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1,3-Dipolar Reactions Involving Corannulene: How Does Its Rim and Spoke Addition Vary?

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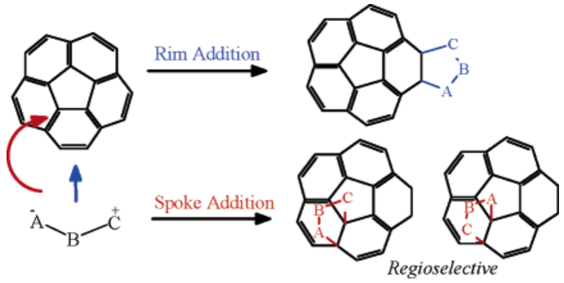

Corannulene undergoes 1,3-dipolar reactions with the dipoles, diazomethane, nitrile oxide, and nitrone through its rim and spoke π bonds; the rim addition yields "one possible" adduct whereas two "regioselective" adducts are formed by spoke addition. Mechanisms of these reactions have been investigated at the B3LYP/6-31G(d) level. Computations show that both rim and spoke additions prefer concerted pathways that lie 2−5 kcal/mol lower in energy than stepwise paths. Stepwise additions can take place in two ways and the activation energies of these two modes differ by 1−2 kcal/mol. A close inspection of the energy profiles reveals that rim addition is more favorable kinetically and thermodynamically than spoke addition in view of lower activation energy and higher exothermicity observed for rim addition. The rim bond of corannulene is more flexible for distortion and also has a stronger double bond (i.e. π-character) than the spoke bond and this facilitates rim addition over spoke addition. Deformation energy analysis also confirms the above through higher deformation in corannulene from the spoke addition when compared to rim addition. In the spoke addition, regio1 reaction is kinetically more favored than regio2 reaction. Attempts to react corannulene in an endohedral fashion have led to the exohedral adduct. Computed activation energies suggest that corannulene acts as a deactivated dipolarophile compared to ethylene. Even more striking is the observation that rim and spoke double bonds in corannulene are part of the local aromatic system but it shows remarkable reactivity compared to benzene despite the loss of aromaticity during the reaction. This is well indicated by computed NICS values. Inclusion of acetonitrile as solvent through the PCM model increases the reaction rate and exothermicity.

Introduction

Corannulenes, bowl-shaped polyaromatic hydrocarbons that were known long before the discovery of fullerenes,[1] have generated intense research activity in recent years.[2,3] It was first synthesized in 1966 by Lawton and Barth,[4] and its X-ray structure was reported by Hanson and coworkers.[5] Corannulene is an attractive system that manifests a compromise between strain and conjugation. Unlike fullerenes, these are open-ended curved π-systems and hence accessibility of both convex and concave faces is possible. Corannulene, despite its substantial curvature, is characterized as a flexible molecule exhibiting rapid bowl-to-bowl inversion in solution as evidenced by dynamic NMR studies.[6] Redox chemistry of it is also very interesting.[7] Mono-, di-, tri-, and tetraanions of corannulene have been generated using controlled reduction by alkali metals, Li and K, and were characterized based on optical absorption, electron paramagnetic resonance

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(EPR), and nuclear magnetic resonance (NMR) spectroscopies.[6]

Computations play a pivotal role in understanding and modeling novel properties of bucky bowls. In particular, theoretical studies concerning the structure and inversion barriers of neutral anions[2e−f] di- and tetraanions of corannulene were reported by Rabideau and co-workers.[8] Recently, the vibronic coupling, the Jahn−Teller effects, and vibrational structures in negatively charged corannulenes have been explored.[9] Annulated corannulenes have often been studied both experimentally[10] and theoretically.[11] Bent π conjugated systems have a different type of electron distribution compared to their planar counterparts, and as a consequence will have different kinds of reactivity.[2a] The π-system exhibiting strain as well as aromaticity in bowl-shaped corannulenes could be effective toward their reactivity like fullerene[12] when compared to the planar systems. However, these curved π-systems mainly show the electron-deficient[12] behavior that arises from their low-lying LUMO and π-conjugative strain overcomes the π-aromaticity.[11k,13] Thus, the conjugated olefins in bucky balls/bowls are shown to undergo readily electrophilic additions.[14] Corannulene is a prototype open-ended curved π-network that offers excellent opportunity to learn these effects and its reactivity toward various organic reagents is also scarce.[2o−q] Only Scott and Preda[2q] have studied the regioselectivity of the corannulene reaction experimentally by dihalocarbene addition and explained the regioselectivity in the reactions through FMOs. Moreover, cycloadditions involving corannulene have neither been accomplished experimentally nor studied theoretically. This has motivated us to theoretically investigate the reactivity of corannulene via the 1,3-dipolar reaction. Since 1,3-dipolar cycloaddition of C_{60}[15] is a key step for making different electronic and photonic[16] materials that attracted a lot of interest in this decade, computational studies have shown that addition of fullerene and nanotube to dipole is shown to be remarkably favorable.[17] Therefore, we deal with the 1,3-dipolar reactions of corannulene with various dipoles viz.

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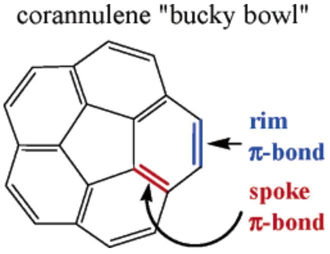

FIGURE 1. Two possible regioselective additions of corannulene are shown by “rim” and “spoke” π-bonds.

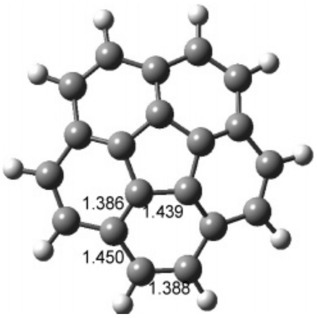

FIGURE 2. The major C−C bond lengths in corannulene calculated at the B3LYP/6-31G(d) level showing with the double bond character of spoke and rim bonds.

diazomethane, nitrile oxide, and nitrone. Corannulene, a multiply π bonded system, can undergo addition in any of its π bonds and “rim” and “spoke” π bond additions are important as shown in Figure 1. Rim vs spoke selectivity, the mechanism of 1,3-dipolar reactions of corannulene, and the factors that govern the regioselectivity are investigated at the DFT level. The purpose of this work is to find out (i) the mechanism for the corannulene 1,3-dipolar reaction, concerted or stepwise, and (ii) the regioselectivity or relative reactivity of rim and spoke π-bonds in the corannulene 1,3-dipolar cycloaddition.

Computational Details

Computations on the mechanism of “rim” and “spoke” addition reactions were carried at the B3LYP/6-31G(d)[18,19] level. The RB3LYP/6-31G(d) method was used to compute the closed shell species on the reaction path and the UB3LYP/6-31G(d) method for open shell species. Houk[20] and Valentin[21] and co-workers have specifically tested the performance of the B3LYP/6-31G(d) method for 1,3-dipolar reaction in comparison with the CASSCF, QCISD optimization and with single point energy calculation at the QCISD(T)/6-31G(d) and CCSD(T)/6-31G(d) levels and concluded that R(U)B3LYP/6-31G(d) geometries as well as energetics are remarkably close to those done at higher levels. These results show that B3LYP/6-31G(d) was not only cost-effective but also well suitable for the present study. Moreover, the value of $\langle s^2 \rangle = 0$. Therefore we have not performed any spin projection calculations here. The stationary point geometries have been characterized by frequency calculations. All transition states have single imaginary frequencies and minima have all real frequencies. All calculations have been performed using the Gaussian 98W[22] program. Deformation energies have been calculated as reported earlier.[23] Loss of aromaticity in the reacting benzenoid ring during both rim and spoke additions can be obtained from Nuclear Independent Chemical Shift[24] (NICS(1)) computed at 1 Å above the geometric center of the hexagonal ring. The NICS(1) values have been evaluated by using the gauge invariant atomic orbital (GIAO) approach at the B3LYP/6-31G(d,p) level and computed as the average magnetic shielding at the center of the hexagonal plane (i.e. 1 Å above the ring). Negative NICS values denote aromaticity, positive values antiaromaticity, and nearly zero values nonaromaticity. The effect of solvent on the concerted reactions has been evaluated using the single point PCM (Polarized Continuum Model) calculations[25] at the SCRF-B3LYP/6-31G(d) level with acetonitrile solvent on the gas-phase geometries.

Results and Discussion

Corannulene undergoes 1,3-dipolar cycloaddition with the dipoles diazomethane, nitrile oxide, and nitrone and predominantly the addition takes place in the rim and spoke bonds. This is in view of the fact that rim (1.388 Å) and spoke bonds (1.386 Å) have higher double bond character than hub (1.439 Å) and flank bonds (1.450 Å) as can be seen from Figure 2. Further, both rim and spoke additions can take place through concerted as well as stepwise pathways in a normal electron demand manner (Scheme 1) showing LUMO-dipolarophile (corannulene) control. Therefore, both pathways are considered for the present investigation as illustrated in Schemes 2−4. The stepwise mechanism can have two modes; either the positive center of the dipole (atom A) reacts first or the negative center (atom C) with corannulene.

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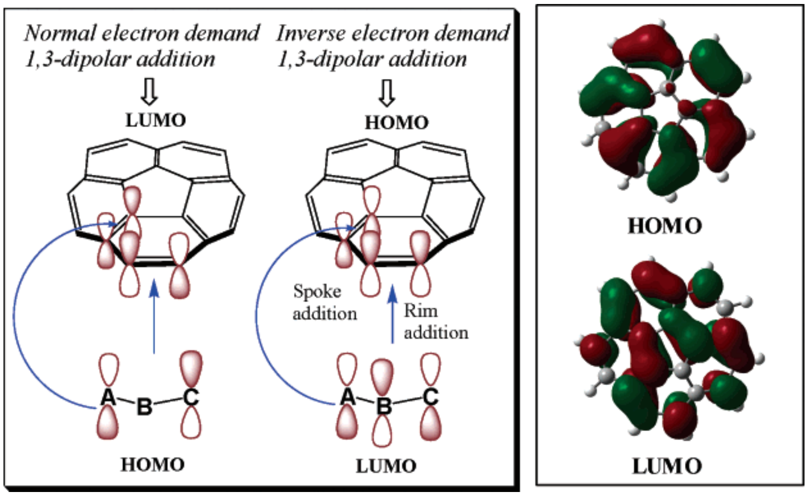
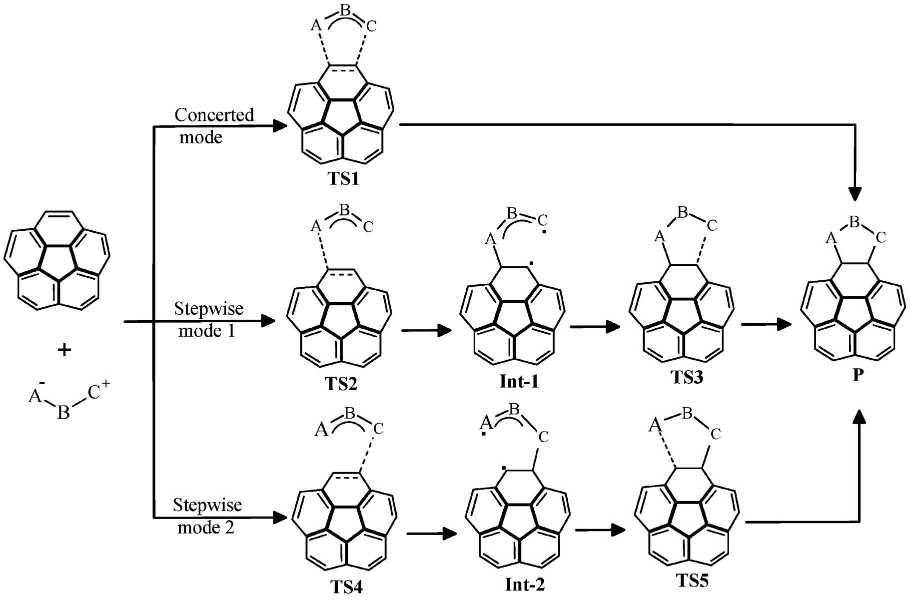
SCHEME 1



SCHEME 2[a]

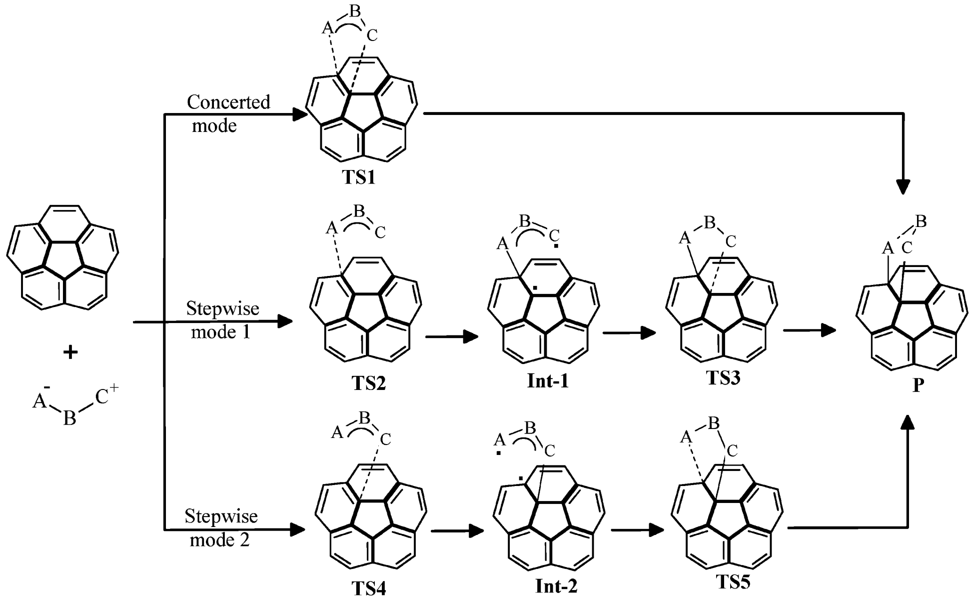


[a] Rim addition of corannulene with 1,3-dipoles, diazomethane, nitrile oxide, and nitrone.

The former is described as **stepwise mode 1** and the latter as **stepwise mode 2**. Later in the second step the intermediate cyclizes to give the adduct. As shown in Schemes 2−4, **stepwise mode 1** involves TS 2, Int1, and TS3 and **stepwise mode 2** involves TS4, Int 2, and TS5. The concerted transition state is denoted as TS1. In total 72 species, 24 stationary point geometries from each dipolar addition, and the relative energies of these species are presented in Table 1. B3LYP/6-31G(d) data reveal that in spoke addition, the regio1 reaction is preferred over the regio2 reaction and therefore spoke-regio1 addition and rim addition alone are considered for further discussion. DFT energy profiles for the three dipolar reactions are presented in Figures 3−5. Calculated deformation energies of the reactants during the initial phase of the reaction are given in Table 2 and computed activation parameters ($\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$) of various species in the reaction path are compiled in Table 3. When dipoles approach corannulene in the endohedral fashion, corannulene flips fast to an exohedral addition and hence no endohedral adduct could be located.

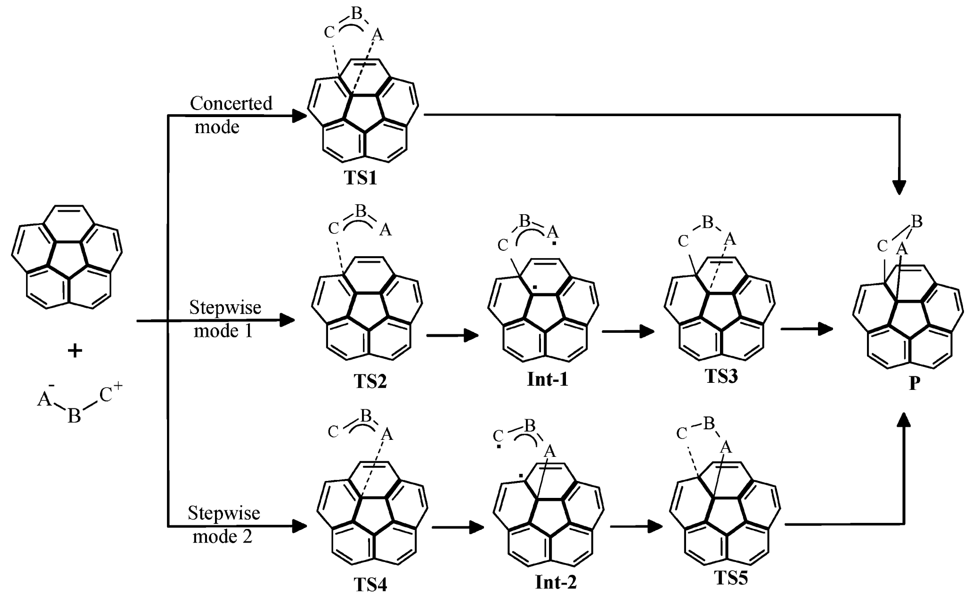
Rim Addition. In corannulene, there are five rim double bonds that are symmetric and therefore only one possible adduct is formed by rim addition of 1,3-dipolar cycloaddition reactions viz. corannulene−diazomethane (reaction 1), corannulene−nitrile oxide (reaction 2), and corannulene−nitrone (reaction 3). DFT activation barriers presented in Figures 3a−5a show that concerted pathways are indeed more preferred by 4.88, 4.96, and 2.61 kcal/mol than the stepwise reactions in Figures 3b−5b. These confirm that reactions 1−3 obviously follow the concerted mechanism as shown in the past experiments.[26] The activation energies (Table 1) further show that in the stepwise mechanism, while stepwise mode 1 is preferred in reaction 1, stepwise mode 2 is preferred in reaction 3. Both these modes have closely lying paths for reaction 2. The reaction exothermicities show that rim

SCHEME 3[a]



[a] Spoke (regio1) addition of corannulene with 1,3-dipoles, diazomethane, nitrile oxide, and nitrone.

SCHEME 4[a]



[a] Spoke (regio 2) addition of corannulene with 1,3-dipoles, diazomethane, nitrile oxide, and nitrone.

adducts of reactions 1 and 2 are more stable, but that of reaction 3 has relatively lower stability compared with that of reactions 1 and 2. In the stepwise mechanism the final step is found to be rate determining in all these reactions. The preference of concerted mechanism can be understood from the deformation of reactants at the TS. The deformation energies (Table 2) reveal that in rim addition the dipole distorts more than corannulene and the concerted process requires lower extents of deformation than the stepwise process. The overall results thus establish that the rim addition prefers the concerted mechanism. Computed activation enthalpies and free energies (Table 3) for concerted and stepwise modes also reflect the same trend. $\Delta S^{\ddagger}$ values computed for the concerted process fall in the range −32 to −33 eu, and this is quite similar to the range observed in ethylene and allene dipolar additions described earlier.[23c,d] NICS-(1) values at the reacting benzenoid ring of corannulene,

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(26) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633. (b) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403. (c) Sustmann, R. *Tetrahedron Lett.* **1971**, *12*, 2721. (d) Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11,* 838. Review: Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569. Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 1−176. (e) Cinquini, M.; Cozzi, F. In *Stereoselective Synthesis*; Helmchen, G., Hoffmann, R. W., Mulzer, J., Schauman, E., Eds.; Georg Thieme: Stuttgart, Germany, 1996; Vol. 5, pp 2953−2987. (f) Houk, K. N.; Yamaguchi, K. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 2, pp 407−450. (g) Padwa, A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991; Vol. 4, pp 1069−1109. (h) Wade, P. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991; Vol. 4, pp 1111−1168.

TABLE 1. B3LYP/6-31G(d) Relative Energies[a] (kcal mol^{-1}) of Various Species on the Reaction Paths of Corannulene with Diazomethane, Nitrile Oxide, and Nitrone Rim and Spoke Addition (Regio1 and Regio2)

	rim addition			spoke addition					
				corannulene + diazomethane		corannulene + nitrile oxide		corannulene + nitrone	
species	corannulene + diazomethane	corannulene + nitrile oxide	corannulene + nitrone	R1	R2	R1	R2	R1	R2
TS1	17.2	15.3	16.1	19.3	20.2	18.4	20.6	17.2	19.7
stepwise 1									
TS 2	22.1	20.2	20.7	21.3	23.8	20.3	23.4	20.1	22.3
Int 1	6.2	7.3	9.2	5.3	6.4	3.2	5.4	8.1	10.3
TS 3	10.3	19.3	13.3	10.4	11.9	10.7	12.3	11.3	13.1
stepwise 2									
TS 4	23.8	21.3	18.7	22.7	24.5	21.4	23.4	19.4	21.9
Int 2	8.3	12.7	8.8	6.3	8.4	7.4	8.2	6.2	8.1
TS 5	13.2	17.0	12.7	11.4	13.9	11.8	12.9	9.4	10.3
product	−17.3	−26.9	−6.0	−9.0	−6.2	−0.7	2.3	−9.3	−4.1

[a] Relative energies are expressed assuming the reactant's energy as zero. For species names refer to Scheme 2 (rim addition), Scheme 3 (spoke regio1 addition), and Scheme 4 (spoke regio2 addition). R1 and R2 in the table represent regio1 and regio2 reactions.

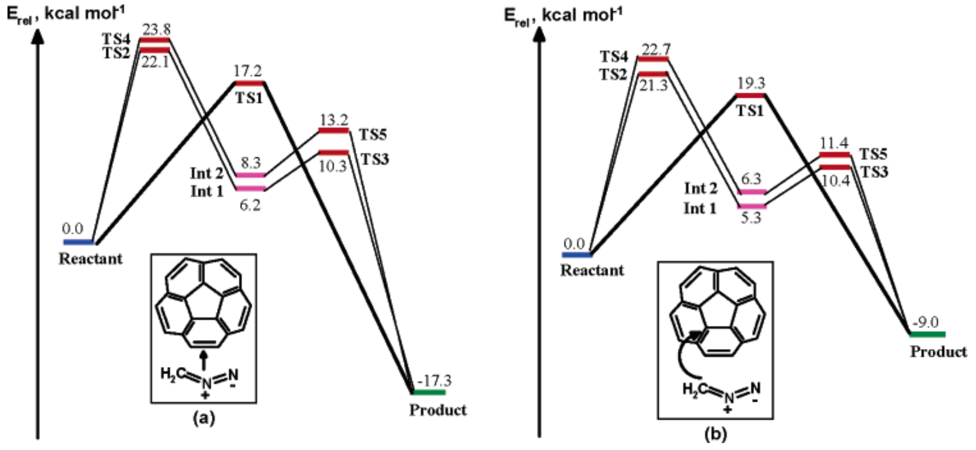

FIGURE 3. Energy profiles (B3LYP/6-31G(d)) for the 1,3-dipolar cycloaddition of (a) corannulene-rim and (b) spoke-regio1 additions to diazomethane shown via concerted (dark line) and stepwise pathways.

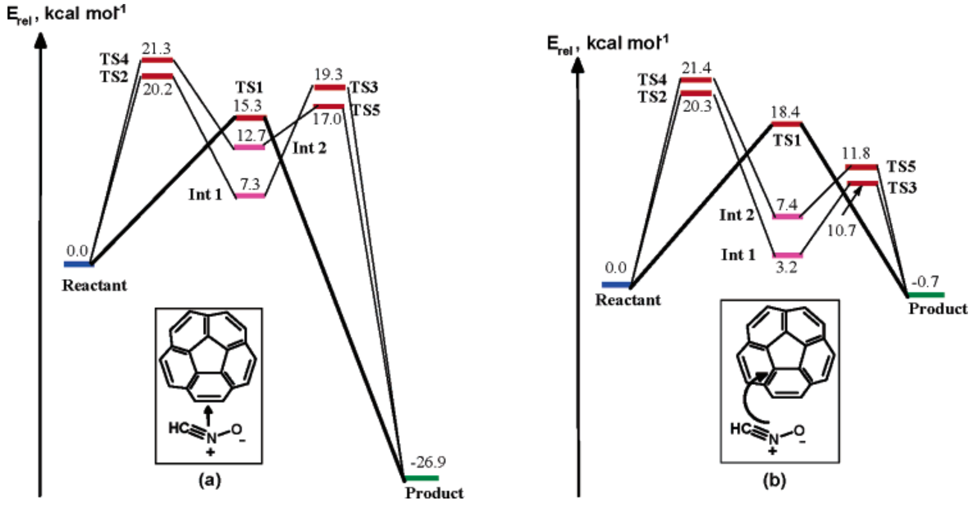

FIGURE 4. Energy profiles (B3LYP/6-31G(d)) for the 1,3-dipolar cycloaddition of corannulene-rim (a) and spoke-regio1 (b) additions to nitrile oxide shown via concerted (dark line) and stepwise pathways.

rim concerted TS, and rim adduct have been calculated to be respectively −6.89,−3.97, and −0.32 ppm and this shows a gradual loss of aromaticity during the course of the reaction.

Spoke Addition. Similar to rim bonds, there are five symmetric spoke bonds and these bonds connect one hub carbon and another rim-quat carbon. Due to this asymmetry additions on this bonds lead to two regio adducts: spoke regio1 and spoke regio2 adducts. Computed barriers data (Table 1) reveal that the spoke regio1 reaction is preferable kinetically over the regio2 reaction. Concerted paths are lower lying than stepwise paths for reactions 1−3. Relative energies of TSs at the B3LYP level (Figures 3b, 4b, and 5b) predict that all the stepwise

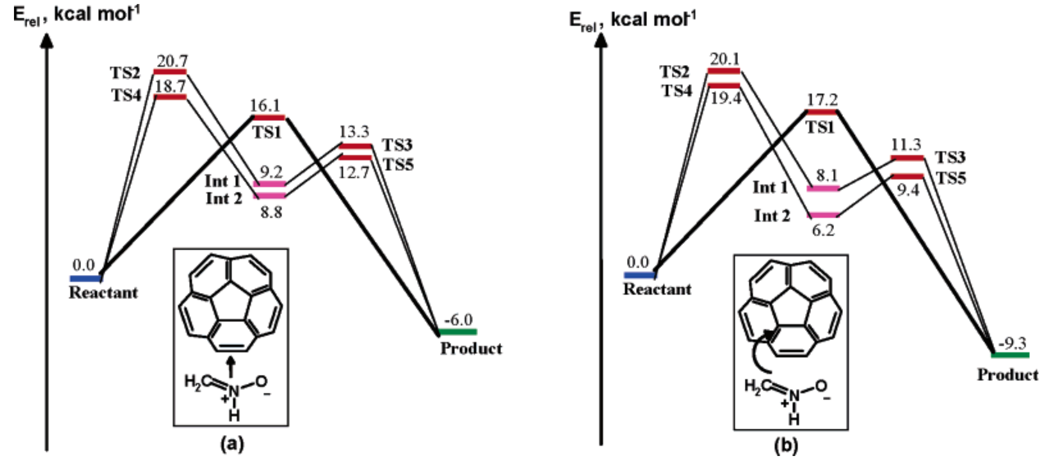

FIGURE 5. Energy profiles (B3LYP/6-31G(d)) for the 1,3-dipolar cycloaddition of corannulene-rim (a) and spoke-regio1 (b) additions to nitrone shown via concerted (dark line) and stepwise pathways.

TABLE 2. B3LYP/6-31G(d) Deformation Energies[a] (kcal mol^{-1}) of the Dipoles and Corannulene in the 1,3-Dipolar Reactions of Corannulene with Diazomethane, Nitrile Oxide, and Nitrone

	corannulene + diazomethane		corannulene + nitrile oxide		corannulene + nitrone	
species	DE1	DE2	DE1	DE2	DE1	DE2
rim addition						
concerted mode: TS 1	10.4	6.3	9.9	5.9	12.8	4.9
stepwise mode 1: TS 2	12.2	7.4	13.4	7.9	13.8	7.8
stepwise Mode 2: TS 4	15.8	7.9	12.9	7.4	11.3	4.2
spoke addition-regio1						
concerted mode: TS 1	11.8	8.7	11.4	8.9	13.3	6.3
stepwise mode 1: TS 2	14.4	9.9	14.3	8.1	14.8	8.3
stepwise mode 2: TS 4	16.3	8.3	13.5	8.8	13.9	8.2

[a] DE1 is the deformation energy of dipole. DE2 is the deformation energy of corannulene. These values have been calculated only for the first stage in each reacting mode, as it is the rate-determining step in all the reactions.

TABLE 3. B3LYP/6-31G(d) Activation Enthalpies as Well as Free Energies (kcal mol^{-1}) and Entropies (cal K·mol^{-1}) Parameters for the 1,3-Dipolar Cycloadditions of Corannulene with Diazomethane, Nitrile Oxide, and Nitrone

	corannulene + diazomethane			corannulene + nitrile oxide			corannulene + nitrone		
species	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
rim addition									
concerted mode									
TS 1	22.9	32.7	−33.0	20.7	30.2	−31.9	21.7	31.5	−32.7
stepwise mode 1									
TS1	26.8	35.3	−28.3	24.3	33.1	−33.2	25.2	32.7	−29.8
TS2	16.4	24.1	−27.6	20.3	29.2	−29.8	19.7	26.4	−30.6
stepwise mode 2									
TS 4	28.8	36.4	−25.4	26.1	35.4	−30.4	21.8	32.	−31.2
TS 5	19.3	28.6	−39.7	21.2	31.7	−31.2	17.3	26.4	−30.9
spoke addition-regio1									
concerted mode									
TS 1	28.1	34.1	−31.2	25.3	30.9	−33.2	21.7	29.7	−28.5
stepwise mode 1									
TS 2	28.8	35.8	−27.9	27.3	31.7	−32.8	26.9	31.2	−32.2
TS 3	17.8	25.7	−31.0	16.2	21.8	−31.2	14.9	20.9	−33.1
stepwise mode 2									
TS 4	29.3	37.2	−32.2	28.7	32.1	−32.4	26.7	31.7	−27.3
TS 5	18.9	25.4	−31.9	16.2	22.7	−30.4	17.1	23.1	−39.9

paths are close lying, and in the stepwise mechanisms, the first step is rate determining. Computed DFT reaction energies (Figures 3b−5b) show that spoke regio1 adducts of reactions 1 and 3 are more stable than that of reaction 2. Deformation energies (Table 2) reveal that concerted processes require a smaller amount of distortion and generally dipoles distort more than corannulene. Calculated activation enthalpies and free energies (Table 1) for concerted and stepwise modes of spoke addition follow the trend predicted by activation energies. Entropies of activation for this reaction fall in the range −28 to −33 eu, which is typical for the 1,3-dipolar cycloadditions considered here.[19] NICS(1) values at the reacting benzenoid rings of corannulene that share the spoke bond, spoke regio1 concerted TS, spoke regio1 adduct have been calculated to be respectively −6.89, −3.93, and −0.27 ppm. Similarly, NICS(1) values for spoke regio2 concerted TS and spoke regio2 adduct have been found to be −2.68 and −0.38 ppm. All these trends in NICS(1) values clearly indicate the loss of aromaticity during the

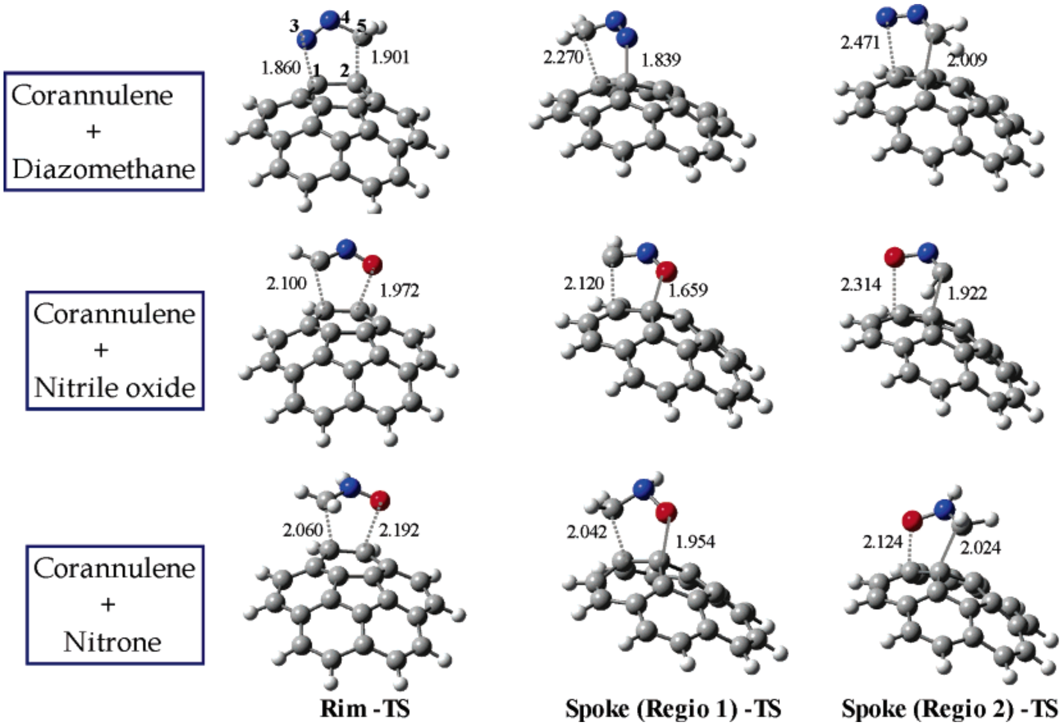

FIGURE 6. Computed transition structures (B3LYP/6-31G*) for the concerted 1,3-dipolar addition of diazomethane, nitrile oxide, and nitrone to both rim and spoke (regio1 and regio2) π-bonds of corannulene along with the bond lengths of forming C⋯C and C⋯X (X = N and O) bonds.

reaction in the reacting benzenoid rings that share the spoke bond in corannulene.

Rim vs Spoke Addition. DFT data listed in Table 1 show that in the reactions 1−3, rim addition is preferred over spoke addition and in spoke addition, regio1 reaction is favored kinetically compared to regio2 reaction. In all these dipolar additions, concerted regio1 paths are lower by 1−3 kcal/mol than the corresponding regio2 paths. DFT results (Figures 3−5) also confirm that (i) rim additions are preferred over spoke additions, (ii) the concerted mechanism is followed in reaction 1−3, and (iii) in the stepwise mechanism, the first step is rate determining while the cyclization step is faster. DFT results (Tables 1 and 3) reveal that the concerted process has a clear preference over stepwise processes with a maximum activation energy difference of 5 kcal/mol and a minimum difference of 2 kcal/mol. In reactions 1 and 2, this selectivity is well resolved while in reaction 3 concerted processes are lower by 2 kcal/mol. Computed DFT exothermicities for rim and spoke additions show that rim adducts are thermodynamically more stable than spoke regio1 adducts of reaction 1 and 2 while spoke regio1 adducts have slightly higher stability over the rim adduct of reaction 3. The overall higher stability of rim adducts over spoke regio1 adducts is due to the strain involved in the new bond formed at hub and rim-quat carbons. Though these carbon atoms have angle strain induced reactivity, their disposition in the middle of the ring system makes it difficult to accommodate any angle/bond length changes during the reaction.

Unlike allene[23c] and ethylene,[23d] corannulene double bonds prefer the concerted mechanism and the deformation energy data (Table 2) reveal that dipoles have to distort more in stepwise paths than in the concerted path. Between rim and spoke addition, the distortion of both dipole and corannulene in the transition state is greater in the latter than in the former and this explains the relative preference of rim over spoke addition. The rim bond is more susceptible to addition than the spoke bond owing to both geometric and electronic criteria. Located at the periphery, the rim bond is quite accessible and can accommodate more pyramidalization at the reacting carbon during the reaction than the spoke bond can. With higher double bond character, rim bonds (NBO pop (π): 1.8 e) are more favored than spoke bonds (NBO pop (π): 1.6 e) for the dipoles to attack. In spoke additions, loss of aromaticity occurs in both benzene rings that share the spoke bond and this also decreases the drive for the reaction. Importantly, corannulene 1,3-dipolar reactions are $\text{LUMO}_{\text{corannulene}}$ controlled and LUMO vectors of rim carbons are larger than those of spoke carbons, and this mainly directs the reaction for rim addition. This can be compared with the preference for spoke addition in the dihalocarbene addition to corannulene reported by Scott and Preda.[2o] In that paper, the authors had explained similarly that the preference of spoke addition was due to larger HOMO vectors on spoke carbons than those on rim carbons. DFT optimized geometries of concerted TSs of rim and spoke regio1 and regio 2 additions presented in Figure 6 indicate that they are relatively early TSs. In all these additions both stepwise modes 1 and 2 have closely low-lying paths and their deformation energy data also support similar extents of distortion in the TS. Calculated activation parameters for reactions 1−3 also explain the same features. Rim and spoke bonds in corannulene are, unlike ethylene and allene, part of the local aromatic system and therefore suffer loss of aromaticity during the reaction. This affects the activation

TABLE 4. Activation and Reaction Energies (kcal mol^{-1}) for the "Concerted" 1,3-Dipolar Reactions of Corannulene with Dipoles Diazomethane, Nitrile Oxide, and Nitrone in Acetonitrile from Single Point Computations at the SCRF(PCM)-B3LYP/6-31G(d) Level on the Gas Phase B3LYP-6-31G(d) Geometry[a]

	diazomethane			nitrile oxide			nitrone		
dipole addition	rim	spoke regio 1	spoke regio 2	rim	spoke regio 1	spoke regio 2	rim	spoke regio 1	spoke regio 2
$\Delta E^{\ddagger}$(gas)	17.2	19.3	20.2	15.3	18.4	20.6	16.1	17.2	19.7
ΔE_r (gas)	−17.3	−9.0	−6.2	−26.9	−0.7	2.3	−6.0	−9.3	−4.1
$\Delta E^{\ddagger}$(solv)	14.2	15.3	19.8	11.3	15.4	18.0	13.3	14.0	16.2
ΔE_r (solv)	−19.8	−11.4	−9.6	−29.1	−2.1	0.3	−8.5	−12.1	−10.7

[a] See gas-phase energies from Figures 3−5.

barrier and adduct stability and hence is responsible for the poor reactivity as compared to ethylene.

Bond Order Analysis on the Nature of Transition States. Computed bond indices for the cycloadditions of three different dipoles (diazomethane, nitrile oxide, and nitrone) to rim and spoke π-bonds of corannulene are listed in Tables S1−S6 (Supporting Information). From these tables, a general trend on the "early" and "late" nature of TS (see Figure 6) has been discussed for both concerted and stepwise mechanisms.

(i) Concerted Mode. Percentages of bond forming (BF$_i$) and cleaving (BC$_i$)[25] at the concerted TS show that the new σ bonds (1−3 and 2−5) are formed roughly 34−41% and 27−33%, respectively, in the concerted TSs. The π bonds (1−2, 3−4, and 4−5) are cleaved around 30−46%, 28−34%, and 31−38%, respectively. Due to the asymmetry of the dipole, the percentages of both the forming and cleaving bonds are unequal.

(ii) Stepwise Mode 1. Considering the first TS, named as TS2, the 1−3 σ bond is formed roughly 38−43% and the 2−5 σ bond is formed 0%, the 1−2 σ bond is cleaved to nearly 90%, the 3−4 bond is cleaved to 35−39%, and the 4−5 bond is cleaved to 52−59% whereas in the intermediate (Int 1), the 1−3 bond is formed completely (100%) and the 2−5 bond is formed to 0% and the 1−2, 3−4, and 4−5 bonds are cleaved to nearly 95%, 39%, and 50%, respectively. But in TS3, the 1−3 bond is formed completely (100%) and the 2−5 bond is formed to 40% and the 1−2, 3−4, and 4−5 bonds are cleaved to nearly 99%, 76%, and 87% respectively.

(iii) Stepwise Mode 2. Here, the 1−3 bonds are formed to a lesser extent compared to the 2−5 bonds. π bonds 1−2, 3−4, and 4−5 are cleaved to nearly 95%, 70%, 90%, respectively. In the concerted mode, the concerted TS and in the stepwise mode the 1st TSs named as TS2 are early TSs. Relatively, concerted TSs are more reactant-like than stepwise TSs and this also supports the concerted mechanism as an early or reactant-like TS implies lower activation energy.

Solvent Effect. The effect of acetonitrile as solvent on the corannulene dipolar reaction has been examined through PCM computations. Activation energies for the concerted processes of rim and spoke(regio 1) additions and reaction energies listed in Table 4 reveal that solvation favors all the reactions kinetically and thermodynamically over gas-phase processes (see Table 3). The calculations demonstrate that solvation lowers the activation barriers for all reactions considered, relative to the gas phase.

Conclusions

Corannulene undergoes 1,3-dipolar cycloadditions with dipoles diazomethane, nitrile oxide, and nitrone to form one rim adduct and two spoke regio adducts. Calculations at the DFT level show that rim additions are more facile over spoke additions and in spoke additions the regio1 reaction is more favorable than the regio2 reaction. Further, calculations confirm the predominance of rim additions over spoke additions. The preference of rim over spoke addition is due to geometric and electronic factors. Rim bonds are at the periphery of the molecule and are easy to access and do not introduce any repulsion during approach. Further during the reaction, pyramidalization of reacting carbons induces geometric distortion which the rim bonds more easily accommodate than the spoke bonds. Electronically rim bonds have higher double bond character than spoke bonds and therefore are more prone to attack by dipoles. The dipolar additions involve initial charge transfer from the HOMO of dipole to the LUMO of corannulene. Larger LUMO vectors on rim carbons also indicate the preference of rim over spoke addition. In all these additions, concerted paths are lower by 2−5 kcal/mol from stepwise paths and stepwise modes 1 and 2 differ by 1−2 kcal/mol. No endohedral adduct could be located as corannulene easily flips into exohedral species during approach. NICS values computed at the centers of the reacting benzenoid ring of corannulene clearly reveal, in both rim and spoke additions, the loss of aromaticity during the reaction in them. The solvent effect on the concerted pathways of such dipolar reactions at the PCM-B3LYP/6-31G(d) level with acetonitrile shows its favorable reaction kinetics and exothermicity over the gas phase.

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Supporting Information Available: NBO polarization and bond populations for corannulene along with bond order analysis tables and the Cartesian Coordinates of both products and transition state geometries calculated at the B3LYP/6-31G(d) level. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) The percent of bond formation and cleavage is defined as [BO(TS)$_i$ − BO(R)$_i$]/[BO(P)$_i$ − BO(R)$_i$] × 100 where "i" can be either a forming or a cleaving bond. See also the references for detailed information. (a) Manoharan, M.; Venuvanalingam, P. *Int. J. Quantum Chem.* **1998**, *66*, 309. (b) Manoharan M.; Venuvanalingam, P. *J. Phys. Org. Chem.* **1998**, *11*, 133.