

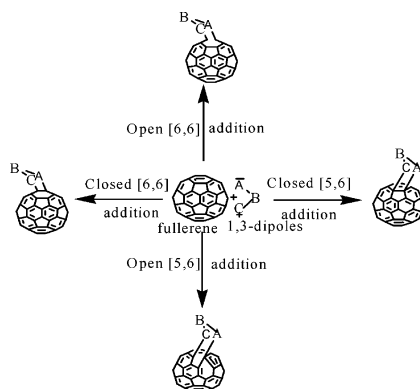
Open versus Closed 1,3-Dipolar Additions of C₆₀: A Theoretical Investigation on Their Mechanism and Regioselectivity

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1,3-Dipolar additions of C₆₀ with dipoles, diazomethane, nitrile oxide, and nitron have been modeled at the B3LYP/6-31G(d,p)//AM1 level, and their mechanism, regiochemistry, and nature of addition are investigated. All of these reactions lead to the formation of fullerene fused heterocycles; theoretically, these reactions can take up four types of additions, viz., closed [6,6], open [5,6], closed [5,6], and open [6,6] additions, and all of them have been examined. Energetics and thermodynamic analysis of these reactions show that closed [5,6] and open [6,6] additions are not probable and that closed [6,6] additions are the most favored ones and follow a concerted mechanism. Experimental evidence that C₆₀-diazomethane reactions yielded closed [6,6] fullerene-pyrazoline provides good support to the theoretical predictions. The observed order of reactivity has been explained based on the double bond character, forcing double bonds in the pentagons of C₆₀, and strain. During the addition, dipoles distort more than C₆₀ and concerted closed [6,6] TSs are found to be more reactant-like or early TS. Inclusion of toluene as solvent through the PCM model increases the reaction rate and exothermicity. NICS values computed at the centers of the reacting benzenoid ring of fullerene clearly reveal, in both open and closed additions, the loss in them of aromaticity during the reaction.

Introduction

C₆₀ is an electron-deficient spherically shaped polyene and is known to undergo a variety of reactions, viz., radical, nucleophilic addition, mono- and polycyclic additions, etc. Fullerene reactions have been studied extensively both experimentally and theoretically by several workers,¹⁻⁴ and the reactivity of fullerene toward various cycloadditions has been well documented by Hirsch⁵ and Silwa⁶ and specifically, 1,3-dipolar cycloadditions involving C₆₀ have been surveyed by Yurovskaya and Ovcharenko⁷ in 1998. In 2002, Yurovskaya and Trushkov⁸ have reviewed further progress on the C₆₀ cycloadditions. 1,3-Dipolar reactions have been used to form fullerene-fused heterocycles and some of these reactions have been modeled.^{9c} Among various dipoles that have been employed to derivatize fullerene, diazo-

methane, nitrile oxide and nitron are very important. Diazoalkanes add to C₆₀ to first form fullerene-fused

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pyrazolines and this on subsequent thermolysis loses N₂ to form methanofullerenes.⁸ The pyrazoline intermediate has been found to be stable and in certain instances, it has been isolated and characterized.⁸ Nitrile oxides and nitrones add to C₆₀ to form fullerene-fused isoxazolines. The ability of C₆₀ to act as a dipolarophile was first reported in 1992.^{9a} Wudl and co-workers^{10a} have performed a systematic study of the reactions of C₆₀ with substituted diazomethanes and proved that C₆₀ is a reactive dipolarophile. Solà and co-workers^{9c} have modeled the reaction of alkyl azides to C₆₀ and subsequent N₂ extrusion and found that the closed [6,6] regio isomer was favored. Though the Diels–Alder reaction of C₆₀ has been modeled by several workers,^{9–12} modeling studies on dipolar addition of C₆₀ are scarce.^{9c} Especially, 1,3 dipolar addition of C₆₀ with diazomethane, nitrile oxide, and nitrene have not been attempted. In the present work therefore, the mechanism of 1,3-dipolar additions of C₆₀ with dipoles diazomethane, nitrile oxide, and nitrene have been specifically investigated. This is important in view of our observations earlier with other dipolarophiles; that is, ethylene and allene preferred stepwise paths and

corannulene chose the concerted path. Second, the regiochemistry of these reactions has been studied by reacting the dipole at 6–6 and 5–6 junctions of C₆₀. Third, C₆₀ reactions at both 6–6 and 5–6 junctions leading to both closed and open adducts have been studied, though earlier studies^{9c} have clearly shown the preference of closed adducts over open ones in cycloadditions.

Computational Details

In view of the large size of the system, full geometry optimizations of the reacting systems have been performed at the AM1^{12a,b} level and single point energy calculations have been performed at the B3LYP/6-31G(d,p)^{12c} level using GAUSSIAN 98.^{12d} Several authors have adopted this strategy to study fullerene systems and their reactions.^{9c} The validity of the B3LYP/6-31G(d,p)//AM1 level was also tested by Solà and co-workers^{9c} by calculating the 1,3-DC of methyl azide to ethylene using different methodologies. The conclusion is that the

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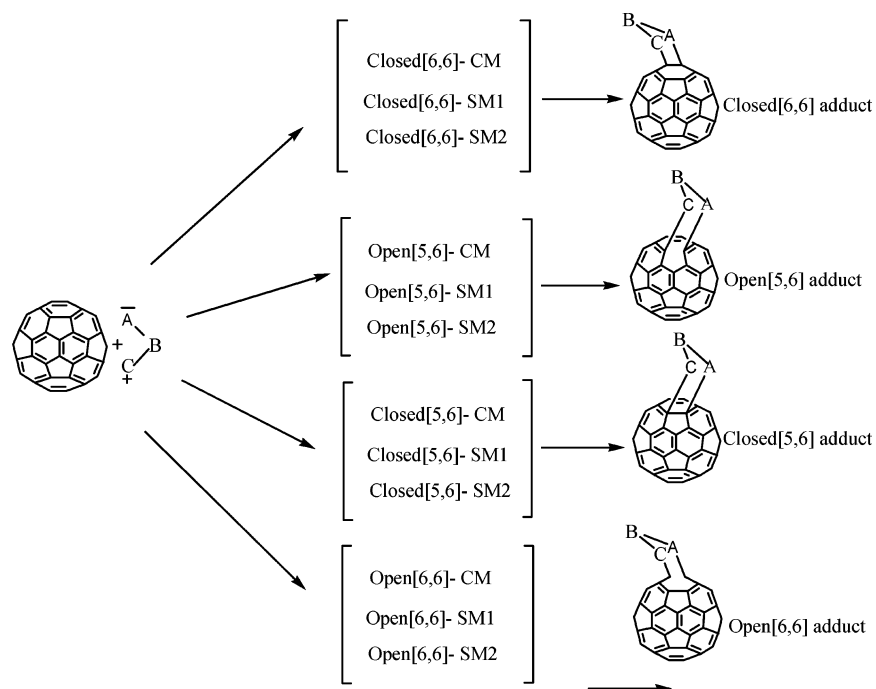
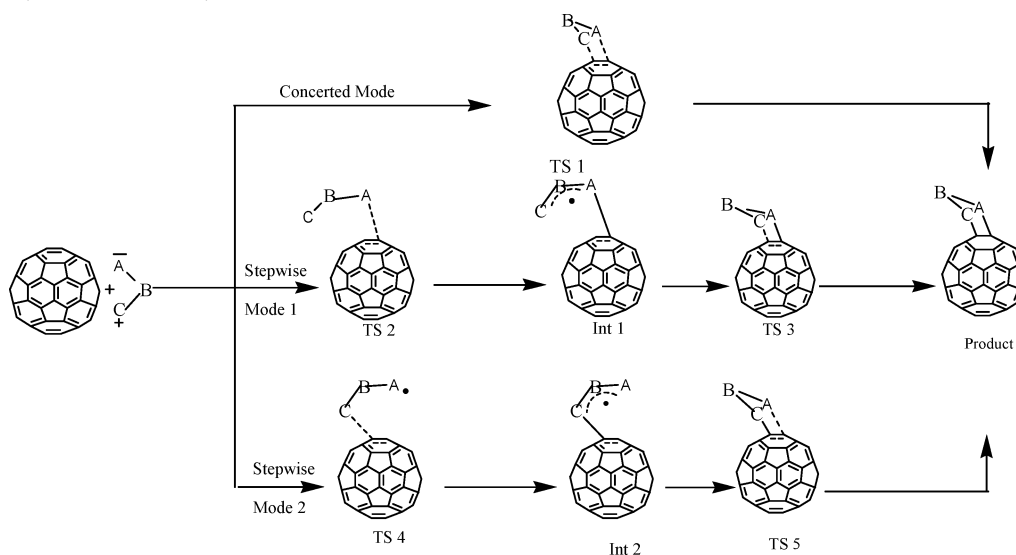
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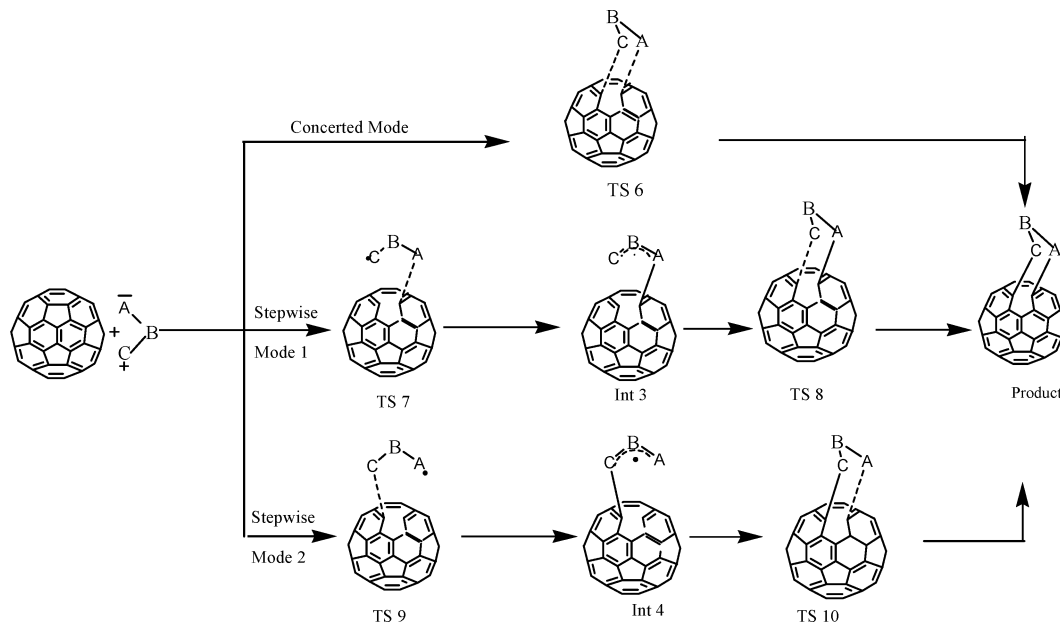
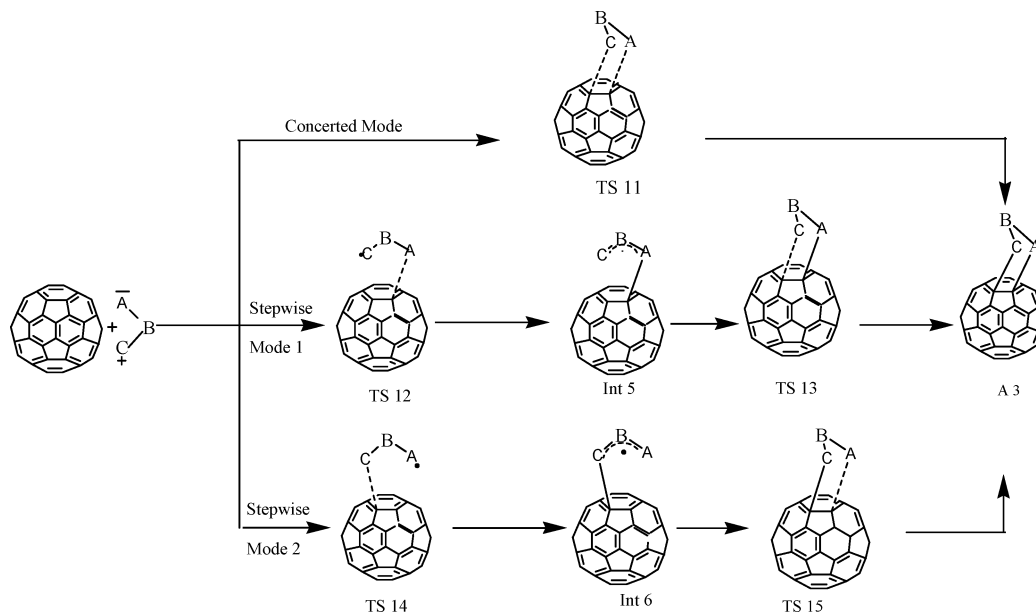
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SCHEME 1. Overall Scheme of the 1,3-dipolar Reaction of C₆₀ with 1,3-dipoles Diazomethane, Nitrile Oxide, and Nitrene**SCHEME 2. Possible Reaction Pathways for Closed [6,6] Cycloadditions of Fullerene with Dipoles, Diazomethane, Nitrile Oxide, and Nitrene**

B3LYP/6-31G(d,p)//AM1 methodology appears to be an acceptable level of calculation for obtaining reasonable estimates of reaction energies and energy barriers for 1,3-DC at low computational cost. Bond orders have been calculated as Wiberg indices¹³ using NBO analysis, and bond indices and deformation energies¹⁴ have been calculated as reported earlier. Activation parameters for all transition states are calculated at the B3LYP/6-31G(d,p) level. In closed additions, only the π bond of the [6,6] or [5,6] junction is cleaved, whereas both π and σ bonds are broken in open additions. This fact is

taken care of in bond order analysis. Loss of aromaticity in the reacting benzenoid ring during both rim and spoke additions can be indicated from nuclear independent chemical shift¹⁵ (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 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 denote antiaromaticity, and nearly zero values denote nonaromaticity. The effect of solvent on the concerted reactions has been evaluated using single point PCM (polarized continuum model) calculations¹⁶ at the SCRF-B3LYP/6-31G(d) level with toluene as solvent on the gas-phase geometries.

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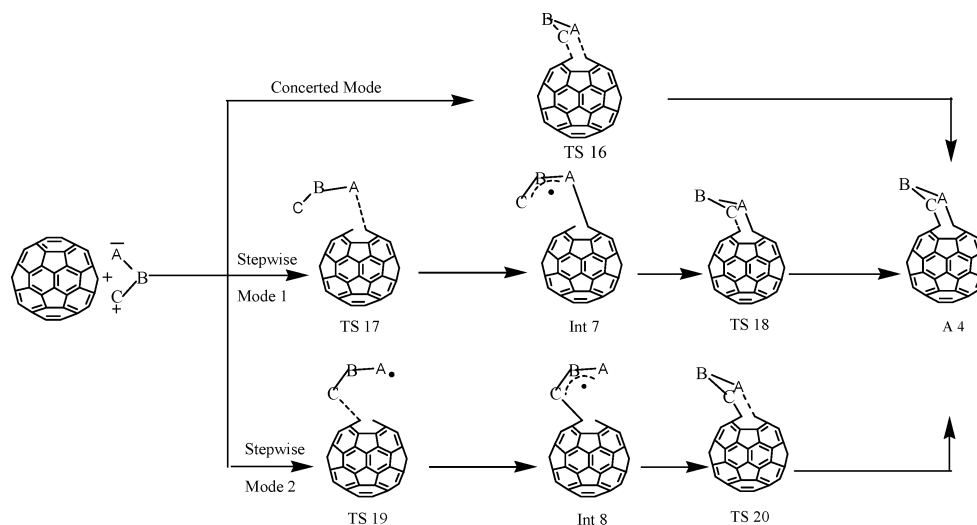
SCHEME 3. Possible Reaction Pathways for Open [5,6] Cycloadditions of Fullerene with Dipoles, Diazomethane, Nitrile Oxide, and Nitrene**SCHEME 4. Possible Reaction Pathways for Closed [5,6] Cycloadditions of Fullerene with Dipoles, Diazomethane, Nitrile Oxide, and Nitrene**

Results and Discussion

C_{60} reacts with 1,3-dipoles, diazomethane, nitrile oxide, and nitrene to give fulleropyrazolines, fullerenoisoxazolines, and substituted fullerenoisoxazolines, respectively. Dipolar addition can occur at the [6,6] or [5,6] bond of fullerene and can form closed and open adducts. Therefore, the reaction can undergo four types of additions, closed [6,6], closed [5,6], open [5,6], and open [6,6] additions, and each of these reactions can follow either concerted or stepwise paths. In the stepwise paths, due to the asymmetry of the dipole, there are two stepwise modes possible: stepwise mode 1 (SM1) and stepwise

mode 2 (SM2) in which, respectively, atom A and C of the dipole reacts first with the dipolarophile. All possible pathways are shown in the overall scheme of the reaction (Scheme 1). In each of the stepwise mode, two transition states and one intermediate are involved, which are shown in Schemes 2–5. The overall scheme describes that there are four concerted paths, one for each type of addition, and eight stepwise paths, two for each type of additions. Therefore, for each dipolar reaction, 20 TSs, 8 INTs, and 4 adducts are considered. Altogether for the 1,3-dipolar reactions with three dipoles, 60 TSs, 24 INTs, and 12 adducts have been located and characterized. The names of the various species are abbreviated in Table 1. As a test case, the stepwise diionic mechanism for the [6,6] closed addition for the C_{60} –diazomethane reaction

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SCHEME 5. Possible Reaction Pathways for Open [6,6] Cycloadditions of Fullerene with Dipoles, Diazomethane, Nitrile Oxide, and Nitron

TABLE 1. Various Species on the Reaction Path and Their Names^a

species	name	species	name
closed [6,6] CTS	TS1	open [5,6] CTS	TS6
closed [6,6] SM1TS1	TS2	open [5,6] SM1TS1	TS7
closed [6,6] SM1TS2	TS3	open [5,6] SM1TS2	TS8
closed [6,6] SM2TS1	TS4	open [5,6] SM2TS1	TS9
closed [6,6] SM2TS2	TS5	open [5,6] SM2TS2	TS10
closed [6,6] SM1Int	INT 1	open [5,6] SM1Int	INT3
closed [6,6] SM2Int	INT 2	open [5,6] SM2Int	INT4
closed [6,6] adduct	A1	open [5,6] Adduct	A2
closed [5,6] CTS	TS11	open [6,6] CTS	TS16
closed [5,6] SM1TS1	TS12	open [6,6] SM1TS1	TS17
closed [5,6] SM1TS2	TS13	open [6,6] SM1TS2	TS18
closed [5,6] SM2TS1	TS14	open [6,6] SM2TS1	TS19
closed [5,6] SM2TS2	TS15	open [6,6] SM2TS2	TS20
closed [5,6] SM1Int	INT5	open [6,6] SM1Int	INT7
closed [5,6] SM2Int	INT6	open [6,6] SM2Int	INT8
closed [5,6] adduct	A3	open [6,6] Adduct	A4

^a CTS, concerted TS; SM1, stepwise mode 1; SM2, stepwise mode 2; INT, intermediate; and A, adduct.

has been explored, and it has been found that the diionic path was not favorable.¹⁷ Therefore the diionic mechanism has not been investigated in other cases. Relative energies of various species on the reaction path are listed in Table 2. Energy profiles and the optimized geometries of the reaction of C₆₀ with nitrile oxide and nitron are given in Supporting Information as Figures S1–S8 and S9–S16, respectively. Earlier reports^{9c} show that in Diels–Alder and 1,3-dipolar additions of C₆₀, the closed [6,6] adduct and open [5,6] adducts are found to be more favored. Computed thermodynamic parameters are compiled in Table 3, and the deformation energies for all the reactions are given in Table 4.

Reaction between C₆₀ and Diazomethane. Thermal addition of diazo compounds to C₆₀ is a more complex process, and depending on the structure of the diazo compound and reaction conditions, a mixture of closed [6,6] and open [5,6] isomeric adducts have been formed.⁸ Generally diazo compounds can react in two ways:

(17) For the [6,6] closed C₆₀–diazomethane reaction, in the stepwise mode 1, ionic TS1, ionic Int, and ionic TS2 have been found to have activation energies of, respectively, 37.12, 16.76 and 26.44 kcal/mol.

(i) 1,3-dipolar cycloaddition followed by N₂ elimination by thermolysis from the pyrazoline intermediate or (ii) initial thermal decomposition of diazo compounds to form carbenes, followed by their concerted addition to the [6,6] double bond of fullerene. In either case, the final product is the methanofullerene. However, simple diazomethane has been found to react by a clear 1,3-dipolar addition path to form a stable pyrazoline adduct.¹¹ⁱ The isolated pyrazolines have been later subjected to thermolysis to give [5,6] bridged fulleroids and trace amounts of closed [6,6] adduct. Our interest here is to investigate the mechanism of 1,3-dipolar cycloaddition of simple diazomethane to C₆₀, and therefore thermal N₂ elimination from the adduct is not considered hereafter. With regard to 1,3-dipolar additions, experimental results indicate that diazomethane attacks the [6,6] ring junctions of C₆₀ and yields a closed [6,6] pyrazoline adduct.¹¹ⁱ Three things about this reaction are not clear, and we addressed them in the present work: (i) Does the dipolar cycloaddition follow a concerted or stepwise mechanism? (ii) What is the reason for the remarkable regioselectivity of the reaction? (iii) What is the relative preference of closed and open additions?

The energy profiles shown in Figures 1–4 and energy data in Table 2 show that in all four types of additions, concerted paths are lying lower than stepwise modes 1 and 2. Free energies of activation listed in Table 3 also favor the concerted mechanism over a stepwise path. Both the activation energies and the activation free energies for the concerted mechanism follows the order closed [6,6] < open [5,6] < closed [5,6] < open [6,6]. Further, the stabilities of the adducts follow the order closed [6,6] > open [5,6] > closed [5,6] > open [6,6]. Computations show that closed [6,6] and open [5,6] adducts are exothermic and closed [5,6] and open [6,6] adducts are endothermic. The above trends show that the closed [6,6] addition is the most favorable kinetically and thermodynamically. This is in excellent agreement with the experimental observation that closed [6,6] pyrazoline adduct was isolated. The instabilities of open [6,6] and closed [5,6] structures are due to the introduction of three and two unfavorable double bonds in five-membered rings.^{9c} As far the regiochemistry of the addition is

TABLE 2. B3LYP/6-31G(d,p)//AM1 Relative Energies of Various Species on the Reaction Paths of Fullerene with Diazomethane, Nitrile Oxide, and Nitron^a

species	fullerene– diazomethane	fullerene– nitrile oxide	fullerene– nitron	species	fullerene– diazomethane	fullerene– nitrile oxide	fullerene– nitron
Closed [6,6] Addition				Open [5,6] Addition			
concerted mode				concerted mode			
TS 1	29.84	27.87	28.99	TS 6	33.76	35.21	39.42
stepwise mode 1				stepwise mode 1			
TS 2	33.46	35.23	32.13	TS 7	35.72	42.32	41.86
Int 1	10.27	16.54	15.42	Int 3	12.96	21.76	21.97
TS 3	25.98	27.21	28.88	TS 8	28.32	31.89	32.46
stepwise mode 2				stepwise mode 2			
TS 4	35.26	36.42	37.21	TS 9	37.56	43.14	39.86
Int 2	13.45	19.76	17.23	Int 4	16.24	22.87	21.73
TS 5	23.78	22.89	21.83	TS 10	26.13	30.76	31.84
A 1	-20.13	-18.73	-19.99	A 2	-15.12	-16.24	-17.32
Closed [5,6] Addition				Open [6,6] Addition			
concerted mode				concerted mode			
TS 11	43.12	45.53	47.92	TS 16	44.28	47.92	49.89
stepwise mode 1				stepwise mode 2			
TS 12	47.21	49.29	50.12	TS 17	48.36	51.34	53.73
Int 5	30.12	29.99	28.10	Int 7	33.49	29.57	29.86
TS 13	35.55	33.43	34.26	TS 18	36.42	35.49	37.29
stepwise mode 1				stepwise mode 2			
TS 14	45.65	50.67	41.22	TS 19	46.13	52.76	43.41
Int 6	24.21	30.01	29.56	Int 7	25.31	32.34	33.17
TS 15	36.82	41.82	39.24	TS 20	37.86	42.79	42.76
A 3	2.24	3.42	5.12	A 4	3.49	5.49	7.32

^a Relative energies of various species are expressed assuming the reactants energy as zero. For species names refer to Scheme 1.

considered, [6,6] junction is preferred over [5,6] junction; this is in view of higher electron density in [6,6] junction than [5,6] junction and better overlaps between frontier orbitals in the [6,6] addition.^{9c} The activation energy values predict that closed additions are the most favorable ones in total agreement with experiment, and next to this, open addition at the [5,6] junction is favored. NICS(1) values at the reacting benzenoid ring of fullerene, closed[6,6] concerted TS, and adduct have been calculated to be -6.92, -4.21, and -0.46 ppm, respectively, and this shows gradual loss of aromaticity during the course of the reaction.

Reaction between C₆₀ and Nitrile Oxide. C₆₀ reacts with various nitrile oxides to form a series of closed [6,6] fullerene-isoxazolines containing diversified substituents.⁸ However, reactions of C₆₀ with simple nitrile oxide have not been experimentally accomplished.⁸ 1,3-Dipolar additions of nitrile oxide with ethylene and allene have been theoretically investigated and a concerted mechanism has been proposed. We have reinvestigated these reactions and shown that these reactions follow stepwise *syn* mechanism. In continuation of that, C₆₀-nitrile oxide cycloaddition is modeled here with a view to understand their mechanism, regiochemistry, and preference for closed and open additions. The energy profiles presented in Figures S1–S4 and computed energy data given in Table 2 clearly show that concerted paths are preferred over stepwise paths 1 and 2 in all four types of additions considered. Free energies of activation listed in Table 3 also reflect the same trend. Both the activation energies and the activation free energies for the concerted mechanism follow the order closed [6,6] < open [5,6] < closed [5,6] < open [6,6]. Further the stabilities of the adducts follow the order closed [6,6] > open [5,6] > closed [5,6] > open [6,6]. The reasons for the instabilities of open [6,6] and closed [5,6] structures have been described in the previous section. The above trends show that closed [6,6]

is the most favorable kinetically and thermodynamically. This is in good agreement with the experimental observation that in the reaction of substituted nitrile oxide with C₆₀, closed [6,6] adducts have been found to be isolated.^{12c} Nitrile oxide reactions follow the same regiochemistry as that of diazomethane; [6,6] junction is preferred over [5,6] junction and the reasons for the preferences are explained in the previous section. Energy profiles (Figures S1–S4) show that closed [6,6] and open [5,6] additions are exothermic and involve lower activation energies, whereas closed [5,6] and open [6,6] additions are endothermic and have high activation barriers. These observations show that closed [5,6] and open [6,6] are not probable and, in the other two, closed [6,6] addition is the most favorable process. NICS(1) values at the reacting benzenoid ring of fullerene, closed [6,6] concerted TS, and adduct have been calculated to be -6.92, -3.72, and -0.39 ppm, respectively, and this shows gradual loss of aromaticity during the course of the reaction.

Reaction between C₆₀ and Nitron. Similar to nitrile oxides, nitrones also undergo 1,3-dipolar cycloadditions with various dipolarophiles to form substituted isoxazolines. Experimental reports on the reaction of simple nitron are very rare because simple nitron is an unstable species. With fullerene, a substituted nitron, namely, *o*-trimethylsilyl nitronates, has been reacted, and the reaction yielded finally fullerenoxazolines.⁸ For comparison, the title reaction has been modeled, and the results are analyzed below with respect to mechanism, regiochemistry, and the type of preferred additions, i.e., closed or open. The energy profiles are presented in Figures S5–S8, and from the computed energy data given in Table 2, it is found that concerted paths are favored over stepwise paths 1 and 2 in all types of preferred additions closed or open. Free energies of activation (Table 3) show the same trend as that of the activation

TABLE 3. Calculated B3LYP/6-31G(d,p)//AM1 Activation Parameters for the 1,3-Dipolar Cycloadditions of Fullerene with Diazomethane, Nitrile Oxide, and Nitrene

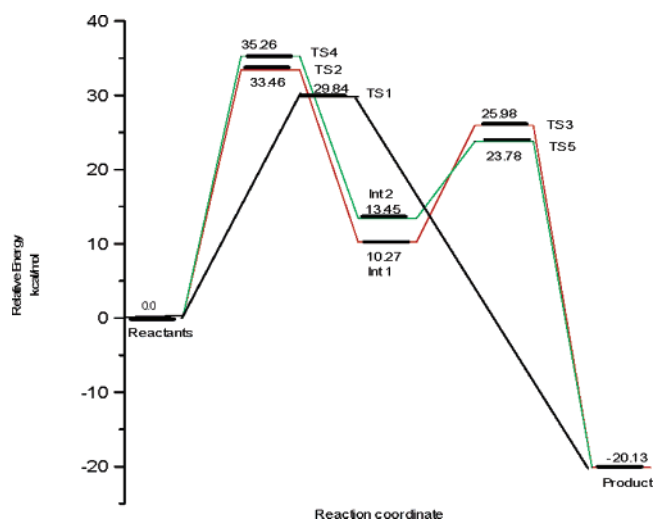
species	C ₆₀ -diazomethane			C ₆₀ -nitrile oxide			C ₆₀ -nitrene		
	ΔG^\ddagger kcal/mol	ΔH^\ddagger kcal/mol	ΔS^\ddagger cal/mol/k	ΔG kcal/mol	ΔH^\ddagger kcal/mol	ΔS^\ddagger cal/mol/k	ΔG kcal/mol	ΔH^\ddagger kcal/mol	ΔS^\ddagger cal/mol/k
Closed [6,6] Addition									
concerted mode TS 1	40.43	31.79	-28.98	38.42	30.72	-25.82	39.99	31.24	-29.35
stepwise mode 1 TS 2	42.74	34.83	-27.18	40.22	31.34	-29.78	41.97	33.86	-27.20
TS 3	38.98	29.34	-32.33	36.43	27.89	-28.64	37.97	29.42	-28.68
stepwise mode 2 TS 4	43.34	34.26	-30.45	41.23	32.86	-28.07	42.48	34.76	-25.89
TS 5	39.12	30.04	-30.45	37.42	26.89	-35.32	38.88	30.34	-28.64
Open [5,6] Addition									
concerted mode TS 6	43.79	34.26	-31.96	39.86	30.79	-30.42	42.16	33.32	-29.65
stepwise mode 1 TS 7	44.76	35.21	-32.03	42.16	33.63	-28.61	42.86	33.16	-32.53
TS 8	40.04	31.79	-27.67	38.14	28.76	-31.46	38.63	29.83	-29.52
stepwise mode 2 TS 9	45.13	39.82	-28.51	42.29	31.63	-35.75	44.16	35.02	-30.66
TS 10	41.87	33.79	-27.10	39.63	29.79	-33.00	39.27	30.06	-30.89
Closed [5,6] Addition									
concerted mode TS 11	46.92	38.17	-29.35	44.43	33.84	-35.52	45.53	37.21	-27.91
stepwise mode 1 TS 12	47.97	37.29	-29.11	45.26	36.79	-28.41	46.45	38.29	-27.37
TS 13	38.48	30.12	-28.03	36.79	25.23	-38.77	37.55	28.63	-29.92
stepwise mode 2 TS 14	48.29	40.26	-28.57	46.37	35.29	-37.16	47.77	39.14	-28.95
TS 15	40.12	31.87	-27.67	39.12	30.79	-27.94	39.55	31.26	-27.80
Open [6,6] Addition									
concerted mode TS 16	49.76	41.26	-28.51	45.21	36.39	-26.22	45.04	34.26	-36.16
stepwise mode 1 TS 17	50.39	43.42	-30.62	48.16	39.92	-27.63	46.13	37.17	-30.05
TS 18	39.96	30.34	-32.27	37.52	29.63	-26.46	38.63	29.75	-29.78
stepwise mode 2 TS 19	51.38	40.72	-35.75	53.79	45.12	-29.79	48.86	40.12	-29.31
TS 20	42.17	33.89	-27.77	40.34	32.17	-27.40	50.14	42.37	-26.06

TABLE 4. Calculated B3LYP/6-31G(d,p)//AM1 Deformation Energies (kcal/mol) of the Dipoles and Fullerene in the 1,3-dipolar Reactions of Fullerene with Diazomethane, Nitrile Oxide, and Nitrene

species	fullerene-diazomethane		fullerene-nitrile oxide		fullerene-nitrene	
	DE1	DE2	DE1	DE2	DE1	DE2
Closed [6,6] Addition						
concerted mode TS 1	18.21	11.23	17.89	12.22	19.22	10.23
stepwise mode 1 TS 2	19.21	12.45	23.43	14.21	21.23	10.99
stepwise mode 2 TS 4	21.26	10.23	25.55	11.22	23.21	11.33
Open [5,6] Addition						
concerted mode TS 6	19.36	14.21	20.31	15.16	20.36	13.14
stepwise mode 1 TS 7	20.21	14.56	24.42	17.35	22.17	12.87
stepwise mode 2 TS 9	22.32	12.56	26.21	13.16	24.17	13.16
Closed [5,6] Addition						
concerted mode TS 11	24.21	19.32	29.55	17.97	24.12	19.56
stepwise mode 1 TS 12	30.17	17.24	30.12	18.33	26.19	20.54
stepwise mode 2 TS 14	30.21	15.29	31.12	17.66	27.44	20.22
Open [6,6] Addition						
concerted mode TS 16	25.23	20.17	30.62	18.96	26.73	20.24
stepwise mode 1 TS 17	28.14	19.76	32.16	19.21	28.32	21.74
stepwise mode 2 TS 19	31.01	17.26	34.73	18.79	30.16	23.21

DE1 is the deformation energy of dipole. DE2 is the deformation energy of fullerene.

energies. The energies follow the order closed [6,6] < open [5,6] < closed [5,6] < open [6,6]. Further, the stabilities follow the order closed [6,6] > open [5,6] > closed [5,6] > open [6,6]. The above trend shows that the closed [6,6] is the most favorable kinetically and thermodynamically.

**FIGURE 1.** Energy profile for the reaction between C₆₀ and diazomethane: closed [6,6] addition.

NICS(1) values at the reacting benzenoid ring of fullerene, closed [6,6] concerted TS, and adduct have been calculated to be -6.92, -4.03, and -0.42 ppm, respectively, and this shows gradual loss of aromaticity during the course of the reaction.

Deformation Energy and Bond Order Analysis. As the trends are similar the above analysis is presented

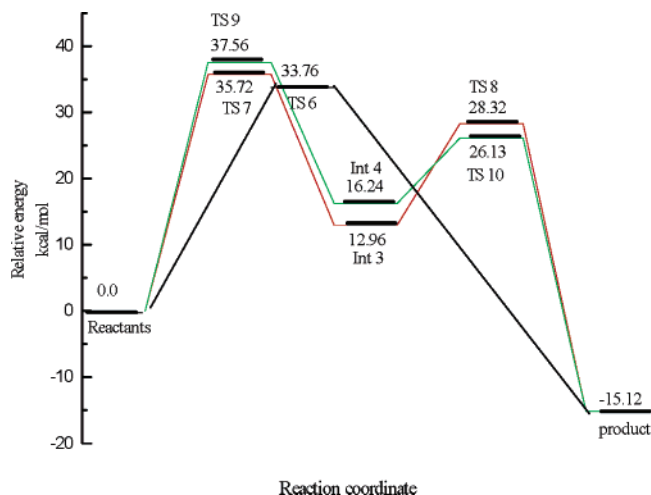


FIGURE 2. Energy profile for the reaction between C₆₀ and diazomethane: open [5,6] addition.

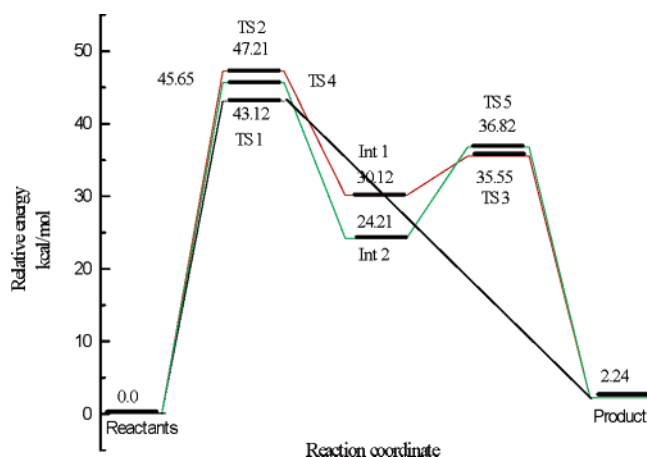


FIGURE 3. Energy profile for the reaction between C₆₀ and diazomethane: closed [5,6] addition.

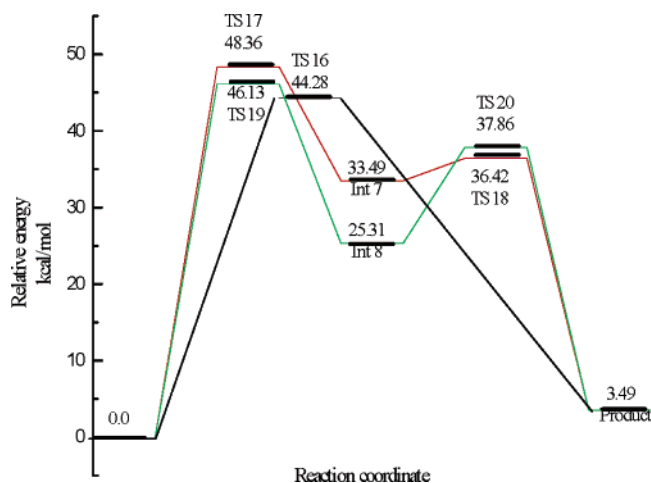


FIGURE 4. Energy profile for the reaction between C₆₀ and diazomethane: open [6,6] addition.

here for all three-dipolar additions in a combined way. Deformation energies listed in Table 4 show that in all types of additions and modes of reaction the dipole

distorts to a greater degree than C₆₀ and the distortion in both the dipole and C₆₀ follow the same order as activation energies or activation free energies show. The deformation of both partners is the lowest in the concerted mode of closed [6,6] addition. Activation entropy values for these reactions fall in the range -25 to -35 eu, and this agrees with the values observed for other 1,3-dipolar additions investigated here. Bond order analysis show that concerted TSs are expectedly asynchronous with C1-C3 bonds and C2-N5 or C2-O5 bonds forming in the range 35-43% and 21-35%, respectively. In closed additions, C1-C2 π bonds break 30-36%, and in open additions, both C1-C2 σ and π bonds break to 100% in the concerted TSs. In the stepwise processes, they are broken more than 82%. The other two cleaving bonds, C3-N4 and N4-N5 in diazomethane and C3-N4 and N4-O5 in nitrile oxide and in nitrene, break to different extents in concerted TSs; in stepwise processes they increasingly break as the reaction progresses. BFC_{av} values of concerted TSs fall in the range 30-38%, showing the early or reactant-like nature of the TS. In closed additions, BFC_{av} of the concerted TSs of the closed [6,6] addition is found to be the lowest. BFC_{av} of other species in a reaction show gradual maturing/breaking of bonds in the reaction. These values have been calculated only for the first stage in each reacting mode, as it is the rate-determining step in all of the reactions.

Solvent Effect. The effect of toluene as solvent on the fullerene dipolar reaction has been examined through PCM computations. Initially as a test case, the effect of toluene solvent on the concerted and stepwise mode 1 biradical and ionic pathways for closed [6,6] addition of C₆₀-diazomethane reaction have been examined, and it has been found that concerted and stepwise biradical paths are slightly stabilized, while the stepwise ionic path shows the destabilizing effect on solvation.¹⁸ The concerted path has been found to be still lower, after the inclusion of solvent effect, compared to stepwise paths. Therefore solvent effect computations have been done only for the concerted mechanism for all four types of addition and for all three dipolar reactions. Activation energies for the concerted processes of open and closed additions and their reaction energies listed in Table 5 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

C₆₀ reacts with diazomethane, nitrile oxide, and nitrene to give, respectively, fullerene pyrazolines and isoxazolines. This addition can take place at [6,6] or [5,6] junctions of C₆₀ and with the reacting [6,6] and [5,6] bonds intact or broken. Thus there are four types of additions possible, which are closed [6,6], closed [5,6],

(18) For the [6,6] closed C₆₀-diazomethane reaction, in the stepwise mode 1, for the biradical path, biradical TS1, biradical Int, and biradical TS2 have been found to have activation energies in toluene of 32.04, 8.76, and 23.99 kcal/mol, respectively. For the same reaction in the ionic path, ionic TS1, ionic Int, and ionic TS2 have been found to have activation energies in toluene 39.89, 17.59, and 27.83 kcal/mol, respectively.

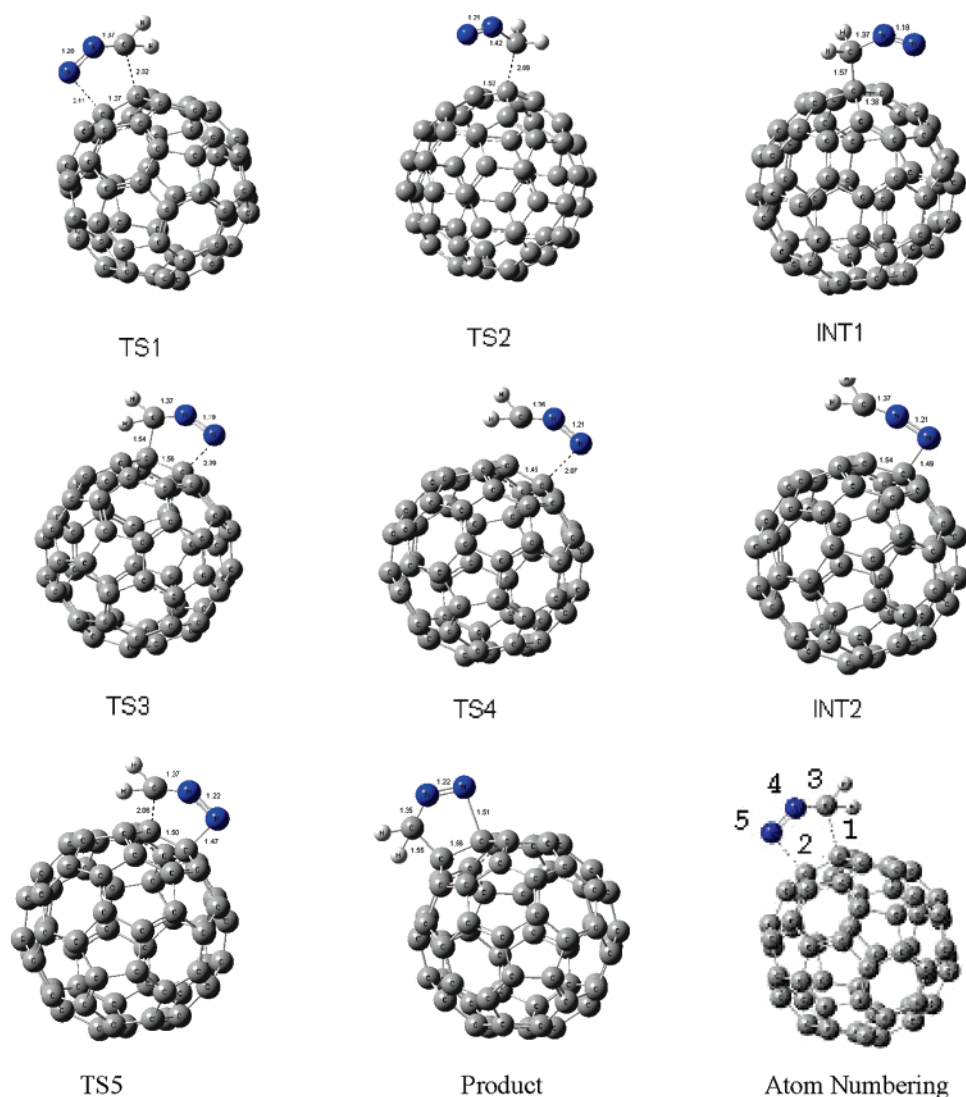


FIGURE 5. AM1 optimized geometries of the reaction of C_{60} with diazomethane: closed [6,6] addition.

TABLE 5. Activation (ΔE^\ddagger) and Reaction Energies (ΔE_r) (kcal mol^{-1}) for the “Concerted” 1,3-Dipolar Reactions of Fullerene with Dipoles Diazomethane, Nitrile Oxide, and Nitron^a

	diazomethane		nitrile oxide		nitron	
	ΔE^\ddagger	ΔE_r	ΔE^\ddagger	ΔE_r	ΔE^\ddagger	ΔE_r
closed [6,6]	27.32	-22.36	25.39	-22.31	26.13	-23.36
open [5,6]	31.96	-18.02	32.92	-18.39	37.56	-19.77
closed [5,6]	40.79	0.98	43.96	1.12	44.23	2.97
open [6,6]	41.97	1.24	45.82	3.16	47.36	4.94

^a In toluene from single point computations at the SCRFP(PCM)-B3LYP/6-31G(d,p) level on gas phase B3LYP/6-31G(d,p)//AM1 geometry.

open [5,6], and open [6,6], leading to corresponding adducts. Each type of addition can follow a concerted or stepwise mechanism, and in the stepwise path, two stepwise modes are possible. All of those reaction paths have been modeled at the B3LYP/6-31G(d,p)//AM1 level, which reveals the following information. All of these types of additions prefer a concerted mechanism, and the energies and free energies of activation follow the order

closed [6,6] < open [5,6] < closed [5,6] < open [6,6]; stabilities of the adduct and exothermicities of the reaction follow the order closed [6,6] > open [5,6] > closed [5,6] > open [6,6]. The above trends indicate that closed [6,6] addition is the most preferred path. Next to this, open [5,6] addition is favored, and the other two types of additions are shown to be not probable. This is in total agreement with experimental observations. Open adducts have to accommodate a lot of strain in the C_{60} fragment due to opening of the [6,6], [5,6] junctions, and closed [5,6] and open [6,6] adducts have to accommodate three and two unfavorable double bonds in five-membered rings of C_{60} . A combination of these factors plus the double bond character of reacting bonds explain the observed order of reactivity. Computed deformation energies show that dipoles distort more than C_{60} initially and deformation of dipoles and C_{60} follow the same order as found in activation barriers. Bond order analysis reveal that (i) concerted TSs are expectedly asynchronous, (ii) concerted TSs of closed [6,6] additions are more reactant-like than other TSs and hence justify the lower activation energies obtained, (iii) TS 1 is the most reactant-like or

early TS, and (iv) in open additions, the [6,6] and [5,6] bonds rupture even at the initial stage of the reaction. Computed thermodynamic parameters show that activation entropies for all of these reactions fall in the range -25 to -35 eu that was observed for 1,3-dipolar additions with ethylene, allene, and corannulene. Solvent effect on the concerted pathways of the dipolar reactions at the PCM-B3LYP/6-31G(d) level with toluene shows its favorable reaction kinetics and exothermicity over gas phase.

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Supporting Information Available: Bond order tables, optimized geometries, energy profiles, and Cartesian coordinates of all geometries calculated at the B3LYP/6-31G(d,p)//AM1 level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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