Intramolecular Effects in the Cycloaddition of Three Ethylenes *vs.* the Diels–Alder Reaction

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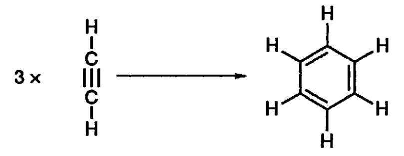
The Diels–Alder (D–A) reaction possesses a much smaller barrier than the cycloaddition of three ethylenes (C-3E) despite the opposite effect of the corresponding reaction exothermicities. These reactions have been studied by means of *ab initio* computations coupled with analysis by the curve-crossing model. It is shown that the intramolecular advantage, exhibited by the D–A reaction, has both electronic and entropic components. The electronic advantage is found to be much more dominant, approximately 26 kcal mol^{-1} at the MP4(FC)/6-31G*//HF/3-21G level of theory. The relationship of the electronic advantage and the notions of 'reactant deformations' and critical distances are explored and quantitated. A simple mechanism which elucidates the origins of the intramolecular electronic effect is presented. The effect is shown to be exerted through a stabilization of the reactant excited state that possesses the bonding features of the product: so called 'the prepared excited state'. The excitation energy gap between the ground state and the prepared excited state is the promotion energy of the reaction and is the root cause of the barrier according to the curve crossing model (ref. 4). The reduction of the promotion energy gap for the Diels–Alder reaction by 124 kcal mol^{-1} results, therefore, in a corresponding reduction of the barrier by *ca.* 26 kcal mol^{-1}. Considerations of the promotion energy gap allow for a semiquantitative estimation of the intramolecular electronic advantage at different distances. It is concluded the electronic advantage of proximity will be smaller than the entropic component unless it is possible to bring the π-bonds into a critical distance which is shorter than *ca.* 2.7 Å.

The trimerization of acetylene to benzene, eqn. (1), is an 'allowed' reaction[1] with an enormous thermodynamic driving force of $\Delta H \approx -140$ kcal‡ mol^{-1}.[2] Despite these favourable features it is puzzling that the computed electronic barrier for the concerted process is very high, being *ca.* 62 kcal mol^{-1} at the MP3/6-31G*//HF/6-31G* level.[2a] In contrast, the Diels–Alder reaction, also an 'allowed' concerted process, but, with a much smaller thermodynamic driving force[3] of -40 kcal mol^{-1}, possesses in comparison a tiny barrier of *ca.* 27.5 kcal mol^{-1}.[3a]

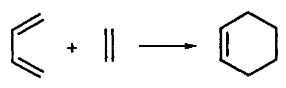


(1)

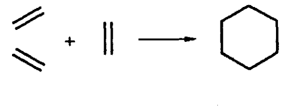
Analyses of the barrier for the trimerization of acetylene have been published before.[2,4] However, what still remains very intriguing is the comparison of the two reactions. Why is it that their relative barriers behave in contrast with the Bell–Evans–Polanyi principle and defy thereby rate–equilibrium relationships? Clearly there is a need to understand the variation of the barrier within a group of isoelectronic 'allowed' reactions, much as we do have a good understanding of the difference between 'allowed' and 'forbidden' reactions.[1]

One difference that comes to mind between eqn. (1) and the Diels–Alder reaction is structural, namely that in the latter reaction two of the π-bonds are intramolecularly linked and somehow cause reduction of the corresponding barrier. But what exactly is this intramolecular advantage? This question is the core of the present paper. To answer the question in a satisfactory manner, it is necessary to model the effect properly and to go back to the mechanism of barrier formation and formulate the intramolecular effect within this mechanism.

A more adequate measure of the intramolecular effect on the barrier requires a comparison of the reaction-pair in eqn. (2) and eqn. (3). Thus eqn. (2) describes the Diels–Alder (D–A) reaction, while eqn. (3) depicts the closest possible *intermolecular* and *isoelectronic* reaction, the cycloaddition of three ethylenes (C-3E). Another important feature of this reaction-pair is the comparison of their reaction exothermicities, ΔH,[5] which again favour the intermolecular cycloaddition. Thus, any potential intramolecular advantage in this reaction-pair must be of a 'pure kinetic' nature which overrides the traditional rate–equilibrium effect.



$\Delta H = -40$ kcal mol^{-1} (2)



$\Delta H = -67$ kcal mol^{-1} (3)

The present work tries to analyse the energetic and entropic aspects of the intramolecular effect, in eqns. (2) and (3), and to trace its origins. The approach is two-pronged, involving *ab initio* computations complemented by curve-crossing analysis of the origin of the barrier.[4,6] As will be shown, the intramolecular effect has both electronic (potential energy) and entropic contributions, with the former contribution being dominant. A simple mechanism which elucidates the origins of the computed intramolecular effect will be constructed and applied for a semiquantitative estimation of the electronic advantage for closely related systems.

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[‡] 1 cal = 4.184 J.

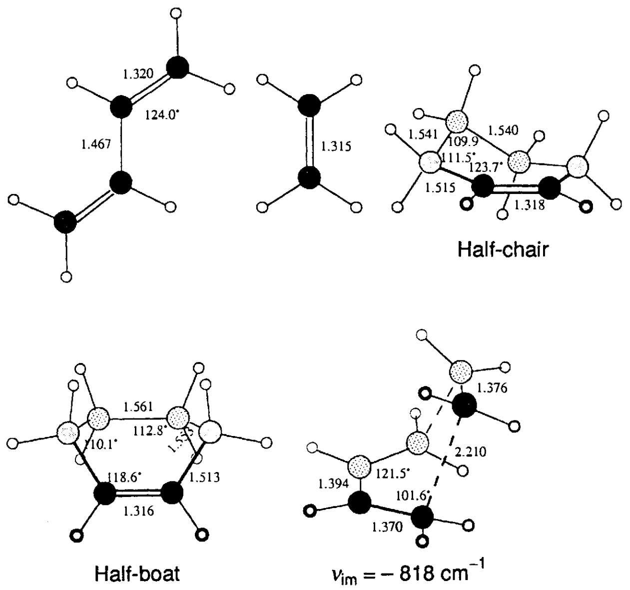


Fig. 1 3-21G optimized geometries for the reactants, transition state and product of the Diels–Alder reaction. The products are shown in their half-chair and half-boat conformations.

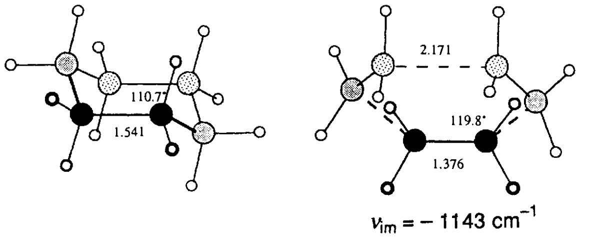


Fig. 2 3-21G optimized geometries for the product and transition state of the cycloaddition of three ethylenes. The geometry of ethylene is shown in Fig. 1.

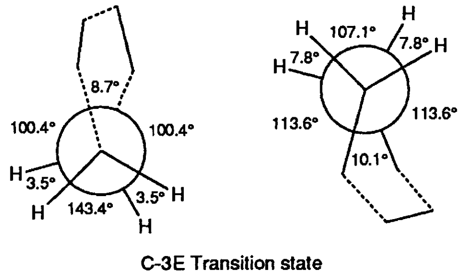


Fig. 3 Newman projections showing the dihedral angles for the transition state of the cycloaddition of three ethylenes (C-3E). Dashed lines correspond to the intermolecular distances between the original ethylene moieties.

Theoretical Methods and Calculations

The geometries of the reactants, products and transition states for the target reactions were optimized by gradient methods and checked by frequency calculations at the restricted Hartree–Fock (RHF) level, using the 3-21G basis set.[7] Correlation energy corrections were evaluated at the 3-21G optimized geometries by use of Møller–Plesset perturbation calculations[8] up to fourth order (MP*n*, n = 2–4). Basis set effects were estimated by single-point calculations with the 6-31G* basis set,[9] at the 3-21G geometries. MP*n* corrections at the 6-31G* basis set level were calculated with the frozen core (FC) approximation. The energies in the various tables are specified using standard notation, *e.g.*, MP4(FC)/6-31G*//HF/3-21G stands for a single-point calculation, on the 3-21G optimized geometry, with the 6-31G* basis set with correlation corrections at the frozen core-MP4 approximation. When MP*n* appears with no parenthetical FC specification this means that the correction also includes the core electrons.

The thermodynamic quantities (ΔH, ΔG, ΔS) were computed by use of the standard GAUSSIAN output based on the rigid-rotor and harmonic oscillator approximations. The work term ($P\Delta V$) was included in the enthalpy and free-energy quantities. The computed ΔS and ΔG were converted to the 1 mol dm^{-3} (1 M) and 298.15 K standard state. The ΔG correction follows from eqn. (4) and from it there follows the ΔS correction.

$$\Delta G_{1M} = \Delta G_{1atm} + 1.895(\Delta n)\ (\text{in kcal mol}^{-1}) \qquad (4)$$

Here Δn refers to the change in the number of moles in the overall reaction or in the activation step (reactants→transition state). The ΔG_{1atm} quantity refers to the standard state at 1 atm pressure. All the thermodynamic quantities were calculated from the frequencies and moments of inertia at the 3-21G level. These contributions were added to the electronic energies at all the computational levels.

The use of the curve-crossing model[4,6,10] requires knowledge of the vertical singlet-to-triplet excitation energies of the reactants. These are the quantities which determine the gaps in the state correlation diagram of the target reaction.[5a,6] The excitation energies for ethylene and butadiene were calculated by use of configuration interaction (CI) methods, *e.g.*, CIS and with the CASSCF method in full π-space. At the most consistent level, the ground-state geometries were optimized at the CASSCF level[11] and the vertical excitation was calculated at the same CAS level. For a given basis set, *e.g.*, 3-21G, this level is denoted by CASSCF/3-21G//CASSCF/3-21G. The highest basis set used for these computations is the 6-31G**.[12]

All the computations were performed with the GAUSSIAN-90 series of programs[13] on IBM/RS6000 (model 550) Workstations of Ben-Gurion University and the Hebrew University.

Results

The main features of the 3-21G optimized structures are shown in Figs. 1 and 2. Our results for the Diels–Alder transition state are in accord with earlier calculations by Houk and collaborators.[14,15] The Diels–Alder reaction product was optimized in both the half-chair and half-boat conformations; the latter being the less stable, but the one which is directly connected with the 'allowed structure' of the transition state. The transition state for the cycloaddition of three ethylenes has D_3 symmetry, intermediate between the geometries of the reactants and the cyclohexane product. However, the mean deviation from a planar structure is quite small, being about ±9° as shown in the Newman projections of the transition state in Fig. 3.

All in all, the two TSs are mutually related in a simple manner. The Diels–Alder transition state involves a supra–supra attack[1] of an ethylene moiety on s-*cis*-butadiene, and likewise the transition state of the three ethylenes cycloaddition involves a supra–supra attack of ethylene on two ethylene moieties which themselves are arranged in a conformation which deviates by *ca.* 8° from an s-*cisoid* arrangement.

The reaction energy change and its various thermodynamic derivatives are collected in Tables 1 and 2 for the HF and MP4 levels. As can be seen from the third column in each table, the zero point energy (E_{ZP}) corrections are not affected much by scaling of the frequencies, and this practice was not utilized further in the other thermodynamic quantities. The basis set and correlation correction calculations have a more pronounced effect on the cycloaddition of three ethylenes, as might be expected. Generally though, the corrections are not overwhelming and the results cluster closely about a mean value. The $\Delta H°$ quantities compare favourably with experimental estimates[5] of

Table 1 Computed[a] reaction energies and entropy for the Diels–Alder reaction, C_4H_6 (s-*trans*) + $C_2H_4 \rightarrow C_6H_{12}$ (half-chair)[b]

Level	ΔE_{el}[c]	$\Delta(E_{el} + E_{ZP})$[d]	ΔH°	ΔG°[e]	ΔS°[e]
HF/3-21G//HF/3-21G	−43.11	−36.68 (−37.32)	−38.66	−27.25	−38.27
MP4/3-21G//HF/3-21G	−43.87	−37.44 (−38.08)	−39.42	−28.01	
HF/6-31G*//HF/3-21G	−42.63	−36.20 (−36.84)	−38.18	−26.77	
MP4(FC)/6-31G*//HF/3-21G	−49.23	−42.80 (−43.44)	−44.78	−33.37	

[a] Energies in kcal mol^{-1}. Entropies in cal mol^{-1} K^{-1}. $T = 298.15$ K. [b] For the process C_4H_6 (s-*trans*)$\rightarrow C_4H_6$ (s-*cis*) $\Delta E_{el} = 2.00$; 2.66 kcal mol^{-1} at the MP4/3-21G//HF/3-21G and MP4(FC)/6-31G*//HF/3-21G levels, respectively, while for the process C_6H_{12} (half-chair)$\rightarrow C_6H_{12}$ (half-boat) the respective values are $\Delta E_{el} = 5.09$; 5.87 kcal mol^{-1}. [c] Electronic energy change. [d] Values in parentheses involve scaling of the frequencies by 0.9. [e] The standard state is 1 mol dm^{-3} at 298.15 K.

Table 2 Computed[a,b] reaction energies and entropy for the cycloaddition of three ethylenes

Level	ΔE_{el}[c]	$\Delta(E_{el} + E_{ZP})$[d]	ΔH°	ΔG°[e]	ΔS°[e]
HF/3-21G//HF/3-21G	−71.50	−60.50 (−61.60)	−63.88	−41.97	−73.48
MP4/3-21G//HF/3-21G	−71.73	−60.73 (−61.83)	−64.11	−42.20	
HF/6-31G*//HF/3-21G	−70.49	−59.49 (−60.59)	−62.87	−40.96	
MP4(FC)/6-31G*//HF/3-21G	−80.92	−69.92 (−71.02)	−73.30	−51.39	

[a] Energies in kcal mol^{-1}. Entropies in cal mol^{-1} K^{-1}. [b] $T = 298.15$ K. [c] Footnotes[c–e] in Table 1 apply here also.

Table 3 Computed[a] activation energies and entropies for the Diels–Alder reaction

Level	$(\Delta E_{el}{}^{\ddagger})$[b]	$\Delta H^\ddagger$	E_a[c,d]	$\Delta G^\ddagger$[d]	$\Delta S^\ddagger$[d,e]
HF/3-21G//HF/3-21G	35.92 (33.21)	37.24	38.43	48.02	−36.17 (−37.87)
MP2/3-21G//HF/3-21G	16.92 (15.02)	18.24	19.43	29.02	
MP3/3-21G//HF/3-21G	23.62 (21.64)	24.94	26.13	35.72	
MP4/3-21G//HF/3-21G	20.54 (18.54)	21.86	23.05	32.64	
HF/6-31G*//HF/3-21G	45.08 (42.02)	46.40	47.59	57.18	
MP2(FC)/6-31G*//HF/3-21G	17.03 (14.39)	18.35	19.55	29.13	
MP3(FC)/6-31G*//HF/3-21G	27.05 (24.46)	28.37	29.56	39.15	
MP4(FC)/6-31G*//HF/3-21G	22.24 (19.58)	23.56	24.75	34.34	

[a] Energies in kcal mol^{-1}. Entropies in cal mol^{-1} K^{-1}. $T = 298.15$ K. [b] Values in parentheses refer to the C_4H_6 (s-*cis*) conformer as the butadiene reactant. All the other data refer to C_4H_6 (s-*trans*). [c] $E_a = \Delta H^\ddagger + mRT$; m = reaction molecularity. [d] Refers to a 1 mol dm^{-3} and 298.15 K standard state. [e] The value in parentheses refers to the C_4H_6 (s-*cis*) reactant.

Table 4 Computed activation energies and entropies for the cycloaddition of three ethylenes[a]

Level	$\Delta E_{el}{}^{\ddagger}$	$\Delta H^\ddagger$	E_a	$\Delta G^\ddagger$	$\Delta S^\ddagger$
HF/3-21G//HF/3-21G	70.98	74.84	76.62	92.43	−58.99
MP2/3-21G//HF/3-21G	42.94	46.80	48.58	64.39	
MP3/3-21G//HF/3-21G	51.49	55.35	57.13	72.94	
MP4/3-21G//HF/3-21G	46.87	50.73	52.51	68.32	
HF/6-31G*//HF/3-21G	81.04	84.90	86.68	102.49	
MP2(FC)/6-31G*//HF/3-21G	42.71	46.57	48.35	64.16	
MP3(FC)/6-31G*//HF/3-21G	55.41	59.27	61.05	76.86	
MP4(FC)/6-31G*//HF/3-21G	48.55	52.41	54.19	70.00	

[a] See comments[a,c,d] in Table 3.

−40 kcal mol^{-1} for the Diels–Alder reaction and −67 kcal mol^{-1} for the three ethylene cycloaddition.

In Tables 3 and 4 are collected activation parameters. The effects of correlation and basis set are now quite large. The change of basis set to 6-31G* is seen to increase the barrier, but the effect is strongly attenuated by correlation correction. The correlation correction oscillates and MP2 seems to overestimate the reduction of the barrier. The extent of reduction is diminished by MP3 and increased again by MP4. This behaviour is analogous to the findings of Bach, Wolber and Schlegel[2a] for the trimerization of acetylene to benzene, and the results of Spellmeyer and Houk[16] for the ring opening of cyclobutene. For our purposes this oscillatory behaviour of MP*n* corrections is not very significant as far as the barrier differences between the two reactions are concerned.

If we take the highest levels (MP4) as representing the most accurate results, we may note that the MP4 and MP4(FC) activation energies, E_a, for the Diels–Alder reaction compare favourably with experimental measurements[3] of 27.5–34.3 kcal mol^{-1}, and with CASSCF calculations by Bernardi, Robb and collaborators.[17,18] Similarly, the entropy of activation data compares well with the experimental range of −34.3 to −41 cal mol^{-1} K^{-1} for the Diels–Alder reaction.[3] No data exist for the trimerization of ethylene, but in view of the good accuracy of the

Table 5 Computed $\pi\pi^*$ type singlet-to-triplet vertical excitation energies (ΔE_{ST}) for ethylene and butadiene

	ΔE_{ST}/kcal mol^{-1}	
Level [a]	Ethylene	Butadiene
CIS=Triplets/6-31G**//HF/6-31G** [b]	86.7	65.6
CASSCF/3-21G//HF/3-21G [b]	107.8	83.5
CASSCF/3-21G//CASSCF/3-21G [c]	102.8	77.8
CASSCF/6-31G**//CASSCF/6-31G** [c]	100.9	—
Experimental [d]	*ca.* 99	*ca.* 74

[a] All CASSCF computations involve all π electrons (two in ethylene, four in butadiene) in all π-type orbitals (b_{3u} and b_{2g} for ethylene, four orbitals on 3-21G level and eight orbitals on 6-31G** level; a_u and b_g for butadiene, eight orbitals on 3-21G level). [b] The singlet ground state is optimized at the RHF/basis set level. [c] The singlet ground state is optimized at the CASSCF/basis-set level. [d] From reference 19(*a*), (*b*).

Table 6 Selected thermochemical quantities[a,b] for the Diels–Alder (D–A) reaction[c] and the cycloaddition of three ethylenes (C-3E)

Reaction	ΔH°	$-T\Delta S^\circ$	$\Delta E_{el}^\ddagger$	$\Delta H^\ddagger$	$-T\Delta S^\ddagger$
D–A [eqn. (2)]	−44.78	11.41	22.24 (20.54)	23.56	10.78
C-3E [eqn. (3)]	−73.30	21.91	48.55 (46.87)	52.41	17.59

[a] All quantities are in kcal mol^{-1} and whenever relevant they refer to the 1 M and 298.15 K standard state. [b] Energies refer to the MP4(FC)/6-31G*//HF/3-21G level. Entropies refer to the HF/3-21G//HF/3-21G level. Parenthetical values refer to the MP4/3-21G//HF/3-21G level. [c] The values for the D–A reaction refer to the C_4H_6 (s-*trans*) conformer as the butadiene reactant.

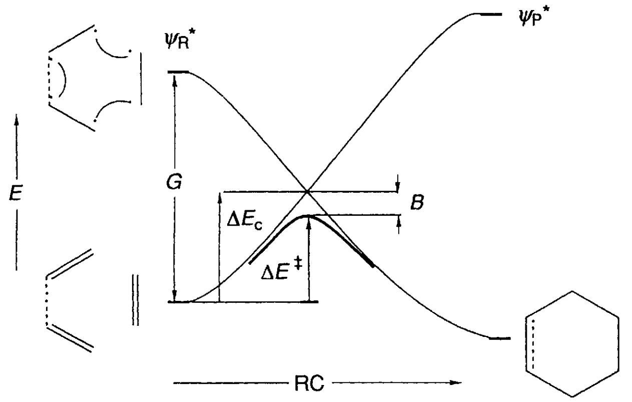


Fig. 4 A VB state correlation diagram for the cycloaddition of three π-bonds (σ-bonds are also shown). Electrons are symbolized by circles and spin-paired electrons are connected by lines. The excited state at the product extreme Ψ_P* is not drawn, for the sake of simplicity. The avoided crossing is shown by a thick line.

computed ΔH° of this reaction, we may assume that the computed MP4 barriers are themselves fairly accurate to serve in the following discussion.

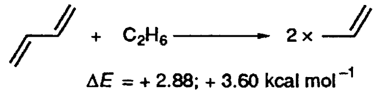
The vertical singlet-to-triplet excitations of ethylene and butadiene are collected in Table 5. It is seen that the results converge toward the experimental values.[19a,b] The best results are obtained at the consistent levels of CASSCF optimization of the ground state and a CASSCF calculation of the triplet state. The excitation energies computed thus are in close agreement with previous CI computations.[19c] Since the computational and experimental values are close we shall use the experimental data in the following discussion.

Discussion

Table 6 compares the thermochemical data for the target reactions at the highest computational level. It is seen that there is an entropic advantage to the D–A reaction. This advantage is approximately 6.8 kcal mol^{-1} which corresponds to *ca.* 5 orders of magnitude in rate constants—close enough to the estimation of Page and Jencks for the comparison of intra- and inter-molecular reactions.[20] Moreover, the entropic advantage is also exerted on the corresponding equilibria, and the effect on the rates is seen to be a fraction of the equilibrium effect—again in full agreement with the analysis of Page and Jencks.[20]

There is another effect in Table 6, and this is the intramolecular electronic advantage which corresponds to the difference of the potential-energy barriers for the two reactions. This electronic advantage is *ca.* 26–30 kcal mol^{-1}, corresponding to 19–21 orders of magnitude in rate constants in favour of the D–A reaction over its putative twin intermolecular reaction, the cycloaddition of three ethylenes (C-3E). This overwhelming electronic advantage is seen to exist despite the opposing effect of the thermodynamic driving force, ΔH°, which clearly favours the C-3E reaction and would have made it faster had rate–equilibrium relationships been dominant. This intramolecular advantage is therefore a 'pure kinetic' property. What we are after now is to elucidate the origins of this effect and to anchor it to some reactant property which lends itself to making future predictions.

Let us first explore the possibility that the effect originates in ground-state destabilization due to the adjacency of the π-bonds in butadiene in comparison with two isolated π-bonds. To answer this question we calculated the ΔE value for the homodesmic[21] reaction in eqn. (5). This reaction is devised so as to eliminate as much as possible the σ effects and to provide the relative stability of the adjacent π-bonds in butadiene *vs.* two free π-bonds. The computed values at the highest levels [MP4/3-21G//HF/3-21G and MP4(FC)/6-31G*//HF/3-21G] are seen to be positive and very small. A similar conclusion is obtained if one considers ΔE of conversion of butadiene + H_2 into two ethylenes while subtracting the σ effects by use of appropriate bond-energy data. Thus, from two different angles, we obtain that the π-bonds are in fact slightly stabilized by being linked in the butadiene molecule.



(5)

ΔE = + 2.88; + 3.60 kcal mol^{-1}

A Curve-crossing Analysis of the Intramolecular Advantage.— Having verified that the intramolecular effect does not originate in repulsive ground-state effects we turn to an analysis of the effect by use of the curve-crossing model as shown in the state correlation diagram in Fig. 4.[4,6] Fig. 4 describes the avoided crossing situation for a general cycloaddition of three π-bonds. In the ground state, two of the moieties are drawn connected by a dotted line which represents either a σ-bond in the D–A reaction or *nothing* in the C-3E reaction. For convenience we use for the two reactions an s-*cisoid* arrangement of the two π-bond fragment which is connected by the dotted line. In the product the dotted line denotes, in turn, either a π-bond or nothing, again depending on the reaction type. The two curves in Fig. 4 intersect along the reaction coordinate and by avoiding the crossing there results a barrier, $\Delta E^\ddagger$, for the cycloaddition reaction.

A key feature in the diagram is the nature of the vertical excited state, Ψ_R*, at the reactant extreme. This excited state is obtained by unpairing each of the three π-bonds of the ground state, below, to a triplet pair while pairing the electrons anew across the inter-fragment linkages. This is exactly the electron pairing mode of the product ground state, and this is why the excited states in the diagram have been called 'image states' or 'prepared excited states' to denote their special relationship to

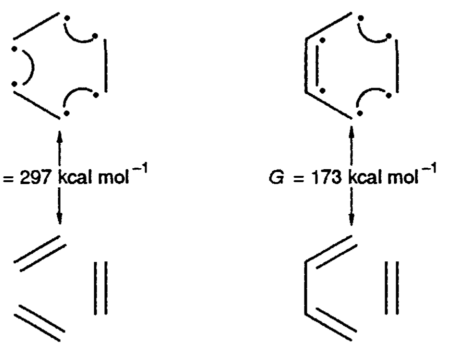
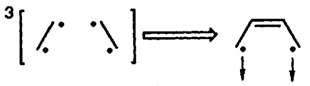


Fig. 5 Excitation gaps for the C-3E and D–A reactions

the ground states of the reactants and products of the reaction. Thus, the Ψ_R* excited state is the prepared excited state of the product at the reactant extreme of the reaction coordinate. The corresponding excitation energy gap between the ground state and the excited state Ψ_R* is denoted in the diagram by the quantity G which is a 'promotion energy' which serves to 'prepare the reactants' for the requisite bond reorganization in the product. This excitation gap is the origin of the barrier, and the magnitude of G is in turn a key element of the barrier height.[6b]

Let us inspect therefore the excitation gaps of the target reactions, as illustrated in Fig. 5 based on the appropriate triplet excitation data in Table 5.[19] The relative magnitudes of the gaps in Fig. 5 provide a clue to the intramolecular electronic effect. Thus, the gap for the D–A reaction is almost half as much in comparison with the corresponding quantity in the C-3E reaction. The energy gap difference is very large, *ca.* 124 kcal mol^{-1}, and since a fraction of it is expressed in the relative barriers this is sufficient to give rise to *ca.* 26 kcal mol^{-1} of intramolecular advantage. Now we may also understand the origins of the enormous barrier in the trimerization of acetylene,[2] eqn. (1). As shown before[4] the excitation gap for this reaction is *ca.* 375 kcal mol^{-1}, even larger than the corresponding gap for the C-3E reaction. In fact, the excitation gap is a good organizing quantity for many barrier data for isoelectronic reactions[10] of the type discussed in this paper.

Why is the energy gap so different in the D–A and C-3E reactions? The answer is in fact already illustrated in Fig. 5. Thus, the excitation gap in the D–A reaction involves the triplet excitations of ethylene and butadiene.[4] In comparison, in the C-3E reaction the gap involves three times the triplet excitation of ethylene. The net difference is seen to originate in the excitation requirements of butadiene compared with the uncoupled π-bonds in two ethylenes. In the case of two ethylenes, the new intermolecular pairing after excitation of the four π-electrons is only a formal spin-pairing with no energetic advantage, and therefore the requisite excitation energy of the two ethylenes is simply the sum of the local singlet-to-triplet excitation energies. In the case of butadiene, however, the new pairing of the four π-electrons creates a new π-bond between the original fragments, while the two triplet electrons reside on the terminal carbons. Thus, the VB structure of the two spin-paired triplets in the two ethylene case is converted into the strongly coupled VB structure of triplet butadiene[19c] as shown schematically in 1 and is substantiated by our CASSCF results which show the dominance of spin density at the terminal carbons.



1

It is seen from 1 that actually two features combine to reduce the triplet energy of butadiene relative to the triplet energy of two ethylenes (which themselves are spin-coupled to a net triplet spin). The first factor is the formation of the central π-bond, and the second is the minimization of the triplet repulsion,[19c] achieved by allowing the triplet electrons to occupy the most distant termini, C1 and C4. This is the mechanism by which the promotion energy gap becomes less costly when two of the three π-bonds are precompressed in the form of butadiene. Since the essence of the reaction is the interchange of the bonding schemes of reactants and products, by means of avoided crossing, then this stabilization of the 'prepared excited state' is expressed in the much lower barrier required to interchange the two bonding schemes along the reaction coordinate. It follows therefore, that the intramolecular electronic advantage originates in a traditional bonding mechanism which stabilizes the reactant excited state that possesses the bonding scheme of the product.

(*a*) *The mechanism of activation.* Let us couch the mechanism of activation in structural terms. With reference to Fig. 4 the origin of the barrier is seen to be the destabilization which the ground state must undergo in order to achieve the requisite resonance with the excited state at the crossing point. Indeed, the barrier can be expressed most generally as in eqn. (6), by the height of the crossing point, ΔE_c, minus the resonance energy, B, at the crossing point.[4,6b]

$$\Delta E^{\ddagger} = \Delta E_c - B \qquad (6)$$

The height of the crossing point can be related to the excitation energy gap and be expressed most generally as a fraction (f) of this gap, that is eqn. (7).

$$\Delta E_c = fG \qquad (7)$$

The destabilizing contributions which enter the crossing point are of two general types.[6d] One contribution involves deformation energies of the reactants due to the need to stretch bonds and deform angles, while the second contribution arises from intermolecular repulsions which are dominated by closed-shell repulsion (*i.e.*, exchange repulsion).[2] Applying eqn. (7) we may expect that the intramolecular catalysis, which is characterized by a reduction of the excitation gap G, will be accompanied by requirements for less reactants-deformation as well as fewer repulsive interactions. Therefore we expect the D–A reaction to possess fewer deformations and fewer repulsive interactions in comparison with the C-3E twin reaction.

(*b*) *Analysis of deformation energies and repulsive interactions.* The role of deformation and repulsive energies can be tested computationally quite easily, and this facility poses the opportunity further to explore the nature of the intramolecular effect. Table 7 displays computed quantities for the two target reactions. Entries 1 and 2 show that the deformation energies of the fragments are larger in the transition state of the C-3E reaction. This is true for each fragment by itself, as well as for the total deformation energy which is seen, from entry 4, to contribute 7.2 kcal mol^{-1} to the total intramolecular advantage.

Entry 3 shows the total energy change of the diethylene portion of the C-3E transition state. It is seen that the ΔE-($C_2H_4 \cdots C_2H_4$) term is larger by 17.6 kcal mol^{-1} than twice the deformation energy quantity of a single olefin, ΔE(C_2H_4) in entry 1. Following a treatment similar to that of Bach, Wolber and Schlegel,[2a] the difference of 17.6 kcal mol^{-1} between the quantities will represent the repulsive interaction between a pair of reactants.

The results of the homodesmic reaction in eqn. (5) show lack of π–π repulsion in butadiene. This is an important conclusion because it indicates that the proximity of the two π-bonds in butadiene also provides a mechanism of eliminating the repulsion. This mechanism probably originates in the π–π* interactions of the polarization and conjugative type,[22]

Table 7 Deformation energies, repulsion energies and curve crossing quantities for the target twin-reactions[a]

		Reaction	
Entry	Quantity	D–A [eqn. (2)]	C-3E [eqn. (3)]
1	$\Delta E(C_2H_4)$[b]	6.48	10.85
2	$\Delta E(C_4H_6)$[b]	18.27 (16.27)	—
3	$\Delta E(C_2H_4 \cdots C_2H_4)$[b]	—	39.29
4	ΔE_{def}[c]	24.75 (22.75)[d]	32.54
5	ΔE_{rep}[e]	*ca.* 35.18	52.77
6	ΔE_c[f]	*ca.* 59.93	85.31
7	f[g]	0.347	0.287
8	B	*ca.* 38.44	38.44[h]
9	$\Delta E^{\ddagger}$	*ca.* 21.49[h] (20.52)[i]	46.87

[a] All energies are in kcal mol^{-1} and are obtained at the MP4/3-21G//HF/3-21G level. [b] ΔE is the energy difference of the specified species in its transition state geometry relative to the corresponding ground state geometry. [c] $\Delta E_{def}(\text{D–A}) = \Delta E(C_2H_4) + \Delta E(C_4H_6)$; $\Delta E_{def}(\text{C-3E}) = 3\,\Delta E(C_2H_4)$. [d] In parentheses are values relative to s-*cis*-butadiene ground-state geometry. [e] $\Delta E_{rep}(\text{C-3E}) = 3[\Delta E(C_2H_4 \cdots C_2H_4) - 2\Delta E(C_2H_4)]$; $\Delta E_{rep}(\text{D–A}) \approx (2/3)\ \Delta E_{rep}(\text{C–3E})$. [f] $\Delta E_c = \Delta E_{def} + \Delta E_{rep}$. [g] $f = \Delta E_c/G$. [h] $\Delta E^{\ddagger} = \Delta E_c - B$; $B = \Delta E_c - \Delta E^{\ddagger}$. [i] MP4 computed value in parentheses. The other value is derived using the equation in footnote *h*.

namely, intrabond as well as interbond π–π* type interactions. It follows therefore that one component of the pair-repulsion will also be absent in the D–A transition state, in comparison with the corresponding transition state in the C-3E reaction. We can therefore estimate the total intramolecular advantage as being the sum of the deformation energy difference and the absent pair-repulsion term. This sum amounts to 25.4 kcal mol^{-1} which compares very well with the computed difference of the corresponding reaction barriers of 26.35 kcal mol^{-1} (at the MP4/3-21G//HF/3-21G level).

Entries 6–8 in Table 7 show the curve-crossing quantities of Fig. 4, estimated from the computational data. Thus, taking the pair-repulsion components to be 17.6 kcal mol^{-1} and reasoning that there exist three such interactions—between the ethylene moieties—in the transition state of the C-3E reaction, provides the total repulsion energy in the transition state, ΔE_{rep} in entry 5. The sum of this term and the ΔE_{def} quantity provides the total destabilization energy of the three ethylene moieties in the C-3E transition state. As reasoned before, this latter quantity is also the height of the crossing point, ΔE_c and is listed in entry 6 for the C-3E reaction. Following eqn. (7) we can obtain the f quantity as the ratio $\Delta E_c/G$. The f thus obtained is in general agreement with values of analogous reactions.[4,10] In a similar manner, by following eqn. (6) we can estimate the resonance energy of the transition state, B, as the difference between the ΔE_c quantity and the barrier. The B obtained value for the C-3E transition state appears in entry 8 and amounts to 38.4 kcal mol^{-1}. A similar treatment of the data of Bach, Wolber and Schlegel[2a] results in a B value of 32.8 kcal mol^{-1} for the trimerization reaction of acetylene [eqn. (1)]. Thus, our derived B value is at least consistent with an analogous reaction.

Let us turn now to the D–A reaction.[23] Since the intermolecular distances in the corresponding transition state are similar to those in the C-3E reaction, we may assume that the pair-repulsion component of 17.6 kcal mol^{-1}, is common to the two reactions. Since we have established that the proximity of the π-bonds in butadiene does not build up repulsion but rather eliminates one such repulsion in the transition state of the D–A reaction, then the total repulsion energy for this transition state is only 35.2 kcal mol^{-1}. This value together with the corresponding deformation energy in entry 4 provides ΔE_c for the D–A reaction in entry 5. If we now further assume a common resonance energy for the two transition states we can derive a value of the barrier for the D–A reaction. The derived value of *ca.* 21.5 kcal mol^{-1} in entry 9 is close to the MP4/3-21G//3-21G computed value in parentheses. This coincidence indicates the consistency of our analysis, though we cannot rule out accidental coincidence.

In summary, the two reactions appear to possess similar curve-crossing parameters B and f, and to differ primarily in their excitation gaps—the promotion energy G. This latter difference dominates the intramolecular electronic effect on the barrier. Thus, the D–A reaction requires less molecular deformation and repulsion to achieve the resonance between the reactant ground state and the prepared excited state, because this excited state is stabilized by bonding due to the proximity of the π-moieties in the butadiene reactant. Quantitatively, this intramolecular advantage is expressed as a sum of 7.2 kcal mol^{-1} of advantage in deformation energy and 17.6 kcal mol^{-1} of advantage in intermolecular repulsion.

A Simple Function for Estimating the Intramolecular Electronic Advantage.—The importance of the excitation gap and its critical dependence on the distance between the reacting moieties is highlighted in the foregoing discussion. What we wish to establish in this section is the dependence of G and hence also of the intramolecular electronic advantage on the distance in a semiquantitative manner which can allow an estimation of the effect and its comparison with the entropic advantage.

Since G depends so critically on the bond-coupling interaction across the termini which are linked in proximity as illustrated in structure **1**, we can construct a simple function which relates the excitation gap to the bond order,[24] n, of the associated termini. This function is eqn. (8) where n varies

$$G_n = G_0(1 - Cn) \qquad (8)$$

between the usual limits: $n = 0$, which corresponds to the infinitely separated π-bonds and $n = 1$, which corresponds to the butadiene limit. The quantity C in the equation is a constant whose value can be determined from the requirement that at $n = 1$ the gap G_1 must equal the corresponding quantity for the D–A reaction. Thus C is given by eqn. (9).

$$C = 1 - (G_1/G_0) = 0.4175 \qquad (9)$$

Similarly, as discussed above, the barrier difference depends on the excitation gap difference. This dependence can be expressed most simply by eqn. (10), where the m is a proportionality factor whose value can be calibrated from the requirement that m should reproduce the barrier difference for the C-3E and D–A reactions. Using the MP4/3-21G//HF/3-21G barriers and the experimental gap difference, we obtain m in eqn. (11).

$$\Delta E_0{}^{\ddagger} - \Delta E_n{}^{\ddagger} = m(G_0 - G_n);\ \Delta E_0{}^{\ddagger} = \Delta E^{\ddagger}\ (\text{at } n = 0) \qquad (10)$$

$$m = 0.2125 \qquad (11)$$

Using this m value and the G_n expression in eqn. (8) we obtain eqn. (12) which expresses the difference in the barriers, relative to the barrier for the intermolecular reaction C-3E, as a function of the excitation gap for this intermolecular limit and of the bond order n between the termini of the π-bonds which are held in proximity, n being the proximity index.

$$\Delta E_0{}^{\ddagger} - \Delta E_n{}^{\ddagger} = 0.088\,72 G_0\, n\ (\text{in kcal mol}^{-1}) \qquad (12)$$

Eqn. (12) is a 'proximity function' that allows us to estimate the intramolecular electronic advantage at different values of the proximity index, n. An interesting question is at what n value would the electronic advantage override the entropic advantage of *ca.* 7 kcal mol^{-1}? According to eqn. (12) this would occur when the bond order between the π-moieties in proximity reached the critical value of $n \geq 0.266$.

The relationship between bond order and actual distance is given by the Pauling relationship,[24b] in eqn. (13).

$$r_n = r_1 - a\ln(n);\; r_1 = r\,(\text{at } n = 1) \qquad (13)$$

This equation allows us to define a critical distance for electronic advantage in the sense specified above, relative to the entropic advantage. The value of the critical distance depends on the value of the Pauling constant a. This constant is commonly assigned a value of 0.3. However, in a recent treatment by Wolfe, Mitchell and Schlegel[25] it has been shown that the Pauling constant may take a range of values, a = 0.6–0.96. We therefore decided to use the entire range of a of 0.3–0.96 and to free thereby our conclusions from a specific bias.

Using the critical bond order value and the C $\cdots$ C distance in butadiene (r_1 = 1.46 Å), we arrive at the critical range of distances in eqn. (14), which shows that in order to achieve a

$$r_n(\text{crit}) \leq (1.86\text{–}2.73)\ \text{Å} \qquad (14)$$

barrier reduction of equal magnitude to the entropic intramolecular advantage, the two π-bonds must be brought into a critical proximity that is smaller than 1.86–2.73 Å. It is seen that despite the fact that we obtain a critical distance which stretches over a range of 1 Å a qualitative feature still emerges quite clearly, that r_n (crit) is quite short; shorter than—or bordering on—the common through-space distance which is *ca.* 2.5 Å in, *e.g.*, divinylmethane. It is mainly *via* through-bond proximity that we can achieve unusually short distances as in butadiene. We may conclude therefore that for the present example of cycloaddition, the electronic component of proximity will generally be smaller than the entropic component unless it is possible to bring the π-bonds into a critical distance which is certainly shorter than 2.7 Å. Thus, while we cannot specify a precise critical distance our approach defines a clear methodology for searching this critical distance and for tracing the origins of the intramolecular advantage on chemical reactivity.

Conclusions

The Diels–Alder (D–A) reaction is significantly less exothermic than the cycloaddition of three ethylenes (C-3E). Despite this thermodynamic disadvantage, the D–A reaction enjoys an overwhelming electronic advantage over the C-3E reaction, reaching a difference of *ca.* 26 kcal mol^{-1} in the corresponding barriers computed at the MP4 level with either the 6-31G* or the 3-21G basis sets. This is electronic catalysis induced by the proximity of the two π-bonds in butadiene. The calculations reveal that the D–A reaction also enjoys an intramolecular entropic advantage of *ca.* 7 kcal mol^{-1} over the C-3E reaction. The presence of the entropic component is in accord with expectations based on the Page–Jencks[1a–c] analysis, that linking in proximity two reacting moieties reduces the loss of entropy along the reaction coordinate.

The adjacent π-bonds in butadiene are shown to be slightly stabilized relative to two isolated π-bonds [eqn. (5)], and therefore the overwhelming electronic advantage does not originate in the ground state effects in the two reactions. Instead this effect is shown to be exerted through a stabilization of the reactant excited state that possesses the bonding features of the product, the so-called 'prepared excited state'. The excitation energy gap between the ground state and the prepared excited state is the promotion energy of the reaction and is the root cause of the barrier according to the curve crossing model.[4,6] The larger the promotion energy the larger, in general, the barrier.

It is argued that the smaller promotion energy gap in the D–A reaction requires less molecular deformation and repulsion to achieve the transition state by the resonance between the ground and the prepared excited states. Our computations show that the intramolecular advantage of the D–A reaction is composed of 7.2 kcal mol^{-1} of advantage in deformation energies and 17.6 kcal mol^{-1} of advantage in repulsive interactions. The notion of less deformation and fewer repulsions inherent in the intramolecular electronic advantage is in general agreement with the views expressed by Dorigo and Houk,[26] and with the analysis of Bach *et al.*[2a]

This understanding of the mechanism by which the electronic advantage operates allows us to construct a simple 'proximity function' [eqn. (12)] which can estimate the intramolecular electronic effect on the reaction barrier at different proximities defined by the bond order between the π-bonds which are held in proximity. This function shows that there exists a critical bond order in which the electronic and entropic advantages become equal. Using bond order–bond length relationships it is possible to define in turn a corresponding 'critical distance' in which this equality of intramolecular effects should occur. This distance turns out to be quite short ($\leq$ 1.86–2.73 Å), and it is concluded that in most common cases of through-space proximity, where the actual distance is longer than the 'critical distance', the observed intramolecular advantage is likely to be dominated by the entropic effect, with a smaller contribution from the electronic effect. While we cannot derive an accurate 'critical distance' our analysis nevertheless provides a clear methodology for calibrating such distances either by computational or experimental studies.

An important effect which occurs at the critical and shorter distances may be deduced from the fact that the two very close π-bonds in butadiene do not maintain between them any significant repulsive interactions [eqn. (5)]. Thus, at the critical distance or closer, the repulsive closed-shell interactions are dissipated through polarization and cross-conjugation of the reacting moieties. Heuristically speaking, by the use of butadiene as a reactant in the cycloaddition of three π-bonds, part of the multibond process is already *virtually* complete at the ground state. It follows therefore that if two reactants can be brought into the critical distance without raising the energy or by compensating the energy rise then the overall barrier of the reaction will be reduced by the electronic effect. This effect, added to the entropic advantage can amount to $\geq$10–11 orders of magnitude in rate enhancement.

Finally, the intramolecular advantage analysed here is reminiscent of the intramolecular reactivity which is amply demonstrated in the literature.[27] The applicability of our conclusions to this broader topic of intramolecularity will be explored in future.

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Supplementary Material

An Appendix which summarizes all geometric details and total energies of all the optimized species for the Diels–Alder reaction and the cycloaddition of three ethylenes, is available from the authors upon request.

References

1 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, NY, 1970.

2 (*a*) R. D. Bach, J. W. Wolber and H. B. Schlegel, *J. Am. Chem. Soc.*, 1985, **107**, 2837; (*b*) K. N. Houk, R. W. Gandour, N. G. Rondan and L. A. Paquette, *J. Am. Chem. Soc.*, 1979, **101**, 6797.

3 (*a*) D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, 1951, **10**, 198; (*b*) M. Uchiyama, T. Tomioka and A. Amano, *J. Phys. Chem.*, 1964, **68**, 1878; (*c*) W. Tsang, *J. Chem. Phys.*, 1965, **42**, 1805; (*d*) J. Sauer and R. Sustman, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 779.

4 S. S. Shaik and P. C. Hiberty in *Theoretical Models for Chemical Bonding*, ed. Z. B. Maksic, Springer, Berlin, 1991; vol. 4, pp. 303–304.

5 J. B. Pedley and J. Rylance, *Computer-Analysed Thermochemical Data: Organic and Organometallic Compounds*, University of Sussex, 1977.

6 (*a*) S. S. Shaik, *J. Am. Chem. Soc.*, 1981, **103**, 3692; (*b*) S. Shaik, *Pure Appl. Chem.*, 1991, **63**, 195; (*c*) A. Pross and S. S. Shaik, *Acc. Chem. Res.*, 1983, **16**, 363; (*d*) S. S. Shaik, H. B. Schlegel and S. Wolfe, *Theoretical Aspects of Physical Organic Chemistry. The S_N2 Mechanism*, Wiley, NY, 1992; (*e*) T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, NY, 1987; pp. 604–608; 359–360.

7 J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.

8 J. S. Binkley, *Int. J. Quantum Chem.*, 1979, **9**, 229; C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

9 P. C. Harriharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

10 S. S. Shaik, P. C. Hiberty, G. Ohanessian and J. M. Lefour, *J. Phys. Chem.*, 1988, **92**, 5086.

11 D. Hegarty and M. A. Robb, *Mol. Phys.*, 1979, **38**, 1795; R. H. E. Eade and M. A. Robb, *Chem. Phys. Lett.*, 1981, **83**, 362.

12 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163.

13 M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, GAUSSIAN 90, Revision J, Gaussian, Inc.: Pittsburgh PA, 1990.

14 (*a*) K. N. Houk, Y.-T. Lin and F. K. Brown, *J. Am. Chem. Soc.*, 1986, **108**, 554; (*b*) F. K. Brown and K. N. Houk, *Tetrahedron Lett.*, 1984, **25**, 4609.

15 M. A. McCarrick, Y.-D. Wu and K. N. Houk, *J. Am. Chem. Soc.*, 1992, **114**, 1499.

16 D. C. Spellmeyer and K. N. Houk, *J. Am. Chem. Soc.*, 1988, **110**, 3412.

17 F. Bernardi, A. Bottoni, M. J. Field, M. F. Guest, I. H. Hillier, M. A. Robb and A. Venturini, *J. Am. Chem. Soc.*, 1988, **110**, 3050.

18 F. Bernardi, A. Bottoni, M. A. Robb, M. J. Field, I. H. Hillier and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1985, 1051.

19 (*a*) A. J. Meyer and R. S. Mulliken, *Chem. Rev.*, 1969, **69**, 639; S. P. McGlynn, T. Azumi and M. Kinoshita, *The Triplet State*, Prentice-Hall, Englewood Cliffs, NJ, 1969; (*b*) D. A. Mosher, W. M. Flicker and A. Kuppermann, *J. Chem. Phys.*, 1973, **59**, 6502; D. F. Evans, *J. Chem. Soc.*, 1960, 1735; (*c*) M. Said, D. Maynau and J. P. Malrieu, *J. Am. Chem. Soc.*, 1984, **106**, 580.

20 (*a*) M. I. Page and W. P. Jencks, *Gazz. Chim. Ital.*, 1987, **117**, 455; (*b*) M. I. Page, *Chem. Soc. Rev.*, 1973, **2**, 295; (*c*) M. I. Page and W. P. Jencks, *Proc. Nat. Acad. Sci. USA*, 1971, **68**, 1678.

21 P. George, M. Trachtman, C. W. Bock and A. M. Brett, *Tetrahedron*, 1976, **32**, 117.

22 L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, 1974, **96**, 1370.

23 For a related analysis in terms of curve crossing, based on total 'exchange' and 'coulomb' VB terms see: (*a*) F. Bernardi, M. Olivucci and M. A. Robb, *Research on Chemical Intermediates*, 1989, **12**, 217; (*b*) F. Bernardi, M. Olivucci, J. J. W. McDouall and M. A. Robb, *J. Chem. Phys.*, 1988, **89**, 6365.

24 (*a*) H. S. Jonston and C. Parr, *J. Am. Chem. Soc.*, 1963, **85**, 2544; (*b*) L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542.

25 S. Wolfe, D. J. Mitchell and H. B. Schlegel, *J. Am. Chem. Soc.*, 1981, **103**, 7694.

26 A. E. Dorigo and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 3698.

27 A. J. Kirby, *Adv. Phys. Org. Chem.*, 1980, **17**, 183.

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