QUANTUMCHEMICAL STUDIES OF REACTIVITY AND ELECTRONIC SPECTRA

I. VALENCE BOND THEORY AND ITS APPLICATION TO ELECTROCYCLIC REACTIONS

II. MOLECULAR ORBITAL CALCULATIONS ON THIOBENZOPHENONE AND RELATED COMPOUNDS

W. Th. A. M. VAN DER LUGT

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN
DE RECTOR MAGNIFICUS DR P. MUNTENDAM,
HOOGLERAAR IN DE FACULTEIT DER GENEESKUNDE,
TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT
TE VERDEDIGEN OP DINSDAG 25 JUNI 1968
TE KLOKKE 15.15 UUR

DOOR

WILHELMUS THEODORUS ANTONIUS MARIA VAN DER LUGT

GEBOREN TE ROTTERDAM IN 1937

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PROMOTOR: PROF. DR L.J. OOSTERHOFF

Aan mijn ouders
Aan mijn vrouw

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CHAPTER I SEMIEMPIRICAL MOLECULAR ORBITAL AND VALENCE BOND THEORY

CHAPTER II APPLICATION OF THE VALENCE BOND THEORY TO ETHYLENE, BUTADIENE AND BENZENE

GENERAL INTRODUCTION

This thesis deals with a comparison of semiempirical molecular orbital and valence bond calculations and the application of these approaches to two topics in organic chemistry:

1. The course of thermal and photoinduced electrocyclic reactions and an analysis of the Woodward-Hoffmann rules.
2. The UV spectra of thiobenzophenone and related compounds.

Up to now entirely theoretical calculations have seldom been performed on problems of interest to experimental chemists, such as for instance the behaviour of molecules in the course of reaction or the response of a molecule to the interaction with an electromagnetic field. In quantumchemistry simple approaches are urgently needed to attack these problems and to interpret experimental results. From this point of view one can understand the increasing interest in semiempirical theories such as the Hückel and the Pariser-Parr-Pople π-electron theories of aromatic molecules. Calculations of this kind have yielded a large number of valuable results. One might imagine that with the increasing influence of high-speed electronic computers these semiempirical approaches in the long run will fade away and will be replaced by ab initio calculations of electronic wave functions from which molecular properties can be determined. There is, however, reason to believe that they will retain their position since irrespective of the greater reliability of ab initio calculations in the quantitative sense, results of semiempirical treatments may be easier to understand and therefore more useful for interpretation and prediction of experiment.

Most applications of semiempirical calculations in organic chemistry have been performed using the Molecular Orbital method. At first sight one may wonder why the use of this method has almost completely overwhelmed that of the Valence Bond theory since so many valuable results have been obtained in terms of valence bond structures, especially with problems concerning chemical reactivity. In the first instance this is because the Molecular Orbital theory provides a simple interpretation of electronic excitation energies and ionization potentials. It is, however, the numerical advantages which have primarily turned the scale in favour of the molecular orbital method. In this thesis both of these methods have been applied to a number of problems in order to obtain a more reliable insight into their relative merits.

Chapter I concerns the introduction of the approximations of Pariser, Parr and Pople[1, 2], which have been used so successfully in the Molecular Orbital theory, into the Valence Bond method. It seemed worth-while to investigate whether this approach makes the Valence Bond method more suitable for calculations with electronic computers than the original approach developed by Heitler, London, Slater and Pauling.

The results of complete valence bond and molecular orbital calculations, using in both cases the same approximations and semiempirical parameters, are given in Chapter II. In addition, in view of the π-electron systems of ethylene, butadiene and benzene, a comparison has been made of the results of some calculations in which only a limited number of valence bond structures or molecular orbital configurations have been taken into account. Special attention will be drawn to the agreement or discrepancies between the experimental absorption bands and the excitation energies which result from these restricted calculations.

In Chapter III the semiempirical Valence Bond method is used for a theoretical study of thermal and photoinduced electrocyclic reactions. The stereochemical course of this kind of reaction has been predicted by the well-known Woodward-Hoffmann rules. The excellent agreement of the theoretical course of the reaction with that determined experimentally is especially surprising for the photochemical process. The explanation given by Woodward and Hoffmann[3] relies on the symmetry of the lowest antibonding molecular orbital, which is occupied in the first excited state by only one electron. A more satisfactory treatment has been given by Longuet-Higgins and Abrahamson[4] who used the molecular orbital approach to characterize states of the molecules, but their considerations are still qualitative. Our calculations aim at a more quantative picture of the reaction.

We have chosen the cyclization of butadiene to cyclobutene as an example in order to obtain more insight into the course of electrocyclic reactions in the ground state and in the excited state. Energy levels have been calculated for butadiene, for cyclobutene and for a large number of intermediate configurations. The potential surfaces thus obtained have been used to discuss the course of the thermal and the photoinduced reaction.

The interpretation of some electronic spectra is given in Chapter IV in terms of the Molecular Orbital method since this approach is much more appropriate for calculations on excited states. The UV spectra of thiobenzophenone and related compounds in methanol and sulfuric acid have been measured and interpreted by Buck[5]. In order to check his conclusions we have performed semiempirical molecular orbital calculations. In addition, the polarographic reduction potentials have been measured so that a comparison could be made between the results of the calculations and two different series of experimental data.

A controversy still exists concerning sulfur-containing molecules, as to whether participation of a 3d orbital of sulfur has to be included in quantum-chemical calculations for a good description of the ground state and the lower excited states of the molecules. In order to contribute to the solution of this problem a 3d orbital of the correct symmetry has been included in the π-electron calculations on the thiobenzophenones.

All the calculations discussed in this thesis have been performed on the computer of the University of Leiden, formerly an Electrologica X1 and at present an IBM 360-50.

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CHAPTER I

SEMIEMPIRICAL MOLECULAR ORBITAL AND VALENCE BOND THEORY

INTRODUCTION

In theoretical discussions of the electronic structure of molecules two widely different approaches are generally recognized. The first of these, and for a long time the most commonly used, is embodied in the Valence Bond (VB) method, which may be regarded as a generalization of the Heitler-London[1] treatment of the hydrogen molecule problem. The building-stones of this theory are the structures of classical chemistry and it is therefore not surprising that the VB theory is particularly attractive from the chemical point of view. Dealing with molecular ground states, it gives a satisfactory description of molecular properties. For example the phenomena of resonance stabilization and reactivities of organic molecules have established the reliability of the theory.

The use of the VB method for molecular excited states is, however, more difficult than for the ground state. Calculations on aromatic molecules performed with the VB method give results in reasonable agreement with energy values for the lowest excited states. These agreements have tended to confirm that the nature of the excited states is well described by the VB method, but the theory fails to give the intensities of spectral transitions: all transitions are predicted to be forbidden. This failure is closely connected with another weakness in the method: the neglect of polar structures in which the electrons are not uniformly distributed. Inclusion of polar structures makes the amount of tedious labour considerable. A large number of ionic structures must be added and the VB method, despite its attraction for the chemist, becomes highly unpractical in numerical calculations.

The second approach, the Molecular Orbital (MO) method, is an extension of the Hartree-Fock method which has been used successfully in quantum mechanical calculations on atoms. Each electron is described by a non-localized wave function, extending over the whole molecule and the problem is now the determination of these one-electron wave functions. The numerical advantages of the MO method are so important, that it is almost exclusively used in present-day calculations. Depending on the purpose of the calculations and the size of the molecules the MO method is performed in two different ways. For small molecules the MO method is used in the non-empirical way, where all of the integrals are explicitly calculated. On the other hand, the semiempirical theories of Hückel and Pariser-Parr-Pople are more attractive for chemists in the study of large molecules. The disadvantage of the MO method is that it is difficult to interpret the results of the calculations in the language of chemical structures which has proved of immense value in chemistry.

The difference between the MO and the VB theory is purely a difference in starting point. Inclusion of all of the excited configurations in the MO theory and inclusion of all of the structures (covalent and polar) in the VB theory *must* yield the same results[2]. Compared with the VB method the MO theory possesses the advantage of giving the best first approximation.

In this Chapter the approximations and adjustments of Pariser, Parr and Pople (PPP) are discussed. For the sake of completeness their application in the MO theory is given in part A, but can also be found in many textbooks[3, 4, 5]. In part B the approach of PPP is introduced in the VB method.

The simplifications of PPP can be justified by the assumption that one employs, in fact, orthogonalized atomic orbitals (Wannier or Löwdin orbitals). The use of the PPP approximations in the VB theory means that the Valence Bond structures are formed from these orthogonalized orbitals while the conventional VB theory is based upon non-orthogonal, atomic orbitals. This reformulated VB theory starting from a set of orthogonalized, atomic orbitals has been developed by McWeeny[6] who applied this method to cyclobutadiene and benzene. This theory has, however, rarely been used since that time and it seems worthwhile to give a simplified version of McWeeny's ideas.

PART A SELF-CONSISTENT FIELD MOLECULAR ORBITAL THEORY.

A1. THE ROOTHAAN EQUATIONS.

Many essential problems in quantum chemistry arise from the fact that the time-independent Schrödinger equation

$$H\Phi = E\Phi \qquad 1.1$$

is generally much too difficult to solve exactly. The theory for π-electron systems treated in this Chapter adopts three basic assumptions.

Assumption A: Magnetic interactions and relativistic effects in the Hamiltonian are neglected.

Assumption B: The Born-Oppenheimer approximation is used, which means that the nuclear and electronic motions are separated.

Assumption C: The π-electrons may be treated independently of the σ-electrons. The π-electrons move in a fixed core containing the nuclei and σ-electrons.

With these assumptions the Hamiltonian for the π-system is

$$\begin{aligned} H &= \sum_i \left\{ -\tfrac{1}{2}\Delta(i) + V(i) \right\} + \sum_{i>j} \frac{1}{r_{ij}} = \\ &= \sum_i H^{\text{core}}(i) + \sum_{i>j} \frac{1}{r_{ij}}. \end{aligned} \qquad 1.2$$

where
$-\frac{1}{2}\Delta(i)$ represents the kinetic energy of electron i
$V(i)$ represents the potential energy of electron i with respect to the fixed core
$\frac{1}{r_{ij}}$ represents the electrostatic repulsion of the electrons i and j.

The self-consistent field method has been originally developed by Hartree and Fock for calculations on atoms. When the number of electrons is even the wave function of the ground state of the system can in most cases be approximated by a closed shell configuration:

$$\begin{aligned} \Phi_0 &= \frac{1}{\sqrt{2n!}} \left| \psi_a(1)\,\bar{\psi}_a(2) \cdots\cdots \psi_n(2n-1)\,\bar{\psi}_n(2n) \right| = \\ &= \left| \psi_a\,\bar{\psi}_a \cdots\cdots \psi_n\,\bar{\psi}_n \right| \end{aligned} \qquad 1.3$$

Each of the space orbitals $\psi_a \ldots . \psi_n$ is occupied by two electrons, one with α spin (ψ_a) and the other with β spin ($\overline{\psi_a}$).

The lowest energy is obtained when the orbitals ψ_i satisfy the equations

$$F(1)\,\psi_i(1) = \epsilon_i\,\psi_i(1) \tag{1.4}$$

where

$$F(1) = H^{\text{core}}(1) + \sum_{j=1}^{n}\left\{2J_j(1) - K_j(1)\right\} \tag{1.5}$$

$$J_j(1)\,\psi_i(1) = \int \psi_j^*(2)\,\frac{1}{r_{12}}\,\psi_j(2)\,\psi_i(1)\,d\tau_2$$

$$K_j(1)\,\psi_i(1) = \int \psi_j^*(2)\,\frac{1}{r_{12}}\,\psi_i(2)\,\psi_j(1)\,d\tau_2$$

The energy corresponding to the wave function Φ_0 is given by

$$E_0 = 2\sum_{i=1}^{n}\epsilon_i - \sum_{i,j=1}^{n}(2J_{ij} - K_{ij}) \tag{1.6}$$

where

$$J_{ij} = \int \psi_i^*(1)\,\psi_j^*(2)\,\frac{1}{r_{12}}\,\psi_i(1)\,\psi_j(2)\,d\tau_1\,d\tau_2$$

$$K_{ij} = \int \psi_i^*(1)\,\psi_j^*(2)\,\frac{1}{r_{12}}\,\psi_j(1)\,\psi_i(2)\,d\tau_1\,d\tau_2$$

The equations 1.4 are the self-consistent field (SCF) or Hartree-Fock equations.

In molecules the one-electron wave functions ψ_i extend over the whole molecule. The molecular orbitals can further be written as linear combinations of atomic orbitals (LCAO):

$$\psi_i = \sum_{\mu} c_{i\mu}\,\varphi_{\mu} \tag{1.7}$$

where φ_μ is an atomic orbital on atom μ. This is the LCAO-SCF method. One usually restricts the set of φ_μ's in calculations on π-electron systems to one p orbital for each atom. When the atomic orbitals φ_μ and coefficients $c_{i\mu}$ are assumed to be real, the equations 1.4 in the LCAO-SCF method are

$$\sum_{\nu} F_{\mu\nu}\,c_{i\nu} = \epsilon_i \sum_{\nu} S_{\mu\nu}\,c_{i\nu} \tag{1.8}$$

where $$F_{\mu\nu} = \int \varphi_{\mu}(1)\, F(1)\, \varphi_{\nu}(1)\, d\tau_1$$

$$S_{\mu\nu} = \int \varphi_{\mu}(1)\, \varphi_{\nu}(1)\, d\tau_1$$

Bij using the expansion in atomic orbitals (equation 1.7) and by neglecting $S_{\mu\nu}$ for $\mu \neq \nu$ the matrix elements $F_{\mu\nu}$ can be written as

$$F_{\mu\nu} = H^{\mathrm{core}}_{\mu\nu} + \sum_{\rho\sigma} P_{\rho\sigma} \left\{ (\mu\nu||\rho\sigma) - \tfrac{1}{2}(\mu\sigma||\rho\nu) \right\} \qquad 1.9$$

where $$H^{\mathrm{core}}_{\mu\nu} = \int \varphi_{\mu}(1)\, H^{\mathrm{core}}(1)\, \varphi_{\nu}(1)\, d\tau_1$$

$$P_{\rho\sigma} = 2 \sum_{i=1}^{n} c_{i\rho}\, c_{i\sigma}$$

$$(\mu\nu||\rho\sigma) = \int \varphi_{\mu}(1)\, \varphi_{\nu}(1)\, \frac{1}{r_{12}}\, \varphi_{\rho}(2)\, \varphi_{\sigma}(2)\, d\tau_1\, d\tau_2$$

$P_{\rho\sigma}$ is the bond order matrix; the diagonal elements are the π-electron densities on the atoms.

The Roothaan equations 1.8 show the characteristic properties of SCF procedures[7]. The problem is to find out the best set of coefficients $c_{i\mu}$. The equations 1.8 have the appearance of linear equations but in fact they are third order equations since the coefficients occur in the operator F. Iteration is the usual technique to solve the equations 1.8: one assumes certain values for the $c_{i\mu}$'s, calculates the matrix F using 1.9, solves the equations and compares the resulting coefficients with the assumed values. If they disagree one substitutes the new values in 1.9 and repeats the procedure until self-consistency is obtained.

Unfortunately, the equations are very complicated because of the presence of the three- an four-center exchange integrals $(\mu\nu||\rho\sigma)$. The number of these integrals is so large that even with modern electronic computers a calculation on the π-electrons of benzene for example, involves a large amount of labour.

A2. THE APPROXIMATIONS OF PARISER, PARR AND POPLE.

A satisfactory semiempirical theory has been independently introduced by Pariser and Parr[8] and by Pople[9]. Some of their assumptions are somewhat similar to those of the Hückel theory. The electronic repulsion is, however, explicitly taken into account, while it is included only in an averaged form in the simple molecular orbital theory. There are three fundamental approximations in the PPP method concerning how to treat the atomic integrals.

1. The first approximation is known as the approximation of zero differential overlap. Whenever the expression $\varphi_\mu(1)\,\varphi_\nu(1)$ $(\mu \neq \nu)$ appears in an integral (except in the resonance integral; see approximation 2), the integral is set equal to zero. This involves:

$$S_{\mu\nu} = \delta_{\mu\nu}$$

$$(\mu\nu\,||\,\rho\sigma) = (\mu\mu\,||\,\rho\rho)\,\delta_{\mu\nu}\,\delta_{\rho\sigma} \qquad 1.10$$

2. The second approximation is concerned with resonance integrals

$$\beta_{\mu\nu} = \int \varphi_\mu(1)\,H^{\mathrm{core}}(1)\,\varphi_\nu(1)\,d\tau_1 \qquad 1.11$$

The resonance integrals are treated as empirical parameters. Furthermore, if the atoms μ and ν are not nearest neighbours, $\beta_{\mu\nu}$ is taken to be zero.

3. The last approximation deals with the one-center electronic repulsion integrals[10]. These integrals are calculated from atomic data

$$(\mu\mu\,||\,\mu\mu) = I_\mu - A_\mu \qquad 1.12$$

where I_μ and A_μ are the valence state ionization potential and the electron affinity, respectively, of the orbital on atom μ. The theoretical value for $(\mu\mu\,||\,\mu\mu)$ is much too large, since it ignores polarization of the core and correlation effects between π-electrons on one atom.

With these simplifications the matrix elements $F_{\mu\nu}$ of equation 1.9 can be written

$$F_{\mu\mu} = H^{\mathrm{core}}_{\mu\mu} + \tfrac{1}{2} P_{\mu\mu}\,\gamma_{\mu\mu} + \sum_{\sigma\neq\mu} P_{\sigma\sigma}\,\gamma_{\mu\sigma}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\,\gamma_{\mu\nu} \qquad 1.13$$

where $\gamma_{\mu\nu} = (\mu\mu || \nu\nu)$.

The integrals $\gamma_{\mu\nu}$ can be evaluated in several ways. Empirical formulae have been developed, for example, by Parr, Pople and Mataga[11].

A final simplification occurs for $H^{\text{core}}_{\mu\mu}$ which can be written in the following form

$$H^{\text{core}}_{\mu\mu} = (\varphi_\mu | -\tfrac{1}{2}\Delta + V_\mu | \varphi_\mu) + \sum_{\sigma \neq \mu} (\varphi_\mu | V_\sigma | \varphi_\mu)$$

$$= U_{\mu\mu} + \sum_{\sigma \neq \mu} (\varphi_\mu | V_\sigma | \varphi_\mu) \qquad 1.14$$

This integral is simplified by two approximations:

1. The one-center core integral $U_{\mu\mu}$ describes the energy of an electron in φ_μ containing the kinetic energy and the interaction with the core of atom μ. If atom μ contributes one π-electron to the system the Goeppert-Mayer-Sklar approximation can be used:

   $$U_{\mu\mu} = -I_\mu \qquad 1.15$$

   If atom μ contributes two π-electrons, $U_{\mu\mu}$ is estimated in some other way.

2. The integrals $(\varphi_\mu | V_\sigma | \varphi_\mu)$ $(\sigma \neq \mu)$ are replaced by

   $$(\varphi_\mu | V_\sigma | \varphi_\mu) = -n_\sigma \gamma_{\mu\sigma}$$

   where n_σ is the number of π-electrons of atom σ participating in the π-electron system. The penetration integrals which describe the interactions with uncharged atoms are neglected.

With these assumptions the SCF equations reduce to

$$\sum_\nu F_{\mu\nu} c_{i\nu} = \epsilon_i c_{i\mu} \qquad 1.16$$

where $F_{\mu\mu} = U_{\mu\mu} + \tfrac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - n_\sigma) \gamma_{\mu\sigma}$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \gamma_{\mu\nu}$$

In practice a self-consistent field calculation starts from the Hückel molecular orbitals as a first approximation of the self-consistent field solution. Values are then chosen for the one-center core integrals, the resonance integrals and the electronic repulsion integrals. The matrix F is calculated and after diagonalization new coefficients are obtained. This prodecure is repeated until there is no change in the coefficients.

Because of the large number of parameters involved, there remains some doubt whether the results are due to a particular choice. However, a well chosen set of parameters can be used successfully in a large number of molecules to predict several physical and chemical properties. This supports the ideas of Pariser, Parr and Pople and makes the method extremely useful for an interpretation and prediction of experimental data.

A3. CALCULATIONS ON EXCITED STATES.

With the SCF equations 1.16 a number of ground state properties of molecules can be calculated. However, one of the main tasks of the molecular orbital theory has been to interpret UV spectra. Because of the vast amount of available data these spectra provide a good test for a semiempirical theory.

Starting from m atomic orbitals a self-consistent field calculation produces m molecular orbitals as linear combinations of the atomic orbitals. In the approximate wave function of the ground state n MO's are occupied by n electrons with α spin and n with β spin. The remaining (m-n) orbitals, the so-called virtual orbitals, can be used to describe electronic excited states of the molecule. The virtual orbitals are, just like the MO's occupied in the ground state, eigenvectors of the SCF Hamiltonian. The use of these SCF MO's instead of e.g. Hückel orbitals substantially simplifies the expressions for the energies of the excited states.

Let us consider the closed shell configuration of the ground state (equation 1.3). As a first approximation an excited state of a molecule can be described by a wave function in which one or more electrons have been promoted out of the orbitals ψ_a, ψ_b, ..., occupied in the ground state, to the virtual orbitals ψ_p, ψ_q, ... In most cases only singly excited states are taken into account. That means that the configuration of the excited states differ from that of the ground state by only one orbital. A singly excited singlet state in which an electron has been promoted from orbital ψ_i to orbital ψ_s is written as the sum of two Slater determinants:

$$\Phi_{i\to s} = \frac{1}{\sqrt{2}} \left\{ \left| \psi_a \bar{\psi}_a \cdots \psi_i \bar{\psi}_s \cdots \right| - \left| \psi_a \bar{\psi}_a \cdots \bar{\psi}_i \psi_s \cdots \right| \right\} \quad 1.17$$

The energy of this function with respect to the ground state is

$$E_{i\to s} - E_0 = \epsilon_s - \epsilon_i - J_{is} + 2K_{is}. \quad 1.18$$

In general, a better description for an excited state can be obtained by taking a linear combination of these excited configurations. This is the configuration interaction method. Again restricting the discussion to singly excited configurations an excited state can be represented by

$$\Phi_A = \sum_{i,s} c_{A,is} \, \Phi_{i\to s} \quad 1.19$$

The energies of the excited states and the coefficients of the configurations are obtained by solving the secular equations

$$\sum_{i,s} c_{A,is} \left(H_{j\to t,\, i\to s} - E_A \delta_{ij} \delta_{ts} \right) = 0 \quad 1.20$$

where $H_{j\to t,\, i\to s} = \langle \Phi_{j\to t} | H | \Phi_{i\to s} \rangle$ 1.21

Non trivial solutions of this set of equations exist only for values E_A, which are the roots of the secular determinant

$$\left| H_{j\to t,\, i\to s} - E \, \delta_{ij} \, \delta_{ts} \right| = 0 \quad 1.22$$

Using the SCF MO's the diagonal elements of eq. 1.22 are given by eq. 1.18 and the off-diagonal elements are

$$H_{j\to t,\, i\to s} = 2(jt||is) - (ij||st) \quad 1.23$$

where $(jt||is) = \int \psi_j(1)\, \psi_t(1) \frac{1}{r_{12}} \psi_i(2)\, \psi_s(2)\, d\tau_1\, d\tau_2$

By expansion of the MO's ψ_i in the set of the atomic orbitals (eq. 1.7) and using the approximation (eq. 1.10) of PPP, the integrals (jt||is) can easily be calculated.

Because of the use of the SCF MO's the interaction elements between the ground state and the singly excited states vanish (theorem of Brillouin). It follows that the energy of the ground state is not influenced by this restricted configuration interaction and that the ground state does not appear in equation 1. 19.

The eigenvalues of the equations 1. 20 represent the excitation energies of the molecule, while the coefficient $c_{A,is}$ is the contribution of configuration $\Phi_{i\rightarrow s}$ to the state Φ_A. The oscillator strength f for an electronic transition between the ground state Φ_0 and an excited singlet state Φ_A is given by

$$f = 1.085 \times 10^{11} \times \nu \times \vec{M}_{OA}^{\;2} \qquad 1.24$$

where ν is the frequency of the transition in cm^{-1}

$\vec{M}_{OA}$ is the transition moment between the states Φ_O and Φ_A

$$\vec{M}_{OA} = \langle \Phi_o \mid \sum_i \vec{r}\,(i) \mid \Phi_A \rangle \qquad 1.25$$

the summation i being over all π-electrons and $\vec{r}(i)$ is the position vector of electron i.

Using the equation 1. 19 and the expansion 1. 7 the oscillator strengths can be calculated. Subject to the neglect of overlap the matrix elements of $\vec{r}$ in the atomic orbital basis are

$$\langle \varphi_\mu (1) \mid \vec{r}\,(1) \mid \varphi_\nu (1) \rangle = \vec{r}_\mu \; \delta_{\mu\nu} \qquad 1.26$$

where $\vec{r}_\mu$ is the position vector of atom μ.

The performance of the calculation of self-consistent field molecular orbitals and excitation energies according to the method of Pariser, Parr en Pople is very suitable for electronic computers. A computer program has been written, in cooperation with drs. J. J. C. Mulder, in Algol 60 for the electronic computer X 1 and converted later into a Fortran IV version for the IBM 360-50.

The results of the calculations for a number of substituted aromatic molecules and carbonium ions are given in Chapter IV. Special attention has been paid to the parameters for the hetero atoms nitrogen, oxygen and sulfur.

A4. JUSTIFICATION OF THE ZERO DIFFERENTIAL OVERLAP APPROXIMATION.

The assumption of zero differential overlap needs a justification. If the atoms μ and ν are at a distance of 1.39 Å the overlap integral of the p orbitals is 0.25 and the electronic repulsion integral $(\mu\mu || \mu\nu)$ is 3.31 e.V. It is therefore surprising that calculated excitation energies in the order of 4 e.V. are in good agreement with experimental data.

Zero differential overlap suggests that orthogonalized atomic orbitals ($\underline{\text{AO}}$) are being used instead of the overlapping atomic orbitals (AO). The $\underline{\text{AO}}$'s can be obtained from the AO's by a orthogonalization procedure proposed by Löwdin[12]:

$$\underline{\varphi} = \varphi \, S^{-\frac{1}{2}} \qquad 1.27$$

where $\varphi = (\mu, \nu, \rho \, \ldots\ldots\ldots)$

$\underline{\varphi} = (\underline{\mu}, \underline{\nu}, \underline{\rho} \, \ldots\ldots\ldots)$

S = the overlap matrix of the AO's.

The advantage of the orthogonalization procedure of Löwdin in comparison with other procedures is that the $\underline{\text{AO}}$'s are very similar to the original atomic orbitals.

If we assume that we are using these $\underline{\text{AO}}$'s as our basis set, the overlap integrals are strictly vanishing. It appears that also the electronic repulsion integrals containing at least one charge distribution with one electron in two different $\underline{\text{AO}}$'s become very small. In table 1-I some values are given for benzene. The AO's are Slater orbitals and the orbitals μ, ν, ρ and σ are situated along the ring in this order. The values are taken from McWeeny[6].

Table 1-I.

Some electronic repulsion integrals for benzene in e.V. using AO's and $\underline{\text{AO}}$'s as basis set.

Integrals	AO's	$\underline{\text{AO}}$'s
$(\mu\mu \| \mu\mu)$	16.93	17.62
$(\mu\mu \| \nu\nu)$	9.03	8.92
$(\mu\mu \| \rho\rho)$	5.67	5.57
$(\mu\mu \| \sigma\sigma)$	4.97	4.88
$(\mu\mu \| \mu\nu)$	3.31	-0.12
$(\mu\mu \| \nu\rho)$	1.87	-0.05
$(\mu\mu \| \rho\sigma)$	1.42	0.04
$(\mu\nu \| \mu\nu)$	0.92	0.09
$(\mu\nu \| \nu\rho)$	0.68	0.02

It can be seen from Table 1-I that neglecting differential overlap is justified by the consideration that we use orthogonalized atomic orbitals. Furthermore, the repulsion integrals which do not contain a charge distribution of the type μ, ν are only slightly influenced by the transformation from AO's to $\underline{\text{AO}}$'s.

PART B THE VALENCE BOND THEORY.

B1 THE CLASSICAL VALENCE BOND THEORY.

The Valence Bond (VB) method was initiated by Heitler and London[1], who were the first to treat the problem of the hydrogen molecule by a quantum-mechanical method. The ground state of H_2 is represented by an antisymmetrized product of atomic wave functions and a singlet spin function.

$$\Phi = \frac{1}{\sqrt{2(1+S^2)}} \sum_P (-1)^P \; P\, a(1)b(2)\; [1,2] \qquad 1.28$$

where a and b are the ls functions of the two hydrogen atoms

[1, 2] is the singlet spin eigenfunction $\frac{\alpha_1\beta_2 - \beta_1\alpha_2}{\sqrt{2}}$

$S = \int a(1)b(1)\, d\tau_1$ assuming that the atomic orbitals are real.

The energy associated with this function is

$$E = \frac{Q + K}{1 + S^2} \qquad 1.29$$

$Q = \int a(1)b(2)\, H\, a(1)b(2)\, d\tau_1\, d\tau_2$ is called the Coulomb integral

$K = \int a(1)b(2)\, H\, b(1)a(2)\, d\tau_1\, d\tau_2$ is called the exchange integral.

The Coulomb as well as the exchange integral contribute to the stability of the hydrogen molecule. It is emphasized that the greater part of the binding energy arises from the exchange term, the Coulomb energy being only 10 - 15 per cent of the total.

The example of the hydrogen molecule shows the way to treat localized bonds in a molecule. The binding energy of a C - H bond and a single C - C bond is nearly constant in a large number of organic molecules. Such bonds can, therefore, be treated with the VB method as separate two-electron problems. If in a molecule the bonds must be drawn in an apparently unique way a function like 1.28 can be written for each bond, the spins perfectly paired. The unnormalized wave function of the molecule is represented by a product of these two-electron VB functions antisymmetrized for all the electrons

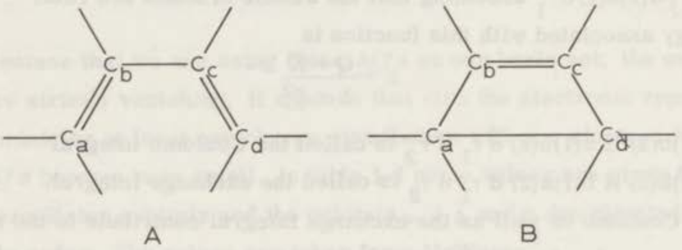
$$\Phi = \sum_P (-1)^P \; P\, a(1)b(2)\, [1,2]\;\; c(3)d(4)\, [3,4] \;\ldots \qquad 1.30$$

Neglecting the overlap integrals of the atomic orbitals, as is usual in applications to larger systems, the energy associated with this structure is found to be

$$E = Q + \sum_{\substack{p,q\\ \text{paired}}} K_{pq} - \tfrac{1}{2} \sum_{\substack{p,q\\ \text{different}\\ \text{pairs}}} K_{pq} \qquad 1.31$$

where K_{pq} is the exchange integral of the atoms p and q. It is clear that the VB method is closely related to the chemical language: the structures.

In many cases, however, there are more possibilities for the covalent structures corresponding to different bond allocations. These must then be allowed to mix for a representation of the state of the molecule. The π-electron system of butadiene may serve as an illustrative example. The π-electron bonds can be drawn in two ways



where
$$\psi_A = \frac{1}{\sqrt{12}} \sum_P (-1)^P \; P\, a(1)b(2)\,[1,2]\; c(3)d(4)\,[3,4]$$
$$\psi_B = \frac{1}{\sqrt{12}} \sum_P (-1)^P \; P\, a(1)d(2)\,[1,2]\; b(3)c(4)\,[3,4]. \qquad 1.32$$

There still exists a third possibility where the spins of a and c and the spins of b and d are paired. It can be shown that the wave function corresponding to this structure is a linear combination of ψ_A and ψ_B. Pauling[13] called the structures A and B "canonical" and Rumer[14] has introduced diagrams in order to select a complete, linear independent set of these canonical structures.

The wave function of butadiene is a linear combination of ψ_A and ψ_B:

$$\Phi = c_A \psi_A + c_B \psi_B \qquad 1.33$$

the constants c_A and c_B chosen in such a way that the energy is minimized in accordance with the variation principle. This gives an explanation for the phenomenon of resonance, one of the most fascinating results of the application of quantum mechanics in chemistry.

In general the energy expression can be written in the form

$$E = Q + \sum_{p,q} d_{pq} K_{pq} \tag{1.34}$$

the coefficients d_{pq} being determined by solution of the secular equations. The Coulomb and exchange integrals are not usually computed but are taken from experimental data.

Representing molecules with a set of covalent structures gives a satisfactory description of the ground state. The approximation will certainly be much worse for excited states. Polar structures in which the electrons are not uniformly distributed must play a more important role for excited states[15]. In addition, the impossibility of obtaining non-zero transition moments is another serious shortcoming of the covalent approximation. Sklar[16] made an attempt to include polar structures in his calculations on benzene and assigned the strong absorption band at 1830 Å to a transition to a purely polar state.

Another defect in the application of the VB method is the neglect of the overlap integrals between the atomic orbitals. Slater[17] has shown that if the exchange integral is evaluated explicitly, the neglect of overlap leads to a positive value. That means that the VB method with neglect of overlap does not give any explanation of chemical bonding.

B2 THE APPROXIMATIONS OF PARISER, PARR AND POPLE IN THE VALENCE BOND THEORY.

It has already been mentioned that the approximations of Pariser, Parr and Pople (PPP) can be justified by the supposition that orthogonalized atomic orbitals (AO) are employed. The introduction of the approximations in the VB theory means therefore that the VB structures are based upon these AO's. This reformulated VB method (the VB method) has been described in a number of papers by McWeeny[6]. The adjustment of the one-center electronic repulsion integrals has not, however, been used in his applications on cyclobutadiene and benzene. The differential overlap has only been neglected in the evaluation of some matrix elements for benzene.

In our treatment we have consistently applied the PPP approximations

(A2) in the VB theory. We will restrict the discussion to singlet states of π-electron systems and assume that the number of orbitals and electrons are equal, although a generalization can be made rather easily.

The state of a molecule is described in the complete valence bond method by a superposition of covalent and polar structures. In a covalent structure there is one electron in each orbital. In the polar structures the electrons are not uniformly distributed, but some orbitals have no electrons and others have two with opposite spin. Inclusion of the polar structures in the VB method is necessary in order to describe bond formation and resonance stabilization. The linearly independent set of covalent structures, the canonical structures, are easily obtained from the diagrams of Rumer. For the polar structures the same rule can be applied to the orbitals occupied by one electron. The ground and excited states of a molecule are represented by a linear combination of the wave functions corresponding to these structures:

$$\Phi = \sum_I A_I \psi_I^{CS} + \sum_J B_J \psi_J^{SP} + \sum_K C_K \psi_K^{DP} + \cdots\cdots \qquad 1.35$$

where ψ_I^{CS} is a covalent structure

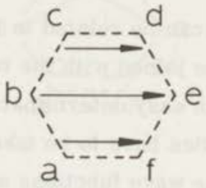
ψ_J^{SP} is a singly polar structure with one positive and one negative charge in the molecule

ψ_K^{DP} is a doubly polar structure with two positive and two negative charges in the molecule.

The energies and the coefficients are determined by the variation method using the π-electron Hamiltonian (equation 1. 2).

In general, a large number of structures is required in the VB method in order to obtain a good description of a state of a molecule. In addition, the number of structures increases rapidly with the size of the molecule. This involves calculating an extensive number of matrix elements of the Hamiltonian taking up much time and tedious labour. Applying the approximations of PPP the matrix elements become very simple although the number remains equally large.

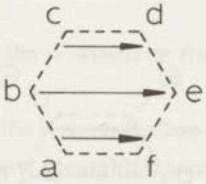
The first task is to accurately fix the sign of the wave functions corresponding to the structures. For the covalent structures (CS) the orbitals are arranged in alphabetic order, electron 1 is assigned to the first orbital, electron 2 to the second and so on. In addition, a graphic picture derived from the Rumer diagrams and introduced by Pauling in the valence bond theory is used. The Dewar structure of benzene for example



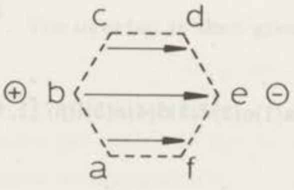
corresponds to the wave function

$$\psi^{CS} = \mathscr{A}\, a(1)b(2)c(3)d(4)e(5)f(6)\,[1,6][2,5][3,4]$$

where $\mathscr{A}$ is the antisymmetrization operator including normalization. Reversal of the direction of an arrow gives an identical wave function except for a change of sign. The wave function of a singly polar structure can be fixed by relating them to the corresponding covalent structure. The orbitals remain in the same order and the orbital of the atom with the positive charge is replaced by that with the negative charge. The spin function is determined by the CS. For example, to the CS of benzene



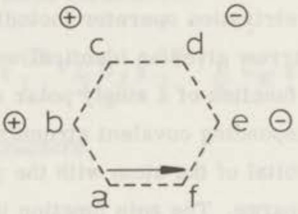
is related the polar structure



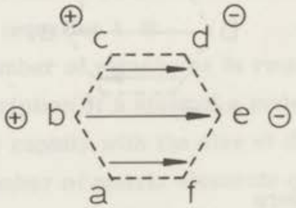
This singly polar structure corresponds to the wave function

$$\psi^{SP} = \mathscr{A}\ a(1)e(2)c(3)d(4)e(5)f(6)\ [1,6]\,[2,5]\,[3,4].$$

A doubly polar structure can be related to two covalent structures since the two positive charges can be joined with the two negative charges in two ways. It will appear that for an easy determination of the matrix elements of the Hamiltonian both possibilities have to be taken into account. In order to take care that in both cases the wave functions are identical the arrows must be directed in such a way that the number of arrow heads on the positive and negative atoms differ by one in the two pictures. For example, the doubly polar structure of benzene



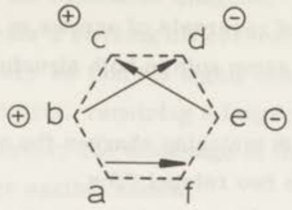
can be represented in two pictures:



with the wave function

$$\psi^{DP} = \mathscr{A}\ a(1)e(2)d(3)d(4)e(5)f(6)\ [1,6]\,[2,5]\,[3,4]$$

and



with the wave function

$$\psi^{DP} = \mathscr{A}\, a(1)d(2)e(3)d(4)e(5)f(6)\ [1,6]\,[2,4][5,3].$$

It can easily be shown that both wave functions are identical. For higher polar structures similar rules have to be used.

Having defined the wave functions of the structures in this unambiguous fashion the problem is to solve the secular equations

$$\sum_J A_J H_{IJ} = E_I \sum_J A_J S_{IJ} \qquad 1.36$$

where $S_{IJ} = \int \psi_I \psi_J \, d\tau$

$$H_{IJ} = \int \psi_I H \psi_J \, d\tau$$

H is the π-electron Hamiltonian (equation 1. 2).

The derivation of the rules for the determination of the elements of the overlap and the Hamiltonian matrix is now straightforward.

The elements of the overlap matrix are unequal to zero if the wave functions ψ_I and ψ_J correspond to structures with the same charge distribution ("matching charges" in the terminology of McWeeny). For two CS's the overlap integral can easily be calculated by the construction of a superposition pattern of the two structures[13]. The overlap is then given by

$$S_{IJ} = (-1)^{\nu}\, 2^{i-n}$$

where i = the number of "islands" in the superposition pattern
n = the number of arrows in a structure
ν = the number of reversals of arrows in order to assign to each electron the same spin in both structures.

For two polar structures with matching charges the overlap integral is equal to the overlap integral of the two related CS's.

The elements of the Hamiltonian matrix do not equal zero if the wave functions ψ_I and ψ_J correspond to structures with matching charges or which differ by one charge shift only.

I. Diagonal elements.
All CS's have the same energy, which we will take equal to zero. The energy of a polar structure is calculated by summation of all repulsions of ⊕ with ⊕ and ⊖ with ⊖ charges and all attractions of ⊕ with ⊖ charges. For each negative charge a one-center repulsion integral is included in the summation. Empirical values of the MO theory can be used for the repulsion and attraction integrals.

II. Non-diagonal elements.
Matching charges: $H_{IJ} = S_{IJ}\, H_{II}$.
One charge shift: let us say that the two structures differ in a charge shift between the atoms e and f. The matrix element is proportional to the resonance integral β_{ef} between the two atoms. Apart from the atoms e and f, charged atoms in the two structures must be joined in the same way by arrows in the diagrams. For SP with SP, DP with DP structures and so on the matrix elements are given by

$H_{IJ} = 2\, S_{IJ}\, \beta_{ef}$ if the two structures differ by the position of the negative charge,

$H_{IJ} = -2\, S_{IJ}\, \beta_{ef}$ if the two structures differ by the position of the positive charge.

For CS with SP, SP with DP structures and so on the matrix elements are given by

$$H_{IJ} = S_{IJ}\, \beta_{ef}\, \sqrt{2}$$

The formulae for the elements of the interaction matrix of the <u>VB</u> structures remain equally simple on introduction of hetero atoms: the diagonal elements contain the one-center core integrals and electronic repulsion integrals, the non-diagonal elements the resonance integrals. A comparison with the molecular orbital theory reveals a striking difference: instead of the simple matrix elements of the VB theory we find the highly complicated expressions of the configuration interaction matrix, requiring a lengthy calculation. The molecular orbital theory has, however, the advantage of the simple first approximation to the ground and lower excited states.

In conclusion we can say that for complete calculations on π-electron systems the VB method is more appropriate than the MO theory. The results of the VB calculations on butadiene and benzene are given in Chapter II and compared with the results of molecular orbital calculations. In addition, the complete VB method has been used in Chapter III in a study of the course of electrocyclic reactions.

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CHAPTER II

APPLICATION OF THE VALENCE BOND THEORY TO ETHYLENE, BUTADIENE AND BENZENE

1. INTRODUCTION

In order to obtain more insight into the merits of the Valence Bond theory, based on orthogonalized atomic orbitals (VB), it has been applied to the π-electron systems of ethylene, butadiene and benzene. For these molecules all singlet structures, 3, 20 and 175 respectively, can be included in the calculations without too much effort.

In all the calculations in this Chapter the electronic repulsion integrals have been taken from Pariser and Parr[1] and the resonance integrals have been calculated from the formula

$$\beta_{ab} = -11.22\, S_{ab} \text{ e.V.}$$

With the same parametrization a complete molecular orbital calculation on benzene has been published by Koutecky et al[2]. Since the results from both methods have to be the same it is easy to verify the correctness of the calculations for benzene. Furthermore, it is interesting to compare a number of restricted VB and MO calculations in which some of the structures and configurations have been omitted.

2. ETHYLENE

Slater[3] has pointed out that the use of orthogonalized atomic orbitals in the Heitler-London treatment of the hydrogen molecule does not lead to a stable ground state unless polar structures are included. It is to be expected that Valence Bond (VB) calculations on the two π-electrons of ethylene using the approximations of Pariser, Parr and Pople will lead to a similar situation.

1. For a valence bond calculation on ethylene three singlet structures are available. Two structures are symmetric (s) and one is antisymmetric (a) with respect to the plane of symmetry perpendicular to the carbon-carbon bond.

covalent structure : $\psi_s^{CS} = \mathscr{A}\, ab\, [1,2]$

polar structures : $\psi_s^{P} = \mathscr{A}(aa+bb)\, [1,2]$

$\psi_a^{P} = \mathscr{A}(aa-bb)\, [1,2]$

where a and b represent the orthogonalized 2p orbitals on the two carbon atoms. Symmetric states are described by linear combinations of the wave functions corresponding to the two symmetric structures. In order to obtain the energies and the coefficients of the structures according to the variation principle a two by two matrix has to be diagonalized:

$$\begin{pmatrix} 0 & 2\beta_{ab} \\ 2\beta_{ab} & \gamma_{aa}-\gamma_{ab} \end{pmatrix}$$

In general, the energy of the state with the highest multiplicity has been chosen as the zero on the energy scale. This turns out to be equal to the energy of the covalent structures within the approximations used.

Taking the carbon-carbon distance equal to 1.34 Å the parameters are

$\beta_{ab} = -\ 3.05$ e. V.

$\gamma_{aa} = \ 10.53$ e. V.

$\gamma_{ab} = \ 7.40$ e. V.

The energies and wave functions for the ground state and excited states are found to be:

ground state : E = -4.73 e. V. $\Phi = 0.79\, \psi_s^{CS} + 0.61\, \psi_s^{P}$

antisymm. excited state: E = 3.13 e. V. $\Phi = \psi_a^{P}$

symm. excited state : E = 7.86 e. V. $\Phi = 0.61\, \psi_s^{CS} - 0.79\, \psi_s^{P}$

Anticipating the discussion in section 5 we can state that chemical binding in the π-bond of ethylene is represented by the interaction of the covalent structure with the symmetric polar structure.

2. For a molecular orbital calculation on ethylene three configurations are available. The MO's are fixed by the symmetry of the molecule:

$$\psi_s = \frac{1}{\sqrt{2}}\,(a+b) \qquad\qquad \psi_a = \frac{1}{\sqrt{2}}\,(a-b).$$

Using these molecular orbitals two symmetric and one antisymmetric singlet configuration can be constructed:

the ground configuration : $\Phi_s^{O} = |\psi_s \overline{\psi}_s|$

the singly excited configuration : $\Phi_a^{SE} = \frac{1}{\sqrt{2}} \left\{ |\psi_s \overline{\psi}_a| - |\overline{\psi}_s \psi_a| \right\}$

the doubly excited configuration: $\Phi_s^{DE} = |\psi_a \overline{\psi}_a|$

Symmetric states are represented by linear combinations of the wave functions corresponding to the ground and the doubly excited configuration. Taking again the energy of the covalent structure as the energy zero the two by two matrix which has to be diagonalized is

$$\begin{pmatrix} \frac{1}{2}(\gamma_{aa} - \gamma_{ab}) + 2\,\beta_{ab} & \frac{1}{2}(\gamma_{aa} - \gamma_{ab}) \\ \frac{1}{2}(\gamma_{aa} - \gamma_{ab}) & \frac{1}{2}(\gamma_{aa} - \gamma_{ab}) - 2\,\beta_{ab} \end{pmatrix}$$

The energies and the wave functions for the ground and excited states are given by:

ground state : $E = -4.73$ e. V. $\quad \Phi = 0.99\,\Phi_s^{O} - 0.13\,\Phi_s^{DE}$

antisymm. excited state: $E = 3.13$ e. V. $\quad \Phi = \Phi_a^{SE}$

symm. excited state : $E = 7.86$ e. V. $\quad \Phi = 0.13\,\Phi_s^{O} + 0.99\,\Phi_s^{DE}$

3. In addition, a valence bond (VB) calculation can be carried out based on the non-orthogonalized atomic orbitals. These orbitals and related parameters can be obtained by transformation of the <u>AO</u>'s with the $S^{+\frac{1}{2}}$ matrix. The results are:

ground state : E = -4.73 e.V. $\Phi = 0.70\,\psi_s^{CS} + 0.45\,\psi_s^{P}$
antisymm. excited state: E = 3.13 e.V. $\Phi = \psi_a^{P}$
symm. excited state : E = 7.86 e.V. $\Phi = 0.92\,\psi_s^{CS} - 1.07\,\psi_s^{P}$

It should be mentioned that the overlap integral between the wave functions corresponding to the covalent and the symmetric polar structure equals 0.50.

The energies of the states resulting from the molecular orbital and the two valence bond calculations are equal and one can easily show that the wave functions are also identical as should be the case. In table 2-I some interesting data have been summarized. The numbers in column 4 represent the overlap between the ground state wave functions resulting on the one hand from the complete calculation and on the other hand from the first approximations according to the different methods. It is clear that the MO method has the advantage of the best first approximation whereas that of the $\underline{\mathrm{VB}}$ method is rather bad.

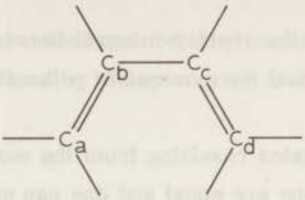
Table 2-I

A comparison of the first approximations according to the $\underline{\mathrm{VB}}$, the VB and the MO method applied to ethylene.

	ground state energy	first excitation energy	overlap
$\underline{\mathrm{VB}}$ first approximation	0 e.V.	3.13 e.V.	0.79
VB first approximation	-2.87 e.V.	6.00 e.V.	0.93
MO first approximation	-4.535 e.V.	7.665 e.V.	0.99
complete calculation	-4.73 e.V.	7.86 e.V.	1.00

3. BUTADIENE.

For a complete π-electron calculation on the singlet states of butadiene twenty structures have to be taken into account in the valence bond theory and twenty configurations in the molecular orbital theory. The calculations have been performed on *cis*-butadiene although it is unstable in favour of the transoid form. The cisoid form, however, is generally accepted as the initial conformation for the photoinduced ringclosure to cyclobutene. In connexion with this electrocyclic reaction which will be treated in Chapter III, we will discuss the results of the calculations on the cisoid form. The excitation energies and the contributions of the VB structures and MO configurations to the states of the molecule are essentially the same for the transoid conformation.



Concerning the geometry we have assumed the molecule to be planar with bond angles 120° and carbon-carbon distances 1.34 Å for C_a-C_b and C_c-C_d and 1.47 Å for C_b-C_c. The parameters are summarized in table 2-II.

Table 2-II

The parameters used in the calculations on *cis*-butadiene.

	r	β	γ
a-b, c-d	1.34 Å	-3.05 e.V.	7.40 e.V.
b-c	1.47 Å	-2.49 e.V.	7.15 e.V.
a-d	2.81 Å	-	4.87 e.V.
a-c, b-d	2.44 Å	-	5.45 e.V.

1. For a complete valence bond calculation twenty structures have to be included:

2 covalent structures : A, B
12 singly polar structures
    4 with adjacent charges and a short bond : C, D, E, F
    4 with adjacent charges or a short bond : G, H, I, K
    4 other structures : L, M, N, O
6 doubly polar structures : P, Q, R, S, T, U.

The meaning of these symbols is explained in figure 2-1.

The energies of the ground state and the two lowest excited states are given in table 2-III, together with the contributions of the structures taking part in these states. One excited state is antisymmetric, the other symmetric with respect to the symmetry plane perpendicular to the C_b-C_c bond. The transition to the antisymmetric excited state has an oscillator strength of 0.31, while the transition to the symmetric state is forbidden. The UV spectrum of *trans*-butadiene reveals that the allowed transition takes place at about 6.0 e.V. For *cis*-butadiene this value will be nearly the same, in agreement with the calculated excitation energy of 5.91 e.V.

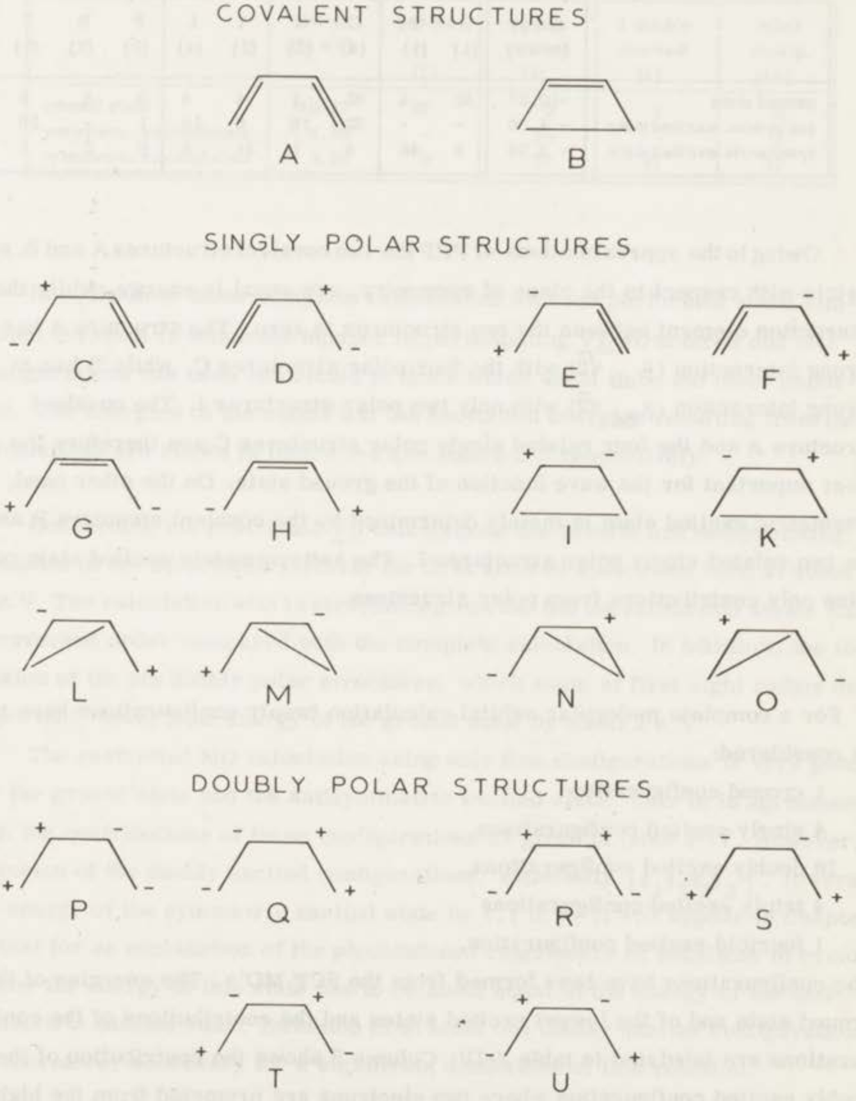


Fig. 2-1. The twenty valence bond structures of butadiene.

Table 2-III

The energies of the ground state and the two lowest excited states of *cis*-butadiene together with the contributions of the VB structures in per cents. The numbers in parentheses represent the number of similar structures.

		covalent		singly polar				doubly polar		
	energy (in eV)	A (1)	B (1)	C (4)	G (2)	I (2)	L (4)	P (2)	R (2)	T (2)
ground state	-10.27	32	4	42	1	4	4	0	5	8
antisymm. excited state	- 4.36	-	-	32	16	6	19	1	-	26
symmetric excited state	- 3.56	4	46	4	1	34	8	0	2	1

Owing to the approximations of PPP the two covalent structures A and B, symmetric with respect to the plane of symmetry, are equal in energy, while the interaction element between the two structures is zero. The structure A has a strong interaction ($\beta_{ab}\sqrt{2}$) with the four polar structures C, while B has a strong interaction ($\beta_{bc}\sqrt{2}$) with only two polar structures I. The covalent structure A and the four related singly polar structures C are therefore the most important for the wave function of the ground state. On the other hand, the symmetric excited state is mainly determined by the covalent structure B and the two related singly polar structures I. The antisymmetric excited state contains only contributions from polar structures.

2. For a complete molecular orbital calculation twenty configurations have to be considered:

1 ground configuration
4 singly excited configurations
10 doubly excited configurations
4 triply excited configurations
1 fourfold excited configuration.

The configurations have been formed from the SCF MO's. The energies of the ground state and of the lowest excited states and the contributions of the configurations are tabulated in table 2-IV. Column 5 shows the contribution of the doubly excited configuration where two electrons are promoted from the highest occupied to the lowest unoccupied molecular orbital: $|\psi_1\bar{\psi}_1\psi_3\bar{\psi}_3|$. This configuration plays an important part in the symmetric excited state.

Table 2-IV

The energies of the ground state and the two lowest excited states of *cis*-butadiene together with the contributions of the MO configurations in per cents. The numbers in parentheses represent the number of configurations.

	energy (in eV)	ground (1)	singly excited (4)	1 doubly excited (1)	other config. (14)
ground state	-10.27	97	0	1	2
antisymm. excited state	- 4.36	-	99	-	1
symmetric excited state	- 3.56	0	57	31	12

In addition to these complete calculations we have performed some simplified versions in which the number of participating VB structures and MO configurations has been restricted to those which seem to be the most important. The energies of the states and the excitation energies resulting from these calculations are shown in figure 2-2 and figure 2-3 respectively.

Concerning the restricted VB calculations the results are disappointing. Inclusion of ten structures predicts the first allowed absorption band at about 11 e.V. The calculation with 14 structures gives the two lowest excited states still in reversed order compared with the complete calculation. In addition, the inclusion of the six doubly polar structures, which seem at first sight rather unimportant, lowers the energy of the ground state by about 2 e. V.

The restricted MO calculation using only five configurations is very good for the ground state and the antisymmetric excited state. This is in agreement with the contributions of these configurations as given in table 2-IV. However, inclusion of the doubly excited configurations, especially $|\psi_1\bar{\psi}_1\psi_3\bar{\psi}_3|$, lowers the energy of the symmetric excited state by 1.7 e. V. It will appear in Chapter III that for an explanation of the photoinduced ringclosure of butadiene to cyclobutene the energy of this state has to be about equal to the energy of the antisymmetric excited state. Inclusion of at least one doubly excited configuration is, therefore, necessary for a significant discussion of this reaction.

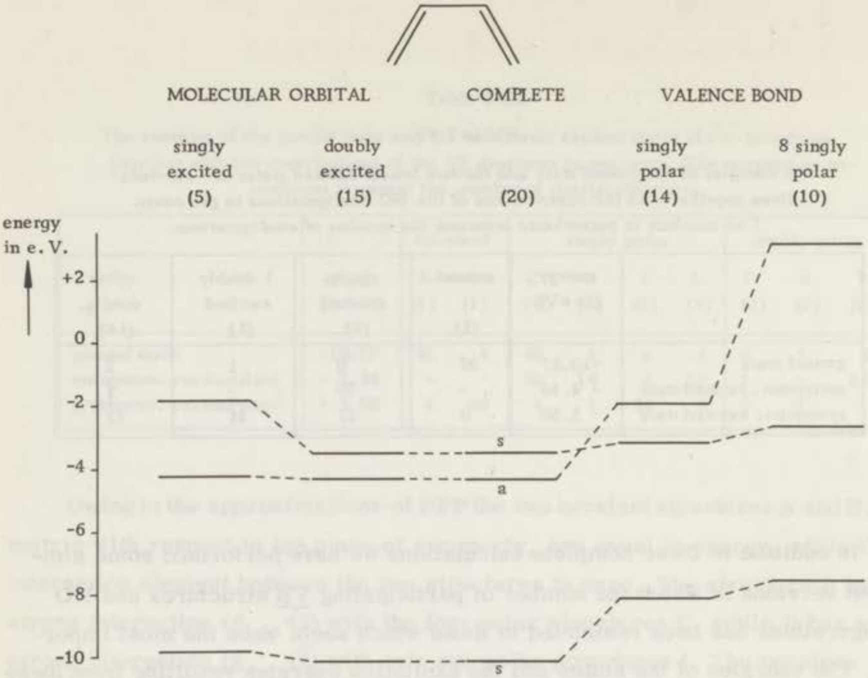


Fig. 2-2. The energies of the ground state and the two lowest excited states of *cis*-butadiene. The numbers in parentheses represent the number of configurations or structures. In all of the MO calculations the ground configuration and in all of the VB calculations the two covalent structures are included.

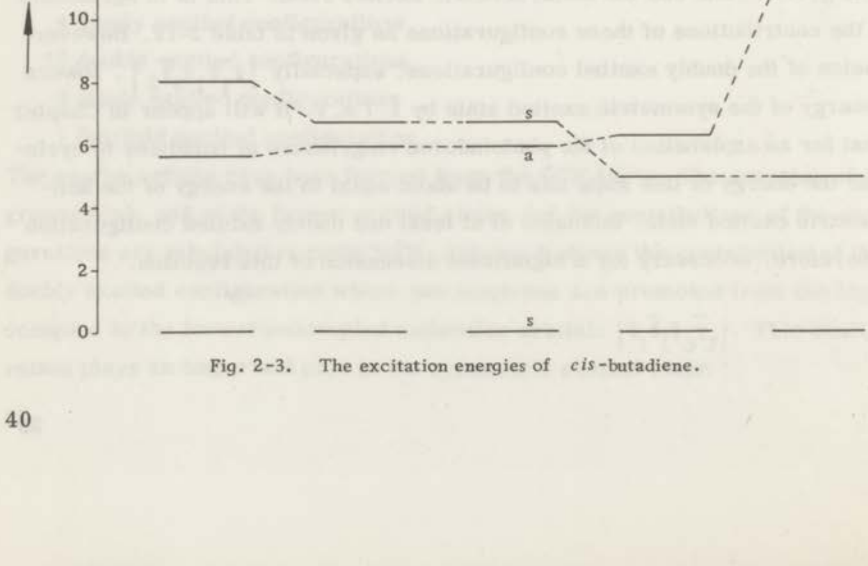


Fig. 2-3. The excitation energies of *cis*-butadiene.

4. BENZENE.

For complete calculations on the π-electron system of benzene 175 structures or configurations are available.

1. The 175 valence bond structures can be arranged in the following way:

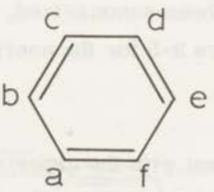
5 covalent structures : 2 Kekulé structures
3 Dewar structures
60 singly polar structures : 24 with adjacent charges
36 with non-adjacent charges
90 doubly polar structures
20 triply polar structures .

Valence bond calculations for benzene with orthogonalized atomic orbitals have been described by McWeeny^4. He has included, however, only 36 of the doubly polar structures and has completely neglected the triply polar structures. In contrast with our parameters McWeeny has used theoretical values for the electronic repulsion integrals.

In our calculations all 175 structures have been included. In order to reduce the order of the matrices which have to be diagonalized, we took advantage of the molecular symmetry. The use of only one plane of symmetry splits the total matrix into a block of 92 and a block of 83. The former consists of matrix elements between symmetric combinations, the latter of elements between antisymmetric combinations with respect to the plane of symmetry.

Applying the rules of Chapter I the matrices can be constructed rather easily. The semiempirical parameters are:

$\beta = -\ 2.805$ e. V.
$\gamma_{aa} = 10.53$ e. V.
$\gamma_{ab} = 7.30$ e. V.
$\gamma_{ac} = 5.46$ e. V.
$\gamma_{ad} = 4.90$ e. V.



The states can be classified according to the symmetry group of the benzene molecule. The states with the lowest energy transforming according to the irreducible representations A_{1g}, B_{1u}, B_{2u}, E_{1u} and E_{2g} are shown in table 2-V. The contributions of the structures have been given together with the energies.

Table 2-V

The energies and the contributions of the VB structures in per cents for the states of benzene.

state	energy	covalent		singly polar		doubly polar	triply polar
		Kekulé	Dewar	adjacent charges	non-adjacent charges		
		(2)	(3)	(24)	(36)	(90)	(20)
A_{1g}	-17.71 e.V.	12	3	33	14	34	4
B_{2u}	-12.50 e.V.	26	-	45	3	23	3
B_{1u}	-11.39 e.V.	-	-	17	20	49	14
E_{1u}	-10.24 e.V.	-	-	21	37	38	4
E_{2g}	- 9.41 e.V.	-	29	41	13	17	0

2. A complete molecular orbital calculation on benzene with the same parametrization has been described by Koutecky et al[2]. The values for the energies of the states are in excellent agreement with our calculations: the differences are always smaller than 0.01 e.V. This suggest that errors which can appear very easily, have been avoided.

In a number of papers[5, 6] Koutecky has also published some restricted molecular orbital calculations including successively singly, doubly and triply excited configurations. We have performed some restricted VB calculations. The results have been summarized, together with those from Koutecky, in figure 2-4 and figure 2-5 for the energies of the states and the excitation energies respectively.

The agreement with the experimental absorption bands is rather good for the complete calculation. The UV spectrum consists of weak bands at 4.8 e.V. and 6.0 e.V. and a strong band at 7.0 e.V., while the calculated values for the forbidden transitions are 5.21 e.V. and 6.32 e.V. and 7.47 e.V. for the allowed one. A lower absolute value for the resonance integral makes the agreement still better. For $\beta = -2.60$ e.V. the calculated excitation energies are 4.76, 5.93 and 7.04 e.V.

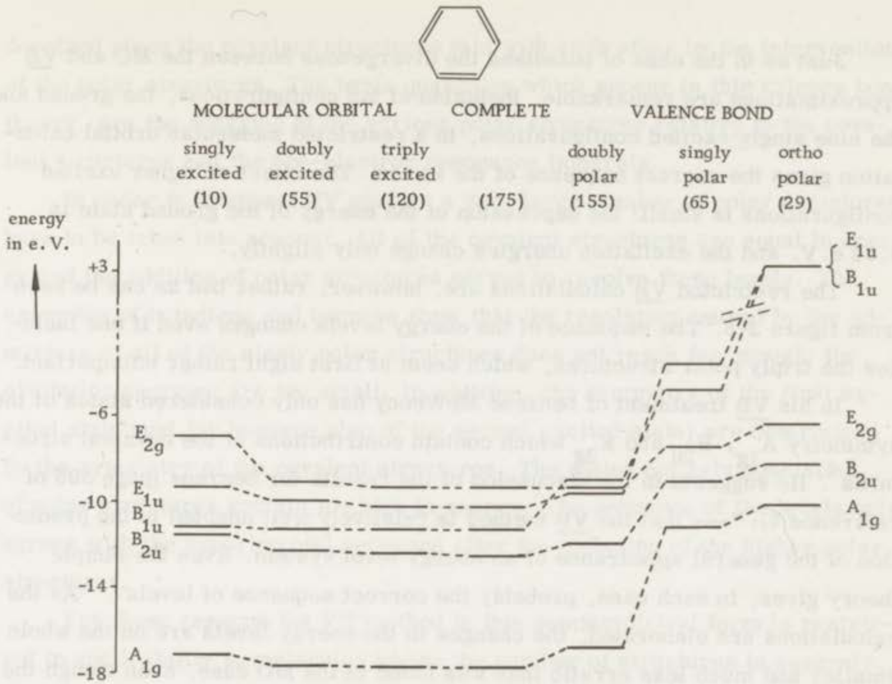


Fig. 2-4. The energies of the ground state and the excited states of benzene. The numbers in parentheses represent the number of configurations or structures. The MO data have been taken from Koutecky.

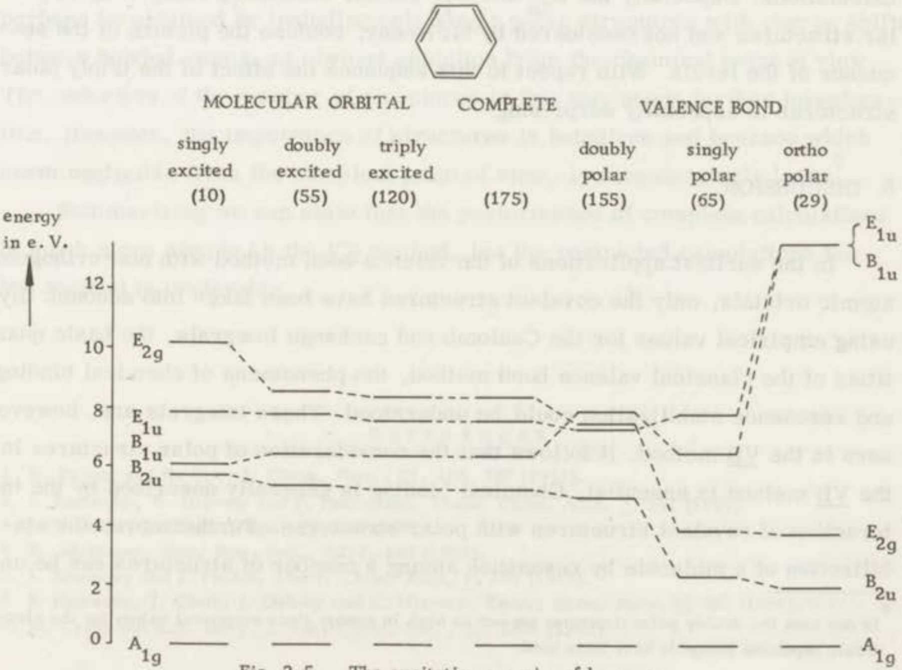


Fig. 2-5. The excitation energies of benzene.

Just as in the case of butadiene the divergences between the MO and VB approximations are remarkable. Inclusion of ten configurations, the ground and the nine singly excited configurations, in a restricted molecular orbital calculation gives the correct sequence of the states. The effect of higher excited configurations is small: the depression of the energy of the ground state is 0.52 e.V. and the excitation energies change only slightly.

The restricted VB calculations are, however, rather bad as can be seen from figure 2-5. The sequence of the energy levels changes even if one includes the triply polar structures, which seem at first sight rather unimportant.

In his VB treatment of benzene McWeeny has only considered states of the symmetry A_{1g}, B_{2u} and E_{2g} which contain contributions of the covalent structures[4]. He suggests in the discussion of the results for benzene (page 306 of reference 4): "--- that the VB method is relatively well adapted to the prediction of the general appearance of an energy level system. Even the simple theory gives, in each case, probably the correct sequence of levels". "As the calculations are elaborated, the changes in the energy levels are on the whole smaller and much less erratic than was found in the MO case, even though the importance of doubly polar structures (which lie at least 25 eV above the ground state) is somewhat disturbing".[*] These suggestions are not confirmed by our calculations. Especially the E_{1u} and B_{1u} states, consisting completely of polar structures and not considered by McWeeny, confuse the picture of the sequence of the levels. With repect to this sequence the effect of the triply polar structures is especially surprising.

5. DISCUSSION.

In the earliest applications of the valence bond method with non-orthogonal atomic orbitals, only the covalent structures have been taken into account. By using empirical values for the Coulomb and exchange integrals, the basic quantities of the classical valence bond method, the phenomena of chemical binding and resonance stabilization could be understood. These integrals are, however, zero in the VB method. It follows that the consideration of polar structures in the VB method is essential. Chemical binding is generally described by the interaction of covalent structures with polar structures. Furthermore, the stabilization of a molecule by resonance among a number of structures can be un-

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[*] In our case the doubly polar structures are not so high in energy since empirical values for the electronic repulsion integrals have been used.

derstood since the covalent structures mix with each other by the intervention of the polar structures. The basic quantities which appear in this valence bond theory, are the energies of the various polar structures relative to the covalent structures and the one-electron resonance integrals.

In order to interpret UV spectra a very large number of polar structures have to be taken into account. All of the covalent structures are equal in energy and the addition of polar structures serves to resolve these levels. The examples of butadiene and benzene show that the resolution caused by the admixture of all of the singly polar structures does not reach far enough: the excitation energies are too small. In addition, the symmetry of the first excited state (and for benzene also of the second excited state) are determined by the symmetry of the covalent structures. The states entirely consisting of polar structures remain too high in energy. The sequence of the levels only agrees with the experimental sequence after the inclusion of the higher polar structures.

For these reasons the VB method in this semiempirical form is restricted in applicability to molecules where the number of structures is severely limited. Concerning conjugated molecules, benzene with 175 singlet structures seems to be the present limit. On the other hand, for molecules with localized bonds a potentially useful selection can be made. A good approximation can perhaps be obtained by including only singly polar structures with charge shifts between bonded atoms: an obvious selection from the chemical point of view. The reduction of the number of structures in this way needs further investigation. However, the importance of structures in butadiene and benzene which seem negligible from the chemical point of view, is discouragingly large[7].

Summarizing we can state that the performance of complete calculations is much more simple in the VB method, but for restricted calculations the MO method is preferable.

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CHAPTER III

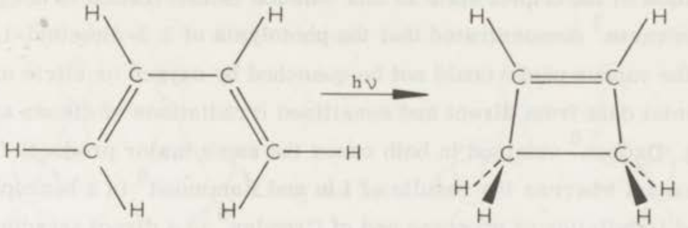
INTERPRETATION OF PHOTOINDUCED ELECTROCYCLIC REACTIONS

1. INTRODUCTION

Besides indicating the general importance of photochemistry as an useful tool in organic syntheses, the investigations in the Vitamin D field have led to the discovery of a highly interesting phenomenon. In a paper by Havinga and Schlatmann[1] the differences in thermal and photoinduced ringclosure of previtamin D have been clearly established. Apart from some other products, pyro- and isopyrocalciferol are formed in the thermal process whereas lumisterol and ergosterol are obtained in the photoinduced reaction. Both reactions are highly stereoselective but the stereoselectivity is different for the two processes. As mentioned in the paper by Havinga and Schlatmann, Oosterhoff pointed out that the symmetry characteristics of the highest occupied molecular orbital of the conjugated hexatriene system might be a factor contributing to the stereochemical difference between the thermal and photoinduced ringclosure. Concerning this suggestion Woodward[2] remarked: "He must have made this suggestion rather casually because Professor Havinga reported it in one of his papers in a single sentence, and the impact of that sentence on organic chemistry was not nearly as great as it deserves to have been".

The insight that symmetry is a general principle governing a large area of chemical reactions was formulated in a number of papers by Woodward and Hoffmann[3]. It forms the contents of the Woodward-Hoffmann rules which will be treated in section 2 in more detail.

Despite the general insight furnished by the Woodward-Hoffmann rules many aspects of the reaction mechanisms remain unexplained. The photochemical cyclization of butadiene to cyclobutene illustrates some of the remaining problems.



The energy scheme pertaining to this reaction, taken from Dauben[4], is given in figure 3-1. In discussing these data Dauben remarks: "When it is considered that in the ground state cyclobutene is about 20 kcal/mole less stable than butadiene, it is evident that the spectroscopic singlet of cyclobutene is about 50-60 kcal/mole higher in energy than the spectroscopic singlet of butadiene. Thus the formation of the spectroscopic singlet state of cyclobutene from a similar state of butadiene is not probable".

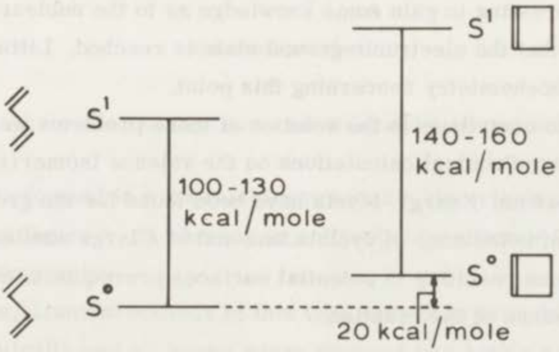


Figure 3-1. Energy scheme for the reaction of butadiene to cyclobutene.

Many suggestions have been made concerning the actual reaction path of photoinduced cyclization reactions. Fonken[5] speculates that the excited singlet state might give rise by internal conversion to a highly vibrationally excited cyclobutene which may thermally revert to butadiene or by collisional deactivation forms stable cyclobutene. Dauben[6] suggests that the spectroscopic singlet state of the diene decays to a "nonspectroscopic" excited singlet state which is stabilized by partial bond formation between C_1 and C_4 of the diene. Participation of the triplet state in this valence isomerization is not probable since Srinivasan[7] demonstrated that the photolysis of 2, 3-dimethyl-1, 3-butadiene in the vapour phase could not be quenched by oxygen or nitric oxide. The experimental data from direct and sensitized irradiations of dienes are rather confusing. Dauben[6] obtained in both cases the same major products from 1, 1-bicyclohexenyl whereas the results of Liu and Hammond[8] in a benzophenone-sensitized irradiation of myrcene and of Crowley[9] in a direct irradiation are different.

The situation is unsatisfactory at least from a theoretical point of view. In fact, from experiment one merely knows that the cyclization reaction of butadiene starts from an excited singlet state and terminates at the ground state of the product. Two important questions remain to be answered: What is the driving force of this reaction:

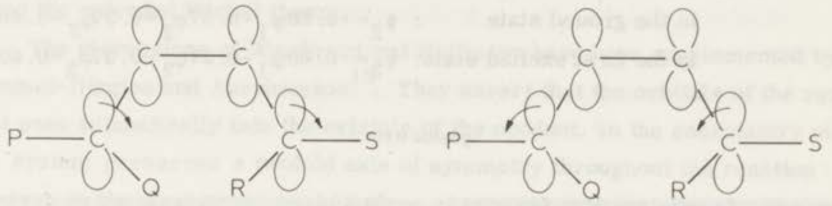
$$S^1_{\text{butadiene}} \longrightarrow [\,?\,] \longrightarrow S^0_{\text{cyclobutene}}$$

and what is the actual path along which the molecule travels to the final state? It is highly interesting to gain some knowledge as to the nuclear configuration at the moment that the electronic ground state is reached. Little is known in the field of photochemistry concerning this point.

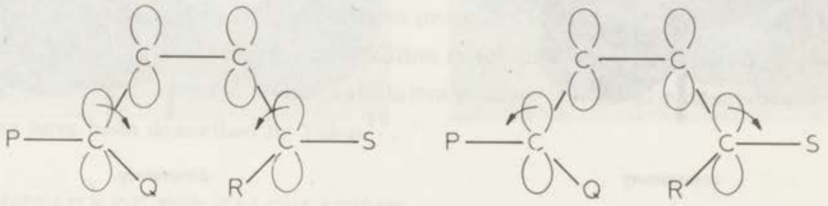
In order to contribute to the solution of these problems we have made a series of quantumchemical calculations on the valence isomerization of butadiene to cyclobutene. Energy levels have been found for the ground state and excited states of butadiene, of cyclobutene and of a large number of intermediate configurations resulting in potential surfaces prerequisite for a discussion of the actual course of the reaction.

2. WOODWARD-HOFFMANN RULES

The process of the valence isomerization of butadiene and cyclobutene is an example of an electrocyclic reaction. Woodward and Hoffmann[3] have defined such a reaction as one leading to the formation of a single bond between the termini of a linear system containing a number of π-electrons and the reverse reaction. The formation of cyclobutene from butadiene can occur in two ways, namely as a conrotatory process where the p orbitals on C_1 and C_4 rotate in the same direction, and as a disrotatory process where the p orbitals rotate in the opposite direction. A pictorial illustration of this terminology is given in figure 3 - 2.



conrotatory processes



disrotatory processes

Figure 3-2. Con- and disrotatory processes for the butadiene-cyclobutene valence isomerization.

If cyclobutene is formed in a conrotatory process a cis orientation is effected for P and R (see figure 3 - 2) whereas in a disrotatory process P and R are finally in the trans position.

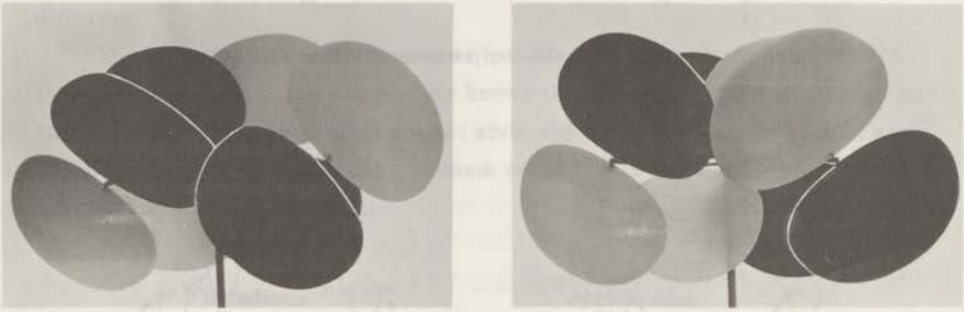
In practice, transformations of this type have been brought about thermally or photochemically and all known cases proceed in a highly stereoselective way. The thermal isomerization of cyclobutene is purely conrotatory [10 - 13] whereas the photoinduced reaction is a disrotatory process[6]. By contrast, the thermal cyclization of hexatrienes is uniquely disrotatory[1] and the photochemical cyclization is conrotatory[1, 14].

Woodward and Hoffmann pointed out that the stereochemical course of an electrocyclic ringclosure is determined by the symmetry of the highest occupied molecular orbital of the open chain reactant. In order to stabilize the transition state of the reaction the termini-atoms have to rotate in such a way that a bonding interaction results in the highest occupied molecular orbital. An application of this rule for the butadiene-cyclobutene isomerization is given in figure 3-3. The highest occupied Hückel molecular orbitals of butadiene are:

in the ground state : $\psi_2 = +0.60\varphi_1 + 0.37\varphi_2 - 0.37\varphi_3 - 0.60\varphi_4$

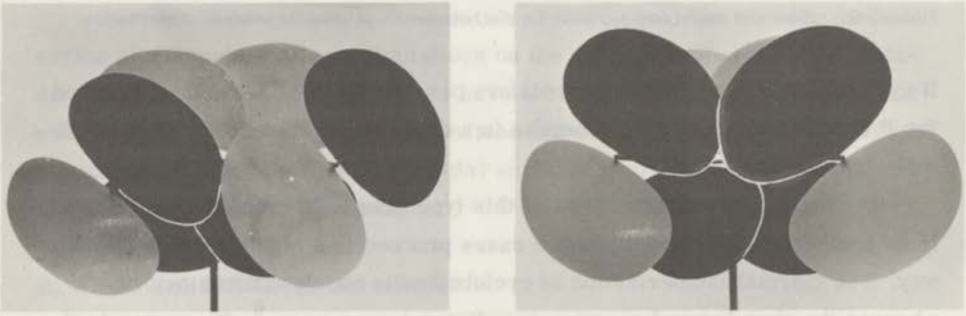
in the first excited state: $\psi_3 = +0.60\varphi_1 - 0.37\varphi_2 - 0.37\varphi_3 + 0.60\varphi_4$

ground state



conrotatory disrotatory

excited state



conrotatory disrotatory

Figure 3-3. The symmetry of the highest occupied molecular orbital in ground and excited state for the butadiene-cyclobutene valence isomerization. In these photographs the positive halfs of the p orbitals are dark and the negative one's are light. The p orbitals on C_2 and C_3 are in a vertical position in the background of all the photographs.

It can be seen from this figure that the thermal reaction should be a conrotatory process and the photochemical reaction disrotatory. For the hexatriene-cyclohexadiene isomerization the situation is just opposite, completely in agreement with the experimental results. The simple symmetry argument was supported in several cases by the results of some quantumchemical calculations using the extended Hückel theory.

The discussions of Woodward and Hoffmann have been supplemented by Longuet-Higgins and Abrahamson[15]. They assert that the orbitals of the reactant pass adiabatically into the orbitals of the product. In the conrotatory mode the system preserves a twofold axis of symmetry throughout the reaction whereas in the disrotatory mode a plane of symmetry is maintained. The orbitals should remain symmetric or antisymmetric with respect to the present element of symmetry. In this way orbital and state correlation diagrams can be constructed in order to follow the course of the reaction qualitatively. The conclusions agree completely with those drawn by Woodward and Hoffmann.

Related selection rules have been proposed for other concerted reactions as for example bimolecular cycloaddition reactions and for reactions involving migrations of σ-bonds[3]. More quantitative studies for the ground-state reactions have been described by Fukui[16].

3. DETAILS OF THE CALCULATIONS.

The determination of potential surfaces has to be the first step in a rigorous discussion on the course and the rate of a chemical reaction. The problem of reactivity has hardly been treated with such a theoretical approach. By using the London equation for the energy Eyring et al[17] calculated in 1935 potential energy surfaces for three hydrogen atoms and other systems consisting of three particles. Although a general insight was obtained into the reaction paths and activation energies of these simple reactions, the method did not appear to be suitable for the problems of interest to organic chemists.

As larger and faster electronic computers became available research into the theoretical background of reactions revived. Ritchie and King[18] have recently published the results of some calculations on the potential energy surfaces for the H_3^- and H_2F^- systems. They applied the LCAO-MO-SCF method, employing Gaussian-type orbitals as basis functions for an easy evaluation of the integrals. Probably because of the amount of computer time required little progress has been made in the computation of potential energy surfaces for reaction systems which involve many electrons. In recent years a number of important contributions have come from the Russian school of which Nikitin is a prominent representative[19].

In order to obtain some insight into the reaction paths of thermal and photoinduced electrocyclic reactions we have calculated potential energy surfaces for the cyclization of butadiene to cyclobutene and the reverse reaction. Energy levels have been calculated for butadiene, for cyclobutene and for a large number of intermediate configurations. Since the number of atoms and electrons is too large for ab initio calculations, we have tackled the problem in a semiempirical way.

Even within a simplified theory it is impracticable to include all conceivable, intermediate configurations into the considerations and we have, therefore, selected three angles which seem to us the most relevant reaction coordinates. These three angles φ, χ and θ are explained in figure 3-4.

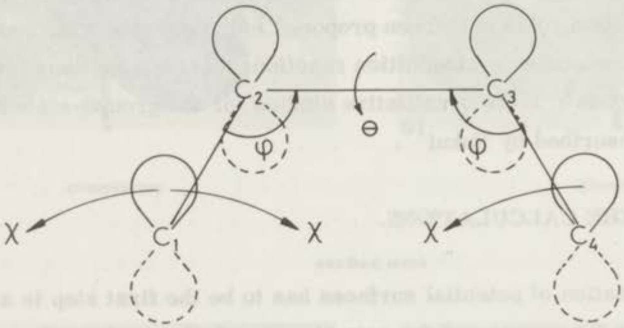


Figure 3-4.

φ : is the angle directly related to the ringclosure; it has been varied from 125° to 90° in steps of 5°.

θ : is a measure for the rotation around the bond between C_2 and C_3; it has been varied from -90° to +90° in steps of 10°.

χ : describes the rotation of the p orbitals on C_1 and C_4; this angle has been varied from 0° to 90°. In the conrotatory process the p orbitals are rotated in the same direction with conservation of a twofold axis of symmetry in the molecule, in the disrotatory process the rotations are in the opposite direction with conservation of a plane of symmetry for $\theta = 0°$.

Using this model the total number of configurations for which the energies have to be calculated still amounts to 4408.

The distances between the carbon atoms C_1-C_2, C_2-C_3 and C_3-C_4 have been kept constant, namely 1.34 Å, 1.47 Å and 1.34 Å respectively and it has been assumed that the carbon atoms C_1 and C_4 retain their trigonal hybridization. These rather drastic simplifications of the model make it in some aspects unrealistic in the neighbourhood of the cyclobutene.

It was assumed that mainly three terms contribute to the changes of the energies and that these three terms may be treated separately:

$$E(\varphi, \chi, \theta) = E_{\text{electronic}} + E_{\text{angle}} + E_{\text{nonbonded}}$$

where $E_{\text{electronic}}$ represents the energy of four electrons as will be explained below,

E_{angle} represents the angle strain energy on the atoms C_2 and C_3,

$E_{\text{nonbonded}}$ represents the energy caused by the nonbonded interactions of the hydrogen atoms.

1. $E_{\text{electronic}}$.

The changes in the electronic structure during the reaction from butadiene to cyclobutene are probably mainly caused by the reorganization of four electrons. The two conjugated double bonds of butadiene pass gradually into the π-bond between C_2 and C_3 and the σ-bond between C_1 and C_4 of cyclobutene. It seems reasonable to consider merely the energy of the four electrons involved in these bonds and to assume that the energy of all other electrons remain constant. The most reliable argument for this assumption is the localized character of the electrons in the other bonds.

The energies of ground and excited states were calculated using the Valence Bond (VB) method with orthogonalized atomic orbitals. This theory has been treated in Chapter I and applied to ethylene, butadiene and benzene in Chapter II. Since it is a four electron ——— four orbital problem, complete Valence Bond calculations involve twenty singlet structures. All these structures were included in all of the calculations.

The same results can of course be obtained from the complete Molecular Orbital theory but two reasons have led us to prefer the Valence Bond procedure. Firstly, the reaction of butadiene to cyclobutene and the reverse are valence isomerizations. These reactions can be considered as a change of the ground state of the molecule from one covalent valence bond structure to the other one. For this reason it seems worth-while to interpret the results of the calculations in terms of valence bond structures. Secondly, for complete calculations the VB method is much more practical than the MO method as has been outlined in Chapter I. The results of MO calculations including only singly excited configurations are unreliable for the photochemical reaction because of the presence of a second excited state in butadiene, which is slightly higher in energy than the first one and which is mainly determined by a doubly excited configuration (see Chapter II).

Since it has been assumed that the carbon atoms C_1 and C_4 retain a trigonal hybridization the σ-bond in cyclobutene is formed in our model from two p_σ orbitals. Concerning the semiempirical parameters, the covalent structures were taken to be equal in energy for all of the nuclear configurations and the electronic repulsion integrals were calculated from the formulae of Pariser and Parr[20]. The resonance integrals were calculated using the formula:

$$\beta_{pq} = -10.4\, S_{pq} \text{ e.V.}$$

For the proportionality constant -10.4 e.V. has been chosen since using this value a very good agreement was obtained for the calculated and experimental absorption bands of benzene (see Chapter II). The resonance integrals are then given by:

$$\beta_{12} = \beta_{34} = -10.4\, S^{\pi}_{12} \cos\chi \text{ e.V.}$$

$$\beta_{23} = -10.4\, S^{\pi}_{23} \cos\theta \text{ e.V.}$$

$$\begin{aligned}\beta_{14} = -10.4\, S^{\pi}_{14} \Big\{ &(\cos\chi \cos\theta \cos\psi \pm \sin\chi \sin\psi)\, x \\ &(\cos\chi \cos\theta \cos\psi + \sin\chi \sin\psi) - \cos^2\chi \sin^2\theta \Big\} \\ -10.4\, S^{\sigma}_{14} \Big\{ &(-\cos\chi \cos\theta \sin\psi \pm \sin\chi \cos\psi)\, x \\ &(\cos\chi \cos\theta \sin\psi - \sin\chi \cos\psi) \Big\} \text{ e.V.}\end{aligned}$$

where S^{π}_{ab} is the overlap integral between two p orbitals with an orientation parallel to each other and perpendicular on $\vec{r}_{ab}$,

S^{σ}_{ab} is the overlap integral between two p orbitals parallel to $\vec{r}_{ab}$,

$\psi = \arc \tan \dfrac{r_{12}\ \sqrt{3}\ \sin\theta}{r_{14}}$,

$\pm$ = the positive sign for the conrotatory process, the negative sign for the disrotatory process.

The overlap integrals have been taken from the tables of Mulliken et al[21].

2. E_{angle}.

The strain associated with the deviation of the bond angle from equilibrium on the carbon atoms C_2 and C_3 has been calculated from the formula:

$$E_{angle} = k\,(\tau - \varphi)^2$$

where k is the bending force constant (the usual factor 1/2 has been left out since the angle strain of two carbon atoms is taken into account),

τ is the "normal" equilibrium value of the bond angle,

φ is the actual value of the angle.

For τ we have chosen 120° and for k 34.4 cal/mole degree^2 which value has been used by Gleicher and von Schleyer[22].

3. $E_{nonbonded}$.

This energy is caused by the interaction of "nonbonded" atoms. In calculating this term only the contribution of the two hydrogen atoms, bonded to carbon atoms C_1 and C_4 and close together in *cis*-butadiene, has been taken into account. The energy has been calculated from a formula also given by Gleicher and von Schleyer[22]. This formula had to be adapted to our model in which the hybridization is artificially kept constant. The two hydrogen atoms appear to be at too short a distance from one another in cyclobutene when this is formed in a disrotatory process. Actually the hybridization of the carbon atoms C_1 and C_4 changes in such a way that the hydrogen atoms bend away from each other. For this reason we have multiplied the formula of reference 22 by a factor $\frac{90^\circ - \chi}{90^\circ}$.

In this way the nonbonded interaction decreases to zero on the formation of cyclobutene when χ is 90°. The formula for the nonbonded interaction now becomes:

$$E_{nonbonded} = \frac{90^\circ - \chi}{90^\circ}\left\{6600\,\exp(-4.08r) - 49.6/r^6\right\}\ \text{kcal/mole}$$

where r is the distance of the two hydrogen atoms in Å.

For each of the 4408 combinations of φ, χ and θ the interaction matrix of the twenty valence bond structures was constructed and diagonalized. The distance of the two hydrogen atoms was calculated using some elementary analytical geometry and the three energy terms were added. A special Fortran program was written in order to perform these calculations on the IBM 360-50. Using this program each nuclear configuration took up only seven seconds on the computer and only one input card was required for the determination of the energies of 19 nuclear configurations.

4. POTENTIAL SURFACES AND REACTION PATHS.

From the treatment of the 4408 nuclear configurations the energies of their ground states and of their excited states are obtained as a function of the angles φ, χ and θ. In order to survey this vast amount of numbers the angle θ was eliminated as an independent variable: for each combination of φ and χ the value of θ which gives the lowest energy for that combination was selected independently for the ground state and the excited states. Two dimensional graphs of the energy as a function of φ and χ can then be made for each state.

As can be seen in Chapter II the first two excited states of butadiene do not differ very much in energy. With the slightly different parametrization used in this Chapter the antisymmetric excited state lies 5.4 e.V. and the symmetric one 6.1 e.V. above the ground state. The remaining 17 excited states are at least 2.0 e.V. higher in energy. The representation of the potential surfaces for the ground state and the two lowest excited states are shown in figure 3-5, 3-6 and 3-7.

1. The thermal reaction.

Let us first discuss the isomerization of butadiene to cyclobutene in the ground state. In fact, the course of the thermal reaction is in the opposite direction since butadiene is more stable than cyclobutene. It is, however, better to start the considerations from butadiene because our model makes the calculations more accurate in the region of the diene. The actual direction of the reaction is simply a question of thermodynamic relations which need not concern us here.

It is evident from figure 3-5 that the disrotatory process of ringclosure is impossible. On the reaction path with the lowest activation energy, the energy still increases from -9.11 e.V. to -4.77 e.V. in the transition state which

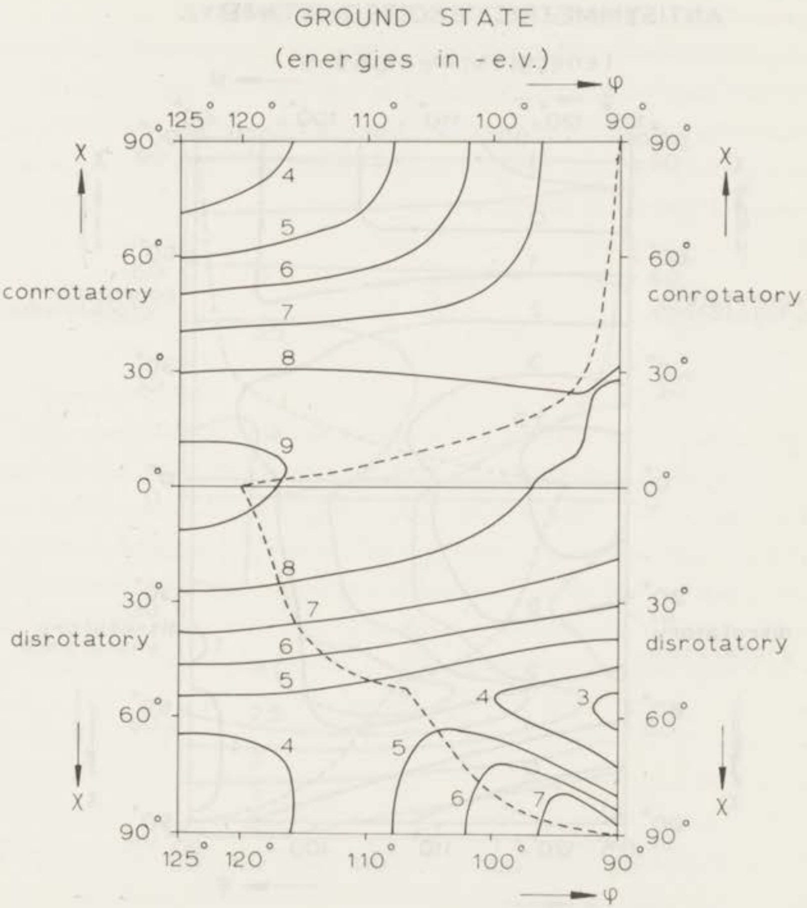


Figure 3-5. Potential surfaces for the ground state.

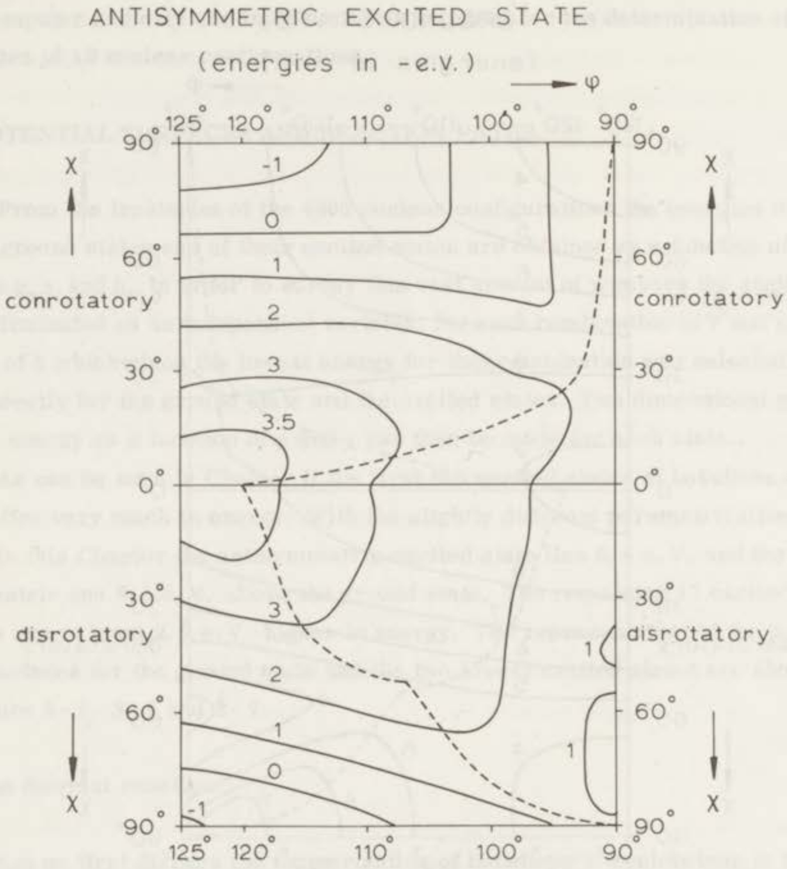


Figure 3-6. Potential surfaces for the antisymmetric excited state.

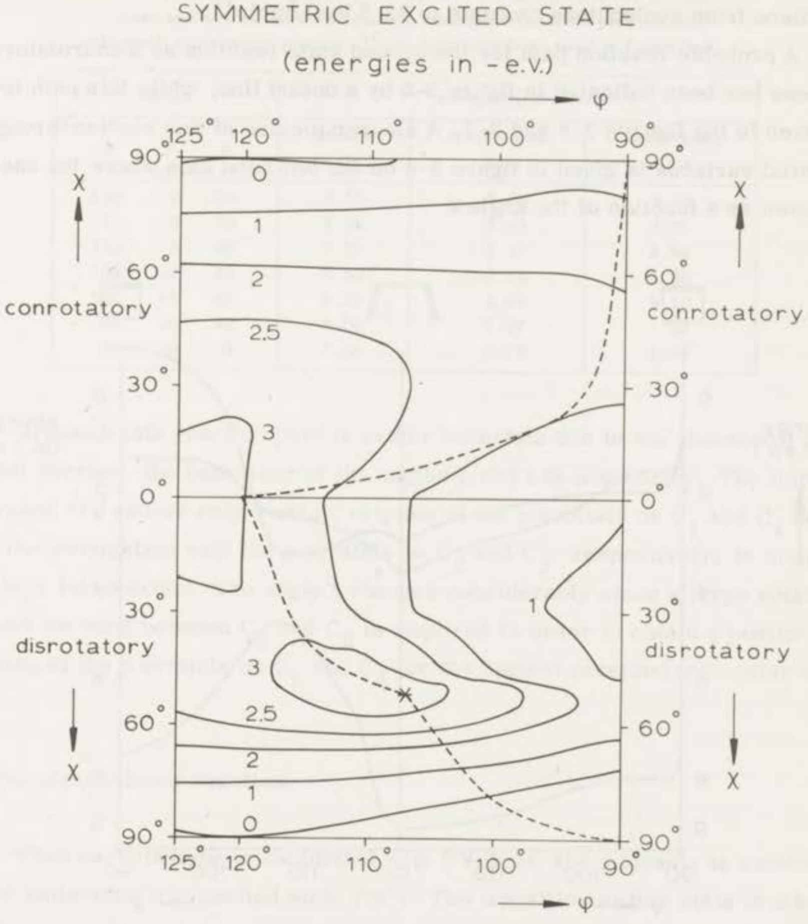


Figure 3-7. Potential surfaces for the symmetric excited state. The asterisk marks the configuration with the lowest energy.

means that an activation energy of 100 kcal/mole is required. In the conrotatory process we find no activation energy at all. The absence of a barrier along the path of minimum energy would mean that cyclobutene is unstable. As has been mentioned already the results of the calculations are rather inaccurate for low values of φ. The experimental activation energy for the formation of butadiene from cyclobutene amounts to 32.5 kcal/mole[12].

A probable reaction path for the ground state reaction as a conrotatory process has been indicated in figure 3-5 by a dotted line, while this path is also given in the figures 3-6 and 3-7. A clearer picture of this section through the potential surfaces is given in figure 3-8 on the left hand side where the energy is shown as a function of the angle φ.

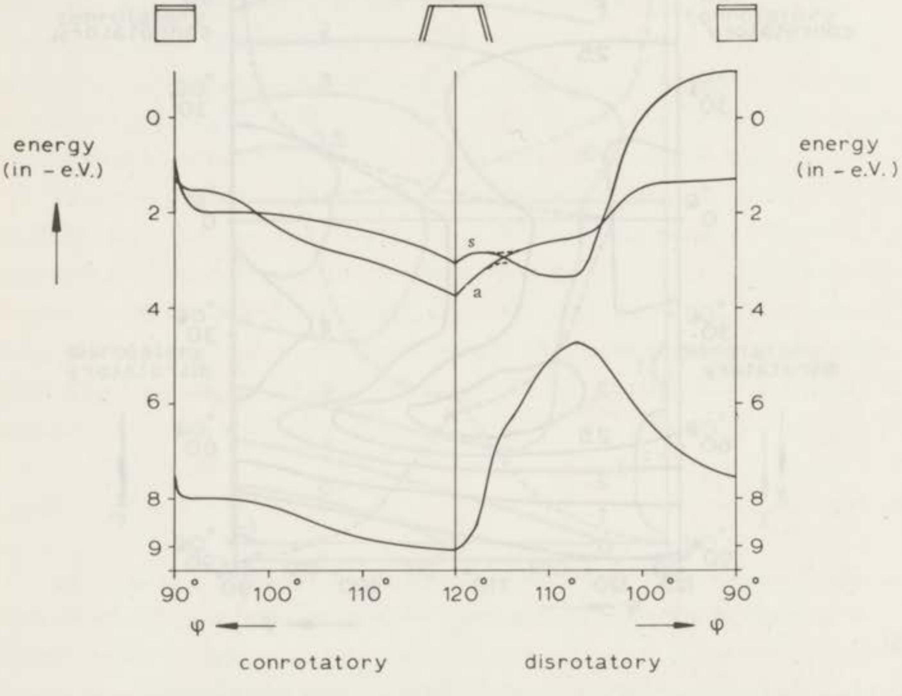


Figure 3-8. The energies of the ground state and of two excited states during the reactions.

As mentioned already, the value of the angle θ was selected independently for the ground state and the excited states. It follows that related points in the figures 3-5, 3-6 and 3-7 (equal value of φ and χ) correspond in general to a different value of θ. In figure 3-8, however, the values of the angles χ and θ are the same for equal φ. The values of the angles φ, χ and θ and of the energies in the ground and the two excited states along this probable, conrotatory reaction path are given in table 3-I.

Table 3-I.

The values of the angles φ, χ and θ and of the energies of the ground state and two excited states along a probable reaction path for the thermal, conrotatory process. These data have been used in figure 3-8.

angles			energies (in e. V.)		
φ	χ	θ	ground state	symm. exc. state	antis. exc. state
120	0	20	9.11	2.92	3.56
115	0	30	8.95	2.63	3.31
110	5	40	8.79	2.37	2.94
105	10	40	8.55	2.18	2.66
100	15	40	8.28	2.03	2.19
95	20	40	8.06	1.97	1.50
90	90	0	7.52	0.79	1.28

Although this reaction path is rather uncertain due to the absence of a potential barrier, the behaviour of the angles χ and θ is noteworthy. The initial decrease of φ causes only a small rotation of the p orbitals on C_1 and C_4 so that the conjugation with the p orbitals on C_2 and C_3, respectively, is maintained to a large extent. The angle θ changes considerably since a large rotation around the bond between C_2 and C_3 is required in order to obtain a positive overlap of the p orbitals on C_1 and C_4 for the highest occupied molecular orbital.

2. The photoinduced reaction.

When *cis*-butadiene is irradiated with UV light, the molecule is excited into the antisymmetric excited state ("a"). The transition to this state is allowed and has according to our calculations an oscillator strength of 0.31. The transition to the symmetric excited state ("s") is forbidden. The UV spectrum of *trans*-butadiene reveals only one absorption band and a transition to the symmetric excited state could not be detected on the interaction with low energy electrons[23]. This supports the idea that the two excited states also in *cis*-butadiene are probably nearly equal in energy.

It can be seen from figure 3-6 that for butadiene in "a" a conrotatory ringclosure is improbable. The energy increases on changing φ and χ and there is in fact no driving force for such a reaction.

The situation for a disrotatory process shows, however, a fundamental distinction. A probable reaction path for a disrotatory ringclosure starting from the antisymmetric excited state has also been indicated in the figures 3-5, 6 and 7 by a dotted line. This section through the potential surfaces is given on the right hand side in figure 3-8[*].

The fundamental distinction is that at $\varphi = 116^{o}$ the antisymmetric and symmetric energy levels intersect. This accidental degeneracy can be lifted by nuclear configurations which deviate from twofold symmetry and the levels no longer cross[**]. Nuclear vibrations cause a molecule in "a" to pass adiabatically into "s" as is shown in figure 3-8 by a dotted line. In this manner the molecular electronic state "a" is converted into "s" in which a disrotatory deformation can proceed. The nuclear configuration will then change in such a way that the electronic energy corresponds to the well[***] in "s" at a value of $\varphi = 107^{o}$, $\chi = 50^{o}$ and $\theta = 0^{o}$. Vibrational energy thus obtained will be distributed over the whole molecule or dissipated by collisions with other molecules.

In this way the molecule is captured in the energy well. From this situation it is supposed to reach the lower potential surface of the ground state. The mechanism of such a transition is not yet known and is connected with the understanding of radiationless processes in molecules. It may very well be that collisions with other molecules are essential for the return to the electronic ground state.

On reaching the electronic ground state the molecule is in a nuclear configuration corresponding to the disrotatory transition state between butadiene and cyclobutene. The reaction can now proceed in two directions: either butadiene or cyclobutene is formed. The reformation of butadiene provides an explanation for the absence of fluorescence and phosphorescence of dienes in liquid solutions. Some interesting data along this probable, disrotatory reaction path starting from the antisymmetric excited state are given in table 3-II.

The behaviour of the angles χ and θ is different from that in the thermal,

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[*] It should be mentioned that "s" terminates into different states of cyclobutene in the two processes.

[**] A rotation of the p orbital of C_1 by 20^{o} and of C_4 by 60^{o}, for example, gives a difference in energy of 0.2 e.V. for the two states.

[***] Since the precise position of the well is required for a sound discussion, the calculations were extended by varying φ from 115^{o} to 105^{o} in steps of 1^{o} and χ from 35^{o} to 55^{o} in steps of 2.5^{o}.

Table 3-II.

The values of the angles φ, χ and $\theta$and of the energies of the ground state and two excited states along a probable reaction path, starting from the antisymmetric excited state, for the photoinduced, disrotatory process. These data have been used in figure 3-8.

angles			energies (in-e. V.)		
φ	χ	θ	ground state	symm. exc. state	antis. exc. state
120	0	0	9.08	3.02	3.69
115	40	0	6.54	3.03	2.90
110	50	0	5.11	3.28	2.59
107	50	0	4.73	3.31	2.53
105	60	0	4.85	2.64	2.32
100	80	0	6.25	-0.13	1.36
95	85	0	7.15	-0.83	1.37
90	90	0	7.52	-1.34	1.28

conrotatory process. A rotation around the bond between C_2 and C_3 does not take place. The nonbonded interaction between the two hydrogen atoms forces a rotation of the two p orbitals on C_1 and C_4.

Concerning the importance of the three terms included in the calculations of the energies, it appears that the contribution of the electronic energy is responsible for the general shape of the potential surfaces. The position of the states with regard to each other is completely determined by this term. The angle strain has been included in order to scale the energies of butadiene and cyclobutene with respect to each other and the nonbonded interaction in order to avoid that hydrogen atoms will come at too short a distance in our model. In figure 3-9 we have given the contribution of the electronic energy and it is clear that conclusions drawn from this figure are essentially the same as those from figure 3-8. Recently the experimental strain energy of cyclobutene is found to be 29 kcal/mole*. The value used in our calculation on cyclobutene is 31 kcal/mole, accidentally in good agreement with the experimental value.

One might doubt whether butadiene in "a" can reach the intersection with "s" since an activation energy of ~ 14 kcal/mole is required which is much too large for a photochemical reaction to proceed in a time comparable to the lifetime. The calculated value for this activation energy depends, however, on the parametrization used in the calculations and, in addition, it will become smaller by the inclusion of asymmetric nuclear configurations.

More general conclusions can be drawn from a theoretical analysis and

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* J.F. Oth, private communication.

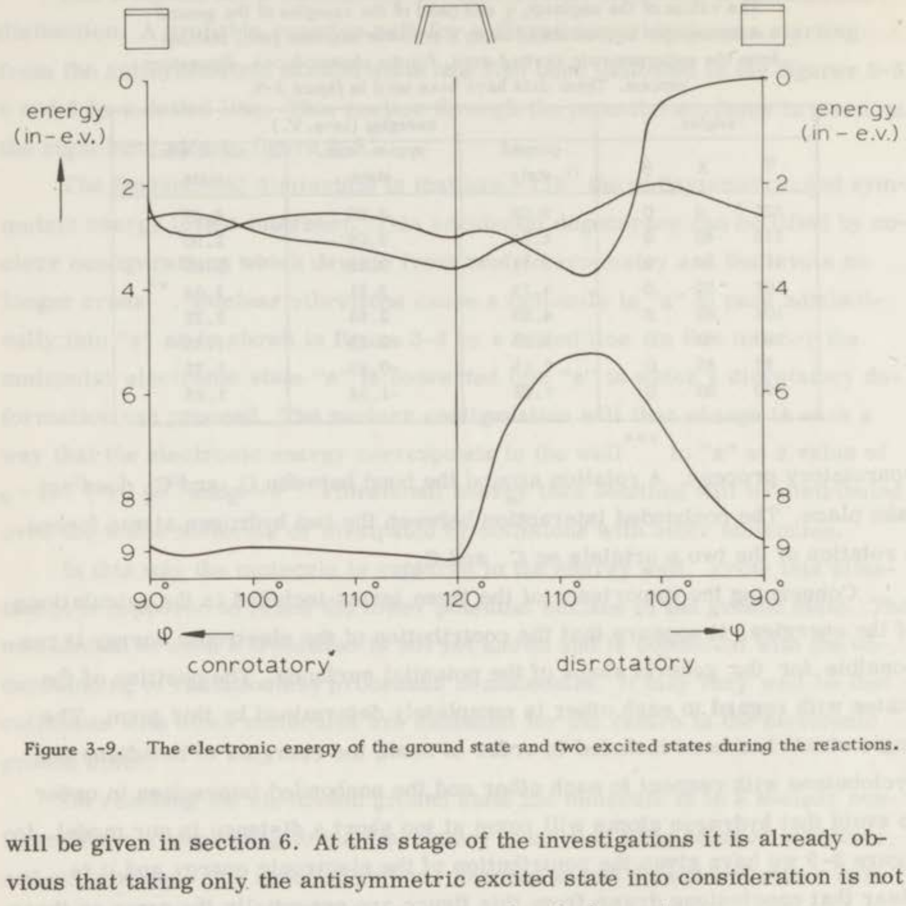

Figure 3-9. The electronic energy of the ground state and two excited states during the reactions.

will be given in section 6. At this stage of the investigations it is already obvious that taking only the antisymmetric excited state into consideration is not sufficient for an interpretation of the photochemical reaction.

5. THEORETICAL ANALYSIS.

The reaction of butadiene to cyclobutene can be considered as a change of the ground state of the molecule from one covalent valence bond structure into the other. This consideration was essentially the reason why we used the Valence Bond method in the quantum chemical calculations. It seems worth-while to calculate the contributions of the valence bond structures along the reaction paths of the thermal, conrotatory and of the photoinduced, disrotatory process.

Contributions of covalent structures (CS) based on orthogonalized atomic orbitals, are generally small as can be seen in the case of butadiene in table

2-III. Contributions of covalent structures based on atomic orbitals are larger. For example a part of the weight of the polar structure (PS) C[*], related to A, turns up in the contribution of A, based on non-orthogonal atomic orbitals. In order to obtain a clearer picture we have added to the weights of the CS those of the related PS. With the CS A are related the PS C and R, with the CS B are related the PS G, I and P. The contributions of the structures L and T have been added partly to A and partly to B.


A


B

The total contributions of the covalent structures A and B thus obtained along the reaction path, are given in table 3-III for the thermal conrotatory process and in table 3-IV for the photoinduced disrotatory process.

Table 3-III.
The contributions of the covalent structures A and B in per cents during the thermal, conrotatory process.

angles			contributions of A and B in per cents					
			ground state		symm. exc. state		antis. exc. state	
φ	χ	θ	A	B	A	B	A	B
120	0	20	88	12	11	89	55	45
115	0	30	88	12	12	88	55	45
110	5	40	88	12	14	86	55	45
105	10	40	84	16	16	84	52	48
100	15	40	80	20	21	79	52	48
95	20	40	75	25	28	72	49	51
90	90	0	4	96	78	22	18	82

The numbers in table 3-III agree with the idea concerning the transition state of the thermal process as mentioned in section 4. Until the reaction is nearly finished the p orbitals on C_1 and C_4 are parallel to those on C_2 and C_3 maintaining the conjugation C_1-C_2 and C_3-C_4: the molecule persists in the valence bond structure A.

The contributions of the covalent structures in the disrotatory process are especially interesting for the behaviour of the wave functions corresponding to the ground state and the symmetric excited state. Following the reac-

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[*] The meaning of the symbols of the structures may be found in figure 2-1.

Table 3-IV.

The contributions of the covalent structures A and B in per cents during the photoinduced, disrotatory process.

angles			contributions of A and B in per cents					
			ground state		symm. exc. state		antis. exc. state	
φ	χ	θ	A	B	A	B	A	B
120	0	0	88	12	12	88	55	45
115	40	0	84	16	11	89	55	45
110	50	0	71	29	25	75	55	45
107	50	0	65	35	30	70	54	46
105	60	0	11	89	90	10	54	46
100	80	0	4	96	100	0	53	47
95	85	0	4	96	100	0	44	56
90	90	0	4	96	100	0	18	82

tion path the electronic ground states related to the nuclear configurations between butadiene and the transition state can be represented by the covalent structure A, whereas for the configurations between the transition state and cyclobutene structure B strongly dominates. The situation in the symmetric excited state is precisely opposite.

This interpretation in terms of valence bond structures is surprisingly simple. Changing the nuclear configuration from butadiene to cyclobutene the energy of the covalent structure A steadily increases whereas the energy of structure B decreases. At the intersection the interaction between the structures has a pronounced effect and the degeneracy is lifted as shown in figure 3-10. In this manner the ground state and the symmetric excited state pass over adiabatically from one valence bond structure into the other as a result of the non-crossing rule.

The shape of the potential surfaces for the disrotatory mode of ringclosure is very similar to the picture which holds for the approach of a Na and a Cl atom. At infinitely large distance the covalent situation is the most favourable. On the approach of the atoms the energy of the ionic term decreases and at the intersection the corresponding wave functions strongly interact. In this way the ground state of the system changes adiabatically from an atomic into an ionic state.

It is instructive to compare the potential surfaces for the disrotatory ringclosure with the simple correlation diagrams as given by Longuet-Higgins and Abrahamson[15]. The diagram pertaining to the disrotatory mode for the inter-

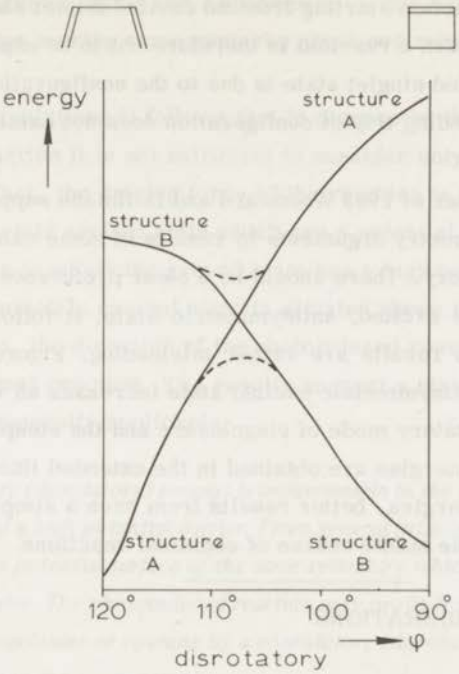

Figure 3-10. A simplified picture of the energies of the ground state and the symmetric excited state in terms of the two covalent valence bond structures for the disrotatory process.

conversion of butadiene and cyclobutene reveals also a potential well in a symmetric excited state. Concerning this well their qualitative considerations are in agreement with the results of our calculations. We would like to stress, however, a dissimilarity of great importance. Our calculations show, in contrast with the qualitative diagram of Longuet-Higgins, that the energy of the symmetric excited state during the photoinduced reaction reaches a lower value than the energy of the antisymmetric excited state. A solution for the problem as posed by Dauben and mentioned in section 1 is found by taking the symmetric excited state into account.

A complete molecular orbital calculation for the nuclear configuration corresponding to the well in the symmetric excited state reveals that the doubly excited configuration $|\psi_1 \bar{\psi}_1 \psi_3 \bar{\psi}_3|$ makes a 65% contribution to this state. Similar calculations as described in this Chapter have been performed on the triplet states including all 15 triplet valence bond structures*. A driving force

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* The calculations have been performed by Mr. R.J. van Santen.

for a cyclization reaction starting from an excited triplet state of butadiene has not been found and such a reaction is therefore not to be expected. The well in the symmetric excited singlet state is due to the configuration $|\psi_1 \bar{\psi}_1 \psi_3 \bar{\psi}_3|$ whereas a corresponding triplet configuration does not exist.

In the first paper of 1965 Woodward and Hoffmann support rather succinctly their simple symmetry arguments by results of some calculations using the extended Hückel theory. There should be a clear preference for disrotatory twisting in the first excited, antisymmetric state. It follows from our calculations that these results are rather misleading. Figure 3 - 6 reveals that the energy of the antisymmetric excited state increases as well in the conrotatory as in the disrotatory mode of ringclosure and the steepness is nearly the same. Since state energies are obtained in the extended Hückel theory by summation of orbital energies, better results from such a simple theory can hardly be expected for the subtle course of chemical reactions.

6. GENERAL CONSIDERATIONS.

In view of the results of the calculations reported in this Chapter we will review once more the different approaches which various authors have used to explain the course of thermal and photoinduced electrocyclic reactions.

The course of these reactions has been interpreted by Woodward and Hoffmann in terms of orbital symmetries. According to their reasoning it is sufficient to consider the symmetry of the highest occupied molecular orbital only. In general, the symmetry of this orbital in the ground state is opposite to that in the lowest excited state. This explains the striking observation that the stereochemistry of photochemical processes is opposite to that observed in thermal reactions.

Many authors have given alternative explanations of the rules formulated by Woodward and Hoffmann. Fukui[24] has used a first-order perturbation calculation for the determination of the change of π-electron energy, Zimmermann[25] has discussed the electrocyclic reactions in terms of Hückel- and Möbius-like systems, whereas Dewar[26] has used aromaticity as a criterion for predicting the course of a reaction. In all these cases the calculations with respect to the photoinduced reaction of butadiene have been performed on the antisymmetric excited state resulting in a stereochemistry opposite to the thermal reaction. A still qualitative but much more detailed treatment has been given by Longuet-Higgins and Abrahamson[15]. We will come back to their considerations after making some remarks about our own results.

From our calculations it follows that in discussing the direction of the photochemical reaction it is not sufficient to consider only the antisymmetric excited state. In fact, the driving force of the reaction is due to the presence of a nearby symmetric excited state which has a potential well in the same nuclear configuration in which the ground state has a high potential barrier. Since the well in the symmetric excited state is situated above the potential barrier in the ground state, the direction of the photoinduced reaction will be opposite to that of the thermal reaction. The results suggest a statement which would seem to us to be generally applicable.

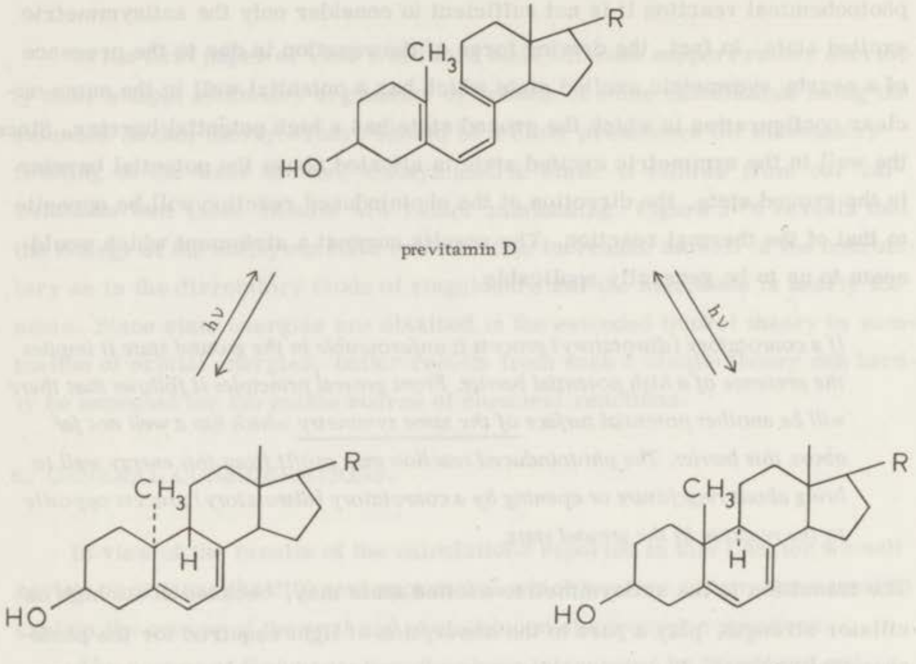
> *If a conrotatory (disrotatory) process is unfavourable in the ground state it implies the presence of a high potential barrier. From general principles it follows that there will be another potential surface of the same symmetry which has a well not far above this barrier. The photoinduced reaction may profit from this energy well to bring about ringclosure or opening by a conrotatory (disrotatory) process opposite to the reaction in the ground state.*

The transition to the antisymmetric excited state may, because of its high oscillator strength, play a part in the absorption of light required for the photochemical process. In our considerations, however, this antisymmetric state is scarcely relevant to the explanation of the course of the photoinduced reaction.

Returning again to the considerations of Longuet-Higgins and Abrahamson we can say that their correlation diagrams are in several respects similar to the potential surfaces resulting from our calculations. Their diagram for the disrotatory interconversion of butadiene and cyclobutene shows a symmetric excited state with a well situated above a high potential barrier in the ground state. However, the importance of this well in providing the driving force to the photochemical reaction cannot be seen from a qualitative description.

Our potential curves may also be used to explain some other photochemical phenomena. Firstly, the presence of a well-in potential energy surfaces of excited states offers an explanation for photochemical transformations in the chemistry of Vitamin D and related substances. On irradiation of previtamin D (P), lumisterol (L) and ergosterol (E) are obtained by conrotatory processes.

Irradiation of L or E only yields P' as primary product whereas a direct conversion of L to E or E to L has not been observed[27, 28].



previtamin D

lumisterol

ergosterol

It follows from these observations that the formation of an excited P molecule from an excited L (E) molecule can be excluded. This conclusion agrees with the picture obtained from our calculations concerning the reaction paths of this kind of photoinduced valence isomerization. An excited L (E) molecule will be captured in a potential well corresponding to a nuclear configuration between L (E) and P. From this situation the molecule reaches the electronic ground state resulting in the formation of L (E) or P whereas the formation of E (L) does not occur.

A second phenomenon for which the well in the symmetric excited state offers an explanation is the absence of fluorescence and phosphorescence of dienes and trienes in liquid solutions. Fluorescence has only been observed in a few cases in glasses at low temperature[27]. Our picture suggests that in liquid solutions a molecule in the antisymmetric excited state very rapidly reaches the well in the symmetric excited state, before interconversion to the ground state with emission of light has occurred.

At present we cannot judge whether our results are generally applicable for the interpretation of photoinduced reactions. Many examples are known where the course of photochemical processes is different from that of the thermal process: such different reactions are observed for instance in heterolytic photosubstitution reactions in aromatic compounds[29]. Although there are experimental and theoretical indications that a photochemical reaction may start from the second electronically excited state[30], it has been assumed in most cases that the reaction starts from the first excited state because of its longer life-time. The reactivity is usually discussed in terms of static electron densities, dynamic localization energies and similar quantities related to the first excited state.

From our calculations it follows that interpretations along the above lines should be regarded with caution. It is possible that for a number of photoinduced reactions the driving force is determined by the behaviour of the potential surface of a higher excited state. Furthermore, one can imagine that after excitation of a molecule into a higher excited state the reaction starts from this state (because of the shape of the potential surface) before radiationless conversion to the first excited state has occurred. If this is the case discussions in terms of properties of the first excited state are inadequate. Extensive studies of photochemical transformations using monochromatic light are therefore very important for a sound discussion of these reactions.

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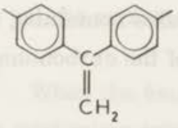
CHAPTER IV

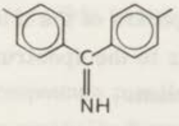
MOLECULAR ORBITAL CALCULATIONS ON THIOBENZOPHENONE AND RELATED COMPOUNDS

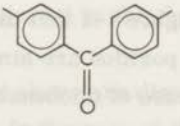
1. INTRODUCTION.

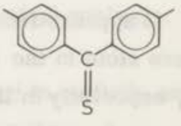
α, α-Diphenylethylene and many substances of related structure show a number of remarkable chemical and physical properties. As early as 1924 Wizinger[1a] has drawn several interesting conclusions from the colour changes that accompany protonation, bromination and several other electrophilic addition reactions. As first recognized by Pfeiffer and Wizinger[1b] the carbonium ions formed are generally accepted as models of intermediates in aromatic substitution reactions.

Later Buck[2] has especially fixed attention on the ultraviolet spectra of α,α-diphenylethylene, the imine, benzophenone and thiobenzophenone and of their related proton complexes. He included the p,p'-dimethoxy and the p,p'-di(dimethyl-amino) substituted analogues in his considerations.









In order to interpret the ultraviolet spectra of these compounds in methanol and sulfuric acid quantumchemical calculations have been performed[*]. Furthermore, the polarographic reduction potentials have been measured. In this

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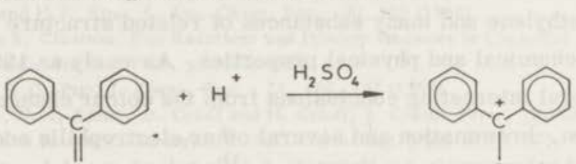
[*] Part of this work will be published in Industrie Chimique Belge, 32, part III (1967).

way the correctness of the calculations can be verified by a comparison with two different sets of experimental data.

From the quantumchemical point of view the most interesting problems arise concerning the sulfur-containing molecules. Since sulfur is an element of the third row of the periodic system it has been suggested many times that the sulfur atom can participate not only with a 3p orbital, but also with a 3d orbital of the correct symmetry. The results of the calculations using only a 3p orbital are in good agreement with the experimental data and suggest that participation of a 3d orbital of the sulfur atom in thiobenzophenones is improbable. In addition, the semiempirical parameters for the sulfur atom are supported by a comparison with theoretical values.

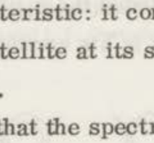
2. ULTRAVIOLET SPECTRA.

When α, α- diphenylethylene is dissolved in sulfuric acid, it accepts a proton from the acid and a carbonium ion is formed.



Comparing the UV spectrum of this solution with the UV spectrum in methanol the first absorption band is found to be shifted to much longer wavelengths and its extinction coefficient is increased about three times[2]. The appearance of the latter spectrum is rather characteristic: it consists of a sharp peak of high intensity with a much smaller satellite at its short wavelength side (cf. figure 4-1 and 4-2 for similar spectra).

It appears from figure 4-1 that the spectra of the molecules containing a hetero atom in the β - position are similar to the spectrum of the carbonium ion, especially in the case of thiobenzophenone.
This can be explained by assuming that the valence bond structure



becomes more important as the electronegativity of X increases and the compounds tend to assume the character of a carbonium ion. The spectra of the four compounds substituted with methoxy groups are given in figure 4-1.

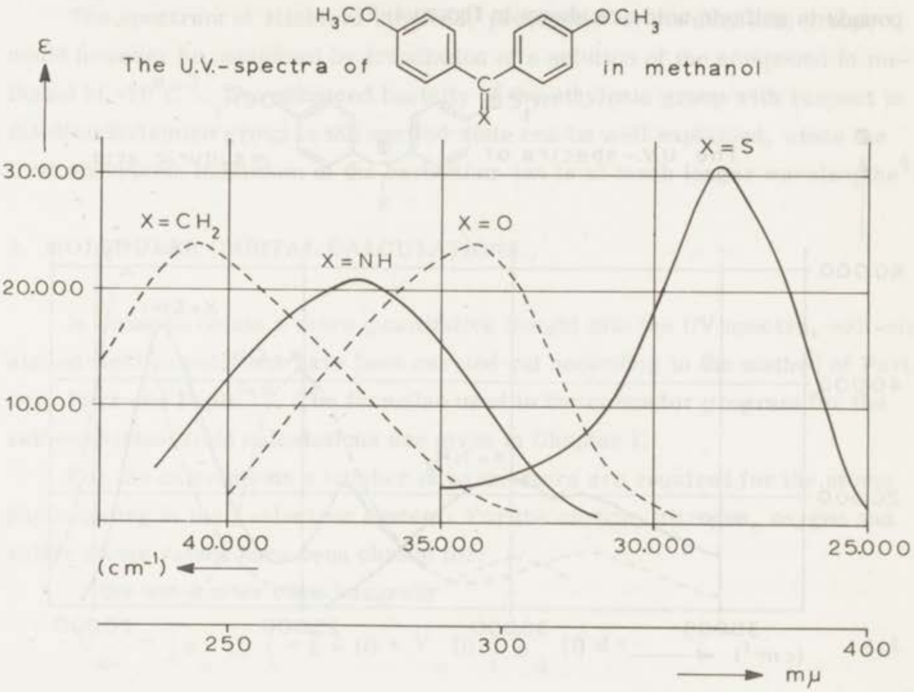


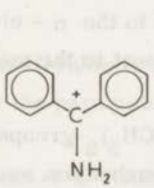
Figure 4-1. The UV spectra of the methoxy substituted compounds in methanol.

One might conclude from these ideas that the sequence of electron affinity is:

$$S > O > NH > CH_2 \qquad (A)$$

As will be explained later this is not supported by the theoretical analysis.

When the four compounds mentioned above are dissolved in sulfuric acid, the carbonium ions are actually formed. In the case of the amine



the positive charge on the central C-atom and the two benzene rings is partly compensated by the electron donating effect of the NH_2-group. The UV spectrum of the amine compared with α,α-diphenylethylene in sulfuric acid is therefore shifted to shorter wavelengths. The spectra of the methoxy substituted compounds in sulfuric acid are shown in figure 4-2.

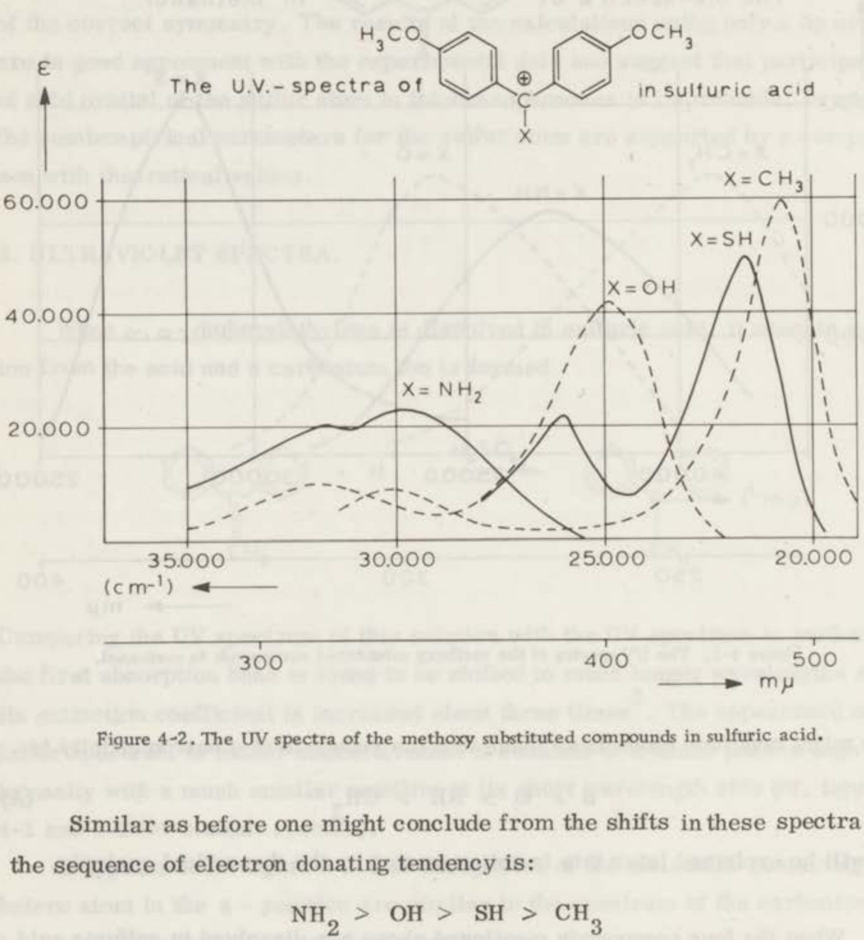


Figure 4-2. The UV spectra of the methoxy substituted compounds in sulfuric acid.

Similar as before one might conclude from the shifts in these spectra that the sequence of electron donating tendency is:

$$NH_2 > OH > SH > CH_3 \qquad (B)$$

This would be in agreement with the sequence of electron affinities (A). The CH_3-group can donate electrons to the π - electron system by hyperconjugation, but this effect is small with respect to the mesomeric effect of the other three groups.

When two OCH_3- or two $N(CH_3)_2$-groups are substituted in the p- and p'-positions, the formation of the carbonium ions is favoured and the bathochromic shifts become more pronounced. Data from the UV spectra in methanol and sulfuric acid are given in table 4-V. With the exception of the imine all of the dimethylamino substituted compounds are protonated in sulfuric acid on the $N(CH_3)_2$-groups.

The spectrum of Michlers ethylene, protonated on the ethylenic group, could however be measured by irradiation of a solution of the compound in methanol at -70°C [3]. The enhanced basicity of the ethylenic group with respect to the dimethylamino group in the excited state can be well explained, since the first absorption maximum of the carbonium ion is at much longer wavelengths[4].

3. MOLECULAR ORBITAL CALCULATIONS.

In order to obtain a more quantitative insight into the UV spectra, self-consistent field calculations have been carried out according to the method of Pariser, Parr and Pople[5,6]. The formulae used in the computer program for the self-consistent field calculations are given in Chapter I.

For the calculations a number of parameters are required for the atoms participating in the π-electron system. For the carbon, nitrogen, oxygen and sulfur atoms values have been chosen for:

the one-center core integrals

$$U_{\mu\mu} = \int \varphi_{\mu}(i)\left\{-\tfrac{1}{2}\Delta(i) + V_{\mu}(i)\right\}\varphi_{\mu}(i)\,d\tau \tag{4.1}$$

the resonance integrals

$$\beta_{\mu\nu} = \int \varphi_{\mu}(i)\,H^{\text{core}}(i)\,\varphi_{\nu}(i)\,d\tau \tag{4.2}$$

the electronic repulsion integrals

$$\gamma_{\mu\nu} = \int \varphi_{\mu}(i)\,\varphi_{\mu}(i)\,\frac{1}{r_{ij}}\,\varphi_{\nu}(j)\,\varphi_{\nu}(j)\,d\tau \tag{4.3}$$

It is reasonable that the parameters conform to two requirements:

A. As far as possible the parameters should harmonize with atomic spectral data.

B. The parameters should be transferable from one molecule to another.

According to these requirements the parameters are chosen in the following way:

1. The one-center core integrals $U_{\mu\mu}$

$U_{\mu\mu}$ is the diagonal matrix element of φ_{μ} with respect to the one-electron Hamiltonian containing the kinetic energy and the effect of the core of atom μ. Let us take n_μ as the number of π-electrons of atom μ participating in the π-electron system.

a. $n_\mu = 1$. In these cases $-U_{\mu\mu}$ should agree with the first ionization potential of atom μ in the valence state (I_μ). For the carbon atom for example we see from figure 4-3

$$I_\mu = \text{I.P.} + \text{P.E.}(C^+) - \text{P.E.}(C) \qquad 4.4$$

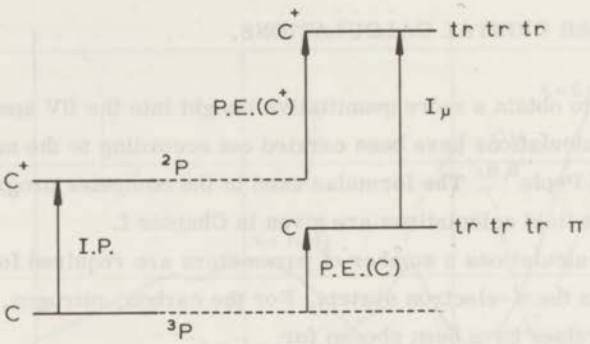


Figure 4-3. Schematic diagram of the energy states of C and C$^+$.

I.P. = the ionization potential for the free atom
P.E.(C) = the energy required to promote the atom C from the ground state to the valence state with three electrons in trigonal hybrids and one electron in a π-orbital.
P.E.(C$^+$) = the energy required to promote C$^+$ from the ground state to the valence state with three electrons in trigonal hybrids.

For the free atom the ionization potentials in the gaseous state have been measured experimentally. The promotion energies can be calculated from spectroscopic data and are tabulated for a number of atoms by Hinze and Jaffé[7]. Using these values we find for I_μ:

carbon	+ 11.16 e.V.
nitrogen	+ 14.12 e.V.
oxygen	+ 17.70 e.V.
sulfur	+ 12.70 e.V.

If we are interested, for example, in molecular ionization potentials knowledge about all I_μ's is necessary. On the other hand, only the differences are important if we want to calculate UV spectra. They are given with respect to carbon in table 4-I.

These differences depend, of course, on the values used for the ionization potentials and the promotion energies. The data change perpetually as new experimental measurements become available. However, the general feature of the semiempirical parameters should agree with the known atomic data. The one-center core integrals used in the calculations are also given in table 4-I.

Table 4-I The valence state ionization potentials and one-center core integrals in e.V. relative to the value of carbon.

	$-\Delta I_\mu$	$\Delta U_{\mu\mu}$
N^+	-2.96	-2.95
O^+	-6.54	-5.98
S^+	-1.54	-1.50

b. $n_\mu = 2$. In these cases $U_{\mu\mu}$ should agree with the second ionization potential in the valence state. It appears that for all the atoms participating with two π-electrons these ionization potentials are too high in energy in order to obtain a good agreement with the UV spectra. The electronegativity of the atoms becomes too large.

We have therefore calculated the $U_{\mu\mu}$'s in the following way. For the difference between $U_{\mu\mu}(X^+)$ and $U_{\mu\mu}(X^{++})$ we take 65% of the difference between the first and second atomic ionization potentials. This choice is rather arbitrary but it is a great asset treating all atoms in the same manner. Using the values from the tables by Moore[8] we find

$\Delta U_{\mu\mu}(N^{++}) = -11.40$ e.V.

$\Delta U_{\mu\mu}(O^{++}) = -17.92$ e.V.

$\Delta U_{\mu\mu}(S^{++}) = -8.80$ e.V.

In addition the inductive effect of the methyl groups in the methoxy and dimethylamino substituents is taken into account by adding 2 e.V. for each methyl group to the $U_{\mu\mu}(X^{++})$.

2. *The resonance integrals $\beta_{\mu\nu}$*

The resonance integrals have been calculated from the formula

$$\beta_{\mu\nu} = \tfrac{1}{2}S_{\mu\nu}\,(U_{\mu\mu} + U_{\nu\nu}) \qquad 4.5$$

where $S_{\mu\nu}$ is the overlap integral of the p orbitals on the atoms μ and ν .

$$S_{\mu\nu} = \int \varphi_{\mu}\,(i)\ \varphi_{\nu}\,(i)\ d\ \tau \qquad 4.6$$

For carbon we have chosen $U_{CC} = -9.60$ e.V. With this value one calculates for a carbon-carbon bond of 1.39 Å: $\beta_{CC} = -2.40$ e.V.

For the carbon-sulfur bond, however, we have taken for the resonance integral 70% of the value calculated from formula 4.5. A justification for this exception is given at the end of this chapter where the parameters of the sulfur are treated in more detail.

3. The electronic repulsion integrals

a. The one-center repulsion integrals.

Pariser[9] introduced for these integrals the empirical formula

$$\gamma_{\mu\mu} = I_{\mu} - A_{\mu} \qquad 4.7$$

where I_{μ} and A_{μ} are the valence state ionization potential and the electron affinity, respectively, of the orbital on atom μ. The values thus obtained are given in table 4-II. For practical reasons we have used another formula

$$\gamma_{\mu\mu} = 3.36 \left\{ Z_{\mu} - 0.35(P_{\mu\mu} - n_{\mu}) \right\} \text{ e.V.} \qquad 4.8$$

where Z_{μ} is the effective nuclear charge calculated from
the well known Slater rules

$P_{\mu\mu}$ is the π-electron density on atom μ.

For the sulfur atom a value of 10.00 e.V. was used for γ_{SS} in agreement with the formula of Pariser. The one-center repulsion integrals for the neutral atoms ($P_{\mu\mu} = n_{\mu}$) are also given in table 4-II .

b. The two-center repulsion integrals.

These integrals have been calculated using the formula

$$\gamma_{\mu\nu} = \frac{14.4}{\dfrac{8.57}{Z_{\mu} + Z_{\nu}} \left[1.4 - 0.025\ (Z_{\mu} + Z_{\nu}) \right]^{-R_{\mu\nu}} + R_{\mu\nu}} \text{ e.V.} \qquad 4.9$$

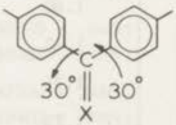
where $R_{\mu\nu}$ is the distance between the atoms μ and ν in Å.

Table 4-II. The one-center electronic repulsion integrals in e.V.

	$I_\mu - A_\mu$	Formula 4.8
C	11.13	10.92
N	12.34	13.10
O	15.32	15.29
S	9.94	10.00

The great advantage of the formulae 4.8 and 4.9, especially for large molecules, is that only a small amount of input data is required for the computer. The formulae have been developed during many calculations on substituted aromatic molecules.

In addition to these empirical parameters the geometry of the molecules is needed. Hanson[10] has found from X-ray data that in bis(p-methoxyphenyl) nitric oxide both anisyl rings are turned through 30°. The non-bonded interaction of the two hydrogen atoms in the ortho position decreases by this rotation. Because of the resemblance to the molecules studied in this chapter the benzene rings are supposed to be turned 30° out of plane.



It was assumed that the C-C distances are 1.39 Å in the two benzene rings, 1.45 Å between the benzene rings and the central carbon atom and 1.34 Å for the $C{=}CH_2$ bond in α,α -diphenylethylene. All parameters and distances used in the self-consistent field calculations are summarized in table 4-III and 4-IV.

Using the self-consistent field molecular orbitals a configuration interaction matrix is calculated of eighteen singly excited singlet configurations. Af-

Table 4-III. The one-center parameters in e.V.

atom	$\Delta U_{\mu\mu}$	$\gamma_{\mu\mu}$
C^+	0	10.92
N^+	-2.95	13.10
O^+	-5.98	15.29
S^+	-1.50	10.00
N^{++}	-11.40	13.10
O^{++}	-17.92	15.29
S^{++}	-8.80	10.00
$(H_3C)_2N^{++}$	-7.40	13.10
$(H_3C)O^{++}$	-15.92	15.29

Table 4-IV. The distances and resonance integrals.

bond	r (in Å)	β(in e.V.)
C = C	1.34	-2.602
	1.39	-2.400
	1.45	-1.877
C = NH	1.28	-2.645
C = O	1.21	-2.539
C = S	1.60	-1.500
$C - NH_2$	1.42	-2.818
C - OH	1.36	-3.005
C - SH	1.75	-1.835
$C - N(CH_3)_2$	1.42	-2.818
$C - OCH_3$	1.36	-3.005

ter diagonalization of this matrix the absorption bands and oscillator strengths are calculated. In a number of cases more configurations were taken into account, but the results only slightly changed. The results of the calculations together with the experimental data are given in table 4-V.

Table 4-V. The calculated absorption bands and oscillator strengths together with the experimental frequencies and extinction coefficients.

UNSUBSTITUTED		
	calculated ν (cm^{-1}) - f	experimental ν (cm^{-1}) - $\varepsilon_{max.}$
$>C = CH_2$	40400 - .34(y)	41000 - 12000
	43600 - .36(x)	
$>C = NH$	41900 - .26(y)	41700 - 13000
	42800 - .36(x)	
$>C = O$	41200 - .39(x)	40000 - 18000
	42200 - .21(y)	
$>C = S$	30800 - .52(y)	31600 - 15800
	37000 - .46(x)	
$>\overset{+}{C} - NH_2$	32600 - .53(x)	34800 - 20000
	36500 - .31(y)	
$>\overset{+}{C} - OH$	28000 - .67(x)	29400 - 24000
	36700 - .18(y)	34500 - 9000
$>\overset{+}{C} - SH$	28700 - .60(x)	25600
	31300 - .48(y)	
$>\overset{+}{C} - CH_3$	23900 - .80(x)	23600 - 37000
	36600 - .13(y)	31800 - 10000

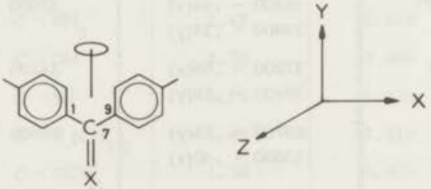
P, P' - METHOXY SUBSTITUTED		
	calculated ν (cm^{-1}) - f	experimental ν (cm^{-1}) - $\varepsilon_{max.}$
$>C = CH_2$	38700 - .46(y)	40800 - 24000
	40200 - .64(x)	
$>C = NH$	38800 - .64(x)	37000 - 21000
	39400 - .35(y)	
$>C = O$	37200 - .66(x)	34200 - 24000
	39400 - .28(y)	
$>C = S$	29700 - .55(y)	28600 - 31000
	33000 - .60(x)	
$>\overset{+}{C} - NH_2$	27800 - .73(x)	29700 - 23000
	32600 - .33(y)	32000 - 20000
$>\overset{+}{C} - OH$	24000 - .86(x)	25000 - 42000
	33000 - .25(y)	31700 - 10000
$>\overset{+}{C} - SH$	24500 - .84(x)	21600 - 50000
	28900 - .44(y)	26000 - 22000
$>\overset{+}{C} - CH_3$	20800 -1.06(x)	20700 - 60000
	33100 - .20(y)	30000 - 9500

Table 4-V (continued).

P,P' - DIMETHYLAMINO SUBSTITUTED		
	calculated ν (cm^{-1}) - f	experimental ν (cm^{-1}) - $\epsilon_{max.}$
$>C = CH_2$	33500 -1.14(x) 34400 - .61(y)	34200 - 31000
$>C = NH$	31900 -1.00(x) 34400 - .48(y)	30600 - 39000
$>C = O$	30600 -1.16(x) 34200 - .42(y)	27000 - 36000 32300 - 10000
$>C = S$	25700 - .87(x) 27800 - .97(y)	23000 - 39000
$>\overset{+}{C} - NH_2$	22400 -1.09(x) 29000 - .51(y)	23100 - 58000 27200 - 22000
$>\overset{+}{C} - CH_3$	18700 - 1.60(x) 30400 - .26(y)	16400 -100000

4. DISCUSSION.

For all of the molecules two strong absorption bands in the long wavelength region were calculated: one polarized in the x-direction and for a small amount in the z-direction and the other in the y-direction. The molecules have a twofold axis of symmetry and the y-direction is chosen along this symmetry axis.



For an interpretation of these absorption bands we consider α,α -diphenyl-ethylene. As a first approximation we neglect the conjugation C_1 - C_7 and C_9 - C_7. The energy levels of the molecule according to the Hückel method are given on the left side of figure 4-4. The molecular orbitals of the degenerate benzene levels are chosen in such a way that the coefficients on the atoms 1 and 9 are zero for one orbital. Introducing the conjugation between the two phenyl rings and ethylene as a perturbation the orbitals will mix in the following ways:

1. The energies of the orbitals with coefficient zero on the atoms 1 and 9 will not be influenced by this interaction. Combined in a symmetric and an antisymmetric way the orbitals ⓐ and ⓢ result.
2. The other four benzene orbitals can be combined with each other in an antisymmetric way. These orbitals a do not mix with the ethylenic orbitals and the energies remain the same. The four symmetric combinations, however, will mix with the orbitals of the ethylenic group resulting in the six new orbitals s.

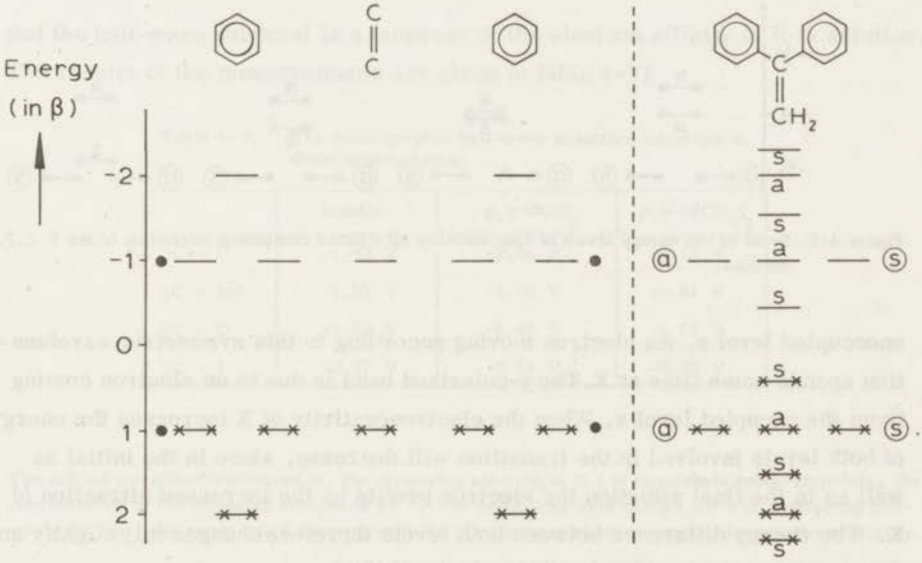


Figure 4-4. Energy levels according to the Hückel method. The levels of the benzene orbitals with coefficient zero on the atoms 1 and 9 are marked by a dot.

On substitution of methoxy or dimethylamino groups in the p- and p'-positions the picture will remain the same. The energy levels involved in the absorption bands of four methoxy substituted compounds are given in figure 4-5. To simplify the figure the levels have been shifted in such a way that the ⓐ and ⓢ levels have the same energy.

Both absorption bands are due to a transition of an electron to the same

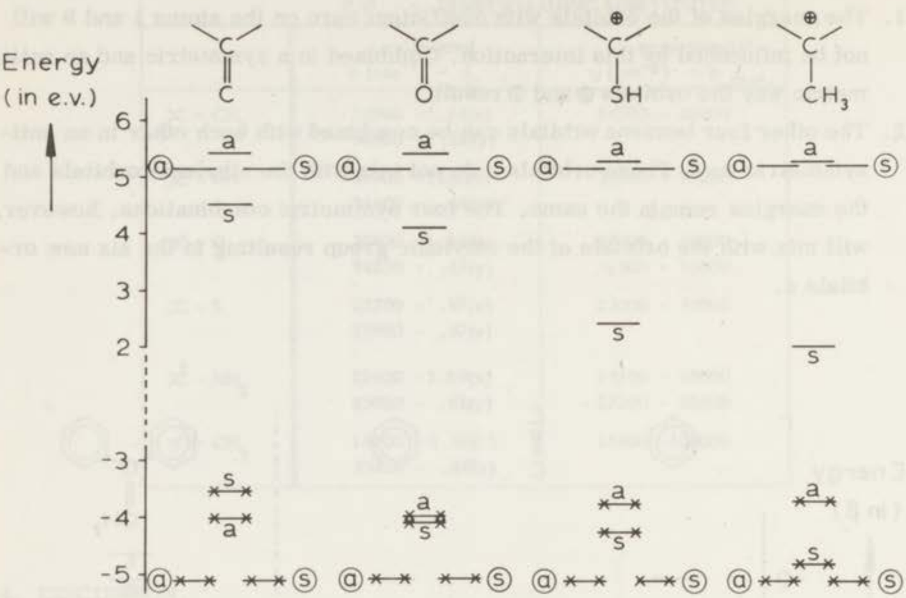


Figure 4-5. Some of the energy levels of four methoxy substituted compounds according to the S.C.F. method.

unoccupied level s. An electron moving according to this symmetric wavefunction spends some time at X. The y-polarized band is due to an electron coming from the occupied level s. When the electronegativity of X increases the energy of both levels involved in the transition will decrease, since in the initial as well as in the final situation the electron profits by the increased attraction of X. The energy difference between both levels therefore changes only slightly and the strong y-polarized band will hardly be shifted.

In the case of the strong x-polarized band, however, the electron comes from the occupied level a. Moving according to this antisymmetric wavefunction it will never be at X and the energy is only slightly influenced by changes in the electronegativity of X. Since the energy of the initial level remains nearly constant and the energy of the final level decreases with increasing electronegativity of X, the x-polarized band will show a pronounced shift to longer wavelengths.

This interpretation agrees with the experimental shifts in the absorption bands. The shift of the first absorption band to longer wavelengths is therefore due to the decrease in energy of the lowest unoccupied energy level.

5. POLAROGRAPHIC MEASUREMENTS.

In the study of UV absorption bands one is primarily interested in differences of energies of occupied and unoccupied levels. It appeared in section 4 that the shift in the UV absorption bands of the compounds is due to the change in energy of the lowest unoccupied level. In order to study this energy more directly the polarographic half-wave reduction potentials were measured[*]. The polarographic reduction is governed by the equilibrium

$$R + e \rightleftarrows R^-$$

and the half-wave potential is a measure of the electron affinity of R in solution. The results of the measurements are given in table 4-VI.

Table 4-VI. The polarographic half-wave reduction potentials in dimethylformamide.

	unsubst.	p,p'-OCH$_3$	p,p'-N(CH$_3$)$_2$
$>$C = C	-1.92 V	-2.04 V	-2.12 V
$>$C = NH	-1.52 V	-1.68 V	-1.81 V
$>$C = O	-1.26 V	-1.46 V	-1.64 V
$>$C = S	-0.57 V	-0.74 V	-0.95 V

The solvent was dimethylformamide, the supporting electrolyte 0.1 M tetraethylammoniumjodide, the concentration of the measured compound 10^{-3}. The reductions were carried out with a dropping mercury electrode, the anode was a mercury pool. In all cases one electron was involved in the reduction.

When the compound is reduced, an electron is accepted in the lowest unoccupied energy level. In these compounds this is the symmetric level, which as already explained is involved in the UV absorption bands. Maccoll[12] showed that the polarographic half-wave reduction potentials of several unsaturated hydrocarbons are linearly correlated with the energy of the lowest unoccupied molecular orbital. This correlation was later confirmed and interpreted by Hoytink et al[13].

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[*] I wish to thank Dr. D.P. den Os for his assistance during the measurements and many helpful discussions.

The energy of this molecular orbital, calculated by using the self-consistent field method, and the half-wave reduction potential of the compounds are shown together in figure 4-6.

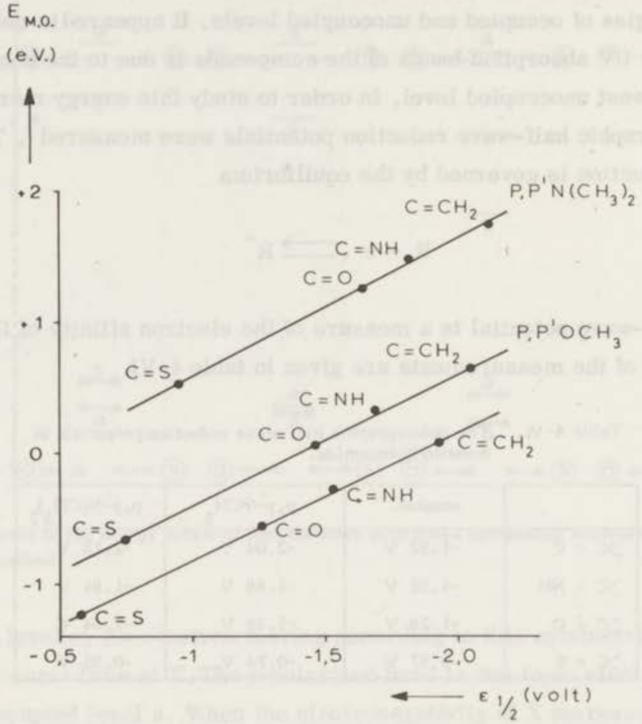
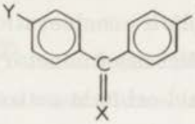


Figure 4-6. Polarographic half-wave reduction potential versus energy of the lowest unoccupied molecular orbital, calculated by the self-consistent field method.

It can be seen that the linear relationship is also valid for the thiobenzophenones and *this justifies the parameters used for the sulfur atom.*

Furthermore, it is remarkable that the slope of the three lines is 45°. This means, that a shift of one e.V. of a calculated energy level, which is the electron affinity of the molecule in vacuo, corresponds to a shift of one Volt in the reduction potential, which can be interpreted as the electron affinity in solution. It follows that the difference in the energy of solvation between the molecule and negative ion, is a constant for each of the four compounds that lie on one line. Perhaps this is due to the common size and shape of the molecules with the same Y and different X.



However, when an unsubstituted and a substituted compound are compared the difference in the energies of solvation of molecule and ion depends on the substituent Y. It appears that the OCH_3- and $N(CH_3)_2$-substituted negative ions are more strongly solvated than the unsubstituted ions. When the calculated electron density on the substituent before and after the reduction is compared, it can be seen that the increase is constant for the four OCH_3-substituted compounds and for the four $N(CH_3)_2$-substituted compounds. The appearance of three lines can therefore be regarded as due to an extra local solvation of the OCH_3- and $N(CH_3)_2$-groups.

6. PARTICIPATION OF 3D ORBITAL AND SEMIEMPIRICAL PARAMETERS FOR SULFUR.

The foregoing results show that the wave functions obtained by the Pariser and Parr theory provide a satisfactory description of the π-electron systems of the molecules under discussion. With respect to the thiobenzophenones two questions remain to be answered.

a. How reasonable is the neglect of the 3d orbital of sulfur?
b. What is the reason that the proportionality constant between the overlap and the resonance integral for the carbon-sulfur bond must be reduced by 30%?

Concerning the first question a controversy still exists as to whether d orbital participation should be included in MO calculations in sulfur-containing aromatic molecules. In most of the considerations thiophene is taken as an illustration. Schomaker and Pauling[14] suggested that resonance forms contributing to the structure of thiophene include those in which the sulfur atom violates the octet rule; i.e. the 3d orbitals are partially occupied in the ground state of the molecule. Longuet-Higgins[15] incorporated this idea in a Hückel MO calculation on thiophene by employing $3p_z$-$3d_{xz}$-$3d_{yz}$ hybrid atomic orbitals on the sulfur atom. This approach has been extended to other sulfur-containing molecules by many authors[16-18]. Although the inclusion of d orbitals on sulfur has proved useful in some cases, many authors believe that sulfur-containing molecules may be treated without their explicit consideration[19-23]. Both of these approaches to the MO study are somewhat unsatisfactory in that the calculations are performed either by omitting the d orbitals entirely or by including their participation arbitrarily.

In order to test the validity of the different approaches Bielefeld and Fitts[24] compared three MO calculations on thiophene. The first considers only the $2p_z$ orbitals on the carbon atoms and the $3p_z$ orbital on sulfur. The second includes two additional orbitals: the $3d_{xz}$ and $3d_{yz}$ atomic orbitals on the sulfur atom. The third calculation adds the $4p_z$ atomic orbital on sulfur to the basic set in the LCAO approximation. The one-center core integrals were approximated by setting them equal to the corresponding atomic valence state ionization potentials. The resonance integrals were calculated using two formulae: one for the carbon-carbon bonds and the other for the carbon-sulfur bonds. Bielefeld and Fitts concluded that the 3d and 4p orbitals on sulfur only participate slightly in the ground state. In all cases a good agreement was obtained with the UV absorption bands although no configuration interaction was taken into account. With respect to the dipole moment, however, the correct value was calculated only by inclusion of 3d orbitals. Since a rather arbitrary value for the σ-moment was assumed this argument in favour of participation of 3d orbitals is not very convincing.

In order to examine the changes of the absorption bands and the energies of the lowest unoccupied molecular orbitals we extended the calculations on the thiobenzophenones by including the 3d orbital. For the difference between the one-center core integrals of the 3p and 3d orbital a value of 8.4 e.V. was assumed in agreement with the excitation energy of the sulfur atom[8]. Inclusion of the 3d orbital causes a very small shift of 10 Å in the first absorption band and the energy of the lowest unoccupied molecular orbital changed about 0.01 e.V.

Concerning the second question, it is noteworthy that in many calculations on thiophene a rather low value for the resonance integral for the carbon-sulfur bond has been assumed in order to obtain agreement with experimental data. Resonance integrals between carbon and a heteroatom of the second row of the periodic system are predicted to a first approximation by proportionality to the overlap integral. The proportionality constant can be calculated from the overlap integral and the estimated resonance integral of the C-C bond in benzene.

The value of $\sim$ -9.6 e.V., resulting from many calculations, can then also be used successfully for C-N and C-O bonds. For the C-S bond, however, a much lower value is necessary for agreement with experimental data (Bielefeld[24] uses -5.6 e.V.).

Sappenfield and Kreevoy[25] remark that the overestimation of the carbon-sulfur resonance integral on the basis of overlap integral ratios may be due to neglect in Slater orbitals of the inner node of the sulfur 3p orbital. The overestimation is caused by the overlap integral and not by the proportionality constant. In order to check up on this possibility the overlap integral was calculated of a 3p orbital of sulfur and a 2p orbital of carbon on a distance of 1.60 Å using the tables of Mulliken, Rieke and Orloff[26]. Three possibilities for the 3p orbital of S were considered:

a. the $3p_S$ is a 3p Slater orbital with an effective nuclear charge (Z) of 5.45. The overlap integral is 0.221.

b. the $3p_S$ is a hydrogen-like 3p orbital (Z = 5.45) with a node in the radial part of the wave function. It can be written as a sum of a 3p and a 2p Slater orbital. The overlap is 0.255.

c. the $3p_S$ orbital of b. is orthogonalized upon the 2p orbital of sulfur with Z = 11.85. The overlap is 0.270.

Thus, there is no overestimation of the overlap integral by neglect of the inner node in a 3p Slater orbital.

Another possibility is that the overlap region of a 3p and a 2p orbital is farther from the nuclei in comparison with two 2p orbitals. The attraction by the nuclei will be smaller and a lower value for the resonance integral results. In order to test this hypothesis theoretical resonance integrals were calculated:

$$\beta_{\mu\nu} = <\mu \left| -\tfrac{1}{2}\Delta \right| \nu> - <\mu \left| \frac{1}{R_\mu} \right| \nu> - <\mu \left| \frac{1}{R_\nu} \right| \nu> \qquad 4.10$$

where the first term is the contribution of the kinetic energy and the other two terms the attraction by the two nuclei μ and ν. Values for these integrals were calculated using the tables of Preuss[27]. For the 3p orbital of sulfur in the carbon-sulfur bond the 3p Slater orbital as well as the hydrogen-like orbital (orthogonalized on the 2p sulfur orbital) was investigated. The results are summarized in table 4-VII. It is evident that the lower proportionality constant between the overlap and the resonance integral for the carbon-sulfur bond is justified using a hydrogen-like 3p orbital on the sulfur atom.

Table 4-VII. The ratio of theoretical resonance and overlap integrals.

bond	distance (in Å)	β theor. (in e.V.)	S	$\frac{\beta_{\text{theor}}}{S}$
C = C	1.39	-4.57	0.250	-18.3
C = N	1.28	-4.68	0.241	-19.4
C = O	1.21	-4.43	0.220	-20.1
C = S (Slater)	1.60	-3.84	0.221	-17.4
C = S (hydrogenlike)	1.60	-3.57	0.270	-13.2

In conclusion, we can say that the 3d orbital in the thiobenzophenones can be neglected. It is as reasonable to omit the 3d orbital of sulfur as for instance the 3p orbital of carbon. Furthermore, the low value for the resonance integral of the C-S bond in comparison with the C-C, C-N and C-O bonds can be understood by calculating theoretical values for the resonance integrals. The same phenomenon will arise in a study of e.g. carbon-phosphor or sulfur-sulfur bonds.

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SAMENVATTING

Het in dit proefschrift beschreven onderzoek heeft tot doel door middel van quantumchemische berekeningen een beter inzicht te verkrijgen in de electronenstructuur en de chemische reactiviteit van organische moleculen. We hebben daarbij niet alleen gebruik gemaakt van de molecular orbital theorie, maar ook van de valence bond methode, die nog maar zelden wordt toegepast voor het interpreteren van experimentele resultaten.

Het veelvuldig gebruik van de molecular orbital theorie in de organische chemie kan grotendeels toegeschreven worden aan de benaderingen en aanpassingen van de parameters door Pariser, Parr en Pople. In hoofdstuk I hebben wij deze methode van aanpak ingevoerd in de valence bond theorie. Het blijkt dat de interactie tussen de covalente en de polaire valence bond structuren wordt bepaald door de resonantieintegralen en de energie van de structuren door de electronen-afstotingsintegralen. Op deze wijze wordt een uiterst overzichtelijk rekenschema verkregen, waarbij de ingewikkelde uitdrukkingen voor de interactieelementen tussen de configuraties van de molecular orbital theorie scherp afsteken.

De nadelen van deze valence bond methode komen in Hoofdstuk II bij de toepassingen op de π-electronen van etheen, butadieen en benzeen echter duidelijk naar voren. Voor de interpretatie van UV spectra bijvoorbeeld, moet bij de berekeningen een zeer groot aantal polaire structuren worden meegenomen, terwijl in de molecular orbital theorie reeds met een gering aantal configuraties de juiste volgorde van de laagste energieniveaus wordt verkregen. Alhoewel het uitvoeren van volledige berekeningen eenvoudiger is met behulp van de valence bond methode, is de bruikbaarheid er van voor grotere moleculen om bovengenoemde redenen aan twijfel onderhevig.

Een toepassing van quantumchemische berekeningen met behulp van de valence bond methode is beschreven in Hoofdstuk III. Het stereoselectieve verloop van thermische en fotochemische cycliseringsreacties werd bestudeerd om na te gaan of de verklaringen van Woodward en Hoffmann op basis van de symmetrie van de hoogst bezette molecular orbital het afwijkende reactiepatroon in grond en aangeslagen toestand juist weergeven. Als voorbeeld werd gekozen de ringsluiting van butadieen tot cyclobuteen. Energieniveaus werden berekend voor *cis*-butadieen, voor cyclobuteen en voor een groot aantal tussenliggende kernconfiguraties, die kunnen optreden tijdens het verloop van de reacties. Met behulp van deze niveaus werden potentiaaloppervlakken, onmisbaar voor een gedetailleerde beschrijving van een chemische reactie, getekend.

Met behulp van deze potentiaaloppervlakken kon worden geconcludeerd dat een disroterende ringsluiting van *cis*-butadieen in de grondtoestand een activeringsenergie vereist van 100 kcal/Mol, zodat de thermische reactie langs deze weg niet mogelijk is. Voor het conroterende proces werd geen activeringsenergie berekend, hetgeen vermoedelijk veroorzaakt wordt door de keuze van het model, aan de hand waarvan de berekingen werden uitgevoerd. De thermische reactie moet, in overeenstemming met het experiment, conroterend verlopen, waarbij in de transition state waarschijnlijk een sterke draaiing om de centrale C-C band plaats vindt.

Het berekende potentiaaloppervlak behorend bij de eerste aangeslagen, antisymmetrische toestand van het *cis*-butadieen geeft geen verklaring voor de fotochemische reactie. Vanuit de kernconfiguratie van *cis*-butadieen neemt de energie in alle richtingen toe en er is daarom geen reden om te veronderstellen dat een cyclisering tot cyclobuteen in deze aangeslagen toestand zou plaats vinden. De verklaring van Woodward en Hoffmann voor het stereoselectieve verloop van de fotochemische reactie op basis van deze antisymmetrische aangeslagen toestand is daarom niet juist.

De berekeningen wijzen daarentegen uit dat de stuwende kracht van de fotochemische ringsluiting gelegen is in het potentiaaloppervlak, behorend bij de tweede aangeslagen toestand van het butadieen. Bij een disroterende ringsluiting profiteert het molecuul van een put in het potentiaaloppervlak van deze symmetrische aangeslagen toestand, waarna de reactie in de grondtoestand kan worden beëindigd. Een analyse met behulp van de bijdragen van valence bond structuren geeft een eenvoudige verklaring voor de juist tegengestelde stereoselectiviteit voor de thermische en de fotochemische reactie.

De UV spectra van difenyletheen, het overeenkomstige imine, benzofenon en thiobenzofenon en van de overeenkomstige dimethoxy en di-(dimethyl)- amino gesubstitueerde verbindingen, opgelost in methanol en zwavelzuur, werden geïnterpreteerd met behulp van self-consistent field molecular orbital berekeningen (Hoofdstuk IV). De benodigde parameters voor de heteroatomen zijn zoveel mogelijk berekend uit de gegevens van de overeenkomstige atoomspectra. Bovendien werden de polarografische reductiepotentialen in dimethylformamide gemeten om de resultaten van de berekeningen ook met deze experimentele gegevens te kunnen vergelijken. Een zeer goede overeenkomst werd verkregen, zowel met de UV spectra als met de reductiepotentialen.

Speciale aandacht werd gewijd aan de parameters van het zwavelatoom in de thiobenzofenonen. Enerzijds werd nagegaan of de 3d orbital een rol speelt in de grondtoestand en in de laagste aangeslagen toestanden van deze verbindingen. Berekeningen met behulp van parameters voor de 3d orbital op basis van de gegevens uit het spectrum van het zwavelatoom tonen aan dat de bijdrage van de 3d orbital verwaarloosbaar klein is. Anderzijds wordt in de literatuur voor de evenredigheidsconstante tussen overlap- en resonantieintegraal van een C-S band in het algemeen een lagere waarde gebruikt dan voor een C-C, C-N of C-O band. Ook bij onze berekeningen was een lagere waarde noodzakelijk om een goede overeenkomst te verkrijgen met de absorptiebanden en reductiepotentialen. De kleinere evenredigheidsconstante kon echter worden gerechtvaardigd door een vergelijking met theoretische waarden voor de resonantieintegralen.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een kort overzicht van mijn academische studie.

Na het behalen van het einddiploma gymnasium β aan het Franciscus College te Rotterdam begon ik in 1955 met de studie aan de Rijksuniversiteit te Leiden. Het candidaatsexamen in de chemie (letter f) werd in oktober 1958 afgelegd. De studie werd daarna voortgezet onder leiding van de hoogleraren dr L.J. Oosterhoff, dr P. Mazur en dr C. Visser. Op de afdeling voor Theoretische Organische Chemie werkte ik onder leiding van dr H.M. Buck aan een onderzoek op het gebied van de fotochemie. Het doctoraalexamen legde ik af in september 1962.

Nadat ik op verzoek van de Rijksuniversiteit te Leiden vrijgesteld was van de vervulling van de militaire dienstplicht, heb ik in 1962 onder leiding van prof. dr L.J. Oosterhoff een aanvang gemaakt met onderzoekingen op het gebied van de quantumchemie. Na eerst van 1962 als assistent verbonden te zijn geweest aan de afdeling voor Theoretische Organische Chemie volgde in 1963 mijn aanstelling tot wetenschappelijk ambtenaar.

Daarnaast ben ik sinds september 1965 voor een beperkt aantal uren als leraar scheikunde verbonden aan het Fioretti-college te Lisse.

De stimulerende gesprekken met de andere leden van de Theoretische afdeling hebben veel bijgedragen tot de totstandkoming van mijn proefschrift. In het bijzonder dank ik dr H.M. Buck voor de vele waardevolle gesprekken en verhelderende discussies. Van het Organisch Chemisch Laboratorium ben ik drs [illegible] zeer erkentelijk voor de [illegible] welke hij mij gaf in de [illegible].

Daarnaast ben ik veel dank verschuldigd aan de medewerkers van het Centraal Reken Instituut voor de hulp bij het schrijven van de computerprogramma's en aan dr [illegible] voor de vele suggesties betreffende het correcte gebruik van de Engelse taal.

De tekeningen werden verzorgd door de heer M. Pison.

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De tekeningen werden verzorgd door de heer M. Pison.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een kort overzicht van mijn academische studie.

Na het behalen van het eindexamen gymnasium β aan het [illegible] College te Amsterdam begon ik in 1955 met de studie aan de Rijksuniversiteit te Leiden. Het candidaatsexamen in de chemie (letter F) werd in oktober 1958 afgelegd. De studie werd daarna voortgezet onder leiding van de hooggeleerden dr L.J. Oosterhoff, dr P. Mazur en dr [illegible]. Op de afdeling voor Theoretische Organische Chemie werkte ik onder leiding van dr H.M. Buck aan een onderzoek op het gebied van de fotochemie. Het doctoraalexamen legde ik af in september 1962.

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Daarnaast ben ik sinds september 1958 voor een [illegible] aantal uren als leraar scheikunde werkzaam aan het [illegible] te Leiden.

De stimulerende gesprekken met de andere leden van de Theoretische afdeling hebben veel bijgedragen tot de totstandkoming van mijn proefschrift. In het bijzonder dank ik dr H.M. Buck voor de vele inspirerende gesprekken en verhelderende discussies. Van het Organisch Chemisch Laboratorium ben ik [illegible] zeer erkentelijk voor de [illegible] wijze waarop hij [illegible] in de [illegible].

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De tekeningen werden verzorgd door de heer W. [illegible].

STELLINGEN

I

Er wordt in leerboeken over quantummechanica onvoldoende op gewezen, dat de absolute waarden van functies f(x), die kwadratisch integreerbaar zijn in het interval $(-\infty, +\infty)$, niet noodzakelijk naar nul streven voor de limiet $x \rightarrow \pm\infty$.

S. Tomonaga, Quantum Mechanics (1966)
L.D. Landau en E.M. Lifshitz, Quantum Machanics (1958)
W. Döring, Einführung in die Quantenmechanik (1955)

II

De bathochrome verschuiving in het UV spectrum, welke optreedt bij de reactie van het protoncomplex van dianisyletheen met broom in zuur milieu, kan met behulp de symmetrie van de molecular orbitals van het protoncomplex worden verklaard.

H.M. Buck, S.J. Oldenburg en L.J. Oosterhoff, Chimia, 20, 324 (1966)

III

Het verdient aanbeveling om bij de bepaling van dipoolmomenten in de aangeslagen toestand polarisatiemetingen van de absorptie en fluorescentie te verrichten.

N.G. Bakhshiev, Optics and Spectroscopy, 13, 24 (1962)

IV

Het verwaarlozen van dubbel-aangeslagen toestanden door Allinger, Gilardeau en Chow doet afbreuk aan hun conclusie, dat de grondtoestand van cyclobutadieen waarschijnlijk een triplet is.

N.L. Allinger, C. Gilardeau en L.W. Chow, Tetrahedron, 24, 2401 (1968)

V

De toepassing van een guard door Dowell en Sharp in hun energiespectrometer heeft een ongunstige invloed op de meetresultaten.

J.T. Dowell en T.E. Sharp, J. Chem. Phys., 47, 5068 (1967)

VI

De in de literatuur gegeven interpretatie van de UV spectra van thiophenol en analoge verbindingen is aan twijfel onderhevig.

A. Mangini en C. Zauli, J. Chem. Soc., 4960 (1956)
H. van Zwet en E.C. Kooyman, Rec. Trav. Chim., 86, 993 (1967)

VII

De wijze waarop Jungen, Labhart en Wagnière de energie en het dipoolmoment van de $n \rightarrow \pi^*$ toestand van formaldehyde berekenen, is onjuist.

M. Jungen, H. Labhart en G. Wagnière, Theor. Chim. Acta, 4, 305 (1966)

VIII

De resultaten van berekeningen met behulp van de extended Hückel theorie zijn, in het bijzonder voor moleculen in een aangeslagen toestand, onbetrouwbaar.

R. Hoffmann, G.D. Zeiss en G.W. van Dine, J. Am. Chem. Soc. 90, 1485 (1968)
W. Adam, A. Grimison, R. Hoffmann en C. Zuazaga de Ortiz, J. Am. Chem. Soc., 90, 1509 (1968)

IX

Het door de commissie den Hertog opgestelde studieprogramma van de organische scheikunde voor het Voorbereidend Wetenschappelijk Onderwijs is te eenzijdig gericht op theoretische aspecten.

X

Het is te betreuren, dat voetbalwedstrijden om de Europa Cup meestal op dezelfde tijd plaats vinden als diners, die gegeven worden ter gelegenheid van promoties aan de Rijksuniversiteit te Leiden.

W. Th. A.M. van der Lugt

Leiden, 25 juni 1968