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SUPERJACENT ORBITAL EFFECTS IN FULVENE CYCLOADDITION REACTIONS

Michael N. Paddon-Row[a], *Kerrie Gell*[b], *and Ronald N. Warrener*[b]

a) Department of Chemistry, New South Wales Institute of Technology
Broadway, N.S.W., 2007, Australia. b) Department of Chemistry,
S.G.S., Australian National University, Canberra, A.C.T., 2600,
Australia.

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The theory of cycloaddition reactions[1a] has been aided greatly by the application of Perturbational Molecular Orbital (PMO) theory[1b] and by the more approximate Frontier Molecular Orbital (FMO) approach[1c]. Essentially these treatments of cycloaddition reactions involve the computation of the stabilization energy (SE) of interaction of the two molecules in the early stages of reaction for different modes of approach. The most favoured product is assumed to be that which is derived from the pathway having the largest SE. In terms of second order PMO theory, this SE is given by the sum over all terms involving interactions between filled and vacant MOs. The contribution of each term towards the total SE is (i) directly proportional to the square of the sum of the products of the coefficients of interacting centres (*coefficient factor*) and (ii) inversely proportional to the energy gap between the interacting MOs (*energy gap factor*, ΔE). In the FMO approximation it is assumed that the predominant stabilization results from that term which contains the smallest ΔE (which obviously involves an HO-LU* interaction), while the corresponding coefficient factor of that term determines the nature of the cycloadduct, in terms of its symmetry favouredness[1c], regioselectivity[3] and periselectivity[4]. Thus the FMO theory neglects all but one term in the summation on the assumption that the ΔE factor is of much greater importance than the coefficient factor in determining the dominant term. However recent work, especially by Berson and Salem[5a-c], has cast doubts on the general applicability of the FMO method particularly in regard to symmetry unfavoured pericyclic reactions. These authors have emphasized the importance of terms which involve interactions between MOs lying below (subjacent) and above (superjacent) the FMO manifold. *Clearly in these cases the coefficient factors are of prime importance.* In one reported case[5d], the coefficient factor in a subjacent orbital interaction term was of such magnitude as to direct the reaction to proceed via an unfavoured route in preference to the favoured pathway (as judged by the usual Woodward-Hoffmann FMO treatment). *We now show that the observed periselectivity of certain fulvene cycloaddition reactions are determined in large by superjacent orbital effects.*

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* HO = Highest Occupied; LU = Lowest Unoccupied; NLU = Next Lowest Unoccupied MO.

Several treatments of regioselectivity and periselectivity have appeared recently[3,4]. Both the Anh and Houk treatments[3,4b,4c] are based on the FMO method whereas our procedure involves the computation of *both* HO-LU terms[4a]. Our reasons for retaining two terms in the SE expression were twofold: (i) it enabled a simple method for predicting substituent effects to be developed and (ii) it reduced the bias that FMO theory gives to the ΔE factor.

Houk and his coworkers[4b] have recently studied the cycloaddition reactions of 6,6-dimethylfulvene (*F*) with cyclopentadiene (*C*), α-pyrone and 2,4-cycloheptadienone and in each case only Diels-Alder type adducts with 6,6-dimethylfulvene acting as the dienophile were isolated. In the same paper, these authors reported that their FMO-based method predicted the formation of the [6+4] adducts. In an attempt to reconcile theory with experiment they extended their treatment to include the other HO-LU term but only in a *qualitative* fashion[6]. That this rationalization is incorrect and that the observed periselectivity is best explained in terms of the superjacent orbital interaction NLU$_F$-HO$_C$ may be exemplified through the reaction between 6,6-dimethylfulvene and cyclopentadiene. Consider the four symmetry favoured cycloaddition modes between 6,6-dimethylfulvene and cyclopentadiene which are outlined below schematically. Table 1 summarizes the relevant Extended Hückel eigenvectors (together with their symmetries) and energies[7] of 6,6-dimethylfulvene. Note that both LU$_F$ and NLU$_F$ have the same pseudo-symmetries at C_2 and C_3 and that the coefficients of the NLU$_F$ at these atoms are large. The interaction energies of the various terms (which are computed via the standard expression[2]) together with the corresponding ΔE values are presented in Table 2. Inspection of these ΔE values reveals that the dominant term according to FMO theory involves the HO$_C$-LU$_F$ orbital

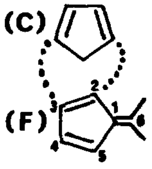
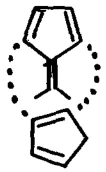
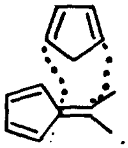
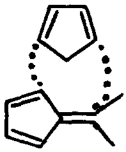
(4+2)	(4+2)	(4+2)	(6+4)
 **MODE I** Observed Product	 **MODE II**	 **MODE III**	 **MODE IV**

Table 1

Atom	NHO	HO	LU	NLU
	(S)	(A)	(S)	(A)
1	0.54	0	0.27	0
2	-0.03	0.56	0.42	0.49
3	0.4	0.38	-0.35	-0.74
6	0.44	0	-0.72	0
E(ev)	-12.5	-12.2	-9.67	-6.5

Table 2

Mode	HO$_C$-LU$_F$	LU$_C$-HO$_F$	Σ	HO$_C$-NLU$_F$	Total SE
(I)	0.138	0.205	0.34	0.16	0.50
(II)	0.118	0.191	0.31	0	0.31
(III)	0.229	0	0.23	0	0.23
(IV)	0.303	0.073	0.38	0.02	0.40
ΔE(ev)	2.61	3.86		5.77	

interaction. It predicts in agreement with Houk's analysis[4b], the formation of the [6+4] adduct (IV) (Col. 2, Table 2). However in contrast with the claim made by these authors[4b] in their attempt to rationalise their experimental observation with the theoretical prediction, our values show that inclusion of the HO_F-LU_C term (Col. 3) *does not alter* the preference for mode IV addition relative to mode I, and that the SE expression still favours IV (Col. 4 Σ). However, this term does contribute significantly towards the stabilization of (I). Despite an unfavourable value of ΔE, the superjacent orbital interaction term (Col. 5) contributes significantly towards the SE of (I) to such an extent that is is *now* the favoured product (Col. 6). It should be noted that these latter two terms which are neglected by the FMO method contribute 73% towards the total computed SE of (I)! Similar results were obtained for the reaction of 6,6-dimethylfulvene with α-pyrone and the 2,4-cycloheptadienone. Inspection of the subjacent orbital (NHO_F - Col. 1, Table 1) interaction term reveals a marked increase in the dienophilicity of the 1,6-bond of 6,6-dimethylfulvene for mode (III) but (I) is still preferred. It was found that the dienophilicities of double bonds in simple alicyclic dienes and trienes such as cyclopentadiene, cyclopentadienone and cycloheptatriene are also increased with respect to the reactivities of the terminal sites with the inclusion of superjacent and subjacent terms - for example inclusion of NHO_C-LU_F and NLU_C-HO_F terms make (II) the next favoured mode.

It appears therefore, that FMO theory overestimates the tendencies of some molecules to enter into cycloaddition reactions as π_n components (n = 4,6...) rather than as π_2 components. This overestimation may be a result of the neglect of a greater proportion of terms when considering the molecule as a π_2 component. For example, consider the cycloaddition reactions of cyclopentadiene. This compound may react either as a π_2 component or as a π_4 component. The constraints of orbital symmetry restrict the number of interacting MOs to two when cyclopentadiene reacts as a π_4 component but in the case of cyclopentadiene reacting as a π_2 component, all four MOs interact favourably (the NHO and the HO orbitals have the same symmetry as have the LU and the NLU MOs). The FMO method thus considers 50% of the MOs in the former case yet it considers only 25% of the MOs in the latter case. An examination of various polyenes reveals that there are fewer MOs of the appropriate pseudosymmetry for reaction as π_n components than there are MOs for reaction as π_2 components. Although FMO theory has led to a better understanding of periselectivity and regioselectivity, we recommend that in its application an inspection of the coefficients of those MOs which lie outside the FMO manifold be carried out.

Finally we emphasize again[4a,8] that the successful interpretation of the PMO based treatments of periselectivity depends very much upon the identification of the products which are formed via kinetic control and this has yet to be verified in the fulvene cycloaddition reactions mentioned in this letter. The reaction of 6,6-dimethylfulvene with cyclopentadienone in relation to this problem has been investigated and the results will appear in due course.

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6. It is by no means clear from their paper[4b] how these authors were able to differentiate between the various [4+2] isomers.
7. Calculations were also performed at the INDO level and the overal conclusions were identical with those obtained from the EHT results.
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