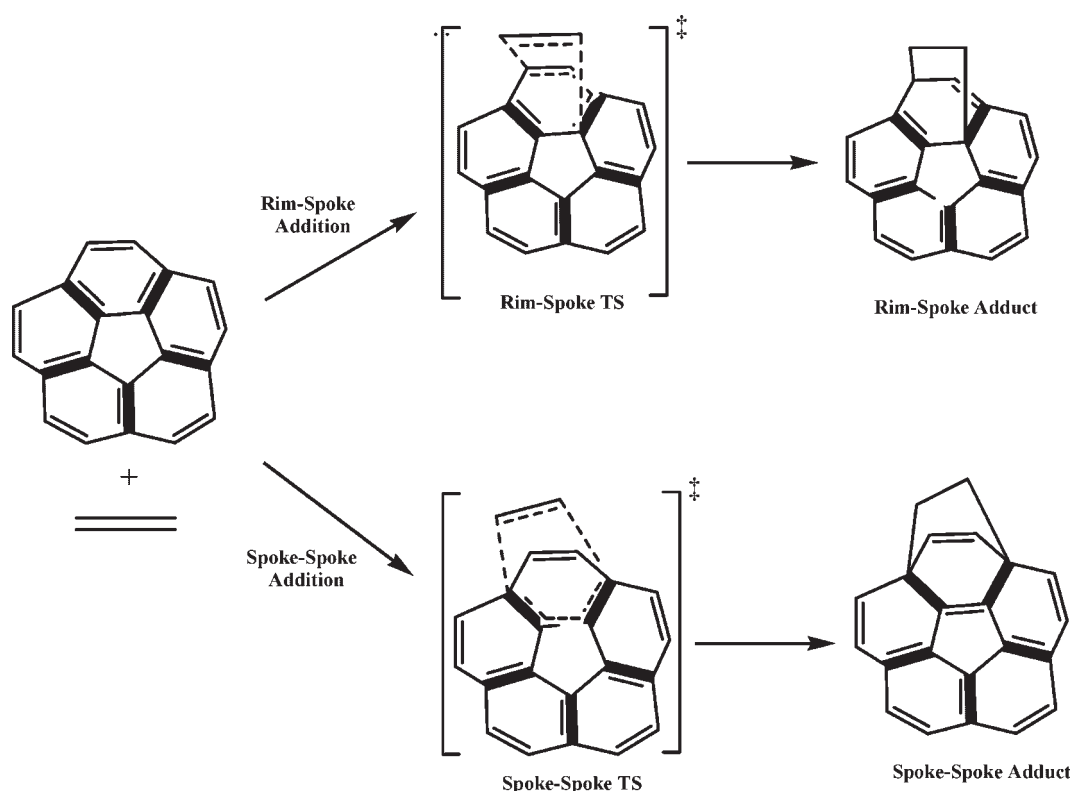
**Scheme 2.** Reaction of corannulene with ethylene

carbon is negatively charged compared to the spoke carbon and is also sterically hindered than the latter. Free energy profile (Fig. 3) and the activation and thermodynamic parameters (Table 2) show that this reaction involves high activation free energy and is endothermic. Comparatively both diene and dienophile distort more indicating that this reaction is more sterically hindered. $BFC_{ave}$ values given in Table 3 indicate that the TS is product like.

From Fig. 1 it is clear that the lobes of the LUMO of corannulene located at the rim carbons are significantly larger than those of the hub carbons and the reactivity at rim positions is much larger compared to spoke carbons. Comparatively, rim addition is kinetically and thermodynamically more favored than spoke addition. Further comparison of this reaction with that of 1,3-butadiene–ethylene shows that corannulene is a less efficient dienophile than ethylene. The latter involves comparatively low activation and reaction energies and passes through a more reactant like TS. The simple reason for this is that the steric involvement in the ethylene reaction is lesser in magnitude and ethylene with its full bond character is obviously more reactive. The double bond of corannulene is a part of local aromatic sextet and this also affects its reactivity.

## Corannulene as diene

Corannulene can also function as a diene where the rim–spoke and spoke–spoke double bonds can act as a diene unit when reacted with dienophiles. Ethylene is chosen to react with corannulene and the reaction scheme is shown in Scheme 2. Frontier orbital energy gap values (Table 2) show that these reactions are inverse electron demand type. Quantum of charge transfer ($q_{CT}$) value for the rim–spoke TS ($-0.029$) for the corannulene–

ethylene reaction confirms this point. $Q_{CT}$ values for the Spoke–Spoke TS exhibit a similar trend.

### Rim–spoke addition

The optimized geometry of the rim–spoke TS (Fig. 2) shows that the reaction passes through asynchronous TS with the rim carbon approaching closer than the hub carbon. The bond lengths of the newly forming $\sigma$ bonds in the rim–spoke TS is much shorter than that found for 1,3-butadiene–ethylene (Fig. 2 (f)). The reaction involves activation free energy of 51.2 kcal mol$^{-1}$ and forms an endothermic product (Table 2). Deformation energies show that higher degree of deformation of both the reactants leads to higher activation energy and activation free energy. Bond order analysis (Table 3) shows that rim bond cleaves up to 76.27% while the spoke bonds break only up to 13.64%. Both $BF_i$ and $BFC_{ave}$ indices indicate that this TS is a late TS.

### Spoke–spoke addition

In the Spoke–spoke addition, both the double bonds involved are endowed with comparatively lower double bond character and located interior of the molecule and this makes the electronic and steric requirements of the reaction very high. This is reflected in the very high activation free energy (Table 2) and deformation energy and further the adduct formed is highly endothermic. The lengths of the newly formed bonds indicated in Fig. 2 (e) reveal that these bonds are more matured and the bond indices (Table 3) reveal that the TS is more product like and this being a very late TS involves high activation energy.

Between rim–spoke and spoke–spoke addition the former is kinetically and thermodynamically more favored. Comparison of
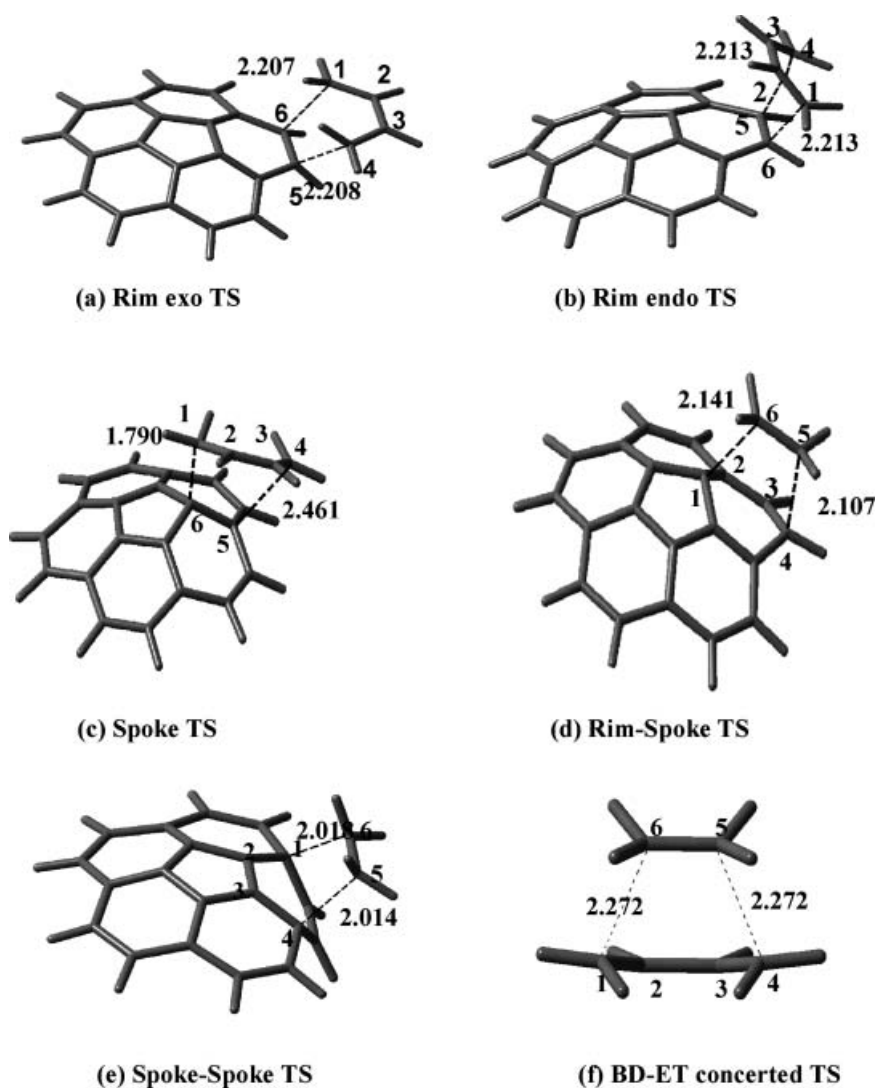
**Figure 2.** B3LYP/6-31G* optimized geometries of the concerted TSs of 1,3-butadiene–corannulene (a–c) and corannulene–ethylene (d, e) and 1,3-butadiene–ethylene (BD–ET) reactions (f)

this reaction with 1,3-butadiene–ethylene reaction shows that corannulene is a less efficient diene compared to 1,3-butadiene. This is due to the reason that (i) corannulene is an electron deficient molecule (ii) its double bonds are not free as it is in 1,3-butadiene. When corannulene is employed as a diene or dienophile, the double bonds involved in the reaction are the part of the local aromatic sextet and during the reactions there is sufficient double bond reorganization in corannulene that increases the energy demand. This does not occur in either 1,3-butadiene or ethylene. Further in the typical cycloaddition partners the double bonds are not only free but also early accessible and flexible to deform. This makes corannulene a less efficient diene than 1,3-butadiene and a less efficient dienophile than ethylene. If the reactivity of corannulene as a diene and dienophile are compared it acts better as a dienophile rather than a diene and it undergoes readily regioselective rim exo addition. When acting as a diene, two double bonds of corannulene are consumed and that involves lot of reorganization, loss of aromaticity and strain compared to dienophile situation where only one $\pi$ bond is consumed. This is the main reason for corannulene acting as a better dienophile than diene. This is consistent with

the conclusions of Chikama *et al.*[32] and Sola and coworkers[33,34] who investigated the reactions of $C_{60}$ with 1,3-butadiene and ethylene. This shows that $C_{60}$ and corannulene behave similarly in Diels Alder cycloaddition.[33,34]

The nature of bonding orbital and its associated stabilization energies are very useful and these quantities can be computed quantitatively using energy decomposition analysis (EDA). The EDA method makes it possible to quantify the contributions of covalent and classical electrostatic interactions to a chemical bond. Hence, an analysis of bonding energetics can be performed by combining a fragment approach to the molecular structure of a chemical system with the decomposition of the total bonding energy. The total bonding energy is the sum of electrostatic interaction ($\Delta E_{ele}$), Pauli ($\Delta E_{pauli}$) repulsion, and orbital interaction energy ($\Delta E_{orb}$). The first two terms, $\Delta E_{ele}$ and $\Delta E_{pauli}$ are added together in a single term called steric energy term.[35] These values are computed for the five TSs and the values are listed in Table 4.

For the reaction with butadiene and the rim carbons (both exo and endo) the steric term summed up to *ca.* $+52$ kcal mol$^{-1}$ while for the spoke carbons it is twice as much ($+103$) indicating a
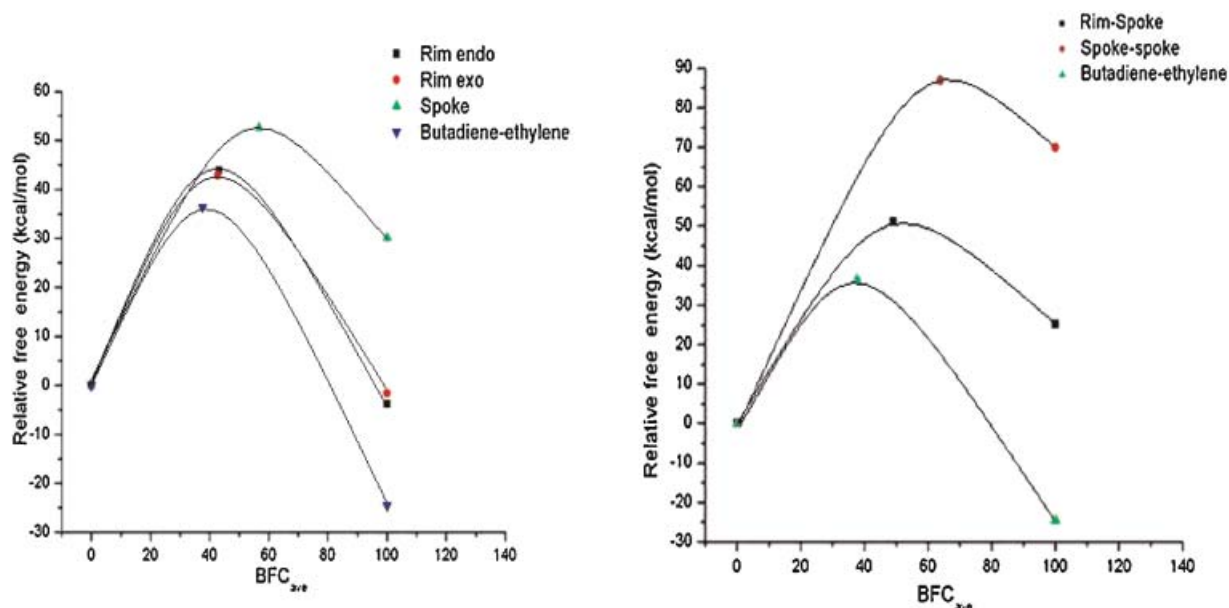
**Figure 3.** Free energy profile for the reaction of corannulene with (a) 1,3-butadiene and (b) Ethylene. Free energy profile for the reaction of 1,3-butadiene and ethylene is given for comparison This figure is available in colour online at www.interscience.wiley.com/journal/poc

strong destabilization or distortion up on the spoke addition. However this destabilization in the spoke addition is largely compensated by the orbital interaction term. This may be due to the formation of a bond in the TS for the spoke reaction and the involvement of neighboring phenyl rings causes a bigger orbital relaxation compared to rim reactions. A similar behavior can be observed for the reaction with ethylene. Additionally the reactions at the spoke carbons lead to distortion in the neighboring phenyl rings which is one reason for the large orbital interaction energies observed and higher activation barrier computed compared to that of the rim additions. The above arguments clearly suggest that corannulene preferentially acts as a dienophile than a diene and this can be due to the involvement of more number of neighboring carbons in the latter

reaction that alter the local aromaticity and strain to a greater extent.

## Effect of substituents

Reactions of isoprene (2-methyl-1,3-butadiene) and chloroprene (2-chloro-1,3-butadiene) with corannulene are monitored theoretically. Expectedly they pass through asynchronous TSs (Fig. 5) and have slightly lower activation energies (Table 5). $\sigma$- and $\pi$-donating tendency of methyl and chloro groups explains this observations.

Finally, we report the rim exo cyclo addition of butadiene to an extended corannulene system namely PEC, ($C_{50}H_{20}$, Fig. 4) which possesses a higher bowl depth compared to corannulene. Its

**Table 2.** Activation, reaction and deformation energies (kcal mol$^{-1}$), thermodynamic parameters at 298.15 K (kcal mol$^{-1}$) and frontier orbital energy (FOE) gap values (eV) computed at B3LYP/6–31G$^*$ level

| Type of addition | Activation energy | Reaction energy | Deformation energy | | Thermodynamical parameters | | | FOE gap$^*$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Diene | Dienophile | $\Delta G^{\ddagger}$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta E_1$ | $\Delta E_2$ |
| 1,3-butadiene–corannulene reaction | | | | | | | | | |
| Rim exo | 28.8 | −15.8 | 24.1 | 11.7 | 42.8 | 29.7 | −44.2 | | |
| Rim endo | 29.9 | −13.9 | 23.2 | 12.1 | 43.9 | 30.7 | −44.4 | 4.62 | 5.12 |
| Spoke | 38.2 | 13.0 | 32.5 | 18.3 | 52.6 | 38.5 | −47.2 | | |
| Corannulene–ethylene reaction | | | | | | | | | |
| Rim–spoke | 37.2 | 7.9 | 25.1 | 14.8 | 51.2 | 37.8 | −44.9 | | |
| Spoke–spoke | 73.9 | 53.9 | 51.7 | 26.9 | 86.9 | 73.9 | −43.6 | 6.45 | 5.69 |
| 1,3-butadiene–ethylene reaction | | | | | | | | | |
| Concerted | 22.4 | −43.1 | 19.7 | 7.9 | 36.4 | 23.4 | −43.6 | 6.70 | 6.43 |

$^*\Delta E_1 = E_{HOMO(diene)} - E_{LUMO(dienophile)}$; $\Delta E_2 = E_{HOMO(dienophile)} - E_{LUMO(diene)}$.

**151**

*J. Phys. Org. Chem.* **2008**, 21 146–154

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**Table 3.** Computed B3LYP/6–31G* bond indices[a] for various TSs involving the cycloaddition reaction of corannulene with butadiene and ethylene

| Reaction | BF$_i$ | | | | BCj | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | C2-C3 | C4-C5 | C6-C1 | BF$_i$ (ave) | C1-C2 | C3-C4 | C5-C6 | BCj (ave) | BFC (ave) |
| Butadiene–Corannulene | | | | | | | | | |
| Rim exo | 33.85 | 40.23 | 40.16 | 38.08 | 47.50 | 47.56 | 49.41 | 48.16 | 43.12 |
| Rim endo | 34.31 | 39.63 | 39.62 | 37.85 | 47.47 | 47.49 | 47.99 | 47.65 | 42.75 |
| Spoke | 45.53 | 72.99 | 31.55 | 50.02 | 49.13 | 75.94 | 64.62 | 63.23 | 56.63 |
| Corannulene + Ethylene | | | | | | | | | |
| Rim–spoke | 48.41 | 51.10 | 43.54 | 47.68 | 76.27 | 13.64 | 61.21 | 50.37 | 49.03 |
| Spoke–spoke | 62.19 | 58.89 | 59.15 | 60.08 | 65.21 | 64.97 | 72.82 | 67.67 | 63.88 |
| 1,3–butadiene–ethylene reaction | | | | | | | | | |
| Concerted | 29.44 | 35.20 | 35.22 | 33.29 | 40.70 | 40.68 | 44.45 | 41.94 | 37.62 |

[a] By definition, bond indices, BF$_i$, and BC$_j$ for various bonds listed above are 0 and 100, respectively for reactants and products. For atom numbering see Fig. 2(a) for butadiene–corannulene reaction and 2(d) for corannulene–ethylene reaction and 2(f) for butadiene–ethylene.

**Table 4.** Energy decomposition analysis (in kcal mol$^{-1}$) for the TSs involved when corannulene behaves as dienophile (with butadiene) and diene (with ethylene)

| Decomposition | 1,3-butadiene with corannulene | | | Corannulene with ethylene | |
| --- | --- | --- | --- | --- | --- |
| | Rim exo | Rim endo | Spoke | Rim–spoke | Spoke–spoke |
| Electrostatic | −41.0 | −39.4 | −83.9 | −55.6 | −77.7 |
| Pauli | +92.9 | +91.0 | +186.5 | +124.9 | +176.0 |
| Orbital | −57.9 | −57.0 | −115.1 | −72.1 | −102.8 |
| Total | −6.1 | −5.4 | −12.5 | −2.8 | −4.5 |

X-ray crystal structure[36] has been very recently published. PEC is a deep orange air stable crystalline solid with an enhanced pyramidalization of the carbon atoms with a p-orbital axis vector (POAV) of 12.6° compared to corannulene (8.3°). It is to be noted that averaged POAV of C$_{60}$ is lower than 12.6°. This indicates the increased bowl depth of PEC and this is the highest bowl depth observed so far.[33] Further it is more electron deficient than corannulene and follows normal electron demand type reaction with butadiene. Due to the preference of exo–metal binding to corannulenes and in our investigations in this paper and in previous work on dipolar cyclo additions suggesting rim exo is the most favorable site, we located the associate transition state for the butadiene–PEC cycloaddition at the rim exo position alone. Besides this due to the large size of the system, calculations were performed using 6–31G basis to reduce the computational cost for this extended corannulene. The optimized structures for the transition states with important geometric parameters are shown in Fig. 5, and the energetic quantities are listed in Table 5.

The activation and reaction energies computed for the reaction of rim exo addition of 1,3-butadiene with PEC (Fig. 5) clearly reveals that this greater bowl depth increased the strain and this resulted in a high barrier (Table 5) and an endothermic adduct. The optimized structure of the PEC (B3LYP/6–31G) is in good
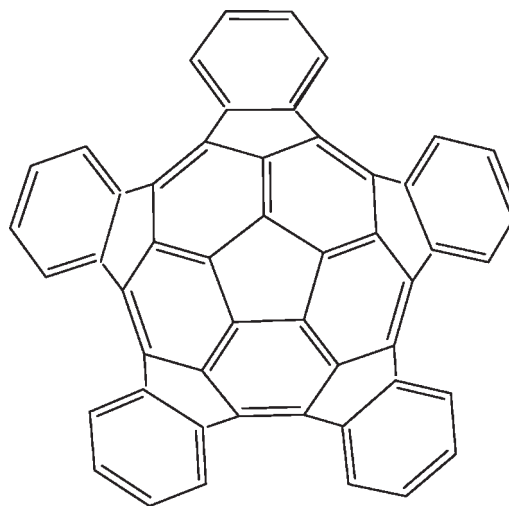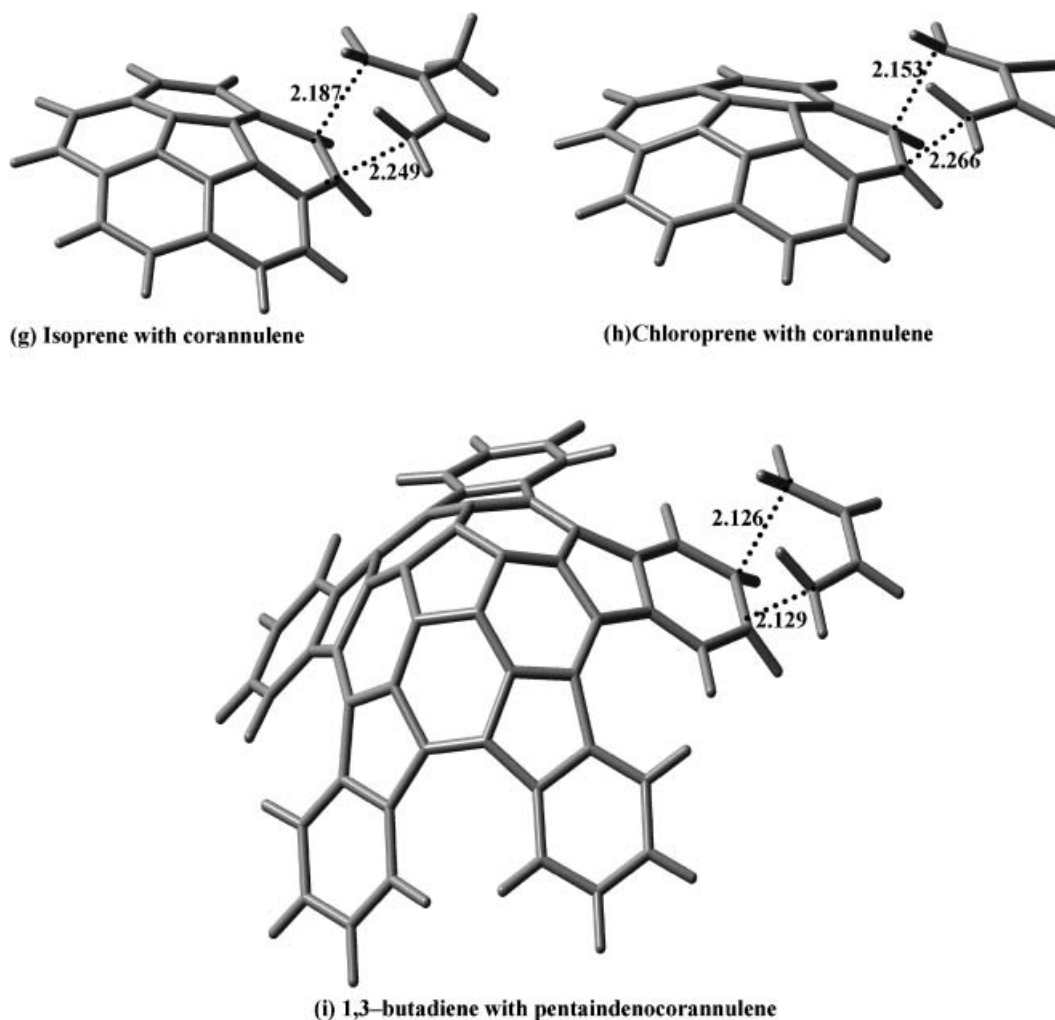


**Figure 4.** Structure of pentaindenocorannulene

(g) Isoprene with corannulene

(h) Chloroprene with corannulene

(i) 1,3–butadiene with pentaindenocorannulene

**Figure 5.** B3LYP/6-31G* optimized geometries of the concerted TSs of substituted 1,3-butadiene with corannulene. B3LYP/6-31G optimized geometries 1,3-butadiene–pentaindenocorannulene cycloaddition

**Table 5.** Computed activation and reaction energies involving the cycloaddition reaction of corannulene with isoprene, chloroprene at B3LYP/6–31G* and the reaction of 1,3-butadiene with pentaindenocorannulene at B3LYP/6–31G level

| | | | FOE gap | |
| --- | --- | --- | --- | --- |
| Type of addition | Activation energy | Reaction energy | $\Delta E_1$ | $\Delta E_2$ |
| 1,3-butadiene–corannulene reaction | | | | |
| Rim exo | 28.8 | −15.8 | 4.62 | 5.12 |
| Isoprene–corannulene reaction | | | | |
| Rim exo | 27.3 | −15.7 | 4.61 | 5.53 |
| Chloroprene–corannulene reaction | | | | |
| Rim exo | 26.2 | −15.9 | 5.10 | 4.92 |
| 1,3-butadiene–pentaindenocorannulene reaction | | | | |
| Rim exo | 39.7 | 7.5 | 3.77 | 4.74 |

agreement with those of the X-ray data and computed structure.[36] The optimized transition state structure shown in Fig. 5 corresponds to the synchronous concerted transition state of this reaction.

# CONCLUSIONS

Corannulene has been tested for its dienophilicity and diene reactivity by computationally following its reactions with typical

*J. Phys. Org. Chem.* **2008,** 21 146–154

153

cycloaddition partners 1,3-butadiene and ethylene. For comparison 1,3-butadiene and ethylene reaction has been investigated. All these reactions have been modeled at B3LYP/6-31G* level. Our study concludes the following points, (i) rim and spoke bonds of corannulene that show higher double bond character are involved in the reaction. Further, rim bonds show better reactivity than spoke bonds since rim bonds have higher double bond character than spoke bonds and are located at the exterior of the molecule permitting easy access to the approaching partner. Reports are available in the literature showing that rim addition occurs in many other cyclizations and addition reactions.[37,38] Regioselectivly rim additions are preferred and particularly rim exo addition is the most favored. (ii) Corannulene acts better as a dienophile than as a diene. Besides, as indicated from NBO analysis lower double bond character and interior location of the reacting double bonds in corannulene makes the electronic and steric requirements much higher and makes it a less efficient diene than 1,3-butadiene and less efficient dienophile than ethylene. Corannulene being an electron deficient system acts as the electron acceptor in both reactions. (iii) These reactions follow concerted mechanism and corannulene reacts in the convex side. (iv) Further, corannulene behaves similarly as $C_{60}$ in the Diels Alder addition. (v) Electron donation by methyl and chloro groups on butadiene slightly favor the rim exo reaction over unsubstituted ones. (vi) The greater bowl depth that leads to more pyramidalized carbon bonds, less HOMO–LUMO gap compared to corannulene (3.15 eV and 4.37 eV) and strained C—C bonds might favor the reaction,[34] but it is interesting to note that the barrier for this reaction is unusually high compared to corannulene.

## Acknowledgements

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