Allene and fluoroallenes as dienophiles in Diels–Alder reactions: an AM1 and PM3 study

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Transition structures and energetics of Diels–Alder reactions of allene with cyclopentadiene and hexachlorocyclopentadiene, and fluoroallenes with cyclopentadiene and furan have been investigated using semiempirical MO methods at AM1 and PM3 levels. Allene and fluoroallenes react through an asynchronous transition structure in which the terminal carbon atom involved in the reaction pyramidalizes and the central carbon atom triangulates and this deformation accounts for almost half the reaction barrier. Allene is found to be a less reactive dienophile compared to ethylene, contrary to expectations, and its reactivity enhances with fluorine substitution up to 1,1-difluoroallene and declines on further substitution of fluorine. Tetrachloroallene is found to be less reactive than allene itself. The reactivity of furan in such cumulene reactions is found to be almost the same as that of cyclopentadiene. While PM3 predictions in certain cases are not reliable AM1 reaction barriers explain reasonably the reactivities and stereochemical preferences of the above reactions.

The Diels–Alder addition of allenes[1–4] provides an attractive approach to the synthesis of various cycloadducts that are useful building blocks of terpenoid natural products.[5] Allenes are cumulated dienes that have a significant 'strain' and thus some enhancement of reactivity in cycloaddition is expected owing to this strain.[4] Cycloaddition reactions of fluoroallenes have been the subject of wide interest since fluorine, as one of the least sterically demanding and most electronically interacting substituent, offers various advantages in probing the mechanism of these reactions. The σ-acceptor and π-donor effects of fluorine on the two allenic π bonds in fluoroallenes is responsible for its directing influence in cycloadditions.[4] It is for this reason that fluoroallenes in cycloaddition reactions have been the subject of several experimental[6] and theoretical investigations.[7–9] While [4 + 2] cycloadditions of fluoroallenes are concerted and FMO controlled,[7a] [2 + 2] cycloadditions are step-wise and thermodynamically controlled. Therefore, they have different regio and stereochemical preferences. Dolbier and co-workers[6] have proposed that the Diels–Alder reactions of fluoroallenes are regiospecific and LUMO dienophile controlled, with reactions occuring only at the C2–C3 π bond.

Extensive investigations on the mechanisms of various Diels–Alder reactions have been performed at different levels of theory.[10,11] Allenes, however, have very rarely been employed[7–9] as addends in Diels–Alder reactions in spite of the fact that cycloadditions of allenes are experimentally well known.[1,4] The reactivity of fluoroallenes in Diels–Alder reactions has been predicted using FMO theory by Dixon and Smart.[8] Rastelli and co-workers[9a] have performed *ab initio* calculations very recently in order to study the mechanisms of 1,3-dipolar cycloadditions of various fluoroallenes with a set of dipoles and also Diels–Alder additions of monofluoroallene with cyclopentadiene and furan. A systematic mechanistic study of [4 + 2] cycloadditions of butadiene with allene and fluoroallenes has been carried out by us using AM1 and PM3 methods[9b] and the reactions showed how fluorine enhances the reactivity of allene. In the present investigation, the reactivity of simple allene with an electron rich and an electron deficient diene, namely cyclopentadiene and hexachlorocyclopentadiene (HCP), has been studied through their reaction mechanism. Further, reactions of fluoroallenes *viz.* monofluoroallene (MFA), 1,1-difluoroallene (DFA), trifluoroallene (TFA), tetrafluoroallene (TTFA) and tetrachloroallene (TTCA) with cyclopentadiene have also been taken up with a view to studying the effect of fluorine and chlorine substitution on the reaction. Though no experimental reports on the reaction of furan with simple allene is known, furan reactions with some substituted allenes have been performed.[2–4] Therefore, in the present work, reactions of furan with certain fluoroallenes have been investigated with a view to comparing the reactivity with those of cyclopentadiene reactions.

Method of computation

All calculations were performed at a semiempirical level with AM1 and PM3 hamiltonians[12] using the MOPAC 6.0[13] program implemented in Micro Vax II and in Silicon Graphics workstations. Baker's Eigenvector Following (EF)[14] routine was used for fully optimizing the geometries of reactants and products. The gradient norm obtained in this procedure is significantly better than the BFGS algorithm. Transition structures (TS) were optimized using the above routine with a TS option. Force field calculations were performed to characterize the stationary points. Equilibrium structures were found to have all positive eigenvalues and first-order saddle points (TSs) were found have only one negative eigenvalue in the diagonalized Hessian matrix. The eigenvectors associated with the negative eigenvalue corresponded to the reaction coordinate.

Results and discussion

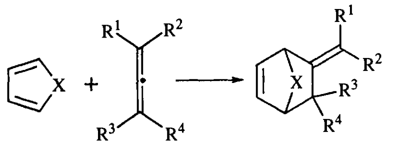
The reactions taken up for the investigation are shown in Fig. 1. Fig. 2 collects the reactions of allene with cyclopentadiene and HCP, and their respective TSs, activation energies and relevant data. Selected geometrical parameters of TSs of Diels–Alder reactions of cyclopentadiene with MFA, DFA, TFA, TTFA and TTCA and those of furan with allene, MFA and DFA are presented in Fig. 3. Computed deformation energies of dienes and dienophiles in the Diels–Alder reactions of allene with cyclopentadiene and HCP, and cyclopentadiene with ethylene, are depicted in Table 1. Calculated frontier orbital energy (FOE) gaps (ΔE_1 and ΔE_2), activation and reaction energies ($\Delta E^{\ddagger}$ and ΔE_r), quantum of charge transfer (q_{CT}) and degree of asynchronicity (α) at the TS of various reactions investigated here are collected in Table 2.

Reactions of allene

Allene is a new kind of dienophile with cumulated double bonds. It is an electron-rich dienophile whose electron-donating capacity matches that of propene. Allene is also referred to as propadiene and is considered to be an unsymmetrically substituted ethylene. Therefore, naturally, a Diels–Alder reaction involving allene as a dienophile should involve an asynchronous TS. Asynchronicity at the TS is due to different rates of maturation of newly forming σ-bonds during the reaction. Allene is relatively electron rich compared with ethylene and therefore, in a normal electron demand reaction, should be less reactive. However, Dolbier[4] anticipates that allene should be relatively more reactive than ethylene on account of the strain associated with the double bond in the cumulene. Pledger[1d] reported that allene required forcing conditions to add to cyclopentadiene to give the adduct in moderate yield. From the above experimental observation one can conclude that the electronic factor overcompensates the strain factor making allene a poor dienophile over ethylene. Further, geometric factors, as will be shown later, make allene less reactive than ethylene. This is correctly predicted by AM1 (PM3) calculations. The energy barrier for the allene reaction (Fig. 2) is greater than for the ethylene reaction (Table 2).

Table 1 Calculated AM1 (PM3) deformation energies (kcal mol^{-1}) of diene (DE$_{\mathrm{I}}$) and dienophile (DE$_{\mathrm{II}}$) in certain Diels–Alder reactions

Reaction	DE$_{\mathrm{I}}$	DE$_{\mathrm{II}}$
Cyclopentadiene–ethylene	16.9 (16.1)	9.9 (8.9)
Cyclopentadiene–allene	14.5 (13.9)	14.5 (13.2)
HCP–allene	20.2 (16.5)	14.7 (12.8)



	R^1	R^2	R^3	R^4	LUMO (eV)
X = CH$_2$, O allene	H	H	H	H	4.39
X = CH$_2$, O MFA	F	H	H	H	3.40
X = CH$_2$, O DFA	F	F	H	H	3.04
X = CH$_2$ TFA	F	F	F	H	3.31
X = CH$_2$ TTFA	F	F	F	F	3.73
X = CH$_2$ TTCA	Cl	Cl	Cl	Cl	—

Fig. 1 Reaction schemes and [DZ + P][8] LUMO values of the dienophile

Allene undergoes [4 + 2] cycloaddition with cyclopentadiene and HCP and reacts through a concerted asynchronous TS as expected. The asynchronicity is due to the fact that one of the reacting carbon atoms in allene is sp^2 hybridized and the other sp hybridized; the former undergoes pyramidalization and the latter triangulation (negative bending) during reaction. Reactions involving cyclopentadiene are normal electron demand reactions as can be seen from the FOE gaps and q_{CT} values presented in Fig. 2 while that of HCP is an inverse electron demand reaction. It is interesting to note from Fig. 2 that in the cyclopentadiene reaction the r2 bond is formed first or is shorter than r1 but in the HCP reaction the r1 bond is found to be shorter than r2. This shows that in the former reaction, the central carbon atom (C2) of allene is more reactive than the terminal carbon atom (C3) while it is the reverse in the HCP reaction. It is understandable from the fact that the central carbon atom in allene is an electrophilic centre while the terminal carbon is a nucleophilic centre.[8] In the cyclopentadiene and furan reactions, allene acts as an electrophile and hence C2 reacts readily over C3 but in the inverse electron demand HCP reaction, allene acts as a nucleophile and the nucleophilic centre in allene C3 reacts first. The *ab initio* charges on the central and terminal carbon atoms of allene computed at the [DZ + P] level[8] are, respectively, + 0.12 and −0.13 and computed AM1 (PM3) charges on C2 and C3 atoms of allene are, respectively, −0.15 (−0.17) and −0.19 (−0.11). It should be noted that while *ab initio* predictions establish clearly the electrophilic nature of the central carbon atom and the nucleophilic nature of the terminal carbon atom, semiempirical methods show the central carbon atom to be relatively electron deficient compared with the terminal carbon atom. TS geometries of such cumulene reactions have some general features and a discussion on the geometric features of TSs is given in a later section.

The deformation energies[15] of diene and dienophile have been calculated and in the light of these, contributing factors to the reaction barriers are analysed. For comparison the above

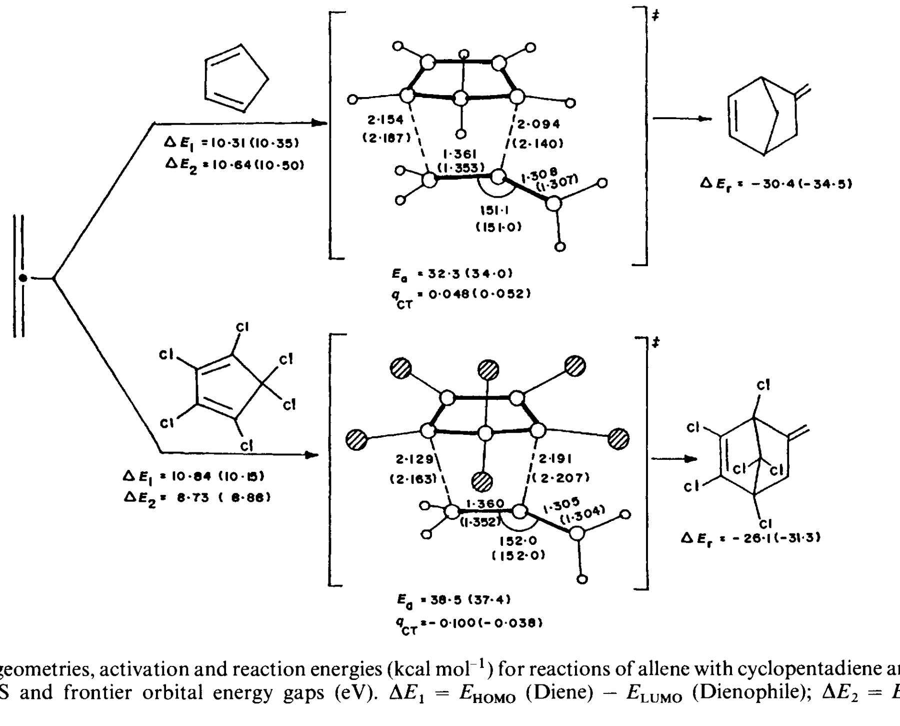


Fig. 2 AM1 (PM3) TS geometries, activation and reaction energies (kcal mol^{-1}) for reactions of allene with cyclopentadiene and HCP, and quantum of charge transfer at TS and frontier orbital energy gaps (eV). $\Delta E_1 = E_{\mathrm{HOMO}}$ (Diene) − E_{LUMO} (Dienophile); $\Delta E_2 = E_{\mathrm{HOMO}}$ (Dienophile) − E_{LUMO} (Diene)

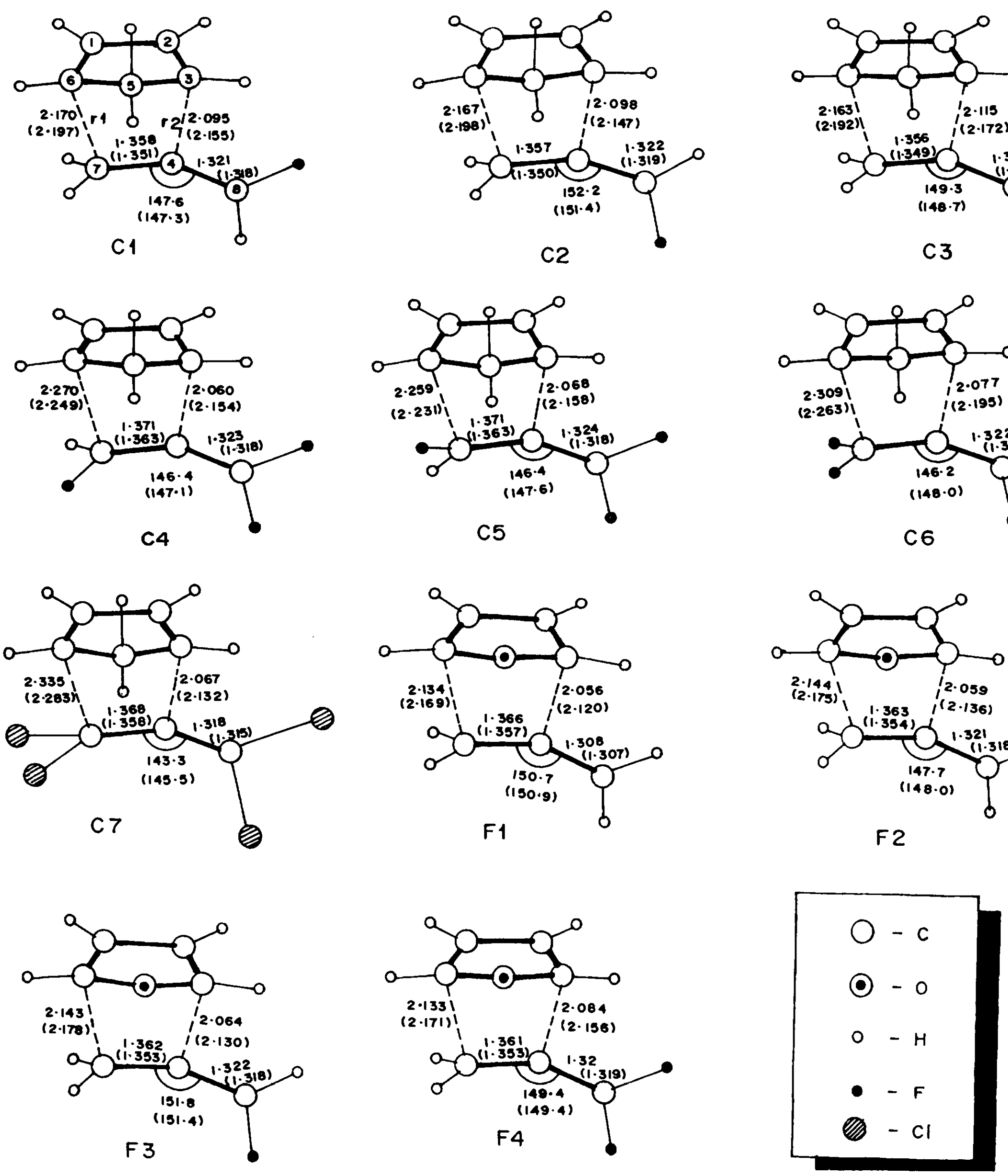


Fig. 3 Computed TSs for the reactions of cyclopentadiene with fluoroallenes and TTCA, and furan with allene, MFA and DFA. Selected geometric parameters from AM1 (PM3) optimized structures

Table 2 Calculated AM1 (PM3) frontier orbital energy gaps (eV), activation and reaction energies (kcal mol^{-1}) and quantum of charge transfer of the Diels–Alder reactions involving cyclopentadiene (CP) and furan (FU) as dienes and fluoroallenes as dienophiles, TS numbers as referred to in Fig. 3

Dienophile	TS	ΔE_1	ΔE_2	q_{CT}[a]	$\Delta E^‡$	ΔE_r	α[b]
CP reactions							
ethylene [22.5][c]		10.52 (10.46)	11.03 (10.97)	0.001 (0.011)	28.5 (32.1)	−26.0 (−26.4)	
MFA, *syn* F	C1	9.86 (9.88)	10.33 (10.42)	0.094 (0.095)	30.2 (32.3)	−35.0 (−37.2)	0.018 (0.010)
MFA, *anti* F	C2			0.079 (0.082)	30.6 (32.0)	−35.1 (−37.5)	0.016 (0.012)
DFA	C3	9.41 (9.42)	10.39 (10.54)	0.126 (0.121)	29.0 (30.7)	−37.1 (−38.8)	0.011 (0.005)
TFA, *exo* F	C4	9.11 (9.06)	11.01 (11.23)	0.139 (0.144)	30.1 (30.6)	−29.3 (−38.1)	0.048 (0.022)
TFA, *endo* F	C5			0.140 (0.141)	30.8 (30.8)	−32.6 (−37.7)	0.044 (0.014)
TTFA	C6	8.74 (8.72)	11.53 (11.77)	0.182 (0.182)	31.7 (30.1)	−31.3 (−40.2)	0.053 (0.015)
TTCA	C7	8.53 (8.88)	10.98 (10.19)	0.217 (0.160)	36.6 (35.3)	−26.7 (−32.0)	0.061 (0.034)
FU reactions							
allene	F1	10.55 (10.49)	10.88 (10.79)	0.064 (0.070)	32.1 (33.5)	−21.1 (−22.8)	0.019 (0.011)
MFA, *syn* F	F2	10.10 (10.02)	10.57 (10.70)	0.110 (0.113)	29.8 (31.4)	−23.6 (−25.3)	0.020 (0.009)
MFA, *anti* F	F3			0.093 (0.099)	30.4 (31.6)	−23.7 (−25.5)	0.019 (0.011)
DFA	F4	9.65 (9.56)	10.63 (10.82)	0.141 (0.138)	28.6 (29.9)	−25.4 (−26.6)	0.012 (0.003)

[a] Quantum of charge transfer at TS from diene to dienophile. [b] Degree of asynchronicity as calculated from |r1 − r2|/(r1 + r2). [c] Experimentally observed barrier, ref. 17.

calculation for cyclopentadiene–ethylene reaction has also been performed (Table 1). The deformation energy of diene–dienophile is calculated as the difference between the energy of the diene–dienophile calculated by the single point method at the geometry of this fragment in the TS and the energy of their equilibrium structures. In this calculation we have taken into account the pyramidalization at the terminal carbon atom and the triangulation at the central carbon and other associated changes in the geometry of dienophile at the TS and consequent deformation of the diene at the TS. The deformation energy of diene (DE_I) of cyclopentadiene and HCP shows that HCP requires slightly more energy for deformation and this leads to a higher activation energy for the HCP reaction. The deformation energy of dienophile (DE_{II}) suggests that ethylene involves a lower deformation energy than allene, in spite of the strain factor in allene referred by Dolbier, and hence the ethylene reaction should have a smaller reaction barrier. Further, allene being electron rich compared with ethylene, is expected to be less reactive than ethylene in a normal electron demand reaction. The reaction barriers of the cyclopentadiene–ethylene reactions presented in Table 2, and cyclopentadiene–allene and HCP–allene reactions presented in Fig. 2 confirm this. The cyclopentadiene–allene reaction is more exothermic than the cyclopentadiene–ethylene reaction whereas the reaction energy of the HCP–allene reaction is comparable to that of the typical cyclopentadiene–ethylene reaction.

Reactions of fluoroallenes

While simple allene is found to be less reactive in normal Diels–Alder reactions, fluoroallenes are much more reactive. This is due to the fact that allene, an electron-rich dienophile, becomes more electron deficient when halogen, OR, COR, CO_2R, SOR and SO_2R (R = H, alkyl and aryl) substitutions are made.[2–4] Halogens especially, being σ-acceptors and π-donor, selectively enhance the reactivity of one of the two cumulated double bonds in allene towards [4 + 2] cycloaddition. This is one of the reasons for which halogens, fluorine in particular, are used as substituents in probing the mechanistic subtleties of Diels–Alder reactions. Among halogens, fluorine has the highest electronegativity and, at the same time, is the best π-donor because of the good match of p orbitals with those of carbon.

Allene has two double bonds that are contiguous but orthogonal to each other. When fluorine substitution is made on allene the electron-donating and -withdrawing characteristics of fluorine operate in different ways on the two double bonds. In MFA and DFA the C1–C2 double bond remains almost unaltered due to the equal but opposing effects of the electron-donating properties of the fluorine lone pairs and inductive withdrawal of fluorine through σ bonds. In contrast, the π and π* orbitals of the C2–C3 double bond are significantly lowered by inductive withdrawal and negative hyperconjugation.[6] In TFA and TTFA, further fluorine substitution at C3 increases the C2–C3 π* level hence the reactivity of TFA and TTFA is expected to decrease down the series. The *ab initio* LUMO energy values predict this trend well as can be noted from Fig. 1.

In our earlier communication [9b] on [4 + 2] cycloadditions of fluoroallenes with butadiene it was shown, based on computed reaction barriers, that the less fluorinated double bond participates preferentially in the cycloaddition. Therefore, we have computed here TSs for reactions in which the less fluorinated double bond is involved. The computed TS geometries for a set of reactions presented in Fig. 3 show certain general features. The torsion angle 3–4–7–6 is typically almost zero throughout and the gliding angles 2–3–4 and 1–6–7 fall in the range 93–96° (94–96°). The fact that there is not much deviation in the above angles from typical reaction cases indicates that steric strain is less at the TS. This is possible because fluorine is sterically less demanding, and cyclopentadiene and furan maintain some rigidity. The newly forming bond r2 at the TS is shorter than r1 leading to asynchronicity and this indicates the greater reactivity of central carbon atom of the allene than the terminal carbon atom. From the degrees of asynchronicity (α) listed in Table 2 for these reactions one can observe that the trend in asynchronicity parallels the trend in reaction barrier. The fluorinated double bond remains undisturbed throughout whereas the less fluorinated double bond shows elongation, indicative of conversion to a σ-bond during the reaction. The reacting terminal sp^2 hybridized carbon atom C3 of fluoroallenes undergoes pyramidalization and the sp-hybridized central carbon atom C2 undergoes triangulation. The distorted angle 7–4–8 in in the TSs fall in the range 143–152° (145–151°). This is due to the fact that during the reaction C3 and C2 carbon atoms of allene rehybridize; the former from sp^2 to sp^3 and the latter from sp to sp^2.

From the FOE gaps ΔE_1 and ΔE_2 listed in Table 2, the reactions of fluoroallenes and TTCA with cyclopentadiene, and furan with MFA and DFA can be classified as normal electron demand types—the diene acting as the electron donor and the dienophile as the electron acceptor. Progressive substitution of fluorine increases the electron deficiency in allene and is therefore expected to increase the reactivity. However, fluorine substitution beyond DFA appears to have the opposite effect since the third fluorine atom at C3 destabilizes C2–C3 π* levels. The FOE gaps listed in Table 2 for these dienophiles show a normal electron demand with continuous decrease in FOE gaps with fluorine substitution. This unexpected trend in prediction is due to a poor estimation of the FMO energy values by semiempirical methods compared to *ab initio* methods. As a consequence a similar trend is predicted by AM1 (PM3) in q_{CT} at the TS. q_{CT} is positive as expected for a normal electron demand reaction and its increases from allene to DFA is understandable but a further increase from DFA to TTFA is unreasonable.

Computed AM1 (PM3) activation energies for reactions of various fluoroallenes with cyclopentadiene and furan (Table 2) are in good agreement with *ab initio* FMO predictions [8] and the available experimental observations;[6] fluorine substitution increases the reactivity up to DFA and further fluorine substitution decreases the reactivity. Though no experimental reports on TFA reactions are available they have been performed with a view to observing the trend on increasing fluorine substitution. AM1 (PM3) barriers have been calculated for cyclopentadiene–TTFA and cyclopentadiene–TTCA reactions, since experimental reports on these reactions are available.[1a–c] While the cyclopentadiene–allene reaction requires forcing conditions to react, the cyclopentadiene–TTFA and cyclopentadiene–TTCA reactions are known to react under less vigorous conditions in quantitative yield. The Semiempirical barrier for the TTFA reaction is slightly lower than that of the allene reaction but the barrier for the TTCA reaction is higher by 4.9 (5.2) kcal/mol^{-1}. TTCA is less reactive than TTFA and this is on account of the increased π electron-donating capacity of chlorine over fluorine. Chlorine, being less electronegative and more electron donating than fluorine, destabilizes the LUMO relatively to a greater extent than fluorine and this in turn makes TTCA less reactive than TTFA. Among these halocumulenes DFA is the most reactive of allenes and its reaction is the most exothermic. Experimental observations in certain reports[2–4] indicate that cyclopentadiene reacts more readily than furan with some substituted allenes, and this has been predicted well by Rastelli and co-workers through their *ab initio* reaction barriers [9a] for MFA reactions with these dienes. The AM1 (PM3) calculations predict that the reaction barrier of furan reactions is found to be almost the same as that of cyclopentadiene reactions (Table 2).

Rastelli and co-workers have recently reported *ab initio* barriers for the reactions of MFA with cyclopentadiene and furan alone. While their HF/3–21G barriers are comparable to AM1 (PM3) barriers presented in Table 2, those calculated at the correlated level are very low. *Ab initio* barriers[9a] explain well the preferred *syn* selectivity in both furan and cyclopentadiene reactions. Though the AM1 (PM3) barriers appear to predict *syn* selectivity in tune with experimental observations and *ab initio* predictions, the differences in the barrier (*syn* and *anti*) are too small (Table 2). For cyclopentadiene the reaction with TFA barriers indicates a slight preference of *exo* products over *endo*.

Conclusions

The mechanism of the Diels–Alder reactions of allene and fluoroallenes with cyclopentadiene and furan, cyclopentadiene–TTCA and HCP–allene reactions have been studied by AM1 and PM3 methods. The reactivities and stereochemical preferences of these reactions have been predicted based on the computed TSs and activation energies. FOE gaps and q_{CT} at the TS predict that reactions of cyclopentadiene and furan with allene and fluoroallenes are of a normal electron demand type, and that of HCP with allene an inverse electron demand reaction. Allene with cyclopentadiene and furan appears to be a nearly normal electron demand reaction. The computed TSs provide the following insight. In the [4 + 2] cycloaddition, the allene acts as an electron rich unsymmetrical alkene reacting through an asynchronous TS. In the normal electron demand reactions, r1 is found to be greater than r2 at the TS while it is reverse in the inverse electron demand reaction. This is due to the differing reactivity of central and terminal carbon atoms of dienophilic allene in the above reactions. In this reaction the terminal carbon atom pyramidalizes ($sp^2 \longrightarrow sp^3$) and the central carbon atom triangulates ($sp \longrightarrow sp^2$). On account of this relatively more deformation energy is required for allene than ethylene and hence it is found to be less reactive than ethylene.

The computed activation barriers indicate that: (i) AM1 (PM3) barriers are reliable to the extent that reactivities and selectivities in a series of related reactions be compared while absolute values have to be treated with caution as has been found even at higher levels of theory.[9a] (ii) Allene is slightly less reactive than ethylene in Diels–Alder reactions with cyclopentadiene. Allene reacts less vigorously with HCP than cyclopentadiene. (iii) Allene reactivity increases on fluorine substitution up to DFA and it declines on further substitution of fluorine. (iv) TTCA is found to be less reactive than allene and fluoroallenes and this may be due to the reason that the LUMO (π^*) of TTCA is, comparatively, destabilized to a greater extent by the π-donating rather than σ-withdrawing influence of the four chlorine atoms present in it. (v) Cyclopentadiene and furan reactivities appear to be similar in allene and fluoroallene reactions. (vi) In reaction with MFA, *syn* selectivity in products is predicted but is less pronounced in barriers. In reaction with TFA the *exo* approach is predicted to be slightly favourable and this is in contrast to the normal expectations in accordance with earlier semiempirical predictions.[16]

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