

# Application of the Cplex-isoelectronic theory to electrocyclisations, sigmatropic rearrangements, cheletropic reactions and antiaromaticity Consistent with Santilli's hadronic chemistry

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## Abstract

The recently proposed Cplex-isoelectronic theory is applied to electrocyclisation/ring opening reactions, sigmatropic rearrangements, cheletropic reactions and antiaromaticity. The Cplex-isoelectronic theory is consistent with the experimental data and makes different predictions from the present quantum chemical methods in some cases, namely a stepwise pathway for the conrotatory photochemical ring opening of 1,3-cyclohexadiene, a concerted photochemical electrocyclisation for 1,3-cyclohexadiene via disrotatory motion, a concerted suprafacial [1,5] sigmatropic shift with inversion for norcaradiene, a concerted suprafacial [1,3] carbon shift with inversion and retention, a concerted suprafacial photochemical [1,5] hydrogen migration, a concerted photochemical [3,3] shift, stabilisation of cyclic  $4n\pi$  electron systems by delocalisation and their excess energy is due only to electronic repulsion and strain, the monohomocyclopropenium and cyclopropenyl cations are not 'aromatic'. The available empirical evidence is consistent with these new 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. It is also consistent with the fact that it is impractical to calculate an exact representation for complex chemical systems using quantum based methods. Replacing double bonds with strained systems, such as the norbornene ring, is predicted to convert stepwise pathways to concerted. © 2007 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

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## 1. Introduction

Recently a new theory of pericyclic chemistry and aromaticity was proposed, the Cplex-isoelectronic theory [1]. This new qualitative theory is based on the chemical level of the reductional hierarchy, in line with the old electronic theory of

Robinson and Ingold, and is not based on quantum mechanics. It makes logical and scientific connections and regularities between known and unknown systems, an approach seen in the emerging area of Complexity theory. The Cplex-isoelectronic theory is consistent with the empirical data. It also makes predictions that are different from the present quantum chemical methods [2] and the experimental evidence, when available, is found to be consistent with this new chemical theory [1]. Nobel prizes have been awarded for the quantum chemical methods. It is conceivable that the present quantum based methods can make inaccurate predictions for *complex* systems due to indeterminacy, assumptions, diversity of factors involved, intractable calculations and chaos [1]. Furthermore Santilli's hadronic mechanics claims that quantum mechanics requires a correction, due to the deep overlap of the wavepackets of the valence electrons at short distance, for molecules with two or

*Abbreviations:* ADEP, antiperiplanar dynamics of isoelectron pairs; AFS, acceptor at the final facial selectivity site; ASIED, acceptor site of initial electron dynamics; CWP-SDSE, continuous when planar-SDSE; 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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more electrons [3]. Expansion of the Cplex-iso-electronic theory into the hadronic and quantum level is for the future once this new theory is fully developed on the chemical level.

The Cplex-iso-electronic theory assumes that isoelectron pairs move in an antiperiplanar manner (ADEP) while single isoelectrons move in a synperiplanar manner (SDSE) [1]. The ADEP process is favoured over the SDSE in most thermal reactions whereas the SDSE is favoured under photochemical conditions. Only in strained systems is synperiplanar dynamics of isoelectron pairs (SDEP) more efficient than the ADEP. These assumptions are deduced from nucleophilic, radical addition,  $S_N2$  and  $S_N2'$  reactions and the anomeric effect. There is direct evidence for these dynamics in pericyclic reactions and in aromatic compounds [1].

The objective of this paper is to outline the Cplex-iso-electronic theory for electrocyclisation/ring opening reactions, sigmatropic rearrangements, cheletropic reactions and antiaromaticity. Again this new theory makes different predictions from the present quantum chemical methods and the available empirical evidence is consistent with the Cplex-iso-electronic theory. This finding is thus consistent with Santilli's hadronic chemistry [3]. Exploring the consistency between the predictions of the Cplex-iso-electronic theory and hadronic chemistry is for future study. Hadronic chemistry converges at least 1000 times faster than the present C.I. calculations and thus can deal more accurately with complex systems compared to the present quantum chemical methods. Hadronic chemistry also permits an exact quantitative representation of the chemical bond thus allowing new predictions for pericyclic reactions and aromatic/antiaromatic compounds to emerge.

## 2. Results and discussion

### 2.1. Electrocyclisations and ring openings

Applying the ADEP concept to the ring opening of cyclobutene results in the electronic mechanism illustrated in 1, Fig. 1. Based on the logic of this theory the C3–C4 single bond undergoes heterolytic fission in the  $1'$  process. The terminus (C-4) with the greatest electron density (DSIED) rotates  $90^\circ$  downwards (as drawn) in a clockwise motion and attacks the C=C bond at C-1. This results in an increase in electron density at the top face of C-2 due to the ADEP process. C-3 (AFS) rotates  $90^\circ$  upwards towards the top face of C-2 resulting in neutralisation of the decrease in electron density at

C-3, formed due to heterolytic fission in the  $1'$  process, and thus prevents charge accumulation which lowers the activation energy and avoids formation of an intermediate. The process occurs in a gradual manner, as in cycloaddition reactions [1], to minimize charge accumulation i.e. the  $2'$  process occurs before the  $1'$  process is completed. This represents a clockwise rotation at C-3 and hence overall conrotatory (rotation in the same direction) motion occurs at the termini. By definition the rotation is asynchronous (semirotatory). Ring opening of cyclobutenes has been shown experimentally to occur in a conrotatory fashion under thermal conditions [4], as predicted by the Cplex-iso-electronic theory. Ring opening has been shown to be unimolecular and insensitive to environmental changes consistent with a concerted pathway. C-3, with its decrease in electron density, cannot rotate first towards and interact with the C=C bond as opposed to C-4 in the  $1'$  process as this would result in the two isoelectron pairs moving on the same face of cyclobutene to neutralise charge accumulation, generating severe electronic repulsion. This is valid for all ring openings/electrocyclisations. In the case of cyclobutene the path of the two isoelectron pairs actually cross [1] in this scenario, which further inhibits this electronic mechanism. This logic implies that the AFS in pericyclic reactions can only be stabilised by electron density arising from the ADEP process.

The cyclobutene ring is strained and thus favours synperiplanar dynamics over antiperiplanar dynamics [1]. The lack of an SDEP process in the ring opening of cyclobutene is due to the paths of the isoelectron pairs crossing [1]. The fact that the SDEP process is not involved implies that the efficiency of the ring opening is reduced. The amount of strain will determine the degree with which the ADEP process can compete with the more favoured SDEP process. The less strained the substrate, the more efficient the ADEP process. More published and systematic empirical data on the addition of nucleophiles to strained systems is required to quantify this, especially from substrates with low steric effects. As the single bond breaks in the  $1'$  process the strain of the cyclobutene ring decreases and hence the efficiency of the ADEP process increases as the ring opening reaction progresses.

Within this new chemical theory if inversion of the electron density at C-4 occurs in the  $1'$  process of the cyclobutene ring opening, the rearrangement is predicted to result in a disrotatory manner. The fact that this does not occur is due to the inversion process destabilizing the  $1'$  process. The  $1'$  process is predicted to be the major factor in the electronic mechanism [1]. Inversion of the electron density at C-4 (DSIED) involves a separation of charge which decreases the stability of both C-3 and C-4, especially C-3 (AFS) as it interacts with the C1–C2 double bond later than C-4. Furthermore destabilisation of the AFS increases the ability of the AFS to interact with the electron density of the C=C double bond which further destabilises the system as discussed above (first paragraph; Section 2.1). Inversion at C-3 (AFS) would also destabilise the AFS. Retention at both C-3 and C-4 in the  $1'$  process insures that both sites stabilize each other until there is a sufficient interaction with the C1–C2 double bond. Retention at the DSIED also means a faster neutralisation of the AFS as inversion adds

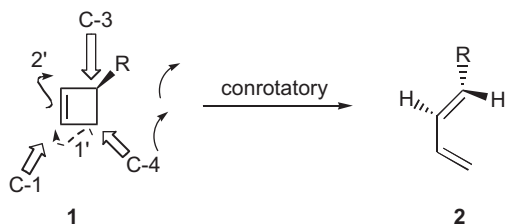


Fig. 1. The ADEP syn FSED electronic mechanism for the concerted ring opening of cyclobutene.

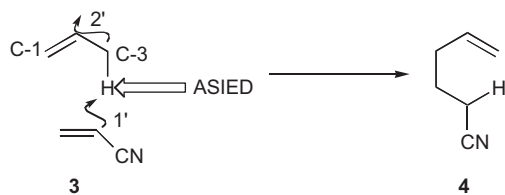


Fig. 2. Hydrogen as the ASIED in the regioselective ene reaction.

an extra time factor. Thus analysis reveals that inversion in the  $1'$  process is highly unstable. This will be referred to as the  $1'$  retention principle. Inversion can occur in all the subsequent  $1'$  processes, because the decrease in electron density is triggered and neutralised by the incoming electron density from the previous  $1'$  process. Literature precedence for this concept can be found in the reaction of the cyclopropane ring with nucleophiles under acid catalysis [5]. The carbon of the cyclopropane ring that is attacked by the nucleophile always occurs with inversion as in  $S_N2$  reactions and the pertinent carbon centre of the cyclopropane ring that reacts with the proton (electrophile) can occur with either inversion or retention with inversion usually favoured. This pathway also occurs without skeletal rearrangement, consistent with a one step pathway [5]. Inversion occurs in the  $2'$  process of the dipolar [3 + 2] cycloaddition [1]. In the case of the ene reaction **3** (Fig. 2) inversion occurs at the carbon of the C–H bond (3-C) in the  $2'$  process. The hydrogen in the ene reaction is similar to the carbon of the cyclopropane ring that is attacked by the nucleophile and 3-C in the ene reaction is similar to the carbon of the cyclopropane ring that bonds with the electrophile.

In the ene reaction the DSIED attacks the strongest bond in the  $1'$  process (C–H as opposed to  $C1=C2$ ) (Fig. 2). This regioselectivity [6] is expounded by a thermodynamic effect, namely breaking the strongest bond first releases the maximum amount of energy which ensures that the subsequent weaker bonds are broken. This also explains the regioselectivity of the 1,3-dipolar cycloaddition where the DSIED in general attacks the negative end of the 1,3-dipole [1]. The negative end is similar to an ionic bond which is stronger than the covalent multiple bond of the 1,3-dipole. As previously discussed, attacking the negative end of the 1,3-dipole is not counter-intuitive [1]. A further conclusive example of this point is the reduction of the 1,3-diphenylallyl dianion radical to the 1,3-diphenylallyl trianion in high yield at ambient temperature [7].

Similar application of the ADEP concept results in a prediction of disrotatory motion (rotation in opposite directions) in the electrocycloislation of the 1,3,5-triene system. Disrotatory motion is observed experimentally [8]. Based on the logic of the Cplex-isoelectronic theory the direction of electron flow is from C-1 to C-2 in the  $1'$  process. C-1 and C-6 rotate in a disrotatory fashion to neutralize the developing charges at the termini, as illustrated by **5** in Fig. 3, thus keeping the activation energy low. By the same logic ring closure of *cis,cis*-1,3,5,7-octatetraene is predicted to be conrotatory, consistent with experiment [9]. Theoretically a thermal concerted disrotatory ring closure of *cis,cis*-1,3,5,7-octatetraene can occur (and for the

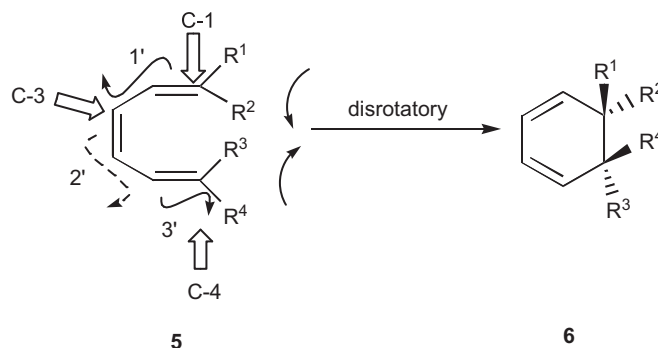


Fig. 3. The ADEP syn FSED electronic mechanism for the concerted disrotatory electrocycloislation of the 1,3,5-triene system **5**.

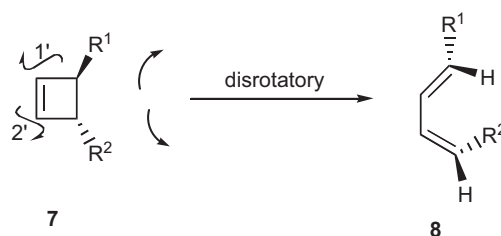


Fig. 4. The SDSE syn FSED electronic mechanism for the concerted ring opening of cyclobutene.

ring opening) via the SDEP syn FSED process. This could be achieved by incorporating the norbornene function or a similarly strained system into all of the double bonds. Strained systems favour the SDEP process [1]. This is a prediction that has not been tested experimentally and thus allows the theory to be tested further.

An SDSE syn FSED process predicts disrotatory motion for all ring openings and electrocycloislations. The SDSE process for cyclobutene is illustrated by **7** (Fig. 4). For the above substrates [4] the thermally induced SDSE mechanism for ring opening is predicted to be inefficient as the single isoelectron character generated in the  $1'$  process is at right angles to the double bond(s), and hence not delocalised, the breaking single bonds are relatively strong, especially for 1,3-cyclohexadiene, and the developing acyclic structure as the single bond breaks in  $1'$  process. As previously discussed these factors determine if the SDSE process is thermally efficient [1]. The photochemically induced ring opening of cyclobutene exhibits disrotatory motion consistent with the existence of an SDSE process [10]. The SDSE process is favoured under photochemical conditions [1]. However, this photochemical reaction is highly complex based on the experimental data [10] and will be discussed in detail in a future publication.

Evidence for a thermal SDSE process is seen in the disrotatory ring opening of bicyclo[2.1.0]pent-2-ene. The activation energy [11] is lower than cyclobutene and the SKIE is small and normal [12], consistent with a concerted process and an alternative reaction mechanism to the ADEP process. The relatively high paramagnetism of bicyclopentene [13] provides

evidence that the substrate has single isoelectron character and thus there will be a bias towards an SDSE process [1]. Furthermore the single bond is relatively weak due to strain, rotation restricted due to the cyclic structure and the reaction intramolecular, which favours an SDSE process [1]. The greater the degree of radical character the faster the reaction will be. Solvent effects are also found by experiment to be absent in these proposed SDSE systems, consistent with a concerted pathway. Observations and deductions lead Jones to suggest that the thermal and photochemical proclivities are linked, in agreement with this new theory [14]. Both are predicted to involve an SDSE process. The ring opening is a Woodward–Hoffmann disallowed transformation [2a]. DFT calculations do predict a concerted process with a transition state of high biradical character [15] but with no prediction of an SDSE syn FSED electronic mechanism. The ring opening of Dewar benzene to give benzene is also a candidate for a concerted SDSE process under thermal conditions. Pyrolysis of Dewar benzenes does give benzene derivatives and under relatively low temperatures [16]. Evidence for the existence of an SDSE process comes from a heavy atom effect observed with chloro derivatives of Dewar benzene under thermal conditions [16a]. These results show that a triplet diradical pathway is not the major pathway involved in the rearrangement and thus provides indirect evidence for a concerted process. The ADEP process is disfavoured due to the formation of 1,3,5-cyclohexatriene with one trans double bond, a highly strained and unknown compound, and thus the SDSE mechanism can emerge and the factors that favour the SDSE process are present. In juxtaposition calculations at the CASSCF(10,10)/6-311G\*\* level of theory predict that the conrotatory process, involving a closed shell transition state, is favoured in which Dewar benzene is directly converted to benzene [17]. The reaction is assumed to be stepwise based on the Woodward–Hoffmann rules [2a] but there is no experimental evidence reported for a stepwise pathway.

The observation of products consistent with conrotatory motion for the photochemical ring closure of trienes **11** to 1,3-cyclohexadienes **9** and the reverse reaction [18], Fig. 5, implies that this reaction does not involve an SDSE process and thus it is not pericyclic in nature. The Woodward–Hoffmann approach [2a] predicts conrotatory motion in a concerted reaction. The following alternative mechanism is proposed and is backed up with experimental evidence (Fig. 5). The ring closure of the triene **11** to the cyclohexadiene ring **9** involves the triene in the conformation in which C-1 and C-6 are on opposite sides of the plane of the C3–C4 double bond. Excitation of this conformation creates radical character in the triene. Interaction through space of the radical character at C-1 and C-6 results in rapid bond formation between the faces of the C-1 and C-6 atoms that point towards each other, creating the stereoisomer that would have arisen from conrotatory motion. Trans FSED is formed at C-3 and C-4 and thus a concerted process is not feasible. Hence intermediate **10** arises.

Direct experimental evidence for this ground state conformation controlled photolysis is reported for 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene [19]. X-ray

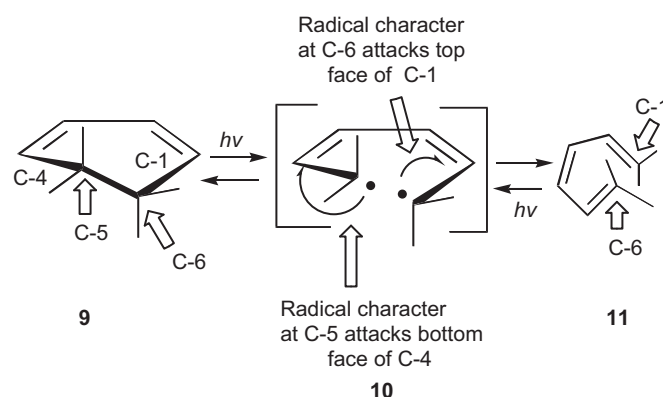


Fig. 5. Proposed mechanism for the photochemical electrocycloisomerization of the 1,3,5-triene system.

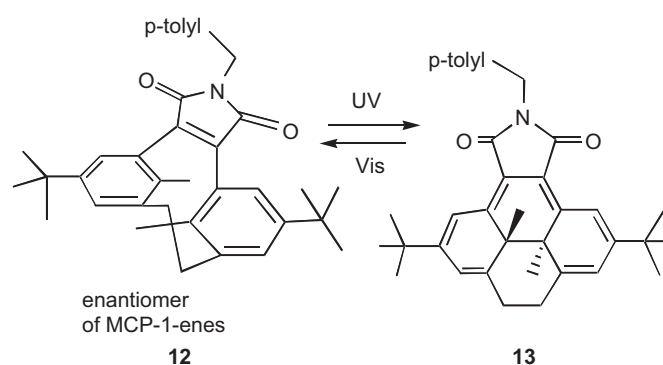


Fig. 6. Evidence for the conformationally controlled stepwise mechanism of the photochemical electrocycloisomerization of the 1,3,5-triene system.

crystallography shows the molecule in the solid state to have the nonplanar conformation. Irradiation of the single crystal resulted in the 'conrotatory' product. Further evidence is illustrated by 1,2-disubstituted [2.2]metacyclophan-1-enes (MCP-1-enes) **12**, (Fig. 6) [20]. Each enantiomer gives a different diastereoisomer [20]. The stereoisomer that is formed in each case corresponds to the tetrahydropyrene product that would arise from bonding between the sides of the aryl ring that face each other in the nonplanar conformation. This enantioselective behaviour was also reported for the 1,2-bis(5-*m*-formyl-phenyl-2-methyl-3-thienyl)perfluorocyclopentene system [21]. If a planar conformation was involved, loss of chirality would be expected. The most efficient concerted process requires the planar conformation. The fact that the ring opening and closing reactions can occur thermally as well as photochemically and the product is not directly formed from the excited state is consistent with an intermediate being involved [22]. The fact that *trans* FSED is generated at C-2 and C-3 in the ring opening of cyclohexadiene is consistent with the observation of a photoproduct from 6-methyl-1,2,3,4,5-pentaphenyl-1,3-cyclohexadiene in which the central bond of the triene isomerises [23]. Experimentalists within this field regard a stepwise pathway as highly probable [22]. An *ab initio* MRD CI investigation [24] of the photochemical isomerisation is consistent with the Woodward–Hoffmann prediction.

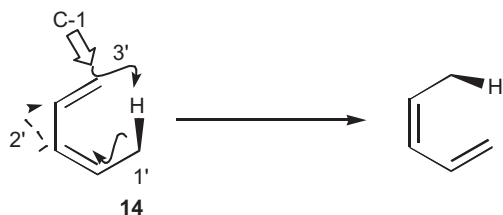


Fig. 7. The ADEP syn FSED electronic mechanism for the concerted [1,5] H sigmatropic shift.

A semiempirical MINDO/3 method predicts a conrotatory diatomic reaction, involving a proposed biradicaloid intermediate; the stereochemistry of which is not due to the orbital conservation requirements [25]. Consistent with the Cplex-iselectronic prediction an intermediate was detected for the spiropyran and spirooxazine systems via photoelectron spectroscopy in a femtosecond experiment in the gas phase [26]. DFT calculations [27] predict a concerted pathway for the spiropyrans whereas CASSCF calculations point to a conical intersection [28].

Assuming this prediction is correct, the concerted disrotatory photochemical electrocycloislation of 1,3,5-hexatriene to 1,3-cyclohexadiene via the SDSE syn FSED electronic mechanism is not observed due to the low concentration of the planar conformation in solution. Furthermore in the planar conformation it would have to compete with the concerted four isoelectron electrocycloislation which results in cyclobutene formation. Dauben et al. have clearly shown that the nonplanar conformation favours ring opening and the planar or near planar conformation favours bicyclo[2.2.0]hex-2-ene formation [18]. Locking the molecules in the planar conformation and varying the wavelength of light in the photochemical reaction may result in the emergence of the concerted disrotatory pathway for the six isoelectron electrocycloislation over the four isoelectron electrocycloislation. This is a prediction that has not yet been tested by experiment.

## 2.2. Sigmatropic rearrangements

The ADEP assumption predicts a suprafacial process for the [1,5] H sigmatropic shift as illustrated by **14** in Fig. 7. Based on the logic of this theory the C5–H bond of *cis*-1,3-pentadiene is orthogonal to the plane occupied by the diene function in the reactive conformation. Heterolytic fission of the C5–H bond occurs in the 1' process with C-5 as the DSIED and H as the AFS. The subsequent ADEP processes results in an increase in electron density on the top face of the C-1 atom (as drawn), pointing towards the face of the H atom (AFS) with the decrease in electron density due to the 1' process. This syn FSED allows rapid neutralisation of the decrease in electron density at the H atom and hence a concerted process is predicted. The movement of electron density is a gradual process as in all pericyclic reactions based on the logic of the Cplex-iselectronic theory, ensuring that no full charge develops [1]. The transfer involves a 'frontside' attack on the H (AFS) in the 3' process. Experimentally a suprafacial process is observed in a first order

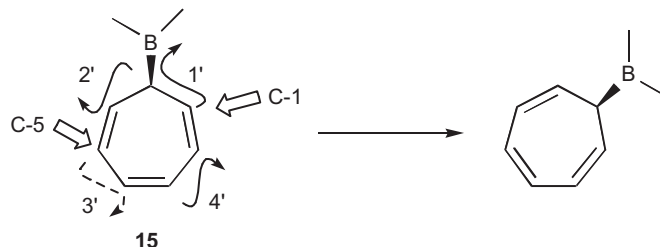


Fig. 8. The ADEP syn FSED electronic mechanism for a concerted suprafacial [1,7] migration.

reaction for the [1,5] H migration of (*S*)-*cis,trans*-3-methyl-7-deutero-octa-4,6-diene under thermal conditions consistent with a concerted process and the ADEP prediction [29]. The single bond breaks in the 1' process as opposed to the double bonds as it ensures the subsequent weaker bonds can be broken (Section 2.1). The orthogonal conformation maximises the ADEP interaction of the C5–H bond with the C3=C4 double bond.

Syn FSED cannot occur for the [1,7] H shift in a suprafacial pathway based on the same logic (the same applies to a [1,3] H migration). An antarafacial migration is possible assuming the required helical type conformation of the triene does not inhibit the ADEP process. Experiments show that the migration is antarafacial [30]. A suprafacial [1,7] migration can occur if the double bond attacks the single bond in the 1' process as illustrated in electronic mechanism **15** (Fig. 8). However, this mechanism is only favoured if the double bond is comparable in energy to the single bond, as discussed above, or if attack on the single bond dramatically lowers its bond strength. Hence a suprafacial [1,7] H migration is not observed [30]. Mechanism **15** can be used to rationalize the experimental observation of a [1,7] migration of boron in the cycloheptatriene system [31]. The C1–C2 double bond attacks the electrophilic boron in the 1' process. The subsequent ADEP processes result in syn FSED at C-2 and C-3 via retention of the electron density at C-7 in the 2' process. The relative bond strength effect is less problematic for **15** compared to the C–H bond system and the electrophilic character of boron provides a strong driving force. The allylic C–B bond energy is estimated at ca. 68 kcal/mol comparable to the C=C 'double' bond energy (i.e. C=C bond energy minus C–C bond energy; approximately 64 kcal/mol) [32]. The 1' process in **15** has characteristics of the oxidation of alkylboranes with the hydroperoxide anion, where electron flow into boron triggers facile heterolytic fission of the C–B bond at ambient temperature [33]. Mechanism **15** also opens up the possibility that a suprafacial [1,7] H migration could be designed. A concerted suprafacial [1,7] H migration can also occur via the SDEP syn FSED process. This could be achieved by incorporating the norbornene function into all of the three double bonds of the triene as strained systems favour the SDEP process. This is a prediction that has not been tested experimentally and thus allows this new theory to be tested further. For this proposed experiment the single bond can break in the 1' process.

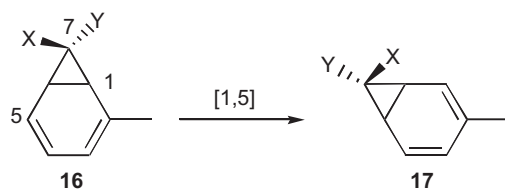


Fig. 9. The [1,5] sigmatropic shift of the bicyclo[4.1.0]heptadiene system **16**.

However, this higher order pericyclic reaction still have to compete with the [1,5] H migration.

Frontside attack on the migrating group gives rise to retention of configuration of the migrating group and backside attack to inversion of configuration based on this new chemical theory. This can occur for both H and C. The Cplex-isoelectronic theory does not differentiate between H and C unlike the Woodward–Hoffmann orbital symmetry approach [2a]. Based on the orbital approach inversion can occur for C but not for H due to the presence of a p-orbital in C. In an overall 1,2 migration, as in the [1,7] migration in the cycloheptatriene system or in the [1,5] migration of the cyclopentadiene system, only retention is expected to be observed with H and C as backside attack is not geometrically feasible. All migrations which involve an overall 1,2 shift have been observed to occur with retention (e.g. cyclopentadiene system) (> 99% stereospecific) [34] as predicted. Retention can occur for C or H in an overall 1,2 migration by an electronic mechanism analogous to **14** or **15**, analogous in terms of the 1' process involved (single or double bond as the DSIED, respectively), if the FSED is syn. If the migration is an overall 1,3 migration backside attack can occur geometrically without inducing the same degree of strain as would be involved in an overall 1,2 migration with inversion. This can occur only by an electronic mechanism analogous to **15** (double bond as the DSIED). The analogous electronic mechanism **14** (single bond as the DSIED) can only give rise to retention as the decrease in electron density occurs at the frontside of the migrating group in the heterolytic fission of the 1' process. This is based on the 1' retention principle (Section 2.1). In the case of the analogous electronic mechanism **15**, in an overall 1,3 migration, backside attack gives rise to inversion of configuration of the migrating group and frontside attack to retention of configuration. Backside attack is predicted to be favoured from an electronic vista, similar to the S<sub>N</sub>2 reaction, due to the lower degree of electronic repulsion. The disadvantage of the overall 1,3 migration is the greater increase in distance between the migrating site and the acceptor site relative to the overall 1,2 migration and thus increases the probability that the overall 1,3 migration may not be concerted. The analogous electronic mechanism **15** is favoured when the double bond and single bond breaking in the 1' process are of similar energy.

In the case of the [1,5] sigmatropic shift of the bicyclo[4.1.0]heptadiene (norcaradiene) system **16** [35], an overall 1,3 migration as shown in Fig. 9, the analogous electronic mechanism **15** can compete with the analogous electronic mechanism **14** as the cyclopropane C–C bond energy (approximately 65 kcal/mol) is comparable to the C=C 'double' bond energy (approx-

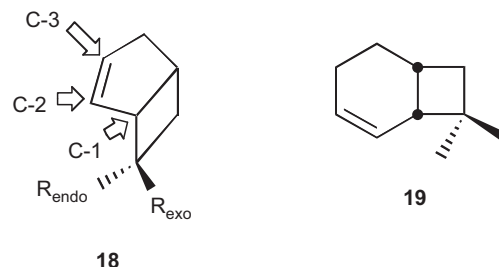


Fig. 10. Bicyclo[3.2.0]hept-2-ene system **18** and the bicyclo[4.2.0]octene system **19**.

mately 64 kcal/mol). The analogous electronic mechanism **14** is less efficient than mechanism **15** because the C7–C1 bond is relatively far from the acceptor site C-5 and hence more charge can accumulate in a retention of configuration pathway. Furthermore the substituents X and Y block access to the frontside of C-7 (rotation required which results in further charge accumulation). As the backside of the C7–C1 bond is closer to C-5 the analogous electronic mechanism **15** is more efficient. This results in inversion of the configuration of the migrating group C-7. In this electronic mechanism inversion of the electron density at C-1 in the 2' process occurs to insure syn FSED at C-4 and C-3 with C-5 as the DSIED. As discussed in Section 2.1 there is precedence for inversion or retention at C-1 [5]. Inversion of stereochemistry at C-7 was reported experimentally with ≥ 95% stereospecificity [35], consistent with this new prediction and a concerted pathway. The Woodward–Hoffmann theory predicts retention for a concerted [1,5] carbon shift [2a]. Ab initio MO calculations predict a diradical transition state for the norcaradiene system [36].

In the case of the [1,3] sigmatropic rearrangement the analogous electronic mechanism **15** must be involved, as opposed to the analogous **14**, to insure syn FSED (i.e. the double bond undergoes heterolytic fission in the 1' process and attacks the migrating group). Thus inversion and/or retention of configuration can occur in a concerted manner for the [1,3] shift based on this new theory. Again this mechanism is not favoured unless the single bond is weak and compatible with the energy of the double bond as discussed above. The analogous mechanism **14** would result in an antarafacial transition state with extreme strain and thus can be ruled out. In fact all the known stereospecific [1,3] C migrations involve very weak migrating single bonds due to strain and annulation, hence the analogous mechanism **15** can emerge. The kinetics of the bicyclo[3.2.0]hept-2-ene system **18** (Fig. 10), shows that retention and inversion occurred with only a factor of 7 between them [37]. Furthermore the stereospecificity factor (inversion and retention) is only of the order 7 and 10 between the 7-*exo* methyl isomer and the 7-*endo* methyl isomer. In the case of the bicyclo[4.2.0]octene system **19** (Fig. 10), the rate of the retention pathway is greater than the inversion pathway and the retention pathway is more stereospecific [37]. These empirical results are consistent with the existence of a concerted process for both the inversion and retention products and thus consistent with the existence of the analogous electronic mechanism

**15.** The migrating single bond of **18** is similar in strength to the double bond which favours the analogous mechanism **15** (in general approximately 270 kJ/mol for a ‘double’ bond and a cyclobutane C–C bond). The relevancy of access to the backside or frontside, based on the Cplex-iso-electronic theory, is consistent with the observation that the suprafacial inversion pathway predominates when the R group is in the *exo-7* position and the suprafacial retention pathway when the R group is in the *endo-7* position [38]. Furthermore a thermal [1,3] shift with retention has been reported for an acyclic system in which the migrating carbon is tertiary, thus backside attack is sterically hindered, and the acceptor site is disubstituted [39]. A further example which illustrates the importance of steric effects has been reported for the 9-methylenespiro[3.5]nona-5,7-diene system [40]. Comparison of activation parameters for the [1,3] shift in restricted and unrestricted vinyl cyclobutanes proves the importance of a specific geometry in the transition state, consistent with a concerted reaction [41]. Furthermore the SKIE are also close to unity. Thus the Cplex-iso-electronic theory provides an electronic mechanism for a concerted pathway for the formation of both the inversion and retention product in the [1,3] C sigmatropic shift. The Woodward–Hoffmann theory predicts that inversion is an allowed pathway whereas retention is disallowed [2a].

The existence of a concerted pathway in the overall [1,3] migration is expected to be determined strongly by the degree of strain in the transition state. The existence and the three-dimensional structure of the monohomocyclopropenium cation [42] and bicyclobutane opens the possibility that carbon ([1,3] C) can tolerate the necessary strain (bridging methylene group over a 3 atom system). Furthermore, bending and stretching modes of the single bond can be involved, as relatively high temperatures are required, up to 573 K, and thus distorted geometries are feasible. Breaking the C2–C3 double bond first in the analogous mechanism **15** adds partial positive charge character to C-2 that should contract the C3–C2 and C2–C1 bonds, bringing the migrating carbon closer to C-3 (consider the monohomocyclopropenium cation). This should relieve some of the strain in the transition state. This may be a crucial factor that further favours the analogous mechanism **15**, aided by the fact that the ‘double’ bond C3=C2 is similar in energy to the migrating single bond. Consistent with the direction of electron flow in the analogous mechanism **15**, the 1,3-sigmatropic migration of boron is known and found to be unimolecular with a substantial negative entropy of activation and an activation energy well below the estimated allylic B–C bond energy [32]. The vinylic B–C bond is both weaker and longer than the C–H bond which favours the analogous mechanism **15** along with the electrophilic character of boron (see above discussion on substrate **15**). In juxtaposition to the Cplex-iso-electronic theory PM3 semi-empirical calculations predict a distinct singlet state biradical intermediate with the stereoselectivity governed by a dynamic effect for the bicyclo[3.2.0]hept-2-ene system [43]. Density Functional Theory calculations deviate towards a concerted pathway for the major stereoisomer involving a diradical transition state with no cyclic conjugation for the [1,3] C migration in the vinylcyclopropane rearrange-

ment [44]. DFT calculations predict a short-lived diradical species moving across a caldera with the major stereoisomer arising due to orbital interactions and dynamic motions in the vinylcyclobutane–cyclohexene rearrangement [45]. Subjacent orbital control has been invoked by quantum chemistry to explain the observation of the Woodward–Hoffmann “forbidden” retention pathway. Despite the quantum based predictions the above experimental data is typical of a concerted pericyclic reaction and thus consistent with the Cplex-iso-electronic theory.

Consistent with the relevancy of the bond length (due to strain in the transition state), bond strength and the existence of a concerted pathway for both inversion and retention, based on the analogous electronic mechanism **15**, is the observation that [1,3] migrations of silyl groups occur, are unimolecular and give both retention and inversion depending on the substrate [46]. The C–Si bond is longer than the C–C bond and the silicon atom is bigger than carbon, furthermore the C–Si bond is weaker and silicon is well known to be susceptible to nucleophiles and able to tolerate electron density ( $S_N2$  reactions and stability of  $\alpha$ -carbanions) as it does in the  $1'$  process [33,47]. The C–Si bond strength is further decreased as the reaction progresses due to the decrease in electron density at the AFS which is  $\beta$  to the breaking C–Si bond. Si is well documented as a strong stabiliser of  $\beta$ -carbocations [33,47]. Thus as the  $1'$  process progresses the C–Si bond becomes even more facile to break. These factors favour the analogous electronic mechanism **15** as well as reducing the strain in the transition state.  $\beta$ -Ketosilanes ( $R_3SiCH_2COR'$ ) rearranges to siloxyalkenes ( $R_3SiOCR' = CH_2$ ) with retention of configuration of the migrating silicon group under first-order kinetics, a [1,3] migration [48]. This migration is even more favoured as the C=O bond is shorter than the C=C bond and this decreases the distance over which the group must migrate. Furthermore, the C=O bond is much stronger than the C–Si bond. Consistent with the direction of electron flow and the  $1'$  process is the negative Hammett reaction constant  $\rho$  reported for  $R'$  (substituent attached to the carbonyl group, i.e. electron donating groups increase the rate) and the positive value for the silicon atom (electron withdrawing groups increase the rate) [49]. In juxtaposition a trigonal bipyramid structured intermediate with the oxygen bound to the silicon (a coplanar 4-membered intermediate) has been predicted by the latest quantum chemical calculations [50]. Ab initio MO calculations also predict a coplanar 4 centred mechanism [51]. A high degree of retention of configuration was also found at the migrating silyl group in ketene silyl acetals using an optically active silyl ester, suggesting a concerted process [52]. It should be noted that a word of caution must be attached at present to the application of the Cplex-iso-electronic theory to third row (and higher) elements such as silicon because the assumptions of this new chemical theory were deduced from reactions and compounds involving the first and second row elements predominately and there is little empirical data-to-date on these reactions and compounds based on the third and higher row elements.

Thermal SDSE syn FSED reactions of the above substrates [28–30,33,34,36–40] of sigmatropic shifts are predicted to be inefficient. All SDSE processes can occur in a suprafacial

manner based on the logic of the Cplex-isoelectronic theory. This contradicts the Woodward–Hoffmann predictions for photochemical migrations [2a]. The thermal [1,3] H shift may also be inhibited due to the shorter C–H bond length and the smaller size of H, compared to the C–C bond, considering the high degree of strain required for a [1,3] transition state. If the bond length (C–H) is a major factor, as well as bond strength, in the thermal [1,3] H shift, implies that the photochemical [1,3] H shift cannot occur in a concerted pericyclic fashion either due to this strain. Photochemical induced [1,3] H migrations are known and consistent with this possibility a carbene mechanism was proven to be involved [53]. The carbene intermediate was trapped. A minor pathway was also observed and was proposed to involve either a direct [1,3] H shift or two consecutive 1,2-hydrogen shifts. The latter mechanism may be involved, or some other alternative. In fact the carbene arises from a 1,2-hydrogen shift, thus such a pathway is feasible. 1,2-H photochemical shifts from the singlet excited state are well documented [54]. Two consecutive shifts or an alternative mechanism must be involved in tetrasubstituted olefins [55], as the carbene mechanism requires an olefinic proton. Both an intramolecular and intermolecular (stepwise) migration was observed for this system. An excited state involving an electron transition from the double bond to an antibonding orbital was postulated [56]. A planar 4-centred photochemical [1,3] migration may also be involved with diradical character. In fact there is no stereochemical study reported that shows the photochemically induced [1,3] H migration is a suprafacial process. From an electronic vista the photochemical [1,3] H shift can occur by a suprafacial concerted pathway via the SDSE syn FSED process. If strain due to the C–H bond length and the size of H does not inhibit the [1,3] H shift, a thermal concerted suprafacial [1,3] H sigmatropic shift could be achieved by incorporating the norbornene function into the double bond. This would involve the SDEP syn FSED process. This prediction has not been tested experimentally. Bond strength is not problematic in this case as the stronger C–H bond breaks in the 1' process. If migration does not occur in this norbornene system it implies that the length of the C–H bond, as well as its bond strength, does impede the thermal [1,3] H sigmatropic shift and a concerted SDSE mechanism cannot occur in the photochemically induced [1,3] H shift due to strain. Ab initio SCF/CI calculations [57] predict that the H transfer in propene involves a planar shift from a twisted conformation with a negative charge on the twisted methylene group whereas CASSCF calculations [58] point to a conical intersection.

Consistent with the SDSE prediction that all photochemical migrations are concerted, the photochemical [1,5] H migration is known experimentally, is relatively facile and numerous, the majority of which have been shown to involve a singlet excited state [59]. A conclusive stereochemical experiment is required to test whether a suprafacial concerted process is involved. Furthermore a planar or near planar diene is required for a concerted pathway. If a concerted [1,5] process is not found it may be due to an inability to compete with the [1,3] H photochemical pathway. The Woodward–Hoffmann rules predicts that a suprafacial photochemical [1,5] H migration is disallowed and

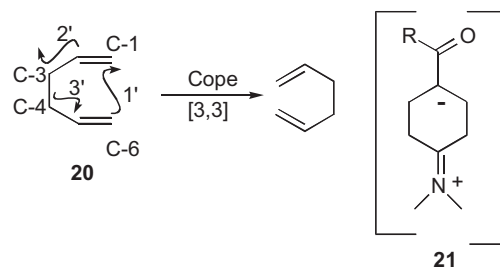


Fig. 11. The ADEP syn FSED electronic mechanism for the Cope Rearrangement. Intermediate **21** formed due to inhibition of the ADEP process.

the antarafacial process is allowed [2a]. The [1,5] antarafacial transition state has been dismissed as effectively “unachievable” from a geometrical vista [59]. Ab initio SCF/CI calculations predict that the H transfer involves a planar shift from a twisted conformation [57]. The predictions of the Cplex-isoelectronic theory pertaining to photochemical reactions are only valid if the singlet excited states has syn coplanar diradical character [1]. At present there is no experimental technique for determining the exact electronic structure of the excited state.

### 2.3. [3,3] Sigmatropic rearrangements

Application of the ADEP concept to the Cope rearrangement results in an electronic mechanism in which the C5–C6 double bond attacks the C1–C2 double bond in the 1' process, as illustrated by **20** (Fig. 11). The resultant facial selectivity at C-2 allows backside attack on the C3–C4 single bond in the 2' process. In the 3' process the build up of electron density at C-4 neutralizes the decrease in electron density at C-5 (AFS) due to the syn FSED. Retention of the electron density occurs at C-4. The single bond (C3–C4) cannot break in the 1' process as electron density builds up on the face of C-6 which points away from the C1–C2 double bond in the 2' process. Thus the Cope rearrangement is not as efficient as it could be due to the fact that the single bond does not break in the 1' process. However, this is less problematic in the Cope rearrangement, compared to the analogous electronic mechanism **15** for the [1,3] migration, as bonds of the same energy break in the 1' process (C6=C5 and C1=C2) of **20** and the resulting decrease in electron density at C-5 (AFS) and the increase in electron density at C-2 will make heterolytic fission of the C3–C4 single bond much more facile than if the single bond was broken in the 2' process where it would behave as the ASIED as it does in the analogous electronic mechanism **15** (Section 2.2). The 1' process is expected to have the major contribution to the activation energy from an electronic vista [1]. This proposed electronic mechanism for the Cope rearrangement is consistent with the experimental observation that substituents at C-2 and C-5 have a greater effect on the rate than at any other position [60]. Donor substituents can provide SEADEF [1], i.e. an anchimeric like effect. The ADEP concept predicts greater rate acceleration for a 2-donor-5-acceptor Cope system than a 2-donor-5-donor system as in the former system the substituents favour the direction of electron flow illustrated in **20**.



The 2-donor pushes isoelectrons in the opposite direction to the 1' process in the 2-donor-5-donor system. A stage can conceivably be reached where the decrease in electron density at C-5 (AFS) is highly stabilised by a strong donor substituent at C-5 and the increase in electron density at C-2 is highly stabilised by a strong electron withdrawing group at C-2, thus interfering with the 'electronic circuit' of the concerted pathway and resulting in an intermediate of type **21** (Fig. 11). It is the role of the isoelectrons involved in the pericyclic circuit to neutralise the AFS. This intermediate has been trapped for systems where the donor is the N-substituted pyrrolidine and the acceptor is a methylester [61].

The ADEP electronic mechanism **20** is different from the current quantum chemical theories. Quantum chemical calculations [(U)B3LYP/6-31G\*] points towards a variable TS geometry involving a contribution from an allyl diradical, a 1,4-diyl structure and an aromatic structure [62]. The greater effect of the 2,5-position is rationalized by a greater resonance contribution from the 1,4-diyl structure than from the allyl biradicaloid. On the same vein the concept of "centauric" and "chameleonic" have been promulgated with the "centauric" model favoured [63]. The diyl hypothesis (biradicaloid) has been predicted by semi-empirical calculations yielding a tight 1,4-diyl intermediate [64]. An aromatic transition state has also been found using semi-empirical calculations [65]. Semi-empirical calculations predict that the biradicaloid TS is favoured over the aromatic transition state whereas ab initio MO calculations predict the opposite. Ab initio modern valence bond calculations predict that the degree of contribution of the diradical, aromatic and bisallyl character to the TS is sensitive to the interallyl distance [66].

Acceleration of the [3,3] rearrangement by a 3-oxyanion substituent (oxy-Cope) is consistent with an expected SEADEF effect [1] at the junction of the 2' and 3' process in **20**. The negative charge on the 3-oxygen helps the incoming isoelectron pair, from the 2' process, break the C3–C4 single bond by electron donation. Thus it is more than a bond weakening effect in the ground state as had been proposed [67]. As the donating ability of the 3-substituent increases a stage will also conceivably be reached where this interferes with the flow of the six isoelectrons involved in the pericyclic reaction. This prediction is born out by the inefficiency of the amino Cope (3-NH<sup>-</sup>) [68] with the SEADEF effect from the NH<sup>-</sup> substituent being too strong at the 2', 3' junction compared to O<sup>-</sup> in the oxy-Cope. Nitrogen is a stronger electron donor than oxygen. Thus side reactions such as deallylation can occur in the amino Cope and it is observed experimentally [68]. In other cases no rearrangement was observed [68] consistent with an inhibited reaction. The fundamentals of the Cplex-isoelectronic theory is inconsistent with the recently proposed paradigm, based on the behaviour of the oxy and amino Cope rearrangements [68a], that the homolytic cleavage model provides a reasonable guide to the ease of a concerted pathway while the heterolytic model provides a guide to a stepwise reaction.

Based on this new theory the barbaralane and semibullvalene systems are predicted as strong candidates for an SDEP process as they have a structure analogous to the norbornene

system [1]. The single bond can thus break in the 1' process, which represents the most efficient process due to the thermodynamic effect discussed above (Section 2.1). This predicted change in the electronic mechanism is consistent with the experimental observation that substituents have a greater effect at the 2,6-positions of barbaralane as opposed to the 3,7-positions (i.e. the reverse to that found for the Cope) [69]. The process is also diamagnetic as measured by a SQUID magnetometer, consistent with the movement of isoelectron pairs [70]. Breaking the single bond in the 1' process is predicted to be a major factor, coupled to the strained bonds and the fixed cisoid conformation of the double bonds, involved in semibullvalene having the lowest activation energy for a Cope rearrangement with fluxional behaviour even at -110°C. The advantage of breaking the single bond in the 1' process is consistent with the fact that the [5,5] sigmatropic shift is favoured over the [3,3] [71], as in the former system the single bond can break in the 1' process of the ADEP pathway to give syn FSED. The SDEP syn FSED electronic mechanism can be invoked by incorporating the norbornene skeleton into the two double bonds of the parent 1,5-hexadiene.

The SDSE process can also result in a concerted [3,3] shift based on the logic of the Cplex-isoelectronic theory and thus opens the possibility that the photochemical [3,3] migration is concerted. The concerted [3,3] shift may be concealed by what is assumed and in some cases, but not all, proven to be a [1,3] migration [72]. In fact the photochemical [3,3] migration may not be observed in most systems because the photochemical [1,3] migration has a lower activation energy, and not because it is a 'forbidden' rearrangement. The photochemical [3,3] migration is disallowed based on the Woodward–Hoffmann approach. The [3,3] shift is a higher order pericyclic process and thus predicted to be less favoured than the [1,3] shift. In general higher order pericyclic reactions have higher activation energies as it takes longer to neutralise the AFS (the AFS can only be stabilised by the final ' process as discussed in Section 2.1) and from a thermodynamic vista more bonds are broken. This is also expected to be related to the fact that the [3,3] migration requires the double bonds to be in the entropy disfavoured cisoid conformation, which is in low concentration in solution. Consistent with this analysis photolysis of tropone adducts, which are locked in the cisoid conformation, resulted in a [3,3] sigmatropic shift [73]. The singlet excited state is involved, a necessary conditions for a concerted reaction [73a].

The obvious connection between the [2,3] sigmatropic shift and the one-step S<sub>N</sub>2' reaction should be adduced for this chemical theory. The [2,3] sigmatropic shift is essentially an intramolecular S<sub>N</sub>2' reaction. The S<sub>N</sub>2' reaction was used to deduce the ADEP assumption [1].

#### 2.4. Antiaromaticity

For cyclic systems with an even number of multiple bonds which cannot achieve syn FSED via the ADEP process, the SDSE process is favoured by the cyclic nature of these species, as the freedom of the single isoelectron centres to rotate and

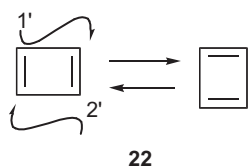


Fig. 12. The SDSE syn FSED electronic mechanism involved in cyclobutadiene: a continuous process.

vibrate is restricted, diradical character in the  $1'$  process is delocalised by the same group and the process is intramolecular. These factors favour the SDSE process [1]. The cyclic systems are known at present as ‘antiaromatic’ molecules ( $4n$  electrons). The SDSE syn FSED process is illustrated for cyclobutadiene **22** in Fig. 12. Evidence for the movement of single isoelectrons in the planar or near planar geometry is seen in the paramagnetic ring current of these molecules [74]. The magnetic field lines are similar to those produced by an electrical current (single isoelectrons) in a metallic loop [75]. The SDSE process allows delocalisation of the isoelectrons which adds stability to the system but as the SDSE process is not as efficient as the ADEP process [1], the rate of the continuous SDSE process is predicted to be dramatically slower. Thus these molecules are predicted not to have RCEDGD stability. RCEDGD is the origin of the high stability of ‘aromatic’ compounds based on the Cplex-isoelectronic theory and is related to the high rate of the continuous ADEP process [1]. This prediction that the rate is slower is backed up by the fact that valence isomerisation is observed in cyclobutadiene by the present experimental techniques and the molecule is a rectangular diene and not a square structure [76]. This prediction is also consistent with the empirical observation that these molecules are destabilised. Furthermore when conformational mobility is possible they are found to be nonplanar as opposed to planar. Thus the inefficiency of the SDSE process is consistent in both pericyclic reactions and in the so-called ‘antiaromatic’ compounds. Valence isomerisation in cyclobutadiene is the SDSE process **22** within this new chemical theory.

In the planar geometry, systems with an even number of multiple bonds are predicted to be destabilised by strong electronic repulsion, as the isoelectrons are close together in a confined space but stabilised by delocalisation (the continuous SDSE syn FSED process). Based on the experimental fact that these molecules are destabilised relative to the open acyclic analogue and the preference for a nonplanar geometry when conformational mobility is possible, electronic repulsion is the major factor for these molecules. This is consistent with the inefficiency of the SDSE process. Strain in the case of cyclobutadiene is also expected to contribute to destabilising the system. Evidence for destabilisation due to electron repulsion in a confined space is seen in the fact that the  $\text{CH}_2=\text{CH}-\text{CH}_2^-$  anion unit of phenalene is more stable than the corresponding benzanthrene i.e. the two vinylic hydrogens are replaced by a fused benzene ring [77]. This is also observed in the gas phase for propene and toluene [77b]. The radical and anion from toluene might be expected to be more stable based on the aromatic character of

the phenyl ring and the greater delocalisation of the radical and anion by the phenyl ring. Thus repulsion between isoelectrons in a confined space is of relatively high magnitude. Quantifying these factors is for future research. On this vein Bauld and Welscher [78] have logically argued that the empirically calculated energies [79] of ‘antiaromatic’ systems are in error and are dramatically smaller than those reported.

Antiaromaticity is strictly defined by present theory as destabilisation by electron delocalisation [80]. Nonaromatic compounds are regarded not to be appreciably stabilized by delocalisation and are highly reactive because of strain and electronic repulsion [80]. Thus based on the Cplex-isoelectronic theory these molecules are neither antiaromatic nor nonaromatic. They will be referred to as CWP-SDSE molecules (continuous when planar-SDSE). They are stabilised by SDSE delocalisation. In contrast quantum chemical theories including high level ab initio methods support the existence of ‘antiaromaticity’ [80–82].

A highly disfavoured SDEP process for unstrained systems, as deduced from the experimental data on which the assumptions of the theory were deduced [1], is consistent with these substrates (even number of multiple bonds) exhibiting a paramagnetic ring current (via SDSE process) as opposed to a diamagnetic current (via SDEP process). The SDSE mechanism is favoured over the SDEP for unstrained systems under thermal conditions [1]. For the strained cyclobutadiene, the SDEP process cannot occur as the paths of the isoelectron pairs cross [1].

## 2.5. Cheletropic reactions

Application of the ADEP concept to the  $[4+2]$  cheletropic reaction results in the electronic mechanism **23** and **24** (Fig. 13). A singlet carbene has both an electrophilic and nucleophilic centre and thus can behave as either the ASIED or the DSIED. In mechanism **23** the singlet carbene acts as the DSIED whereas in mechanism **24** the carbene is the ASIED. Only mechanism **23** results in syn FSED and thus a concerted pathway is feasible. The same logic applies to the *retro* process, i.e. the cycloelimination. Mechanism **23** is a suprafacial and disrotatory process, which is consistent with the experimental evidence for the  $[4+2]$  cheletropic reaction [83]. The  $[4+2]$  cheletropic reaction is by definition asynchronous, as are all concerted reactions involving the ADEP process. The Woodward–Hoffmann rules also predict a suprafacial and disrotatory process [2a]. Ab initio MO calculations predict a synchronous path [84].

In the case of the  $[2+2]$  cheletropic reaction syn FSED can only be achieved if the singlet carbene acts as the ASIED in the  $1'$  process **25** (Fig. 13). Mechanism **25** is an A-SE2 type mechanism, which is known to give syn addition [1]. To avoid the paths of the isoelectron pairs crossing the ASIED has only to attack from one end (AFS) of the double bond as opposed to the centre, a sliding type mechanism. Experimentally the  $[2+2]$  cheletropic reaction is stereospecific and suprafacial, consistent with a concerted reaction [85]. Furthermore a linear free energy study shows that the carbene is electrophilic in the transition state with only modest charge development, consistent with the predicted direction of electron flow in **25** and a concerted

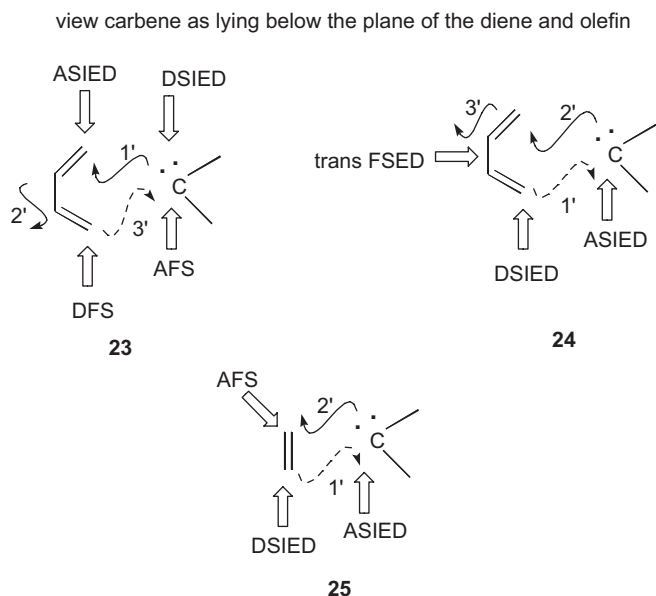


Fig. 13. The ADEP syn FSED electronic mechanism for the concerted [4+2] and [2+2] cheletropic reaction.

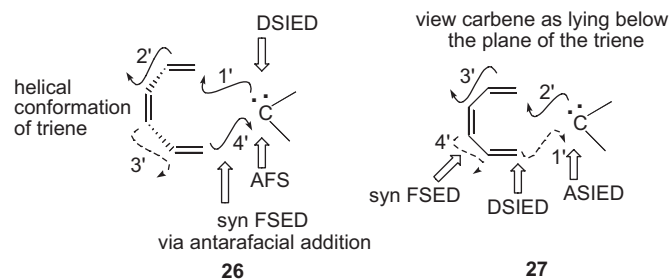


Fig. 14. The ADEP syn FSED electronic mechanism for the concerted [6+2] cheletropic reaction.

pathway [86]. The reaction constants are also similar to that found in  $S_N2$  reaction [86]. The  $S_N2$  reaction was used to deduce the ADEP assumption [1]. To explain the suprafacial pathway Woodward and Hoffmann invoke a 'nonlinear' reaction pathway involving a deformed substrate [2a]. The linear mode, which is generally the most efficient, predicts an antarafacial process [2a].

For the [6+2] cheletropic reaction, syn FSED is obtained in an antarafacial mode when the singlet carbene acts as the DSIED as illustrated by **26** (Fig. 14). This antarafacial mode requires a nonplanar helical type conformation which is geometrically feasible. The antarafacial mode is not geometrically feasible for the [2+2] and [4+2] cheletropic reactions. A suprafacial pathway achieves syn FSED via the carbene behaving as the ASIED, **27** (Fig. 14). Experimentally both antarafacial and suprafacial pathways are observed [85], in agreement with the Cplex-isoelectronic theory. Consistent with both pathways being concerted and having similar electronic mechanisms, the reactions are found to be stereospecific and the enthalpy of activation is similar for both pathways

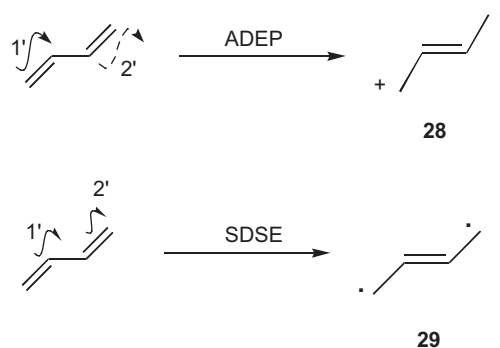


Fig. 15. Unstable electronic structures **28** and **29** created by the ADEP and SDSE processes in 1,3-butadiene.

(difference is 0.2 kcal/mol). The suprafacial pathway has a far greater and more negative entropy of activation (+0.2 versus  $-18$  eu) consistent with the requirement of the less favoured, from an entropy vista, planar conformation in the transition state [85]. However, it should be noted that the authors claimed experimental complications due to isothermal control problems and thus there is some doubt about the kinetic parameters for the suprafacial pathway. The Woodward and Hoffmann rules predict that the antarafacial pathway is linear and the suprafacial nonlinear [2a]. The linear mode is generally the most efficient [2a].

## 2.6. Alternating polyenes

The ADEP and SDSE processes for 1,3-butadiene create the unstable zwitterion **28** and diradical **29** electronic structures, respectively, (Fig. 15). The Cplex-isoelectronic theory rests on the fact that charged and radical species are in general far less stable than the neutral species [1]. Thus this new chemical theory rules out delocalisation as a major factor in the structure of butadiene. As this is a qualitative theory at present, delocalisation cannot be ruled out completely. Delocalisation is at best minimal. The ADEP process is favoured as opposed to the SDSE [1]. This prediction of a low degree of delocalisation via the ADEP mechanism, or possibly a complete lack of, explains why the length of the C1–C2 bond (1.34 Å) is very close in length to the double bond of ethylene (1.32 Å) [87]. A 4 kcal/mol stabilisation of butadiene relative to an isolated double bond is also consistent with a low degree of delocalisation or a lack of [87]. Hence, the shortening of the C2–C3 bond length, compared to ethylene, by approximately 0.06 Å may not be due to delocalisation but some other factor(s). The same applies to the favoured planar conformation of 1,3-butadiene. Evidence that the planar conformation of butadiene may not be as a result of delocalisation is found in the X-ray crystal structure of *syn*-planar oxalic acid, assuming packing forces are not the determining factor in the crystal [88]. The C–C bond length is the same as in ethane, consistent with no delocalisation, but the *syn*-oxalic acid is still planar.

Assuming delocalisation is not involved in butadiene one possible rationale for the planar structure lies in minimising

electronic repulsion by having the two isoelectron pairs as far apart as possible in line with the valence shell electron pair repulsion theory. Minimum electronic repulsion is achieved in the planar transoid conformation. The transoid conformation also has a steric advantage. Electronic repulsion can be reduced further if the isoelectron pairs are on opposite sides of the carbon framework at the same time. When one isoelectron pair is above the plane, the other is below but each isoelectron pair can be both above and below the plane. Movement of the isoelectron pairs around the C–C bonds would be synchronised in this model. This facial aspect of the isoelectron pairs is a new postulate never previously considered. In this case shielding by the carbon nuclei add stability as well as the increased distance between the nonplanar isoelectron pairs. The concept of the isoelectron pairs occupying opposite sides of the carbon framework at the same time explains why the planar or near planar geometry is favoured in the cisoid conformation [89]. Increasing the dihedral angle by rotation of the C2–C3 bond brings the isoelectron pairs closer together and thus increases electronic repulsion. This rotation also results in repulsion between the carbon nuclei on the sides of the plane in which the isoelectron pairs do not exist. The shortening of the C2–C3 bond in the planar conformation can be expounded by the greater electronegativity of the vinyl carbon and geminal nonbonded interactions [87] as well as this reduced electronic repulsion effect. Other factors may also be involved. These factors could also account for the 4 kcal/mol stabilisation. It is not necessary to include delocalisation to explain these observations [87]. The reason for the bond shortening of the C2–C3 bond in 1,3-butadiene relative to butane remains unsettled based on present theory [87]. The three arguments are based on resonance ( $\pi$  bond delocalisation) (conjugation), hybridisation and geminal nonbonded interactions. MP2/6-31G\* and MP3/6-31G\*\* calculations [90] agree with Hückel theory that delocalisation is involved whereas other quantum chemical calculations [91] predict hybridisation as the major factor. In juxtaposition NDDO calculations predicts that hybridisation is not very significant [92]. The planarity of butadiene has been proposed as evidence for delocalisation [87]. Further experiments are required to elucidate the true origin of the structure of 1,3-butadiene. In the delocalisation ADEP process **28**, electrons move in the same manner and in the same direction as they move across the diene in the proposed Diels Alder electronic mechanism [1]. Thus even if there is some degree of delocalisation in dienes, it does not dramatically change the proposed electronic mechanism of the Diels–Alder reaction or conclusions made from it [1].

Electronic structures **28** and **29** arise from valence tautomerism (fluxional) via the ADEP and SDSE processes. Alternatively butadiene may exist as a single structure (stable state) with ADEP/SDSE characteristics. Experiment at present cannot distinguish between rapid valence tautomerism and such a stable state. This theory should not be confused with canonical or resonance structures which is a method of obtaining a trial wavefunction in valence bond theory. Resonance structures are imaginary.

Molecules that can stabilize electronic structures **28** and **29** are predicted to show some degree of delocalisation via the

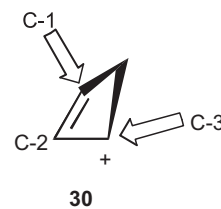


Fig. 16. The monohomocyclopropenium cation **30**.

ADEP/SDSE processes. This logic implies that allylic anions, cations, and radicals (SDSE) will exhibit a high degree of delocalisation as is found by experiment [87]. This also applies to 1,3-dipoles. It will be referred to as ‘nonneutralised FSED delocalisation’. It is relevant to both the valence tautomerism situation and the stable state. Under photochemical conditions the SDSE mechanism **29** is favoured and the more alternating double bonds present the greater the stability of **29**. This explains why as the number of alternating double bonds increase the wavelength of light absorbed increases.

The monohomocyclopropenium cation **30** (Fig. 16), [42] cannot benefit from RCEDGD stability as syn FSED is not feasible [1] and thus is predicted not to be ‘aromatic’. The diamagnetism can be explained by nonneutralised FSED delocalisation with the isoelectron pair also moving through the space between C-1 and C-3. This allows the positive charge to be spread over 3 atoms (C-1–C-3) as opposed to two atoms (C-1, C-3) if the 1,3-interaction was not involved. It is this ability to spread the positive charge over three atoms, as opposed to ‘aromaticity’ as in the Hückel theory and the latest quantum chemical methods, which explains the structure and stability of the homocyclopropenium cation. This also applies to the cyclopropenyl cation. Hence an aromatic molecule must generate a diamagnetic field in the presence of an applied field but its presence does not imply aromaticity. The anisotropic structure of the induced diamagnetic ring currents in these systems [42] implies valence tautomerism as oppose to a single state for these cations. *Moving* isoelectrons create an anisotropic effect [75]. The cyclopentadienyl cation also can only benefit from nonneutralised FSED delocalisation. Its instability and ground-state triplet diradical structure [93] provides further evidence that electronic repulsion between isoelectron pairs in a confined spaced is of relatively high magnitude (Section 2.4). The positive charge shortens the single bonds by an inductive effect. This brings the two isoelectron pairs closer together.

### 2.7. Ring opening of bicyclobutane

Ring opening of bicyclobutane **31** to 1,3-butadiene is predicted to give two isomers **32** and **33** by the ADEP process (Fig. 17). In the formation of **32** the initial electron motion involves heterolytic fission of the C1–C2 bond, followed by rotating in the direction of the *exo* position, which allows backside attack to occur on the C3–C4 bond (backside is favoured in  $S_N2$  reactions). To prevent electron density accumulation the latter C3–C4 bond rotates towards the *endo* position to

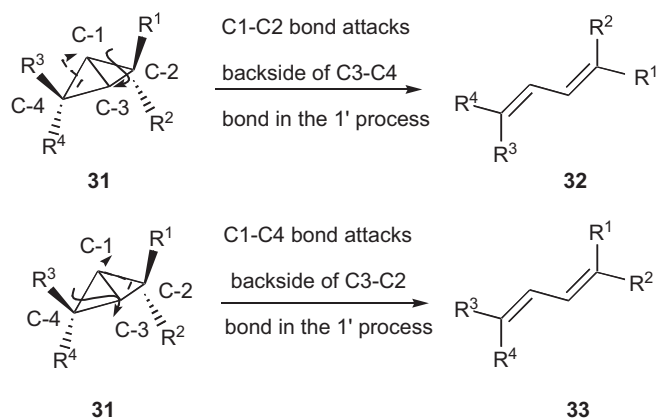


Fig. 17. Predictions for the ring opening of bicyclobutane **31** based on the ADEP process.

neutralize the electron density deficiency at C-1. This is a gradual process as in all concerted reactions. The same logic applies to the formation of **33**. The isomers formed experimentally (**32** and **33**) [94] are as predicted by the ADEP concept. Analysis based on the Woodward–Hoffmann correlation diagrams prove possible only for two of the three modes of ring opening [2a,95]. The mode which lacks the necessary symmetry element to analyse this reaction proves to be the one that is observed experimentally. The Cplex-isoelectronic prediction is also different from the electronic mechanism proposed by semi-empirical [96] and ab initio calculations [97].

## References

- [1] Cloonan MO. *Int J Hydrogen Energy*, 2007;32:159–71.
- [2] [a] Woodward RB, Hoffmann R. *Angew Chem Int Ed Engl* 1969;8: 781–853; [b] Fukui K. *Angew Chem Int Ed Engl* 1982;21:801–9; [c] Wiest O, Montiel DC, Houk KN. *J Phys Chem A* 1997;101:8378–88.
- [3] Santilli RM, Shillady DD. *Int J Hydrogen Energy* 1999;24:943–56.
- [4] Winter REK. *Tetrahedron Lett* 1965;1207–1212.
- [5] Burritt A, Coxon JM, Steel PJ. *J Org Chem* 1995;60:7670–3.
- [6] [a] Albisetti CJ, Fisher NG, Hogsed MJ, Joyce RM. *J Am Chem Soc* 1956;78:2637–41; [b] Snider BB, Conn RSE, Sealfon S. *J Org Chem* 1979;44:218–21.
- [7] Boche G, Buckl K. *Angew Chem Int Ed Engl* 1978;17:284–5.
- [8] Marvell EN, Caple G, Schatz B, Pippin W. *Tetrahedron* 1973;29:3781–9.
- [9] Huisgen R, Dahmen A, Huber H. *J Am Chem Soc* 1967;89:7130–1.
- [10] Leigh WJ. *Can J Chem* 1993;71:147–55.
- [11] Brauman JI, Golden DM. *J Am Chem Soc* 1968;90:1920–1.
- [12] Baldwin JE, Reddy PV, Schaad LJ, Hess Jr BA. *J Am Chem Soc* 1988;110:8555–6.
- [13] Hsu SL, Andrist AH, Gierke TD, Benson RC, Flygare WH, Baldwin JE. *J Am Chem Soc* 1970;92:5250–8.
- [14] Jones II G, Turbini LJ. *J Org Chem* 1976;41:2362.
- [15] Özkan I, Kinal A, Balci M. *J Phys Chem* 2004;108:507–14.
- [16] [a] Lechtken P, Breslow R, Schmidt AH, Turro NJ. *J Am Chem Soc* 1973;95:3025–7; [b] Wingert H, Irgartinger H, Kallfab D, Regitz M. *Chem Ber* 1987;120:825–38.
- [17] Havenith RWA, Jenneskens LW, van Lenthe JH. *J Mol Struct Theochem* 1999;492:217–24.
- [18] Dauben WG, Kellogg MS, Seeman JI, Vietmeyer ND, Wendschuh PH. *Pure Appl Chem* 1973;33:197–215.
- [19] Kobatake S, Shibata K, Uchida K, Irie M. *J Am Chem Soc* 2000;122:12135–41.
- [20] Takeshita M, Yamato T. *Angew Chem Int Ed Engl* 2002;41:2156–7.
- [21] Yamamoto S, Matsuda K, Irie M. *Angew Chem Int Ed Engl* 2003;42: 1636–9.
- [22] [a] Sheepwash MAL, Mitchell RH, Bohne C. *J Am Chem Soc* 2002;124:4693–700; [b] Mitchell RH, Ward TR, Chen Y, Wang Y, Weerawarna SA, Dibble PW. et al. *J Am Chem Soc* 2003;125:2974–88.
- [23] Woolsey NF, Radonovich LJ, Saad FM, Brostrom M. *J Org Chem* 1984;49:1937–41.
- [24] Share PE, Kompa KL, Peyerimhoff SD, Van Hemert MC. *J Chem Phys* 1988;120:411–9.
- [25] Pichko VA, Simkin BY, Minkin VI. *J Org Chem* 1992;57:7087–92.
- [26] Poisson L, Raffael KD, Soep B, Mestdagh J-M, Buntinx G. *J Am Chem Soc* 2006;128:3169–78.
- [27] Sheng Y, Leszczynski J, Garcia AA, Rosario R, Gust D, Springer J. *J Phys Chem B* 2004;108:16233–43.
- [28] Celani P, Bernardi F, Olivucci M, Robb MA. *J Am Chem Soc* 1997;119:10815–20.
- [29] Roth WR, König J, Stein K. *Chem Ber* 1970;103:426–39.
- [30] Wu K-M, Okamura WH. *J Org Chem* 1990;55:4025–33.
- [31] Gridnev ID, Tok OL, Gridneva NA, Bubnov YN, Schreiner PR. *J Am Chem Soc* 1998;120:1034–43.
- [32] Hancock KG, Kramer JD. *J Am Chem Soc* 1973;95:6463–5.
- [33] Thomas SE. *Organic synthesis, the role of boron and silicon*. Oxford: Oxford University; 1991.
- [34] Boersma MAN, deHaan JW, Kloosterziel H. *Chem Commun* 1970;1168–9.
- [35] Klärner F-G. *Top Stereochem* 1984;15:1–35.
- [36] Kless A, Nendel M, Wilsey S, Houk KN. *J Am Chem Soc* 1999;121: 4524–5.
- [37] Berson JA, Holder RW. *J Am Chem Soc* 1973;95:2037–8.
- [38] [a] Bender JD, Leber PA, Lirio RR, Smith RS. *J Org Chem* 2000;65: 5396–402; [b] Berson JA, Nelson GL. *J Am Chem Soc* 1967;89:5503–4.
- [39] Cookson RC, Kemp JE. *J Chem Soc Chem Commun* 1971;385–6.
- [40] Gajewski JJ, Paul GC. *J Org Chem* 1990;55:4575–81.
- [41] Gajewski JJ, Gitendra CP. *J Org Chem* 1991;56:1986–9.
- [42] Paquette LA. *Angew Chem Int Ed Engl* 1978;17:106–17.
- [43] Carpenter BK. *J Am Chem Soc* 1995;117:6336–44.
- [44] Nendel M, Sperling D, Wiest O, Houk KN. *J Org Chem* 2000;65: 3261–8.
- [45] Northrop BH, Houk KN. *J Org Chem* 2006;71:3–13.
- [46] [a] Kwart H, Slutsky J. *J Am Chem Soc* 1972;94:2515–6; [b] Zhang LC, Kabuto C, Kira M. *J Am Chem Soc* 1999;121:2925–6.
- [47] Brook MA. *Silicon in organic, organometallic, and polymer chemistry*. New York: Wiley; 2000.
- [48] Brook AG, MacRae DM, Limburg WW. *J Am Chem Soc* 1967;89: 5493–5.
- [49] Brook AG. *J Organomet Chem* 1975;86:185–92.
- [50] Kwart H, Barnette WE. *J Am Chem Soc* 1977;99:614–6.
- [51] Takahashi M, Kira M. *J Am Chem Soc* 1999;121:8597–603.
- [52] Shiina I, Nagasue H. *Tetrahedron Lett* 2002;43:5837–40.
- [53] Hixson SS, Tausta JC, Borovsky J. *J Am Chem Soc* 1975;97:3230–2.
- [54] Motschieder K, Gudmundsdottir A, Toscano JP, Platz M, Garcia-Garibay MA. *J Org Chem* 1999;64:5139–47.
- [55] Kropp PJ, Fravel Jr HG, Fields TR. *J Am Chem Soc* 1976;98:840–1.
- [56] Peijnenburg WJGM, Buck HM. *Tetrahedron* 1988;44:4927–40.
- [57] Dormans GJM, Buck HM. *J Mol Struct Theochem* 1986;136:121–38.
- [58] Wilsey S, Houk KN. *J Am Chem Soc* 2000;122:2651–2.
- [59] [a] Mousseron-Canet M, Mousseron M, Legendre P. *Bull Soc Chim France* 1964;31:50–3; [b] Kiefer EF, Tanna CH. *J Am Chem Soc* 1969;91:4478–80; [c] Pettit WA, Wilson JW. *J Am Chem Soc* 1977;99:6372–9; [d] McCullough JJ, McClory MR. *J Am Chem Soc* 1974;96:1962–3; [e] Manning JC, McClory MR, McCullough JJ. *J Org Chem* 1984;49: 919–30; [f] Wilson RM, Patterson WS, Austen SC, Ho DM, Krause JA, Bauer J. *J Am Chem Soc* 1995;117:7820–1;

- [g] Woolfe GJ, Melzig M, Schneider S, Dorr FC. *J Chem Phys* 1983;77:213–21;
- [h] Ramamurthy V, Liu RSH. *J Org Chem* 1976;41:1862–7.
- [60] [a] Wehrli R, Schmid H, Bellus D, Hansen H-J. *Helv Chim Acta* 1977;60:1325–56;
- [b] Dewar MJS, Wade Jr LE. *J Am Chem Soc* 1977;99:4417–24.
- [61] Gompper R, Wagner H-U. *Angew Chem Int Ed Engl* 1988;27:1437–55.
- [62] Hrovat DA, Chen J, Houk KN, Borden WT. *J Am Chem Soc* 2000;122:7456–60.
- [63] Doering W, von E, Wang Y. *J Am Chem Soc* 1999;121:10967–75.
- [64] Dewar MJS, Ford GP, McKee ML, Rzepa HS, Wade Jr LE. *J Am Chem Soc* 1977;99:5069–73.
- [65] Dewar MJS, Jie C. *Acc Chem Res* 1992;25:537–43.
- [66] Blavins JJ, Cooper DL, Karadakov PB. *J Phys Chem A* 2004;108:194–202.
- [67] Evans DA, Baillargeon DJ. *Tetrahedron Lett* 1978;34:3315–8 3319–22.
- [68] [a] Young Yoo H, Houk KN, Lee JK, Scialdone MA, Meyers AI. *J Am Chem Soc* 1988;110:205–6;
- [b] Sprules TJ, Galpin JD, MacDonald D. *Tetrahedron Lett* 1993;34:247–50.
- [69] [a] Jackman LM, Ibar G, Freyer AJ, Görlach Y, Quast H. *Angew Chem Int Ed Engl* 1984;23:604;
- [b] Günther H, Runsink J, Schmickler H, Schmitt P. *J Org Chem* 1985;50:289–93.
- [70] Seefelder M, Heubes M, Quast H, Edwards WD, Armantrout JR, Vaughan Williams R. et al. *J Org Chem* 2005;70:3437–49.
- [71] Wender BA, Ternansky RJ, McNSieburth S. *Tetrahedron Lett* 1985;26:4319–22.
- [72] [a] Manning TDR, Kropp PJ. *J Am Chem Soc* 1981;103:889–97;
- [b] Cookson RC, Gogte VN, Hudec J, Mirza NA. *Tetrahedron Lett* 1965;44:3955–9.
- [73] [a] Sasaki T, Kanematsu K, Hayakawa K, Kondo A. *J Org Chem* 1973;38:4100–8;
- [b] Tezuka T, Miyamoto R, Mukai T, Kabuto C, Kitahara Y. *J Am Chem Soc* 1972;94:9280–2.
- [74] [a] Untch KG, Wysocki DC. *J Am Chem Soc* 1967;89:8386–7;
- [b] Farquhar D, Leaver D. *Chem Commun* 1969;24–5.
- [75] Young HD, Freedman RA. *University physics with modern physics*. 10th ed., Reading, MA: Addison-Wesley Publishing; 2000 [Chapter 28 and 29].
- [76] Maier G, Kalinowski H-O, Euler K. *Angew Chem Int Ed Engl* 1982;21:693–4.
- [77] [a] McMillen DF, Golden DM. *Ann Rev Phys Chem* 1982;33:493–532;
- [b] Bausch MJ, Gostowski R, Jirka G, Selmarten D, Winter G. *J Org Chem* 1990;55:5805–6.
- [78] Bauld NL, Welscher TL, Cessac J, Holloway RL. *J Am Chem Soc* 1978;100:6920–4.
- [79] Breslow R. *Acc Chem Res* 1973;6:393–8.
- [80] Breslow R. *Angew Chem Int Ed Engl* 1968;7:565–70.
- [81] Glukhovtsev MN, Bach RD, Laiter S. *J Mol Struct Theochem* 1997;417:123–9.
- [82] Kuwajima S. *J Am Chem Soc* 1984;106:6496–502.
- [83] [a] Ašperger S, Hegedić D, Pavlović D, Borčić S. *J Org Chem* 1972;37:1745–9;
- [b] Mock WL. *J Am Chem Soc* 1975;97:3666–70.
- [84] [a] Bencivenni L, Ramondo F, Quirante JJ. *J Mol Struct Theochem* 1995;330:389–93;
- [b] Suárez D, Sordo TL, Sordo JA. *J Org Chem* 1995;60:2848–52.
- [85] Mock WL. *J Am Chem Soc* 1975;97:3673–9.
- [86] Couch EV, Landgrebe JA. *J Org Chem* 1972;37:1251–3.
- [87] J. March, *Advanced organic chemistry*, 4th ed. New York: Wiley-Interscience; 1992. p. 30–3.
- [88] Leiserowitz L, Nader F. *Angew Chem Int Ed Engl* 1972;11:514–5.
- [89] Fisher JJ, Michl J. *J Am Chem Soc* 1987;109:1056–9.
- [90] Wiberg KB, Rosenberg RE, Rablen PR. *J Am Chem Soc* 1991;113:2890–8.
- [91] Skaarup S, Boggs JE, Skancke PN. *Tetrahedron* 1976;32:1179–81.
- [92] Miyazaki T, Shigetani T, Shinoda H. *Bull Soc Jap* 1971;44:1491–6.
- [93] Saunders M, Berger R, Jaffe A, McBride JM, O'Neill J, Breslow R. et al. *J Am Chem Soc* 1973;95:3017–8.
- [94] Closs GL, Pfeffer PE. *J Am Chem Soc* 1968;90:2452–3.
- [95] Mulder JJC. *J Am Chem Soc* 1977;99:5177–8.
- [96] Dewar MJS. *J Am Chem Soc* 1984;106:209–19.
- [97] Shevlin PB, McKee ML. *J Am Chem Soc* 1988;110:1666–71.