The role of cumulenic strain on the kinetic and thermodynamic control of the Diels–Alder reactions involving allenes as dienes

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Diels–Alder cycloaddition reactions of vinylallene and diallene with ethylene, acrylonitrile, maleic anhydride, *p*-benzoquinone and 1,4-naphthaquinone have been investigated at the semiempirical level and with limited *ab initio* and DFT calculations. Calculations predict that these reactions are concerted processes and these cumulated dienes are less reactive than the non-cumulated diene. With increase in cumulenic strain the reactivity decreases while the exothermicity of the reaction increases. This happens because the transition states occur 'early' and the cumulenic strain is therefore released only when the reaction proceeds from transition state to product. Deformation energy analysis explains that these cumulated dienes have to deform to a greater extent during the reaction and thus are responsible for the increase of the activation energy. Activation barriers predict the reactivity trends, regio- and stereo-selectivities reasonably.

Introduction

Allenes are known to undergo Diels–Alder reactions,[1–6] which are preparatively very useful and mechanistically interesting. Similar to alkenes these cumulenic addends also take part in less well known photochemical and acid and metal catalysed Diels–Alder reactions.[1,2] Unlike alkenes, allenes, owing to their double olefinic character and unusual stereochemical properties, show considerable mechanistic diversity; suitably substituted allenes can react to give complicated mixtures of regio- and stereo-isomers.[1,3] Such synthetic and mechanistic importance has led to the accumulation of a substantial body of knowledge on allene reactions. Yet, theoretical studies on the mechanism of their reactions are rare. Allenes undergo [4+2] cycloaddition[3] in a concerted fashion and for a long time the concerted nature of these reactions has been deduced from kinetic, stereochemical and isotopic labelling studies alone and only recently have theoretical techniques been employed to prove the mechanism through location of transition states (TS). Hydrocarbon Diels–Alder reactions of various dienes and dienophiles have been thoroughly investigated[7–9] using various theoretical methods in recent years but those involving allenes as dienophiles have attracted attention only very recently.[9] The present report is a theoretical study on the mechanism of Diels–Alder reactions of allenic dienes with a selected set of dienophiles.

Allenes can act as dienes[1,5,6] or dienophiles[2–4] in Diels–Alder reactions. For them to act as dienes they have to be a part of a conjugated system. Penta-1,2,4-triene or vinylallene (VA) and hexa-1,2,4,5-tetraene or diallene (DA) are such cumulenic diene systems and they are the simplest and most typical members of this class of dienes. VA and DA have been chosen as dienes for the present investigation and these cumulenic dienes, besides being simple, show considerable regio- and stereo-chemical variety in their reaction and have been experimentally studied[5,6] extensively. This is the first theoretical report of the mechanism of their Diels–Alder reactions. Ethylene (ET), acrylonitrile (AN), maleic anhydride (MA), *p*-benzoquinone (BQ) and 1,4-naphthaquinone (NQ) have been chosen as dienophiles as experimental reports on their reactions with VA and DA are available.[1,5,6] For comparison, reactions of butadiene (BD) with the same dienophiles have been carried out. The typical reactions—those of BD, VA and DA with ET—have been studied at the semiempirical, *ab initio* and DFT levels of theory to observe the relative performance and reliability of predictions at these different levels. Other reactions have been studied at the semiempirical level only. The VA reaction with AN was investigated to observe the regioselectivity in VA reactions. In this paper, we focus on the following points: (*i*) the relative reactivity of cumulenic dienes over simple dienes; (*ii*) the role of strain factor associated with the cumulenic bond on the barrier and reaction energy; (*iii*) the reactivity trend when different dienophiles are reacted with cumulated dienes.

Computational details

AM1 and PM3 computations[10] have been done using the MOPAC 6.0[11] package implemented on a Micro Vax II and using MOPAC routines available in INSIGHT II implemented on a Silicon Graphics IRIS workstation. For selected sets of reactions, *ab initio* computations have been performed using the GAUSSIAN 94W program.[12] Reactant, product and transition state (TS) geometries of the above reactions have been optimized at the AM1, PM3 and HF/3-21G[13] levels and single point energy computations have been done on HF/3-21G geometries with 6-31G*[14] basis set at the DFT Becke3LYP level.[15] Baker's eigenvector following (EF) routine[16] has been extensively used for location of stationary points at the semiempirical level but both EF and Berny algorithms have been used in HF/3-21G computations. The EF procedure has been found to be far better both in terms of fast convergence and quality of the converged geometries.[9b,9c,17] As usual stationary points have been characterized through FORCE calculations/frequency analysis. Deformation energy analysis of the activation barrier has been done as detailed in our previous reports.[9c,17]

Results and discussion

Reaction scheme with TS geometries for the typical reactions—ET with BD, VA and DA—is presented in Fig. 1. AM1-(PM3)[HF/3-21G]{Becke3LYP/6-31G*//HF/3-21G} frontier orbital energy (FOE) gaps, q_{CT} values, reaction and activation energies for the above reactions are also given in Fig. 1. AM1(PM3) optimized TSs for the other reactions of VA and DA are presented in Fig. 2 and Fig. 3 respectively. As reactions of BD with the selected set of dienophiles have been carried out for comparing relative reactivity, the corresponding TSs are not

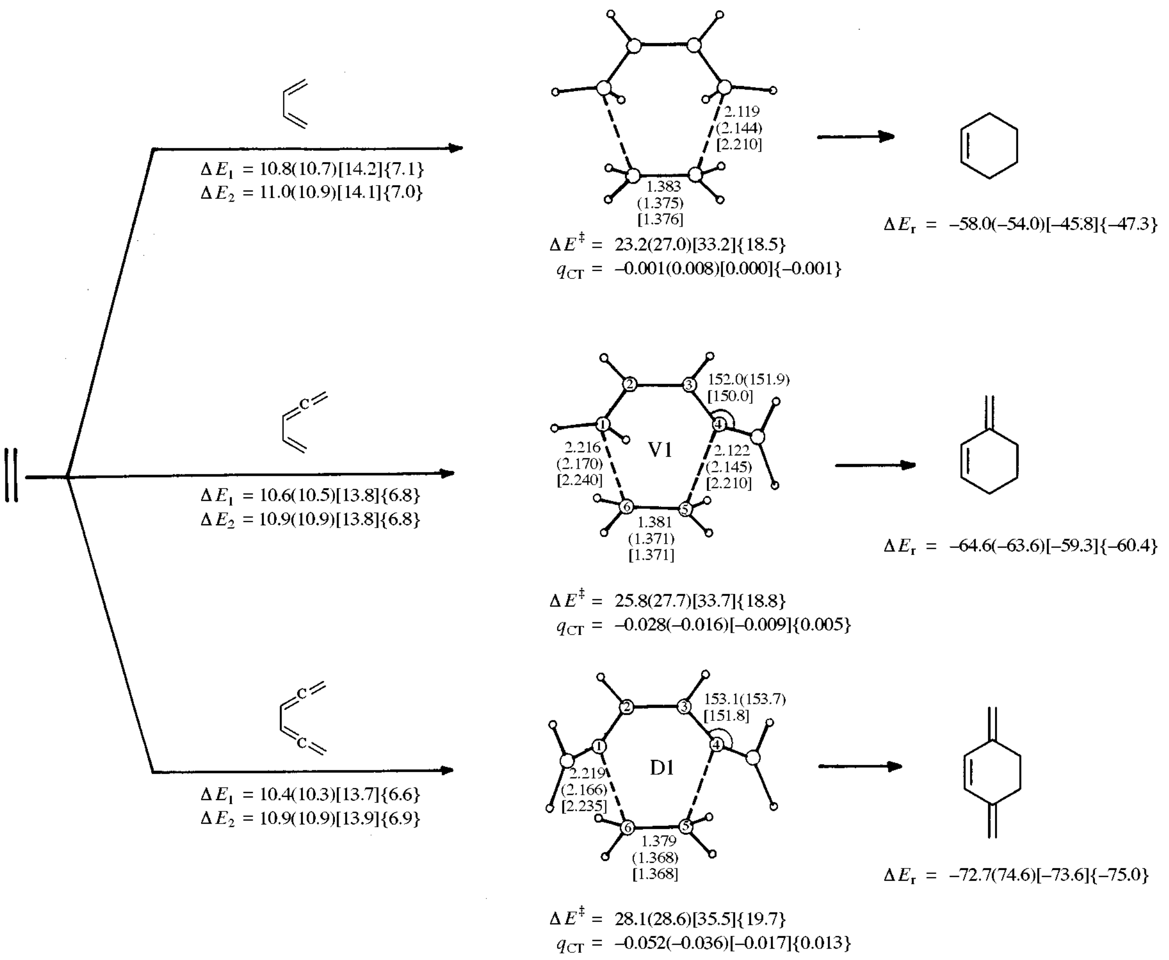

Fig. 1 TS geometries, frontier orbital energy gaps (eV),† q_{CT},‡ activation and reaction energies (kcal mol^{-1}) for the Diels–Alder reactions of ethylene with BD, VA and DA calculated from AM1(PM3) [HF/3-21G] {Becke3LYP/6-31G*//HF/3-21G} models

† $\Delta E_1 = E_{HOMO}$(diene) − E_{LUMO}(dienophile) and $\Delta E_2 = E_{LUMO}$(diene) − E_{HOMO}(dienophile); ‡ quantum of charge transfer from diene to dienophile at the TS

Table 1 Degree of asynchronicity (a) and selected geometric parameters from AM1(PM3) optimized TSs for the reactions involving VA and DA with various dienophiles

TS	a^a	$\theta_1{}^b$ (°)	$\theta_1{}^b$ (°)	$\varphi_1{}^b$ (°)	$\varphi_2{}^b$ (°)
V1	0.001 (0.006)	101.2 (101.4)	98.2 (98.6)	−3.4 (−0.9)	4.4 (4.7)
V2	0.040 (0.035)	101.4 (101.2)	96.3 (98.0)	2.5 (6.7)	6.2 (6.1)
V3	0.036 (0.030)	102.4 (102.6)	97.4 (98.2)	0.0 (−1.8)	4.8 (3.8)
V4	0.058 (0.033)	98.5 (99.8)	98.1 (97.2)	−16.4 (−14.1)	0.0 (1.0)
V5	0.042 (0.028)	99.2 (100.5)	100.0 (100.0)	−4.4 (0.9)	3.0 (4.8)
V6	0.022 (0.012)	97.7 (98.5)	95.7 (95.1)	−9.6 (−6.5)	1.7 (2.2)
V7	0.007 (0.001)	100.2 (101.4)	99.1 (99.7)	0.0 (0.0)	3.9 (4.2)
V8	0.019 (0.033)	98.3 (99.5)	96.3 (97.3)	−8.0 (−16.4)	1.8 (0.0)
V9	0.008 (0.004)	102.3 (102.3)	99.8 (99.7)	−5.5 (−1.6)	4.1 (4.0)
V10	0.018 (0.004)	98.5 (99.0)	96.3 (97.0)	−8.1 (−3.3)	1.8 (2.2)
V11	0.007 (0.004)	102.6 (102.5)	100.0 (99.9)	−6.0 (−1.6)	4.1 (4.0)
D1	0.000 (0.000)	99.9 (100.2)	99.9 (100.2)	0.0 (0.0)	0.0 (0.0)
D2	0.077 (0.050)	100.4 (99.4)	96.9 (98.7)	18.6 (17.3)	5.8 (4.4)
D3	0.048 (0.028)	102.0 (102.2)	97.4 (99.1)	0.0 (−4.0)	1.5 (0.0)
D4	0.000 (0.000)	95.7 (96.2)	95.7 (96.2)	0.0 (0.0)	0.0 (0.0)
D5	0.000 (0.000)	99.3 (100.8)	99.3 (100.8)	0.0 (0.0)	0.0 (0.0)
D6	0.000 (0.000)	96.3 (96.7)	96.3 (96.7)	0.0 (0.0)	0.0 (0.0)
D7	0.000 (0.000)	101.0 (101.3)	101.0 (101.3)	0.0 (0.0)	0.0 (0.0)
D8	0.000 (0.000)	96.4 (96.8)	96.4 (96.8)	0.0 (0.0)	0.0 (0.0)
D9	0.000 (0.000)	101.2 (101.5)	101.2 (101.5)	0.0 (0.0)	0.0 (0.0)

[a] $a = |a - b|/(a + b)$, a and b are the newly forming bonds. [b] $\theta_1 = \angle$C3–C4–C5; θ_2 = C1–C6–C5; φ_1 = C4–C5–C6–C1; φ_2 = C1–C2–C3–C4.

included here. The degree of asynchronicity and selected geometric parameters of TSs of VA and DA reactions are collected in Table 1. AM1(PM3) FOE gaps, q_{CT} values, activation and reaction energies, and deformation energies of dienes and dienophiles at the TSs for the reactions of BD, VA and DA with dienophiles *viz.* AN, MA, BQ and NQ are summarized in Table 2. The reactions considered in this paper can be discussed under two headings; first the typical reactions, the reactions of BD, VA and DA with ethylene, and secondly the reactions of the above dienes with other dienophiles, namely AN, MA, BQ and NQ. In the first section the relative reactivity of the cumulated dienes and the factors influencing their reactivity are discussed

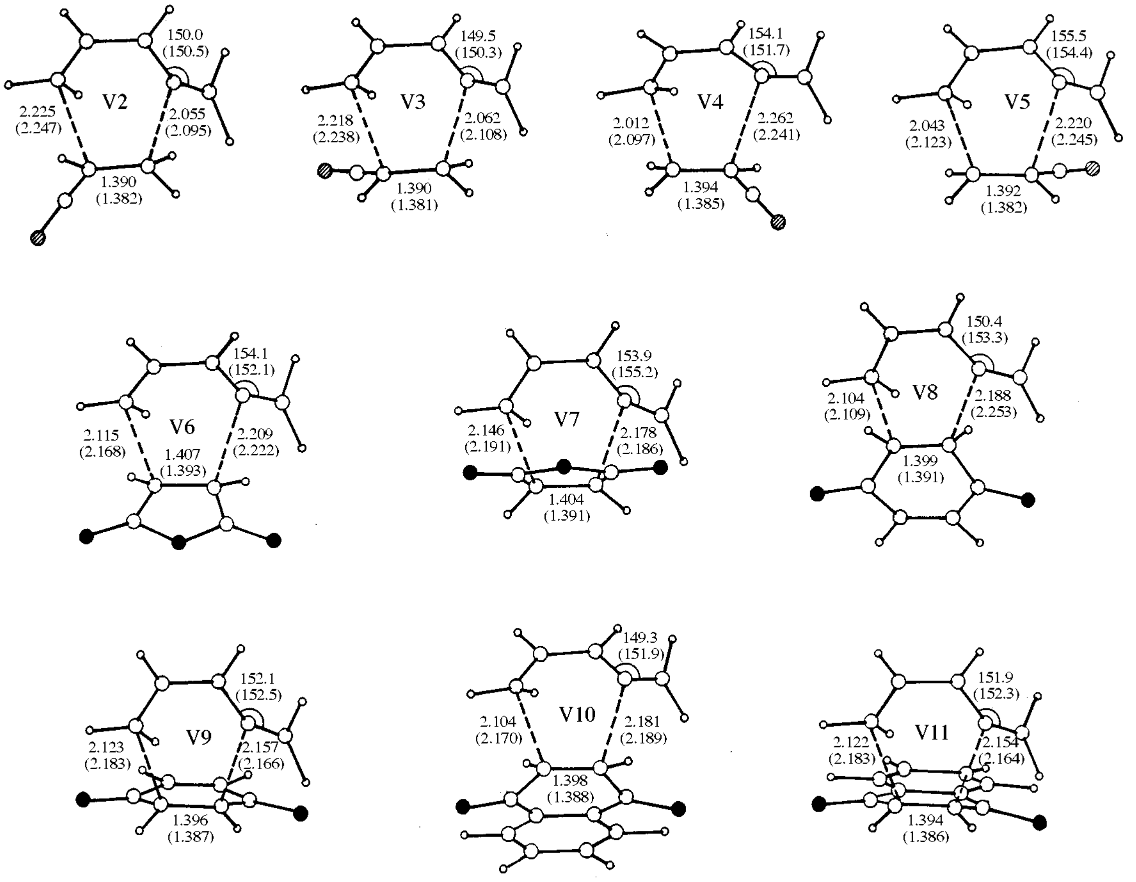

Fig. 2 AM1(PM3) optimized TSs for the reactions of VA with AN, MA, BQ and NQ

and in the subsequent section the regio- and stereo-selectivities of the reactions of VA and DA with various dienophiles are discussed.

Reactions of BD, VA and DA with ET

VA and DA are electron rich dienes compared to BD as their HOMO values indicate (Table 3) and the FOE gaps and q_{CT} values show that the title reactions are neutral electron demand reactions. If the computed activation energy for the BD–ET reaction is calibrated against the experimental value, 27.5 kcal mol^{-1} (1 cal = 4.184 J),[18] semiempirical methods seem to perform better while HF/3-21G calculation overestimate the barrier and the chosen DFT model underestimate it; at the semiempirical level the performance with PM3 is better. As for reaction energies HF/3-21G and DFT values are lower while AM1 and PM3 values are slightly higher and closer to each other. Activation energies presented in Fig. 1 predict that the diene reactivity decreases with cumulenic strain, BD being the most reactive and DA the least reactive among them and the reactivity differences are found to be small. At the same time reaction energy (Fig. 1) increases notably with cumulenic strain. This reminds us of our earlier observations[9b,c] that allene, a cumulenic dienophile, was found to be less reactive than the simple dienophile ET and allene reaction with BD was more exothermic than ET reaction with BD. It is therefore clear that Diels–Alder reactions of cumulenic dienes or dienophiles are kinetically less favoured and thermodynamically more favoured than those of simple dienes or dienophiles. But this is contrary to normal expectation[3] that cumulenic systems should be more reactive than the simple system on account of the strain associated with the cumulenic part. All these reactions are highly exothermic and have reactant-like TSs (Fig. 1) as one would normally expect, based on Hammond's postulate.[19] But the increase of activation energy with the increase in exothermicity observed in the present set of reactions appears to be a contradiction to the postulate.[19] The apparent differences between the expectation and our observation can be explained as follows. It is true that cumulenic systems are associated with strain and this strain will have its effect on the barrier if a considerable amount of it is released in the TS. The observation that the activation energy is not altered much but reaction energies differ considerably with increase in cumulenic strain indicates that much of the strain is released only in the later phase; that is when the reaction proceeds from TS to product. This can be well accounted for by the observation that all the TSs obtained for these reactions are 'early' or reactant-like retaining most of the strain. Deformation energy analysis provides a clue as to why the activation energy increases with cumulenic strain instead of decreasing as expected. The deformation energy of diene DE1 and dienophiles DE2 computed for the title reactions presented in Table 2 show that cumulenic dienes involve higher deformation energy and so also does ET when combined with cumulenic dienes and this should have increased the barrier. The increase in DE1 seems to be proportional to the cumulenic strain and DE2 also distorts to a greater degree when reacting with cumulenic diene.

The degrees of asynchronicity, selected geometric parameters listed in Table 1 and values presented in Fig. 1 show that BD and DA reactions have synchronous TSs owing to their symmetry while the TS of the VA reaction is asynchronous. The lengths of the newly forming bonds (C4 $\cdots$ C5 and C6 $\cdots$ C1) and breaking ethylenic π bond (C5–C6) in the TS of these reactions (Fig. 1) are comparable to those obtained for the prototype reaction.[7a–c] It can be noted from the TSs presented in Fig. 1 that with the increase of cumulenic strain the ethylenic π bond is cleaved to a lesser degree and correspondingly the forming bonds also develop to a smaller extent. Therefore from BD to DA, the corresponding TSs are more and more reactant-like. In VA reaction, the terminal carbon atom rehybridizes from sp^2 to sp^3 and the cumulenic carbon atom from sp to sp^2 and as a result the former pyramidalizes and the latter triangulates. It can also be understood from the fact that the cumulenic carbon

Table 2 Calculated AM1(PM3) frontier orbital energy gaps, quantum of charge transfer, activation and reaction energies, and deformation energy of diene (DE1) and dienophile (DE2) at the TS for the reactions of AN, MA, BQ and NQ with various dienes, BD, VA and DA

Dienophile	ΔE_1/eV	ΔE_2/eV	TS	q_{CT}	$\Delta E^{\ddagger}$/kcal mol^{-1}	DE1/kcal mol^{-1}	DE2/kcal mol^{-1}	ΔE_r/kcal mol^{-1}
BD reactions								
ET: 27.5[a]						15.9 (14.1)	9.9 (9.2)	
AN, *exo*	9.43 (10.80)	11.35 (11.01)		0.084 (0.074)	24.3 (27.9)	15.5 (14.1)	10.9 (10.4)	−52.1 (−48.8)
AN, *endo*				0.089 (0.078)	24.9 (28.4)	15.7 (14.2)	11.2 (10.8)	
MA, *exo*	7.76 (8.03)	12.51 (11.22)		0.194 (0.151)	20.7 (25.2)	13.5 (12.0)	10.1 (10.1)	−56.9 (−50.4)
MA, *endo*				0.199 (0.157)	22.0 (26.0)	13.8 (12.5)	10.9 (11.0)	
BQ, *exo*	7.64 (7.87)	11.36 (11.29)		0.161 (0.120)	23.9 (28.8)	16.0 (13.8)	10.8 (10.8)	−46.8 (−43.0)
BQ, *endo*				0.166 (0.127)	24.8 (29.7)	16.6 (14.5)	11.4 (11.6)	
NQ, *exo*	7.83 (8.05)	10.74 (10.66)		0.156 (0.112)	24.4 (28.8)	16.0 (13.9)	11.0 (10.6)	−46.2 (−42.5)
NQ, *endo*				0.163 (0.121)	25.5 (30.0)	16.7 (14.5)	11.8 (11.6)	
VA reactions								
ET						17.1 (15.7)	12.8 (11.3)	
AN, *R*1-*exo*	9.20 (9.06)	11.25 (11.14)	V2	0.056 (0.049)	26.5 (28.6)	17.0 (15.9)	10.1 (9.3)	−58.6 (−58.1)
AN, *R*1-*endo*			V3	0.059 (0.053)	27.0 (28.9)	17.4 (16.1)	10.4 (9.5)	
AN, *R*2-*exo*			V4	0.066 (0.051)	28.5 (30.6)	16.9 (16.4)	11.7 (10.5)	−60.0 (−59.7)
AN, *R*2-*endo*			V5	0.068 (0.057)	27.2 (29.1)	16.5 (15.4)	11.0 (9.8)	
MA, *exo*	7.53 (7.70)	12.41 (11.11)	V6	0.182 (0.133)	22.9 (27.8)	15.2 (14.6)	10.9 (10.3)	−66.5 (−62.3)
MA, *endo*			V7	0.179 (0.139)	24.0 (27.0)	15.3 (13.8)	11.2 (10.1)	
BQ, *exo*	7.42 (7.54)	11.26 (11.17)	V8	0.137 (0.114)	28.8 (33.3)	18.5 (16.5)	12.1 (10.7)	−52.8 (−52.9)
BQ, *endo*			V9	0.140 (0.104)	27.9 (30.6)	17.7 (15.8)	11.5 (10.5)	
NQ, *exo*	7.60 (7.72)	10.64 (10.54)	V10	0.131 (0.085)	28.4 (32.3)	18.6 (16.9)	12.3 (10.9)	−52.2 (−52.5)
NQ, *endo*			V11	0.136 (0.098)	28.6 (30.9)	18.0 (15.9)	11.7 (10.5)	
DA reactions								
ET						18.7 (17.0)	12.6 (10.4)	
AN, *exo*	9.02 (8.85)	11.81 (11.12)	D2	0.041 (0.030)	30.8 (31.4)	18.2 (17.9)	10.9 (9.8)	−66.5 (−68.9)
AN, *endo*			D3	0.043 (0.036)	29.6 (29.9)	18.5 (16.9)	10.4 (8.8)	
MA, *exo*	7.36 (7.49)	12.35 (11.09)	D4	0.164 (0.114)	26.9 (30.8)	17.8 (17.1)	12.3 (10.9)	−74.6 (−73.7)
MA, *endo*			D5	0.160 (0.124)	27.1 (28.3)	17.0 (15.0)	11.5 (9.4)	
BQ, *exo*	7.24 (7.33)	11.20 (11.15)	D6	0.108 (0.068)	34.2 (36.0)	21.4 (19.7)	13.4 (11.7)	−59.3 (−62.0)
BQ, *endo*			D7	0.115 (0.086)	31.4 (31.9)	19.5 (17.0)	11.7 (9.7)	
NQ, *exo*	7.43 (7.50)	10.58 (10.52)	D8	0.102 (0.052)	35.0 (36.0)	21.7 (19.7)	13.5 (10.5)	−58.5 (−61.5)
NQ, endo			D9	0.111 (0.080)	32.0 (32.0)	19.8 (17.1)	12.0 (9.7)	

[a] Experimental activation barrier, ref. 18.

Table 3 *E*(HOMO) value of BD, VA and DA[a]

Diene	E(HOMO)/eV
BD	−9.375 (−9.574) [−9.121] {−6.449}
VA	−9.150 (−9.247) [−8.749] {−6.2150}
DA	−8.974 (−9.033) [−8.661] {−6.041}

[a] For use of ( ), [ ], { }, see Fig. 1 caption.

is more nucleophilic[1] than the terminal carbon and hence the former carbon reacts faster than the latter one to give a strong new σ bond (C4 · · · C5). In the DA reaction, both diene carbon atoms that form σ bonds during the reaction are cumulenic carbon atoms and are sp hybridized, and they rehybridize from sp to sp^2. Therefore, both carbon atoms undergo triangulation. This is revealed by the corresponding angles shown in the TSs V1 and D1 presented in Fig. 1 and these values indicate that the bending is approximately 30°. Very low values of φ_1 and φ_2 suggest that there is not much twist from the C_s plane and distortion from planarity of the diene. There is almost 10° change in the glide angles θ_1 and θ_2 of V1 and D1 from the ideal value 90° and this can be attributed to the repulsion by the cumulenic bond outside the diene part and ET.

Reactions of VA and DA with AN, MA, BQ and NQ

The reactions of a set of electron deficient dienophiles *viz*. AN, MA, BQ and NQ are considered here. FOE gaps and q_{CT} values presented in Table 2 for the reactions of these dienophiles with BD, VA and DA predict that they are all normal electron demand reactions and MA is the most reactive dienophile in the set as expected. The trend in diene reactivity and the relative exothermicity of these reactions (Table 2) for any dienophile in the set is as expected and can be explained as above. Therefore the discussion will focus on the regio- and stereo-selectivity of the reactions through computed activation energy. The TSs of the reactions of MA, BQ and NQ with DA are synchronous and those of VA are asynchronous for the aforementioned reactions. But TSs of AN with both dienes are asynchronous on account of the asymmetry of the dienophile. Selected geometric parameters listed in Table 1 indicate that the glide angles θ_1 and θ_2 are slightly greater while the twist angle φ_1 is lower in *endo* TSs than in *exo* TSs. The bending angles of allene at the TS shown in Figs. 2 and 3 are found to be in the range 148–158° (150–155°). The extent of triangulation of the cumulenic carbon atoms at the TS found in the structures V2–V11 and D2–D9 is almost the same. The twist angle φ_1 and distortion of the diene (φ_2) at the TS in DA reaction are found to be nearly zero. Small changes are noted in the TSs of VA reactions and this may be due to a lack of symmetry in VA.

Among the reactions with various dienophiles considered here, that of MA is found to be the most favoured kinetically as well as thermodynamically and this is in accordance with earlier observations.[20] AN differs from other dienophiles employed here in that two regioselective products 5-cyano-3-methylenecyclohexene and 4-cyano-3-methylenecyclohexene are possible and there are four regioselective TSs (V2–V5) obtained; TSs V2 and V3 lead to the 5-cyano derivative while V4 and V5 lead to 4-cyano derivative. Computed activation energies predict that the formation of the former regioselective product is relatively favoured over the latter and is in good agreement with the experimental observations.[1] In all these reactions, both *endo* and *exo* selective TSs leading to a single product are possible[1,5,6] and the *endo* TS is generally stabilized by secondary orbital interaction and should therefore be preferred.[20] Both AM1 and PM3 barriers show a clear preference of *exo* TS in BD reactions

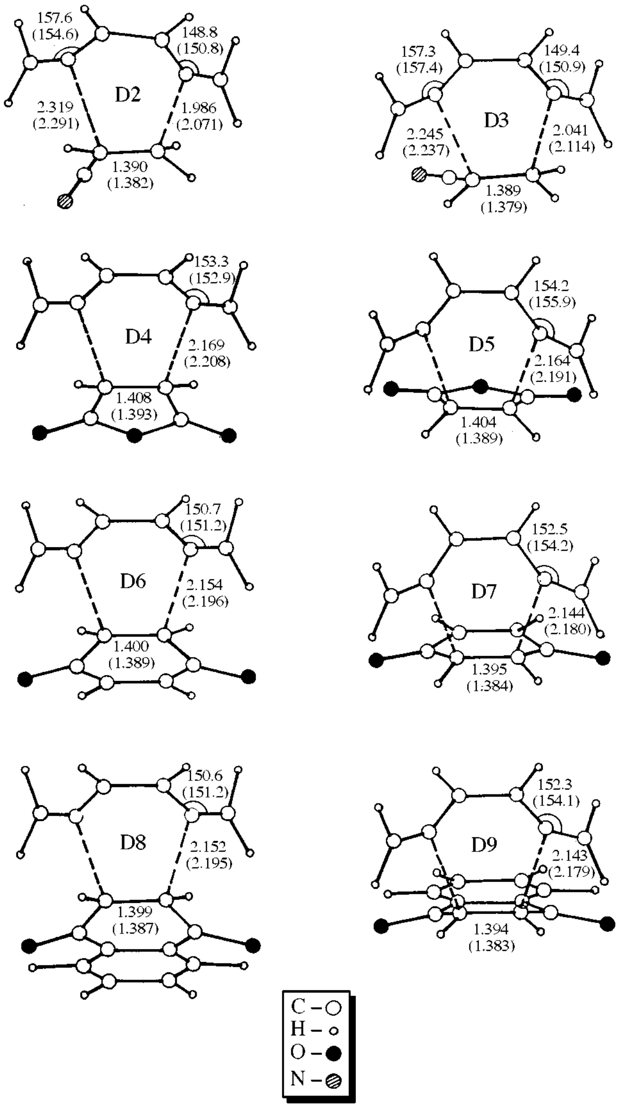

Fig. 3 Computed AM1(PM3) TSs for the reactions of DA with AN, MA, BQ and NQ

and *endo* preference in DA reactions and mixed trend in VA reactions. Here, PM3 seems to predict correctly the *endo* preference in each reaction compared to AM1. Deformation energy analysis shows that both diene and dienophile deform to different extents at the *exo* and *endo* TSs, and DE1 and DE2 values are relatively low in the majority of the reactions of VA and DA considered here for the *endo* approach. The relatively higher positive value of q_{CT} (Table 2) for *endo* TS in the reactions considered over the *exo* TS shows further evidence for the *endo* preference in the reaction. Computed activation energies for the BQ and NQ reactions are almost equal but experimentally[19] BQ is observed to be slightly more reactive than NQ as a dienophile.

Conclusions

AM1 and PM3 computations reveal that VA and DA undergo Diels–Alder reactions with a host of dienophiles ET, AN, MA, BQ and NQ through a concerted process. The geometries of the TSs show that in the TS the reacting cumulenic carbons rehybridize from sp to sp^2 resulting in triangulation and the reacting terminal carbon atom rehybridizes from sp^2 to sp^3 leading to pyramidalization. These cumulated dienes are found to be slightly less reactive than simple dienes and the reactivity decreases with increase of cumulenic strain instead of increasing as anticipated. This apparently contradictory trend is due to the fact that the cumulenic strain is not fully released in the TS. Instead it appears to get released in the later phase of the reaction, when the TS is converted into the product. It is for this reason the exothermicity of these reactions increases with cumulenic strain of the diene. While *ab initio* calculations at the HF/3-21G level overestimate the barrier DFT calculations with the Becke3LYP functional underestimate it. Deformation energy analysis shows that cumulated dienes have to undergo increased deformation compared to a simple diene (BD) during the formation of the TS and even a simple dienophile like ET deforms to a relatively greater extent while reacting with cumulated dienes. In the set of dienophiles chosen MA is predicted to be the most reactive as expected. In the reaction of VA with AN, there are two regioselective products possible and 5-cyano derivative is preferentially formed. In all the reactions, two stereoselective TSs are possible and the *endo* TSs are reasonably favoured over *exo* TSs.

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