Computational Investigation of the Competition between the Concerted Diels−Alder Reaction and Formation of Diradicals in Reactions of Acrylonitrile with Nonpolar Dienes

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Ⓢ *Supporting Information*

ABSTRACT: The energetics of the Diels−Alder cyclo-addition reactions of several 1,3-dienes with acrylonitrile, and the energetics of formation of diradicals, were investigated with density functional theory (B3LYP and M06−2X) and compared to experimental data (Hall et al., *J. Org. Chem.* **1993**, 58, 7049−7058). For the reaction of 2,3-dimethyl-1,3-butadiene with acrylonitrile, the concerted reaction is favored over the diradical pathway by 2.5 kcal/mol using B3LYP/6-31G(d); experimentally, this reaction gives both cycloadduct and copolymer. The concerted cycloaddition of cyclo-pentadiene with acrylonitrile is preferred computationally over the stepwise pathway by 5.9 kcal/mol; experimentally, only the Diels−Alder adduct is formed. For the reactions of

(*E*)-1,3-pentadiene and acrylonitrile, both cycloaddition and copolymerization were observed experimentally; these trends were mimicked by the computational results, which showed only a 1.2 kcal/mol preference for the concerted pathway. For the reactions of (*Z*)-1,3-pentadiene and acrylonitrile, the stepwise pathway is preferred by 3.9 kcal/mol, in agreement with previous experimental findings that only polymerization occurs. M06−2X is known to give more accurate activation and reaction energetics (Pieniazek, et al., *Angew. Chem. Int.* **2008**, 47, 7746−7749), but the energies of diradicals are too high.
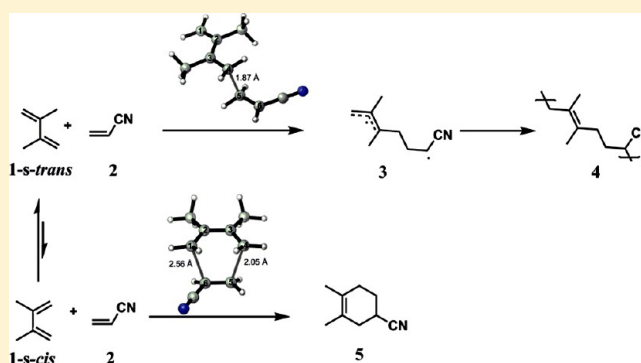
INTRODUCTION

The competition between the Diels−Alder cycloaddition and spontaneous polymerization reactions of butadienes with ethylenes has long been a topic of interest and investigation.[1a] The mechanism of the Diels−Alder reaction is known generally to be concerted, while the stepwise mechanism via diradicals, which could initiate the polymerization, has an activation barrier only a few kcal/mol higher in energy.[1]

Copolymerizations accompanying the Diels−Alder reaction have been previously observed and described. In 1945, Koningsberger and Salomon observed spontaneous copoly-merization of butadiene and 2,3-dimethyl-1,3-butadiene with styrene and acrylonitrile. For the reaction of 2,3-dimethyl-1,3-butadiene and acrylonitrile, the Diels−Alder cycloaddition predominated under normal conditions. Polymerization pre-dominates in the presence of initiators such as benzoyl peroxide and diazoaminobenzene.[2]

Competition between cycloaddition and copolymerization was also observed by Jenner and Rimmelin, who examined the high pressure cyclodimerization of 2,3-dimethyl-1,3-butadiene.[3] These authors deduced that there is participation of a nonconcerted mechanism that has an activation energy several kcal/mol higher in energy than the concerted.[3]

Li, Padias, and Hall measured the kinetics of a series reactions of 1,3-dienes with acrylonitrile and determined the relative amounts of copolymer and cycloadduct formed.[4] These studies included dienes that formed both cycloadduct and copolymer (2,3-dimethyl-1,3-butadiene, isoprene, (*E*)-1,3-pen-tadiene, 1,3-cyclohexadiene, and 1,2-dimethylenecyclohexane), dienes that formed only cycloadduct (cyclopentadiene and 1,2-dimethylenecyclopentane), and dienes that only formed copolymer ((*Z*)-1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene, and verbenene). Among these dienes that gave mixtures, 2,3-dimethyl-1,3-butadiene gave the highest yield of polymer.[4] At 80 °C, spontaneous copolymerization occurs at almost the same rate as cycloaddition, and at 100 °C, cycloaddition predominates (Table 1).

It was proposed by Hall et al. that the conformation of the diene was an important factor in determining the outcome of this reaction, and that the s-*trans* conformation of the diene was significantly favored over the s-*cis* conformation because of the clashing of the methyl groups in the s-*cis* form.[4] This conformational preference would favor diradical formation

Table 1. Rate Constants for Cycloaddition and Copolymerization of 2,3-Dimethyl-1,3-butadiene (2,3-DMB), 1,3-Cyclohexadiene (CHD), and Verbenene (VB)[4] with Acrylonitrile

diene	temp (°C)	cycloaddition k_c (L mol^{-1} s^{-1})	copolymerization k_{poly} (L mol^{-1} s^{-1})
2,3-DMB	80	1.45×10^{-6}	1.72×10^{-6}
2,3-DMB	100	10.3×10^{-6}	7.71×10^{-6}
CHD	70	3.16×10^{-7}	1.3×10^{-7}
VB	100	–	6.09×10^{-7}

(Scheme 1). Indeed (Z)-1,3-pentadiene and verbenene, which cannot form the s-cis diene, only give polymerization.

Scheme 1
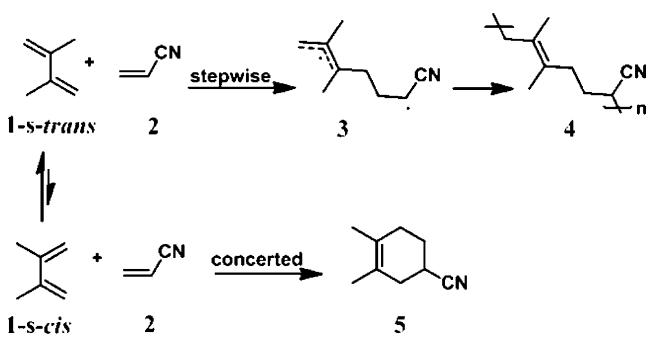
Using density functional theory, we have explored the reactions of 2,3-dimethyl-1,3-butadiene and (E)-1,3-pentadiene, dienes that form both cycloadduct and copolymer with acrylonitrile. We also investigated the reactions of cyclopentadiene, which only forms cycloadduct, and (Z)-1,3-pentadiene, a diene that only forms copolymer.

Our group has conducted several previous studies of the reactions of butadiene and ethylene. These theoretical studies have ranged from semiempirical methods to ab initio techniques, CASSCF,[1a−c] and density functional theory. The relative energies of the concerted and stepwise mechanisms of Diels−Alder reactions of butadiene and ethylene predict the stepwise path is 2.3−7.7 kcal/mol higher than that of the concerted pathway depending on the method used.[1]

Sakai and Okumura investigated substituent effects on the reactions of butadiene and ethylene and calculated the impact of substituents on the stabilization of transition states and diradical intermediates.[5] They determined the activation energies for the concerted and stepwise reactions between a phenyl- or cyano-substituted butadiene and a substituted ethylene. For monosubstituted systems, the energies of the transition states of the concerted reaction were lower than those of the stepwise reactions, but the effects of substituents on the energy barriers of the stepwise reactions were greater than the effects on the concerted.[5]

■ COMPUTATIONAL METHODS

Density functional theory (DFT) calculations were performed using the programs Gaussian03 and 09.[6] All structures were fully optimized using the B3LYP hybrid functional[7] with the 6-31G(d)[8] basis set, and all stationary points were verified by vibrational frequency analysis. Free energies are for 298K and 1 atm. The reactions of 2,3-dimethyl-1,3-butadiene and acrylonitrile were also investigated using M06−2X/6-311+G(d,p).[9] We and others have established that M06−2X gives

better $\Delta G^{\ddagger}$ and ΔG_{rxn} values for concerted cycloadditions.[11,12] However, in the course of this investigation, we observed that UM06−2X seems to overestimate the energies for diradicals (open-shell systems). Since the main purpose of this study is to evaluate the energy difference between diradical polymerization and concerted cycloaddition, the B3LYP functional is emphasized in our analysis.

■ RESULTS

2,3-Dimethyl-1,3-butadiene and Acrylonitrile. We first explored the conformations of the diene. The relative energies of the s-cis and s-trans conformations of 2,3-dimethyl-1,3-butadiene are given in Figure 1. Hall and co-workers proposed

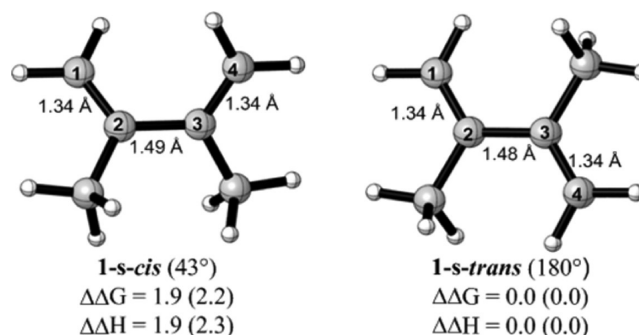**Figure 1.** Calculated structures and relative energies of s-cis and s-trans conformers of 2,3-dimethyl-1,3-butadiene using B3LYP and M06−2X (shown in parentheses) in kcal/mol.

that the conformation of the diene was an important factor in determining the outcome of this reaction, and that the preference for the s-trans conformation would favor diradical formation. The s-trans conformation is 1.9 kcal/mol more stable than the s-cis conformation. The s-cis conformer is nonplanar, with a C=C−C=C dihedral angle of 43°. Interestingly this difference is less than that of 1,3-butadiene itself, where the s-trans conformation is 3.7 kcal/mol more stable than the s-cis at the B3LYP/6-31G(d) level, similar to experimental and computational values of about 3 kcal/mol in the literature.[12] The s-cis conformation of 1,3-butadiene has a dihedral angle of 30°. Using M06−2X, it was found that the s-trans conformer of 2,3-dimethyl-1,3-butadiene is 2.2 kcal/mol more stable than the s-cis conformer.

The exo (**TS1-exo**) and endo (**TS2-endo**) transition states for the Diels−Alder cycloaddition of 2,3-dimethyl-1,3-butadiene and acrylonitrile were located (Figure 2). The two conformers of the product were also located. Using B3LYP, **TS1-exo** has the lowest activation barrier of 33.2 kcal/mol, which is 0.4 kcal/mol lower in energy than **TS2-endo**. In **TS1-exo**, the forming C1−C6 bond is 0.51 Å longer than the forming C4−C5 bond. **TS2-endo** is slightly less asynchronous, with the C1−C6 bond being 0.45 Å longer than the C4−C5 forming bond.

M06−2X optimizations were also carried out for this case. The geometries at the two levels are very similar. B3LYP overestimates the energies of the Diels−Alder transition states and products relative to reactants, consistent with previous benchmarking studies.[10,11]

To understand the effect of the methyl groups of the diene and the cyano group of the dienophile on the parent reaction (butadiene and ethylene), we investigated the reactions of 1,3-butadiene and acrylonitrile and the reactions of 2,3-dimethyl-1,3-butadiene and ethylene (Scheme 2, Table 2).
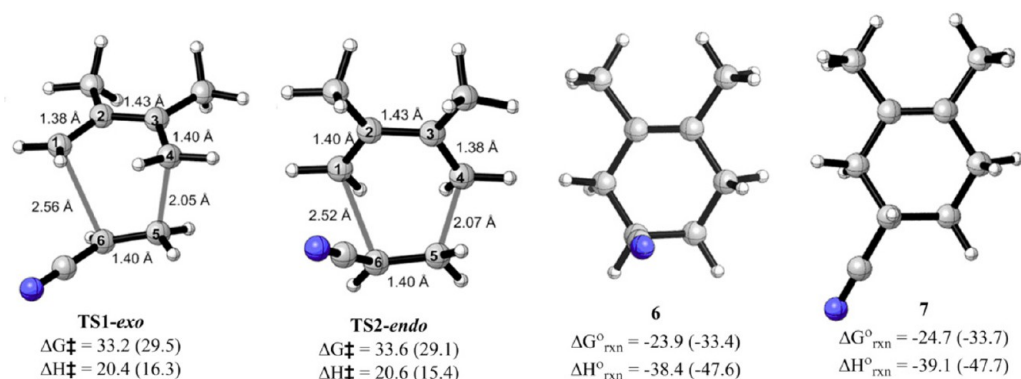
Figure 2. **TS1**-*exo* and **TS2**-*endo* and two conformers, **6** and **7**, of products for the reactions of 2,3-dimethyl-1,3-butadiene and acrylonitrile using B3LYP and M06−2X (shown in parentheses) in kcal/mol.
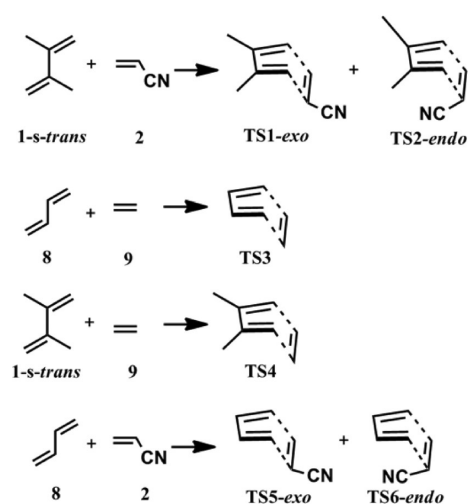
Scheme 2

Table 2. Calculated Relative Energies (kcal/mol) for TS1-exo, TS2-endo, TS3, TS4, TS5-exo, and TS6-endo using B3LYP/6-31G(d)

entry	diene	dienophile	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$
TS1-*exo*	1	2	33.2	20.4
TS2-*endo*	1	2	33.6	20.6
TS3	8	9	36.3	23.4
TS4	1	9	36.5	24.1
TS5-*exo*	8	2	34.0	20.6
TS6-*endo*	8	2	34.8	24.1

The reaction of butadiene and ethylene has an activation energy of 36.3 kcal/mol (**TS3**). Previous computational studies have been carried out on this reaction at this (B3LYP/6-31G*) and other methods.[1,11] **TS3** has a $\Delta H^{\ddagger}$ of 23.4 kcal/mol, which is very similar to experimental (23.2) and computational (24.9) literature values.[1c,11] Johnson et al. recently reported a CCSD(T) value of 24.6 kcal/mol.[11b] As shown in Table 2, methyl groups on the diene slightly increase the activation energy of **TS4**. Comparing **TS5**-*exo* to **TS3**, the cyano group lowers the activation barrier by 2−3 kcal/mol. The presence of both the methyl groups on butadiene and the cyano group on ethylene lower the barrier by 3 kcal/mol, larger than the sum of the individual substituent effects (Figure 3).

The transition states for all possible stepwise additions of 2,3-dimethyl-1,3-butadiene to acrylonitrile were calculated (Figure
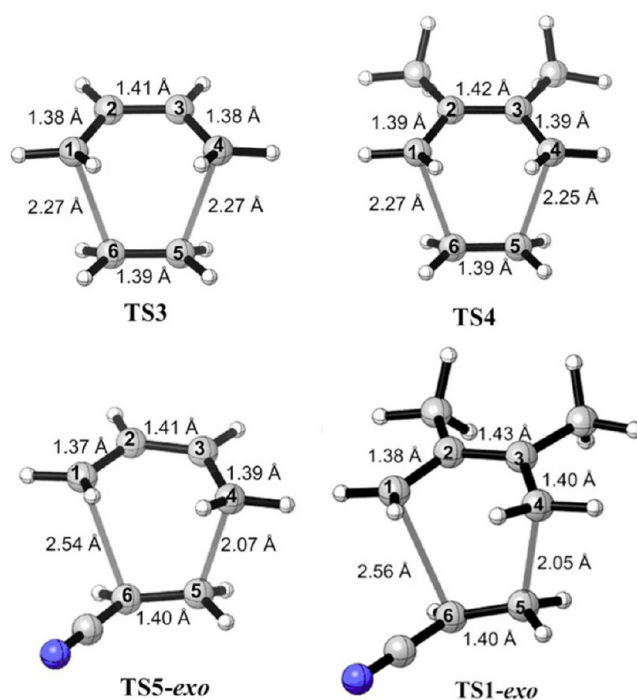

Figure 3. Optimized geometries and bond lengths (Å) of **TS3**, **TS4**, **TS5**-*exo*, and **TS1**-*exo* calculated using B3LYP.

4). This included the examination of transition states involving both the s-*cis* and s-*trans* conformers of the diene as well as the
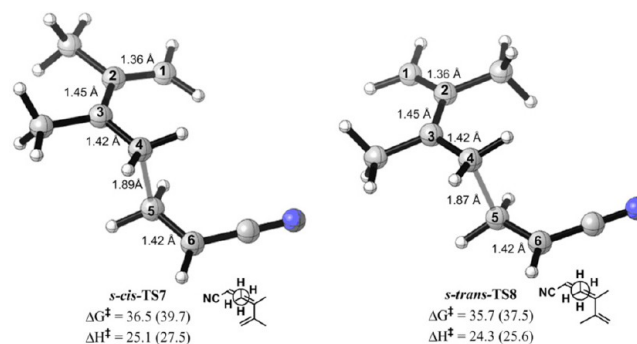

Figure 4. s-*cis*-**TS7** and s-*trans*-**TS8** for the stepwise addition transition states of 2,3-dimethyl-1,3-butadiene and acrylonitrile using B3LYP and M06−2X (shown in parentheses) in kcal/mol.

three conformers about the forming C−C bond of the diradical intermediate. The activation energies of the transition structures were located in the range from 35 to 39 kcal/mol, and the lowest energy transition state (**s-trans-TS8**) has an energy of 35.7 kcal/mol. The M06−2X energy is 37.5 kcal/mol. This transition state results from the addition of the s-trans conformation of the diene to acrylonitrile in an anti-periplanar arrangement (Figure 4). The lowest energy transition state resulting from the addition of the s-cis conformer of 2,3-dimethyl-1,3-butadiene (**s-cis-TS7**) is 1−2 kcal/mol higher in energy.

The effects of substituents on the stepwise reaction were investigated (Scheme 3). This included study of the reactions

Scheme 3
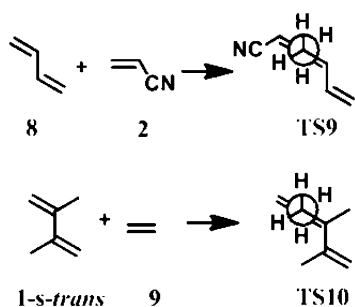
of 1,3-butadiene and acrylonitrile and the reactions of 2,3-dimethyl-1,3-butadiene and ethylene (Table 3). The table also

Table 3. Calculated Relative Energies (kcal/mol) and $\langle S^2 \rangle$ Values for s-cis-TS7, s-trans-TS8, TS9, and TS10 in kcal/mol

entry	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\langle S^2 \rangle$
s-cis-TS7	37.7	25.9	0.31
s-trans-TS8	35.7	24.2	0.46
TS9	35.4	23.9	0.48
TS10	43.4	32.4	0.60

lists the $\langle S^2 \rangle$ values, which are usually greater than zero in open shell singlet diradicals and are indicative of some triplet spin contamination. In the case of 1,3-butadiene with acrylonitrile, the lowest energy transition state (**TS9**) resulted from the addition of the s-trans conformer of the diene to acrylonitrile in an antiarrangement, similar to the stepwise addition of **1-s-trans** and acrylonitrile (**s-trans-TS8**). **TS9** has an activation barrier of 35.4 kcal/mol, suggesting that the presence of methyl groups on the diene is slightly destabilizing.

The most energetically unfavorable transition state of the stepwise addition of dimethylbutadiene and ethylene has an activation barrier of 43.4 kcal/mol (**TS10**). This barrier is 7.7 kcal/mol higher in energy than **s-trans-TS8**, indicating that the cyano group has a very large stabilizing effect on the transition state. Like **s-trans-TS8** and **TS9**, **TS10** also results from a s-trans conformation of the diene and the antiarrangement about the forming bond.

The diradical intermediates resulting from **s-cis-TS7** and **s-trans-TS8** were also located. The s-trans product (**10**) was found to have the lowest energy of 30.7 kcal/mol (Figure 5). The s-cis (**11**) and s-trans (**10**) diradical products have the same energy. M06−2X calculations give the very similar energetics.
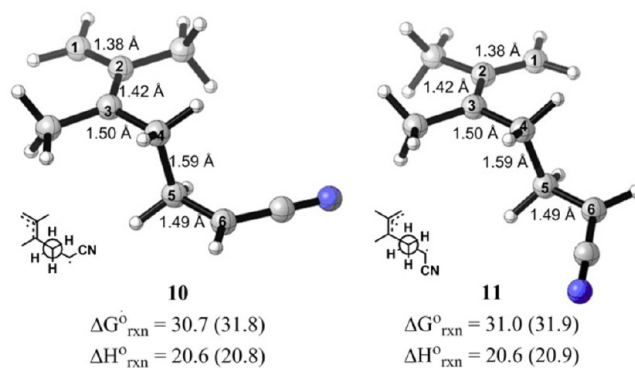
10
$\Delta G^{\circ}_{rxn} = 30.7 \, (31.8)$
$\Delta H^{\circ}_{rxn} = 20.6 \, (20.8)$

11
$\Delta G^{\circ}_{rxn} = 31.0 \, (31.9)$
$\Delta H^{\circ}_{rxn} = 20.6 \, (20.9)$

Figure 5. s-trans (**10**) and s-cis (**11**) diradicals for the reactions of 2,3-dimethyl-1,3-butadiene and acrylonitrile using B3LYP and M06−2X (shown in parentheses) in kcal/mol.

Cyclopentadiene and Acrylonitrile. The reaction of cyclopentadiene with acrylonitrile gives only the Diels−Alder adduct experimentally. No copolymerization occurred (Scheme 4).[4]

Scheme 4
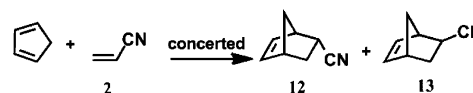
The endo and exo transition states of the Diels−Alder reaction were located (Figure 6). These transition states are essentially isoenergetic, with the exo transition state having a slightly lower activation barrier of 30.7 kcal/mol. This is consistent with previous experimental observations and
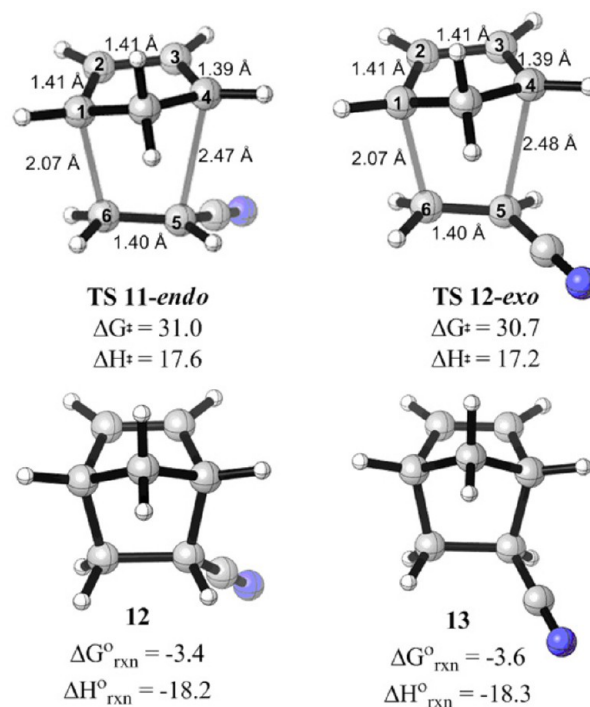
TS 11-endo
$\Delta G^{\ddagger} = 31.0$
$\Delta H^{\ddagger} = 17.6$

TS 12-exo
$\Delta G^{\ddagger} = 30.7$
$\Delta H^{\ddagger} = 17.2$

12
$\Delta G^{\circ}_{rxn} = -3.4$
$\Delta H^{\circ}_{rxn} = -18.2$

13
$\Delta G^{\circ}_{rxn} = -3.6$
$\Delta H^{\circ}_{rxn} = -18.3$

Figure 6. Calculated relative energies of the Diels−Alder transition states **TS11-endo** and **TS12-endo**, and products **12** and **13** of the reactions of cyclopentadiene and acrylonitrile in kcal/mol.

computational studies.[13] The *endo* (**12**) and *exo* (**13**) Diels–Alder adducts were also found to have very similar energies.

For the stepwise reaction of cyclopentadiene, we attempted to locate all possible conformations of the transition state and product. The only transition structure found has an anti arrangement about the forming bond (Figure 7). The diradical
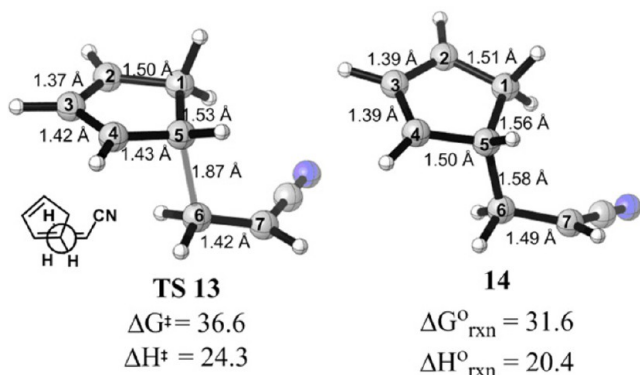

TS 13
$\Delta G^{\ddagger} = 36.6$
$\Delta H^{\ddagger} = 24.3$

14
$\Delta G^{\circ}_{rxn} = 31.6$
$\Delta H^{\circ}_{rxn} = 20.4$

Figure 7. Calculated energies of the diradical transition state (**TS13**) and intermediate (**14**) for the reactions of cyclopentadiene and acrylonitrile in kcal/mol.

transition state has an activation barrier of 36.6 kcal/mol, and the intermediate is 5 kcal/mol lower than the transition state. The stepwise pathway has a 6 kcal/mol higher barrier than the concerted Diels–Alder process, consistent with experimental observations that only the Diels–Alder product is formed.

(E)-1,3-Pentadiene and Acrylonitrile. The concerted and stepwise pathway for the reactions of (*E*)-1,3-pentadiene and acrylonitrile were investigated. Experimentally, it was found that both the cycloadduct and copolymer were formed for this reaction (Scheme 5). The cycloadduct obtained was a mixture of the two expected regioisomers **16** and **17** in a 62:38 ratio.[4]

Scheme 5
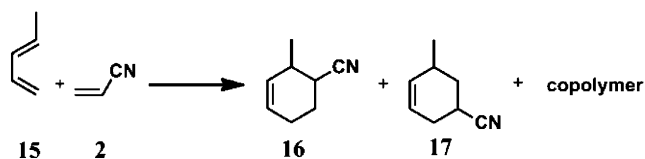
We first located the s-*cis* and s-*trans* conformations of (*E*)-1,3-pentadiene (**15**). The s-*trans* conformation was found to be 3.3 kcal/mol more stable than the s-*cis* conformation (Figure 8). The s-*trans* conformer was found to be planar with a C=C—C=C dihedral angle of 0°, while the s-*cis* conformer had a dihedral angle of 29.6°.

The transition states for both regioisomers of the cycloaddition reaction were located. As expected, the transition state for formation of the *ortho*-isomer (**TS15-exo**) has the lowest barrier of 33.5 kcal/mol (Figure 9). The products are shown in Figure 10.

For the stepwise reaction of (*E*)-1,3-pentadiene and acrylonitrile, the transition states of all possible stepwise additions were calculated. Like our findings from the investigation of the diradical formation of 2,3-dimethyl-1,3-butadiene and acrylonitrile, the reactions of the s-*trans* conformation of (*E*)-1,3-pentadiene were systematically lower in energy than those of the s-*cis* conformer with acrylonitrile.
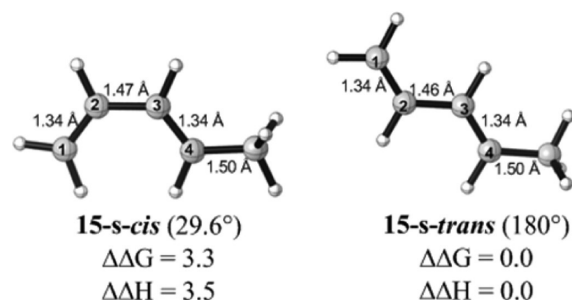

15-s-cis (29.6°)
$\Delta\Delta G = 3.3$
$\Delta\Delta H = 3.5$

15-s-trans (180°)
$\Delta\Delta G = 0.0$
$\Delta\Delta H = 0.0$

Figure 8. Optimized geometries and relative energies of s-*cis* and s-*trans* conformers of (*E*)-1,3-pentadiene in kcal/mol.

TS 14-endo
$\Delta G^{\ddagger} = 34.3$
$\Delta H^{\ddagger} = 21.1$

TS 15-exo
$\Delta G^{\ddagger} = 33.5$
$\Delta H^{\ddagger} = 20.0$

TS 16-endo
$\Delta G^{\ddagger} = 36.7$
$\Delta H^{\ddagger} = 23.0$

TS 17-exo
$\Delta G^{\ddagger} = 35.9$
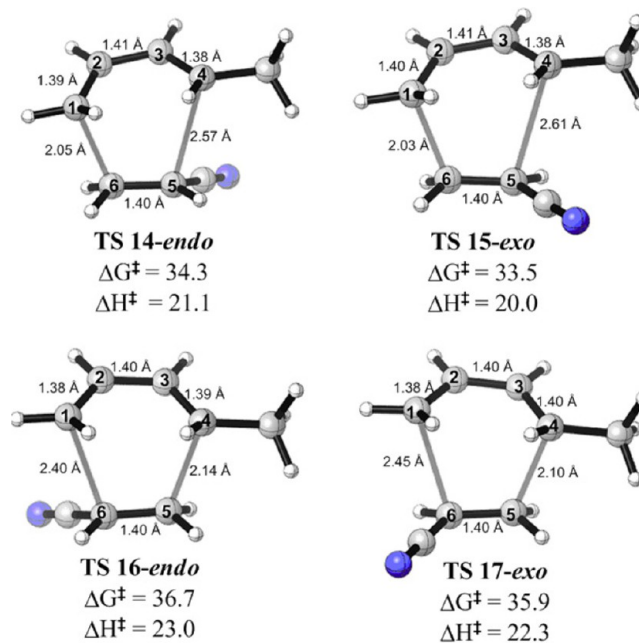$\Delta H^{\ddagger} = 22.3$

Figure 9. Optimized geometries and activation barriers for the cycloaddition reaction of (*E*)-1,3-pentadiene and acrylonitrile in kcal/mol.

The lowest energy transition state for cycloaddition (**TS18**) was found to have an anti-periplanar arrangement of the double bonds about the forming C—C bond (Figure 11). The diradical intermediate, **18**, is 5 kcal/mol below **TS18**.

The Diels–Alder transition state was found to be preferred over the diradical transition state by 1.2 kcal/mol. This is consistent with the formation of both the Diels–Alder adduct and copolymer observed experimentally.

(Z)-1,3-Pentadiene and Acrylonitrile. The reaction of (*Z*)-1,3-pentadiene and acrylonitrile was observed to prefer the stepwise pathway and produced only copolymer experimentally (Scheme 6).[4]

The energetics of both the s-*cis* and s-*trans* conformations of the reactant (*Z*)-1,3-pentadiene were investigated computationally. It was determined that the s-*trans* conformer was preferred by 3.1 kcal/mol (Figure 12).

The *endo* and *exo* transition states of both regioisomers were then located (Figure 13). **TS21-exo** was found to be slighty more energetically favorable than the other transition states obtained with an activation barrier of 37.9 kcal/mol. While all the transition structures exhibited an asynchronous nature, **TS21-exo** was the most asynchronous and had a difference of 0.87 Å between its forming C—C bonds. This could be due to
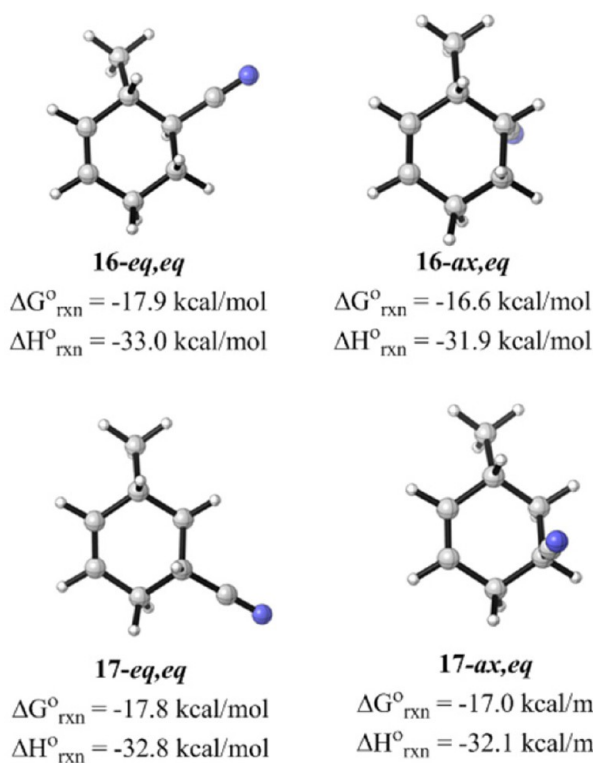
16-eq,eq
$\Delta G^{\circ}_{rxn} = -17.9$ kcal/mol
$\Delta H^{\circ}_{rxn} = -33.0$ kcal/mol

16-ax,eq
$\Delta G^{\circ}_{rxn} = -16.6$ kcal/mol
$\Delta H^{\circ}_{rxn} = -31.9$ kcal/mol

17-eq,eq
$\Delta G^{\circ}_{rxn} = -17.8$ kcal/mol
$\Delta H^{\circ}_{rxn} = -32.8$ kcal/mol

17-ax,eq
$\Delta G^{\circ}_{rxn} = -17.0$ kcal/mol
$\Delta H^{\circ}_{rxn} = -32.1$ kcal/mol

Figure 10. The optimized geometries and relative energies of the of 4-cyano- (**16**) and 5-cyano-3-methyl-cyclohexene (**17**) in kcal/mol.

TS 18
$\Delta G^{\ddagger} = 34.7$ kcal/mol
$\Delta H^{\ddagger} = 23.3$ kcal/mol

18
$\Delta G^{\circ}_{rxn} = 30.0$
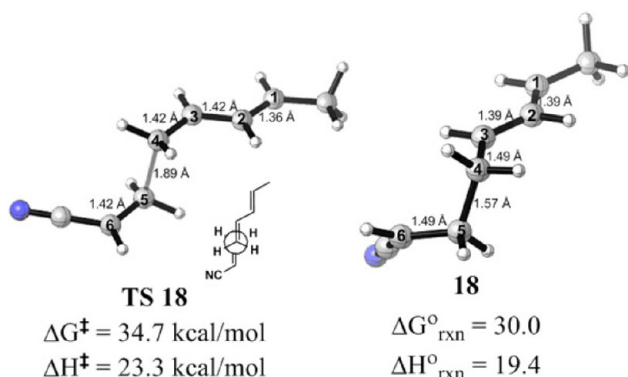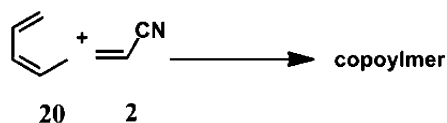$\Delta H^{\circ}_{rxn} = 19.4$

Figure 11. The optimized geometries and relative energies **TS18** and **18** for the reactions of (E)-1,3-pentadiene and acrylonitrile in kcal/mol.

Scheme 6

the methyl and cyano substituents of C4 and C5 both being *exo*. The products formed from these transition states were also located (Figure 14).

The stepwise pathway of this reaction was also investigated. All conformations of possible stepwise additions of (Z)-1,3-pentadiene to acrylonitrile were explored. Once again, the diradical from the s-*trans* conformer of the diene formed with a substantially smaller activation barrier than that for the s-*cis* conformer. The diradical transition state with the lowest energy
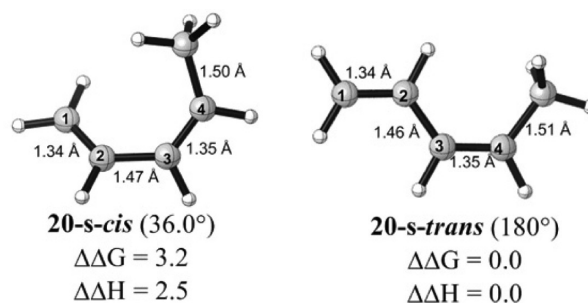

20-s-cis (36.0°)
$\Delta\Delta G = 3.2$
$\Delta\Delta H = 2.5$

20-s-trans (180°)
$\Delta\Delta G = 0.0$
$\Delta\Delta H = 0.0$

Figure 12. Calculated structures and relative energies of s-*cis* and s-*trans* conformers of (Z)-1,3-pentadiene in kcal/mol.

TS 20-endo
$\Delta G^{\ddagger} = 38.9$
$\Delta H^{\ddagger} = 26.9$

TS 21-exo
$\Delta G^{\ddagger} = 37.9$
$\Delta H^{\ddagger} = 24.8$

TS 22-endo
$\Delta G^{\ddagger} = 39.9$
$\Delta H^{\ddagger} = 27.5$

TS 23-exo
$\Delta G^{\ddagger} = 39.2$
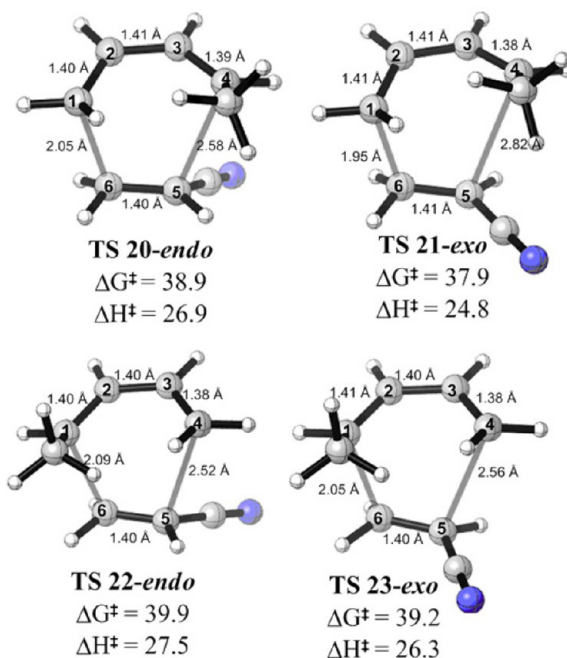$\Delta H^{\ddagger} = 26.3$

Figure 13. Calculated structures and relative energies of **TS20**-*endo*, **TS21**-*exo*, **TS22**-*endo*, and **TS23**-*exo* for the reaction of (Z)-1,3-pentadiene and acrylonitrile in kcal/mol.

(**TS24**) was found to have an energy barrier of 34.0 kcal/mol (Figure 15). The resulting diradical intermediate (**23**) was found to have an energy of 27.8 kcal/mol, which was 6.2 kcal/mol lower in energy that its transition state.

Pathways to Polymerization and Barriers to Ring Closure. The fates of the diradical intermediates formed in reactions of nonpolar 1,3-dienes with acrylonitrile were also investigated. The diradicals may either ring-close to give cyclobutanes, revert to reactants, or react with a diene or alkene to initiate copolymerization. We studied the diradicals resulting from the reactions of 2,3-dimethyl-1,3-butadiene, (E)-1,3-pentadiene, and (Z)-1,3-pentadiene with acrylonitrile (Scheme 7). The diradical intermediate resulting from cyclopentadiene and acrylonitrile was not considered, because the barrier to formation of diradicals is considerably higher than that of the concerted reaction.

We located the barrier of rotation and subsequent ring closure for the diradical **10** from the reaction of 2,3-dimethyl-1,3-butadiene and acrylonitrile. The transition state for the rotation about the C2−C3 bond from an anti-periplanar to syn conformation is 6.4 kcal/mol. The transition state for the cyclization to cyclobutane (**TS26**) was found to have a low
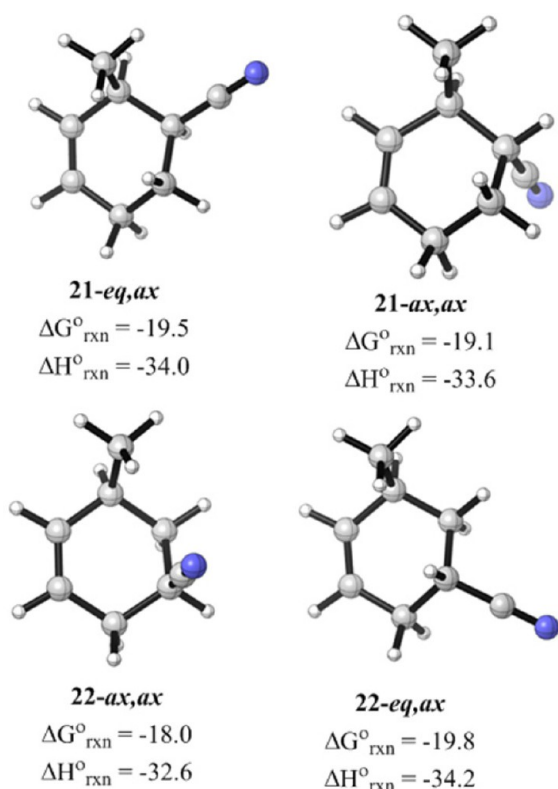
21-eq,ax
$\Delta G^{\circ}_{rxn} = -19.5$
$\Delta H^{\circ}_{rxn} = -34.0$

21-ax,ax
$\Delta G^{\circ}_{rxn} = -19.1$
$\Delta H^{\circ}_{rxn} = -33.6$

22-ax,ax
$\Delta G^{\circ}_{rxn} = -18.0$
$\Delta H^{\circ}_{rxn} = -32.6$

22-eq,ax
$\Delta G^{\circ}_{rxn} = -19.8$
$\Delta H^{\circ}_{rxn} = -34.2$

Figure 14. The optimized geometries and relative energies of the of 4-cyano- (**21**) and 5-cyano-3-methyl-cyclohexene (**22**) in kcal/mol.

TS 24
$\Delta G\ddagger = 34.0$
$\Delta H\ddagger = 23.7$

23
$\Delta G^{\circ}_{rxn} = 27.8$
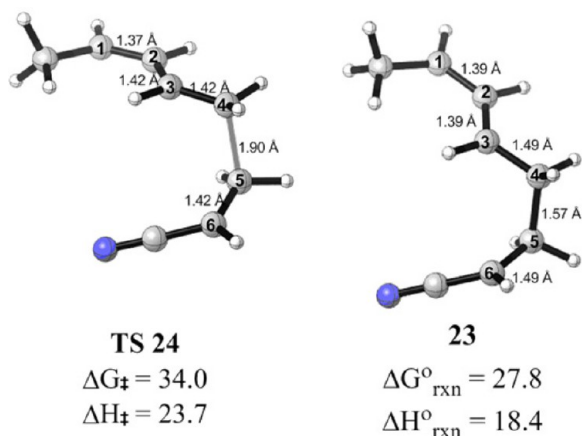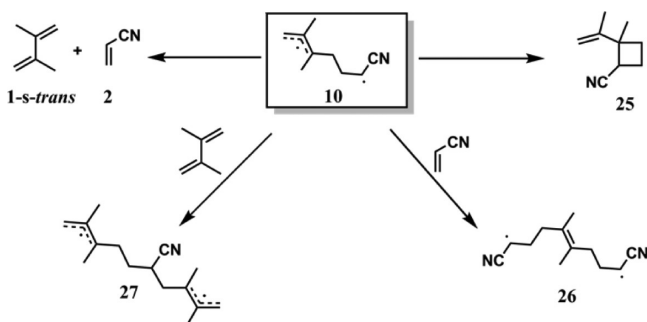$\Delta H^{\circ}_{rxn} = 18.4$

Figure 15. Diradical transition state and intermediate for the reactions of (Z)-1,3-pentadiene and acrylonitrile in kcal/mol.

Scheme 7

barrier of 4.7 kcal/mol, and the reaction is exergonic to give **25** with an energy of −26.3 kcal/mol (Figure 16). The diradical
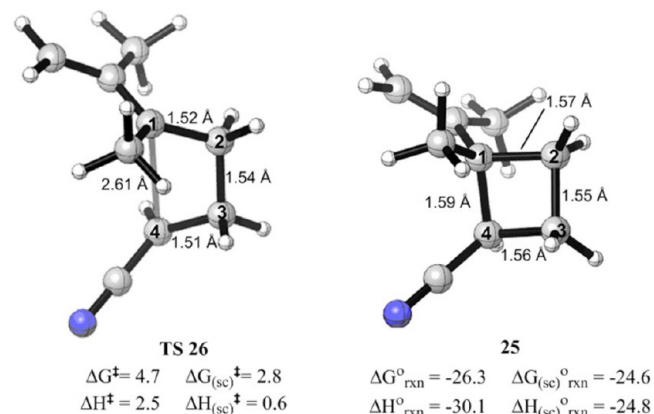

TS 26
$\Delta G^{\ddagger} = 4.7$　　$\Delta G_{(sc)}^{\ddagger} = 2.8$
$\Delta H^{\ddagger} = 2.5$　　$\Delta H_{(sc)}^{\ddagger} = 0.6$

25
$\Delta G^{\circ}_{rxn} = -26.3$　　$\Delta G_{(sc)}^{\circ}{}_{rxn} = -24.6$
$\Delta H^{\circ}_{rxn} = -30.1$　　$\Delta H_{(sc)}^{\circ}{}_{rxn} = -24.8$

Figure 16. The energies of the transition state (**TS26**) and product (**25**) for the ring closure of diradical intermediate **10** in kcal/mol.

10, the transition states and intermediates for cleavage, polymerization, and cyclization are all spin contaminated. The energies for the pure singlet states were calculated using the method of Yamaguchi et al.:[14]

$$\Psi_{(UB)} = c_s\,^1\phi + c_T\,^3\phi$$

$$^1E_{(SC)} = {}^1E_{(SC)} + f_{SC}[{}^1E_{(UB)} - {}^3E_{(UB)}]$$

$$f_{SC} = \frac{c_T{}^2}{1 - c_S{}^2} \approx \frac{{}^1\langle S^2\rangle}{{}^3\langle S^2\rangle - {}^1\langle S^2\rangle}$$

Diradical **10** and **TS26** were found to have $\langle S^2\rangle$ values of 0.96 and 0.83, respectively. Spin correction to estimate the energy of the singlet diradicals gives energies of 2.8 kcal/mol for the cyclization of the diradical and gives an energy of −24.6 kcal/mol for the product **25**.[14,15] Additionally, the transition state for the cleavage of diradical **10**, **s-trans-TS8**, was found to have an energy of 2.5 kcal/mol (Figure 17).

We also explored various pathways by which the diradical can initiate copolymerization. This included the addition of acrylonitrile at C-1 or of 2,3-dimethyl-1,3-butadiene at C-6. For the addition of acrylonitrile to **10**, adding at C-1 had a
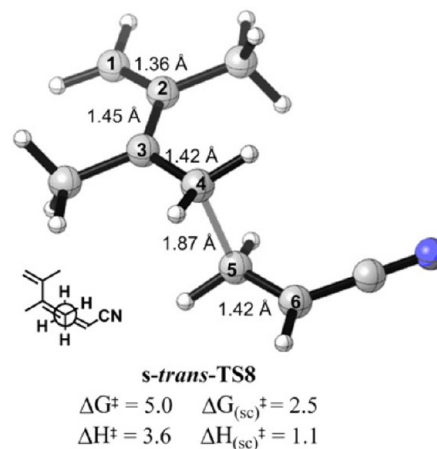

s-trans-TS8
$\Delta G^{\ddagger} = 5.0$　　$\Delta G_{(sc)}^{\ddagger} = 2.5$
$\Delta H^{\ddagger} = 3.6$　　$\Delta H_{(sc)}^{\ddagger} = 1.1$

Figure 17. The energies of the transition state **s-trans-TS8** for the cleavage of diradical **10** in kcal/mol.

barrier of 20.2 kcal/mol (**TS27**). **TS27** leads to the product **26**, which has an energy of 0.8 kcal/mol (Figure 18). Spin correction gave a barrier of 21.1 kcal/mol, leading to the product that has an energy of 2.4 kcal/mol.
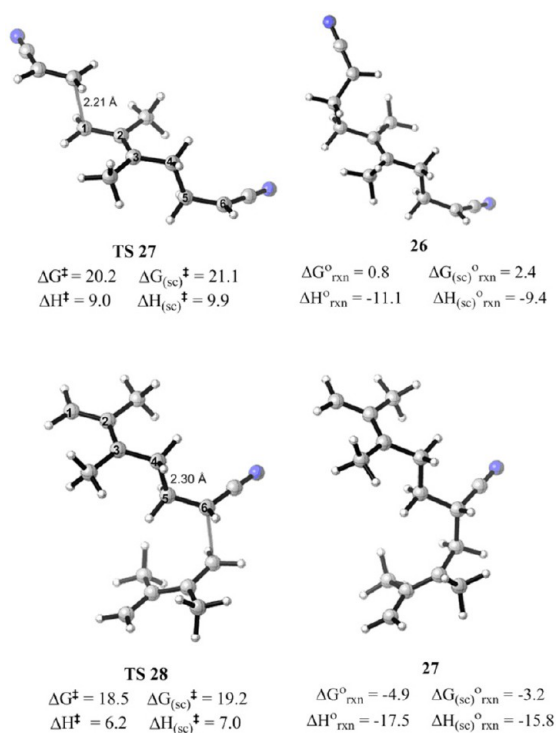

TS 27
$\Delta G^{\ddagger} = 20.2 \quad \Delta G_{(sc)}^{\ddagger} = 21.1$
$\Delta H^{\ddagger} = 9.0 \quad \Delta H_{(sc)}^{\ddagger} = 9.9$

26
$\Delta G^{o}_{rxn} = 0.8 \quad \Delta G_{(sc)}^{o}{}_{rxn} = 2.4$
$\Delta H^{o}_{rxn} = -11.1 \quad \Delta H_{(sc)}^{o}{}_{rxn} = -9.4$

TS 28
$\Delta G^{\ddagger} = 18.5 \quad \Delta G_{(sc)}^{\ddagger} = 19.2$
$\Delta H^{\ddagger} = 6.2 \quad \Delta H_{(sc)}^{\ddagger} = 7.0$

27
$\Delta G^{o}_{rxn} = -4.9 \quad \Delta G_{(sc)}^{o}{}_{rxn} = -3.2$
$\Delta H^{o}_{rxn} = -17.5 \quad \Delta H_{(sc)}^{o}{}_{rxn} = -15.8$

Figure 18. The energies of the transition states and products formed from the reaction of diradical **10** with acrylonitrile and with 2,3-dimethyl-1,3-butadiene in kcal/mol.

The barrier for the addition of the diene to C6 has an energy of 18.5 kcal/mol. This transition state led to the most favorable diradical intermediate (**27**). Spin corrected calculations show that the barrier is 19.2 kcal/mol, leading to the product that has an energy of −3.2 kcal/mol.

■ DISCUSSION

Li, Padias, and Hall measured the kinetics of the reactions of dienes and acrylonitrile described here. These include dienes that form both cycloadduct and copolymer (2,3-dimethyl-1,3-butadiene, isoprene, (*E*)-1,3-pentadiene, 1,3-cyclohexadiene, and 1,2-dimethylenecyclohexane) and dienes that form only cycloadduct (cyclopentadiene and 1,2-dimethylenecyclopentane). In addition, some dienes only form copolymer ((*Z*)-1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene, and verbenene). The reaction of 2,3-dimethyl-1,3-butadiene and acrylonitrile gave the highest yield of alternating copolymer of all of the 1,3-dienes, which produced both copolymer and cycloadduct.

We investigated main reactions of interest, those of dimethyl butadiene and acrylonitrile, with B3LYP and M06−2X density functionals. While the M06−2X functional generally shows lower mean errors than most other methods for concerted cycloadditions,[10,11] M06−2X was found to slightly overestimate the energies of the diradical transition states relative to the closed-shell concerted transition states. For the concerted pathway, M06−2X single point calculations were consistent with trends shown in previous benchmarking studies of the Diels−Alder reaction.[10,11] The Diels−Alder transition states and products are consistently lowered by approximately 5 and 10 kcal/mol using M06−2X, respectively. The slight overestimation of the diradical transition states along with the expected lowering of the Diels−Alder transition states resulted in the energy difference between pathways being 8.4 kcal/mol. Using B3LYP, polymerization via a diradical pathway was calculated to be less favored than the Diels−Alder cycloaddition by 2.5 kcal/mol.

For the reaction of 2,3-dimethyl-1,3-butadiene and acrylonitrile, the methyl substituents on butadiene and the cyano group on acrylonitrile lower the activation barrier of the Diels−Alder cycloaddition. The methyl groups have only a very small effect on concerted (0.8 kcal/mol) and stepwise (0.3 kcal/mol) reactions. The presence of CN has a substantial effect on lowering the energy of the concerted Diels−Alder transition state (3.3 kcal/mol) and an even larger effect on the stepwise transition state (7.7 kcal/mol). Although the presence of substituents assists in lowering both the stepwise and concerted
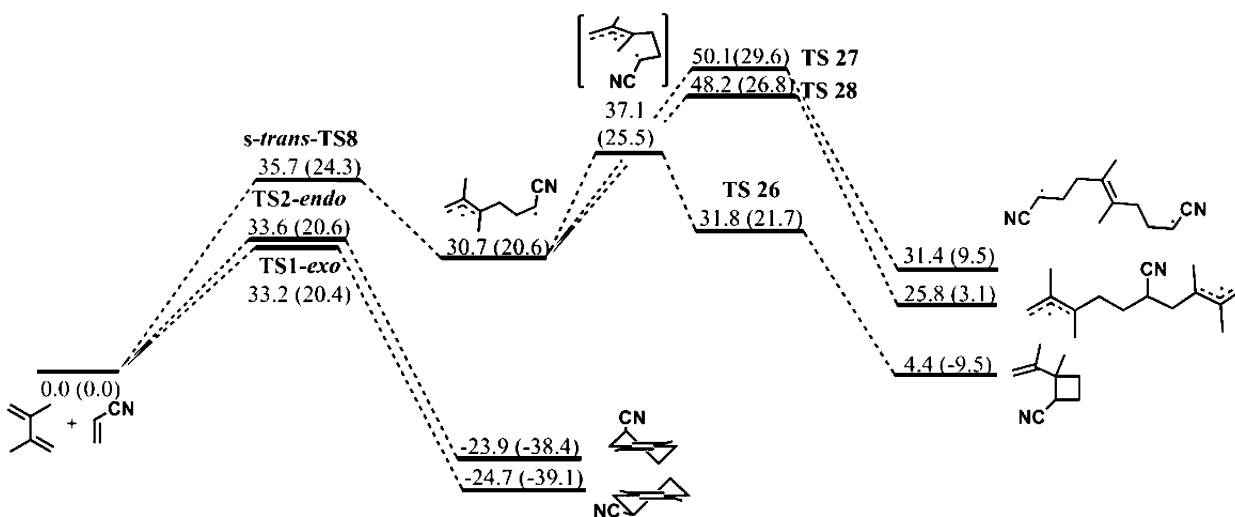

Figure 19. Relative free energies and enthalpies (in parentheses) for the reactions of 2,3-dimethyl-1,3-butadiene and acrylonitrile in addition to possible reactions of **10** (with spin corrections) using B3LYP/6-31G(d) in kcal/mol.

pathways, the concerted pathway remains the lowest (Figure 19).

We also studied the possible reactions of the diradical. Ring closure to give cyclobutane via **TS26** had the lowest activation barrier of 2.8 kcal/mol. Experimentally, the cyclobutane adduct is never isolated, because the cyclobutane readily reverts to reactants and then to the thermodynamically more stable Diels−Alder adduct. The additions of the diene and dienophile to various positions of the diradical were also explored. Addition of the diene to the C6 position of the diradical (**TS28**) had the lowest energy of 17.5 kcal/mol above the diradical. The addition of acrylonitrile at the C1 position of the diradical (**TS27**) had an activation barrier of 19.4 kcal/mol.

The reaction of cyclopentadiene with acrylonitrile gives only the Diels−Alder cycloadduct experimentally (Figure 20).
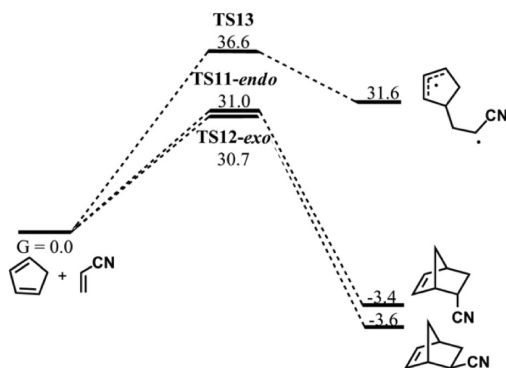

Figure 20. Relative free energies (kcal/mol) of reactants, transition structures, diradical intermediates, and products for the reactions of 1,3-cyclopentadiene and acrylonitrile using B3LYP/6-31G(d).

Computationally, it was found that the Diels−Alder transition states were lowest in energy, with **TS12-exo** being slightly lower in energy by 0.3 kcal/mol. The only diradical transition state (**TS13**) had a barrier of 5.9 kcal/mol higher than that of the **TS12-exo**.

This energy difference, along with the energetics of the resulting products support the experimental findings of Hall et al.[4] Cyclopentadiene is constrained in a s-*cis* conformation of the diene, which more readily can undergo the Diels−Alder reaction. The formation of a diradical intermediate from cyclopentadiene is disfavored since the concerted transition state has a low distortion energy due to the constraint of the reactant into the cisoid, transition state-like geometry.

The reaction of (*E*)-1,3-pentadiene and acrylonitrile (Figure 21) gives both cycloaddition and polymerization experimentally. The lowest energy Diels−Alder transition state (**TS15-exo**) was found to have an activation barrier of 33.5 kcal/mol, while the lowest energy diradical transition state (**TS18**) was calculated to have a barrier of 34.7 kcal/mol, only 1.2 kcal/mol higher in energy.

The reaction of (*Z*)-1,3-pentadiene and acrylonitrile was observed experimentally to produce only the copolymer. Our computational findings illustrate that the diradical transition state **TS24** is 3.9 kcal/mol lower in energy than the Diels−Alder transition state (Figure 22), because of the considerable distortion of the diene necessary to achieve a concerted transition state geometry.

Initiation of polymerization by a few diradicals can give significant amounts of copolymer; comparable quantities of copolymer and cycloadduct are obtained because of significant
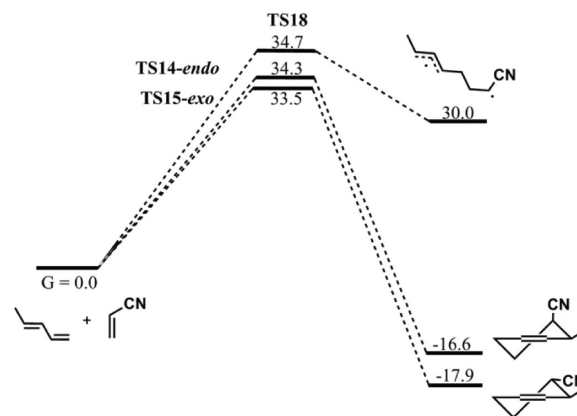

Figure 21. Relative free energies (kcal/mol) of reactants, transition structures, diradical intermediates, and *ortho*-cycloadducts for the reactions of (*E*)-1,3-pentadiene and acrylonitrile using B3LYP/6-31G(d) .
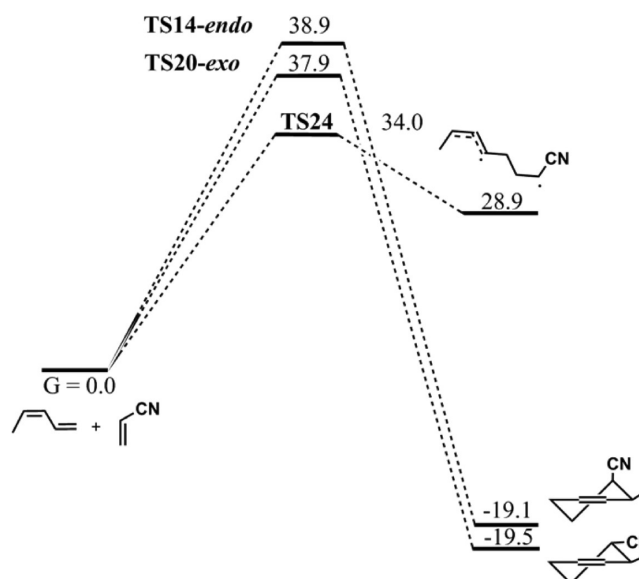

Figure 22. Relative free energies (kcal/mol) of reactants, transition structures, diradical intermediates, and *ortho*-cycloadducts for the reactions of (*Z*)-1,3-pentadiene and acrylonitrile using B3LYP/6-31G(d).

chain lengths in the radical polymerization. The ratio of the rate of cycloaddition to the rate of diradical formation can be calculated from the kinetic equations derived in the Supporting Information. This is based upon the steady-state approximation. For the reactions of 2,3-dimethyl-1,3-butadiene with acrylonitrile, the ratio of cycloaddition to diradical formation was calculated to be 530. This analysis is consistent with the computational findings that show a difference of 2.5 kcal/mol between the diradical formation and cycloaddition activation energies. The results of the present study are in accord with those of our earlier work on competition between 1,3-dipolar cycloaddition of a thiocarbonyl ylide and polymerization of the dipolarophile.[16]

Polymerization is a highly amplifying method of trapping reactive intermediates. Although the activation barriers for polymerization (the addition of monomeric units to the diradical intermediate) are high, we believe this is in part due to the overestimation of the negative entropy of activation for

the bimolecular process. This complication in calculating the entropy of activation, $\Delta S^{\ddagger}$, in solution has been investigated by various groups.[17-19] The problem arises from use of standard states and computations of entropies in solution; calculations of entropy are complicated by the fact that there is less free volume in solution than in the gas phase.[17] While these errors are relevant to both cycloaddition and copolymerization, they are perhaps more complex in polymerizations.

CONCLUSION

Using density functional theory, the energetics for the reactions of several 1,3-dienes with acrylonitrile were investigated. The reaction of 2,3-dimethyl-1,3-butadiene with acrylonitrile gives both cycloadduct and copolymer experimentally, and computational findings show the barriers for cycloaddition and diradical formation are comparable. It was previously proposed that the preferred conformation of an acyclic diene was an important factor in determining the outcome of the reaction, but we have found that the conformation of the diene is a minor contributor to the cycloaddition barrier, while cyclopentadiene does favor the concerted reaction because of its constraint into a geometry resembling the transition state.

In the reaction of cyclopentadiene and acrylonitrile, only the Diels−Alder adduct is formed experimentally; these trends were supported by computational results, which showed that the concerted cycloaddition is preferred over the stepwise pathway by 5.9 kcal/mol. For the reactions of (E)-1,3-pentadiene and acrylonitrile, both cycloaddition and copolymerization were observed experimentally. The computational results are in good agreement, predicting only a 1.2 kcal/mol preference for the concerted pathway. In the reactions of (Z)-1,3-pentadiene and acrylonitrile, the stepwise pathway is preferred by 3.9 kcal/mol, and experimentally, only polymerization occurs.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the calculation of the ratio of rates of cycloaddition to diradical formation. Cartesian coordinates and energies of all reported structures and model systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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