Regiospecific cyclodimerizations of arylacetylenes : a spectroscopic and quantumchemical study

REGIOSPECIFIC CYCLODIMERIZATIONS
OF ARYLACETYLENES

A SPECTROSCOPIC AND QUANTUMCHEMICAL STUDY

A. E. VAN DER HOUT-LODDER

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CHAPTER I

GENERAL INTRODUCTION

This thesis describes the reactions of aryl-substituted
acetylenes with proton acids and transition metal ions. Both
reactions represent cyclodimerization reactions of acetyle-
nes. The presence of proton acids leads to formation of pro-
tonated cyclobutadienes(cyclobutenyl cations), whereas the
reaction with transition metal ions affords the correspon-
ding metal complexed cyclobutadienes.

One of the interesting aspects of these cycloadditions
consists of the selectivity of the cyclodimerization process,
whereby only one of the possible cyclodimers is formed. This
kind of specificity is often called regiospecificity, which
according to Hassner(1968) implies a directional preference
for the formation of bonds. Stimulated by these results we
also investigated the dimerization of the cyclobutadiene
metal complexes. In this reaction a striking regiospecifi-
city has also been observed.

The course of these reactions can be derived from the
fundamental theory for concerted cycloaddition reactions as
put forth by Woodward and Hoffmann(1969). The regiospecifi-
city governing the cyclodimerization of acetylene derivati-
ves has been explained in this thesis by the fact that sub-
stituent effects lead to an unsymmetrical transition state.

These matters are clarified by first considering the
reaction of acetylene with a proton. According to Woodward
and Hoffmann a vinyl cation is initially formed which sub-

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sequently reacts with a second molecule acetylene. If the
reaction would proceed in a suprafacial(s) manner, which
involves bond formation or rupture on the same face of the
double bond, the transition state would be isoconjugate with
cyclobutadiene. As this transition state is anti-aromatic,
the reaction is "forbidden" ($_\pi 2_s + _\pi 2_s$ reaction). A reaction,
however, in which one of the components reacts in an antara-
facial(a) manner, defined as occuring on opposite faces of
the double bond, is "allowed" ($_\pi 2_s + _\pi 2_a$ reaction). One out-
of-phase overlap is present in the transition state which
is isoconjugate with "anti-Hückel" cyclobutadiene and con-
sequently aromatic. Maximum overlap of the relevant orbital
lobes is obtained if the two reactants approach each other
orthogonally (Fig.1.1).
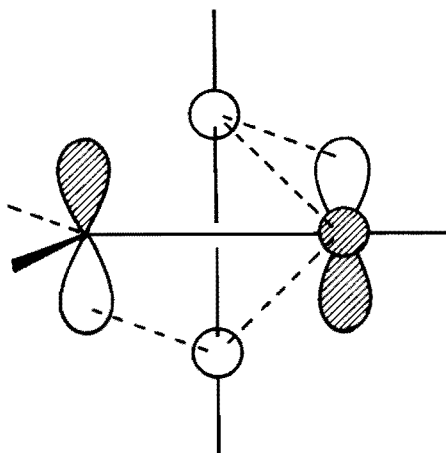
Fig.1.1 Orthogonal approach of a molecule acetylene and a
       vinyl cation.

    It is to be expected, that this orthogonal transition
state will cause a high energy of activation due to the
framework distortions required in maintaining an effective
orbital overlap. However, in the reaction of an acetylene
with a vinyl cation, the empty orbital of the vinyl cation
contributes two strong bonding interactions with the π-
orbitals of the acetylene forming a kind of cyclopropylium

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ion intermediate, thereby lowering the transition state
energy considerably. This theory gives a satisfactory ratio-
nalization of the fact that the cyclodimerization of diaryl-
acetylenes under the influence of proton acids requires only
a very small energy of activation. This has been confirmed
in our investigations.

The cyclodimerization of diarylacetylenes in the presence
of proton acids shows a non-vicinal regiospecificity, which
means that in the product the same substituents are situated
opposed to each other. The regiospecificity of these reac-
tions can be explained by the polar nature of the transition
state, resulting from attack of the preferentially formed vi-
nyl cation on a polarized acetylenic molecule.

The reactions of diarylacetylenes with transition metal
ions show the same regiospecificity as with proton acids. On
the other hand, the reaction of t-butylphenylacetylene with
transition metal ions affords the 1,2-di-t-butyl-3,4-diphe-
nylcyclobutadiene complex(Avram et al.,1969 and Hosokawa et
al., 1969). The vicinal regiospecificity of this reaction
should probably be attributed to steric factors. In this
respect, it is interesting that the reaction of t-butylphe-
nylacetylene with proton acids leads to the non-vicinal cy-
clobutenyl cation. The structure of the 1,3-diphenyl-2,4-di-
t-butylcyclobutenyl cation has been determined with the ^{13}C
NMR technique.

The tetra-arylcyclobutadiene complexes, obtained from the
reaction of diarylacetylenes with transition metal salts,
offer the interesting possibility to study also the mecha-
nism of the dimerization of tetra-arylcyclobutadienes to
octa-arylcyclo-octatetraenes.The observed regiospecificity
is perhaps attributable to the fact that in this $_{\pi}2_s+_{\pi}4_s$
process endo dimerization is favoured over the exo combina-
tion due to secondary orbital interactions in the transi-
tion state.

Chapter II offers a summary of the quantumchemical me-
thods used in this thesis. The LCAO-MO-SCF method is descri-

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bed together with the approximations leading to the π-electron theory of Pariser, Parr and Pople (PPP) and the CNDO-2 method which includes all valence electrons.

In chapter III experimental evidence is presented for the regiospecific formation of tetra-arylcyclobutenyl cations from diarylacetylenes by reaction with acids. The structure analysis of the tetra-arylcyclobutenyl cations is mainly based on PMR measurements; in addition the ^{13}C NMR spectra of the cyclobutenyl cations with ^{13}C enrichment of the cyclobutenyl ring are given. The chemical shift of these cyclobutenyl ^{13}C atoms could be related to the charge on these carbon atoms. The obtained charge densities are used to test our quantumchemical calculations.

In chapter IV the experimental UV spectra of the tetra-aryl-cyclobutenyl cations are discussed in relation to the UV spectra which are calculated with the PPP method. Different geometric and theoretical models have been used for these calculations. The charges obtained from ^{13}C NMR together with the experimental UV spectra were used to test the different models. From these calculations it became clear that π-overlap across the cyclobutenyl ring had to be taken into account. Therefore we propose that these cations can be regarded as homocyclopropenyl cations.

In chapter V the mechanism of the cyclodimerization reaction has been considered. CNDO-2 calculations have been performed on the reaction between a molecule acetylene and a vinyl cation using different models for the transition state. The regiospecificity of the reaction between acetylene with different substituents and the related vinyl cation can qualitatively be explained by a polarization of the acetylenic bond. This concept has been confirmed by PPP calculations.

Chapter VI concerns the reactions of diarylacetylenes and t-butylphenylacetylene with transition metal ions. A reaction mechanism is proposed, explaining the opposed regiospecificity of these reactions. Photochemical excitation

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of the tetra-arylcyclobutadiene complexes leads to the for-
mation of tetra-arylcyclobutenyl cations. From the struc-
ture of these cations, the sequence of the aryl groups in
the cyclobutadiene complexes can be established. By use of
^{13}C NMR it is shown, that the reaction of t-butylphenylace-
tylene with protons also proceeds in a non-vicinal regio-
specific way.

In chapter VII, the formation of octa-arylcyclo-octate-
traenes from the tetra-arylcyclobutadiene complexes, descri-
bed in chapter VI, is reported. Also this cyclodimerization
proceeds regiospecifically. In order to explain the regio-
specificity of the latter process, CNDO-2 calculations have
been carried out, showing that the endo reaction of two mo-
lecules cyclobutadiene is favoured over the exo reaction.
This is in agreement with the qualitative predictions of
Woodward and Hoffmann.

In chapter VIII the method of preparation of the compounds
used in this thesis is reported. Some reactions of the te-
tra-arylcyclobutenyl cations are discussed. It appears that
the electronegativity of the counter ion of the acid deter-
mines whether electrophilic or nucleophilic attack on the
acetylenic bond predominates. In the case of a nucleophilic
attack no cyclodimerization occurs but the normal addition
product is formed.

CHAPTER II

SUMMARY OF THE QUANTUM CHEMICAL METHODS USED FOR THE INTER-
PRETATION OF REACTIVITY AND SPECTROSCOPIC DATA.

II.1. *Introduction.*

The use of quantumchemical calculations can provide an ex-
planation of chemical reactions. In the first place, the ex-
tent and manner of electron delocalization may aid in predic-
ting the tendency of the molecule to undergo a certain reac-
tion. On the other hand, it is also possible to calculate the
energy along the preferred pathway of a chemical reaction. An
estimate of the energy of activation can be obtained by compa-
ring the total energy of the reacting molecules with the ener-
gy of a suitable model for the transition state. Quantumchemi-
cal methods can also be applied to the calculation of physical
properties of a molecule. From ground-state calculations one
can obtain charge densities, bond orders, dipole moments or
ionization potentials, whereas a calculation on excited states
allows the interpretation of the electronic absorption spec-
trum (UV spectrum) of a molecule.

In this thesis two quantumchemical methods have been used,
which are based on the MO-SCF scheme (Hartree, 1928; Fock,
1930) and the use of atomic orbitals as basis functions (LCAO
method) according to Roothaan (1951). For conjugated molecu-
les, the π-electron theory of Pariser, Parr (1953) and Pople
(1953) has been applied. A calculation on the ground state
provides charge densities, which can be compared with the
experimentally determined charge densities from ^{13}C NMR.

Furthermore, the UV spectra of conjugated molecules can theoretically be obtained by the use of the virtual orbitals of the SCF calculation of the ground state combined with a configuration interaction treatment (CI). The π-electron theory has also been applied to some transition state calculations.

For this purpose however, calculations with the CNDO-2 method of Pople and Segal (1966) are more suitable, because all valence electrons are included in the calculation. Steric interactions and transition state strain are properly described by this method.

In this chapter a survey of the LCAO-MO-SCF method will be offered together with the approximations which lead to the π-electron theory of Pariser, Parr and Pople and the CNDO-2 method of Pople and Segal.

II.2. *The LCAO-MO-SCF method for closed shell molecules.*

The electronic energy of the ground state of a closed shell molecule with 2n electrons is given by the expectation value of the energy

$$\langle \chi_0 | H | \chi_0 \rangle \qquad \qquad 2.1$$

If only kinetic energy and Coulomb terms are taken into account and furthermore the Born-Oppenheimer approximation (1927) is assumed to be valid, the Hamiltonian operator is given by

$$H = \sum_i^{2n} H^{core}(i) + \sum_{i<j}^{2n} \frac{1}{r_{ij}} \qquad \qquad 2.2$$

in which $H^{core}(i)$ is a one-electron operator, representing a sum of kinetic energy and attraction by the nuclei and $1/r_{ij}$ is a two-electron operator, which represents the mutual repulsion between electrons i and j.

The wave function of the ground state is described by one Slater determinant, which exhibits the required antisymmetry (Pauli's principle, 1927) with respect to interchange of

two electrons

$$\chi_0 = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} \psi_1(1)\ \alpha(1) & \psi_1(1)\beta(1) & \cdots & \psi_n(1)\alpha(1) & \psi_n(1)\beta(1) \\ & & & & \\ \psi_1(2n)\alpha(2n) & \psi_1(2n)\beta(2n) & \cdots & \psi_n(2n)\alpha(2n) & \psi_n(2n)\beta(2n) \end{vmatrix} \qquad 2.3$$

A shorter notation for a Slater determinant is

$$\chi_0 = \frac{1}{\sqrt{(2n)!}} \left| \psi_1(1)\bar{\psi}_1(2) \cdots \psi_n(2n-1)\bar{\psi}_n(2n) \right| = \left| \psi_1\bar{\psi}_1 \cdots \psi_n\bar{\psi}_n \right| \qquad 2.4$$

in which ψ indicates spin α and $\bar{\psi}$ indicates spin β.
The energy of the ground state is now given by

$$E = \left\langle \chi_0 \middle| H \middle| \chi_0 \right\rangle = \left\langle \left| \psi_1\bar{\psi}_1 \cdots \psi_n\bar{\psi}_n \right| H \middle| \psi_1\bar{\psi}_1 \cdots \psi_n\bar{\psi}_n \right| \right\rangle \qquad 2.5$$

For convenience the following quantities will be defined

$$\varepsilon_k^{core} = \left\langle \psi_k(1) \middle| H^{core}(1) \middle| \psi_k(1) \right\rangle \qquad 2.6$$

$$J_{kl} = \left\langle \psi_k(1)\psi_k(1) \middle| \frac{1}{r_{12}} \middle| \psi_l(2)\psi_l(2) \right\rangle = \left\langle \psi_k(1) \middle| J_l(1) \middle| \psi_k(1) \right\rangle \qquad 2.7$$

J_{kl} is called the Coulomb integral and describes the mean repulsion between two electrons, one in orbital ψ_k the other in orbital ψ_l. This term is independent of the position of the electrons with respect to each other, no correlation being taken into account. The Coulomb operator J_l is defined by 2.8.

$$J_l(1)\psi_k(1) = \int \psi_l^*(2) \frac{1}{r_{12}} \psi_l(2)\psi_k(1)d\tau_2 \qquad 2.8$$

$$K_{kl} = \left\langle \psi_k(1)\psi_l(1) \middle| \frac{1}{r_{12}} \middle| \psi_k(2)\psi_l(2) \right\rangle = \left\langle \psi_k(1) \middle| K_l(1) \middle| \psi_k(1) \right\rangle \qquad 2.9$$

K_{kl} is called the exchange integral, because it arises from a product of terms, in which one exchange of orbitals has taken place. The exchange operator K_l is defined by 2.10.

$$K_l(1)\psi_k(1) = \int \psi_l^*(2) \frac{1}{r_{12}} \psi_k(2)\psi_l(1)d\tau_2 \qquad 2.10$$

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By virtue of the normalization of the Slater determinants, one obtains as the sum of all one-electron terms

$$\sum_k^n \left[\langle \psi_k(1) | H^{core}(1) | \psi_k(1) \rangle + \langle \bar{\psi}_k(1) | H^{core}(1) | \bar{\psi}_k(1) \rangle \right] = 2 \sum_k^n \varepsilon_k^{core} \qquad 2.11$$

The two-electron terms yield the sum of three terms 2.12, 2.13 and 2.14.

$$\sum_k^n \langle \psi_k(1) \psi_k(1) | \frac{1}{r_{12}} | \bar{\psi}_k(2) \bar{\psi}_k(2) \rangle = \sum_k^n J_{kk} \qquad 2.12$$

$$\sum_{k<l}^n \left[\langle \psi_k(1) \psi_k(1) | \frac{1}{r_{12}} | \psi_l(2) \psi_l(2) \rangle + \langle \bar{\psi}_k(1) \bar{\psi}_k(1) | \frac{1}{r_{12}} | \psi_l(2) \psi_l(2) \rangle + \right.$$

$$\left. + \langle \psi_k(1) \psi_k(1) | \frac{1}{r_{12}} | \bar{\psi}_l(2) \bar{\psi}_l(2) \rangle + \langle \bar{\psi}_k(1) \bar{\psi}_k(1) | \frac{1}{r_{12}} | \bar{\psi}_l(2) \bar{\psi}_l(2) \rangle = \right.$$

$$\sum_{k \neq l}^n 2 J_{kl} \qquad 2.13$$

$$- \sum_{k<l}^n \left[\langle \psi_k(1) \psi_l(1) | \frac{1}{r_{12}} | \psi_k(2) \psi_l(2) \rangle + \langle \bar{\psi}_k(1) \bar{\psi}_l(1) | \frac{1}{r_{12}} | \bar{\psi}_k(2) \bar{\psi}_l(2) \rangle \right]$$

$$= - \sum_{k \neq l}^n K_{kl} \qquad 2.14$$

The summation is restricted in order to avoid counting the repulsions twice over. The minus sign in 2.14 arises, because one interchange of electrons has taken place in comparison with 2.13. The effect of the exchange term is that the repulsion between two electrons with parallel spins is lowered. This kind of correlation is introduced by Pauli's principle (1927). This effect forms the basis of Hund's rule. The expression for the total energy is now

$$E = 2 \sum_k^n \varepsilon_k^{core} + \sum_k^n J_{kk} + \sum_{k \neq l}^n (2 J_{kl} - K_{kl}) \qquad 2.15$$

From the definition of the integrals it follows that $J_{kk} = K_{kk}$. Adding $J_{kk} - K_{kk}$ to 2.15 gives the Hartree-Fock energy

$$E = 2 \sum_k^n \varepsilon_k^{core} + \sum_k^n \sum_l^n (2 J_{kl} - K_{kl}) \qquad 2.16$$

The expression for the orbital energy likewise becomes

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$$\varepsilon_k = \langle \psi_k | H | \psi_k \rangle = \varepsilon_k^{core} + \sum_1^n (2J_{kl} - K_{kl}) \qquad 2.17$$

Summation of 2.17 over k and combining with 2.15 gives the alternative expressions for the total energy 2.18 and 2.19.

$$E = 2 \sum_k^n \varepsilon_k - \sum_k^n \sum_l^n (2J_{kl} - K_{kl}) \qquad 2.18$$

$$E = \sum_k^n (\varepsilon_k + \varepsilon_k^{core}) \qquad 2.19$$

The problem now is to find the single determinant of the type 2.4, which gives rise to the lowest ground state energy. Equation 2.16 must be minimized with respect to the ψ_k, subject to the condition $S_{kl} = \langle \psi_k | \psi_l \rangle = \delta_{kl}$. The solution to this problem is obtained by solving the Hartree-Fock equations

$$F(1)\psi_k(1) = \varepsilon_k \psi_k(1) \qquad 2.20$$

where the Hartree-Fock operator is given by

$$F(1) = H^{core}(1) + \sum_k^n \left[2J_1(1) - K_1(1) \right] \qquad 2.21$$

The Hartree-Fock equations are coupled equations, one has to know the set ψ_k in order to know the F-operator. This problem is solved by an iterative process, first a set ψ_k is estimated, then 2.20 is solved which yields a new set ψ_k and this process is iterated until two succesive solutions are identical or nearly identical.

In order to enable solution of 2.20 for molecules, the molecular orbitals are written as a linear combination of atomic orbitals (LCAO) according to Roothaan (1951). So we have

$$\psi_k = \sum_\nu c_{k\nu} \phi_\nu \qquad 2.22$$

The molecular orbitals are indicated with ψ and the indices k, l, s, t; the atomic orbitals with ϕ and the indices μ, ν, ρ, σ.

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If we insert 2.22 into 2.20, multiply on the left by ϕ_μ and integrate, we obtain

$$\sum_\nu c_{k\nu} F_{\mu\nu} = \epsilon_k \sum_\nu c_{k\nu} S_{\mu\nu} \qquad\qquad 2.23$$

in which

$$F_{\mu\nu} = \left\langle \phi_\mu(1) \,\middle|\, F(1) \,\middle|\, \phi_\nu(1) \right\rangle \qquad\qquad 2.24$$

$$S_{\mu\nu} = \left\langle \phi_\mu(1) \,\middle|\, \phi_\nu(1) \right\rangle \qquad\qquad 2.25$$

From 2.23 follows

$$\sum_\nu c_{k\nu} (F_{\mu\nu} - \epsilon_k S_{\mu\nu}) = 0 \qquad\qquad 2.26$$

Equations 2.26 are simultaneous equations for the unknown $c_{k\nu}$. A non-trivial solution exists if

$$|F_{\mu\nu} - \epsilon_k S_{\mu\nu}| = 0 \qquad\qquad 2.27$$

The ϵ_k (k=1,2..n) are the solutions of 2.27. The coefficients $c_{k\nu}$ of the expansion in atomic orbitals can be obtained from 2.26. The matrix elements $F_{\mu\nu}$ follow from 2.17 using the expansion in atomic orbitals

$$\epsilon_k = \left\langle \psi_k \,\middle|\, H \,\middle|\, \psi_k \right\rangle = \sum_\mu \sum_\nu c_{k\mu} c_{k\nu} F_{\mu\nu} \qquad\qquad 2.28$$

$$\epsilon_k = \sum_\mu \sum_\nu c_{k\mu} c_{k\nu} H_{\mu\nu}^{core} + \sum_l \sum_\mu \sum_\nu \sum_\rho \sum_\sigma 2 c_{k\mu} c_{k\nu} c_{l\rho} c_{l\sigma}$$
$$\left[\left\langle \mu\nu \,\|\, \rho\sigma \right\rangle - \tfrac{1}{2} \left\langle \mu\rho \,\|\, \nu\sigma \right\rangle \right] \qquad\qquad 2.29$$

in which

$$H_{\mu\nu}^{core} = \left\langle \phi_\mu \,\middle|\, H^{core} \,\middle|\, \phi_\nu \right\rangle \qquad\qquad 2.30$$

and

$$\left\langle \mu\nu \,\|\, \rho\sigma \right\rangle = \left\langle \phi_\mu(1) \phi_\nu(1) \,\middle|\, \frac{1}{r_{12}} \,\middle|\, \phi_\rho(2) \phi_\sigma(2) \right\rangle \qquad\qquad 2.31$$

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Introducing the expression for the bond order

$$P_{\rho\sigma} = 2 \sum_{1}^{n} c_{1\rho} c_{1\sigma} \qquad\qquad 2.32$$

and equalization of 2.28 and 2.29 yields

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\rho}\sum_{\sigma} P_{\rho\sigma}\left[\langle\mu\nu\|\rho\sigma\rangle - \tfrac{1}{2}\langle\mu\rho\|\nu\sigma\rangle\right] \qquad 2.33$$

II.3. *The π-electron method of Pariser, Parr and Pople.*

Pariser, Parr and Pople have developed a theory for π-electrons in conjugated molecules. In the π-electron approximation, the σ-electrons make up the core, while the more loosely bound π-electrons are moving in the potential field of this core. The effect of the non-polarizable core is represented in the Hamiltonian by $H^{core}(i)$. The basis set of atomic orbitals consists of Slater $2p_z$ atomic orbitals. As a first approximation for the SCF procedure the Hückel MO's are used. Pariser, Parr and Pople have introduced a number of approximations, which facilitate the calculation enormously.

A. Zero-differential overlap in all two-electron integrals

$$\langle\mu\nu\|\rho\sigma\rangle = \langle\mu\mu\|\rho\rho\rangle\,\delta_{\mu\nu}\,\delta_{\rho\sigma} \qquad\qquad 2.34$$

$$S_{\mu\nu} = \delta_{\mu\nu} \qquad\qquad 2.35$$

This simplifies the F matrix to

$$F_{\mu\mu} = H_{\mu\mu}^{core} + \tfrac{1}{2}P_{\mu\mu}\langle\mu\mu\|\mu\mu\rangle + \sum_{\sigma\neq\mu} P_{\sigma\sigma}\langle\mu\mu\|\sigma\sigma\rangle \qquad 2.36$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} - \tfrac{1}{2}P_{\mu\nu}\langle\mu\mu\|\nu\nu\rangle \qquad\qquad 2.37$$

B. The resonance integrals $H_{\mu\nu}^{core}$ are treated as empirical parameters and are then called $\beta_{\mu\nu}$. Furthermore, if atoms μ and ν are not nearest neighbours $\beta_{\mu\nu}=0$.

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C. $H_{\mu\mu}{}^{core}$ must be simplified, because these terms are depen-
dent on the environment in the molecule and the same para-
meter cannot be used for atoms in a different environment.

$$H_{\mu\mu}{}^{core} = \left\langle \phi_\mu \left| -\tfrac{1}{2}\nabla^2 + V_\mu \right| \phi_\mu \right\rangle + \sum_{\sigma \neq \mu} \left\langle \phi_\mu \left| V_\sigma \right| \phi_\mu \right\rangle \qquad 2.38$$

The kinetic energy and the attraction by the nucleus of ϕ_μ
itself is given by the negative value of the valence state
ionization potential $= W_\mu$. The attraction of an electron in
ϕ_μ with core σ is taken to be

$$-Z_\sigma \left\langle \mu\mu \, \| \, \sigma\sigma \right\rangle$$

in which Z_σ is the core charge of nucleus σ, which is equal
to the number of π-electrons that the nucleus contributes.
So,

$$H_{\mu\mu}{}^{core} = W_\mu - \sum_{\sigma \neq \mu} Z_\sigma \left\langle \mu\mu \, \| \, \sigma\sigma \right\rangle \qquad 2.39$$

Under these approximations the F matrix takes the form

$$F_{\mu\mu} = W_\mu + \tfrac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - Z_\sigma) \gamma_{\mu\sigma} \qquad 2.40$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \qquad 2.41$$

in which $\gamma_{\mu\nu} = \left\langle \mu\mu \, \| \, \nu\nu \right\rangle$
The SCF equations now take the simple form

$$\sum_\nu c_{k\nu} F_{\mu\nu} = \varepsilon_k c_{k\mu} \qquad 2.42$$

The total energy including the nuclear replusion term

$$\sum_{\mu < \nu} Z_\mu Z_\nu \gamma_{\mu\nu} \qquad 2.43$$

is given by

$$E_\pi = \sum_\mu P_{\mu\mu} (W_\mu + \tfrac{1}{4} P_{\mu\mu} \gamma_{\mu\mu}) + 2 \sum_{\mu < \nu} P_{\mu\nu} \beta_{\mu\nu} +$$

$$+ \sum_{\mu < \nu} \left[(P_{\mu\mu} - Z_\mu)(P_{\nu\nu} - Z_\nu) - \tfrac{1}{2} P_{\mu\nu}^{\,2} \right] \gamma_{\mu\nu} \qquad 2.44$$

If we wish to calculate the UV spectra of π-electron com-
pounds, it is necessary to give a description of excited
states. For this purpose, it is convenient to use the vir-
tual orbitals obtained in the SCF calculation of the ground
state. In our case only singly excited configurations have
been considered.

A singly excited state, in which for example an electron
of MO ψ_k has been promoted to MO ψ_s, can be described by the
difference of two Slater determinants:

$$^1\chi_{k \to s} = \frac{1}{\sqrt{2}} \left[| \ldots \psi_k \bar{\psi}_s \ldots | - | \ldots \bar{\psi}_k \psi_s \ldots | \right] \qquad 2.45$$

The energy of this excited state with respect to the ground
state is given by

$$\left\langle ^1\chi_{k \to s} \,|H|\, ^1\chi_{k \to s} \right\rangle - \left\langle \chi_0 |H| \chi_0 \right\rangle \qquad 2.46$$

After promotion of this electron the gain in energy with
respect to the ground state is given by

$$\varepsilon_s^{core} + \sum_{i \neq k}^{n} (2J_{is} - K_{is}) + J_{ks} + K_{ks} = \varepsilon_s - J_{ks} + 2K_{ks}$$
$$2.47$$

But, with respect to the ground state the following energy
is lost

$$\varepsilon_k^{core} + \sum_{i \neq k}^{n} (2J_{ik} - K_{ik}) + J_{kk} = \varepsilon_k \qquad 2.48$$

Therefore the energy difference 2.46 is

$$^1E_{k \to s} - E_0 = \varepsilon_s - \varepsilon_k - J_{ks} + 2K_{ks} \qquad 2.49$$

To obtain a good description of singly excited states, it is
necessary to take a linear combination of singly excited
configurations. This is called the configuration interaction

(CI) method. The singly excited state χ_A is now written

$$^1\chi_A = \sum_{ks} c_{A,ks} \, ^1\chi_{k \to s} \qquad\qquad 2.50$$

The coefficients in this linear combination are determined by the variation principle. The following set of secular equations has to be solved, which also yields the energies of the excited states.

$$\sum_{ks} c_{A,ks} (H_{k \to s, 1 \to t} - E_A \, \delta_{kl} \, \delta_{st}) = 0 \qquad\qquad 2.51$$

in which

$$H_{k \to s, 1 \to t} = \left\langle \, ^1\chi_{k \to s} \, |H| \, ^1\chi_{1 \to t} \, \right\rangle \qquad\qquad 2.52$$

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

$$|H_{k \to s, 1 \to t} - E_A \delta_{ks} \delta_{1t}| = 0 \qquad\qquad 2.53$$

The diagonal elements of this secular determinant are given by 2.49, the off-diagonal elements are

$$H_{k \to s, 1 \to t} = 2\left\langle \psi_k \psi_s || \psi_1 \psi_t \right\rangle - \left\langle \psi_1 \psi_k || \psi_t \psi_s \right\rangle \qquad\qquad 2.54$$

The values of these integrals over MO's can be obtained by using the expansion in AO's and the approximations of PPP. The big advantage of the use of the virtual SCF MO's lies in the fact, that the ground state is not altered by CI with singly excited configurations. In other words, the off-diagonal elements between ground state and singly excited configurations are zero.

The oscillator strength f for an electronic transition between the ground state χ_0 and an excited state χ_A is given by

$$f = 1.085 \times 10^{11} \times \nu \times \vec{M}_{OA}^2 \qquad\qquad 2.55$$

in which ν is the frequency of the transition in cm^{-1}.
$\vec{M}_{OA}$ is the transition moment between the states χ_0 and χ_A.

$$\vec{M}_{OA} = \langle \chi_0 | \sum_i (r_i) | \chi_A \rangle \qquad 2.56$$

The summation is over all electrons and r(i) is the position
vector of electron i.

The parameter set, developed by Van der Lugt (1967, 1968)
has been used in all calculations, except in some cases, where
the difference is clearly indicated. The parameters have been
chosen in an empirical way so as to fit the UV spectra of a
series of aromatic compounds.

Description of the parameters:
1. The parameter W_μ should agree with the negative value of
the first valence state ionization potential in the case of
the nucleus contributing one π-electron to the π-system. The
value of W_μ for carbon is slightly adapted, but the differen-
ce between the W_μ of other elements and carbon has not been
changed. The adapted value of W_μ is indicated with α. In the
case of the nucleus contributing 2π-electrons, the value of
α should be related to minus the second ionization potential
in the valence state. It is observed that this value for α
is much too low to obtain good agreement with experimental
UV spectra. For the difference between $\alpha(X^+)$ and $\alpha(X^{++})$ 65%
of the difference between the first and second ionization
potential is taken.
2. The resonance integrals $\beta_{\mu\nu}$ have been taken from the
Mulliken formula

$$\beta_{\mu\nu} = \tfrac{1}{2}S_{\mu\nu}(\alpha_\mu + \alpha_\nu), \text{ if } \mu \text{ and } \nu \text{ are nearest neighbours}$$
$$2.57$$

Furthermore, $\beta_{\mu\nu} = 0$, if μ and ν are not nearest neighbours.
The approximation $S_{\mu\nu} = \delta_{\mu\nu}$ is not used in the formula for
$\beta_{\mu\nu}$.
3. The electronic repulsion integrals.

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For the one-centre repulsion integrals, the empirical formula of Pariser (1953)

$$\gamma_{\mu\mu} = I_\mu - A_\mu \qquad\qquad 2.58$$

is for practical reasons replaced by

$$\gamma_{\mu\mu} = 3.36 \left[Z_\mu^* - 0.35(P_{\mu\mu} - Z_\mu) \right] \qquad\qquad 2.59$$

which yields about the same values as the formula of Pariser.
Z_μ^* = effective nuclear charge calculated from Slater's rules.
$P_{\mu\mu}$ = π-electron density on atom μ.
The two-centre repulsion integrals have been calculated using the formula

$$\gamma_{\mu\nu} = \frac{14.4}{\dfrac{8.57}{Z_\mu^* + Z_\nu^*} \left[1.4 - 0.025 \ (Z_\mu^* + Z_\nu^*)\right]^{-R_{\mu\nu}} + R_{\mu\nu}} \qquad\qquad 2.60$$

Values of the parameters.

Atom	α (in eV)	γ (in eV)	bond	r in Å	β (in eV)	Z^*
C^+	-9.6	10.92	C=C	1.34	-2.602	3.25
				1.39	-2.400	
				1.45	-1.877	
N^+	-12.55	13.10	C=NH	1.28	-2.645	3.90
O^+	-15.52	15.29	C=O	1.21	-2.539	4.55
N^{++}	-21.00	13.10	C-NH$_2$	1.42	-2.818	3.90
O^{++}	-27.52	15.29	C-OH	1.36	-3.005	4.55
$(H_3C)_2N^{++}$	-17.00	13.10	C-N(CH$_3$)$_2$	1.42	-2.818	3.90
$(H_3C)O^{++}$	-25.52	15.29	C-O(CH$_3$)	1.36	-3.005	4.55

As a first approximation of the MO's the Hückel MO's are used. According to equations 2.40 and 2.41 the SCF matrix

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is calculated, then 2.27 is solved and from 2.26 a new set
of MO's is calculated. This process is iterated until two
succeeding bond order matrices are nearly identical.

II.4. *The CNDO-2 method.*

In the CNDO-2 calculation the Slater AO's of all valence
electrons are used as basis set. The effect of the other
electrons is reflected in H^{core}. With the exception of hy-
drogen and lithium more than one orbital per atom is taken
into account. It is required, that the calculations are in-
variant under a rotation of the Cartesian axes. If approx-
imations are introduced the rotational invariance must be
conserved.

1. In the CNDO-2 method the approximation of zero-dif-
ferential overlap is used, as was the case in the PPP method.
For this reason equations 2.35, 2.36 and 2.37 are valid.

$$S_{\mu\nu} = \delta_{\mu\nu} \qquad\qquad 2.61$$

$$F_{\mu\mu} = H_{\mu\mu}^{core} - \tfrac{1}{2} P_{\mu\mu} \left\langle \mu\mu \,\|\, \mu\mu \right\rangle + P_{\sigma\sigma} \left\langle \mu\mu \,\|\, \sigma\sigma \right\rangle \qquad 2.62$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} - \tfrac{1}{2} P_{\mu\nu} \left\langle \mu\mu \,\|\, \nu\nu \right\rangle \qquad\qquad 2.63$$

2. If the zero-differential overlap approximation is in-
troduced and we wish to preserve the rotational invariance,
it is necessary to take

$$\left\langle \mu\mu \,\|\, \nu\nu \right\rangle = \gamma_{AB} \qquad \begin{array}{l}\text{for all } \phi_\mu \text{ on atom A} \\ \text{all } \phi_\nu \text{ on atom B}\end{array} \qquad 2.64$$

Furthermore we define

$$P_{BB} = \sum_\sigma{}^B P_{\sigma\sigma} \qquad \phi_\sigma \text{ on atom B} \qquad 2.65$$

where P_{BB} represents the total electron density associated
with atom B. Equations 2.62 and 2.63 now simplify to

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$$F_{\mu\mu} = H_{\mu\mu}^{core} - \tfrac{1}{2}P_{\mu\mu}\gamma_{AA} + \sum_B P_{BB}\gamma_{AB} \qquad \phi_\mu \text{ on atom A} \qquad 2.66$$

$$F_{\mu\nu} = H_{\mu\nu}^{core} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \qquad \phi_\nu \text{ on atom B} \qquad 2.67$$

3. In evaluating $H_{\mu\nu}^{core}$, $S_{\mu\nu}$ is not taken equal to the unit matrix, but the values calculated over Slater orbitals are used.
$H_{\mu\nu}^{core}$ is taken proportional to the overlap integral as was the case in the PPP method.

$$H_{\mu\nu}^{core} = \beta_{AB}^{0} S_{\mu\nu} \qquad\qquad 2.68$$

However, in contrast to the PPP method, $H_{\mu\nu}^{core}$ is not taken equal to 0, if μ and ν are not neighbours.
To preserve rotational invariance β_{AB}^{0} is only dependent on the nature of atoms A and B.
4. $H_{\mu\mu}^{core}$ is approximated in the same way as in the PPP method by

$$H_{\mu\mu}^{core} = W_\mu - \sum_{B \neq A} Z_B \gamma_{AB} \qquad\qquad 2.69$$

Under these approximations, equations 2.66 and 2.67 become

$$F_{\mu\mu} = W_\mu + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\,\gamma_{AA} + \sum_{B \neq A}(P_{BB} - Z_B)\,\gamma_{AB} \qquad 2.70$$

$$F_{\mu\nu} = \beta_{AB}^{0}\, S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \qquad \mu \neq \nu \qquad\qquad 2.71$$

W_μ is taken from observed atomic energy data, the ionization potential I and the electron affinity A. The theoretical expressions for these quantities are respectively

$$-I_\mu = W_\mu + (Z_A - 1)\,\gamma_{AA} \qquad \phi_\mu \text{ on atom A} \qquad 2.72$$

$$-A_\mu = W_\mu + Z_A \gamma_{AA} \qquad \phi_\mu \text{ on atom A} \qquad 2.73$$

W_μ is taken from the average of expressions 2.72 and 2.73, in order to account satisfactorily for the tendency of an atomic orbital to acquire and to lose electrons. So

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$$-\tfrac{1}{2}(I_\mu + A_\mu) = W_\mu + (Z_A - \tfrac{1}{2})\gamma_{AA} \qquad 2.74$$

Introducing 2.74 into 2.72 gives 2.75

$$F_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + \left[(P_{AA}-Z_A) - \tfrac{1}{2}(P_{\mu\mu}-1)\right]\gamma_{AA} +$$

$$\sum_{B \neq A}(P_{BB}-Z_B)\gamma_{AB} \qquad 2.75$$

$$F_{\mu\nu} = \beta^0_{AB}S_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\gamma_{AB} \qquad 2.76$$

It should be noted, that expression 2.76 is even applicable when ϕ_μ and ϕ_ν are located on the same atom A, when $S_{\mu\nu}=0$ and γ_{AB} is replaced by γ_{AA}.
The total energy is given by a sum of monatomic and diatomic terms

$$\varepsilon_{tot} = \sum_A \varepsilon_A + \sum_{A<B} \varepsilon_{AB} \qquad 2.77$$

in which

$$\varepsilon_A = \sum_\mu^A P_{\mu\mu}W_\mu + \tfrac{1}{2}\sum_\mu^A \sum_\nu^A (P_{\mu\mu}P_{\nu\nu} - \tfrac{1}{2}P_{\mu\nu}^2) \qquad 2.78$$

$$\varepsilon_{AB} = \sum_\mu^A \sum_\nu^B (2P_{\mu\nu}\beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}^2\gamma_{AB}) + (Z_A Z_B R_{AB}^{-1} \quad -$$

$$P_{AA}Z_B\gamma_{AB} - P_{BB}Z_A\gamma_{AB} + P_{AA}P_{BB}\gamma_{AB}) \qquad 2.79$$

To start the SCF procedure an initial estimate of the F matrix is taken.

$$F_{\mu\mu}^{(0)} = -\tfrac{1}{2}(I_\mu + A_\mu) \qquad 2.80$$

$$F_{\mu\nu}^{(0)} = \beta^0_{AB}S_{\mu\nu} \qquad \mu \neq \nu \qquad 2.81$$

After diagonalization of F the SCF-MO's are obtained. With these MO's the bond orders are calculated, which are used to form a new F matrix. The process is stopped if the electronic energy converges to 10^{-6}.

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Values of the parameters.

element	$\frac{1}{2}(I_s + A_s)$ (eV)	$\frac{1}{2}(I_p + A_p)$ (eV)	$-\beta_A^o$ (eV)	eff-nuclear charge z^*	core charge z
H	7.176		9	1.2	1
Li	3.106	1.258	9	1.3	1
Be	5.946	2.563	13	1.95	2
B	9.594	4.001	17	2.60	3
C	14.051	5.572	21	3.25	4
N	19.316	7.275	25	3.90	5
O	25.390	9.111	31	4.55	6
F	32.272	11.080	39	5.20	7

To reduce the amount of empirical parametrization β_{AB}^o is taken to be:

$$\beta_{AB}^o = \tfrac{1}{2}(\beta_A^o + \beta_B^o)$$

The values are selected to give the best fit with ab-initio calculations.

CHAPTER III

STRUCTURE ANALYSIS OF AND CHARGE DISTRIBUTION IN TETRA-ARYL-
CYCLOBUTENYL CATIONS BY USE OF PROTON AND ^{13}C MAGNETIC RESO-
NANCE MEASUREMENTS.

III.1. *Introduction.*

This chapter deals with the proton and ^{13}C magnetic reso-
nance measurements of a number of tetra-arylcyclobutenyl
cations. With the NMR technique it could be established that
the reactions of diarylacetylenes with strong proton acids
like CF_3COOH, H_2SO_4 or HSO_3F yield tetra-arylcyclobutenyl
cations in a non-vicinally regiospecific way. To study this
regiospecificity, diarylacetylenes with different substitu-
ents at the para positions were dissolved in strong proton
acids yielding the cyclobutenyl cations I, II, III and IV
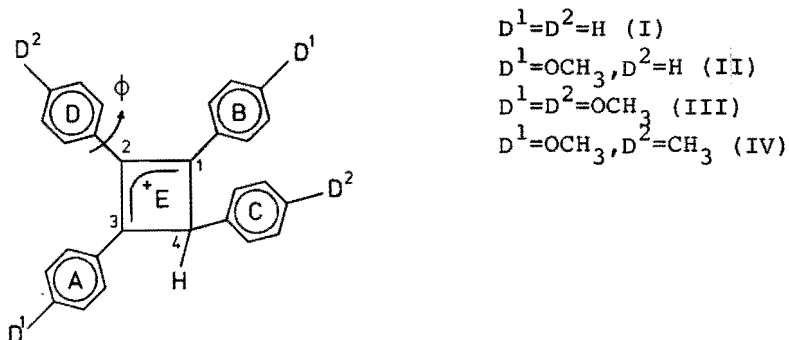respectively (Fig. 3.1).

$D^1=D^2=H$ (I)
$D^1=OCH_3, D^2=H$ (II)
$D^1=D^2=OCH_3$ (III)
$D^1=OCH_3, D^2=CH_3$ (IV)

Fig. 3.1 A tetra-arylcyclobutenyl cation.

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X-ray diffraction measurements carried out by Bryan (1964) on a related compound (4-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate) show that in this type of cation ring D is turned 57° out of the plane formed by rings A, B and E (Fig. 3.1). With these considerations in mind, one may expect the NMR spectra of the tetra-arylcyclobutenyl cations to display three different signals with relative intensities 2:1:1 due to the equivalent rings A and B, ring C and ring D respectively.

Experimental evidence that the results of the X-ray diffraction measurements are also valid for the tetra-arylcyclobutenyl cations in solution has been obtained from proton-deuteron exchange experiments. In the tetra(p-methoxyphenyl) cyclobutenyl cation deuterium could be introduced into one p-methoxyphenyl ring. Most probably ring C (at the saturated carbon atom) is deuterated, while ring D by partial conjugation with the rings A, B and E bears part of the positive charge, thereby impeding attack by a deuteron.

The ^{13}C NMR spectra of cyclobutenyl cations III and IV with ^{13}C enrichment in the cyclobutenyl ring were measured. The ^{13}C shift can be correlated with the charge on the carbon atoms. The experimental charge density forms an important criterion for testing the different models of the SCF calculations.

III.2. *Proton magnetic resonance measurements.*

A. 1,2,3,4-tetra(p-methoxyphenyl)cyclobutenyl cation.

The PMR spectrum of compound III in CF_3COOH is shown in Fig. 3.2. The spectrum displays the signal of the alipathic proton at 5.58 ppm. The expected three signals of the OCH_3 protons appear only partly separated as two signals at 4.16 ppm and 4.00 ppm with relative intensities 1:3.
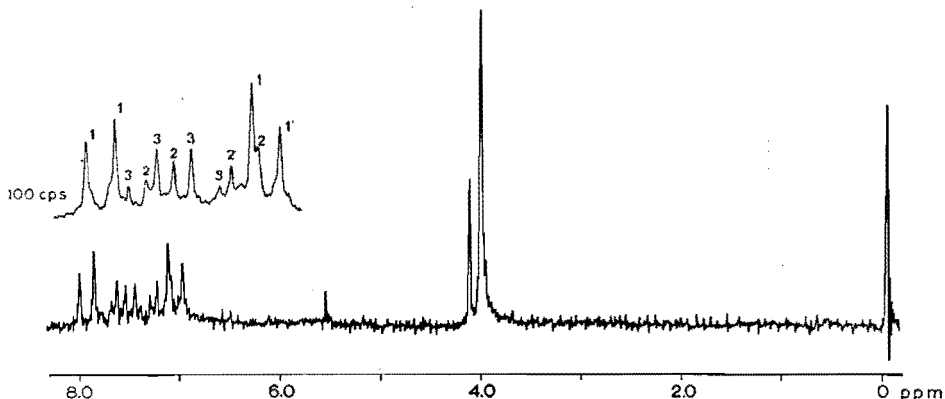
Fig. 3.2 1,2,3,4-tetra(p-methoxyphenyl)cyclobutenyl cation
in CF_3COOH. Shifts in ppm downfield from TMS.

The ratio of the relative intensities is H(aliph.):H(OCH$_3$):H
(arom.)=1:12:16. A more detailed analysis of the phenyl re-
gion is also given in Fig. 3-2. Three different AA'BB' sub-
spectra are present, which are almost quartets, because the
coupling constants $J_{AA'}$, $J_{BB'}$ and $J_{AB'}$ ($=J_{A'B}$) are small
(Richards and Schaefer, 1958).
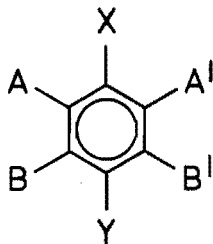
Bij double resonance measurements it was shown of which sig-
nals each quartet consists. Irradiation of the frequency of
one signal of the quartet resulted in an enhanced absorption
of the other signals of the same quartet.
     The signals represented by (1) are due to the equivalency
of rings A and B. This can be concluded from the intensities
of the lines and the fact that most of the positive charge

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is delocalized into rings A and B, resulting in the lowest field signals of the protons ortho with respect to the cyclobutenyl ring. However, no decision could be made as to which of the signals (2) and (3) is due to ring C or D.

This problem has been solved by proton-deuteron exchange experiments, in which deuterium was selectively introduced in ring C. In the same experiment the signals of the OCH_3 protons became separated and can, moreover, be indentified (see section III.3.).

The PMR spectrum of III in HSO_3F at $-60^{\circ}C$ shows oxygen protonation of two of the four OCH_3 moieties (Fig. 3.3).
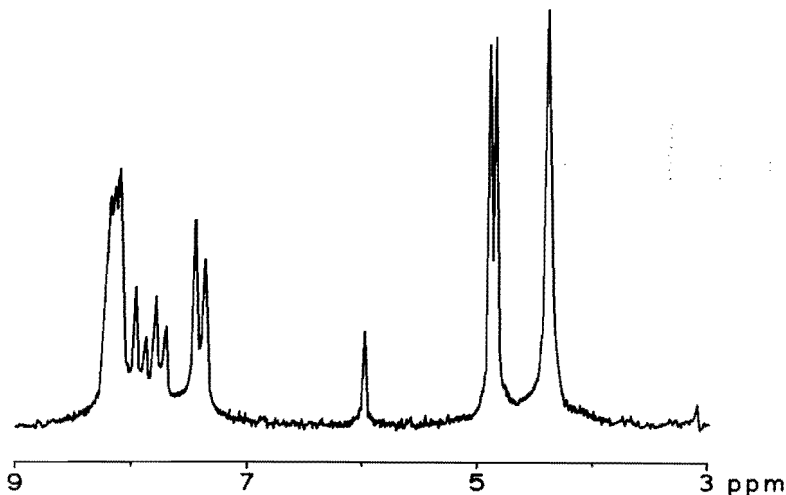
Fig. 3.3 1,2,3,4-tetra(p-methoxyphenyl)cyclobutenyl cation in HSO_3F. Shifts in ppm downfield from TMS.

A doublet present at 4.85 ppm (J=5 cps) is due to the protonated OCH_3 groups, whereas the singlet at 4.37 ppm arises from the unprotonated OCH_3 groups. The relative intensities of these signals are 1:1. These values can be compared with a chemical shift of 4.80 ppm (J=2.7 cps) of the O-protonated OCH_3 groups in 4-methylanisole (Brouwer et.al., 1966). It appears, that the OCH_3 groups of rings C and D have been protonated, as the signals of rings A and B indicated with (1) in Fig. 3.2 are not changed, whereas changes in the absorptions indicated with (2) and (3) are observed.

From this experiment it follows that the conjugation of ring D with the positively charged system is relatively small. Information obtained from proton-deuteron exchange points to some positive charge being present in ring D. Therefore, all evidence is in agreement with the results of the X-ray diffraction on a related compound (Bryan, 1964), which gave a value of $57°$ for the angle of rotation of ring D.

B. 1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl)cyclobutenyl cation.

The PMR spectrum of this cation in CF_3COOH gives evidence of the regiospecificity of the cyclodimerization process and is illustrated in Fig. 3.4.
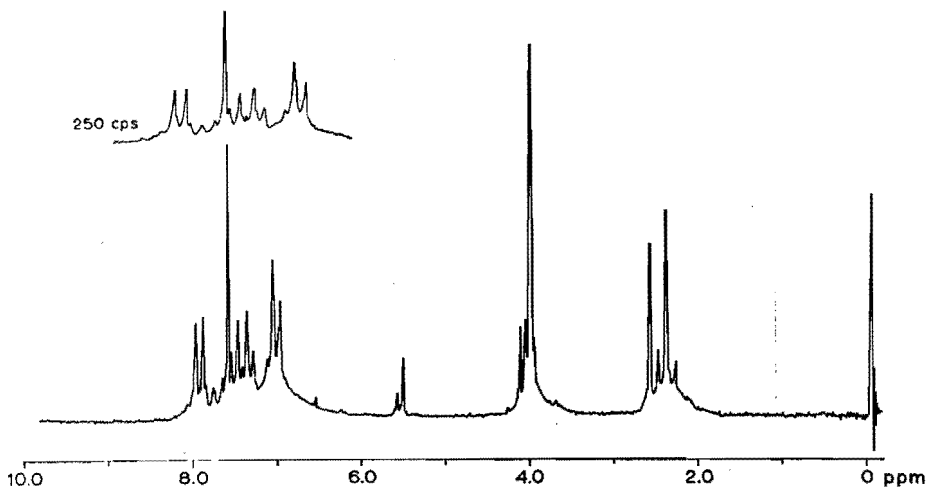

Fig. 3.4 1,3-di(p-methoxyphenyl)2,4-di(p-tolyl)cyclobutenyl cation in CF_3COOH. Shifts in ppm downfield from TMS.

One major peak at 4.00 ppm is present, ascribable to the OCH_3 groups of rings A and B. The signals of the OCH_3 groups of rings C and D are located at 2.40 and 2.60 ppm. The ratio of the relative intensities is H(aliph.):H(OCH_3):H(CH_3):H(arom.)=

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1:6:6:16. In the phenyl region the signals of the AA'BB'
quartet of the equivalent rings A and B are found at the
same ppm values as in compound III. One more quartet and
one singlet are present in the phenyl region, these being
due to the protons of rings C and D. It is not certain,
which signals belong to which.

C.   1,3-di(p-methoxyphenyl)-2,4-diphenylcyclobutenyl cation.

The PMR spectrum of the cation in CF_3COOH shows one sig-
nal of the OCH_3 protons at 3.98 ppm and the aliphatic proton
at 5.74 ppm. The phenyl region exhibits an AA'BB' quartet
of rings A and B at the same ppm values as does compound III
and a singlet at 7.70 ppm due to the phenyl protons of rings
C and D. From this spectrum it can be concluded, that the
cyclodimerization of (p-methoxyphenyl)phenylacetylene in the
presence of proton acids also proceeds regiospecifically.

D. 1,2,3,4-tetraphenylcyclobutenyl cation.

The PMR spectrum of this cation in HSO_3F at $-60^{O}C$ dis-
plays the aliphatic proton at 6.10 ppm, while the phenyl re-
gion yields an unresolved multiplet. The spectrum has been
recorded in HSO_3F, as diphenylacetylene yields this cation
only in HSO_3F and not in CF_3COOH. This finds its origin in
the lower basicity of diphenylacetylene in comparison with
the other acetylenes. Doorakian and Freedman (1968) prepa-
red the same cation by reaction of cis- and trans- 3-bromo-
1,2,3,4-tetraphenylcyclobutenes with $SnCl_4$. The signal of
the aliphatic proton occurs in this case at 5.9 ppm. The
difference is probably caused by solvent effects.

III.3. *Proton-deuteron exchange experiments.*

Reaction of di(p-methoxyphenyl)acetylene with CF_3COOD
yields the 4-deutero-1,2,3,4-tetra(p-methoxyphenyl) cyclo-
butenyl cation (VI). The PMR spectrum of VI is presented in

Fig. 3.5 and is identical with the spectrum of III, except
for the fact that the aliphatic proton is replaced by a deu-
teron.

Fig. 3.5 4-deutero-1,2,3,4-tetra(p-methoxyphenyl)cyclobu-
        tenyl cation in CF_3COOD. Shifts in ppm downfield
        from TMS.

Deuteron attack in the phenyl ring is expected to be the
easiest on carbon atoms with a large electron density (De
Bie and Havinga, 1965). Refluxing VI in CF_3COOD for 80 hours
results in 80% deuteration of the ortho positions (with re-
spect to the OCH_3 group) of one phenyl ring. In ring C no
positive charge is present, implying that ring C is deutera-
ted, thus affording VII.

VII
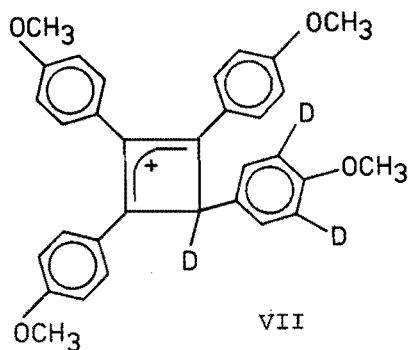
The PMR spectrum of VII is given in Fig. 3.6.

Fig. 3.6 Compound VII in CF$_3$COOD. Shifts in ppm downfield
from TMS.

Deuteration of ring C replaces the AA'BB' quartet by an
apparent singlet, because J$_{H-H}$ and J$_{H-D}$ are small. It can
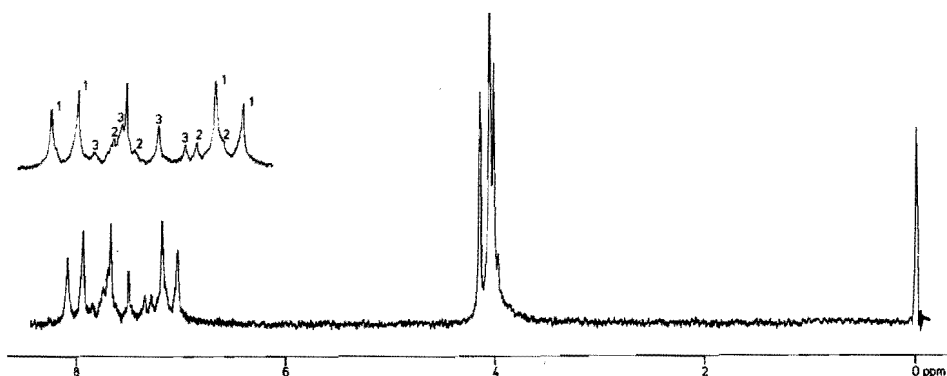now be concluded, that the signals represented by (2) belong
to ring C and the quartet represented by (3) must be due to
ring D. The signals of the OCH$_3$ protons are now separated
and can also be assigned. The ortho deuteration of ring C
produces a small shift difference for the OCH$_3$ group atta-
ched to it. This signal now appears at high field with re-
spect to the other OCH$_3$ groups. The lowest field signal must
be attributed to the OCH$_3$ protons of ring D.

No deuterium is introduced in ring D, thus indicating
that ring D takes part in the conjugation. This is in agree-
ment with the results of the X-ray analysis on a related
compound and has important consequences for the SCF calcula-
tions of the UV spectra (see chapter IV).

Proton-deuteron exchange experiments with compound IV
yielded no exchange at the ring protons in CF$_3$COOD or in
CF$_3$COOD/D$_2$SO$_4$ mixtures. This would be consistent with a
structure having a p-tolyl group instead of the much more
basic p-methoxyphenyl group at the saturated carbon atom.

As it is difficult with the present equipment to record ^{13}C NMR spectra of non-enriched compounds, acetylenes with ^{13}C enrichment of the acetylenic carbon atoms have been prepared.

An 1:1 mixture of 1-*p*-methoxyphenyl-2-*p*-tolyl(1-^{13}C)acetylene and 1-*p*-methoxyphenyl-2-*p*-tolyl(2-^{13}C)acetylene (60% enrichment) was dissolved in CF_3COOH. A number of cyclobutenyl cations IV are formed with none, one or two ^{13}C atoms in the cation. Statistically therefore 30% ^{13}C enrichment is present in all carbon atoms of the cyclobutenyl ring.

Examination of the spectrum of IV in CF_3COOH showed three distinct signals at 140.3 ppm, 73.5 ppm and 45.5 ppm upfield from CS_2 as an external standard. Under the experimental conditions the signals of non-enriched carbon atoms were just barily visible in the noise. The low field signal was more intense that the other two. However, quantitative results are difficult to obtain from ^{13}C NMR spectra under complete noise-decoupling of all proton spins due to possibly different Overhauser effects for different carbon atoms (La Mar, 1971). Moreover, direct couplings between the ring carbon atoms interfered with the results.

It does seem justified, however, to assign the low field signal to C_1 and C_3, the 73.5 ppm signal to C_2 and the 140.3 ppm signal to C_4.

In the same way compound III with ^{13}C enrichment of the cyclobutenyl carbon atoms was prepared from di(*p*-methoxyphenyl)acetylene with 60% ^{13}C enrichment of one of the acetylenic carbon atoms. The low field signals of C_1 and C_3 now appear at 46.1 ppm, the C_2 signal at 73.5 ppm and the C_4 signal at 141.4 ppm.

The ^{13}C shifts of the cyclobutenyl cations can be related to the π-charge on the cyclobutenyl carbon atoms. Spiesecke and Schneider (1961) obtained a linear relationship for aromatic systems in which an unit charge causes a shift of 160 ppm relative to benzene. The resulting π-electron densities

are given in table 3.1.

Table 3.1

Compound	atom	^{13}C-shift[+]	^{13}C-shift relative to benzene	excess charge	π-dens.
III	C_1, C_3	46.1	-18.9	-0.12	0.88
	C_2	73.3	8.3	0.05	1.05
IV	C_1, C_3	45.5	-19.5	-0.12	0.88
	C_2	73.5	8.5	0.05	1.05

[+] The ^{13}C shifts were measured in ppm upfield from CS_2 (the ^{13}C shift of benzene= +65 ppm).

The π-electron densities were used to test the different geometric and theoretical models for the SCF calculations according to the method of Pariser, Parr and Pople. (See chapter IV).

CHAPTER IV

THE EXPERIMENTAL AND CALCULATED ELECTRONIC ABSORPTION SPEC-
TRA OF TETRA-ARYLCYCLOBUTENYL CATIONS

IV.1. *Introduction*

   The experimental UV spectra of the tetra-arylcyclobute-
nyl cations show a single strong absorption band situated
in the visible region. The UV spectra have also been calcu-
lated with the π-electron method of Pariser, Parr and Pople
(see chapter II) with configuration interaction of 40 sing-
ly excited configurations. As a geometric model, the re-
sults of the X-ray diffraction on a related compound(Bryan,
1964) were used (see Fig.4.1).
   From the calculations, it appears, that two absorption
bands are always predicted, if the phenyl ring at C_2 is
turned through 60°. These two transitions result from an
interaction of ring D with the system formed by rings A,B
and E. If one turns ring D through 90°, this interaction is
absent and only one absorption band is calculated. However,
in chapter III it was shown that this geometry is preclu-
ded in tetra-arylcyclobutenyl cations. Therefore, efforts
directed at improving the correlation with the experimental
UV spectra, using as a geometric model the results of the
X-ray diffraction were undertaken.
   Inclusion of overlap of the π-orbitals on atoms 1 and 3,
which are close to each other in the cyclobutenyl ring led
to an improvement of the calculated spectra. For this rea-
son, these cations can better be considered as homocyclo-

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propenyl cations.

Furthermore, two additional models for the calculation have been used, which are based on the fact, that in the cyclobutenyl ring an angle of 90° is present, which will cause a hybridization intermediate between that of benzene and cyclopropane. The fact, that ring D is turned 60° out of plane brings about, that the π-σ separation is not strictly valid. In the first of these two models, an external σ-orbital of the homocyclopropenyl ring has been included in the calculation. This orbital is allowed to mix with the components of the π-orbitals of ring D, which are in the plane of the homocyclopropenyl ring. In the second model, we have accounted for the deshielding hybridization with respect to benzene by a lowering of the one centre core integrals in the cyclobutenyl ring.

The calculation using the model with inclusion of an external σ-orbital gives the best UV spectra. However, if comparison is made between the calculated π-electron densities and the experimental ones, obtained from ^{13}C NMR, one sees that only in the cases, where the one centre core integrals have been lowered, good agreement for the π-electron densities is obtained. Though in this latter calculation two absorption bands are predicted, one is very strong in comparison with the other, when 1-3 overlap is included. It is our conclusion therefore, that the model using lower one centre core integrals in the cyclobutenyl ring and 1-3 overlap, is to be preferred.

IV.2. *Experimental electronic absorption spectra*

The electronic absorption spectra of the deeply coloured tetra-arylcyclobutenyl cations have been measured. The absorption maxima(λ) and the molar extinction coefficients(ε) are given in table 4.1.

The UV-spectrum of I can be compared with the UV spectrum of the 4-bromo-1,2,3,4-tetraphenylcyclobutenyl cation(λ_{max}= 482 nm, ε=50.000) obtained by Freedman on dissolving 3,4-

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dibromo-tetraphenylcyclobutene in H_2SO_4.

Table 4.1

UV spectra of tetra-arylcyclobutenyl cations

Cyclobutenyl cation	Acid	λ (nm)	ε
1,2,3,4-tetraphenyl (I)	HSO_3F (-60°)	470	(14.000)
1,3-di(p-methoxyphenyl)-2,4-diphenyl (II)	CF_3COOH	520	34.000
1,2,3,4-tetra(p-methoxyphenyl) (III)	CF_3COOH	523	45.000
1,3-di(p-methoxyphenyl)-2,4-di-(p-tolyl) (IV)	CF_3COOH	520	36.000

For numbering of the substituents see Fig.3.1.

IV.3. *Calculated electronic absorption spectra and π-electron densities, making use of different models for the calculation.*

A. Calculation based on the X-ray determined geometry of a related compound.

Following the X-ray diffraction measurements by Bryan (1964) on a related compound, a model for the calculation was chosen in which ring D is turned through 60° (see Fig. 4.1). The UV spectra and π-electron densities calculated with this model are given in table 4.2.

For compound I no experimental π-electron density is available. The experimental π-electron density of compound IV should be compared with the calculated π-electron density of compound II because the inductive effect of the methyl group in the p-tolyl ring is neglected in the calculation. The experimental π-electron densities have been taken from section III.4 and are given between brackets in table 4.2. From the table it can be seen that the calculated π-electron densities on carbon atoms 1 and 3 are too low.

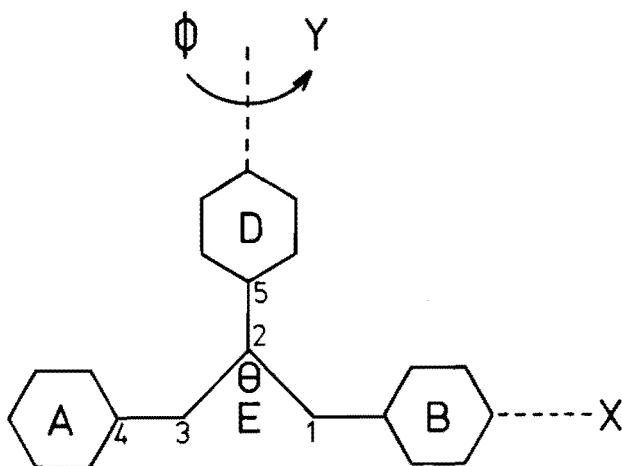In the visible region two transitions are calculated,

Fig.4.1

$\phi = 60°$, $\beta_{2-5} = \beta_{3-4} \, x\cos\phi$

$\angle\theta = 90°$

The C-C distances were taken to be:

1.39 Å in the benzene rings

1.45 Å between the benzene rings and the cyclobutenyl ring

1.45 Å in the cyclobutenyl ring

All parameters have values as discussed in chapter II.

Table 4.2

Compound	λ(nm)	f	π-electron dens. C_1 and C_3	π-electron dens. C_2
I	524	0.84	0.70	1.02
	436	0.42		
II	549	1.35	0.73(exp. 0.88)	1.04(exp.1.05)
	405	0.10		
III	585	0.70	0.73(exp. 0.88)	1.02(exp.1.05)
	494	0.74		

f is the oscillator strength. All transitions are polarized in the X-direction.

while in the experimental UV spectrum only one absorption band is present.

The two absorption bands correspond to electronic transitions from the two highest occupied levels, which are symmetrical, to the lowest unoccupied level which is antisymmetrical (symmetry operation is a rotation of 180° around the Y-axis). The two symmetrical levels result from an interaction of the highest occupied symmetrical level of the system formed by rings A,B and E with the highest occupied symmetrical level of ring D. This can be seen from the picture of the energy levels according to the Hückel method (Fig.4.2, first two columns).

In compound II the interaction of the two symmetrical levels is small due to the great difference in energy between these levels. The second transition therefore has a low oscillator strength. However, in compounds I and III the difference between the interacting levels is small and the coefficients are about equally distributed over the MO's of the resulting levels. This causes a marked increase in the oscillator strength of the second transition.

B. Calculation based on a model in which no interaction is present between ring D and the remainder of the π-electron system (Fig.4.1 $\phi=90^O$).

In part A it was shown that the two calculated absorption bands arise through interaction of ring D with the remainder of the system. Clearly, this interaction can be removed by turning ring D through 90° in which case $\beta_{2-5}=0$. The UV spectra and π-electron densities calculated with this model are given in table 4.3.

In this case, the π-electron densities on carbon atoms 1 and 3 are also too low. The UV spectra calculated with $\phi=90^O$ show indeed one absorption band and are in excellent agreement with the experimental UV spectra.

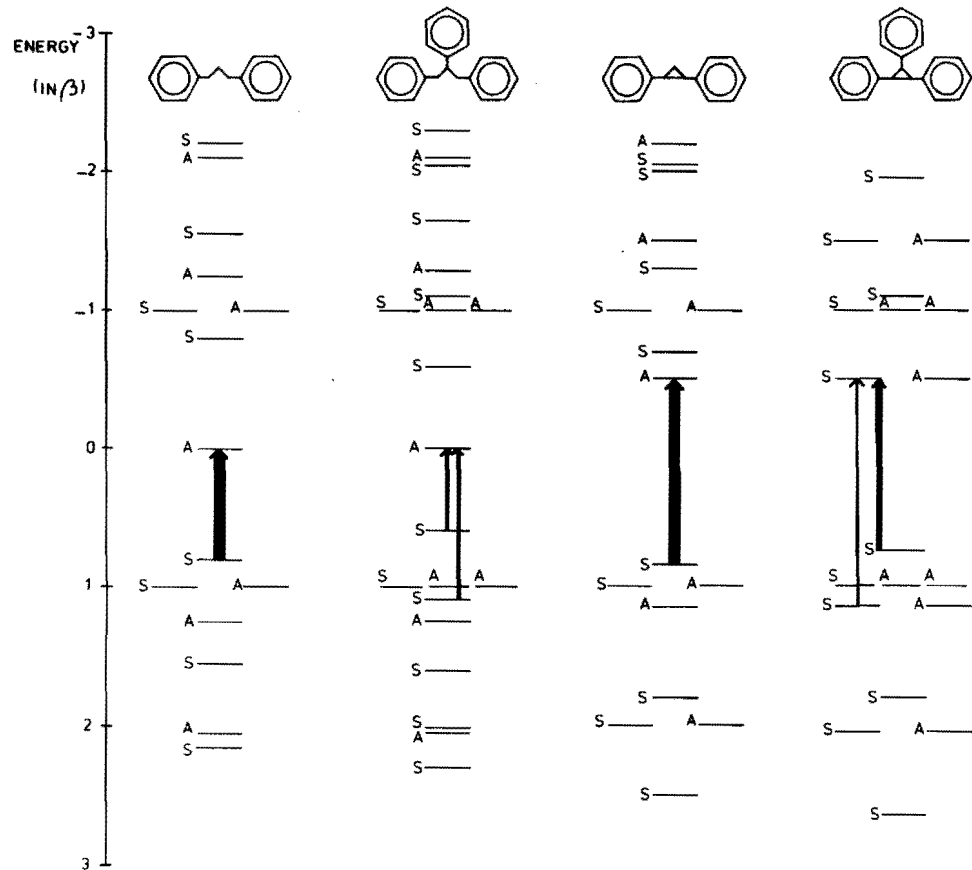Some doubt might exist whether the results of the X-ray diffraction(on an analogous compound) are valid in solution.

Fig.4.2 Energy levels according to the Hückel method. All β's between neighbours had the value 1 in the Hückel calculation.

Table 4.3

Compound	λ(nm)	f	π-electron dens. C_1 and C_3	π-electron dens. C_2	
I	492	1.26	0.70	1.02	
II	538	1.48	0.72	1.04	
III	537	1.45	0.73	1.03	

All transitions are polarized in the X-direction

The conclusive proof that ring D is not turned through 90° was obtained from proton-deuteron exchange experiments (see section III.3). No deuterium was introduced in ring D, while in this experiment deuterium was incorporated in the ring at the saturated carbon atom. This points to positive charge being present in ring D and therefore that conjugation is involved. For this reason this model has been rejected and further calculations have been carried out, all using the geometry of Fig.4.1($\phi=60^{\circ}$).

C. Calculation in which the overlap integral between carbon atoms 1 and 3 is taken into account (homoconjugation).

In the geometry of the cyclobutenyl ring the carbon atoms 1 and 3 are closer together than is normally the case with non-neighbours. Therefore this overlap should not be neglected. Using the formulas of Mulliken et.al.(1949) the overlap integral for this carbon-carbon distance was calculated to be 0.065 and from 2.57 the resonance integral was obtained: $\beta_{1-3}= -0.624$ eV. The calculation is based on the geometry of the X-ray diffraction($\phi=60^{\circ}$). The results are shown in table 4.4.

From the Hückel energy levels (see Fig.4.2) it can be seen that the absorption bands with inclusion of 1-3 overlap show a hypsochromic shift in comparison with the case where no 1-3 overlap is taken into account. Conjugation with ring D causes also in cases where 1-3 overlap is included splitting of the highest occupied symmetrical level;

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Table 4.4

Compound	λ (nm)	f	π-electron dens. C_1 and C_3	π-electron dens. C_2	
I	437	1.08	0.70	0.95	
	373	0.21			
II	473	1.41	0.72	0.97	
	348	0.03			
III	485	1.06	0.73	0.96	
	424	0.38			

All transitions are polarized in the X-direction

in this case two absorption bands are calculated.

However, inclusion of 1-3 overlap has the effect that the oscillator strength of the second transition decreases to a rather large extent; at the same time the oscillator strength of the first transition greatly increases. From this calculation it can be concluded that the introduction of 1-3 overlap yields a considerable improvement of the calculated UV spectra. Therefore we presume that homoconjugation is involved in cyclobutenyl cations (homocyclopropenyl cations) (see Fig.4.3).
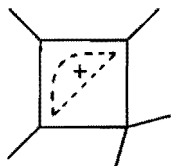

Fig.4.3 A homocyclopropenyl cation

The π-electron densities are still too low in this calculation and two more attempts are described in sections D and

E to improve the UV spectra and the calculated π-electron densities.

D. Inclusion of one σ-orbital on carbon atom 2 in the calculation.

The σ-π distinction used as an approximation in the π-electron approximation of Pariser, Parr and Pople is not valid when, as in our case, a phenyl ring is turned out of the plane formed by the remainder of the π-system. The π-orbitals of the turned phenyl ring can now be factorized in a part lying in the plane of the other π-electrons and a part lying in the plane of the σ-core. Matrix elements between σ and π atomic orbitals are now non zero, because the π-orbitals have a component in the plane of the σ-electrons.

The hybridization of the σ-electrons in the cyclobutenyl ring(or with 1-3 overlap homocyclopropenyl ring) might resemble the hybridization in cyclopropane. The bond angle of 90° is intermediate between the ideal bond angle for sp^2 hybridization(120°) and the bond angle of the cyclopropane ring(60°).

The hybridization in a cyclopropane ring has been discussed by Walsh (1947). Walsh assumed that the carbon atoms of cyclopropane were sp^2 hybridized, with two of the hybrids being used to form C-H bonds. The third hybrid points toward the centre of the cyclopropane ring and contributes to the internal σ MO's. The remaining p-orbitals form external σ MO's in the plane of the cyclopropane ring. The energy levels of the internal and external σ MO's are shown in Fig.4.4.

The hybridization in the cyclobutenyl ring can be described in a similar way. First, we assume the carbon atoms to be sp hybridized, one hybrid forming the C-phenyl bond, one hybrid pointing towards the centre of the ring(internal σ MO's). Of the two remaining p-orbitals, one is in the plane of the ring forming external σ MO's, one perpendicular to the plane forming π MO's.

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S_3 S_3 ———

A_3 A_3 ———

A_2 A_2 ———

A_1
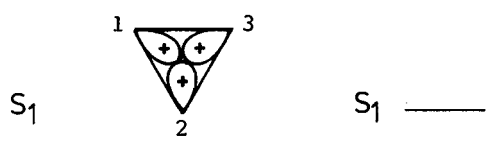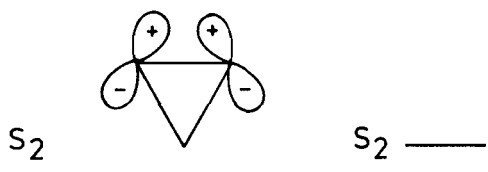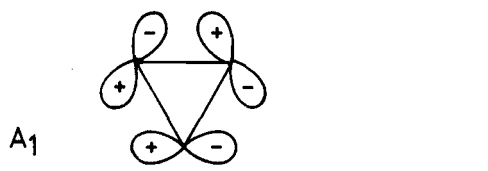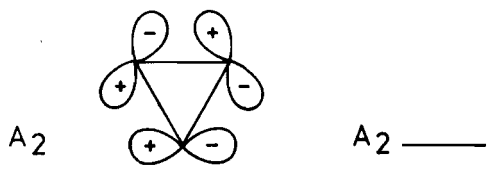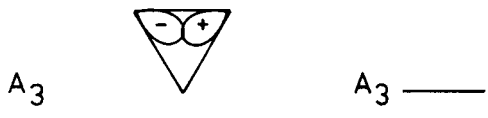
On streching the C_1-C_3 bond, the antisymmetric level is lowered in energy, while the symmetric level is going up in energy

S_2 S_2 ——— A_1 ——— - - - - S_2 ———
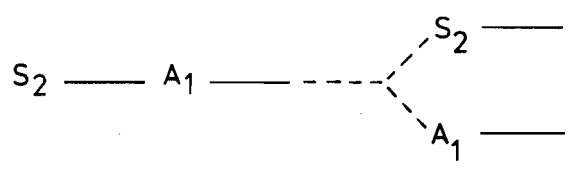
A_1 ———

S_1 S_1 ———

Fig.4.4 Energy levels of internal and external MO's in cyclo-
         propane.

The occupied external σ MO, which is antisymmetrical, has
the appropriate symmetry to mix itself into the component
in the plane of the cyclopropane ring of the phenyl π-
orbitals. For program-technical reasons, this external
σ MO is described as an AO, occupied by 2 electrons on car-
bon atom 2.
When ring D is turned through 60°, the angle between this
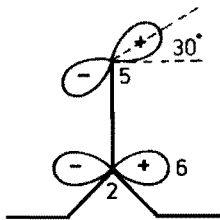σ AO and the phenyl π-orbitals is 30°(see Fig.4.5).

Fig.4.5

The resonance integral β_{5-6} is taken to be $\cos 30^{\circ} \times 0.5 \times S_{5-6}$
$(\alpha_5 + \alpha_6)$, in which $S_{5-6} = 0.1955$.
To account for the fact that the core electrons are lower
in energy than the π-electrons, a lower value for the σ AO
is taken in comparison with the π-orbitals. The value of
the one-centre repulsion integral is lowered to account
for the fact that the electrons are in fact delocalized
over the MO. Without 1-3 overlap, the best results are ob-
tained when α_6 has the value -17 eV. As a consequence
$\beta_{5-6} = -2.25$ eV.
The one-centre repulsion integral γ_{6-6} was given the value
8 eV, the two-centre repulsion integral γ_{2-6} was also taken
to be 8 eV. The results of this calculation are shown in
table 4.5.
When 1-3 overlap was taken into account, the best results
were obtained with $\alpha_6 = -16.3$ eV. These are given in table
4.6.

    Only one transition is calculated in the visible region
in agreement with the experimental UV spectra. The π-elec-

Table 4.5

Compound	λ (nm)	f	π-density C_1 and C_3	π-density C_2
I	508	1.27	0.72	0.99
II	573	1.57	0.77	1.02
III	563	1.57	0.74	1.11

$\alpha_6 = -17$ eV, $\beta_{1-3}=0$, $\beta_{5-6}=-2.25$ eV, $\gamma_{6-6}=8$ eV, $\gamma_{2-6}=8$ eV.

Table 4.6

Compound	λ (nm)	f	π-density C_1 and C_3	π-density C_2
I	439	1.30	0.72	0.93
II	507	1.60	0.76	0.96
III	498	1.55	0.73	1.05

$\alpha_6 = -16.3$ eV, $\beta_{1-3} = -0.624$ eV, $\beta_{5-6} = -2.25$ eV, $\gamma_{6-6}=8$ eV,

$\gamma_{2-6}=8$ eV.

tron densities on C_1 and C_3 are in this calculation also too low. The positions of the first absorption bands are in good agreement with the experimental UV spectra. From these calculations it is not clear whether 1-3 overlap is important. In both cases the parameters can be chosen in such a way as to fit the experimental spectrum.

E. Lowering of the one-centre core integrals of carbon atoms 1,2 and 3.

The hybridization of the cyclobutenyl ring, described in section D has a deshielding effect on the cyclobutenyl ring carbon atoms. As a result of this deshielding with respect to benzene the π-electrons are more attracted by the core, which justifies a lower value of the one-centre core inte-

grals in comparison with benzene. The best results were ob-
tained when $\alpha_1=\alpha_2=\alpha_3$ had the value -11 eV. Without 1-3 over-
lap the results of the calculation are given in table 4.7
and with inclusion of 1-3 overlap in table 4.8.

Table 4.7

Compound	λ (nm)	f	π-density C_1 and C_3	π-density C_2
I	584	0.84	0.77	1.07
	495	0.52		
II	649	1.57	0.86	1.06
	501	0.26		
III	897	0.12	0.86	1.06
	609	1.71		

$\alpha_1=\alpha_2=\alpha_3=$ -11 eV, other α-C= -9.6 eV, $\beta_{1-3}=$ 0

Table 4.8

Compound	λ (nm)	f	π-density C_1 and C_3	π-density C_2
I	500	1.12	0.76	1.00
	423	0.15		
II	584	1.66	0.84	1.02
	427	0.07		
III	683	0.27	0.84	1.01
	552	1.47		

$\alpha_1=\alpha_2=\alpha_3=$ -11 eV, other α-C= -9.6 eV, $\beta_{1-3}=$ -0.624 eV

Only from this type of calculation a good agreement with
the experimental ^{13}C charges is obtained. In this case
1-3 overlap had to be taken into account to obtain a reaso-
nable value for the absorption maximum.

From all described calculations, the ones given in table
4.8 show the best results. The charge densities agree fa-

vourably with the experimental ones and, although the cal-
culated UV spectra show two absorption bands, one of the
two is very strong as compared to the other.

CHAPTER V

CALCULATIONS ON DIFFERENT MODELS FOR THE TRANSITION STATE
OF THE REACTION BETWEEN A DIARYLACETYLENE AND A DIARYLVINYL
CATION.

V.1. *Introduction*

The cyclodimerization of diarylacetylenes under the in-
fluence of proton acids has been described in chapter III.
This process can essentially be regarded as the reaction be-
tween an acetylene and a vinyl cation. According to Woodward
and Hoffmann(1969), this reaction constitutes a $_\pi2_s+_\pi2_a$ pro-
cess, in which the empty orbital of the vinyl cation reduces
the transition state energy considerably. The quantitative
effect of this empty orbital has been investigated by com-
paring the latter process with the reaction of two molecules
ethylene and acetylene respectively. In section V.2. a num-
ber of CNDO-2 calculations give a quantitative insight in
these processes.

The regiospecificity of the cyclodimerization of diaryl-
acetylenes in the presence of proton acids is initially
caused by the preferential formation of that diarylvinyl
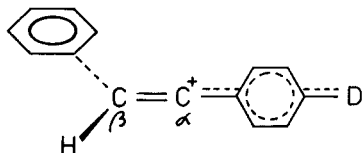cation which is of lowest energy.

Fig.5.1 A diarylvinyl cation

In a diarylvinyl cation (Fig.5.1),the empty p-orbital on
the α-carbon atom is conjugated with the benzylic π-system,
which is perpendicular to the olefinic bond and the β-phenyl

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group. The diarylvinyl cation in which the positive charge
is delocalized over the phenyl ring with the more electron-
donating para substituent is preferentially formed. In sec-
tion V.3 SCF calculations according to the method of Pari-
ser, Parr and Pople are given, thereby affording a confir-
mation of this concept. The solvolysis experiments of Mil-
ler and Kaufmann(1968) on triaryliodoethylenes are also con-
sistent with this proposed structure for the vinyl cation.

The vinyl cation subsequently reacts with a second mole-
cule acetylene. PPP calculations have been carried out on
the reaction between a(p-methoxyphenyl)phenylvinyl cation
and (p-methoxyphenyl)phenylacetylene. In (p-methoxyphenyl)
phenylacetylene, the carbon atom to which the phenyl group
is attached is more basic than the carbon atom to which a
p-methoxyphenyl group is attached due to the mesomeric elec-
tron-donating effect of the p-methoxy moiety. This carbon
atom preferentially forms the bond with the carbon atom
bearing the positive charge in the vinyl cation. The speci-
ficity of the reaction is completely explained by this me-
chanism.

V.2 *CNDO-2 calculations concerning the reaction of acetyle-
ne with a vinyl cation.*

The reaction between an acetylene molecule and a vinyl
cation is mechanistically related to the reaction between
two molecules of ethylene or acetylene.

Let us first consider the reaction between two molecules
ethylene. According to the principle of conservation of or-
bital symmetry (Woodward and Hoffmann,1969) the reaction be-
tween two molecules ethylene which approach each other along
the path of maximum symmetry (Fig.5.2) is "forbidden".
This result can be arrived at by constructing a full orbital
correlation diagram. It is also possible to explain the
allowedness or forbiddenness of a reaction in terms of aro-
maticity. According to this reasoning(Dewar,1971 and refe-
rences cited therein) this 4-electron system is isoconjuga-
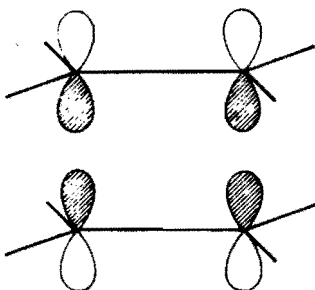te with cyclobutadiene and therefore anti-aromatic. To in-

Fig.5.2 Parallel approach of two molecules ethylene.

troduce aromaticity one resonance integral has to be nega-
tive($-\beta$). Therefore the $_{\pi}2_s+_{\pi}2_a$ reaction is allowed. The ge-
ometry for the transition state of the allowed $_{\pi}2_s+_{\pi}2_a$ pro-
cess clearly must differ from that of the symmetry forbid-
den combinations. Maximum overlap of the relevant orbital
lobes can be achieved if the ethylene molecules approach
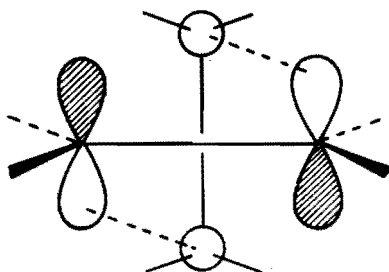each other orthogonally(Fig.5.3).

Fig.5.3 Orthogonal approach of two ethylene molecules.

   The same considerations apply to the reaction between
two molecules acetylene and to the reaction of a molecule
acetylene with a vinyl cation. CNDO-2 calculations have
been carried out for the symmetry forbidden ($_{\pi}2_s+_{\pi}2_s$) and
symmetry allowed ($_{\pi}2_s+_{\pi}2_a$) processes. All bond angles and

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bond lengths have been kept constant in the calculations.
For the C-C distances were taken 1.20,1.27 and 1.34 Å, for
the C-H distances 1.06, 1.09 and 1.09 Å for acetylene, vi-
nyl cation and ethylene respectively (Lathan et.al.,1971).

As energy lowering rearrangements in the reacting mole-
cules will occur, it is not possible to extend the calcula-
tions to the region where the reactants have approached
each other to about 1.8-1.5 Å. However, by this type of cal-
culation, one can establish which mechanism will lead to
bonding interactions. A picture of the energy along the re-
action path for the symmetry forbidden parallel approach
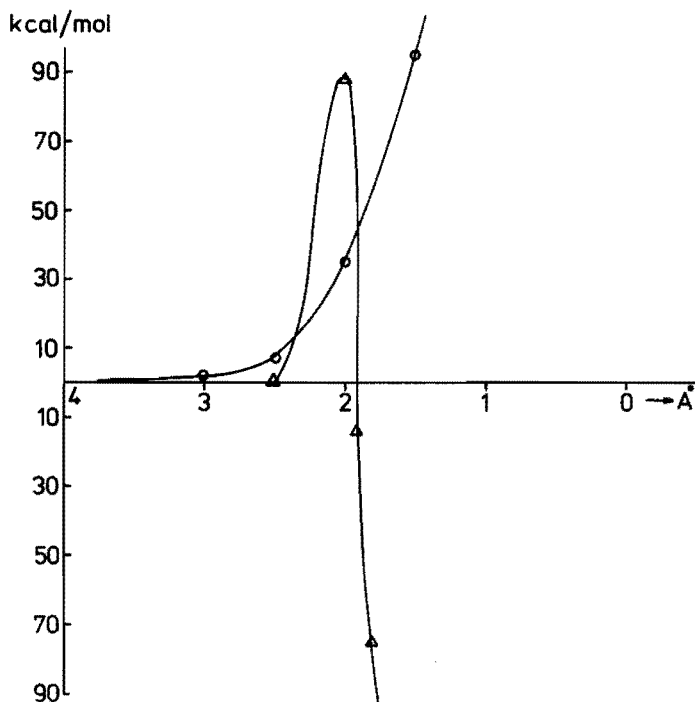and the orthogonal approach of two molecules ethylene is
given in Fig.5.4.

Fig.5.4 Interaction energy as a function of the distance
between the two ethylene molecules.

In both cases an increase in energy is calculated. In the
case of the symmetry forbidden combination this result is
easily understood. The energy increase for the orthogonal
approach is caused by steric hindrance of the hydrogen atoms
and by framework distortions required in maintaining an ef-
fective orbital overlap.

If the approach of two molecules acetylene is considered
the steric hindrance effect is much smaller. The results of
the CNDO-2 calculations (Fig.5.5) show that the orthogonal
$\pi^2_s + \pi^2_a$ approach is initially accompanied by a lowering of
the energy. At closer distances, the framework distortions
cause a positive interaction energy. The symmetry forbidden
parallel approach shows the expected increase in energy.
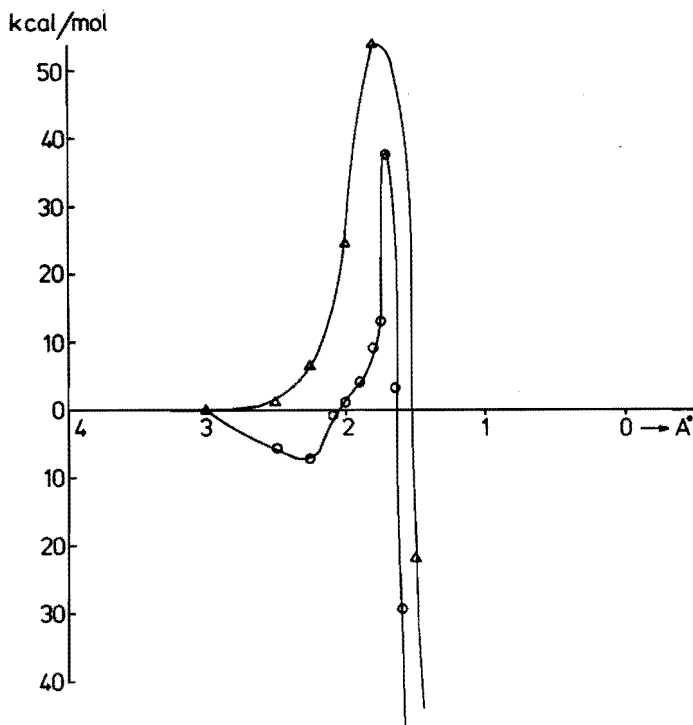

Fig.5.5 Interaction energy as a function of the distance
        between two molecules acetylene

Woodward and Hoffmann have qualitatively suggested that
the transition state energy of a $_\pi 2_s +_\pi 2_a$ reaction is signi-
ficantly lowered, if the $_\pi 2_a$ component is a vinyl cation, as
the empty p-orbital of the vinyl cation forms two bonding
interactions with the acetylenic π-orbitals (Fig.5.6).
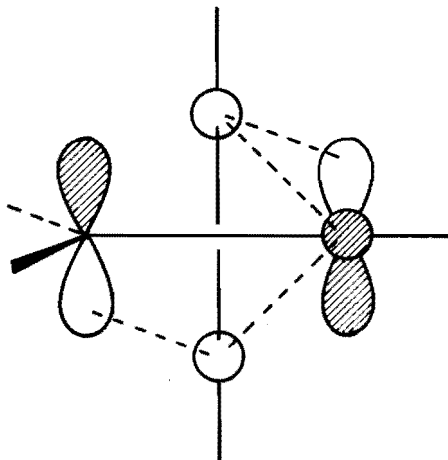

Fig.5.6 Orthogonal approach of a molecule acetylene and a
         vinyl cation.

CNDO-2 calculations show that the energy decreases quickly,
in the case of the acetylene and the vinyl cation approaching
one another orthogonally (Fig.5.7). One can gain an insight
into the quantitative effect of the empty orbital of the
vinyl cation by comparing the latter process with the ortho-
gonal approach of two molecules of acetylene. For the acety-
lene-vinyl cation reaction the energy decreases to a much
larger extent, although the hydrogen-hydrogen repulsions are
stronger.

These results are in sharp contrast with the calculations
of Wagner and Gompper (1971) carried out with the MINDO-2
program (Dewar and Haselbach, 1970). They calculate an ener-
gy barrier for the acetylene-vinyl cation approach in the geo-
metry proposed by Woodward and Hoffmann. Therefore, they sug-
gest an alternative transition state, in which the acetylene
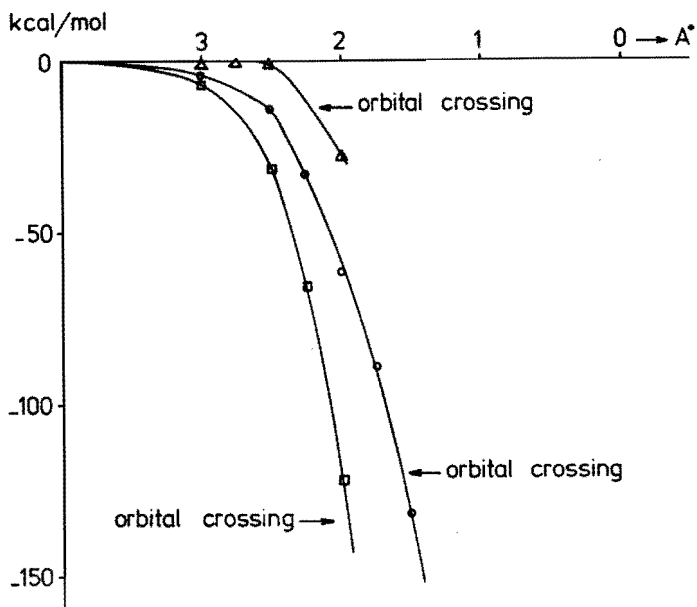is situated above the empty orbital of the vinyl cation
(Fig.5.8).

Fig.5.7 Interaction energy as a function of the distance
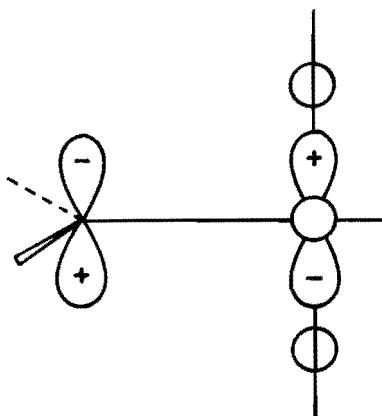   between an acetylene and a vinyl cation.

Fig.5.8 Approach of an acetylene and a vinyl cation accor-
        ding to Wagner and Gompper.

In this situation the interactions with the empty p-orbital are still stronger. However, here an additional $1,2^+$ sigmatropic shift is required to obtain the observed cyclobutenyl cation.

Using the model of Fig.5.8, we have carried out CNDO-2 calculations which show a more favourable interaction energy than for the Woodward-Hoffmann approach. In Fig.5.7 a comparison of the CNDO-2 results is given for both models. In both cases between 1.8 and 1.5 Å an orbital crossing takes place, whereby the "empty" orbital becomes bonding instead of anti-bonding and is filled. Therefore, at distances closer than 1.8 Å the calculations lose their meaning.

In our opinion, the concerted path predicted by Woodward and Hoffmann appears to be the most probable mechanism for this reaction. Taking into account the energy required for the $1,2^+$ sigmatropic shift and the rearrangement effects which may be different for both models, leads to the conclusion, that the energy differences for both models are too small to discard the Woodward-Hoffmann model, which has proven its general validity.

V.3. *Calculations by the method of Pariser, Parr and Pople on a number of di- and triarylvinyl cations.*

The reaction of diarylacetylenes with proton acids leads initially to formation of a diarylvinyl cation. Experimental evidence being present on triarylvinyl cations, calculations on both kinds of cation have been carried out.

Miller and Kaufman (1968) obtained triarylvinyl cations as intermediates upon solvolyzing triaryliodoethylenes. Introduction of an electron-donating substituent in the phenyl ring attached to the carbon atom bearing the iodine atom led to a considerably enhanced solvolysis rate. No such effect was registered when an electron-donating substituent was introduced into the β-phenyl rings.

We have carried out some calculations according to the method of Pariser, Parr and Pople on these triarylvinyl cat-
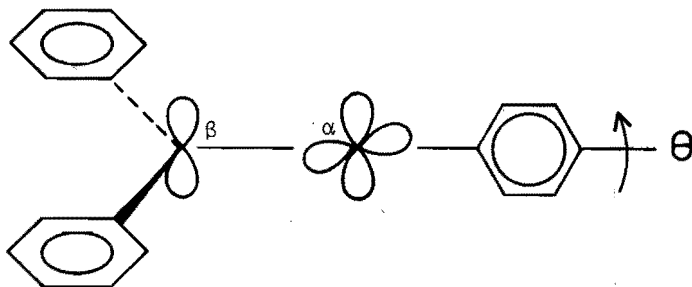
ions, using the model shown in Fig.5.9.

Fig.5.9 Model of a triarylvinyl cation. The β-phenyl rings
        are twisted 30° with respect to the molecular plane
        (Hanson, 1953).

The α-phenyl ring was taken to be perpendicular to the ole-
finic bond. (ϕ=90°). In the triphenylvinyl cation 64% of the
positive charge is localized in the empty p-orbital. The re-
mainder of the positive charge is present in the α-phenyl
ring. It has been calculated that the isomer with a p-methoxy
group in the α-phenyl ring is lower in energy than the isomer
with a p-methoxy substituent in the β-phenyl ring. These re-
sults would offer a rationale for the rate enhancement repor-
ted in the former case by Miller and Kaufmann and their sugges-
tions about the structure of these triarylvinyl cations.

    In our case a diarylvinyl cation is formed (one β-phenyl
ring is replaced by a proton in Fig.5.9). Calculations on
diarylvinyl cations lead to the same results as those obtai-
ned for triarylvinyl cations. In the case of the diarylvinyl
cations, the β-phenyl ring is taken as lying in the plane of
the ethylenic bond, as no steric hindrance of the ortho pro-
tons is present. The positive charge is for 61% localized in
the empty p-orbital, if the α-phenyl ring is turned through
90°.

    Different angles of rotation of the α-phenyl ring were con-
sidered. In the case that ϕ=90°. the lowest energy is obtained.
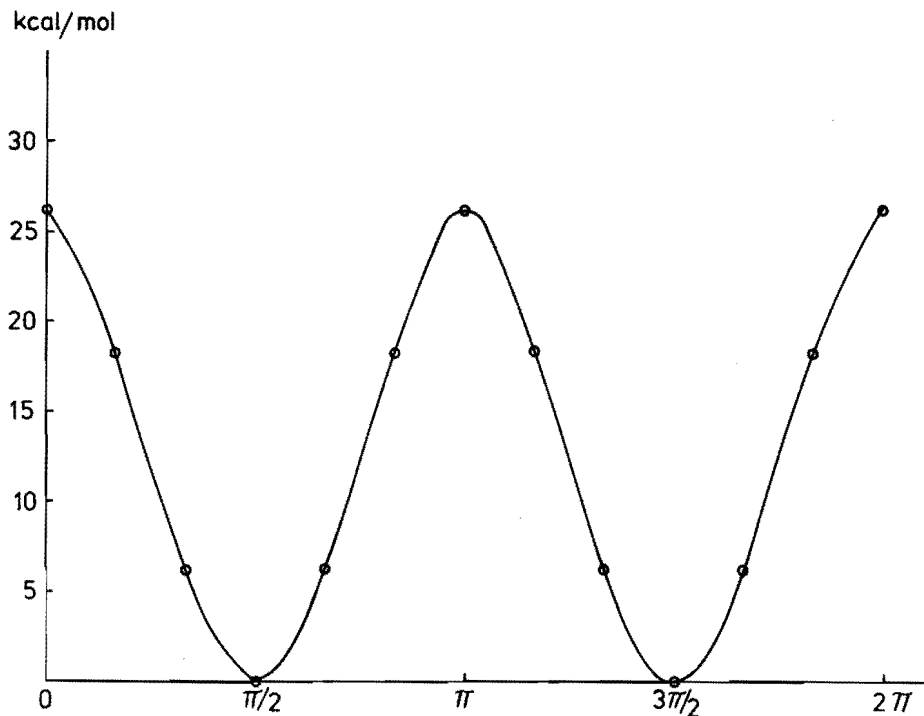
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(Fig.5.10).

kcal/mol

Fig.5.10 Energy as a function of the angle of rotation (ϕ)
          in the diphenylvinyl cation.

The amount of positive charge in the "empty" orbital is not
very dependent of the angle of rotation of the α-phenyl ring.
When the angle of rotation is in between $0°$ and $90°$, also mix-
ing with the β-phenyl levels is possible. However, the energy
level of the empty p-orbital remains anti-bonding. In the
case $\phi=0°$, the α-ring is in conjugation with the ethylenic
bond and the positive charge is fully localized in the empty
orbital.

     If the energy of two isomeric (p-methoxyphenyl)phenylvinyl
cations is compared with each other, the one having the p-
methoxy substituent in the α-phenyl ring is lower in energy
than the one having this substituent in the β-phenyl ring.
The p-methoxy substituent in the α-phenyl ring is conjugated

with the empty orbital, thereby stabilizing the positive
charge.The preferential formation of this vinyl cation is
responsible for the observed regiospecificity of the subse-
quent cyclodimerization reaction.

V.4. *PPP calculation on the reaction between a (p-methoxy-
phenyl)phenylacetylene and a (p-methoxyphenyl)phenyl
vinyl cation.*

In section V.3. it was shown that of two possible isomeric
diarylvinyl cations the one with the more electron-donating
para substituent at the α-phenyl ring is of lower energy.
To explain the regiospecificity of the formation of the
tetra-arylcyclobutenyl cations, this diarylvinyl cation must
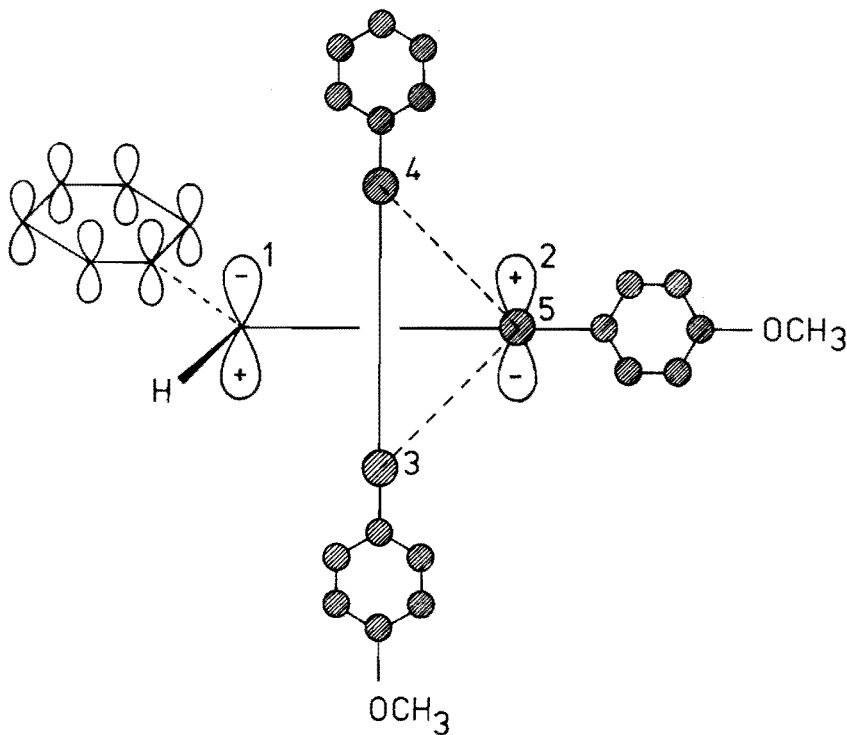react in a specific way with a molecule acetylene.

Fig. 5.11 Transition state for the reaction between a (*p*-
methoxyphenyl)phenylvinyl cation and (*p*-methoxy-
phenyl)phenylacetylene.

A calculation according to the PPP method on the reaction between a (p-methoxyphenyl)phenylvinyl cation and a (p-methoxyphenyl)phenylacetylene has been carried out. In Fig.5.11 the transition state is pictured.

When the two molecules have approached each other to 2,5 Å, the bond orders between the empty p-orbital and the acetylenic carbon atoms are $p_{3-5}=0.2439$ and $p_{4-5}=0.2580$. The absolute value of the bond orders p_{1-3} and p_{1-4} are both 0.0405. The specificity of this reaction therefore is determined by the transition state bond strengths of orbitals 4 and 5, which prepare the path for the bond formation between orbitals 2 and 4.

CHAPTER VI

REACTIONS OF TRANSITION METALS WITH ARYLACETYLENES

VI.1. *Introduction*

Cyclodimerization of arylacetylenes can be accomplished under the influence of transition metal ions, resulting in cyclobutadiene metal complexes (Pollock and Maitlis,1971). The reaction of two unsymmetrical acetylenes(p-methoxyphenyl-p-tolylacetylene and (p-methoxyphenyl)phenylacetylene) with bis(benzonitrile)PdCl$_2$ exhibits a similar regio-specificity as has been established in proton acids. The sequence of the aryl groups in the tetra-arylcyclobutadiene complexes appeared to be non-vicinal (section VI.4.).

Photochemical excitation of these complexes in CF$_3$COOH produces 4-chloro-tetra-arylcyclobutenyl cations. The structure of these cations has been determined with UV and PMR measurements (section VI.4). An interesting feature of this reaction is the greater basicity of the cyclobutadiene ring in the excited state complex as compared to the ground state. In section VI.3 a description of the bonding in the ground state and excited state of cyclobutadiene-PdCl$_2$ complexes is given, which explains this phenomenon.

Only one example of a cyclobutadiene complex obtained from an unsymmetrical acetylene has been reported hitherto. Avram et al.(1969) and Hosokawa et al.(1969) describe independently the formation of 1,2-di-*t*-butyl-3,4-diphenylcyclobutadiene -PdCl$_2$ on treatment of *t*-butylphenylacetylene with bis(benzonitrile)PdCl$_2$.The vicinal regiospecificity

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of this reaction contrasts with our observations for unsymmetrical diarylacetylenes.

Of very special interest, therefore, is the reaction of t-butylphenylacetylene with proton acids. It appears that in this case the non-vicinal cycloaddition product is formed. With the ^{13}C NMR technique, it could be unequivocally established that the 1,3-diphenyl-2,4-di-t-butylcyclobutenyl cation is formed on dissolution of t-butylphenylacetylene in HSO_3F at -70° (section VI.4).

In order to clarify these divergent results, the differences in the reaction mechanisms with proton acids and transition metal ions are discussed in section VI.2. An explanation of the different behaviour of t-butylphenylacetylene in the presence of transition metal ions is proposed which is based on steric considerations.

VI.2. *Mechanism explaining the regiospecificity of the reactions of arylacetylenes with transition metal ions.*

For the reaction of acetylenes with transition metal ions Maitlis(1971) has proposed the following reaction mechanism(Fig.6.1):
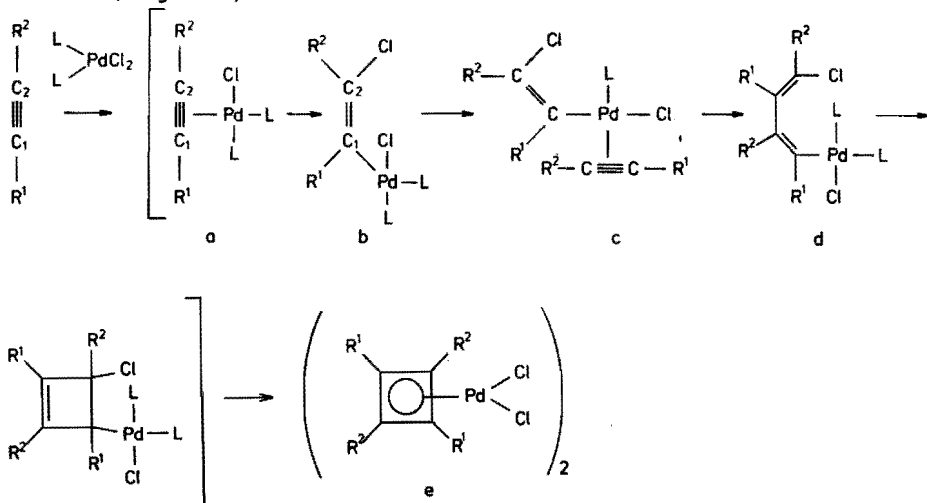

Fig.6.1 Reaction mechanism for the reaction of acetylenes with Pd(II) complexes

The acetylenic compound forms initially a π-complex with PdL$_2$Cl$_2$(L=benzonitrile)(a), which by cis ligand insertion into the Pd-Cl bond is converted into a σ-vinyl intermediate(b). A second molecule of acetylene is complexed with Pd(II) in complex(c). This leads, after a second cis insertion, to a butadiene complex(d), which subsequently forms a cyclobutadiene-PdCl$_2$ π-complex in dimeric form(e).

If this reaction is carried out with diphenylacetylenes having different substituents at the para positions, only electronic forces will govern this cyclodimerization. In the case R^1=phenyl,R^2=p-methoxyphenyl, the acetylenic compound is polarized in such a way that C$_1$ bears a fractional negative charge and C$_2$ a fractional positive charge. This leads to the assumption, that in both insertions an asymmetric π-complex is involved, yielding intermediates in which Pd(II) is attached to C$_1$. This stabilization is of the same type as the preferential attack of a proton on C$_1$(see chapter V). Consequently, in the cyclobutadiene complex, the substituents R^1 are situated opposed to each other, which is also the case for R^2.

The different behaviour of t-butylphenylacetylene should in our opinion be attributed to steric factors. According to Maitlis, the rate determining step in the cyclodimerization mechanism is the formation of the σ-vinyl intermediate (b). We propose, that in the case of t-butylphenylacetylene attack of Pd(II) on the carbon bearing a t-butyl group is impossible by steric hindrance of the bulky t-butyl group. Hence, the σ-vinyl intermediate(f) is formed, which gives the cyclobutadiene complex(g) by reaction with a second molecule t-butylphenylacetylene.
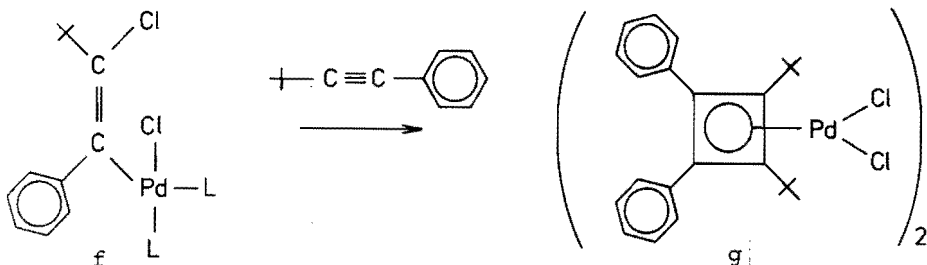
This supposition is supported by the fact, that di-*t*-butyl-
acetylene yields only the acetylene-$PdCl_2$ complex on treat-
ment with bis(benzonitrile)$PdCl_2$ (Hosokawa et al.,1969).
Furthermore, Maitlis(1971) proposes as intermediate the σ-
complex(f) for the reaction of *t*-butylphenylacetylene with
$(C_2H_4)(PdCl_2)_2$, which affords the 1-methyl-2-phenyl-3-
chloro-3-*t*-butyl-π-allyl palladium chloride(Hosokawa et al.,
1969).

VI.3 *Bonding in diene Pd complexes*

    In section VI.1 an irradiation experiment is described,
from which it appears that the basicity of the cyclobuta-
diene ring in the complex is greater in the excited state
than in the ground state. This interesting feature can be
explained by a consideration of the bonding in the complex-
es.
    The bonding of the cyclobutadiene ring to the metal is
performed in the following way(Cotton,1953). The totally
symmetric cyclobutadiene orbital $\psi_1(=\phi_1+\phi_2+\phi_3+\phi_4)$ mixes
with a combination of the 5s and 5 p_z orbitals of the metal,
thus forming a σ-bond. This σ-bond involves some electron
transfer from the cyclobutadiene ring to the metal. The de-
generate orbitals $\phi_1-\phi_3$ and $\phi_2-\phi_4$ of cyclobutadiene, both
occupied by one electron combine with the $4d_{xz}$ and $4d_{yz}$
doubly occupied orbitals of the metal respectively, forming
a π-bond. From this mixing two bonding and two anti-bonding
levels result. As only four electrons can be accomodated in
the bonding levels, the two remaining electrons are used to
fill the metal $4d_{z^2}$ orbital. Also this process will involve
charge transfer from the ring to the metal. The empty orbi-
tal ψ_4 of cyclobutadiene$(\phi_1-\phi_2+\phi_3-\phi_4)$ can form a bond with
the $4d_{x^2-y^2}$ orbital of the metal. This gives rise to elec-
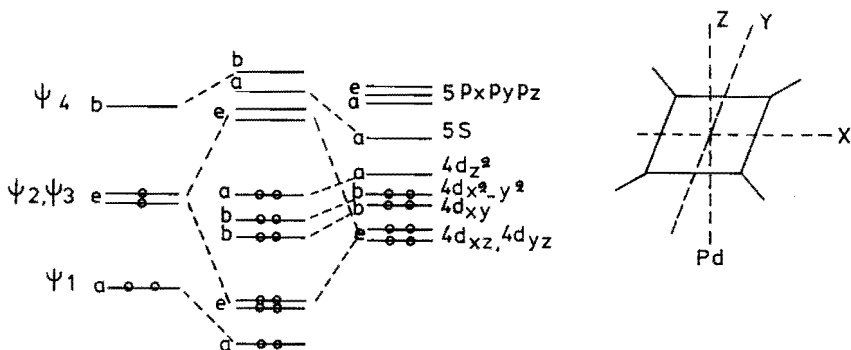tron transfer from the metal to the ring(back-donation).

Fig.6.2 Orbital correlation diagram of cyclobutadiene with
      Pd(II).

From the foregoing it can be concluded that excitation
of the complex to the lowest unoccupied levels(e) will be
accompanied with a charge transfer from the metal to the
cyclobutadiene ring. This leads to an enhanced basicity of
the cyclobutadiene ring in the excited complex in comparison
with the ground-state complex. Electrophilic attack of a
chloronium ion is therefore facilitated by electron excita-
tion.

VI.4 *Evidence of the ordering of the substituents in the*
      cyclobutadiene-PdCl$_2$ complexes. ^{13}*C NMR of the 1,3-*
      diphenyl-2,4-di-t-butylcyclobutenyl cation.

p-Methoxylphenyl-p-tolylacetylene and (p-methoxyphenyl)
phenylacetylene treated with bis(benzonitrile)PdCl$_2$ in etha-
nol/chloroform yield concatenated cyclobutadiene complexes
(more than one PdCl$_2$ unit per cyclobutadiene ring), which
are converted with HCl in CHCl$_3$ into the normal cyclobuta-
diene complexes(Fig.6.3).

$R^1 = p\text{-methoxyphenyl}$
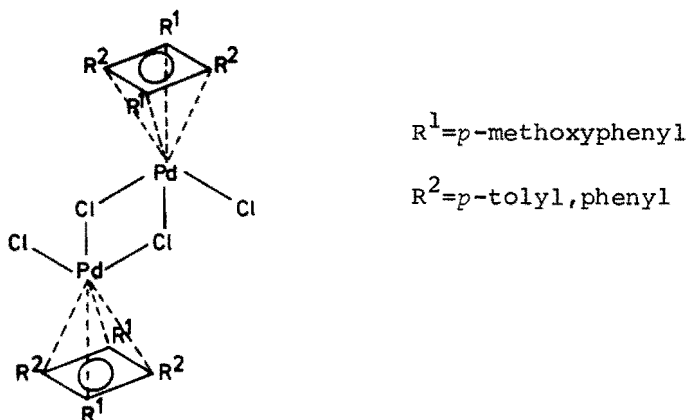
$R^2 = p\text{-tolyl, phenyl}$

Fig.6.3 Cyclobutadiene complex

The ordering of the substituents in the cyclobutadiene rings could be established by the following experiments.

The cyclobutadiene complexes of p-methoxyphenyl-p-tolyl-acetylene and (p-methoxyphenyl)phenylacetylene were dissolved in CF_3COOH and irradiated with UV light. The orange solutions turned purple and the UV spectra indicated that 1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl)cyclobutenyl cations ($\lambda_{max}=520$ nm) and 1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl)-cyclobutenyl cations($\lambda_{max}=520$ nm) had been formed respectively. For the latter compound it has been possible to build up a NMR concentration of cations by means of irradiation. The PMR spectrum is identical with that of the 1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl) cyclobutenyl cation(Fig.3.4), only the signal of the aliphatic proton is absent. Therefore, we suggest that a 4-chloro-1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl)cyclobutenyl cation(VIII) is formed, due to intramolecular chloronium transfer from the metal to the cyclobutadiene ring.

Reaction of the di(p-methoxyphenyl)-di(p-tolyl) cyclobutadiene complex with triphenylphosphine in air yields only one di(p-methoxyphenyl)-di(p-tolyl) furan, in which the four

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substituents are non-equivalent. This compound is to be ex-
pected from the oxydation of the intermediate 1,3-di(p-
methoxyphenyl)-2,4-di(p-tolyl)cyclobutadiene. The irradia-
tion experiments are consistent with this result, clearly
indicating that the ordering of the substituents is non-
vicinal.

Avram and Hosokawa report independently the formation of
1,2-di-t-butyl-3,4-diphenylcyclobutadiene-PdCl$_2$ from t-
butylphenylacetylene and bis(benzonitrile)PdCl$_2$. The struc-
ture of this cyclobutadiene complex was derived from the
hydrogenation product, 1,2-di-t-butyl-3,4-diphenylcyclobut-
1-ene. A similar conclusion for the sequence of the substi-
tuents(phenyl,t-butyl) could be arrived at by treating the
complexes with triphenylphosphine in air, which yields two
isomeric furans.
Both products are obtained by oxydation of one intermediate,
1,2-di-t-butyl-3,4-diphenylcyclobutadiene.

t-Butylphenylacetylene, dissolved in HSO$_3$F at -70° yields
the 1,3-diphenyl-2,4-di-t-butylcyclobutenyl cation (IX).
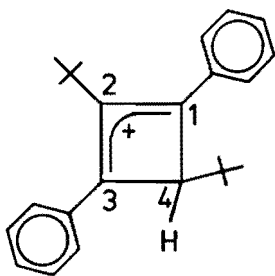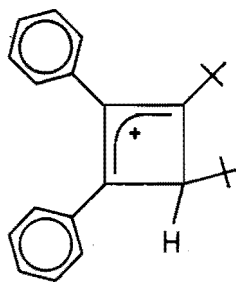
IX   X

The PMR spectrum in HSO$_3$F at -70° displays the signals of
the t-butyl protons at 1.45 and 1.96 ppm and the aliphatic
proton at 4.89 ppm. The latter value gives an indication that
this proton is present at a carbon bearing a t-butyl group.
The PMR spectrum does not allow a definite distinction be-

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tween structures IX and X, since in both systems the t-
butyl groups are non-equivalent.

^{13}C NMR of this compound in HSO$_3$F at -70°, taken under
conditions of complete noise-decoupling of all proton spins,
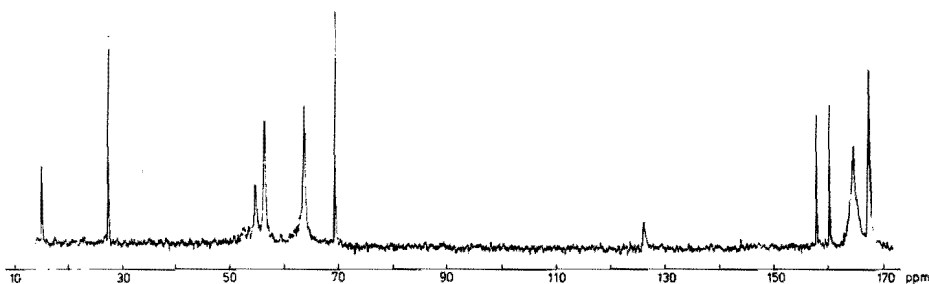show that compound IX is present(Fig.6.4).

Fig.6.4 ^{13}C NMR of IX in HSO$_3$F at -70°. Shifts in ppm up-
field from CS$_2$, measured from CD$_3$OD, which was also
used as external deuterium lock.*

From this spectrum, it can be concluded that the two phe-
nyl groups are equivalent. The signals of the para, ortho
and meta carbons are found at 54.9, 56.6 and 63.9 ppm respec-
tively, while the α-carbon atom is present at 69.6 ppm. Under
conditions of selective decoupling of the t-butyl proton
spins, the signals of the para, ortho and meta carbons appear
to be doublets, whereas the α-carbon atom remains a singlet.
The signal of C$_4$ is present at 126.0 ppm, which is 15.4 ppm
downfield compared with the tetra(p-methoxyphenyl)cyclobute-
nyl cation. This substituent effect is of the expected magni-
tude. The two t-butyl groups are clearly not equivalent. The
signals appear at 157.9, 160.3 (quaternary carbon atoms),
165.1 and 167.5 ppm (methyl carbon atoms). The equivalent
carbons C$_1$ and C$_3$ show one signal at 27.7 ppm, while the
signal of C$_2$ is displayed at 15.4 ppm. If the Spiesecke-
Schneider(1961) correlation between charge and ^{13}C shift is

used(section III.4), a positive charge of 0.22 units is found on C_1 and C_3.

In principle, ^{13}C NMR chemical shifts contain diamagnetic(σ_d) and paramagnetic(σ_p)terms(Ramsey,1950). Only σ_p may, in fact, be correlated directly with charge densities. In our previous examples(section III.4), the four substituents were all substituted aromatic rings, where σ_d's will be very similar. Intrinsic difficulties arise when aromatic rings have to be compared with e.g.tertiary butyl groups. Approximation of σ_d according to Mason(1971), who only included the effect of neighbour atoms leads to identical results for both groups which does not seem very probable. Extending the approximation over the total groups also happens to lead to similar results. A different and more promising approach is offered by comparing chemical shifts in model compounds like 1-phenylalkanes and 2,2-dimethylalkanes. In this way, one arrives at a difference in σ_d of about 13 ppm between a phenyl and a t-butyl substituent.

From the foregoing, it may be concluded that the chemical shift of 15.4 ppm of C_2 must be corrected with about 13 ppm for the difference in diamagnetic shielding between a t-butyl group and a phenyl group. A value of 28 ppm is now obtained, which indicates that on C_2 about the same amount of positive charge is present as on C_1 and C_3(0.22 unit). This clearly indicates, that homoconjugation is present in this cation. Olah(1970) arrived at the same conclusion for the 4-chloro-tetramethylcyclobutenyl cation, although his calculation of the charge distribution seems doubtful.

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CHAPTER VII

OCTA-ARYLCYCLO-OCTATETRAENES.

VII.1 *Introduction.*

Tetra-arylcyclobutadiene-PdCl$_2$ complexes, treated with tri-phenylphosphine under nitrogen atmosphere, yield octa-aryl-cyclo-octatetraenes (Pollock and Maitlis, 1971). Although spe-culations about radical intermediates for this reaction have been reported (Sandel and Freedman, 1968), the cyclobutadiene intermediates could be trapped by Diels-Alder reaction with cyclopentadiene and methyl phenylacetylenecarboxylate (Cook-son and Jones, 1965).

The tetra-arylcyclobutadiene-PdCl$_2$ complexes described in chapter VI (Fig.6.3),(R^1=p-methoxyphenyl,R^2=p-tolyl,phenyl) have been used to investigate the mechanism of this reaction. It is known that in these complexes the different substitu-ents are situated in a non-vicinal way (Chapter VI).

Reaction of one of these complexes with triphenylphosphine under nitrogen atmosphere yields only one cyclo-octatetraene. From ^{13}C NMR it can be established that the vicinal cycload-dition product is formed (Section VII.2). The regiospecifici-ty of this reaction can be explained by a concerted $_\pi 4_s + _\pi 2_s$ mechanism in which the endo transition state is favoured over the exo transition state.

In section VII.3 CNDO-2 calculations are given, which con-firm this qualitative concept.

*Regiospecific formation of octa-arylcyclo-octatetra-
enes from cyclobutadiene-PdCl$_2$ complexes.*

From the reaction of 1,3-di(p-methoxyphenyl)-2,4-di(p-
tolyl)cyclobutadiene-PdCl$_2$ with triphenylphosphine under ni-
trogen only one cyclo-octatetraene is obtained. This has been
established by thin layer chromatography with a number of
solvents. Also by means of analytical high-speed liquid chro-
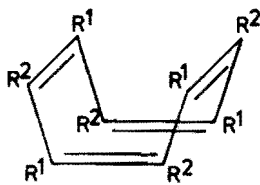matography on a Hupe+Busch LC type UFC 1000 only one compound
could be detected under different operation conditions.

By use of ^{13}C NMR it could be determined which of the two
possible cyclo-octatetraenes (XIA, XIB, R^1=p-methoxyphenyl,
R^2=p-tolyl) is present.
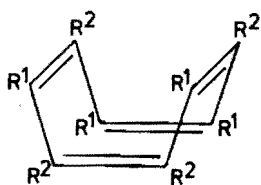
XIA   XIB

The ^{13}C NMR spectrum showed a multiplet centered at 51.2 ppm
upfield from CS$_2$ (Fig.7.1). This multiplet clearly contains
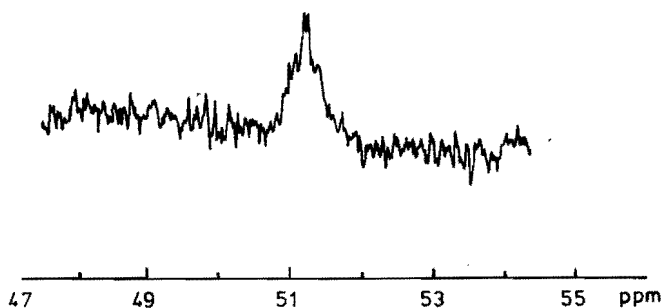more than two lines thereby excluding structure XIB. Most pro-

47   49   51   53   55 ppm

Fig.7.1 ^{13}C NMR spectrum of the carbon atoms of the cyclo-
octatetraene ring of XIA.

bably, four partially overlapping singlets are present due to
four pairs of ring carbon atoms. This indicates the formation
of XIA.

From the reaction of 1,3-di(p-methoxyphenyl)-2,4-diphenyl-
cyclobutadiene-$PdCl_2$ with tri(n-butyl)phosphine under nitro-
gen atmosphere also structure XIA(R^1=p-methoxyphenyl, R^2=
phenyl) was obtained. The ^{13}C NMR spectrum shows a multiplet
at 51.2 ppm of the octatetraene ring carbon atoms, which
consists again of more than two lines. Furthermore, two non-
equivalent types of phenyl rings and p-methoxyphenyl rings
are present. Of both types of rings the α and ortho carbon
atoms each appear as two signals, while the meta and para
carbon atoms each appear as one signal. This is only consis-
tent with structure XIA.

VII.3 *CNDO-2 calculation on possible transition states for the dimerization of two molecules cyclobutadiene.*

The regiospecificity of the cyclodimerization of two cy-
clobutadienes can be explained by the preference for endo
addition over exo addition in the transition state. The se-
lection rules of Woodward and Hoffmann require that this cy-
clodimerization proceeds as a $_\pi2_s+_\pi4_s$ process. The endo tran-
sition state is predicted to be stabilized by secondary bon-
ding orbital interactions.

Fukui (1971) has demonstrated that secondary orbital in-
teractions among the occupied molecular orbitals of the re-
actants will contribute only in a very minor way to the to-
tal energy of the transition state, since the energy of some
levels will be increased while the energy of other levels
will be decreased. The significant interactions will arise
from the symmetry allowed mixing of unoccupied with occupied
levels. The most important contribution is obtained from the
mixing of the highest occupied molecular orbital (HOMO) with
the lowest unoccupied molecular orbital (LUMO).
In Fig. 7.2 it can be seen that in the cyclodimerization of
cyclobutadiene the secondary orbital interactions between

the HOMO and the LUMO of both reactants are bonding, which affords a lowering of the transition state energy. These interactions are absent in the alternative exo process.

CNDO-2 calculations on a number of possible transition states for the endo and the exo process provide a confirmation of the qualitative considerations just presented.

A series of calculations was carried out in which the cyclobutadiene molecules were placed on a distance of 3 Å of each other, whereby the angle θ was varied (Fig.7.3).

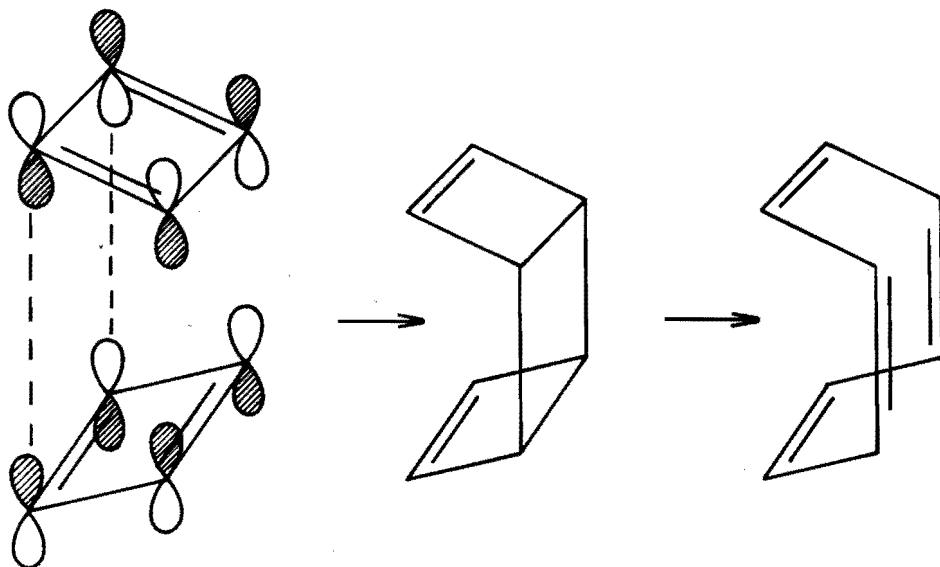

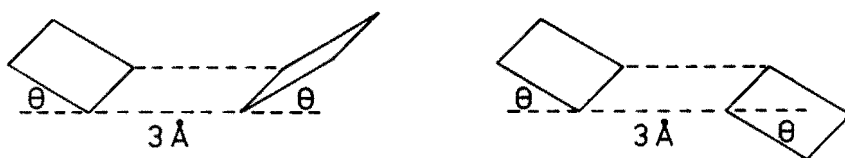Fig.7.2 Secondary interactions in the endo cyclodimerization of cyclobutadiene.

Fig.7.3 Models for the calculations of the endo and the exo process.

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From the calculations, it appears that the endo process is
more favourable than the exo process for any value of θ. The
most favourable situation is $\theta=90^\circ$ for both the exo and the
endo process. However, in view of the product cyclo-octate-
traene in which $\theta=45^\circ$ (Pawley, et al., 1964), it seems
doubtful whether this situation resembles the transition
state.

kcal/mol
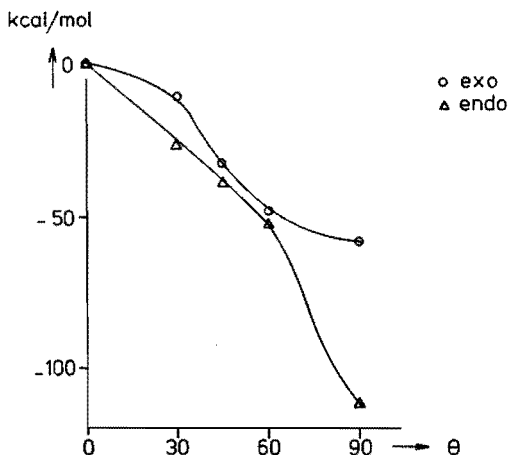
Fig.7.4 Transition state energy for different values of θ.

   Furthermore, it has been established that in the actual
position of the cyclobutadiene rings in the complex (distan-
ce between the rings is about 5 Å, $\theta=90^\circ$) the endo orienta-
tion is 10 kcal lower in energy than the exo orientation. It
seems possible that the cyclobutadiene rings, after removal
of the transition metal salts with triphenylphosphine, react
from the arrangement which was present in the complex. Since
we know the structure of the formed cyclo-octatetraenes, the
relative orientation of the cyclobutadiene rings in the metal
complex is now established (Fig.6.3).

CHAPTER VIII

EXPERIMENTAL

VIII.1 *Cyclobutenyl cations.*

The cyclobutenyl cations were prepared by dissolving the
corresponding acetylenes in acids with a weak nucleophile as
anion, like CF_3COOH, H_2SO_4 or HSO_3F. Efforts to crystallize
the tetra-arylcyclobutenyl cations were unsuccesfull, since
tetra-arylfurans are easily formed by reaction with the anion
of the acid (Section VIII.3).

This reaction requires the use of acids with a weakly nu-
cleophilic anion, because otherwise a nucleophilic attack on
the acetylenic bond will almost certainly occur. If di(p-
methoxyphenyl)acetylene is dissolved in liquid HBr at -70°
the tetra(p-methoxyphenyl)cyclobutenyl cation is formed in
small amounts only. However, Br^- attack on the triple bond
followed by rapid protonation, yielding the 1-bromo-1,2-di
(p-methoxyphenyl)ethene, predominates (Section VIII.3).

It is clear that also the basicity of the acetylenic com-
pound determines whether nucleophilic or electrophilic attack
occurs. Viehe (1967) obtained bromocyclobutenyl cations on
treatment of alkynylamines with Br_2, whereas diarylacetylenes
yield 1,2-dibromo-1,2-diarylethenes on reaction with Br_2
(Section VIII.3). Kinetic experiments with diphenylacetylene
have shown that the latter reaction proceeds by an initial

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nucleophilic attack (Sinn, 1957).

VIII.2 *Tetra-arylcyclobutadiene-PdCl₂ complexes and octa-arylcyclo-octatetraenes.*

The tetra-arylcyclobutadiene-PdCl$_2$ complexes were prepared from the corresponding acetylenes by reaction with bis⁻(benzonitrile)PdCl$_2$. If this reaction is carried out in CHCl$_3$/C$_2$H$_5$OH, concatenated forms of the cyclobutadiene complexes crystallize (Pollock and Maitlis, 1971). These concatenated complexes are converted into the normal cyclobutadiene complexes by treatment with HCl in CHCl$_3$ (Section VIII.3).

The octa-arylcyclo-octatetraenes are obtained by refluxing the tetra-arylcyclobutadiene complexes in anhydrous benzene with triphenylphosphine or tri(n-butyl)phosphine under nitrogen atmosphere. In the presence of air the corresponding tetra-arylfurans are formed.

VIII.3 *Experimental data.*

A. Starting materials
1,2-diphenylacetylene was commercially available.

1,2-di(p-methoxyphenyl)acetylene and *1-p-methoxyphenyl-2-p-tolylacetylene* were prepared as described for the ^{13}C enriched compounds.

1-p-methoxyphenyl-2-phenylacetylene (m.p.63°) was prepared by reaction of 1-p-methoxyphenyl-1,2-dibromo-2-phenylethane and C$_2$H$_5$ONa in a sealed tube at 130°.

1,2-di(p-methoxyphenyl) (1-^{13}C)acetylene.
1.45 g di(p-methoxyphenyl)ketone was added to the Grignard reagent (0.2 g Mg, 1 g (^{13}C)methyl iodide (60% enrichment), 10 cc ether). Decomposition with aqeous HCl, extraction with ether/CHCl$_3$ and recrystallization from alcohol yielded 1,1-

di(p-methoxyphenyl)-2-bromo(2-^{13}C)ethene. 1,2-Di(p-methoxy-phenyl)(1-^{13}C)acetylene (m.p. 141°-143°) was prepared from the latter compound and C_2H_5ONa in a sealed tube at 130°.

Mixture of 1-p-methoxyphenyl-2-p-tolyl(1-^{13}C)acetylene and 1-p-methoxyphenyl-2-p-tolyl(2-^{13}C)acetylene.
By the same method as described above 1-p-methoxyphenyl-1-p-tolyl-2-bromo(2-^{13}C)ethene was prepared. The reaction with C_2H_5ONa in a sealed tube at 130° scrambled the labelling. The ^{13}C NMR spectrum of the labelled acetylene in $CHCl_3$ revealed that the ^{13}C isotope was about equally divided over the ace-tylenic carbon atoms. This could be established by comparison with the ^{13}C NMR spectrum of the unlabelled 1-p-methoxyphenyl-2-p-tolylacetylene, which exhibits two signals in the acety-lenic region at 104.1 and 104.6 ppm upfield from CS_2.

1-t-Butyl-2-phenylacetylene (liq.) was prepared by the action of *t*-butylbromide on phenylacetylenemagnesium bromide in ether.
The preparations of these compounds with original literature have been described by us (Lodder et al., 1970, Van der Hout-Lodder et al., 1972).

B. Details of the reactions described in this thesis.
1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl)cyclobutadiene-PdCl$_2$.
1 g p-methoxyphenyl-p-tolylacetylene dissolved in a mixture of 24 cc C_2H_5OH and 4 cc $CHCl_3$ was added to a solution of 1 g bis(benzonitrile)PdCl$_2$ in 4 cc $CHCl_3$. 0.8 g of a red-brown complex separated after 24 hours, which probably is a conca-tenated form of the cyclobutadiene complex. This red-brown complex was dissolved in 20 cc $CHCl_3$ and HCl gas was bubbled through. After 24 hours red crystals of 1,3-di(p-methoxyphe-nyl)-2,4-di(p-tolyl)cyclobutadiene-PdCl$_2$ had separated.

1,3-di(p-methoxyphenyl)-2,4-diphenylcyclobutadiene-PdCl$_2$.
The same procedure was followed as described for 1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl)cyclobutadiene-PdCl$_2$.

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1,2,4,7-tetra(p-methoxyphenyl)-3,5,6,8-tetra(p-tolyl)cyclo-octatetraene.

4.2 g 1,3-di(p-methoxyphenyl)-2,4-di(p-tolyl)cyclobutadiene-
PdCl$_2$ was refluxed in anhydrous benzene. 5 g triphenylphosphi-
ne was added under nitrogen atmosphere. After 8 hours of re-
fluxing, the reaction was stopped. After filtration of triphe-
nylphosphine-PdCl$_2$ and removal of the solvent in vacuo, the
resulting oil was crystallized with C$_2$H$_5$OH. Yield 1.8 g (60%).
(See also Van der Hout and Buck, 1972).

*1,2,4,7-tetra(p-methoxyphenyl)-3,5,6,8-tetraphenylcyclo-octa-
tetraene.*

0.8 g 1,3-di(p-methoxyphenyl)-2,4-diphenylcyclobutadiene-
PdCl$_2$ was refluxed in anhydrous benzene. Under nitrogen at-
mosphere 1 g tri(n-butyl)phosphine was added. After 8 hours
the solvent was removed in vacuo. Bis(tri-n-butyl)phosphine-
PdCl$_2$ was washed out of the residue with petroleum ether. Af-
ter crystallization with C$_2$H$_5$OH 0.3 g of the cyclo-octatetra-
ene resulted.

Formation of 1-bromo-1,2-di(p-methoxyphenyl)ethene.
Di(p-methoxyphenyl)acetylene was dissolved in liquid HBr at
-70°C yielding a purple solution. The solvent HBr was allowed
to evaporate at room temperature, whereupon the purple oil
was dissolved in CCl$_4$ under nitrogen. The only compound iso-
lated was 1-bromo-1,2-di(p-methoxyphenyl)ethene(m.p. 95°,
C$_{16}$H$_{15}$O$_2$Br from mass spectroscopy) PMR δ 3.80 (OCH$_3$,s) δ 7.16
(H,s) δ 7.2-7.6 (phenyl,m).

Formation of 1,2-dibromo-1,2-di(p-methoxyphenyl)ethene.
Di(p-methoxyphenyl)acetylene was dissolved in nitromethane. A
purple solution resulted from which white crystals of 1,2-di-
bromo-1,2-di(P-methoxyphenyl)ethene (m.p. 194°, C$_{16}$H$_{14}$O$_2$Br$_2$
from mass spectroscopy) separated. PMR δ 3.95 (OCH$_3$,s) δ 7.0-
7.7 (phenyl,m).

Formation of 1,2,3,4-tetra(p-methoxyphenyl)furan.

Di(p-methoxyphenyl)acetylene was dissolved in CF_3COOH, which resulted in the formation of the 1,2,3,4-tetra(p-methoxyphenyl)cyclobutenyl cation (PMR spectrum). CF_3COOH was removed in vacuo leaving a purple oil. Dissolving this oil again in CF_3COOH yielded the same PMR spectrum as before. Under nitrogen atmosphere CCl_4 was added to this purple oil. After some time a white compound crystallized (m.p. 220°, $C_{32}H_{28}O_5$ from mass spectroscopy) which was identified as tetra(p-methoxyphenyl)furan. PMR δ 3.76 (OCH_3), δ 6.63-7.45 (phenyl,qq).

C. Instrumental data.

The PMR spectra were recorded with a Varian HA-100 and a Varian A-60 spectrometer. The ^{13}C NMR spectra (25.1Mc/s) were taken on a Varian HA-100 spectrometer.

The UV spectra were measured with a Cary spectrophotometer.

The calculations discussed in this thesis have been performed initially on the computer of the University of Leiden, an IBM 360-50, later on the IBM 360-75 of Philips Computer Centre, by teletype from the Technological University Eindhoven.

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SUMMARY

Diarylacetylenes can be cyclodimerized to tetra-arylcyclo-
butenyl cations under the influence of proton acids. In this
study it was shown by NMR that these reactions proceed via a
non-vicinal regiospecific pathway. The experimental UV spectra
of the cations were compared with the theoretical spectra,
calculated according to the LCAO-MO-SCF method of Pariser,
Parr and Pople. Homoconjugation in these cations was thereby
predicted theoretically and observed experimentally. As a con-
sequence, these ions can better be regarded as homocycloprope-
nyl cations.

An explanation of the regiospecificity of this reaction is
given, starting from an allowed $_\pi 2_s + _\pi 2_a$ process (orthogonal
transition state). The preferentially formed vinyl cation re-
acts with a polarized molecule of acetylene. This was also
confirmed by CNDO-2 and PPP calculations on the transition
state of this reaction.

Under the influence of Pd(II) ions diarylacetylenes exhibit
a similar cyclodimerization. Tetra-arylcyclobutadiene-PdCl$_2$
complexes are formed in a non-vicinal regiospecific process.
The mechanism of this reaction, however, differs fundamental-
ly from the reaction with proton acids (cis-insertion).

In this context the behaviour of t-butylphenylacetylene is
interesting. Under the influence of proton acids this acety-
lenic compound forms the non-vicinal cycloaddition product.
On the other hand, the reaction with Pd(II) ions yields the
cyclobutadiene complex in which the substituents are in a vi-
cinal position. A possible explanation can be found in the
steric hindrance of the t-butyl group, which impedes Pd(II)
attack on the t-butyl substituted acetylenic carbon.

The tetra-arylcyclobutadiene complexes, thus obtained, can
be converted to octa-arylcyclo-octatetraenes by reaction with
triphenylphosphine. This conversion was also studied. The sub-
stitution pattern of the formed octatetraene was determined by
means of ^{13}C NMR. From this it could be concluded that the re-
action proceeds probably in a converted way via an endo $_\pi 4_s +$
$_\pi 2_s$ mechanism.

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SAMENVATTING

Onder invloed van protonzuren is het mogelijk diarylacety-
lenen te cyclodimeriseren tot tetra-arylcyclobutenyl kationen.
Met behulp van NMR-metingen werd vastgesteld dat deze reaktie
een niet vicinale regiospecificiteit vertoont. De UV-spektra
van deze tetra-arylcyclobutenyl kationen werden vergeleken
met de spektra die berekend werden volgens de LCAO-MO-SCF me-
thode van Pariser, Parr en Pople. Zowel experimenteel als
theoretisch kon vastgesteld worden, dat in deze kationen ho-
mokonjugatie optreedt. Dientengevolge is het beter deze io-
nen te beschouwen als homocyclopropenyl kationen.

Een verklaring voor de specificiteit van deze reaktie werd
gegeven, uitgaande van een toegestaan $_{\pi}2_s + _{\pi}2_a$ proces (ortho-
gonale transition state). Het vinyl kation, dat bij voorkeur
gevormd wordt, reageert met een gepolariseerd molekuul ace-
tyleen. Dit werd onder meer bevestigd door CNDO-2 en PPP be-
rekeningen aan de transition state van deze reaktie.

Onder invloed van Pd(II) ionen vertonen diarylacetylenen
een soortgelijke cyclodimerisatie. Er worden tetra-arylcyclo-
butadieen-PdCl$_2$ komplexen gevormd, waarbij wederom een niet
vicinale regiospecificiteit optreedt. Het mechanisme van deze
reaktie evenwel verschilt principieel van de reaktie met pro-
tonzuren (cis insertie).

In dit verband is het gedrag van t-butylphenylacetyleen
interessant. Onder invloed van protonzuren vormt dit acety-
leen het niet-vicinale cycloadditieprodukt. De reaktie met
Pd(II) ionen daarentegen levert het cyclobutadieen komplex,
waarin de substituenten een vicinale positie innemen. Een mo-
gelijke verklaring hiervoor is de sterische hindering van de
t-butyl groep, die Pd(II) aanval op de acetyleen koolstof,
waaraan de t-butyl groep gesubstitueerd is, verhindert.

De verkregen tetra-arylcyclobutadieen komplexen boden de
mogelijkheid het mechanisme te onderzoeken van de omzetting
in octa-arylcyclo-octatetraenen met behulp van triphenylphos-
phine. Het substitutie patroon van het gevormde octatetraeen
kon met behulp van ^{13}C NMR bepaald worden. Hieruit kon worden
gekonkludeerd dat de reaktie waarschijnlijk "concerted" ver-
loopt via een endo $_{\pi}4_s + _{\pi}2_s$ mechanisme.

DANKWOORD.

Gaarne wil ik op deze plaats mijn dank betuigen aan allen die aan de tot standkoming van mijn proefschrift hebben bijgedragen. In de eerste plaats gaat mijn dank uit naar mijn ouders, die het mij mogelijk hebben gemaakt een academische studie te volgen. De stimulerende gesprekken met de leden van de afdeling theoretische organische chemie te Leiden en later de afdeling physische organische chemie te Eindhoven heb ik zeer op prijs gesteld. Belangrijke steun bij de uitvoering van dit onderzoek heb ik ontvangen van Mej. P.L.A. Everstijn en de Heer R.J. de Knegt uit Leiden en later van Mevr. E.W.A. Krijzer-Kraak uit Eindhoven.
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LEVENSBERICHT

Na het behalen van het einddiploma gymnasium β aan het Libanon Lyceum te Rotterdam begon ik in september 1963 met mijn studie aan de Rijksuniversiteit te Leiden. Het kandidaatsexamen in de scheikunde met bijvakken wiskunde, natuurkunde en biologie (letter G) legde ik in juni 1966 af. Mijn studie werd voortgezet op de afdeling voor theoretische organische scheikunde van Prof.Dr. L.J. Oosterhoff. Onder leiding van Dr. H.M. Buck verrichtte ik een onderzoek naar de kinetiek van termolekulaire reakties en naar associatieverschijnselen.
In november 1968 legde ik het doktoraalexamen af in de theoretische organische chemie met als bijvakken numerieke wiskunde en theoretische natuurkunde.

Gedurende de periode januari 1969-juni 1970 was ik als doktoraal-assistent in dienst van de Rijksuniversiteit te Leiden. Hierna werd ik als wetenschappelijk medewerkster verbonden aan de afdeling theoretische organische chemie in dienst van Z.W.O. (S.O.N.) tot 1 januari 1971, op welke datum ik in dezelfde funktie aangesteld werd bij de Technische Hogeschool te Eindhoven.

STELLINGEN

I

De door Hellwinkel bij ESR metingen aan het bis-2,2'-
bifenylfosfonium radikaal verkregen fijnstruktuur
dient niet aan het fosfonium radikaal te worden toe-
geschreven.
D.Hellwinkel,Ber.,102,528 (1969).

II

De manier waarop Landau e.a. vaststellen via welk a-
toom verbindingen van het type XYZPO aan metaal ionen
zullen coördineren is onjuist.
M.A.Landau,V.V.Sheluchenko en S.S.Dubov,J.Struct.Chem.
SSSR,11, 467 (1970).

III

Tot nu toe vormden de chemische verschuiving en de
koppelingskonstanten de enige analytisch bruikbare
parameters bij ^{13}C NMR.Het is te verwachten,dat bin-
nenkort de longitudinale relaxatietijd T_1 van verge-
lijkbaar belang zal worden.

IV

De ESR spektra, die Kolodny en Bowers gemeten hebben
van het charge-transfer komplex van 2,3-dichloro-5,6-
dicyano-1,4-benzochinon met p-fenyleen diamine, wijzen
er niet op, dat naast de radikalen van donor en accep-
tor nog een radikaal afkomstig van het charge-transfer
komplex aanwezig is.
N.H. Kolodny en K.W. Bowers, J.Am.Chem.Soc., 94, 1113
(1972).

V

Het is niet mogelijk de grootte van de metaal-zuurstof-
fosfor bindingshoek(M-O-P) vast te stellen zonder een
röntgen struktuur te bepalen.

M.Schafer en C.Curran, Inorg. Chem., $\underline{4}$, 623 (1965).

P.M.Mullins, Can.J. Chem., $\underline{49}$, 2719 (1971).

VI

De konklusie van Klages en Roth,dat het relaxatiegedrag
van alkoholen in verdunde oplossingen van apolaire oplos-
middelen door een verdeling van relaxatietijden wordt
gegeven,is aanvechtbaar.

G.Klages en N.Roth, Z. Naturforsch. $\underline{23^{\underline{a}}}$, 171 (1968).

VII

De fosforsplitsing van het bij de reaktie tussen tri-
phenylfosfine en tetrachlorobenzochinon gevormde radikaal
is niet in overeenstemming met het gepostuleerde phenoxy-
O-fosfonium radikaal.

E.A.C.Lucken,F.Ramirez,V.P.Catto,D.Rhum en S.Dershowitz,
Tetrahedron $\underline{22}$, 637 (1966).

VIII

Aan de maximumsnelheid op Corsica dient streng de hand
gehouden te worden teneinde het uitsterven van de
neushoornkever te voorkomen.

A.E. van der Hout-Lodder   Eindhoven,12 september 1972.