

A quantumchemical study of symmetry controlled reactions in organic systems

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A QUANTUMCHEMICAL STUDY
OF SYMMETRY CONTROLLED REACTIONS
IN ORGANIC SYSTEMS

W.A.M. CASTENMILLER

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PROEFSCHRIFT

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GEBOREN TE RAAMSDONK

Dit proefschrift is goedgekeurd
door de promotoren
prof. dr. H.M. Buck
en
prof. dr. D.H.W. den Boer

"Hier wordt gener waarheid gezegd,
hier wordt der wetenschap gepleegd".

Prof. Prlwytzkofski

in

Heer Bommel en de gekikkerde vorst.

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CHAPTER ONE

INTRODUCTION

In this thesis a quantumchemical study is presented on the potential energy surfaces of organic systems. The total energy of a molecule consisting of N nuclei is a function of the $(3N-6)$ coordinates which describe the geometry of the atoms in the molecule. When the energy is plotted as a function of the $(3N-6)$ coordinates, one can construct the potential energy hypersurface. A stable compound or intermediate is represented as a minimum on the surface. The transition state for a reaction between two compounds A and B is found as a saddlepoint on the surface between two valleys leading to the two minima A and B.

The total energy of a molecule can be evaluated using quantumchemical methods. From the results of successive calculations one can construct the energy hypersurface. By minimizing the energy with respect to the geometrical variables it is possible to detect a local or global energy minimum. The minimization of the energy can be achieved using parabolic approximation formulas, i.e. by successively minimizing the energy as a function of each geometrical variable. In a much faster procedure the gradient of the energy can be minimized with respect to all the geometrical parameters.

A transition state on the surface can be located using two different approaches. In the reaction coordinate method one of the geometry parameters is chosen to be the reaction coordinate. This parameter is varied in small steps from the value in compound A to the value in B. At each step the energy is minimized with respect to all other variables. In

this way a reaction path over the surface is constructed. On the path the energy passes a barrier between A and B. The barrier height is considered to be the activation energy for the reaction after neglect of the zero-point vibrational energy terms. It is essential that a suitable parameter is chosen to be the reaction coordinate. When a small change in this parameter should be accompanied by a large change in the energy and the other parameters, an incorrect description of the reaction path is obtained.

Alternatively, it is possible to locate a transition state by minimizing the gradient of the energy. This minimization generally leads to a stationary point on the surface. By evaluating the matrix of the force constants of the system at the stationary point, it is possible to decide what kind of stationary point has been obtained. At an energy minimum the matrix has no negative eigenvalues. At a transition state there is just one negative eigenvalue. When two or more negative eigenvalues are found, one is dealing with a local energy maximum. The gradient minimization technique should be incorporated in the computer program used for the quantumchemical evaluation of the energy.

The construction of the total energy hypersurface is rather cumbersome because of the large number of geometrical variables involved. Usually, approximations are made with respect to some of these parameters. For instance, carbon-hydrogen bond lengths in hydrocarbon systems are fixed at a constant value. When an element of symmetry is present in the system under study, the number of independent geometrical variables is lowered substantially. Local energy minima within a certain symmetry point group can be detected rapidly. It is necessary to evaluate the force constants matrix or to repeat the geometry optimization with a lower symmetry constraint in order to determine the nature of the stationary point obtained. When the symmetry of a transition state can be assumed a priori and when this transition state is more symmetric than both the react-

ant and the product, it is possible to locate such a transition state by direct minimization of the energy within the appropriate symmetry point group. Then the nature of this stationary point should also be determined unambiguously. In this thesis, extensive use is made of the symmetry properties of the local minima (ground states) and transition states in the investigations of the potential energy surfaces.

The symmetry properties of organic systems can govern the stereochemical course of their reactions. Woodward and Hoffmann have developed a qualitative theory to predict the selectivity in this type of reactions, based on the principle of Conservation of Orbital Symmetry. When an element of symmetry is present in the system, the Molecular Orbitals of the reactant and the product can be classified as symmetric or antisymmetric with respect to this element of symmetry. In an allowed (thermal) reaction all occupied MO's of the reactant should correlate with occupied MO's of the product. When a reaction can occur in two distinct stereochemical modes, it is possible to predict which is the allowed mode.

The symmetry properties of the MO's are used to construct orbital correlation diagrams, which give an indication of the stereochemistry of the reactions. Another type of orbital diagrams can be used to study the relative stabilization resulting from the interaction of two molecules or fragments in a larger system. The MO's of both fragments which have identical symmetry properties can combine to form the MO's of the resulting molecule. Orbital interaction diagrams have been used frequently throughout this study.

In Chapter 2 of this thesis a description is given of the quantumchemical methods which have been applied. Extensive use has been made of the semiempirical MINDO/3 method which was developed recently. A very efficient gradient minimization technique is included in the MINDO/3 computer program. The results are supported by calculations

using the more rigorous STO-3G and 4-31G ab initio methods. A parabolic approximation method was used for the geometry optimizations in the ab initio calculations.

Chapter 3 presents a study on the potential energy surface of the $C_6H_5^+$ system. A large number of local energy minima can be detected on the surface within the various symmetry point groups. Evidence is found for a relatively stable nonclassical pyramidal structure with C_{5v} symmetry, which has a carbenoid character. Some reactions between the $C_6H_5^+$ species are studied using the theory of orbital isomerism. In this theory the symmetry properties of the MO's are used in a more extensive way, enabling an easy prediction on the allowed or forbidden character of rearrangement reactions between a large series of isomers.

In Chapter 4 and 5 the theory on symmetry governed reactions presented by Woodward and Hoffmann has been applied more directly in the study of electrocyclic and sigmatropic reactions. In Chapter 4 the stereochemical course of electrocyclic reactions is studied when they are influenced by a second π -electron system at a short distance. The ring opening reaction of cyclobutene to yield butadiene when perturbed by an ethylene molecule is used as a model system. It has been investigated if the forbidden disrotatory ring opening reaction should become allowed upon interaction with the ethylene π system.

Chapter 5 is devoted to the study of [1,3], [1,5] and [1,7] sigmatropic shift reactions in both cyclic and acyclic hydrocarbon systems. Hydrogen, methyl, fluorine and silyl have been chosen as the shifting groups. The reactions can occur in a suprafacial way (via a C_s -symmetric transition state) or in an antarafacial way (via a C_2 -symmetric transition state). Quantitative support has been obtained for the qualitative predictions on the stereochemistry of the reactions. The shift of a fluorine substituent is found to proceed in an "inversion-type" mechanism.

In this thesis some species have been studied which

contain highly coordinated carbon atoms. In Chapter 3 a few compounds are described in which an antiaromatic ring system is stabilized by interaction with an apical fragment which contains a pentacoordinated or hexacoordinated carbon atom. In the transition states for methyl shifts discussed in Chapter 5 the shifting carbon atom is also pentacoordinated. In Chapter 5 in addition a study is presented on the pentacoordinated CH_5^+ and SiH_5^+ cation systems.

CHAPTER TWO

QUANTUMCHEMICAL CALCULATIONS

2.1 Ab initio calculations

In the quantumchemical calculations the Molecular Orbital theory has been employed in the closed shell single determinant formalism¹. The Born-Oppenheimer approximation is applied, assuming the nuclei in the molecule to remain at fixed positions. An approximation to the exact solution of the nonrelativistic Schrödinger equation can be obtained in the Hartree-Fock SCF method, using a variational treatment to minimize the total energy of the system. This method has been worked out by Roothaan in the LCAO-MO procedure. The Molecular Orbitals are expanded as linear combinations of the atomic orbital basis set functions.

For the STO-3G² and 4-31G³ ab initio calculations we have employed the GAUSSIAN70 computer program available from the Quantum Chemistry Program Exchange⁴. In the STO-3G method² a minimal basis set is used consisting of the valence shell and inner shell atomic orbitals of the atoms in the molecule. These basis functions are indicated as Slater-Type Orbitals (STO). Each STO is approximately described as a contracted Gaussian function: a fixed linear combination of 3 primitive Gaussian functions. The use of Gaussian instead of Slater functions facilitates the evaluation of the two-electron repulsion integrals. In the 4-31G method³ an extended basis set is used. Each valence shell orbital is described by two contracted Gaussian basis functions. A fixed combination of three primitive Gaussians represents the inner part of the orbital and the outer part is described using only one primitive Gaussian. Inner shell orbitals are represented by one contracted Gaussian as a linear

combination of 4 primitive functions.

In the ab initio calculations a large number of two-electron repulsion integrals has to be evaluated. The total number of these integrals is proportional to m^4 , where m is the number of primitive Gaussian basis functions. The amount of computer time necessary increases rapidly for larger molecules. On the Burroughs 7700 computer at the Eindhoven University of Technology Computing Centre one standard STO-3G calculation on a C_3H_5F molecule requires about 4 minutes, while a 4-31G calculation takes about 40 minutes. An STO-3G calculation requires about 11 minutes for a C_5H_8 system and about 50 minutes for a C_6H_5 system.

As input for the calculations the GAUSSIAN70 program only requires the total charge and multiplicity of the molecule and the atomic number and coordinates of the atoms. No 3d-type orbitals can be incorporated. Up to 35 atoms or 70 STO's or 240 primitive Gaussians can be treated. In the STO-3G method the atoms up to the third row of the periodic system can be handled, and the 4-31G method can be applied only to the elements H, B to F, and P to Cl. A simple parabolic approximation procedure is included to minimize the energy with respect to one geometrical parameter. In the evaluation of the integrals no use is made of the symmetry point group of the system. All integrals are evaluated again for each point on the surface, none of them are retained from calculations on previous points.

2.2 MINDO/3 calculations

2.2.1 Approximations in the MINDO/3 method

Semiempirical MO procedures have been developed in order to avoid the calculation of a large number of integrals as in the ab initio methods. Many of these integrals are neglected and others are obtained from parametrical

approximation formulas. A valence basis set is used consisting of one Slater-type function for each atomic orbital of the valence shell. The inner shell electrons are not taken into account. The nucleus and the inner shell electrons are considered as a point charge called the core.

The Modified Intermediate Neglect of Differential Overlap (MINDO) method is based on the INDO approximation developed by Pople⁵. The final scheme to obtain the elements of the matrix representation of the Fock operator F_{pq} (which is diagonalized in the SCF procedure) is:

$$F_{pp}^{kk} = U_{pp} + \sum_q P_{qq} \left[\langle pq | pq \rangle - \frac{1}{2} \langle pp | qq \rangle \right] + \sum_{l \neq k}^N (P_{ll} - Z_l) \gamma_{kl} \quad (2.1)$$

$$F_{pq}^{kk} = \frac{1}{2} P_{pq} \left[3 \langle pp | qq \rangle - \langle pq | pq \rangle \right] \quad (2.2)$$

$$F_{pq}^{kl} = \beta_{pq}^{-\frac{1}{2}} P_{pq} \gamma_{kl} \quad (2.3)$$

The indices p and q represent the basis functions ϕ_p and ϕ_q , k and l represent the atoms on which the functions are centered and N is the number of nuclei. The first summation in (2.1) is over the functions ϕ_q centered on the same atom k as ϕ_p . P_{pq} is an element of the density matrix. The total electron density on an atom k is given as

$$P_{kk} = \sum_p P_{pp} \quad (2.4)$$

summing over all functions ϕ_p on k . Z_k is the charge of the core of atom k .

The two-electron repulsion integrals are given as

$$\langle pq | rs \rangle = \langle \phi_p(\mu) \phi_q(\nu) | \frac{1}{r_{\mu\nu}} | \phi_r(\mu) \phi_s(\nu) \rangle \quad (2.5)$$

where $r_{\mu\nu}^{-1}$ is an operator representing the repulsion between two electrons μ and ν . γ_{kl} is the average two-electron repulsion between two electrons in two basis functions

ϕ_p and ϕ_q on the atoms k and l , independent of the type of basis functions

$$\gamma_{kl} = \langle \phi_p^k(\mu) \phi_q^l(\nu) | \frac{1}{r_{\mu\nu}} | \phi_p^k(\mu) \phi_q^l(\nu) \rangle \quad (2.6)$$

All three- and four-center integrals have been neglected. U_{pp} is the one-electron one-center integral and β_{pq} is the one-electron two-center resonance integral.

In the MINDO/3 method developed by Dewar⁶ the following assumptions are made to evaluate the integrals in (2.1-3):

- a) because only s- and p-type orbitals are taken into account (3d orbitals are not incorporated in the method), six different types of one-center repulsion integrals (involving s, p_x and p_y orbitals) should be distinguished⁵: $g_{ss} = \langle ss | ss \rangle$; $g_{sp} = \langle sp_x | sp_x \rangle$; $g_{pp} = \langle p_x p_x | p_x p_x \rangle$; $g_{pp'} = \langle p_x p_y | p_x p_y \rangle$; $h_{sp} = \langle ss | p_x p_x \rangle$; $h_{pp'} = \langle p_x p_x | p_y p_y \rangle$. All other integrals (also involving p_z orbitals) are of a similar type. In the MINDO/3 method these integrals are obtained⁷ using the procedure of Oleari⁸. Upon introducing this parametrization, the method is no longer invariant under rotation of the coordinate system. It has been assumed that the errors introduced are only small.
- b) the two-center integrals γ_{kl} are evaluated from an empirical formula

$$\gamma_{kl} = \left[r_{kl}^2 + \frac{1}{4} \left(\frac{1}{g_k} + \frac{1}{g_l} \right)^2 \right]^{-\frac{1}{2}} \quad (2.7)$$

where r_{kl} is the distance between the atoms k and l and g_k is the averaged value of the 16 one-center repulsion integrals over the atom k

$$g_k = \frac{1}{16} (g_{ss} + 3g_{pp} + 6g_{sp} + 6g_{pp'}) \quad (2.8)$$

- c) for the one-center integrals U_{pp} for s and p orbitals small adjustments were made to the values given by Oleari⁸ (these modifications have not been reported in the literature⁶).
- d) the resonance integral is evaluated as

$$\beta_{pq}^{kl} = \beta_{kl}^0 S_{pq} (I_p^k + I_q^l) \quad (2.9)$$

where I_p^k is the valence state ionization potential for an electron in an s or p orbital, obtained from experimental data. S_{pq} is the overlap integral between ϕ_p and ϕ_q , which is evaluated analytically over valence orbitals using Slater functions

$$S_{pq}^{kl} = \langle s_k(\mu) | s_l(\nu) \rangle \quad (2.10)$$

The parameters β_{kl}^0 have been chosen empirically (vide infra).

- e) the orbital exponents ζ_s^k and ζ_p^k for s and p orbitals, used in the evaluation of S_{pq} , have been chosen empirically.
- f) the core-core repulsion E_{rep}^{kl} between the cores of the atoms k and l, which is added to the total electronic energy E_{el} , is obtained from an empirical formula

$$E_{rep}^{kl} = Z_k Z_l \left[\gamma_{kl} + \left(\frac{1}{r_{kl}} - \gamma_{kl} \right) f(r_{kl}) \right] \quad (2.11)$$

which satisfies the limiting conditions

$$E_{rep}^{kl} = Z_k Z_l \gamma_{kl} \quad \text{for } r \rightarrow \infty \quad (2.12)$$

$$E_{rep}^{kl} = \frac{Z_k Z_l}{r_{kl}} \quad \text{for } r \rightarrow 0 \quad (2.13)$$

The formula f is chosen as

$$f(r_{k1}) = \exp(-\alpha_{k1} r_{k1}) \quad (2.14)$$

except for repulsions between hydrogen and N or O, where

$$f(r_{k1}) = \alpha_{k1} \exp(-r_{k1}) \quad \text{with } k=H \text{ and } l=N \text{ or } O \quad (2.15)$$

The parameters α_{k1} are chosen empirically.

2.2.2 The MINDO/3 computer program

The MINDO/3 procedure is available in the MINDO/3 computer program⁹. The SCF iteration procedure is carried out until the energy converges within 10^{-4} eV (0.0023 kcal/mol) and until the largest change in the diagonal elements of the density matrix is smaller than 10^{-4} . The dominating factor in the computation time now is the repeated diagonalization of the Fock matrix (2.1-3) in the SCF procedure. The computation time is proportional to m^3 , where m is the number of basis functions. One MINDO/3 calculation on the B7700 computer requires about 50 seconds for a C_8H_{12} system and about 8 seconds for C_3H_5F . The heat of formation of the molecule at $25^\circ C$ is evaluated as

$$\Delta H_f = E_{e1} + \sum_{k<1} \sum_{l=1}^N E_{rep}^{kl} - \sum_k E_k + \sum_k \Delta H_f^O(k) \quad (2.16)$$

where E_k is the energy of the free atom k obtained from a separate MINDO/3 calculation and $\Delta H_f^O(k)$ is the standard heat of formation of atom k obtained from thermodynamic data.

The values of the empirical parameters α_{k1} , β_{k1}^O , ζ_s^k and ζ_p^k have been obtained from a least squares fit to experimental data, to give the best fit for heats of formation, bond lengths and bond angles in a set of standard molecules. For instance, a set of 20 hydrocarbon molecules was used to

obtain the parameters for carbon and hydrogen⁶. In the program the parameter values are available for the elements H and B to F, and furthermore for the second row elements (with neglect of 3d orbitals) Si to Cl, but only in combination with H, C and the element itself. Up to 30 atoms or 50 orbitals can be handled. The input for the program is similar to that for the GAUSSIAN70 program.

Some of the options available in the MINDO/3 program include:

- the geometry of the molecule can be given in polar coordinates, making use of the symmetry in the system.
- geometry parameters can be optimized, leading to a minimum on the energy surface. A very efficient procedure is available using the gradients of the energy. The gradients are calculated by the method of finite differences while the density matrix P_{pq} is held constant, so no additional SCF calculations are necessary. The computation time is proportional to the number of geometrical parameters to be optimized.
- a reaction path on the surface can be constructed.
- for closed shell ground state calculations a 2x2 configuration interaction (CI) calculation can be carried out with one closed shell doubly excited state.
- single determinant open shell calculations can be performed.

Prior to the development of the MINDO/3 method several preliminary MINDO versions have been reported. In each of them the Slater values were used for the orbital exponents ζ^5 , and formula (2.15) was replaced by (2.14). For each method another parameter set for α_{k1} and β_{k1}^0 was determined.

- The original MINDO/2 method¹⁰ differs from MINDO/3 in using the INDO formulas for the six one-center repulsion integrals⁵ and in different values for the one-center integrals U_{pp} and g_k (2.8).
- Upon extension of this method to include fluorine as well⁷, the one-center repulsion integrals and g_k were determined just as in the MINDO/3 method, but other

- values were used for U_{pp} .
- For hydrocarbons, another method was developed termed MINDO/2¹¹, which differs from ref. 7 in using different formulas for β_{pq}^{kl} (2.9) and E_{rep}^{kl} (2.11) with respect to C-H or H-H interactions.
 - The latter method was extended by inclusion of a 2x2 CI procedure (MINDO/CI)¹². Formula (2.9) was used again for β_{pq}^{kl} and different values were taken for U_{pp} and ζ .
- All these methods can be considered as precursors for the MINDO/3 procedure. The MINDO/3 method is claimed to be the endpoint for semiempirical treatments based on the INDO approximation⁶.

2.2.3 Evaluation of MINDO/3 results

In recent years many results have been published from MINDO/3 calculations on a large variety of molecules and reactions. The method is claimed to give better results than any other semiempirical procedure⁶. Its predictions generally are comparable to those of the STO-3G ab initio method. Most of the data have been reported in publications by Dewar and co-workers, including some reviews^{13,14}. Only a few objective reviews of MINDO/3 results have been given^{15,16}. Some standard objections against the use of semiempirical methods like MINDO/3 have been discussed¹⁷. The average errors in numerical data for various properties have been presented¹⁸.

In the calculation of optimized molecular geometries the MINDO/3 method is reported to predict bond lengths with an average accuracy of 0.021 Å for a set of 256 molecules¹⁸. C-H bonds are predicted too long by 0.02 Å and C-C bonds are too short by about 0.015 Å. Results for bond angles are less satisfactory. An average error of 5.5° is reported for a set of 104 angles¹⁸ or 4.2° for a set of 78 angles¹⁵ and 8.7° for a set of 23 angles¹⁹. Skeleton bond angles generally are predicted to be too large, methylene H-C-H angles are given about 6° too small. The geometry of

ring systems is predicted to be too flat.

Good results are obtained from the MINDO/3 method for the heats of formation ΔH_f , when compared to experimental values. An average error of 6 kcal/mol is reported for a set of 193 different compounds⁶, or 11 kcal/mol for a selected set of 138 molecules¹⁸. For 4 different types of molecules a systematic error of more than 10 kcal/mol is reported²⁰: for acetylene-type molecules and for small ring systems, ΔH_f is too low, and for aromatic molecules and compact globular molecules like neopentane or adamantane, ΔH_f is too high. Barriers for rotation around double bonds are predicted well, but too low barriers are found for rotation around single bonds. The results reported in the original papers on the MINDO/3 method were obtained using the slowly converging SIMPLEX geometry optimization procedure. These data contain small errors when compared with results from the faster gradient minimization procedure in the final version of the program. In this thesis all results are obtained using the latter method, unless indicated otherwise.

The MINDO/3 method is claimed to predict the energies of transition states just as good as those of ground states, and to give a good description of potential energy surfaces. For 185 different reactions, the mechanism is found to be in line with experimental results¹⁸. Most of the activation energies for over 50 reactions are predicted within 5 kcal/mol from the experimental values. The activation energies for 14 electrocyclic reactions are given with the same accuracy²¹, only the transition state for the conrotatory ring opening of cyclobutene is found to be 16.5 kcal/mol too high¹³. For the Diels-Alder reaction of butadiene with ethylene to give cyclohexene, MINDO/3 predicts an asymmetrical transition state and a biradicaloid reaction mechanism²², while ab initio calculations with and without inclusion of configuration interaction predict a symmetrical transition state. This discrepancy was found to originate from the assumptions made in the INDO method²³.

The errors in the MINDO/3 values for overall heats of reaction are found to depend mainly on the errors for the individual species in the reactions. Good results can be obtained, depending on the type of reactions studied, such as isomerization, hydrogenation or bond separation reactions^{16,24}.

The MINDO/3 method is found to give reliable results for carbocations as well. The data obtained from various kinds of semiempirical and ab initio calculations on carbocations have been extensively reviewed¹⁵. MINDO/3 is reported to give a successful description of nonclassical carbocations²⁵. Some data reported in the original papers are found to be incorrect²⁶.

For molecules containing heteroatoms such as N, O and F, generally good results are obtained from the MINDO/3 method²⁷. When two neighbouring atoms contain lone pairs, the resulting heat of formation is systematically too low and the bond length is too short. The accuracy in geometries and energies for other systems is similar to that in results for hydrocarbon systems. For calculations including the elements Si to Cl, satisfactory results are obtained as well, although 3d orbitals are not included in the method. It has been reported that fluorine has a tendency to be bi-coordinated in MINDO/3 calculations²⁶. In Chapter 5 of this thesis it will be shown that MINDO/3 results for molecules containing fluorine should be interpreted with great caution. The original parameter set for boron has recently been rejected²⁸.

Difference charge densities calculated from the MINDO/3 method are found to be similar to those resulting from ab initio methods. STO-3G generally predicts more $C^{\delta-}H^{\delta+}$ polarization than MINDO/3. MINDO/3 can incorrectly predict the presence of high-energetic occupied σ -type MO's. Good results from MINDO/3 have been obtained for a large variety of ground state molecular properties⁶.

2.3 The report of numerical data

The following should be noted about the numerical data reported throughout this work. The heats of formation and the energy differences are always given in kcal/mol, where $1 \text{ kcal/mol} = 4.18400 \cdot 10^3 \text{ J/mol}$. Interatomic distances are given in Å ($1 \text{ Å} = 10^{-10} \text{ m}$), angles in degrees. In spite of the well-known uncertainties in the MINDO/3 results (see Section 2.2.3), all numerical data in this thesis are given in one place of decimal for energies and bond angles and in three places of decimal for bond lengths. Dihedral angles are reported using the notation A-B-C-D for the dihedral angle of atom A rotated clockwise around the axis B-C out of the plane (B,C,D). Charge densities and orbital occupancies are given as the number of electrons. Difference charge densities are corrected for the number of electrons in the valence state of the free atom, a positive number indicates a positively charged atom. In the orbital interaction diagrams presented in the Figures, the orbital energy levels are not drawn on scale. Only the most important interactions between the orbitals have been indicated.

CHAPTER THREE

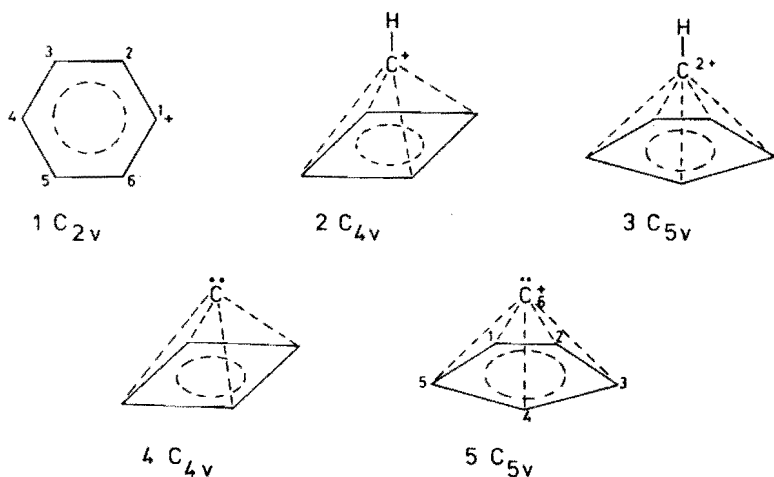
A STUDY ON THE $C_6H_5^+$ POTENTIAL ENERGY SURFACE

3.1 Introduction

In recent years a large number of studies has been devoted to carbocation systems. An experimental approach usually is restricted to the investigation of carbocations as transient species, because the isolation of carbocation salts is impossible. Solutions of carbocations in superacid media have been studied frequently. Information about the structures and their reactions can be obtained from NMR techniques. The heats of formation of positively charged species can be determined from mass spectrometric experiments, but in this case it is rather difficult to obtain structural information. Experimental work on carbocations has been reviewed by Olah and v. R. Schleyer¹.

Carbocations are appropriate subjects for quantum-chemical investigations. Nonempirical and semiempirical MO techniques have been applied to single cationic species, but complete potential energy surfaces of certain cationic systems have also been generated. A survey of the literature up to 1975 has been given by Radom². The MINDO/3 procedure and the STO-3G and 4-31G ab initio methods have been applied most frequently. Most carbocationic structures containing up to 4 carbon atoms have been investigated systematically and much work has also been performed for larger systems. In this Chapter an investigation of a part of the potential energy surface of the $C_6H_5^+$ system is presented. Until recently, theoretical and experimental interest was aimed only at the phenyl cation 1 derived from benzene.

Recently, evidence has been obtained for hydrocarbon structures containing carbon atoms with a coordination



number higher than four. Some examples are the C_{4v} -symmetrical $C_5H_5^+$ system 2³ and the related C_{5v} -symmetrical $C_6H_6^{2+}$ dication 3⁴. Also the C_5H_4 carbene structure 4 derived from 2⁵ can be considered as containing a penta-coordinated apical carbon atom, if the carbenic orbital is assumed to be the fifth ligand. The stabilization of the antiaromatic basal ring in 2 and 3 by interaction with the apical fragment has been explained qualitatively with the aid of orbital interaction diagrams. Similar to the carbene 4 derived from 2 a $C_6H_5^+$ carbene 5 could exist derived from 3, containing a hexacoordinated carbon atom.

The phenyl cation 1 is supposed to play a role as a possible intermediate in reactions of benzenediazonium systems (see Section 3.2.2). Our interest in the phenyl cation intermediacy during these reactions and in the possible existence of the pyramidal carbene structure 5 led us to perform a more extensive theoretical investigation of a part of the $C_6H_5^+$ singlet ground state potential energy surface. The use of ab initio methods to investigate the surface of such a large system is hampered because of the amount of computer time required. Therefore we had to confine ourselves to a semiempirical study. The MINDO/3 method

has been chosen because it has been applied successfully to study energy surfaces of various carbocationic systems². Occasionally, we have also performed STO-3G ab initio calculations. Recently, an unpublished MINDO/3 study on the $C_6H_5^+$ surface has been mentioned in the literature⁶.

In our MINDO/3 study a complete optimization of all the geometrical parameters has been included within the symmetry point group assumed for each structure under investigation. For each energy minimum obtained the calculation was repeated with a lower symmetry constraint to check if the stationary point on the surface was a minimum or a saddlepoint. For the geometries the following assumptions have been made unless indicated otherwise:

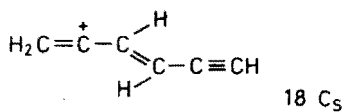
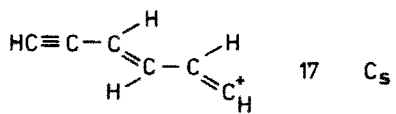
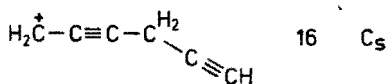
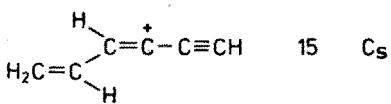
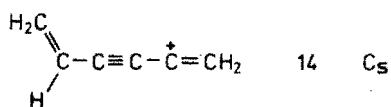
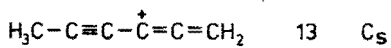
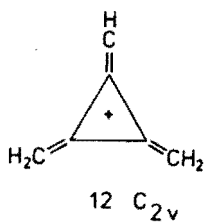
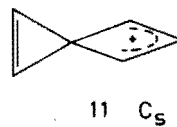
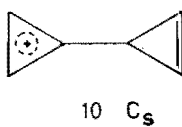
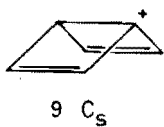
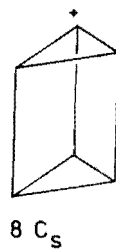
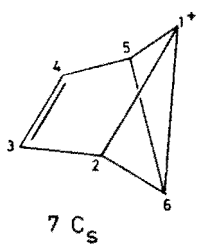
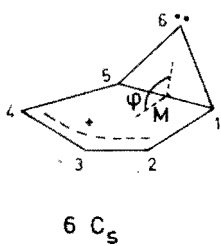
- C-H bond lengths were fixed at 1.09 Å.
- a planar arrangement was imposed on sp^2 -hybridized carbon atoms.
- for CH_2 groups local C_{2v} symmetry was assumed.

For the STO-3G calculations the geometry obtained from the MINDO/3 procedure was taken as a starting point. Then only a few parameters were reoptimized because of limitations in computer time. Details on the geometry optimizations will be given in Section 3.3.

3.2 Relative energies

3.2.1 Local energy minima

Some of the energy minima located on the potential energy surface may be represented by the structures 1 and 5-17. The electronic configuration of the various species will be discussed in detail in Section 3.4. The MINDO/3 heats of formation are presented in Table 3.1. It is not certain that all the acyclic structures 13-17 represent local energy minima (see Section 3.3.3). From this survey containing 14 species, it is clear that the phenyl cation is the most stable cyclic structure on the surface. For the acyclic system 13 a similar energy is found, but



higher heats of formation are predicted for all other acyclic structures. Many more $C_6H_5^+$ systems are feasible, but we have not tried to perform a complete study. These results are corroborated by an unpublished MINDO/3 study on more than 40 isomers of $C_6H_5^+$, which predicts 1 to be the most stable one⁶.

In Table 3.1 are included the relative energies from STO-3G calculations on a few species that are most important in the discussions following. The STO-3G energy values for the compounds 6 and 7 are interchanged compared with the MINDO/3 results. This might be due to the fact that the MINDO/3 geometry was taken for 7 without further geometry optimization. It should be mentioned that the acyclic system 18 was found to be 17 kcal/mol higher than 1 from 4-31G calculations⁶.

The relative energy found for system 5 from ab initio calculations should be corrected because of the fivefold rotational symmetry. The symmetry number σ indicates the number of rotational symmetry operations possible within the system. An extra term should be added to the entropy of the system, which is equal to $-R \ln \sigma = -5.76 \text{ J/}^\circ\text{K.mol}$, because σ equals 5 in 5. A similar correction does not apply to MINDO/3 results, because the parameters in the MINDO/3 method have been fitted to experimental heats of formation.

3.2.2 Occurrence of the phenyl cation

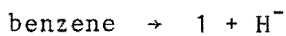
The phenyl cation 1 is the only $C_6H_5^+$ species which has been studied experimentally using mass spectrometry. Reported heats of formation vary widely: 266⁷, 285⁸ and 270 kcal/mol⁹, the latter value is considered to be reliable⁶. It is not certain that all data are related to 1, since acyclic isomers could not be ruled out. A value of 292 kcal/mol for 1 has been obtained from thermodynamic data¹⁰. 4-31G calculations lead to 280 kcal/mol⁶, which is 35 kcal/mol higher than the MINDO/3 value. The heat of

Table 3.1

Absolute and relative heats of formation

	MINDO/3		STO-3G
<u>1</u>	244.8	0	0
<u>5</u>	281.6	36.8	24.5
<u>6</u>	307.6	62.8	44.3
<u>7</u>	299.5	54.7	53.0
<u>8</u>	355.6	110.8	
<u>9</u>	294.8	50.0	
<u>10</u>	281.4	36.6	
<u>11</u>	298.7	53.9	
<u>12</u>	277.0	32.2	
<u>13</u>	244.8	-0.01	
<u>14</u>	252.9	8.1	
<u>15</u>	269.8	25.0	
<u>16</u>	270.0	25.2	
<u>17</u>	296.4	51.6	

reaction calculated from the MINDO/3 method for the process

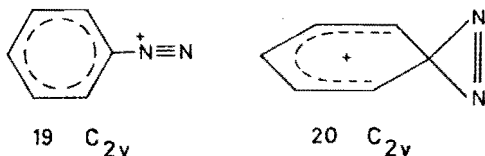


equals 316.6 kcal/mol ($\Delta H_f(\text{benzene}) = 28.8$ and $\Delta H_f(\text{H}^-) = -532.6$ kcal/mol) which is in good agreement with the value of 303 kcal/mol found experimentally¹¹.

From the calculated heats of formation in Table 3.1 it can be concluded that in the mass spectrometric experiments structure 1 indeed is formed and not an acyclic system like 17. Solvolytic experiments on benzene systems substituted with good leaving groups failed to generate 1 or its derivatives as an intermediate¹². 1 has been formed from halobenzenes in ion cyclotron resonance spectroscopy experiments and some of its reactions have been studied¹³.

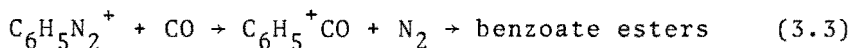
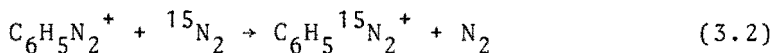
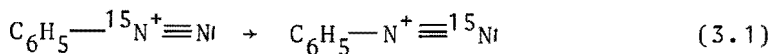
The phenyl cation has been postulated to exist as a

reaction intermediate in nucleophilic displacement reactions on the benzenediazonium cation 19¹⁴. The solvolysis reaction of 19 (with an experimental activation energy of



28.3 kcal/mol¹⁵) can be accompanied to a small extent by three possible ancillary reactions¹⁶:

- rearrangement of the (labeled) nitrogen atoms (3.1),
- exchange of the diazonium nitrogen with external labeled molecular nitrogen dissolved under high pressure (3.2),
- exchange with external carbon monoxide (3.3).



In all these reactions formation of a transient phenyl cation is the first step. It has been postulated that the nucleophilic substitution proceeds via a molecule-ion pair ($C_6H_5^+ \cdots N_2$) mechanism¹⁵⁻¹⁷, which would provide the possibility for other reactions of the phenyl cation.

We have performed some exploratory MINDO/3 calculations on $C_6H_5N_2^+$ systems to study the intermediacy of 1 in these reactions. The heat of formation of 19 was found to be 170.7 kcal/mol and the geometry parameters are in good agreement with data from X-ray experiments¹⁸. The spiro-type nitrogenbenzenium cation 20 is a shallow minimum on the energy surface, being 49.7 kcal/mol higher than 19. The activation energy for the rearrangement of the N_2 fragment in 19 by rotation in the plane perpendicular to the phenyl ring is predicted to be 56.9 kcal/mol. For the linear

fragmentation of 19 to yield 1 and N_2 a much higher barrier is predicted.

The MO calculations are always related to isolated systems in the gas phase. The effect of surrounding molecules, solvent or counterion is not taken into account. The mechanism postulated for the reactions (3.1-3) involving a molecule-ion pair cannot be substantiated by this type of calculations. It would be necessary, for instance, to include the first shell of solvent molecules in the calculations to obtain more reliable quantitative predictions.

3.3 Geometries

3.3.1 The phenyl cation and the pyramidal system 5

A large number of theoretical studies has been devoted to the (planar) C_{2v} -symmetrical phenyl cation 1⁶. The MINDO/3 geometry is given in Table 3.2, together with the reported STO-3G structure (with C-H bond lengths fixed at

Table 3.2
Geometry parameters for 1 and 5

<u>1</u>			<u>5</u> ^a		
	MINDO/3	STO-3G ⁶		MINDO/3	STO-3G
C_1-C_2	1.352	1.347	C_1-C_2	1.456	1.427
C_2-C_3	1.429	1.403	C_1-M	1.239	1.214
C_3-C_4	1.408	1.394	C_6-M	1.164	1.345
$C_6-C_1-C_2$	145.4	144.9	C_1-C_6	1.700	1.819
$C_1-C_2-C_3$	104.4	103.6	H_1-C_1-M	172.9	171.4
$C_2-C_3-C_4$	123.1	125.6			
$C_3-C_4-C_5$	119.6	116.8			
$H_2-C_2-C_1$	130.0	128.2			
$H_3-C_3-C_2$	114.8	115.8			

^aM is the centre of the five-membered ring

1.08 Å)⁶. The mutual differences between these geometry parameters are not important. This was concluded from an STO-3G calculation using the MINDO/3 optimized geometry parameters as input. The energy found is even 2.0 kcal/mol lower compared with the result from the STO-3G optimization⁶. Apparently, a C-H distance of 1.09 Å is a more appropriate choice. Lowering of the symmetry constraint to C₅ led to higher energies on both the MINDO/3 and STO-3G⁶ energy surfaces.

Next in importance on the C₆H₅⁺ hypersurface is the C_{5v}-symmetrical nonclassical pyramidal structure 5. The geometry parameters are included in Table 3.2. From the STO-3G method a notably larger distance between the apical C₆ atom and the cyclopentadienyl ring is predicted. Similar results have been found for the corresponding parameter in the nonclassical pyramidal structures 2-4^{5,19,20}, see Table 3.3. In 5 the hydrogen atoms in the ring are bent slightly upwards, which leads to an increase in the overlap between the ring π orbitals and the apical carbon atom. This feature has also been noted in results for 2-4^{3,5,20,21}. MINDO/3 calculations predict an energy rise for various deviations from the C_{5v} symmetry. Similar results were obtained from the STO-3G method when the C₆ carbon atom was moved off the fivefold axis, while the positions of the ring atoms were fixed.

Table 3.3

Results for pyramidal systems 2-5: distance between the apical fragment and the basal ring, and total overlap population

	Distance		Overlap population STO-3G
	MINDO/3	STO-3G	
<u>5</u>	1.164	1.355	0.359
<u>3</u>	1.084	1.210 ¹⁹	0.598 ¹⁹
<u>4</u>	1.245	1.318 ⁵	0.480
<u>2</u>	1.179	1.198 ²⁰	0.672

Table 3.4

Geometry parameters of the bicyclo[3.1.0]hexenyl compounds 6 and 21.

M is the centre between C₁ and C₅. Assumed values are given between parentheses.

	<u>6</u>		<u>21</u>	
	MINDO/3	STO-3G	MINDO/3	STO-3G ²²
C ₁ -C ₅	1.666	1.483	1.547	1.483
C ₁ -C ₂	1.466	(1.463)	1.484	1.463
C ₂ -C ₃	1.404	(1.391)	1.410	1.391
C ₁ -C ₆	1.449	1.584	1.518	1.617
C ₅ -C ₁ -C ₂	101.7	105.4	104.7	105.4
C ₁ -C ₂ -C ₃	114.8	(110.2)	110.7	110.2
C ₂ -C ₃ -C ₄	107.1	(108.7)	109.2	108.7
C ₃ -M-C ₁ -C ₂	-1.0	(0)	(0)	(0)
C ₆ -C ₁ -C ₅ -C ₄ (φ)	142.5	93.0	117.1	104.4
H ₁ -C ₁ -C ₂	113.9	(120.9)		120.9
H ₁ -C ₁ -C ₂ -C ₅	140.6	155.0		155.0
H ₂ -C ₂ -C ₁	119.9	(124.3)	(127.6)	124.3
H ₂ -C ₂ -C ₁ -C ₅	175.8	(180)	(180)	(180)
H ₃ -C ₃ -M	(180)	(180)	(180)	(180)
C-H	(1.09)	(1.09)	(1.09)	(1.10)
H ₁ -C ₁ -C ₅			(127.6)	125.8
H ₅ -C ₅ -C ₁ -C ₄			138.3	
H ₆ (exo)-C ₆ -M	-	-	(125.5)	120.7
H ₆ (endo)-C ₆ -M	-	-	(125.5)	122.2

3.3.2 The structure of the bicyclic system 6

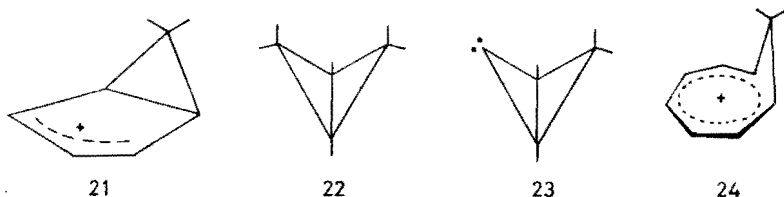
Another minimum on the potential energy surface is the C_s bicyclic structure 6, which can be described as the 6-carbenic species derived from the bicyclo[3.1.0]hexenyl cation 21. MINDO/3 calculations predict an almost planar cyclopentenyl ring in 6. The geometry parameters of 6 and 21 obtained from MINDO/3 and STO-3G calculations are given in Table 3.4. For the STO-3G calculations on 6 we have taken the geometry parameters of 21²². Then five parameters were optimized successively for 6: the distances C_1-C_5 and C_1-C_6 , angle $C_5-C_1-C_2$ and the dihedral angles $C_6-C_1-C_5-C_4$ (ϕ) and $H_1-C_1-C_2-C_5$. Only the angle ϕ (93°) led to a notable deviation from the value in 21 (104.4°).

For some parameters in 6, rather large differences exist between the results from the MINDO/3 and STO-3G methods. In Table 3.5 the values of the dihedral angle ϕ

Table 3.5
Geometry parameters of bicyclic systems

	MINDO/3	STO-3G
Dihedral angle		
<u>6</u>	142.5	93.0
<u>21</u>	117.1	104.4 ²²
<u>22</u>	130.5	117.4 ²³
<u>23</u>	148.5	129.0 ²³
<u>24</u>	117.9 ²⁴	103.0 ²²
Ring-fused linkage		
<u>6</u>	1.666	1.483
<u>21</u>	1.547	1.483 ²²
<u>22</u>	1.555	1.469 ²³
<u>23</u>	1.643	1.547 ²³
<u>24</u>	1.621 ²⁴	1.512 ²²

and the ring-fused linkage C_1-C_5 are summarized, together with results for the corresponding parameters in other bicyclic systems for which STO-3G results were reported in the literature: 21²², bicyclobutane C_4H_6 22²³, bicyclo-[1.1.0]butan-2-ylidene C_4H_4 23²³ and the homotropenylium cation $C_8H_9^+$ 24^{22,24}. It is noted that the MINDO/3 method



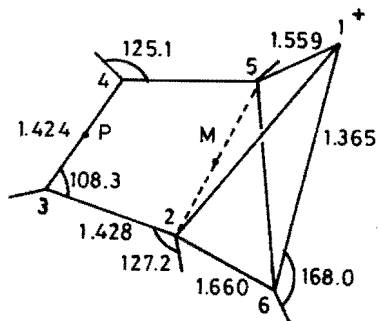
always predicts larger values for the ring-fused linkage than STO-3G calculations. The angle ϕ is about 15° larger in the MINDO/3 structures, but this does not explain the large discrepancy found for this parameter in 6. Additional MINDO/3 calculations show that reduction of ϕ in 6 to a value of 120° leads to an energy rise of only 3.1 kcal/mol, while the C_1-C_5 distance is reduced to 1.575 Å. Apparently, the MINDO/3 potential energy surface is rather flat in the vicinity of the local minimum 6, and the dihedral angle of 143.5° is much too large. The MINDO/3 method is known to be unreliable for the calculation of bond angles (see Chapter 2).

3.3.3 Other energy minima

Furthermore, we have studied cationic structures derived from the C_6H_6 valence isomers Dewar benzene, benzvalene and prismane. The three C_s -symmetrical $C_6H_5^+$ cations, viz. the 1-benzvalenyl cation 7, the prismanyl cation 8 and the 1-Dewar-benzenyl cation 9, are all found to be local minima on the MINDO/3 energy surface. The geometry parameters are indicated in Figure 3.1. Although the geometries of the cations do show some notable differences in comparison with the neutral parent hydrocarbons, there is no indication that they should be described as nonclassical

Figure 3.1

MINDO/3 optimized structures

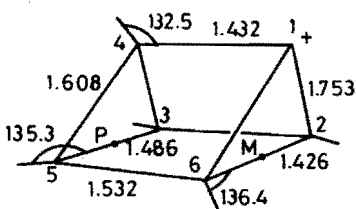


7 $C_2-C_5 = 2.321 \text{ \AA}$

$\psi = C_1-M-P = 146.6^\circ$

$C_6-M-P = 138.2^\circ$

M and P are situated in the mirror plane



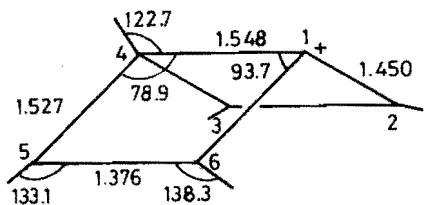
8 $C_1-M-P = 86.1^\circ$

$C_4-P-M = 89.9^\circ$

$H_5-C_5-C_3-C_2 = 163.9^\circ$

$H_2-C_2-C_6-C_5 = 176.5^\circ$

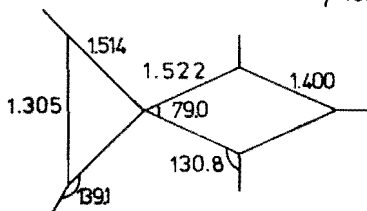
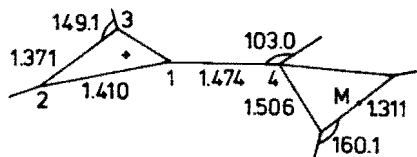
M and P are situated in the mirror plane



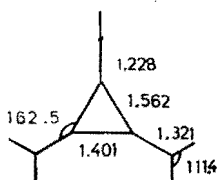
9 $C_6-C_1-C_4-C_3 = 126.3^\circ$

10 $C_1-C_4-M = 133.8^\circ$

M is situated in the mirror plane



11



12

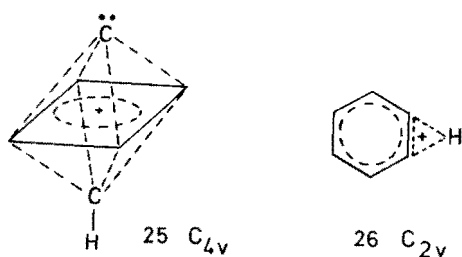
ions. The bond lengths adjacent to the cationic centre are shortened compared to the C_6H_6 structures.

In 7, the lowest unoccupied MO is localized on C_1 and is moved away from the double bond, so there is no bis-homoaromatic interaction, as for instance in the 7-norborn-enyl cation. In 8 the C_1 - C_2 distance is very large (1.753 Å) and the positive charge is delocalized over the entire system by means of σ interaction. In structure 9 the Dewar-benzene geometry is seriously distorted, allowing the cationic centre C_1 to acquire more sp^2 character, the lowest unoccupied MO (LUMO) being localized on C_1 .

More local energy minima may be detected on the $C_6H_5^+$ potential energy surface, for instance the structures 10-12 (see Figure 3.1). In the cyclopropenyl cyclopropenium cation 10 the three-membered rings are similar in structure to cyclopropene and the cyclopropenium cation (which has a bond length of 1.388 Å), respectively. The positive charge is concentrated in the cyclopropenium π system and the central bond length of 1.474 Å does not suggest an interaction between the two ring systems. The [1,2] hydrogen migration from C_4 to C_1 would require an activation energy of 13.3 kcal/mol (MINDO/3).

For 11 C_{2v} symmetry has been assumed. For the parent $C_4H_5^+$ cyclobutenium cation MINDO/3 calculations predict a much larger ring puckering angle (31°)² than an STO-3G study (10°)². The positive charge in 11 is concentrated mainly at the terminal atoms of the allyl system, evidence for charge transfer between the perpendicular ring systems is lacking. Compound 12 was found to be planar and to have C_{2v} symmetry. The positive charge is fully concentrated in the σ -type orbitals, the highest occupied MO (HOMO) of the system resembles the HOMO in butadiene.

We have also studied the hypothetical C_{4v} -symmetrical bipyramidal system 25. This structure was found not to represent a local energy minimum. The C_{2v} -symmetrical structure 26 was reported⁶ to be 77 kcal/mol (STO-3G) or 44 kcal/mol (MINDO/3) higher than 1. However, this system probably re-



presents the transition state for the [1,2] hydrogen migration in 1.

In this study 5 acyclic $C_6H_5^+$ structures (13-17) are included out of the 14 possibilities. These systems were selected because they represent the various manners in which the 5 hydrogen atoms can be bound to the carbon chain. The carbon atoms were assumed to lie in one plane in an all-trans conformation. The position of the hydrogen atoms along the carbon chain has not been optimized, they were assumed to be bonded in the way indicated. Therefore, it is not certain that 13-17 all represent a local energy minimum. The most important resonance structure is depicted. It is found that a less extended conjugation of the π system leads to a higher energy. The linear system 13 has the lowest heat of formation (equal to 1). Structure 17 with all hydrogen atoms bonded to different carbon atoms is closely related to 1, since it could be formed from 1 in mass spectrometric experiments. Because 17 is so much higher in energy, the experimental heats of formation mentioned earlier are most likely related to the cyclic structure 1 and not to an open system. Extensive hydrogen migration would be necessary in the rearrangement from 17 to 13.

3.4 Electronic structures and orbital interaction diagrams

3.4.1 The phenyl cation

Many theoretical studies have been devoted to the

question whether the phenyl cation 1 has a singlet or a triplet ground state. MINDO/3⁶ and corrected STO-3G and 4-31G calculations⁶ predict a singlet ground state. The effect of substituents on the relative energies of the singlet and triplet states has also been studied²⁵. The difference charge densities for the singlet state from the MINDO/3 and STO-3G methods are given in Table 3.6.

Table 3.6

Difference charge densities from the MINDO/3 and STO-3G methods, respectively

	<u>1</u>	<u>5</u>	<u>6</u>	<u>7</u>
C ₁	0.376 0.300	0.084 -0.004	-0.063 -0.111	0.107 0.113
C ₂	-0.048 -0.046		0.296 0.107	0.060 -0.018
C ₃	0.099 -0.003		-0.125 -0.068	0.064 0.020
C ₄	-0.016 -0.022			
C ₆		0.070 0.119	0.188 0.236	0.147 0.009
H ₁		0.102 0.181	0.115 0.170	
H ₂	0.144 0.192		0.064 0.175	0.092 0.168
H ₃	0.078 0.147		0.112 0.151	0.093 0.157
H ₄	0.093 0.142			
H ₆				0.127 0.223

The phenyl cation is found to be a σ -type cation: the STO-3G method predicts 0.79 positive charge units to be concentrated in the C₁ p _{σ} orbital, while the charge in the π orbitals of C₁ to C₄ equals -0.21, 0.02, 0.06 and 0.06, respectively. The HOMO is a π -type MO, while the LUMO is located mainly at the C₁ p _{σ} orbital. The positive charge is stabilized by through-bond σ interaction, leading to delocalization mainly on the ortho hydrogen atoms. The electronic structure of 1 is discussed more extensively in ref. 6.

3.4.2 Stabilization of antiaromatic ring systems in pyramidal structures

Analysis of the STO-3G charge densities in 5 illustrates the stabilizing effect of the apical carbon atom on the antiaromatic cyclopentadienyl cation. The charge density in the π orbitals of the ring is reduced because of transfer of 0.35 electrons from C_6 . Simultaneously, 0.23 electrons are transferred from the σ framework of the ring towards C_6 . Concerning the charge transfer with respect to the apical atom, there is a π donation of 0.69 electrons from C_6 towards the ring, accompanied by a σ backdonation of 0.57 electrons. The positive charge is delocalized over C_6 and the hydrogen atoms. All MINDO/3 results are similar to those of the STO-3G calculations, except that the charge transfer effects of C_6 on the ring are predicted to be somewhat larger: 0.56 electrons π donation and 0.49 electrons σ backdonation.

The strong bonding interaction between C_6 and the ring is indicated also by the STO-3G overlap populations given in Table 3.7. The total overlap population of 0.359 between

Table 3.7
STO-3G overlap populations between the apical atom and the basal ring in 5

	Ring	π	σ	Total
C_6	π	0.379	0.020	0.399
	σ	0.054	-0.094	-0.040
Total		0.433	-0.074	0.359

C_6 and the ring may be compared with corresponding populations in the analogous nonclassical structures 2-4. In the carbenic species 4 and 5 the overlap populations are smaller than in the saturated systems 2 and 3, because of the

correlation with the distance between the apical atom and the ring (see Table 3.3).

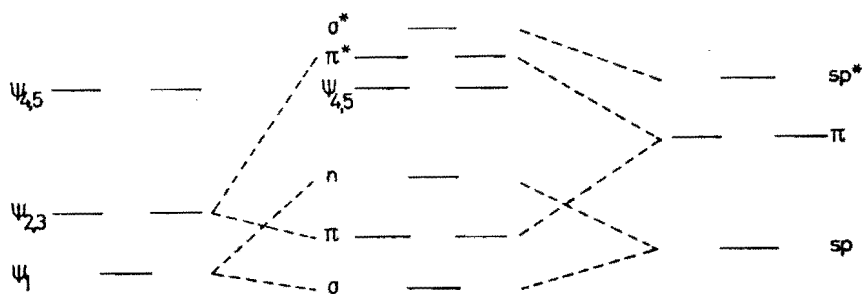
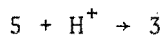


Figure 3.2 Orbital interaction diagram of 5

The relative stability of the pyramidal structure 5 can be illustrated by the orbital diagram in Figure 3.2 for the interaction between a hypothetical sp-hybridized apical carbon atom (at right) and the cyclopentadienyl cation ring (at left). The orbital energy levels for 5 in the Figure (in the middle) are based on STO-3G calculations, the MINDO/3 method predicts the σ^* MO to be lower in energy than the pair of π^* MO's. Similar diagrams have been given for the pyramidal systems 2³ and 3⁴. The two electrons in the degenerate orbitals $\psi_{2,3}$ of the antiaromatic ring are stabilized due to the interaction with both C_6 π orbitals. The HOMO is the nonbonding C_6 carbenic σ orbital. The STO-3G p_σ coefficient of 0.47 in 5 is somewhat smaller than in other singlet carbenes.

In its reactions, 5 should also exhibit its carbenic nature. The C_6 carbenic orbital could interact with an empty acceptor orbital of the appropriate symmetry, for instance a proton. The reaction



is exothermic by 69.1 kcal/mol (MINDO/3). Interaction of C_6 with a σ -electron donating species leads to a destabilizing four-electron interaction: linear correlation of a

carbene with an electron donor is forbidden. In spite of its positive charge of +0.12, the apical carbon atom behaves as a nucleophilic site.

The orbital diagrams for 2, 3 and 5 are similar to diagrams used in a discussion of the structure of C_{4v}^- symmetrical pentacoordinated transition-metal complexes²⁶. The orbitals of the organic pyramidal systems resemble the s, p and d orbitals of the metal atom, but the energy levels differ. Based on orbital diagrams, Hart²⁷ has argued that 3 should be more stable than 2 compared with the parent antiaromatic basal ring. Similarly, 5 is predicted to be more stable than 4. Ab initio calculations predict 4 to be the lowest C_5H_4 species on the energy surface⁵.

3.4.3 Interactions in system 6

The electronic structure of the bicyclic carbene 6 should be compared with that of the parent structure 21, discussed by Hehre²². He describes the interaction of the HOMO and LUMO π orbitals of the allyl cation system with the two degenerate Walsh-type HOMO's of the cyclopropane ring, see Figure 3.3. Both interactions should result in a

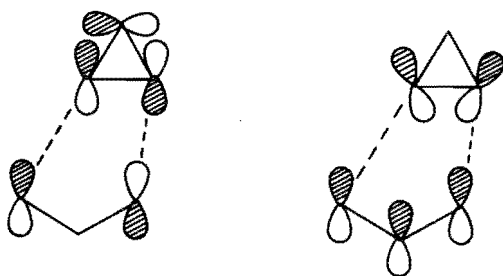


Figure 3.3 Interaction of the HOMO and LUMO π orbitals of the allyl cation with the degenerate pair of Walsh-type HOMO's of the cyclopropane ring in 6 and 21. At left HOMO-LUMO interaction (antisymmetric), at right HOMO-HOMO interaction (symmetric).

shortening of the C₁-C₅ bond. This qualitative analysis is confirmed by STO-3G calculations, which predict the C₁-C₅ distance in 21 (1.483 Å)²² to be shorter than the bond length in cyclopropane (1.502 Å)²⁸. However, the MINDO/3 bond length in 21 (1.547 Å) is larger than in cyclopropane (1.504 Å). In 6 the Walsh orbitals of the cyclopropane ring interact with the doubly occupied σ orbital on C₆. This should lead to a lowering of the occupied symmetric Walsh orbitals, while the antisymmetric orbitals are not influenced. This implies that the destabilizing interaction at right in Figure 3.3 should diminish, leading to a decrease of bonding electron density between C₁ and C₅ and a C₁-C₅ bond longer than in 21, see Table 3.4.

The calculations on 6 do not indicate any direct homoconjugational interaction between C₆ and the allyl π system, since the corresponding overlap populations are almost zero. Analysis of the HOMO shows that the carbenic orbital at C₆ is moved out of the plane of the cyclopropane ring only over an angle of 14° towards the allyl system. There is no indication for a "foiled-reaction" methylene in 6²⁹. The value of the dihedral angle φ should be in the same order of magnitude as in 21, albeit diminished because of the absence of hydrogen repulsion. The STO-3G method predicts a very small value of only 93°. Most of the positive charge is located at the terminal orbitals of the allyl π system (0.75 charge units) and 0.24 charge units are located at C₆ through σ interaction. Generally, 6 displays the same antiaromatic character in the cyclopentenyl cation ring as does the parent cation 21²².

3.5 Rearrangements on the energy surface

3.5.1 The concept of orbital isomerism

Apart from the study of local energy minima on the C₆H₅⁺ potential energy surface, we have also considered rearrangements between the various isomers. Some theoretical

aspects of allowed and forbidden rearrangements have been discussed by Dewar using the concept of orbital isomerism³⁰. A symmetry forbidden reaction is characterized by an orbital crossing between the HOMO and the LUMO. Any collection of isomeric species can be divided into sets in such a way that members of the same set can be converted without a HOMO-LUMO crossing; these species are termed homomers. The interconversion of species of two different sets (lumomers) always involves a HOMO-LUMO crossing and should be a forbidden reaction in the ground state. For MO calculations on these reactions, CI with the lowest doubly excited singlet state should be included. Generally, these reactions can take place only via an asymmetric reaction path, requiring a very high activation energy. The loss of symmetry during the reaction does not imply that a reaction between lumomers should become allowed. The HOMO-LUMO crossing in a forbidden reaction occurs regardless of the symmetry retained on the reaction path.

The $C_6H_5^+$ species can be divided into sets of homomers that have the same number of symmetric and antisymmetric occupied and virtual MO's with respect to the common symmetry element: the mirror plane in the C_s symmetry point group. The total number of symmetric valence shell MO's depends on the number of atoms lying in the mirror plane (for a compound C_xH_y with C_pH_q atoms in the mirror plane, this number is equal to $2x + p + \frac{1}{2}(y + q)$). For the C_{2v} -symmetrical species 1 and 11 there are two possible mirror planes. Table 3.8 presents the total number of symmetric and antisymmetric MO's for the systems 1 and 5-11. Compounds with a different total number of symmetric MO's cannot be transferred into each other under retention of the appropriate mirror plane. The first three rows of the Table present the sets of homomers with the same number of occupied symmetric MO's.

According to these predictions, 1 and 9 should be homomers. However, for the transformation from 9 to 1 a bond is being broken which is situated in the mirror plane.

Table 3.8

Total number of symmetric (S) and antisymmetric (A) valence shell MO's with respect to a mirror plane

	Occupied		Virtual		Total	
	S	A	S	A	S	A
<u>9</u> , <u>1</u> (mirror plane perpendicular to the ring)	8	6	9	6	17	12
<u>5</u> , <u>6</u> , <u>7</u>	9	5	8	7	17	12
<u>8</u> , <u>10</u>	10	4	7	8	17	12
<u>11</u> (mirror plane through the cyclopropene ring)	10	4	10	5	20	9
<u>11</u> (mirror plane through the cyclobutenium ring)	11	3	9	6	20	9
<u>1</u> (mirror plane through the ring)	11	3	12	3	23	6

Therefore, this mirror plane cannot be determining for the stereoselectivity of this reaction. The reaction Dewar benzene \rightarrow benzene is known to be forbidden and the same should be true for the reaction of 9 to 1.

The concerted rearrangement from 8 to 10 would imply the simultaneous breaking of the C₂-C₃ and C₅-C₆ bonds in 8 (see Figure 3.1). The reaction of the parent 3,3'-bicyclopropenyl leading to Dewar benzene was found to proceed in a diradical mechanism³¹, the concerted [2+2] cycloaddition to form prismane is a forbidden reaction. Therefore, one would expect the rearrangement from 8 to 10 also to be forbidden. However, these systems are found to be homomers with respect to the mirror plane which is determining for the stereoselectivity of the [2+2] cycloaddition reaction. We conclude that the concept of orbital isomerism presents a necessary but not sufficient condition which should be satisfied for a reaction to be allowed.

3.5.2 MINDO/3 calculations on reaction paths

We have not performed any calculations on the rearrangements 9 → 1 and 8 → 10. Preliminary MINDO/3 calculations on the reaction between 1 and 6, retaining C_s symmetry and using the dihedral angle ϕ in 6 as the reaction coordinate, resulted in conversion towards a doubly excited state, indicating orbital crossing. Extensive calculations were performed on interconversions between the homomers 5, 6 and 7. The activation energies found are presented in Figure 3.4. It should be noted that the heat

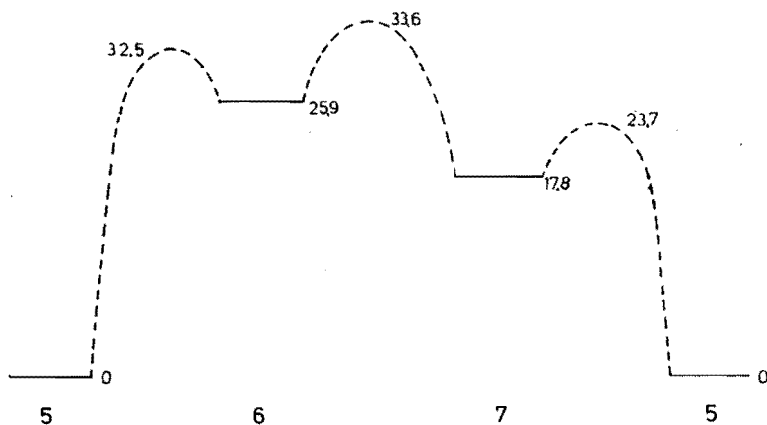


Figure 3.4 MINDO/3 relative energies for reactions between 5, 6 and 7

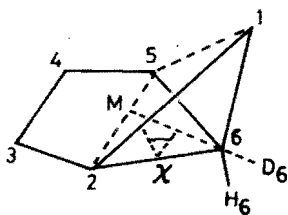
of formation of 6 could be in error by a few kcal/mol because of the incorrectly located minimum on a rather flat energy surface (STO-3G calculations predict 6 to be lower in energy than 7 after a geometry optimization).

For the calculations on the reaction between 5 and 6 the mirror plane was retained and the atoms C₁ to C₅ and H₃ were assumed to lie in one plane. The dihedral angle ϕ in 6 was taken as the reaction coordinate, varying from 142.5° in 6 to 49.3° in 5 in steps of 10°. All 9 remaining

geometry parameters have been optimized for each value of ϕ . The transition state was found for $\phi = 100^\circ$; it resembles the bicyclic system.

For the rearrangement between 5 and 7 the mirror plane was also maintained in the calculations and the atoms C_2 to C_5 and H_2 to H_5 (in 7) were assumed to lie in one plane. The angle $\psi = C_1-M-P$ in 7 (see Figure 3.1) was taken as the reaction coordinate, varying from 146.6° in 7 to 71.8° in 5 in steps of 10° . The angle H_6-C_6-M was assumed to vary linearly with ψ and all 8 remaining parameters were optimized. In the transition state ψ equals 115° . Of the 6 electrons in the three σ bonds to C_1 in 7, two electrons are incorporated in the carbenic orbital at C_6 in 5, while the other electrons support the bonding interaction between C_1 and the ring.

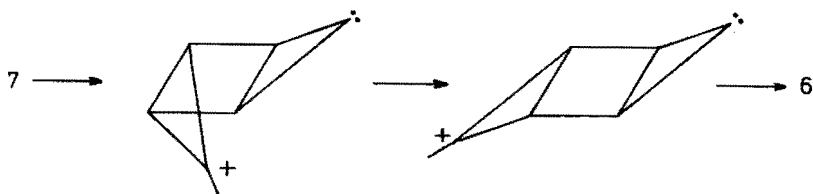
In the MINDO/3 calculations on the rearrangement from 7 to 6 the mirror plane has not been retained. The C_6 carbon atom of 7 enters the plane of C_2 to C_5 (and H_3 to H_5), while the C_1-C_5 bond is being broken simultaneously, finally yielding the carbenic σ electrons at C_6 in 6. The dihedral angle $\chi = C_1-C_2-C_6-C_5$ is taken as the reaction coordinate, varying from 57.4° in 7 to 143.5° in 6 in steps of 10° . The transition state with $\chi = 100^\circ$ can be depicted as follows:



where M is defined as the projection of C_6 on the C_2-C_5 axis. Five parameters have been optimized for each value of χ , viz. the distances C_2-M , C_6-M and C_1-C_6 and the angles $C_1-C_6-C_2$ and $C_6-M-C_2-C_3$. The following assumptions have been made: H_3 and H_4 are situated on the bisector, the angle $H_5-C_5-C_4$ is equal to the angle $H_4-C_4-C_5$, and the

angle $H_6-C_6-D_6$ has the constant value of 35.5° (just as in both 7 and 6; D_6 is a dummy atom in the plane (C_2, C_6, C_5), which is perpendicular to the plane (H_6, D_6, C_6)). The 8 remaining parameters (the distances C_2-C_3, C_3-C_4 and C_4-C_5 , the angles $C_4-C_3-C_2, C_5-C_4-C_3, H_2-C_2-C_3$ and $D_6-C_6-C_5$ and the dihedral angle $H_2-C_2-C_3-C_4$) were assumed to vary linearly with χ . The backward reaction of 6 to 7 could formally be depicted as an attack of the carbenic σ orbital at C_6 on the most electron-deficient site of the allyl cation at C_2 ; upon activation the methylene reaction is not "foiled" anymore.

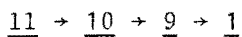
The rearrangement from 7 to 6 under retention of the mirror plane could proceed via 5. An alternative route retaining symmetry is feasible, in which the (C_6-H_6) fragment would move under the plane in which the atoms C_2 to C_5 are situated:



However, this mechanism is not very likely.

Since 6 is the highest energy species (at least on the MINDO/3 surface) within this set of homomers, rearrangement from 6 can proceed rather easily, requiring an activation energy of about 7 kcal/mol. The reaction to 5 could take place directly or via 7. Compound 5 is the most stable species and requires a much higher activation energy for rearrangement. Reactions of system 5 probably could be studied experimentally starting from benzvalene-type precursors or systems related to 6. A path via 5 would lead to complete scrambling of the five carbon atoms in the ring.

It should be noted that Weiss and Andrae³² have studied the possible reaction sequence



Experimentally they have accomplished the first step only. In this reaction the mirror plane is not retained. The second step is a conversion between lumomers and it has not been detected by the authors.

CHAPTER FOUR

ELECTROCYCLIC REACTIONS INFLUENCED BY A NEIGHBOURING π SYSTEM

4.1 The ring opening reaction of a carbenoid cyclopropyl ring system

The stereoselectivity of electrocyclic ring opening and ring closure reactions in hydrocarbon systems has been described by Woodward and Hoffmann¹, based on the principle of Conservation of Orbital Symmetry.

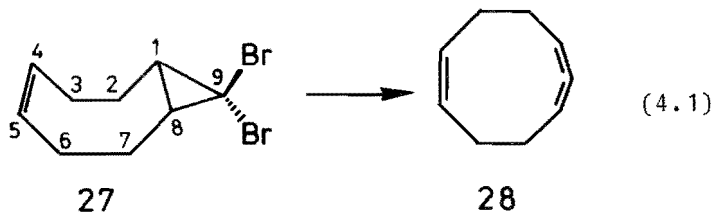
The reactions can occur either in a disrotatory or a conrotatory way, when the terminal carbon atoms rotate in the same direction or in opposite directions, respectively. The reaction is characterized by an element of symmetry present in the transition state: a twofold rotational axis for the conrotatory mode or a mirror plane for the disrotatory mode. The stereochemistry is determined from an orbital correlation diagram, indicating the symmetry of the MO's of the system with respect to the current symmetry element. In a concerted allowed reaction the occupied MO's of the reactant all correlate with occupied MO's of the product having the same symmetry. In a forbidden reaction an orbital crossing occurs between an occupied and a virtual MO having a different symmetry. Woodward and Hoffmann predict a $4n$ π -electron system to close thermally in the conrotatory way. Systems with $4n+2$ π electrons react in the disrotatory mode. For photochemical processes the stereoselectivity is reversed. These qualitative predictions have been extended by Longuet-Higgins, who considered the symmetries of the total electronic states of the system².

The selection rules have been borne out in many experiments.

Some studies have been devoted to the question how the stereoselectivity of these electrocyclic reactions could be influenced and eventually reversed:

- when the allowed mode is prohibited from steric reasons, the reaction could eventually occur either in a concerted (symmetrical) forbidden way³, or in a nonconcerted asymmetrical way via a biradical-like transition state.
- the influence of electron donating or accepting substituents introduced in the hydrocarbon chain has been analysed using a perturbational approach and a configuration interaction treatment⁴.
- the introduction of heteroatoms in the chain will affect the MO's and the stereoselectivity⁵.
- the relative positions of the orbital energy levels could change upon incorporation of the π system into a larger conjugated molecule.
- a symmetry forbidden reaction could become allowed after complexation with a transition metal compound which also causes a change in the MO energy levels⁶.
- other possibilities for the stabilization of forbidden transition states have been indicated⁷.

Recent experimental work⁸ has suggested that a disrotatory ring opening reaction occurs in the bicyclo [6.1.0] - nonene compound 27 leading to the allene 28.



Upon reaction of 27 with butyllithium in THF at -95°C the 9-lithio-9-bromo-substituted derivative is formed in the first step. Ionization at low temperatures leads to a lithium cation and a carbenoid cyclopropyl anion which could behave as a free carbanion



Opening of the carbenoid cyclopropyl ring leads to the allene 28. The presence of the double bond at the C₄-C₅ atoms was shown to be of crucial importance for the reaction to occur at very low temperatures⁸. The ring opening of the 4 π electron system in the cis-fused cyclopropyl anion ring would have to take place in the forbidden disrotatory mode and therefore should be precluded. The reaction (4.1) is suggested to occur via a bishomoaromatic transition state 29,



29

where the 4 π -electron system is extended by two more π electrons through the interaction with the neighbouring double bond⁸. The disrotatory reaction of a 6 π -electron system is allowed.

In the model for the reaction taking place via 29 three assumptions are essential:

- the cyclooctene ring has a boat conformation, so the distances C₁-C₄ and C₅-C₈ are only small.
- the C₄-C₅ π -electron system is oriented so as to give an appreciable interaction with C₁ and C₈.
- C_s symmetry is maintained throughout in the disrotatory ring opening reaction.

Bishomoaromatic interactions like in 29 are frequently

being encountered in organic species which constitute an energy minimum on a potential energy surface. Now a similar interaction is suggested for the first time to provide "anchimeric assistance" in a transition state.

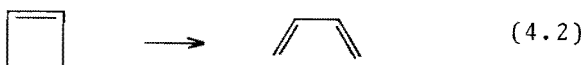
By these experimental findings we were led to investigate theoretically whether a neighbouring π system would be able to influence and eventually reverse the stereochemistry of an electrocyclic reaction in the way outlined above. The ring opening reaction of a carbenoid cyclopropyl system has never been the object of a theoretical analysis. MO calculations using the INDO method have been performed on the ring opening of cyclopropylidene to yield allene⁹. The reaction was found to proceed via a "mixed-mode" mechanism: the ring opening takes place in a disrotatory way in the initial stage, and evolves in the conrotatory way in the final stage of the reaction.

In an MO study on the transition state 29 of reaction (4.1) the following complications are to be taken into account:

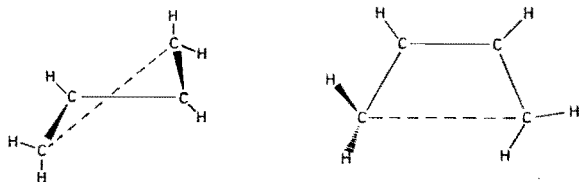
- a large computation time is required to perform even a single semiempirical SCF MO calculation for the $C_9H_{12}Br^-$ anion.
- the influence of the lithium cation near the C_9 atom might be important.
- the geometrical arrangement of the bromine substituent at C_9 is uncertain.
- in most current MO procedures the elements Br and Li cannot be handled.
- the C_4-C_5 π -electron system possibly cannot acquire the optimal conformation for the bishomoaromatic interaction.
- the boat conformation of the cyclooctene ring leads to an increase in the ring strain of the system.
- a large part of the molecule (the 4 methylene groups) is of no importance to the model.

Therefore, it was decided to study a much more simple model system. We have chosen the electrocyclic reaction of cyclobutene to give butadiene (4.2), which has been fre-

quently investigated using theoretical methods^{10,11}. The



thermal ring opening reaction of this 4π -electron system is predicted to proceed in the conrotatory mode from both qualitative theory¹ and quantitative studies. MINDO/3¹¹ calculations predict an energy difference of 16.6 kcal/mol between the transition states (TS) for the disrotatory (at right) and conrotatory mode (at left). The conrotatory



TS was found to have C_2 symmetry, but the disrotatory reaction proceeds via an asymmetric TS in which only one of the methylene groups has rotated.

4.2 Computational procedures

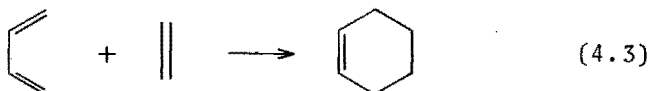
In this Chapter we describe an MO study of reaction (4.2) when influenced by an ethylene molecule in its vicinity. Two approaches have been used:

- a MINDO/3 study including geometry optimization of the potential energy surfaces of the C_4H_6 and C_6H_{10} systems with respect to the electrocyclic reaction.
- a perturbational treatment of the interactions between ethylene and the C_4H_6 system. Simple second order perturbation theory is applied based on results from INDO calculations without geometry optimization¹².

The MINDO/3 and INDO calculations were performed in the single determinant formalism. A forbidden reaction is characterized by a crossing between the highest occupied and lowest unoccupied MO's (HOMO-LUMO crossing) and by a simultaneous crossing of the two lowest single determinant

potential energy surfaces¹. This is accompanied by a sudden change in the total energy, the MO energy levels and the geometrical parameters. From the single determinant potential energy surface it is possible to decide if one is dealing with an allowed or a forbidden reaction.

A part of the C_6H_{10} potential energy surface has been studied intensively in the past, viz. the Diels-Alder reaction of ethylene with butadiene leading to cyclohexene (4.3). In contrast with ab initio studies, MINDO/3 calculations erroneously predict this reaction to proceed via an



asymmetrical TS (see Chapter 2). The $[3,3]$ sigmatropic reaction of 1,5-cyclohexadiene (Cope rearrangement) and the reaction between bicyclo[2.2.0]hexane and hexadiene have been studied using the MINDO/3 method¹³. Now we have investigated the system ($C_4H_6 + C_2H_4$).

The geometry of the C_6H_{10} model system is described in Figure 4.1. C_s symmetry was assumed to be maintained throughout for the disrotatory reaction (the x,z plane being the mirror plane) and C_2 symmetry was retained for the conrotatory mode (with the twofold axis in the x direction). In the Figure the disrotatory arrangement is depicted, the atoms C_1 to C_4 are situated in the x,y plane. Because of the assumed symmetry, the centre P of the ethylene molecule is always situated in the x,z plane. The orientation of the C_2H_4 fragment is being described by α , the rotational angle χ around the M-P axis ($\chi = 0^\circ$ for C_5-C_6 parallel to C_1-C_4) and the inclination angle ψ of the π orbitals towards the cyclobutene fragment ($\psi = 0^\circ$ for P-Q perpendicular to the (C_5,P,M) plane). β is the dihedral angle $C_1-C_2-C_3-C_4$ for the conrotatory mode and γ is the dihedral

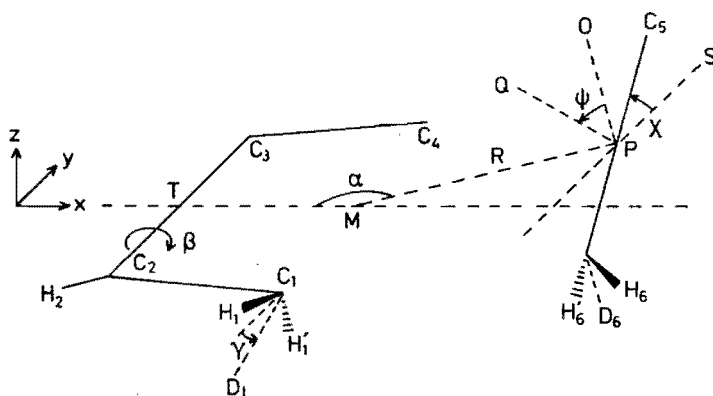


Figure 4.1 Geometry of the C_6H_{10} system

Explanation of the angles:

$$\alpha = \text{P-M-T}$$

$$\beta = \text{C}_1\text{-C}_2\text{-C}_3\text{-C}_4$$

$$\gamma = 180 - (\text{D}_1\text{-C}_1\text{-C}_2\text{-C}_3)$$

$$\chi = \text{S-P-C}_5$$

$$\psi = \text{O-P-Q}$$

M is the centre between C_1 and C_4 , P-S is parallel to $C_1\text{-C}_4$, P-M, P-O and P- C_5 are mutually perpendicular.

angle $(180 - (\text{D}_1\text{-C}_1\text{-C}_2\text{-C}_3))$. For a conrotatory reaction $\alpha = 180^\circ$ because of the C_2 symmetry. In the calculations the C-H distances were taken equal to 1.08 Å. H_2 and H_3 were situated on the bisector of the appropriate carbon skeleton angle and for the methylene groups local C_s symmetry was assumed.

From qualitative theories it can be predicted that a stabilizing interaction between two fragments or molecules can result from a combination of an occupied MO of one fragment and a virtual MO of the other fragment¹⁴. The HOMO's and LUMO's are most important because of the smaller orbital energy difference between them. When an element of symmetry is present in the system, the two combining MO's

should have the same symmetry with respect to this element.

Table 4.1 presents the symmetry of the most important orbitals of ethylene, butadiene and cyclobutene with

Table 4.1

Symmetry of the σ and π MO's in ethylene, butadiene and a partially opened cyclobutene ring with respect to the current symmetry element: S = symmetric, A = antisymmetric

Disrotatory mode (α irrelevant, C_S)

Butadiene		Cyclobutene		Ethylene			
ψ_4	A	π^*	A	$\chi = 0^\circ$		$\chi = 90^\circ$	
ψ_3	S	σ^*	A	(ψ irrelevant)		$\psi = 0^\circ$	$\psi = 90^\circ$
ψ_2	A	σ	S	π^*	A	A	π^* S
ψ_1	S	π	S	π	S	A	π S

Conrotatory mode ($\alpha = 180^\circ$, χ irrelevant, C_2)

Butadiene		Cyclobutene		Ethylene			
ψ_4	S	π^*	S	$\psi = 0^\circ$		$\psi = 90^\circ$	
ψ_3	A	σ^*	A	π^*	S	π^*	A
ψ_2	S	σ	S	π	A	π	S
ψ_1	A	π	A				

respect to the mirror plane and the rotational axis. ψ_1 to ψ_4 are the π -type MO's in butadiene. For cyclobutene, a partially opened ring has been taken, where the σ and σ^* MO's between C_1 and C_4 constitute the HOMO and LUMO, respectively (in the equilibrium structure the HOMO and the LUMO are the π -type orbitals). It is seen from the Table, that a conrotatory electrocyclic reaction in the C_4H_6 system is allowed because of the corresponding symmetry of the occupied MO's.

In Table 4.1 is given the symmetry of the π and π^* orbitals of ethylene in various orientations, described by the angles χ and ψ . With respect to the HOMO-LUMO inter-

actions between ethylene and the C_4H_6 system, it is seen that $\chi = 0^\circ$ leads to a stabilizing interaction with butadiene in C_s symmetry. This implies that the Diels-Alder reaction (4.3) proceeds in the suprafacial mode. When the ring opening reaction (4.2) proceeds in the conrotatory way, the largest stabilizing interaction arises when $\psi = 0^\circ$. However, these qualitative considerations are not sufficient to derive reliable predictions about the interactions in 29. We have performed a more quantitative investigation on the model described in Figure 4.1.

4.3 Comparison of the MINDO/3 potential energy surfaces for C_4H_6 and C_6H_{10}

4.3.1 The ring opening reaction of cyclobutene

Reaction (4.2) has been studied before by Dewar using the MINDO/3 method¹¹. He only reports a few geometry data for the transition state (TS), which is asymmetric for the forbidden disrotatory reaction. We have repeated the MINDO/3 calculations to obtain more insight into the C_4H_6 potential energy surface.

For the allowed conrotatory reaction the methylene rotation angle γ was found to be unsuitable as a reaction coordinate because it gave rise to large discontinuities on the reaction path. When γ increases from 0° (cyclobutene), the energy rises steadily until γ equals 90° in a seriously distorted cyclobutene system with $\beta = 42^\circ$. Starting from butadiene ($\gamma = 90^\circ$) the energy rises when γ decreases, leading to the but-2-en-1,4-diyl biradical. The energy falls suddenly between $\gamma = 20^\circ$ and 10° , when the ring is closed. A better choice for the reaction coordinate proved to be the distance parameter $r = (C_1-C_4)$ with simultaneous optimization of all other geometry parameters in C_2 symmetry¹⁵. A smooth reaction path is obtained leading over a transition state with $r = 2.06 \text{ \AA}$, in agreement with the reported results¹¹ obtained from minimization

of the scalar gradient of the energy. Table 4.2 presents the heats of formation and the values of β and γ found for the various points on the reaction path. The calculated

Table 4.2

Heats of formation and geometry parameters along the reaction path for the conrotatory ring opening reaction of cyclobutene

	r	ΔH_f	γ	β
Cyclobutene	1.543	35.9	0	0
	1.80	53.3	0.0	0.0
(see text)	1.90	64.5	0.0	0.0
	2.00	76.2	0.2	0.0
	2.04	80.8	0.5	0.5
TS	2.06	86.1	42.0	0.8
	2.08	85.9	50.6	36.3
	2.20	80.0	67.7	36.0
(see text)	2.40	65.5	77.7	31.1
	2.80	42.8	88.6	9.5
Butadiene	3.270	34.6	90	0

activation energy for the ring opening reaction (50.3 kcal/mol) is similar to the reported MINDO/3 value (49.0 kcal/mol)¹¹; an experimental value of 36.0 kcal/mol has been found¹¹. Two points on the reaction path with $r = 1.90$ and 2.40 \AA were selected for further investigations. Geometry data are given in Table 4.3. The parameters for the transition state have been taken from the literature¹¹ with a subsequent optimization of 2 (not reported) parameters for the methylene hydrogen atoms.

For the disrotatory reaction an asymmetrical transition state is predicted¹¹. However, this investigation now is aimed at the influence of a neighbouring ethylene moiety on the ring opening reaction, to see whether a concerted disrotatory mode could be invoked. Therefore, we have in-

Table 4.3

Geometry parameters for selected points on the reaction surface for the cyclobutene ring opening reaction

Conrotatory	Cyclobutene	r=1.9	TS	r=2.4	Butadiene
r	1.543	1.900	2.060	2.400	3.270
C ₁ -C ₂	1.511	1.486	1.390	1.336	1.333
C ₂ -C ₃	1.351	1.351	1.410	1.451	1.464
C ₁ -C ₂ -C ₃	93.6	100.6	101.6	108.8	132.6
β	0	0.2	26.0	29.6	0
D ₁ -C ₁ -C ₂	137.1	148.4	160.9	173.6	180
H ₁ -C ₁ -H ₁ '	105.2	109.1	107.5	106.8	110.5
γ	0	0.2	42.0	77.7	90

Disrotatory	A	C	TS	D	B
	γ=30°	RC=¼	RC=½	RC=¾	γ=50°
r	1.567	1.872	2.200	2.735	3.284
C ₁ -C ₂	1.508	1.439	1.385	1.323	1.340
C ₂ -C ₃	1.351	1.390	1.430	1.447	1.457
C ₁ -C ₂ -C ₃	94.1	99.6	106.1	119.1	133.0
D ₁ -C ₁ -C ₂	134.4	140.1	143.1	161.5	181.6
H ₁ -C ₁ -H ₁ '	99.6	107.4	107.6	109.0	110.5
γ	30	11.2	22.5	56.2	50

vestigated a hypothetical symmetrical reaction path. C_s symmetry was imposed throughout in these calculations. The dihedral angle γ taken as a reaction coordinate again leads to a discontinuous reaction path. When γ decreases from 90°, the butadiene is transformed into the open biradical and the energy rises steadily. The "reaction paths" are indicated in Figure 4.2. When γ increases from 0°, the energy falls suddenly between γ = 60° and 70°, when the ring is opened. Similar complications result when r is taken as the reaction coordinate. Starting from cyclobutene,

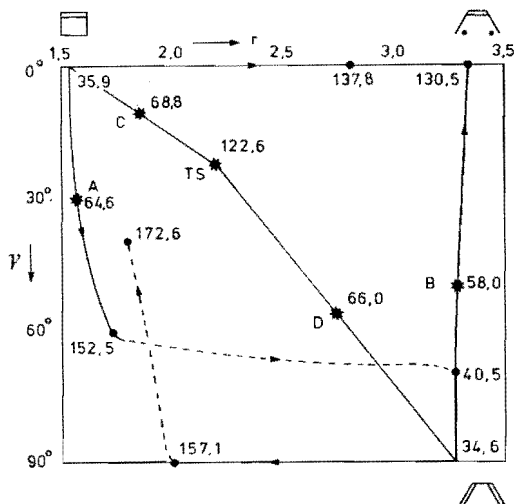


Figure 4.2 Reaction paths on the potential energy surface for the disrotatory reaction between cyclobutene and butadiene. Some energy values have been indicated in the Figure in kcal/mol.

the energy rises with increasing r while γ remains equal to 0° , finally yielding the but-2-en-1,4-diyl biradical again. When r decreases in butadiene, a rather high energy emerges and γ remains equal to 90° until $r = 2.0$ Å, when the methylene groups rotate instantly. The high energy value probably is related to the orbital crossing.

Two points in the initial and final stage of the disrotatory reaction, characterized by values of 30° and 50° for γ (taken as a reaction coordinate) and indicated as A and B in Figure 4.2, have been selected for further investigations. Because of the orbital crossing it was not possible to approximate a symmetrical transition state through geometry variations. Therefore, we have taken a geometry based on averaged parameters from the asymmetrical

transition state in the literature¹¹, which leads to an "activation energy" of 86.7 kcal/mol (the reported MINDO/3 value with respect to the asymmetrical TS is 55.6 kcal/mol¹¹). From interpolation of the geometrical parameters between the TS (where the reaction coordinate is assumed to be 1/2) and the initial and final states (followed by optimization of the H₁-C₁-H₁' bond angle), two more points C and D on the surface have been selected that could be characterized by a value of $\frac{1}{4}$ and $\frac{3}{4}$ for the hypothetical reaction coordinate RC. The geometries of these five selected points on the potential energy surface are given in Table 4.3. The heats of formation are indicated in Figure 4.2. Although these 5 points are only situated in the vicinity of the symmetrical reaction path, we can assume that the influence of the neighbouring ethylene group on the reaction path parallels the effect on these five selected points.

4.3.2 The C₆H₁₀ potential energy surface

For the calculations on the C₆H₁₀ system C_s and C₂ symmetry has been assumed for the disrotatory and conrotatory modes, respectively. For the distance R the values of 2.5, 3.0 and 3.5 Å have been selected and for the angle χ the values 0° and 90° were taken. The geometry parameters of the selected points on the C₄H₆ reaction paths given in Table 4.3, have been taken as the starting configurations. The first series of these calculations concerned those systems characterized by a value of $r = 1.9$ and 2.4 Å for the conrotatory mode and by a value of $\gamma = 30$ and 50° (A and B) for the disrotatory mode. For these points on the surface all geometrical parameters in the combined system have been optimized. It was found that the geometry of the C₄H₆ fragment deviates only little from the values given in Table 4.3. Therefore, in the second series of calculations on the other selected points all parameters in this fragment were fixed at their value in the Table, except

for the angle $H_1-C_1-H_1'$. The optimal value of ψ was found to be 90° for both $\chi = 0^\circ$ and $\chi = 90^\circ$ throughout the entire reaction path. This indicates that the most favourable orientation of the ethylene π orbitals is towards the C_4H_6 system. In all systems studied the geometry of the ethylene molecule is found to be rather similar: $C_5-C_6 = 1.321 \text{ \AA}$ and $H_5-C_5-H_5' = 111^\circ$. The average value of the angle $D_5-C_5-C_6$ equals 175° , which indicates that the methylene hydrogen atoms are slightly bent away leading to decreased repulsions and an increased interaction of the π orbitals with C_1 and C_4 . The combined C_6H_{10} system can be effectively described using only three parameters: R , α and χ (when $\psi = 90^\circ$).

For the conrotatory mode the angle α was set equal to 180° because of the C_2 symmetry. The change in α along the disrotatory reaction path is given in Table 4.4. Only the averaged values of α are given, because α is found to be almost independent of R (deviation $\pm 1^\circ$). When the butadiene π system is developing, α moves towards a value similar to the value of 119° found from ab initio calculations on the transition state of the Diels-Alder reaction (4.3)^{16,17}.

Table 4.4

The value of the parameter α for the disrotatory reaction in the C_6H_{10} system, averaged over three values of R

	$\chi=0^\circ$	$\chi=90^\circ$
Cyclobutene	180.0	180.0
$\gamma=30^\circ$ (A)	154.6	149.9
$RC=\frac{1}{4}$ (C)	172.2	170.1
TS	161.5	158.1
$RC=\frac{3}{4}$ (D)	129.7	132.6
$\gamma=50^\circ$ (B)	136.4	139.9
Butadiene	118.0	122.7

For all points studied on the C_6H_{10} potential energy surface it is found that the total heat of formation is higher than that of the two separated fragments. The MINDO/3 energy differences for $\chi = 0^\circ$ are given in Table 4.5.

Table 4.5

Energy differences between C_6H_{10} systems and the separated ($C_4H_6 + C_2H_4$) fragments for $\chi = 0^\circ$

Conrotatory	R=2.5	R=3.0	R=3.5
Cyclobutene	35.7	12.9	4.6
r=1.9	32.8	12.1	4.4
TS	32.9	12.3	4.5
r=2.4	35.3	13.7	5.0
Butadiene	36.6	13.5	

Disrotatory	R=2.5	R=3.0	R=3.5
Cyclobutene	36.8	13.5	5.0
$\gamma=30^\circ$ (A)	32.9	12.2	4.4
RC= $\frac{1}{4}$ (C)	32.3	11.8	4.3
TS	28.9	10.6	3.9
RC= $\frac{3}{4}$ (D)	19.8	8.6	3.4
$\gamma=50^\circ$ (B)	20.0	8.4	3.3
Butadiene	26.2	10.1	3.8

The heats of formation are lower for $\chi = 90^\circ$ by a small but constant amount of about 2.9, 1.1 and 0.3 kcal/mol for $R = 2.5, 3.0$ and 3.5 \AA , respectively. These data have been omitted from the Table.

The energy differences in Table 4.5 are seen to be dependent mainly on the value of R . The combination of the two fragments at a certain distance results in an almost uniform rise in energy over the entire reaction path. Because the distinct points selected are situated only in

the vicinity of a reaction path, we may conclude that the approach of the ethylene molecule leads to a constant rise in energy of the whole C_4H_6 potential energy surface, mainly depending on the separation R between the two fragments. The energy gap is only somewhat smaller for the developing butadiene system in the disrotatory mode. Even in the forbidden symmetrical transition state very close to the crossing point, the energy change does not differ significantly from that at other points on the surface. No significant differences are found between the energies for the disrotatory and conrotatory ring opening reactions. An optimal value of $\psi = 90^\circ$ does not correspond to the bishomoaromatic system depicted in 29.

The above conclusion is corroborated by a study of the orbital energy levels of the C_4H_6 fragment. In the initial stage of the ring opening reaction the σ and π MO's change their positions, and also the σ^* and π^* MO's are interchanged. In the disrotatory path an orbital crossing takes place in the transition state region. From the results on the C_6H_{10} system it is clear that the energy levels are only little influenced by the approaching ethylene molecule, no significant change occurs. The orientation of the ethylene molecule (as indicated by the angle χ) does not appear to have any effect, in spite of the qualitative analysis given in Table 4.1.

We conclude that our calculations do not support a bishomoaromatic transition state as in 29. The ring opening reaction (4.1) does not occur in a concerted disrotatory way. Most likely a "mixed-mode" (nonconcerted) mechanism can give a more appropriate description of the reaction. Free rotation of the terminal carbon atoms in 27 is hampered because of the presence of the cyclooctene ring. The conformation of this ring system is uncertain. No clear explanation can be given for the crucial influence of the C_4-C_5 double bond in 27 in order to invoke the cyclopropyl ring opening at very low temperatures. Even-

tually, conformation effects in the eight-membered ring might be important.

4.4 The perturbational approach

The perturbational calculations are based on the method given by Dewar to obtain the stabilization energy for the union of two π systems¹⁴. In our model the perturbation is represented by an increase in the resonance integrals between C_1 and C_6 and between C_4 and C_5 (see Figure 4.1). From Table 4.1 it can be concluded which combinations of MO's of both molecules do not give any contribution to the stabilization energy because they have a different symmetry.

INDO calculations have been performed on the separated fragments to yield the orbital energy levels and the eigenvectors which are required in the perturbational treatment. For cyclobutene a geometry was chosen with a partially broken C_1 - C_4 bond ($r = 2.1 \text{ \AA}$) and for the methylene rotation angles γ values of $\pm 30^\circ$ were imposed in the disrotatory and conrotatory modes. No geometry optimization was performed. The resonance integrals were obtained from INDO calculations on the combined system (without geometry optimization). For the orientation of the ethylene fragment the following parameter values have been selected:

- $\chi = 0^\circ$.
- $\alpha = 120^\circ$ and 180° .
- $R = 2.0$ and 2.4 \AA .
- $\psi = 0^\circ, 40^\circ$ and 85° .

The INDO energy results are of little value because of the lack of geometry optimization and because the method is not very reliable. The lowest energy values were found for $R = 2.4 \text{ \AA}$, for $\psi = 85^\circ$ and for $\alpha = 120^\circ$ in the disrotatory mode. The average (second order) stabilization energy found from the perturbational calculations is in the order of 33 kcal/mol, when R equals 2.4 \AA . The energy contributions resulting from the HOMO-LUMO combinations

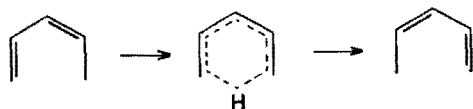
are found to be zero in the disrotatory mode from symmetry reasons (see Table 4.1) and are only very small in the conrotatory mode. The total stabilization energy is rather similar for the disrotatory and conrotatory arrangements. No clearcut predictions emerge about the selectivity of the ring opening reaction when influenced by an ethylene molecule. The application of simple perturbation theory apparently is insufficient for this type of investigations.

CHAPTER FIVE

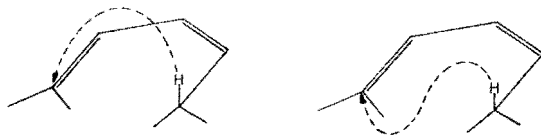
THE STEREOSELECTIVITY OF SIGMATROPIC REACTIONS

5.1 Qualitative theories

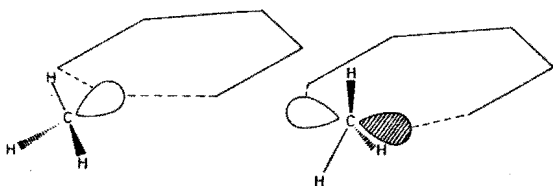
Sigmatropic reactions can be defined as intramolecular conversions occurring via migration of a σ bond flanked by one or two π -electron systems. When the two atoms, where the new σ bond is formed in the product, have the positions i and j in the conjugated carbon chains with respect to the originally bonded atoms in the reactant, the reaction is described as a sigmatropic $[i,j]$ shift. When i equals 1, only one π system is involved as in the $[1,5]$ hydrogen shift in pentadiene.



The π -electron system can be a linear chain or a cyclic conjugated system consisting of a j -membered ring. The reaction can occur in two stereoselective modes: in a suprafacial way, when the migrating group remains on the same side of the π system (at left), or in an antarafacial way, when the group moves to the other side of the π system (at right).



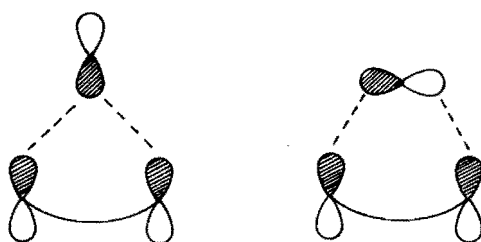
A sigmatropic shift of an sp^3 -hybridized group like CH_3 can occur with either retention (at left) or inversion (at right) of configuration of the tetragonal atom.



It is imperative that all these reactions occur in an uncatalysed concerted process in which the bond-breaking and bond-formation are taking place simultaneously, and not in a two-step pathway via an ionic or biradical intermediate. Several reviews on sigmatropic reactions have been published¹⁻⁴.

The transition state (TS) of a sigmatropic reaction can be characterized by the presence of an element of symmetry. For a suprafacial TS this is the mirror plane through the shifting group and the middle of the conjugated carbon chain, which is perpendicular to the chain (C_s symmetry). In an antarafacial TS a twofold rotational axis is present through the shifting group and the centre of the carbon system (C_2 symmetry).

Woodward and Hoffmann have worked out a theoretical analysis of stereoselectivity, based on the principle of Conservation of Orbital Symmetry¹. For sigmatropic reactions a perturbational argument is applied dealing with the Highest Occupied MO's (HOMO's) of the interacting fragments: the carbon chain and the shifting group. In the TS of a thermally allowed reaction the (singly occupied) HOMO's of both fragments should have the same symmetry with respect to the current symmetry element. The allowed mode for a reaction with inversion of stereochemistry (at right) is just opposite to the allowed mode for a reaction with retention of stereochemistry (at left) or for a hydrogen shift, because of the different symmetry of the important orbital of the shifting group which is involved in the bond-breaking and bond-formation process. In photochemical (excited state) reactions more MO's should be taken into



account because of the transition of electrons to virtual orbitals.

Woodward and Hoffmann predict the following selection rules¹: thermal allowed $[1,3]$ and $[1,7]$ shifts (with retention) occur in an antarafacial way, while $[1,5]$ shifts occur suprafacially. These predictions have been borne out in many experiments. In the allowed reactions the transition state can be considered to have (either Hückel or Möbius) aromatic character. By using the Orbital Phase Continuity Principle⁵ or equivalent treatments⁶ the MO's in the transition state can be related to those of the initial and final states of the reaction in which no symmetry element is present anymore: in an allowed reaction the occupied MO's of the reactant should gradually evolve to those of the product.

Berson and Salem⁷ have argued that in systems where the allowed reaction is prohibited by steric reasons, the reaction proceeds specifically in the "forbidden" mode. The stereoselectivity is now determined by the second highest occupied MO. This phenomenon has been termed Subjacent Orbital Control. For instance, a suprafacial $[1,3]$ methyl shift in 1-butene should normally occur with inversion of configuration: the methyl p orbital and the second allyl π orbital ψ_2 both are antisymmetric with respect to the mirror plane (see Figure 5.1). When this mode is precluded, for instance from steric reasons, the TS for a shift with retention of configuration can also be appreciably stabilized through the interaction of the p orbital

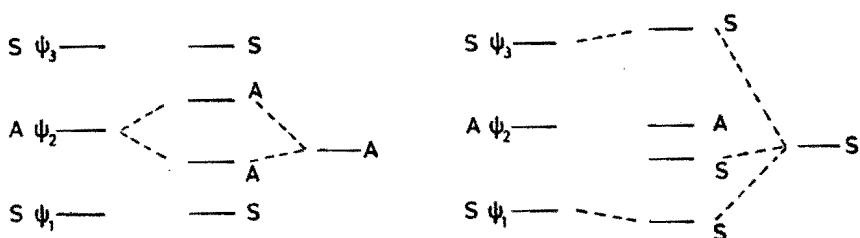


Figure 5.1 Molecular Orbital diagram for the transition state of a suprafacial $[1,3]$ CH_3 shift in 1-butene, occurring with inversion (at left) and retention (at right) of configuration. S and A denote symmetric and antisymmetric orbitals with respect to the mirror plane.

with the lowest allyl orbital ψ_1 , both being symmetric. The "forbidden" mode is favoured over a two-step diradical pathway. This model has been confirmed by experiments⁸.

Epiotis has analysed the effect of Configuration Interaction (CI) on pericyclic reactions⁹⁻¹¹. For sigma-tropic shifts the interactions between the two pairs of terminal atoms in the carbon chain and the shifting group are considered. The relative energies of the resulting electronic states depend on the donor or acceptor type character of both interacting fragments. When their electron donating or accepting abilities do not differ (as in hydrogen or methyl shifts in hydrocarbons), the stereoselectivity predicted is the same as in the Woodward-Hoffmann one-configuration model. When the properties of both fragments differ strongly (as in halogen shifts), the relative energies of the basis configurations are changed, the lowest state now corresponding to a transition of the unpaired electron from the donor to the acceptor fragment. A polar $[1,3]$ shift then should proceed with retention of stereochemistry, in contrast with the predictions of Woodward and Hoffmann. Thermal $[1,5]$ shifts should proceed with retention both in the polar and the nonpolar case.

Epiotis also discusses the concept of toposelectivity¹¹. For instance, in 5,5,5-trisubstituted-1,3-pentadiene three different groups can undergo a sigmatropic [1,5] shift. The electronic nature of the substituents and the sterical factors involved will determine which group migrates.

Apart from these electronic effects, other factors are involved when shifts occurring with retention or inversion of configuration are to be compared. A TS with retention leads to little repulsion between the shifting group and the terminal methylene hydrogen atoms. Moreover, an inversion mechanism requires a severe change in the hybridization of the shifting atom. From these non-electronic factors, a retention mechanism should be favoured.

5.2 Molecular Orbital calculations

5.2.1 A survey of literature results

So far, only a few Molecular Orbital calculations have been published on sigmatropic reactions in linear alkenes. Bingham and Dewar¹² have carried out MINDO/CI calculations (including CI with the lowest doubly excited state) on the [1,3] hydrogen shift in propene and the [1,5] H shift in 1,3-pentadiene. The geometries of the ground states and the symmetrical TS were optimized. The activation energies found are 49.2 kcal/mol for the suprafacial shift in propene and 28.3 and 37.0 kcal/mol for the suprafacial and antarafacial shift in pentadiene, respectively. Calculations using the MINDO/2 method without CI were reported to give erroneous results¹³.

The theory of Epiotis has been worked out in two papers^{14,15}. INDO and STO-4G ab initio calculations have been performed for the allyl⁺...F⁻ ion pair¹⁴. For the allyl cation a fixed geometry was taken and the fluorine atom was kept at a distance of 1.8 Å above the line connecting C₁ and C₃. No geometry optimization has been carried out and no activation energies have been reported. Subja-

cent Orbital Control was found to be unimportant for this polar [1,3] shift. This work was extended to methyl shifts (with retention of stereochemistry)¹⁵ assuming the CH₃ atoms lying in one plane at a distance of 2.03 Å above the carbon chain. It was found that stabilization through CI can be important in both polar and nonpolar suprafacial [1,3] shifts occurring with retention, not in shifts with inversion.

A similar geometry model has been used in INDO calculations with inclusion of CI on the suprafacial methyl and chlorine [1,3] shifts in propene¹⁶. A planar geometry was assumed for the allyl fragment. Three possible pathways were selected for the rearrangement of the substituent in a plane parallel to the allyl fragment. The position of the chlorine atom was varied in a plane at 1.8 Å above the allyl skeleton. The tetrahedral methyl group was situated at a distance of 1.4 or 1.5 Å above the plane with the singly occupied p lobe directed perpendicular to this plane. Calculations were performed on the C_s-symmetrical transition state halfway the reaction path and on the initial stage of the reaction, corresponding to a value of $\frac{1}{4}$ for a hypothetical reaction coordinate. It was found that the methyl [1,3] shift (with retention of configuration) could approximately be described by two successive [1,2] shifts via the allyl C₂ atom in a one-step process, while chlorine shows a direct [1,3] shift. No overall reaction energies were reported.

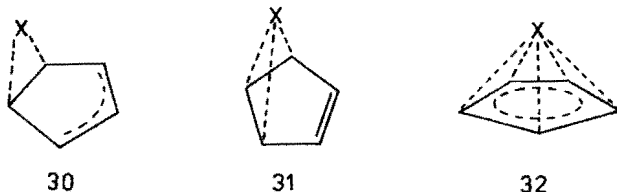
MO calculations on sigmatropic shifts in cyclic conjugated systems have been performed by Shchembelov and Ustynyuk¹⁷⁻²⁰. CNDO/2 and MINDO/2 calculations are reported on suprafacial hydrogen, methyl and silyl shifts with retention of configuration in cyclopentadiene. Three models were discussed, characterized by a two-coordinated shifting group X in the TS for a [1,5] shift (30), a three-coordinated group in the TS for a [1,3] shift (31) and by a C_{5v}-symmetrical TS with a five-coordinated group (32) which would lead to scrambling of X over all five ring positions.

Table 5.1

Activation energies calculated for suprafacial sigmatropic shifts in cyclic systems

System	Group	Shift	Method	ΔE_a	Ref.
Cyclopentadiene	H	[1,5]	CNDO/2	10.2	20
"	H	<u>31</u>	"	61.1	17
"	H	<u>32</u>	"	101.2	17
"	CH ₃	<u>30</u>	"	-7	18
"	SiH ₃	<u>30</u>	CNDO/2 ^a	6.0	20
"	SiH ₃	<u>32</u>	"	29.1	19
"	H	[1,5]	MINDO/2	18.4	18
"	CH ₃	[1,5]	"	27.6	18
"	H	[1,5]	CNDO/2	10.0	21
"	H	[1,5]	INDO	17.2	21
Cyclohexadiene	H	[1,5]	"	31	22
Cycloheptatriene	H	[1,5]	"	37	22
Cyclopentadiene	H	[1,5]	MINDO/3	28.3	28
Methylcyclopentadienes:					
<u>33</u> → <u>34</u>	H	[1,5]	"	28.3	27
<u>33</u> → <u>35</u>	H	[1,5]	"	29.8	27
<u>34</u> → <u>33</u>	H	[1,5]	"	28.1	27
<u>35</u> → <u>33</u>	H	[1,5]	"	21.3	27
<u>35</u> → <u>35</u>	CH ₃	[1,5]	"	46.4	27

^a Without inclusion of 3d orbitals



The geometry of these states has been optimized within the assumed C_s or C_{5v} symmetry point group. The resulting activation energies are given in Table 5.1. CNDO/2 calculations predict the transition state for a $[1,5]$ CH_3 shift (30) to be even 7 kcal/mol lower than the ground state¹⁸. The original calculations on the SiH_3 shift predict 32 to be the absolute energy minimum on the surface¹⁹. Apparently, this is caused by an unrealistically large contribution from the 3d orbitals on the silicium atom in the CNDO/2 method, favouring a highly coordinated situation. The calculations mentioned in the Table were carried out with neglect of 3d orbitals. The experimentally found activation energies for $[1,5]$ shifts in cyclopentadiene are 24, 43 and 14 kcal/mol for $X=H$, CH_3 and SiH_3 , respectively². For the H and SiH_3 shifts the complete reaction path has been calculated using the CNDO/2 method²⁰. The structures 31 and 32 do not correspond to a real transition state. No reaction path was found for an antarafacial $[1,5]$ shift.

Similar CNDO/2 and INDO calculations have been performed by de Dobbelaere et al.²¹⁻²⁴, who have studied the suprafacial $[1,5]$ hydrogen shift in several cyclic diene systems and the $[1,3]$ H shift in cyclopropene. Full geometry optimizations have been carried out for the transition states, assuming C_s symmetry. Results are given in Table 5.1. In the TS of the cyclohexadiene and cycloheptatriene



systems the carbon atoms not involved in the $[1,5]$ shift are bent away out of the plane of the conjugated pentadienyl system.

Su²⁵ has studied the fluxional behaviour of organometallic compounds where a substituted metal atom is displaced over the positions of a cyclopentadienyl ring by consecutive $[1,3]$ or $[1,5]$ shifts. Orbital and state correlation diagrams were given for the C_s symmetrical transition state using the π orbitals of the cyclopentadienyl ring (see Figure 5.2). The symmetric metal atom

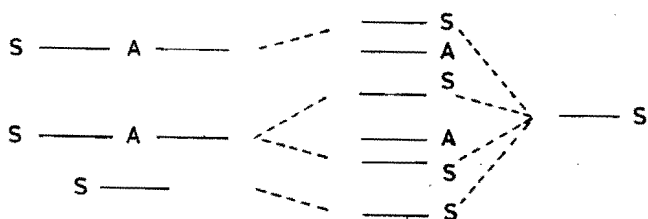


Figure 5.2 Molecular Orbital diagram for the transition state of a sigmatropic shift in cyclopentadiene. S and A denote symmetric and antisymmetric orbitals with respect to the mirror plane.

orbital (at right in the Figure) combines with one orbital of a pair of degenerate π MO's (at left), thereby lifting the degeneracy. The metal atom orbital contributes to the subjacent MO of the resulting system, not to the HOMO. However, in a polar sigmatropic shift the metal orbital could be lower in energy than the pair of degenerate π HOMO's. In this case state correlation diagrams predict an open shell singlet to be the lowest state for the separated fragments, while the lowest state of the resulting system is of the closed shell type, having a different symmetry. Therefore, polar sigmatropic shifts in cyclopentadiene systems are thermally forbidden as a consequence of the (near-)degeneracy of the π orbitals. Using a perturbational approach, it was further shown that a $[1,5]$ shift is

favoured over a [1,3] shift.

Su has also analysed which organometallic groups should give rise to shifts with retention and/or inversion of configuration²⁵. An inversion mechanism could arise when the shifting group in the TS is bicoordinated using either both lobes of a p-type orbital or both the originally bonded p orbital and an empty orbital by expansion of the valence shell. The fluxional behaviour of group IV organometallic groups such as silyl has been extensively reviewed²⁶. No details of the reaction mechanisms were reported.

De Dobbelaere^{23,24} has confirmed the orbital correlation diagrams of Su²⁵ by applying semiempirical calculations. The approach using the π orbitals of a cyclic conjugated ring system seems justified, because the hydrogen atoms, which are linked to the terminal atoms of the conjugated carbon chain in the TS of cyclopropene and cyclopentadiene, are bent out of the plane of the carbon system only over an angle of 5° and 7°, respectively. So the near-degeneracy of the π HOMO's is almost left intact. Even when the (homo-conjugational) overlap between the terminal atoms decreases, the hydrogen orbital still contributes to the subjacent MO. In the TS of the [1,5] H shift in cycloheptatriene with zero overlap between the terminal atoms, the near-degeneracy is lifted sufficiently to yield the π orbitals of a truly open pentadienyl system.

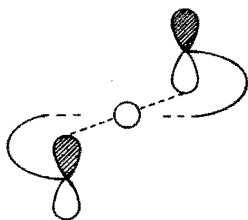
Recently, preliminary MINDO/3 calculations have been reported on [1,5] shifts in cyclopentadiene and the 1-, 2- and 5-methyl derivatives 33, 34 and 35, respectively²⁷⁻²⁸. No geometrical details were given. For the hydrogen and methyl shifts in cyclopentadiene an activation energy of 28.3 and 46.4 kcal/mol was found, respectively. These data are in very good agreement with the experimental values of 24 and 43 kcal/mol. Results are presented in Table 5.1. MINDO/3 calculations have also been performed for the hydrogen shifts in the $C_7H_8^+$ cycloheptatriene molecular cation²⁹. The reported activation energies are 54.9 kcal/mol for the [1,5] shift and only 13.8 kcal/mol for the

[1,2]shift over a planar ring system.

Finally, it should be noted that a classical approach using the Principle of Least Motion gives correct predictions for the stereoselectivity of sigmatropic reactions³⁰.

5.2.2 Model systems for sigmatropic reactions

In all the qualitative models discussed so far and also in some quantitative studies¹⁴⁻¹⁶ only the π orbitals of the alkene system are being taken into account. Usually the interaction between only one orbital of the shifting group with these π orbitals is being studied to predict the stereoselectivity of the reactions. Some crude geometrical assumptions are being made about suprafacial and antarafacial transition states or about retention and inversion of configuration. No serious attention was given to the question how the shifting group is bound to the terminal atoms in the TS. The geometrical arrangement at the terminal carbon atoms has not been considered. With one (ill-documented) exception¹², only a rather vague idea has been expressed on the possible occurrence of antarafacial shifts in linear systems. Usually a Möbius-type arrangement of the carbon chain is suggested.



For sigmatropic shifts in linear systems no extensive theoretical studies have been performed. A few quantitative studies have been reported on shifts in cyclic systems, but some of the results are questionable^{17,18}. The theoretical work reported so far is not in line with the wealth of experimental data available.

In this study we have undertaken a systematic quantitative investigation of sigmatropic reactions in order to obtain a consistent picture for $[1,j]$ shifts in both linear and cyclic systems. MO calculations have been performed for the shifts of several substituent groups in a series of hydrocarbon systems. The results are used to test the adequacy of the simplified qualitative models that have been given to explain the stereoselectivity of these reactions. It was also investigated if reliable quantitative predictions could be obtained from semiempirical and ab initio methods.

The following reactions have been studied:

- hydrogen, methyl and fluorine shifts in linear conjugated systems: $[1,3]$ shifts in 3-substituted propene, $[1,5]$ shifts in 5-substituted (Z)-1,3-pentadiene and $[1,7]$ shifts in 7-substituted (Z,Z)-1,3,5-heptatriene. Both suprafacial and antarafacial reactions have been studied, and methyl shifts occurring both with retention and inversion of configuration on the shifting methyl carbon atom have been taken into account.
- hydrogen, methyl and silyl $[1,5]$ shifts in 5-substituted cyclopentadiene and 1,3-cyclohexadiene, occurring in a suprafacial way with retention of configuration.

No effort was made to study the problem of toposelectivity directly by determining the migratory aptitude of two geminal substituents in one model system. By our choice of the transition state we have implicitly chosen the substituent which is the shifting group. A much more elaborate study of the potential energy surface would be necessary if one wants to determine explicitly which one of two possible reactions is favoured. Similarly, no direct comparison has been made between $[1,j]$ and $[1,j+2]$ shifts within the same model, because this would also lead to serious complications.

In this study only simplified model systems have been considered. For all reactions the ground states and transition states of the molecules have been studied using the

MINDO/3 method including a (usually complete) geometry optimization within the appropriate symmetry point group. For a few smaller systems STO-3G and 4-31G ab initio calculations have also been performed.

Unless indicated otherwise, the following general assumptions have been made in the geometry optimization studies:

- for a suprafacial transition state C_s symmetry was assumed and for an antarafacial TS C_2 symmetry. No attention was paid to asymmetrical reaction paths for forbidden reactions.
- local C_{2v} symmetry was assumed for sp-hybridized -CH- groups and for CH_2 groups in ground state molecules or in an sp^3 hybridization.
- local C_s symmetry was assumed for CH_2 groups in the transition states of the alkene systems.
- C-H bond lengths were set equal to 1.10 Å (1.08 Å in ab initio calculations). This assumption was based on the results from geometry optimizations reported in the literature³¹.

It is expected that all the assumptions concerning the geometry of the hydrogen atoms only have a small effect on the total heats of formation of the molecules studied.

5.3 Sigmatropic shifts in linear compounds

5.3.1 Ground states of the alkene systems

For the MINDO/3 calculations on the ground states of linear alkenes substituted with a group X=H, CH_3 or F we have taken the planar all-cis conformation of the carbon chain which can be assumed to form the initial conformation for the sigmatropic reaction. The C-X bond was assumed perpendicular on the plane of the carbon chain to avoid repulsion effects from the terminal vinyl group. This conformation is intermediate between the syn and gauche rotational isomers. For systems with X=H and for 1-butene the syn conformation was assumed to be the starting point

for the reaction, because of the diminished repulsion between the terminal atoms. It should be stressed that the lowest energy all-trans conformation was not selected to represent the ground state of the alkenes in these reactions. All parameters with respect to the carbon skeleton have been optimized, except for 4 parameters in heptatriene (taken from pentadiene) and 5 parameters in the substituted heptatrienes (taken from the parent heptatriene).

The C-C distances in the carbon chain have values of about 1.350 Å for double bonds, 1.330 Å for terminal vinyl bonds and 1.460 Å for C(sp²)-C(sp²) single bonds. The values for the C(sp²)-CH₂X bond lengths are 1.480, 1.465 and 1.500 Å for X=H, F and CH₃, respectively, while the C-X bond lengths are 1.517 Å for X=CH₃ and 1.383 Å for X=F. A value of 111.3° is found for the F-C-C angle. For the vinyl methylene group the H-C-C angle was always found to be very close to 124°, the other sp² hydrogen atoms are situated near the appropriate bisector. All these data are in good agreement with MINDO/3 results in the literature^{31, 32}.

As expected, the only notable deviation from standard data is seen in the carbon skeleton angles as a direct consequence of the assumed planar all-cis conformations. The angle of 131.9° in propene (3.0° larger than the reported MINDO/3 value³¹) increases to 136.8° in 1-butene upon introduction of the syn methyl group. The average angle in the pentadiene systems equals 135.3° and in the heptatriene molecules the average value is 137.0° for the two outer angles and 142.5° for the three inner angles. The heptatriene angles are too large as a result of the geometry assumptions. It is found that the angles in 1,3-hexadiene with the methyl group in the syn conformation are about 5° larger than in the perpendicular arrangement, leading to a rise in energy of 7.1 kcal/mol. Similarly, the heat of formation of syn-1-butene is 5.6 kcal/mol larger than the reported MINDO/3 value for the anti-isomer³¹.

These features are caused by the increased nonbonded repulsions in the planar all-cis models. However, the discrepancies are small compared to the activation energies found for the sigmatropic reactions, as will be seen below. One could argue that the carbon skeleton angles in heptatriene could be reduced by allowing deviations from planarity in the carbon chain. This would certainly result in lower heats of formation; however, this extension of the model has not been considered.

5.3.2 Transition state geometries

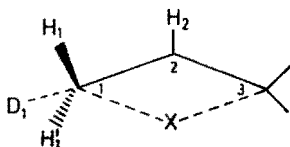
The most important MINDO/3 geometry parameters for the transition states are given in Tables 5.2-5.4, together with the numbering system of the atoms. D_1 is a dummy atom on the bisector of the $H_1-C_1-H_1^1$ angle. Geometry optimization was complete (including the methyl groups) within the C_s or C_2 symmetry. In the Tables and text, S and A denote suprafacial and antarafacial shifts, R and I indicate retention and inversion of configuration, respectively.

At this point some remarks should be made first. In this Chapter we refer to the geometry optimization of a transition state: the geometry is varied until a state with minimal energy has been found. This minimum can be found because we have implicitly applied some symmetry constraint, such as the C_s or C_2 symmetry, for the system under study. The TS is the energy minimum within the C_s or C_2 subspace of the total $(3N-6)$ -dimensional potential energy surface for a molecule consisting of N nuclei. On the total surface the TS is a saddlepoint between two valleys leading to two energy minima. Sometimes we will refer to the TS as a minimum, without explicitly mentioning the symmetry constraint.

Furthermore, in this study another type of saddlepoint is encountered. For instance, the antarafacial TS for the hydrogen shift in pentadiene was found to be planar, being

Table 5.2

MINDO/3 geometry of transition states for sigmatropic [1,3] shifts of a group X in propene, where X=H, CH₃, F



	H		CH ₃ , S ^a		F	
	S	A	R	I	S	A ^b
C ₁ -C ₃	2.561	2.128	1.689	2.324	2.323	2.224
C ₁ -C ₂	1.409	1.403	1.473	1.452	1.411	1.408
X-C ₁	1.714	1.376	1.715	1.657	1.464	1.493
C ₁ -C ₂ -C ₃	130.8	98.6	70.0	106.4	110.8	104.4
C ₁ -X-C ₃	96.7	101.2	77.9	89.0	105.0	96.4
X-C ₃ -C ₁ -C ₂	78.7	180	173.1	160.0	129.3	180
D ₁ -C ₁ -C ₂	172.4	158.9	143.5	143.2	155.7	163.2
D ₁ -C ₁ -C ₂ -C ₃	91.4	149.3	177.9	159.0	135.3	180.0
α ^c	-3.6	0	-27.9	43.0	30.9	0

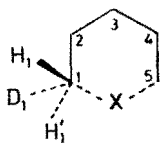
^a See text

^b Stationary point, see text

^c H₂ out of plane bending angle, see text

Table 5.3

MINDO/3 geometry of transition states for sigmatropic [1,5] shifts of a group X in 1,3-pentadiene, where X=H, CH₃, F

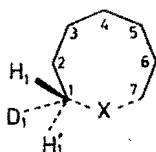


	H		CH ₃ ,S		CH ₃ ,A		F	
	S	A ^a	R	I ^a	R	I	S	A
C ₁ -C ₅	2.525	2.618	2.462	2.896	2.716	2.843	2.758	2.686
C ₁ -C ₂	1.413	1.452	1.437	1.466	1.456	1.458	1.415	1.408
C ₂ -C ₃	1.402	1.397	1.398	1.398	1.393	1.399	1.400	1.404
C ₁ -C ₂ -C ₃	121.4	123.8	121.5	124.5	122.6	123.4	121.5	123.2
C ₂ -C ₃ -C ₄	119.6	120.1	118.6	126.6	123.8	122.8	127.0	119.0
C ₁ -C ₂ -C ₃ -C ₄	15.0	0	9.2	0	8.0	16.9	6.5	27.2
X-C ₁	1.365	1.354	1.701	1.628	1.605	1.639	1.452	1.459
C ₁ -X-C ₅	135.4	150.5	92.7	125.7	115.6	120.3	145.1	164.6
D ₁ -C ₁ -C ₂	147.0	123.6	132.2	134.9	130.6	128.3	158.0	151.3
D ₁ -C ₁ -C ₂ -C ₃	138.6	180	133.7	180	162.8	146.1	145.7	123.8
X-C ₅ -C ₁ -C ₂	101.2	-	128.4	180	-	-	172.9	-

^a Stationary point, see text

Table 5.4

MINDO/3 geometry of transition states for sigmatropic [1,7] shifts of a group X in 1,3,5-heptatriene, where X=H, CH₃, F



	H		CH ₃ ,S		CH ₃ ,A		F	
	^a S	A	R	I	R	^b I	S	A
C ₁ -C ₂	1.432	1.409	1.459	1.451	1.438	1.460	1.400	1.406
C ₂ -C ₃	1.382	1.397	1.382	1.385	1.391	1.379	1.398	1.397
C ₃ -C ₄	1.406	1.403	1.406	1.408	1.404	1.409	1.399	1.405
C ₁ -C ₂ -C ₃	134.1	130.4	132.0	132.8	130.8	136.5	134.2	130.6
C ₂ -C ₃ -C ₄	136.2	132.7	137.4	137.0	132.4	139.4	134.1	135.3
C ₃ -C ₄ -C ₅	132.6	132.1	133.6	137.2	128.7	137.2	131.9	131.4
C ₁ -C ₂ -C ₃ -C ₄	0	13.5	11.2	15.6	13.6	0	31.0	13.6
C ₂ -C ₃ -C ₄ -C ₅	0	11.8	11.6	13.4	14.0	0	16.6	13.8
X-C ₁	1.250	1.329	1.611	1.649	1.682	1.618	1.451	1.450
C ₁ -X-C ₇	184.4	158.3	110.8	124.6	110.6	151.9	144.6	163.3
D ₁ -C ₁ -C ₂	145.3	145.3	128.1	123.6	126.9	129.5	146.7	152.7
D ₁ -C ₁ -C ₂ -C ₃	180	113.5	125.0	127.4	92.4	180	116.8	119.8
X-C ₇ -C ₁ -C ₂	0	-	116.6	122.2	-	-	90.5	-

^a Stationary point, see text

^b See text

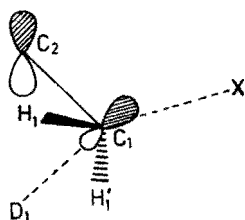
higher in energy than the suprafacial TS with a $C_1-C_2-C_3-C_4$ dihedral angle of 15° . For the A system C_2 symmetry was assumed. The planar system (with C_{2v} symmetry) is an energy minimum only within the C_{2v} and C_2 subspaces. But when we pass from the C_{2v} subspace to the (larger) C_s subspace (for the suprafacial system), the energy decreases. This means that the C_{2v} state is another type of stationary point on the potential energy surface. It is possible to detect stationary points on the potential energy surface by minimizing the gradient of the total energy. From the number of negative eigenvalues obtained on diagonalizing the force constants matrix in the stationary point one can determine if one is dealing with an energy minimum (no negative eigenvalues), a transition state (only one negative eigenvalue) or another type of stationary point (more than one negative eigenvalue)³³. This type of calculational techniques has not been employed in this study. The C_{2v} states discussed above will be further referred to as a "stationary point" on the surface, not to be confused with a real transition state for a sigmatropic shift.

A full geometry search of the potential energy surface of pentadiene without any restrictions leads to a stationary point for the hydrogen A shift. A similar situation is found for the methyl S I shift in pentadiene and the hydrogen S shift in heptatriene. The geometries have been included in the Tables for comparison. The important consequences will be discussed below. We have also calculated the C_{2v} symmetrical states for all systems, the data are omitted from the Tables.

For the transition states of the hydrogen and methyl shifts in pentadiene and heptatriene, it is found that the C-C distances all have values typical for unsaturated systems.

The C_1-C_2 distance is somewhat larger because of the vicinity of the group X. The C_2-C_3 and C_3-C_4 distances in the heptatriene systems are almost equal indicating complete delocalization of the π electrons. The heptatriene

dihedral angles are all found to be rather similar, except for a planar TS found for the methyl A I shift (vide infra). The angle $D_1-C_1-C_2$ can vary between 128° (sp^3 hybridization on C_1) and 180° (complete sp^2 hybridization). For the hydro-



gen shifts an intermediate value of about 146° is found, while for a methyl shift the CH_2 group is almost fully sp^3 hybridized. The dihedral angle $D_1-C_1-C_2-C_3$ gives an indication for the extent of π -orbital conjugation between C_1 and C_2 , its value varies between 90° for maximal overlap and 180° for zero overlap and complete sp^3 hybridization on C_1 . It is found that for the predicted allowed transition states there exists much more π -orbital conjugation than for the forbidden TS. For the methyl S shift in heptatriene this dihedral angle has a value of 126° for both R and I, because the developing orbital on C_1 is directed towards the methyl carbon atom above the plane (C_1, C_2, C_6, C_7). The $X-C_1$ distance is somewhat larger than a normal bonding distance: 1.35 \AA for $X=H$ and 1.64 \AA for $X=CH_3$. The MINDO/CI method predicts the $H-C_1$ distance in pentadiene to be 1.297 and 1.267 \AA for the S and A TS, respectively¹². For methyl I shifts the CH_3 group is situated much closer to the carbon chain as compared to R states, leading to a larger overlap of its p orbital with the terminal atoms. Simultaneously the distance between the terminal atoms is found to be larger, resulting in decreased nonbonded repulsions. For methyl R shifts the p orbital is directed towards the middle between the terminal atoms.

The hydrogen A shift in propene can be characterized

by the small $C_1-C_2-C_3$ angle of only 99° . The methylene groups are situated in a position so as to give a rather large overlap of the C_1 valence orbital with the shifting hydrogen. Of course a genuine Möbius-type arrangement cannot be reached in a propene system from steric reasons. In the TS for the hydrogen S shift the H atom is situated above the three-carbon plane having an overlap with C_2 as well. This is reminiscent of the model used by Epiotis^{14,15}. In the suprafacial TS in propene the H_2 out of plane bending angle α has also been optimized: α is positive when H_2 is on the same side of the plane as the shifting group X. For the H S shift H_2 is situated slightly below the plane: $\alpha = -3.6^\circ$. It should be noted that the inclusion of this parameter in the geometry optimization is highly important. If α is assumed to be zero the energy minimum found has a heat of formation of 25 kcal/mol above the TS, even though the difference in α is very small. The C_3H_5 fragment is almost planar. The H- C_1 distance of 1.714 Å is notably larger than the value of 1.593 Å found from the MINDO/CI method¹².

For the CH_3 shifts in propene no TS with a reasonably adequate geometry is found. With inversion of configuration the A state leads over a planar stationary point to the S minimum. In this minimum, however, α is found to be 43° , while the C_1-X-C_3 angle is only 89° . Similarly, the methyl R shift leads to a minimum resembling a homocyclopropane system with a $C_1-C_2-C_3$ angle of only 70° . We conclude that no transition state can be found, because the system collapses to some four-membered puckered ring system which probably is an energy minimum only within the applied symmetry constraints. The geometries found are included in Table 5.2 for comparison. This complication was not encountered in earlier studies because of the crude geometry models that have been used¹⁴⁻¹⁶.

Most geometry parameters for the fluorine shift transition states have values similar to those found for the H and CH_3 shifts. The average F- C_1 distance equals 1.455 Å, somewhat larger than the normal MINDO/3 bond length of 1.383 Å³².

The angle $D_1-C_1-C_2$ in the fluorine systems is notably larger than in the hydrocarbon systems, the average value is 153° . The TS for the H and F shifts in heptatriene are almost equal. In the pentadiene S TS the $F-C_5-C_1-C_2$ dihedral angle has a large value of 173° . In the propene system the equivalent dihedral angle equals 129° , notably differing from the values of 90° assumed by Epiotis^{14,15} or 106° found in INDO calculations¹⁶. However, in the heptatriene TS the value is 90° . In the fluorine S TS in propene the carbon skeleton angle is rather small and α equals 31° . The A shift leads to a stationary point, not a TS.

5.3.3 Ab initio calculations

Some sigmatropic reactions have been studied using the STO-3G and 4-31G ab initio methods. The ground state of propene has also been calculated by Radom et al.³⁴. The C-H distances found have values of 1.081, 1.085 and 1.088 Å, very close to the value of 1.08 Å assumed throughout this work. For 3-fluoropropene these propene parameters³⁴ have been taken with a C-F distance of 1.36 Å. This structure is in very good agreement with the experimental data for the syn isomer³⁵. The perpendicular arrangement has been estimated to be 2.2 kcal/mol higher in energy than the syn minimum from ab initio calculations³⁶. An STO-3G geometry optimization was carried out for the S and A transition states of the hydrogen and fluorine [1,3] shifts in propene by successive optimization of the geometry parameters (8 for a suprafacial TS and 6 for an antarafacial TS). The resulting geometries are given in Table 5.5. The STO-3G parameters have been used as input to perform one single 4-31G calculation. For the C-F distance in 3-fluoropropene the 4-31G optimum value of 1.412 Å for CH_3F was taken³⁷. We have also carried out one single STO-3G calculation on the S and A TS for the [1,5] hydrogen shift in pentadiene, using the MINDO/3 geometries. The suprafacial TS is found to be 98.9 kcal/mol lower in energy than the

Table 5.5

STO-3G geometries for transition states of sigmatropic [1,3] shifts of a group X in propene, where X=H, F

	H		F	
	S	A	S	A
C ₁ -C ₃	2.549	2.187	2.122	2.165
C ₁ -C ₂	1.421	1.418	1.397	1.468
X-C ₁	1.738	1.393	1.674	1.510
C ₁ -C ₂ -C ₃	127.6	100.9	98.9	95.0
C ₁ -X-C ₃	94.3	103.4	78.7	91.6
X-C ₃ -C ₁ -C ₂	72.8	180	143.8	180
D ₁ -C ₁ -C ₂	169.1	147.7	159.5	158.6
D ₁ -C ₁ -C ₂ -C ₃	90.9	135.0	145.2	180 ^a
α ^b	-5.0	0	31.5	0
H ₁ -C ₁ -D ₁	59.5	55.2	53.6 ^a	53.2

^aValue taken from the MINDO/3 geometry

^bH₂ out of plane bending angle

stationary point. More extensive ab initio calculations have not been performed because of the amount of computer time necessary.

The STO-3G geometry of the hydrogen S TS in propene is found to be strikingly similar to the MINDO/3 result. The same resemblance is seen for the A TS, where only the D₁ angles have slightly different values. The fluorine A shift is assumed to proceed via a stationary point as was found with MINDO/3. The geometries from both methods are in fairly good agreement. Only for the fluorine S TS some notable discrepancies are seen. STO-3G calculations predict a large F-C₁ distance of 1.674 Å and a dihedral angle F-C₃-C₁-C₂ of 143.8°. The overall correspondence for geometry parameters between the STO-3G and MINDO/3 methods is

rather satisfying for X=H, but less agreement is found for X=F.

5.3.4 Activation energies

The heats of formation calculated from the MINDO/3 method for the ground states (GS) and TS for the sigmatropic reactions are calculated in Table 5.6. Values not

Table 5.6

MINDO/3 heats of formation for sigmatropic [1,j] shifts of the group X=H, CH₃, F

	H	F	CH ₃ ,R	CH ₃ ,I
Propene [1,3]	GS	7.3	-40.1	6.6
	TS S	97.5	-59.7	(100.9) (112.4)
	TS A	83.4	(- 5.8)	- -
Pentadiene [1,5]	GS	22.6	-25.2	19.6
	TS S	70.7	-12.6	102.9 (123.3)
	TS A	(105.0)	-51.6	123.8 115.5
Heptatriene [1,7]	GS	43.0	- 5.0	40.4
	TS S	(101.9)	-38.4	130.2 129.1
	TS A	68.5	-15.3	117.1 129.0

Values between parentheses do not correspond to a real transition state, see text.

corresponding to a genuine TS are given between parentheses. From the geometry and energy data we conclude that some of the transition states are only very shallow minima on the potential energy surface. For the methyl A R shift in pentadiene, some dihedral angles in the TS differ substantially from those in the planar stationary point, but the

heat of formation found is only 0.5 kcal/mol lower. In the TS for the fluorine S shift in pentadiene both the F atom and the C_3-H_3 fragment deviate only little from the plane of the remaining carbon atoms. This probably also is only a shallow minimum. For the CH_3 I shift in heptatriene we find equal energies for the S and A TS, the difference being only 0.06 kcal/mol, but the geometries differ considerably because the A TS is planar, while the S system is bent in a boat-type conformation. Since the antarafacial TS is the lower energy state, it cannot be considered to be a "stationary point". Apparently, in the C_s subspace there is a shallow maximum between the planar C_{2v} geometry and the suprafacial TS, which is a local energy minimum.

From the data in Table 5.6 and from the ab initio results the activation energies for the sigmatropic shifts are obtained. Results are collected in Table 5.7 for those systems for which a real transition state has been found.

Table 5.7
Activation energies for sigmatropic $[1,j]$ shifts

MINDO/3

	H		F		CH_3,R		CH_3,I	
	S	A	S	A	S	A	S	A
Propene $[1,3]$	90.2	76.1	-19.6	-	-	-	-	-
Pentadiene $[1,5]$	48.1	-	12.6	-26.4	93.3	104.2	-	95.9
Heptatriene $[1,7]$	-	25.6	-33.4	-10.3	89.8	76.7	88.7	88.6

Ab initio

Propene $[1,3]$

	H			F		
	S	A	$\Delta(S-A)$	S	A	$\Delta(A-S)$
STO-3G	159.0	134.8	24.2	112.9	129.2	16.3
4-31G	120.1	112.4	7.7	94.6	138.6	44.0

The selectivity of the reactions can be seen from the difference in activation energies for a reaction occurring in the allowed and forbidden modes predicted from qualitative theories. In Table 5.8 the MINDO/3 energy differences are given between the transition states for the suprafacial and antarafacial modes, and between the TS of a methyl shift occurring with retention and inversion of configuration. STO-3G energy differences are included in Table 5.7.

Table 5.8

Differences in MINDO/3 activation energies between forbidden and allowed sigmatropic shifts

Suprafacial and antarafacial shifts

	H	F	CH ₃	
			R	I
Propene [1,3]	14.1	-	-	-
Pentadiene [1,5]	-	-38.9	10.9	-
Heptatriene [1,7]	-	-23.0	13.1	-0.1

Methyl shifts with retention and inversion of configuration

	S	A
Pentadiene [1,5]	-	8.3
Heptatriene [1,7]	1.1	11.9

From Table 5.7 it is concluded that MINDO/3 calculations generally predict high activation energies for hydrogen and methyl shifts. [1,3] H shifts in propene are not reported to occur². It has been found experimentally that the activation energy for the [1,3] H shift in 2-butene should be higher than 63 kcal/mol, which is the activation energy for the observed cis-trans isomerization³. The MINDO/3 value of 90.2 kcal/mol thus may constitute an

overestimate of maximally 27 kcal/mol. It also is 41.0 kcal/mol higher than the result reported from MINDO/CI calculations^{1,2}. The same method predicts the activation energy for the hydrogen S shift in pentadiene to be 19.8 kcal/mol lower than the MINDO/3 result. From the sparse results reported from MINDO/CI it is not clear whether the A TS is a real transition state (as stated by the authors) or a stationary point (if the geometry would be planar), since insufficient geometry data are available. The MINDO/CI heat of formation for this antarafacial TS is 45.6 kcal/mol lower than the MINDO/3 result^{1,2}. Experimentally an activation energy of 35.4 kcal/mol is found for the hydrogen S shift in pentadiene², while values of 31-36 kcal/mol are reported for shifts in other open diene systems^{2,4}. The MINDO/3 result apparently is about 13 kcal/mol too high. A low activation energy of 26 kcal/mol is found for the antarafacial [1,7] H shift in heptatriene, in agreement with experimental values ranging from 15 to 26 kcal/mol².

Resulting activation energies for methyl shifts are all higher than 75 kcal/mol. Alkyl shifts in pentadiene and heptatriene systems are not reported to occur^{2,3,8}; either fragmentation reactions or the much faster hydrogen shifts are found to be favoured. This is in accordance with the high activation energies calculated, which are of the same order as the normal carbon-carbon bond energies of 80-85 kcal/mol^{3,6}. It should be noted that the geometry optimization always leads to a bonding transition state. No indication of a dissociative process has been obtained. The high heats of formation found from MINDO/3 could probably be related to the rather small interatomic distances between C₁ and the shifting group as predicted from this method.

For the fluorine shifts the MINDO/3 method remarkably predicts many transition states to have a lower energy than the corresponding ground states. Clearly the parameter set for fluorine in the MINDO/3 program is insufficient. In the set of molecules used to derive these para-

meters some alkenes have been included with the F atom(s) substituted in α position, not in β position³². In another study it has been mentioned that fluorine has the propensity to be bicoordinated in MINDO/3 calculations³⁹. This is in full agreement with our findings, which predict the transition states with bicoordinated fluorine to be more favourable than the ground states. However, MINDO/3 results even more intriguingly predict the three "forbidden" transition states to be much lower than the "allowed" modes, the A shift in propene leading to a stationary point. This result will be discussed below.

The predicted activation energies for the hydrogen shifts in propene from both ab initio methods are much higher than the MINDO/3 values. Since no experimental data are available (vide supra), we cannot say which of the three methods gives more reliable results. For the fluorine shifts also very high activation energies have been found from the ab initio methods. It should be noted that the selectivity predictions from the semiempirical and ab initio methods are in good agreement, the differences in activation energy all being of the same order. The ab initio methods also predict the fluorine [1,3] shift to occur in the suprafacial mode.

For the hydrogen and methyl shifts the MINDO/3 method always correctly predicts the allowed modes to have the lower activation energies as compared to the forbidden modes. Those systems for which a stationary point has been found (the A [1,5] H shift in pentadiene, the methyl S I shift in pentadiene and the S [1,7] H shift in heptatriene) are all predicted to correspond to a forbidden reaction. The shallow energy minimum found for the methyl A R shift in pentadiene also corresponds to a forbidden mode. The methyl shifts in propene are not considered here, since the calculations lead to structures which cannot represent a genuine TS for a sigmatropic shift, as has been noted before.

For those H or CH₃ shifts where two real transition

states can be compared, we see that the MINDO/3 energy differences determining the selectivity in Table 5.8 all fall in a remarkably narrow range of 8-14 kcal/mol. All stationary points found are at least 8 kcal/mol higher in energy than the corresponding TS of the allowed reactions. Experimentally a lower limit of 8 kcal/mol has been found for the difference between the S and A hydrogen shifts in pentadiene⁴⁰. The only anomaly in Table 5.8 arises from the methyl S I shift in heptatriene. From the small energy differences found with respect to this system no predictions can be made about the stereochemistry. A clear explanation is not available; maybe the geometry optimization on the MINDO/3 potential energy surface did not lead to the correct energy minimum (see discussion before). Although the absolute activation energies found from MINDO/3 are rather high, the method is quite successful in the predictions on stereoselectivity. This might be due to the cancelling of similar errors in the comparison of two systems that have some resemblance to each other. In both transition states that are to be compared the X-C₁ distance might be too small, leading to a high heat of formation. We think that the selectivity predictions are highly significant and that this method is to a certain extent a useful tool for the study of sigmatropic reactions in linear systems. Similar considerations can be made with respect to the ab initio methods. Good correspondence with the semiempirical results was obtained.

5.3.5 Electronic configurations

In Table 5.9 the difference charge densities are given for the shifting group in the transition state. Values for the stationary points are included for comparison. It is clear that for the allowed modes of the hydrogen and methyl shifts the difference charge density on X always is more negative than for the forbidden modes. Because of the concerted nature of the allowed reactions two partial bonds

Table 5.9

Difference charge densities on the shifting group X in sigmatropic shifts, and total orbital occupancies in the fluorine $2p_y$ orbital. Values between parentheses do not correspond to a real transition state.

MINDO/3

		Propene	Pentadiene	Heptatriene
H	S	0.218	-0.008	(-0.059)
	A	-0.028	(0.141)	0.000
CH ₃ ,R	S	-	-0.008	0.251
	A	-	0.280	0.001
CH ₃ ,I	S	-	(0.326)	0.079
	A	-	0.058	0.291
F	S	-0.308	-0.336	-0.259
	A	(-0.378)	-0.254	-0.353
F,2p _y				
	S	1.406	1.571	1.397
	A	(1.574)	1.412	1.689

Propene , ab initio

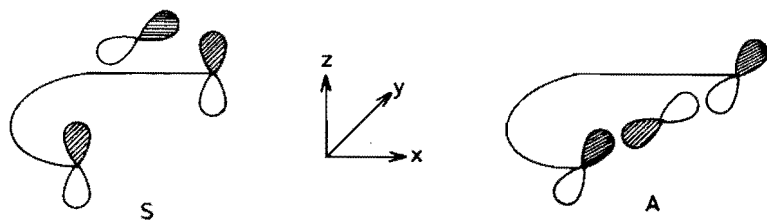
	H		F		
	S	A	GS	TS,S	TS,A
STO-3G	0.217	0.100	-0.154	-0.143	(-0.047)
4-31G	0.336	0.182	-0.455	-0.467	(-0.448)

are connecting the shifting group X: one bond being broken and the other bond being formed. In the allowed reactions these bonds will have more bonding character than in the forbidden modes, where the bonds should be more anti-bonding. This could probably result in a higher electron density on X in the allowed modes.

De Dobbelaere has discussed the concept of aromaticity

for the TS of sigmatropic shifts in cyclic systems²⁴. The aromaticity model predicts the allowed TS in cyclopentadiene to have 6π electrons in a cyclic conjugated system and a positively charged group X, while a forbidden mode would lead to 4π electrons in the ring and negative charge on X. From calculations on hydrogen shifts in cyclopropene and cycloheptatriene negative charges on the shifting group were found²⁴. From our results on linear systems it is clear that here the allowed reactions are not related to an aromatic transition state. The distances between the terminal carbon atoms are larger than 2.3 \AA , so the corresponding overlap integrals are almost zero. In all the allowed transition states the group X is more negatively charged than in the forbidden modes. So the aromaticity model does not apply to sigmatropic reactions in linear alkene systems.

In Table 5.9 are also included the MINDO/3 orbital occupancies for the $2p_y$ orbital of the shifting fluorine atom in the TS. Both lobes of this orbital are directed towards the π lobes of the terminal carbon atoms as indicated below. The $2p_y$ orbital is antisymmetric with respect



to the mirror plane and the twofold rotational axis of the transition states. The $2p_y$ orbital has a large overlap with each of the terminal atoms. The charge in this orbital clearly parallels the total charge on fluorine. The orbital occupancy of the fluorine $2s$ orbital is about 1.98, while the $2p_x$ and $2p_z$ orbitals each contain about 1.9 electrons. Apparently, the $2p_y$ orbital is the singly occupied HOMO which determines the behaviour of a shifting fluorine atom, while the $2s$, $2p_x$ and $2p_z$ orbitals together can be regarded

to constitute the lone pairs. The overlap of the π lobe of the terminal carbon atoms with the $2p_y$ orbital is much larger than with the $2p_{x,z}$ MO, which is directed towards the centre between the terminal atoms, and which is lying in the x,z plane. The shift of a fluorine orbital proceeds similar to that of a methyl group with inversion of configuration. The stereochemistry of a fluorine shift is just opposite to that of a hydrogen shift.

This mechanism occasionally has been suggested in the literature^{16,25,41,42}, but only a few experiments on halogen shifts are reported². Epiotis assumed the $2p_y$ orbital to contain a fluorine lone pair leading to additional stabilization of the allyl system¹⁴. In his model, the $2p_z$ orbital might be favoured as the crucial orbital for the rearrangement because of the crude geometry assumptions made. From the MINDO/3 results it is clear that a polar [1,3] sigmatropic shift can occur with inversion. This conclusion is in contrast with the work of Epiotis^{9-11,14}. Although the polarities of fluorine and allyl are different, there is no indication for a retention mechanism stabilized through CI. More extended calculations including CI would be necessary for a more definite conclusion.

From the MINDO/3 calculations it is shown unambiguously that all fluorine sigmatropic shifts proceed with "inversion of configuration". Activation energies calculated from MINDO/3 and the STO-3G and 4-31G ab initio methods clearly lead to this conclusion, which is fully supported by the resulting charge densities in the $2p_y$ orbital. Of course for fluorine one cannot really speak of "inversion of configuration". Because of its spherical symmetry the fluorine atom can always obtain the most favourable electronic configuration in the transition state, which leads to the $2p_y$ orbital being involved in the sigmatropic reaction, because it has the largest overlap with the terminal carbon atoms. This conclusion, based on electronic factors, can be extended to all atoms where a $2p$ orbital is involved, i.e. all atoms except hydrogen. Entirely consistent with

this view, the suprafacial [1,3] shifts of alkyl⁸ and silyl³⁸ groups are reported to occur with inversion.

Experimentally, it might be impossible to distinguish between the "retention" and "inversion" modes for a fluorine shift. For every model compound where a shift under "retention" could be proposed, the "inversion" mechanism should always be considered as a serious alternative. When sufficient experimental data on activation energies for fluorine shifts in a large series of molecules should be available, it might be possible to derive a definite conclusion about the reaction mechanism. From a practical point of view it is not really important which mechanism does apply for fluorine.

It should be pointed out that in the calculations on methyl shifts the reaction mechanism was imposed by choosing the geometry of the CH₃ group within a certain symmetry point group, thereby making it possible to calculate the activation energy for both reactions. A similar procedure is impossible for fluorine, because always the most favourable electronic configuration is obtained. When a shifting carbon atom is substituted with other groups than hydrogen, for instance methyl or phenyl, the inversion mechanism should become more difficult with the increasing bulkiness of the shifting group. Moreover, the larger change in hybridization also disfavours an inversion mechanism.

From the difference charge densities on the shifting fluorine atom in Table 5.9 no conclusions can be derived about the selectivity of the reactions. Charge differences between the S and A transition states are only small. The charges are similar to the values in the ground state (the MINDO/3 method predicts a charge of -0.347 for F in the ground states). Both ab initio methods predict widely differing charges for fluorine, probably as a result of the quality of the basis set.

We have also studied the nature of the various Molecular Orbitals in the transition state, especially the

HOMO's which are determining the selectivity. From the MINDO/3 MO's we see that the allowed transition states can be characterized by the orbital pattern given in Figure 5.3.

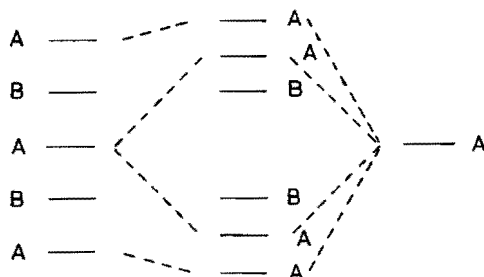


Figure 5.3 Molecular Orbital diagram for the transition state of allowed sigmatropic shifts in linear alkenes. A and B denote two types of symmetry with respect to the current symmetry element.

At left in the diagram the set of π orbitals of the alkene system is indicated, with alternating symmetry with respect to the crucial symmetry element. At right the determining orbital of the shifting group is indicated, which in an allowed mode has the same symmetry as the (singly occupied) HOMO of the π system. The combination of these two MO's produces two new MO's which in all systems are found to be the second highest occupied and the second lowest virtual MO of the resulting system, as has been noted before by Su²⁵ and de Dobbelaere²³. This situation is found to exist in all the allowed modes for both hydrogen, methyl and fluorine shifts in propene, pentadiene and heptatriene. For fluorine the crucial orbital is seen to be the $2p_y$ orbital, again indicating the "inversion of configuration". For the forbidden modes it is not possible to present a general orbital pattern. In a planar geometry the in-plane orbitals of the shifting group do not combine with the π orbitals, while the terminal carbon atoms do not participate in the π conjugation.

In the S hydrogen shift in propene, the hydrogen orbital combines with the lowest allyl π orbital. This feature has been described as Subjacent Orbital Control⁷, see Figure 5.1. For the corresponding fluorine shift the orbital diagram is given in Figure 5.4. It is clear that the combination of ψ_2 with $2p_y$ results in a larger splitting of the orbital energy levels than the splitting from the $(\psi_1+2p_{x,z})$ combination. A larger splitting is (among other

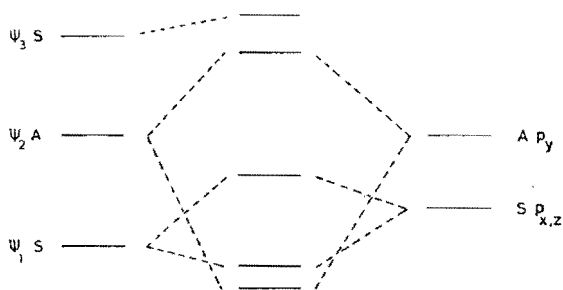


Figure 5.4 Molecular Orbital diagram for the transition state of the suprafacial $[1,3]$ fluorine shift in propene. S and A denote symmetric and antisymmetric orbitals with respect to the mirror plane.

factors) caused by a more effective overlap between the two combining orbitals. The diagram again shows that the fluorine $2p_y$ orbital can be more effective in determining the stereochemistry of the reactions. All MO diagrams from the ab initio calculations are in good correspondence with the MINDO/3 results.

From INDO calculations¹⁶ on the suprafacial $[1,3]$ chlorine shift in propene an MO diagram was derived similar to Figure 5.4. In this case the interactions were studied between a chloride anion and an allyl cation. No difference charge densities were given for the individual chlorine AO's.

These results should be considered with caution, since no geometry optimization has been carried out.

To investigate the relative importance of configuration interaction in the transition states we have tried to perform MINDO/3 calculations including CI with the lowest doubly excited singlet state⁴³ on the TS for hydrogen and methyl shifts in propene and pentadiene. However, this led to convergence difficulties; it was not possible to carry out a geometry optimization. It has been reported that MINDO3/CI calculations can lead to convergence difficulties⁴³.

5.4 Sigmatropic [1,5] shifts in cyclic systems

5.4.1 Geometries

MINDO/3 calculations have been performed on suprafacial hydrogen, methyl and silyl [1,5] shifts in cyclopentadiene and 1,3-cyclohexadiene. No study has been made of possible transition states for [1,3] shifts (31) or for scrambling over the cyclopentadienyl ring (32). These structures have been found from CNDO/2 calculations not to correspond to a real transition state for X=H or SiH₃²⁰. For the CH₃ and SiH₃ shifts only the reactions have been studied with retention of configuration, since this is the allowed mode for a suprafacial [1,5] shift. Reactions with inversion should proceed in the antarafacial way and this clearly is impossible for steric reasons. The possibility of a CH₃ or SiH₃ shift proceeding with inversion in these systems has never been discussed in the literature¹⁷⁻²⁰.

C_{2v} symmetry was assumed for the ground state of the cyclopentadiene ring system and C₂ symmetry for the cyclohexadiene ring. The CH₃ and SiH₃ groups with a tetrahedral geometry were placed in a conformation with minimal non-bonded repulsions both in the GS and the TS. All the C-H and Si-H distances were taken as 1.090 and 1.465 (optimum value in SiH₄) Å, respectively. The geometry parameters of

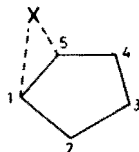
the ground state systems are not reported here. The parameters for the methyl and silyl systems were almost identical to those in the hydrogen-substituted analogues. For the X-C₁ distances values of 1.518 and 1.880 Å were found for X=CH₃ and SiH₃, respectively. In 5-silylcyclopentadiene the ring puckering angle was also optimized in C_s symmetry, but the ring was found to be almost planar (1.8° puckered). MINDO/3 results for the geometry of cyclopentadiene are in better agreement with experiment⁴⁴ than reported CNDO/2¹⁷ or MINDO/2¹⁸ calculations. Good agreement was also obtained with MINDO/2 results for X=CH₃¹⁸ and with experimental data for X=SiH₃⁴⁵. The cyclohexadiene ring was found to have a planar geometry, in sharp contrast with the experimental⁴⁶ value of 18° for the torsional angle between the double bonds. Imposing this value of 18° led to an energy rise of 2.9 kcal/mol and to small changes in the geometry parameters. The MINDO/3 potential energy surface appears to be rather flat in the vicinity of the energy minimum. The MINDO/3 method usually predicts too flat geometries for six-membered ring systems (see Chapter 2).

For the transition states C_s symmetry was assumed, in line with the suprafacial mode of the reactions. Resulting geometries are collected in Tables 5.10 and 5.11, together with results from other methods. In the cyclopentadiene systems the ring is found to be almost planar. The C₁-C₅ distance equals 1.50 Å, the C₁-C₂ and C₂-C₃ distances are similar indicating π-electron delocalization. For the C₃ atom a planar configuration was assumed. H₂ is moved slightly out of the carbon plane in the direction of X. The H₁ out of plane bending is larger when X=CH₃ or SiH₃ because of the increased repulsion. The X-C₁ distances are about 0.21 Å larger than the normal bond lengths and they are similar to the values in the TS of the linear systems (see Table 5.3). Good agreement is found with results from CNDO/2¹⁷ and MINDO/2¹⁸ calculations, the MINDO/3 interatomic distances being somewhat larger.

In the transition states of the cyclohexadiene systems

Table 5.10

Geometry of transition states for sigmatropic [1,5] shifts of the group X in cyclopentadiene, where X=H, CH₃, SiH₃



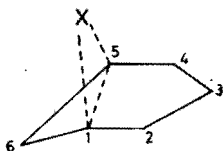
Reference	H			CH ₃		SiH ₃
	b	17	18	b	18	b
Method	MINDO/3	CNDO/2	MINDO/2	MINDO/3	MINDO/2	MINDO/3
C ₁ -C ₅	1.497	1.470	1.471	1.484	1.456	1.508
C ₁ -C ₂	1.425	1.404	1.386	1.440	1.385	1.440
C ₂ -C ₃	1.413	1.393	1.401	1.412	1.418	1.413
C ₅ -C ₁ -C ₂	106.8	107.1	106.6	106.7	106.7	106.0
C ₁ -C ₂ -C ₃	108.0	107.5	108.4	108.2	108.3	109.4
C ₂ -C ₃ -C ₄	110.3	110.9	a	110.0	a	109.0
X-C ₁	1.309	1.279	1.297	1.745	1.671	2.077
X-C ₅ -C ₁ -C ₂	104.8	104.3	107.4	115.9	111.6	117.0
180-(C ₃ -C ₂ -C ₄ -C ₅)	0.8	0.4	-2.8	2.0	0.0	3.7
H ₁ -C ₁ -C ₂	127.3	126.0	a	123.1	a	120.5
H ₁ -C ₁ -C ₅		125.5	125.6		126.2	
180-(H ₁ -C ₁ -C ₂ -C ₅)	-9.6	a	a	-23.2	a	-33.3
180-(H ₁ -C ₁ -C ₅ -C ₂)		-10.5	-12.4		-21.4	
H ₂ -C ₂ -C ₁	124.8	125.6	a	124.3	127.7	124.2
(H ₂ -C ₂ -C ₁ -C ₅)-180	1.4	-0.6	a	2.5	0.0	2.9

^a Not reported

^b This study

Table 5.11

Geometry of transition states for sigmatropic [1,5] shifts of the group X in 1,3-cyclohexadiene, where X=H, CH₃, SiH₃. ^a Value taken from the hydrogen analogue. ^b Not reported.



	H		CH ₃	SiH ₃
	MINDO/3	INDO ²⁴	MINDO/3	MINDO/3
C ₁ -C ₅	2.201	1.77	2.152	2.288
C ₁ -C ₂	1.423	1.43	1.439	1.435
C ₂ -C ₃	1.409	1.39	1.408	1.410
C ₁ -C ₆	1.516	1.48	1.519	1.529
X-C ₁	1.420	1.30	1.891	2.213
C ₅ -C ₁ -C ₂	94.0	101.3	94.7	92.2
C ₁ -C ₂ -C ₃	117.6	111.2	117.2	119.5
C ₂ -C ₃ -C ₄	116.8	114.5	116.1	116.6
C ₆ -C ₁ -C ₂	120.6	116.8	117.2	114.9
C ₁ -C ₆ -C ₅	93.0	73.3	90.2	96.9
X-C ₅ -C ₁ -C ₂	99.2	100.6	111.2	110.3
C ₆ -C ₁ -C ₅ -C ₂	132.0	114.5	124.5	126.3
180-(C ₃ -C ₂ -C ₄ -C ₅)	-3.3	-5.0	-1.4	-2.4
H ₁ -C ₁ -C ₂	118.7	119.8	116.3	115.2
H ₆ -C ₆ -H ₆	103.8	108.7	a	a
H ₂ -C ₂ -C ₁	120.1	123.7	a	a
(H ₂ -C ₂ -C ₁ -C ₅)-180	14.1	b	a	a
180-(H ₁ -C ₁ -C ₂ -C ₅)	15.4	b	5.6	-4.3

the C_1-C_2 and C_4-C_5 bonds are found to be almost parallel. The C_1 to C_5 carbon chain resembles an open pentadienyl system, the distance between the terminal atoms is about 2.2 Å. The C_3 carbon atom is slightly bent away from the group X. The $X-C_1$ distances are about 0.34 Å larger than the normal bond lengths for $X=H$ or CH_3 and 0.19 Å larger for $X=SiH_3$. These bond lengths are also larger than the corresponding bonds in the TS for shifts in pentadiene and cyclopentadiene. Because of repulsion effects, the $X-C_5-C_1-C_2$ dihedral angle is larger for $X=CH_3$ or SiH_3 , while the angle $C_6-C_1-C_5-C_2$ is smaller. Parameters for the hydrogen atoms at C_6 and C_2 were fixed at the optimum values for $X=H$. H_2 is moved in the direction of X, the position of H_1 is strongly dependent on X.

INDO calculations^{22,24} predict an unrealistically small value of 1.77 Å for the C_1-C_5 distance in the TS for the H shift in cyclohexadiene. This would imply that in order to achieve a sigmatropic shift the C_1-C_5 distance should be diminished by about 0.74 Å from the GS value of 2.51 Å, thereby causing a severe deformation of the carbon ring. This is in contradiction with a simple approach based on the Principle of Least Motion³⁰. The CNDO/2 and INDO methods are known to be biased towards formation of three-membered rings because of the underestimation of ring strain. This is clear also from a geometry optimization of cycloheptatriene, which leads to the bicyclic norcaradiene²⁴.

5.4.2 Stereoselectivity

Resulting activation energies from the MINDO/3 and other methods are given in Table 5.12, together with experimental data (see also Table 5.1). MINDO/3 results for the H and CH_3 shifts in cyclopentadiene are superior to results from the other methods. Our activation energies are somewhat smaller than data reported from other MINDO/3 calculations^{27,28}. The reason for this discrepancy is not

Table 5.12

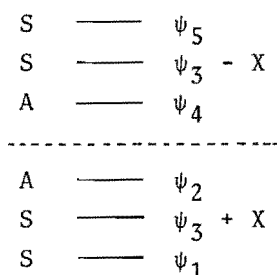
Activation energies for sigmatropic [1,5] shifts in cyclopentadiene and cyclohexadiene

Group	Method	ΔE_a	Ref
Cyclopentadiene			
H	CNDO/2	10.2	20
	INDO	17.2	21
	MINDO/2	18.4	18
	MINDO/3	27.7	a
	MINDO/3	28.3	28
	Exp	24.3	2
CH ₃	MINDO/2	27.6	18
	MINDO/3	49.4	a
	MINDO/3	46.4	27
	Exp	43.0	2
SiH ₃	MINDO/3	25.8	a
	Exp	13.7	2
Cyclohexadiene			
H	INDO	31	24
	MINDO/3	55.0	a
	Exp	39	24
CH ₃	MINDO/3	93.0	a
SiH ₃	MINDO/3	54.5	a

^aThis study

clear. For the silyl shift in cyclopentadiene the predicted activation energy is too high. Rather high values are found also for the shifts in cyclohexadiene. The INDO results for the activation energies are satisfying, in spite of the unrealistic geometry of the cyclohexadiene TS.

The MO pattern in the TS of the cyclic systems is similar to that of the suprafacial shift in an open pentadiene system:



ψ_1 to ψ_5 are the π -type MO's in the carbon chain. This diagram is characteristic for an allowed reaction (see Figure 5.3). The symmetrical ψ_3 π orbital of the pentadienyl system combines with the (s or p_z) orbital of the shifting group X. The antisymmetrical orbitals ψ_2 and ψ_4 become the HOMO and LUMO of the TS. There are two exceptions: for the H shift in cyclopentadiene the two lowest virtual orbitals are interchanged, and for the silyl shift in cyclohexadiene the two highest occupied orbitals are reversed. However, this does not affect the stereoselectivity.

The C_1 - C_5 distance of 2.2 Å in the cyclohexadiene TS is somewhat smaller than in the open pentadiene systems: 2.525 and 2.462 Å for the suprafacial H and CH_3 R shifts, respectively (see Table 5.3). This is caused obviously by the bridging methylene group. The overlap integral between the terminal π orbitals in the cyclohexadiene TS is about 0.04 and the corresponding bond-order is zero. In the open pentadiene TS the overlap integral between the terminal π lobes, which are directed somewhat more towards the

shifting hydrogen atom, is of the same order. We conclude that there is no homoconjugation between the terminal atoms in the cyclohexadiene TS.

Table 5.13 contains the difference charge densities on the shifting group X in the GS and TS. In the cyclopentadiene molecules X carries about 0.06 electrons less in the TS. Although this charge transfer effect is rather small, it suggests a transition state with an aromatic cyclopentadienyl anion ring and a positively charged shifting group²⁴. It can be concluded that sigmatropic

Table 5.13

MINDO/3 difference charge densities on the shifting group

		H	CH ₃	SiH ₃
Cyclopentadiene	GS	-0.016	0.010	0.058
	TS	0.061	0.094	0.111
Cyclohexadiene	GS	-0.031	-0.002	0.047
	TS	-0.056	-0.019	0.025

shifts in fully closed cyclic systems (i.e. a rearrangement towards the neighbouring carbon atom in the framework) proceed via a TS with a contribution from an aromatic charge transfer structure. This conclusion is supported by INDO²³ and MINDO/3 calculations on the TS for the [1,3] hydrogen shift in cyclopropene, which predict difference charge densities of -0.13 and -0.15, respectively, on the shifting hydrogen atom.

In the cyclohexadiene systems the shifting group in the TS is found to be slightly more negative than in the GS, see Table 5.13. Apparently, the aromaticity model does not apply here and the shifting group is purely covalently bound in the TS. INDO calculations predict no charge transfer in the TS for the [1,5] H shift in cycloheptatriene²². In the "half-open" cyclic systems like cyclohexadiene, cycloheptadiene and cycloheptatriene, the [1,5] shifts

should be considered as occurring in an open linear conjugated system, in which the terminal atoms are bridged by a second fragment. There is no charge transfer effect in the TS and there is no overlap between the terminal atoms.

The aromaticity model for fully closed cyclic conjugated transition states could be extended to systems where the conjugation in the ring is diminished, i.e. when there is homoconjugation²⁴. The distance between the terminal atoms in the TS should be small enough (up to about 1.8 Å) to give an appreciable overlap. A possible model reaction is the [1,7] hydrogen shift in 1,3,5-cyclooctatriene. The TS should be described as a negatively charged hydrogen atom with a homotropenylium cation (compound 24 in Chapter 3). The C₁-C₇ distance in 24 is equal to 1.621 Å (see Table 3.5) and the system is considered to be a homoaromatic cation^{46a}.

Breslow has studied the [1,5] hydrogen shift in 5-halocyclopentadienes⁴⁷. He found that the halogen substituent slows the reaction, the effect is larger for iodine than for chlorine. It was suggested that local positive charge would be involved in the TS for the hydrogen shift and that the TS would have antiaromatic cyclopentadienyl cation character. However, another interpretation was also proposed⁴⁷. Moreover, because the halogen atom is bent out of the plane of the ring, both inductive and mesomeric effects should be taken into account. We have not performed any calculations on H or F shifts in 5-fluorocyclopentadiene in view of the incorrect MINDO/3 results for fluorine compounds (see Section 5.3).

Little attention has been paid to theoretical studies of sigmatropic (fluxional) rearrangements in organometallic compounds. Experimental data have been reviewed for shifts concerning elements of group IV (like Si) occurring in hydrocarbon systems like cyclopentadiene, cycloheptadiene and indene²⁶. Su²⁵ has made some predictions about the fluxional behaviour of a wide variety of organometallic

compounds. Ab initio calculations⁴⁸ have shown that cyclopentadienyllithium C_5H_5Li has a C_{5v} -symmetric structure with the lithium atom above the centre of the cyclopentadienyl ring. Apparently, the model description given for sigmatropic shifts in 5-lithiocyclopentadiene is not realistic²⁵. The C_{5v} structure of C_5H_5Li is similar to that of the pyramidal $C_6H_5^+$ carbene system 5 described in Chapter 3.

5.4.3 Calculations on pentacoordinated cation compounds

De Dobbelaere²⁴ has discussed sigmatropic $[1,5]$ shifts in relation to the C_1-X-C_5 angle at the shifting group in the TS. A larger angle is correlated with a retarding effect in the reaction. Pentacoordinated cations like CH_5^+ were used as a model. The migrating CH_3 group which is bi-coordinated with both terminal atoms in the TS has been compared with a CH_5^+ cation in the most favourable C_s symmetry. The CNDO/2 method (including 3d orbitals) has been used for silicium compounds. The MINDO/3 method does not incorporate 3d orbitals, and the parameter set for Si has been derived consistently. To test the performance of the MINDO/3 method for pentacoordinated silicium compounds, we have compared the results from calculations on CH_5^+ and SiH_5^+ with CNDO/2 and ab initio results. Three different geometry structures have been optimized with D_{3h} , C_{4v} and C_s symmetry. We have not investigated if they all correspond to energy minima. From a preliminary MINDO/3 study⁴⁹ it has been reported that the C_s structure is the only minimum on the CH_5^+ surface. For the CNDO/2 calculations a computer program has been applied in which the SIMPLEX algorithm is included for the geometry optimization²⁴.

Table 5.14 contains the relative energies for CH_5^+ structures obtained from CNDO/2, MINDO/3 and three different ab initio calculations (ordered in increasing quality of the basis set used) and the estimated Hartree-Fock limit⁵². In Table 5.15 results for SiH_5^+ are compiled.

Table 5.14

Relative energies for CH_5^+ structures with respect to the C_s structure

Method	CNDO/2	MINDO/3	STO-3G	4-31G	Dyczmons	HF-limit
Ref	a	a	50	51	52	52
D_{3h}	-35.0	11.4	6.3	7.2	16.6	16.9
C_{4v}	-38.2	7.5	1.9	4.5	9.0	8.8

^aThis study

Table 5.15

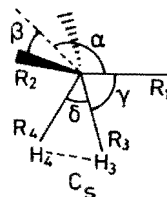
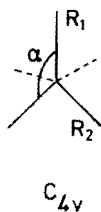
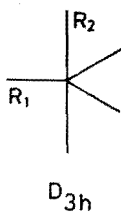
Relative energies for SiH_5^+ structures

Method	CNDO/2	MINDO/3	Hartmann ⁵³
D_{3h}	172.8	52.6	0
C_{4v}	102.8	47.8	1.9
C_s	0	0	-

All the reported data correspond to geometry optimized structures. Many of the geometry data are compiled in Table 5.16.

The CNDO/2 method clearly gives insufficient results for the relative energies of both species. The MINDO/3 method yields relative energies for the CH_5^+ species that are even better than those from ab initio methods with a small basis set. The only available result on SiH_5^+ (an ab initio calculation using one-center electron functions) predicts the D_{3h} and C_{4v} structures to be rather close in energy⁵³, in line with MINDO/3 results. The MINDO/3 heat of formation of 216.2 kcal/mol for the C_s structure is in good agreement with the reported experimental value of 217-233 kcal/mol⁵⁴. For CH_5^+ a similar correspondence has

Table 5.16

Geometries of XH_5^+ structures, where X=C, Si

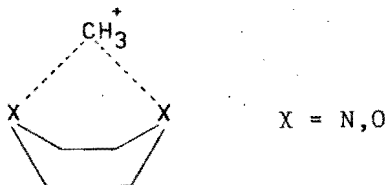
	CH_5^+				SiH_5^+		
	CNDO/2	MINDO/3	4-31G	Ref. 52	CNDO/2	MINDO/3	Ref. 53
D_{3h}							
R_1	1.135	1.120	1.100	1.096	1.623	1.487	1.570
R_2	1.115	1.126	1.118	1.117	1.633	1.494	1.585
C_{4v}							
R_1	1.111	1.100	1.071	1.094	1.540	1.457	1.585
R_2	1.118	1.133	1.117	1.130	1.640	1.498	1.582
α	112.1	113.6	136.1	113.1	139.0	116.5	104.0
C_s							
R_1	1.171	1.109	1.086	1.089	1.616	1.462	
R_2	1.159	1.103	1.077	1.082	1.623	1.462	
R_3	1.249	1.250	1.242	1.268	1.879	1.807	
R_4	1.410	1.245	1.241	1.273	1.927	1.808	
α	116.1	110.8	131.6	135.0	118.0	116.7	
β	62.6	64.6	58.1	57.9	60.1	73.2	
γ	96.2	83.3	84.8	77.7	91.3	86.9	
δ	40.6	42.0	40.1	40.8	24.5	25.7	
H_3-H_4	0.935	0.894	0.851	0.856	0.809	0.804	

been found^{4,9}.

From the resulting geometry data we conclude that both the CNDO/2 and MINDO/3 methods give fairly good results for CH_5^+ . For SiH_5^+ systematic differences for the Si-H distances are found, but bond angles are in good agreement. From the results it seems fully justified to perform MINDO/3 calculations on pentacoordinated silicium compounds without including 3d orbitals in the basis set.

From Table 5.16 it is concluded that the $\text{H}_3\text{-H}_4$ bond length in the C_s -symmetric arrangement has a constant value in both CH_5^+ and SiH_5^+ . The value of the angle δ only depends on the X-H bond length. The C_s structure is best described as a σ -type complex of a CH_3^+ cation with H_2 . Apparently, the angle δ is not related to the $\text{C}_1\text{-X-C}_5$ angle in the TS for sigmatropic shifts.

Recently, CNDO/2 and STO-3G calculations have been performed on the methyl rearrangement between two substituted heteroatoms in hydrocarbon cation systems^{5,5}. The transition state contains a pentacoordinated carbon atom



in the shifting methyl group, which resembles the CH_5^+ cation. It was found that retention of configuration for the methyl group with local C_s symmetry in the TS is more favourable than inversion of configuration with local C_{2v} symmetry in the TS. Most likely, this is caused by the unfavourable rehybridization effect in the reaction path for the inversion mechanism.

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SUMMARY

In this thesis a quantumchemical investigation of the stereoselectivity of organic reactions governed by symmetry is presented. Qualitative predictions on the stereochemistry can be made based on the principle of Conservation of Orbital Symmetry. Ground states and transition states of the reacting molecules have been located on the potential energy hypersurface for the lowest electronic singlet state. The Molecular Orbital calculations have been performed using the semiempirical MINDO/3 method and the STO-3G and 4-31G ab initio procedures.

A number of local energy minima has been detected on the $C_6H_5^+$ potential energy surface. The phenyl cation is found to be the most stable cyclic compound, followed by a pyramidal nonclassical structure, in which an anti-aromatic cyclopentadienyl cation ring is stabilized by interaction with an apical carbon atom. Qualitative predictions are offered for the allowed or forbidden character of rearrangement reactions between the various isomers using the theory of orbital isomerism. Most of the results are supported by the MO calculations.

The stereochemistry of the ring opening reaction of cyclobutene, when influenced by a vicinal ethylene molecule has been studied as a model system for a possible change in the stereoselectivity. The ethylene molecule was found to have a similar effect on the conrotatory and disrotatory reactions. No evidence was found for a change in the stereochemistry upon extension of the π -electron system by two more electrons.

Sigmatropic shift reactions in cyclic and acyclic

molecules have been studied, occurring both in a suprafacial and in an antarafacial way. H, F, CH₃ and SiH₃ have been chosen as the shifting groups and for the methyl shifts reactions with retention and inversion of configuration have been considered. Very good agreement is found between the qualitative predictions and the quantitative results. A MINDO/3 energy difference of 8-14 kcal/mol is obtained between the activation energies for comparable allowed and forbidden reactions. The shift of a fluorine atom proceeds via an "inversion-type" mechanism. The transition state for suprafacial shifts in cyclic systems can be described by a mesomeric charge transfer contribution which contains a ring system with aromatic character.

SAMENVATTING

In dit proefschrift wordt een quantumchemisch onderzoek beschreven naar de selektiviteit van organische reacties welke wordt bepaald door de symmetrie van het systeem. Kwalitatieve voorspellingen over de stereochemie kunnen worden afgeleid met behulp van het principe van Behoud van Orbital Symmetrie. Grondtoestanden en transitie states van de reagerende molekulen werden gelokaliseerd op het potentiaaloppervlak van de laagste elektronische singlettoestand. De Molecular Orbital berekeningen werden uitgevoerd met behulp van de semi-empirische MINDO/3 methode en de STO-3G en 4-31G ab initio procedures.

Een aantal lokale energieminima zijn gevonden op het $C_6H_5^+$ potentiaaloppervlak. Het fenyl kation is de meest stabiele cyclische verbinding, gevolgd door een pyramidale niet-klassieke structuur, waarin een anti-aromatische cyclopentadienyl kation ring wordt gestabiliseerd door interactie met een apikaal koolstofatoom. Kwalitatieve voorspellingen worden gegeven over het toegestaan of verboden karakter van omleggingsreacties tussen de verschillende isomeren met behulp van de theorie van orbital isomerie. De meeste resultaten worden ondersteund door de MO berekeningen.

De stereochemie van de ringopeningreactie van cyclobuteen onder invloed van een naburig etheenmolekuul is bestudeerd als een modelsysteem voor een mogelijke verandering in de selektiviteit. De invloed van het etheenmolekuul was gelijk voor de conroterende en disroterende reacties. Er werden geen aanwijzingen gevonden voor een verandering in de stereochemie door een uitbreiding van

het π -systeem met twee extra elektronen.

Verder werden bestudeerd suprafaciale en antarafaciale sigmatrope reacties in cyclische en niet-cyclische molekulen. H, F, CH_3 en SiH_3 zijn gekozen als de verhuizende groepen en methylverhuizingen met zowel retentie als inversie van configuratie werden bestudeerd. Een zeer goede overeenstemming werd gevonden tussen de kwalitatieve voorspellingen over de stereochemie en de kwantitatieve resultaten. Met behulp van de MINDO/3 methode werd een energieverval van 8-14 kcal/mol verkregen tussen de aktiveringsenergieën voor vergelijkbare verboden en toegestane reacties. De verhuizing van een fluoratoom vindt plaats via een "inversie"-mechanisme. De transition state voor suprafaciale verhuizingen in cyclische systemen kan worden beschreven door een mesomere charge-transfer structuur met aromatisch karakter voor het ringsysteem.

CURRICULUM VITAE

De schrijver van dit proefschrift werd op 3 juni 1950 geboren in Raamsdonksveer. Na het behalen van het eindexamen gymnasium β aan het Sint-Oelbert gymnasium in Oosterhout (N.B.) werd in 1967 begonnen met de studie aan de afdeling Scheikundige Technologie van de TH Eindhoven. Het afstudeeronderzoek werd verricht in de vakgroep Organische Chemie onder leiding van prof. dr. H.M. Buck. In september 1972 werd het ingenieursexamen met lof afgelegd. Daarna werd in dezelfde groep begonnen met het onderzoek beschreven in dit proefschrift.

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STELLINGEN

1. Het tijdsverschil tussen de bestraling van H_2CO en het verschijnen van CO kan op bevredigende wijze worden verklaard door het optreden van een oxacarbeen als intermediaire structuur.

P.L. Houston, C.B. Moore, J. Chem. Phys.,
65, 757 (1976)

2. In leerboeken over quantummechanica wordt onvoldoende aandacht besteed aan de dimensie van de golffunctie.
3. Bij zogenaamde intramoleculaire processen wordt het belang van intermoleculaire effecten onderschat.

W.J. Bouma, D. Poppinger, L. Radom,
J. Amer. Chem. Soc., 99, 6443 (1977)

4. Bij het berekenen van UV overgangsenergieën en dipoolmomenten wordt vaak geen rekening gehouden met de invloed van nulpuntsvibraties.
5. De structuur van kationen onder langlevende condities kan niet zondermeer gerelateerd worden aan de structuur van de transition state tijdens solvolysereacties.

G.A. Olah, G.K.S. Prakash, G. Liang,
J. Amer. Chem. Soc., 99, 5683 (1977)

6. Het valt te betreuren, dat sommige wetenschappelijke conferenties en summer schools in belangrijke mate worden ondersteund door de NATO.

7. Het verdient aanbeveling om een genormaliseerde methode vast te stellen voor het beschrijven van de geometrische structuur van een molecuul.

8. Seidman en Maciel beweren ten onrechte, dat zij sterisch geïnduceerde ^{13}C chemical shifts kunnen berekenen.

K. Seidman, G.E. Maciel, J. Amer. Chem. Soc., 99, 659 (1977)

9. Achteruitkijkspiegels op fietsen kunnen een belangrijke bijdrage leveren aan de verkeersveiligheid.

10. Vysotskii et al. houden ten onrechte geen rekening met de mogelijkheid, dat bij de reactie van PCl_3 met 1,5-diketonen ook een 1,3,2-dioxafosfolaanring kan ontstaan.

V.I. Vysotskii, U.G. Chuprakova, M.N. Tilichenko, Zh. Obshch. Khim., 46, 785 (1976); J. Gen. Chem. USSR (Engl. Transl.), 46, 783 (1976)

11. De artsenopleiding in Nederland wordt ten onrechte de studierichting der medicijnen genoemd.