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A new electronic theory of pericyclic chemistry and aromaticity is proposed: The Cplex-isoelectronic theory. Consistent with Santilli's hadronic chemistry

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Abstract

A new electronic theory of pericyclic chemistry and aromaticity, in line with the Robinson/Ingold electronic theory, is proposed. It is referred to as the Cplex-isoelectronic theory. This represents the first successful theory that is not based on quantum mechanics. There are three assumptions in this theory (1) ADEP, (2) SDEP and (3) SDSE. The ADEP assumption refers to isoelectron pairs moving in an antiperiplanar mode in relation to the plane of the molecule. SDEP relates to isoelectron pairs moving in a synperiplanar mode and SDSE refers to single isoelectrons moving in a synperiplanar mode. These assumptions are deduced from nucleophilic, radical addition, S_N2 and S_N2' reactions and the anomeric effect. Application of the ADEP concept to pericyclic reactions is supported by Complexity theory and backed up by direct empirical evidence from 1,3-dipolar cycloaddition reactions involving nitronates and by its ability to predict the experimental data. The heavy atom effect provides experimental evidence for the SDSE mode in pericyclic reactions. The HOMO Diels–Alder is consistent with the SDEP concept. Evidence for the assumptions in aromatic compounds is found in the observation of a diamagnetic ring current in the presence of an applied field and in the applicability of the Biot–Savart law. The Cplex-isoelectronic theory makes different predictions from the present quantum chemical methods in some cases, namely the existence of suprafacial concerted thermal [2 + 2], [4 + 4], [6 + 2] and [6 + 6] cycloadditions, suprafacial concerted photochemical [4 + 2] and [6 + 4] cycloadditions, stepwise [2 + 2 + 2] cycloadditions of ethyne, diamagnetic ring currents for some cyclic systems with $4n\pi$ electrons. The available empirical evidence is consistent with these predictions. This finding is consistent with Santilli's hadronic chemistry which proposes that the present quantum chemical theories require the addition of a small correction factor for molecules with two or more electrons.
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1. Introduction

In 1999 Santilli proposed a new theory for the structure of H_2 based on hadronic mechanics, which assumes that the electrons involved in the chemical bond overlap to create a singlet quasi-particle state called the isoelectronium [1]. Hadronic chemistry permits an exact representation of the binding energy of H_2 from axiomatic principles, without ad hoc modifications of the theory, and increases the speed in computer calculations by at least 1000-fold compared to a C.I. calculation [1,2]. Hadronic mechanics is not only potentially of immense theoretical importance but it also predicts new clean energy sources at the level of elementary particles, at the nuclear level and at the molecular level [2]. There is empirical evidence for these predictions even though this area of research is still relatively new [1,2]. Hadronic mechanics is proposed as a 'covering' theory of quantum mechanics. It claims that quantum mechanics is exact for the hydrogen atom but requires a correction, due to the deep overlap of the wavepackets of the valence electrons at short distance, for molecules with two or more electrons [2]. The basic axioms of quantum mechanics do not cover this interaction [2].

Abbreviations: ADEP, antiperiplanar dynamics of isoelectron pairs; AFS, acceptor at the final facial selectivity site; ASIED, acceptor site of initial electron dynamics; DFS, donor at the final facial selectivity site; DSIED, donor site of initial electron dynamics; FSED, final facial selectivity of electron density; RCEDGD, rate of continuous electron dynamics greater than delocalisation; SEADEF, substituent electronic assistance in the direction of the electron flow; SDSE, synperiplanar dynamics of single isoelectrons; SDEP, synperiplanar dynamics of isoelectron pairs.

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For *complex* chemical systems, in calculating an exact representation based on quantum methods, the computer time required reaches prohibitive amounts, even with supercomputers. Thus the present quantum chemical methods are prone to making inaccurate predictions for complex systems due to the use of approximations, assumptions, diversity of factors involved, intractable calculations, computational limitations and indeterminacy. This is augmented by chaos where small variations in the input can result in dramatically different outputs. Complex systems, where many factors are interacting, are especially prone to chaos. A slight increase in the activation energy of one step of a multi-pathway reaction, for example, could result in the emergence of a completely different product. If the isoelectronium concept is valid it increases the probability even further that the present quantum chemical methods can make inaccurate predictions. These factors become even more pronounced and inhibitive as the complexity of the system increases.

It is in the areas of pericyclic reactions and aromaticity that the quantum-based methods have seen their greatest growth in chemistry since the 1950s. These methods include the Woodward–Hoffmann [3], the FMO [4] and the modern ab initio approaches [5], all of which have received the Nobel prize in chemistry. Based on the above logic it is feasible that these quantum-based approaches make imprecise predictions for these *complex* chemical systems. This paper proposes a new electronic theory of pericyclic chemistry and aromaticity that makes different predictions from the present quantum chemical methods. The experimental evidence, when available, is consistent with these new predictions. Thus this new chemical theory represents independent research that is consistent with Santilli's hadronic chemistry. This theory will be referred to as the Cplex-isoelectronic theory (Cplex is an abbreviation for Complex). The term 'iso' is used as hadronic chemistry provides an origin, an attractive force and a quantitative representation for the chemical bond and is a covering theory of quantum mechanics [1,2].

The Cplex-isoelectronic theory of pericyclic chemistry and aromaticity is in line with the old electronic theory of Robinson and Ingold [6]. The Robinson's and Ingold's electronic theory of organic chemistry has a strong empirical basis and successfully rationalises a vast degree of experimental data and thus represents a firm foundation on which to develop a new theory. The concept of electronegativity for example provides insights into radical stabilities, electrophilic aromatic substitutions, steric effects, conjugative stabilisation in unsaturated systems, rotational barriers, molecular and electronic structure yet it does not build on any of the electronic properties of atoms that results from the Schrödinger equation and is still a subject of current research [7]. Although Robinson's and Ingold's theory is still used profusely by the experimental organic chemist in trying to understand and predict complex chemical reactions, it lost a lot of its strength as a theory due to the fact that no one was able use it to successfully rationalise pericyclic reactions and aromaticity during the 1950s and 1960s when the Woodward–Hoffmann and the FMO approaches emerged. Concepts and principles used within this old electronic theory can be understood, in principle, in terms of hadronic or quantum mechanics. By definition the fundamentals of the old electronic theory do not conflict with the fundamentals of hadronic chemistry or quantum mechanics. They exist on different levels of the 'reductional hierarchy', in the same way that Darwinism exists on the biological level.

The Cplex-isoelectronic theory, like Darwinism and the Robinson/Ingold theory, is qualitative, making logical and scientific connections between known and unknown systems (within the chemical level), an approach seen in the emerging area of Complexity theory [8]. There is still a place for such qualitative theories for complex systems considering the above discussion in relation to the present quantum chemical methods. In fact Fukui stated that "chemistry inevitably depends on analogy through experience due to the formidable complexity" [4]. As this new theory is based on the chemical and not the quantum level it is less prone to making inaccurate predictions as there are less factors involved. Expansion into the hadronic and quantum level is for the future, either in a qualitative or quantitative form, when the theory is fully developed on the chemical level.

In this paper the Cplex-isoelectronic theory will be applied to some of the major areas of pericyclic chemistry and aromaticity to show its validity. Due to the limitation on length within this journal it will be expanded upon in detail in subsequent papers, including all areas of pericyclic chemistry and 'aromaticity'/'antiaromaticity'. These papers will also show that this new chemical theory makes further predictions that are different from the present quantum chemical methods.

2. Results and discussion

2.1. Hypostasis and assumptions of the theory

Anti addition is favoured, under conditions of kinetic control, when nucleophiles undergo addition reactions with multiple bonds [9], Fig. 1. This could be rationalized by a steric effect; the incoming nucleophile and subsequent electrophile are at a maximum separation in this antiperiplanar geometry. However, it is conceivable that an electronic factor is also involved, namely that the isoelectron pairs (isoelectronium) move more efficiently in an antiperiplanar manner, i.e. the isoelectron pair of the multiple bond moves on the opposite side of the plane of the molecule to the isoelectron pair of the incoming nucleophile. This is a logical assumption, as this dynamic effect would minimize electron repulsion as the electron density moves on opposite sides of the plane, thus lowering the overall energy of the system. To distinguish from the steric factor the term ADEP (antiperiplanar dynamics of isoelectron pairs) will be used to refer to the electron dynamics specifically. A list of acronyms is given at the end of this paper. The term 'isoelectron pair' is used instead of 'electron pair' as hadronic chemistry provides an origin, an attractive force and a quantitative representation for the chemical bond and is a covering theory of quantum mechanics as discussed above. The Robinson/Ingold

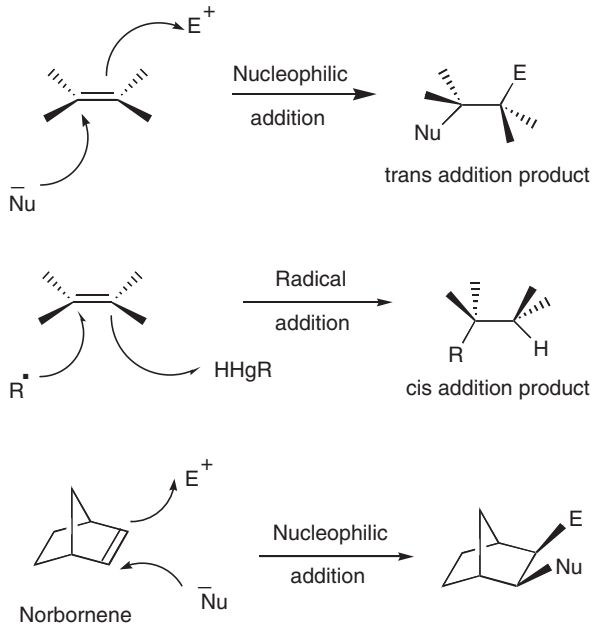

Fig. 1. Trans addition of nucleophiles and cis addition of radicals to multiple bonds. The syn addition of nucleophiles to norbornene.

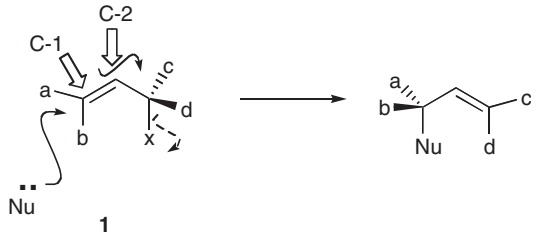

Fig. 2. Evidence for the ADEP assumption based on the S_N2' reaction.

electronic theory uses the term 'electron pair' and without any underlying structure.

Evidence that the antiperiplanar geometry could be related to an electronic factor is seen in the so-called anomeric effect [10]. As this effect is contrasteric, the antiperiplanar geometry must be related to an electronic effect. Evidence that an electronic effect is involved when isoelectron pairs *move* is seen in the S_N2' reaction. The leaving group departs from the same face that the nucleophile adds on to. This is illustrated by **1** (Fig. 2). This contrasteric effect not only implies that an electronic factor is involved in dynamic processes that involve isoelectron pairs but it also implies that it is greater than the steric factor. Based on this assumption the increase in electron density occurs on the face of C-2 that points away from the incoming nucleophile (at C-1) due to the ADEP process. This facial aspect of the electron density at C-2 results in the leaving group (X) syn to the incoming nucleophile so that backside attack on the C3-X bond can occur. Backside attack is confirmed in S_N2 reactions. Syn addition and a one step pathway has been confirmed experimentally in the S_N2' reaction [11]. The term stereoelectronic control invokes a steric effect and the molecular orbital concept [10]. Thus the term ADEP will be used as it refers specifically to the dynamics of isoelectrons only and does not invoke the orbital concept or steric effects.

Radicals undergo syn (cis) addition under kinetic control [12], Fig 1. This contrasteric result implies that an electronic effect is operating. Radicals are well established in exhibiting stereochemical and regiochemical behaviour, as opposed to being highly reactive and unselective entities as is often perceived. Radical reactions involve single isoelectrons. Thus it could be assumed that single isoelectrons move more efficiently in a synperiplanar manner. The term SDSE (synperiplanar dynamics of single isoelectrons) will be used. It refers specifically to the dynamics of isoelectrons only and does not invoke the orbital concept or a steric effect. This theory is not "empirical" or "phenomenological" [8a]. Mechanisms/rationales for the assumptions can be provided for within the chemical level i.e. using the fundamentals of chemistry, in line with the old electronic theory of Robinson, Ingold, Lapworth, Meerwein etc. developed during the early 20th century and which has a strong empirical basis [6].

In conjunction with the experimental data on which the assumptions of this theory are deduced from, the ADEP process is more efficient than the SDSE. The empirical data shows that radical additions to multiple bonds are in general far less stereospecific than nucleophilic additions [9,12].

Based on the experimental data syn nucleophilic addition is favoured for strained cyclic systems such as norbornene and cyclobutene [13], Fig. 1. This implies that an SDEP process (synperiplanar dynamics of isoelectron pairs) is preferred over the ADEP for strained systems.

The fact that nucleophilic addition to unstrained systems give low yields of the syn addition product, in many cases 0% [9], and there is evidence that syn addition products arise via enol intermediates and via inversion of carbanion intermediates with increased lifetimes, as syn addition arises more in non-polar aprotic solvents as opposed to proton-donating solvents [9], implies that the SDEP process has a high activation energy for unstrained systems. In fact there is no conclusive evidence that an SDEP process has been observed for unstrained systems i.e. that syn products arise directly as opposed to inversion or rotation of an intermediate formed from the ADEP process.

Considering that, in general, kinetic syn addition is confirmed in radical addition reactions and in high yields and the yield of the syn addition product is much less in unstrained systems, with no conclusive evidence for a direct syn addition product (kinetic syn product) implies that the SDSE mechanism is favoured over the SDEP mechanism for unstrained systems.

Application of the ADEP/SDSE/SDEP concept to pericyclic reactions, as well as aromaticity, is supported by Complexity theory (regularities/connections occur within and between systems) [8] and is backed up by direct empirical evidence (see Sections 2.3, 2.5 and 2.7) as well as its ability to predict the experimental data.

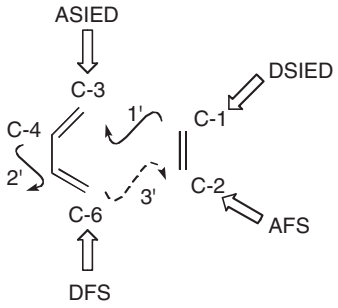

Fig. 3. The ADEP syn FSED electronic mechanism of the Diels–Alder concerted cycloaddition.

2.2. The ADEP syn FSED electronic mechanism of the concerted cycloaddition

Applying the ADEP concept to the concerted Diels–Alder [4 + 2] reaction results in the electronic mechanism illustrated in Fig. 3 (view the dienophile, C2 = C1, as lying below the plane of the diene). The double bonds of butadiene are assumed to be localized (see subsequent paper). Based on the logic of the assumption the olefin 'initiates' the cycloaddition by acting as a nucleophile or isoelectron source. This will be referred to as the 1′ process and the nucleophilic center, C-1, as the DSIED (donor site of initial electron dynamics). The diene acts as the electrophile in the 1′ process and the center, C-3, will be referred to as the ASIED (acceptor site of initial electron dynamics). The 1′ process results in an increase in electron density on the face of C-4 that points away from the dienophile (olefin) due to the antiperiplanar dynamics of the isoelectron pairs (ADEP). This increase in electron density at C-4 acts as a nucleophilic center and attacks the C5–C6 double bond. This ADEP process results in an increase in electron density on the face of C-6 that points towards the dienophile. Thus the decrease in electron density at C-2 of the dienophile, due to the 1′ process, can be neutralized rapidly by the increase in electron density at C-6 because the electron density at C-6 is pointing directly towards the top face of C-2. This facial aspect of the electron flow at the C-6 and C-2 terminus will be referred to as the FSED (final facial selectivity of electron density). In this case the increase in electron density at C-6 and the decrease in electron density at C-2 occur on the faces of the atoms that point towards each other. This will be referred to as 'syn FSED'. It is this syn FSED concept that expounds why the reaction is concerted. It prevents charge accumulation. Charged species are in general far less stable than the neutral species. Thus developing charge increases the activation energy and minimizing the degree of charge results in pathways of relatively low activation energy. A concerted reaction, based on this new electronic theory, is proposed to involve an ADEP process with syn FSED. To illustrate electron density moving on the bottom face of the molecule a dashed curved arrow is used arbitrarily and a plain curved arrow for dynamics on the top face. In the 1′ process electron density moves above the plane of the dienophile, as drawn, and thus a plain curved arrow is invoked. In the 3′ process electron density moves below the plane of the diene and thus a dashed curved arrow is used. The plane of the electron source is arbitrarily considered as opposed to the electron sink. As in the Robinson electron theory the curved arrows imply the movement of electrons only and not the nuclei. C-6 of the diene will be referred to as the DFS (donor at the final facial selectivity site) and C-2 of the dienophile as the AFS (acceptor at the final facial selectivity site).

Within the logic of this theory the movement of electron density is also a gradual process, which prevents charge accumulation, i.e. no site develops a full negative or position charge at any stage in the reaction. The 2′ process has begun before the 1′ process is complete and the 3′ process has begun before the 2′ process is complete. As no charge accumulates, solvent polarity has little effect on the rate of cycloaddition as is found experimentally. In conjunction with the experimental data on which the assumptions of this theory are deduced from, the ADEP mechanism for thermal pericyclic reactions is predicted to be favoured over the SDSE and SDEP as discussed above (Section 2.1).

Based on this electronic mechanism the majority of the activation energy in relation to the contribution from the electronic mechanism (there is also a thermodynamic contribution to the transition state from the exothermic reaction) is predicted to be involved in the 1′ process. This is because, once the isoelectrons begin to move the process begins to drive itself, as electron density moves towards a region of low electron density (AFS). Within the ADEP syn FSED theory the transition state is asynchronous by definition (see Section 2.3 on KIE's and Section 2.4 for empirical evidence). This prediction is different from the predictions of the present quantum chemical methods. Bond making at the DSIED-ASIED terminus is always in advance of bond making at the DFS–AFS terminus (syn FSED cannot be achieved otherwise), including the parent Diels–Alder.

Based on the ADEP assumption the dienophile must behave as the DSIED for a concerted reaction to occur. In a reaction pathway in which the diene behaves as the DSIED (C-3), the FSED at C-2 and C-6 is not syn. The increase in electron density at C-2 of the dienophile occurs on the face pointing away from the diene and thus is unable to neutralize the decrease in electron density on the diene and thus charge begins to build up. This 'trans FSED' cannot result in a concerted process and such an interaction is predicted to involve a stepwise pathway.

The behaviour of the dienophile as an electron donor in the 1′ process and subsequently as an electron acceptor in the 3′ process, in the proposed concerted mechanism, and the order in which they occur is similar to an electrophilic addition to a multiple bond, but without full charges or an intermediate developing. As the 1′ process is predicted to be the slowest part in the overall electronic mechanism it is essentially an A-SE2 type mechanism [14]. Consistent with this new electronic mechanism of pericyclic reactions the A-SE2 mechanism involving multiple bonds (no bridging intermediate possible as H involved) is highly stereospecific and syn, syn is increasingly favoured at low temperatures and by weakly donating solvents as well as by increasing the concentration of HX [15]. Thus not only is a facial aspect to the decrease in electron density at the AFS possible but it is syn to the DSIED based on the

experiment data of electrophilic addition reactions. Thus there is precedence for all parts of the proposed electronic mechanism.

The ADEP theory focuses on avoiding the accumulation of charge, both negative and positive, especially via the syn FSED mechanism, and the SDSE theory focuses on avoiding the accumulation of single isoelectrons (radical character) whereas the Woodward–Hoffmann and FMO theories [3,4] focus on avoiding bonding electrons in the reactants moving into antibonding orbitals in the product. The linear combination of atomic orbitals approach (LCAO) for polyene systems results in the molecular orbitals having the symmetry of p-orbitals. P-orbitals have a + and − phase, above and below the plane. For concerted reactions, orbitals with the same phase must overlap, as this allows a bonding situation to arise. The + and − symbols do not refer to charge, but to the amplitude of the wave. It is this aspect, coupled to coincidence that explains why the Woodward Hoffmann and the FMO approaches make similar predictions to the ADEP/SDEP/SDSE theory in some cases. The symmetry above and below the plane is analogous to the facial aspect of the electron density at the DFS-AFS terminus in the ADEP theory. This is purely a scientifically unconnected analogy; orbital symmetry/MO and the ADEP and syn FSED concepts are completely different. The orbital symmetry at both of the bonding termini must be considered in the MO approach. In the ADEP theory the emergence of a concerted reaction is essentially determined by the facial aspect of electron density at only one terminus, the DFS–AFS terminus.

None of the modern MO quantum chemical techniques, as well as VB and DFT methods, invokes the ADEP concept and the syn FSED concept in pericyclic reactions and aromatic compounds [5]. There is no direct connection stated, by quantum chemists, between the ab initio MO theory of the S_N2' reaction [11c] and pericyclic reactions and aromaticity. Furthermore, in MO theory the *trans* bending that occurs when a nucleophile attacks a multiple bond is due to an interaction between the σ_{CH} and the π^* LUMO and is not due to the dynamics of the electron pairs [9c]. Thus this new theory is different from the present quantum chemical methods.

2.3. Evidence for the ADEP syn FSED theory

1,3-Dipoles have also been shown to be subject to *trans* addition with nucleophiles [16] and thus the ADEP concept applies. Experimental evidence for the involvement of the ADEP process in concerted reactions comes from the [3 + 2] cycloadditions of nitronate **2** with acrylonitrile **3** under conditions of kinetic control (Fig. 4) [17]. Based on the logic of this theory the dipolarophile behaves as the DSIED for syn FSED to occur. The carbon directly bonded to the cyano group in **3** is assumed to behave as the DSIED because it is the more nucleophilic end of the dipolarophile. Thus the negative end of the dipole, oxygen, behaves as the ASIED [see Section 2.4, paragraph 2, in relation to this aspect]. Nucleophilic attack at the ASIED (1′ process) results in inversion of the negative charge on the oxygen, via electron repulsion from the DSIED,

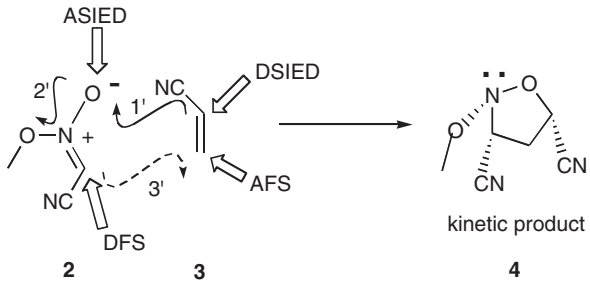

Fig. 4. Empirical evidence for the ADEP syn FSED electronic mechanism.

followed by a transfer of the isoelectron pair onto the central nitrogen of the 1,3-dipole (2′ process). This is an S_N2-type process with the isoelectron pair as the 'leaving group' (nucleofuge) (2′ process; the same type of arrow is used in the S_N2 reaction to signify bond breaking), departing on the opposite side of the 1,3-dipole to the electron density coming from the DSIED. This transfer results in a 'nucleophilic attack' of the isoelectron pair on the C═N double bond and hence the electron density increases on the face of the C of the 1,3-dipole **2** that points towards the dipolarophile **3**, via the ADEP process. Thus syn FSED is achieved and the reaction is concerted. To achieve syn FSED the isoelectron pair on the oxygen (ASIED) in the 2′ process must move on the face of the dipole that is opposite to the incoming dipolarophile. Thus the lone pair on the central nitrogen will be *trans* to the incoming dipolarophile. This is found experimentally in the product [17]. The nitrogen lone pair in the isoxazolidine **4** is on the side opposite to the incoming dipolarophile **3**. The reaction is found by experiment to be under kinetic control, the invertomers are stable under the reaction conditions (barrier to inversion in the range 29–30 kcal/mol) and the phenomena independent of the stereochemistry of the dipole. Furthermore, the cyano group lies in the *endo* position in the transition state and is as predicted *trans* to the lone pair in the product. Dipole **2** has been shown to be stereospecific with *cis* dideuterated methyl acrylate and dimethyl malonate, consistent with a concerted process [17]. Thus there is direct experimental evidence for the ADEP syn FSED electronic mechanism in concerted reactions. Thus not only has a connection between the assumptions and pericyclic reactions been noted, in line with complexity theory [8], but there is direct experimental evidence.

The ADEP transition state for the Diels–Alder has S_N2-like character (note assumption of theory) and thus the secondary kinetic isotope effects (SKIEs) are predicted to be similar to those observed for S_N2 reactions (of the order 0.95 to 1.06 per α deuterium) [18]. This is consistent with the observation that the Diels–Alder cycloadditions exhibit inverse SKIEs (< 1.0) that are close to unity [19]. The fact that the SKIE is different at the ASIED and the DFS is consistent with the ADEP asynchronous transition state. There is no conclusive experimental evidence for the origin of SKIE's in general. As the reaction moves from the S_N1 to the S_N2 end of the spectrum the SKIE becomes more inverse [18]. It could thus be assumed that a more inverse SKIE relates to a greater build up of electron

density (this could be equated to a greater degree of pyramidalization). If this assumption is valid it implies that there is a greater build up of electron density at the DFS than at the ASIED in the transition state. This is consistent with the 1′ process as the major factor in the transition state, the flow of electron density is towards the DFS as a result of the 1′ process. In the 1′ and 2′ processes combined, the electron density at the ASIED remains essentially constant. The DFS–AFS interaction is less advanced in the transition state. Consistent with this theory is the empirical observation that as the nucleophilicity of the DSIED increases (electron withdrawing ability of the substituent attached to C-1 increases) the inverse SKIE at the DFS increases whereas the value at the ASIED remains essentially constant [19a]. The importance of the 1′ process and the direction of electron flow also explains why the SKIEs are greater for the diene than the dienophile. Furthermore, the fact that the SKIEs are close to unity is consistent with the fact that charge does not accumulate.

2.4. Regioselectivity

The proposed electronic mechanism for the Diels–Alder reaction (Section 2.2) predicts that the introduction of a substituent on the diene that can aid the movement of the isoelectrons across the diene will increase the efficiency of the pericyclic process. This logic allows the regioselectivity and rate increase with electron rich dienes to be predicted. In conjunction with this the preference for the 'ortho' product **7** over the 'meta' **8** in the Diels–Alder cycloaddition (a so-called 'normal' DA) [20] is related to electronic assistance from the 1-substituent in the diene **5**, similar to the concept of anchimeric assistance (Fig. 5). The donating ability of the diene substituent helps the DSIED to assist the isoelectrons, at the ASIED, in the direction of the DFS. Experimental evidence for the existence of anchimeric assistance is well established [14]. The term SEADEF (substituent electronic assistance in the direction of the electron flow) will be used. This prediction is consistent with the observation that as the electron donating ability of the substituent increases the rate of reaction also increases. Preference for the 'para' product **10** in the case of 2-substituted butadienes **9** is in accordance with assistance to the direction of electron flow from the substituent (Fig. 5). In the formation of the 'meta' product (1,3-disubstituted) the electron donating effect of the substituent is antagonistic to the direction of electron flow. Thus the greater reactivity of 1-substituted dienes **5** over 2-substituted species **9** reflects the fact that the SEADEF effect in the transition state is over two double bonds for the former but only over one double bond for the latter. The substituent assists four isoelectrons towards the AFS when in the 1-position but only two isoelectrons when in the 2-position. Furthermore, and probably the major factor, the substituent in the 1-position is closer to the terminus at which the 1′ process occurs and thus it has a much greater effect on lowering the activation energy. The SEADEF effect is predicted to be a transition state effect, as is the similar neighbouring group mechanism with examples of the principle of increasing demand [14], and not a ground state effect.

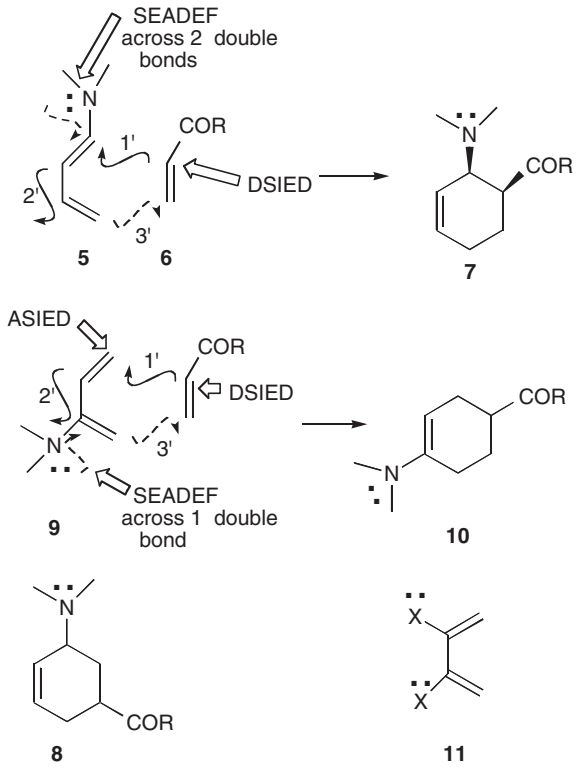

Fig. 5. Origin of the Diels–Alder regioselectivity.

Thus the experimental observation of enhanced reactivity between dienes with electron donating groups and dienophiles with electron withdrawing substituents is predicted by the proposed electronic mechanism. As the electron donating ability of the donor in the 2-position increases, the rate of reaction increases, consistent with a greater degree of SEADEF. The lower reactivity of symmetrically donor-substituted dienes such as **11** (Fig. 5) compared to the unsymmetrical analogues **9** can thus be easily rationalized, as the second donor group in **11** is antagonistic to the direction of electron flow. Evidence for this direction of electron flow is seen in the SKIE data, as discussed in Section 2.3, and in the kinetic data (see later in this section).

The fact that electron rich dienes act as the ASIED in the 1′ process is not counter-intuitive [21]. The same applies to 1,3-dipolar cycloaddition reactions where the negative end of the 1,3-dipole behaves as the ASIED, as in the [3 + 2] cycloaddition of nitronate **2** with acrylonitrile **3** (Fig. 4). It has been conclusively shown that a nitrogen anion attacks a carboxyl anion (a delocalised anion) under mild conditions [21a–c]. This is not an isolated example as the 2,4,6-trinitrobenzyl anion attacks the nitro group (a delocalised negative charge) of fluorotrinitromethane, also under mild conditions [21d]. It has been proposed that a sulphur anion attacks a nitro group in the reduction of aromatic nitro compounds by sodium trimethylsilanethiolate [21e]. Furthermore, it has been conclusively shown by experiment that fluoride, oxyanions (anion–dianion reaction), amines and other nucleophiles attack the PO_3^{2-} group [21f]. This mode is also favoured by the fact that charge does not build up as a consequence of the 1′ process, the 2′ process is involved.

Furthermore, as electron donation from the DSIED increases the degree of electronic repulsion in the 1′ process decreases due to the increasing pull from the AFS. For these exothermic reactions the thermodynamic contribution to the transition state will also counteract this electronic repulsion. Furthermore, with electron rich dienes the substituent provides SEADEF to the 1′ process. This is a crucial factor based on the proposed electronic mechanism. Evidence for this direction of electron flow is seen in the SKIE data, as discussed in Section 2.3, and in the kinetic data (next paragraph).

Experimental evidence that the 1′ process is the major factor involved in the activation energy from an electronic vista, and the direction of electron flow predicted in the 1′ process, is seen in the observation that 1,1-dicyanoethylene reacts 43,269 times faster than acrylonitrile in the Diels–Alder reaction whereas 1,2-dicyanoethylene reacts only 78 times faster than acrylonitrile [22]. The cyano groups in the 1,1-position increase the nucleophilicity of the DSIED whereas in the 1,2-system the electron withdrawing effect of the substituents are antagonistic. The CN in the 2-position (1,2-system; dienophile) increases the electron affinity of the AFS as it is directly bonded and this favours the flow of electron density from the DFS to the AFS as well as from the ASIED to the DFS. Thus the CN substituent has a far greater effect on the DSIED–ASIED interaction than on the AFS–DFS interaction. This proves that the 1′ process is the major factor in the electronic mechanism as well as the direction of electron flow, as does the SKIE data (Section 2.3).

2.5. The SDSE syn FSED concerted process

Within this theory the concerted [4 + 2] cycloaddition, as well as the [3 + 2], can also occur by an SDSE process as the FSED is syn. This is illustrated in Fig. 6. Half-headed curved arrows are used to denote the movement of single isoelectrons. It is also feasible to have the arrow in the 1′ process going in the opposite direction (i.e. from diene to dienophile; see subsequent paper). In both cases the FSED is syn. As discussed in Section 2.1 the ADEP mechanism is predicted to be favoured over the SDSE process under thermal conditions based on the experimental data on which the assumptions are deduced from. Hence the thermal Diels–Alder reaction involves the ADEP process illustrated in Fig. 3 and not the SDSE process, Fig. 6.

Evidence for the claim of the existence of a ‘radical-type’ concerted phenomena (SDSE) is seen in the stereospecific addition of singlet diradicals, such as **12** (Fig. 7), to unsaturated systems [23]. All SDSE processes are concerted, as the FSED is always syn. As predicted both [2 + 2] and [4 + 2] cycloadditions were observed with cyclopentadiene and the diradical **12** [24]. The SDSE process could in theory be synchronous or asynchronous unlike the ADEP process, which is by definition asynchronous. The diradical must be a singlet (opposite spins) as the theory assumes that a chemical bond involves isoelectrons with opposite spins.

Based on the experimental data of the assumptions, the SDSE syn FSED is predicted to be generally disfavoured under thermal conditions. However, as the 1′ process is the major factor in

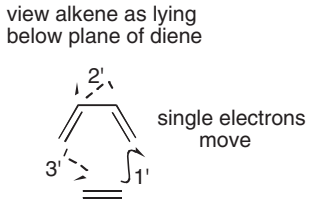

Fig. 6. The SDSE syn FSED electronic mechanism for the concerted [4 + 2] cycloaddition.

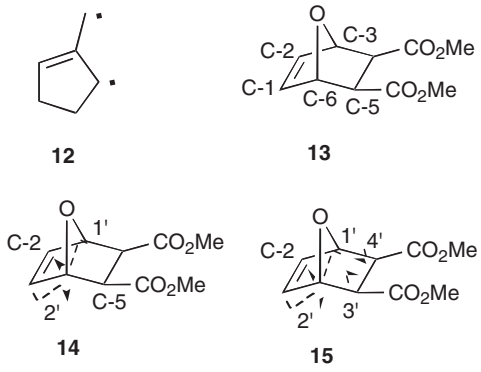

Fig. 7. Singlet diradical **12**, 7-Oxabicyclo[2.2.1]hept-2-ene **13** and electronic mechanisms **14,15**.

the transition state from an electronic vista, as discussed above, the SDSE mechanism should become more favoured if the diradical character generated in the 1′ process can be maintained syn (same face of the atoms) coplanar (same plane).

In the diradical **12** [23,24], the single isoelectrons are delocalised by the same group and thus can be maintained coplanar. Hence the addition reactions of **12** are stereospecific. Based on this logic the weaker the bond the lower the reaction temperature required and therefore the ability to maintain the single isoelectron character syn coplanar increases. A geometry, which prevents rotation of the single isoelectron centre, should also favour an SDSE process under thermal conditions. An intramolecular reaction as opposed to an intermolecular also favours the SDSE mechanism, as there is less time for a large degree of radical character to build up, for rotation and inversion to occur. Geometrical constraints, delocalisation by the same group, a weak bond and an intramolecular reaction are thus predicted to favour the SDSE syn FSED electronic mechanism as they help maintain the single isoelectron character in the 1′ process syn coplanar. These factors become important when the ADEP mechanism cannot achieve syn FSED and thus the SDSE mechanism can emerge. Only if a molecule has a high degree of single isoelectron character (a full diradical such as **12** for example) is a bias towards the SDSE mechanism over the ADEP predicted.

Experimental evidence for an SDSE process in pericyclic reactions comes from the observation of a substantial heavy atom effect (HAE) in the [4 + 2] cycloreversion of 7-oxabicyclo[2.2.1]hept-2-ene **13** (Fig. 7) [25]. KIE data, the entropy of activation, activation volume and the stereospecificity

implies that the reaction is concerted with an early transition state as opposed to a biradical or a biradicaloid intermediate [25,26]. The HAE, which is well established by experiment, implies that singlet radical character is involved. In this case the ADEP process is not the most efficient process as a norbornane-type skeleton is present, the SDEP process is favoured (based on the assumption of theory). However, the SDEP process, illustrated in **14**, Fig. 7, cannot occur in a concerted fashion. In this case dashed arrows are used arbitrarily when the isoelectrons move on the same side of the longest bridge (*endo*), plain arrows when they move anti to the bridge (*exo*) and plain arrows when coplanar with the bridge. Attack of the C3–C4 bond on the C2–C1 double bond in the 1′ process results in an increase in electron density on the *endo* face of C-1 due to the SDEP process. Thus backside attack on the C6–C5 single bond cannot occur and hence the SDEP process cannot give rise to a concerted pathway. Frontside attack is not favoured in S_N2 reactions. However, the SDSE process can occur in a concerted process as illustrated in **15**. Singlet diradical character at C-6 and C-3, generated in the 1′ process, is potentially syn coplanar due to interaction with the same C2–C1 double bond and the same oxygen lone pair (a captodative-type interaction [14]). Furthermore, the formation of the aromatic furan ring should lower the energy required to break the single bonds, the bonds are thus relatively weak. The reaction is also intramolecular. All of these factors favour an SDSE mechanism as discussed above. The heavy atom converts the singlet entity, as it traverses the concerted pathway, into a triplet which is the source of the emergence of the nonstereospecificity via a stepwise pathway.

Syn coplanar single isoelectron diradical character can in theory be generated from multiple bonds if the isoelectrons selectively absorb energy so that the molecule stays 'cold' from a vibrational and rotational vista. Photochemical conditions can achieve such an objective (known as the Franck–Condon Principle) as the isoelectrons selectively absorb the radiation. Thus under photochemical conditions the SDSE syn FSED electronic mechanism is predicted to be favoured and more efficient than under thermal conditions. Photochemical conditions are well know to generate radical character and research in the area of molecular reaction dynamics reveals similar transition states, from product angular distributions, for the reaction between a hydrogen atom (radical) and Cl_2 (atom–molecule reaction) and the photo dissociation of Cl_2 (a photon–molecule reaction: $h\nu + Cl_2$) [27]. This theory does not make any predictions about the electronic structure of the excited state of any molecule. The theory is only relevant when singlet coplanar diradical character is generated. The excited state must be a singlet (opposite spins) as the theory assumes that a chemical bond involves an isoelectron pair with opposite spins. A triplet (same spins) excited state is predicted to result in a stepwise pathway, consistent with the experimental findings.

The photochemical [2+2] cycloaddition has been found to be stereospecific when singlet excited states are involved [28], consistent with a concerted SDSE syn FSED process. The [4 + 4] photochemical cycloaddition has been reported and also found to be stereospecific [29]. It is with the photochemical [4 + 2] cycloaddition that the SDSE predictions (predicts all reactions are concerted from an electronic vista) differ from the present quantum chemical methods [3–5], the latter predicts a disallowed process. A stereospecific photochemical [4 + 2] cycloaddition has been reported for 9-cyanoanthracene and diastereoisomers *trans, trans*-2,4-hexadiene and *cis,cis*-2,4-hexadiene with empirical evidence for the involvement of a singlet excited state, consistent with a concerted pathway [30]. The reaction was also stereospecific for *cis*- and *trans*-1,3-pentadiene with 9-anthraldehyde as the diene. Other examples of stereospecific photochemical [4 + 2] cycloadditions, involving the singlet excited state, have been reported as well as an efficient [4 + 2] photocycloreversion with a similar efficiency to the analogous [4 + 4] cycloreversion [31].

Empirical evidence that the photochemical [4 + 2] cycloaddition is concerted arises with the observation of an 'excited' cyclopentadiene intermediate in the femtosecond study of norbornene [32]. This observation, which is consistent with a concerted photochemical *retro* Diels–Alder pathway, has been interpreted by the latest quantum chemical method in terms of a stepwise pathway involving a conical intersection structure, a stepwise pathway being consistent with the Woodward and Hoffmann rules [32b].

The observation of all three types of cycloaddition reactions with anthracene [30], namely [2 + 2], [4 + 2] and [4 + 4], is consistent with the prediction that all SDSE processes are concerted. Photolysis of anthracene and 9-cyanoanthracene with 1, 3, 5-cycloheptatriene gave all four possible cycloadducts, [2 + 2], [4 + 2], [4 + 4] and [6 + 4] [29]. In contrast the [6 + 4] cycloaddition is predicted to be stepwise by quantum chemical theory, including the modern methods. However, there is no empirical evidence available to support a concerted or stepwise pathway for photochemical [6 + 4] cycloadditions. Furthermore, the type of excited state involved has not been reported. The involvement of exciplexes and the orientation of reactants in exciplexes is also crucial information in elucidating photochemical reaction mechanisms.

The [2 + 2] cycloaddition cannot be concerted based on the ADEP theory as syn FSED cannot be achieved. This is illustrated in Fig. 8. This proclivity for the thermal [2 + 2] cycloaddition has been confirmed experimentally for many substrates [33]. In relation to the SDSE mechanism the diradical character is generated from strong bonds, the diradical character is not delocalised by the same group, they are free to rotate as the substrates are acyclic and the reactions are intermolecular. Thus the SDSE mechanism is not favourable for these substrates under thermal conditions. A stepwise pathway

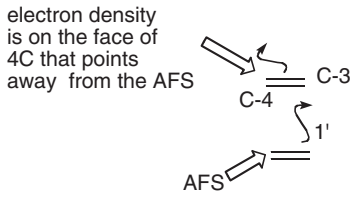

Fig. 8. Origin of the stepwise thermal [2 + 2] cycloaddition.

observed by experiment is consistent with the assumption that the SDSE process is in general inefficient. Furthermore, in the stepwise pathways the zwitterionic intermediates are strongly stabilised and thus have relatively low activation energies. Concerted [2 + 2] cycloadditions are predicted if the factors that favour the SDSE mechanism are present. There is experimental evidence to back up this prediction. Stereospecific [2 + 2] cycloadditions have been observed between cyclopentyne and substituted alkenes (*cis*-1-methoxy-1-propene, *cis*- and *trans*-2-butenes) under thermal conditions suggesting a concerted process [34]. For both cyclopentyne and benzyne the single isoelectron centres are syn coplanar based on geometrical constraints and the bonds are very weak (IR data), thus the SDSE process is feasible although the reactions are intermolecular. The existence of the concerted SDSE process explains why norbornadiene and benzyne exhibits both a [4 + 2] and [2 + 2] cycloaddition [35]. Solvent polarity does not have a dramatic effect on the ratio between the two cycloadditions, which suggests that the [2+2] cycloaddition is concerted. Benzyne is also found to exhibit highly stereoselective [2 + 2] cycloadditions [36]. An SDSE concerted process is also possible, due to restricted rotation of the single isoelectron centres and weak bonds due to strain, in the intramolecular *retro* [2 + 2] of quadricyclane. Although the reaction is forbidden based on the Woodward-Hoffmann theory [3], it does occur on heating [37]. The reaction also occurs photochemically [14] consistent with the possibility that an SDSE mechanism can exist for this system. Stepwise pathways are expected to compete as the radical character of the substrate increases. The present quantum chemical methods do not predict the existence of a suprafacial concerted pericyclic pathway for the [2 + 2] cycloaddition [3–5,34].

Although norbornyne and cyclopentyne are strained substrates, the SDEP mechanism cannot occur for the [2 + 2] cycloaddition due to more than just electronic repulsion of the two isoelectron pairs moving in a confined space. Based on the logic of this theory it is also due to the fact that the paths of the isoelectron pairs cross, they have to occupy the same space at the same time, as the isoelectron pair of the double bond has to move in the direction of the incoming isoelectron pair of the other double bond. The SDSE mechanism is applicable to strained substrates based on the assumptions (Section 2.1).

The [6 + 4] cycloaddition can occur by a concerted ADEP process with the triene as the DSIED as illustrated by **16** in Fig. 9. The cycloaddition have been reported experimentally and with evidence for a concerted pathway [38]. The [8 + 2] reaction is predicted to be concerted with the two isoelectron component as the DSIED, **17**, Fig. 9. The reaction is known and with no solvent effect consistent with a concerted pathway [3]. Syn FSED cannot be achieved for the [4+4] cycloaddition based on the ADEP theory as illustrated in **18**. This explains the observation of a [4 + 2] cycloaddition as opposed to a [4 + 4] interaction in the Diels–Alder environment. The [6 + 6] cycloaddition does not create syn FSED either; **19**, Fig. 9. The [6 + 2] cycloaddition cannot occur in a concerted ADEP manner no matter which unit is the DSIED; **20**, Fig. 9. In the case of the [4 + 4], [6 + 2] and [6 + 6] cycloadditions the SDSE syn FSED is favoured based on delocalisation of

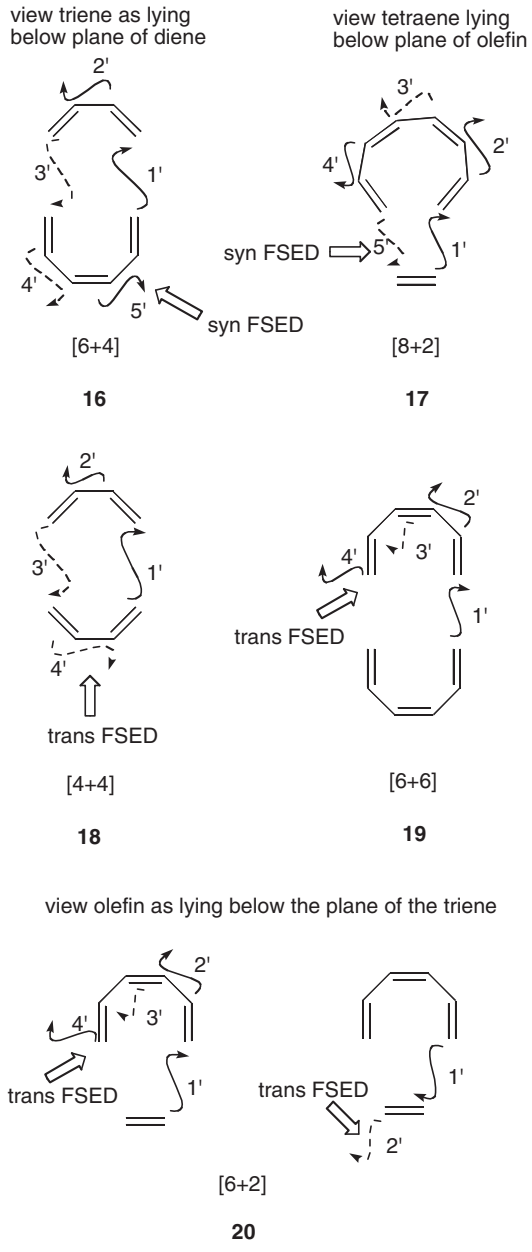

Fig. 9. Application of the ADEP concept to the [6+4], [8+2], [4+4], [6+6] and [6 + 2] cycloaddition reactions.

the diradical by the same double bond or polyene function and the substrates are often cyclic but disfavoured as the bonds are strong and the reactions intermolecular. Which factors win out is not obvious and is best decided at present by comparing to known SDSE systems, in line with complexity and the above statement by Fukui (Introduction) [4]. Whether concerted (SDSE) or not such reactions would have to compete with the Diels–Alder reaction, and in the case of the [6 + 6] cycloaddition it would also have to compete with the [6 + 4] cycloaddition, both of which involve the more efficient ADEP process. Furthermore, higher order pericyclic reactions are predicted to be less favoured than the [4 + 2] and [2 + 2] cycloadditions as it takes longer to neutralize the AFS. In fact the fulvene

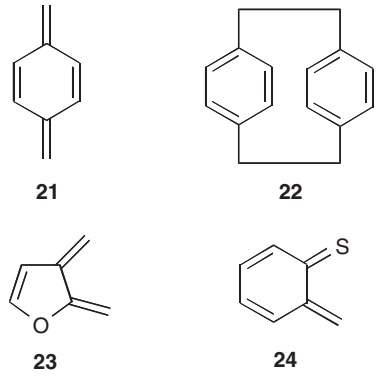

Fig. 10. Intermediate **21** that gives rise to the [6 + 6] cycloadduct **22**; Intermediates **23** and **24** that gives rise to [4 + 4] cycloadducts.

substrates mentioned in the Woodward and Hoffmann paper [3] in relation to their prediction for the [6 + 2] cycloaddition gave the [4 + 2] and [8 + 2] cycloadducts instead. The higher order SDSE mechanisms would also be disfavoured over the SDSE mechanisms for the [4+2] and [2+2] cycloadditions. The most stable diradical structure of the polyene would also be expected to be a deciding factor on which reaction would emerge.

Consistent with this prediction from the ADEP/SDSE syn FSED theory that the so-called "forbidden" reactions, based on the present quantum chemical methods [3–5], can occur in a concerted pathway for some substrates via the SDSE syn FSED electronic mechanism and should be observed when the "allowed" pathways are not available, numerous examples of the [6 + 6] and [4 + 4] cycloadditions have been reported [39] and many of these substrates contain the factors that favour an efficient SDSE process. The presumed intermediate **21**, Fig. 10, gave the adduct **22** [39a] consistent with a [6+6] cycloaddition and it's found to be a general reaction. In this case a [4 + 2] ADEP cycloaddition cannot occur as there is no cisoid diene unit. A concerted [6 + 4] ADEP cycloaddition cannot occur, as it is not geometrically possible, the bonding termini are too remote in the transition state. The [8 + 2] cycloaddition cannot exist, as the tetraene unit is not connected to allow the ADEP process to occur. Hence the SDSE syn FSED mechanism could emerge for the thermal [6 + 6] cycloaddition, which is not impeded by geometry or how the triene unit is connected and is favoured by the fact that the product is aromatic. The diradical character is stabilized by the same unit, the bonds are weak due to the aromatic character and the structure has a cyclic unit. Thus the concerted SDSE syn FSED mechanism is feasible. Evidence that such molecules have a tendency towards single isoelectron (radical) character is seen in the ESR studies of a bis-imidazole derivative and Tschitschibabin's hydrocarbon. A [4 + 4] cycloadduct was observed for **23** [39b] in a quantitative yield and for the thiophene analogue. These are also substrates that would favour the SDSE mechanism. Other examples have been reported including the sulphur system **24** and o-xylylene [39c]. A [4 + 2] cycloaddition in these cases is generally not favoured as aromaticity can only be regained in part of the molecule. In the case of **23** the lack of a solvent polarity effect on the rate of dimerization, the low activation enthalpy and the highly negative activation entropy are consistent with a typical concerted reaction [39b]. The SKIE are negative at both termini [39b], which is also consistent with a concerted reaction, with values similar to that found for ozone (an SDSE process and considered to be concerted) [40]. Despite these facts this reaction is assumed by the authors [39b] to be stepwise, mostly likely due to the Woodward and Hoffmann predictions [3]. The [4+4] and [6+6] SDSE processes are favoured as the bonding termini coincide, and thus there is less chance for radical build up. As the radical character of these substrates increase stepwise pathways are expected to emerge, and also as the energy gap from the singlet to the triplet decreases. It is also feasible that thermal cycloadditions that are concerted, via the ADEP mechanism, have a competing concerted pathway, with higher activation energy, involving the SDSE syn FSED mechanism. The SDEP mechanism is predicted to have much higher activation energy than the SDSE, as the systems are not strained, and thus stepwise pathways with lower energies may emerge before it does. In fact there is no conclusive evidence for the SDEP process in unstrained systems based on the empirical data on which the assumptions are deduced from (Section 2.1).

A concerted [4 + 4] cycloaddition, via the SDEP syn FSED process, could be achieved by incorporating strained systems such as the norbornene skeleton into the 4 double bonds. However, it would still have to compete with the [4 + 2] DA cycloaddition. This could potentially be avoided by a steric factor (as dienophile is trisubstituted) or by introducing one. This is a prediction that has not yet been tested experimentally. This new prediction can also be applied to the [6 + 2] and [6 + 6] cycloadditions. The present quantum chemical methods do not predict the existence of a thermal suprafacial pericyclic reaction for the [4 + 4] cycloaddition [3–5].

2.6. SDEP syn FSED electronic mechanism

Strong evidence for this new chemical theory is also to be found in the HOMO Diels–Alder cycloaddition involving norbornadiene. As discussed in Section 2.1 strained systems such as norbornene favour the SDEP process as opposed to the ADEP (Fig. 1). The two double bonds of the norbornadiene system and the dienophile are close to being coplanar in the proposed transition state of the HOMO Diels–Alder, as illustrated by **25**, Fig. 11, and thus conventional arrows are used, but with 1′, 2′ and 3′ included to distinguish from the conventional meaning. In this geometry an ADEP process cannot create syn FSED, as illustrated in **26**, Fig. 11. The electron density that builds up at C-3, as a result of the ADEP process, points away from C-4. However, the reaction can occur in a concerted manner by the SDEP process. Thus the HOMO Diels–Alder can occur in a concerted fashion, via the SDEP syn FSED electronic mechanism, as strained systems favour the SDEP over the ADEP. Based on the logic of the theory the norbornadiene system behaves as the ASIED. The HOMO DA cycloaddition has been found to be stereospecific and stereoselective implying a concerted process [41]. Thus the HOMO DA is a testimony to the validity of the assumptions and their application to pericyclic reactions. The fact that the ADEP process cannot create the correct FSED,

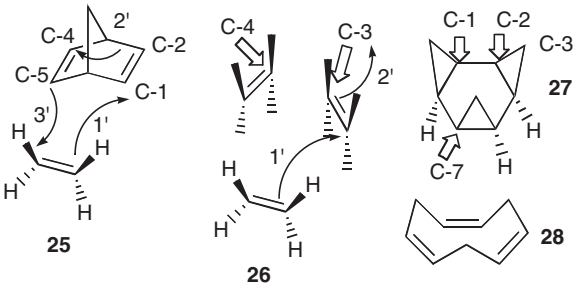

Fig. 11. The SDEP syn FSED electronic mechanism **25** of the HOMO DA. Origin of the stepwise [2+2+2] cycloaddition **26**. A concerted retro [2+2+2] cycloaddition involving **27**, via the SDSE syn FSED electronic mechanism, with **28** as the product.

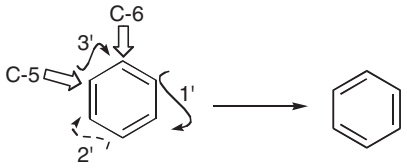

Fig. 12. The ADEP syn FSED electronic mechanism involved in 'aromaticity': a continuous process.

as illustrated in **26**, is consistent with the [2 + 2 + 2] cycloaddition involving ethylene and ethyne following a stepwise pathway based on the experimental evidence (temperatures in excess of 400 °C and occurs only to a small extent) [42]. Such unstrained systems are subject to the ADEP process and the SDEP process is highly disfavoured for unstrained substrates. The lack of an SDEP process is consistent with the fact that there is no conclusive evidence for the SDEP process in the experimental data on which the assumptions were derived. In these cases the reaction cannot occur by a concerted SDSE syn FSED mechanism either, as the factors that favour this mechanism are not present (Section 2.5). This Cplex-isoelectronic prediction is consistent with the fact that the activation energy for the trimerisation of acetylene (six isoelectrons) is higher than the activation energy for the six 'electron' Diels–Alder reaction [42a] and they do not fit the Bell–Evans–Polanyi principle, which suggests the reactions are not related, consistent with different mechanisms. It can also be adduced that in the case of acetylene the trimerization is highly exothermic, yet it is not observed [42b]. In juxtaposition the [2 + 2 + 2] cycloaddition is thermally allowed based on the Woodward-Hoffmann rules [3]. Modern ab initio calculations also predict a concerted pathway for the trimerization of acetylene [42b], despite the experimental data [42]. Houk and Bach have attributed this to a high activation energy barrier due to the very large closed shell electron repulsion between the out of plane π-bonds but Birney's ab initio calculations have refuted this, predicting that stabilization due to aromaticity is greater than any closed-shell repulsion [42d].

All the thermal stereospecific *retro* [2+2+2] cycloadditions reported [43] involved the cyclohexane ring annulated with the either the cyclopropane and/or the cyclobutane rings, an example is illustrated in **27**, Fig. 11 which gives product **28**. As the bonds are very weak (C2–C4, C5–C6, C8–C1), the reaction intramolecular and rotation restricted due to the cyclic structure (product is cyclic) the SDSE mechanism is favourable under thermal conditions. The stereospecificity of these *retro* reactions is in agreement with an SDSE process.

2.7. Aromaticity

Application of the ADEP/SDEP/SDSE assumptions to 'aromaticity' is supported by Complexity theory (connections/regularities exist within and between systems) [8]. This new chemical theory defines 'aromaticity' as a continuous ADEP/syn FSED process within a planar loop. In relation to benzene, the face of C-6 on which a decrease in electron density occurs due to the 1′ process corresponds to the same face of C-5 on which an increase of electron density occurs, as illustrated by in Fig. 12. This syn FSED allows double bond character to be generated at C6-C5. An ADEP mechanism is predicted to be involved as opposed to an SDSE as the former is more efficient. The 1′ process can begin from either above or below the plane with equal probability. Experimental evidence for the movement of isoelectron pairs in a loop is seen in the observation of a diamagnetic ring current when an external magnetic field is applied to benzene [14]. The magnetic field lines and the anisotropic effect are similar to those produced by an electrical current in a metallic loop when placed in a magnetic field [44]. The main difference is that the ring current is diamagnetic as isoelectron pairs are involved in aromatic compounds as opposed to single isoelectrons which are involved in an electrical current. It is well established by experiment that radicals (single isoelectrons) are paramagnetic and molecules with isoelectron pairs are diamagnetic. The Biot–Savart law has been applied successfully to both benzene and current carrying metallic loops, which proves the validity of the connection [45]. Based on the logic of this theory, neutral molecules with an odd number of double bonds ($4n + 2$ isoelectrons), in a single planar loop are predicted to be aromatic and this agrees with experiment [14].

The continuous ADEP process delocalises the six isoelectrons, which stabilises the system. However, stability due to delocalisation reaches a maximum once the isoelectrons are moving sufficiently faster than an approaching reactant. Stability due to delocalisation does not increase as the rate of the ADEP process increases beyond this rate, as an approaching reactant still feels the average force of a single and 'double' bond no matter what the rate is. However, beyond delocalisation this increasing rate of the continuous ADEP process is predicted to add further stability and it is expected to have the greatest potential for increasing the stability of the molecule. An approaching reactant would have to slow the rate of the ADEP process to interact with the isoelectrons and as the rate of the continuous process increases it will become even more difficult to interact with the isoelectrons and thus stability increases, unlike the delocalisation stability. This will be referred to as RCEDGD (rate of continuous electron dynamics greater than delocalisation) stability. The six isoelectrons become 'locked' in this rapid cycle. The RCEDGD and delocalising processes

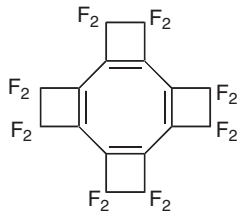

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Fig. 13. Perfluorotetracyclobutacyclo-octatetrene ring system **29**.

explain the low reactivity of benzene relative to alkenes and the tendency to undergo substitution reactions as opposed to addition and it is the RCEDGD stability of the ADEP process that is predicted as the major factor as opposed to delocalisation. Considering the high efficiency of the ADEP process the continuous process is expected to be rapid. Evidence that the ADEP process is extremely rapid and that its rate provides the greatest source of stabilisation in benzene is seen in the fact that present experimental techniques (e.g. NMR, X-ray crystallography), which are subject to a time scale, observe an equal degree of electron density at each point along the benzene ring (they observe an average due to the high rate).

Based on this new chemical theory, systems with an even number of double bonds ($4n$ isoelectrons), with the exception of cyclobutadiene (as electron paths cross in an SDEP process; see Section 2.5), are predicted to exhibit a diamagnetic ring current (implies movement of isoelectron pairs) if an SDEP process is involved. This could be achieved, based on the logic of this theory (see Sections 2.1 and 2.6), by annulation with strained rings such as the four membered rings or norbornene-type systems. A continuous SDEP syn FSED process explains why the planar perfluorotetracyclobutacyclo-octatetrene ring system **29**, (Fig. 13) which has eight electrons ($n = 2$), is diamagnetic (which violates Hückel's rules) and why the system is delocalised (it is also planar) as suggested by the bond lengths (bond alternation is relatively small, a difference of 0.08 Å) [46]. This will be referred to as SDEP-Aromaticity. The present quantum chemical methods predict that perfluorotetracyclobutacyclo-octatetrene is a localised structure with a closed-shell singlet electronic configuration [47]. These quantum chemical calculations also predicts that a delocalised structure would be diradicaloid, a "disjoint" singlet diradical [47c]. CTOCD-DZ (modern Hartree–Fock methods) calculations [47c] predict that the ring **29** has a paratropic ring current (antiaromatic), in contradistinction to the empirical data.

Based on this theory benzene is either a rapid equilibrium between two 1,3,5-cyclohexatriene structures, and thus an average structure is observed by the present experimental techniques, or the single bond framework is constant. The former case is similar to the Kekulé model of benzene except that the Kekulé model lacks an intimate mechanism by which the electrons can move [48]. The electron was not discovered when Kekulé proposed his model. This theoretical possibility involves valence tautomerism (fluxional), via the ADEP syn FSED electronic mechanism. The concept of having the single bonds equal is seen in the outer-sphere electron transfer mechanism where the lowest energy pathway for electron transfer between complexes occurs when the metal-ligand bond distances are the same [49]. Considering that spectroscopy techniques are subject to a time scale (thus an average may be observed) and present analysis of the spectroscopic data is strongly dependant on theory [50], it is not unequivocal to which of the two alternative proposals is valid. This and other features including 'antiaromaticity' will be discussed in a future publication.

As a final point it should be noted that the Cplex-isoelectronic theory, in its present qualitative form, is like all qualitative theories, prone to some degree of *a posteriori* rationalization in some cases. This can be seen, for example, in deciding whether a thermal reaction can occur via a concerted SDSE syn FSED electronic mechanism or by a stepwise pathway. This is not necessarily a limitation in juxtaposition to the present theories, based on the following statement by Dewar "The problems of chemistry cannot be solved, and will not be solved in the forseeable future, by a priori quantum mechanical calculation" [51]. According to Dewar all present quantum methods, including ab initio method, are wholly empirical and the only way of discovering which level of theory is sufficient is by comparing with experiment [52]. This stems from the fact that it is impractical to calculate an exact representation for complex chemical systems, especially chemical reactions, based on present methods and technologies. Some of these a posteriori rationalizations can be removed when more knowledge about the experimental data, on which the assumptions are deduced from, is discovered. On this vein the emergence of Hadronic chemistry is highly promising as convergence occurs at least 1000 times faster than the present C.I. calculations [1,2]. Furthermore, as Hadronic chemistry permits an exact quantitative representation of the chemical bond it can make new predictions for pericyclic reactions and aromatic compounds. Exploring the consistency between the predictions of the Cplex-isoelectronic theory and hadronic chemistry is for future study.

References

[1] Santilli RM, Shillady DD. Int J Hydrogen Energy 1999;24:943–56.
[2] Santilli RM. Foundations of hadronic chemistry, with applications to new clean energies and fuels. Dordrect: Kluwer Academic Publishers; 2001.
[3] Woodward RB, Hoffmann R. Angew Chem Int Ed Engl 1969;8:781–853.
[4] Fukui K. Angew Chem Int Ed Engl 1982;21:801–9.
[5] Wiest O, Montiel DC, Houk KN. J Phys Chem A 1997;101:8378–88.
[6] [a] Robinson R. Quatrieme Conseil de la Inst Chim Solvay 1931; 423; [b] Ingold CK. Chem Rev 1934;15:225–4.
[7] Matsunaga N, Rogers DW, Zavitsas AA. J Org Chem 2003;68:3158–72.
[8] [a] Gell-Mann M. The quark and the Jaguar: adventures in the simple and the complex. Abacus, 1995; [b] Bertz SH. New J Chem 2003;27:860–9.
[9] [a] Dickstein JL, Miller SI. In: Patai S, editor, The chemistry of the carbon–carbon triple bond part 2. New York: Wiley; 1978; [b] Abramovitch RA, Singer SS. J Org Chem 1976;41:1712–7; [c] Strozier RW, Caramella P, Houk KN. J Am Chem Soc 1979; 101:1340–3.
[10] Deslongchamps P. Stereoelectronic effects in organic chemistry, Elmsford, New York: Pergamon; 1983.
[11] [a] Magid RM, Fruchey OS. J Am Chem Soc 1979;101:2107–12; [b] La Cruz TE, Rychnovsky SD. J Chem Soc Chem Commun 2004; 168–9;

[c] Houk KN, Paddon-Row MN, Rondan NG. J Mol Struct (Theochem) 1983;103:197–208.
[12] [a] Giese B, Lachhein S. Angew Chem Int Ed Engl 1982;21:768–9;
[b] Giese B, Meixner J. Tetrahedron Lett 1977;18:2783–4;
[c] Giese B, González-Gómez JA, Lachhein S, Metzger JO. Angew Chem Int Ed Engl 1987;26:479–80.
[13] [a] Watson WH, Marchand AP, Sivappa R. ARKIVOC 2004;iii:66–73;
[b] Afarinkia K, Mahmood F. Tetrahedron Lett 2000;41:1287–90.
[14] March J. Advanced organic chemistry. 4th ed., New York: Wiley; 1992.
[15] [a] Becker KB, Grob CA. Synthesis 1973;789–90;
[b] Fahey RC, McPerson CA. J Am Chem Soc 1970;92:2445–53.
[16] Hegarty AF. Acc Chem Res 1980;13:448–54.
[17] [a] Grée R, Tonnard F, Carrié R. Tetrahedron 1976;32:675–82;
[b] Grée R, Tonnard F, Carrié R. Tetrahedron 1976;32:683–8;
[c] Tufariello JJ. In: Padwa A, editor, 1,3-Dipolar cyloaddition chemistry, vol. 2. New York: Wiley; 1984. p. 83–168 [chapter 9].
[18] Westaway KC. Isot Org Chem 1987;7:275–392.
[19] [a] Gajewski JJ, Peterson KB, Kagel JR. J Am Chem Soc 1987;109: 5545–6;
[b] Gajewski JJ, Peterson KB, Kagel JR, Jason Huang YC. J Am Chem Soc 1989;111:9078–81.
[20] Sauer J. Angew Chem Int Ed Engl 1967;6:16–33.
[21] [a] Hegarty AF, Bruice TC. J Am Chem Soc 1969;91:4924;
[b] Hegarty AF, Bruice TC. J Am Chem Soc 1970;92:6575–88;
[c] Menger FM, Thanos TE, Lynn JL. J Org Chem 1974;39:1771–2;
[d] Sitzmann ME, Kaplan LA, Angres I. J Org Chem 1977;42:563–4;
[e] Hwu JR, Wong FF, Shiao MJ. J Org Chem 1992;57:5254–5;
[f] Kirby AJ, Dutta-Roy N, da Silva D, Goodman JM, Lima MF, Roussev CD, et al. J Am Chem Soc 2005;127:7033–40.
[22] Sauer J, Wiest H, Mielert A. Chem Ber 1964;97:3183–207.
[23] [a] Corwin LR, McDaniel DM, Bushby RJ, Berson JA. J Am Chem Soc 1980;102:276–87;
[b] Little RD, Muller GW, Venegas MG, Carroll GL, Bukhari AA, Patton L, et al. Tetrahedron 1981;37:4371–83;
[c] Liu W-D, Chi C-C, Pai I-F, Wu A-T, Chung W-S. J Org Chem 2002; 26:9267–75.
[24] Siemionko R, Shaw A, O'Connell G, Little RD, Carpenter BK, Shen L, et al. Tetrahedron Lett 1978;38:3529–32.
[25] Telan LA, Firestone RA. Tetrahedron 1999;55:14269–80.
[26] Jenner G, Papadopoulos M, Rimmelin J. J Org Chem 1983;48:748–9.
[27] Zewail A, Bernstein R. In: Zewail A, editor, The chemical bond: structure and dynamics. London: Academic Press; 1992. p. 223–79.
[28] Yamazaki H, Cvetanovié RJ, Irwin RS. J Am Chem Soc 1976;98: 2198–205.
[29] Yang NC, Yates RL, Masnovi J, Shold DM, Chiang W. Pure Appl Chem 1979;51:173–80.
[30] [a] Yang NC, Libman J, Barrett Jr L, Hui MH, Loeschen RL. J Am Chem Soc 1972;94:1406–8;
[b] Yang NC, Shold DM, McVey JK. J Am Chem Soc 1975;97:5006–8
[31] [a] Kaupp G. Angew Chem Int Ed Engl 1972;11:718–9;
[b] Schuster GB, Kim J-I. J Am Chem Soc 1990;112:9635–7;
[c] Yang NC, Chen M-J, Chen P, Mak KT. J Am Chem Soc 1982;104: 853–5;
[d] Yang NC, Chen M-J, Chen P. J Am Chem Soc 1984;106:7310–5;
[e] Saltiel J, Dabestani R, Sears Jr DF, McGowan WM, Hilinski EF. J Am Chem Soc 1995;117:9129–38;
[f] Nakayama T, Nagahara T, Miki S, Hamanoue K. J Photochem Photobiol A 2000;133:11–20.
[32] [a] Horn BA, Herek JL, Zewail AH. J Am Chem Soc 1996;118:8755–6;
[b] Wilsey S, Houk KN, Zewail AH. J Am Chem Soc 1999;121: 5772–86.
[33] Huisgen R. Acc Chem Res 1977;10:117–24.
[34] Gilbert JC, Baze ME. J Am Chem Soc 1984;106:1885–6.
[35] Heaney H, Jablonski JM. Tetrahedron Lett 1967;28:2733–5.
[36] [a] Wasserman HH, Solodar AJ, Keller LS. Tetrahedron Lett 1968; 5597–600;
[b] Jones M, DeCamp MR. J Org Chem 1971;36:1536–9.
[37] Oth JFM. Recl Trav Chim Pays-Bas 1968;87:1185–95 [CA 70:28174d].
[38] Garst ME, Roberts VA, Houk KN, Rondan NG. J Am Chem Soc 1984;106:3882–4.
[39] [a] Ito Y, Miyata S, Nakatsuka M, Saegusa T. J Org Chem 1981;46: 1043–4;
[b] Chou C-H, Trahanovsky WS. J Am Chem Soc 1986;108:4138–44;
[c] Wintgens V, Netto-Ferreira JC, Casal HL, Scaiano JC. J Am Chem Soc 1990;112:2363–7.
[40] Choi H-S, Kuczkowski RL. J Org Chem 1985;50:901–2.
[41] Kobuke Y, Sugimoto T, Furukawa J, Fueno T. J Am Chem Soc 1972;94:3633–5.
[42] [a] Ioffe A, Shaik S. J Chem Soc Perkin Trans 2 1992; 2101–7;
[b] Houk KN, Gandour RW, Strozier RW, Rondan NG, Paquette LA. J Am Chem Soc 1979;101:6797–802;
[c] Lindstedt RP, Skevis G. Combust Sci Tech 1997;125:73–137;
[d] Wagenseller PE, Birney DM, Roy D. J Org Chem 1995;60:2853–9.
[43] [a] Spielman W, Kaufmann D, de Maijere A. Angew Chem Int Ed Engl 1978;17:440–1;
[b] Mohler DL, Vollhardt KPC, Wolff S. Angew Chem Int Ed Engl 1990;29:1151–3.
[44] Young HD, Freedman RA. University physics with modern physics, 10th ed., Reading, MA: Addison-Wesley Publishing; 2000 [chapter 28 and 29].
[45] Haddon RC. Tetrahedron 1972;28:3613–33.
[46] Einstein FWB, Willis AC, Cullen WR, Soulen RL. J Chem Soc Chem Commun 1981;526–8.
[47] [a] Baldridge KK, Siegel JS. J Am Chem Soc 2001;123:1755–9;
[b] Klärner F-G. Angew Chem Int Ed Engl 2001;40:3977–81;
[c] Fowler PW, Havenith RWA, Jenneskens LW, Soncini A, Steiner E. Angew Chem Int Ed Engl 2002;41:1558–60.
[48] Kekulé A. Ann Chem Pharm 1866;137:129.
[49] Cotton FA, Wilkinson G. Advanced inorganic chemistry, 5th ed. New York: Wiley-Interscience; 1988. p. 1318–34 [chapter 29].
[50] Ermer O. Angew Chem Int Ed Engl 1987;26:782–4.
[51] Dewar MJS. J Phys Chem 1985;89:2145–50.
[52] Dewar MJS, Jie C. Acc Chem Res 1992;25:537–43.