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Theoretical study on the mechanism and reactivity of fluorocumulenes in [4+2] cycloadditions

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Abstract

Semi-empirical molecular orbital calculations have been used to investigate the transition structures and energetics of the [4+2] cycloaddition reactions of butadiene with allene, monofluoroallene, 1,1-difluoroallene and trifluoroallene. Geometry optimizations have been performed with both AM1 and PM3 Hamiltonians and on the basis of the computed transition state geometries and activation energies, the favoured stereochemical preferences of the reactions and the reactivity of fluorallenes have been predicted. The reactivity order found agrees well with ab initio predictions based on LUMO energies and experimental observations.

Keywords: Fluoroallene; Cycloaddition; Diels–Alder reaction; Transition structure; Semi-empirical calculations

1. Introduction

Allenes are known to undergo cycloaddition reactions with greater ease than alkenes because of the presence of the considerably strained cumulenic double bonds. Fluroallene addends in cycloaddition reactions have been the topic of several experimental [1–5] and theoretical [6,7] investigations, since fluorine has been used as a mechanistic probe in studying these reactions. Although reports have been published of selectivity studies based on an FMO approach [1,7], the mechanisms of these cycloadditions have not been studied systematically to date, i.e. the transition structures (TS) for such reactions have not been characterized. In the present communication, the mechanism of the Diels–Alder processes of various fluoroallenes with butadiene and the reactivity of such cumulenes are thoroughly discussed in relation to the computed results.

2. Method of computation

The concerted [4+2] cycloaddition reactions of butadiene with allene, monofluoroallene (MFA), 1,1-difluoroallene (DFA) and trifluoroallene (TFA) depicted in Scheme 1 have been subjected to a computational study. All calculations have been undertaken at a semi-empirical level with AM1 and PM3 Hamiltonians [8–10]. The TS search has been made using an eigenvector following the EF procedure [11] available in MOPAC 6.0. The TS geometries have been characterized by examining the Hessian matrix for only one imaginary vibrational frequency.

3. Results and discussion

Computed reaction barriers and degrees of asynchronicity of TSs for these reactions are collected in Table 1, reaction energies are shown in the reaction scheme and TSs are presented in Fig. 1. It should be noted that the calculated results are presented in the AM1 (PM3) format. For allenes involved in [4+2] cycloadditions, either double bond of the allene may be incorporated theoretically into the ring. However, in fluoroallene cycloadditions, it has been observed experimentally that only the less fluroinated double bond is incorporated into the ring. Ab initio computations also predict the same point and our investigations confirm this. However, TSs corresponding to both reaction types, noted as A and B in Table 1, have been investigated in order to observe any difference. Since the results indicate that reaction type B is a less favourable pathway, the geometries of the TSs of these reactions are not discussed in this paper. Activation energies for both types of reaction are presented in Table 1 for comparative purposes. Whilst allene (**1**) and DFA (**3**) [1] generate only one exocyclic cycloadduct (4-methylene-cyclohexene),

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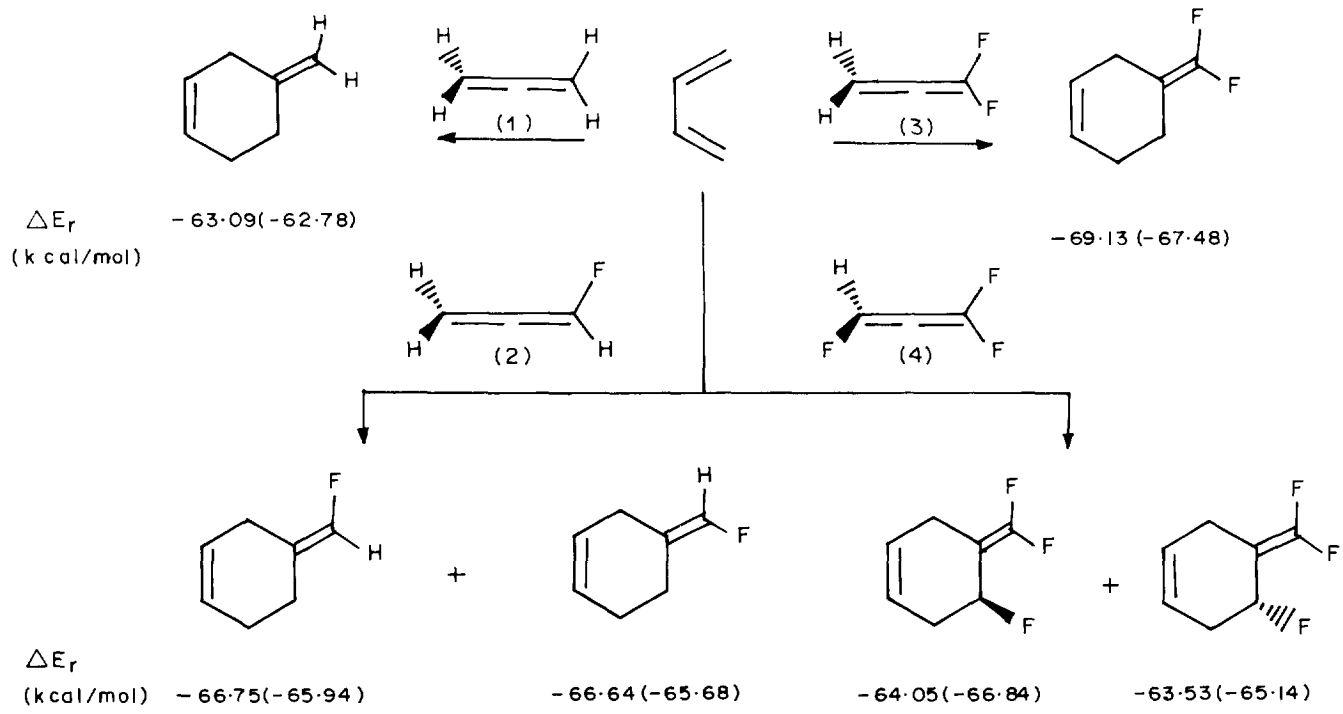


Scheme 1.

MFA (**2**) [2] can generate both *syn*- and *anti*-selective adducts. In addition TFA (**4**) can lead to *endo*- and *exo*-selective adduct formation. For these reasons, the corresponding six TSs have been characterized (Fig. 1).

The computed TS geometries 1–6 show the following interesting features. Generally, AM1 and PM3 results show a difference in TS bond lengths of ca. 0.01–0.09 Å. The concerted mechanisms found in these reactions resemble that for the reaction between butadiene and ethylene [12,13], with the former showing slight asynchronicity in the newly forming σ-bonds. This may be due mainly to perturbation by the cumulenic double bonds. The degree of calculated asynchronicity [14] is listed in Table 1 for each TS. The asynchronicity is more pronounced in structures 5 and 6. In the TS, the allene moiety is distorted from linearity but all the three carbon atoms are in the same plane, the calculated C5–C4–C7 angle being in the range 143–150°. Two TSs have been characterized in the reaction of TFA, one corresponding to the *endo* product and another due to the *exo* product. Of these two TS geometries, the *exo* structure 6 shows a slight twisting from planarity with the torsion angle C3–C4–C5–C6 being 15.8° (8.0°).

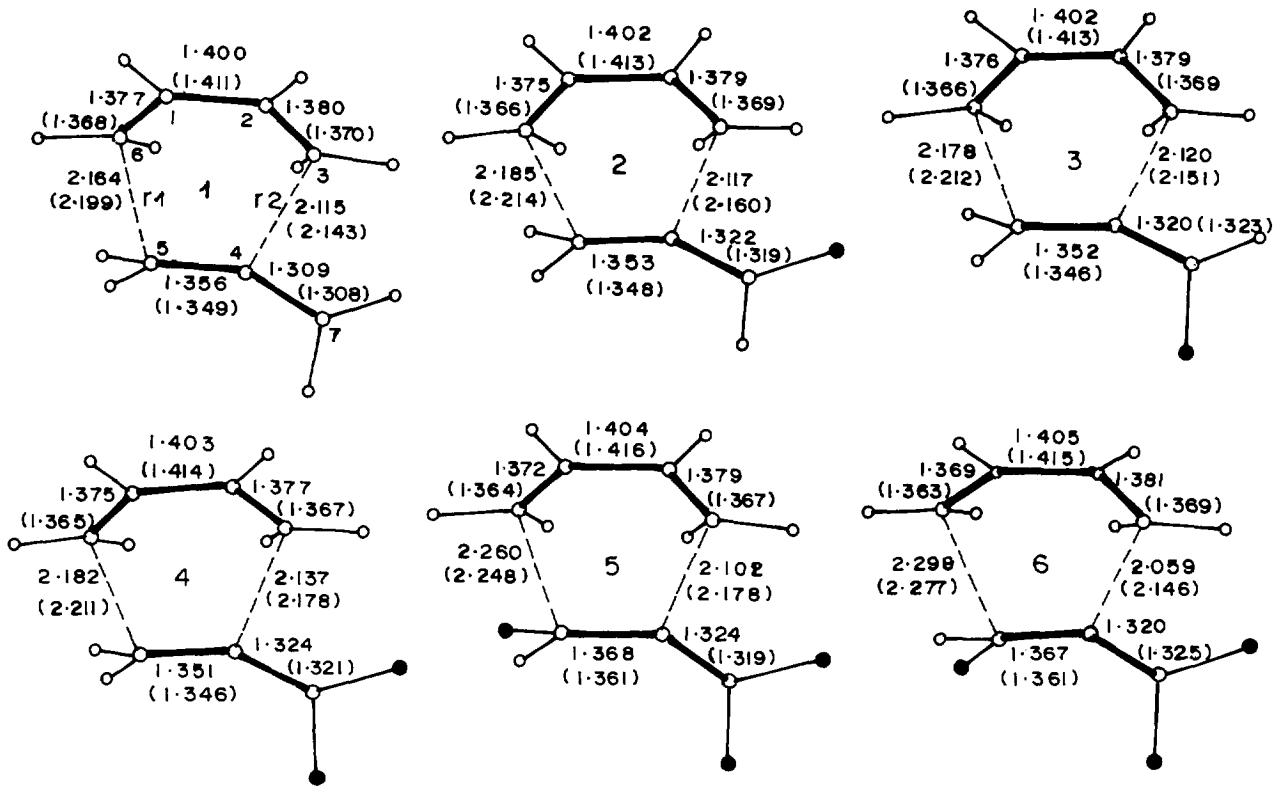
Generally, fluorine enhances the reactivity of allenes in [4+2] reactions and the cycloaddition is regiospecific with respect to fluoroallenes [4,5], with the C2–C3 bond being exclusively incorporated into the ring. Computed activation energies for both reactions, i.e. that in which the C1–C2 π^*-orbital is involved and the other where the C2–C3 π^*-orbital is involved, referred to respectively as B and A in Table 1, show that only the latter reaction type is preferred. Hence, throughout the discussion below the former reaction path is not considered.

In moving from allene to DFA [7], the LUMO which is predominantly the C2–C3 π^*-orbital is progressively stabilized with increasing fluorine substitution, and hence the reactivity is expected to increase in the same order. This trend is

Table 1
Calculated AM1 (PM3) activation energies (kcal mol^{-1}) and degrees of asynchronicity for the reaction of butadiene with allene and various fluoroallenes

Dienophile (A) [a]	TS [b]	α [c]	E_a	Dienophile (B) [d]	E_a
allene	1	0.011 (0.013)	27.9 (29.0)		
MFA, *syn* F	2	0.016 (0.012)	26.1 (27.8)	MFA, *endo* F	29.9 (29.3)
MFA, *anti* F	3	0.013 (0.014)	26.1 (27.1)	MFA, *exo* F	28.5 (28.8)
DFA	4	0.010 (0.008)	25.0 (26.3)	DFA	30.9 (28.8)
TFA, *endo* F	5	0.036 (0.016)	27.4 (26.9)	TFA, *syn* F	29.4 (27.8)
TFA, *exo* F	6	0.055 (0.030)	26.3 (26.6)	TFA, *anti* F	29.6 (27.4)

[a] Reaction where the C2–C3 π^*-orbital is involved.
[b] TS numbers as referred to in Fig. 1.
[c] Degree of asynchronicity calculated from the TS distances r_1 and r_2, i.e. $\delta r/(r_1+r_2)$.
[d] Reaction where the C1–C2 π^*-orbital is involved.



	1	2	3	4	5	6
5–4–7	148·9(149·6)	144·8(144·6)	149·6(149·5)	146·3(145·7)	143·6(144·4)	143·8(144·1)
3–4–5–6	0·0(0·0)	−1·4(1·0)	1·1 (0·0)	2·8(0·0)	−3·2 (−2·3)	15·8(8·0)
2–3–4–7	129·0(125·6)	129·5(124·9)	129·2(125·8)	130·3(125·7)	131·7(128·3)	112·1 (117·0)

Fig. 1. Computed transition structures for the reaction of fluoroallenes with butadiene and selected geometric data from AM1 (PM3) optimized structures.

clearly reflected in the computed reaction barrier. In TFA the third fluorine atom destabilizes [7] the C2–C3 π^*-orbital, and TFA is therefore expected to show less reactivity than DFA. This is also clearly seen from the calculated activation energies. The AM1 and PM3 results show a mixed trend when the reactivities of MFA and TFA are compared alone but it is clear that the reactivity of TFA is near that of MFA in the series. Reported ab initio results [7] based on LUMO values predict that TFA is slightly more reactive than MFA, and this trend is well predicted by the PM3 results. Thus, the computed reaction barriers indicate that DFA is the most reactive component in these cycloadditions with the reaction of DFA being the most exothermic [−69.13 (−67.48) kcal mol^{-1}]. The relative preference of the [4+2] cycloaddition over the [2+2] reaction of fluoroallenes will be reported elsewhere.

In conclusion, the TS geometries for the concerted cycloadditions of fluoroallenes with butadiene have been characterized for the first time. In all cases, the TS is found to be nearly asynchronous with the allene moiety being distorted from linearity in the structure. Computed AM1 and PM3 results confirm that (i) only the C2–C3 bond is incorporated into the ring in such cycloadditions and (ii) increased fluorine substitution in the allenes up to DFA increases the reactivity, with TFA being predicted to be less reactive than DFA.

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