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**ELECTRON SPIN RESONANCE
SPECTROSCOPIC STUDIES OF
RADICAL CATION REACTIONS**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Sheng Dai

December, 1990

THESE
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.D253

献给我的
父母及妻子

Dedicated to my parents
and my wife Huimin Luo for their love

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ABSTRACT

The work completed in this thesis is summarized as follows. Theoretical Work: (1) a spin Hamiltonian suitable for interpretations and theoretical analyses of ESR spectra in this work is derived by using the general effective Hamiltonian theory in the usual Schrödinger representation, (2) the Permutation Indices method is extended to obtain the dynamic exchange equations used in ESR lineshape simulation, (3) the correlation between β -hydrogen coupling constants and their geometric orientations is derived through the use of a perturbation method, (4) the three electron bond model is extended to rationalize unimolecular rearrangements of radical cations. Experimental Work: (1) the ring-closed radical cations of 9,10-octalin oxide and syn-sesquinorbornene oxide have been characterized by ESR spectroscopy in the CFCl_3 matrix at low temperature. The ESR spectra of the former radical cation exhibit a novel alternating linewidth effect arising from an internal relation between the coupling constants for the four equivalent pairs of hydrogens,¹ (2) the self-electron-transfer rate constants between the methyl viologen dication and cation have been determined by dynamic ESR lineshape simulations at room temperature in allyl alcohol, water, methanol and propargyl alcohol solvents. Correlation diagrams between solvent parameters and rate constants reveal that the

work-function term dominates the activation energy,² (3) the radical cation formed by the radiolytic oxidation of allylamine in Freon matrices at 77 K is shown to be the 3-iminiopropyl distonic species (3-iminium-1-propyl radical) resulting from a symmetry-allowed 1,2-hydrogen shift in the parent radical cation,³ (4) the nucleophilic endocyclization of the but-3-en-1-ol radical cation to the protonated tetrahydrofuran-3-yl radical was observed in the radiolytic oxidation of but-3-en-1-ol in Freon matrices,⁴ (5) ESR studies of the radiolytic oxidation of 1,5-hexadiyne have resulted in the first spectroscopic characterization of the radical cation Cope rearrangement, the 1,5-hexadiyne radical cation isomerizing to the 1,2,4,5-hexatetraene radical cation at 77 K in Freon matrices,⁵ (6) ESR studies show that the symmetric(C_{2v}) bicyclo[3.3.0]-octa-2,6-diene-4,8-diyl (a bridged 1,4-bis-homobenzene species) radical cation is produced by the radiolytic oxidation of semibullvalene in Freon matrices. The magnitudes of the coupling constants clearly establish the $^2B_2$ state as the ground-state electronic structure, and this corresponds closely to the transition structure for the degenerate Cope rearrangement of the neutral semibullvalene molecule,⁶ (7) the 3,4-dimethylenecyclobutene radical cation has been characterized as a $^2B_1$ state by ESR spectroscopy, prepared by the radiolytic oxidation of the parent compound in Freon matrices. The ring-opening of the 3,4-dimethylenecyclobutene radical cation to

the 1,2,4,5-hexatetraene radical cation was observed in the photolysis of the 3,4-dimethylenecyclobutene radical cation, (8) the cyclooctatetraene radical cation generated by radiolytic oxidation photoisomerizes to the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation identical to the species produced directly from the radiolytic oxidation of semibullvalene. This isomerization can be interpreted as a symmetry-allowed electrocyclic reaction where the lowest Koopmans (^2E) excited state of the reactant correlates directly with the $^2B_2$ ground state of the product.⁷

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CHAPTER 1

INTRODUCTION

This dissertation focuses on two kinds of problems in radical chemistry. The first is to study the dynamics of radical cations in the condensed phase (electron transfer and configuration dynamics) and to interpret the experimental results by dynamic computer simulation. The second is to study the special reactivity of radical cations in the condensed phase. The experimental results are rationalized with both frontier orbital theory and quantum chemical calculations using the AMPAC (Austin Molecular Package) program.

Radical cations are those species formed by the one-electron oxidation or ionization of neutral molecules.



Recently, the chemistry of radical cations has aroused wide interest.⁸ They are involved in a variety of fundamental chemical processes including redox, electrochemical, and photochemical reactions as well as many catalytic chemical transformations. Their distinct chemical properties even find some direct applications in synthesis.⁹ Hence it is important to understand the structure and chemistry of these species.

A large amount of thermodynamic data has been acquired on gas-phase radical cations through the use of

photoelectron spectroscopy(PES) and mass spectrometry(MS). The former also gives information about molecular orbital Koopmans energies of radical cations from measurement of the vertical ionization energies of the parent molecules. Recently, there has been some exciting progress in studies of radical cations in the gas phase. Much detailed rotational and vibrational spectroscopic information of some gas-phase radical cations has become available by the use of modern laser spectroscopic techniques.¹⁰ Some of these studies, notably those by PES and MS techniques, can certainly provide important insights to the radical cation chemistry in the condensed phase. However, much other information of interest, such as the spin distribution of the singly-occupied frontier orbitals is very hard to obtain directly from the gas-phase spectroscopic techniques. Moreover, there are some fundamental differences between gas-phase and condensed-phase processes. In the condensed phase, large numbers of matrix or solvent molecules can act as a vast heat bath to provide either sources or sinks for energy. When reactants and products are separated by an energy barrier, for example, solvents provide the fluctuating energy to climb over the barrier, and they can absorb the excess energy of the products. Solvents also create and impede molecular motion so that solute molecules are locked in cages(cage effect). They sometimes even play a role in determining the reaction potential surface. In a word, the chemical processes of

solute molecules in the condensed phase are coupled with those of solvents(Fig.(1-1)). In contrast, molecules in gas phase are relatively more isolated from the environment. One effect due to this isolation is that excess energies produced in chemical processes of the gas phase can not be easily dissipated and often end up with the fragmentation of radical cations. Therefore, direct condensed-phase studies of the radical cations can provide vital information about the structure and reactivity of these species.

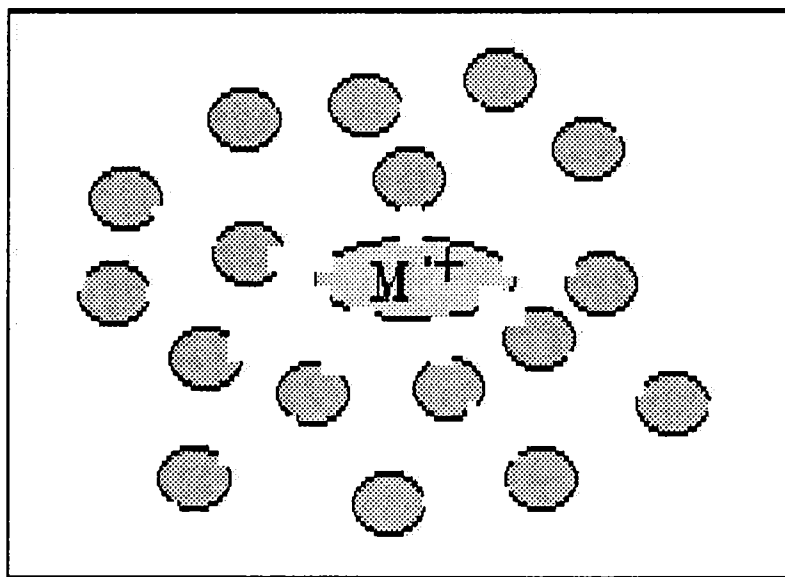


Fig.(1-1). Coupling between solvent and solute molecules.

Several spectroscopic methods have been developed to observe radical cations in the condensed phase.^{8,11,12,13,14,15,16} Since radical cations are normally very reactive and

transient, the spectroscopic techniques used to observe them generally belong to three categories: (1) fast time-resolved spectroscopies of transient radical cation species;^{12,15,16} (2) indirect measurement of after-effects induced by the short presence of radical cations;^{8a,14,16} (3) direct continuous wave(CW) spectroscopies of trapped or stable radical cations.^{8b,8d,8e,13} The analogies among the above methods and animal behavior studies are shown in Fig.(1-2). The fast time-resolved optical spectroscopy¹⁵ and time-domain ESR¹⁶ are examples of the first group. On the other hand, the CIDNP^{8a} and FDMR¹⁴ are examples of the second. The ESR and electronic absorption spectroscopy(EA) of trapped or stable radical cations,^{8d,11} which were adopted in this work as main experimental tools, belong to the last group.

The spectrometers used in ESR and EA studies are commercially available. The use of the ESR method allows determination of the unpaired electron distribution of the semi-occupied-molecule-orbital(SOMO), which in turn helps to characterize the structure of the radical. On the other hand, EA studies can determine the orbital energy difference between two molecular orbitals(MO) involved in an allowed single-electron transition and sometimes the symmetries of these orbitals may be deduced from the intensity of the transition. For Koopmans transitions, EA data can often be correlated with the gas-phase PES data of the corresponding neutrals when geometry changes of the radical cations

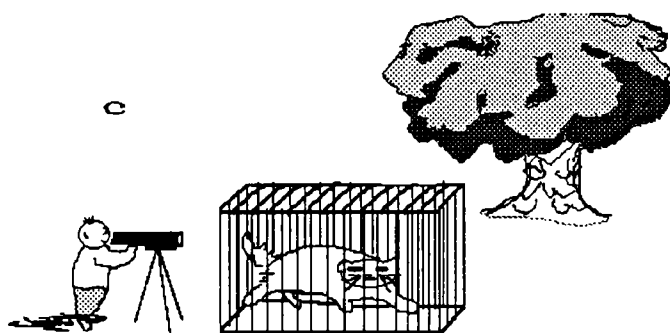
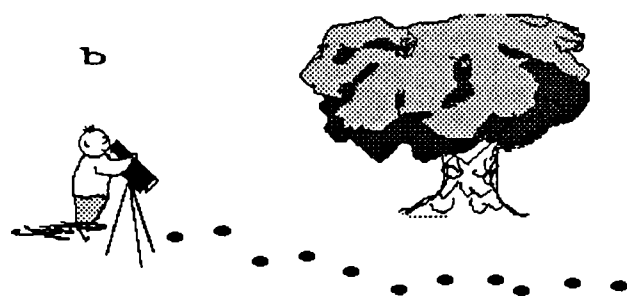
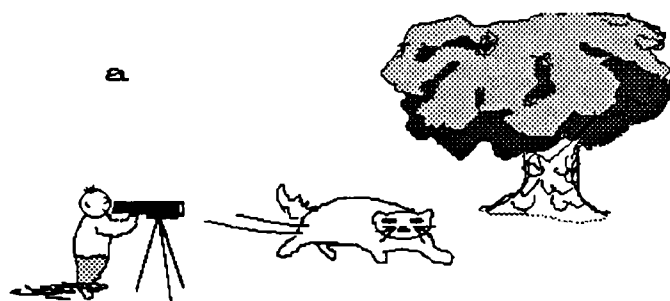
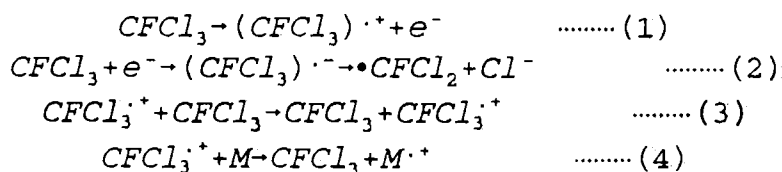


Fig.(1-2). Three ways of studying animal behavior. a, transient; b, aftereffects; c, trapped.

relative to their neutral molecules are taken into account. Fig.(1-3) shows the general information obtained from PES, EA and ESR studies of radical cations and their mutual relations.

The one-electron oxidation can be induced by many methods. For example, relatively unreactive radical cations such as those of aromatic compounds can be generated in solution by the traditional chemical and electrochemical oxidation of the parent neutral molecules.¹³ The method used in this work is that of radiolytic oxidation.^{8d,11} This method was first used in 1966 by Hamill and Shida to generate aromatic radical cations in alkyl halide matrices for optical studies.¹⁷ In 1979, the technique was extended by Shida and Kato to generate radical cations for ESR studies from a wider variety of molecules by using Freon matrices.¹⁸ In this method, radical cations are produced by exposing the dilute solution of a substrate in Freon matrices to the high energy radiation at 77 K. The essence of the method is summarized in reactions (1)-(4) for the most popular matrix(CFCl_3). The substrate radical cation($\text{M}^{\bullet+}$) is produced at 77 K via electron



transfer from the substrate molecule to the matrix radical cation generated by the radiolytic oxidation followed by electron self-exchange reactions. Provided the substrate

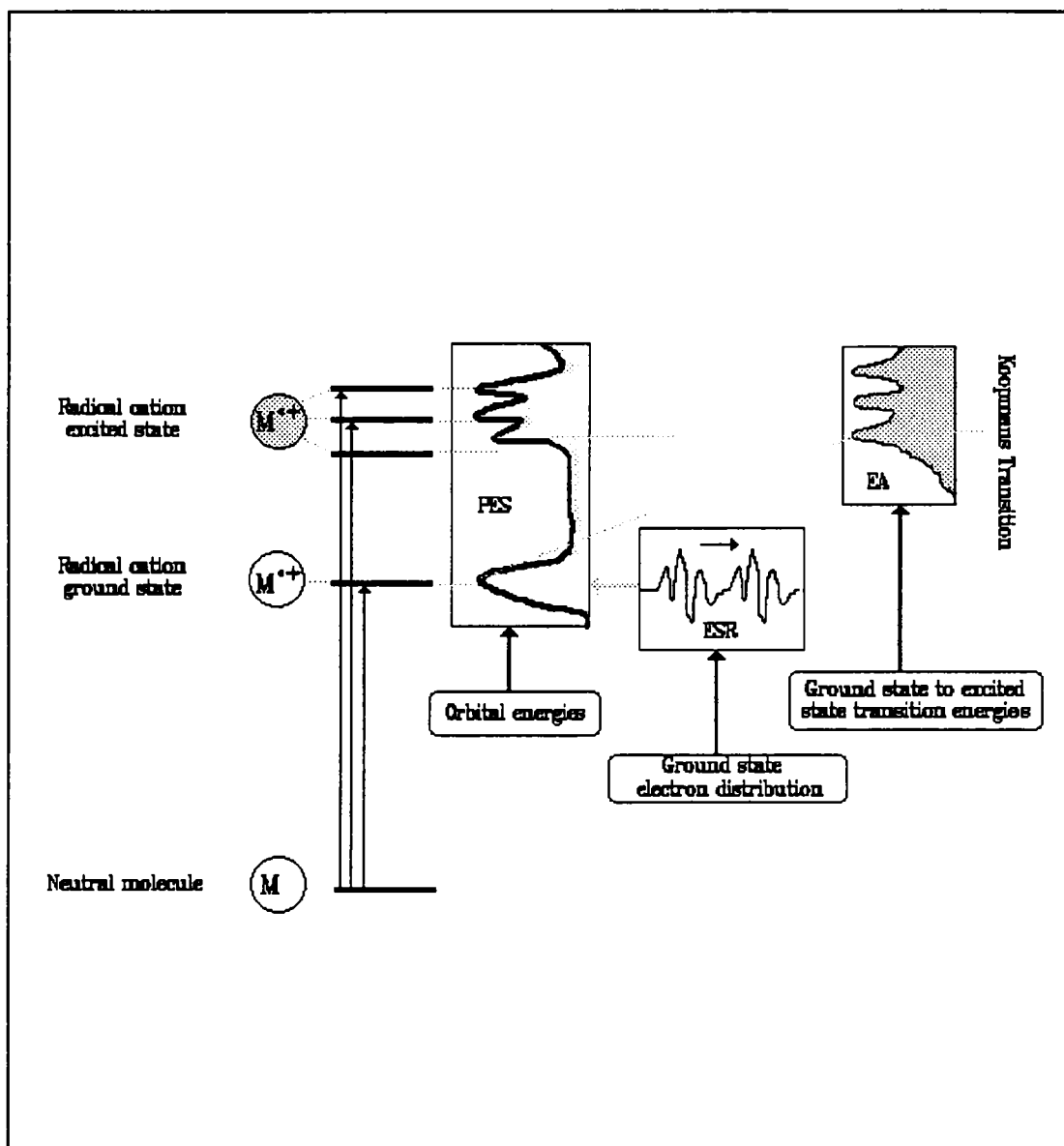


Fig.(1-3). A schematic diagram showing general information obtained from PES, EA and ESR studies of radical cations, and their mutual relations.

molecule has an ionization potential less than that of the solvent, and provided it does not form clusters in the frozen solution, M^+ will be formed. This method is more gentle compared to the ionization methods in the gas phase since only the relatively low-energy electron transfer processes are involved and the excess energy released in step (4) can be easily degraded through the matrix vibrations. Normally only the parent radical cations or rearranged ones are produced at 77 K. Such generated radical cations can be easily studied by ESR and EA spectroscopies since Freon matrix radicals give rise to very broad ESR features which do not seriously interfere with solute ESR spectra and have no absorption peaks in UV-visible ranges of interest.

CHAPTER 2

THEORY OF ELECTRON SPIN RESONANCE

Introduction

Electron spin resonance spectroscopy is a well-established spectroscopy,¹⁹ which provides information about interactions among unpaired electrons, couplings between unpaired electrons and magnetic nuclei, interactions between unpaired electrons and a magnetic field, and spin-orbital couplings. The progression from theory to parameter evaluation can be summarized in Fig.(2-1).

From Fig.(2-1), it can be seen that the fundamental ESR spectral theory begins with the proposition of a **spin Hamiltonian**. What is the spin Hamiltonian? The spin Hamiltonian, like the Hückel Hamiltonian in π -electron theory, AM1 Hamiltonian in valence-electron theory, and the ligand-field Hamiltonian in coordination chemistry, is an example of so-called model or effective Hamiltonians, most of which were first proposed phenomenologically. The aim of using the spin Hamiltonian is to simplify the ESR spectral analysis, i.e., to extract information from the ESR spectra to the least number of parameters like g and a (spin-nuclear coupling constant). In some sense, it is not very different from using polynomials to fit curves in mathematics where mathematical

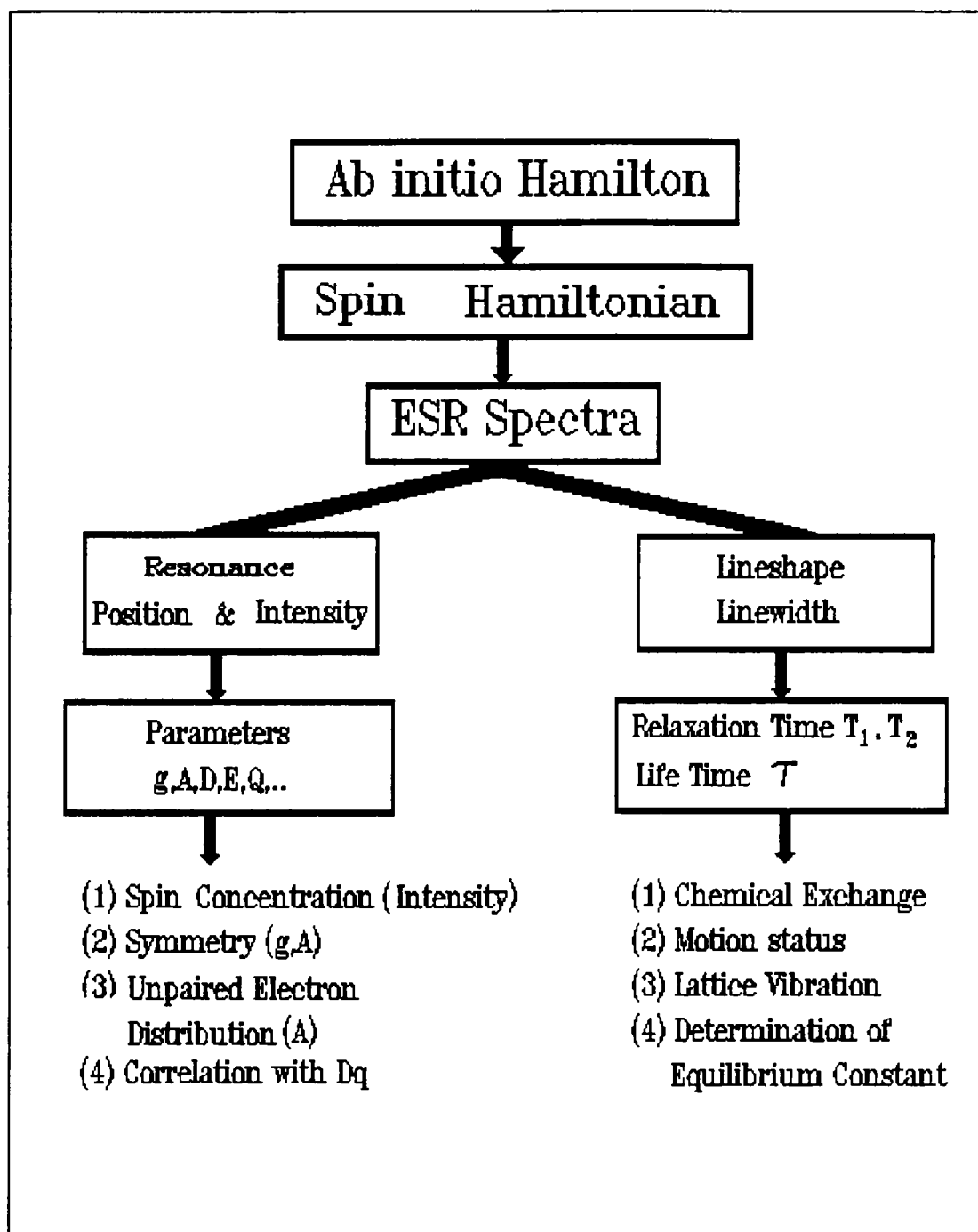


Fig.(2-1). Flow chart of ESR studies.

information hidden in the curve is transferred into coefficients of the polynomials. These parameters (g and a) play a similar role in the spin Hamiltonian as α and β do in the Hückel Hamiltonian which are used to interpret electronic spectra of conjugated organic compounds. The only difference in form between the spin Hamiltonian and the Hückel Hamiltonian is the domain of the energy spectra probed as shown in Fig 2-2. We now consider how the **spin Hamiltonian** can be derived from the ab initio Hamiltonian of the system.

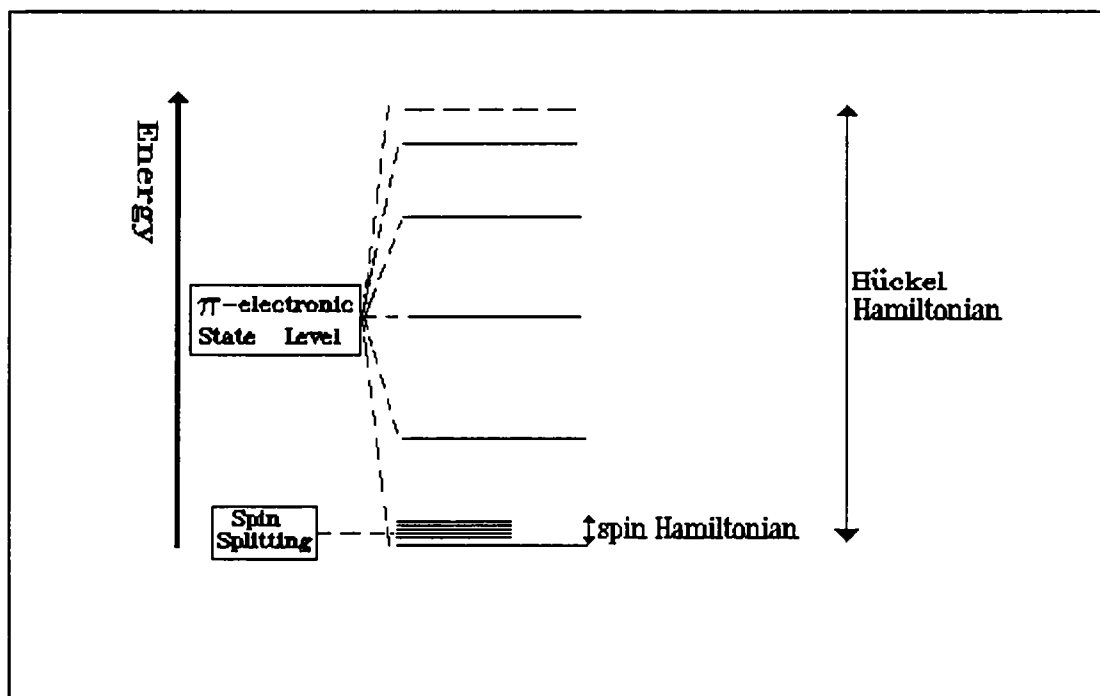


Fig.(2-2). Different spectral domains of interest for Hückel Hamiltonian and spin Hamiltonian.

In general, the derivation methods can be divided into two groups: (1) by symmetry arguments;²⁰ (2) by perturbation calculations.^{20b} Koster and Statz pioneered the former method,²¹ while the latter method was first employed by Pryce and Abragam,²² and is discussed in several text books.^{19c, 19d, 19e}

Recently some different perturbation schemes have been proposed to derive the spin Hamiltonian. Notably, Slichter used the Van Vleck unitary transformation method in his classical book.²³ The essence of this method is to provide a new eigen-basis which can decouple the spectral domain of interest from the rest of the system. The effective or model Hamiltonian theory has been employed by Stevens in his very general derivation of the spin Hamiltonian describing spin-spin exchange interactions in the solid state physics.²⁴ The highlight of this method is its generality and systematic character. However, the derivation was formulated in the second quantization representation, making it difficult to understand. The aim of the first part of this chapter is to derive the spin Hamiltonian used later in this dissertation via the Stevens method, but to formulate the derivation in the Schrödinger representation. While the final results are the same as those given in standard books,¹⁹ the derivation methods employed are different.

The second part of this chapter is devoted to the theory of ESR lineshapes. The fundamental theory is well established,^{19d,25} and will not be repeated in detail in this dissertation. Here, the **Permutation Indices method** proposed by Kaplan and Fraenkel²⁶ for dynamic NMR problems is generalized to evaluate exchange terms in dynamic ESR problems.

Part I. Theory of Spin Hamiltonian

In this part, the general model or effective Hamiltonian theory²⁷ is used to derive the spin Hamiltonian. The general theory is reviewed briefly in section A , followed by its application to the Spin Hamiltonian derivation in Section B. Finally, the physical and chemical interpretations of parameters introduced in Spin Hamiltonian are discussed.

Section A. General Effective Hamiltonian Theory²⁷

Suppose a Hamiltonian of a system has the following structure :

$$H=H_0+V\cdots\cdots\cdots(2.1a-1)$$

where H_0 is the zeroth-order Hamiltonian and V is a perturbation. We shall leave the definition of H_0 and V open for the moment, and assume only that they are Hermitian operators. H_0 has a complete set of eigenfunctions and corresponding real eigenvalues.

$$H_0|n\rangle_0=E_n^0|n\rangle_0\cdots\cdots\cdots(2.1a-2)$$

We are concerned with the solution of the stationary Schrödinger equation,

$$H|\psi_n\rangle=E_n|\psi_n\rangle\cdots\cdots\cdots(2.1a-3)$$

inside a certain vectorial space with d-dimensions, which is

in our spectroscopy observation domain. Only a few energy levels and eigenvectors of H are of interest, for instance valence orbital energies. A common practice in such cases is to introduce an effective Hamiltonian H_{eff} , which operates only inside a small designed vectorial space manifold, whose dimension d is equal to the number of the energy levels we are interested in. This manifold is called the model space. The concept of the effective Hamiltonian is illustrated diagrammatically in Fig.(2.1a-1).

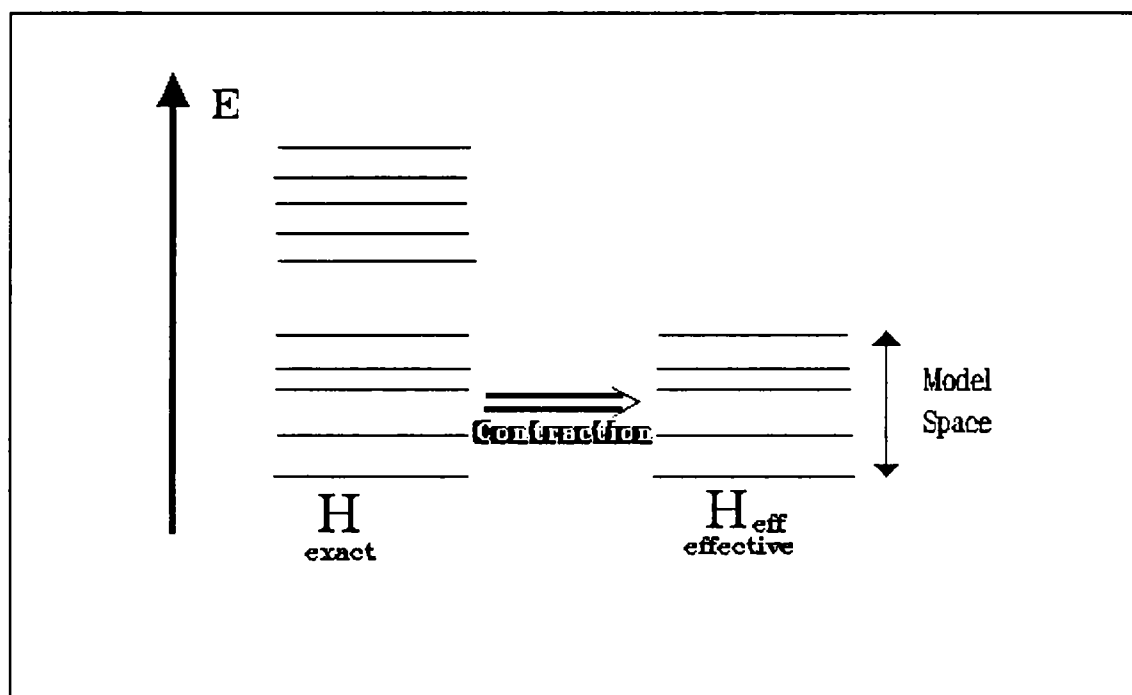


Fig.(2.1a-1). Exact and effective Hamiltonian.

The exact eigenvalues of the actual Hamiltonian and those of the effective Hamiltonian H_{eff} coincide within a subset of the entire spectrum of H . The eigenvectors of H_{eff} are denoted by $|\Psi_n^0\rangle$, which is the projection of $|\Psi_n\rangle$ to the model space. There is a one-to-one correspondence between the

exact solutions $|\Psi_n\rangle$ in the actual space and the approximate solutions $|\Psi_n^0\rangle$ in the model space by means of the so-called wave operator Ω :

$$|\Psi_n\rangle = \Omega |\Psi_n^0\rangle \quad \text{..... (2.1a-4) .}$$

We introduce a projection operator associated with the model function,

$$P = \sum_{n=1}^{n=d} |\Psi_n^0\rangle \langle \Psi_n^0| \quad \text{..... (2.1a-5) .}$$

The corresponding projection operator for the complementary part of the formulated space, called the orthogonal space or the Q space, is

$$Q = 1 - P = \sum_{m \neq (1, \dots, d)} |\Psi_m^0\rangle \langle \Psi_m^0| \quad \text{..... (2.1a-6) .}$$

The model functions are normally nonorthogonal, since they are projections of orthogonal functions on a smaller space. Nevertheless, we can always find "dual" functions $|\Psi_n'^0\rangle$ in the model space, satisfying the "biorthogonality condition"^{28,27b,27a}

$$\langle \Psi_n'^0 | \Psi_l^0 \rangle = \delta(n, l) \quad \text{..... (2.2a-7) .}$$

We can then rewrite the projection operator for the model space as

$$P = \sum_{n=1}^d |\Psi_n^0\rangle \langle \Psi_n'^0| \quad \text{..... (2.1a-8) .}$$

The operator P evidently destroys any functions in the Q

space, and leaves all functions in P space unaffected. If the so-called "intermediate normalization"^{27a} is used, one can obtain

$$|\psi_n^0\rangle = P|\psi_n\rangle \dots\dots\dots (2.1a-9)$$

This is just the reverse of Eq.(2.1a-4). The properties of P and Ω are shown in Fig.(2.1a-2).

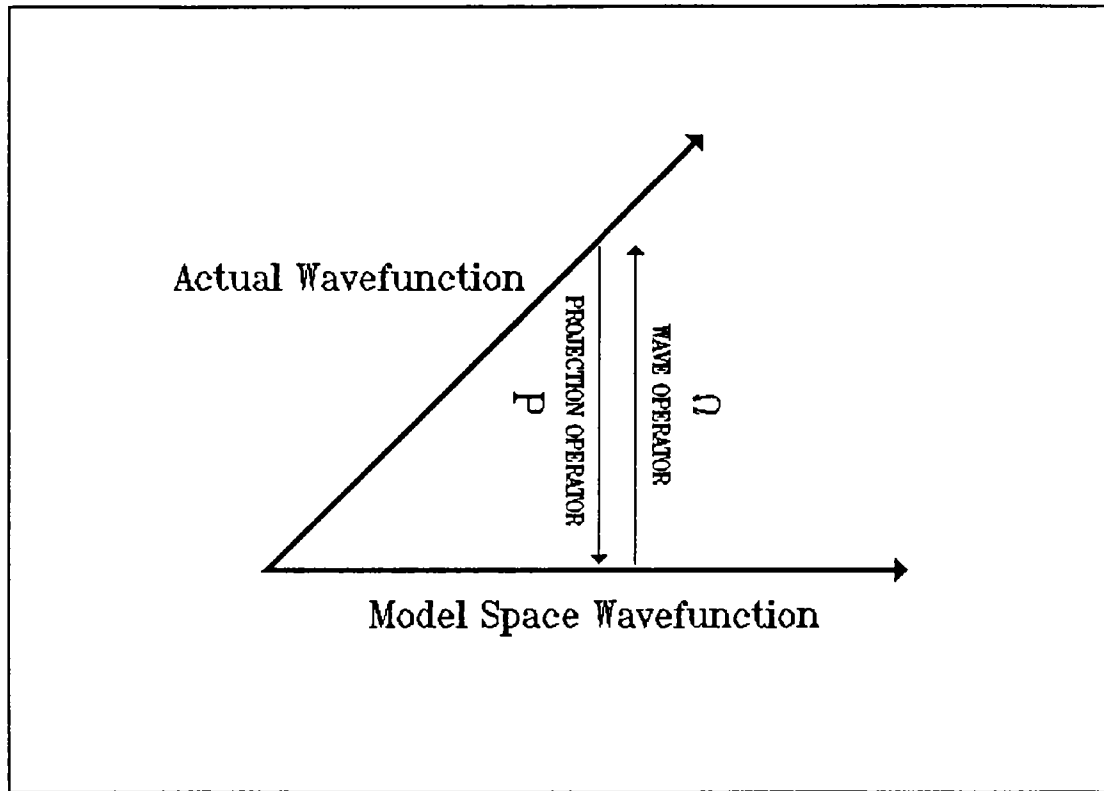


Fig.(2.1a-2). Properties of Ω and P.

Substitution of Eq.(2.1a-4) to Eq(2.1a-3) yields,

$$H\Omega|\psi_n^0\rangle = E_n|\psi_n\rangle \dots\dots\dots (2.1a-10)$$

where $n=1, \dots, d$. Multiplying both sides of Eq.(2.1a-10) with P gives

$$PH\Omega|\psi_n^0\rangle = E_nP|\psi_n\rangle \dots\dots\dots (2.1a-11)$$

Using Eq.(2.1a-9), the above equation can be reduced to:

$$PH\Omega|\psi_n^0\rangle=E_n|\psi_n^0\rangle\cdots\cdots\cdots(2.1a-12)$$

By definition, we have:

$$H_{eff}|\psi_n^0\rangle=E_n|\psi_n^0\rangle\cdots\cdots\cdots(2.1a-13)$$

By comparison between Eq.(2.1a-12) and Eq.(2.1a-13), the following key operator equation of this section can be deduced.

$$H_{eff}=PH\Omega\cdots\cdots\cdots(2.1a-14)$$

It can be seen clearly from Eq(2.1a-12) and Eq.(2.1a-13) that although H_{eff} only operates in the model space, it has the same eigenvalues as H in the corresponding actual space. As mentioned before that since $|\psi_n^0\rangle$'s are normally not orthogonal, H_{eff} is not Hermitian. It is very inconvenient to use non-hermitian operators which sometimes produce imaginary eigenvalues. The following recipe can be used to transform the above effective Hamiltonian to a Hermitian operator.²⁹

As

$$\langle\psi_i|\psi_j\rangle=\langle\psi_i^0|\Omega^+\Omega|\psi_j^0\rangle=N_{ii}\delta_{ij}\cdots\cdots\cdots(2.1a-15)$$

where N_{ii} is a normalization constant, the orthogonality feature of the above equation enables us to construct an orthonormal basis,^{27a,27c,29}

$$|\Phi_n\rangle=(\Omega^+\Omega)^{-\frac{1}{2}}|\psi_n^0\rangle N_{n,n}^{-\frac{1}{2}}\cdots\cdots(2.1a-16).$$

The effective Hamiltonian in this new basis is:

$$\tilde{H}_{eff} = (\Omega^\dagger \Omega)^{\frac{1}{2}} H_{eff} (\Omega^\dagger \Omega)^{-\frac{1}{2}} \quad \text{..... (2.1a-17) .}$$

Since the new basis is orthonormal, H_{eff} is Hermitian. The only unknown in Eq.(2.1a-17) is the wave operator Ω . This wave operator can be obtained by the solution of a nonlinear integral equation^{27a,27b,30}, which is omitted in this dissertation due to the mathematical complexity involved. The detailed solution can be found in the literature.^{27a,27b,30} Then, the following effective Hamiltonian can be obtained based on the perturbation solution of the nonlinear integral equation involving the wave operator:

$$\begin{aligned} \tilde{H}^{(0)} &= PH_0P, \\ \tilde{H}^{(1)} &= PVP, \\ \tilde{H}^{(2)} &= PVSVP, \\ \tilde{H}^{(3)} &= P[VSVSV - \frac{1}{2} (VS^2VPV + VPVS^2V)] P, \\ &\vdots \end{aligned} \quad \text{(2.1a-18)}$$

where

$$S = \frac{(I-P)}{(E^0 - H^0)} \quad \text{..... (2.1a-19) .}$$

The total Hermitian effective Hamiltonian is

$$\tilde{H}_{eff} = \sum_p \tilde{H}^{(p)} \quad \text{..... (2.1a-20) .}$$

Section B. Derivation of the Spin Hamiltonian

The basic Hamiltonian of a paramagnetic species in a

magnetic field can be generally decomposed as follows :¹⁹

$$H = H_0 + V \quad \text{..... (2.1b-1)}$$

$$H_0 = \text{All non-magnetic interactions} \quad \text{..... (2.1b-2)}$$

$$\begin{aligned} V = & \lambda L \cdot S \quad \text{Spin-orbital Interaction} \\ & + \beta_e (L + g_e S) \cdot H \quad \text{Zeeman Interaction} \\ & + g_N \beta_N I \cdot H \quad \text{Nuclear Zeeman Interaction} \\ & + \left(\frac{8}{3}\right) g_e g_N \beta_e \beta_N \delta(r) I \cdot S \quad \text{Fermi Interaction} \\ & + S \cdot D \cdots S \quad \text{Electron Dipole-dipole Interaction} \\ & + I \cdot A \cdots S \quad \text{Electron-nuclear Dipole-Dipole Interaction} \\ & \text{..... (2.1b-3)} \end{aligned}$$

where A'' and D'' are :

$$A'' = - (g \beta g_N \beta_N) \begin{bmatrix} \frac{r^2 - 3x^2}{r^5} & \frac{-3xy}{r^5} & \frac{-3xz}{r^5} \\ \frac{-3xy}{r^5} & \frac{r^2 - 3y^2}{r^5} & \frac{-3yz}{r^5} \\ \frac{-3xz}{r^5} & \frac{-3yz}{r^5} & \frac{r^2 - 3z^2}{r^5} \end{bmatrix} \quad \text{..... (2.1b-4)}$$

$$D'' = \frac{1}{2} (g^2 \beta^2) \begin{bmatrix} \frac{r^2 - 3x^2}{r^5} & \frac{-3xy}{r^5} & \frac{-3xz}{r^5} \\ \frac{-3xy}{r^5} & \frac{r^2 - 3y^2}{r^5} & \frac{-3yz}{r^5} \\ \frac{-3xz}{r^5} & \frac{-3yz}{r^5} & \frac{r^2 - 3z^2}{r^5} \end{bmatrix} \quad \text{..... (2.1b-5) .}$$

The ground state ($\equiv |0\rangle$) of H_0 is generally non-degenerate. For the ESR experiment, the projection operator of the model space is

$$P = |0\rangle P_S P_I \langle 0| \quad \text{..... (2.1b-6)}$$

where

$$P_S = \sum_{\substack{m_s=S \\ m_s=-S}}^{m_s=S} |m_s\rangle\langle m_s| = 1 \quad \dots (2.1b-7)$$

$$P_I = \sum_{\substack{m_I=I \\ m_I=-I}}^{m_I=I} |m_I\rangle\langle m_I| = 1 \quad \dots (2.1b-8)$$

Based on Eq.(2.1a-18), the second-order effective Hamiltonian of the system is

$$\tilde{H}_{eff} = \langle 0|V|0\rangle P_S P_I - \sum_{n \neq 0} \frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_n^0 - E_0^0} P_S P_I \quad (2.1b-9)$$

Using Eq.(2.1b-7) and (2.1b-8), the above equation is reduced to

$$\tilde{H}_{eff} = \langle 0|V|0\rangle - \sum_{n \neq 0} \frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_n^0 - E_0^0} \quad (2.1b-10)$$

As the ground state $|0\rangle$ is orbitally nondegenerate,

$$\langle 0|L|0\rangle = 0 \quad \dots (2.1b-11)$$

Hence the first term of Eq.(2.1b-10) gives

$$\begin{aligned} \langle 0|V|0\rangle &= g_e \beta_e S \cdot H + (g_N \beta_N) I \cdot H \\ &+ \left(\frac{8}{3}\right) g_e g_N \beta_e \beta_N \langle 0|\delta(r)|0\rangle I \cdot S + S \cdot D \cdot S \\ &+ I \cdot A \cdot S \quad \dots (2.1b-12) \end{aligned}$$

where

$$A = - (g_e \beta_e g_N \beta_N) \begin{bmatrix} \langle \frac{r^2 - 3x^2}{r^5} \rangle & \langle \frac{-3xy}{r^5} \rangle & \langle \frac{-3xz}{r^5} \rangle \\ \langle \frac{-3xy}{r^5} \rangle & \langle \frac{r^2 - 3y^2}{r^5} \rangle & \langle \frac{-3yz}{r^5} \rangle \\ \langle \frac{-3xz}{r^5} \rangle & \langle \frac{-3yz}{r^5} \rangle & \langle \frac{r^2 - 3z^2}{r^5} \rangle \end{bmatrix} \quad \dots (2.1b-13)$$

$$D' = \frac{1}{2} (g_e^2 \beta_e^2) \begin{bmatrix} \langle \frac{r^2 - 3x^2}{r^5} \rangle & \langle \frac{-3xy}{r^5} \rangle & \langle \frac{-3xz}{r^5} \rangle \\ \langle \frac{-3xy}{r^5} \rangle & \langle \frac{r^2 - 3y^2}{r^5} \rangle & \langle \frac{-3yz}{r^5} \rangle \\ \langle \frac{-3xz}{r^5} \rangle & \langle \frac{-3yz}{r^5} \rangle & \langle \frac{r^2 - 3z^2}{r^5} \rangle \end{bmatrix} \quad \dots (2.1b-14).$$

If the orbital interaction part of V, which has no contributions in the first term (first-order perturbation) of Eq.(2.1b-10), dominates in the second term (second-order perturbation) of Eq.(2.1b-10), then

$$\frac{\langle 0|V|n\rangle\langle n|V|0\rangle}{E_n^0 - E_0^0} \sim (\beta_e H + \lambda S)^T \cdot \left(\sum_{n \neq 0} \frac{\langle 0|L|n\rangle\langle n|L|0\rangle^T}{E_n^0 - E_0^0} \right) \cdot (\beta_e H + \lambda S) \quad \dots (2.1b-15).$$

Noting that

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} (x, y, z) = \begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix} \quad \dots (2.1b-16),$$

the middle part of Eq.(2.1b-15) can be written in the form of a matrix or the second-rank tensor:

$$\sum_{n \neq 0} \frac{\langle 0|L|n\rangle\langle n|L|0\rangle^T}{E_n^0 - E_0^0} = \begin{bmatrix} \Lambda_{xx} & \Lambda_{xy} & \Lambda_{xz} \\ \Lambda_{yx} & \Lambda_{yy} & \Lambda_{yz} \\ \Lambda_{zx} & \Lambda_{zy} & \Lambda_{zz} \end{bmatrix} = \Lambda \quad \dots (2.1b-17).$$

The ij th element of the tensor Λ is given by

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n^0 - E_0^0} \quad \dots (2.1b-18)$$

where L_i and L_j are orbital angular momentum operators

appropriate to the x,y, or z directions. Substitution of Eq.(2.1b-17) into Eq.(2.1b-15) yields

$$\text{Second term of Eq. (2.1b-10)} \approx -(\beta_e^2 H \cdot \Lambda \cdot H + 2\lambda \beta_e H \cdot \Lambda \cdot S + \lambda^2 S \cdot \Lambda \cdot S) \quad \text{..... (2.1b-19)}$$

The first term of Eq.(2.1b-19) can be neglected because of the independence of spin operators. The combination of Eq.(2.1b-19) with Eq.(2.1b-12) results in the key equation of this section, i.e., the Effective Hamiltonian or Spin Hamiltonian:

$$\begin{aligned} \tilde{H}_{eff} = & \beta_e H \cdot (g_e 1 + 2\lambda \Lambda) \cdot S + \lambda^2 S \cdot \Lambda \cdot S \\ & + \beta_N g_N I \cdot H + \left(\frac{8}{3}\right) g_e g_N \beta_e \beta_N \langle 0 | \delta(r) | 0 \rangle I \cdot S \\ & + S \cdot D' \cdot S + I \cdot A \cdot S \quad \text{..... (2.1b-20)} \\ = & \beta_e H \cdot g \cdot S + S \cdot D \cdot S \\ & + \beta_N g_N I \cdot H + a I \cdot S \\ & + I \cdot A \cdot S \end{aligned}$$

where

$$\begin{aligned} g &= g_e 1 - 2\lambda \Lambda & (2.1b-21) \\ D &= -\lambda^2 \Lambda + D' & (2.1b-22) \\ a &= \left(\frac{8}{3}\right) g_e g_N \beta_e \beta_N \langle 0 | \delta(r) | 0 \rangle & (2.1b-23). \end{aligned}$$

Section C. Meanings of the parameters in Spin Hamiltonian

Compared to the derivation by the symmetry argument, one of the advantages of using the general effective Hamiltonian theory to obtain the spin Hamiltonian is that the parameters introduced have explicit physical meanings attached to them. This makes the extraction of the physical or chemical

information from experimentally measured parameters simple. However, since only values of isotropic g and a parameters are used mainly in this dissertation, the physical meaning of all other parameters will not be discussed.

Based on Eq.(2.1b-21), the isotropic g value is given by:

$$\begin{aligned}
 g &= g_e + \Delta g \\
 &= g_e + \left(\frac{\Delta g_{xx} + \Delta g_{yy} + \Delta g_{zz}}{3} \right) \\
 &= g_e - \left(\frac{2}{3} \right) \lambda \sum_{n \neq 0} \sum_{i=x,y,z} \frac{\langle 0 | L_i | n \rangle \langle n | L_i | 0 \rangle}{E_n^0 - E_0^0} \quad \text{..... (2.1c-1)}
 \end{aligned}$$

The absolute deviation of the g value from that of the free electron g_e is governed by three factors, namely, the numerator $|\langle 0 | L_i | n \rangle|^2$, the denominator $(E_n^0 - E_0^0)$, and λ .

The numerator, which is similar in structure to the transition matrix in spectroscopy, is closely related to the symmetry properties of both the ground state $|0\rangle$ and the excited state $|n\rangle$, always has a positive value, and relates to couplings between the ground state and excited states induced by spin-orbital interaction.

The denominator, which is equal to the energy difference between the excited state $|n\rangle$ and the ground state $|0\rangle$, is also a positive quantity. As this energy difference becomes smaller, the contribution of the excited state $|n\rangle$ to Δg gets greater.

The sign of Δg is determined by that of λ . The sign of λ is dependent on the nature of the transition that intermixes the ground molecular-orbital state $|0\rangle$ with the

excited molecular-orbital state $|n\rangle$. Any transition that removes the single unpaired electron of a radical from its ground-state orbital must transfer it to an unoccupied orbital because all other occupied orbitals have electron pairs. In this case, λ is taken to be positive. The most common transition of this type is to an antibonding molecular orbital. If the induced mixing of the ground state $|0\rangle$ with an excited state $|n\rangle$ involves a transfer of an electron from one of the subjacent occupied orbitals into the SOMO, the associated λ is taken to be negative. In a sense, the sign of Δg is to a first approximation governed by the relative magnitudes ΔE_1^0 and ΔE_2^0 if the corresponding numerators are approximately equal. This implies that the sign of Δg can be used to probe the gaps to the LUMO and HOMO from SOMO, as shown in Fig.(2.1c-1). The magnitude of the spin-orbital coupling constant λ is directly proportional to the fourth power of the nuclear charge, Z , which implies that Δg is very small for atoms having a small Z , e.g., carbon.

The isotropic coupling constant a is given by

$$a = \left(\frac{8}{3}\right) g_e g_N \beta_e \beta_N \langle 0 | \delta(r) | 0 \rangle \quad \dots (2.1c-2)$$

where $\langle 0 | \delta(r) | 0 \rangle$ is just the electron probability density of the ground state at the nucleus. Since only the s-atomic orbital has a non zero value at the nucleus, the magnitude of the coupling constant a of a nucleus is proportional to the population of its s atomic orbital in SOMO. Usually, there

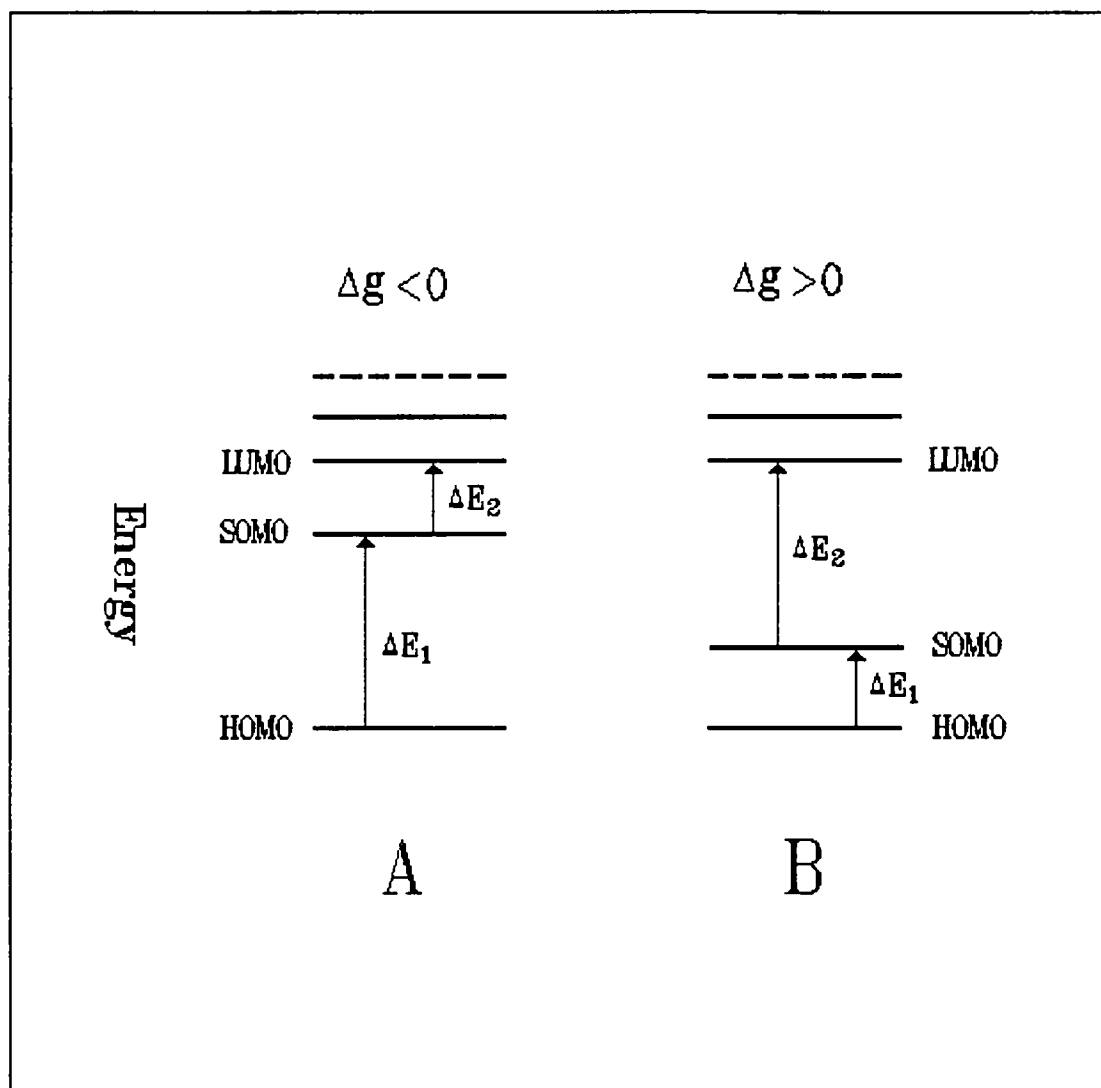


Fig.(2.1c-1). Sign of Δg . Case A: $\Delta g < 0$; Case B: $\Delta g > 0$.

are two mechanisms, polarization and hyperconjugation, which can induce spin in s-orbital or s-component in SOMO. Isotropic couplings to α -hydrogens are largely induced by the former mechanism, while the latter mechanism is the predominant mechanism to induce isotropic couplings to β -hydrogens. Isotropic couplings to β -hydrogens are closely related to radical geometries through the Heller-McConnell equation:¹⁹

$$a_{\beta} = (B_1 + B_2 \cos^2 \theta) \rho_{\pi} \quad \text{..... (2.1c-3)}$$

where B_1 is a constant arising possibly from spin polarization contribution and $B_2 \cos(\theta)$ is the angular dependent hyperconjugative contribution. The proofs of Eq.(2.1c-3) and other rules concerning the spin-distribution are given in Appendix 1.

Part II. Theory of Lineshape

In ESR experiments, detected signals are proportional to the imaginary part of the total complex transverse magnetization, with an absorption lineshape given by:^{19d,25a,25c}

$$\begin{aligned} A(\omega) &= \text{Im}[\text{Trace}(\rho(S_x + iS_y))] \\ &= \text{Im}[\text{Trace}(\rho S_+)] \end{aligned} \quad (2.2-1)$$

where ρ is a so-called spin density operator. It is clear from the above equation that we need to calculate the density matrix elements of ρ in order to calculate ESR lineshapes. In section A, the basic density matrix theory is briefly reviewed, and this is followed by the derivation of the equation of motion for a radical spin density operator in the absence of chemical exchange. The equation of motion under the influence of exchange is derived in section B. In section C, the **Permutation Indices** method developed for NMR chemical exchange problems by Kaplan and Fraenkel is generalized to evaluate explicitly chemical exchange terms in ESR density matrix motion equations.

Section A. Basic Theory of the Density Matrix^{19d,25a,25c,23,31}

The density operator is defined as follows:

$$\rho = \sum_{\Psi} P_{\Psi} |\Psi\rangle \langle \Psi| \quad \dots\dots (2.2a-1).$$

Here the summation can be discrete or continuous, and P_{Ψ} is the fraction of systems corresponding to the state vector $|\Psi\rangle$.

For state vectors of the form

$$|\Psi\rangle = \sum_n c_n^{\Psi} |n\rangle \dots\dots\dots (2.2a-2)$$

Eq.(2.2a-1) reduces to

$$\rho = \sum_{\Psi} P_{\Psi} \sum_n \sum_m c_n^{\Psi} c_m^{\Psi*} |n\rangle \langle m|, \quad \dots\dots (2.2a-3)$$

where $|n\rangle$ is a certain basis set. The matrix elements of ρ can be defined as follows:

$$\rho_{nm} = \sum_{\Psi} P_{\Psi} c_n^{\Psi} c_m^{\Psi*} |n\rangle \langle m| \dots\dots\dots (2.2a-4).$$

This is called the ensemble average in statistical mechanics.

Then

$$\rho = \sum_{nm} \rho_{nm} |n\rangle \langle m| \dots\dots\dots (2.2a-5)$$

The equation of motion of the density operator (and hence that of the matrix elements) is readily determined from the

Schrödinger equation:

$$\begin{aligned}\dot{\rho} &= \frac{\partial \rho}{\partial t} = \sum_{\Psi} P_{\Psi} \{ |\Psi\rangle\langle\Psi| + |\Psi\rangle\langle\Psi| \} \\ &= -\frac{2\pi i}{h} \sum_{\Psi} P_{\Psi} \{ H|\Psi\rangle\langle\Psi| - |\Psi\rangle\langle\Psi|H \} \\ &= -\frac{2\pi i}{h} [H, \rho] \dots\dots\dots (2.2a-6)\end{aligned}$$

where the commutator

$$[H, \rho] = H\rho - \rho H \dots\dots\dots (2.2a-7) .$$

The ijth density matrix element ρ_{ij} is

$$\begin{aligned}\dot{\rho}_{ij} &= -\frac{2\pi i}{h} \langle i | H\rho - \rho H | j \rangle \\ &= -\frac{2\pi i}{h} \sum_k \{ H_{ik}\rho_{kj} - \rho_{ik}H_{kj} \} \dots\dots\dots (2.2a-8) .\end{aligned}$$

Section B. Equation of Motion Under Chemical Exchange^{19d,25a,26,32}

The above equation (2.2a-8) describes only the equation of motion for the radical spin density operator without chemical exchange. In this section, the general motion equation of the density matrix under the influence of chemical exchange is derived.

Let

$P(t)$ = the probability that a molecule survives a time t without undergoing a chemical exchange.

Since a molecule has no chance of exchange in a time $t \rightarrow 0$, $P(0) = 1$. This is the so-called initial condition, which will later be used to integrate the differential equation. Let τ be the lifetime of the radical under a chemical exchange. Then :

$k dt = (1/\tau) dt$ = the probability that a molecule undergoes a chemical exchange between t and $t + dt$.

The quantity k is thus the probability per unit time that a radical undergoes an exchange, and is nothing but a first-order rate constant. We assume that k is independent of time. Knowing the rate constant for exchange, it is possible to calculate the survival probability $P(t)$. This is done by noting that the probability that a molecule survives a time $t + dt$ without exchange must be equal to the probability that this radical survives a time t without exchange multiplied by

the probability that it does not undergo an exchange in the subsequent time interval t and $t+dt$. This statement is equivalent to the following mathematical equation:

$$P(t+dt) = P(t) \left(1 - \frac{1}{\tau} dt\right) \dots\dots\dots (2.2b-1) .$$

Hence

$$P(t) + \frac{dP(t)}{dt} dt = P(t) - \frac{P(t)}{\tau} dt \dots\dots\dots (2.2b-2)$$

or

$$\frac{1}{P(t)} \frac{dP(t)}{dt} = -\frac{1}{\tau} \dots\dots\dots (2.2b-3) .$$

By noting the initial condition mentioned above, the integration of eq (2.2b-3) yields

$$P(t) = e^{-\frac{t}{\tau}} \dots\dots\dots (2.2b-4) ,$$

which is the well-known relaxation equation for a first-order process. Multiplication of $P(t)$ by $1/\tau$ gives

$e^{-t/\tau} dt/\tau$ = the probability that a radical, after surviving without exchanges for a time t , undergoes an exchange in the time interval between t and $t+dt$.

Therefore, the average spin density operator of a radical i under the influence of exchange is,

$$\langle \rho^i \rangle = \frac{1}{\tau_i} \int_0^\infty \rho^i(t, t_0) e^{-\frac{\theta}{\tau_i}} d\theta \dots\dots\dots (b-5)$$

where $\theta = t - t_0$, and $\rho(t, t_0)$ is the solution of eq(2.2a-8). By direct differentiation of Eq.(2.2b-5) one obtains³³

$$\begin{aligned} \frac{d\langle \rho^i \rangle_{av}}{dt} &= \frac{1}{\tau_i} \int_0^\infty \left(\frac{\partial \rho^i(t, t-\theta)}{\partial t} \right)_{t-\theta} e^{-\frac{\theta}{\tau_i}} d\theta \\ &- \frac{1}{\tau_i} \int_0^\infty \left(\frac{\partial \rho^i(t, t-\theta)}{\partial \theta} \right)_{t-\theta} e^{-\frac{\theta}{\tau_i}} d\theta \dots\dots\dots (2.2b-6) . \end{aligned}$$

The first term on the right is simply an average over the side of Eq.(2.2a-8), and the second term can be integrated by parts. Thus,

$$\begin{aligned} \frac{d\langle \rho^i(t) \rangle_{av}}{dt} &= \frac{2\pi i}{h} [\langle \rho^i(t) \rangle_{av}, H^i] + \frac{\rho^i(t_0, t_0) - \langle \rho^i(t) \rangle_{av}}{\tau_i} \\ &\dots\dots\dots (2.2b-7) . \end{aligned}$$

For the sake of convenience, the average bracket is omitted in the following discussion. If one wants to include other relaxation effects, one can either add the proper terms from Bloch's general master equation^{23,25a} to the above equation or include some suitable phenomenological relaxation terms.

Section C. Evaluation of $\rho^i(t_0, t_0)$

The above Eq. (2.2b-7) is not self-consistent if one does not know $\rho^i(t_0, t_0)$. $\rho^i(t_0, t_0)$ is a density operator just after the formation of radical i from other radicals or chemical species. The Permutation Indices method,²⁶ i.e., the "backward" approach can be employed to evaluate matrix elements of this operator. This method uses the chemical and basis function description of chemical exchange processes, which in a sense attaches chemical meanings to the abstract mathematical permutation transformation. The rationalization of this method can be found in the literature. Although it is developed for NMR exchange problems, it can be naturally "transplanted" into ESR exchange problems virtually without change, except for singling out one nuclear spin basis and relabeling it as an electron spin basis. In this way, all formulas developed for NMR problems can be adopted for analogous ESR problems. This "adoption" is now illustrated by a specific example.

Consider the conformation change:

$$\begin{array}{ccc} A & = & A \\ abc & & acb \\ a'b'c' & = & a'c'b' \end{array} \quad (2.2c-1)$$

where a represents the nuclear spin state not involved in exchange and b and c represent the nuclear spin states

involved in exchange. According to the Permutation Indices method, $\rho^A(t_0, t_0)$ in this basis is

$$\rho_{abc, a'b'c'}^A(t_0, t_0) = \rho_{acb, a'c'b'}^A(t) \quad (2.2c-2).$$

If a is singled out and considered to be an unpaired electron spin state in the radical, Eq(2.2c-2) automatically becomes the exchange term of the corresponding ESR problem. The insertion of Eq.(2.2c-2) into Eq.(2.2b-7) then results in the self-consistent equation of motion for the density operator. A specific example of this exchange process in ESR is shown in Fig.(2.2c-1).

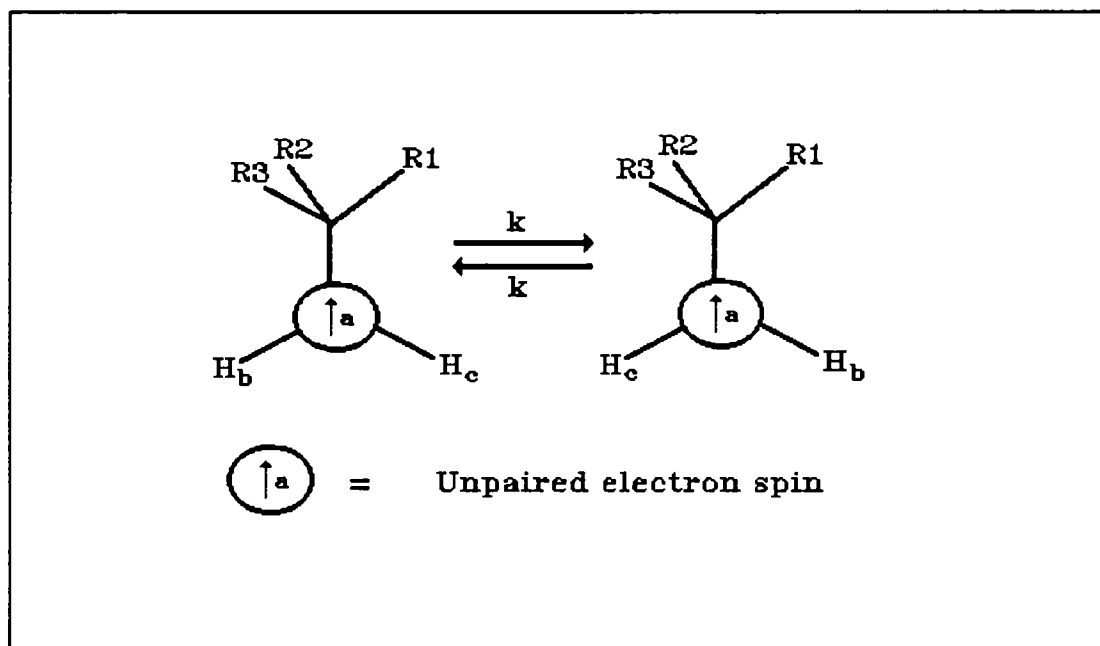


Fig.(2.2c-1). An example of radical chemical exchanges.

Further examples of using this method to evaluate $\rho^i(t_0, t_0)$ will appear later in Chapter 4. The method of solving the motion equation naturally varies with different problems.

Sometimes analytical solutions are available for simple chemical exchange problems. However, only numerical solutions are available for more complicated cases. Excellent discussions about the methods of solution can be found in the literature.^{26,34}

CHAPTER 3

EXPERIMENTAL TECHNIQUES

Part I. Sample Preparations

Section A. ESR Sample Preparation

Fig.(3.1a-1) shows a typical ESR quartz tube used in this work before seal-off at the constriction D(vide infra). It is composed of three parts as seen in Fig.(3.1a-1). The main part is a synthetic quartz(Spectrosil or Suprasil) tube(A), which is connected to a pyrex tube(C) through a graded seal(B). There is a constriction(D) at the top of the graded seal, which makes the tube easy to seal off. The pyrex tube is connected to a ground joint(E) so that the whole tube can be easily connected to the vacuum line. The size of the quartz tube is made to fit our γ -source cavity. There are two reasons to choose the quartz tube instead of the normal pyrex tube. The first is that normal pyrex and quartz tubes can develop some ESR signals after irradiation. The second is that some pyrex tubes have some iron(III) mixed in their

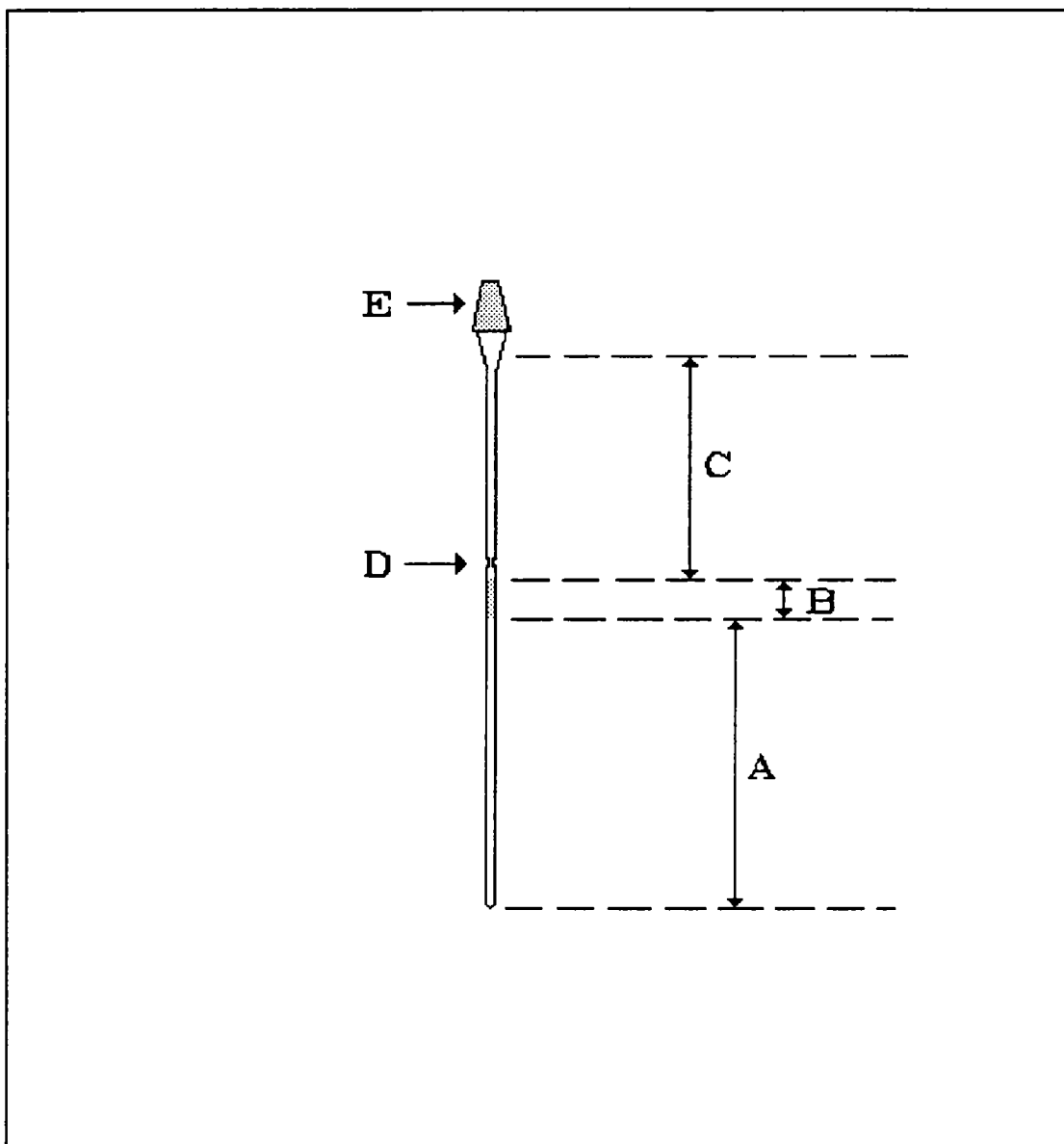


Fig.(3.1a-1). An ESR tube. A, quartz tube; B, graded seal; C, pyrex tube; D, constriction; E, ground glass joint.

composition. As a result, the sample ESR signal would overlap with that of the iron(III), and make the spectral analysis more difficult.

Fig.(3.1a-2) shows the vacuum line used in the ESR sample preparation and synthesis work. It was cleaned every two or three weeks for maintenance.

Before the sample was transferred into the tube, the quartz tube was flamed under vacuum. After it had cooled to room temperature on the vacuum line, it was ready for sample preparation. Normally there were two ways to transfer a solute substrate to the tube according to its physical properties (boiling point, state and air-sensitivity). If the sample was not air-sensitive, the tiny amount(ca. 2-5 mg) of the solute substrate can be readily transferred into the tube by using a spatula for solid samples or a capillary tube made from the standard pipet (Fig.(3.1a-3)) for liquid samples. On the other hand, if the sample was air-sensitive, it was handled by the standard break-seal(Fig.(3.1a-4)) technique. Fig.(3.1a-4) shows the typical break seal used in this work. The sample was transferred to the ESR tube from the break seal by vacuum transfer.

After the solute substrate was introduced into the ESR tube, it was degassed with two freeze-pump-thaw cycles to remove possible residual oxygen in the sample. Then, a Freon solvent was introduced from a glass reservoir by vacuum transfer. The common Freon solvents used in this work were

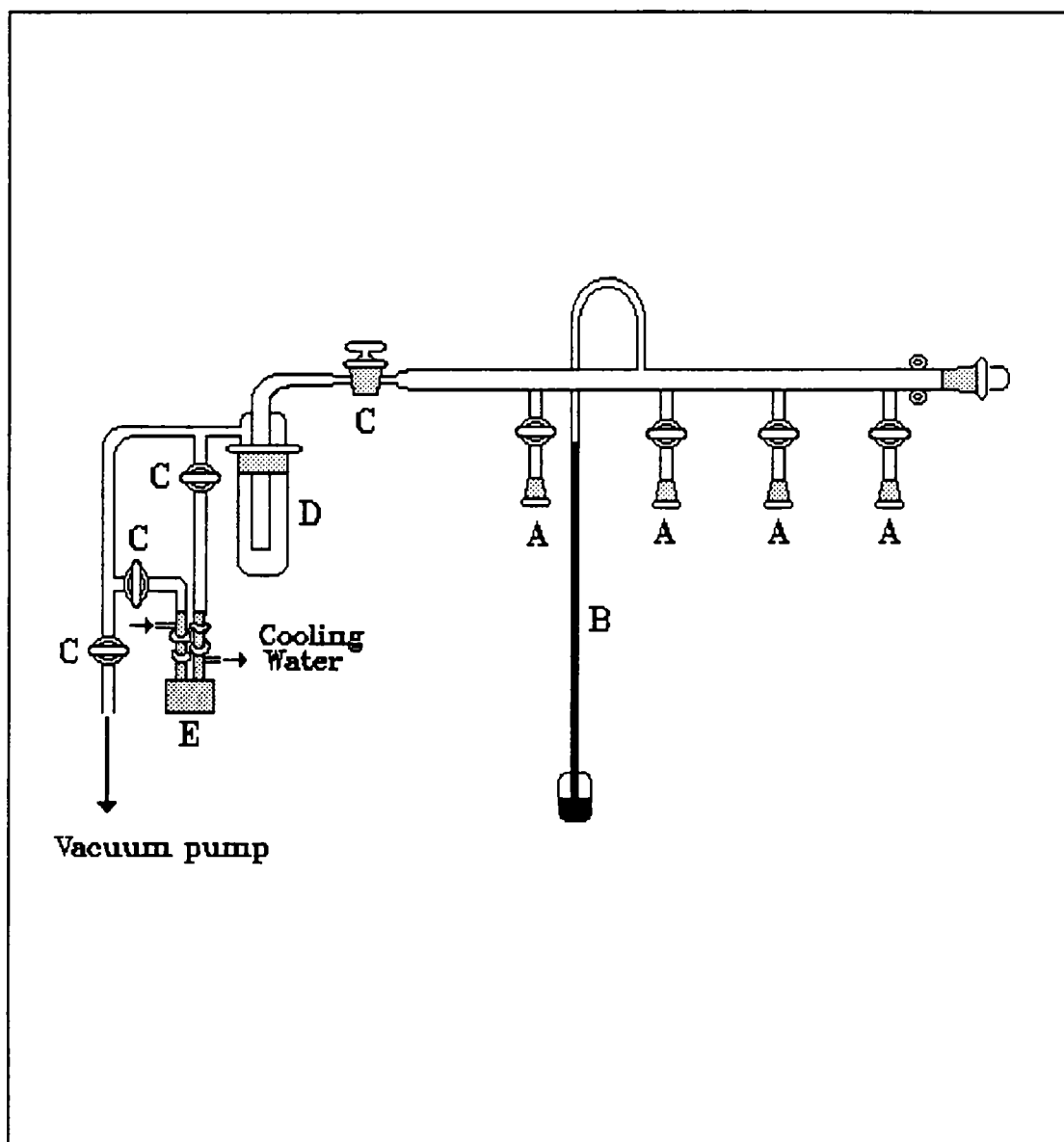


Fig.(3.1a-2). The vacuum line used during the course of these studies. A, ground glass joints with stopcocks to connect ESR tubes; B, Mercury manometer; C, Stopcocks; D, trap; E, oil diffusion pump.

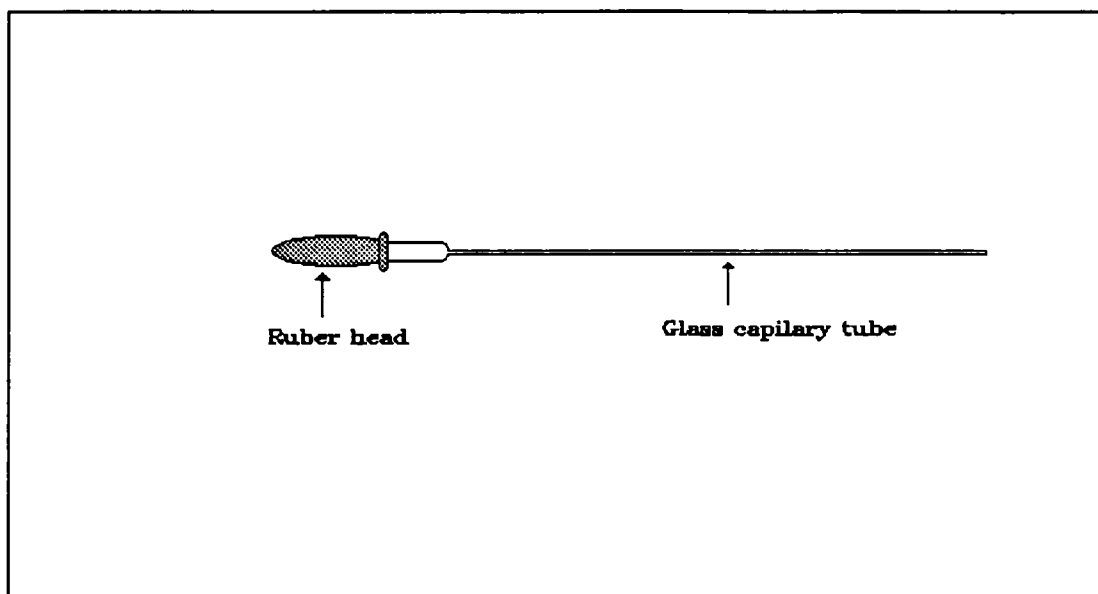


Fig.(3.1a-3). A typical capillary tube used in the sample preparation.

CF_3CCl_3 , CFCl_3 and $\text{CFCl}_2\text{CF}_2\text{Cl}$. The solvent had been previously degassed with similar freeze-pump-thaw cycles. The optimum volume ratio between the solvent and solute was normally around 200:1 but varied with different samples. It was very important to use the optimum ratio since low solute concentrations may only give rise to weak signals whereas high concentrations can result in ESR signals from radical products of ion-molecule reactions.

After the solvent was introduced, the dilute solution was degassed with 3-5 freeze-pump-thaw cycles. Then the ESR tube was cooled with liquid nitrogen and sealed at the constriction (D in Fig.(3.1a-1)) under vacuum. The sealed tube was slowly warmed up to room temperature. The sample preparation was completed by shaking the tube so as to make the solute evenly distributed in the solvent.

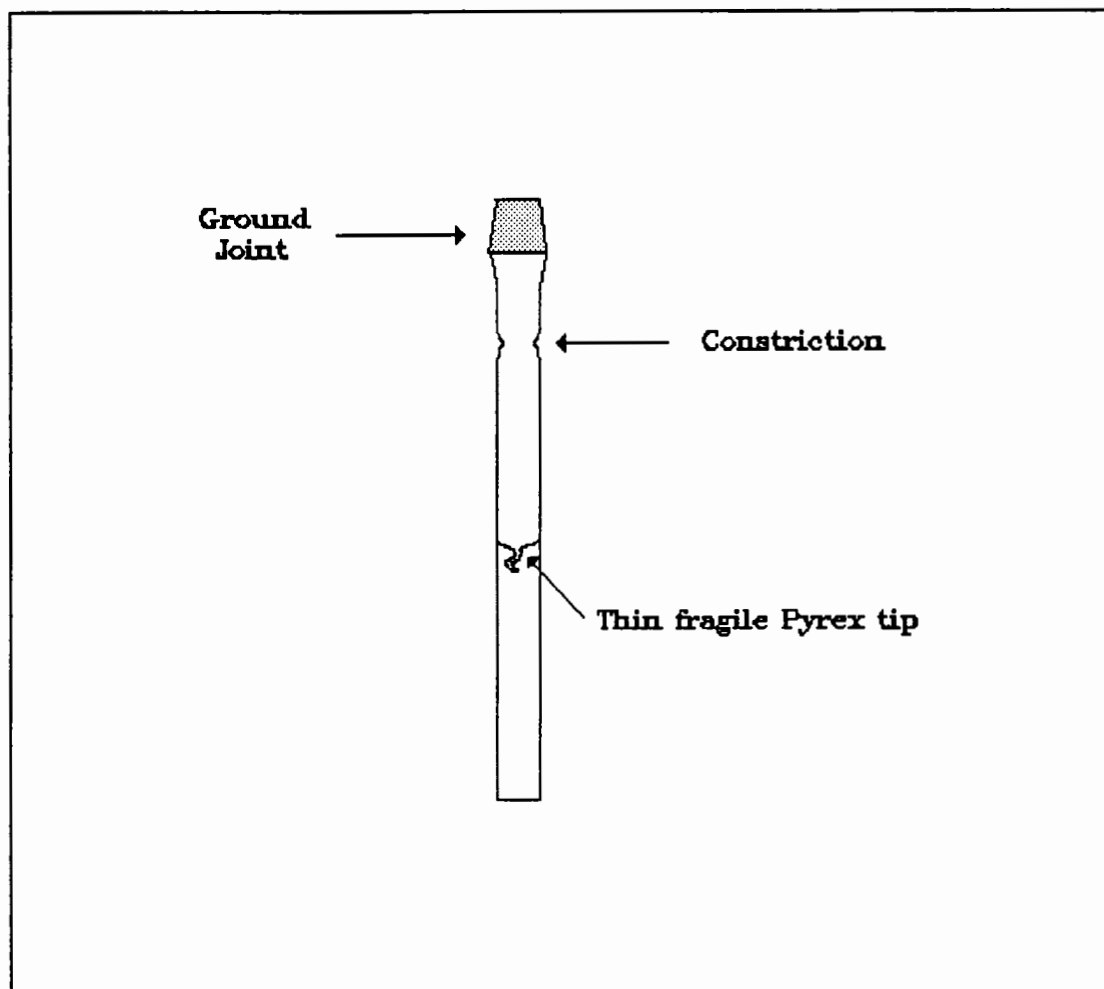


Fig.(3.1a-4). Break seal.

The prepared sample was quickly quenched in liquid nitrogen which was contained in the irradiation dewar. The size of the dewar was made to fit the compartment of the γ -source(Atomic Energy of Canada Ltd.). Then the dewar was carefully put into the γ -source for the irradiation. This γ -source was reloaded on September 14, 1971 and had a certified dose rate of 0.463 Mrad/hr on that date. During the course of this work, the total irradiation dose for a sample was around 0.25 Mrad.

Section B. Sample Preparation for EA Spectra³⁵

A special thin quartz cell used in our optical measurement is shown in Fig.(3.1b-1). The EA sample preparation procedure was the same as that of ESR. However , the volume ratio between the sample and solvent was around 5% which was much higher than that of ESR. A mixture of CFCl_3 and $\text{CF}_2\text{BrCF}_2\text{Br}$ with a 1:1 volume ratio was usually chosen as the solvent since it can form a nice transparent glass at low temperature so as to minimize the light scattering.

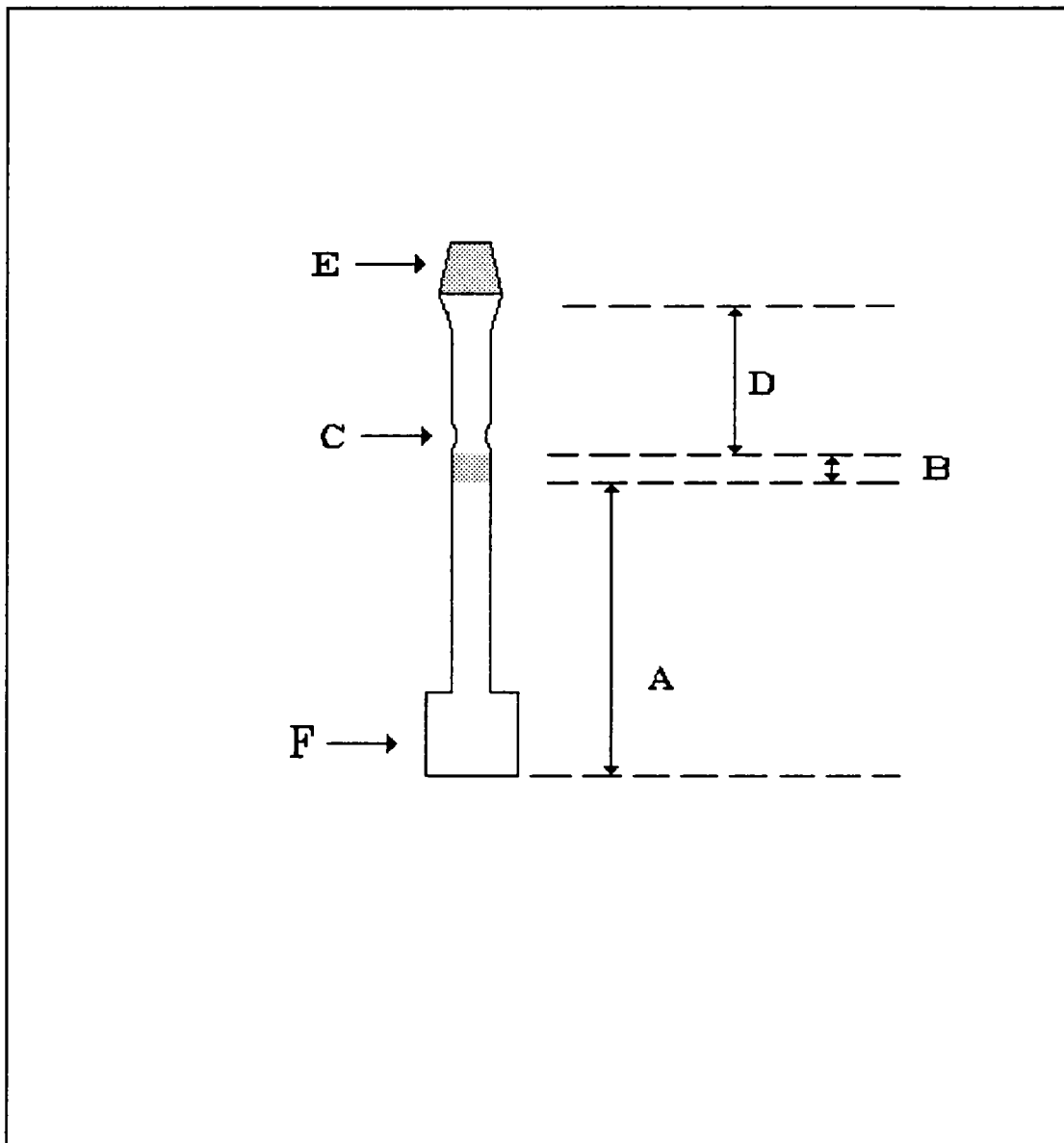


Fig.(3.1b-1). A low-temperature UV cell. A, quartz tube; B, graded seal; C, constriction; D, pyrex tube; E, ground glass joint; F, thin UV quartz cell.

Part II. Spectral Measurements

Section A. ESR measurements

After the prepared ESR sample was γ -irradiated in a dewar containing liquid nitrogen for about six hours, it was ready for ESR measurement. The dewar which contained the ESR sample tube was removed from the γ source. Then the irradiated ESR tube was quickly transferred from the irradiation dewar to an insert dewar within the ESR cavity, which had been cooled to 80 K by a hybrid variable temperature unit constructed previously in this laboratory. The ESR instrument used in this work was a Bruker 200-D spectrometer installed in 1982. Fig.(3.2a-1) shows a block diagram of the whole experimental system.

The sample temperature was slowly increased from 80 K to about 160 K by the temperature variable unit. Spectra were recorded at intervals corresponding to five-degree temperature increases until the matrix softening point when ion-molecule reactions often took place. The matrix softening point was different for each matrix. Table (3.2a-1) tabulates the softening points for the common Freon solvents. If a

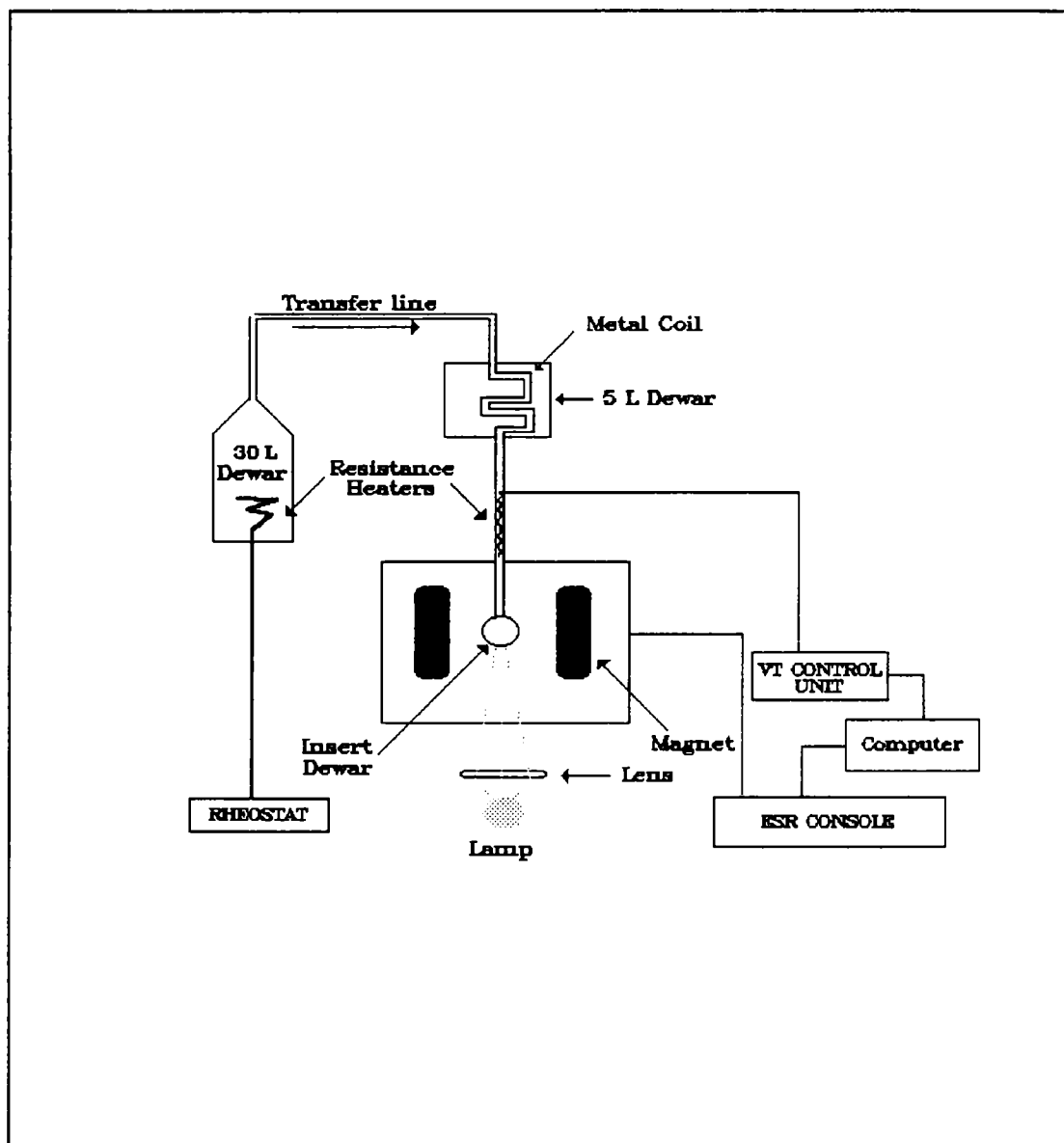


Fig.(3.2a-1). Schematic diagram of the experimental setup.

change occurred in the ESR spectrum during the warm-up process, the sample was cooled back to the previous temperature to see whether the change was reversible. A reversible change is normally attributable to loss of anisotropy induced by molecular motions or to dynamic conformation change in the radical, while the irreversible change indicates that a thermal-induced chemical reaction of the radical has taken place.

Table (3.2a-1). Freon solvents and their softening point at which ion-molecule reactions take place.

Solvent	Softening Point
CFCl_3	~160 K
CF_3CCl_3	~145 K
$\text{CF}_2\text{ClCFCl}_2$	~115 K
$\text{CFCl}_2\text{CFCl}_2$	~140 K
$\text{CF}_2\text{ClCCl}_3$	~160 K

Since the ESR cavity had a removable front cover, the photobleaching experiment can be easily conducted in situ. A UV lamp and a tungsten lamp were employed as the light sources. A pump was used to evacuate the toxic gases produced by the generation of UV light. The light was focused into the ESR cavity with a 15cm-diameter lens through the adjustment of the relative position between the lamp and the lens. The

selective bandwidth photobleaching was achieved by appropriate Corning filters. The sample tube was frequently rotated to ensure an even light exposure.

Section B. Electronic Absorption(EA) Spectral Measurement of Radical Cations at 77 K³⁵

The apparatus for the low temperature EA measurement was constructed previously in this laboratory. Fig.(3.2b-1) and its legend give the details for construction. The dimensions were based on the compartment size of Cary Model 14R or similar spectrometers.

The liquid nitrogen was allowed to fill the dewar(A) through a normal paper filter, which was followed by the insertion of the γ -irradiated sample into the dewar. The whole apparatus was assembled like Fig.(3.2b-1) and was positioned properly in the compartment of the spectrometer. The reason for filtering the liquid nitrogen was to remove ice particles which can cause light scattering and reduce light transmission. The liquid nitrogen bubbling in the dewar can cause noise in EA measurements. Before starting measurements, the apparatus was evacuated by pump from outlet(I) for about 1 minutes. This can efficiently eliminate bubbling of the liquid nitrogen by destroying bubbling centers. Then an appropriate neutral density screen (Cary

Instrument) was chosen to attach to the reference light path to balance the absorption into the right range. The spectrometer was tuned according to the instrument manual. Finally, the spectra were recorded.

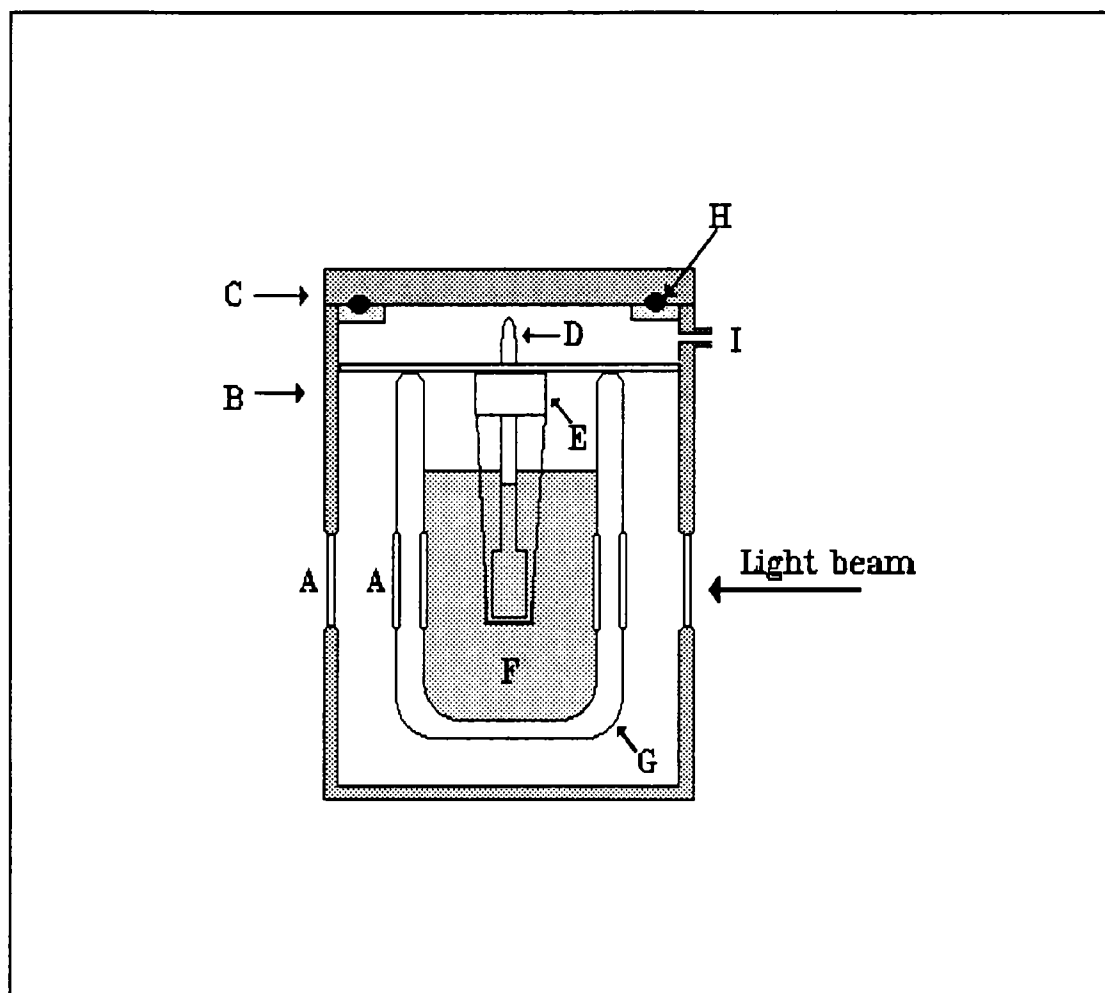


Fig.(3.2b-1). Optical dewar for use at 77 K. A, suprasil windows; B, brass can(vacuum tight); C, removable brass top; D, sample; E, sample holder; F, liquid nitrogen; G, double-walled dewar; H, o-ring seal; I, gas outlet.

Part III. Computer Calculations

Section A. Computer Simulations of ESR Spectra

The static ESR spectral simulation package was developed by the author based on his early work,³⁶ which consisted of the second-order perturbation calculation of the resonance position and the convolution of a Gaussian or Lorentzian lineshape. The largest total multiplicity of nuclear spins, which can be handled by this program, was 220 due to the limitation of the computer memory. Both isotropic and anisotropic ESR spectra can be readily simulated. The package was written in BASIC language, which was compiled by the Microsoft BASIC compiler (Version 1.0) on an IBM-AT computer.

The dynamic ESR spectral simulation programs were written in FORTRAN by the author according to the well-known theory discussed in Chapter 2. The two-site dynamic ESR simulation program was run on IBM-AT, while the electron transfer dynamic lineshape simulation program was run on the mainframe UTK-VAX computer.

Section B. Semiempirical Calculations

The AMPAC program package used in this work was sent to us by Prof. Nelsen. This program was originally developed by Dewar's group^{37a} and modified by Dr. T. Clark^{37b} to include AUHF (Annihilated Unrestricted Hartree-Fock procedure) and NCG (Neutral at Cation Geometry) calculations besides the original commands (e.g. AM1, MNDO, UHF, ...). It was installed on the mainframe VAX by the author to carry out geometry optimization, location of transition states, and predictions of EA transitions. Since the INDO calculation normally gives better unpaired-electron spin distribution than AM1 or other semiempirical methods implemented in AMPAC, a standard version of the INDO program³⁸ was also installed by the author on the VAX computer to carry out a single point calculation of the radical spin distribution using the AMPAC-optimized geometry. The original input format of the QCPE INDO program was modified to be adapted to the output file of AMPAC so that the single point calculation was made very convenient. The optimized geometries were checked by either MM2 or PCMODEL program, which were kindly provided to the author by Prof. Bartmess and Prof. Lane, respectively.

Part IV. Chemicals

The chemicals used in this work are listed in Table (3.4-1) along with their suppliers. 1,6-dideuterio-1,5-hexadiyne, 3,4-dimethylenecyclobutene, 1,2,4,5-hexatetraene, N,N-dideuterio-allylamine and but-3-en-1-ol-d were synthesized in this laboratory according to either literature procedures or adaptations of standard methods. These preparations are briefly described below.

(1) Preparation of 1,6-dideuterio-1,5-hexadiyne³⁹

An ether solution of methyllithium(30 ml, 1.4 M) obtained from Aldrich was added dropwise to a solution of 1.5 g(1.8 ml) 1,5-hexadiyne(Lancaster Synthesis) in 18 ml of ether, which was kept at -40 °C under stirring for about 10 minutes. The methane gas, which was liberated during the addition, was safely handled by the standard three needle technique(Fig.(3.4-1)).⁴⁰ The mixture was stirred for an additional 0.5 h at room temperature to allow the complete formation of a white precipitate. Then the mixture was recooled to 0 °C and 1.3 g(1.7 ml) of methyl alcohol-d(Aldrich) was slowly added. After the addition was finished, the mixture was stirred at room temperature for 1 h. The white precipitate was removed by filtration. The filtrate was concentrated by distillation through a helices-packed column

Table (3.4-1). Chemicals used and their suppliers

Supplier	Compounds
Aldrich Chemical Company, Inc.	Trichlorofluoromethane 1,1,1-Trichlorotrifluoroethane 1,1,2-Trichlorotrifluoroethane 1,2,2,2-Tetrachlorodifluoroethane But-3-en-ol 3-Methylbut-3-en-ol Prop-2-enylamine(allylamine) Cyclooctatetraene Methylviologen dichloride hydrate
Alpha Division Ventron Corporation	1,5-Hexadiyne
Fluka Chemical Corp.	N,N-Dimethylallylamine
Lancster Synthesis	1,5-Hexadiyne
Wiley Organics	But-3-en-1-ol 3-Methylbut-3-en-1-ol
Prof. S. Nelsen Dept. of Chem. Univ. of Wisconsin Madison, WS 53706	syn-Sesquinorbornene oxide
Prof. T. Bally Inst. Chem. Phys. Univ. Fribourg Suisse Perolles, CH-1700 Fribourg, Switzerland	9,10-Octalin oxide
Synthesised in this Laboratory during the course of this work.	But-3-enyl methyl ether But-3-en-ol-d N,N-Dideuterioallylamine 3,4-Dimethylenecyclobutene 1,2,4,5-Hexatetraene 1,6-Dideuterio-1,5-hexadiyne Semibullvallene

at 40 °C. The pure compound was separated by preparative GC (8 ft x 1/4 in. SE-30 on Chromosorb W-HP, column 100 °C, 100 mL/min) and examined by ^1H NMR spectroscopy.

(2) Preparation of 3,4-dimethylenecyclobutene⁴¹

The pyrolysis apparatus used in this experiment is shown in Fig.(3.4-2). 1,5-hexadiyne was added dropwise to a 100-ml three-necked flask immersed in an oil bath maintained at 105 °C. A dry helium stream slowly carried the diyne vapor through an electrically heated reaction vessel kept around 375 °C. It was comprised of a vertically mounted Pyrex tube packed with glass helices. The heater temperature was

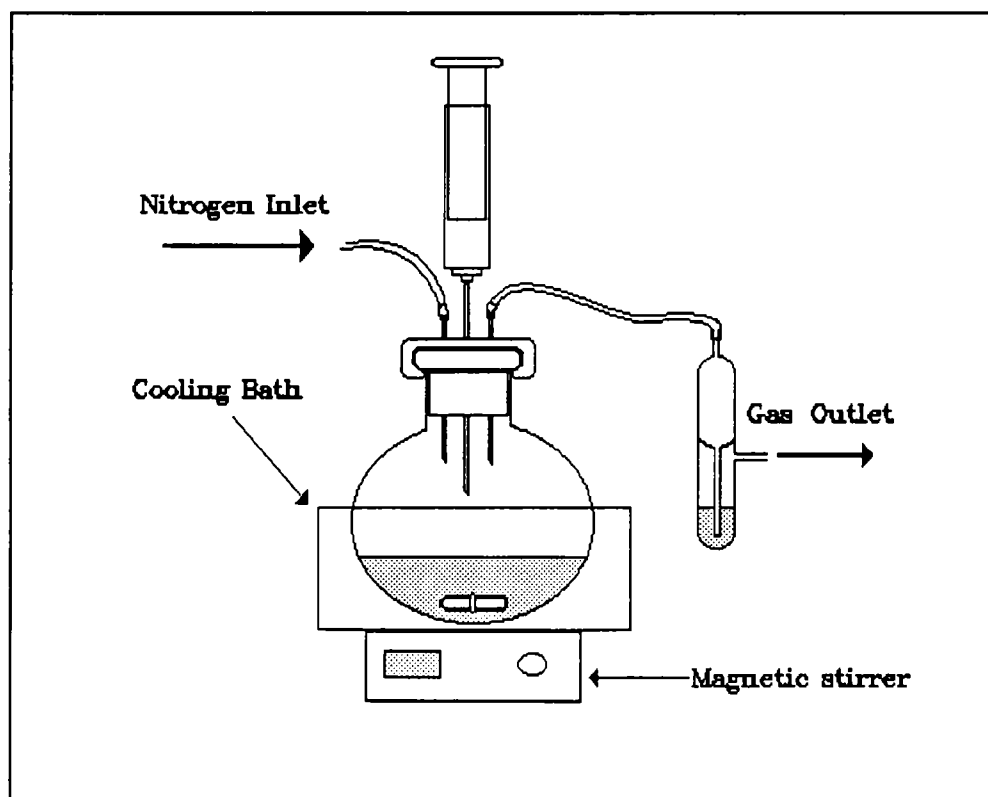


Fig.(3.4-1). The three needle technique.

calibrated by a thermocouple. The products were collected by condensation in a dry ice trap. The final product was checked by 90-MHz ^1H NMR spectroscopy.

(3) Preparation of 1,2,4,5-hexatetraene⁴²

A 500 ml three-necked round-bottom flask was equipped with a reflux condenser connected with a drying tube containing anhydrous calcium chloride, a dropping funnel and a thermometer. The flask was charged with 0.16 g of mercury chloride and 9.7 g of magnesium which had been crushed with a mortar and pestle, and the apparatus was flushed with nitrogen while being flamed externally to remove traces of moisture. Then, 55 ml of anhydrous ethyl ether along with 1.5 ml of propargyl bromide was added to the cooled flask. The anhydrous ethyl ether was obtained by distilling ether in sodium turnings under drying nitrogen atmosphere, while the propargyl bromide was prepared by the distillation of its 80% solution in toluene (Aldrich). During the addition, the ether started to reflux, indicating formation of the Grignard reagent. Then, the mixture was cooled to 5°C in an ice-salt bath and stirred vigorously as a solution of 45 g (30 ml) of propargyl bromide in 185 ml of anhydrous ether was added dropwise. The reaction temperature should be in the range of 5°C and 10°C during the addition. The cooling bath was removed, and the dark green mixture stirred for an additional 20 min at room temperature. A 0.7 g portion of finely pulverized, dry copper (I) chloride was added, and the

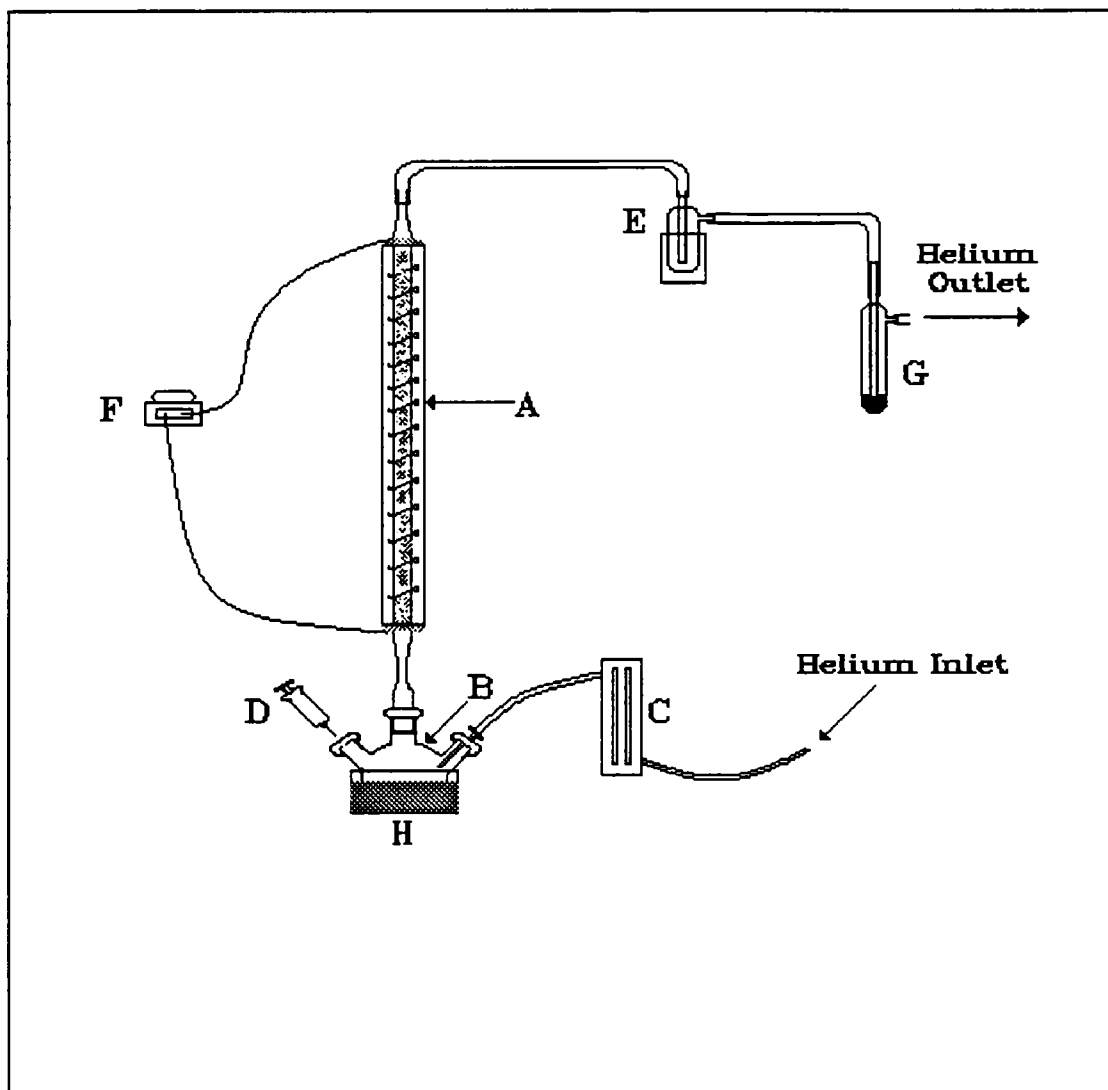


Fig.(3.4-2). The pyrolysis apparatus. A, reaction tube; B, three-necked flask; C, gas flowmeter; D, sample injection needle; E, dry-ice trap; F, voltage variable transformer; G, paraffin oil bubbler; H, oil bath.

mixture was stirred for additional 10 min at room temperature and cooled again to 5°C with an ice-salt bath. Stirring was continued while a solution of 45 g (30 ml) of propargyl bromide in 30 ml of ether was added at a rate such that the internal temperature was kept around 20°C. The mixture became almost black, and separated into two phases when the stirrer had stopped. The cooling bath was removed, and stirring was continued for 15 min at room temperature to complete the dimerization. The reaction mixture was cooled to 0°C with an ice-salt bath and stirred vigorously as 67 ml of 1 N aqueous hydrochloric acid was added. The two-phase mixture was warmed to room temperature, and another 34 ml of 1 N hydrochloric acid was added. The ether layer was separated and washed with three 100-ml portions of water by using a separation funnel. The exposure of the ether layer to the open-air should be avoided during the above handling since 1,2,4,5-hexatetraene was air-sensitive. A few crystals (0.1 g) of hydroquinone was added to stabilize the reddish solution, which was then dried with anhydrous potassium carbonate. The drying agent was filtered, and the filtrate was concentrated to a volume of ca. 120 ml by distillation under nitrogen at atmospheric pressure at 40-45°C. The concentrate was purified by vacuum transfer. The final product was a colorless solution, which was stabilized by adding another 0.1 g of hydroquinone. The pure compound was obtained readily by the preparative GC(8 ft x 1/4 in. 10% carbowax 20M on Chromosorb W-HP, column 50 °C).

The GC peak of 1,2,4,5-hexatetraene came in the second to the solvent ether peak. The GC-purified product was characterized by NMR ^1H spectroscopy.

(4) Preparation of N,N-dideuterioallylamine
and but-3-en-1-ol-d

The two compounds were prepared by standard deuterium exchange. 1 equiv of the nondeuterio parent compound (Aldrich) was stirred with 10 equiv of D_2O overnight. Then a small amount of sodium chloride was added to accelerate the organic and water phase separation. The organic layer was dried with sodium sulfate. The final product was examined by ^1H NMR spectroscopy.

(5) Preparation of but-3-enyl methyl ether

The standard Williamson procedure was followed in the synthesis of but-3-enyl methyl ether. 1 equiv of fresh sodium was placed in a flask and 10 equiv of but-3-en-1-ol was added at room temperature. This resulted in a brownish solution. Then 1 equiv of methyl iodide was slowly added to the stirred solution. The precipitates formed during the addition were removed by filtration. The crude ether product was obtained by the distillation of the filtrate at 80-90 °C. The pure compound was separated by preparative GC (8 ft x 1/4 in. SE-30 on Chromosorb W-HP, column 110 °C, 100 mL/min).

(6) Preparation of semibullvalene⁴³

Semibullvalene was synthesised by the photolysis of cyclooctatetraene in the vapor state. It was carried out in a Rayonet apparatus equipped with 6 RPR 3500-Å lamps. A Pyrex

vessel, 38 cm long and 8.5 cm in diameter fashioned with a 4 cm cold finger at the bottom and a glass joint at the top, was employed for the photolysis. A charge of 0.25 g cyclooctatetraene was added to the cold finger by vacuum transfer. The cold finger was cooled with liquid nitrogen and the vessel was sealed under vacuum. The vessel was suspended at the center of the Rayonet reactor by a wire attached to two glass ears on the cold finger. The top of the reactor was covered with aluminum foil. The sample was irradiated for 4 days at the ambient temperature achieved by the heat generated by the lamps (65~70 °C). After the termination of the photolysis, the cold finger was inserted into liquid nitrogen so that the final product condensed in it. Then the glass finger was cut off and transferred into a vacuum line for further processing. The final product was examined by ^1H NMR spectroscopy with a purity of ca. 95%.

Chapter 4

ESR Studies of Dynamic Changes in Radical Cations

Introduction

The general theory developed in Chapter 2 is applied in this chapter to elucidate two dynamic ESR problems encountered in our radical cation studies. The first problem is the dynamic conformational change of a ring-closed oxirane radical cation, while the second is concerned with the dynamic characterization of the electron transfer between the methyl viologen dication(MV^{2+}) and its radical cation($MV^{\cdot+}$).

Part I. ESR Characterization of Ring-Closed Oxirane Radical Cation via a Novel Alternating Line Width Effect

It has been experimentally demonstrated that the radical cation formed from oxirane under both gas-phase and solid-state condition is the rearranged planar $C\cdots\cdots C$ ring-opened oxallyl isomer.⁴⁴⁻⁵⁶ Since the Freon technique used in generating the radical cation in the latter solid-state case⁵¹⁻⁵⁶ involves only low-energy positive hole-transfer processes between solvent and solute at liquid-nitrogen

temperature as discussed in Chapter 1, the facile ring-opening reaction under such conditions implies that the activation energy for the reaction should be small. This was later confirmed by high-level ab initio calculations.⁵⁷⁻⁶³ One corollary resulting from this low activation barrier to the ring opening is that only the ring-opened form can be detected spectroscopically from monocyclic and bicyclic oxiranes. However, in polycyclic oxiranes where steric constraints prevent C·····C opening and twisting at the carbons of the oxirane ring, topological ring-closed cyclic cations should become accessible.⁵² In this part, the first ESR characterization of topologically ring-closed oxirane cations with a formal one-electron C-C bond is reported. The compounds used in this study were 9,10-octalin oxide (11-oxatricyclo[4.4.1.0^{1,6}]undecane) (1) and syn-sesquinorbornene oxide (2). The former has a flexible structure with a potential to undergo a dynamic conformational change as shown in Fig.(4.1-1), while the latter(Fig.(4.1-2)) is a totally rigid molecule with no possibility of undergoing any dynamic conformational change.

In the following, the application of the general theory developed in Chapter 2 to the simulation of the dynamic ESR profile of (1) is first presented in Section A, which is then used to elucidate and interpret the ESR spectra in Section B. Finally in Section C, some discussions about the electronic structures are given.

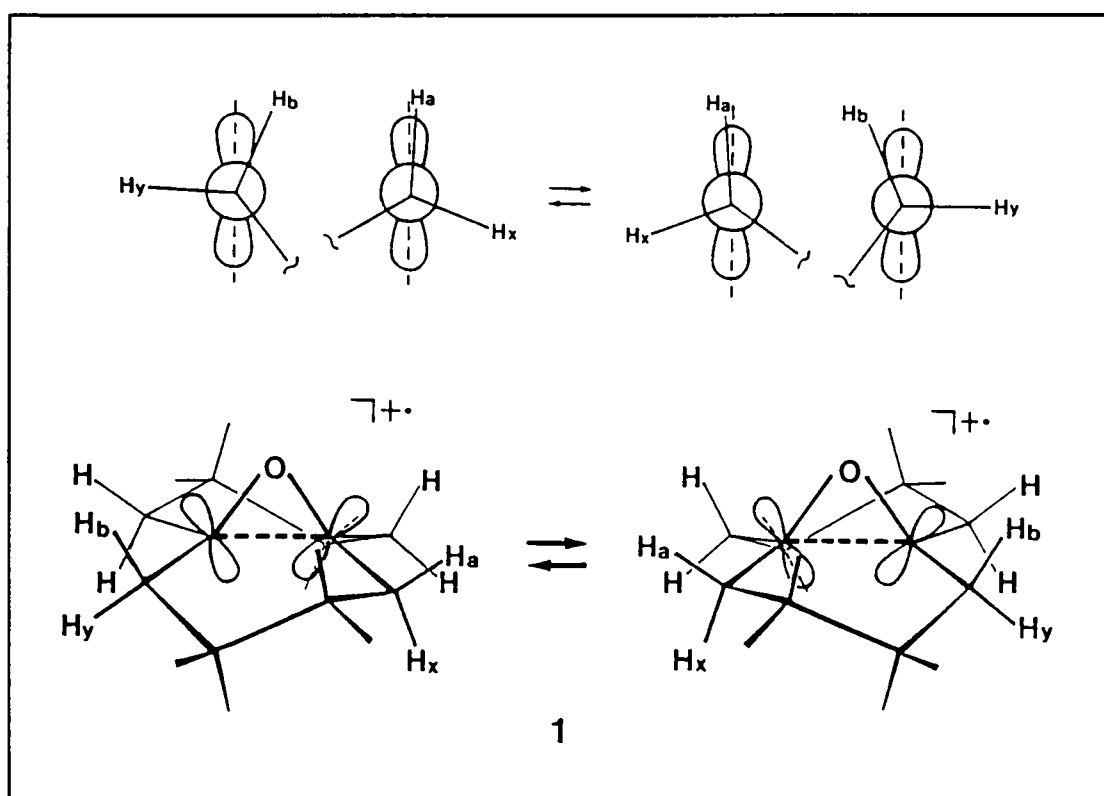


Fig.(4.1-1) Conformation change of 9,10-octalin oxide [11-oxatricyclo[4.4.1.0^{1,6}]undecane] (1) radical cation.

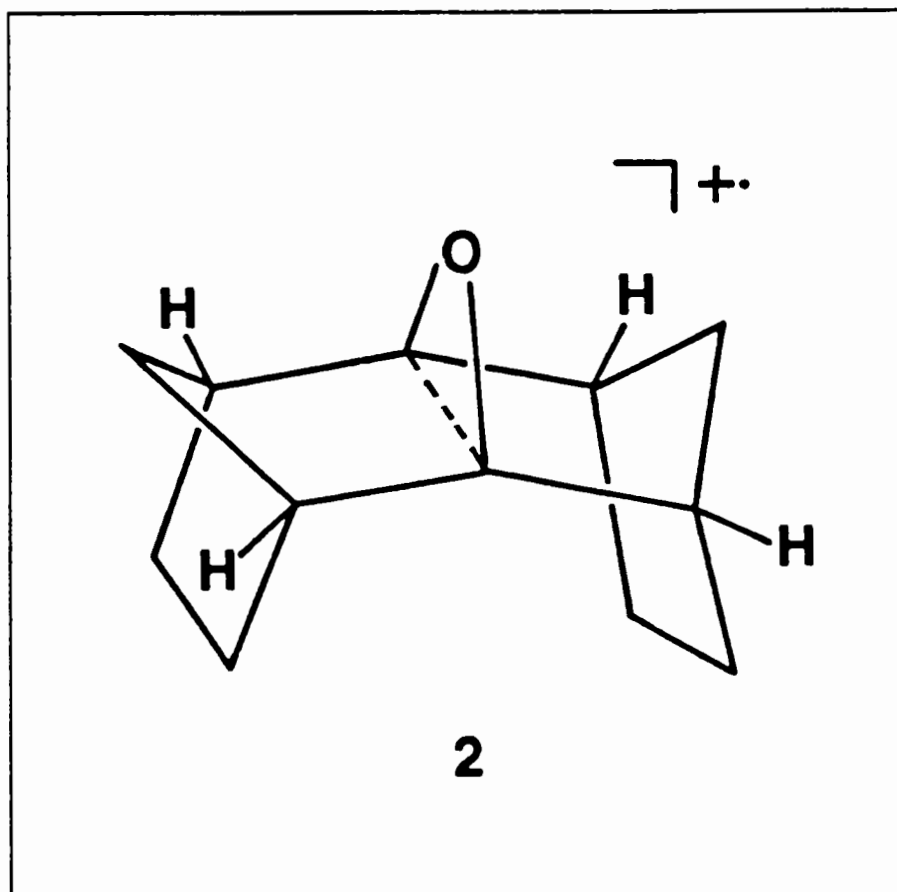


Fig.(4.1-2) The steric conformation of syn-sesquinorbornene oxide (2) radical cation.

Section A. Dynamic Simulation of ESR Lineshape of (1)

According to Eq.(2.2-1), the absorption lineshape is given by

$$A(\omega) = \text{Im}[\text{Trace}(\rho S_+)] \quad \text{..... (4.1a-1) .}$$

In the electron spin basis, the matrix representation of S_+ is

$$S_+ = \begin{array}{c|cc} & |\alpha\rangle & |\beta\rangle \\ \hline \langle\alpha| & 0 & 1 \\ \langle\beta| & 0 & 0 \end{array} \quad \text{..... (4.1a-2) .}$$

Based on this matrix, Eq.(4.1a-1) can be reduced to:

$$A(\omega) = \text{Im} \sum_n \rho_{\alpha n \beta n} \quad \text{..... (4.1a-3)}$$

where the indices α and β are unpaired electron-spin indices as usual and n represents all possible nuclear spin configurations. According to Eq.(2.2b-7), the equation of motion for the density operator is

$$\frac{d\rho}{dt} = \frac{2\pi i}{h} [\rho, H] + \frac{1}{\tau} \{\rho(t_0, t_0) - \rho\} - \frac{\rho}{T_2} \quad \text{..... (4.1a-4)}$$

where a new term $(-\rho/T_2)$ is added to account for the natural linewidth, and the spin Hamiltonian(H) is given by

$$\frac{2\pi H}{h} = g\beta [(\omega_0 - \omega) S_z + \omega_1 S_x] + \sum_j a_j I_{jz} S_z \quad \text{..... (4.1a-5) .}$$

Here $\omega_0/\gamma_e = H_0$ corresponds to the magnetic field, $\omega_1/\gamma_e = H_1$ the magnetic-field component of the microwave field, and $\omega/\gamma_e = H$ the applied variable magnetic field. Following the recipe proposed in Section C of Chapter 2 to evaluate $\rho(t_0, t_0)$, consider the degenerate conformation change:

$$\begin{array}{cc} (1) & \rightleftharpoons & (1) \\ \alpha\{abxy\} & & \alpha\{bayx\} \\ \beta\{abxy\} & & \beta\{bayx\} \end{array} \quad (4.1a-6)$$

where α and β are the electron spins and a,b,x and y the nuclear spins with labels following Fig.(4.1-1). According to the Permutation Indices method, $\rho(t_0, t_0)$ in the above basis is

$$\rho_{\alpha\{abxy\}, \beta\{abxy\}}(t_0, t_0) = \rho_{\alpha\{bayx\}, \beta\{bayx\}}(t) \quad \dots\dots\dots (4.1a-7) .$$

If the applied magnetic field is slowly varied, the steady state condition

$$\dot{\rho}_{\alpha\{abxy\}, \beta\{abxy\}} = 0 \quad \dots\dots\dots (4.1a-8)$$

can be applied. Thus, Eq.(4.1a-4) is transformed into the following two simultaneous equation:

$$\begin{aligned} & \rho_{\alpha\{abxy\}, \beta\{abxy\}} \left[i(\omega_{\alpha\{abxy\}, \beta\{abxy\}} - \omega) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \frac{\rho_{\alpha\{bayx\}, \beta\{bayx\}}}{\tau} \\ & + i\omega_1 (\rho_{\alpha\{abxy\}, \alpha\{abxy\}} - \rho_{\beta\{abxy\}, \beta\{abxy\}}) = 0 \quad \dots\dots\dots (4.1a-9) ; \end{aligned}$$

$$\begin{aligned} & \rho_{\alpha\{bayx\}, \beta\{bayx\}} \left[i(\omega_{\alpha\{bayx\}, \beta\{bayx\}} - \omega) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \frac{\rho_{\alpha\{abxy\}, \beta\{abxy\}}}{\tau} \\ & + i\omega_1 (\rho_{\alpha\{bayx\}, \alpha\{bayx\}} - \rho_{\beta\{bayx\}, \beta\{bayx\}}) = 0 \quad \dots\dots\dots (4.1a-10) . \end{aligned}$$

These equations can be rewritten as

$$\rho_{\alpha\{abxy\}, \beta\{abxy\}} + \frac{\rho_{\alpha\{abxy\}, \beta\{abxy\}} + \rho_{\alpha\{bayx\}, \beta\{bayx\}}}{\tau \left[i(\omega_{\alpha\{bayx\}, \beta\{bayx\}} - \omega) - \frac{1}{T_2} - \frac{2}{\tau} \right]} + \frac{i\omega_1 (\rho_{\alpha\{abxy\}, \alpha\{abxy\}} - \rho_{\beta\{abxy\}, \beta\{abxy\}})}{\left[i(\omega_{\alpha\{abxy\}, \beta\{abxy\}} - \omega) - \frac{1}{T_2} - \frac{2}{\tau} \right]} \quad \dots (4.1a-9)$$

$$\rho_{\alpha\{bayx\}, \beta\{bayx\}} + \frac{\rho_{\alpha\{abxy\}, \beta\{abxy\}} + \rho_{\alpha\{bayx\}, \beta\{bayx\}}}{\tau \left[i(\omega_{\alpha\{bayx\}, \beta\{bayx\}} - \omega) - \frac{1}{T_2} - \frac{2}{\tau} \right]} + \frac{i\omega_1 (\rho_{\alpha\{bayx\}, \alpha\{bayx\}} - \rho_{\beta\{bayx\}, \beta\{bayx\}})}{\left[i(\omega_{\alpha\{bayx\}, \beta\{bayx\}} - \omega) - \frac{1}{T_2} - \frac{2}{\tau} \right]} \quad \dots (4.1a-10) .$$

The addition of Eq.(4.1a-10) to Eq.(4.1a-9) followed by algebraic rearrangement yields :

$$\sum_{s=1}^2 \rho_s = \frac{i\omega_1 (\rho_{\alpha\{abxy\}, \alpha\{abxy\}} - \rho_{\beta\{abxy\}, \beta\{abxy\}}) f_{s=1}}{\left(1 - \frac{1}{\tau} \sum_{s=1}^2 f_s\right)} + \frac{i\omega_1 (\rho_{\alpha\{bayx\}, \alpha\{bayx\}} - \rho_{\beta\{bayx\}, \beta\{bayx\}}) f_{s=2}}{\left(1 - \frac{1}{\tau} \sum_{s=1}^2 f_s\right)} \quad \dots (4.1a-11)$$

where

$$s=1 = \langle \alpha\{abxy\}, \beta\{abxy\} \rangle \quad \dots (4.1a-12)$$

$$s=2 = \langle \alpha\{bayx\}, \beta\{bayx\} \rangle \quad \dots (4.1a-13)$$

$$f_s = \frac{1}{T_2} + \frac{2}{\tau} - i(\omega_s - \omega) \quad \dots (4.1a-14) .$$

Because the electron Zeeman term usually dominates the spin Hamiltonian of the system, the following approximation relation is obvious:

$$\begin{aligned}\rho_{\alpha n, \alpha n} - \rho_{\beta n, \beta n} &\approx e^{-\frac{\alpha \beta_e g H}{kT}} - e^{-\frac{\beta \beta_e g H}{kT}} \\ &= C \\ &= \text{Independent of } n \quad \dots\dots (4.1a-15)\end{aligned}$$

where n is any possible nuclear spin configuration. Insertion of this relation to Eq.(4.1a-11) gives

$$\sum_{s=1}^2 \rho_s = \frac{i\omega C \sum_{s=1}^2 f_s}{(1 - \frac{1}{\tau} \sum_{s=1}^2 f_s)} \quad \dots\dots (4.1a-16).$$

Similarly, we can obtain the same expression for other possible nuclear spin configurations needed in Eq.(4.1-3). Then, Eq.(4.1a-3) can be evaluated so that the lineshape is calculated. Although Eq.(4.1a-16) looks very complicated, its evaluation can be easily programmed.

Section B. Results

The radical cation of 9,10-octalin oxide (11-oxatricyclo-[4.4.1.0^{1,6}]undecane) (1) was generated radiolytically in CFCl₃ at 77 K, and its ESR spectrum showed a reversible temperature dependence below the softening point (165 K) of this matrix, as illustrated in Fig.(4.1b-1). This strongly indicated that a conformational dynamic process was involved. A degenerate conformational change between the two

most stable half-chair transoid ring conformations⁶⁴ shown in Fig.(4.1-1) was most likely to be responsible for this spectral temperature dependence. In terms of this stable half-chair conformation, the rigid-limit spectrum at low temperature is expected to show hyperfine coupling to the four completely equivalent pairs of β -hydrogens represented by H_a , H_b , H_x , and H_y . Based on this model, the low temperature ESR spectra can be analyzed with the help of computer simulation. The hfcs obtained in this way are given in Table (4.1a-1). However, the real test for this assignment comes from whether or not these hfcs can be used to simulate the experimental high-temperature ESR spectra only through the adjustment of the lifetime value(τ) for the conformational change.

As seen from Fig.(4.1-1), the dynamic ring flipping gives rise to the interconversion of H_a and H_b and of H_x and H_y . The usual result of this exchange in the above spin system is to selectively broaden the $M_I=\pm 1$ components in both the primary ($2H_a, 2H_b$) and secondary ($2H_x, 2H_y$) quintets. Consequently, the unbroadened lines corresponding to the coalescence spectrum normally constitute a triplet of triplets, the apparent splittings being twice the quintet splittings. However, the experimental coalescence spectrum at 160 K (Fig.(4.1b-1)) also shows a doublet of doublets with precisely the same splittings as for the triplets mentioned above. These extra lines are in fact the $M_I=\pm 1$ components of

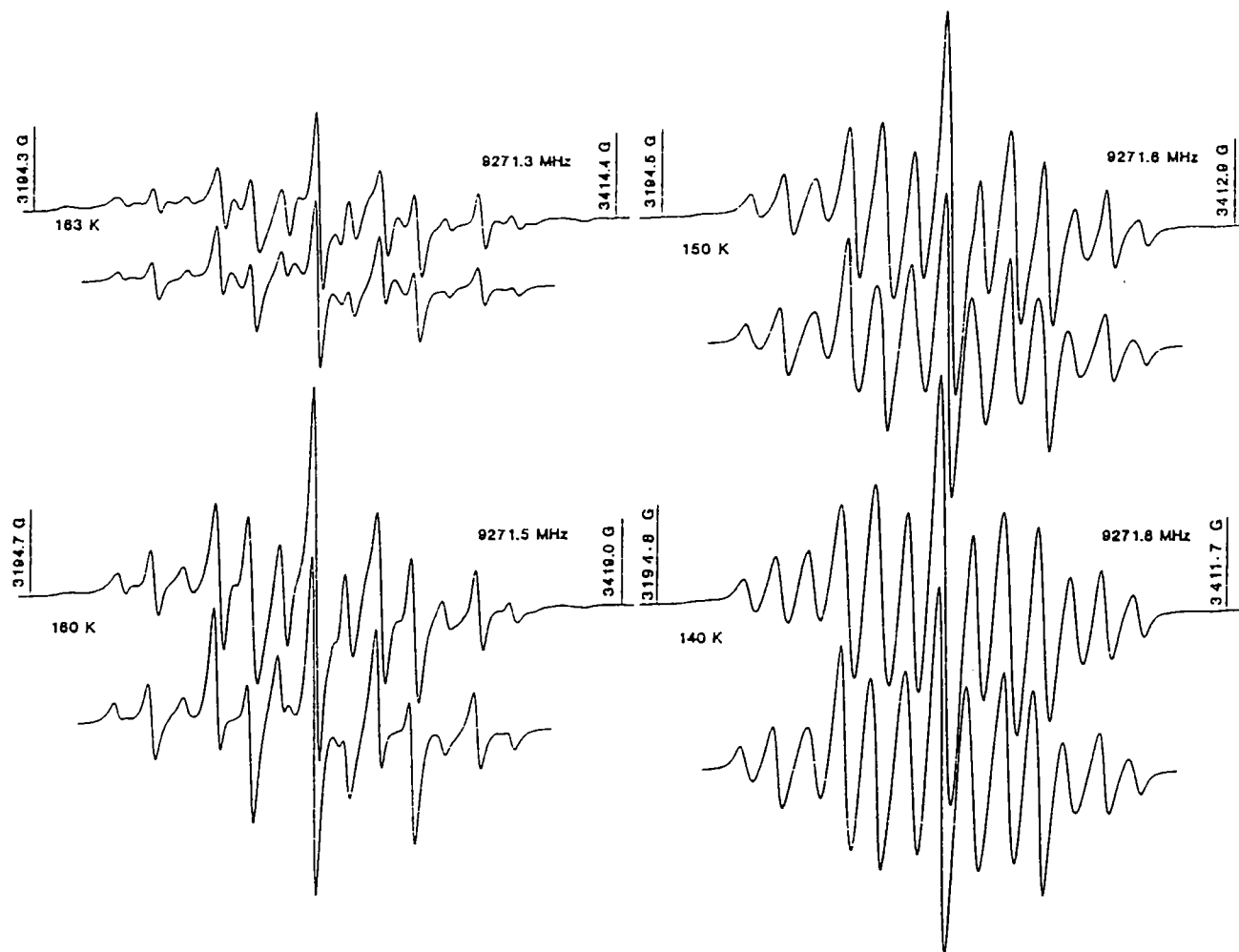


Fig.(4.1b-1). First-derivative ESR spectra of the 9,10-octalin oxide radical cation in CFCl_3 . The simulated spectra (see text) by using the parameters in Table (4.1b-1), a line width of 2.7 G, and rate constants for ring inversion in (**1**) of $7.1 \times 10^7 \text{ s}^{-1}$ (163 K), $5.6 \times 10^7 \text{ s}^{-1}$ (160 K), $2.5 \times 10^7 \text{ s}^{-1}$ (150 K), and $1.11 \times 10^7 \text{ s}^{-1}$ (140 K).

the primary quintet with a substructure corresponding to the $M_I=\pm 1$ components of the secondary quintet. In other words, the spectrum shows an alternating substructure of triplets and doublets arising from a change of parity in the line-width alternation.

This unusual line broadening phenomenon is in fact expected from the above hfc assignments. Since the coupling constants (Table (4.1b-1)) have the following internal relation

$$a(2H_a) - a(2H_b) = a(2H_x) - a(2H_y) \quad \text{..... (4.1b-1)}$$

this establishes that the position of line components meeting the condition

$$M_I(2H_a) + M_I(2H_x) = M_I(2H_b) + M_I(2H_y) \quad \text{..... (4.1b-2)}$$

will remain invariant upon exchange. This rationale is illustrated with the aid of the stick plots in the correlation diagram of Fig.(4.1b-2). Thus, the 140-K spectrum in Fig.(4.1b-1) corresponds to the 13 line groups for the rigid-limit spectrum in plot a, while the coalescence spectrum at 160 K fits the reconstruction in plot c of line components whose resonances remain unaltered by exchange (plots a and b). Simulations of the temperature-dependent spectra were made by using the method of Section 1. The perfect agreement between the experimental spectra and the calculated spectra strongly supports the above hfc assignments. Moreover, the interconversion rate constants

used to obtain the fits in Fig.(4.1b-1) obeyed an Arrhenius relation with $A=5.6 \times 10^{12} \text{ s}^{-1}$ and $E_a=3.66 \text{ kcal mol}^{-1}$ (Fig.(4.1b-3)). These parameters are very similar to those reported for ring inversion in the cyclohexyl radical⁶⁵ and the cyclohexanesemidione radical anion.⁶⁶

As a simple corollary of the above explanation, the addition of the two extra single methylene bridges in the rigid radical cation of syn-sesquinorbornene oxide (2) should eliminate the conformational interconversion observed for (1). In agreement, its ESR spectrum (Fig.(4.1b-4)) showed no temperature dependence and consisted of a quintet from coupling to the four equivalent bridgehead hydrogens (Table (4.1b-1)).

Since one of the characteristics of oxygen-centered radicals is that of g-anisotropy, the failure to observe significant g-anisotropy in the low-temperature ESR spectra of (1) and (2) implies that (1) and (2) are carbon-centered rather than oxygen-centered radical cations. This is in fact also consistent with the observed angular-dependent couplings for hydrogens in β positions with respect to the oxirane ring carbons. However, high-level ab initio MO calculations predicted a $^2B_1$ ground state instead of the analogous carbon-centered $^2A_1$ state for the ring-closed parent oxirane cation.⁶³ This change in the state ordering on going to these rigid species is expected since the effect of alkylation is known to destabilize the a_1 relative to the b_1 orbital in methylated

Table (4.1b-1). ESR and Related Parameters for the Radical Cation Cations of 9,10-Octalin Oxide (1) and syn-Sesquinorbornene Oxide (2) in a CFCl_3 Matrix

radical cation	β - ^1H hyperfine couplings ^a /G	$\text{H}_\beta\text{C}_\beta\text{C}_\alpha\text{P}_\alpha$ dihedral angles ^b /deg	$\text{H}_\beta\text{C}_\beta\text{C}_\alpha\text{P}_\alpha$ dihedral angles ^c /deg	<u>g</u>
<u>1</u>	35.8 (2H_a)	± 4.4 (5.2)	± 7.3	2.0050
	25.8 (2H_b)	± 32.6 (32.3)	± 27.7	
	11.5 (2H_x)	± 124.4 (124.4)	± 122.6	
	1.5 (2H_y)	± 87.4 (78.2)	± 89.0	
<u>2</u>	24.2 (4H_β)	$\pm (36.3)$		2.0069

^aThe estimated uncertainty in the hyperfine couplings is ± 1.5 G for 1 and ± 0.5 G for 2. ^bCalculated from the hyperfine couplings assuming the Heller-McConnell $\cos^2\theta$ equation,^d a planar configuration at C_α , and that the H_aCH_x and H_bCH_y phase angles are both equal to 120 degrees. Using these assumptions and the Powell method^e for a non-linear least-squares error minimization, the proportionality constant in the $\cos^2\theta$ equation^d was also determined to be 36.1 G. The θ values in parentheses were calculated directly from the couplings using this latter value. ^cAM1-UHF^f calculated values for the optimized geometry having $d(\text{C}_\alpha, \text{C}_\alpha') = 2.244$ Å and planar α -carbons. ^dHeller, C.; McConnell, H. M. J. Chem. Phys. 1960, 32, 1535. ^ePowell, M. T. D. Comput. J. 1964, 7, 303. ^fDewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc., 1985, 107, 3902.

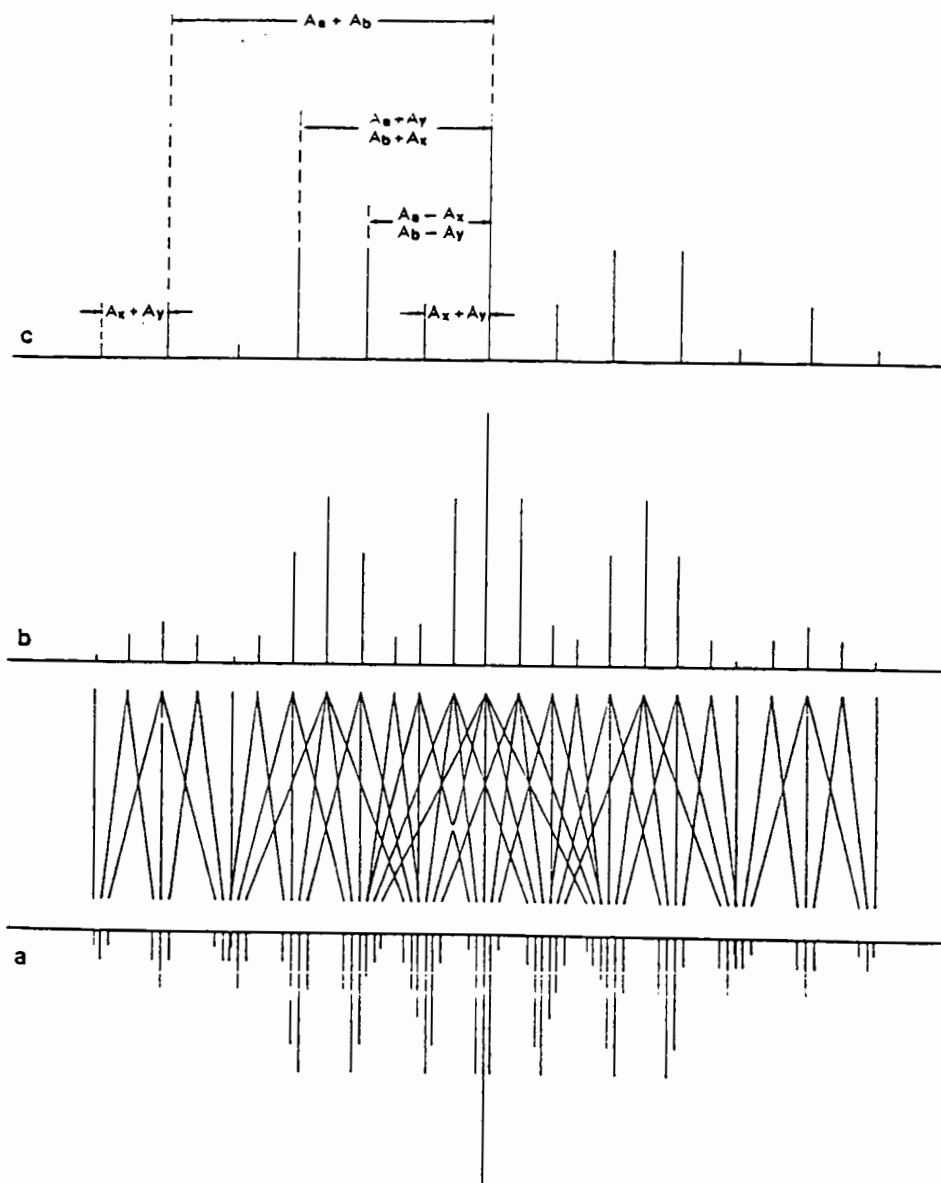


Fig.(4.1b-2). Stick diagram reconstructions of the 9,10-octalin oxide (1) spectra for (a) slow, (b) fast, (c) intermediate rates of exchange between $2H_a$ and $2H_b$ and between $2H_x$ and $2H_y$. The intensities of the line components in stick plot b are shown at half scale, and the lines connecting the components in plots a and b show the correlations between nuclear spin states.

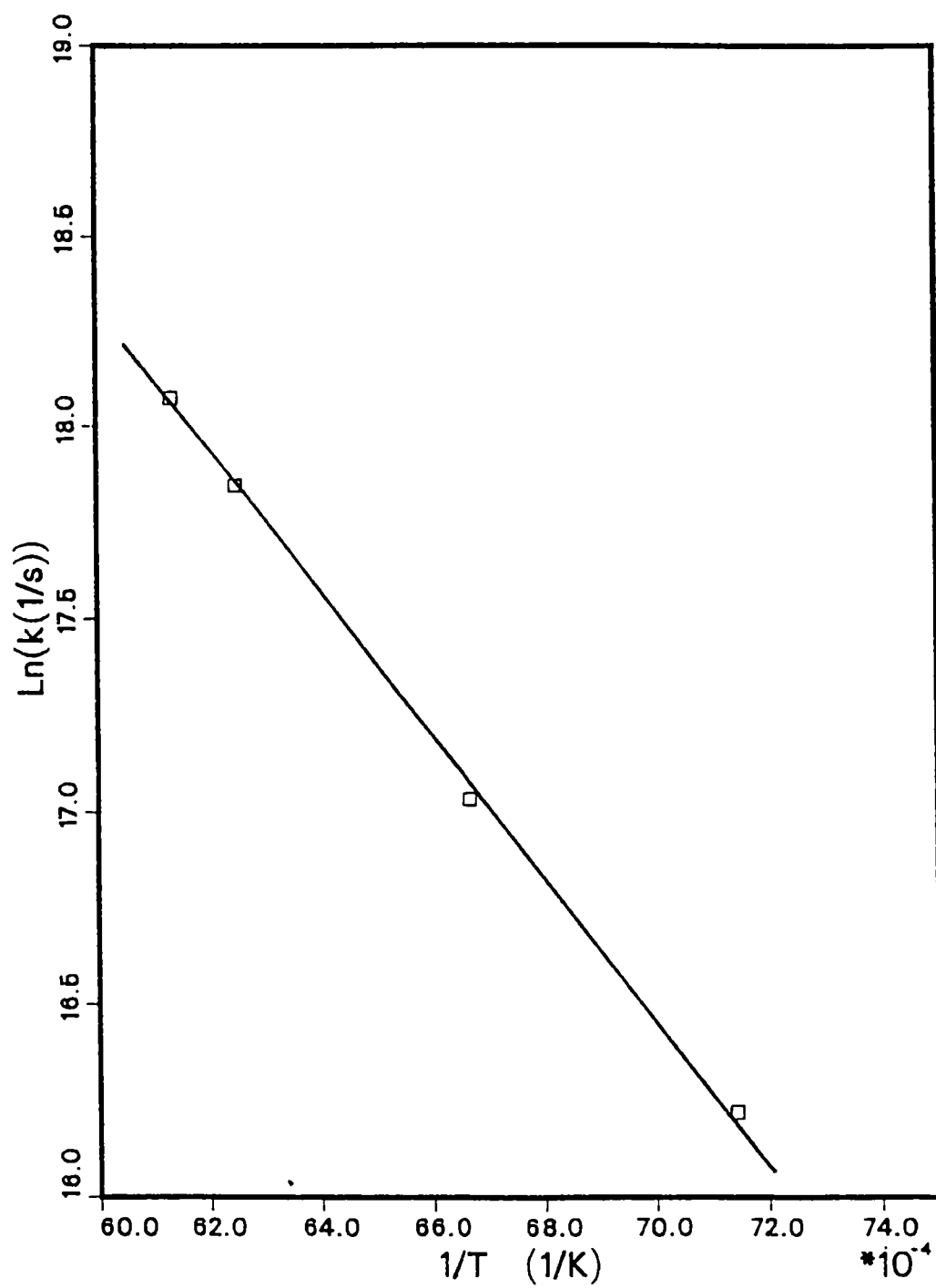


Fig.(4.1b-3). $\ln(k_{ex})$ vs. $1/T$ plot.

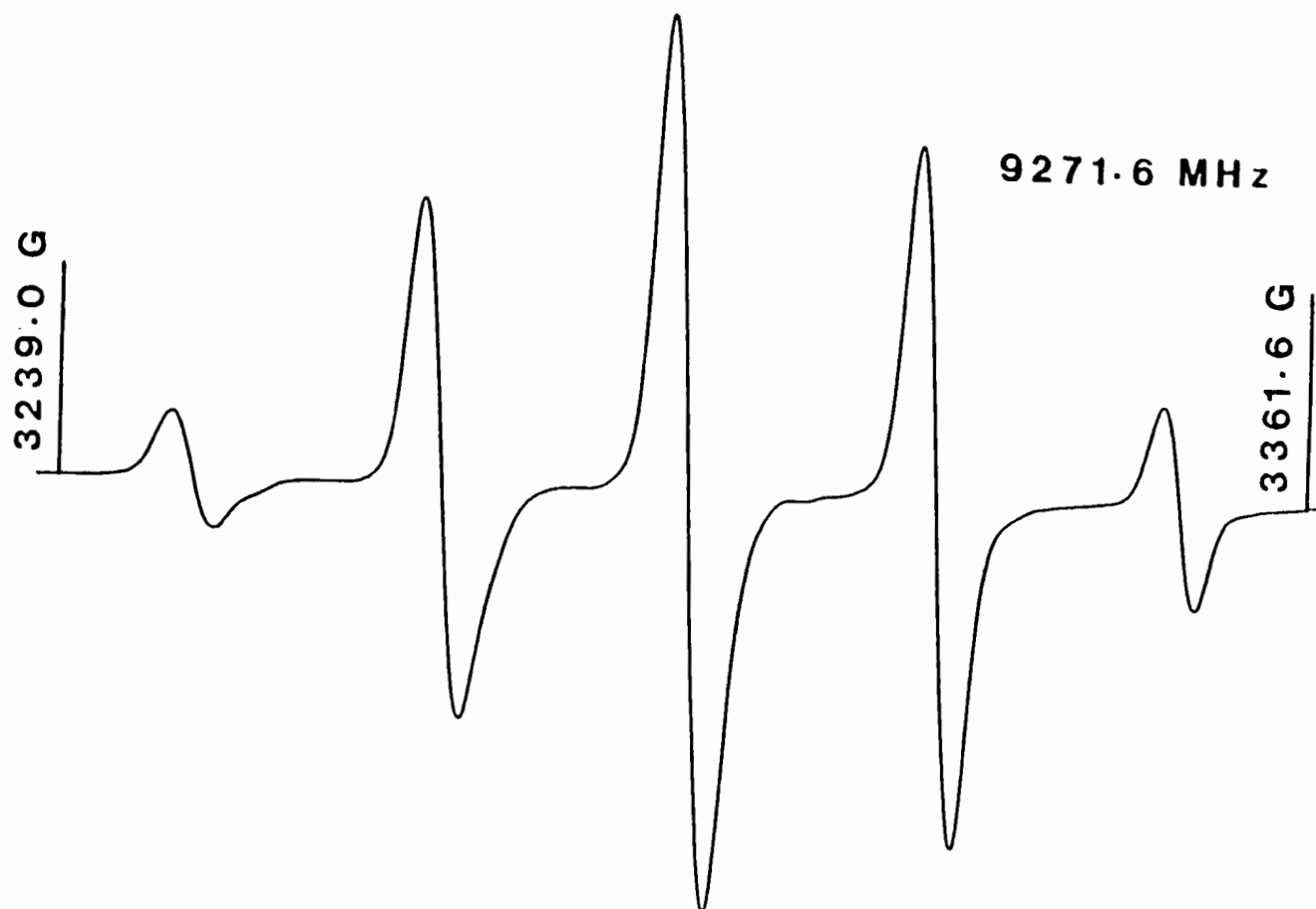


Fig.(4.1b-4). First-derivative ESR spectrum of the syn-sesquinorbornene oxide radical cation in CFCl_3 matrix at 142 K. The cation was produced by γ -irradiation of a 1 mol % solution of the parent compound at 77 K for a dose of 0.5 Mrad.

oxiranes.⁶⁷

Section C. Discussion

In order to give further theoretical evidence for the above assignment, an AM1 calculation was employed. Fig. (4.1c-1) shows the AM1-optimized geometry of (1). In agreement with the experimental results, AM1 calculations predict that (1) has the carbon-centered ^2A state as the ground state with a transoid half-chair conformation. Also, the calculation results reveal that the spin density is largely concentrated in the two p-orbitals of the α -carbons which assume a nearly planar conformation with a highly elongated $C_\alpha-C_\alpha$ bond distance of 2.24 Å. Clearly, the C-C bond must be very weak in these intermediate $CC(\sigma)$ species, and their observation is due to the steric effect which prohibits rotation about the C-O bonds to the more stable oxallyl radical cation. The calculated dihedral angles between the β -hydrogens and the corresponding α -carbon p-orbitals where most of the spin is located are in an excellent agreement with those deduced from the ESR analysis by the Powell non-linear regression method (Table (4.1b-1)).

If the $CC(\sigma)$ bond is assumed to be the main reaction coordinate for the elongation, the potential energy curve

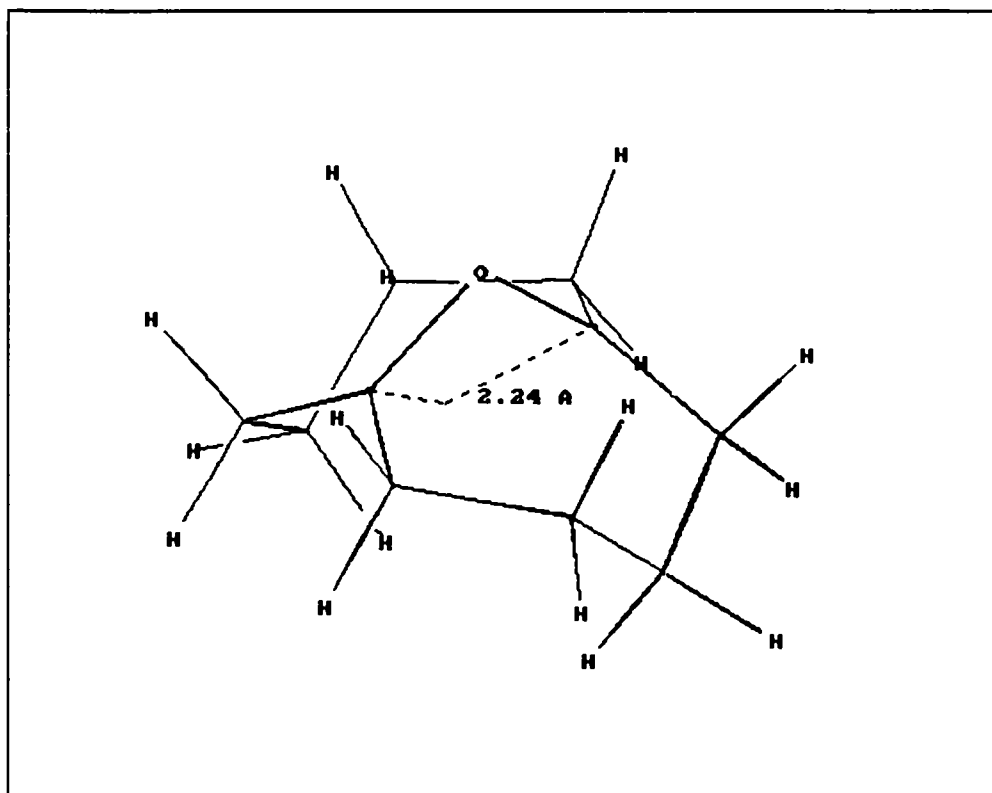


Fig.(4.1c-1). AM1-optimized geometry of the 9,10-octalin oxide radical cation(1).

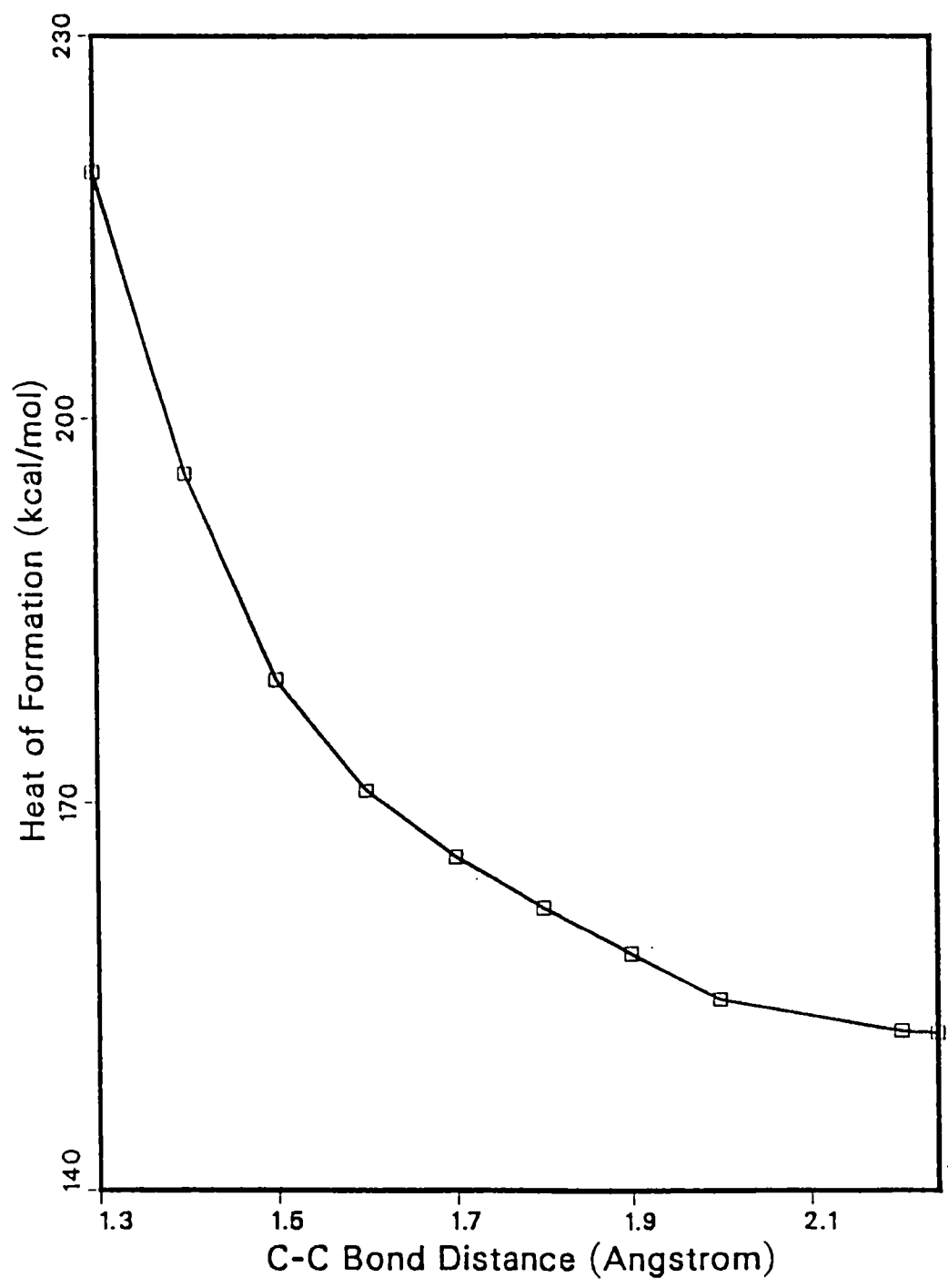


Fig.(4.1c-2). Reaction coordinate calculation of the 9,10-octalin oxide radical cation elongation process using C_a-C_a' distance as a reaction coordinate.

(Fig.(4.1c-2)) along the reaction coordinate can be calculated. The results indicate that the parent radical cation (1) can easily relax to the elongated structure without any activation energy.

A similar $^2A_1$ electronic structure was found for syn-sesquinorbornene oxide radical cation (2) in the AM1 studies. The corresponding AM1-optimized geometry is shown in Fig.(4.1b-3). The elongation of the $C_\alpha-C_\alpha$ bond is again observed with a bond length of 2.01 Å. The calculated potential energy curve(Fig.(4.1b-4)) during the elongation is similar to that of (1). This suggests that the elongation might be a general phenomenon in radical cations of ethylene oxide derivatives with similar geometries.

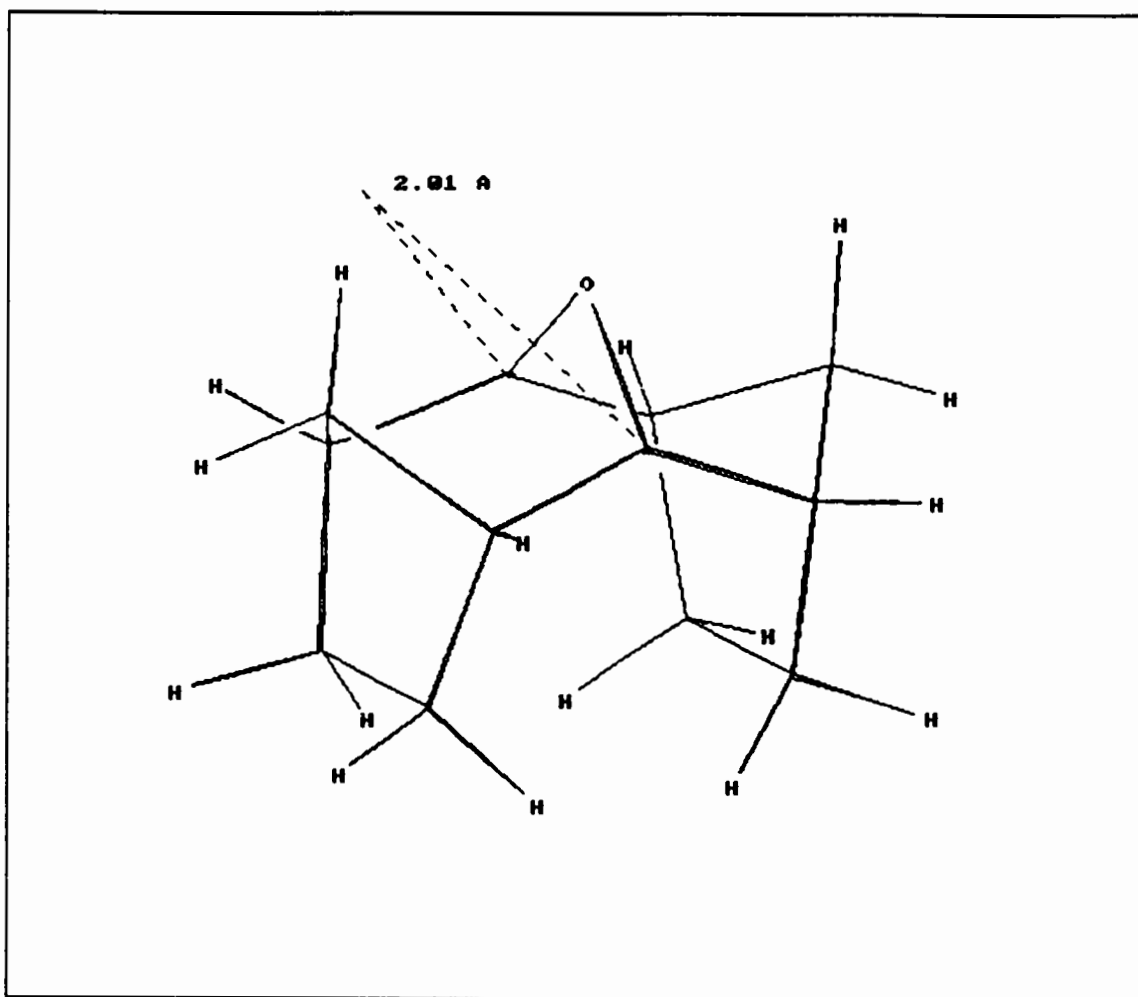


Fig.(4.1c-3). AM1-optimized geometry of the syn-sesquinorbornene oxide radical cation (2).

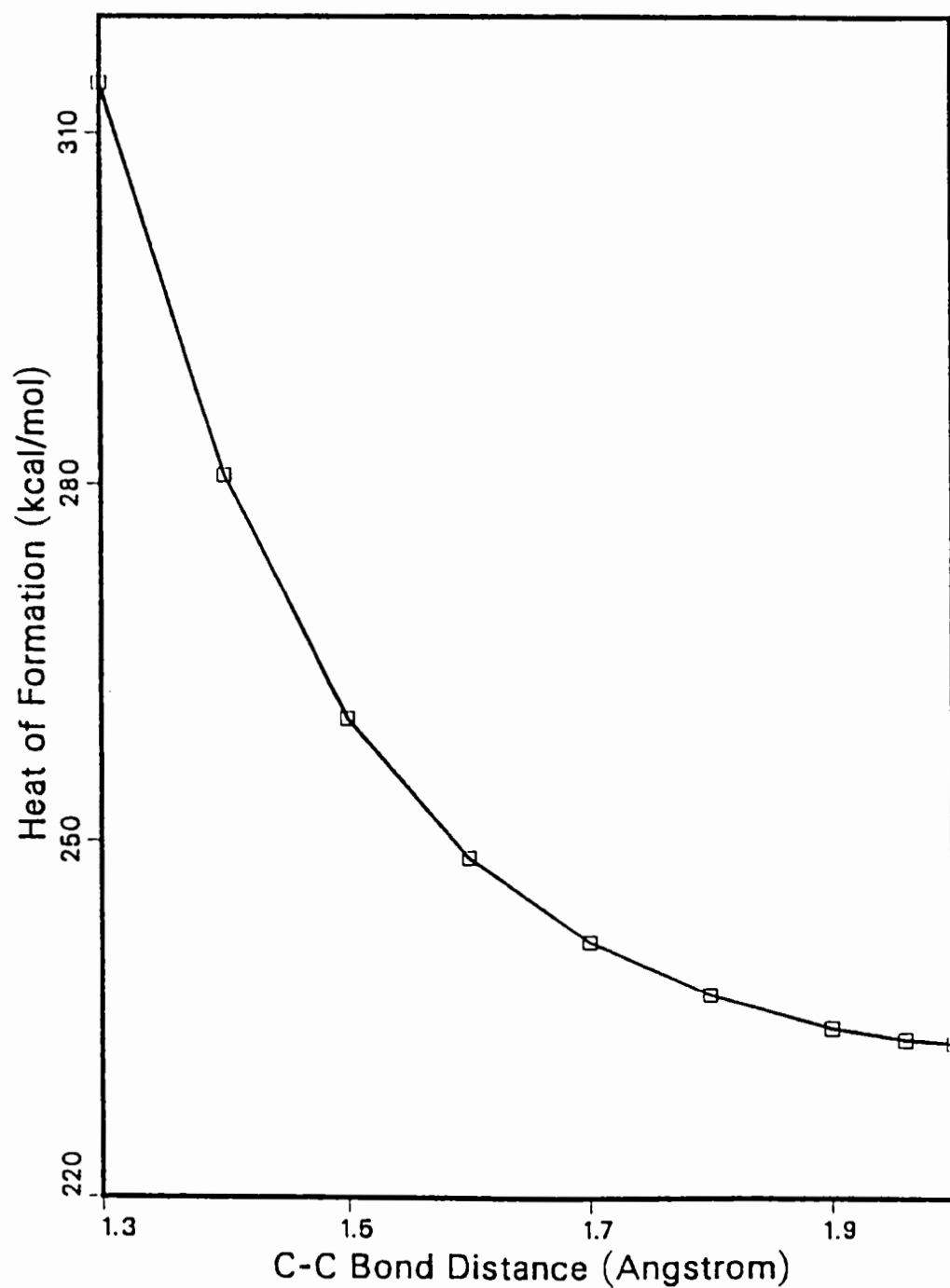
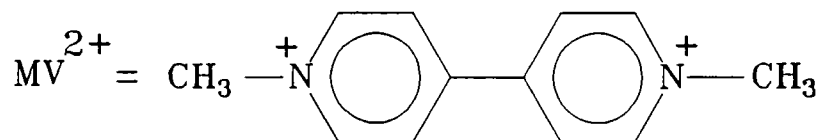
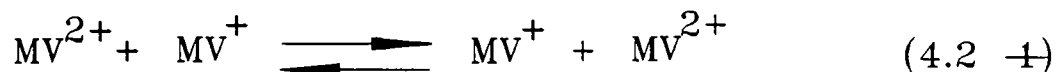


Fig.(4.1c-4). Reaction coordinate calculation of the syn-sesquinorbornene oxide radical cation elongation process using C_a-C_a distance as a reaction coordinate.

Part II. ESR Studies of Electron Transfer Between Methyl Viologen Dication and Its Radical Cation

Methyl viologen dication (MV^{2+}) has been extensively used in herbicides,⁶⁸ as redox indicators⁶⁹ and as mediators in photosensitive electron-transfer reactions for the solar energy conversion and storage.⁷⁰ Recently, methyl viologen was used in our laboratory and elsewhere as an effective photoinduced electron acceptor in TiO_2 colloid studies.⁷¹ In all these applications, it is important to know the rate constant for the electron-self-exchange reaction between MV^{2+} and $MV^{\bullet+}$ (Eq.(4.2-1)). This need was also reflected in some recent publications.⁷²



There have been many reports on the measurement of this rate constant (k_{et}) in the literature, and large discrepancies exists among them. An estimate of $8.4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ has been made for this self-exchange rate constant in acetonitrile

solvent by Bock et al according to their electron-transfer quenching experiment involving $\text{Ru}(\text{bpy})_3^{2+*}$ and MV^{2+} .⁷³ The calculation of this value has been reassessed and a value of $8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ in water solvent was found.⁷⁴ Later, these findings were properly questioned by Tsukahara et al⁷⁵ who reported that k_{et} was about $10^8 \text{ M}^{-1}\text{s}^{-1}$ based on the experimental measurement of a cross electron-transfer rate constant between two viologens and the use of Marcus's cross relationship. To sum up, the above results were obtained either through indirect measurements or idealized models. In contrast, Rieger et al approached the subject more directly and tried to determine k_{et} quantitatively in methanol solvent by a direct NMR line broadening measurement.⁷⁶ This measurement was based on the following Eq.(4.2-2)

$$\Delta T_2^{-1} = \frac{k_{\text{et}} [P]}{1 + 4k_{\text{et}}^2 [D]^2 / A^2} \quad \text{..... (4.2-2)}$$

where ΔT_2^{-1} is a linewidth change caused by the electron transfer, [D] and [P] are concentrations of the diamagnetic and paramagnetic exchange partners respectively, and A is an electron-nuclear hyperfine coupling constant in angular frequency units. Clearly an accurate determination of k_{et} by the use of Eq.(4.2-2) requires knowledge of the hfcs(A), [P] and [D] as well as linewidths. Since [P] is very difficult to measure due to high radical reactivities, it is often set to be an optimization parameter in nonlinear regressions as was done in the measurement by Rieger et al. This reduces the

accuracy of the whole method considerably if only a few well-resolved NMR peaks exist. In the case of MV^{2+} , three proton-NMR peaks can be observed experimentally, two (the NMR signals corresponding to protons in the two pyridine rings) of them overlapping strongly. Accordingly, the measurement of k_{et} for $MV^{2+/.+}$ by Rieger et al was essentially equivalent to using three experimental points to obtain two unknown parameters, which was clearly not very accurate. This prompted us to use a more accurate ESR method to redetermine the electron-transfer rate between the methyl viologen dication and cation. In this context, ESR determinations of this rate constant (k_{et}) in water, methanol, allyl alcohol and propargyl alcohol solvents through dynamic ESR-lineshape simulations are reported. Since the model used in this direct ESR measurement only involves determinations of the radical lifetime(τ) and of $[D]$, inherently more accurate results would be expected as compared to the corresponding NMR method.⁷⁷

According to classical theories of electron transfer,⁷⁸ an electron-transfer process is a kinetic process in which solvents play an important rule. A theoretical expression has been given by Marcus to correlate electron-transfer rates to solvent parameters.⁷⁸ Extensive measurements of rate constants involving electron transfers between organic radical cations and their neutral molecules(**cn**), or between organic anion radicals and their neutral molecules(**an**) in various solvents

have been made, notably by the groups of Grampp⁷⁹ and Nelsen⁸⁰. Normally, a very nice agreement between theories and experiments has been found for these systems. However, little work^{79d,80b} has been done to study organic cation-dication(cd) electron-transfer reactions. The MV²⁺/MV^{•+} system studied in this part is an example of (cd)-systems. Careful studies of this system can therefore provide us some information on general reaction properties in (cd)-systems.

Section A. Density Matrix Formulation of ESR Linshapes Under the Influence of Electron Transfer

Considering a general homogeneous (cc) electron transfer reaction



we can write down the following equation of motion for the density operator of the radical cation :

$$\frac{\partial \rho^{C^{•+}}}{\partial t} = \frac{2\pi i}{h} [\rho^{C^{•+}}, H] + \frac{1}{\tau} \{ \rho^{C^{•+}}(t_0, t_0) - \rho^{C^{•+}} \} - \frac{\rho^{C^{•+}}}{T_2} \quad \text{..... (4.2a-2)}$$

where τ is the lifetime of the radical cation and is given by

$$\frac{1}{\tau} = k_{ec} [C^{2+}] \quad \text{..... (4.2a-3) .}$$

The homogeneous electron transfer reaction(Eq. (4.2a-1)) is an

example of the following general abstract exchange equation:

$$AB + A \rightleftharpoons A + AB \quad (4.2a-4)$$

Spin state	$a\alpha$	a	a	$a\alpha$
	$a\beta$	a	a	$a\beta$

where B can be a proton in NMR proton-exchange experiments or an unpaired electron in ESR electron-exchange experiments. In our case, we regard B as an unpaired electron with electron-spin states α and β . Based on the Permutation Indices method, the following results can be derived by the simple indices switch^{26b} according to Eq.(4.2a-4)

$$\rho_{\alpha a, \beta a}^{C^*}(t_0, t_0) = \sum_n \rho_{\alpha n, \beta n}^{C^*} \rho_{a, a}^{C^{2*}} \quad \dots\dots\dots (4.2a-5)$$

where n represents all possible nuclear configurations. Inserting Eq.(4.2a-5) in Eq.(4.2a-2), and using the same steady-state condition as that used in section A of Part I results in the following N simultaneous equations:

$$\rho_{\alpha a, \beta a}^{C^*} \left[i(\omega_{\alpha a, \beta a} - \omega) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \frac{\sum_n \rho_{\alpha n, \beta n}^{C^*} \rho_{aa}^{C^{2*}}}{\tau} + i\omega_1 (\rho_{\alpha a, \alpha a}^{C^*} - \rho_{\beta a, \beta a}^{C^*}) = 0$$

$\dots\dots\dots (4.2a-6);$

$a=1, 2, \dots, N.$

where N is the total number of nuclear spin configurations. The insertion of the so-called "high temperature" condition

$$\rho_{aa}^{C^{2*}} = \frac{1}{N} \quad \dots\dots\dots (4.2a-7)$$

to Eq.(4.2a-6) gives

$$\rho_{\alpha a, \beta a}^{C^{*}} + \frac{\sum_n \rho_{\alpha n, \beta n}^{C^{*}}}{N\tau \left[i(\omega_{\alpha a, \alpha a} - \omega) - \frac{1}{T_2} - \frac{1}{\tau} \right]} + i\omega_1 (\rho_{\alpha a, \alpha a}^{C^{*}} - \rho_{\beta a, \beta a}^{C^{*}}) = 0 \quad \dots (4.2a-8) .$$

Adding the above N equations together gives :

$$A(\omega) = Im \sum_n \rho_{\alpha n, \beta n}^{C^{*}} \\ \sim Im \left\{ -\omega_1 C \frac{\sum_n f_{\alpha n, \beta n}}{1 - \sum_n f_{\alpha n, \beta n}} \right\} \quad \dots\dots\dots (4.2a-9)$$

where

$$C = \rho_{\alpha a, \alpha a}^{C^{*}} - \rho_{\beta a, \beta a}^{C^{*}} \quad \dots\dots\dots (4.2a-10)$$

$$f_{\alpha n, \beta n} = \frac{1}{\left[i(\omega_{\alpha n, \beta n} - \omega) - \frac{1}{T_2} - \frac{1}{\tau} \right]} \quad \dots\dots\dots (4.2a-11) .$$

With Eq.(4.2a-9), we can easily calculate the ESR spectra of an electron-transfer system. It should be pointed out that Eq.(4.2a-9) was first derived by Norris through another method.⁸¹

Section B. Results

Traces of MV^{+} which have a light blue color were generated in the four chosen solvents through the photoinduced reduction of the corresponding dilute solution of MV^{2+} by visible light from a tungsten lamp for a very short

period(3-4 seconds).⁷¹ In the case of water as the solvent, 2-3 drops of sodium hydroxide solution(1 M) were added to the corresponding dication solution to assist the photoreduction.^{76,82} Since only a very small amount of $MV^{\cdot+}$ was produced, ESR lineshape broadening caused by possible dimerization between two radical cations could be avoided and the concentration of methyl viologen dication could well be assumed to be unchanged. All ESR spectra were recorded at 298 K. The ESR spectra of $MV^{\cdot+}$ at various concentrations of MV^{2+} in methanol are shown in Fig.(4.2b-1a) and Fig.(4.2b-1b), where the simulated spectra obtained by fitting the experimental spectra via the adjustment of the parameter τ are also presented. The ESR spectra of $MV^{\cdot+}$ in the other three solvents are similar to those in methanol although the measured life times(τ 's) vary greatly with different solvents at an approximately equal dication concentration.

Bimolecular electron transfer rate constants(k_{et} 's) in the four solvents were determined by linear least-square fittings according to Eq.(4.2a-3). A typical result from such fitting is shown in Fig.(4.2b-2). The measured electron transfer rate constants(k_{et} 's) in all four solvents are listed in Table (4.2b-1) along with the solvent dielectric constant ϵ and refractive index n .

Table (4.2b-1). Properties of the solvents and experimental electron-transfer rate constants $k_{et}(MV^{\cdot+}/MV^{2+})$ at 298 K.

Solvents	Dielectric Constant ϵ^{83}	Refractive Index n^{83}	$10^{-8} k_{et}$ ($M^{-1} s^{-1}$)
Water	1.3325029	78.36	4.19±0.06
Methanol	1.32652	32.66	1.96±0.08
Allyl Alcohol	1.4135 ^{83b}	21.6	1.01±0.08
Propargy Alcohol	1.4300	24.5	0.69±0.06

Section C. Discussion

According to classical electron-transfer theories, an electron-transfer rate constant can be expressed in the following general form for a homogeneous electron-transfer reaction:⁷⁸

$$k_{et} = Z_0 T^{\frac{1}{2}} \exp\left(-\frac{\Delta G^*}{RT}\right) \quad \text{..... (4.2c-1)}$$

where

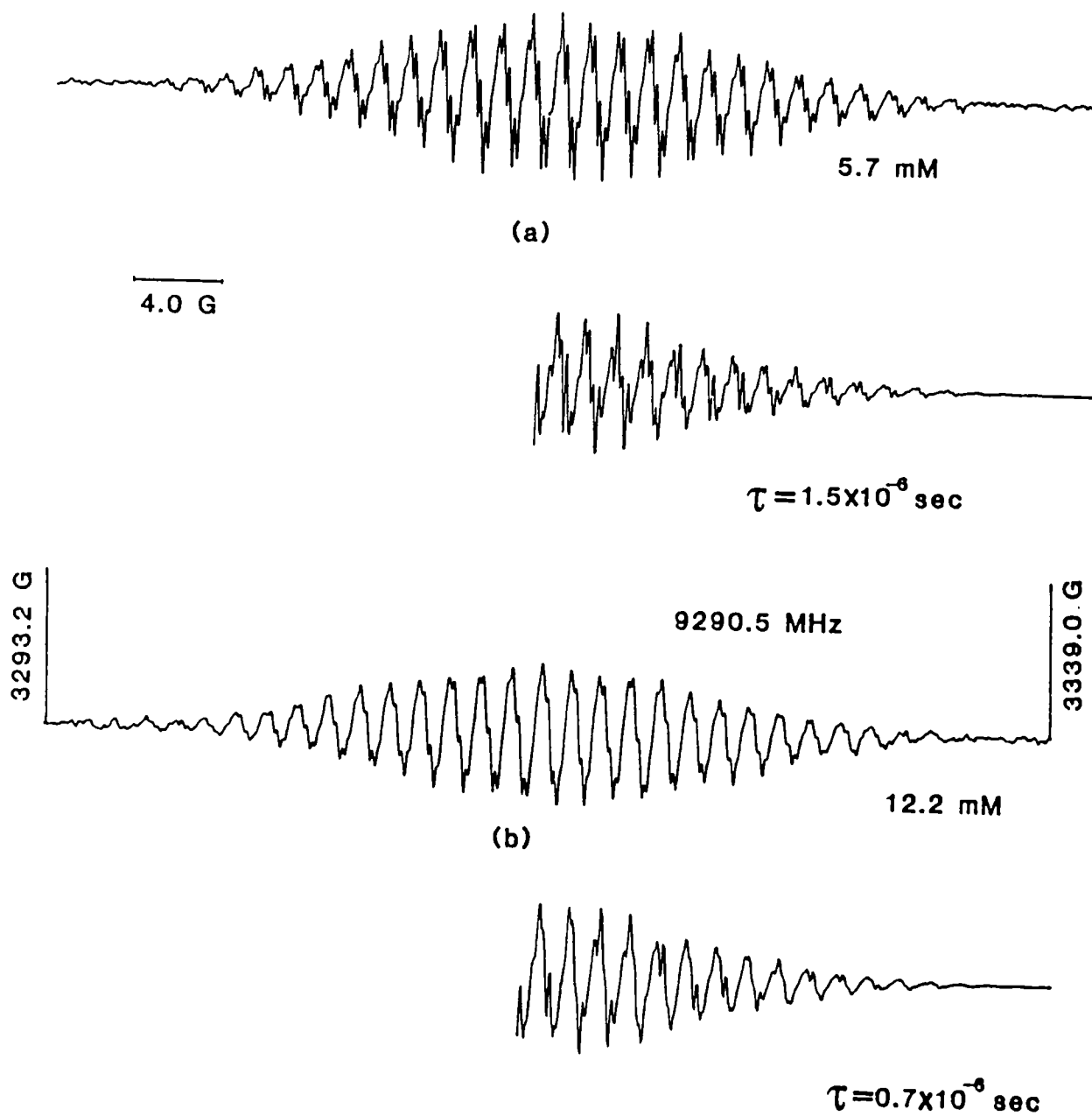


Fig.(4.2b-1a). First-derivative ESR spectra of the methyl viologen radical $MV^{\bullet+}$ in methanol. The simulated spectra shown beneath the experimental spectra.

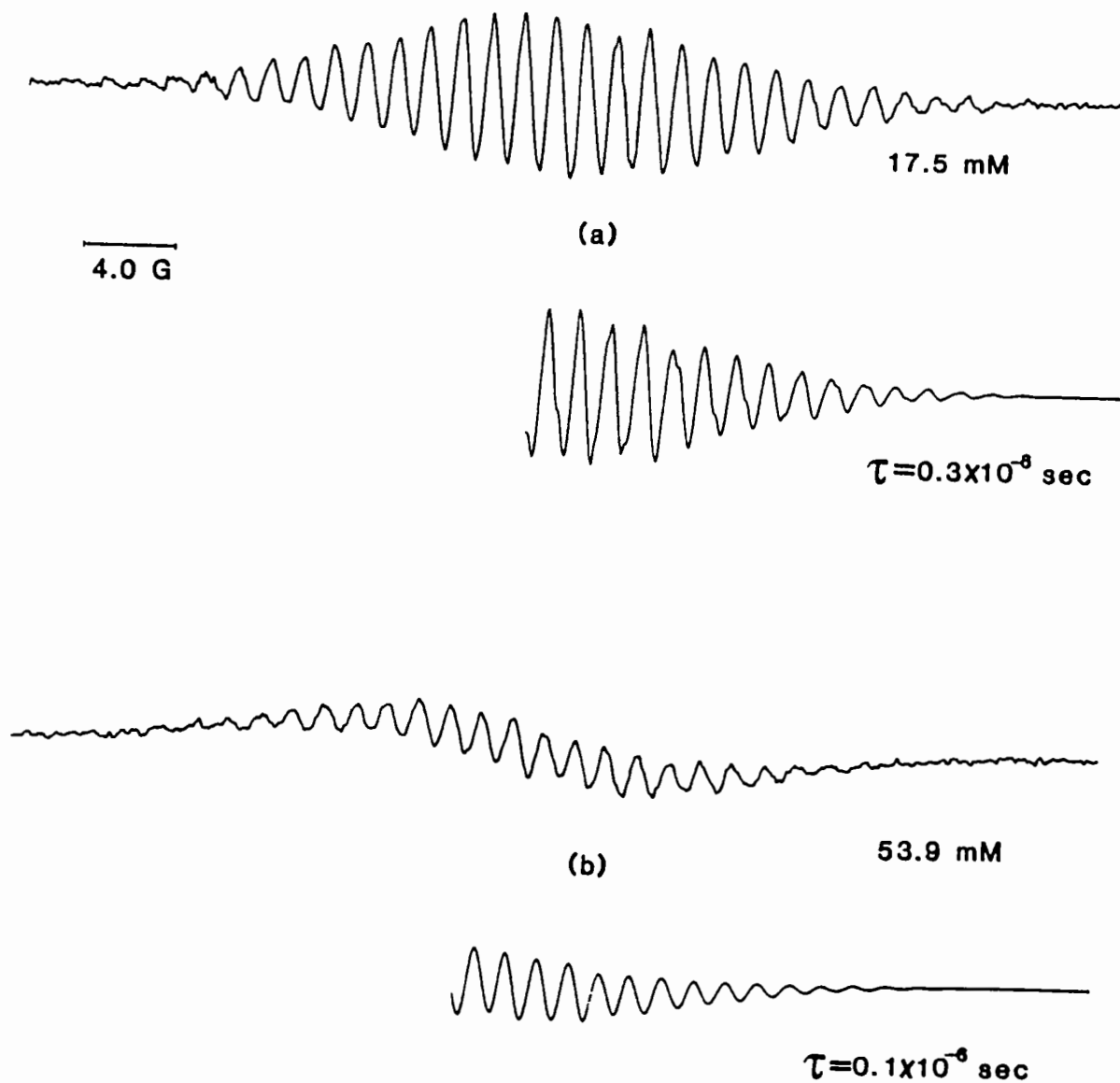


Fig.(4.2b-1b). First-derivative ESR spectra of the methyl viologen radical $MV^{\cdot+}$ in methanol. The simulated spectra shown beneath the experimental spectra.

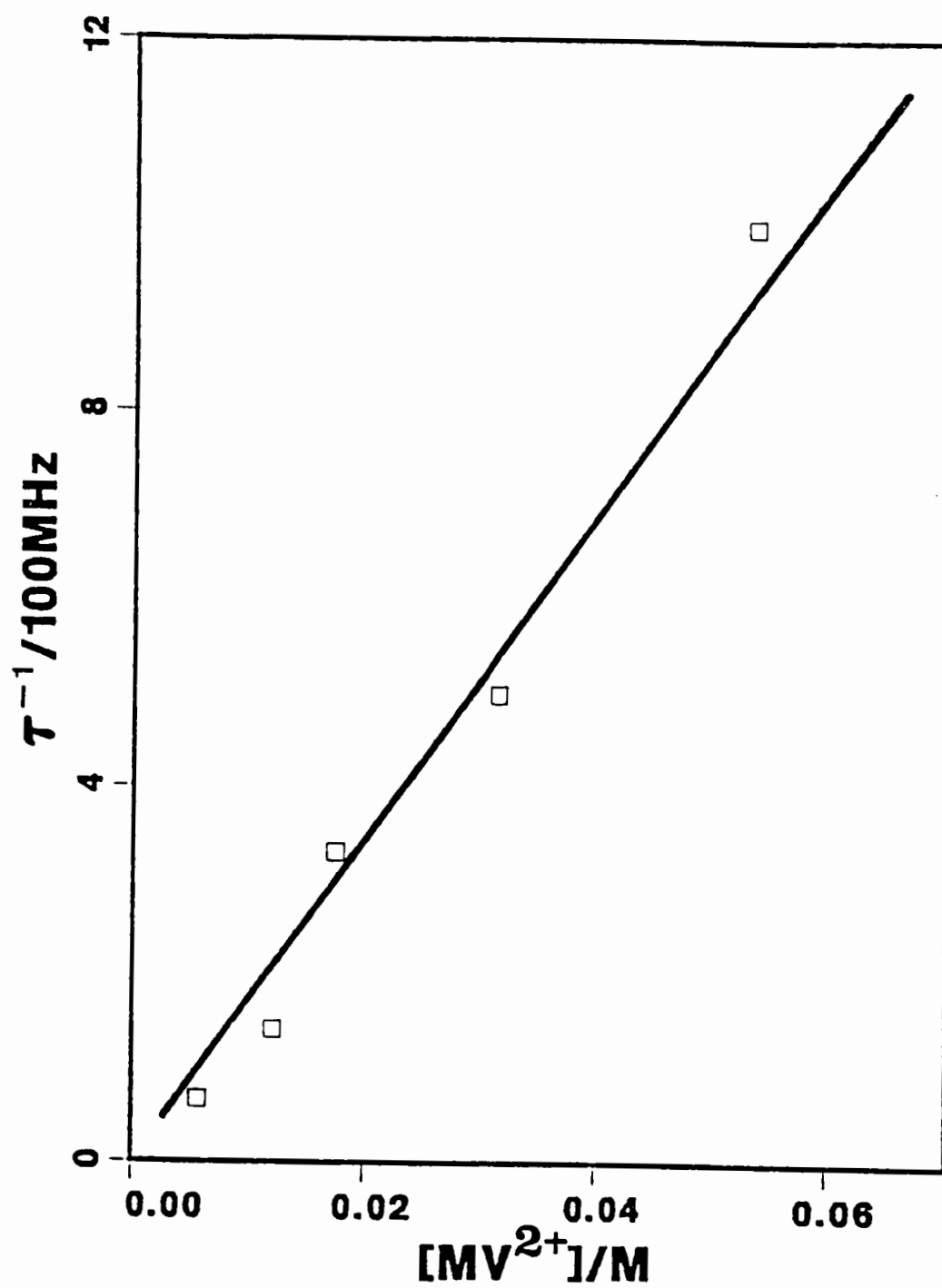


Fig.(4.2b-2). Inverse of the $MV^{\bullet+}$ life-time at 298 K as plotted against concentrations of $[MV^{2+}]$ in methanol.

$$\Delta G^* = W + \frac{(\lambda_o + \lambda_i)}{4} \quad \text{..... (4.2c-2)}$$

$$W = \text{Work Function} \quad \text{..... (4.2c-3)}$$

$$\lambda_o = \text{Outer Sphere Reorganization Energy} \quad \text{..... (4.2c-4)}$$

$$\lambda_i = \text{Inner Sphere Reorganization Energy} \quad \text{..... (4.2c-5) .}$$

Usually, the parameter λ_i can be regarded as being solvent-independent. The outer-sphere reorganization energy λ_o is given by :

$$\lambda_o = 332.4 g(r, d) \gamma, \text{ kcal/mol} \quad \text{..... (4.2c-6) .}$$

Here $g(r, d)$ is a distance parameter where r is the radius of reactants at the transition state and d is the distance between two reacting spheres at the transition state, and the solvent polarity parameter γ is given by

$$\gamma = \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad \text{..... (4.2c-7)}$$

where n and ϵ are the refractive index and the dielectric constant, respectively. $g(r, d)$ is always a positive solvent-independent quantity. Accordingly, the γ vs $\ln(k_{et})$ correlation diagram should be approximately a straight line with a negative slope if λ_o dominates ΔG^* as compared to W . This is usually the case for organic (cn) and (an) systems, where the work function can be safely omitted. Our experimental data (Fig. (4.2c-1)) certainly do not follow this prediction. This rules out the usual γ -dominating model.

On the other hand, the work function term W is given by :

$$W = \frac{664.85f}{\epsilon d} \quad \text{..... (4.2c-8)}$$

where f is a dimensionless constant usually less than one to account for the ionic strength effect, and d is the distance between the two reactants in the transition state as defined above. The implication of Eq.(4.2c-8) is that k_{et} increases with $1/\epsilon$, and the $\ln(k_{et})$ vs $1/\epsilon$ diagram will be approximately a straight line if W predominates over ΔG^* . As shown in Fig.(4.2c-2), the experimental result is nicely consistent with this model. Although the diagram is not a perfect straight line, the trend is correct. Using the slope of Fig.(4.2c-2) and taking the value of f as 0.7, an approximate d -value of 16 Å is estimated according to Eq.(4.2c-8). This approximately agrees with the relatively large size of the reactant molecules.

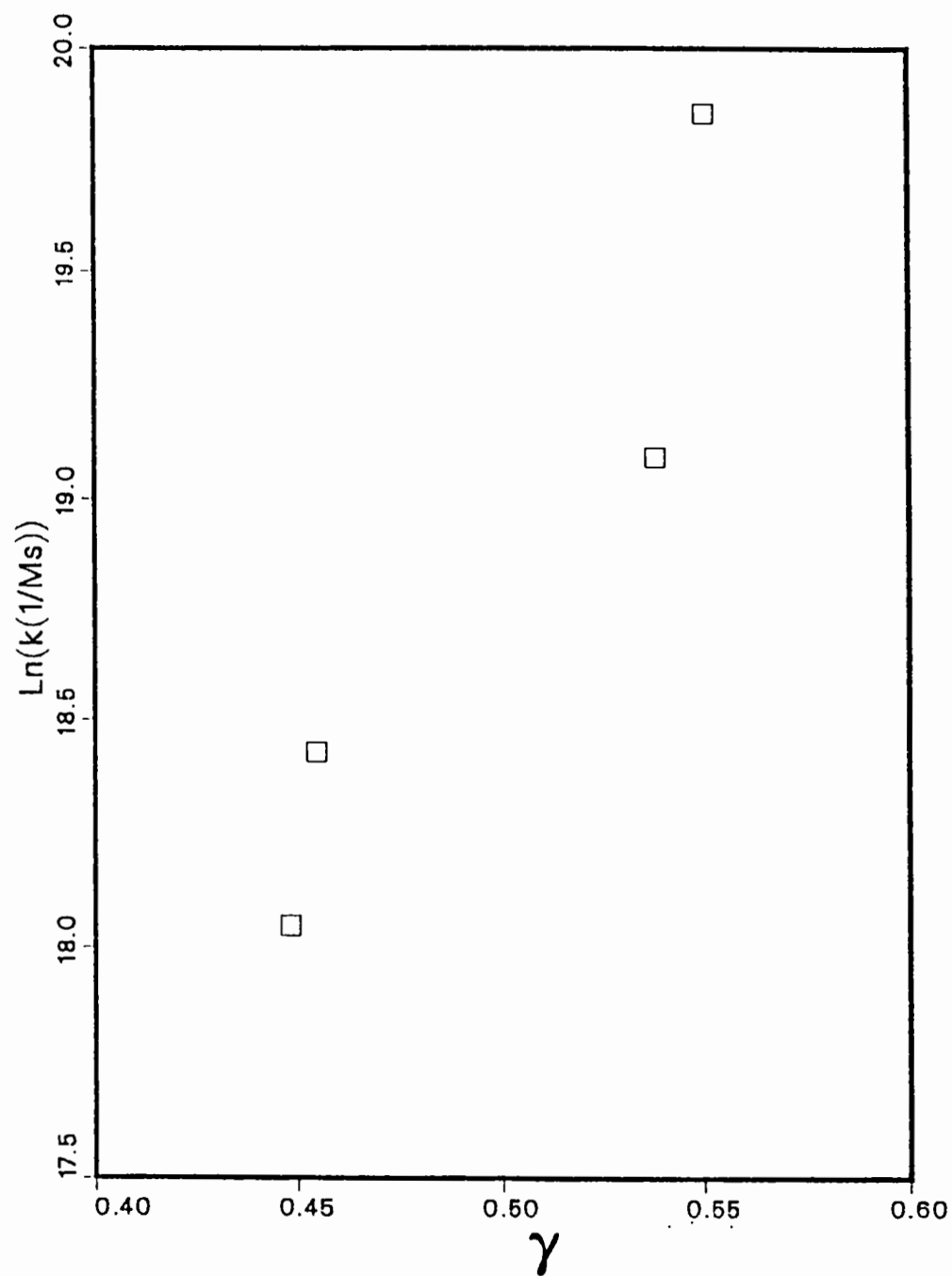


Fig.(4.2c-1). Electron transfer rate constant between $\text{MV}^{\cdot+}$ and MV^{2+} at 298 K plotted against γ .

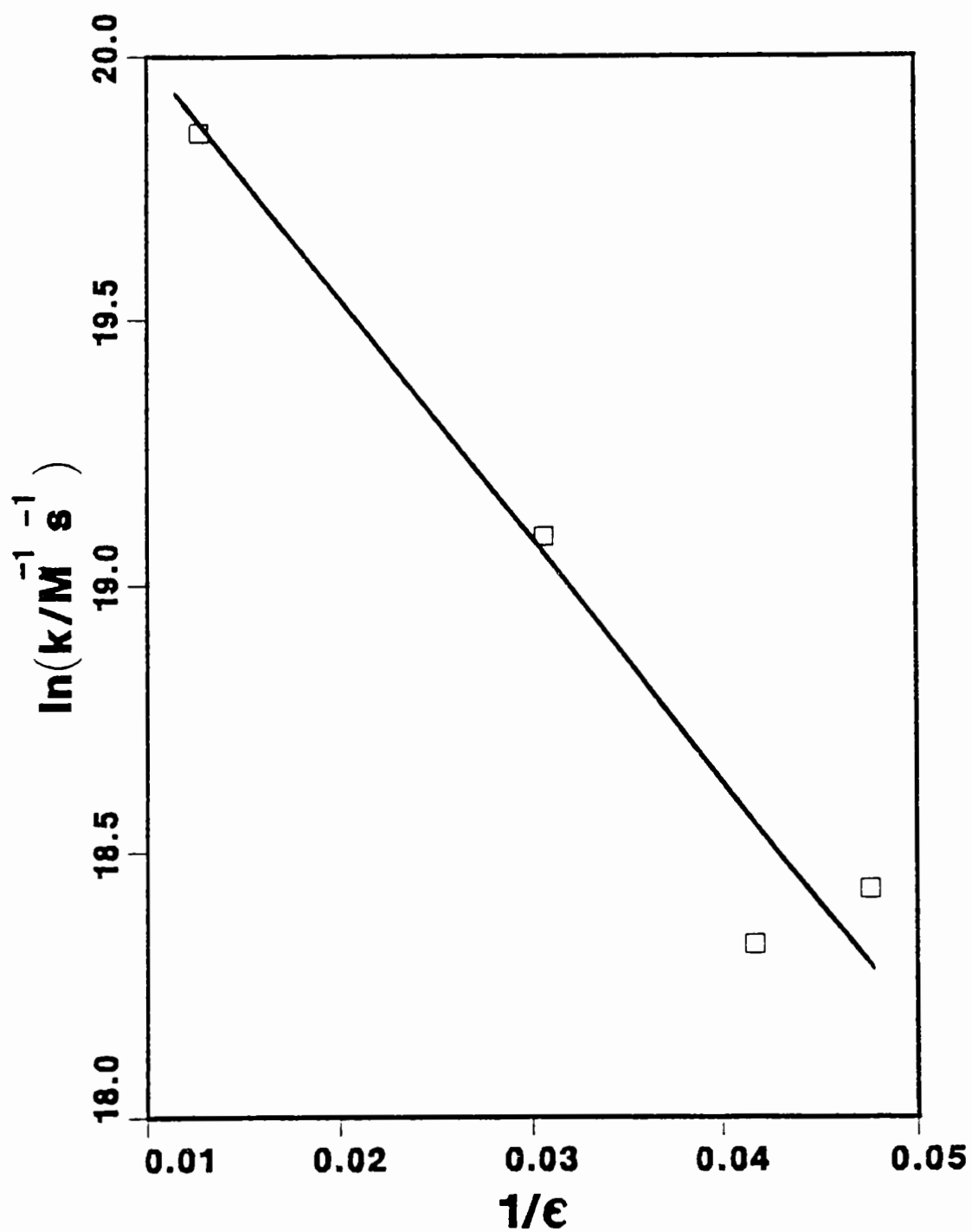


Fig.(4.2c-2). Electron transfer rate constant between $MV^{\cdot+}$ and MV^{2+} at 298 K plotted against ϵ .

CHAPTER 5

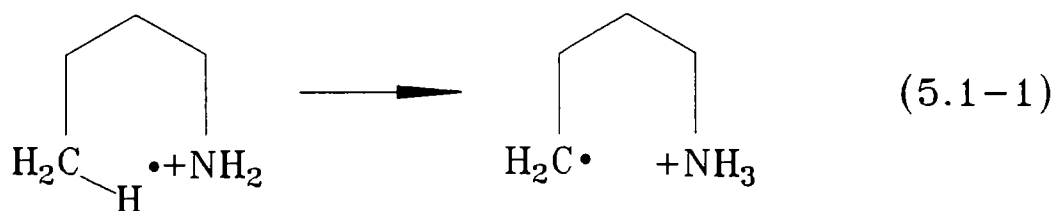
CHEMICAL REACTIONS OF RADICAL CATIONS

Introduction

In this Chapter, several new unimolecular thermal rearrangement reactions of radical cations are reported. The experimental results include radical cation 1,2-hydrogen transfer reactions (sigmatropic reactions), a cyclization reaction induced by nucleophilic attack, a Cope rearrangement, and a reaction involving cyclopropane ring-opening. In addition to their potential uses in future hole-induced syntheses, these new reactions can help us understand the kinds of fundamental principles governing the rearrangement reactions of radical cations. In particular, we want to test whether orbital symmetry or frontier orbital theory, which plays an important part in rationalizing neutral molecule reactions, plays a similar role in describing radical cation reactions. We also hope to find out if there is any special driving force in radical cation processes which is unavailable in the parent neutral molecule.

**Part I. ESR Evidence for the Rearrangement
at 77 K of Ionized Allylamine to the Distonic
Radical Cation $\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$**

It is well known that nitrogen-centered amine radical cations can easily undergo a 1,5-intramolecular hydrogen transfer from carbon to nitrogen both in the gas phase⁸⁴⁻⁸⁹ and in the condensed phase.⁹⁰⁻⁹¹ These and analogous reactions have been extensively studied recently by different groups, notably that of Radom,^{84,89} and can be well classified as radical abstraction reactions. The Hofmann-Löffler rearrangement⁹² (Reaction (5.1-1)) is an example, where the driving force of the reaction comes from the formation of a strong N-H bond in the substituted ammonium ion of the product.⁹³⁻⁹⁴ In this part, a totally different type of hydrogen migration in an unsaturated amine radical cation is reported, where the driving force of the reaction comes from the formation of a substituted iminium cation ($\text{RCH}=\text{NH}_2^+$) resulting from the 1,2-shift of a β -hydrogen atom to the γ, δ - unsaturated group.



Section A. Results

The ESR spectrum produced after γ -irradiation of prop-2-enylamine (allylamine) in the CF_3CCl_3 matrix is shown in Fig.(5.a-1a). It is composed of a well-resolved triplet of triplets with coupling constants of 22.7 G and 16.9 G respectively. Each triplet has a 1:2:1 intensity pattern, which indicates that two different groups of hydrogens are involved, every group consisting of two equivalent hydrogens. Since the 22.7 G coupling constant is reminiscent of typical α -hydrogen coupling constants in carbon-centered radicals, the spectrum can be assigned to a $\text{RCH}_2\text{CH}_2\cdot$ radical.⁹⁵ This assignment implies that a rearrangement has occurred in the parent radical cation. In order to confirm the rearrangement, N-dideuterioallylamine was synthesized. The ESR spectrum obtained from the radiolytic oxidation of its CF_3CCl_3 solid solution(Fig.(5.1a-1b)) is identical to that obtained from the nondeuterated allylamine. This clearly rules out any

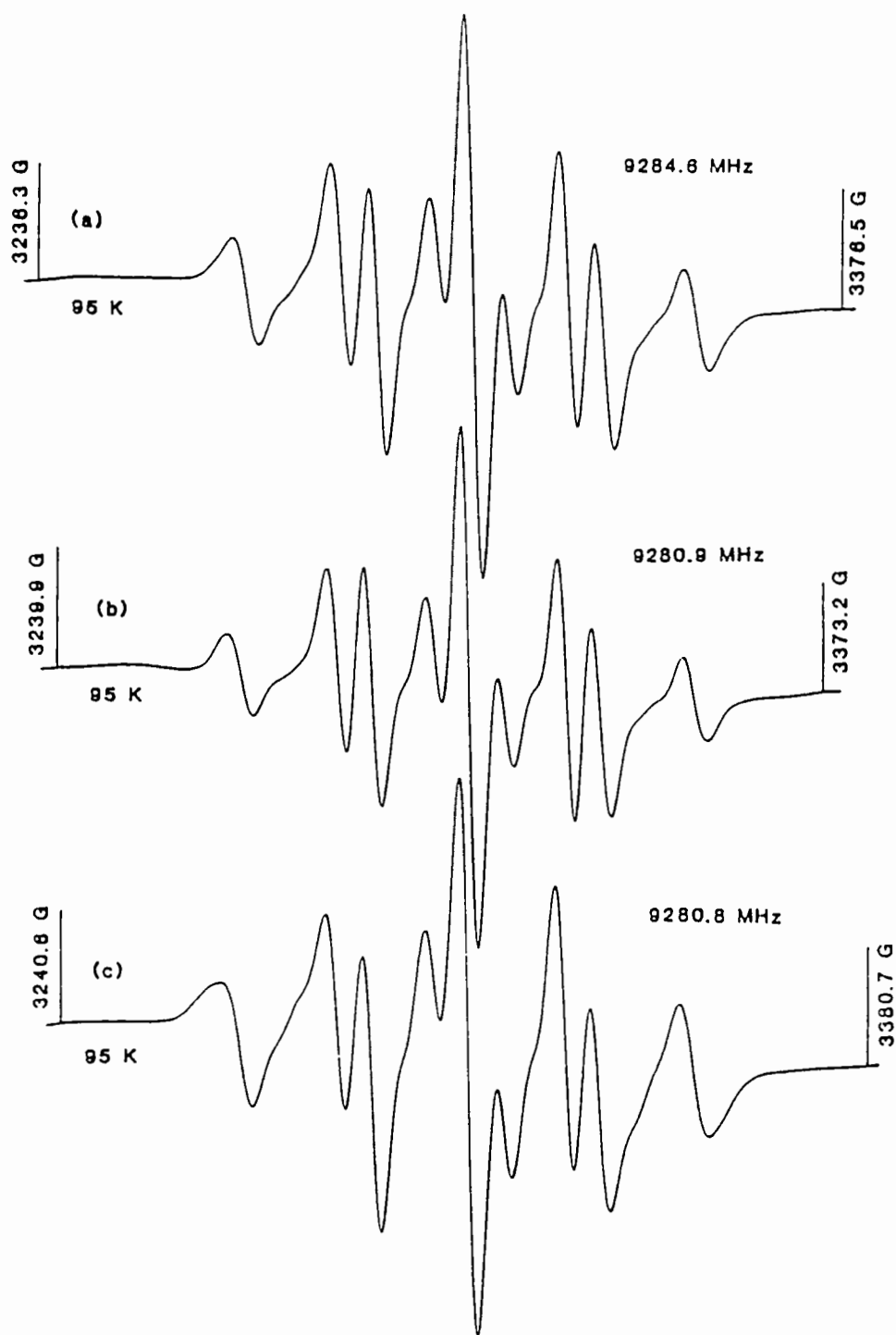


Fig.(5.1a-1). First-derivative ESR spectra at 95 K of the radical cations produced by γ -irradiation at 77 K of dilute solid CF_3CCl_3 solutions of (a) allylamine, (b) N,N-d_2 -allylamine, and (c) cyclopropylamine.

possibility for the parent nitrogen-centered radical cation to the signal carrier, but is consistent with the above assignment.

It has been demonstrated in an earlier work⁹⁶ that the cyclopropylamine radical cation undergoes a facile ring-opening reaction to give the distonic radical cation $\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$. Since this species is an isomer of the allylamine radical cation and has a $\text{RCH}_2\text{CH}_2\cdot$ structure, it could well be identical to the product of the allylamine radical cation rearrangement. In fact, the ESR spectra of the radical cations derived from radiolytic oxidation of cyclopropylamine and allylamine are indistinguishable from each other in CF_3CCl_3 (Fig.(5.1a-1a,c)), $\text{CF}_2\text{ClCFCl}_2$ (Fig.(5.1a-2a,b)), and CFCl_3 (Table (5.1a-1)) when measured under the same conditions. This coincidence clearly suggests that the same signal carrier is involved. Based on these observations, a rearrangement mechanism (Reaction (5.1a-1)), involving a simple hydrogen 1,2-sigmatropic shift can be proposed for the allylamine radical cation.

Other evidence supporting this rearrangement comes from the corresponding high-temperature(>110 K) ESR spectrum in the $\text{CF}_2\text{ClCFCl}_2$ matrix, which shows an 80 G doublet ESR pattern. The spectrum can be assigned to the propane-1-iminyl radical $\text{CH}_3\text{CH}_2\text{CH}=\text{N}\cdot$ caused by an ion-molecule reaction involving the loss of a proton followed by an intramolecular H transfer,⁹⁶ the spectrum being identical to that produced

Table (5.1a-1). ESR parameters for the propan-1-iminium-3-yl distonic radical cation produced by radiolytic oxidation of allylamine, and N,N-d₂-cyclopropylamine in Freon matrices.

Radical cation	Substrate	Solvent	T/K	Hyperfine couplings/G ^a	g_{iso}	Reference
$\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$	$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	CF_3CCl_3	140	22.6(2H _α), 17.4(2H _β)	2.0027	This work
			95	22.7(2H _α), 16.9(2H _β)	2.0026	This work
$\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{ND}_2^+$	$\text{CH}_2=\text{CHCH}_2\text{ND}_2$	CF_3CCl_3	140	22.7(2H _α), 17.5(2H _β)	2.0027	This work
			87	22.6(2H _α), 16.8(2H _β)	2.0027	This work
$\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$	$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	CFC_2Cl_3	150	22.6(2H _α), 17.2(2H _β)	2.0026	This work
$\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$	$\underline{c}\text{-C}_3\text{H}_5\text{NH}_2$	CF_3CCl_3	140	22.6(2H _α), 17.6(2H _β)	2.0026	This work
			95	22.6(2H _α), 17.0(2H _β)	2.0027	This work
			80-140	22.6(2H _α), 17.0 ^b (2H _β)	2.0026	96
$\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{ND}_2^+$	$\underline{c}\text{-C}_3\text{H}_5\text{ND}_2$	CF_3CCl_3	130	22.6(2H _α), 17.4(2H _β)	2.0027	This work
			100	22.5(2H _α), 17.1(2H _β)	2.0026	This work
$\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$	$\underline{c}\text{-C}_3\text{H}_5\text{NH}_2$	CFC_2Cl_3	150	22.6(2H _α), 17.1(2H _β)	2.0026	This work
			80-160	22.5(2H _α), 17.0(2H _β)	2.0027	96

^a 1 G=10⁻⁴ T. ^b The slight temperature dependence of the β-hydrogen hyperfine coupling constant for $\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2$ in CF_3CCl_3 observed in the present work was not reported in ref.96.

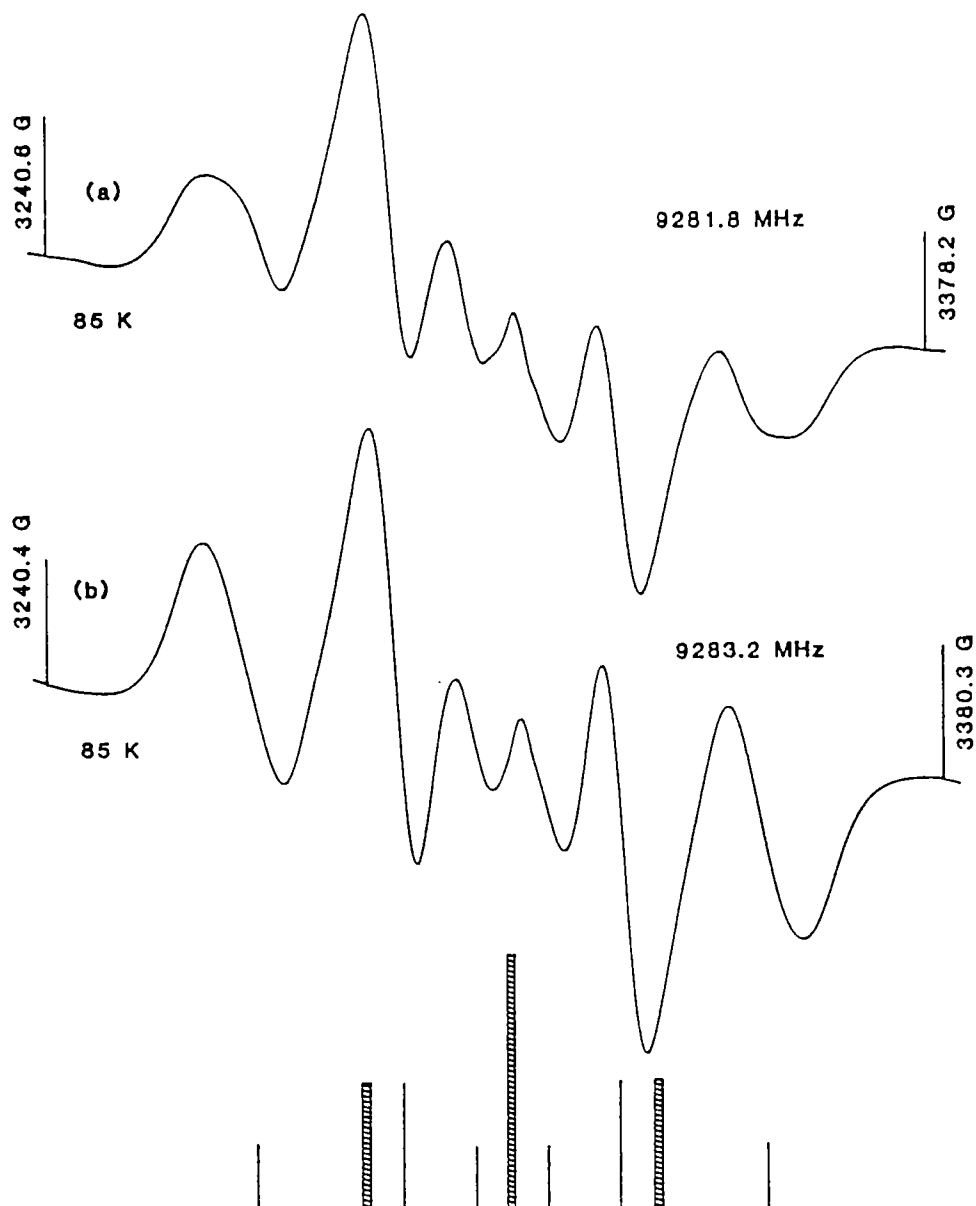
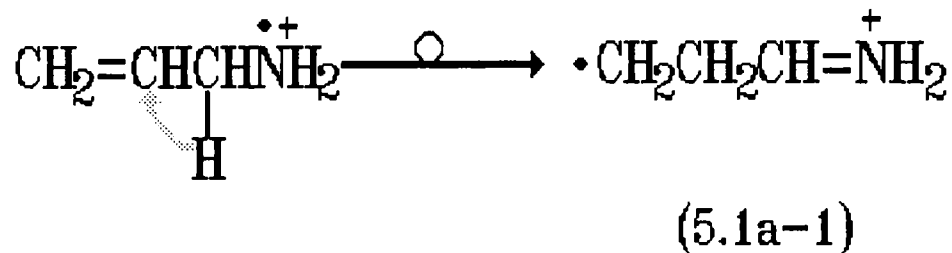


Fig.(5.1a-2). First-derivative ESR spectra at 85 K of the radical cations produced by γ -irradiation at 77 K of dilute solid $\text{CF}_2\text{ClCFCl}_2$ solutions of (a) allylamine and (b) cyclopropylamine. The stick diagram reconstruction shows a triplet of triplets with the $\underline{M}_I(2H_\beta)=0$ lines ($A(2H_\beta) < A(2H_\alpha)$) represented by bars to indicate the broadening of these components in the low-temperature spectra. These spectra became better resolved at higher temperatures before the onset of ion-molecule reactions at 105 K (see text), all nine components (cf. Fig.(5.1a-1)) being clearly observed under these conditions in each spectrum.

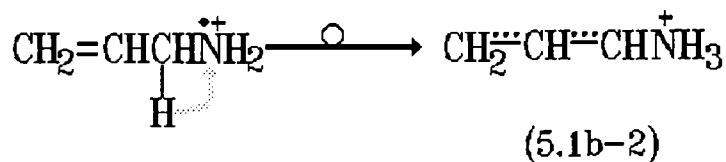
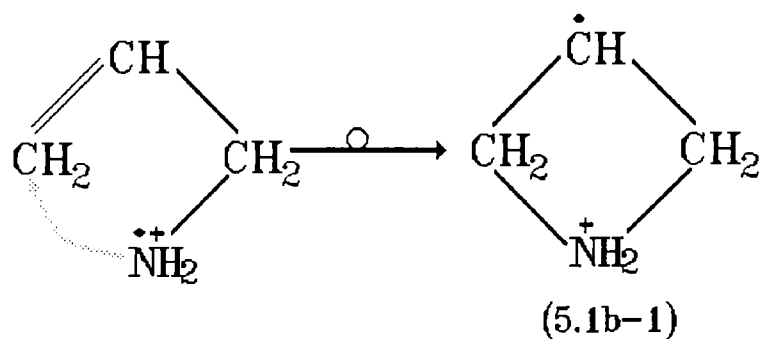


in the corresponding experiments from cyclopropylamine through a similar mechanism under the same conditions. This observation of the parallel secondary processes provides a strong basis for the identification of the rearranged distonic species. If the rearrangement to the distonic species had not occurred, the most probable ion-molecule reaction product of the parent allylamine radical cation would be $\text{CH}_2=\text{CH}-\text{CHNH}_2^+$, which clearly can not explain the observed large doublet.

A close comparison of the spectra in CF_3CCl_3 and CFCl_3 with those in $\text{CF}_2\text{ClCFCl}_2$ shows that although the total spectral widths are roughly the same, the lineshapes in the two matrices are different. This difference can be reconciled by the introduction of the selective line-broadening effect in $\text{CF}_2\text{ClCFCl}_2$ (Fig.(5.1a-2)) on the $\underline{M}_1(2H_\beta)$ components, which is a common phenomenon in the $\text{RCH}_2\text{CH}_2\cdot$ radical.⁹⁷

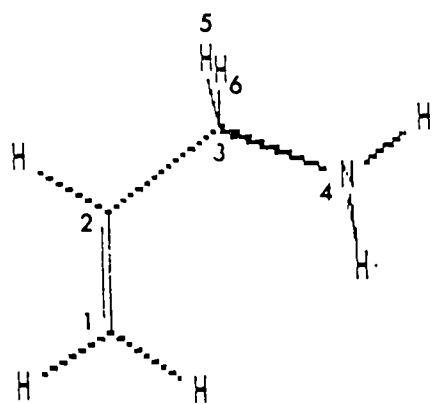
Section B. Discussion

Despite clear evidence for the presence of the distonic species $\cdot\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2^+$, two mechanistic problems remain unresolved. First, why does the parent allylamine radical cation prefer to undergo reaction (5.1a-1) to reaction (5.1b-1) and (5.1b-2) ? Specifically, in term of hydrogen transfer, why does hydrogen prefer this rearrangement orientation to that of forming the distonic species $\text{CH}_2^-\text{CH}^-\text{CHNH}_3^+$? Is the reason kinetic or thermodynamic ?

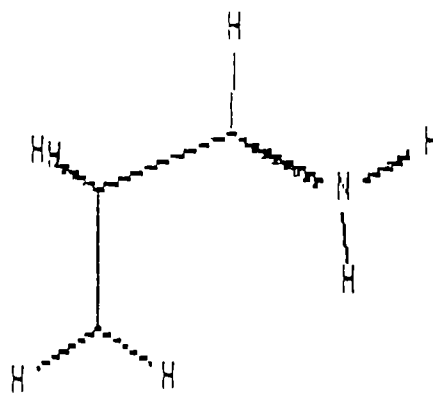


To answer these questions, detailed UHF-AM1 calculations were conducted. All equilibrium geometries were determined by minimizing the total energy with respect to all geometrical parameters using the standard Davidon-Fletcher-Powell procedure. The transition states were located by the usual reaction coordinate method and refined by minimizing the scalar gradient of the energy. All the stationary points were checked by calculating and diagonalizing the Hessian(Force constant) matrix, to verify the presence of six near zero eigenvalues but one negative value for transition states.^{37c} The optimized equilibrium structures along with the transition states are shown in Fig.(5.1b-1a,b). Their corresponding calculated heats of formations are listed in Table (5.1b-1). Based on Table (5.1b-1) and reaction coordinate calculations, the relative potential energy profile of intramolecular rearrangement reactions can be obtained as shown in Fig.(5.1b-2).

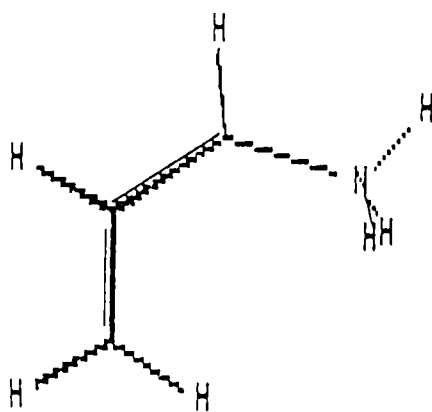
The species (1), (2), (3), (4) and (5) are various equilibrium structures for the potential energy surface located by the AM1 calculation. It can be seen from Table (5.1b-1) that the cyclized species (5) is 1.07 kcal/mol higher in energy than the parent radical cation (1). This shows that there is no thermodynamic driving force for the cyclization reaction (5.1b-1). Moreover, the calculated activation energy for this process (29.81 kcal/mol) is very large compared to the other two reactions (vide infra).



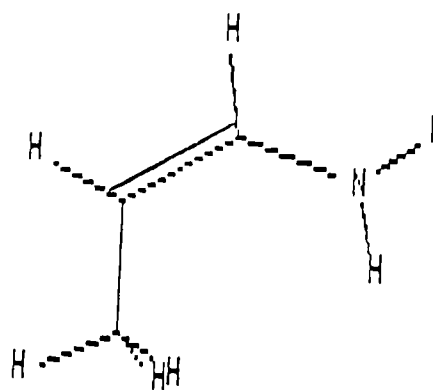
(1)



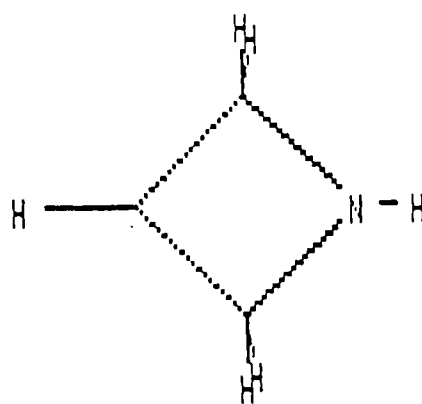
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(3)

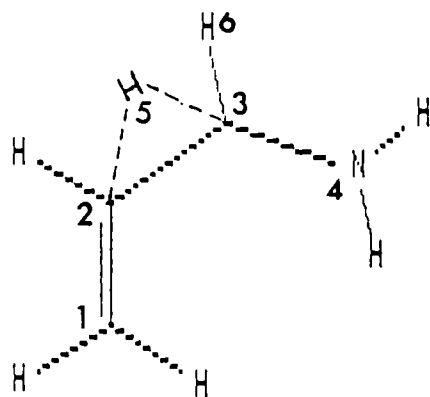


(4)

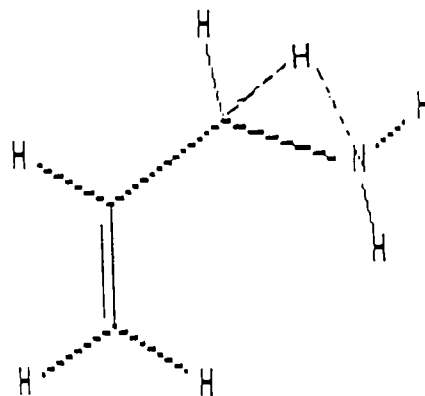


(5)

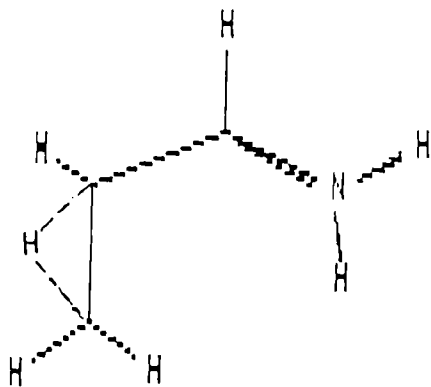
Fig.(5.1b-1a). AM1-UHF optimized equilibrium structures.



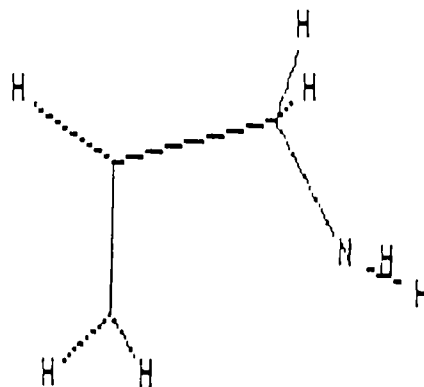
(6)



(7)



(8)



(9)

Fig.(5.1b-1b). AM1-UHF optimized transition structures.

Table (5.1b-1). The number of negative imaginary vibration modes (NIMAG), Heats of formation and relative energies for the species (1)-(9).

Species	NIMAG	Heat of Formation (kcal/mol)	Rel. Energy (kcal/mol)
(1)	0	206.08	0
(2)	0	186.93	-19.15
(3)	0	184.15	-21.93
(4)	0	176.27	-29.81
(5)	0	207.15	1.07
(6)	1	223.01	16.93
(7)	1	231.19	25.11
(8)	1	214.07	7.99
(9)	1	235.89	29.81

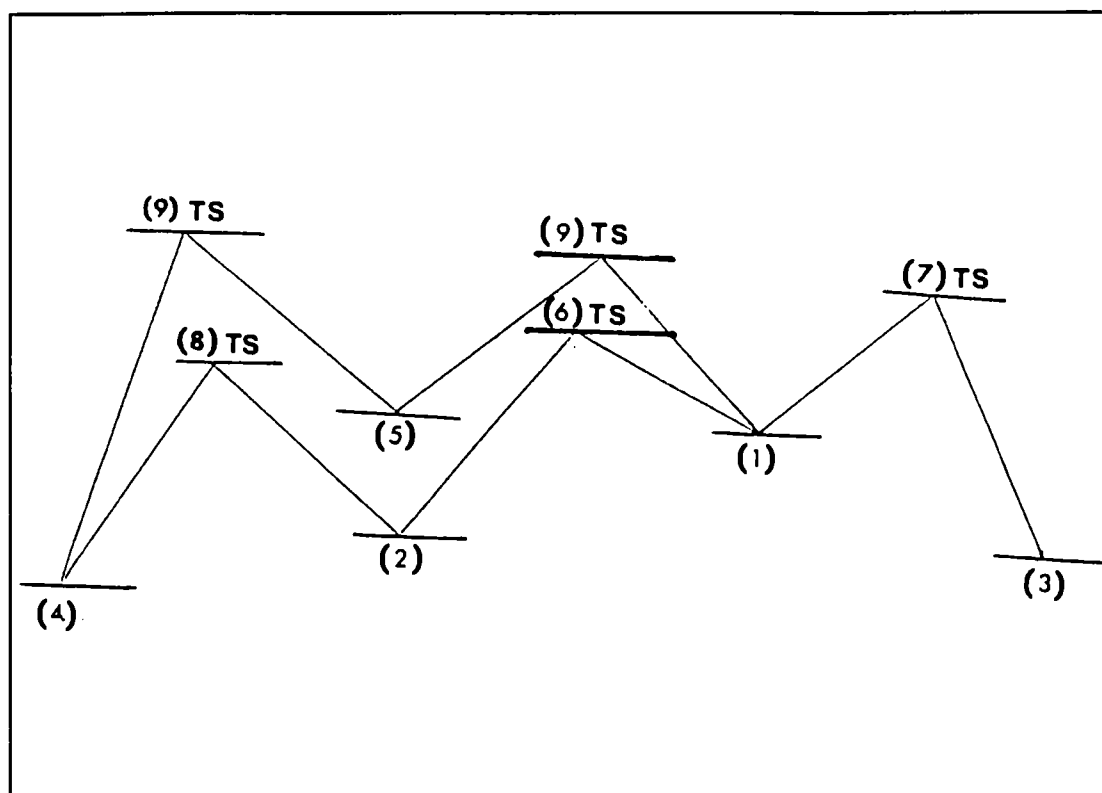


Fig.(5.1b-2). The relative energy diagram.

Therefore, we can safely neglect it.

On the other hand, the hydrogen transfer reactions (5.1a-1) and (5.1b-2) are both found to be exothermic. Surprisingly reaction (5.1b-2) is 2.72 kcal/mol more exothermic than the experimentally observed reaction (5.1a-1). This implies that the actual reaction is governed by kinetic control. This is in fact confirmed by AM1 calculations which indicate that the activation energy of the former reaction is ca. 8 kcal/mol larger than that of the latter (Table (5.1b-1)). At the same time, it is perhaps hard to understand that although the unpaired electron or hole is originally located on the nitrogen atom of the parent radical cation as shown in Table (5.1b-2) for calculation results and

by photoelectron spectroscopic studies,^{98,99} the hydrogen prefers to shift from the neighboring carbon to the olefin site. However, using the ideas of frontier-orbital theory,¹⁰⁰ the transition state can be formulated in terms of two fragments, i.e., a hydrogen atom and $\text{CH}_2=\text{CH}-\text{CH}=\text{NH}_2^+$ (Table (5.1b-2)), in which case the in-phase character of the two central neighboring carbon p orbitals in the LUMO of $\text{CH}_2=\text{CH}-\text{CH}=\text{NH}_2^+$ clearly assists the experimentally observed hydrogen shift orientation. In contrast, a hydrogen shift to the nitrogen is not forced by the nodal properties of the LUMO (Fig.(5.1b-3)). The calculated small activation energy can be intuitively ascribed to the contribution of the resonance structure 2 as shown in Fig.(5.1b-4). In order to confirm this point, a similar hydrogen transfer reaction of the radical cation $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2\text{NH}_2^+$ was studied computationally. The calculated activation energy in this latter case was 8.54 kcal/mol smaller than that of the corresponding hydrogen shift reaction of the allylamine radical cation, which is consistent with the assumption of the resonance stabilization of the transition state. In contrast, the activation energy for hydrogen transfer reaction of the radical cation $\text{CH}_2=\text{CH}-\text{CH}_2\text{NMe}_2^+$ is 13.84 kcal/mol larger than that of the allylamine radical cation. The high activation energy implies the absence of the hydrogen shift at low temperature, which has been confirmed by our unpublished experimental results.

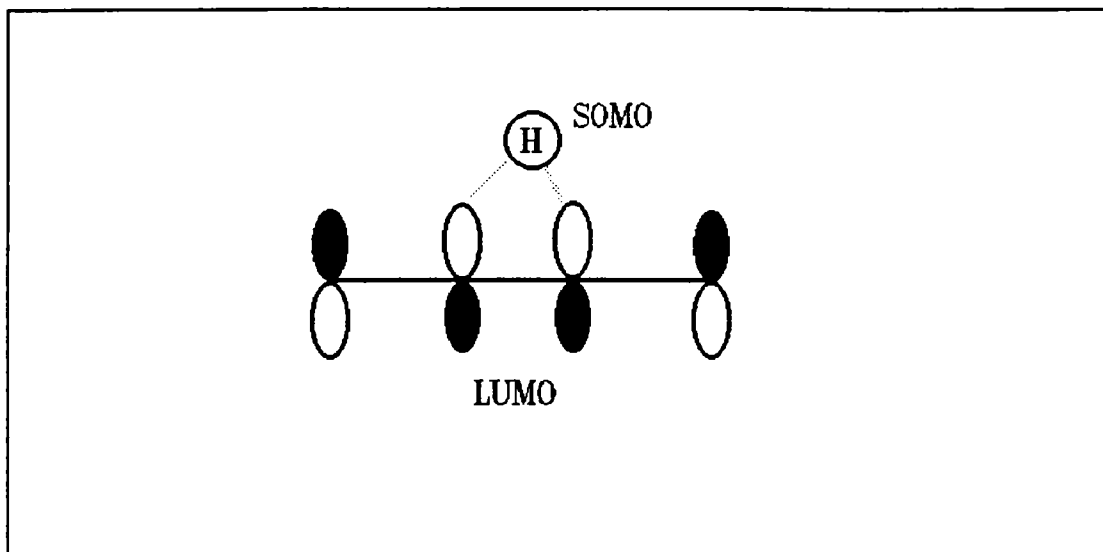


Fig.(5.1b-3). The frontier orbitals of the hydrogen 1,2-shift.

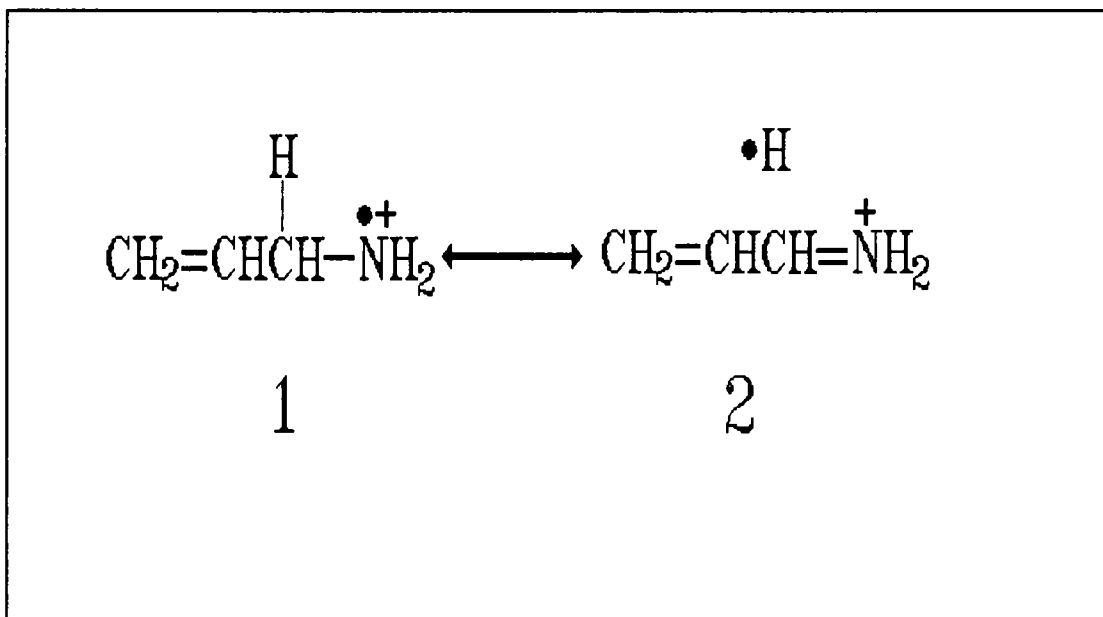


Fig.(5.1b-4). Resonance structures of the allylamine radical cation.

The species (2) may undergo further hydrogen 1,2-shift to give (4) which is 10 kcal/mol lower in energy than (2). However, the calculated activation energy for the reaction is very high (33.1 kcal/mol), which prevents the distonic species (2) from any further reaction.

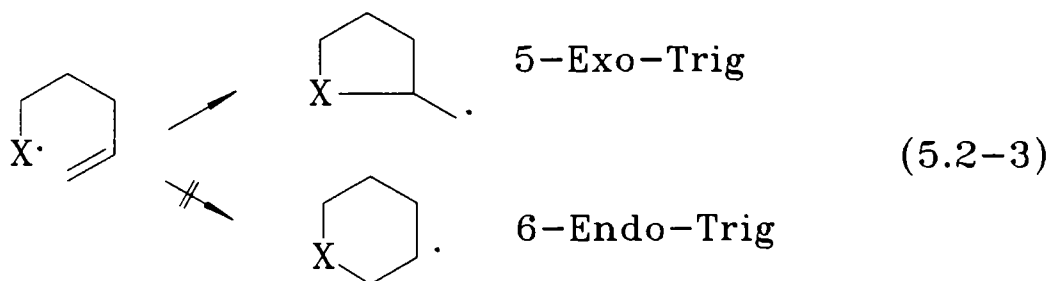
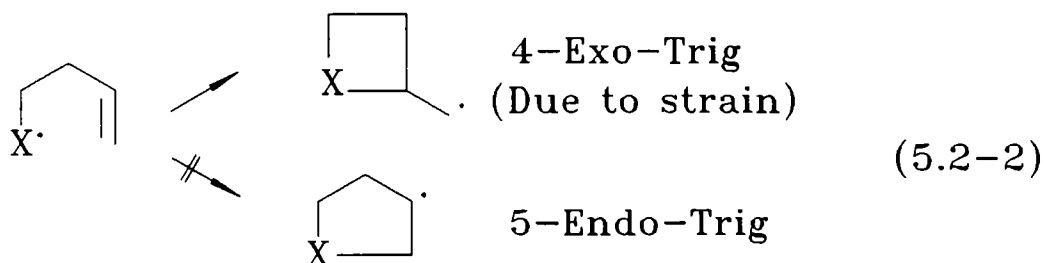
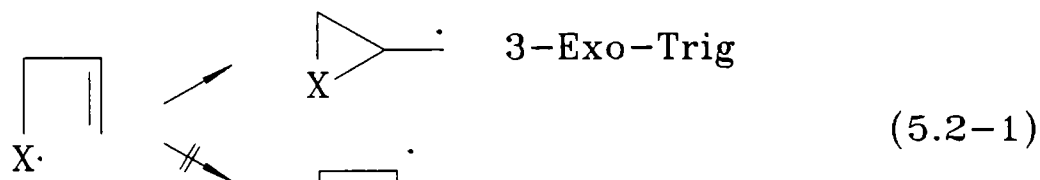
In conclusion, our AM1 calculations indicate that the allylamine radical cation (1) is more likely to undergo hydrogen 1,2-shift to the olefin site than to the cationic radical site. This transfer preference can be attributed to the LUMO phase property of the $\text{CH}_2=\text{CH}-\text{CH}=\text{NH}_2^+$ cation.

Table (5.1b-2). Atomic-orbital spin populations of the (1), (2) and (6) calculated by an INDO method using AM1-optimized geometries.

Species	p(C1)	p(C2)	p(C3)	p(N4)	s(H5)	s(H6)
(1)	-0.037	0.034	-0.057	0.957	0.063	0.070
(2)	0.979	-0.010	0.003	-0.001	0.022	-0.000
(6)	0.741	-0.291	0.053	0.276	0.290	0.006

**Part II. An ESR Study of Radical Cation Cyclization
in the Radiolytic Oxidation of But-3-en-1-ol Solutions
in Freon Matrices**

The cyclization reaction is one of the most fundamental processes in organic chemistry. Some general rules have been proposed based on many experimental results concerning normal organic or neutral radical cyclization reactions. The following reactions (5.2-1)-(5.2-3), where the nomenclature is based on Baldwin's paper,¹⁰¹ show the general rule for neutral radical cyclization reactions. Whether this rule can be extended to the corresponding radical cation cyclization reactions is still an unresolved question. Recently, it has been found that the 1,5-hexadiene radical cation can undergo a facile 6-endo cyclization to form the cyclohexane-1,4-diyl radical cation instead of the 5-exo cyclization for neutral radicals.¹⁰² This result clearly contradicts the above rule for neutral radicals. In this part, another interesting example involving 5-endo cyclization of but-3-en-1-ol radical cation is reported along with a surprising fragmentation reaction of neutral alkoxyl radical in Freon matrices.



Section A. Results

The spectrum a in Fig.(5.2a-1) shows ESR signals from the radicals produced by the radiolytic oxidation of but-3-en-1-ol in the CF_3CCl_3 matrix at 77 K. As indicated by the stick diagram, the main pattern is composed of a well-resolved 1:4:6:4:1 quintet (34.8 G(4H)) of doublets (22.6 G(2H)). These coupling constants are almost identical to those of the tetrahydrofuran-3-yl radical¹⁰³ as listed in Table (5.2a-1). This strongly suggests that an 5-endo

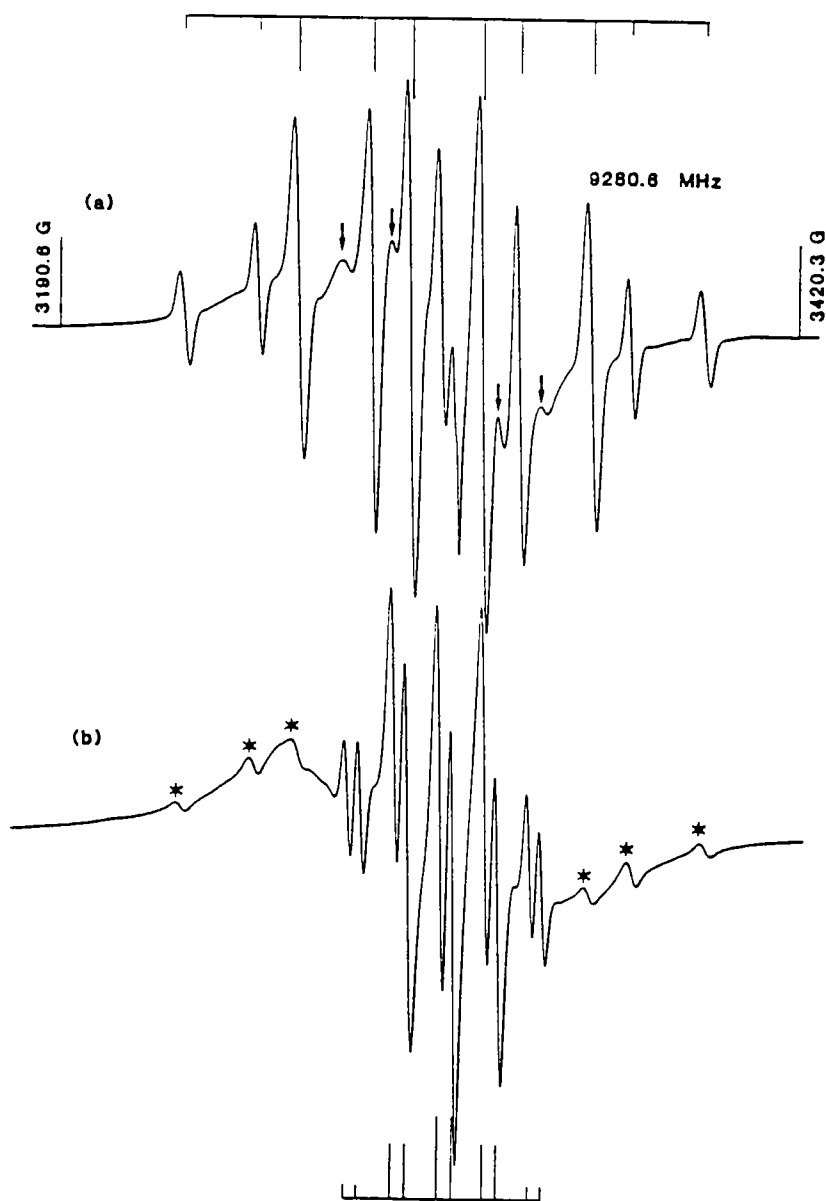


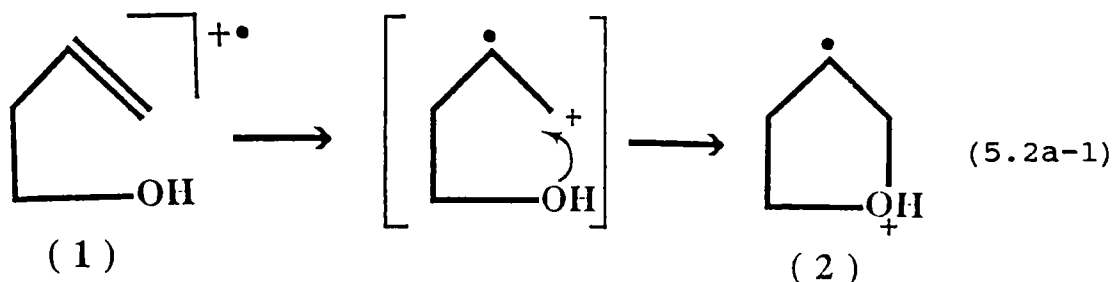
Fig.(5.2a-1). First-derivative ESR spectra of radicals produced by γ -irradiation at 77 K of dilute (1 mol %) solid solutions of but-3-en-1-ol (a) in CF_3CCl_3 , recorded at 144 K, and (b) in $\text{CF}_2\text{ClCFCl}_2$, recorded at 115 K. The dominant hyperfine pattern in (a) represented by the upper stick diagram reconstruction is that of the protonated tetrahydrofuran-3-yl radical, while the weaker signals represented by arrows are spectral components of the allyl radical. Conversely, the intense pattern in (b) is from the allyl radical (lower stick diagram) while the weaker signals marked by asterisks are from the protonated tetrahydrofuran-3-yl radical. Similar results were obtained with solutions prepared from but-3-en-1-ol samples (99%) obtained from Wiley Organics and the Aldrich Chemical Company.

Table (5.2a-1). ESR parameters for radicals produced by radiolytic oxidation of but-3-en-1-ol and 3-methyl-but-3-en-1-ol in Freon matrices.

Radical cation or radical	Substrate	Solvent	T/K	Hyperfine couplings/G ^a	g_{iso}	Ref.
(2)	but-3-en-1-ol	CF ₃ CCl ₃	140	22.6(1H _α), 34.8(4H _β)	2.0030	This work
Tetrahydrofuran-3-yl	tetrahydrofuran	CF ₂ ClCFC1 ₂	110	21.5(1H _α), 35.4(4H _β)	2.0025	103
(4)	but-3-en-1-ol	CF ₂ ClCFC1 ₂	115	14.4(4H) ^c , 4.1(1H)	2.0030	This work
(4)	propylene	CF ₂ ClCFC1 ₂	115	14.4(4H) ^c , 4.1(1H)	2.0029	<u>b</u>
(3-methyl-2)	3-methyl-but-3-en-1-ol	CF ₃ CCl ₃	140	24.8(3H _{Me}), 31.5(4H _β)	2.0031	This work
(2-methyl-4)	3-methyl-but-3-en-1-ol	CF ₂ ClCFC1 ₂	120	14.1(4H) ^c , 3.2(3H _{Me})	2.0030	This work

^a1G' = 10⁻⁴T. ^bX.-Z. Qin and F. Williams, unpublished work. ^cThe exo and endo hydrogen couplings were indistinguishable.

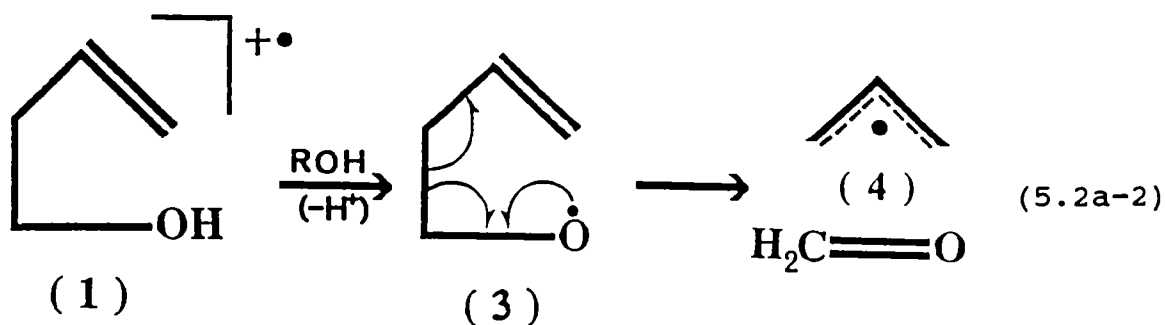
cyclization of the but-3-en-1-ol radical cation (1) to the distonic species (2) (Reaction (5.2a-1)) takes place since (2) has the same radical center as the tetrahydrofuran-3-yl radical.



Similar oxidation studies were carried out in the Freon CFCl_3 , $\text{CF}_2\text{ClCFCl}_2$, and $\text{CFCl}_2\text{CFCl}_2$ matrices. The CFCl_3 experiment gave a poorly-resolved spectrum, and only the outer lines of the proposed radical cation (2) could be recognized. On the other hand, the spectrum from radicals produced in the $\text{CF}_2\text{ClCFCl}_2$ matrix (Fig. (5.2a-1b)) surprisingly gave a clear set of lines from another radical in addition to the much weaker signals from (2). The stronger group of signals consists of a pattern from quintet [$\underline{A}(4\text{H})=14.4$ G] of doublets [$\underline{A}(1\text{H})=4.1$ G], which is indistinguishable from that of the well-known neutral allyl radical produced from the ion-molecule reaction of propene in the same matrix. This indicates that a fragmentation reaction leading to the allyl radical has occurred. The results obtained in $\text{CFCl}_2\text{CFCl}_2$ were

intermediate between those in CF_3CCl_3 and $\text{CF}_2\text{ClCFCl}_2$, the spectra consisting of signals of comparable intensity from (2) and the allyl radical. It should also be pointed out that a closer examination of Fig.(5.1a-1a) shows that besides the strong signals of (2), there is a group of much weaker ones (marked with arrows) that match perfectly with the signals of the allyl radical. Clearly, a very small portion of the parent but-3-en-1-ol underwent the fragmentation even in this matrix.

These results in the haloethane matrices illustrate that a process leading to allyl radical formation obviously competes with the cyclization reaction of the but-3-en-1-ol radical cation. This competition could be explained by considering that there are different degrees of solute clusterings through hydrogen bonding in different matrices. Under radiolytic oxidation, these alcohol clusterings may give rise to proton transfer from the alcohol radical cation to a neighboring molecule in the cluster, resulting in the formation of the alkoxyl neutral radical (3).¹⁰⁴ The radical (3) in turn undergoes a well known β -carbon scission reaction to give the allyl radical (4) and formaldehyde (Reaction (5.2a-2)).¹⁰⁵



Similar studies on 3-methylbut-3-en-1-ol solutions (98%, Wiley Organics) also gave the two corresponding radicals, consistent with the above model. However, in this case the relative signal intensity of the cyclized radical was smaller in all the matrices. Nevertheless, the largest ratio of the cyclized to allyl radical was obtained in the CF_3CCl_3 matrix. This in turn implies that the degree of clustering is most inefficient in CF_3CCl_3 . This is not surprising considering the fact that the CF_3CCl_3 molecule has the largest electric dipole moment amongst these matrix molecules, making it most able to disperse the alcohol molecules. In order to further establish the proposed cyclization, methyl but-3-enyl ether was synthesized. The spectrum obtained from its γ irradiated Freon solutions possessed a similar pattern as that of (2), which is exactly what is expected from the cyclization model.

Section B. Discussion

The AM1 calculation on the system indicates that the cyclization of (1) to (2) is exothermic by 11 kcal/mol. If we choose the distance between the oxygen and the terminal carbon of the ethylene as the reaction coordinate, the calculated endo cyclization is a down-hill process with no activation energy barrier (Fig.(5.2b-1)). The geometry-optimized cyclized structure is shown in Fig.(5.2b-2). In contrast, a similar reaction coordinate calculation (Fig.(5.2b-3)) on the exo cyclization using the distance between the oxygen and the non-terminal carbon of the ethylene as the reaction coordinate indicates that the exo cyclization is an uphill process with no thermodynamic driving forces.

These semi-empirical calculation results correlate well with our experimental findings. However, Davies and his coworkers¹⁰⁶ have reported only exo cyclizations for their protonated alkoxyl radical systems which can formally be thought of as radical cations. This contradiction may be related to the distribution of the unpaired electron. In our case, both photoelectron spectroscopy¹⁰⁷ and AM1 calculations indicate that the unpaired electron is mainly distributed on the double bond, denoting that the endo cyclization is

virtually a nucleophilic addition reaction as formulated in reaction (5.2a-1). In fact, a very similar nucleophilic addition mechanism has recently been suggested¹⁰⁷ on the basis of product analyses to explain why the regioselectivity previously observed for the cyclization of pent-4-en-1-ol induced by certain oxidants¹⁰⁷ differs from that obtained for the cyclization of the corresponding alkoxy radical.¹⁰⁸ In the case of Davies and his coworkers, however, the unpaired electron is located on the oxygen, so the cyclization would be expected to follow the rule of the neutral radical like that of neutral alkoxy radicals.^{109,110}

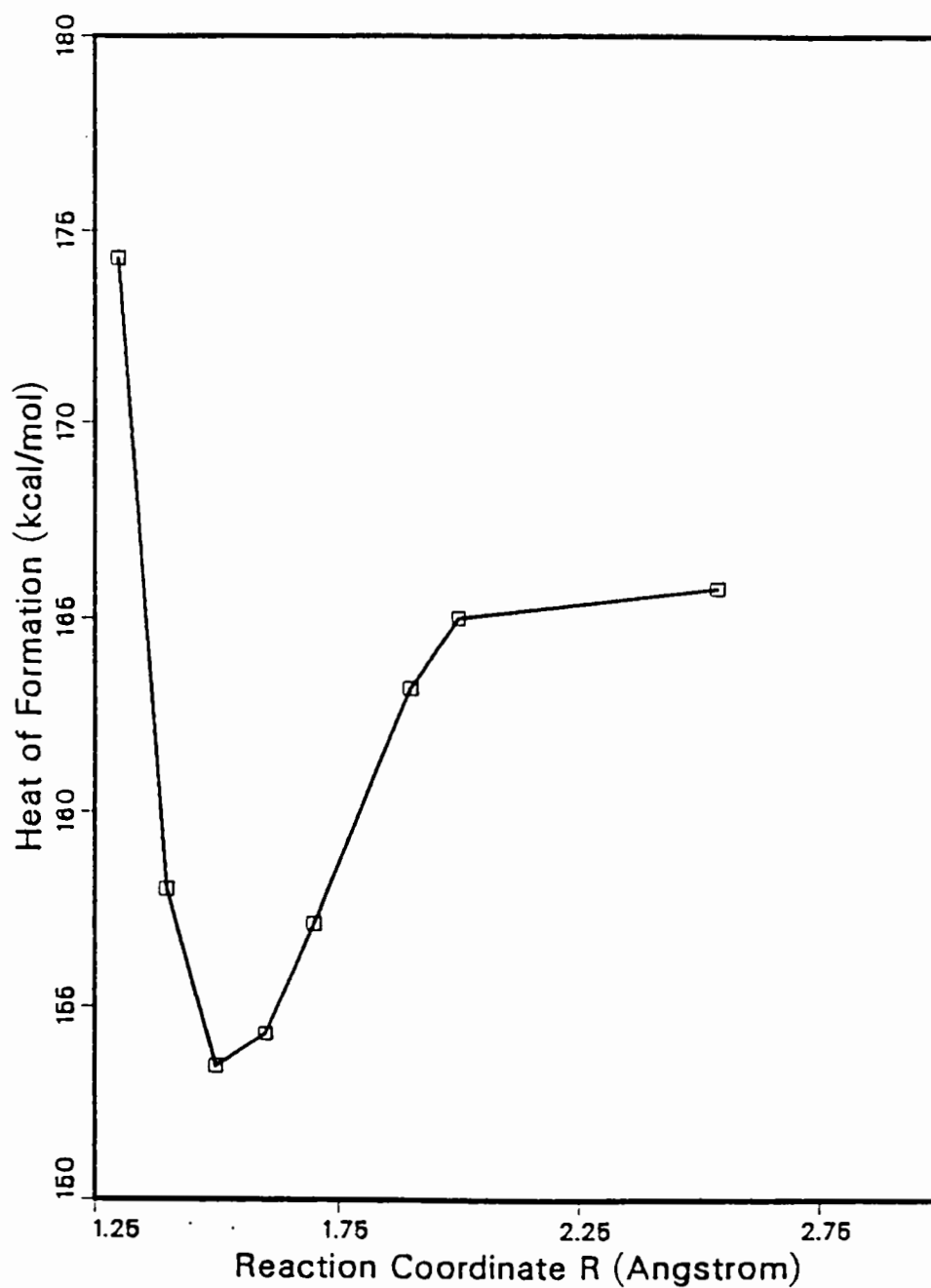


Fig.(5.2b-1). The reaction coordinate calculation for the endo cyclization of the but-3-en-1-ol radical cation, where R represents the distance between the oxygen and terminal carbon of the ethylene group.

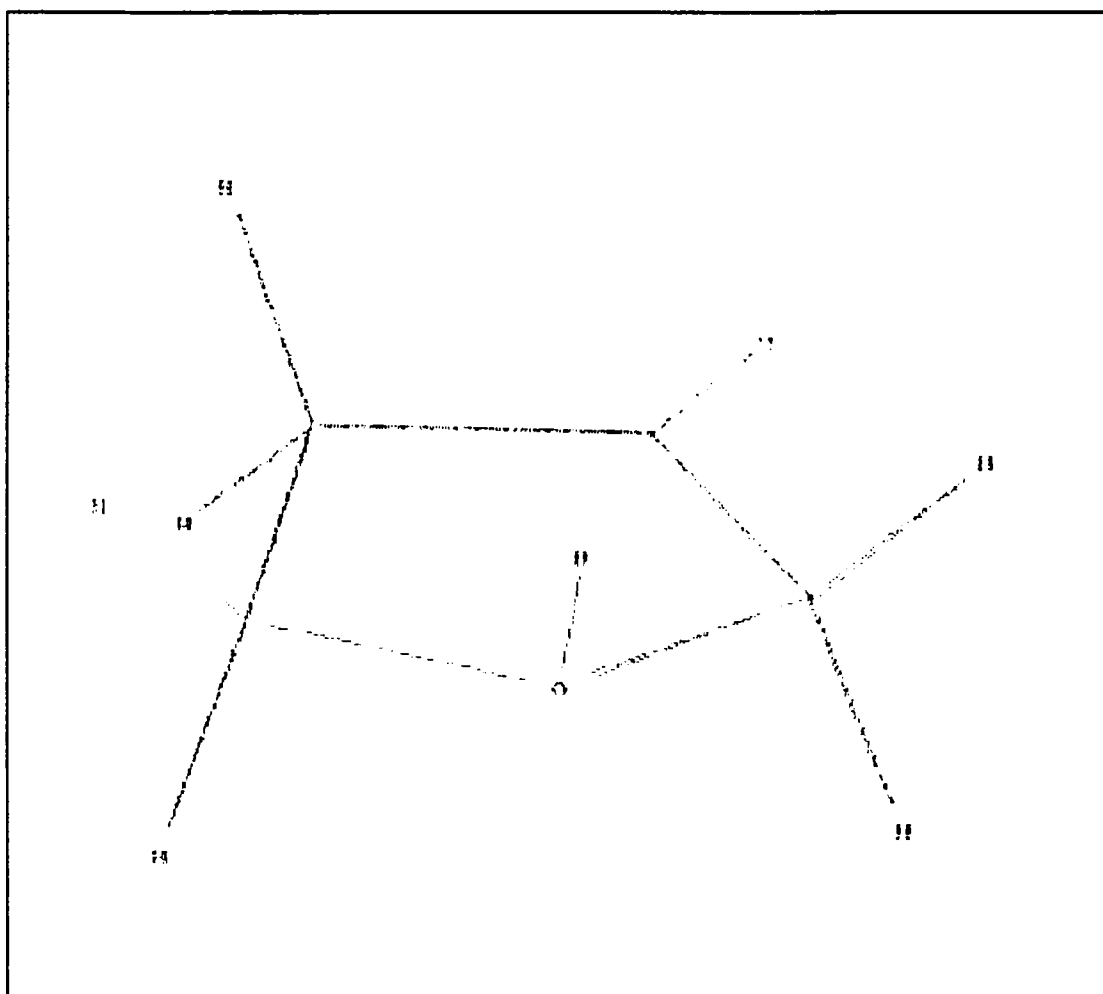


Fig.(5.2b-2). The AM1-UHF optimized equilibrium geometry for the cyclized But-3-en-1-ol radical cation.

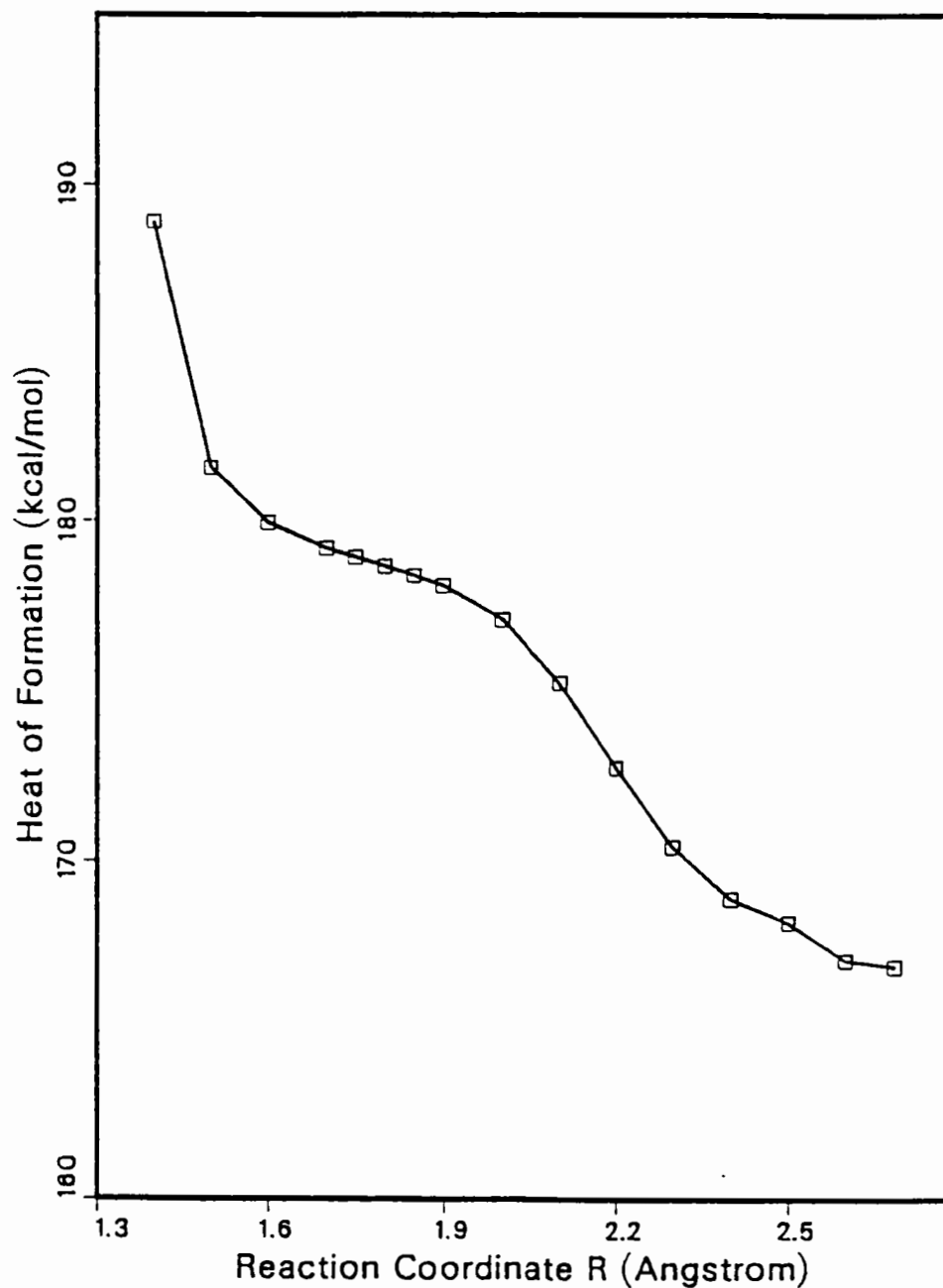


Fig.(5.2b-3). The reaction coordinate calculation for the exo cyclization of the but-3-en-1-ol radical cation, where R represents the distance between the oxygen and non-terminal carbon of the ethylene group.

**Part III. Cope Rearrangement of 1,5-Hexadiyne Radical
Cation to 1,2,4,5-Hexatetraene (Bis(allene))
Radical Cation at 77 K**

Recently, it has been discovered that some neutral pericyclic organic reactions can be catalysed by one electron oxidations.^{8c} These radical cation reactions have found some applications in organic and even natural product synthesis⁹ through the work of Bauld and his coworkers. The Diels-Alder reaction of butadiene radical cation with various dienophiles is an example,^{8c} where almost no activation energy for the reaction has been found. In this part, a spectroscopic study of another radical cation pericyclic reaction involving the nondegenerate radical cation Cope rearrangement of 1,5-hexadiyne to 1,2,4,5-hexatetraene at 77 K is presented. The fact that the reaction occurs at such a low temperature (77 K) contrasts with the high temperature (>473 K) needed in the corresponding neutral Cope rearrangement.¹¹¹ This implies an extremely low activation barrier for the radical cation Cope rearrangement.

Based on product analyses, Miyashi et al recently suggested a radical cation degenerate Cope rearrangement to explain a 1:1 photostationary mixture of 2,5-diphenyl-1,5-hexadiene-1,1,6,6-d₄ and 2,5-diphenyl-1,5-hexadiene-3,3,4,4-d₄ produced from the photolysis of the solution of the former in the presence of 9,10-dicyanoanthracene.¹¹² However, the recent

studies¹⁰² on the 1,5-hexadiene radical cation demonstrate that the potential surface of the 1,5-hexadiene radical cation is the inverse of that of the corresponding neutral molecule, indicating that the cyclohexa-1,4-diyl radical cation is more stable (34 kcal/mol according to the calculation¹¹³) than the parent 1,5-hexadiene radical cation. This stability provides a driving force for the cyclization, but prevents the subsequent retrocyclization required to complete the Cope reaction. It therefore seems likely that the radical cation degenerate Cope rearrangement conjectured by Miyashi et al proceeds via a back electron transfer to form the neutral cyclohexane-1,4-diyl precursor, which then undergoes the ring opening reaction to form the rearranged hexadiene.¹¹⁴ Similar findings¹¹⁵ in the literature concerning radical cation Cope rearrangements can also be attributed to this back electron transfer. To sum up, no clearcut example of any radical cation Cope rearrangement has been reported.

Section A. Results

As shown in Fig.(5.3a-1a), the ESR spectrum produced from the radiolytic oxidation of the parent 1,5-hexadiyne (1) in the CF_3CCl_3 matrix is composed of a quintet ($a(4\text{H})=28.6 \text{ G}$)

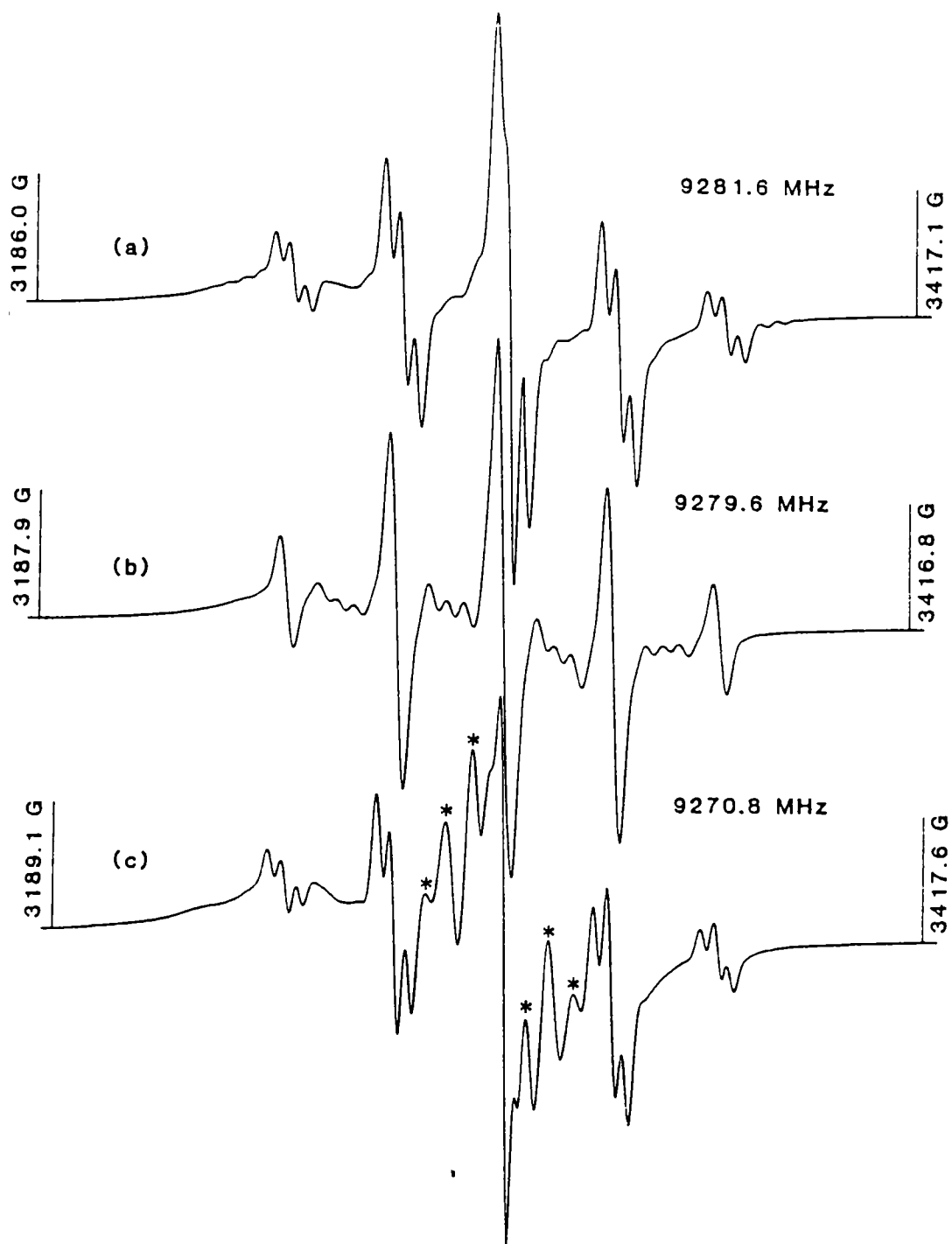


Fig.(5.3a-1). ESR spectra assigned to 1,2,4,5-hexatetraene radical cations obtained from γ -irradiated (dose, ca. 0.25 Mrad) CF_3CCl_3 solutions of (a) 1,5-hexadiyne, (b) 1,6-dideuterio-1,5-hexadiyne, and (c) 1,2,4,5-hexatetraene at 130 K. The concentrations were ca. 1 mol % and the samples were irradiated at 77 K. Only reversible spectral changes resulting from line narrowing were observed between 77 K and the matrix softening point of ca. 150 K. The spectral components denoted by asterisks in (c) originate from other radicals.

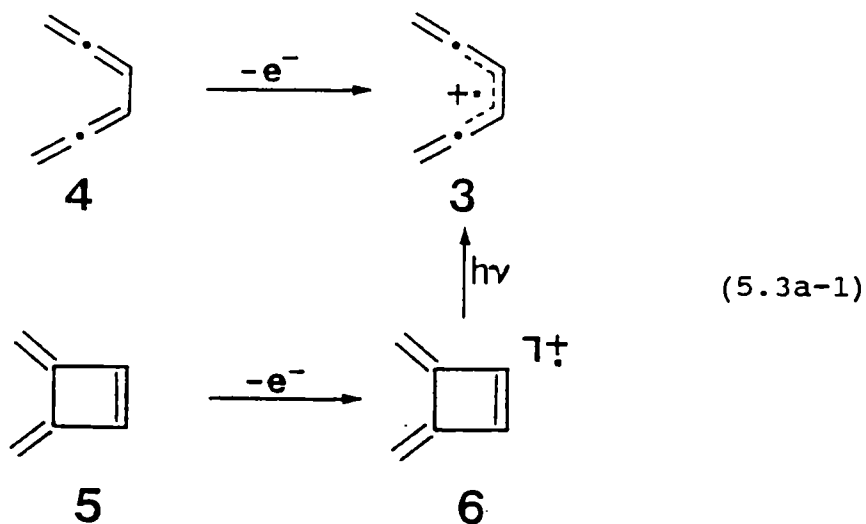
of triplets ($a(2H)=3.8$ G) with a g factor of 2.0024, and is totally different from the poorly defined spectra usually obtained from the radiolytic oxidation of alkyne molecules.^{11c} This suggests that a rearrangement may have occurred.

Because certain alkyne radical cations can easily react with the corresponding neutral molecules to form cyclobutadiene radical cation derivatives,^{8b,11c} the bicyclo[2.2.0]hexa-1,3-diene radical cation should be considered as a possible signal carrier. However, based on Davies's and Shiotani's work,^{8b,11c} the β -hydrogen hfcs in this kind of structure are in range of 6-12 G, which is far away from the experimental value 28.6 G. Accordingly, the bicyclo[2.2.0]hexa-1,3-diene can be safely neglected. The 5,6-dihydro-1,4-benzyne (2) and 3,4-dimethylenecyclobutene (6) radical cations can be ruled out by a similar argument.

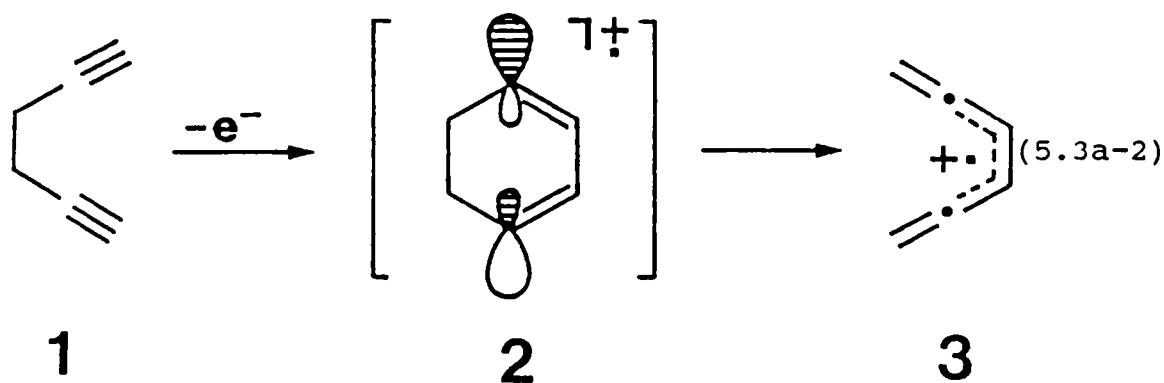
The observed pattern can be nicely explained however by invoking the 1,2,4,5-hexatetraene radical cation (3) as the signal carrier, which is another isomer of (1). The SOMO of (3) is essentially similar to that of the butadiene radical cation.¹¹⁶ The triplet substructure can be assigned to the two inner hydrogens in the butadiene part of (3), and the quintet to the four β hydrogens that form π' orbitals parallel to the butadiene π orbitals. An INDO calculation using the AM1-UHF optimized geometry of the 1,2,4,5-hexatetraene radical cation confirmed this $a_2(\pi)$ -SOMO with couplings of 44.8 G(4H) and 1.6 G(2H). This is qualitatively consistent with the

experimental results. In order to further verify this assignment, the 1,2,4,5-hexatetraene was directly synthesized. Its radical cation ESR spectra are identical to those produced from the radiolytic oxidation of 1,5-hexadiyne, which clearly establishes that the same radical cation is involved.

Further support for this assignment comes from a photolysis study of the 3,4-dimethylenecyclobutene radical cation with visible light. The spectrum produced from the photobleaching of the 3,4-dimethylenecyclobutene is shown in Fig.(6.1a-1), and is essentially identical to that obtained from the radiolytic oxidation of 1,5-hexadiyne. This photochemical reaction (Reaction (5.3a-1)) is similar to the well-known photoinduced cyclobutene radical cation ring-opening reactions.¹¹⁷



In order to understand how this rearrangement occurs, the 1,6-dideuterio-1,5-hexadiyne was synthesized. As shown in Fig.(5.3a-1b), the spectrum produced from the radiolytic oxidation of 1,6-dideuterio-1,5-hexadiyne consists of five lines with the same coupling constant as that of the quintet of the corresponding non-deuterated radical cation. This result not only is consistent with the assignment to the 1,2,4,5-hexatetraene radical cation (3) , but also clearly establishes the Cope rearrangement(reaction (5.1a-2)) as the reaction mechanism for the isomerization of (1) $\cdot^+$ to (3).



Section B. Discussion

If the plane of symmetry element which bisects the 3,4- σ bond of the 1,5-hexadiyne radical cation is preserved during the reaction (5.3a-2),¹¹⁸ the qualitative orbital symmetry

correlation diagram for this Cope reaction can be drawn as shown in Fig.(5.3b-1). According to the Woodward-Hoffmann rules,¹¹⁹ this correlation diagram indicates that the reaction is thermally allowed. Many attempts to carry out the AM1-UHF reaction coordinate calculation of reaction (5.3a-2) using the distance between the two terminal carbons(1,6) as the main reaction coordinate failed due to the divergence of SCF at a point between the radical cation (1) and (2). However, it has been found that (2) can easily relax to (3) with almost no activation energy.

The calculated heats of formation for the radical cation (1), (2), (3), (6) and bicyclo[2.2.0]hexa-1,3-diene radical cation at their optimized geometries with certain symmetry constraints are tabulated in Table (5.3b-1) along with some experimental estimations. These results indicate that reaction (5.3a-2) is thermodynamically favorable with a large negative reaction enthalpy (-46 kcal/mol). On the contrary, the bicyclo[2.2.0]hexa-1,3-diene radical cation is higher in energy than the 1,5-hexadiyne radical cation, indicating that it cannot be derived from thermal isomerization of (1)⁺. This strongly supports the experimental assignment. It is interesting that (2) is found lower in energy than the parent radical cation (1). This phenomenon very much resembles the stability of cyclohexane-1,4-diyl radical cation relative to the 1,5-hexadiene radical cation. In Part V of this Chapter, a qualitative theory to

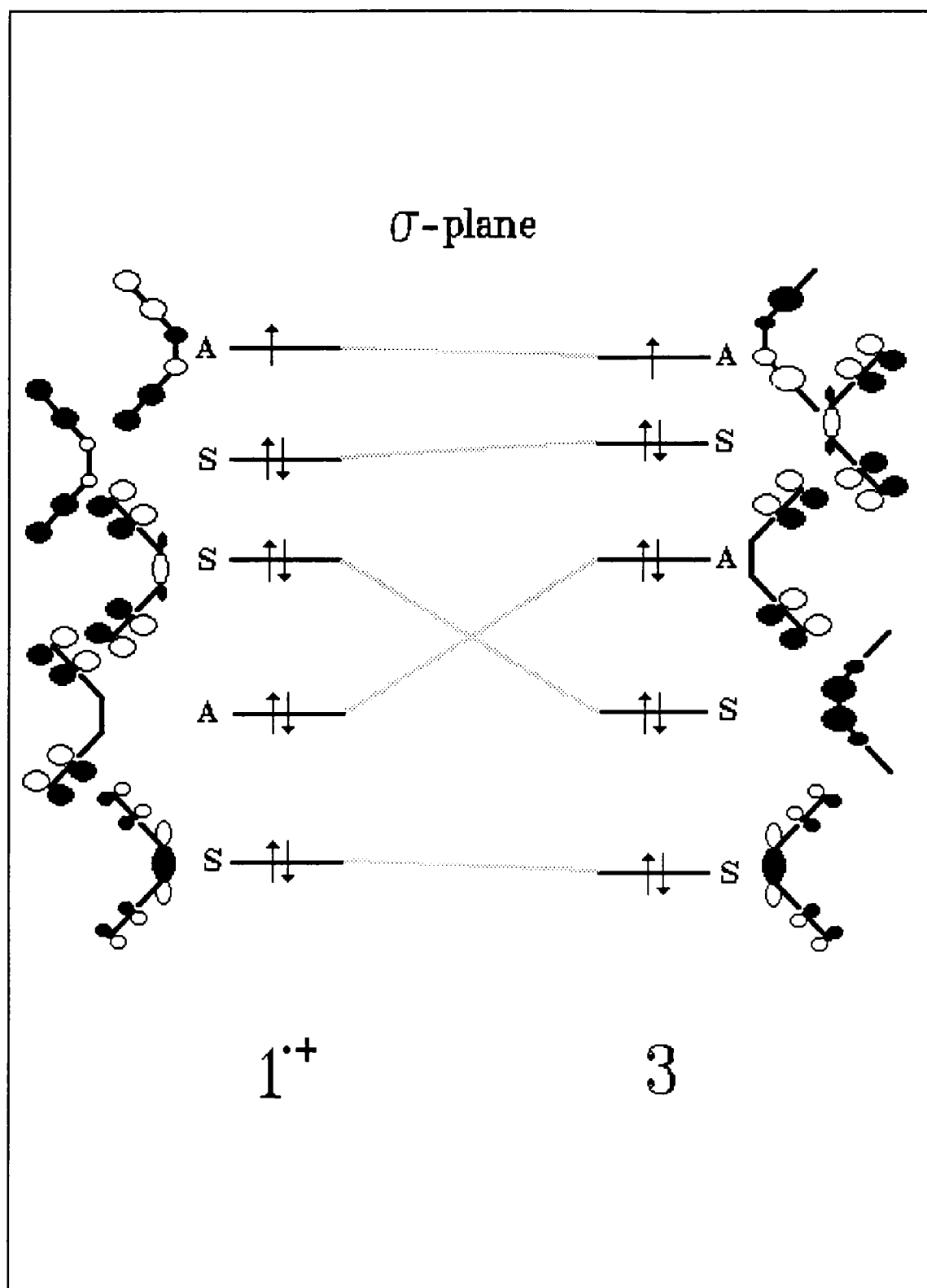


Fig.(5.3b-1). Orbital symmetry correlation diagram for the isomerization of $(1)^{\bullet+}$ to (3) .

Table (5.3b-1). Heats of Formation of 1,5-Hexadiyne Radical Cation and Its Possible Isomers at 298 K.

Radical Cation Isomer	Point Group Used in Calculation ^a or Experimental Determination ^b	ΔH_f (kcal mol ⁻¹)
1,5-Hexadiyne (1 ⁺ ·)	C _{2h} (<i>anti</i> , <i>planar</i>)	328.4
	C _{2v} (<i>syn</i> , <i>planar</i>)	327.5
	Expt.	329 ± 2 ^b
Bicyclo[2.2.0]hexa-1,3-diene	C _{2v}	348.6
3,4-Dimethylenecyclobutene (6)	C _{2v}	294.7
5,6-Dihydro-1,4-benzyne (2)	C _{2v}	319.6 ^c
		312.0 ^d
	C _s	311.9
1,2,4,5-Hexatetraene (3)	C _{2v} (<i>s-cis</i>)	282.2
	Expt.	295 ± 5 ^{b,e}

^aAM1-UHF method (ref 37). ^bFrom ΔH_f of neutral molecule and gas-phase ionization potential: Rosenstock, H.M.; McCulloh, K.E.; Lossing, F.P. *Adv. Mass Spectrometry* 1978, 7B, 1260.
^cSymmetrical charge distribution. ^dUnsymmetrical charge distribution. ^eBased on estimated ΔH_f for neutral molecule.

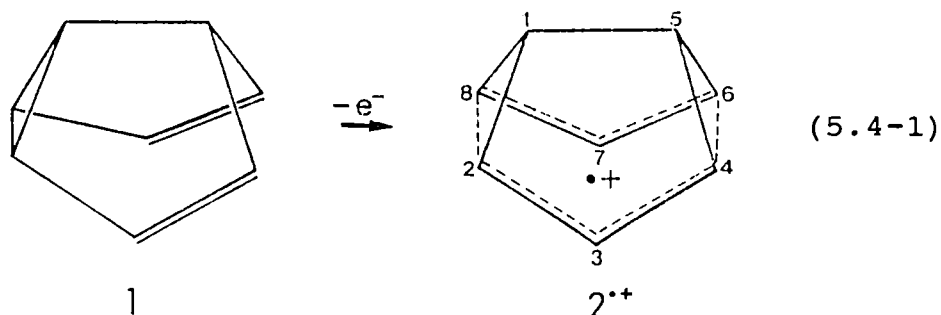
rationalize this stability is developed.

Part IV. ESR Evidence for the 1,4-bishomobenzene

Structure of C_{2v} Ring-Opened Semibullvalene

(Biscyclo[3.3.0]octa-2,6-diene-4,8-diyl) Radical Cation

It is well known that semibullvalene (**1**) can undergo a rapid degenerate Cope rearrangement¹²⁰ on the NMR time scale even at $-150\text{ }^{\circ}\text{C}$ through a boat transition state with a 4.8 kcal/mol activation energy.¹²¹ There have been several efforts^{120,122,123} to invert the potential surface by introducing suitable substituents to (**1**) so as to obtain the "transition state" as a stable compound. In Hoffmann's terminology,¹²² this would correspond to a negative activation energy for the Cope rearrangement. So far, attempts to fulfill this goal have not met with success.^{120,123} In this part, an inversion of the potential surface of (**1**) realized by the radiolytic oxidation of (**1**) to its radical cation is reported. Essentially, the radical cation produced by the vertical ionization undergoes a facile ring-opening reaction to the stable delocalized bicyclo[3.3.0]octa-2,6-diene-4,8-diyl or 1,4-bishomobenzene radical cation in Freon matrices (Reaction (5.4-1)).



Bishomoaromatic radical cations of this type were first suggested by Roth and Abelt¹²⁴ as the precursors responsible for the CINDP patterns observed from the neutral recombination products of photoinduced electron-transfer between a series of bridged bicyclo[5.1.0]octadi-2,5-enes and electron acceptors. However, CINDP results of this kind are indirect and cannot provide first-hand information on the electronic structure. To our knowledge, no direct spectroscopic measurement has been reported on a bishomobenzene radical cation resulting from two strongly interacting allyl systems, although some other biallylic radical cations have been studied by EA¹²⁵ (Electronic Absorption) and ESR spectroscopy.¹²⁶

Section A. Results

As shown in Fig.(5.4a-1), the ESR spectrum of the radical cation produced by radiolytic oxidation of a solid solution of (1) in the $\text{CF}_2\text{ClCFCl}_2$ matrix consists of a well resolved triplet ($a(2\text{H})=36.2$ G) of quintets ($a(4\text{H})=7.7$ G) with a g factor of 2.0029(3). The signals persisted up to 110 K with no major change. Above 110 K, the signal started to decay due to the usual ion-molecule reactions¹⁰³ in this particular matrix. The spectrum of the ion-molecule reaction product,

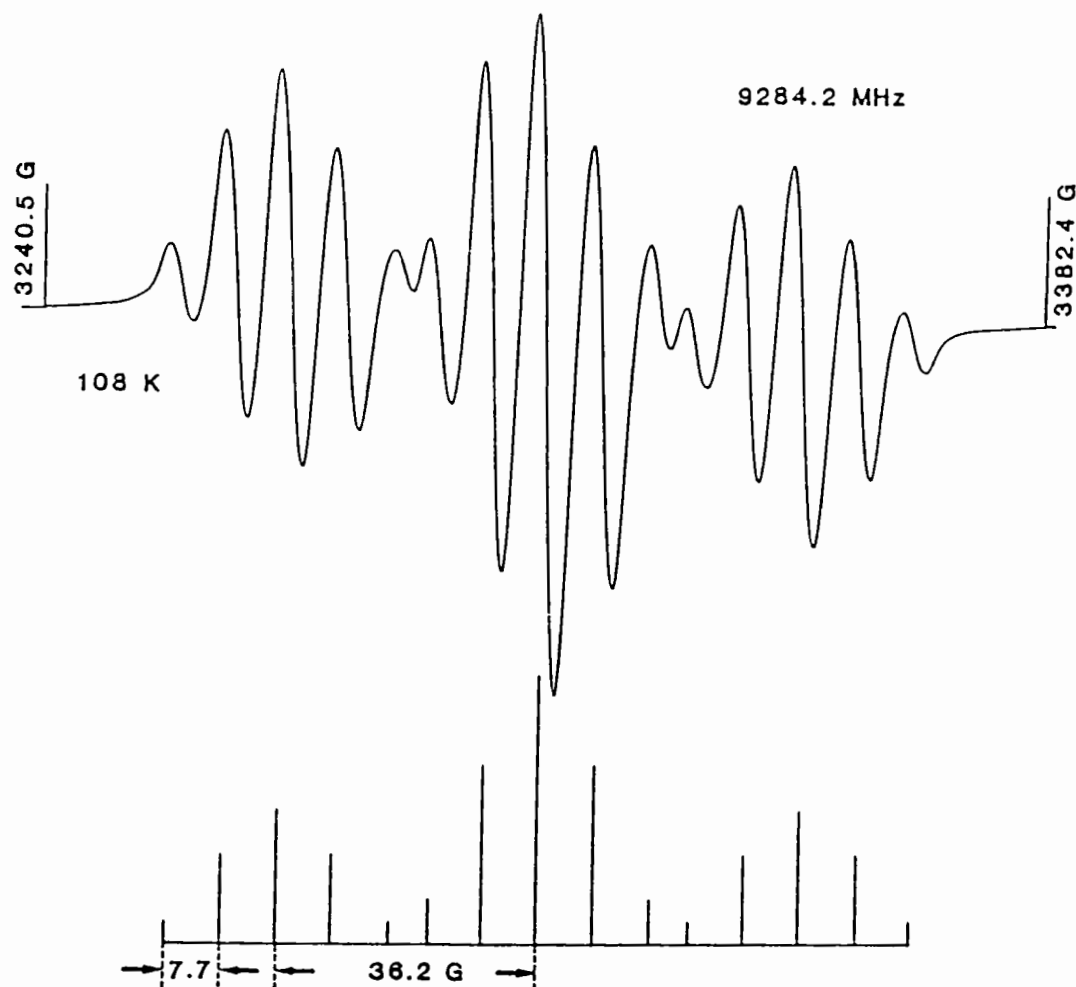


Fig.(5.4a-1). First-derivative ESR spectrum obtained from a solid solution of semibullvalene(<1 mol%) in $\text{CF}_2\text{ClCFCl}_2$ after γ -irradiation (dose, 0.25 Mrad) at 77 K. The stick diagram represents the line components of the C_{2v} bridged 1,4-bishomobenzene radical cation derived by the cyclopropane ring opening of the semibullvalene radical cation.

which is better resolved at 150 K, consists of a doublet ($a(1H)=35.5$ G) of triplets ($a(2H)=14.4$ G) pattern with a g factor of 2.0025. The most probable candidate for this secondary radical product is the neutral radical species produced by loss of a hydrogen proton from the C(5) position of semibullvalene, for which the larger coupling can be assigned to the β -hydrogen at C(1), and the smaller couplings to the hydrogens at C(4) and C(6).

The spectra obtained from the CF_3CCl_3 and $CFCl_3$ matrices were virtually identical to that from $CF_2ClCFCl_2$ (<110 K) except for different linewidths. In the former matrices, however, the observed ESR signals were unchanged until the softening point of the matrices (145 K and 160 K, respectively).

The two sets of equivalent hydrogens in the ESR pattern (Fig.(5.1a-1)) observed prior to the ion-molecule reaction clearly indicates a highly symmetric paramagnetic species, which implies that a rearranged radical cation is formed. It has been found before that the cyclopropane ring of a radical cation can under certain circumstances undergo a the ring opening reaction.¹²⁷⁻¹²⁸ For (1), this corresponds to ring-opening caused by the weakening of the C(2)-C(8) σ -bond upon ionization of an electron from the a' HOMO shown in Fig.(5.4a-2). It is very similar to the ring-opening found for bicyclo[2.1.0]pentane (Fig.(5.4a-2)). Thus, the ring-opened radical cation (2) with C_{2v} symmetry and a highly

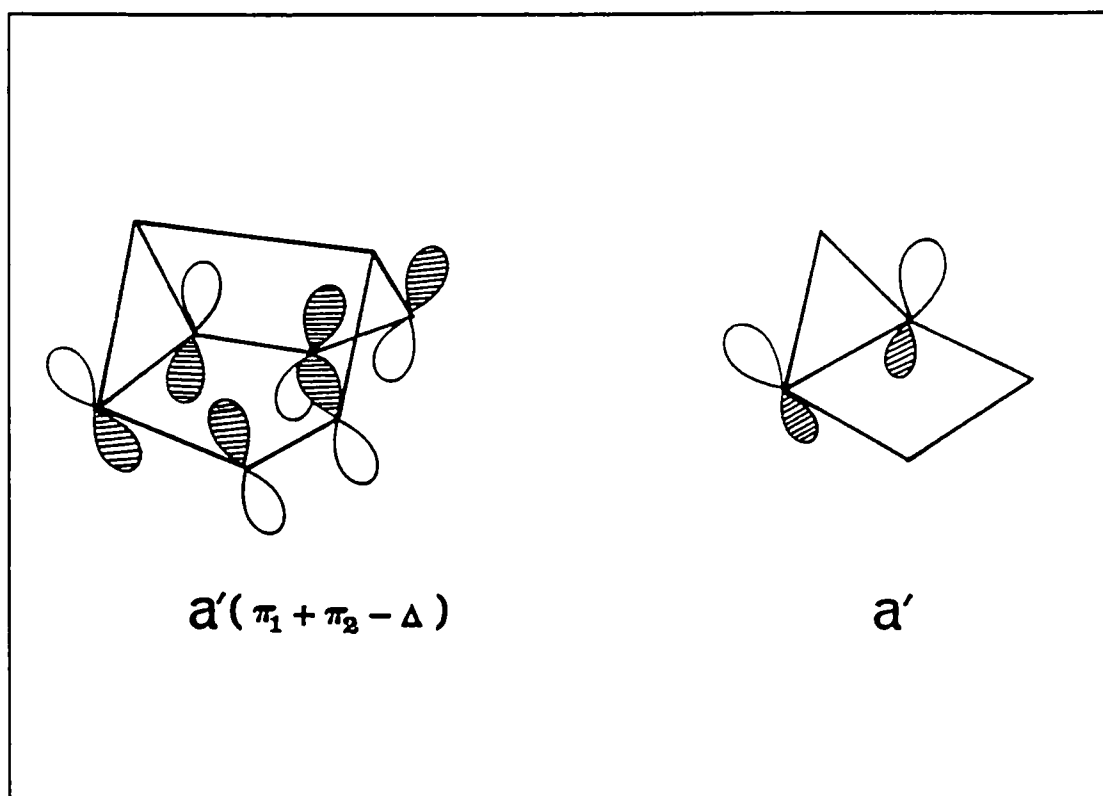


Fig.(5.4a-2). The diagram of the MO responsible for the semibullvalene radical cation ring-opening and the MO responsible for the bicyclo[2.1.0]pentane radical cation ring-opening.

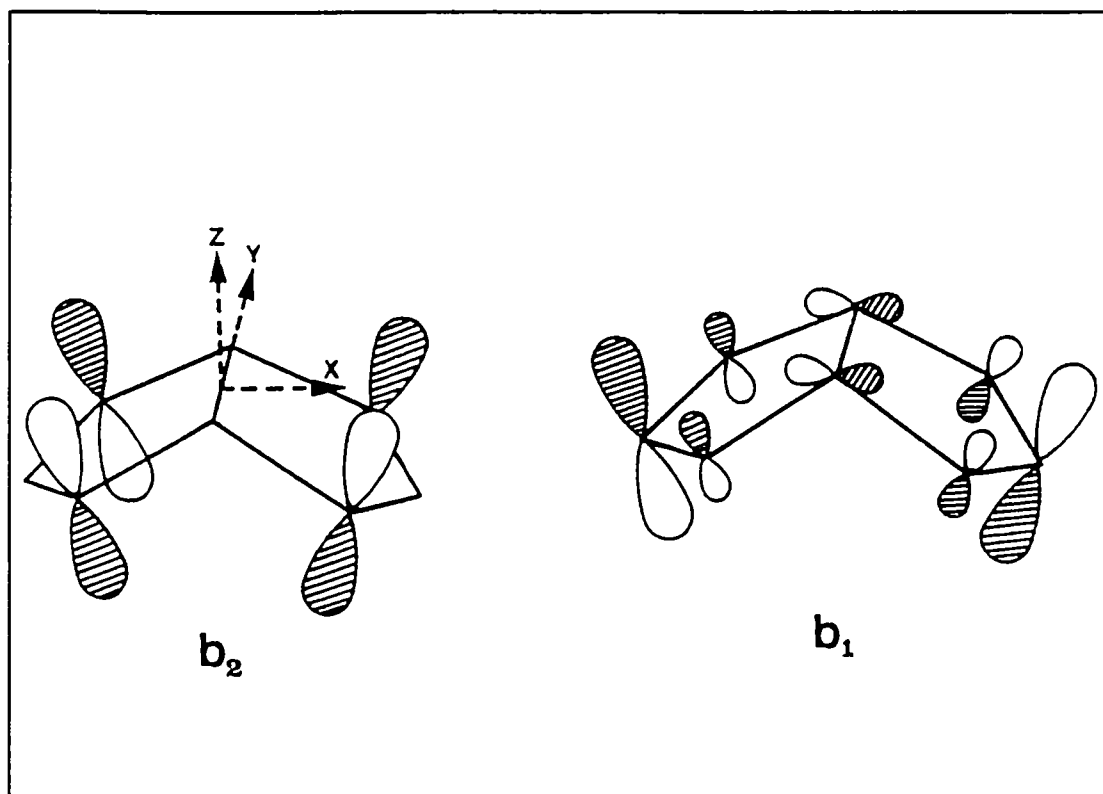


Fig.(5.4a-3). Two MO diagrams of the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation.

delocalized electronic structure is clearly the best candidate for the spectrum of interest. The two most likely SOMOs for this radical cation are shown in Fig.(5.4a-3). Since the b_1 orbital possesses a ZY nodal plane through the bridgehead hydrogen, the largest hfcs would be to the α -hydrogens at (3) and (7). This certainly cannot explain the observed large $a(2H)$ value of 36.2 G since the maximum value of α -hydrogen coupling constants for unit spin is always less than 30 G. In contrast, the measured hfcs can be easily rationalized by choosing the b_2 orbital as the SOMO. In this case, the 36.2 G hfcs can be assigned to the two bridgehead β -hydrogens at (1) and (5), while the 7.7 G couplings correspond to the four allylic α -hydrogens at the C(2), C(4), C(6) and C(8) positions. The remaining two hydrogens at position C(3) and C(7) would be expected have very small couplings (less than linewidths) as they are in the XZ nodal plane. Using the AM1-optimized geometry, an INDO calculation predicted hfcs of 57.2 G for the two β -hydrogens, -7.1 G for ones at C(2),C(4),C(6) and C(8), and 3.4 G for ones at C(3) and C(7). These results are in qualitative agreement with this assignment of the $^2B_2$ state to 2^+ . The relatively large discrepancy between the calculated and experimental β -coupling constant is not unusual since INDO calculations often overestimates β -hydrogen couplings by a factor of about 1.5 as seen from the last part.

The small 7.7 G coupling constant to four allylic

hydrogens clearly rules out a static charge-localized structure with a weak interaction between allyl radical and allyl cation moieties as being the signal carrier. However, a time-averaged C_{2v} structure produced by the rapid dynamic intramolecular electron transfer between the two equivalent sites remains a possibility. In other words, whether the signal carrier has the potential surface like Fig.(5.4a-4a) (resulting from the weak interaction) or Fig.(5.4a-4b) (resulting from the strong interaction) still remains open. This ambiguity can be cleared by considering the β -hfcs value of the two bridgehead protons. Since the coefficients of SOMO at C(2) and C(8) for the unsymmetric structure can be approximated as 0.5 and 0.0, the coupling constant of the two bridgehead protons can be evaluated by the following formula (Eq.(5.4a-1)):¹²⁹

$$a(2H_{\beta}) = B(0.5^{\frac{1}{2}} + 0.0^{\frac{1}{2}})^2 \cos^2(\theta) \quad \text{..... (5.4a-1) .}$$

Substituting $\theta=31.4$ degree according to the AM1-UHF optimized bishomobenzene radical cation geometry (Fig.(5.4a-5)) and $B=48$ G into Eq.(5.4a-1) gives an 18 G coupling constant for the two bridgehead protons, which is clearly remote from the experimental results. On the other hand, for the symmetric delocalized structure the coefficient of the b_2 SOMO at C(2) and C(8) is 0.25 with the same sign. The coupling constant of the two bridgehead protons is given by :

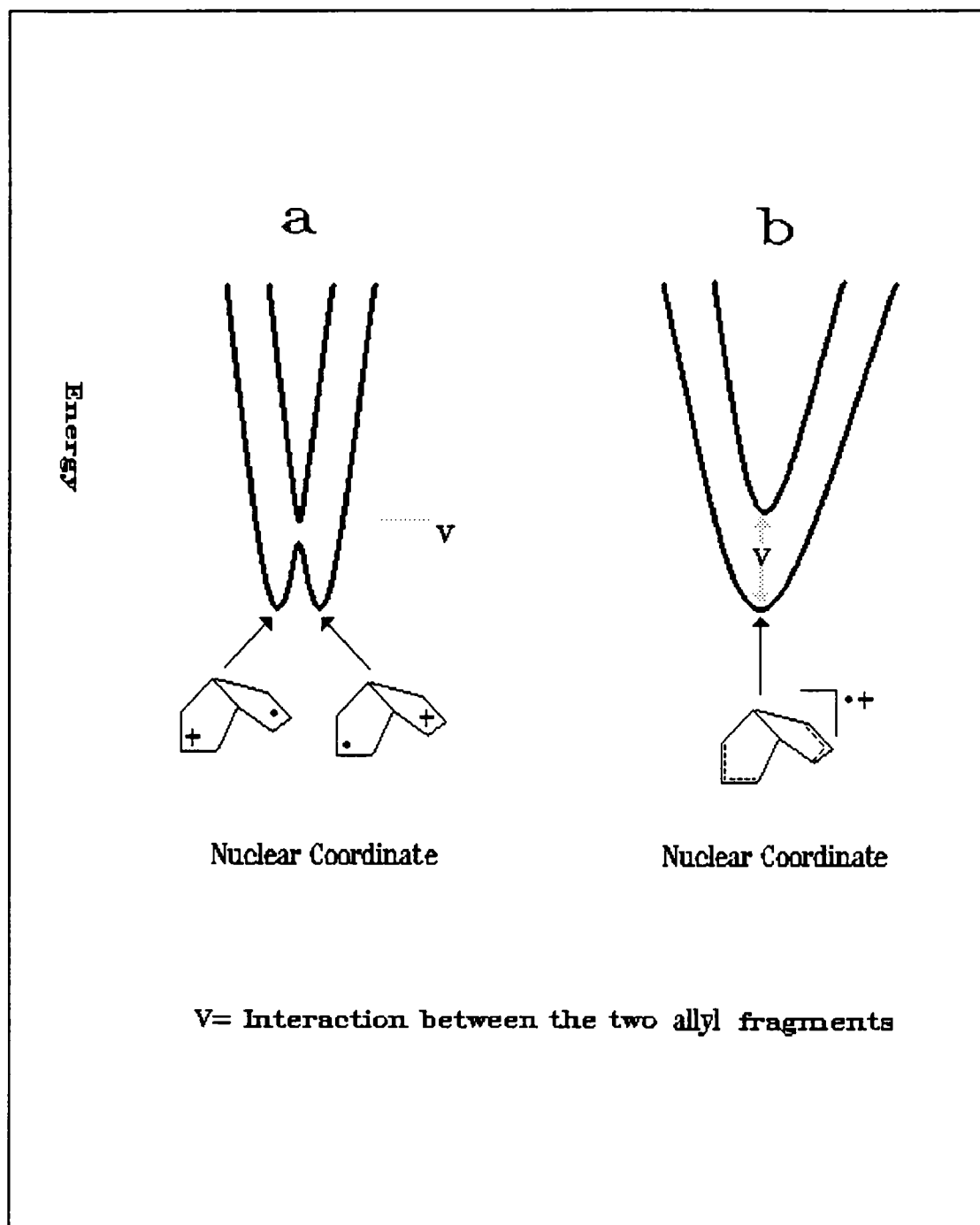


Fig.(5.4a-4). Qualitative cross sections of potential hypersurfaces for (a) a localized and for (b) a delocalized bishomobenzene radical cation.

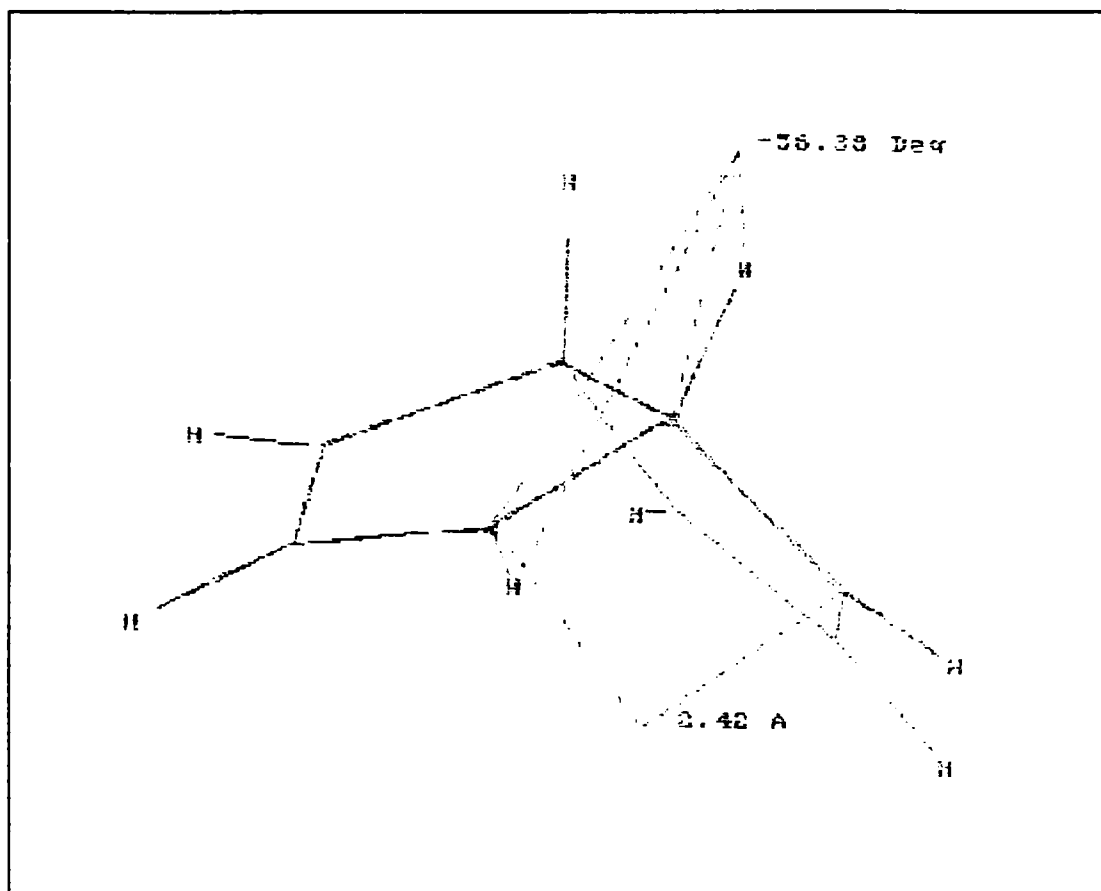


Fig.(5.4a-5). The AM1-UHF optimized bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation geometry with no symmetry constraint.

$$a(2H_9) = B(0.25^{\frac{1}{2}} + 0.25^{\frac{1}{2}})^2 \cos^2(\theta) \quad \text{..... (5.4a-2) .}$$

This gives a value of 36 G for the bridgehead coupling constant after substituting the same values for θ and B as before. This agrees perfectly with the experimental value. Therefore, the symmetric radical cation is composed of two strong interacting allyl fragments with delocalized charge and radical centers. As shown in Fig.(5.4a-6), Its valence structure should therefore be formulated as a mesomeric resonance between $2a^{\bullet+}$ and $2b^{\bullet+}$ instead of the equilibrating species.

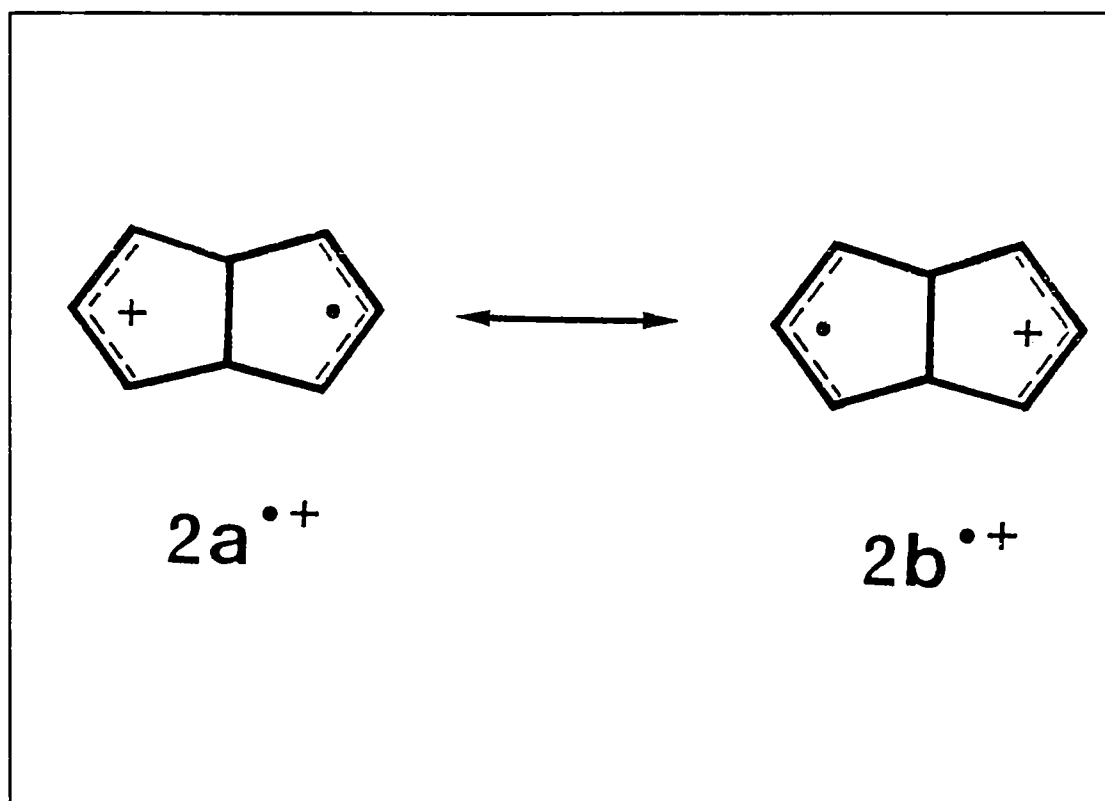


Fig.(5.4a-6). Mesomeric resonance representation of the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation.

The degree of interaction(V) between the two allyl fragments can be determined from the first transition in the EA spectrum, based on the qualitative MO diagram for (2)^{•+} (Fig.(5.4a-7)). The measured first transition of the EA spectrum at 77 K is a broad band with a peak value at 635 nm. This value is a little larger than that observed from the rearranged species of the dicyclopentadiene radical cation.¹²⁵ In the present case, rigid geometric arrangement for interaction makes the two allyl fragments interact more strongly in radical cation (2) relative to the rearranged radical cation of dicyclopentadiene.¹²⁵

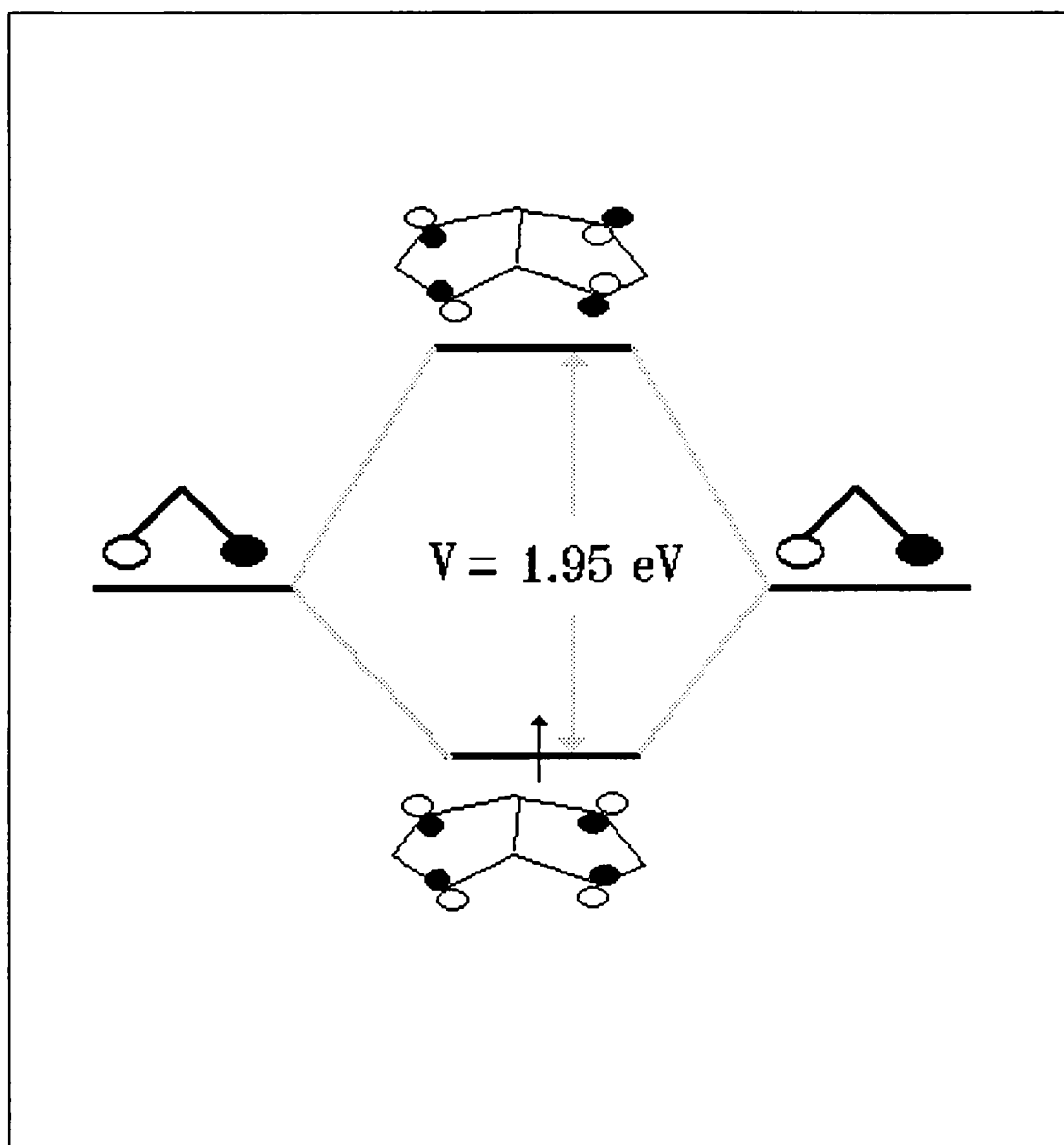
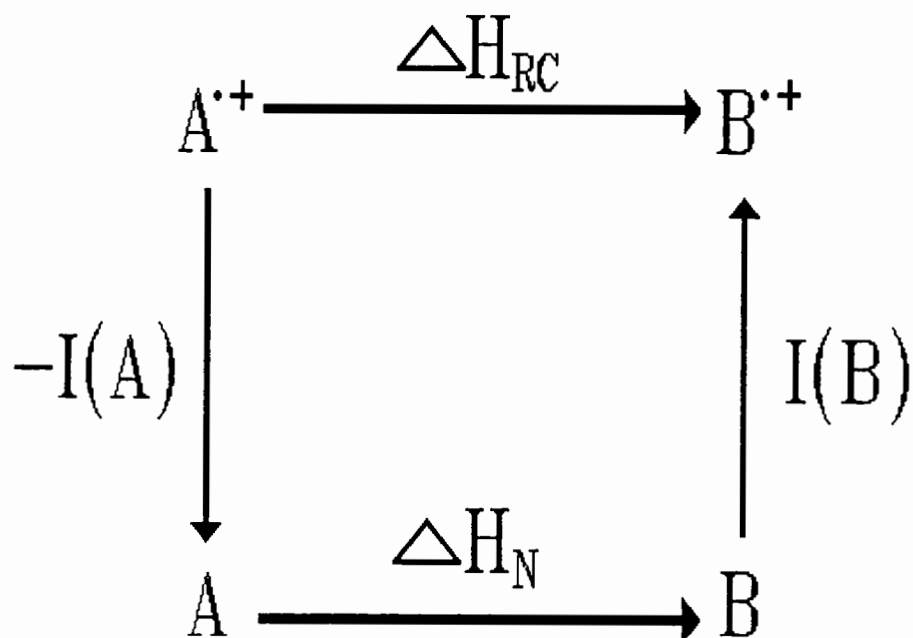


Fig.(5.4a-7). Qualitative MO interaction diagram for the 1,4-bishomobenzene radical cation.

Section B. Discussion

For a general unimolecular radical cation reaction ($A^{\cdot+} \rightarrow B^{\cdot+}$), the following thermal cycle can be constructed,



based on which the reaction enthalpy for the radical cation reaction is

$$\Delta H_{RC} = I(B) - I(A) + \Delta H_N \quad \text{..... (5.4b-1)}$$

where

ΔH_{RC} =Radical Cation Reaction Enthalpy (5.4b-2)

$I(A)$ =Ionization Potential of Neutral A (5.4b-3)

$I(B)$ =Ionization Potential of Neutral B (5.4b-4)

ΔH_N =The Corresponding Neutral Reaction Enthalpy ... (5.4b-5) .

Eq.(5.4b-1) indicates that in order to make the reaction ($A^{\cdot+} \rightarrow B^{\cdot+}$) thermodynamically favorable, the difference ($I(A) - I(B)$) between the first ionization potentials of the neutral A and B should be larger than the corresponding neutral reaction enthalpy (ΔH_N). In the case of our Reaction (5.4-1), the neutral reaction enthalpy is equal to the activation enthalpy for the Cope rearrangement with the experimental value 0.21 eV.¹²¹ The ionization potential difference can be obtained from the recent high level ab initio CI calculation results¹³⁰ which gave a value of -9.37 eV and a value of -7.33 eV for the HOMO energies of (1) and (2) respectively. Based on Koopmans theory, the orbital energy can be approximately regarded as the negative value of the ionization potential of the molecule. Therefore, the first ionization potential difference between (1) $^{\cdot+}$ and (2) $^{\cdot+}$ is around 2.04 eV, which is far larger than 0.21 eV. This gives rise to a reaction enthalpy of around -40 kcal/mol so as to establish a thermodynamic driving force for the reaction (5.1-1).

Now consider the kinetic aspect. If the symmetry plane bisecting the C(2)-C(8) σ -bond is preserved during the reaction, the thermal isomerization of (1) $^{\cdot+}$ to (2) $^{\cdot+}$ is symmetry-allowed according to the orbital correlation diagram

(Fig.(5.4b-1)).^{119,131} This implies that a low reaction barrier is expected for the isomerization. In fact, both one-dimensional and two-dimensional AM1-UHF reaction coordinate calculations choosing the C(2)-C(8) distance in 1-D, and degenerate C(2)-C(8) and C(4)-C(6) in 2-D as the reaction coordinates indicate no activation barrier encountered during the ring-opening (Fig.(5.4b-2) and Fig.(5.4b-3)). If the parent semibullvalene radical cation is assumed to have the C(2)-C(8) distance equal to 1.5 Å, the AM1 calculated reaction enthalpy is 41 kcal/mol, which agrees well with the above estimated value.

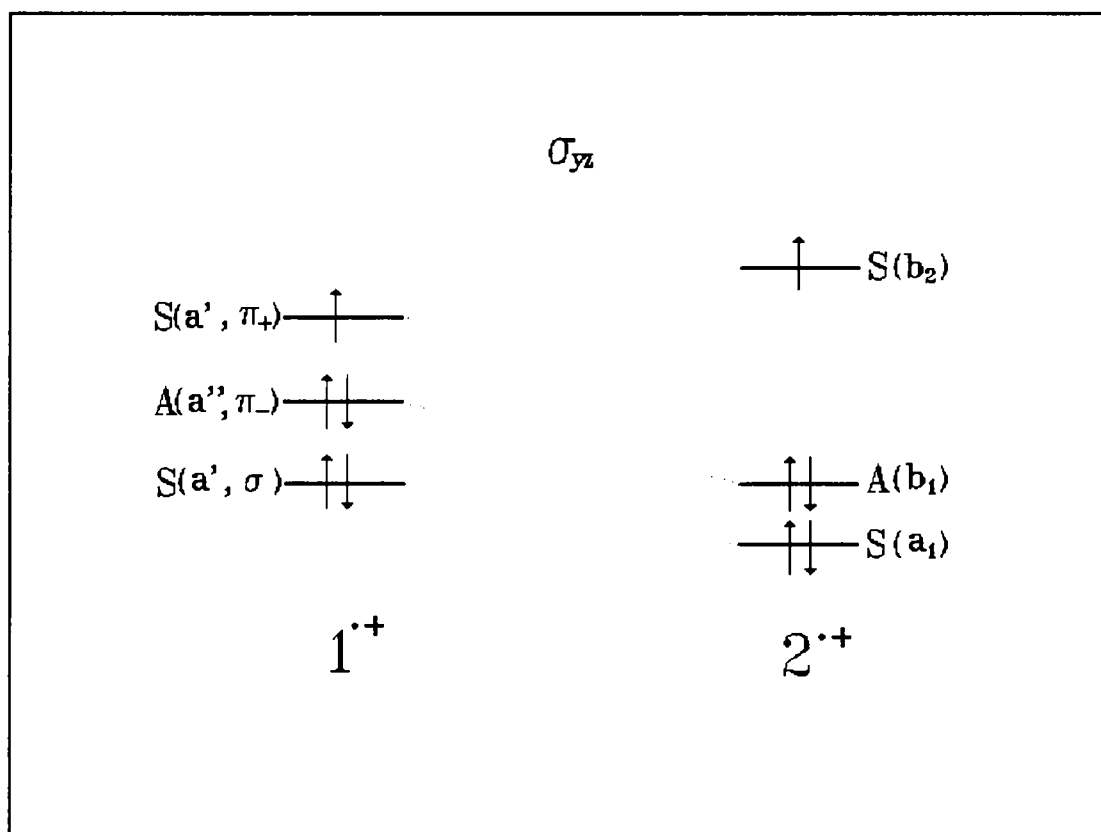


Fig.(5.4b-1). Orbital symmetry correlation diagram for the ring-opening of the semibullvalene radical cation to the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation.

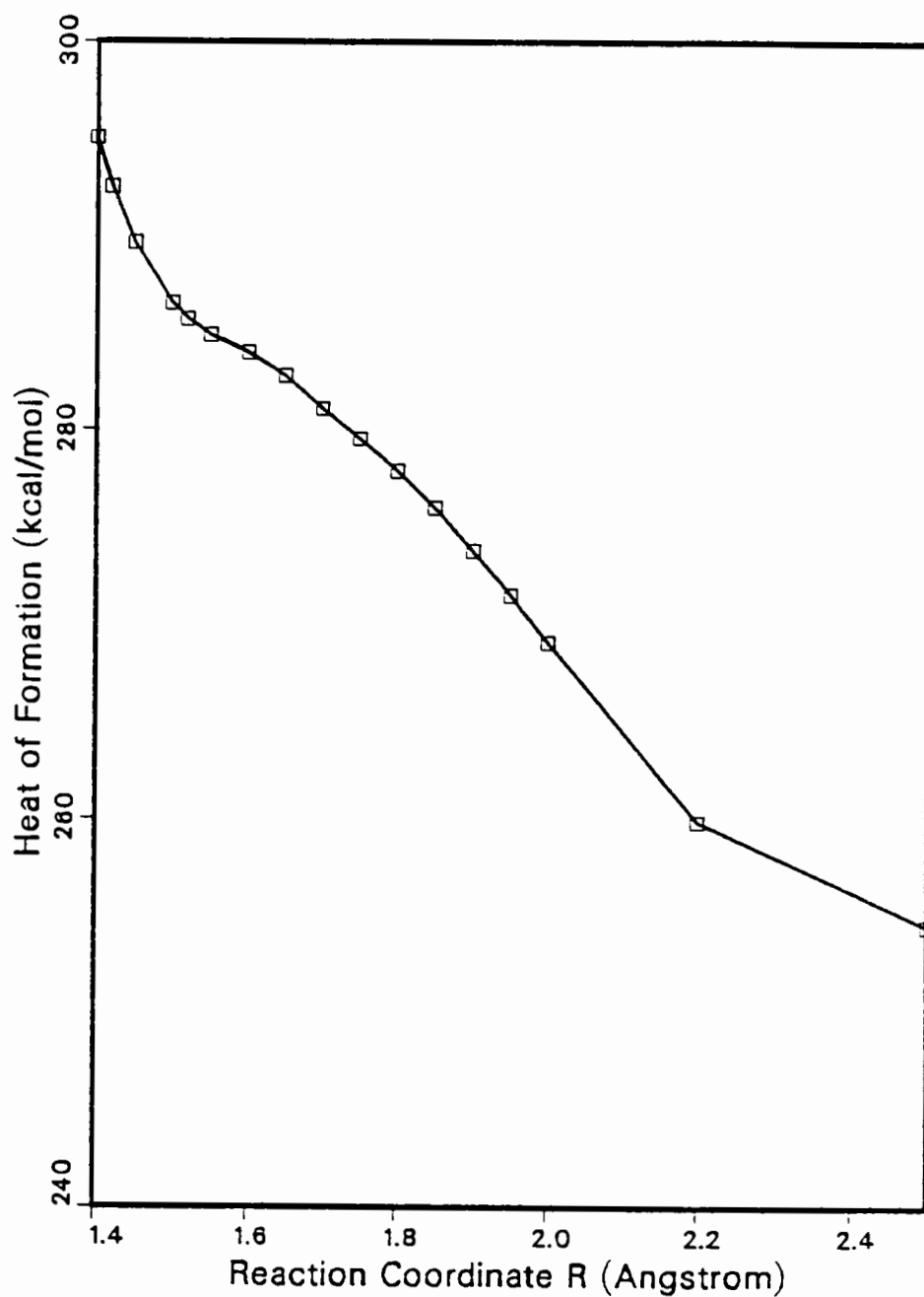


Fig.(5.4b-2). Potential energy curve of the heat of formation versus reaction coordinate R for the ring-opening of the semibullvalene radical cation calculated with AM1-UHF. The reaction coordinate R is chosen to be the distance between C(2) and C(8).

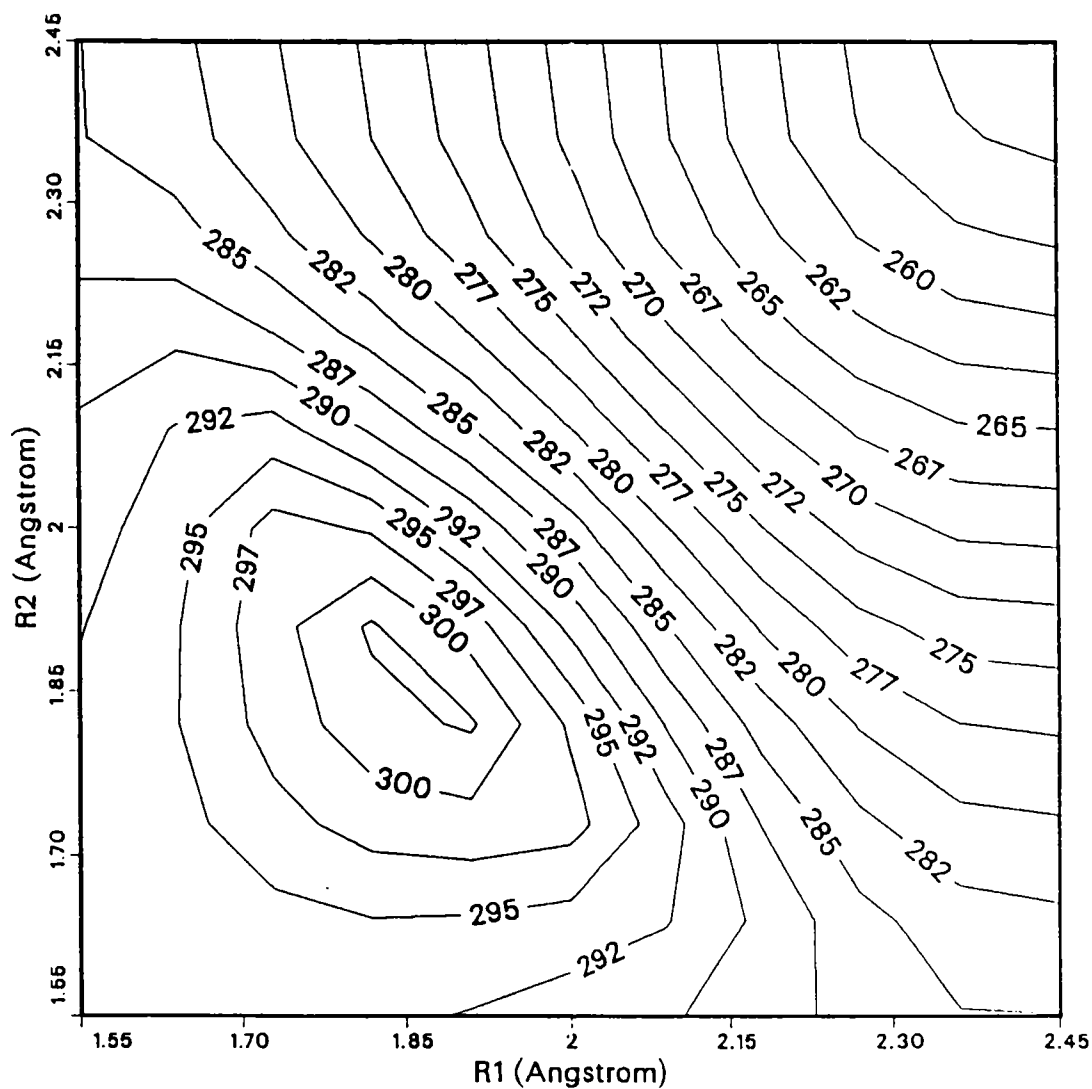


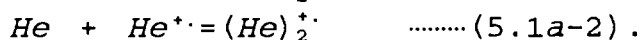
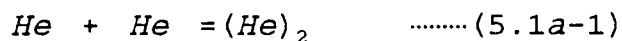
Fig.(5.4b-3). Potential energy contour map of the heat of formation(kcal/mol) versus reaction coordinate R1 and R2 for the ring-opening of the semibullvalene radical cation calculated with AM1-UHF. The reaction coordinate R1 and R2 are chosen to be the distance between C(2) and C(8), and C(4) and C(6) respectively.

Part V. A Unique Reaction Channel Available for Radicals

A radical is defined as a species with an odd electron. This open-shell electronic structure makes it different from normal diamagnetic molecules in both physical properties and reactivities. The unimolecular reactions discussed in the above four parts clearly demonstrate the distinct reaction trends or thermodynamic driving forces associated with radical cations, which are not found in the corresponding neutral molecules. Although these phenomena can be rationalized through quantum chemical calculations, it is very easy for nonspecialists to get lost in pages of computer print-outs and lose the insight into the physical principles governing reactions. What an experimentalist needs is a simple, qualitative, straight-forward and yet powerful rule-of-thumb to help him to understand and predict chemical changes of radicals. In the following, a qualitative rule will be developed to rationalize the driving force for the reactions in the above four parts. Other examples of unimolecular radical changes in the literature can be treated in a similar manner. This idea is derived from the generalization of the net stabilization effect resulting from a bimolecular interaction between a radical and a nonradical, i.e., the concept of the three electron bond.¹³²

Section A. Basic Theory

Consider the following two dimerization processes:



It is well known that the first reaction is a thermodynamically unfavorable process while the second is a strongly favorable one with a reaction enthalpy of around $-57 \text{ kcal mole}^{-1}$.¹³³ This dissimilarity is rooted in the one-electron difference between the two reactions, which can easily be rationalized by noting that while the $(\text{He})_2$ molecule has a net zero bond order due to the same number of electrons in bonding and antibonding molecular orbitals (Fig.(5.5a-1a)), $(\text{He})_2^{\bullet}$ has a net 0.5 bond order due to the one-electron difference in the bonding and antibonding orbitals (Fig.(5.5a-1b)). This significance of 0.5 bond order for radical interactions will now be explored in a general way.

By analogy to this helium prototype case, many other facile bimolecular dimerization reactions involving radicals can be explained. This so-called three-electron interaction model is certainly not new in the literature, as indicated by the following examples. Thus, Bauld et al¹³⁴ employed this concept to rationalize the "dimerization" between an olefin

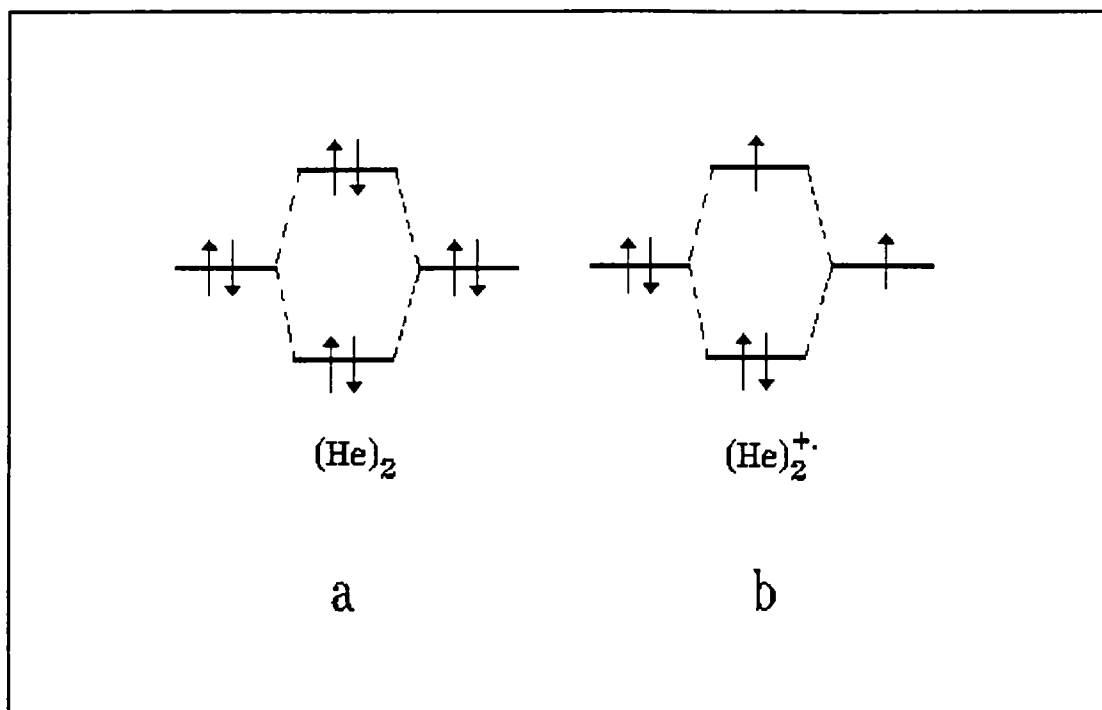


Fig.(5.5a-1). Orbital splitting diagram.

molecule and the corresponding olefin radical cations. Similarly, Asmus¹³⁵ used it to explain the dimerization between sulfur-containing molecules and their corresponding radical cations. Also, Clark¹³⁶ used this concept for rationalizing the ab initio computational stability of H_2SSH_2^+ and H_2SClH^+ relative to their fragments. Furthermore, Rossi¹³⁷ has discussed this concept while investigating the interaction between aryl radicals and nucleophiles. The interest of the present work is to examine if there is any possibility to generalize this model further to elucidate the course of unimolecular radical cation processes, including both geometry changes and reactions.

Let us rationalize the above He-He⁺ dimerization process from a different angle, i.e., consider it as an unimolecular

process. Imagine that two He atoms are held together to form a supramolecule whose molecular orbital description is shown in Fig.(5.5a-2). Now, we ask what happens when an electron is

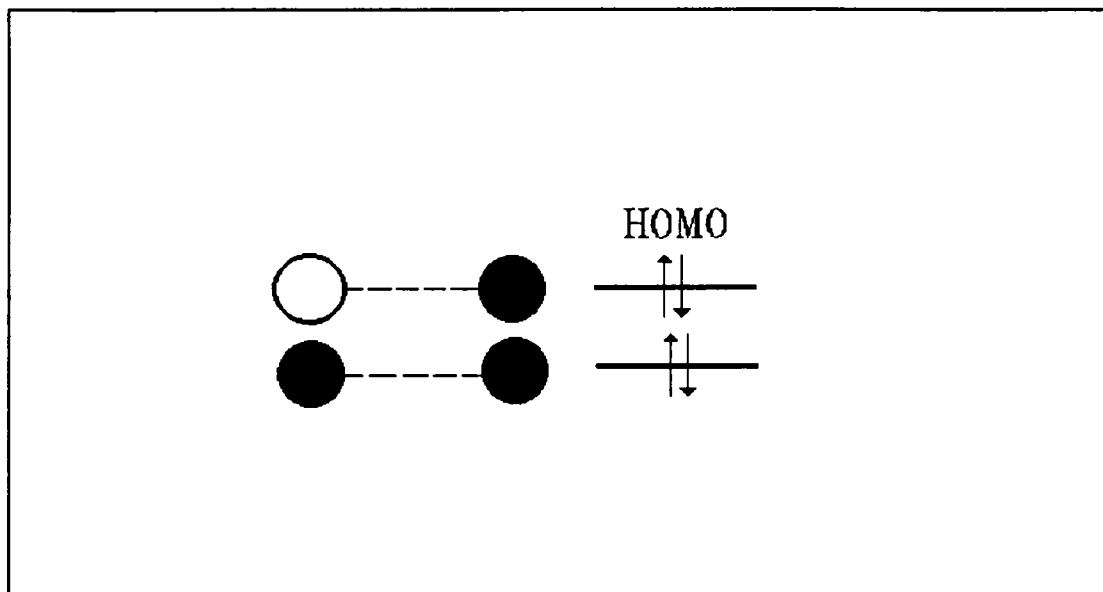


Fig.(5.5a-2). MO description of the imagined Helium dimer.

ejected from the molecule. If we choose the bond distance as the reaction coordinate and vary its length, a Walsh diagram (Fig.(5.5a-3)) can be constructed easily. It can be seen clearly from Fig.(5.5a-3) that the energy of the in-phase MO drops with the decrease of the bond length(R) due to the overlap of the atomic orbitals while that of the out-of-phase MO (SOMO) rises due to the anti-bonding interaction. As the low-energy orbital is doubly occupied, there is a net stabilization for this process. Hence, the bond distance in the radical cation will contract relative to that for the neutral molecule, which, of course, is the same prediction as that given by the three-electron model. Although this

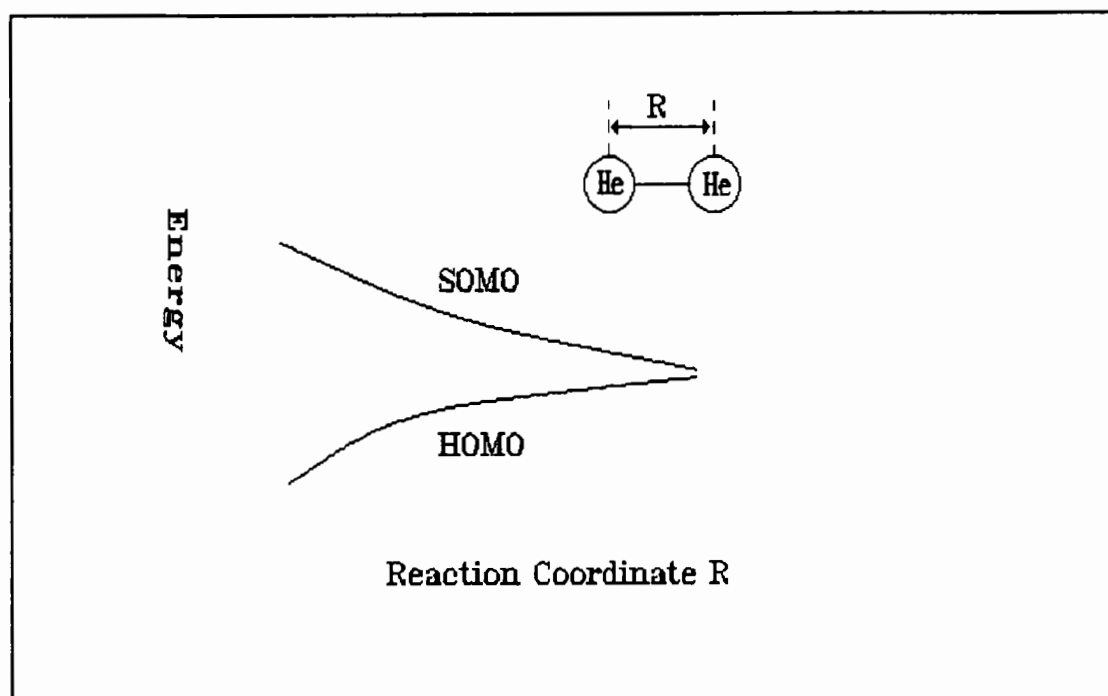


Fig.(5.5a-2). Changes in MO energies during the contraction of the $(\text{He})_2^+$ radical cation.

reformulation seems redundant because all bimolecular processes involving radicals can be similarly explained by invoking the general concept of the three-electron bond, there is a very useful implication hidden in the above treatment which is that the 3-electron bond model can be easily extended to cover unimolecular radical changes. All unimolecular processes of radicals have a tendency to take advantage of this "0.5-bonding principle", which can be put more precisely as

There is a special potential reaction channel available for a radical by means of which the overall energy is lowered as a result of a decrease in doubly-occupied MO energies which accompanies the destabilization of the SOMO energy change.

In the following section, we will apply this generalized three-electron bond model (GTEBM) to the problems of orbital reorganization in unimolecular processes in order to understand some radical reactions in the above four parts and in the literature.

Section B. Examples

1. Planarization of the NH_3 radical cation.¹³⁸

It has been known that although the neutral NH_3 molecule has a pyramidal structure, its radical cation has a planar structure. This observation can be rationalized by GTEBM as shown in Fig.(5.5b-1). The increase of the $\text{SOMO}(\text{sp}^3 \rightarrow \text{p})$ orbital energy during the planarization is compensated by the decrease of the three doubly-occupied σ -orbital energies caused by the hybridization change in the nitrogen atom($\text{sp}^3 \rightarrow \text{sp}^2$). Hence the planarization is favorable.

2. 1,2-Hydrogen shift of the allylamine radical cation.

As shown in Part I of this chapter, the allylamine radical cation can undergo the facile 1,2-hydrogen shift to form the distonic species $\bullet\text{CH}_2\text{CH}_2\text{CH}=\text{NH}_2$. Based on GTEBM, the thermodynamic driving force can be attributed to the formation of $\text{C}=\text{N}$ double bond and hybridization change associated with the nitrogen as shown in Fig.(5.5b-2).¹³⁹

3. The cyclization of the but-3-en-1-ol radical cation.

While the cyclization causes the breaking of the SOMO double bond in the but-3-en-1-ol radical cation, this energy gain is nicely compensated by the formation of a new σ -bond from the oxygen lone pair electrons (Fig.(5.5b-3)). According to GTEBT, the cyclization is thermodynamically favorable.

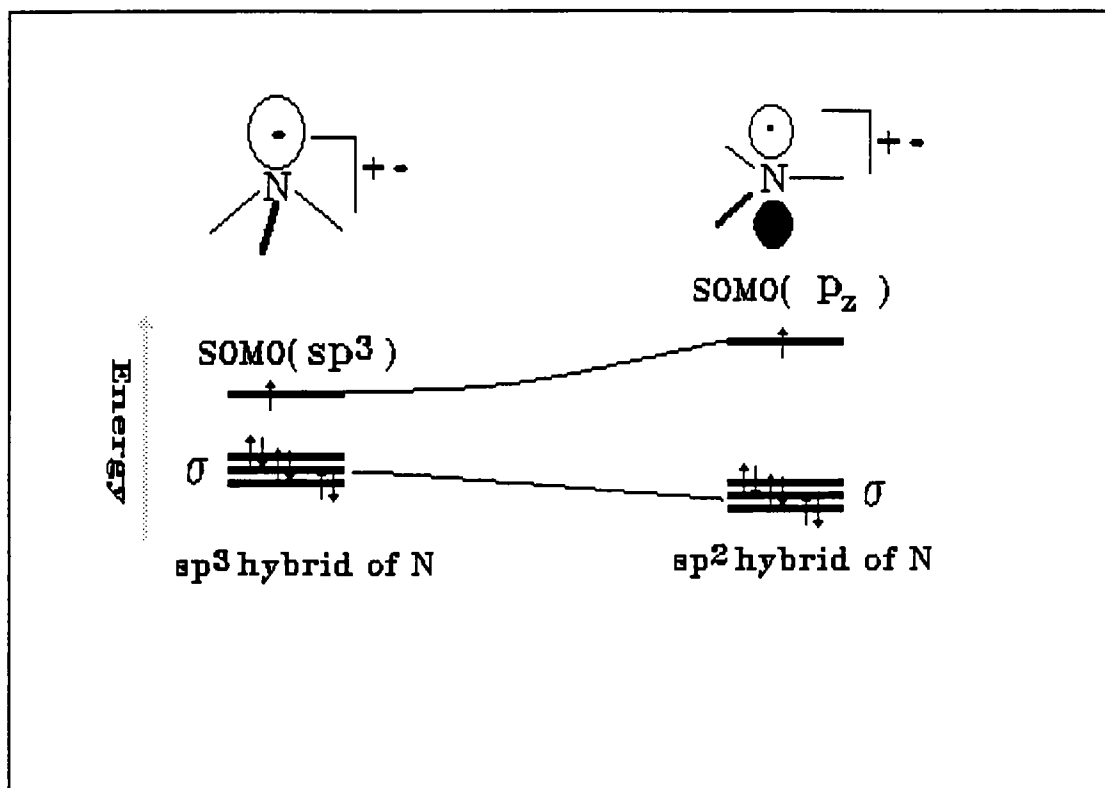


Fig.(5.5b-1). Changes in orbital energies during the process of the planarization.

4. Facile ring-opening of cyclopropane ring in the semibullvalene radical cation

The driving force for this ring-opening reaction has been rationalized in Part IV of Chapter 5 through the use of Eq.(5.4b-1) derived from the thermal cycle. In terms of GTEBM, this driving force can equivalently be attributed to the drops of the orbital energies of the two doubly-occupied HOMOs(b_2 and a_1 orbitals) in the bishomobenzene radical cation as compared to those of the corresponding doubly-occupied a'' and a' orbitals in the parent semibullvalene radical cation, as shown in Fig.(5.4b-1).

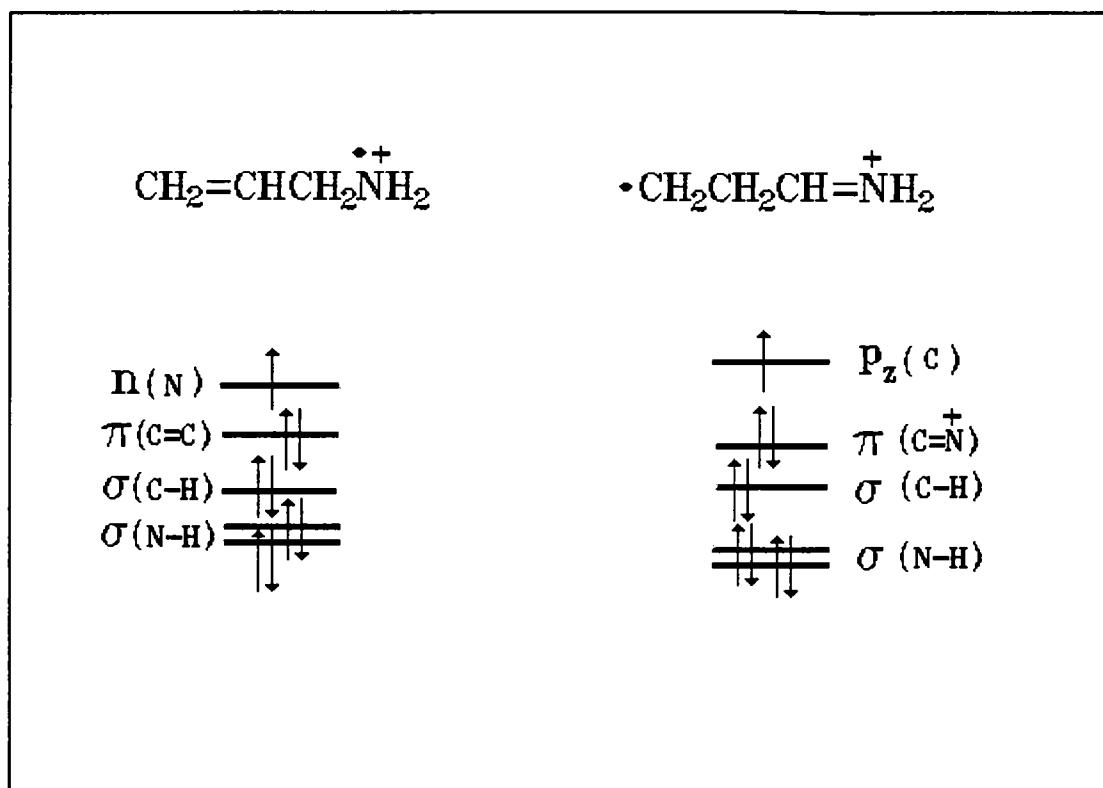


Fig.(5.5b-2). Changes in orbital energies during the 1,2-hydrogen transfer in the allylamine radical cation.

5. The cyclization of the 1,5-hexadiene radical cation.¹⁰²

As mentioned above, the 1,5-hexadiene radical cation can undergo an endo cyclization reaction to form the cyclohexane-1,4-diyl radical cation, which approximately corresponds to the transition state of the neutral molecule Cope rearrangement. This striking inversion relationship between the neutral and radical cation potential surfaces can be easily understood by invoking GTEBT. Fig.(5.5b-4) shows the qualitative orbital energy changes associated with the reaction. As seen from Fig.(5.5b-4), the energy increase of the non-bonding SOMO orbital of cyclohexane-1,4-diyl radical cation is well compensated by the energy decrease of the

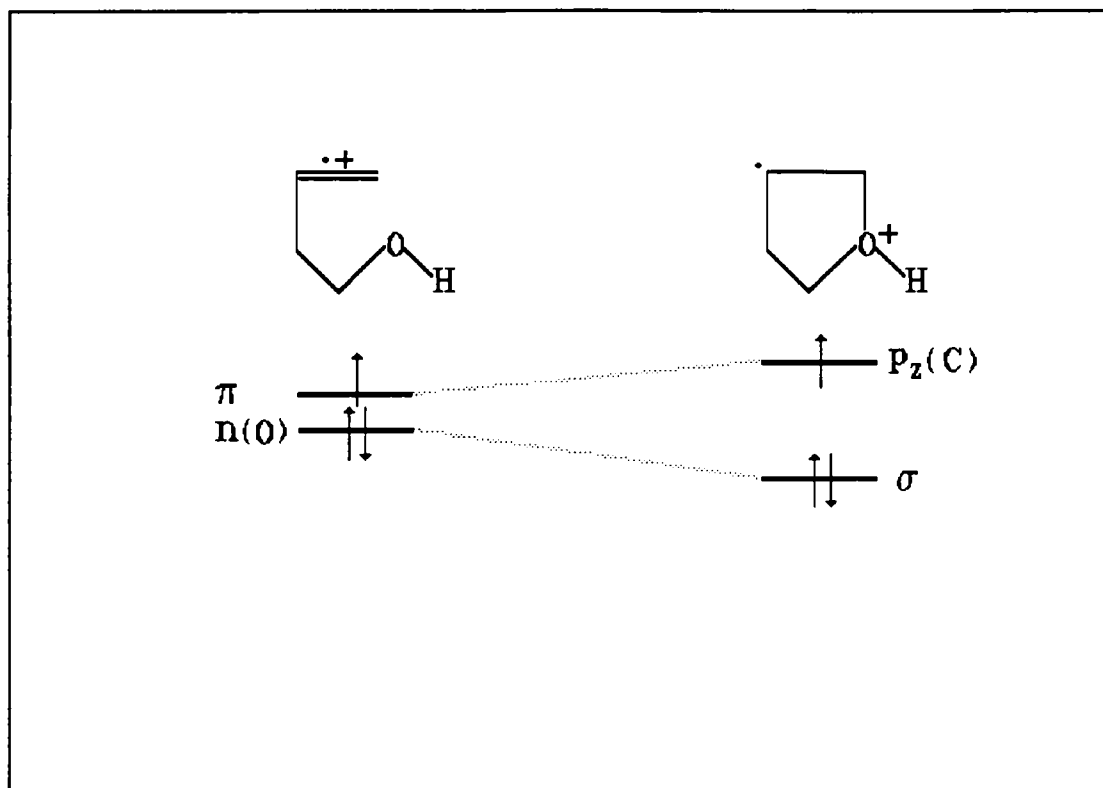


Fig.(5.5b-3). Changes in orbital energies during the endocyclization of the but-3-en-1-ol radical cation.

strong σ -orbital relative to the π -orbital energies of the parent radical cation. Clearly, the formation of the doubly-occupied strong σ -orbital provides the driving force for the reaction.

6. Energetic relation between the 5,6-dihydro-1,4-benzyne and the 1,5-hexadiyne radical cations.

As found through the AM1 calculation in Part III, the 5,6-dihydro-1,4-benzyne radical cation was lower in energy than the 1,5-hexadiyne radical cation. This phenomenon is very similar to the potential energy inversion discussed in 4. From the perspective of GTEBM, the driving force can be similarly attributed to the formation of the low energy doubly-occupied σ -bond(Fig.(5.5b-5)).

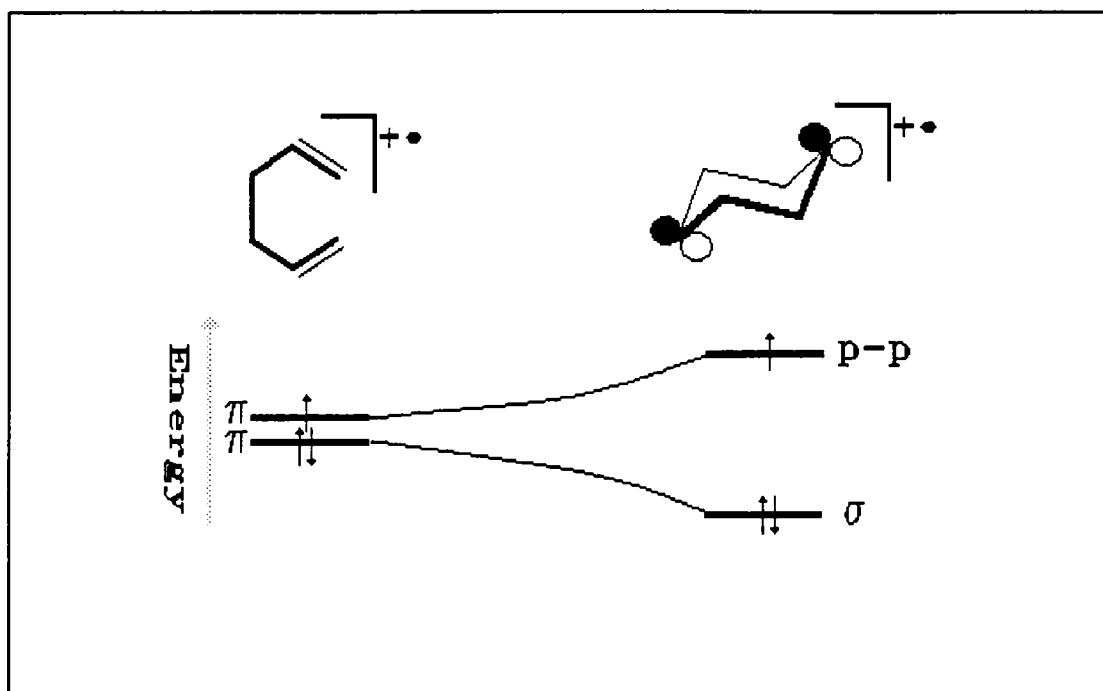


Fig.(5.5b-4). Changes in orbital energies during the endo cyclization of the 1,5-hexadiene radical cation.

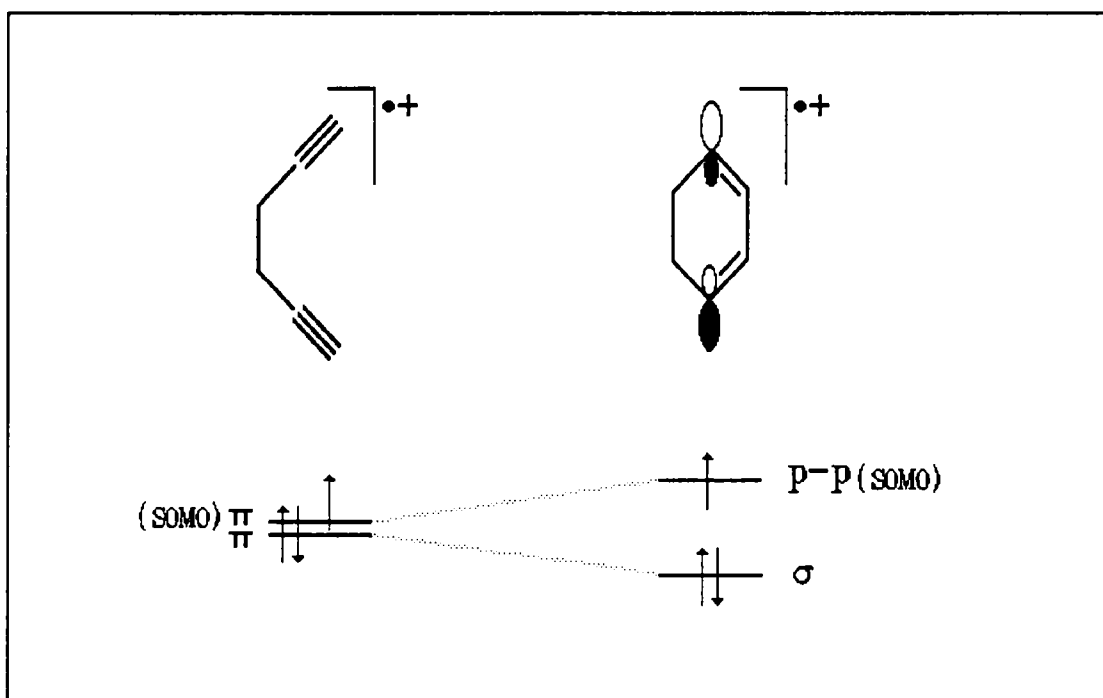


Fig.(5.5b-5). Changes in orbital energies during the endo cyclization of the 1,5-hexadiyne radical cation.

7. The partial planarization of the cycloheptatriene radical cation.

Recently, it has been found through the ESR experiment and AM1 calculation that the cycloheptatriene radical cation had a planar π -frame instead of the tub-like structure of its neutral molecule.¹⁴⁰ The occupied π -orbitals can be approximately constructed as in Fig.(5.5b-6) based on the simple LCAO. According to these qualitative MO diagrams, the orbital energy change directions can be easily derived during the planarization. The energies of the two doubly-occupied π -orbitals, especially the doubly-occupied a-orbital, will drop due to the more favorable overlaps among the neighboring π -p orbitals. Conversely the energy of the SOMO orbital will rise due to the reduction of the favorable in-phase through-space orbital interaction between the two terminal p orbitals in the π system. The process(Fig.(5.5b-7)) is thermodynamically favorable according to GTEBM.

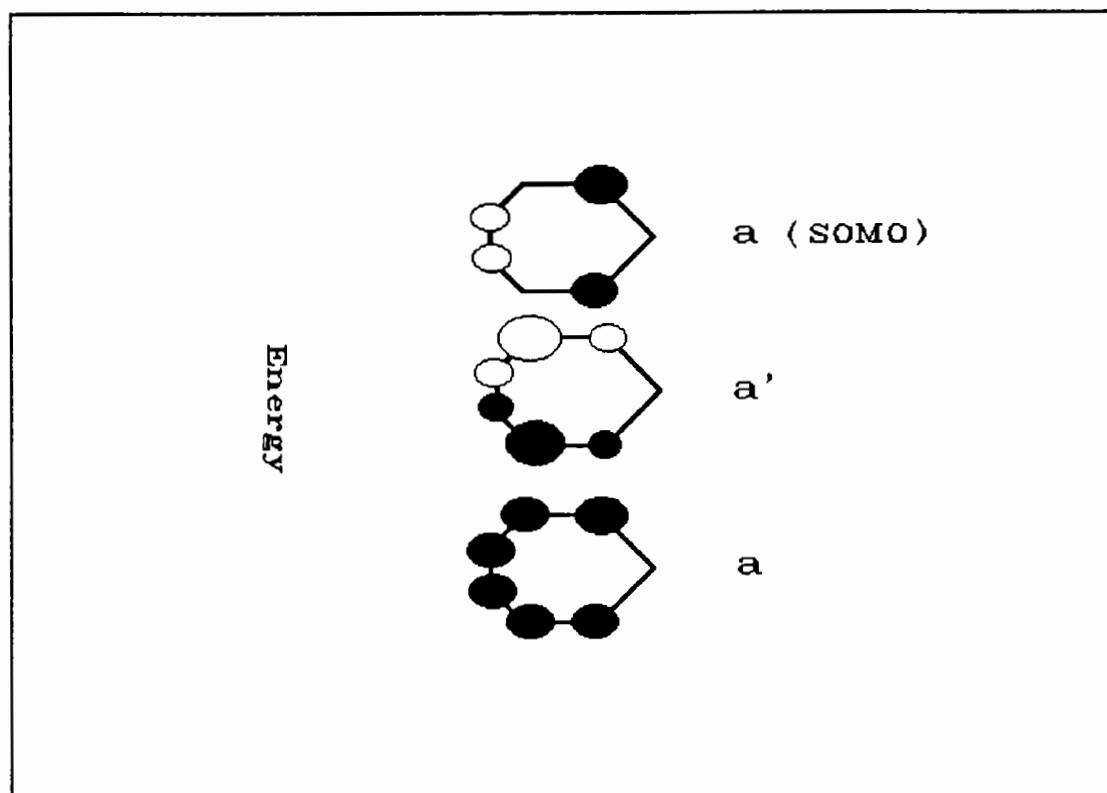


Fig.(5.5b-6). The approximate MO diagram of the cycloheptatriene radical cation.

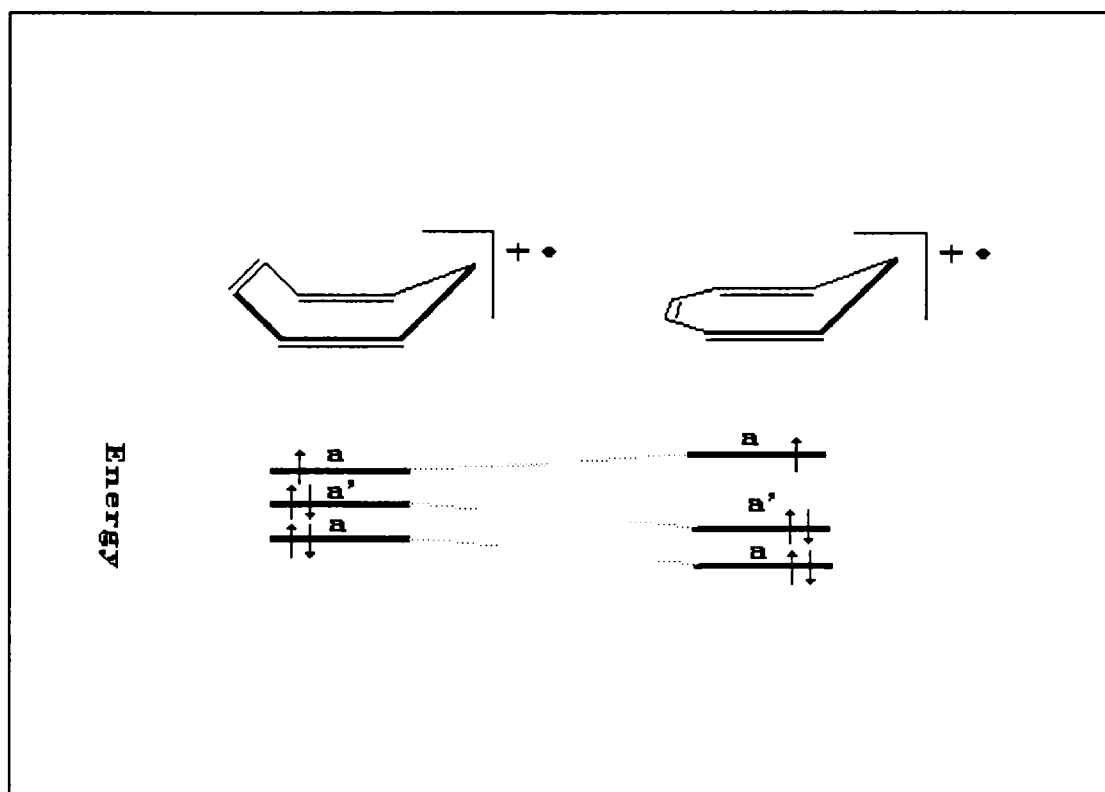


Fig.(5.5b-7). Changes in orbital energies during the planarization of the cycloheptatriene radical cation.

CHAPTER 6

RADICAL CATION PHOTOCHEMICAL REACTIONS

Introduction

This chapter is divided into two parts. The first part is devoted to the studies of the photoinduced ring-opening reaction of the 3,4-dimethylenecyclobutene radical cation, and the second part describes the photoinduced ring-closure reaction of the cyclooctatetraene radical cation. The general goal is to understand the fundamental principles governing radical cation photochemical reactions. Specifically, we want to test the validity of the Woodward-Hoffmann orbital symmetry rules as applied to radical cation photoreactions. This test is more stringent than that described in the preceding chapter since the radical cation photoreaction sometimes involves a Koopmans transition(Fig.(6-1)) which is unavailable in its neutral counterpart. The results below provide evidence for the existence of radical cation reactions dictated by the symmetry rules, although the general applicabilities of the Woodward-Hoffmann rules to radical cation reactions have recently been quite properly questioned.¹⁴¹

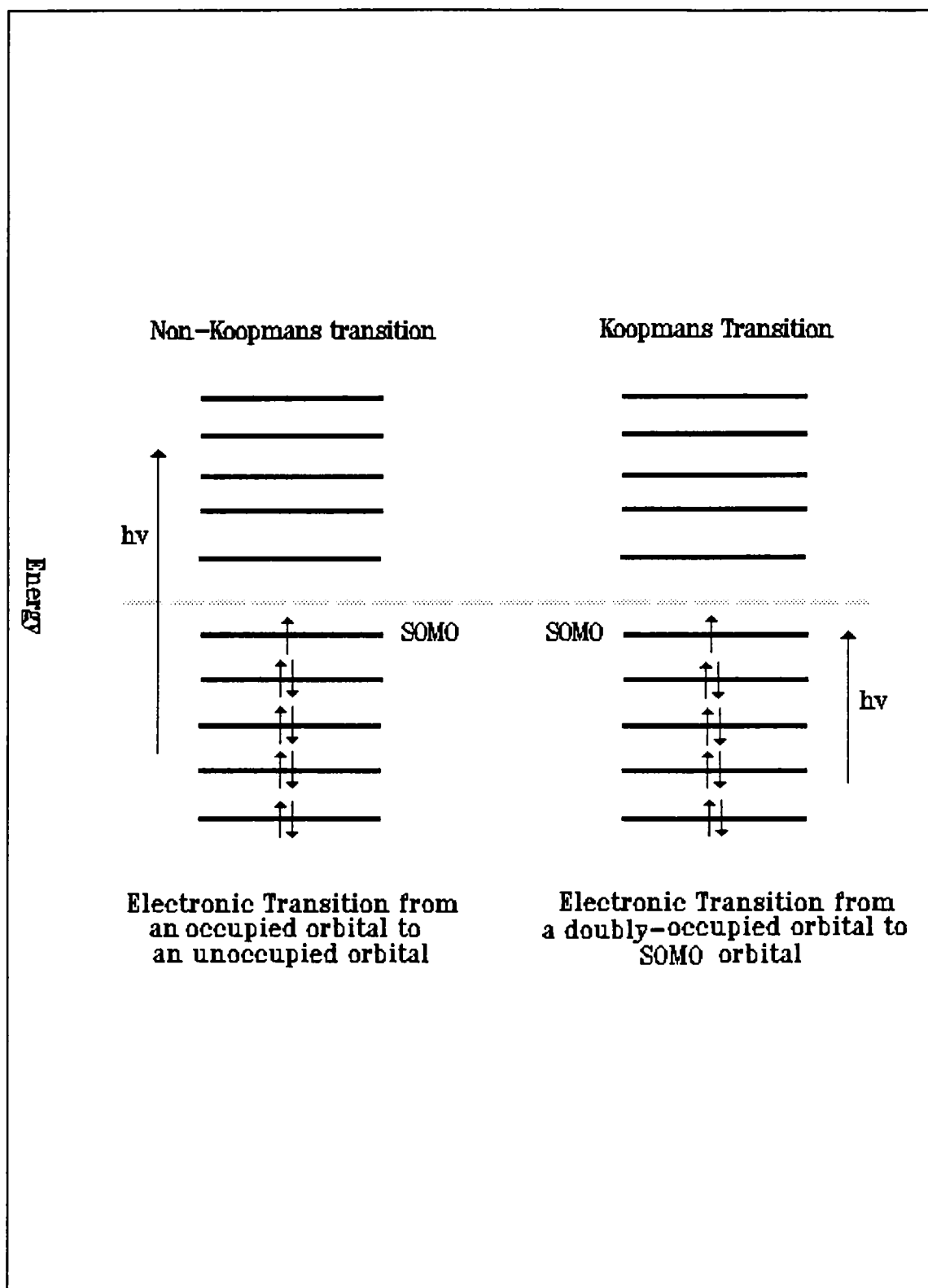
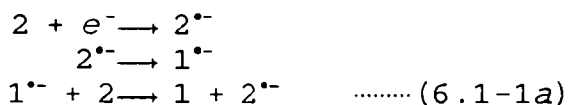


Fig.(6-1). Definitions of Non-Koopmans and Koopmans transitions.

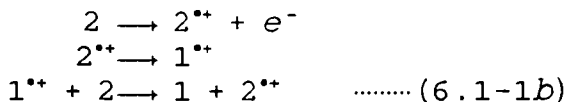
**Part I. The Photoinduced Ring-Opening of the
3,4-Dimethylenecyclobutene Radical Cation to the
1,2,4,5-Hexatetraene(Bisallene) Radical Cation at 77 K**

3,4-Dimethylenecyclobutene (1) is an interesting C₆H₆ isomer. It was first synthesized by Blomquist and Maitlis.¹⁴² Later, Huntsman et al. discovered that thermal pyrolysis of 1,5-hexadiyne quantitatively produced 3,4-dimethylenecyclobutene.¹¹¹ The reaction mechanism consisted of two steps: first, 1,5-hexadiyne molecule was transformed to 1,2,4,5-hexatetraene (2) via a rapid Cope rearrangement, which then underwent a thermal electrocyclic ring-closure of 2 to 1. More recent studies¹⁴³ have provided evidence that the latter ring-closure reaction in liquid solution phase can be accelerated by the presence of both electron-donating(e.g. cuprous salts) and electron-accepting(e.g. tris(4-bromophenyl)aminium cation) reagents. This led to a proposition^{143c,d} that a radical-initiated chain process(Reaction (6.1-1a) and (6.1-1b)) may be involved in

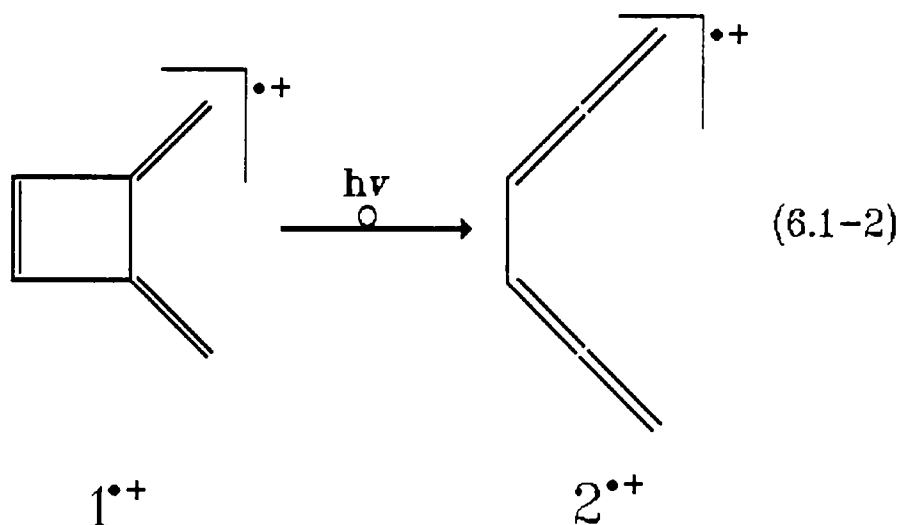
Radical Anion:



Radical Cation:



the ring-closure reaction with a radical-anion or radical-cation intermediate. Therefore, it was of interest to study the 3,4-dimethylenecyclobutene radical cation reaction directly. In this part, the photoinduced ring-opening of the 3,3-dimethylenecyclobutene (Reaction (6.1-2)) discovered recently in this laboratory is reported along with some computational(AM1) studies. Our results indicate that Reaction (6.1-2) is not only photo-allowed but also thermodynamically favorable, which suggests that the proposed radical cation chain mechanism (Reaction (6.1-1b)) is very unlikely.



Section A. Results

As shown in Fig.(6.1a-1a), the ESR spectrum of the radical produced from the radiolytic oxidation of the dimethylenecyclobutene in CF_3CCl_3 consists of seven well-resolved lines ($a(6\text{H})=6.6$ G) with an approximate 1:6:15:20:15:6:1 intensity ratio. When the sample was heated to the matrix softening point (150 K) from 77 K, no change in the spectral pattern was observed except for the spectral linewidth undergoing a reversible narrowing. This indicated that no thermal reactions had taken place. This nice ESR pattern with small hfcs suggests that six nearly equivalent α -hydrogens are involved, which implies that the most likely signal carrier is the parent radical cation. The qualitative SOMO orbital of the parent radical cation (Fig.(6.1a-2)) constructed from the interactions between π -orbitals of an ethylene fragment and π -orbitals of a butadiene fragment does suggest the possibility for the six α -hydrogens to have the approximately same coupling constant. In fact, the INDO calculation (Fig.(6.1a-3)) using the AM1-UHF-optimized geometry confirmed the above SOMO and predicted almost the same coupling constants for all six hydrogens with an average value of 6.3 G, which agrees very well with the experimental value of 6.6 G. These observations clearly establish the

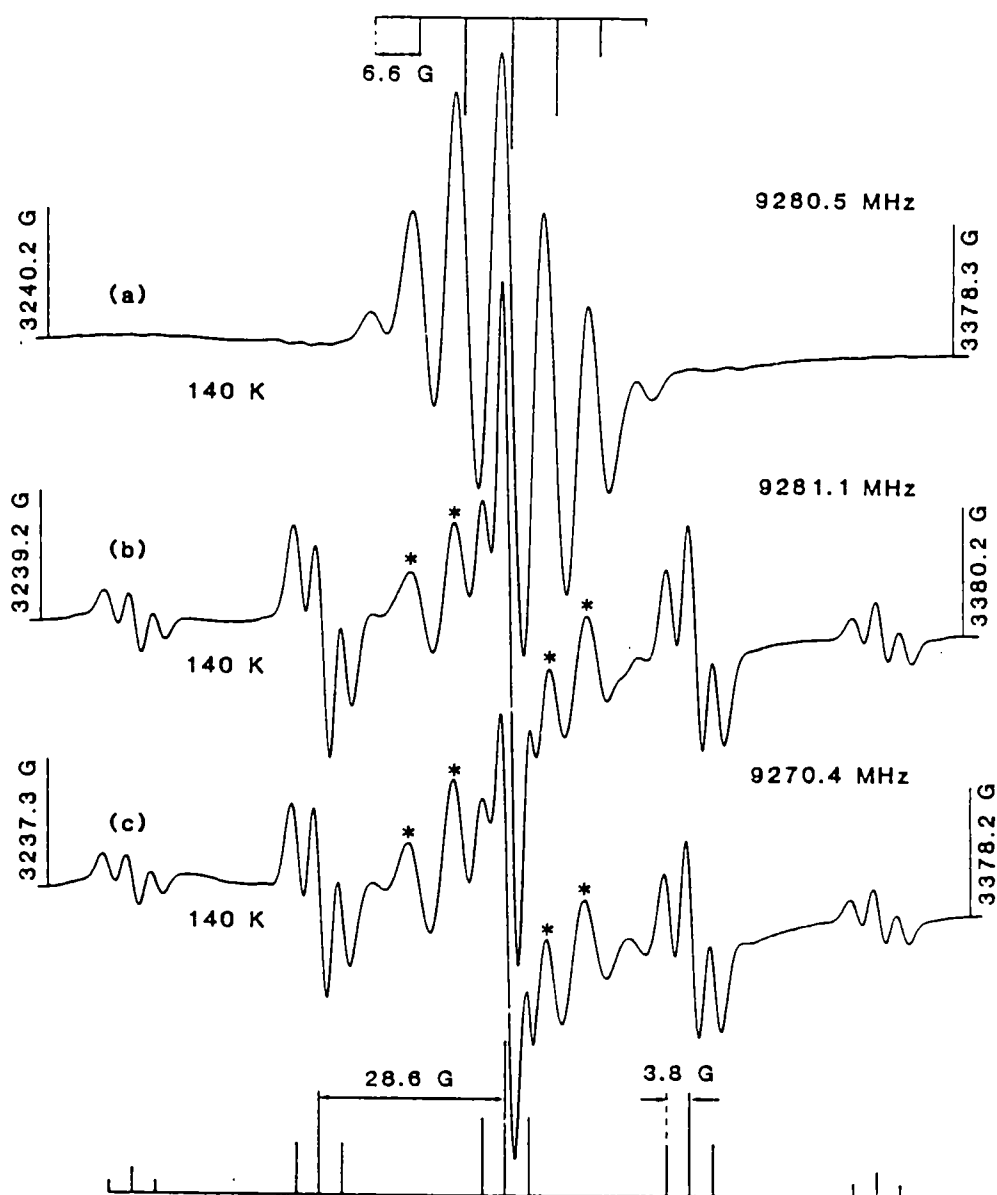


Fig.(6.1a-1). First-derivative ESR spectra recorded at 108 K from a 77 K γ -irradiated (dose, 0.25 Mrad) solid solution (0.5 mol %) of 3,4-dimethylenecyclobutene (a) before and (b) after exposure to visible light ($\lambda > 480$ nm) from a tungsten lamp, and of 1,2,4,5-hexatetraene (c) in CF_3CCl_3 . The spectrum (a) is assigned to the parent 3,4-dimethylenecyclobutene radical cation, while spectra in (b) and (c) are assigned to the 1,2,4,5-hexatetraene radical cation. The weaker signals denoted by asterisks in spectrum b are due to the residual signals of the parent 3,4-dimethylenecyclobutene radical cation.

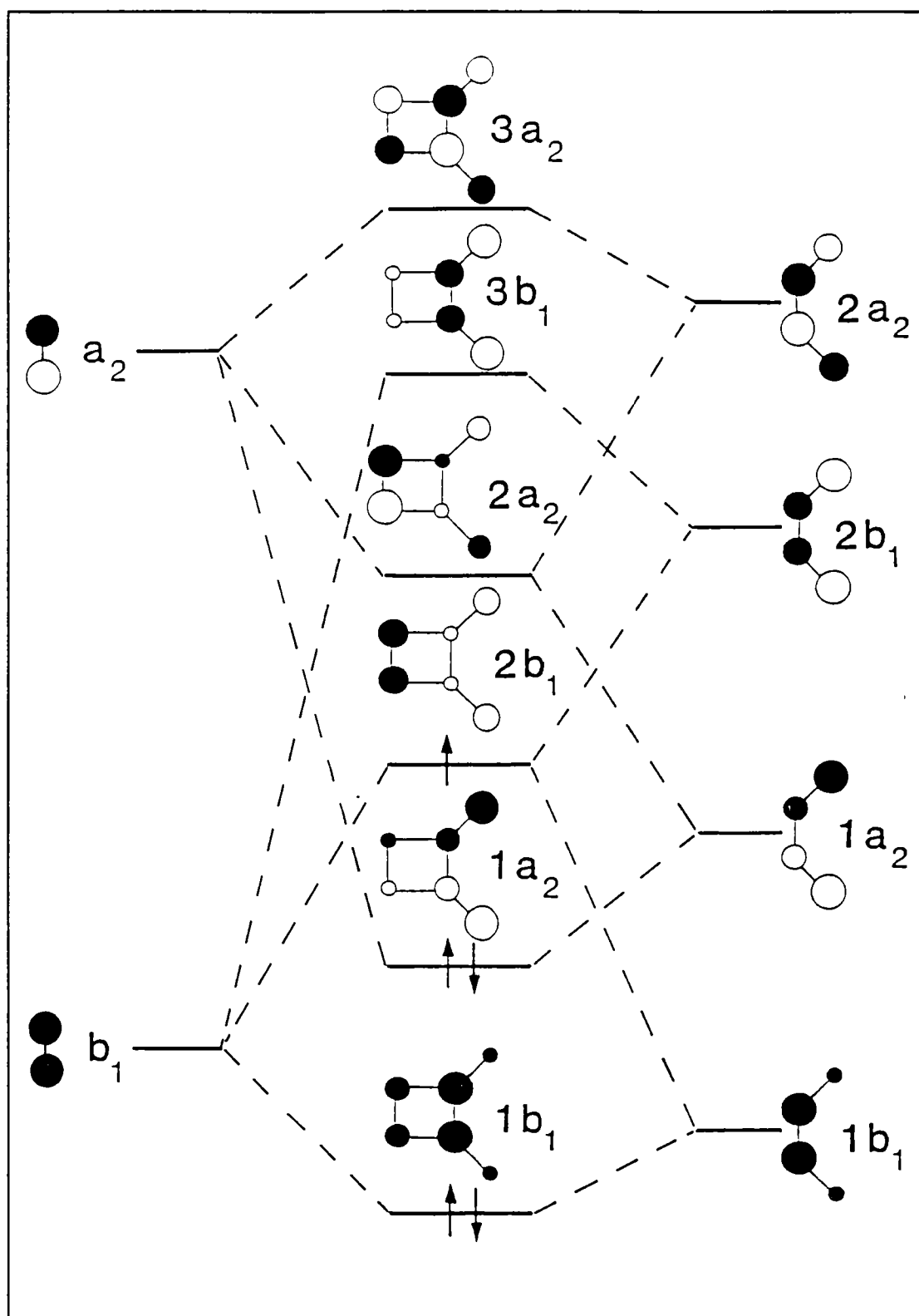


Fig.(6.1a-2). The MO diagram for the 3,4-dimethylenecyclobutene radical cation resulted from the fragment MO-orbital interactions.

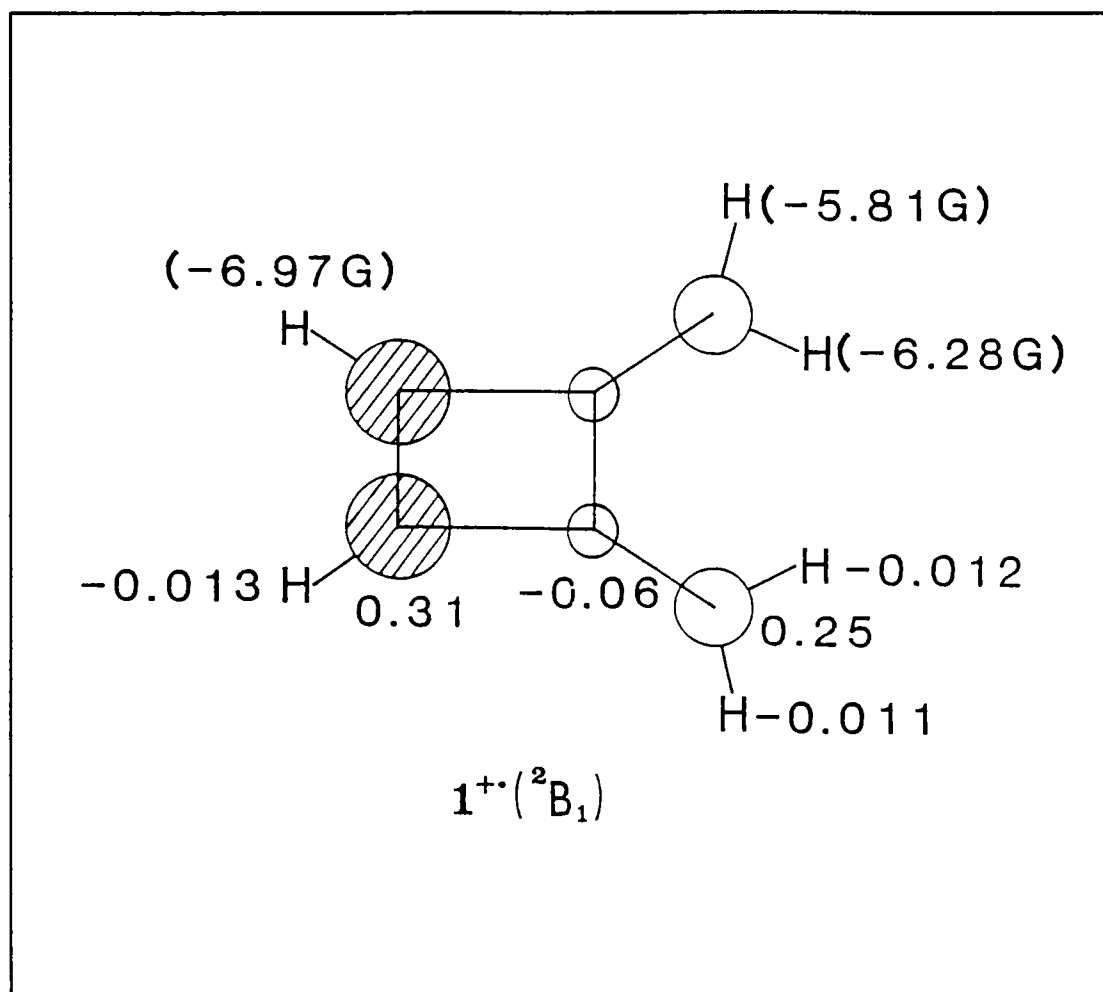


Fig.(6.1a-3). The INDO-calculated SOMO atomic orbital coefficients and coupling constants of the 3,4-dimethylenecyclobutene radical cation.

parent dimethylenecyclobutene radical cation as the signal carrier.

Upon being photobleached by visible light from a tungsten lamp for 15 minutes, the seven-line spectrum irreversibly changed to a quintet ($a(4H)=28.6$ G) of triplets ($a(2H)=3.8$ G), which is exactly the same spectral pattern as that obtained from the 1,2,4,5-hexatetraene radical cation in the same matrix. This strongly indicates that the dimethylenecyclobutene $1^{\cdot+}$ had rearranged to the latter radical cation $2^{\cdot+}$ through photo-excitation, as shown in Reaction (6.2-2).

Similar results were found in the $CF_2ClCFCl_2$ matrix at low temperature (77 K-110 K). Above 110 K, the spectrum of the parent radical cation started to change to a complicated pattern in this matrix. This was presumably due to the expected ion-molecule dimerization since the resulting spectrum was the same as that produced from the radiolytic oxidation of 3,4-dimethylenecyclobutene in the CF_3CCl_3 matrix when a relatively high concentration of dimethylenecyclobutene was employed. The photoisomerization in CF_3CCl_3 was also reproduced in $CFCl_3$ except for the relatively weaker ESR intensity of the photoproduct. This may be due to the low solubility of the 1,2,4,6-hexatetraene in this particular matrix at low temperature.

Section B. Discussion

As discussed in Part III of Chapter 5, the thermal stability of the 1,2,5,6-hexatetraene radical cation is calculated to be greater than that of the 3,4-dimethylenecyclobutene radical cation by 12.5 kcal/mol according to the AM1-derived heats of formation. This implies that there is a thermodynamic driving force available for the ring-opening reaction. This reaction trend contrasts with that of the corresponding neutral reaction where the opposite ring-closure reaction is thermodynamically favorable.^{111,143} No thermal isomerization was, however, observed in the accessible temperature ranges of the three matrices (<160 K), which means that there exists an activation barrier to the thermal ring-opening reaction. In agreement with this observation, the Woodward-Hoffmann orbital symmetry rules¹¹⁹ indicate that neither the conrotatory ring-opening nor the disrotatory ring-opening is a symmetry-allowed thermal reaction. In the disrotatory case where the plane of symmetry bisecting the broken σ bond is preserved, the ground state $^2A_2$ of the reactant $1^\cdot$ is correlated to the $^2B_1$ non-Koopmans excited state of the product $2^\cdot$ (Fig.(6.1b-1)), while in the conrotatory opening where the C_2 axis is preserved, the

ground state is connected to the Koopmans excited state ${}^2B_1$ of the product(Fig.(6.1b-2)). In contrast, both kinds of ring-openings are photo-allowed, as seen from Fig.(6.1b-3) and Fig.(6.1b-4). This is consistent with the experimental observation of the photoreaction. The photoinduced conrotatory ring-opening involves a Koopmans transition, whereas the photoinduced disrotatory opening requires a non-Koopmans transition. The NCG(Neutral at Cation Geometry) calculation of 1^+ predicts that the first electronic transition is of the Koopmans type with a peak value at 1211.8 nm and a normalized transition moment equal to 0.4990. However, selective band photobleaching experiments indicated that no photoisomerization was induced with light in this near IR range($\lambda > 840$ nm). On the other hand, photobleaching using light between 400 and 840 nm resulted readily in the photoisomerization. This indicated that the non-Koopmans transition is more likely to be responsible for Reaction (6.1-2) in our experimental conditions.

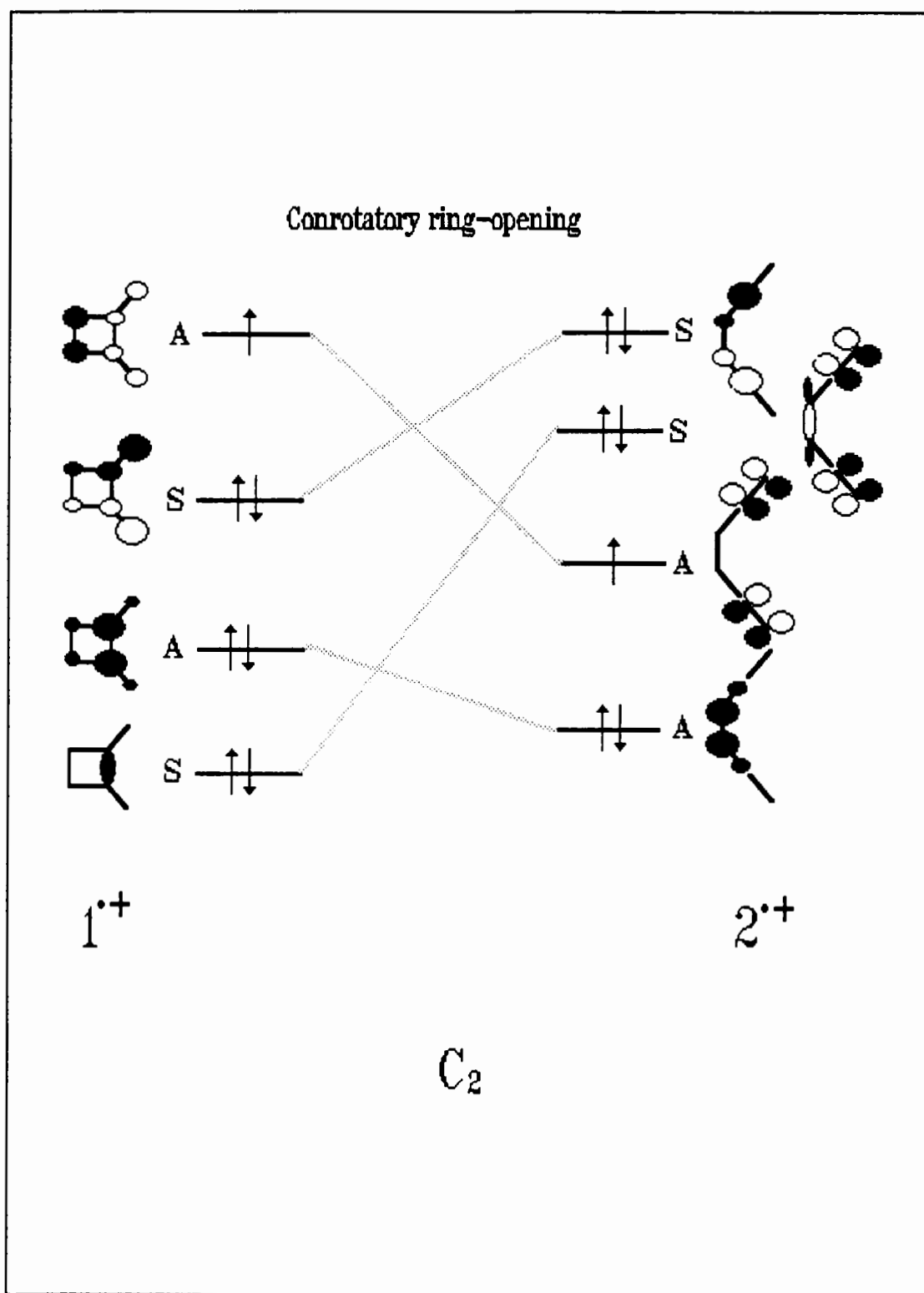


Fig.(6.1b-1). Orbital symmetry correlation diagram for the thermal conrotatory ring-opening of the 3,4-dimethylenecyclobutene radical cation to the 1,2,4,5-hexatetraene radical cation.

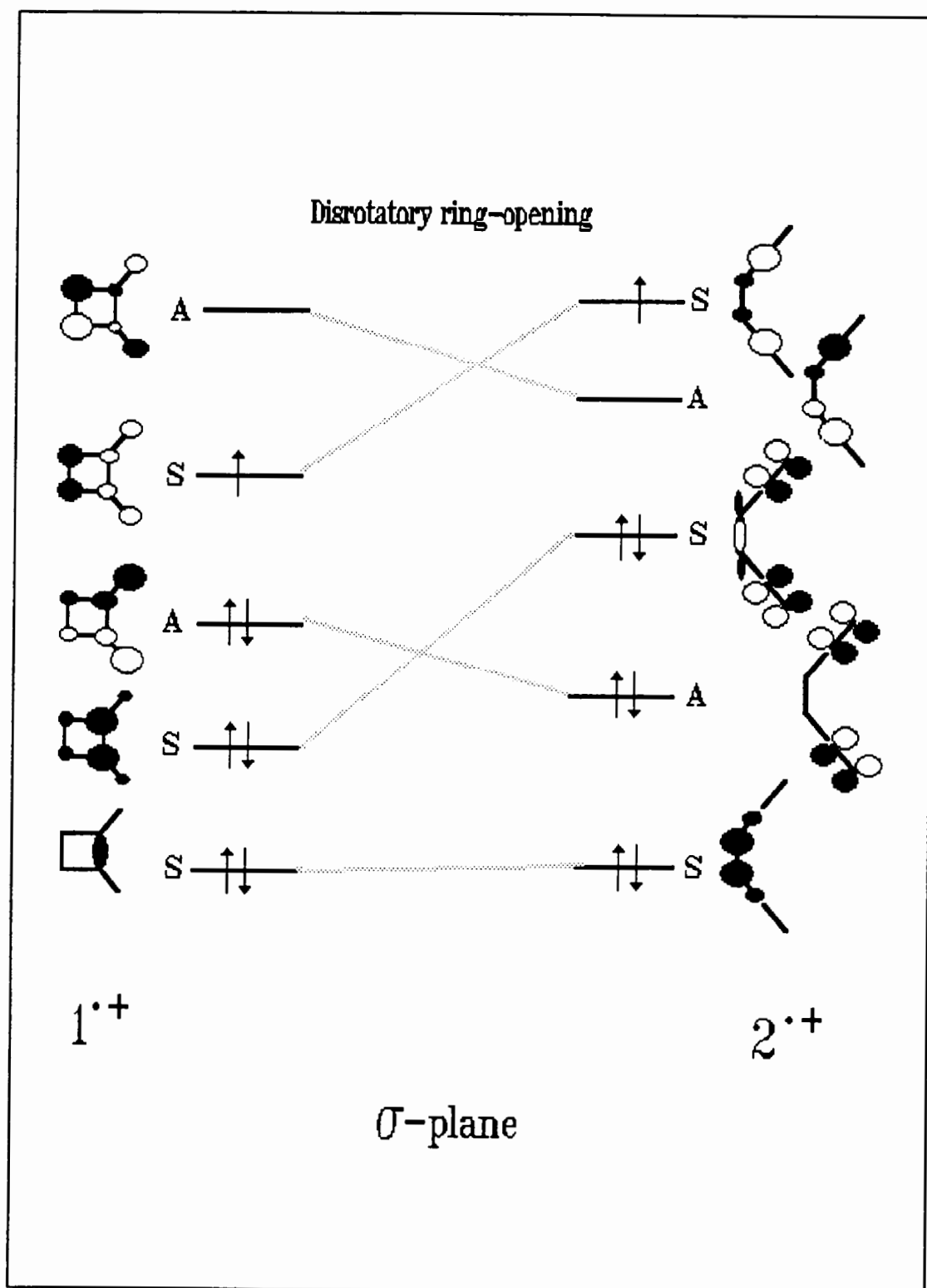


Fig.(6.1b-2). Orbital symmetry correlation diagram for the thermal disrotatory ring-opening of the 3,4-dimethylenecyclobutene radical cation to the 1,2,4,5-hexatetraene radical cation.

Photoinduced conrotatory ring-opening

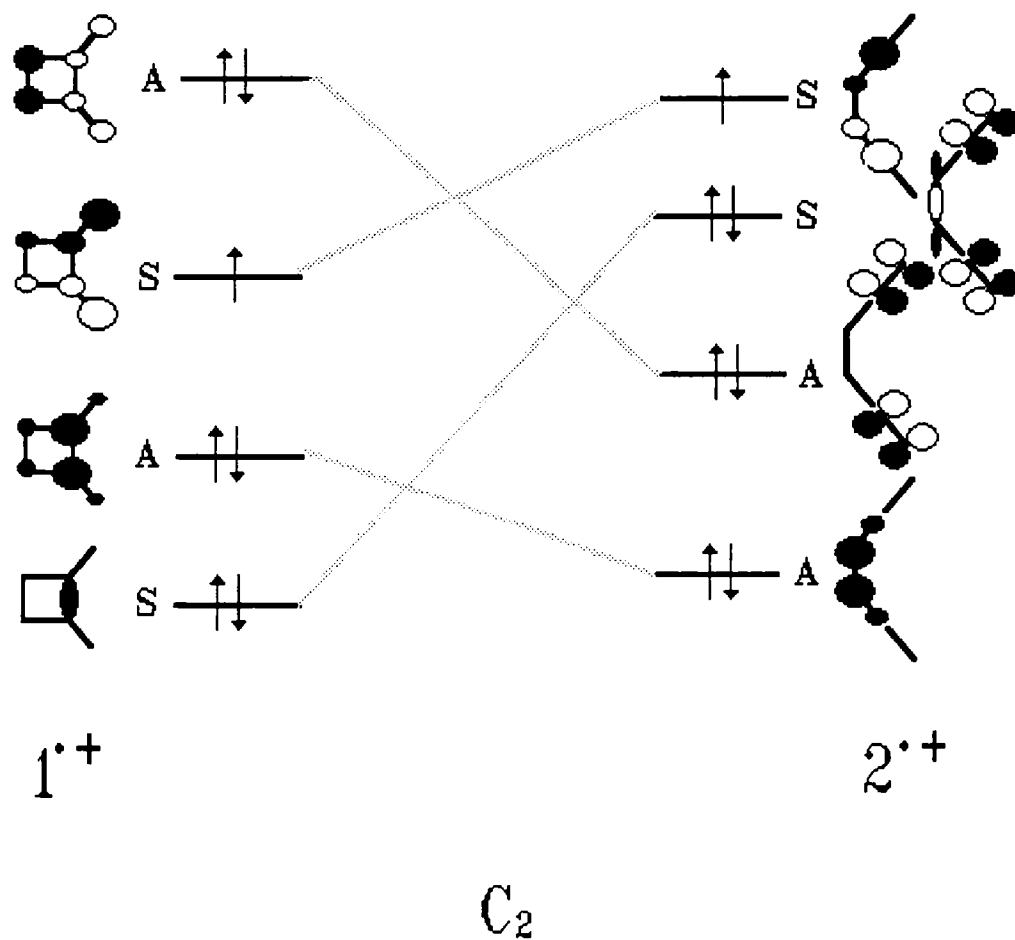


Fig.(6.1b-3). Orbital symmetry correlation diagram for the photoinduced conrotatory ring-opening of the 3,4-dimethylenecyclobutene radical cation to the 1,2,4,5-hexatetraene radical cation.

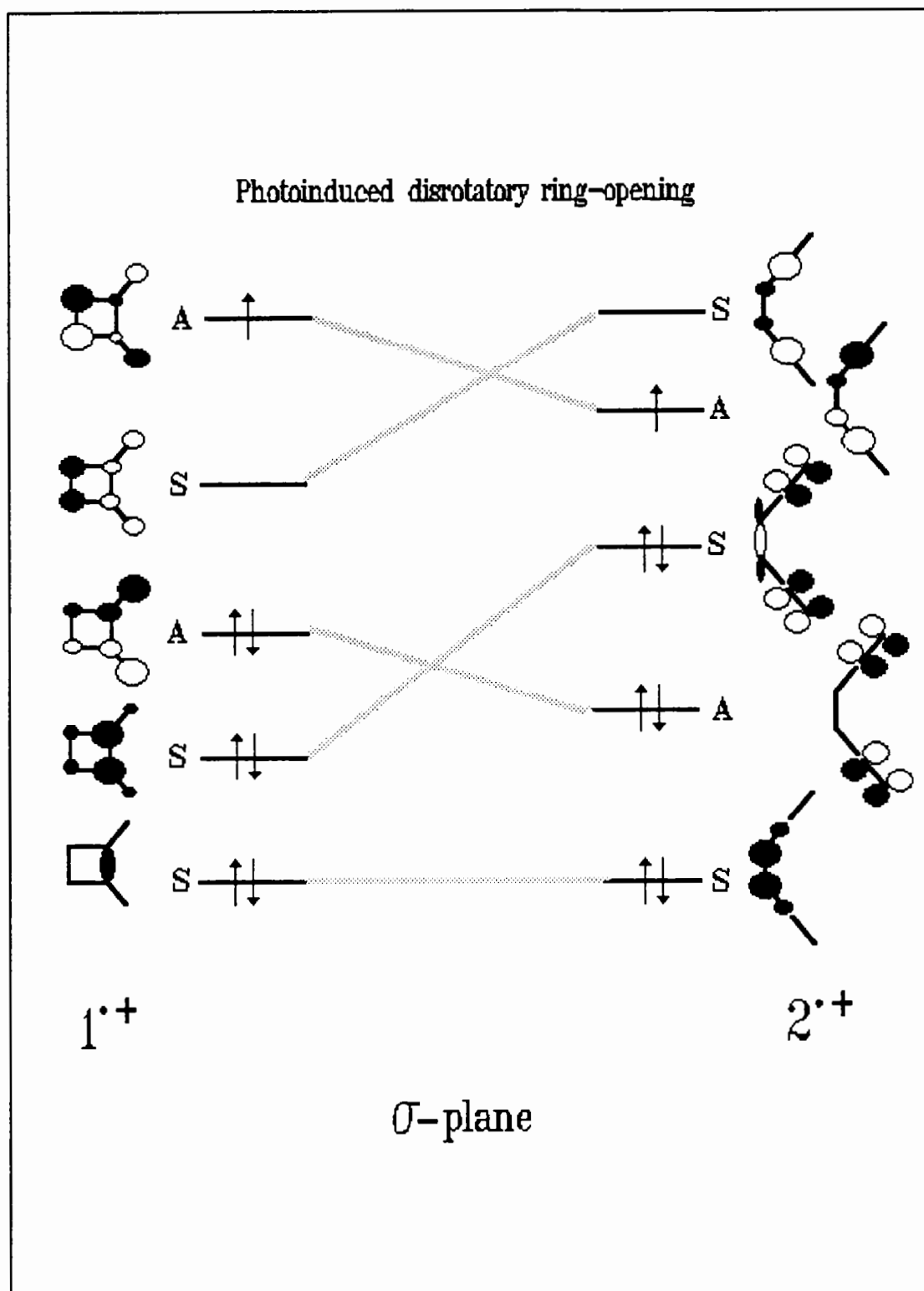
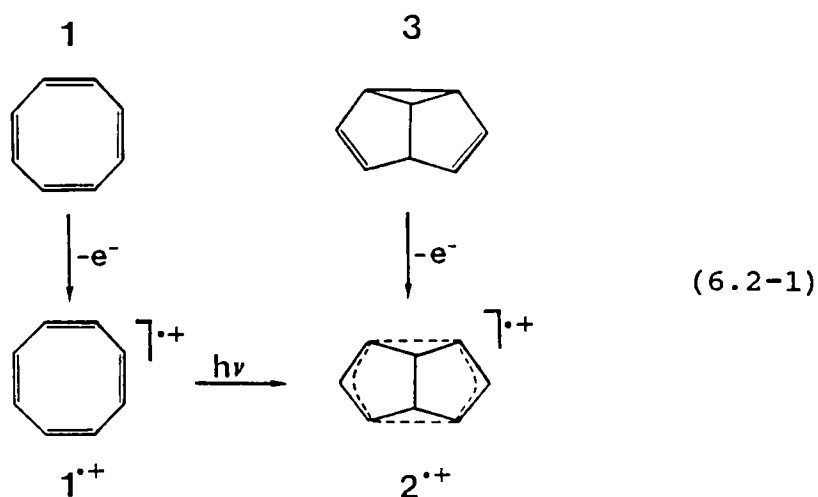


Fig.(6.1b-4). Orbital symmetry correlation diagram for the photoinduced disrotatory ring-opening of the 3,4-dimethylenecyclobutene radical cation to the 1,2,4,5-hexatetraene radical cation.

**Part II. Photoinduced Electrocyclic 1,5-Closure of the
Cyclooctatetraene Radical Cation to
a Bridged 1,4-Bishomobenzene
(Bicyclo[3.3.0]octa-2,6-diene-4,8-diyl) Radical Cation**

Cyclooctatetraene(COT) is an interesting classical nonaromatic compound with a nonplanar tub-like geometry.¹²³ Both thermal and photochemical isomerizations of the neutral molecule have been intensively studied.¹²³ Reactions of the corresponding dication methyl derivatives have also been studied by Olah, Paquette and their coworkers.¹⁴⁴ In contrast, the reactivities of the COT radical cation are virtually unknown. In this part, our recent discoveries on the photoinduced 1,5-closure of the COT radical cation ($1^{\cdot+}$) to the bridged 1,4-bishomobenzene(bicyclo[3.3.0]octa-2,6-diene-4,8-diyl) radical cation $2^{\cdot+}$ at 77 K in Freon matrices(Reaction (6.2-1)) are described.



It should be pointed out that the striking photochromatic effect associated with the photo reaction (6.2-1) was first discovered by Shida and Iwata.¹⁴⁵ However, these authors attributed it to the conformation change of the COT radical cation instead of the isomerization reaction.

Section A. Results

Cyclooctatetraene was γ -irradiated at 77 K in $\text{CF}_2\text{ClCFCl}_2$ matrix. As shown in Fig.(6.2a-1a), a broad single ESR line was produced with an approximately 8-12 G linewidth, which is the same as the total ESR width of the parent D_{2d} tub-like radical cation in the liquid state reported by Dessau.^{146,147} This strongly indicates that the same signal carrier is involved, since the fine structure from the small 1.5 G coupling constant found in the liquid state would be broadened out by the large linewidth in the low-temperature solid matrix. No change in the spectral pattern was observed when the sample was warmed up to the matrix softening point, except for the spectral linewidth undergoing a reversible line narrowing due to molecular motions. Upon photobleaching by visible light from a tungsten lamp, the red color of the initial sample rapidly turned blue. Similarly, the ESR spectrum changed irreversibly to a triplet($a(2H)=36.2$ G)-of-

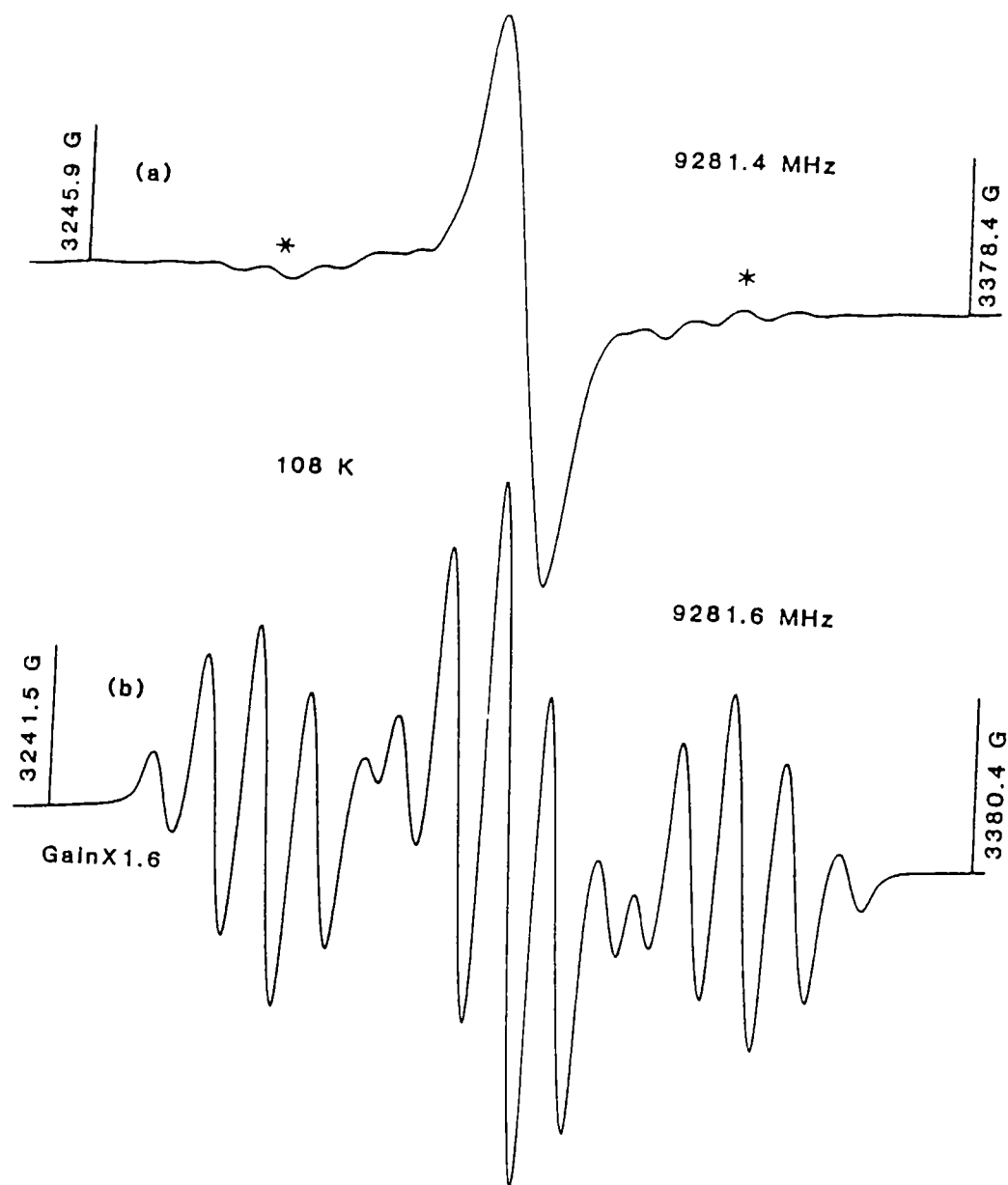


Fig. (6.2a-1). First-derivative ESR spectra recorded at 108 K from a 77-K γ -irradiated (dose, 0.25 Mrad) solid solution (0.5 mol%) of cyclooctatetraene in $\text{CF}_2\text{ClCFCl}_2$ (a) before and (b) after exposure to visible light ($\lambda > 480$ nm) from a tungsten lamp. The spectra in a and b are assigned to the cyclooctatetraene and bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cations, respectively. The weak signals denoted by asterisks in spectrum a occur at approximately the same line positions as the strong photoinduced signals in b.

quintets($a(4H)=7.7$ G) pattern with a g-value equal to 2.0029(3) as shown in Fig.(6.2a-1b). Both the final spectrum and the sample color were identical with those of the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation produced independently from semibullvalene under the same conditions(see Part IV of Chapter 5). This clearly indicates that Reaction (6.2-1) had occurred. The same photochemical reaction was also found in the other two matrices (CF_3CCl_3 and $CFCl_3$).

The EA studies in the Freon mixture matrix ($CFCl_3+CF_2BrCF_2Br$; equivolume solution) confirmed the findings by Shida and Iwata.¹⁴⁴ The UV spectrum of $1^{\cdot+}$ had a strong absorption band in the visible region($\lambda_{max}=507$ nm). Upon photobleaching with visible light from a tungsten lamp, this band was replaced by two bands with λ_{max} values at 399 nm and 635 nm and a group of low-intensity sharp peaks around 550 nm. The two former bands matched very well with the EA spectrum of $2^{\cdot+}$ generated independently from 3, and this again confirms the ESR evidence for the photoisomerization. The latter low-intensity peaks are assigned tentatively to linear polyenes produced from photobleaching.

Section B. Discussion

If no large geometric changes are involved in going to the parent radical cation from its neutral molecule, the EA band associated with a Koopmans transition should be approximately equal to the neutral molecule IP difference between the two occupied orbitals involved in the transition(Fig.(6.2b-1)). The IP values of the $5a_1$ and $7e$ orbitals are 8.42 eV and 9.78 eV respectively,¹⁴⁷ giving rise to a 1.36 eV(911 nm) difference. This is clearly inconsistent with our experimental value of 2.45 eV(507 nm), which in turn implies that a relatively large geometric change has occurred. In fact, the AM1 calculations do reflect a large geometric difference between the radical cation(Fig.(6.2b-2)) and the neutral molecule(Fig.(6.2b-3)). The AM1-optimized geometry of the COT radical cation is more flat than that of the neutral molecule as seen from the marked dihedral angle in Fig.(6.2b-2) and (6.2b-3). This radical cation planarization effect can be easily rationalized by considering the qualitative occupied π -MO diagram¹²³ (Fig.(6.2b-4)). As the molecule begins to undergo the planarization, the energy of the SOMO orbital rises due to both the decrease of the in-phase through-space interactions between the two pairs of transoid ethylene π -orbitals and the

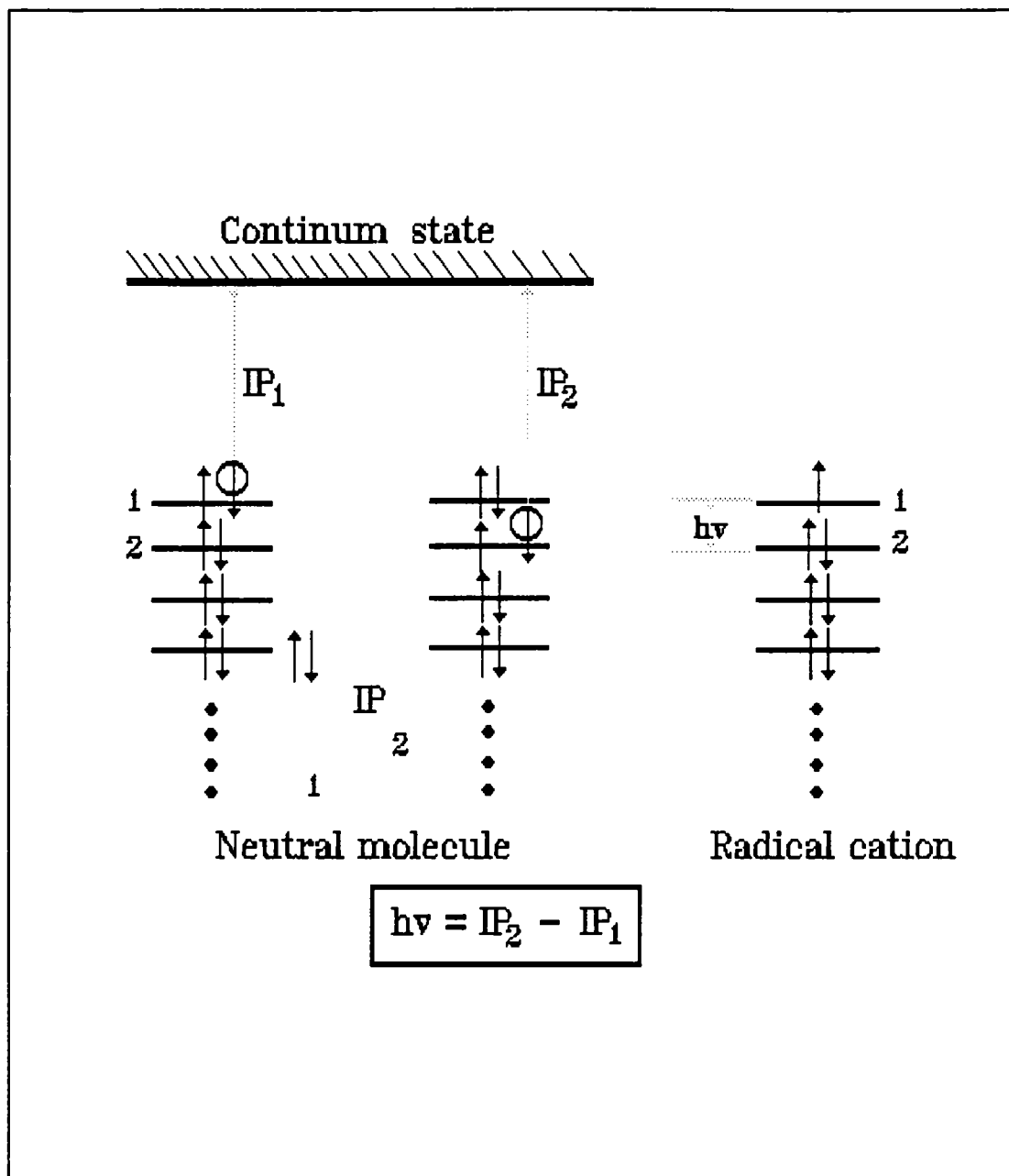


Fig.(6.2b-1). The relationship between IP's of a neutral molecule and its radical cation EA transition.

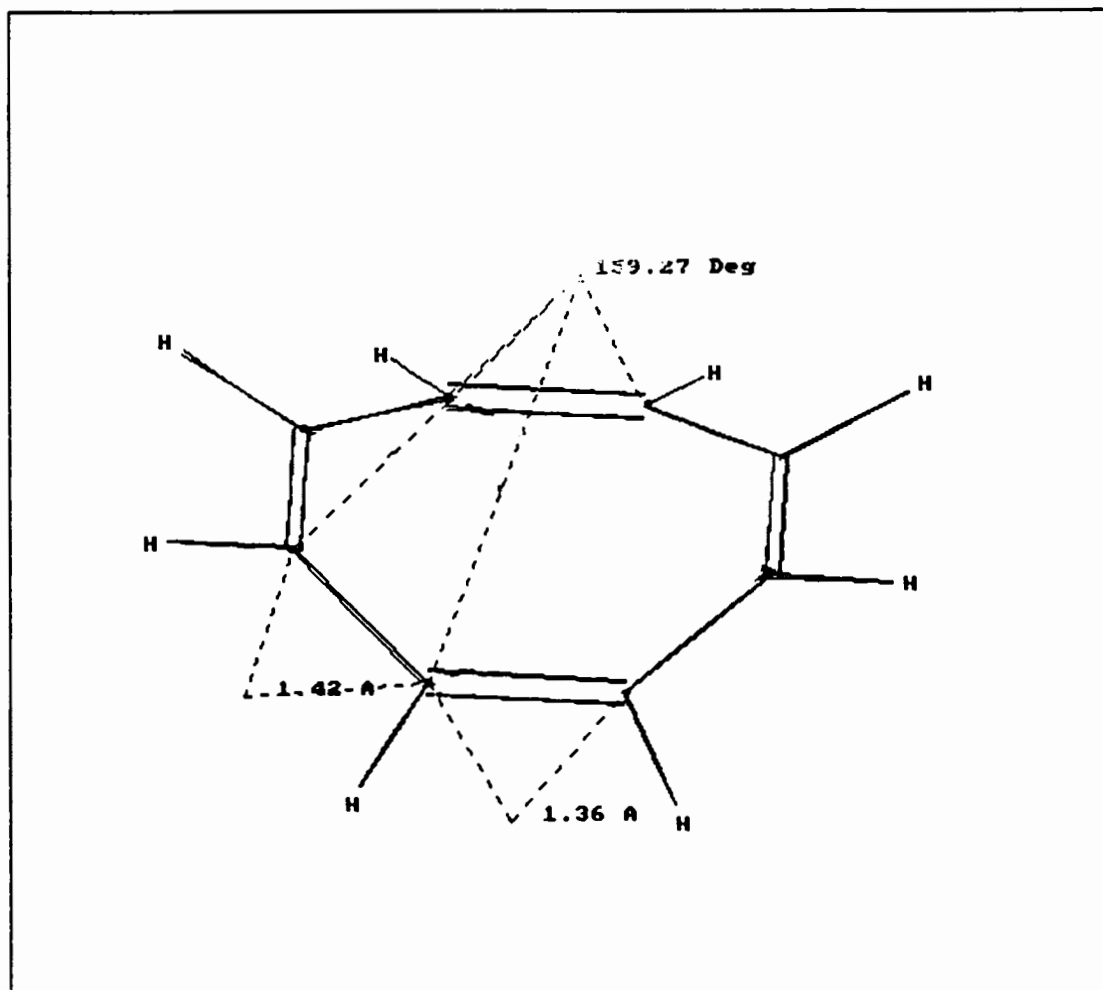


Fig.(6.2b-2). The AM1-UHF optimized cyclooctatetraene radical cation geometry with a D_{2d} symmetry constraint.

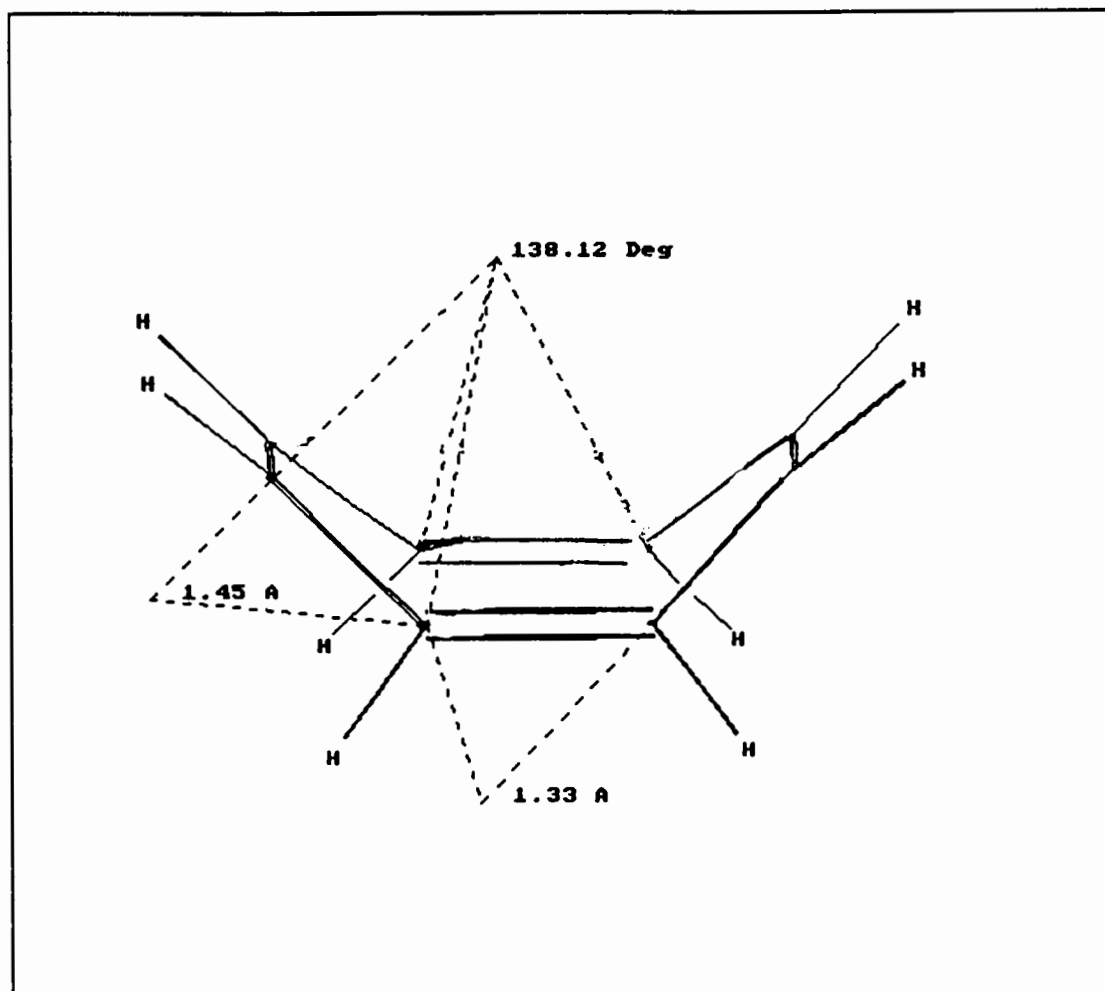


Fig.(6.2b-3). The AM1-optimized cyclooctatetraene neutral molecule geometry with a D_{2d} symmetry constraint.

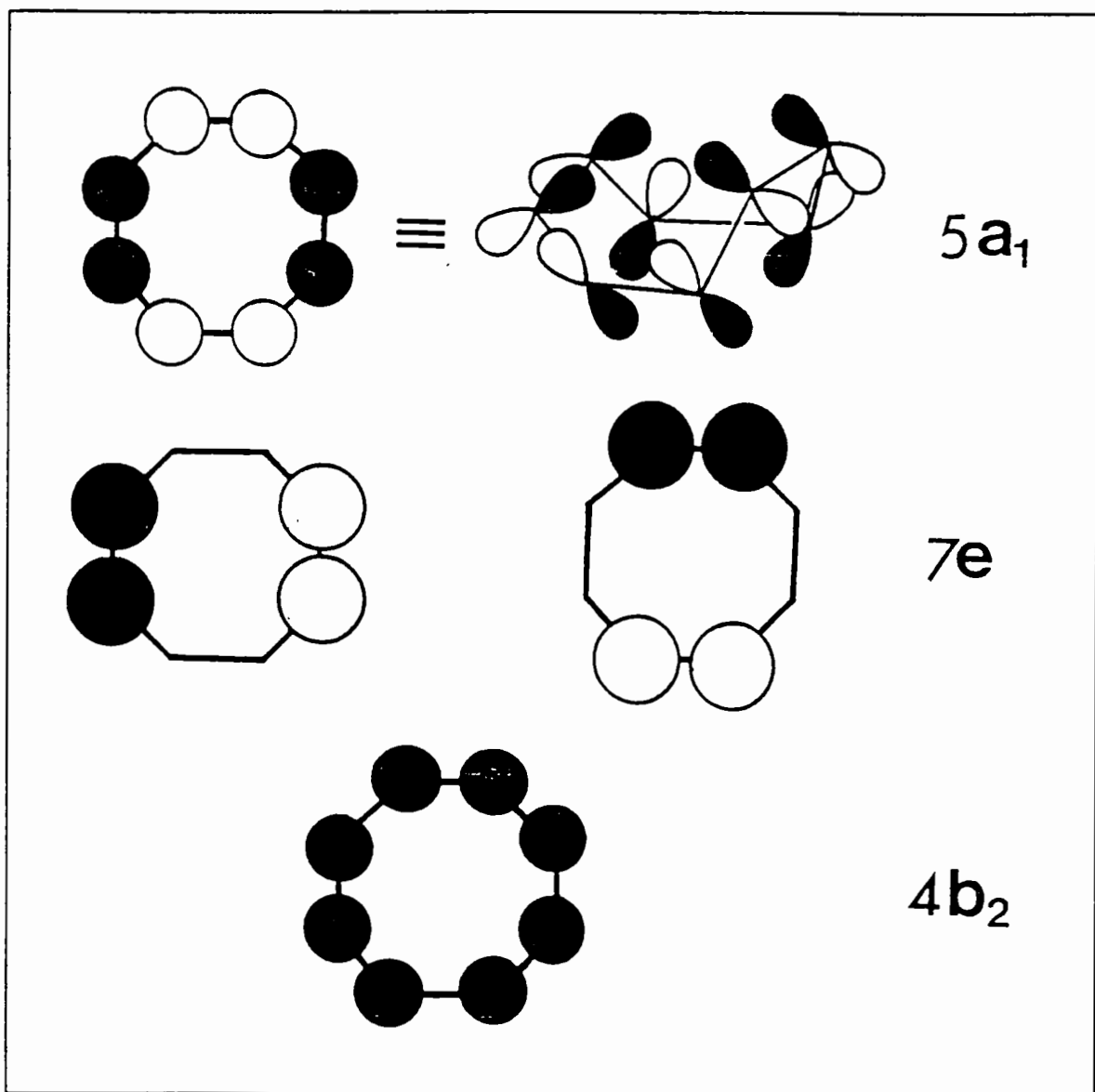


Fig.(6.2b-4). The qualitative occupied π -orbitals of cyclooctatetraene.

increase of the out-of-phase neighboring p-orbital interactions. This energy increase is, however, compensated by the energy descents of the doubly-occupied subjacent π -orbitals caused by the increasing in-phase interactions among the neighboring p-orbitals. Based on GTEBM developed in Part V of Chapter 5, the planarization is thermodynamically favorable. One corollary induced from this planarization is the increase in the energy gap between the $5a_1$ and $7e$ orbitals, which nicely rationalizes the above contradiction between the EA transition value and the corresponding IP difference. A more quantitative support for the assignment of this electronic transition comes from the NCG calculation using AM1-optimized radical cation geometry, which gives the first transition value of 505 nm with a large 0.45 transition moment. This agrees very well with the experimental EA transition value of 507 nm.

If the C_2 symmetry around the principal axis that bisects the forming bridge σ -bond(C_1 - C_5) is preserved during Reaction (6.2-1), the orbital correlation diagram can be constructed as in Fig.(6.2b-5) where the orbitals are labeled as symmetric(**S**) or antisymmetric(**A**) with respect to this C_2 operation. It is evident from Fig.(6.2b-5) that the ${}^2A_1(\pi)$ ground state of the COT radical cation with the configuration $(4b_2)^2(7e)^4(5a_1)^1$ cannot adiabatically correlate with the ground state ${}^2B_2$ of the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation having the configuration $(a_1(\sigma))^2(a_1(\pi))^2$

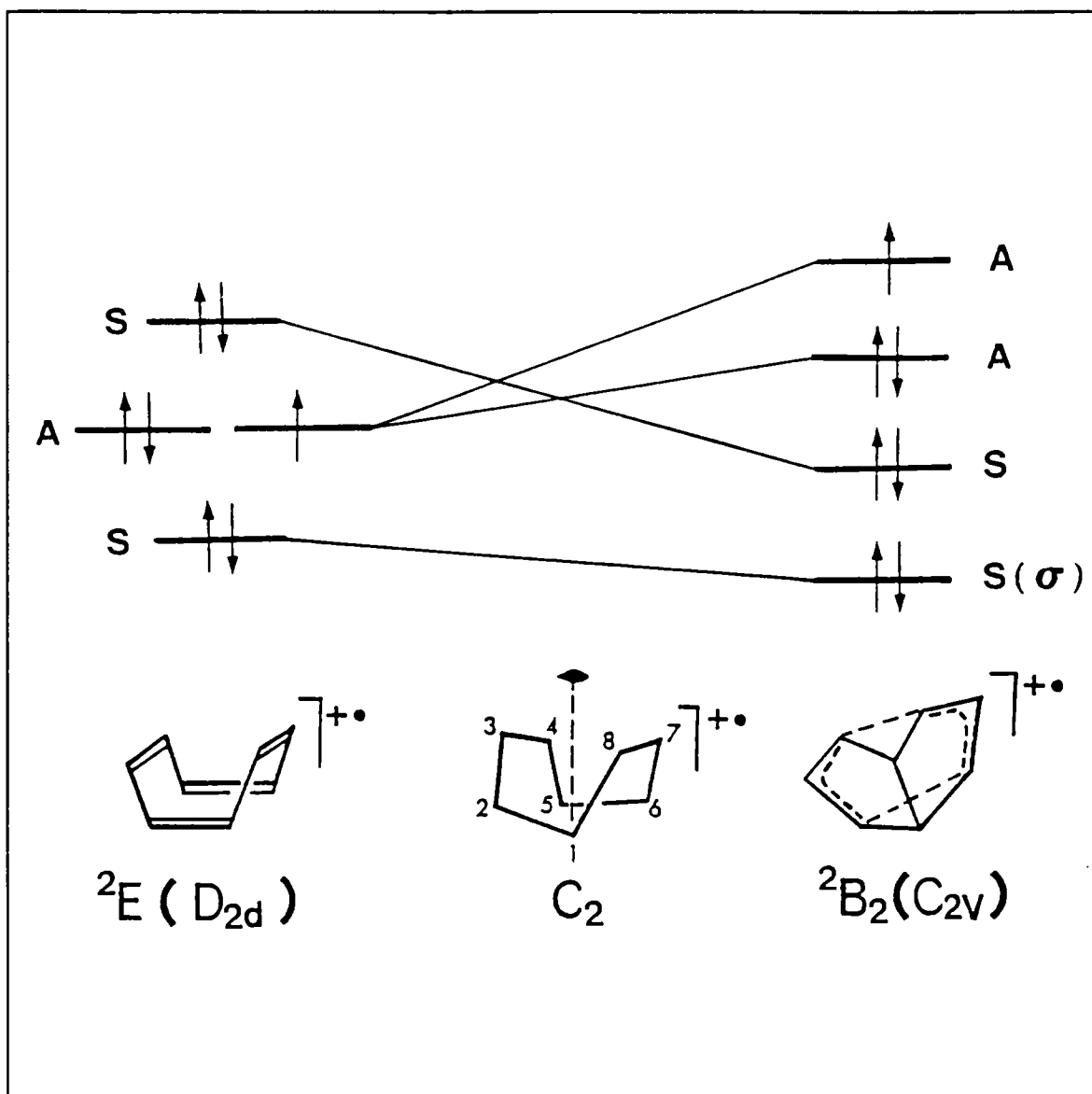


Fig.(6.2b-5). Orbital symmetry correlation diagram for the 1,5-closure of the cyclooctatetraene radical cation to the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation.

$(b_1(\pi))^2(b_2(\pi))^1$.¹²² This is consistent with the failure to observe the thermal isomerization of the COT radical cation in the accessible matrix temperature ranges of the three matrices. However, the lowest excited ${}^2E$ state produced by the EA transition from $7e$ to $5a_1$ can correlate adiabatically with the ground state of the final product(Fig.(6.2b-5)). This is clearly the most likely reaction channel causing Reaction (6.2-1).

The AM1 calculation results for 1^+ is very close to those of the MINDO/2 calculation by Dewar and his coworkers.¹⁴⁷ It is quite surprising to find out that the calculated heat of formation of 1^+ (250.16 kcal/mol) is 6.54 kcal/mol smaller than that of 2^+ (256.7 kcal/mol). This implies that no thermal driving force is available for the reaction. Therefore, the reaction is fully activated by the photoinduced electronic transition. Finally, it should be pointed out that the ring closure of 1^+ is analogous to the conversion of methyl-substituted COT dications to the corresponding bicyclic[3.3.0] derivatives found by Olah, Paquette and their coworkers.¹⁴⁴ However, the correlation diagram shown in Fig.(6.2b-5) indicates that the ring closure of the dicationic COT derivatives is neither thermally allowed nor photo-allowed, as pointed out by Olah et al.¹⁴⁴ This implies that the ring closure might involve the corresponding radical cations as intermediates(Reaction (6.2b-1)), which would undergo a reaction similar to Reaction

(6.2-1) under the influence of ordinary light.

1*=methyl derivatives of COT;

2*=methyl derivatives of 1,4-bishomobenzene;

1*→1*·+e⁻ Oxidation;

1*·→2*· Photoisomerization ... (6.2b-1);

2*·→2*2*+e⁻ Oxidation.

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APPENDIXES

Appendix I

Introduction

Magnitudes of β -coupling constants are very important in identifying radical conformations. This is based on relationships between coupling constants and the corresponding spin distributions. The famous Heller-McConnell equation¹ is an example of such relations. The purpose of this Appendix is to develop a general scheme to derive them.

General Theory

It is well known that β -coupling constants are mostly induced by hyperconjugation between a SOMO orbital and the corresponding σ -orbital in β -position or interaction between the two orbitals in general terms. This orbital interaction can be treated by the usual perturbation theory.^{2,3}

Suppose that the unpaired electron is localized in orbital ψ_A^0 which interacts with a doubly-occupied orbital ψ_B^0 as shown in Fig.(I-1).

According to the perturbation theory,^{2,3} perturbed wavefunction for the unpaired electron is as following:

$$\Psi'_A = t_{AA}\Psi_A + t_{AB}\Psi_B \quad \dots\dots (II-1) .$$

To the second order, the mixing coefficients can be expanded as

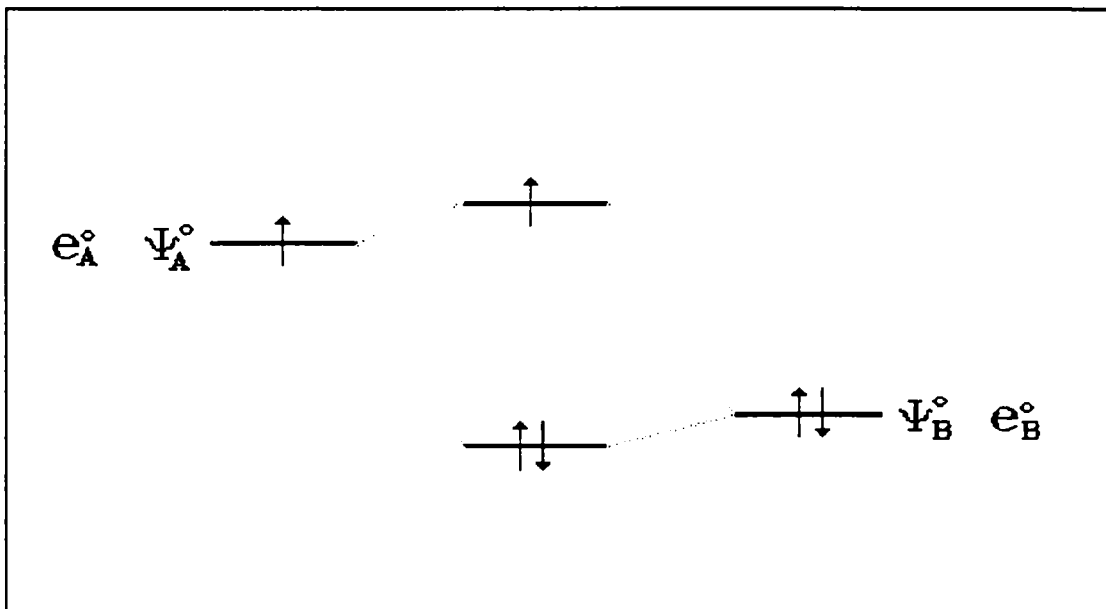


Fig.(I-1). Orbital interaction diagram.

$$t_{AA} \approx t_{AA}^0 + t_{AA}^{(1)} + t_{AA}^{(2)} \quad \text{..... (II-2) ;}$$

$$t_{AB} \approx t_{AB}^0 + t_{AB}^{(1)} + t_{AB}^{(2)} \quad \text{..... (II-3) .}$$

The various terms of the mixing coefficients are given by:^{2,3}

$$t_{AB}^{(2)} = t_{AB}^0 = 0 \quad \text{..... (II-4) ;}$$

$$t_{AB}^{(1)} = \frac{\tilde{\Delta}_{AB} - e_A^0 \tilde{S}_{AB}}{(e_A^0 - e_B^0)} \propto \frac{-\tilde{S}_{AB}}{(e_A^0 - e_B^0)} \quad \text{..... (II-5) ;}$$

$$t_{AA}^0 = t_{AA}^{(1)} = 0 \quad \text{..... (II-6) ;}$$

$$t_{AA}^{(2)} = -(\tilde{S}_{AB} t_{AB}^{(1)} + \frac{1}{2} (t_{AB}^{(1)})^2) \quad \text{..... (II-7)}$$

where

$\tilde{\Delta}_{AB}$ = Orbital interaction energy;
 e_A^0, e_B^0 = Unperturbed orbital energies;
 $\tilde{S}_{AB}$ = Overlap integral.

Actually, only the coefficient t_{AB} is important in our discussions. It has the following obvious relationship with a β -coupling constant:

$$\begin{aligned}
 a &= \text{const.} \cdot t_{AB}^2 \\
 &= \text{const.} \cdot \frac{\tilde{S}_{AB}^2}{(e_A^\circ - e_B^\circ)^2} \quad \text{..... (II-8) .}
 \end{aligned}$$

According to the above equation, it is clear that the β -coupling constant is directly proportional to the squared overlap integral and conversely proportional to the squared energy gap. All β -coupling constants induced by hyperconjugation can be rationalized by these two fundamental criteria. In the following section, we first use this general equation to prove the Heller-McConnell equation, which is then followed by the derivation of Whiffen's effect in cyclohexadienyl radicals. These two applications clearly demonstrate the power of Eq.(II-8).

Applications

A. Proof of Heller-McConnell equation

Suppose that the unpaired electron is localized in the pure p orbitals and interaction with a σ orbital, which is schematically shown in Fig.2. According to the treatment in II, the coupling

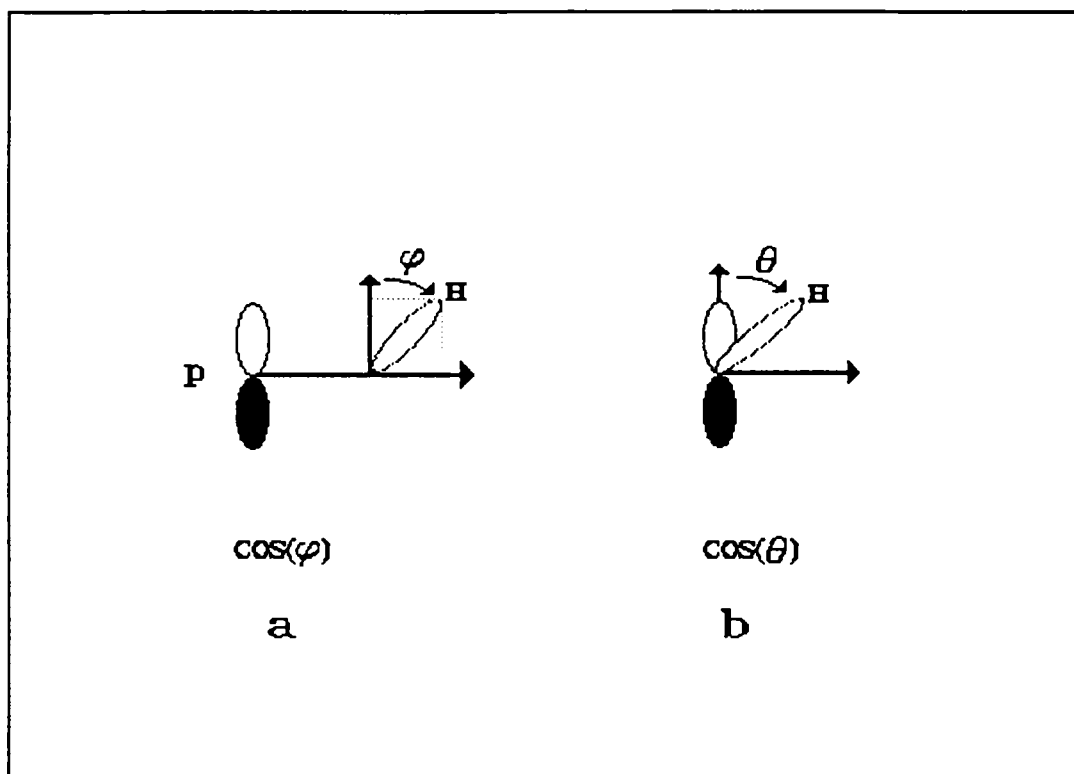


Fig.(I-2). Hyperconjugation interaction diagram. a, side view; b, Newman projection.

constant for the β -hydrogen can be expressed as follows:

$$a^{\beta} \propto t_{p\sigma}^2 = \frac{\tilde{S}_{p\sigma}^2}{(e_p^{\circ} - e_{\sigma}^{\circ})} \quad \dots\dots (III-1).$$

The key step to reduce this equation to the form of Heller-McConnell equation is the separation of the overlap integral to two parts, i.e., the angular part and radial part^{4,5,6} as shown in Eq.(III-2). This idea is, to some extent, the same

$$\tilde{S}_{p\sigma} = R(r) \cdot A(\theta, \phi) \quad \dots\dots\dots (III-2)$$

as Angular Overlap Model^{4,5,6} which is frequently used in inorganic chemistry. The separation in our case is really easy. Through the usual vector analogy of the orbital as

shown in Fig.2, the following expression is obvious:

$$\tilde{S}_{p\sigma} = R(r) \cdot \cos\phi \cdot \cos\theta \quad \text{.....(III-3)}.$$

Since the ϕ and $R(r)$ are constant for normal organic compounds, the following equation can be obtained:

$$\tilde{S}_{p\sigma} = \text{const.} \cdot \cos\theta \quad \text{.....(III-4)}.$$

By inserting this equation to Eq.(III-1), we can readily derive the following equation:

$$a^{\beta} = \text{const.} \cdot \cos^2\theta \quad \text{.....(III-5)}.$$

which is nothing but the Heller-McConnell equation.

B. Whiffen's Effect in Cyclohexadienyl radical

It is well known that cyclohexadienyl as shown in Fig.3

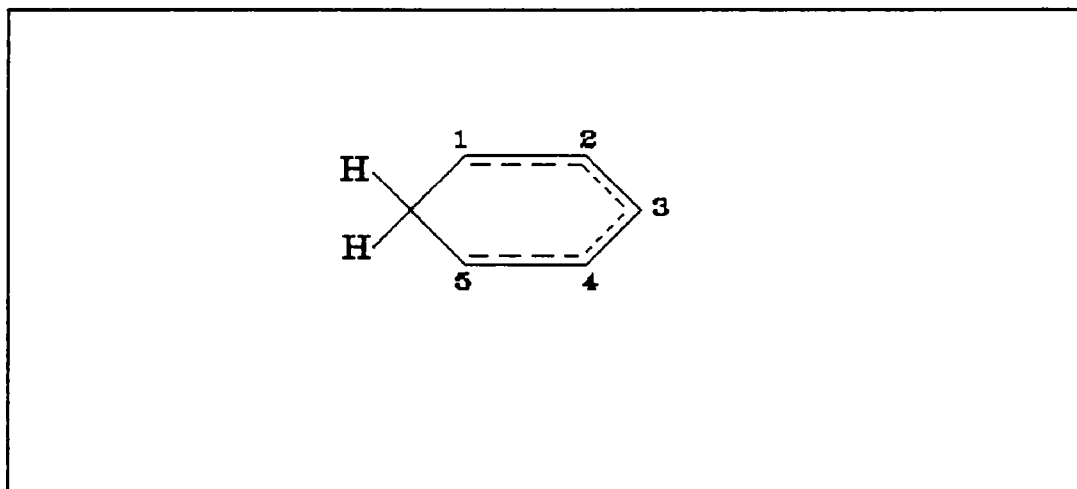


Fig.(I-3). Cyclohexadienyl radical.

has the following approximate SOMO:

$$\Psi^{\circ}_s = C_1P_1 + C_2P_2 + C_3P_3 + C_4P_4 + C_5P_5 \quad \text{.....(IV-1)}$$

with the symmetry restriction

$$C_1 = C_5 \quad \dots\dots (IV-2) .$$

According to section II, the coupling constant of β -hydrogen can be expressed as follows:

$$a^{\beta} \propto t_{\Psi_s^{\sigma}}^2 = \frac{\tilde{S}_{\Psi_s^{\sigma}}}{(e_{\Psi_s^{\sigma}} - e_{\sigma}^{\circ})^2} \quad \dots\dots (IV-3)$$

where we have:

$$\begin{aligned} \tilde{S}_{\Psi_s^{\sigma}} &= \int \Psi_s^{\sigma} \sigma d\tau \\ &= c_1 \int p_1 \sigma d\tau + c_2 \int p_2 \sigma d\tau + c_3 \int p_3 \sigma d\tau + c_4 \int p_4 \sigma d\tau + c_5 \int p_5 \sigma d\tau \\ &= 2c_1 \int p_1 \sigma d\tau + S_{2\sigma} + S_{3\sigma} + S_{4\sigma} \quad \dots\dots (IV-4) . \end{aligned}$$

We can simplify this equation by assuming that overlap integral $S_{2\sigma}$, $S_{3\sigma}$ and $S_{4\sigma}$ can be neglected because of the long distance. Hence, we have the final equation:

$$a^{\beta} \propto (2C_1)^2 S_{1\sigma}^2 \quad \dots\dots (IV-5)$$

which was first derived by Whiffen through other method.

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Appendix II

Further Studies on Radical Cation Hydrogen Transfer Reactions

Introduction

Allyl alcohol has a very similar structure to that of allylamine. This made us think that the allyl alcohol radical cation might undergo a hydrogen-transfer reaction similar to that described for the allylamine radical cation in Part I of Chapter 5. Unfortunately, the allyl alcohol radical cation forms clusters very easily in Freon matrices, probably due to hydrogen bond formation among intermolecular hydroxyl groups so that no clear ESR signals could be obtained. However, the ability to form hydrogen bonds can be easily removed by replacing the hydroxyl group by a methoxyl group to form the corresponding methyl ether compound which retains the main electronic feature of allyl alcohol. This prompts us to study reactions of the allyl methyl ether radical cation.

Results and Discussions

Fig. (II-1a) and (II-1b) give ESR spectra obtained from the radiolytic oxidation of allyl methyl ether and allyl methyl- d_3 ether in the CF_3CCl_3 matrix. The two spectra are

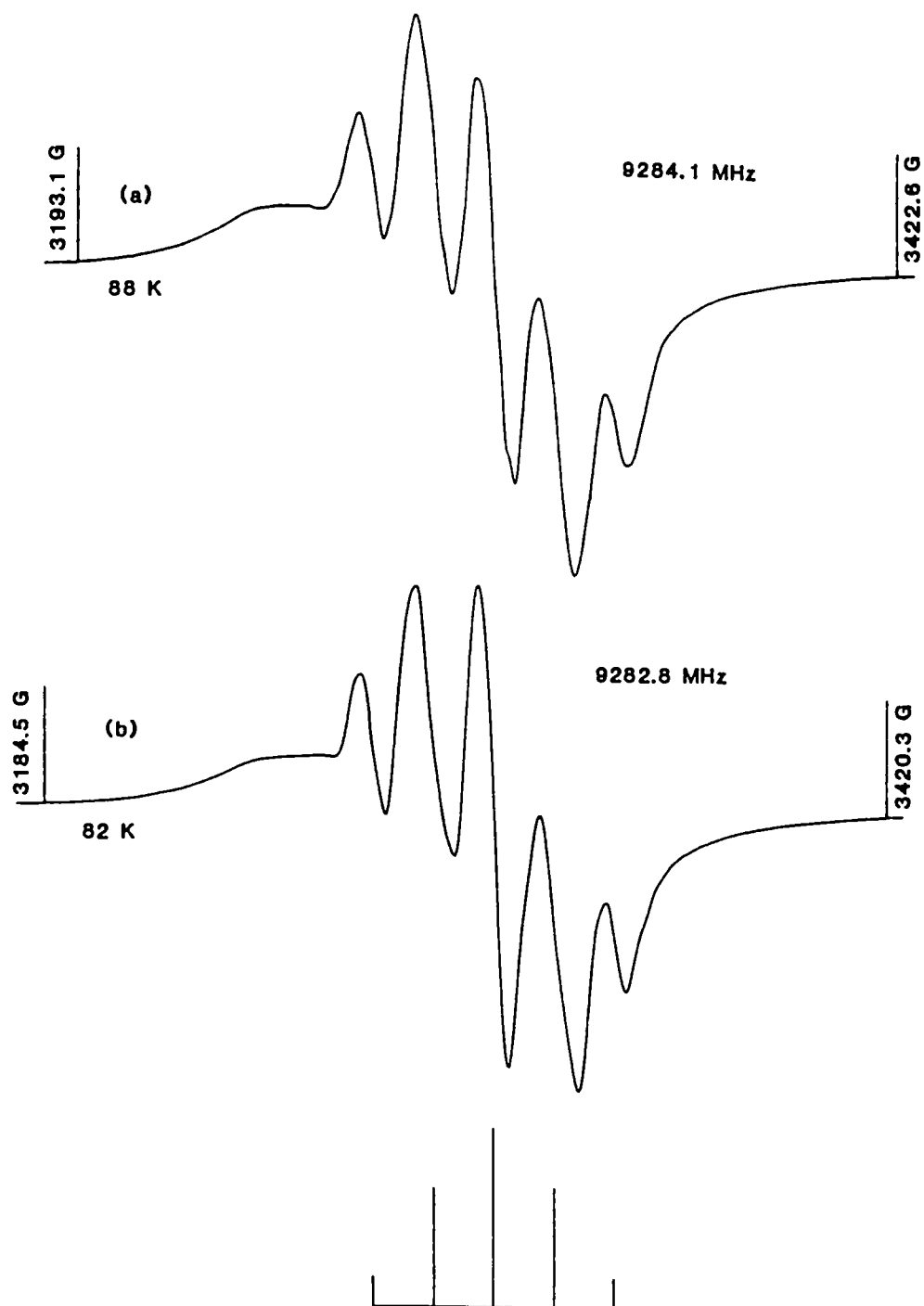


Fig.(II-1). First-derivative ESR spectra of the radical cation distonic species produced by γ -irradiation at 77 K of dilute solid CF_3CCl_3 solutions of (a) allyl methyl ether at 88 K, (b) allyl methyl- d_3 ether at 82 K.

indistinguishable from each other and consist of a quintet pattern(17.3 G) with an approximate 1:4:6:4:1 intensity ratio. Since the deuteration has no effect on the spectral appearance, the radical center is clearly not near the methyl group. Our results on the allylamine system made us think that the $\cdot\text{CH}_2\text{CH}_2\text{CH}=\overset{+}{\text{OCH}_3}$ radical cation(2) is the signal carrier. This quintet comes from the unresolved triplet($2H_\alpha$) of triplets($2H_\beta$) with approximately the same hyperfine coupling constants. In fact, both the total spectral width and the coupling constant are very close to those of the propan-1-iminium-3-yl distonic radical cation, and those of radicals with a similar structure.¹ Upon warming up to 120 K, the quintets of Fig.(II-1a) and (II-1b) irreversibly changed to Fig.(II-2a) and (II-3a) respectively. The pattern of Fig.(II-3a) is relatively simple due to the deuteration of the three methyl protons and can be assigned to be a doublet(5.4 G) of doublets(15.1 G) of quartets(23.1 G) through the help of computer simulation. Accordingly, the coupling constant(6.0 G) of the three methyl protons can be then extracted from Fig.(II-2a). These parameters are very similar to those of the $\text{CH}_3\text{CH}=\overset{+}{\text{CHOR}}$ radical cation^{2,3} and the spectra are therefore assigned to the corresponding $\text{CH}_3\text{CH}=\overset{+}{\text{CHOCH}_3}$ radical cation formed by a further intramolecular 1,2-hydrogen transfer reaction of the $\cdot\text{CH}_2\text{CH}_2\text{CH}=\overset{+}{\text{OCH}_3}$ radical cation. Upon warming up above the softening point(145 K) of the CF_3CCl_3 matrix, a different well-resolved spectrum

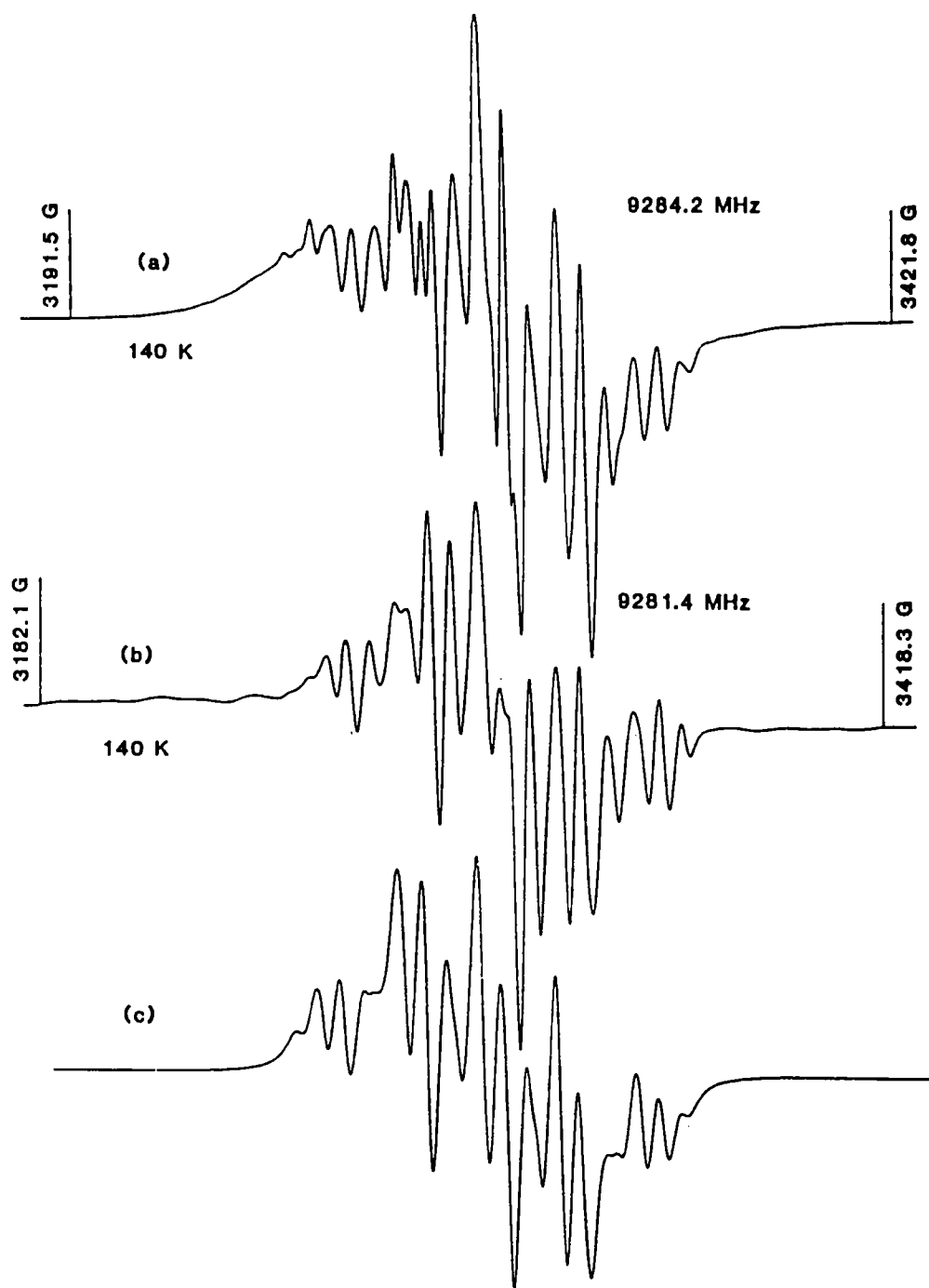


Fig.(II-2). First-derivative ESR spectra of the $\text{CH}_3\text{CH}^{\bullet+}\text{=CHOCH}_3$ radical cation at 140 K produced by γ -irradiation at 77 K of dilute solid solutions of allyl methyl ether (a) in CF_3CCl_3 and (b) in CFCl_3 . Figure (c) is the corresponding computer simulation based on the parameters in Table (II-1).

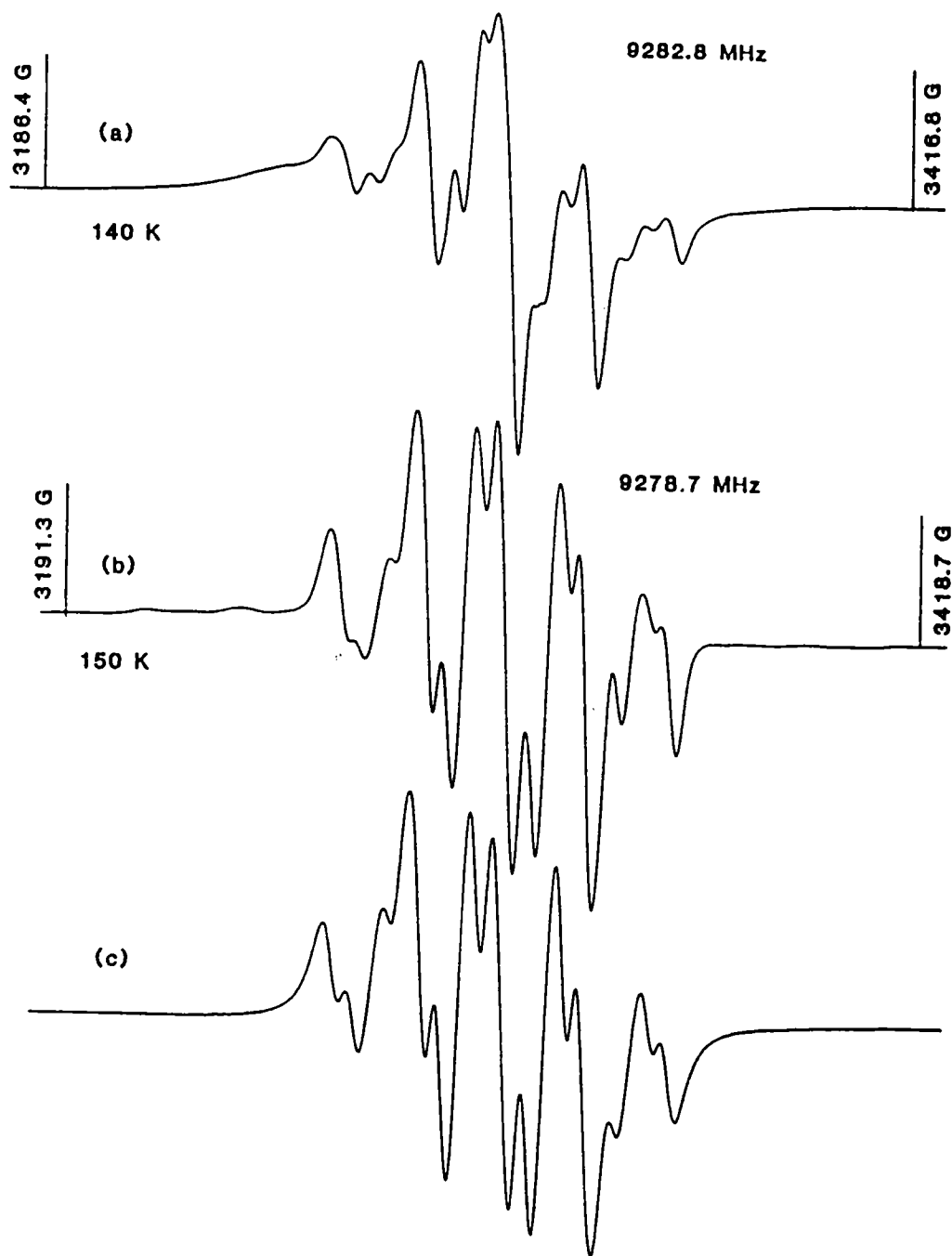
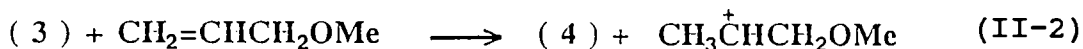
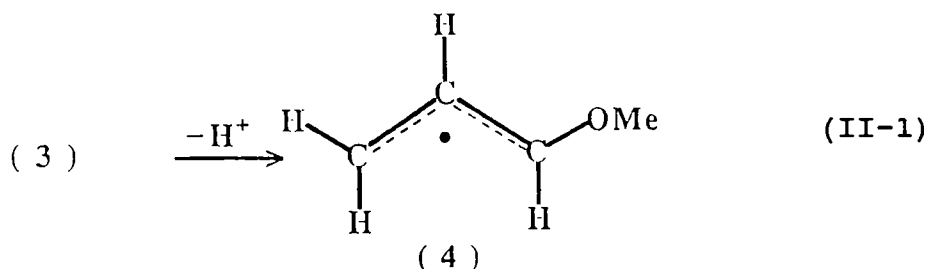


Fig.(II-3). First-derivative ESR spectra of the $\text{CH}_3\text{CH}=\text{CHOCD}_3^{\bullet+}$ radical cation produced by γ -irradiation at 77 K of dilute solid solutions of allyl methyl- d_3 ether (a) in CF_3CCl_3 , recorded at 140 K, and (b) in CFCl_3 , recorded at 150 K. Figure (c) is the corresponding computer simulation using the parameters in Table (II-1).

(Fig.(II-4)) consisting of doublet(3.3 G) of quartets(13.0 G) was observed. This spectrum can easily be assigned to the $\text{CH}_2=\text{CH}-\text{CHOCH}_3$ radical(4)⁴ produced by the following two possible ion-molecule reactions(Reaction (II-1) and (II-2)). The photobleaching experiments in this matrix indicated that the above radical cation isomerization from (2) to (3) could also be induced by visible light from a tungsten lamp.



On the other hand, a totally different low-temperature ESR spectrum was observed from the radiolytic oxidation of allyl methyl ether in the CFCl_3 matrix as shown in Fig.(II-5a). This spectrum is very similar to ESR spectra of olefin radical cations.⁵ Hence, we assign it to the parent radical cation(1). On raising the temperature to 110 K, the above spectrum irreversibly changed into a poorly-resolved five-line pattern similar to Fig.(II-1a). This implies that the

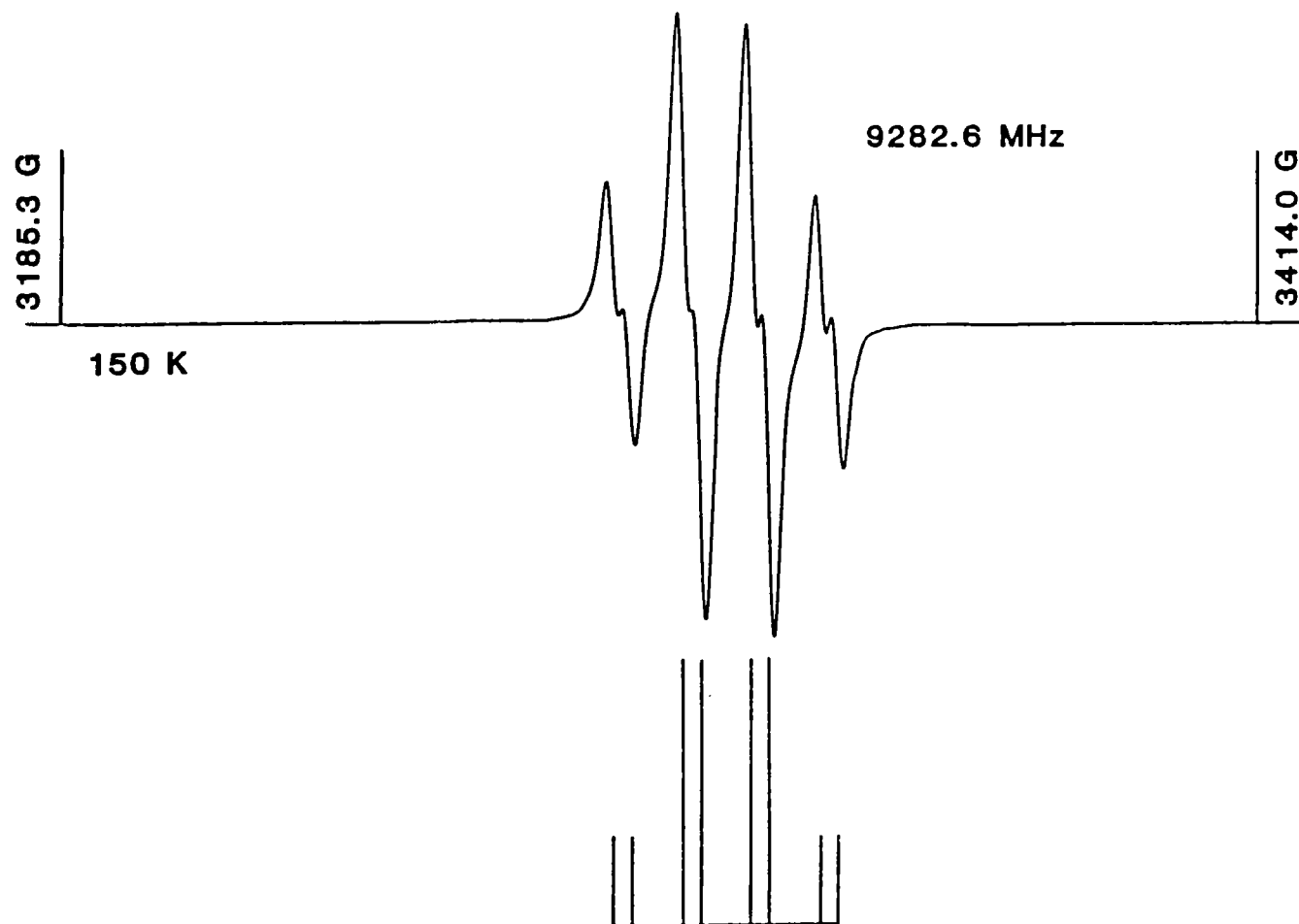


Fig. (II-4). First-derivative ESR spectra of the $\text{CH}_2\text{-}\dot{\text{C}}\text{H-CHOCH}_3$ radical recorded at 150 K in the CF_3CCl_3 matrix.

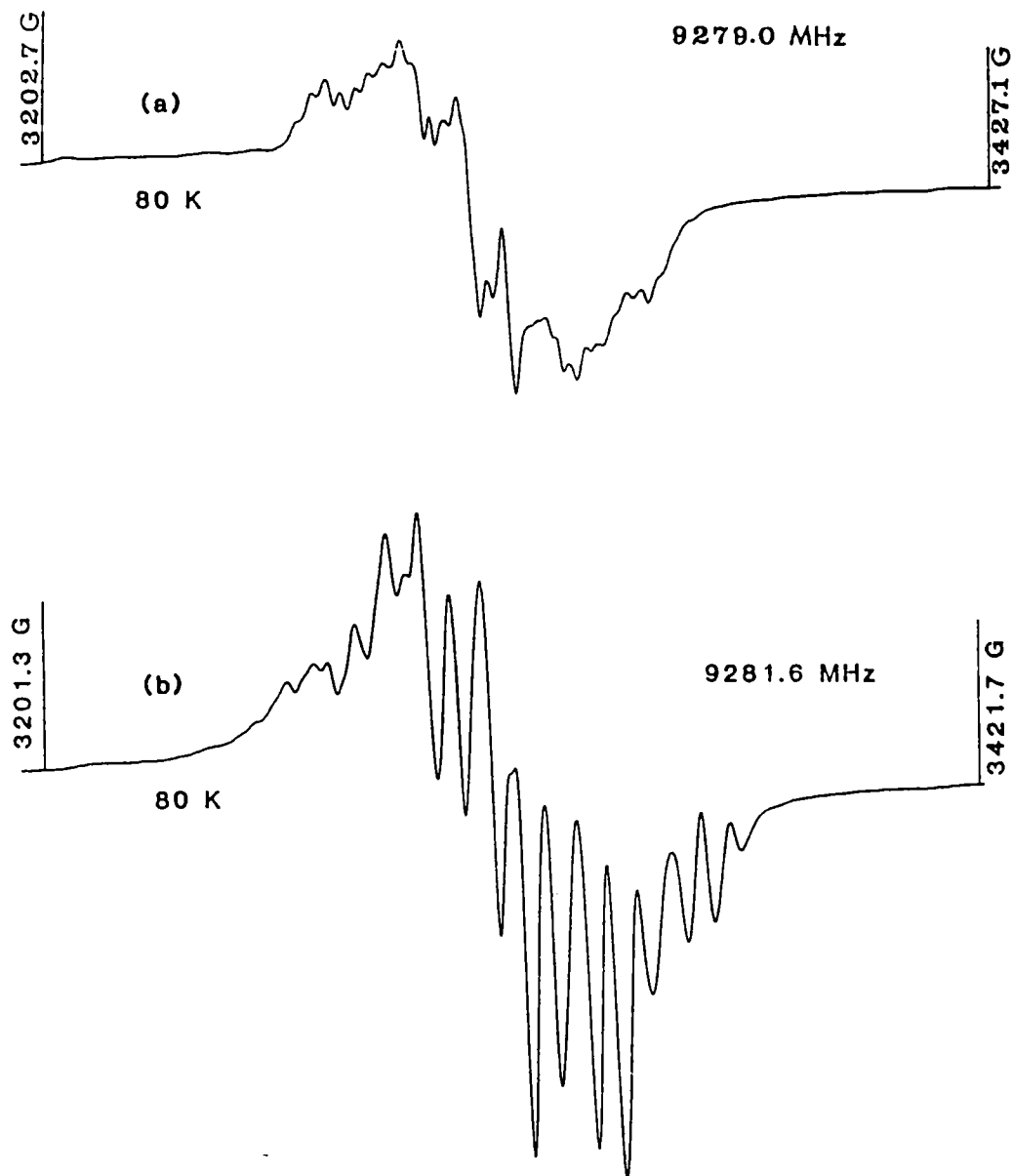


Fig.(II-5). First-derivative ESR spectra at 80 K produced by γ -irradiation at 77 K of dilute solid CFCl_3 solutions of allyl methyl ether (a) before, and (b) after photobleaching with visible light from a tungsten lamp. The spectra in a and b are assigned to the allyl methyl ether radical cation and the $\text{CH}_3\text{CH}=\text{CHOCH}_3$ radical cation, respectively.

1,2-hydrogen-transfer isomerization from the parent radical cation(1) to the distonic species(2) had taken place. Further increase of the sample temperature results in another irreversible change. The five-line pattern was replaced by a more complex spectrum(Fig.(II-2b)) which is identical to Fig.(II-2a). This indicated that the rearrangement of the distonic species $\bullet\text{CH}_2\text{CH}_2\text{CH}=\overset{+}{\text{O}}\text{CH}_3$ (2) to the $\text{CH}_3\text{CH}=\overset{\bullet+}{\text{CHOCH}_3}$ radical cation(3) also occurred in the CFCl_3 matrix. The photobleaching experiments indicate that the isomerization of (1) to (3) can be directly induced by visible light without appearance of the intermediate five-line spectrum, as shown in Fig.(II-5b).

To sum up, the above results in the two Freon matrices are described in scheme 1, and the hfcs of the corresponding radicals are listed in Table (II-1). The rearrangement of (1) to (2) is virtually the same as that discovered for the allylamine radical cation. This agrees well with our initial expectation. Finally, it should be pointed out that no hydrogen transfer reactions have been observed in similar experiments with the allyl methyl sulfide radical cation, and only the parent radical cation was detected. This might be related to the relative stability of sulfur-centered radical cations.

Scheme 1

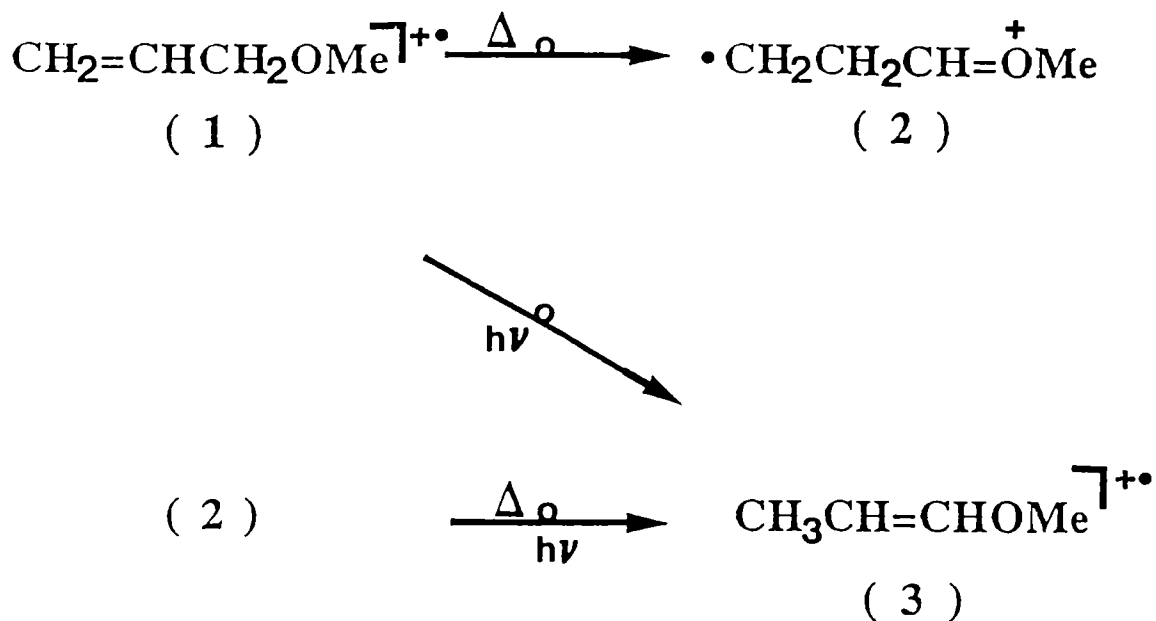


Table (II-1). ESR parameters for the radical cation (1), the radical cation (2), the radical cation (3) and the neutral radical (4) in Freon matrices.

Radical Cation	Hyperfine couplings/G
$\text{CH}_2^{\cdot+}=\text{CHCH}_2\text{OCH}_3$ ⁶	23.5(1H), 11.0(1H), 6.0(1H), 39.0(1H), 14.5(1H)
$\cdot\text{CH}_2\text{CH}_2\text{CH}=\overset{+}{\text{O}}\text{CH}_3$	17.3
$\text{CH}_3\text{CH}=\overset{+}{\text{C}}\text{HOCH}_3$	23.1(3H), 15.1(1H), 5.4(1H), 6.0(3H)
$\text{CH}_2^{\cdot-}\text{CH}^--\text{CHOCH}_3$	13.0(3H), 3.3(1H)

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6. This is a tentative assignment neglecting the long-range couplings from the three methyl protons. The parameters were obtained based on the best fitting between the experimental spectrum(non-deuterated) and the simulated one. The parameters are very similar to those of radical cations with the similar structure⁵. However, the corresponding ESR spectrum from the deuterated compound suggested that the three methyl protons were weakly coupled. Clearly, more precise assignment should consider these long-range couplings from the protons of the methyl group.

VITA

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