

# Lawrence Berkeley National Laboratory

## LBL Dissertations

**Title**

THE ELECTRON SPIN RESONANCE SPECTRA OF RADICAL ANIONS IN LIQUID AMMONIA

**Permalink**

<https://escholarship.org/uc/item/2m21n4vz>

**Author**

Levy, Donald Harris.

**Publication Date**

1965

Thesis/dissertation

**University of California**

**Ernest O. Lawrence**  
**Radiation Laboratory**

**TWO-WEEK LOAN COPY**

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

THE ELECTRON SPIN RESONANCE SPECTRUM OF RADICAL ANIONS IN  
LIQUID AMMONIA

**Berkeley, California**

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory  
Berkeley, California

AEC Contract No. W-7405-eng-48

THE ELECTRON SPIN RESONANCE SPECTRA OF RADICAL  
ANIONS IN LIQUID AMMONIA

Donald Harris Levy

(Ph.D. Thesis)

January 1965

CONTENTS

|                                                                               |    |
|-------------------------------------------------------------------------------|----|
| Abstract . . . . .                                                            | v  |
| I. Introduction . . . . .                                                     | 1  |
| II. Theory and Chemistry of Radical Anions . . . . .                          | 4  |
| A. Previous Theoretical Work . . . . .                                        | 4  |
| B. Previous Chemical Work . . . . .                                           | 8  |
| III. Ammonia Systems . . . . .                                                | 12 |
| A. Metal-Ammonia Solutions . . . . .                                          | 12 |
| B. Electrolysis in Liquid Ammonia . . . . .                                   | 14 |
| C. Chemical Reactions in Liquid Ammonia . . . . .                             | 15 |
| IV. Experimental Techniques . . . . .                                         | 16 |
| A. Electrolysis Cell . . . . .                                                | 16 |
| B. Cooling System . . . . .                                                   | 19 |
| C. ESR Spectrometer . . . . .                                                 | 20 |
| D. Typical Procedure . . . . .                                                | 21 |
| E. Chemicals . . . . .                                                        | 23 |
| V. Results and Discussion . . . . .                                           | 26 |
| A. Butadiene . . . . .                                                        | 26 |
| B. Methyl and Methylene Coupling Constants . . . . .                          | 35 |
| C. Justification of the Hyperconjugation Model:<br>Cycloheptatriene . . . . . | 70 |
| D. Nitrosobenzene and Nitrobenzene . . . . .                                  | 83 |
| E. Cyclooctatetraene . . . . .                                                | 89 |
| Acknowledgements . . . . .                                                    | 91 |
| Appendices                                                                    |    |
| I. Fortran II Computer Program ESR IV . . . . .                               | 92 |

|                                                |     |
|------------------------------------------------|-----|
| II. Fortran IV Computer Program M0 . . . . .   | 105 |
| III. Calculations on Radical Cations . . . . . | 121 |
| References . . . . .                           | 125 |
| Figure Captions . . . . .                      | 130 |

# THE ELECTRON SPIN RESONANCE SPECTRA OF RADICAL ANIONS IN LIQUID AMMONIA

Donald Harris Levy

Inorganic Materials Research Division, Lawrence Radiation Laboratory,  
Department of Chemistry, University of California,  
Berkeley, California

## ABSTRACT

January 1965

A new technique for the generation of pi-bonded radical anions by means of continuous electrolysis in liquid ammonia has been developed, and the experimental procedures are described in detail. The radical anion of 1,3-butadiene has been prepared by this method and its electron spin resonance spectrum has been observed. The measured proton hyperfine coupling constants are compared to those predicted by several theoretical calculations.

The radical anions of isoprene, 1,3-cyclohexadiene and 2,3-dimethylbutadiene have been prepared and their ESR spectra have been observed. A theory for deriving methyl and methylene proton coupling constants from a knowledge of the unpaired spin density distribution is developed and used to predict the coupling constants of these and other methyl and methylene containing radical anions. The unpaired spin distribution is calculated using a hyperconjugation model and several simple LCAO molecular orbital theories. A small correction for spin exchange polarization is taken into account. It is shown that a simple extension of Huckel theory can be used to successfully predict the methyl and methylene proton

coupling constants of all the radical anions considered.

An inequivalence of the methylene protons in dimethylbutadiene radical anion has been observed. To explain this the usual molecular orbital treatments have been modified by using an expanded basis set including the 3d carbon atomic orbitals. These are shown to be of the correct symmetry to account for the observed anisotropy.

The radical anion of 1,3,5-cycloheptatriene has been prepared and the hyperfine coupling constants measured. The methylene proton coupling constant has been assigned by monodeuteration of the methylene group. The wavefunction of the unpaired electron in this molecule is shown to have a node at the methylene protons and consequently any hyperfine coupling is due to a combination of spin exchange polarization and electron correlation. The small contribution of electron correlation is estimated by an approximate self-consistent field calculation, and the remaining hyperfine coupling is taken as a measure of the spin exchange polarization. A correction term useful for accounting for spin polarization effects in other radicals is derived. The fact that this term is small provides a justification of the hyperconjugation model used previously.

The ESR spectra of the nitrosobenzene and nitrobenzene radical anions have been observed in liquid ammonia. The nitrosobenzene radical anion shows two ortho and two meta proton coupling constants which may be explained by either of two simple theoretical models. One model involves non-bonded interactions introducing off-diagonal Hamiltonian matrix elements between non-bonded atoms, and the other involves an electron polarization effect which produces small changes in the on-diagonal matrix elements. These have been described previously as the  $\beta$ - and  $\alpha$ -effects.

The nitrobenzene radical anion was prepared in liquid ammonia as a reference and to compare solvent shifts.

The radical anion of cyclooctatetraene was prepared in liquid ammonia and is shown to be much more stable in this solvent than in any previously used. Small coupling constant solvent shifts were observed which, because of the symmetry of the molecule, can only be attributed to a solvent perturbation of the sigma-pi interaction.

## I. INTRODUCTION

Molecular quantum mechanics and the general problem of molecular electronic structure is fundamental to all of chemistry, and it is not surprising that it has received considerable attention ever since the introduction of quantum mechanics itself. The recent general availability of high speed computing machinery has led to a proliferation of theoretical calculations which has brought this field to the point where quite sophisticated self-consistent field calculations appear in the organic chemistry literature, and the more advanced calculations of "theoretical" chemists involve so much computation that they are almost entirely divorced from conventional chemical concepts and any notion of chemical intuition. One unfortunate aspect of this wealth of theoretical computation is that the theoretician is beginning to outstrip the experimentalist and many calculations are yielding results for which the corresponding experimental data are not available. One frequently finds the theoretician forced to compare his latest calculation to the "best Hartree-Fock calculation" rather than to experimental results simply because the experimental results do not exist.

One promising source of the necessary data has been relatively new areas of radio frequency spectroscopy. Their utility lies in the fact that it usually is possible to separate out small terms from the molecular Hamiltonian which to a very high degree of approximation do not effect the molecular energy or wave function but which do contain parameters which depend upon the molecular wave function. Since these smaller terms are usually much more easily solved than the complete Hamiltonian one can obtain very accurate measurements of the values of the parameters

which appear in them. If one can then relate the parameters to the molecular wave function one has a measure, at least in parts of the molecule, of the wave function itself. Coulson described these small terms as "measuring rods, able to be placed within the electronic charge-cloud without affecting it."<sup>1</sup>

A specific technique that has provided a great deal of data of this nature has been the measurement of the electron spin resonance (ESR) spectra of organic radical ions and neutral radicals in solution. The motional narrowing of the absorption line due to the rapid tumbling in solution allows a very great degree of resolution and causes the anisotropic terms in the Hamiltonian to average to zero, thus simplifying the interpretation of the spectrum. The interaction of the electronic and nuclear paramagnetism produces a great deal of hyperfine structure in the spectrum which can be readily analyzed in terms of a set of hyperfine coupling constants that are related to the electronic structure of the molecule. The problem of determining this relationship is complex but not impossible, and one is now able to get a reasonable estimation of the value of the molecular wave function from the measured hyperfine constants.

One of the severe restrictions on this technique is the experimental difficulty of preparing the necessary paramagnetic species. A survey of the literature impresses one with the fact that the theoreticians and the experimentalists are not working on the same kinds of molecules. This is illustrated by the fact that the molecules which are experimentally easily reducible to the radical anion are those with the larger conjugated pi-electron systems and are difficult to treat theoretically. Conversely the molecular species that are interesting and tractable theoretically are extremely unstable and difficult to prepare. Thus the theoreticians deal with such species as methyl, allyl, and ethylene while the

experimentalists make measurements on anthracene, tetracene, etc. It was in an attempt to develop experimental techniques that would help close this gap between theoreticians and experimentalist that the following work was undertaken.

## II. THEORY AND CHEMISTRY OF RADICAL ANIONS

### A. Previous Theoretical Work

As mentioned above it is possible to separate the complete molecular Hamiltonian into various terms which are non-interacting. It is customary for ESR work to write the complete Hamiltonian as

$$H = H_0 + H' \quad (1)$$

where  $H_0$  contains all the electrostatic interactions and  $H'$  contains the spin orbit, magnetic field, and hyperfine terms. Treating  $H'$  as a perturbation it is possible to derive an operator  $H_s$  (the "spin Hamiltonian") which lifts the spin degeneracy within the ground manifold of  $H_0$ . Although the coefficients of the operators appearing in  $H_s$  are averages of various orbital matrix elements, the operators themselves are spin operators and hence  $H_s$  operates only in the space of the electronic and nuclear spin variables. The derivation of  $H_s$  for atoms has been treated by Pryce,<sup>2,3</sup> and has been lucidly reviewed by Bleaney and Stevens<sup>4</sup> and again by Pake.<sup>5</sup> Stone<sup>6</sup> has shown that this treatment cannot be applied directly to molecules due to the fact that the theory is not invariant to a gauge transformation which changes the point in space about which the electronic angular momenta are referred. However, he has derived a similar theory for molecules which is gauge invariant.

The results of these treatments is that the Zeeman term of the spin Hamiltonian describing the interaction of the electronic magnetic moment and an applied magnetic field  $\bar{H}$  is given by

$$H_z = \beta \bar{H} \cdot g \cdot \bar{S} \quad (2)$$

where  $\beta$  is the Bohr magneton,  $\bar{S}$  is the electron spin operator, and  $g$  is a second-rank tensor which is derived from the theory and contains orbital angular momentum matrix elements arising from the spin-orbit interactions. In liquid systems the rapid tumbling of the paramagnetic species usually averages out any anisotropies in the  $g$  tensor and it may usually be replaced by a scalar,  $g$ .

In molecular radicals the low symmetry caused by the strong molecular electric field almost completely quenches any orbital magnetism, which results in the complete removal of most orbital degeneracy. Any degeneracies remaining due to whatever molecular symmetry exists tend to be removed by the Jahn-Teller effect.<sup>7</sup> The result of this is that the  $g$ -value for molecular radicals tends to be very close to 2.00229, the  $g$ -value of the free electron. While a theory<sup>8</sup> has been developed to account for deviations from the free electron  $g$ -value, very little information about the electronic structure of the molecule can be obtained from these extremely small deviations.

The Hamiltonian for the interaction of the electronic and nuclear angular momenta is expressed as<sup>9</sup>

$$H = \sum_n g_e g_n \beta \left\{ \frac{\mathbf{S}_e \cdot \mathbf{I}_n}{|\mathbf{r}_e - \mathbf{r}_n|^3} - \frac{3(\mathbf{S}_e \cdot \mathbf{r})(\mathbf{I}_n \cdot \mathbf{r})}{|\mathbf{r}_e - \mathbf{r}_n|^5} - \frac{8\pi}{3} \mathbf{S}_e \cdot \mathbf{I}_n \cdot \delta(\mathbf{r}_e - \mathbf{r}_n) \right\} \quad (3)$$

The notation is standard and is defined in Ref. 9. The first two terms in the brackets arise from the classical dipole-dipole interaction of the electronic and nuclear magnetic moments. It has been shown by Weissman<sup>10</sup> that for molecules undergoing rapid tumbling in solution this part of the interaction vanishes. The term remaining arises from the Fermi contact interaction<sup>11</sup> and is not averaged out by any molecular motion.

In organic pi-radicals the energy splittings caused by this term are extremely small (of the order of 10 mc.). However as noted above these radicals have very small spin-orbit couplings and this produces long relaxation times and a very highly resolved spectrum. Consequently even these small splittings can be fully resolved and a great deal of information may be obtained.

It is easily seen that the effective spin Hamiltonian consisting of the Zeeman term and the Fermi contact term may be solved to define the position of the lines in the ESR spectrum in terms of a set of parameters  $A_i$ , the hyperfine coupling constants, where for the  $i$ th magnetic nucleus

$$A_i = \left( \frac{8\pi g\beta \mu_i}{3 I} \right) \delta_i \quad (4)$$

where

$$\delta_i \equiv \langle \Psi | \sum_k \delta(\vec{r}_{ki}) S_{kz} | \Psi \rangle / S_z \quad (5)$$

In this expression  $\delta(\vec{r}_{ki})$  is the Dirac delta function of the distance between electron  $k$  and nucleus  $i$  and  $\delta_i$  might be looked upon as the unpaired spin density at the magnetic nucleus  $i$ . Thus from the experimental values of the coupling constant  $A_i$  one gets easily and accurately the unpaired spin density at the  $i$ th magnetic nucleus.

Unfortunately for most pi-bonded molecules this is not a very interesting quantity in itself (with certain exceptions to be treated later). The reason for this is that almost all theoretical treatments of pi-bonded molecules begin with an assumption that the pi-sigma separation approximation is valid. This approximation assumes that the total molecular wave function may be written as

$$\Psi = A[\Psi_\sigma \Psi_\pi] \quad (6)$$

where  $\Psi_{\sigma}$  and  $\Psi_{\pi}$  are functions of only the sigma and only the pi-electron coordinates (space and spin) respectively and A is the antisymmetrization operator with respect to pi and sigma electron interchange.<sup>12</sup> Since the unpaired electron in pi-radicals is a pi-electron in this approximation all the nuclei lie at a node of  $\Psi_{\pi}$  and therefore the pi-sigma approximation implies that  $\delta_i$  and  $A_i$  are both exactly zero. The fact that there is any hyperfine interaction observed at all indicates a departure from pi-sigma separability. Of course the minute energies involved indicate that the pi-sigma interaction is very small, and that its neglect is unimportant in comparisons with other approximations that must be made in any molecular theory. Nonetheless in order to compare experimental coupling constants with such a theory it is necessary to have an additional relationship between the experimental numbers and the wave function  $\Psi_{\pi}$ .

This relationship in aromatic protons was discussed by McConnell<sup>13,14</sup> who theoretically examined the hyperfine interaction in a C-H fragment of an aromatic hydrocarbon. He postulated an exchange polarization mechanism whereby the unpaired pi-electron on the carbon atom polarized the sigma-electrons in the C-H bond resulting in a net unpaired spin density at the proton. His treatment involved admixing a small amount of an excited configuration  $\phi$  with the ground state wave function. The configuration  $\phi$  involved the antibonding valence bond function where the two sigma-electrons in the C-H bond have parallel spins. This treatment led to the approximate relationship

$$A_i = Q \rho_i \quad (7)$$

where  $\rho_i$  is the probability of finding the unpaired electron on the carbon atom to which the *i*th proton is bonded (frequently referred to as

the unpaired spin density at the  $i$ th carbon atom), and  $Q$  is a constant defining the sigma-pi interaction. In both a simple valence bond or molecular orbital derivation  $Q$  is proportional to the quantity  $(J_{ph} - J_{ps})/E$  where

$$J_{ps} = \langle p_1 s_2 | \frac{e^2}{r_{12}} | s_1 p_2 \rangle \quad (8)$$

and  $E$  is the energy of the excited configuration above the ground configuration. Here  $p$  is a  $2p_z$  atomic orbital centered on the carbon atom,  $h$  is an  $sp^2$  hybrid orbital centered on the carbon atom and directed toward the proton, and  $s$  is the  $1s$  atomic orbital of the proton. A more complicated expression for  $Q$  has been derived using a theory generalized to the case of polyatomic pi-electron radical systems.<sup>15</sup>

Colpa and Bolton<sup>16</sup> have extended the theory by considering the C-H fragment and including the effect of excess charge in addition to that of unpaired spin in attempt to explain certain anomalous trends which develop when Eq. (7) is applied. Their derivation has led to the relationship

$$A_i = (Q_0 + k\epsilon_i)\rho_i \quad (9)$$

where  $\epsilon_i$  is the excess charge density on the  $i$ th carbon atom and  $K$  is a theoretical constant. Giacometti et al.<sup>17</sup> have tried to explain these same anomalies by including nearest neighbor interactions with the C-H fragment.

The first treatment of hyperfine interaction due to magnetic nuclei other than protons was by McLachlan et al.<sup>18</sup> who removed a few minor restrictions from McConnell's theory and generalized this theory to include all magnetic nuclei lying in the nodal plane of a pi-radical. The particular importance of such a theory is that now  $C^{13}$  and  $N^{14}$  splittings

could also be related to the molecular electronic structure. Their theory yielded the result that

$$A_i = \text{tr}(Q^i \rho) \quad (10)$$

where  $\rho$  is the pi-electron spin density matrix and  $Q^i$  is a hyperfine coupling matrix whose elements depend upon  $\sigma$ - $\Pi$  exchange integrals and excited sigma triplet states. An expanded theory which considered not only the C-H fragment but in addition treated the 1s carbon electrons and all the electrons in the three bonds of the  $sp^2$  hybridized carbon atom was developed by Karplus and Fraenkel.<sup>19</sup> This theory, which is applicable to any many-electron atom such as  $N^{14}$ , gave the prediction that

$$A_i = (S^C + \sum_{j=1}^3 Q_{CX_j}^C) \rho_C + \sum_{j=1}^3 Q_{X_jC}^C \rho_j \quad (11)$$

Here C is an  $sp^2$  hybridized carbon atom that is bonded to three atoms,  $X_j$  ( $j = 1, 2, 3$ ) and  $\rho$  and  $\rho_j$  ( $j = 1, 2, 3$ ) are the pi-electron spin densities on atoms C and  $X_j$  respectively.  $S^C$  accounts for the contribution of the 1s electrons of the carbon atom and the Q's for that of the remaining electrons. The theory can be used for any atom, A, by defining a set of parameters  $Q_{BC}^A$  which result from the interaction between the bond BC and the pi-electron spin density on atom B.

#### B. Previous Chemical Work

The first observed ESR spectra of radical anions were reported by Weissman and co-workers in a series of papers primarily concerning the naphthalene negative ion.<sup>20-22</sup> Since then quite a large number of papers have appeared reporting the ESR spectra of specific radicals. The literature on this subject prior to 1958 has been summarized quite nicely by

Ingram<sup>9</sup> in his chapter on stable free radicals (Chapter 5). However much of the high resolution work in this field has been done since the publication of Ingram's book and unfortunately, to the best of the author's knowledge, no single comprehensive review of the literature since 1958 has been written. A series of annual reviews covering the previous year's work has been published<sup>23-27</sup> and in some ways helps to fill this gap. A recent translation of the book by Al'tshuler and Kozyrev<sup>28</sup> gives a more recent review although his table of molecules studied is taken verbatim from Ingram.<sup>9</sup> Carrington<sup>29</sup> has written an introductory review of this area which contains references to much of the most significant recent literature, but it is not intended to be a complete listing of all recent work. A complete bibliography of all ion-radicals studied (including subject or formula index) would be of considerable use but is unfortunately outside the scope of this work. Somewhat more to the point, there follows a brief review of the techniques developed for the generation of radical anions.

The first solutions of radical anions were prepared by the chemical reduction of the parent species (A), by alkali metals (M) using an inert ether solvent such as tetrahydrofuran (THF). The detailed experimental procedure for such chemical reductions has been described in the literature.<sup>30-31</sup> The equilibrium reaction involved is



and in cases where the factor limiting the production of the anion is a small electron affinity for A, this technique is still perhaps the best available.\*

---

\* Probably the best example of the extreme reducing power of these solutions is the recent generation of the cyclopropane radical anion.<sup>32</sup>

On the other hand, in many cases, the production of the anion is limited by other factors such as polymerization or additional reaction, and in these cases direct chemical reduction leaves something to be desired. The technique of electrolytic reduction was first used by Geske and Maki<sup>33</sup> for the production of the nitrobenzene radical anion and represented a considerable improvement for many interesting cases. Geske and Maki used an intra muros technique whereby the radicals were generated in an electrolytic cell placed directly in the microwave cavity of the ESR spectrometer. More recently Rieger et al.<sup>34</sup> have carried out the electrolysis outside the microwave cavity and transferred the electrolyzed solution to the cavity via a flow system.

The electrolytic method of generating negative ions has a number of distinct advantages over the older technique of chemical reduction:

- 1). The possibility of hyperfine interaction between the unpaired electron and the magnetic nucleus of the alkali metal used as a reducing agent is eliminated since very large cations can be used.
- 2). The complications of ion pairing are minimized by the use of a solvent of high dielectric constant.
- 3). The potential at which the reduction is carried out is easily and continuously variable.
- 4). The difficulty of purifying and manipulating small amounts of alkali metals is eliminated.
- 5). Continuous electrolysis offers the possibility of generating an observable steady state concentration of radicals that would otherwise be too reactive to observe.

Electrolytic reductions are usually carried out in a glass cell between a mercury pool cathode and some reference anode, frequently a

saturated calomel electrode. In addition to a small amount (ca.  $10^{-2}$  -  $10^{-3}$  molar) of the parent molecule the solvent contains sufficient supporting electrolyte to make it conductive. The supporting electrolyte usually has a large cation, such as found in the tetra-alkylammonium salts, to reduce ion pairing. It is obvious that the choice of solvent is critical since it represents the principle source of unwanted side reactions. Previous to this work acetonitrile,<sup>33</sup> dimethylformamide,<sup>34</sup> dimethyl sulfoxide,<sup>35</sup> water,<sup>36</sup> and ethanol-water mixtures<sup>37</sup> have been used as solvents. These were chosen because they were obtainable in high purity and were relatively inert to the supporting electrolyte, the radical anion, and the parent molecule. Besides this they were capable of dissolving and dissociating a large enough amount of a supporting electrolyte to make the resulting solution conductive. In spite of these advantages there are two essential difficulties involved with all of the solvents thus far mentioned. First the solvents themselves are reducible at the high reduction potentials necessary to produce the more unstable radicals, and consequently the radicals themselves are never generated. Second the relatively high freezing point of all these solvents makes it impossible to cool the solutions much below room temperature. It has long been known from chemical reduction work that many radicals are stabilized by cooling and are observable only at low temperature.<sup>31,32</sup> Thus although the technique of electrolytic reduction had many advantages of its own, it is lacking the two principle advantages of chemical reduction, namely a large reduction potential and the ability to cool the reducing solutions. It was the desire to combine the advantages of both the chemical and electrolytic methods that led us to examine the possibility of using liquid ammonia as an electrolytic solvent.

### III. AMMONIA SYSTEMS

#### A. Metal Ammonia Solutions

It has long been known that liquid ammonia will dissolve certain metals (primarily the alkali and alkaline earth metals) to produce blue, paramagnetic solutions. Several reviews of these fascinating solutions have been written to which the reader is referred for a detailed discussion of their properties.<sup>38-41</sup> The discussion below is limited to a summary of the various theories about the nature of the reducing species present in these solutions.

One of the earliest models for the solution of a metal in ammonia was postulated by Kraus<sup>42</sup> who suggested that the solution reaction be represented by the equation



where both the metallic cation ( $\text{M}^+$ ) and the electron ( $\text{e}^-$ ) were solvated. This model was based upon the fact that the dilute solutions are extremely conductive and that the negative carrier transference number is about seven times that of the positive carrier, implying a very small mobile negative carrier.\*

Later measurements on bulk magnetic susceptibility<sup>43</sup> showed that the molar susceptibility decreased as the concentration of metal increased and indicated that a further reaction was necessary to account for the pairing

---

\* This model is still generally agreed to be correct for very dilute solutions, and Kraus's electrochemical data are probably the only data available on these solutions that is universally accepted as being accurate.

of spins. A model proposed by Ogg<sup>44-45</sup> postulated that the unpaired electron of Eq. (13) existed in a solvent cavity and that a pairing reaction



produced singlet electron pairs inside a solvent cavity.

A more recent model by Becker, Lindquist, and Alder<sup>46</sup> postulates four species in chemical equilibrium. The first two species are the metal ion and solvated electron of the earlier theories. In addition they postulate the existence of a "monomer", M, which consists of an alkali metal ion surrounded by approximately six oriented ammonia molecules with an electron circulating around the metal ion on the protons of the ammonia molecules. The concentration of this monomer is governed by the equilibrium reaction



Finally they postulate that two monomers can come together to form a singlet dimer, M<sub>2</sub>. The reaction for the formation of the dimer is



and is analogous to the formation of Na<sub>2</sub> in the gas phase. The fact that the paramagnetic species has something to do with the metal cation was confirmed by the NMR Knight shift measurements of McConnell and others.<sup>47,48</sup>

Gold, Jolly, and Pitzer<sup>49</sup> have combined certain features of the Ogg and Becker models and have proposed still another model for these solutions. Their model retains the concept of an electron cavity and proposes that the monomer of the Becker model is simply an ion pair between the electron cavity and a metal cation. The diamagnetic species analogous to the Becker dimer is a quadrupolar assembly consisting of two ion pairs with the wave functions of the two electrons overlapping sufficiently to

produce a singlet ground state. This model was an attempt to explain certain spectral data<sup>49</sup> indicating that the absorption spectra follow Beer's law and are independent of the alkali metal used.

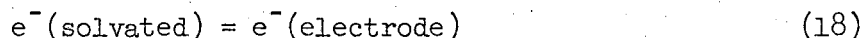
From even a brief survey of the current literature it is obvious that none of these theories is conclusive and the issue is still open to considerable question. In order not to prejudice the argument in the following experimental description we shall follow the convention of Laitinen and Nyman<sup>50</sup> and refer to any and all paramagnetic species in these solutions by the single name "electron".

#### B. Electrolysis in Liquid Ammonia

Several workers have investigated the electrolysis of solutions of tetra-alkyl ammonium salts in liquid ammonia. Forbes and Norton<sup>51</sup> measured the cathode potential for the reaction



where R was one of several different alkyl groups. They found the cathode potential to be essentially independent of the alkyl group used and came to the conclusion that the actual cathode reaction was



Laitinen and Nyman<sup>50</sup> studied the polarography of these salts in liquid ammonia at both mercury and platinum electrodes. They found that a polarographic wave with no limiting current occurred at essentially the same voltage for all the quaternary salts studied. They came to the conclusion that the only cathode reaction was a dissolution of electrons into the solution and they referred to this as the "electron electrode".

Doyle<sup>52</sup> studied the ESR spectrum of a frozen solution of electrolyzed

tetramethyl ammonium iodide in liquid ammonia and found that it was paramagnetic and that the ESR spectrum consisted of a single line with a width of 2.5 gauss. We have taken the ESR spectra of liquid solutions of electrolyzed tetramethyl ammonium iodide and found them to be similar to solutions of sodium in liquid ammonia (see below). These ESR experiments along with the polarographic data show rather conclusively that the reduced species in the tetra-alkyl ammonium salt solutions is similar to the reduced species in the alkali metal solutions.

### C. Chemical Reactions in Liquid Ammonia

The production of radical anions by dissolving organic molecules in metal-ammonia solutions has long been postulated by organic chemists. Polymerization and hydrogen abstraction reactions involving unsaturated hydrocarbons have been assumed to proceed via a radical-anion mechanism, and this type of reaction has been thoroughly studied.<sup>53,54</sup> In fact, in his original observation of the ESR spectrum of a radical anion<sup>22</sup> Weissman compared the production of the anion in tetrahydrofuran with the solution of sodium in ammonia. A thorough review of organic chemistry in liquid ammonia has recently been written.<sup>54</sup> This review, which was brought to the author's attention after the experiments described below were completed, anticipates many of the results described below and suggests many possibilities for future research.

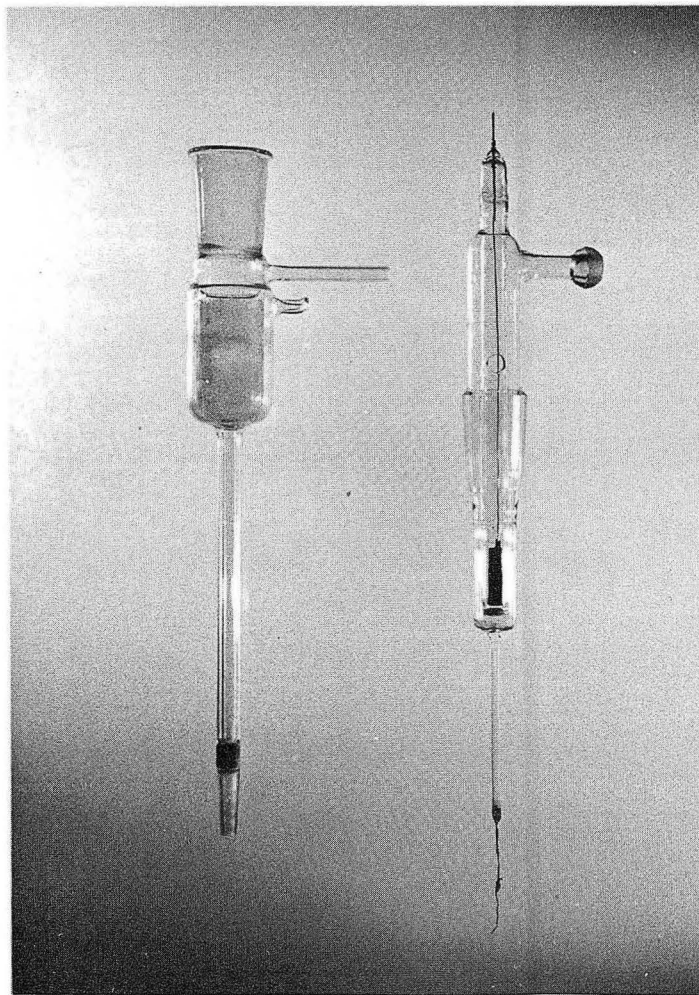
#### IV. EXPERIMENTAL TECHNIQUES

##### A. Electrolysis Cell

A photograph of the cell and Dewar in which the electrolysis was carried out is shown in Fig. 1 and a diagram of this equipment is shown in Fig. 2. The platinum wire cathode is sealed into the lower tube by a pressure glass-to-metal seal and made vacuum tight with epoxy resin cement.\* The lower tube, which is the only part of the cell that is placed in the microwave cavity, is made of quartz and is connected to the Pyrex part of the cell with a graded seal. The anode is contained in the inner tube and consists of a cylinder made of platinum foil and attached via a platinum wire to the tungsten wire that is sealed into the glass at the top of the cell. There is a hole in the inner tube above the level to the ammonia to allow easy cleaning of the anode compartment and to equalize the pressure throughout the cell. The anode and cathode compartments are separated by a glass frit to prevent the iodine produced at the anode from diffusing back into the cathode tube. The end of the lower tube is raised slightly from the bottom of the cell proper to prevent any solid supporting electrolyte from falling into the lower tube. The cell is connected to the vacuum line through a ball and socket joint and is held in place in its supporting Dewar by the large standard taper joint. The overall length of the cell is roughly 30 cm. and the length of the lower tube is roughly 10 cm. When filled to the operating point the cell contains 5-10 ml. of solution.

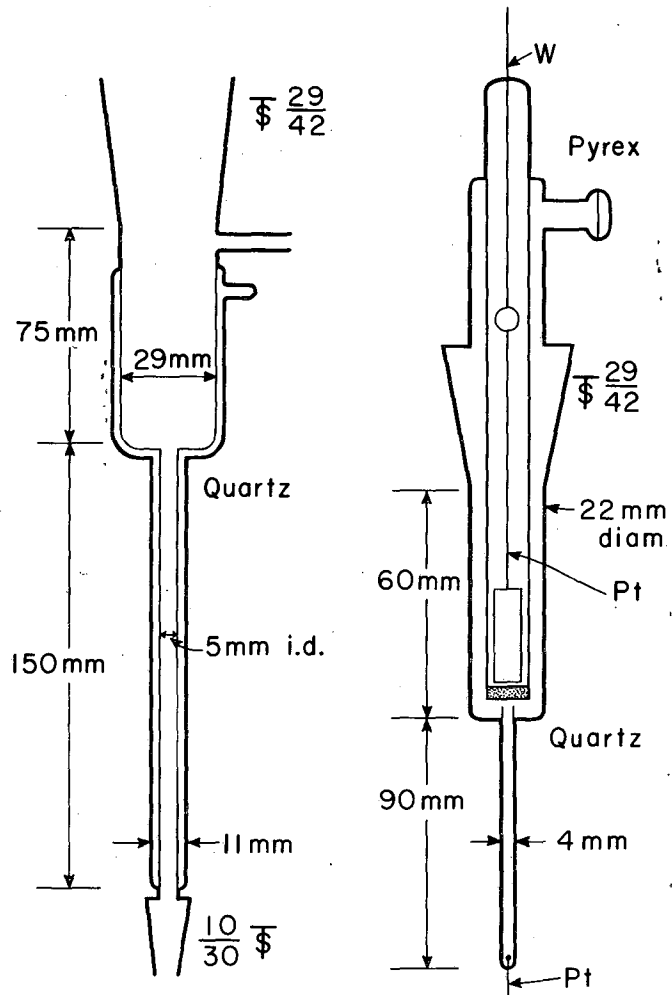
---

\* Armstrong Products Company C-3 resin was used. Some care must be shown in the selection and application of these cements since certain cements are paramagnetic, and all cements are paramagnetic if insufficiently cured.



ZN-4694

Fig. 1



MU-33781

Fig. 2

The electrolysis voltage was supplied by a voltage regulated power supply. A simple potentiometer circuit was used to vary the electrolysis voltage and either the voltage or current could be continuously monitored by a voltmeter connected either across the cell or across a 1000 ohm resistor which was in series with the cell.

#### B. Cooling System

When in use the cell is placed in the unsilvered quartz Dewar and the entire assembly is held rigid in the microwave cavity by a Teflon collet and aluminum collar fitting onto the stacks of the cavity. Since the ammonia solutions are quite lossy it is important that the sample tube be placed as nearly as possible in the node of the microwave electric field. With the platinum cathode approximately half way into the cavity a satisfactory loaded cavity Q was possible.

A transfer Dewar was connected to the lower standard taper of the sample Dewar via a ball joint elbow, and cold nitrogen gas was blown through the Dewar, past the cell, and out the top. The nitrogen gas was boiled from a reservoir of liquid nitrogen by means of an electric immersion heater, and the temperature of the cell was controlled by the amount of current passed through the heater. The temperature of the cell for a given heater power is of course a function of the heat loss in the specific Dewar arrangement used. With the Dewars used in these experiments a power dissipation of approximately 32 watts in the heater would maintain the cathode at the freezing point of the solutions used (approximately  $-78^{\circ}\text{C}.$ ). When necessary the temperature of the cathode was measured by a thermocouple wrapped around the lower tube of the cell. Quite large temperature gradients between the top and bottom of the cell were unavoidable but these did not prove inconvenient. Since the section of the Dewar inside the cavity must

be unsilvered there was considerable heat loss, and dry air was blown through the cavity to prevent condensation of moisture. The temperature variation with this system was less than one degree over the time necessary to complete the measurement of a complete spectrum.

### C. ESR Spectrometer

The ESR spectra were obtained on a conventional X-band reflection spectrometer employing 100 kc. magnetic field modulation and phase detection. With the exception of modifications mentioned below the spectrometer has been previously described.<sup>55</sup> The DC magnetic field was provided by a Pacific Electric Motors twelve inch electromagnet driven by a current stabilized power supply. The field homogeneity and power supply stability were such that there was less than a .001% field variation over a cylinder volume one inch in diameter. Of course, the effective sample volume in the cavity was much less than this, and field homogeneity over the sample was correspondingly higher. The magnetic field was slowly swept by a Hewlett-Packard low frequency function generator which was modified so that sweeps as slow as 2 hrs. per cycle (1 hr. per sweep) could be obtained with no sacrifice in linearity. The sample was contained in a Varian rectangular cavity, Model V-4531, operating in the  $TE_{012}$  mode with a loaded resonance frequency of approximately 9.2 gc.

Magnetic field intensity measurements were made with a marginal proton oscillator using a water sample doped with 0.1 M copper ion. To prevent instability caused by mechanical vibration, a rigid coaxial line was used between the oscillator and the sample coil, and the oscillator was remotely tuned by varying the bias voltage on a varactor diode in the oscillator tank circuit. The diode was thermally insulated to prevent instability and the bias voltage was provided by mercury cells. The

position of a given line was measured by adjusting the magnetic field until it was in the middle of the line, tuning the NMR oscillator to the middle of the proton resonance, and counting the oscillator frequency on a Hewlett-Packard frequency counter. The oscillator was stable to several parts in  $10^7$  over the period of time necessary to make a single measurement and was consequently never a major source of error. The principle source of error in measuring the position of a given line was in determining exactly the middle of the line.

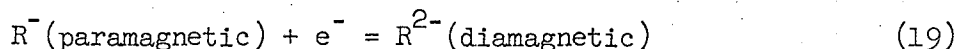
In making  $g$  value measurements the microwave frequency was measured with a Hewlett-Packard transfer oscillator and frequency counter.

#### D. Typical Procedure

At the start of each run a small amount of supporting electrolyte was placed in the cell. When tetramethylammonium iodide was used enough was placed in the cell to produce a saturated solution (0.0023 M at  $-78^\circ\text{C}.$ ). With the other salts used a saturated solution was probably obtained. At this point the cell was connected to the vacuum system and thoroughly evacuated. A calibrated volume was filled to a known pressure with sample, and the cell was cooled almost to liquid nitrogen temperature. At this point the vacuum system was sealed off from the pumps and the sample was allowed to distill over into the cell. The progress of the distillation could be followed by monitoring the pressure on a thermocouple gauge attached to the vacuum system. When a non-volatile sample was involved it was placed directly in the cell before evacuation. After the distillation was complete a small amount of ammonia was distilled into the cell, the cell was warmed to somewhere below the freezing point of ammonia, and the rest of the ammonia was distilled in. It was found that if the ammonia was distilled into the cell at liquid nitrogen

temperatures, it tended to crack the lower tube. After enough ammonia had been distilled over to cover the platinum anode, the cooling was shut off, the cell was allowed to warm, and the solution was stirred by the bubbles evolving from the bottom of the lower tube. When the solution had been thoroughly stirred the cell was again cooled so that the temperature of the lower tip was just above the freezing point of the solution. The freezing and thawing could be followed both by monitoring the current through the cell and by observing the change in cavity Q and frequency produced when the sample froze. After the cell was filled the system was allowed to sit until it had reached thermal equilibrium (approximately 20 minutes) and the cavity resonance frequency had stopped drifting.

The optimum electrolysis voltage varied with the concentration and nature of the sample used. To obtain the best signal-to-noise ratio the highest possible voltage was used to produce the highest steady state concentration of radicals. However at too high a voltage there are two mechanisms which tend to again decrease the signal-to-noise ratio. First the "electron" line which appears tends to overlap and obscure the radical spectrum. Second the higher concentration of electrons produces the diamagnetic dianion and reduces the radical concentration by the following reaction.



A typical example of voltage and concentration would be a solution 0.005 M in butadiene electrolyzed at a potential of -25 volts.

Because the radicals examined by this technique are unstable some care must be used to optimize the experimental conditions. Extremely small steady state radical concentrations are generated under the best of circumstances and it takes very little reactive impurity to reduce

these concentrations to the point where no signal is observed. Therefore all glassware must be scrupulously clean and the ammonia and supporting electrolyte must be of very high purity. After acquiring an experimental technique the experiments on a given molecule under a given set of experimental circumstances became quite reproducible. However the optimum conditions varied widely from molecule to molecule and a good bit of trial and error was necessary in order to achieve the best signal-to-noise ratio. The choice of supporting electrolyte seemed to be particularly critical. With butadiene the spectrum is almost unobservable when using sodium iodide although a very good signal-to-noise ratio could be obtained using tetramethylammonium iodide. With most of these radicals we were operating at the limits of the spectrometer's sensitivity and consequently these considerations determine not simply the quality of the spectrum but whether or not one sees any signal at all.

#### E. Chemicals

The tetramethyl-, tetraethyl-, and tetrabutylammonium iodides were Southwestern Analytical Chemicals polarographic grade. They were stored continuously in vacuo over magnesium perchlorate and were used without further purification. Some Eastman White Label tetramethylammonium iodide was also used. It was recrystallized from a four to one ethanol-water mixture and also stored in vacuo. The tetra-n-propylammonium perchlorate was made by titrating a 10% aqueous solution of Eastman tetra-n-propylammonium hydroxide with Baker and Adamson perchloric acid. The water insoluble salt was thoroughly washed with cold water and dried in vacuo. Baker and Adamson sodium iodide was dried at 110°C. and used without further purification.

Matheson reagent grade ammonia was used without purification. This grade is quoted as having a minimum purity of 99.99% and in the author's experience this is probably fairly accurate. The dimethyl ether used was Matheson research grade and when it was used as a mixed solvent sufficient sodium metal was added to the solution to produce the bronze metallic sodium-ammonia phase. The mixture was allowed to sit in contact with the sodium overnight and was degassed before being distilled into the electrolysis cell.

The deuterated cycloheptatriene was prepared in the following manner. Equimolar portions of cycloheptatriene and triphenyl methyl bromide were allowed to react in a liquid  $\text{SO}_2$  solution at approximately  $-17^\circ\text{C}$ . After the reaction was complete the solvent was removed by vacuum distillation. The cycloheptatrienyl bromide produced was dissolved in dimethyl ether and allowed to react overnight at dry ice temperature with lithium aluminum deuteride. The product was distilled off and purified by bulb to bulb distillation on the vacuum line. A vapor phase chromatogram of the product showed only one peak with the same retention time as the undeuterated material. An NMR spectrum of the deuterated material matched that reported by Jensen and Smith<sup>56</sup> for 7-deuterocycloheptatriene.\*

The sources of other chemicals used are listed below. The volatile samples were purified by bulb to bulb distillation on the vacuum line and all others were used without further purification.

Butadiene - Phillips Petroleum Company Research Grade

Isoprene - Phillips Petroleum Company Research Grade

---

\* The author is indebted to Miss Carolyn Talcott for carrying out the synthesis of the deuterated cycloheptatriene, and to Professor F. R. Jensen for suggesting the method.

Cyclohexadiene - Matheson, Coleman, and Bell Technical Grade

2,3 dimethyl butadiene - Matheson, Coleman, and Bell Practical Grade

Nitrobenzene - Eastman Organic Chemicals, White Label

Nitrosobenzene - Aldrich Chemicals

Hexatriene - Aldrich Chemicals

Cyclooctatetraene - Aldrich Chemicals

Cycloheptatriene - Prepared by Professor F. R. Jensen's research  
group.\*

---

\* The author would like to thank Professor Jensen and his group for the sample of cycloheptatriene.

## V. RESULTS AND DISCUSSION

### A. Butadiene

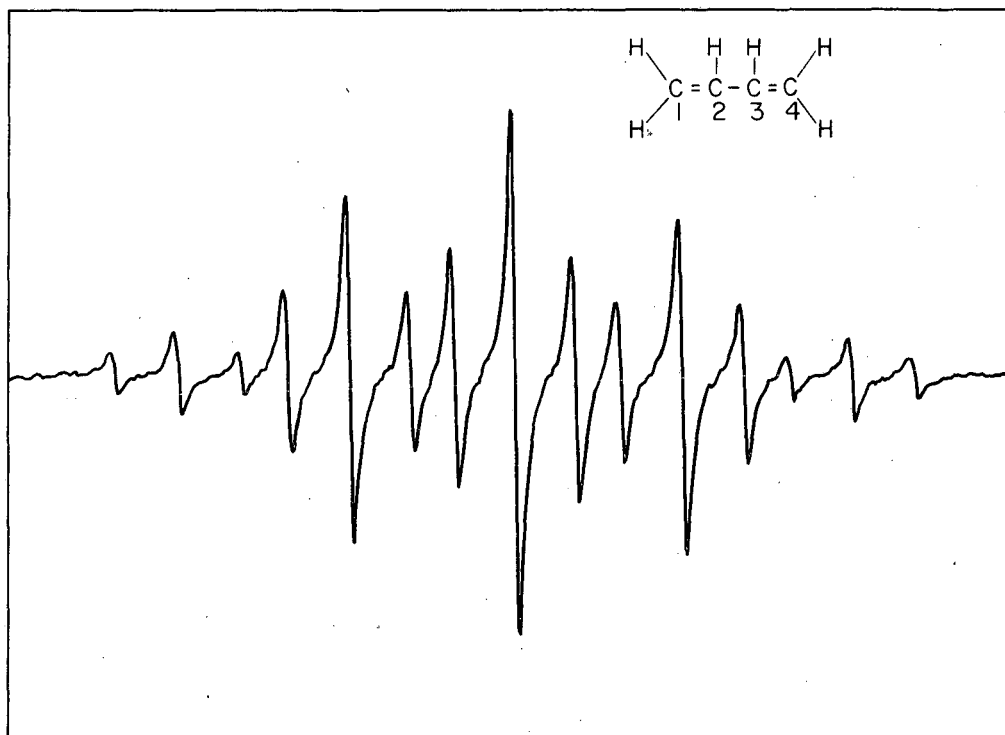
The ESR spectrum of the butadiene radical anion was obtained by electrolyzing a  $5 \times 10^{-3}$  M solution of butadiene in liquid ammonia at  $-78^{\circ}\text{C}$ . The solution was saturated with tetramethylammonium iodide.\* The spectrum obtained and the numbering of the atoms is shown in Fig. 3.

The spectrum is seen to consist of five groups of three lines each. If the two protons attached to the end carbon atoms are equivalent then only two proton coupling constants could be expected. Since the coupling constant  $A_1 (=A_4)$  is greater than  $A_2 (=A_3)$  then one would expect five sets of triplets as is experimentally observed.

The spectrum was measured several times over a range of microwave power and field modulations and the coupling constants in Table I were obtained. The difference in field between Lines 1 and 2 were the same as between Lines 14 and 15 thus showing that second order terms in the spin Hamiltonian could be neglected. The field difference between the points of maximum slope of the center line at  $-78^{\circ}\text{C}$ . is 0.3 gauss.

\*

The ESR spectrum of this solution without the butadiene consisted of a single very intense line of 0.21 gauss halfwidth. The  $g$  value of the line was 2.0007. When the electrolysis voltage was turned off the electron line slowly decayed following a zero order rate law.



MU-32841

Fig. 3

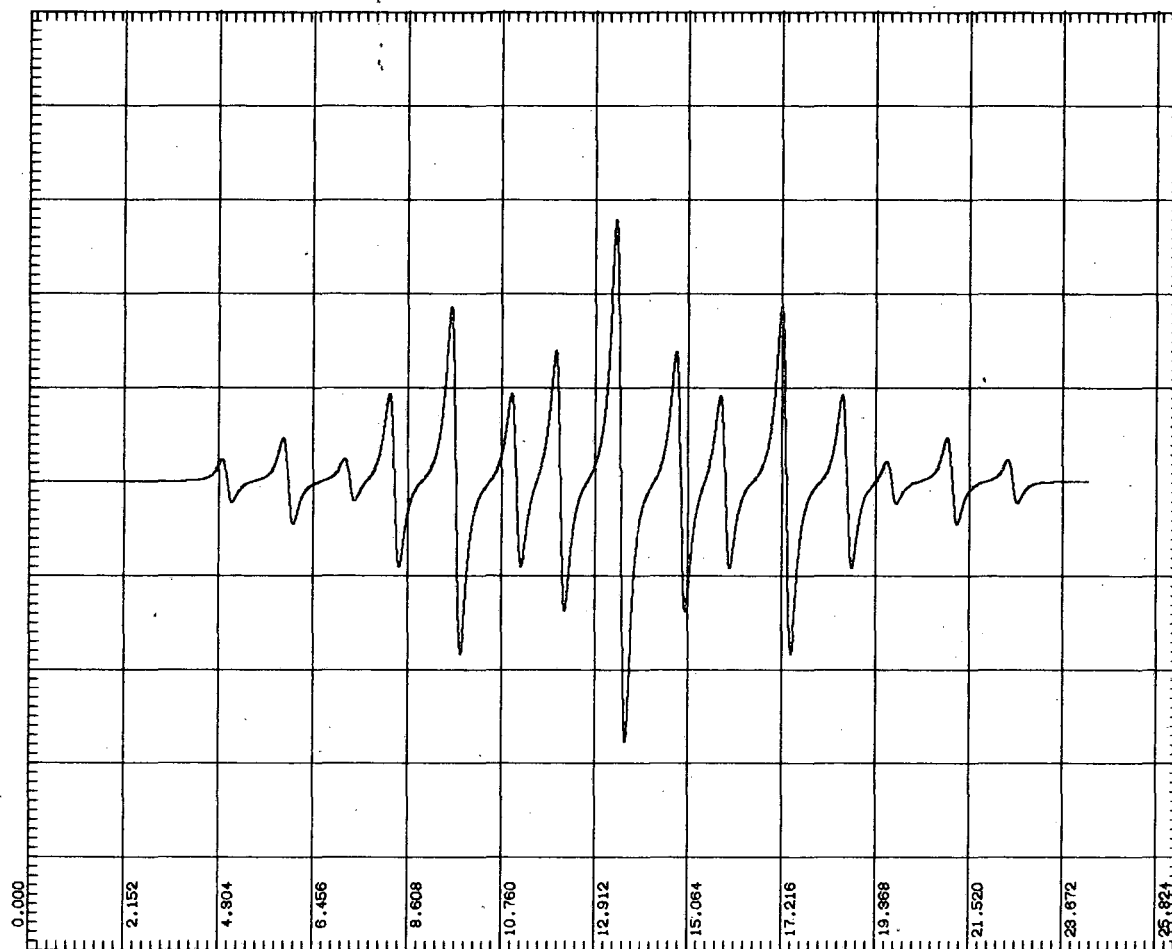
Table I. Observed Data for 1,3-Butadiene

|                 |   |                   |       |
|-----------------|---|-------------------|-------|
| $A_1$           | = | $7.617 \pm 0.005$ | gauss |
| $A_2$           | = | $2.791 \pm 0.007$ | gauss |
| $Q(\text{Av.})$ | = | $20.82 \pm 0.02$  | gauss |
| Linewidth       | = | 0.37              | gauss |
| $g$             | = | 2.0024            |       |

Using these values and assuming a Lorentzian lineshape a theoretical spectrum was calculated. This calculation was performed on an IBM 7094 Computer and the results were plotted on a California Computer Company digital x-y plotter. The plot is shown in Fig. 4 and as can be seen the agreement between the observed and calculated spectrum is excellent. Details of the calculation are given in Appendix I.

The line width of the spectrum was not found to vary with temperature within our experimental accuracy between  $-78^{\circ}$  and  $-68^{\circ}\text{C}$ . The lifetime of the radical anion was determined by measuring the decay of the signal after the removal of the electrolysis current. At  $-78^{\circ}\text{C}$ . the decay was found to follow first-order kinetics with a half-life of 2 sec. Since the signal-to-noise ratio depends greatly upon the experimental conditions, this implies that the half-life probably depends upon the temperature and solute. We have no indication that the observed line width is due to electron exchange with neutral butadiene, but it is possible that solute concentration or other factors may be the primary source of line width. Unlike conventional solvents, in this medium chemical exchange with the solvent itself is possible and may be responsible for these rather wide lines. It has been shown that an exchange mechanism of this sort can effect the apparent values of the coupling constants.<sup>91</sup> However, calculations performed on the butadiene radical anion show that the maximum effect in this radical would be approximately the same as the experimental uncertainty in the coupling constant measurements.<sup>92</sup> Magnetic field inhomogeneity was not a source of line width.

The molecule 1,3-butadiene has been considered<sup>57,58</sup> as a model system for pi-electron molecular orbital calculations. The observed values of the proton coupling constants can be related to theoretical



MUB-2276

Fig. 4

spin densities with Eq. (7) if the  $Q$  values are known. Recent evidence<sup>16</sup> indicates that the  $Q$  for every carbon position must be calculated taking into account a variation of  $Q$  with charge density. In our case since we know the proton coupling constant for every carbon atom an average  $Q$  value can be exactly determined. Thus by symmetry, we know that

$$\rho_1 + \rho_2 = 0.5 \quad (20)$$

and so

$$Q(A_v) = 2(A_1 + A_2) = 20.82 \text{ gauss} \quad (21)$$

This value is particularly small and is therefore consistent with Eq. (9) where  $Q$  in radical anions should decrease with the charge density. If one also considers the values of  $Q(C_8H_8^-) = 25.67^{59}$  and  $Q(C_6H_6^-) = 22.50$ ,<sup>31</sup> there appears to be a nearly linear decrease of  $Q$  with charge density. The three radical anion  $Q$  values indicate that in Eq. (9),  $K$  should be close to 40 and  $Q$  around 30.0 gauss while Colpa and Bolton<sup>16</sup> obtained  $K = 17$  and  $Q_0 = 31.2$  gauss from other data. It is quite possible that changes in the hybridization of the C-H orbitals are partly responsible for these low values of  $Q$ . The trend with charge density is moderately close to that expected from Colpa and Bolton's equation, but a rather large  $K$  value must be assumed.

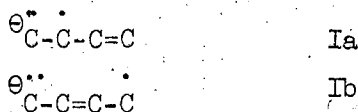
Giacometti et al.<sup>17</sup> have obtained satisfactory agreement for the radical ions considered by Colpa and Bolton and for  $C_6H_6^-$ . In the later case agreement was only obtained if overlap was included in the usual Huckel treatment. If we apply the equations recommended by Giacometti et al. to the usual Huckel orbitals<sup>60</sup> for butadiene radical anion, the

predicted proton coupling constants are  $A_1 = 9.8$  gauss and  $A_2 = 3.8$  gauss. These values are essentially unchanged by the inclusion of overlap as recommended by Giacometti et al. These coupling constants are both about 25% larger than the observed ones, and it does not seem that this treatment has any advantage over that of Colpa and Bolton even if overlap is included.

If we neglect the variation of  $Q$  with charge density, a direct comparison of the experimental value of  $A_1/A_2$  with theoretical values of  $\rho_1/\rho_2$  can be made. In Table II such a comparison is given for a series of one-electron molecular orbital wave functions. It can be seen that simple Huckel theory gives a most satisfactory agreement.

The inclusion of d-orbitals by Sover and Kauzman<sup>61</sup> is an interesting extension of Huckel theory. The d-orbital value in Table II is the sum of p and d-electron spin densities. Since the Q values would not be expected to be identical for these two kinds of orbitals, the spin density ratio shown in Table II is of only qualitative significance. The three SCF values fall far short of the mark and a considerable improvement must be made in this theory to approach Huckel theory for spin density calculations.\*

Some interesting valence bond structures can be drawn for our radical anion as follows:



\* <sup>62</sup>Hayes has performed a SCF calculation on the 5 electron pi system for the butadiene radical anion and gotten 3.39 and 2.97 as values for the ratio  $\rho_1/\rho_2$  for the cis and trans isomer respectively. The author does not know the details of this calculation.

Table II. Comparison with Theory

---

---

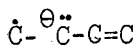
| $A_1/A_2$ (expt.) = $2.729 \pm 0.007$ |                                              |
|---------------------------------------|----------------------------------------------|
| $\rho_1/\rho_2$ (cal.)                | Theory                                       |
| 2.615                                 | Simple Huckel Theory                         |
| 2.219                                 | Huckel Theory with<br>variable $\beta$       |
| 2.9                                   | Huckel Theory with<br>d-orbital <sup>a</sup> |
| 1.9                                   | SCF (without net charge) <sup>b</sup>        |
| 1.6                                   | SCF (with net charge) <sup>c</sup>           |
| 2.97                                  | SCF (with net charge) <sup>d</sup>           |

---

|              |                                     |
|--------------|-------------------------------------|
| <sup>a</sup> | Ref. 17                             |
| <sup>b</sup> | Ref. 1                              |
| <sup>c</sup> | L. Goodman by private communication |
| <sup>d</sup> | Ref. 62                             |

---

---



II

Structures Ia and Ib are those of a substituted allyl radical and simple valence bond arguments would predict that  $\rho_1/\rho_2 = 2$ . Since structures of the type II do not place the odd electron at all on the middle carbon atoms, the inclusion of these structures can only increase  $\rho_1/\rho_2$ . Since simple resonance considerations would give a greater importance to the structures of Type I, one would predict that  $\rho_1/\rho_2 > 2$  and it should not be too far above the lower limit. The valence bond structures also predict that the negative charge should be even more concentrated on the end carbon atoms than is the spin.

The simple Huckel theory can also be modified for the fact that the radical anion should have two  $\beta$  values.<sup>60</sup> Since the bond between the middle carbon atoms is the longer one it should also have the smaller resonance integral. The assumption that  $\beta$  is proportional to the overlap integral  $S$  will lead to this type of variation. The bond length data of Almenningen et al.<sup>87</sup> and the overlap integrals of Mulliken et al.<sup>70</sup> lead to values of 0.9 and 1.1 for the values of the resonance integrals of the end and middle carbon-carbon bonds respectively. We have performed a Huckel calculation using these matrix elements and have found that this calculation gives a value of  $\rho_1/\rho_2 = 2.219$ . This modification is in the wrong direction to compensate for a correction based upon the variation of  $Q$  with spin density where we expect that  $Q_1 < Q_2$ , but at the present time there is considerable uncertainty about the variation of  $Q$  with either charge density or spin density.

## B. Methyl and Methylene Coupling Constants

As we have seen the hyperfine splittings due to protons attached to pi-bonded carbon atoms can be analyzed theoretically by simple and straightforward means (e.g. Eqs. (7 & 9)). However splittings due to protons attached to aliphatic substituents such as methyl or methylene\* groups involve some additional theoretical considerations. There are two problems that arise when one considers aliphatic substituents. The first is a question as to how any unpaired spin density gets into the aliphatic group. The second is that, given a mechanism for getting unpaired spin density into the aliphatic group, how does one then calculate the hyperfine coupling constants from a knowledge of this spin density distribution.

The model most recently used with considerable success<sup>63,64</sup> to account for methyl hyperfine splittings is that of hyperconjugation with the methyl group itself. This model mixes the pi molecular orbitals of the conjugated system with orbitals of the correct symmetry centered on the methyl group and this extends the conjugated system. The result is a flow of electrons between the methyl group and the unsaturated part of the molecule and a net unpaired spin density on the methyl group. An alternate model is that of spin exchange polarization similar to that used by McConnell<sup>13</sup> to explain the production of unpaired spin density at the hydrogen nuclei in the plane of a pi-radical. In this model the unpaired pi-electron remains in the unsaturated part of the molecule but produces unpaired spin density at the methyl protons via polarization of

---

\* Of course we are here referring to  $sp^3$  bonded methylene carbons and not to  $sp^2$  carbons which are a part of the pi-system such as in butadiene.

the sigma electrons in the C-H methyl bond. This polarization may be either direct or through a polarization of the sigma electrons in the carbon-carbon bond. In this section we shall assume that the principle mechanism for methyl and methylene coupling constants is hyperconjugation, and that the effects of spin polarization may be accounted for by a small correction term. In the next section we shall provide some justification for this assumption and shall derive the correction term from experiments on cycloheptatriene.

As was mentioned in the last section, the simple Huckel molecular orbital treatment of conjugated systems has been remarkably successful in interpreting the ESR spectra of alternate hydrocarbons. This theory has been explained quite simply by Streitwieser<sup>60</sup> whose notation we will use in the following discussion. Because of the success of this method it is desirable to attempt to include the hyperconjugation model within the general Huckel framework. This was first done by Mulliken et al.<sup>65</sup> in the following manner. They assumed that the 1s atomic orbitals of the hydrogens could be combined in some manner to produce a pseudo atomic orbital,  $Z$ , which was centered on the hydrogens and was of the correct symmetry to combine with the  $2p_z$  atomic orbitals of the unsaturated carbon system. The  $H_3$  pseudo-atom was then considered as a part of the substituent group  $C'-C-H_3$  where  $C'$  was the unsaturated carbon to which the methyl group was attached. Thus by assuming off-diagonal matrix elements connecting  $C'$  with  $C$  and  $C$  with  $H_3$ , and on-diagonal elements for  $C$  and  $H_3$  the hyperconjugating methyl group could be included in the usual Huckel calculation.

It was pointed out by Coulson and Crawford<sup>66</sup> that because the C- $H_3$  bond was so short, the assumption that  $S_{ij} = \delta_{ij}$  ( $\delta_{ij}$  is the Kronecker

delta), usually made in the Huckel approximation, is no longer valid and that the calculation should be carried out using the complete overlap matrix,  $\tilde{S}$ . They made the assumption that the off-diagonal S and H matrix elements were proportional to each other and that both were proportional to bond length. With the S and H values thus derived and with some fairly arbitrary values for the on-diagonal H matrix elements they performed a series of calculations.

Bolton and co-workers<sup>63</sup> modified Coulson's method in an attempt to be able to include the effects of non-vanishing overlap elements in the methyl group without adding the additional computational difficulties that are encountered when overlap is included for the entire pi-system. They formed two molecular orbitals for the methyl group by combining the atomic orbitals on C and H<sub>3</sub> using overlap and the parameters of Coulson and Crawford. This of course involved only two by two matrices and was a fairly simple calculation even including overlap. It turned out that the resulting anti-bonding molecular orbital was so high in energy that they felt it could be neglected. This meant that the methyl group could be treated as a heteroatom where the bonding molecular orbital now became the pseudo atomic orbital. The previous calculation provided the matrix elements connecting it to the unsaturated system, and the usual Huckel calculation could be performed with neglect of overlap since the overlap of the methyl group had already been included.

Colpa and deBoer<sup>64</sup> examined the absolute magnitudes of the coupling constants predicted by the theory of Bolton et al and came to the conclusion that the neglect of the anti-bonding molecular orbital was unjustified since it led to values of the coupling constants which were considerably lower than those observed experimentally. Their contention

was that the only reasonable way to treat the hyperconjugation model was to perform the full overlap calculation of Coulson and Crawford. The calculation starts with the matrix eigenvalue equation

$$\tilde{H}\tilde{C} = \tilde{S}\tilde{C}\tilde{E} \quad (22)$$

Following the method of Lowdin<sup>67</sup> we can rearrange Eq. (22) to the following form

$$H'C' = C'E \quad (23)$$

where

$$H' = S^{-\frac{1}{2}}HS^{-\frac{1}{2}} \quad (24)$$

and

$$C = S^{-\frac{1}{2}}C' \quad (25)$$

Thus the problem is reduced to the usual Huckel form and the transformation  $S^{-\frac{1}{2}}$  can be used to transform the resulting eigenvector matrix  $C'$  into the molecular eigenvector matrix  $C$ . The matrix  $S^{-\frac{1}{2}}$  may either be computed from the series expansion as was done by Lowdin or by application of a quite general theorem.<sup>68</sup> The theorem states that for any matrix  $A$  which can be diagonalized by a transformation,  $T$ , according to the following equation,

$$T^{-1}AT = A_D \quad (26)$$

any function  $f(A)$  is given by

$$\text{Tr}(A_D)T^{-1} = f(A) \quad (27)$$

where

$$(f(A_D))_{aa} = f((A_D)_{aa}) \quad (28)$$

for all values of  $a$ .

In spite of the success of simple Huckel theory there are certain effects which it cannot explain. The principle effect is that of negative spin density in which the closed shell pi-electrons are polarized by the odd electron to produce a net negative spin density at points in the molecule where the unpaired electron wave function is small or vanishing. This correlation effect arises from the electron-electron repulsion term in the molecular Hamiltonian which is neglected completely by Huckel theory. In order to account for negative spin density and other electron correlation effects McLachlan<sup>69</sup> proposed an approximate self-consistent field theory which took electron correlation into account in a simple and straightforward manner. His theory led to the following formula for the spin density:

$$\rho_r = C_{ro}^2 - \lambda \sum_c \Pi_{rs} C_{so}^2 \quad (29)$$

where  $C_{ro}$  is the Huckel coefficient of the odd orbital on atoms r,  $\Pi_{rs}$  is the mutual polarizability of atoms r and s, and  $\lambda$  is a constant derived from the theory to be about equal to 1. We have combined the theory of McLachlan with the hyperconjugation model of Mulliken<sup>65</sup> in an attempt to account for correlation effects in the methyl group.

Once one has calculated the electronic wave function with one of the above methods there still remains the problem of calculating the hyperfine coupling constant for comparison with experiment. Colpa and deBoer<sup>64</sup> have touched briefly on this problem but their treatment is sketchy and the method they used to obtain their results is not obvious. We have extended their treatment to provide a specific formula for the coupling constants of methyl and methylene protons.

We first consider the case of methylene protons. The methylene

group consists of one hydrogen atom above the nodal plane of the pi-system and one hydrogen atom below the nodal plane. If we denote the normalized 1s atomic orbitals centered on these two atoms as  $\phi_{1s}^U$  and  $\phi_{1s}^L$  respectively we can combine them to form one pseudo atomic orbital of the correct symmetry to combine with the pi-orbitals of the rest of the molecule. This pseudo atomic orbital is

$$\Pi_H = N(\phi_{1s}^U - \phi_{1s}^L) \quad (30)$$

where the normalization constant N is given by

$$N = \frac{1}{\sqrt{2(1-S_{UL})}} = .834 \quad (31)$$

The overlap integral  $S_{UL}$  is taken from the tables of overlap integrals of Mulliken et al.<sup>70</sup> and assumes the bond lengths and angles shown in Fig. 5.

In the LCAO approximation the molecular orbital in which the unpaired electron moves is given by

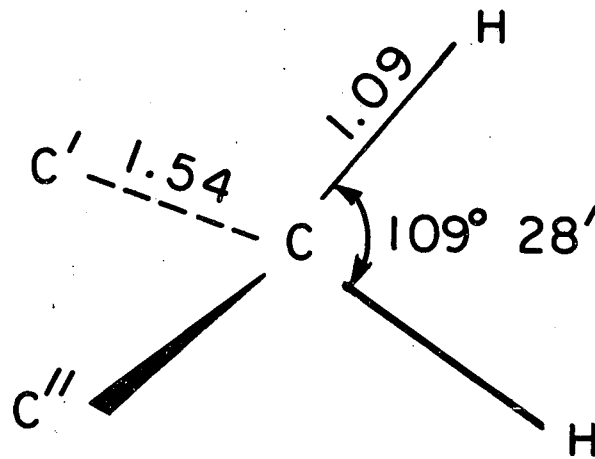
$$\Psi_o = \sum_i c_{oi} \Psi_i \quad (32)$$

where the  $\Psi_i$ 's are the atomic orbitals including the  $2p_z$  orbitals on each of the carbons and the pseudo atomic orbital  $\Pi_H$  on the hydrogens. Then the spin density at either of the methylene protons is given by

$$\rho(\rho) = \sum_{l,m} c_{ol} c_{om} \Psi_l(\rho) \Psi_m(\rho) \quad (33)$$

in the case where overlap is included or by

$$\rho(\rho) = \sum_l c_{ol}^2 \Psi_l(\rho)^2 \quad (34)$$



MU-35076

Fig. 5

where the assumption of zero differential overlap is made. Using the atomic orbitals listed in Table III an expression for the total spin density at the proton can be evaluated. In order to convert this to a coupling constant one must multiply the total spin density by

$$\frac{A_{\text{Hydrogen Atom}}}{[\phi_{1s}(p)]^2} = \frac{508 \text{ gauss}}{2.161} = 235.1 \quad (35)$$

The only important terms in the series expressions given by Eqs. (33 & 34) are those involving the coefficients of the pseudo orbital ( $C_H$ ), the methylene carbon ( $C_C$ ), and the two carbons to which the methylene is attached ( $C_{C'}$  and  $C_{C''}$ ). Of these terms the  $C_C^2$  and  $C_{C''}^2$  terms are also negligible. The resulting expression for methylene coupling constants is given by

$$A_{\text{methylene}} = 327C_H^2 + 19.8C_C^2 + 161C_C C_H + (5.95C_H + 1.46C_C)(C_{C'} + C_{C''}) \text{ gauss} \quad (36)$$

If overlap has been neglected only the first two terms of this expression need be used.

The theory of methyl group coupling constants is similar to that of methylene except that the lack of symmetry with respect to the nodal plane of the pi system complicates things somewhat. These complications have been worked out quite explicitly by Chesnut<sup>71</sup> who has accounted for the chemical equivalence of the methyl protons by averaging over various static configurations of the methyl group. We have used Chesnut's method to provide a formula for evaluating methyl group coupling constants from a knowledge of spin distribution. Our values for the significant P matrix elements (defined in Ref. 71) are given in Table IV and the formula to

Table III. Atomic Orbitals.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} = 1.47 \ell^{-1.89r}$$

$$\psi_{2p_z} = N r \ell^{-\frac{3.25r}{2a_0}} \sin \theta = 9.32 r \sin \theta \ell^{-3.08 r}$$

Table IV. Important  $\Gamma$  Matrix<sup>71</sup> Elements

| $\begin{matrix} j \\ i \end{matrix}$ | 1       | 2       | 3      |
|--------------------------------------|---------|---------|--------|
| 1                                    | 0.00077 | 0.00207 | 0.0085 |
| 2                                    |         | 0.056   | 0.229  |
| 3                                    |         |         | 0.935  |

which they lead is

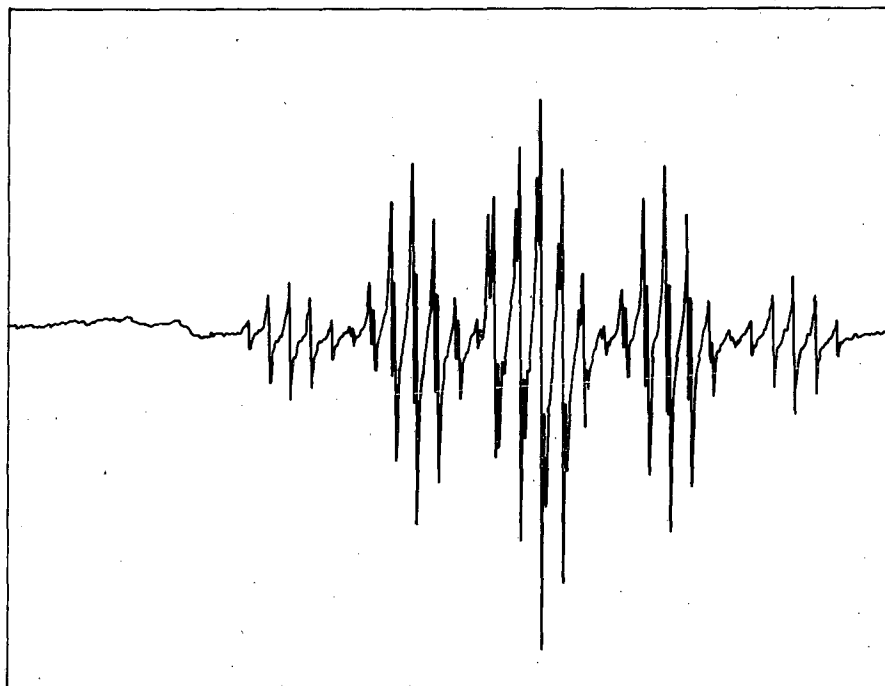
$$A_{\text{methyl}} = 219.8c_H^2 + 13.17c_C^2 + 107.7c_{HC} + 3.997c_{HC} + 0.973c_{CC}, \text{ gauss} \quad (37)$$

Here again if overlap is neglected only the first two terms need be considered.

In order to test the above theories several methyl or methylene containing radical anions were prepared and their ESR spectra measured. The radical anion of 2,3-dimethyl 1,3-butadiene was prepared by electrolysis of a 0.01 M solution of the parent hydrocarbon dissolved in a solution of liquid ammonia saturated with tetramethylammonium iodide. At low voltages (e.g. 10 volts) the spectrum consisted of five septets of rather wide lines. As the voltage was raised (e.g. 30 volts) the lines narrowed and the lines of the inner septets were further split to give the spectrum shown in Fig. 6. If the voltage was raised even further (e.g. 100 volts) the line width remained roughly constant but the spectrum became considerably weaker. If the voltage were at this point reduced to the intermediate level the spectrum would grow very rapidly and then decay to the level it originally had when the voltage was at an intermediate (e.g. 30 volt) level. We interpret this behavior as evidence for the formation of a relatively stable diamagnetic dianion which is in equilibrium with the electron and the radical anion according to the following equation:



As the voltage is raised the production of excess electrons shifts the equilibrium to the left and causes the radical anion concentration to



MU-32839-A

Fig. 6

decrease and the steady state dianion concentration to increase to quite a high level. When the voltage is again reduced the production of electrons is decreased, the steady state concentration of electrons drops, and the equilibrium shifts rapidly to the right. The initial high concentration of the dianion represents an excellent reducing agent and a high concentration of the radical anion results via the equilibrium



Eventually the supply of excess of dianion is exhausted and the concentration of the radical anion is governed by the equilibrium



and drops to its original value.

The line width versus electrolysis voltage characteristics of this system raise some interesting questions as to the source of line width in this radical. Unlike butadiene and most other radicals investigated, the source of line width in fairly concentrated solutions (0.01 M) appears to be due to an electron exchange relaxation mechanism between the radical and the neutral parent molecule similar to that occurring in more conventional solvents. The effect of increasing the voltage is to lower the concentration of the neutral molecule in the immediate vicinity of the electrode\* via equilibria 38-40. When the neutral species concentration is decreased the line width also decreases. Just why the mechanism that produces the relatively large line widths in most other species does not

---

\* In most of these radicals the lifetimes are so short that they can diffuse only a very short distance from the electrode before being destroyed. Consequently the ESR spectrum is a measure of conditions in the immediate vicinity of the cathode.

operate here is open to question. If the principal source of line width in ammonia solutions is electron exchange with the solvent or the solute cation, it may be that the effect of the methyl groups in this molecule is to sterically block the approach of solvent or solute molecules and thus inhibit this source of relaxation.

The fact that the linewidth of dimethylbutadiene is far narrower than that of any other radical we have observed in ammonia solution is at least not inconsistent with such a theory.

A spectrum consisting of five septets could be readily assigned to the splittings caused by four equivalent methylene protons and six equivalent methyl protons. However the additional small splittings of the inner septets can only be accounted for by assuming a slight inequivalence of the methylene protons which produces two sets of two equivalent protons. On that basis the spectrum can be completely assigned with the coupling constants given in Table V. The theoretical spectrum calculated from these coupling constants is shown in Fig. 7.

The usual treatments for hyperfine coupling constants as given in Eqs. (7 & 9) predict a single pi-sigma interaction parameter for any given carbon and consequently imply that all protons attached to a given carbon should have the same coupling constant even if they are geometrically unequivalent. This conclusion is generally true and only one other case of unequivalent protons attached to the same carbon has been reported. Fessenden and Schuler<sup>72</sup> have noted that the two methylene proton coupling constants in the allyl radical differ by 0.10 gauss. In order to explain this phenomenon an extension of the usual treatments of sigma-pi interaction is necessary.

Table V. Observed Data for 2,3-Dimethylbutadiene

---



---

|                          |       |
|--------------------------|-------|
| $A_1 = 7.033 \pm 0.003$  | gauss |
| $A'_1 = 7.241 \pm 0.003$ | gauss |
| $A_2 = 1.200 \pm 0.002$  | gauss |
| Linewidth = 0.099        | gauss |
| $g = 2.0020$             |       |

---



---

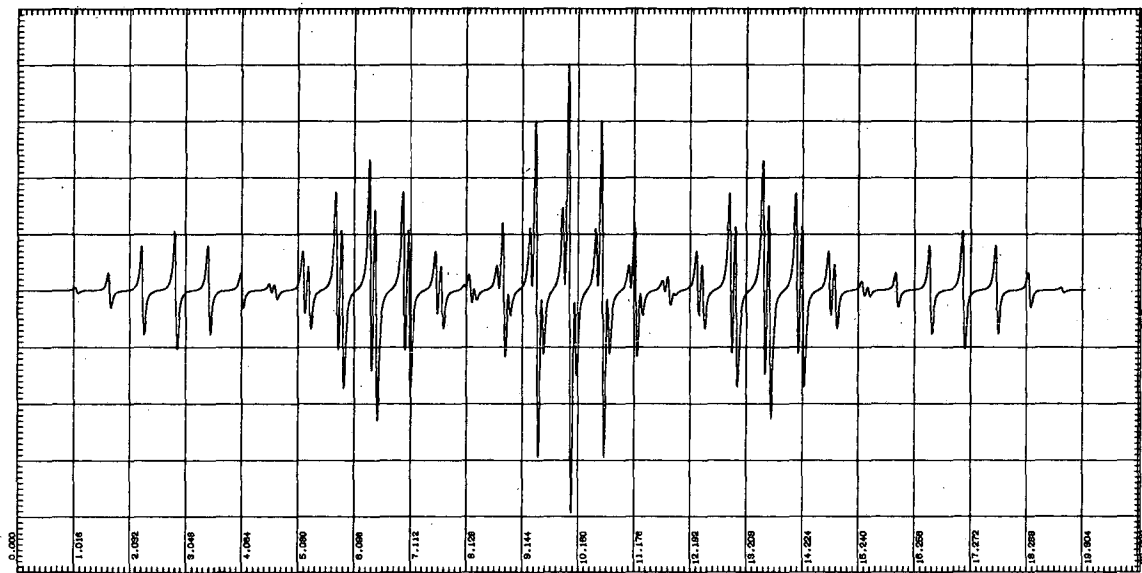
see Fig. 12 for numbering

Inasmuch as the  $2p_z$ -atomic orbitals of carbon are invariant to any arbitrary rotation about an axis normal to the molecular plane, no molecular orbital scheme involving only these  $2p_z$ -orbitals as basis functions can explain the observed difference. The most straightforward expansion of the basis set to include functions of the appropriate symmetry would be to include the carbon atomic d orbitals as was done by Sovers and Kauzmann.<sup>61</sup> They considered only the effect of the d orbitals on the electron distribution in the pi-system itself and neglected their effect on the pi-sigma interactions. Thus their calculations cannot explain the different coupling constants but can serve as the starting point for further calculations of the effect of d orbitals on the sigma system.

It can be shown<sup>61</sup> that of the five d-orbitals only two, the  $d_{xz}$  and  $d_{yz}$ , are of the correct symmetry to combine with the  $2p_z$ -orbitals. Thus the molecular orbital in which the odd electron moves can be expressed

as

$$\psi_o = \sum_{i=1}^N [c_{oi} \phi_{p_z}^i + c'_{oi} \phi_{d_{yz}}^i + c''_{oi} \phi_{d_{xz}}^i] \quad (41)$$



MU8-2277

Fig. 7

By considering only the  $\text{CH}_2$  fragment composed of carbon atom  $j$  and two hydrogens it is clear that there exists a coordinate system such that either  $\phi_{\text{d}}^j_{\text{yz}}$  or  $\phi_{\text{d}}^j_{\text{xz}}$  vanishes. This is of course equivalent to transforming the coefficients  $C'$  and  $C''$  from the arbitrary coordinate system in which they were originally defined to a new coordinate system which in general is not the same as the coordinate system defined by the two C-H bonds. This produces the anisotropy which can account for the different coupling constants.

Using Sovers and Kauzmann's values for the coefficients of the d orbitals of butadiene, the principle d axis system is rotated from the bond axis system by approximately  $3^\circ$ . Myers<sup>73</sup> has shown that by making certain reasonable assumptions the  $3^\circ$  anisotropy would produce a difference in coupling constants on the order of 0.05 gauss in butadiene. This difference would have been too small to even produce a measurable line intensity anomaly with the limited resolution we were able to achieve with butadiene.

There are two mechanisms which could account for the larger anisotropies in dimethylbutadiene. First of all the methyl groups, through a hyperconjugation or inductive effect, will distort the pi system and alter the d orbital coefficients. By this mechanism the principal axis system of the d orbitals might be further shifted from the bond axis system. The second mechanism which might be important would be the steric effect of the methyl groups. This steric effect would tend to distort the molecular geometry itself and thus produce further anisotropy. The first effect might be looked upon as a shifting of the d orbital principal axis system, and the second effect might be looked upon as a shifting of the bond axis system. Since the total anisotropy depends upon the difference between

these two either could produce the observed effect. Unfortunately all of the usual techniques for measuring bond angles and distances give very little information about carbon hydrogen bond angles, and the second effect would be difficult to measure with the methods now available. Calculations are in progress to determine the magnitude of the first mechanism in dimethylbutadiene and to see how large a geometric distortion would be necessary to account for the observed differences.

The radical anion of 1,3-cyclohexadiene was prepared by electrolyzing a 3-millimolar solution of cyclohexadiene in liquid ammonia. The solution was saturated with tetramethylammonium iodide. In this case the optimum signal-to-noise ratio was produced with a rather high electrolysis voltage (ca. 60 volts). The resulting spectrum with the electron superimposed is shown in Fig. 8. At first sight the spectrum appears quite complex but the assignment is aided by the fact that only three distinct coupling constants are involved. The total width of the spectrum imposes the constraint that

$$\text{Total width} = \sum_{n=1}^N I_n A_n \quad (42)$$

where  $I_n$  and  $A_n$  are the spin and coupling constant of the nth magnetic nucleus respectively. This constraint allows one to determine the 3rd coupling constant if the first two are known so the problem of assigning the spectrum is really a two parameter problem. The outermost triplet indicates that one of the coupling constants is given by the spacing of the lines in the triplet and a not unreasonable guess for a second coupling constant would be the distance between the first and fourth lines. The coupling constants derived from this assignment are given in Table VI and the theoretical spectrum calculated from them and shown in Fig. 9

Table VI. Observed Data for Cyclohexadiene

---



---

|                          |       |
|--------------------------|-------|
| $A_1 = 1.996 \pm 0.009$  | gauss |
| $A_2 = 8.212 \pm 0.011$  | gauss |
| $A_3 = 11.114 \pm 0.012$ | gauss |
| Linewidth = 0.233        | gauss |
| $g = 2.0025$             |       |

---

See Fig. 12 for numbering

---

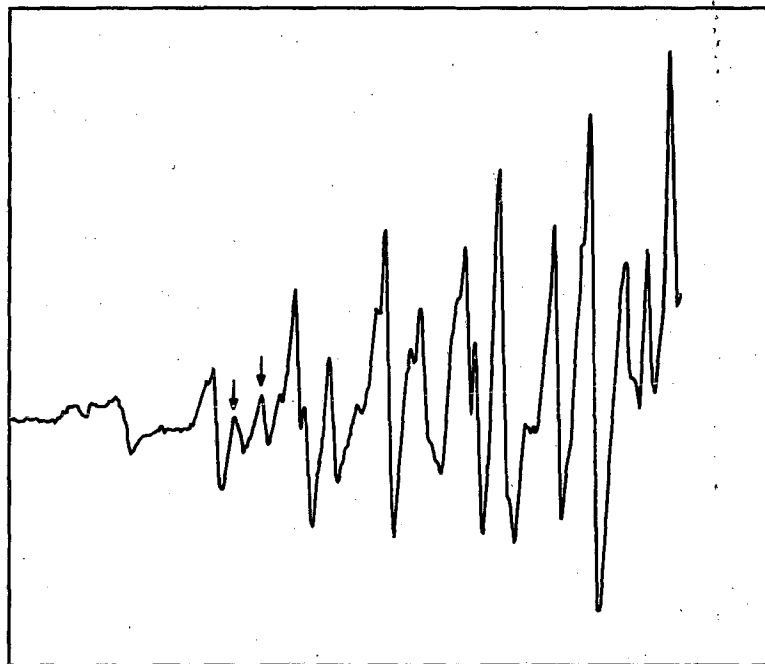


---

is seen to agree with the experimental spectrum.

The radical anion of isoprene was prepared by electrolyzing a 0.01 M solution of the parent molecule in liquid ammonia. Enough tetraethylammonium iodide was added to produce a saturated solution. Since tetraethyl ammonium iodide is much more soluble in liquid ammonia than the tetramethyl salt, the resulting saturated solution is more conductive. The best spectrum shown in Fig. 10 was produced at rather high electrolysis voltages (ca. 80 volts). At these voltages a large electron line is superimposed upon the isoprene spectrum. By lowering the electrolysis voltage the electron line could be eliminated and this did not change the radical anion spectrum.

Unfortunately in this case the assignment of the spectrum is not a trivial matter. Assuming that the protons on any given methyl or methylene group are equivalent or almost equivalent, the spectrum should be able to be assigned with four coupling constants. After considerable effort to assign the spectrum by the usual intuitive method an attempt was made at a systematic approach to the problem. To begin with it is clear from the



MU-35077

Fig. 10

spin Hamiltonian that in general every distinct coupling constant in any given radical is represented by the distance between the outermost line in the spectrum and one of the interior lines. The constraint imposed by Eq. (42) places an upper limit on the value of the largest coupling constant. In the case of isoprene this limit requires the largest coupling constant to be represented by the distance between the outermost line and one of the interior lines up to and including line number 23. Thus the four coupling constants must be chosen from the set of 22 numbers given by the positions of the lines 2 through 23 (defining the position of line 1 as zero). This limits the number of possible assignments to around  $10^5$  and the problem of checking each of them (with the aid of a computer) becomes tractable.

Most of the combinations are ruled out because they do not satisfy Eq. (42). Each of the  $10^5$  combinations were checked and only those which produced a total spectrum width within the range (experimental width  $\pm R$ ) were saved. With  $R = 2\%$  of the experimental width there were 208 combinations that satisfied this criterion. Seven specific critical lines were chosen in the experimental spectrum and each of the 208 remaining combinations were tested to see if they would predict a line at each of the seven experimental positions  $\pm R'$ . With  $R' = 1\%$  of the total spectrum width only three combinations satisfied this criterion. The complete spectrum predicted by each of these three combinations was calculated and none of them agreed with the experimental spectrum. Thus within the accuracy of the experimental data there was no possible assignment of four coupling constants that would predict all the lines in the spectrum.

The cause of the difficulty is lines 4 and 5 indicated by arrows in Fig. 10. If the existence of these lines is ignored a very good

assignment can be made for the rest of the spectrum with the coupling constants listed in Table VII. The theoretical spectrum based on these coupling constants is shown in Fig. 11 and may be seen to be in excellent agreement with the rest of the experimental spectrum. This excellent fit and the fact that the assignment agrees so well with the predictions of molecular orbital theory (see below) have led us to the conclusion that lines four and five are anomalous, perhaps caused by impurities, and that the assignment given in Table VII is indeed correct.

We have performed a series of calculations on the three molecules mentioned above and on several other molecules containing methyl or methylene groups for which experimental data exists in the literature. For each molecule we have done a simple Huckel hyperconjugation calculation both including and neglecting overlap, a modified overlap calculation,<sup>63</sup> and an approximate self consistent field calculation.<sup>69</sup> In all of these calculations we have started with the methyl parameters of Coulson and Crawford<sup>66</sup> which are given in Table VIII. The numbering of the atoms is shown in Fig. 12 and the results for the four different calculations are given in Tables IX-XII. The computer program used to perform these calculations is discussed in Appendix II.

Using the results of these calculations one can calculate the predicted theoretical coupling constants. The hyperconjugation contribution to the methyl and methylene coupling constants,  $A_H$ , is given by Eqs. (36 & 37). In addition to this one must consider the contribution of spin exchange polarization,  $A_p$ . Following the treatments of McConnell<sup>15</sup> and Colpa<sup>64</sup> we shall assume that this contribution takes the form

$$A_p = Q_p \rho' \quad (43)$$

Table VII. Observed Data for Isoprene

|                        |       |
|------------------------|-------|
| $A_1 = 7.91^a \pm .03$ | gauss |
| $A_2 = 3.42 \pm .03$   | gauss |
| $A_5 = 3.10 \pm .03$   | gauss |
| $A_6 = 6.50^a \pm .03$ | gauss |

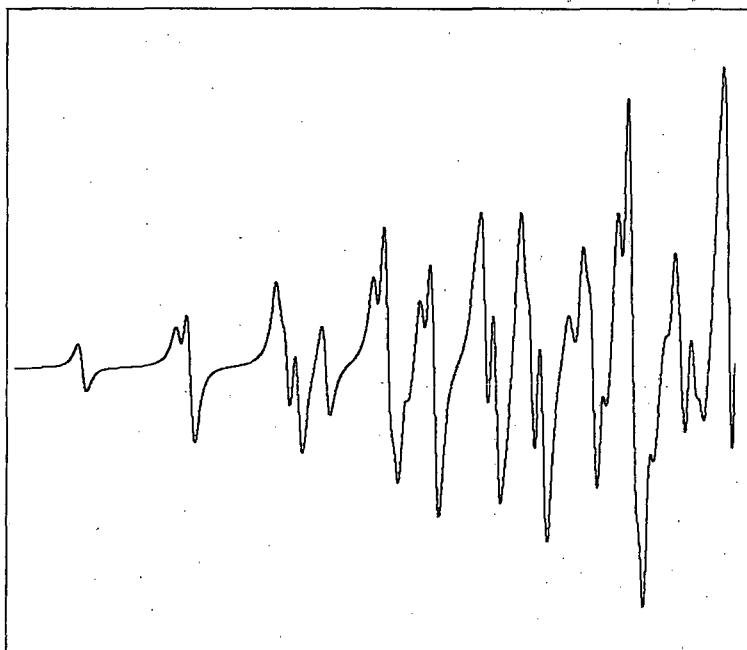
<sup>a</sup> Assigned on the basis of theoretical calculation.

See Fig. 12 for numbering.

Table VIII. Methyl Group Parameters

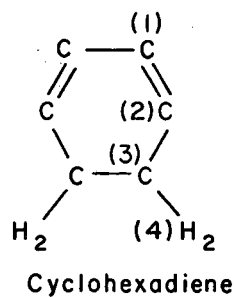
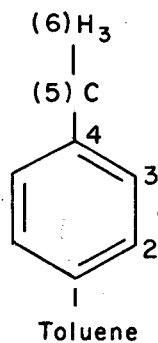
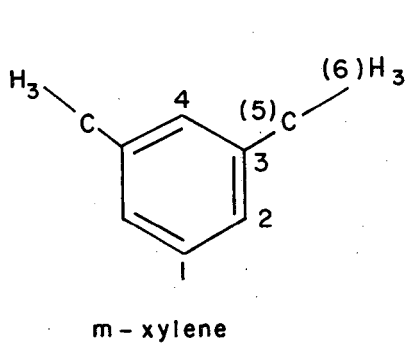
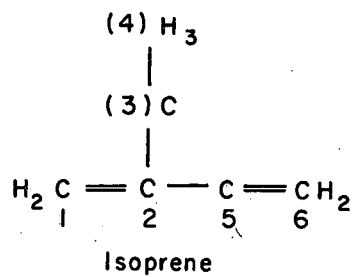
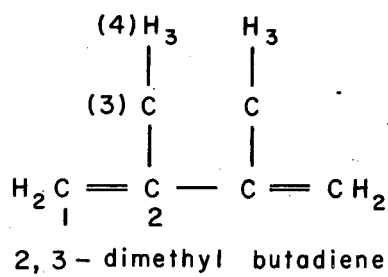
| Parameter                  | Coulson & Crawford Value <sup>66</sup> |
|----------------------------|----------------------------------------|
| $H_H$                      | -0.5                                   |
| $H_C$                      | -0.1                                   |
| $H_{H-C}$                  | 2.00                                   |
| $H_{C-C'}$                 | 0.76                                   |
| $H_{ij}/S_{ij} \ i \neq j$ | 4.0                                    |

<sup>a</sup> Ref. 66



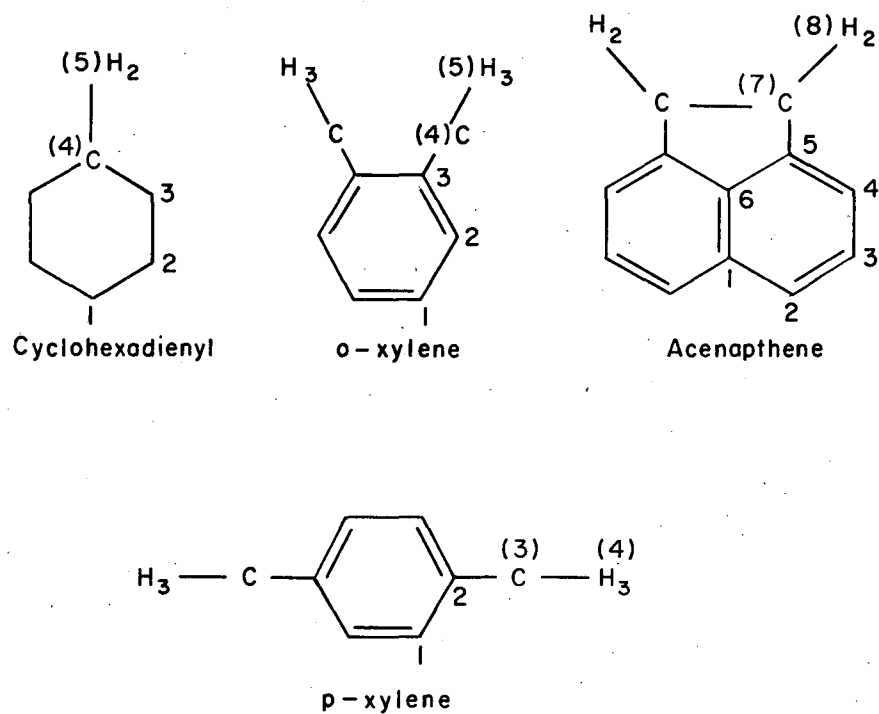
MU-35056

Fig. 11



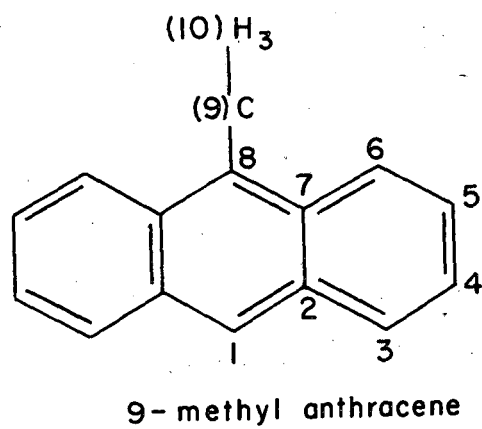
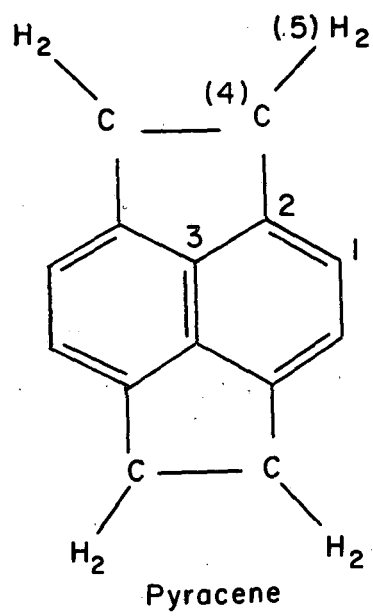
MU-35080

Fig. 12a



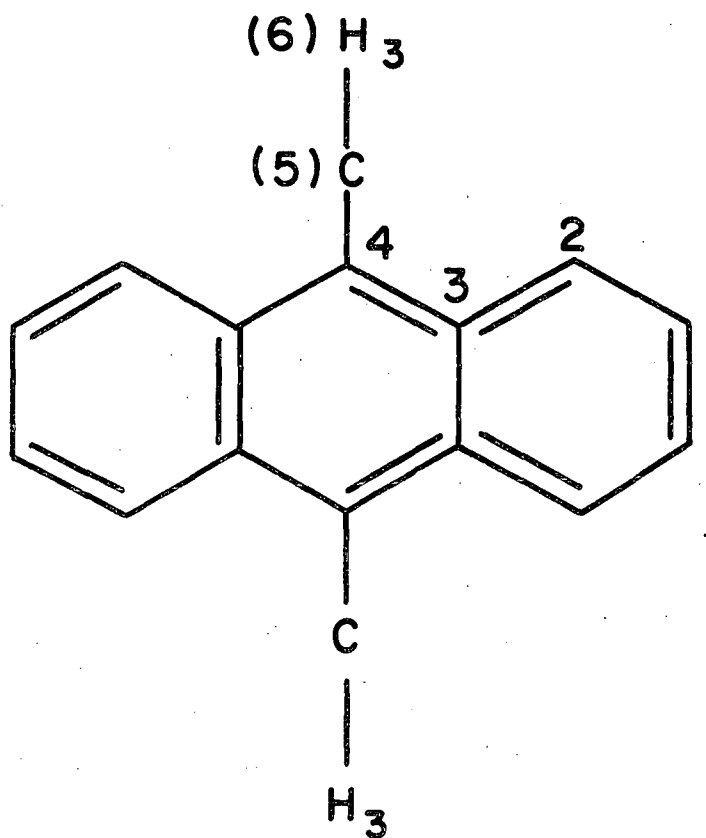
MU-35081

Fig. 12b



MU-35078

Fig. 12c



9,10 dimethyl anthracene

MU-35079

Fig. 12 d

Table IX. Hückel Molecular Orbital Coefficients Neglecting  
Overlap For Radical Anions

| Radical Anion<br>$C_i$            | $i$     |         |         |         |         |         |         |         |        |        |
|-----------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|--------|--------|
|                                   | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9      | 10     |
| 2,3 dimethyl<br>butadiene         | .59080  | -.36243 | -.00793 | .13976  |         |         |         |         |        |        |
| Isoprene                          | .59852  | -.36850 | -.00822 | .14215  | -.36539 | .59346  |         |         |        |        |
| 1,3 cyclo-<br>hexadiene           | -.35438 | .56933  | .00193  | -.22390 |         |         |         |         |        |        |
| Toluene <sup>a</sup>              | .00000  | -.50000 | .50000  | .00000  | .00000  | .00000  |         |         |        |        |
| Cyclohexa-<br>dienyl <sup>b</sup> | .52765  | -.02131 | -.52593 | .08395  | .40052  |         |         |         |        |        |
| o-xylene <sup>c</sup>             | .28743  | -.57119 | .27646  | .02869  | -.11778 |         |         |         |        |        |
| m-xylene <sup>c</sup>             | .55930  | -.27594 | -.28703 | .58177  | -.02975 | .12226  |         |         |        |        |
| p-xylene <sup>a</sup>             | -.50000 | 0       | 0       | 0       |         |         |         |         |        |        |
| Acenaphthene                      | 0.00000 | -.41544 | .25434  | .25972  | -.41355 | 0.00000 | -.00875 | .15599  |        |        |
| Pyrene                            | .25154  | -.40421 | .00000  | -.00816 | .15257  |         |         |         |        |        |
| 9 methyl<br>anthracene            | -.43215 | .09000  | .30679  | -.21779 | -.21608 | .30779  | .08787  | -.43440 | .00684 | .16399 |
| 9,10 dimethyl<br>anthracene       | -.21416 | .30389  | .08694  | -.42717 | .00655  | .16128  |         |         |        |        |

See Fig. 12 for numbering

a) Antisymmetric orbital; b) Not an anion; c) Symmetric orbital

Table X. McLachlan<sup>a</sup> SCF Spin Densities for Radical Anions

| Radical Anion \ $\rho_i$     | i         |         |         |         |         |         |         |        |         |        |
|------------------------------|-----------|---------|---------|---------|---------|---------|---------|--------|---------|--------|
|                              | 1         | 2       | 3       | 4       | 5       | 6       | 7       | 8      | 9       | 10     |
| 2,3 dimethyl butadiene       | .44097    | .05582  | -.00614 | .00935  |         |         |         |        |         |        |
| Isoprene                     | .45253    | .06020  | -.00639 | .00996  | .05365  | .43005  |         |        |         |        |
| 1,3 cyclohexadiene           | .06382    | .39142  | -.01433 | .05909  |         |         |         |        |         |        |
| Toluene                      | b .38308  | .03610  | .05824  | .37253  | -.01122 | .06693  |         |        |         |        |
|                              | c -.38378 | .46268  | .45230  | -.37998 | -.00264 | -.06357 |         |        |         |        |
| Cyclohexadienyl <sup>d</sup> | .35912    | -.10667 | .36418  | -.03949 | .16534  |         |         |        |         |        |
| o-xylene <sup>c</sup>        | -.07091   | .68814  | -.09563 | -.00476 | -.01684 |         |         |        |         |        |
| m-xylene <sup>c</sup>        | .66512    | -.10156 | -.06874 | .71951  | -.00483 | -.01217 |         |        |         |        |
| p-xylene                     | b .04739  | .35360  | -.01074 | .06236  |         |         |         |        |         |        |
|                              | c .46114  | -.36083 | -.00214 | -.05932 |         |         |         |        |         |        |
| Acenaphthene                 | -.03497   | .21409  | .04325  | .05130  | .20478  | -.03361 | -.00672 | .02759 |         |        |
| Pyrene                       | .04699    | .19858  | -.03214 | -.00640 | .02691  |         |         |        |         |        |
| 9 methyl anthracene          | .24110    | -.02193 | .11243  | .03374  | .03296  | .11293  | -.02163 | .23740 | -.00799 | .03249 |
| 9,10 dimethyl anthracene     | .03281    | .11021  | -.02073 | .23137  | -.00769 | .03172  |         |        |         |        |

a) Ref. 69.  $\lambda = 1.00$ ; b) Antisymmetric orbital; c) Symmetric orbital; d) Not an anion  
See Fig. 12 for numbering

Table XI. Bolton et al.<sup>a</sup> Modified Overlap Molecular  
Orbital Coefficients for Radical Anions

| Radical Anion \ $C_i$        | $i$     |         |         |         |         |         |         |        |         |         |
|------------------------------|---------|---------|---------|---------|---------|---------|---------|--------|---------|---------|
|                              | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8      | 9       | 10      |
| 2,3 dimethyl butadiene       | .58241  | -.38633 | .06282  | .05587  |         |         |         |        |         |         |
| Isoprene                     | .56883  | -.36376 | .05986  | .05324  | -.39355 | .61542  |         |        |         |         |
| 1,3 cyclohexadiene           | .35163  | -.59989 | .07507  | .06676  |         |         |         |        |         |         |
| Toluene <sup>b</sup>         | .00000  | .50000  | .50000  | .00000  | .00000  | .00000  |         |        |         |         |
| Cyclohexadienyl <sup>c</sup> | .54579  | -.07020 | .52774  | .21499  | .19119  |         |         |        |         |         |
| o-xylene <sup>b</sup>        | -.28169 | .56989  | -.30137 | .04158  | .03698  |         |         |        |         |         |
| m-xylene <sup>b</sup>        | .58917  | -.30095 | -.28171 | .55150  | .03889  | .03459  |         |        |         |         |
| p-xylene <sup>b</sup>        | -.50000 | .00000  | .00000  | .00000  |         |         |         |        |         |         |
| Acenaphthene                 | .00000  | -.40673 | .28365  | .20891  | -.42935 | .00000  | .09450  | .08404 |         |         |
| Pyrene                       | .44298  | -.26220 | -.34023 | .05475  | .04869  |         |         |        |         |         |
| 9 methyl anthracene          | .41132  | -.09225 | -.30925 | .23096  | .20566  | -.32321 | -.06069 | .44267 | -.08058 | -.07166 |
| 9,10 dimethyl anthracene     | -.21782 | .32198  | .06384  | -.41635 | .07455  | .06630  |         |        |         |         |

a) Ref. 63; b) Antisymmetric orbital; c) Not an anion.

Table XII. Hückel Molecular Orbital Coefficients Including  
Overlap for Radical Anions

| Radical Anion<br>$C_i$            | $i$     |         |         |         |         |         |         |        |         |         |
|-----------------------------------|---------|---------|---------|---------|---------|---------|---------|--------|---------|---------|
|                                   | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8      | 9       | 10      |
| 2,3 dimethyl<br>butadiene         | .64084  | -.39121 | -.01423 | .15240  |         |         |         |        |         |         |
| Isoprene                          | .65178  | -.40027 | -.01489 | .15604  | -.39465 | .64263  |         |        |         |         |
| 1,3 cyclo-<br>hexadiene           | -.38223 | .61114  | .02136  | -.24583 |         |         |         |        |         |         |
| Toluene <sup>a</sup>              | 0       | -.57735 | .57735  | 0       | 0       | 0       |         |        |         |         |
| Cyclohexa-<br>dienyl <sup>b</sup> | .52769  | -.02089 | -.52603 | .08230  | .40056  |         |         |        |         |         |
| o-xylene <sup>a</sup>             | .33094  | -.65647 | .31482  | .04208  | -.13879 |         |         |        |         |         |
| m-xylene <sup>c</sup>             | .63862  | -.31384 | -.33016 | .67182  | -.04405 | .14545  |         |        |         |         |
| p-xylene <sup>a</sup>             | .57735  | 0       | 0       | 0       |         |         |         |        |         |         |
| Acenaphthene                      | .00000  | -.45033 | .27405  | .28356  | -.44661 | .00000  | -.01550 | .16788 |         |         |
| Pyrene                            | -.27219 | .43550  | .00000  | .01433  | -.16373 |         |         |        |         |         |
| 9 methyl<br>anthracene            | .45672  | -.09480 | -.32346 | .22908  | .22836  | -.32388 | -.09391 | .45766 | -.00286 | -.17345 |
| 9,10 dimethyl<br>anthracene       | -.22539 | .31915  | .09263  | -.45031 | ..00273 | .17067  |         |        |         |         |

a) Antisymmetric orbital; b) Not an anion; c) Symmetric orbital

where  $\rho'$  is the total spin density on the unsaturated carbon to which the methyl or methylene group is attached. Of course in the case of a methylene group one must add the spin densities on the two carbon atoms to which the group is attached to get the total spin density  $\rho'$ . As is shown in the next section a good estimate for  $Q_P$  in the case of a methylene group would be 2.78 gauss, and we assume that this is also valid for a methyl group. Since, as shown by Colpa,<sup>64</sup> the hyperconjugation and spin polarization mechanisms act with opposite signs the total theoretical coupling constant  $A$  is given by

$$|A| = \left| |A_H| - |A_P| \right| \quad (44)$$

Using this equation we have calculated the series of theoretical coupling constants shown in Table XIII.

The methyl substituted benzenes (toluene and the xylenes) present an additional complication. It is well known that the six-fold symmetry of benzene requires that the first two anti-bonding molecular orbitals be degenerate. In this case the molecular wave function of the unpaired electron can be described only by a linear combination of the two degenerate orbitals. The methyl group in toluene and the xylenes can be looked upon as a perturbation on the six-fold symmetry, and the effect of this perturbation is to lift the degeneracy of these two levels. The magnitude of the perturbation is such, however, that the two levels are not split very much (e.g.  $0.025 \beta_0$  in toluene) and there is still a vibronic mixing of these two near degenerate states. For simplicity we have ignored this additional mixing with the following exceptions. The approximations in these calculations are such that the inaccuracies in energy of the molecular orbitals are far larger than the splitting between

Table XIII. Calculated and Experimental Methyl and Methylene Coupling Constants for Radical Anions

| Radical Anion                | Expt. <sup>a</sup> | Huckel without overlap | McLachlan           | Bolton overlap | Huckel with overlap |
|------------------------------|--------------------|------------------------|---------------------|----------------|---------------------|
| 2,3 dimethyl butadiene       | 1.200              | 3.61                   | 1.82                | .59            | 4.22                |
| Isoprene                     | (3.42)             | 3.73                   | 1.94                | .55            | 4.42                |
| 1,3 cyclohexadiene           | 11.114             | 14.30                  | 17.99               | 1.09           | 16.98               |
| Toluene                      | <sup>75</sup> 0.79 | 0.00                   | (0.57) <sup>b</sup> | 0.00           | 0.00                |
| Cyclohexadienyl <sup>c</sup> | <sup>64</sup> 47.7 | 53.83                  | 51.26               | 19.47          | 53.68               |
| o-xylene                     | <sup>74</sup> 2.00 | 2.36                   | 3.50                | .18            | 3.19                |
| m-xylene                     | <sup>75</sup> 2.26 | 2.54                   | 2.55                | .16            | 3.51                |
| p-xylene                     | <sup>75</sup> 0.10 | 0.00                   | (.52) <sup>b</sup>  | 0.00           | 0.00                |
| Acenaphthene                 | <sup>64</sup> 7.53 | 6.89                   | 8.34                | 3.01           | 7.80                |
| Pyracene                     | <sup>64</sup> 6.58 | 6.60                   | 8.14                | .99            | 7.44                |
| 9-methyl anthracene          | <sup>63</sup> 4.27 | 5.22                   | 6.38                | 1.13           | 5.77                |
| 9,10 dimethyl anthracene     | <sup>63</sup> 3.88 | 5.05                   | 6.23                | .95            | 5.58                |

a) Superscripts give reference number.

b) Computed from  $\rho = \rho_{\text{Antisymmetric}} + \rho_{\text{symmetric}}$

c) Not an anion

the two near degenerate orbitals. Consequently the calculation is unable to predict which of the two is really lower in energy. We have therefore in each case chosen the one that gives the best fit to the experimental data not only at the methyl groups but at the various ring protons. It turns out that there is never any ambiguity as to which is the "best" orbital. The implication of this is that while the simple calculation cannot predict which orbital is lower there is still not very much mixing, and that one of the orbitals still gives a fair approximation to the true wave function.<sup>88</sup> The only exception to this is the self consistent field calculation on toluene and paraxylene. These two molecules to a first approximation have nodes through the methyl groups and the inclusion of electron-electron interactions leads to two near degenerate orbitals such that neither of them provide even an approximate description of the unpaired orbital. In this case only, we have calculated the methyl group coupling constant from a wave function  $\Psi$  where

$$\Psi = \Psi_1 + \Psi_2 \quad (45)$$

and  $\Psi_1$  and  $\Psi_2$  are the two near degenerate orbitals. These approximations represent a simple approach to a quite complicated subject that has been considered in detail elsewhere.<sup>93</sup>

The results listed in Table XIII are quite gratifying and indicate that the simple Huckel theory is capable of predicting not only ring coupling constants but also those due to methyl and methylene protons. Of the cases considered with simple Huckel theory none are wildly in error and most provide better agreement with experiment than would be expected from such a simple theory. It is interesting to note that with but one exception the Huckel theory predicts coupling constants slightly larger than those actually observed. This indicates that the calculation

could be further improved by altering the parameters of Coulson and Crawford to reduce the extent of the hyperconjugation somewhat. This is not terribly surprising since these parameters are quite arbitrary and would be expected to be somewhat in error. The utility of the theory lies in the fact that ~~it is not very~~ sensitive to the choice of matrix elements, and that any reasonable selection can be expected to lead to reasonable results. An example of this may be seen in the fact that even with this inaccurate choice of matrix elements the calculation is very successful in predicting the relative magnitudes of coupling constants in several pairs of similar molecules (e.g. ortho and meta xylene, methyl and dimethyl anthracene, methyl- and dimethylbutadiene, pyracene and acenaphthene, etc.).

The inclusion of the effect of electron-electron repulsion in the McLachlan calculation does not seem to lead to a significant improvement in agreement. Here again the effects of hyperconjugation seem to be somewhat overemphasized and an adjustment of the parameters so as to scale down this effect would probably be in order. The one case in which the McLachlan calculation does offer a significant improvement over the simple Huckel theory is that of dimethylbutadiene where the McLachlan calculation more nearly predicts the quite small methyl coupling constant.

One obvious conclusion of these calculations is that the theory of Bolton et al.<sup>63</sup> does indeed predict coupling constants that are far lower than those actually observed. This behavior was predicted by Colpa and deBoer<sup>64</sup> and certainly seems to be born out by comparison with a large number of experimental coupling constants. Thus if one wishes to include the effects of overlap the only effective method appears to be the complete overlap calculation including overlap between the unsaturated carbon atoms.

However the inclusion of overlap in any form appears to add little to the calculation and in fact seems to give a somewhat worse fit than the same calculation performed while neglecting overlap. This has generally been the case for purely aromatic calculations and seems to carry over to the case of hyperconjugation.

Using McConnell's relationship (Eq. (7)) one can also compare the unsaturated proton coupling constants with the predictions of the above calculations if the value of the parameter  $Q$  is known. Assuming that  $Q$  has the same value as in the case of butadiene (20.82) we have calculated the predicted values for the unsaturated protons of dimethylbutadiene, isoprene, and cyclohexadiene. There are shown in Table XIV. Here again a fair agreement can be obtained with any of the theories used. Since the Huckel, overlap, and modified overlap theories differ primarily in how they treat the effect of the methyl substituent one would expect them to give essentially identical results for the unsaturated protons and this is seen to be the case. The McLachlan self-consistent field calculation in many cases corrects the simple Huckel theory in the proper direction but tends to overcorrect. More satisfactory results could probably be obtained by lowering the value of  $\lambda$  used in this calculation thus reducing the effects of electron correlation. It should be noted that the Huckel and Bolton theories give different predictions as to which of the methylene groups in isoprene have the larger coupling constant. It would be of some interest to measure the spectrum of the deuterated molecule (if it can be prepared) to determine experimentally which is larger.

The calculations described above can also be performed for the case of the radical cation. Unfortunately we have no new experimental data to

Table XIV. Calculated and Experimental Unsaturated  
Coupling Constants for Radical Anions<sup>a</sup>

| Molecule                   | Position <sup>b</sup> | Expt. | Huckel<br>without<br>overlap | McLachlan | Bolton<br>overlap | Huckel<br>with<br>overlap |
|----------------------------|-----------------------|-------|------------------------------|-----------|-------------------|---------------------------|
| 2,3 dimethyl-<br>butadiene | 1                     | 7.137 | 7.27                         | 9.18      | 7.06              | 7.24                      |
| Isoprene                   | 1                     | 7.91  | 7.46                         | 9.42      | 6.74              | 7.49                      |
|                            | 5                     | 3.10  | 2.78                         | 1.29      | 3.22              | 2.74                      |
|                            | 6                     | 6.50  | 7.33                         | 8.95      | 7.89              | 7.28                      |
| Cyclohexa-<br>diene        | 1                     | 1.996 | 2.61                         | 1.33      | 2.57              | 2.59                      |
|                            | 2                     | 8.212 | 6.75                         | 8.15      | 7.49              | 6.61                      |

a) Calculated assuming  $Q = 20.82$

b) See Fig. 12 for numbering

offer in a field distinguished by a lack of such data and the results of these calculations are therefore consigned to Appendix III.

#### C. Justification of the Hyperconjugation Model: Cycloheptatriene

In the last section we showed that methyl and methylene proton coupling constants could be satisfactorily explained by a hyperconjugation model. Several investigators have offered arguments to support the theory that the hyperconjugation model is the only model that can explain these coupling constants. Bolton and co-workers<sup>63</sup> postulated that the pairing principle of Huckel theory,<sup>76,77</sup> which predicts that the radical cations and anions of a given alternate hydrocarbon should have very similar ESR spectra, would be carried over to methyl coupling constants

if these coupling constants arose via a spin polarization mechanism. However if hyperconjugation were the principle mechanism there would be no reason for cation and anion methyl coupling constants to be equal. They took the experimental fact that they are not equal as evidence that the principle mechanism was indeed hyperconjugation. From their calculation they predicted a series of ratios  $A_{\text{methyl}}^+ / A_{\text{methyl}}^-$  which were in good agreement with the experimental ratios. However, as we have seen, the absolute magnitude of their coupling constants is seriously in error and this throws some doubt on their whole theory.

Colpa and deBoer<sup>64</sup> used a corrected hyperconjugation theory and were able to successfully predict both the anion/cation ratios and the absolute magnitude of the coupling constants in a number of cases. In addition, they performed a configuration interaction calculation on the  $C'-CH_2$  fragment ( $C'$  being the unsaturated carbon to which the methylene group is attached) to obtain an estimate of the magnitude of the spin exchange polarization mechanism. They found that the spin polarization contribution to methylene coupling constants could be given by

$$A = Q_{SP} \rho_{C'} = -1.1 \rho_{C'} \quad (46)$$

and that this  $Q$  value was far too small to account for the large coupling constants observed. They point out that the approximations in such a calculation naturally leave the numerical results in some doubt. Nonetheless, they felt that the order of magnitude of the results substantiated their main argument.

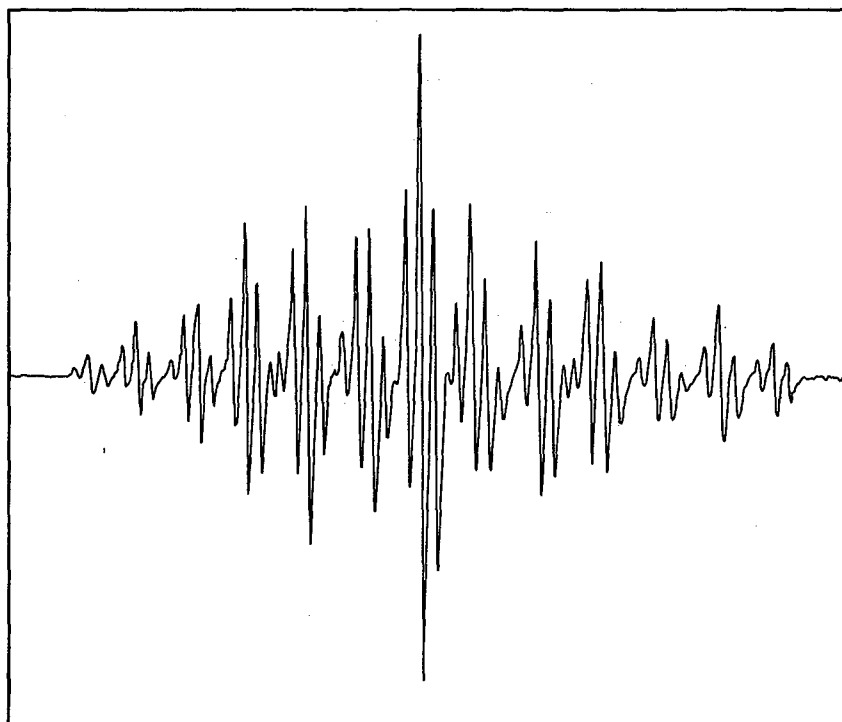
The ESR spectrum of the cycloheptatriene radical anion offers a striking experimental confirmation of the importance of hyperconjugation. Moreover from the hyperfine coupling constants it is possible to obtain a quantitative measure of the magnitude of  $Q_{SP}$ . This is brought about

by the fact that symmetry considerations require the first anti-bonding molecular orbital of cycloheptatriene to have a node passing down the symmetry axis which goes through the methylene carbon. This means that for reasons of symmetry there can be no hyperconjugation contribution to the methylene coupling constant, and consequently any resulting coupling constant can only be the result of spin polarization or electron correlation.

We have prepared the cycloheptatriene radical anion by electrolyzing a three millimolar solution of the parent hydrocarbon dissolved in a solution of liquid ammonia. The solution was saturated with tetramethylammonium iodide. No electron appeared at electrolysis voltages up to 100 volts but at the higher voltages a bubbling occurred at the cathode presumably due to some decomposition reaction. The spectrum obtained is shown in Fig. 13.

The spectrum is moderately complicated but the assignment is made considerably easier by the fact that the two outermost triplets are so well resolved. As in the case of cyclohexadiene a reasonable guess would be that one coupling constant is given by the distance between the two triplets and one coupling constant is given by the spacing within either triplet. Since there are only four coupling constants in the problem these guesses plus the total width constraint leaves but one coupling constant undetermined. This last coupling constant may then be determined by trial and error with very little difficulty. The resulting assignment is given in Table XV, and the theoretical spectrum calculated from this assignment is shown in Fig. 14. As can be seen there is excellent agreement between the theoretical and experimental spectrum.

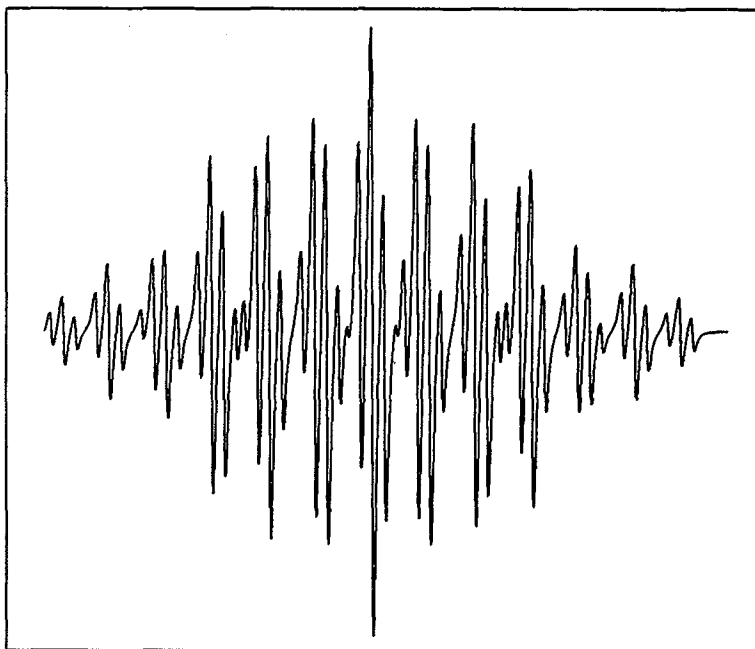
With no further experiments it is impossible to assign which of the coupling constants in Table XV are associated with which protons.



MU-35082

Fig. 13

CYCLONEPTATRIENE



MU-25057

Fig. 14

Table XV. Observed Coupling Constants for Cycloheptatriene

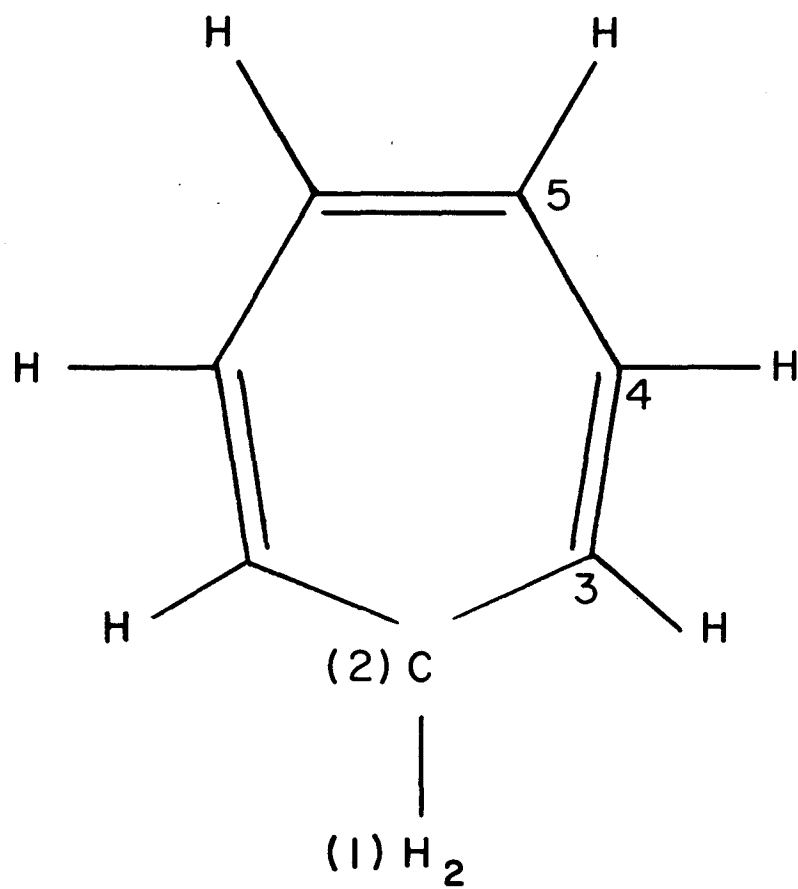
|                         |       |
|-------------------------|-------|
| $A_2 = 2.16 \pm 0.03$   | gauss |
| $A_3 = 7.64^a \pm 0.02$ | gauss |
| $A_4 = 0.59^a \pm 0.03$ | gauss |
| $A_5 = 4.90^a \pm 0.01$ | gauss |

<sup>a</sup> Assigned on the basis of theoretical calculation  
See Fig. 15 for numbering

be seen from Fig. 15 the molecule contains four sets of two symmetrically equivalent protons each. In order to determine which coupling constant was associated with the methylene protons we prepared the radical anion of cycloheptatriene in which one of the methylene protons had been replaced by a deuterium. The ESR spectrum of this deuterated species is shown in Fig. 16. The coupling constant of a deuteron is given by

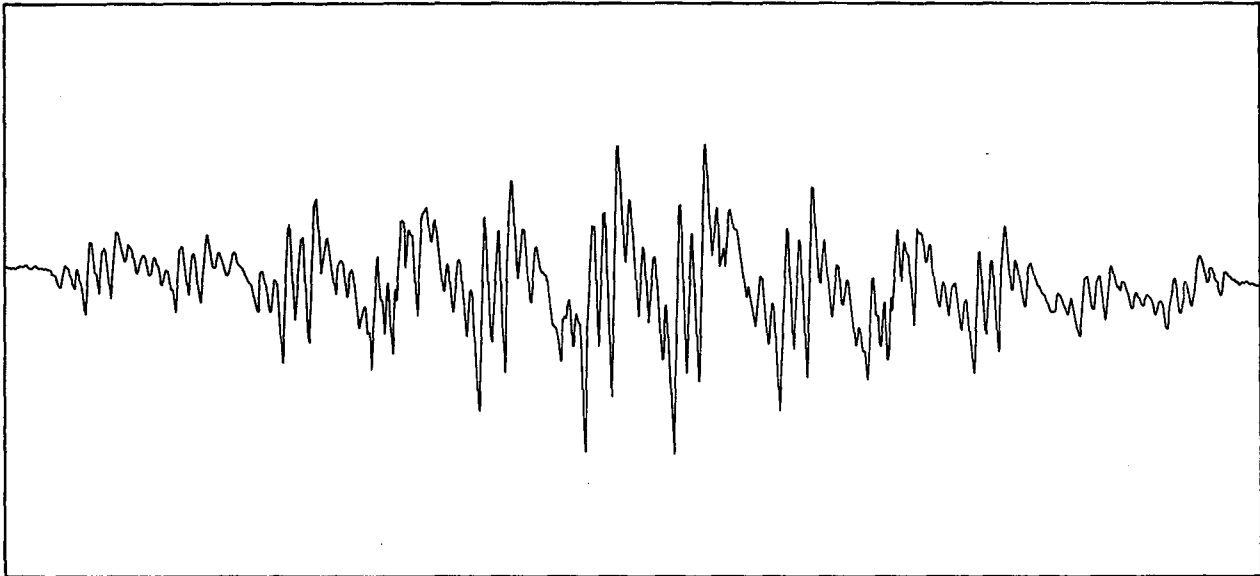
$$A_D = \frac{\mu_D}{\mu_H} \frac{I_H}{I_D} A_H = 0.1535 A_H \quad (47)$$

where the  $\mu$ 's are the magnetic moments as they are commonly tabulated, the  $I$ 's are the spins of the deuteron and proton, and  $A_H$  is the coupling constant for a proton occupying the same position in the molecule. From this it is possible to calculate the four possible spectra expected from the deuterated species. These are shown in Fig. 17. A comparison of



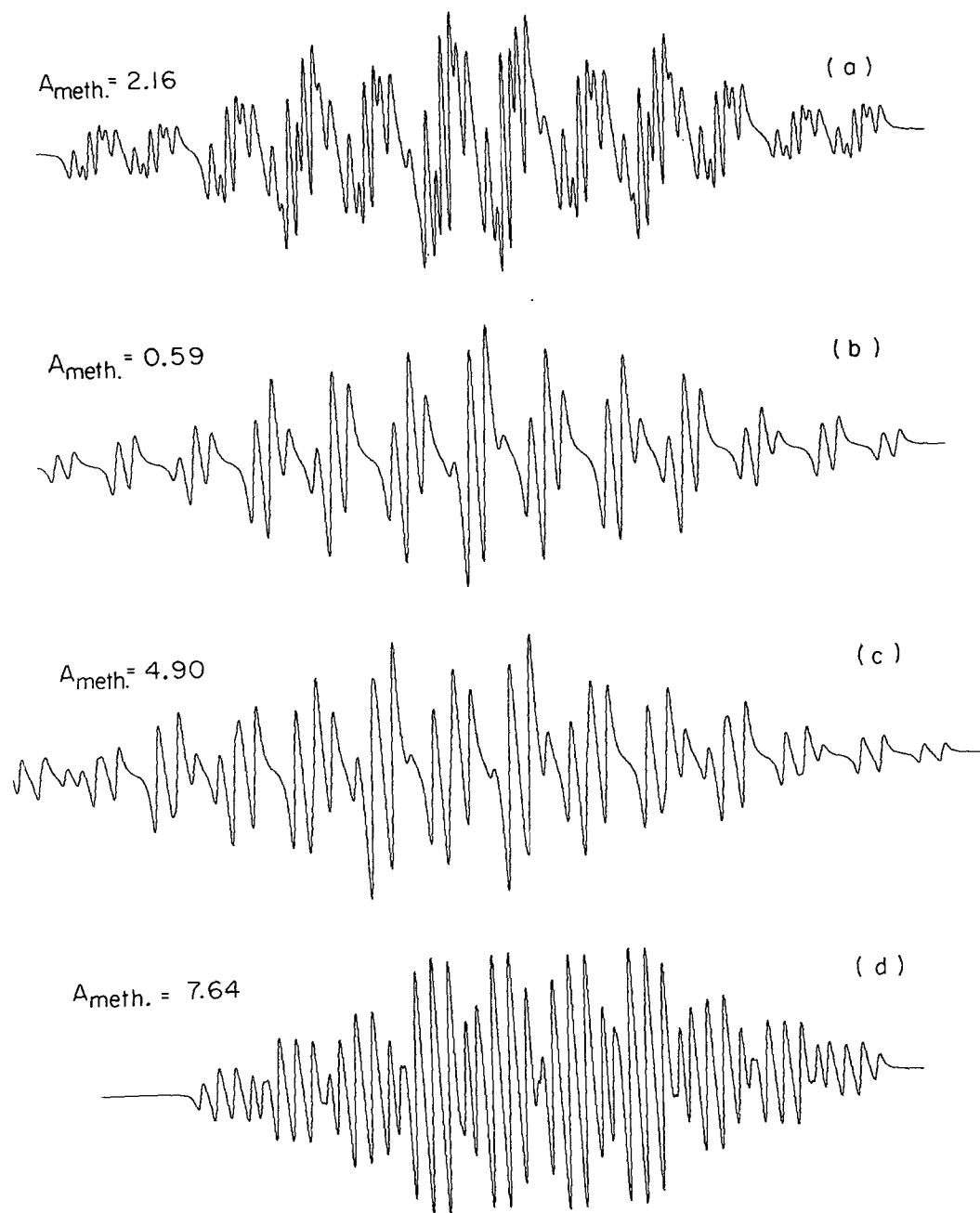
-MU-35083

Fig. 15



MUB-4950

Fig. 16



MUS-4951

Fig. 17

Figs. 16 and 17 clearly shows that the methylene proton coupling constant is 2.16 gauss. The other coupling constants cannot be assigned directly from the experimental spectra but can be assigned with considerable confidence from the following theoretical considerations.

We have performed the same series of calculations that was described in the last section on cycloheptatriene. The numbering system used is shown in Fig. 15 and the results of these calculations are given in Table XVI. Of course, since there is a node at the methylene group the results of the three non-correlation calculations will be the same since they differ only in their treatment of hyperconjugation. These calculations indicate that there is a large spin density on the two carbon atoms to which the methylene is attached, and the largest experimental coupling constant tends to confirm this fact. If spin polarization were the principle mechanism for producing unpaired spin density on the methylene groups of all radicals we would expect a very large methylene coupling constant in the cycloheptatriene radical anion similar to that which one finds in cyclohexadienyl, cyclohexadiene, and similar radicals. The fact that the methylene coupling constant is only 2.16 gauss confirms the fact that hyperconjugation, which in this case is absent, is generally the principle mechanism for methylene coupling constants.

The fact that hyperconjugation is not effective in this radical allows us to obtain an experimental value for the constant  $Q_{SP}$ . The McLachlan calculation predicts that essentially all the spin density is in the unsaturated part of the molecule and that the spin density at position 4 is negative. Assuming that this is correct we can obtain a value for  $Q$  given by

Table XVI. Molecular Orbital Coefficients and Calculated Spin Densities in Cycloheptatriene Radical Anion

| Position <sup>a</sup> | Huckel Coefficient | McLachlan Spin Density <sup>b</sup> |
|-----------------------|--------------------|-------------------------------------|
| 1                     | 0                  | -0.00095                            |
| 2                     | 0                  | -0.00338                            |
| 3                     | -0.52112           | 0.35819                             |
| 4                     | 0.23192            | -0.02280                            |
| 5                     | 0.41791            | 0.16677                             |

a) See Fig. 15 for numbering

b) Reference 69.  $\lambda = 1.00$

$$Q = 2 \sum_{i=3}^5 A_i = 23.90 \quad (48)$$

Using this  $Q$ , the experimental coupling constant  $A_3$ , and Eq. (7) one finds that the unpaired spin density on carbon 3 is 0.320 and the total unpaired spin density adjacent to the methylene group is 0.639. The total methylene coupling constant consists of a small hyperconjugation part and a larger spin polarization part. Using the spin densities predicted by the McLachlan calculation and Eq. (36) we can estimate the electron correlation induced hyperconjugation contribution to be 0.38 gauss. As has been mentioned the spin polarization and hyperconjugation coupling constants are ordinarily of opposite sign, but in this case the hyperconjugation is caused by a negative spin density, the two effects add, and the spin polarization coupling constant is

$$|A_{SP}| = |A_{total} - A_{hyperconjugation}| = 1.78 \text{ gauss} \quad (49)$$

This coupling constant and the adjacent spin density determined above may be inserted into Eq. (46) to give the value  $Q_{SP} = 22.78$  gauss. This is remarkably close to Colpa and deBoer's calculated value of -1.1 when one considers the approximate nature of their calculation. It has been suggested<sup>78-80</sup> that aliphatic coupling constants are a function of the angle  $\theta$  between the normal to the pi system nodal plane and the C'-C-H plane, and that the relationship is given by

$$A = B_0 + B_1 \cos^2 \theta \quad (50)$$

The parameter  $B_0$  in this formula is the same as our  $Q_{SP}$  and to the best of the author's knowledge this is the first experimental determination of this quantity.

Using the  $Q$  value given in Eq. (48), the theoretical spin densities, and McConnell's relationship one can calculate a set of theoretical coupling constants for the unsaturated part of the cycloheptatriene radical anion. This has been done and the results are shown in Table XVII. As can be seen there is a reasonable agreement between theory and experiment. The self-consistent field theory is particularly useful to explain the quite low coupling constant of carbon number 4, although again one gets the feeling that perhaps the value of  $\lambda$  should be reduced to reduce the electron correlation effect.

An obvious experiment that suggests itself is to measure the ESR spectrum of the 1,3,5-hexatriene radical anion. Here again one could take advantage of the fact that the hyperconjugation in cycloheptatriene is symmetry forbidden. Thus the only difference between the pi-electron

Table XVII. Calculated and Observed Unsaturated Coupling Constants for Cycloheptatriene Radical Anion<sup>a</sup>

| Position <sup>b</sup> | Expt. | Huckel | McLachlan |
|-----------------------|-------|--------|-----------|
| 3                     | 7.64  | 6.49   | 8.56      |
| 4                     | 0.59  | 1.29   | 0.54      |
| 5                     | 4.90  | 4.17   | 3.99      |

a) Calculated assuming  $Q = 23.90$

b) See Fig. 15 for numbering

distribution in hexatriene and cycloheptatriene would be the inductive effect of the methylene group. In most methyl or methylene groups the electron distribution is perturbed by combined hyperconjugation and inductive effects and the separating of these two effects is a matter of considerable theoretical interest. In this pair of molecules the hyperconjugation effect is nonexistent and a comparison of the unsaturated proton coupling constants in the two molecules should provide an experimental measurement of the inductive effect alone.

Unfortunately our efforts in this direction have been only partially successful. We have attempted to prepare the radical anion of hexatriene by electrolyzing solutions of hexatriene dissolved in various concentrations in liquid ammonia. Various supporting electrolytes were used in an attempt to increase the lifetime of the radical. In this series of experiments only one succeeded in producing even a weak spectrum and even this one was not reproducible. A very rough measurement indicated that

the two largest coupling constants were 7.3 and 4.2 gauss. The lack of resolution and sensitivity made the measurement of the third coupling constant very difficult but the lack of readily observable splittings probably places an upper limit of 0.5 gauss on it. There are some very poorly resolved lines that could be the result of a coupling constant of around 0.5 gauss.

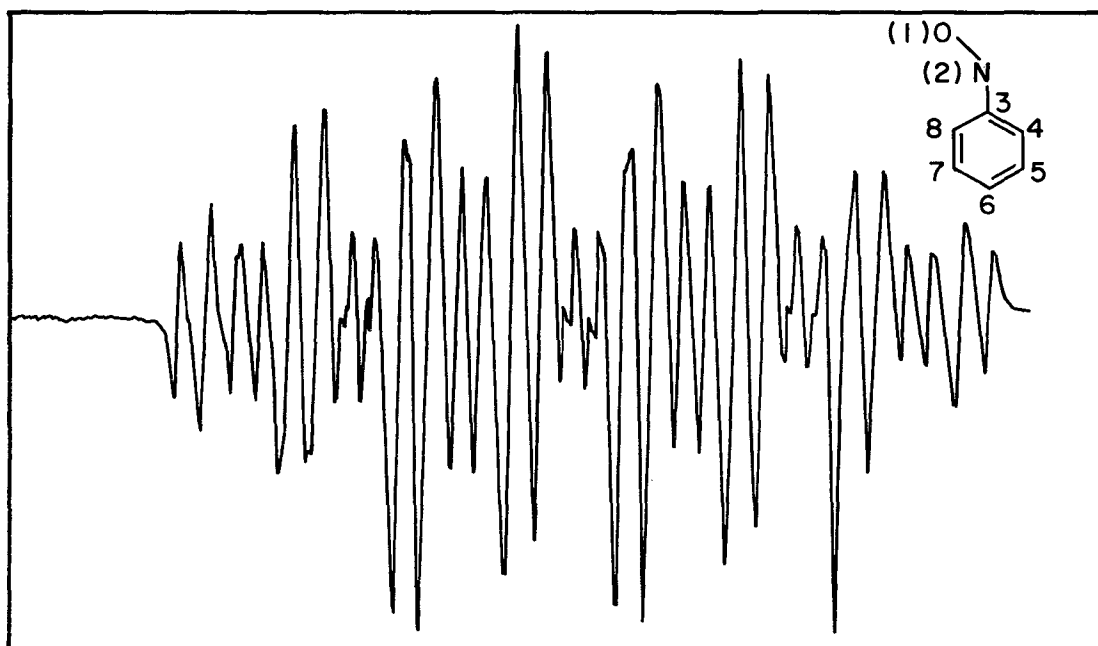
No really quantitative conclusions can be drawn from these very poor data. The fact that the hexatriene coupling constants seem to be so close to the cycloheptatriene coupling constants indicates that the inductive effect of the methylene group is small. This is not unreasonable in view of the fact that the model used in the previous section completely neglected any inductive effects and was still relatively successful in predicting unsaturated coupling constants. The fact that both large coupling constants in hexatriene are smaller than the corresponding cycloheptatriene coupling constants is interesting. The change is probably large enough to be real and not just an experimental error and it could be caused by one of two effects. First of all the sigma-pi interaction could have changed in such a manner as to lower the  $Q$  value. If this were the case and if the third coupling constant were still 0.6 and caused by negative spin density the  $Q$  for hexatriene would have to be around 21.8. Changes in  $Q$  of this order are certainly not impossible but it seems to be a rather large shift for two such similar molecules. The more likely explanation would be that the effect of eliminating the methylene group was to rearrange the pi-electron density such that the spin density at position 4 (position 2 in hexatriene) was no longer negative. A positive spin density coupling constant of 0.4 gauss at position 2 would be sufficient to account for the shifts in the larger coupling constants without any change in the value

of Q. The comparison of Huckel, McLachlan, and experimental coupling constants in Table XVII. indicates that electron correlation has a considerable effect in cycloheptatriene, and it would not be surprising that this correlation effect would be sensitive to the removal of the methylene group. Obviously better data are needed for more quantitative arguments and further work along this line is in progress.

#### D. Nitrosobenzene and Nitrobenzene

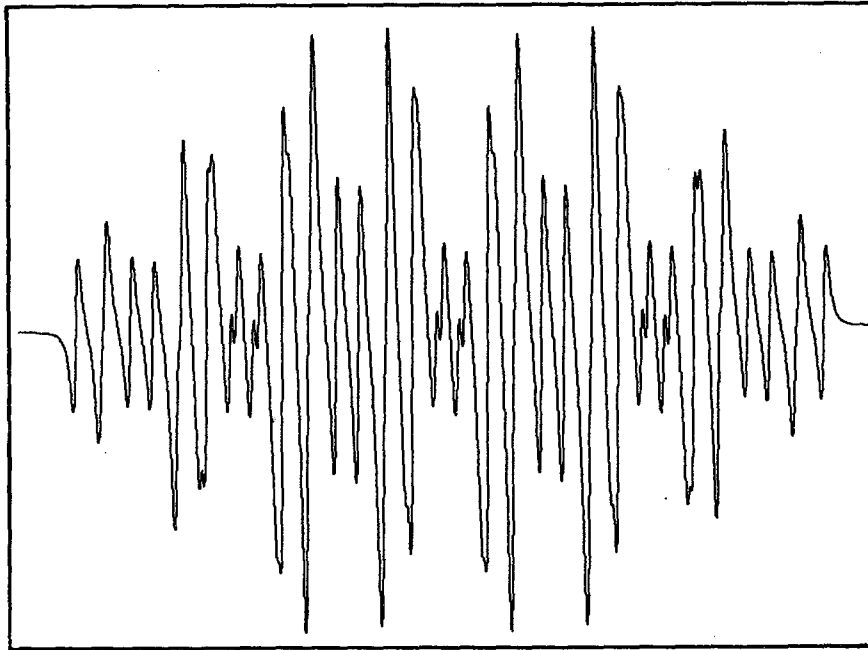
We have prepared the radical anions of nitrosobenzene ( $C_6H_5NO$ ) and nitrobenzene ( $C_6H_5NO_2$ ) by electrolysis in liquid ammonia solution. The nitrosobenzene radical anion shows two ortho and two meta proton coupling constants which can be explained by simple theoretical models. The nitrobenzene radical anion was prepared in liquid ammonia as a reference and to compare solvent shifts.<sup>81</sup>

The observed spectrum of the reddish-brown nitrosobenzene radical anion is shown in Fig. 18. This radical appears to be quite stable at  $-78^\circ C$ . in liquid ammonia solution. It is far more stable than any of the other radicals so far discussed and is probably more stable than even nitrobenzene. The spectrum consists of 30 principal lines which are further split by small amounts. On the basis of the 30 principal lines one can readily determine the  $N^{14}$ , the single para proton, and average values for both the ortho and meta coupling constants. The larger value can be assigned to the ortho protons in analogy to nitrobenzene. The additional splittings can only be accounted for if it is assumed that nitrosobenzene has two ortho protons differing by 0.30 gauss. A similar difference for the meta protons of 0.18 gauss can be determined from the intensity ratios within its triplets. The calculated spectrum in Fig. 19



MU-35084

Fig. 18



MU-35085

Fig. 19

shows the excellent agreement with experiment for the coupling constants given in Table XVIII.

The two ortho and two meta coupling constants must arise from the effects of a non-linear C-N-O group. This group must be held fairly rigidly in a planar conformation or else the difference in coupling constants would be averaged out by rapid internal rotation. This is similar to the case of nitrobenzene, but the symmetry of nitrobenzene does not allow us to determine directly the effects of the N-O bond on the coupling of the ring protons.

A theoretical interpretation of this effect can be included in a Huckel LCAO molecular orbital calculation of the spin densities in either of two ways. One can either utilize a small resonance integral between the oxygen and the nearby ortho carbon (between positions 1 and 8) or describe the polarization effects of the nitroso group by changing the Coulomb integral of one ortho carbon atom. Rieger and Fraenkel<sup>84</sup> used the latter method and Stone and Maki<sup>84</sup> used both methods to account for similar asymmetries in substituted benzaldehydes. Stone and Maki referred to these as the  $\beta$ - and  $\alpha$ -effects respectively. If one uses the approximate configuration treatment of McLachlan with the parameters recommended by Rieger and Fraenkel<sup>81</sup> but with  $\delta_N = \frac{1}{3} \delta_N^{60}$  and with  $r_{18} = 0.05$  or  $\delta_8 = -0.07$  then one obtains the theoretical proton coupling constants given for nitrosobenzene in Table XVIII.

It can be seen from Table XVIII that either a small value for the resonance integral between the oxygen and its nearby ortho carbon or a small change in the nearby ortho carbon Coulomb integral yields a satisfactory explanation of the two ortho and meta coupling constants. As previously observed<sup>84</sup> these two effects are seen to work in opposite directions and we are unable to distinguish between them. An arbitrary

Table XVIII. Coupling Constants for Nitrosobenzene and Nitrobenzene Radical Anions<sup>a</sup>

| Position   | Obs. <sup>b</sup> | $\beta$ effect <sup>d</sup> | Cal. <sup>c</sup> | $\alpha$ effect <sup>e</sup> |
|------------|-------------------|-----------------------------|-------------------|------------------------------|
| Nitrogen-2 | 7.97±.01          | -                           | -                 | -                            |
| Para H-6   | 2.97±.02          | 4.43                        |                   | 4.54                         |
| Ortho H-4  | { 3.84±.02        | 3.68                        |                   | 4.02                         |
| -8         | { 4.14±.02        | 4.03                        |                   | 3.67                         |
| Meta H-5   | { 0.96±.02        | 1.08                        |                   | 1.22                         |
| -7         | { 1.14±.02        | 1.22                        |                   | 1.06                         |

<sup>a</sup> Absolute magnitudes in gauss

<sup>b</sup> Bracketed values may be interchanged

<sup>c</sup> Calculated with  $\delta_O = 1.4$ ,  $\delta_N = 0.733$ ,  $r_{NO} = 1.67$ ,  $r_{CN} = 1.2$ , and  $Q_{CH}H = 23.7$ . The meta positions have negative spin density.

<sup>d</sup> Using  $r_{CO} = 0.05$  between positions 1 and 8.  $\rho_1 = 0.2629$ ,  $\rho_2 = 0.3138$ ,  $\rho_3 = 0.0086$ .

<sup>e</sup> Using  $\delta_8 = -0.07$ .  $\rho_1 = 0.2652$ ,  $\rho_2 = 0.3121$ ,  $\rho_3 = 0.0026$ .

adjustment of parameters can improve the agreement with the values in Table XVIII particularly for the para position. This effect may be seen in Table XIX where we have listed the results obtained by performing the McLachlan calculation with various values of  $\delta_N$ .

Table XIX. Calculated<sup>b</sup> Proton Coupling Constants  
for Nitrosobenzene Radical Anion<sup>a</sup>

| Value of $\delta_N$ | 4    | 5    | Position<br>6 | 7    | 8    |
|---------------------|------|------|---------------|------|------|
| 0.80                | 3.59 | 1.07 | 4.26          | 1.23 | 3.99 |
| 1.00                | 3.41 | 1.08 | 3.81          | 1.22 | 3.77 |
| 1.20                | 3.20 | 1.07 | 3.36          | 1.20 | 3.53 |
| 1.40                | 2.97 | 1.07 | 2.92          | 1.18 | 3.28 |
| 1.60                | 2.74 | 1.07 | 2.49          | 1.16 | 3.02 |
| 1.80                | 2.51 | 1.07 | 2.06          | 1.15 | 2.76 |
| 2.00                | 2.29 | 1.08 | 1.64          | 1.15 | 2.51 |
| 2.20                | 2.10 | 1.10 | 1.24          | 1.15 | 2.28 |
| Expt.               | 3.84 | 0.96 | 2.97          | 1.14 | 4.14 |

<sup>a</sup> Absolute magnitudes in gauss.

<sup>b</sup> Calculated with  $\delta_O = 1.4$ ,  $r_{NO} = 1.67$ ,  $V_{CN} = 1.2$ ,  $Q = 23.7$ , and  $r_{18} = 0.06$ .

In Table XX we give our observed values for the radical anion of nitrobenzene in liquid ammonia. The radical anion was prepared by the electrolytic reduction of a  $5 \times 10^{-3}$  M solution 0.1 M in sodium iodide. The spectrum was independent of temperature from  $-40$  to  $-78^\circ\text{C}$ . Also given are values for nitrobenzene dissolved in dimethylformamide,<sup>81</sup> acetonitrile,<sup>33</sup> and 50% water in acetonitrile,<sup>82</sup> respectively. It can be seen from Table XX that the solvent shift for nitrobenzene in liquid ammonia is intermediate between acetonitrile and 50% water in acetonitrile.

Ludwig *et al.*<sup>82</sup> have recently related the large solvent shifts for nitrobenzene radical anion to the formation of hydrogen bonds with the solvent. Since acetonitrile and liquid ammonia have essentially the same value for their dielectric constants the shift cannot be explained entirely by the simple polarity of the solvent. Since liquid ammonia is a more protic solvent than is acetonitrile, its position in the solvent shifts in Table XX is consistent with some type of hydrogen bonding. However, it can also be seen from Table XX that the calculation of Reiger and Fraenkel<sup>81</sup> which is based upon a variable oxygen coulomb integral is a very satisfactory qualitative interpretation of the shift in the nitrogen and proton coupling constants in a wide variety of solvents.

#### E. Cyclooctatetraene

By far the most dramatic solvent effect which we have observed in liquid ammonia is in the radical anion of cyclooctatetraene. This radical has been prepared by Katz and Strauss<sup>83</sup> by alkali metal reduction in tetrahydrofuran. They observed a spectrum due to eight equivalent protons with a coupling constant of  $3.209 \pm 0.007$  gauss. From the intensity of the radical spectrum they concluded that the equilibrium for the disproportionation reaction

Table XX. Nitrobenzene Radical Anion Coupling  
Constant Solvent Shifts

| Position             | Ammonia | Dimethyl-<br>formamide <sup>a</sup> | Acetonitrile <sup>b</sup> | 50% H <sub>2</sub> O<br>in<br>CH <sub>3</sub> CN <sup>c</sup> |
|----------------------|---------|-------------------------------------|---------------------------|---------------------------------------------------------------|
| N                    | 11.46   | 9.70                                | 10.32                     | 13.59                                                         |
| Para                 | 3.89    | 4.03                                | 3.97                      | 3.54                                                          |
| Ortho                | 3.42    | 3.36                                | 3.39                      | 3.44                                                          |
| Meta                 | 1.11    | 1.07                                | 1.09                      | 1.12                                                          |
| <sup>a</sup> Ref. 81 |         |                                     |                           |                                                               |
| <sup>b</sup> Ref. 33 |         |                                     |                           |                                                               |
| <sup>c</sup> Ref. 82 |         |                                     |                           |                                                               |



was shifted far to the right.

We have prepared the radical anion of cyclooctatetraene by electrolysis of a dilute solution of the hydrocarbon in liquid ammonia. The solution was saturated with tetramethylammonium iodide. The spectrum was found to be that of eight equivalent protons with coupling constant  $3.278 \pm 0.004$  gauss. The one striking feature of the spectrum was its high intensity and extreme stability.\* Although no quantitative measurements

\* The radical spectrum was so strong, that trace amounts of hydrocarbon remaining in the vacuum system contaminated the system, and nothing but cyclooctatetraene spectra could be produced for several days after the initial experiment.

were made it seems safe to conclude that the effect of switching solvents from tetrahydrofuran to ammonia was to shift equilibrium 51 drastically to the left. The effect was so pronounced that it is doubtful that this can be looked upon as a solvent perturbation. It seems more likely that the entire chemistry including ion dissociation and perhaps even geometry of the molecular species changes when ammonia is used. Further work on the chemistry of this system is now in progress.<sup>89</sup>

One additional interesting feature of this system is the change in coupling constant of 0.069 gauss. Although far larger coupling constant solvent shifts have been previously observed,<sup>81</sup> symmetry considerations in this molecule require a different mechanism than is usually thought to be responsible. Ordinary solvent shifts are usually regarded as arising from a redistribution of the unpaired pi-electron spin density caused by solvent perturbations. Since coupling constants are related to unpaired spin density distribution by Eq. (7) this would bring about a coupling constant shift. In this molecule however symmetry considerations require that one-eighth of the odd electron reside on each carbon atom. Thus the quantity effected by the solvent perturbation is the sigma-pi interaction parameter  $Q$ . This  $Q$ -shift is small ( $\Delta Q = 0.55$  gauss) as would be expected but is certainly larger than experimental error. A variation of the  $Q$  of the benzene radical anion with temperature has been observed by Fessenden and Ogawa.<sup>90</sup> The variation in this case is about the same order of magnitude as we have observed in cyclooctatetraene and is in the direction of producing lower  $Q$  values at lower temperatures. Although a detailed theoretical consideration of these effects is complex and quite outside the scope of this work, we note that a mechanism involving ion pairing would be consistent with the direction of the shift in both of these cases.

#### ACKNOWLEDGMENTS

I am indebted to Professor Rollie J. Myers for his constant encouragement and expert advice throughout the course of this work.

The exchange of ideas with my colleagues and their frequent assistance has been an invaluable aid which I gratefully acknowledge.

Mrs. Pat Cookson has been particularly helpful in coping with the bureaucracy when it threatened to overwhelm us. I am further indebted to her for typing this thesis.

I wish to thank my wife for proofreading, editing, tea and sympathy.

This work was completed under the auspices of the United States Atomic Energy Commission and the Lawrence Radiation Laboratory.

APPENDIX I

Fortran II Computer Program ESR IV

The theoretical calculations and drawings in chapter four were done with the aid of the computer program ESR IV. This program uses the same basic method of calculation as the program ESR III developed by Stone and Maki<sup>84</sup> with the exception that ESR III will handle directly only 4 equivalent  $I = \frac{1}{2}$  and 3 equivalent  $I = 1$  nuclei while ESR IV will handle any number of equivalent nuclei.\* The principal difference is in the output.

ESR IV has deleted the three types of output available in ESR III and uses a California Computer Co. digital x-y plotter as an output device. The program makes use of the binary subroutine package J6 XYP2 MOD<sup>85</sup> which is usable only on an IBM 7094 computer. The 7094 produces a tape which is used as input to an IBM 1401 (or 1460) computer which drives the plotter. The 1401 is under control of the IBM 1401 PARASITE PLOT Program and any future changes in this program will probably require changes in ESR IV.

There are two basic outputs available with ESR IV. The first produces a plot of the spectrum with the name of the problem lettered above it for identification and nothing else. All input information is written on the 7094 monitor print tape for ordinary 1403 printing. The second output in addition provides a one-inch grid with the horizontal axis labeled in gauss and prints the input data on the graph itself to the right of the spectrum if the spectrum involves only one species. If more than one species is involved, the program leaves room for printed data to be stapled next to the spectrum and prints the input data on the 1403.

\*

The author would like to thank Drs. Stone and Maki for a listing and deck of their program.

The second output is rather elegant but uses a great deal of plotter time (up to 15 minutes per graph) to draw the grid and print the input data. The first output is not quite as pleasing but probably uses a maximum of 30 seconds of plotter time. In regard to 7094 time, ESR IV is somewhat faster than ESR III regardless of which output is used.

The data cards are divided into group A, which applies to the entire problem, and group B, which applies to one species. There must be a set of group B for each species to be superimposed, and they are stacked in any order after group A. Definitions of all input variables are given after the following list of data cards. Each card must be included unless otherwise indicated.

| <u>FORMAT</u> | <u>CONTENTS</u>         | <u>COMMENTS</u>          |
|---------------|-------------------------|--------------------------|
|               | Group A                 |                          |
| (12A6)        | ANAME(I), I = 1,12      |                          |
| (214)         | NSPEX, KSHAPE           |                          |
| (2F12.6, I12) | GPI, HIY, LETTER        |                          |
|               | Group B                 |                          |
| (12A6)        | BNAME(I), I = 1,12      |                          |
| (214)         | NA, NB                  |                          |
| (3F12.6)      | WEIGHT, WLINE, PHASE    |                          |
| (6(I4, F8.3)) | NQA(I), A(I), I = 1, NA | May be omitted if NA = 0 |
| (6(I4, F8.3)) | NQB(I), A(I), I = 1, NB | May be omitted if NB = 0 |

As many calculations may be stacked on top of each other as desired.

At the end of the entire data deck there must be two blank cards.

Definitions of Input Variables

ANAME                    The name of the problem. This will be lettered across the top of the graph.

NSPEX                   The total number of species whose spectra are to be superimposed.

KSHAPE                  If zero, Lorentzian lineshape selected; Gaussian lineshape for non-zero.

GPI                     Horizontal scale of spectrum in gauss per inch.

HIY                     Height of largest peak of experimental spectrum in inches. Must be less than ten.

LETTER                  If zero, output consists of spectrum and title only.  
If non-zero, grid and input data plotted.

BNAME                   The name of each species. Will be printed or typed above the input data for that species.

NA                      The total number of different coupling constants with  $I = \frac{1}{2}$ .

NB                      The total number of different coupling constants with  $I = 1$ .

WEIGHT                  The relative abundance of the species. If there is only one species any positive number may be used.

WLINE                   The linewidth in gauss.

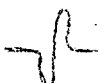
PHASE                   If +1.0 lines will look like this:   
If -1.0 lines will look like this: 

NQA(I)                  The number of equivalent  $I = \frac{1}{2}$  nuclei having the Ith coupling constant.

A(I)                    The Ith coupling constant for nuclei with  $I = \frac{1}{2}$ , in gauss.

NQB(I) }  
B(I)                    The corresponding variables for nuclei with  $I = 1$ .

Example: The use of ESR IV is illustrated by the following example.

The experimental spectrum appears to consist of 2 species with the same g-factor. Species A, in 20% abundance has hyperfine structure from 5 equivalent nitrogens with  $A = 2.35$  gauss. The linewidth is 0.135 gauss. Species B, in 80% abundance, has hyperfine structure from 2 equivalent protons, with  $A = 3.59$  gauss. The linewidth is 0.180 gauss. The highest line measures 4.25 inches peak-to-peak, and the total width of the spectrum is 14.72 inches. Full output is desired, and the lines look like this: 

The data cards will appear exactly as shown below, where - represents a blank space.

-FICTITIOUS-EXAMPLE

---2---0

-----0.399-----4.252-----1

-SPECIES-A

---0---1

-----2.000-----0.135-----+1.0

---5---2.350

-SPECIES-B

---1---0

-----8.000-----0.180-----+1.0

---2---3.590

Blank }  
Blank } (if this is the only spectrum being run)

It will be noted that with clever handling of the input data one can produce the full spectrum, deal with nuclear spins greater than 1, deal

with two or more species of different  $g$  value, and do various other things not explicitly written into the program.

The listing of the Fortran program is as follows:

```

* 400207 EPR      3   DCN LEVY
*   LABEL
CEPRV SPECTRUM SIMULATOR PROGRAM
C STATEMENT NUMBERS USED IN THE FOLLOWING PROGRAM ARE 1-180, 230-232, 551,
C 610-615, 711, 1001-1005, 1101, 1106, 1111-1112, 1201-1207, 1301-1302,
C 1304-1307, 1401-1419, 1751, 1801-1806, 2601-2610, 2800, 2802, 3001-3010,
C 3101-3105, 3107, 5001, 5006, 6001-6005, 7001-7010, 8001-8023, 9003-9018
  DIMENSION ANAME(13), YA(3,6000), BNAME(13), NQA(50), A(50),
  INQR(50), R(50), SCALE(2), HOLD(22), ALPHA(12)
  FREQUENCY 612(320),22(0,1,10),27(0,3,1),38(0,1,10),
  139(4),43(0,3,1),44(1),58(320),64(0,1,10),65(4),71(3000),
  172(8,10,3,1),78(8,10,3,1),79(1,0,5),82(1,0,5),84(1,0,5),87(1,0,5),
  189(1,0,5),91(1,0,5),94(1,0,5),96(1,0,5),98(1,0,5),100(1,0,5),
  1112(0,3,1),113(1),119(3000),120(0,0,5),128(0,0,5),129(1,0,5),
  1131(1,0,5),134(1,0,5),136(1,0,5),138(1,0,5),140(1,0,5),143(1,0,5),
  1145(1,0,5),147(1,0,5),149(1,0,5),151(1,0,5),153(1,0,5),166(5000),
  1174(5000),179(5000),711(0,1,10)
  FREQUENCY 2602(5), 2604(10,1,2), 3002(1), 3004(10, 1, 2),
  13101(0, 15, 1), 3102(0, 2, 1), 3103(0, 15, 1), 3104(0,15,1),
  13105(0,15,1), 9015(4,1,2), 9017(0,1,5), 9008(10), 3107(0,1,1),
  18001(0,3,1), 8007(0,15,1), 8014(0,1,10), 8015(5), 7003(0,1,100),
  18018(0,3,1), 8019(1), 7007(0,1,100), 6002(20), 1801(5000),
  1 1406(0, 1, 1), 1407(0, 1, 1), 1408(0, 1, 1), 1401(0, 1, 1),
  1 1402(0, 1, 1), 1403(0, 1, 1), 1404(0, 1, 1), 1405(0, 1, 1),
  1 1409(0, 1, 1)
  PRINT 11
11 FORMAT (23H MOUNT BLANK TAPE ON B5 )
  CALL PAUSE
  1 CALL CALSET (15)
  2 FORMAT (3F12.6)
B   3 ANAME(1)=606060070230
  4 FORMAT(12A6)
  5 READ INPUT TAPE 2,4,(ANAME(I),I=2,13)
  7 READ INPUT TAPE 2,8, NSPEX, KSHAPE
  711 IF (NSPEX) 231, 231, 9
  9 READ INPUT TAPE 2, 12, GPI, HIY, LETTER
  3102 IF (NSPEX - 1) 1401, 1401, 6
  1401 IF (LETTER) 10, 6, 10
  6 WRITE OUTPUT TAPE 3, 2800
  2800 FORMAT (11HINPUT DATA )
  WRITE OUTPUT TAPE 3, 2802
  2802 FORMAT (2H )
  WRITE OUTPUT TAPE 3,4,(ANAME(I),I=2,13)
  8 FORMAT (2I4)
B   10 BNAME(1) = 606060070230
  12 FORMAT (2F12.6, 1I2 )
  13 NSPEC=0
  14 NHAFFMX=0
  15 DC 16 I=1,6000
  16 YA(3,I)=0.0
  17 NSPEC=NSPEC+1
  18 READ INPUT TAPE 2,4,(BNAME(I),I=2,13)
  3103 IF (NSPEX - 1) 1402, 1402, 19
  1402 IF (LETTER) 20, 19, 20
  19 WRITE OUTPUT TAPE 3,4, (BNAME(I), I=2,13)
  20 READ INPUT TAPE 2,8,NA,NB

```

```

21 READ INPUT TAPE 2,2, WEIGHT, WLINE, PHASE
22 IF (NA) 27,27,23
23 READ INPUT TAPE 2,24,(NQA(I),A(I),I=1,NA)
24 FORMAT(6(I4,F8.3))
3104 IF (NSPEX - 1) 1403, 1403, 25
1403 IF (LETTER) 2601, 25, 2601
25 WRITE OUTPUT TAPE 3,26,(NQA(I),A(I),I=1,NA)
26 FORMAT (10X,13,27H EQUIVALENT, I=0.5, WITH A= ,F12.6,6H GAUSS )
C STATEMENTS NUMBERED TWENTY-SIX HUNDRED TAKE CARE OF THE
C POSSIBILITY OF MORE THAN 4, I=0.5, EQUIVALENT COUPLING CONSTANTS
2601 NTA=NA
2602 DO 2610 L=1, NTA
2603 NTEMP = NQA(L) - 4
2604 IF (NTEMP) 2610, 2610, 2605
2605 NQA(L) = NQA(L) - 4
2606 NA = NA + 1
2607 NQA(NA) = 4
2608 A(NA) = A(L)
2609 GO TO 2603
2610 CONTINUE
27 IF (NR) 3101, 3101, 28
28 READ INPUT TAPE 2,24,(NCB(I),B(I),I=1,NB)
3105 IF (NSPEX - 1) 1404, 1404, 29
1404 IF (LETTER) 3001, 29, 3001
29 WRITE OUTPUT TAPE 3,30,(NCB(I),B(I),I=1,NB)
30 FORMAT (10X,13,27H EQUIVALENT, I=1.0, WITH A= ,F12.6,6H GAUSS )
C STATEMENTS NUMBERED THREE THOUSAND TAKE CARE OF THE POSSIBILITY
C OF MORE THAN 3 EQUIVALENT, I=1, COUPLING CONSTANTS
3001 NTB = NB
3002 DO 3010 L=1, NTB
3003 NTEMP = NCB(L) - 3
3004 IF(NTEMP) 3010,3010,3005
3005 NCB(L) = NCB(L) - 3
3006 NB = NB + 1
3007 NCB(NB) = 3
3008 B(NB) = B(L)
3009 GO TO 3003
3010 CONTINUE
3101 IF (NSPEX - 1) 1405, 1405, 31
1405 IF (LETTER) 33, 31, 33
31 WRITE OUTPUT TAPE 3,32,WEIGHT,WLINE
32 FORMAT(10X,15HSPECIES WEIGHT= F12.6,15H AND LINEWIDTH= F12.6,
16H GAUSS )
33 DO 35 I=1,2
34 DO 35 J=1,6000
35 YA(I,J )=0.0
36 WID=0.0
37 TENS=1.0
38 IF (NA) 43,43,39
39 DO 42 I=1,NA
40 ANQ=NQA(I)
41 WID=WID+(ANQ*A(I))
42 TENS=TENS*(2.0**ANQ)
43 IF (NB) 48,48,44
44 DO 47 I=1,NB
45 BNQ=NCB(I)

```

```

46 WID=WID*(2.0*BNQ*B(I))
47 TENS=TENS*(3.0**BNQ)
48 HAF=WID/2.0
49 NI=WLINE/0.005
50 NGEN=16*NI
51 NORG=8*NI
52 ORIGIN=0.005*FLCAIF(NORG)
53 NHAF=NORG+IR(HAF/0.005)
54 W=WLINE
55 TENFAC=PHASE*WEIGHT/TENS
551 IF (KSHAPE) 611,56,611
56 TA=-16.*(W**3)
57 TP=3.*(W**2)
58 DO 61 I=1,NGEN
59 XI=I
60 XA=(XI*0.005)-ORIGIN
61 YA(1,I)=(TENFAC*TA*XA)/((4.*(XA**2)+TP)**2)
610 GO TO 62
611 TA=-(W**2)
612 DO 615 I=1,NGEN
613 XI=I
614 XA=(XI*0.005)-ORIGIN
615 YA(1,I)=TENFAC*(XA/TA)*EXP((XA**2)/TA)
62 LENGTH=NGEN
63 NY=1
64 IF (NA) 112,112,65
65 DO 111 K=1,NA
66 NEQ=NQA(K)
67 KUPL=A(K)/0.005
68 LENGTH=LENGTH+(NEQ*KUPL)
69 LENGTH=XMINOF(LENGTH,NHAF)
70 AK=A(K)
71 DO 106 I=1,LENGTH
72 GO TO (76,75,74,73),NEQ
73 I4=I-IR(4.*AK/.005)
74 I3=I-IR(3.*AK/.005)
75 I2=I-IR(2.*AK/.005)
76 I1=I-IR(AK/.005)
77 YPLUS=0.0
78 GO TO (79,82,87,94),NEQ
79 IF(I1) 102,102,80
80 YPLUS=YA(NY,I1)
81 GO TO 102
82 IF (I1) 102,102,83
83 YPLUS= 2.*YA(NY,I1)
84 IF (I2) 102,102,85
85 YPLUS= YPLUS+YA(NY,I2)
86 GO TO 102
87 IF (I1) 102,102,88
88 YPLUS=3.*YA(NY,I1)
89 IF (I2) 102,102,90
90 YPLUS=YPLUS+3.*YA(NY,I2)
91 IF (I3) 102,102,92
92 YPLUS=YPLUS+YA(NY,I3)
93 GO TO 102
94 IF (I1) 102,102,95

```

```
95 YPLUS=4.*YA(NY,I1)
96 IF (I2) 102,102,97
97 YPLUS=YPLUS+6.*YA(NY,I2)
98 IF (I3) 102,102,99
99 YPLUS=YPLUS+4.*YA(NY,I3)
100 IF (I4) 102,102,101
101 YPLUS=YPLUS+YA(NY,I4)
102 GO TO (105,103),NY
103 YA(1,I)=YA(2,I)+YPLUS
104 GO TO 106
105 YA(2,I)=YA(1,I)+YPLUS
106 CONTINUE
107 GO TO (108,110),NY
108 NY=2
109 GO TO 111
110 NY=1
111 CONTINUE
112 IF (NB) 165,165,113
113 DO 164 K=1,NB
114 NEQ=NQB(K)
115 KUPL=B(K)/.005
116 LENGTH=LENGTH+2*NEQ*KUPL
117 LENGTH=XMINOF(LENGTH,NHAF)
118 BK=B(K)
119 DO 159 I=1,LENGTH
120 GO TO (125,123,121),NEQ
121 I6=I-IR(6.*BK/.005)
122 I5=I-IR(5.*BK/.005)
123 I4=I-IR(4.*BK/.005)
124 I3=I-IR(3.*BK/.005)
125 I2=I-IR(2.*BK/.005)
126 I1=I-IR(BK/.005)
127 YPLUS=0.0
128 GO TO (129,134,143),NEQ
129 IF (I1) 155,155,130
130 YPLUS=YA(NY,I1)
131 IF (I2) 155,155,132
132 YPLUS=YPLUS+YA(NY,I2)
133 GO TO 155
134 IF (I1) 155,155,135
135 YPLUS=2.*YA(NY,I1)
136 IF (I2) 155,155,137
137 YPLUS=YPLUS+3.*YA(NY,I2)
138 IF (I3) 155,155,139
139 YPLUS=YPLUS+2.*YA(NY,I3)
140 IF (I4) 155,155,141
141 YPLUS=YPLUS+YA(NY,I4)
142 GO TO 155
143 IF (I1) 155,155,144
144 YPLUS=3.*YA(NY,I1)
145 IF (I2) 155,155,146
146 YPLUS=YPLUS+6.*YA(NY,I2)
147 IF (I3) 155,155,148
148 YPLUS=YPLUS+7.*YA(NY,I3)
149 IF (I4) 155,155,150
150 YPLUS=YPLUS+6.*YA(NY,I4)
```

```

151 IF (15) 155,155,152
152 YPLUS=YPLUS+3.*YA(NY,15)
153 IF (16) 155,155,154
154 YPLUS=YPLUS+YA(NY,16)
155 GO TO (158,158),NY
156 YA(1,I)=YA(2,I)+YPLUS
157 GO TO 159
158 YA(2,I)=YA(1,I)+YPLUS
159 CONTINUE
160 GO TO (161,163),NY
161 NY=2
162 GO TO 164
163 NY=1
164 CONTINUE
165 IREAD=NHAF+1
166 DO 168 I=1,NHAF
167 IREAD=IREAD-1
168 YA(3,I)=YA(3,I)+YA(NY,IREAD)
169 IF (NHAF-NHAFMX) 172,172,170
170 NHAFMX=NHAF
171 NORGMX=NORG
172 IF (NSPEX-NSPEC) 173,173,17
173 YMAX=0.0
174 DO 178 I=1,NHAFMX
175 YY=YA(3,I)
1751 YY=ABS(YY)
176 IF (YY-YMAX) 178,178,177
177 YMAX=YY
178 CONTINUE
179 DO 180 I=1,NHAFMX
  AMULT = HIY/(2.0*YMAX)
180 YA(3,I) = AMULT*YA(3,I) + 5.0
1806 GRALN=FLOATF(NHAFMX)*0.005*(1.0/GPI)+1.0
C   STATEMENTS 9014-9018, 9011 LETTER THE PROBLEM NAME ACROSS
C   THE TOP OF THE GRAPH
9014 LETHIT=XFIXF(10.0*GRALN/72.0)
9015 IF(LETHIT-4) 9017, 9017, 9016
9016 LETHIT = 4
9017 IF(LETHIT) 9018, 9018, 9003
9018 LETHIT=1
9003 CALL SETGPH(GRALN, 10.0, 0.50)
1406 IF (LETTER) 9004, 9012, 9004
9004 CALL FRAME (0.10, 0.10)
9005 DO 9007 I=1,3, 2
9006 CALL XLN(0.0, GRALN, FLOATF(I), 0.0)
  CALL XLN (GRALN, 0.0, FLOATF(I + 1), 0.0)
9007 CONTINUE
  DO 1111 I = 6, 8, 2
  CALL XLN ( 0.0, GRALN, FLOATF(I), 0.0)
  CALL XLN (GRALN, 0.0, FLOATF(I + 1), 0.0)
1111 CONTINUE
9012 JEND = XFIXF(GRALN) - 1
1407 IF (LETTER) 9008, 9011, 9008
9008 DO 9010 I=1, JEND, 2
9009 CALL YLN (0.0, 10.0, FLOATF(I), 0.0)
  CALL YLN(10.0, 0.0, FLOATF(I + 1), 0.0)

```

```

9010 CONTINUE.
3107 IF(JEND - 2*(JEND/2)) 1112, 1112, 9011
1112 CALL YLN(0.0, 10.0, FLOAT(JEND + 1), 0.0)
9011 CALL LTR(0.0, 10.1, LETHIT, 0, ANAME)
1408 IF (LETTER) 8001, 1409, 8001
C   STATEMENTS 8001-8023 PUT THE REST OF THE LETTERING, BUT NONE OF THE
C   HOLERITH NUMBERING, ON THE GRAPH
8001 IF (KSHAPE) 1001, 1002, 1001
81001 ALPHA(1) = 011030272164
B   ALPHA(2) = 626231214560
B   ALPHA(3) = 433145256230
B   ALPHA(4) = 214725606060
8002 CALL LTR (GRALN + 1.0, 10.3, 1, 0, ALPHA)
8003 GO TO 1003
81002 ALPHA(1) = 020030434651
B   ALPHA(2) = 254563713121
B   ALPHA(3) = 456043314525
B   ALPHA(4) = 623021472560
8004 CALL LTR (GRALN + 1.0, 10.3, 1, 0, ALPHA)
81003 ALPHA(1) = 031030504651
B   ALPHA(2) = 317146456321
B   ALPHA(3) = 436062232143
B   ALPHA(4) = 251360606060
B   ALPHA(5) = 606060272164
B   ALPHA(6) = 626260472551
B   ALPHA(7) = 603145233060
8005 CALL LTR (GRALN + 1.0, 10.1, 1, 0, ALPHA)
5001 CALL LTRNUM (GPI, GRALN + 2.7, 10.1, 1, 0)
5006 CALL LTRNUM (HIY, GRALN + 2.3, 9.9, 1, 0)
B   ALPHA(1) = 031130432151
B   ALPHA(2) = 272562636043
B   ALPHA(3) = 314525136060
B   ALPHA(4) = 606060606031
B   ALPHA(5) = 452330256260
B   ALPHA(6) = 472521421463
B   ALPHA(7) = 461447252142
8006 CALL LTR (GRALN + 1.0, 9.9, 1, 0, ALPHA)
8007 IF(NSPEX-1) 8008, 8013, 8008
8008 CALL YLN (0.0, 10.0, GRALN + 7.0, 0.0)
8009 CALL YLN (0.0, 10.0, GRALN + 22.0, 0.0)
B   ALPHA(1) = 030730634646
B   ALPHA(2) = 604421457060
B   ALPHA(3) = 624725233125
B   ALPHA(4) = 626063466043
B   ALPHA(5) = 256363255160
B   ALPHA(6) = 314547646360
B   ALPHA(7) = 242163216060
8010 CALL LTR (GRALN + 9.0, 5.6, 3, 0, ALPHA)
B   ALPHA(1) = 021030626321
B   ALPHA(2) = 474325606370
B   ALPHA(3) = 472524603145
B   ALPHA(4) = 476463602421
B   ALPHA(5) = 632160302551
B   ALPHA(6) = 256060606060
8011 CALL LTR (GRALN + 8.8, 6.2, 3, 0, ALPHA)
8012 GO TO 1004

```

```
8013 CALL LTR (GRALN + 1.0, 9.0, 1, 0, BNAME)
8014 IF(NA) 7001,8018,7001
7001 WIDTH = GRALN + 2.0
7002 DEPTH = 8.8
8015 DO 8017 I = 1, NA
7003 IF(DEPTH - 1.0) 7004, 7004, 7006
7004 DEPTH = 8.8
7005 WIDTH = WIDTH + 6.0
7006 DEPTH = DEPTH - 0.2
B   ALPHA(1) = 040230606060
B   ALPHA(2) = 255064316521
B   ALPHA(3) = 432545637360
B   ALPHA(4) = 311300330573
B   ALPHA(5) = 606631633060
B   ALPHA(6) = 211360606060
B   ALPHA(7) = 606060602721
B   ALPHA(8) = 646262606060
8016 CALL LTR (WIDTH, DEPTH, 1, 0, ALPHA)
1201 CALL BINCON (HOLD)
1202 WRITE OUTPUT TAPE 3, 1203, NQA(I)
1203 FORMAT (I6)
B1204 SCALE(1) = 60606060630
1205 SCALE(2) = HOLD(1)
1206 CALL LTR (WIDTH - 0.4, DEPTH, 1, 0, SCALE)
1207 CALL LTRNUM (A(I), WIDTH + 3.0, DEPTH, 1, 0)
8017 CONTINUE
8018 IF(NB) 8019, 1005, 8019
8019 DO 8021 I=1,NB
7007 IF (DEPTH - 1.0) 7008,7008,7010
7008 DEPTH = 8.8
7009 WIDTH = WIDTH + 6.0
7010 DEPTH = DEPTH - 0.2
B   ALPHA(1) = 040230606060
B   ALPHA(2) = 255064316521
B   ALPHA(3) = 432545637360
B   ALPHA(4) = 311301330073
B   ALPHA(5) = 606631633060
B   ALPHA(6) = 211360606060
B   ALPHA(7) = 606060602721
B   ALPHA(8) = 646262606060
8020 CALL LTR (WIDTH, DEPTH, 1, 0, ALPHA)
1301 CALL BINCON (HOLD)
1302 WRITE OUTPUT TAPE 3, 1203, NQB(I)
B1304 SCALE(1) = 60606060630
1305 SCALE(2) = HOLD(1)
1306 CALL LTR (WIDTH - 0.4, DEPTH, 1, 0, SCALE)
1307 CALL LTRNUM (B(I), WIDTH + 3.0, DEPTH, 1, 0)
8021 CONTINUE
B1005 ALPHA(1) = 020330433145
B   ALPHA(2) = 256631246330
B   ALPHA(3) = 136060606060
B   ALPHA(4) = 606060272164
B   ALPHA(5) = 626260606060
8022 CALL LTR (GRALN + 1.1, 8.8, 1, 0, ALPHA)
1106 CALL LTRNUM (WLINE, GRALN + 2.1, 8.8, 1, 0)
8023 CALL YLN (0.0, 10.0, WIDTH + 8.0, 0.0)
```

```

B1004 ALPHA(1) = 053000330000
      ALPHA(2) = 006060606060
      6001 CALL LTR (-0.05, 0.25, 1, 1, ALPHA)
            JEND = JEND + 1
      6002 DO 6005 I=1, JEND
      6003 BER = FLOATF(I)*GPI
      6004 CALL LTRNUM (BER, FLOATF(I) +0.15, 0.15, 1, 1)
      6005 CONTINUE
      1419 GO TO 9013
      1409 IF (KSHAPE) 1410, 1412, 1410
      1410 WRITE OUTPUT TAPE 3, 1411
      1411 FORMAT ( 19H GAUSSIAN LINESHAPE )
      1418 GO TO 1414
      1412 WRITE OUTPUT TAPE 3, 1413
      1413 FORMAT ( 21H LORENTZIAN LINESHAPE )
      1414 WRITE OUTPUT TAPE 3, 1415, GPI
      1415 FORMAT ( 20H HORIZONTAL SCALE = , F12.6, 15H GAUSS PER INCH )
      1416 WRITE OUTPUT TAPE 3, 1417, HIY
      1417 FORMAT ( 16H LARGEST LINE = , F12.6, 20H INCHES PEAK-TO-PEAK )
      9013 CALL CURVE(0, 0, 0.0, 0, 0.0, GRALN, 0.0, 10.0, 1)
      1801 DO 1805 I=1, NHAFTX
      1802 XPT = 1.0/GPI*0.005*FLOATF(I)
      1803 YPT = YA(3,I)
      1804 CALL PLOTPT(XPT, YPT)
      1805 CONTINUE
      230 GO TO 3
      231 CALL NDPLT
      232 CALL EXIT
      END

```

```

*      LABEL
      1 FUNCTION IR(X)
      2 Y=INTF(X)
      3 D=ABSF(X-Y)
      4 IF (D-.5) 5,7,7
      5 IR=Y
      6 RETURN
      7 IF (X) 8,10,10
      8 IR=Y-1.
      9 RETURN
     10 IR=Y+1.
     11 RETURN
      END

```

```

*      LABEL
      SUBROUTINE LTRNUM (ANUM, XBEG, YBEG, LHIGH, LINE)
      DIMENSION SCALE(2), HOLD(22)
      1 CALL BINCON (HOLD)
      2 WRITE OUTPUT TAPE 3, 3, ANUM
      3 FORMAT (F6.3)
      4 SCALE(1) = 606060600630
      5 SCALE(2) = HOLD (1)
      6 CALL LTR (XBEG, YBEG, LHIGH, LINE, SCALE)
      RETURN
      END

```

## APPENDIX II

### Fortran IV Computer Program MO

The four different molecular orbital calculations described in chapter four were performed with the Fortran IV program package MO. This program will perform a Huckel LCAO calculation (with or without overlap) or a McLachlan SCF calculation depending on the values of the input data. It will also calculate methyl, methylene, or ring coupling constants from the calculated wavefunctions.

The heart of the program is the SHARE subroutine HDIAG which performs the matrix diagonalizations. The routine has been changed from Fortran II to Fortran IV and the statements from 1000 through 1001 inclusive have been added but other than that the routine is unchanged. The subroutine METHYL contains the formulae for calculating the methyl and methylene coupling constants and the date on which these formulae were last changed. The date appears on the output and allows one to easily keep track of which formulae were used in any given calculation. The subroutines XEMERR and SETFPT are monitor subroutines which suppress the error comments which are ordinarily printed out on underflows. These routines are specifically designed for the LRL 7044 IBSYS monitor<sup>86</sup> and may be superfluous or undefined with a different monitor.

The input data for a single calculation consists of two control cards and the input H and S matrix cards. The first card contains the name of the molecule and has the format 12A6. The second card defines the type of calculation and contains the following data fields:

| <u>FIELD</u> | <u>CONTENTS</u> |
|--------------|-----------------|
| I2           | N               |
| F6.3         | ALAM            |

|        |                                              |
|--------|----------------------------------------------|
| F6.3   | Q                                            |
| I2     | IORBIT                                       |
| 8(4I2) | (IH(I), IC(I), ICPRM(I), ICDPRM(I), I = 1,8) |

The definitions of these input variables are as follows:

|           |                                                                                                                                                          |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| N         | The order of the H and S matrices.                                                                                                                       |
| ALAM      | The value of lambda in the McLachlan SCF calculation. If zero, no McLachlan calculation is performed.                                                    |
| Q         | The value of the sigma-pi interaction parameter from which ring coupling constants are calculated. If zero, ring coupling constants are not calculated.  |
| IORBIT    | The orbital of the odd electron in the radical cation. If zero, IORBIT is assumed to be $N/2$ if N is even, $N/2 - \frac{1}{2}$ if N is odd.             |
| IH(I)     | The number of the hydrogen atom in the Ith methyl or methylene group.                                                                                    |
| IC(I)     | The number of the carbon atom in the Ith methyl or methylene group.                                                                                      |
| ICPRM(I)  | The number of the carbon atom to which the Ith methyl or methylene group is attached.                                                                    |
| ICDPRM(I) | The number of the second carbon atom to which the Ith methylene group is attached. If the Ith group is a methyl this is left blank or set equal to zero. |

As stated, all of this information goes on a single card whose format statement is (I2, 2F6.3, 36I2).

After the two control cards there follows the stack of cards giving the input H-matrix. Each non-zero matrix element  $H_{ij}$  is listed on a separate card with format (2I4, F 64.10). The first two fields contain the values of I and J respectively and the third field contains the value of the matrix element. At the end of the H-matrix deck a blank card is inserted. If an overlap calculation is to be done the S-matrix deck follows

the H matrix deck in the same manner. Only the off-diagonal overlap elements need be given. If the calculation is to be done neglecting overlap a blank card is inserted in place of the overlap deck. Of course when doing a McLachlan calculation there must be no overlap deck.

As an example of the use of this program we consider an overlap calculation performed on the molecule 2-methylcyclohexadiene-1,3 using the parameters of Coulson and Crawford. We wish to do a Huckel calculation both with and without overlap and a McLachlan calculation with lambda equal to 1.0. Further we wish to calculate all methyl and methylene coupling constants and all unsaturated proton coupling constants assuming a Q of 20.0. The numbering of the atoms is shown in Fig. 20. The data cards will appear exactly as shown below, where - represents a blank space.

2-METHYLCYCLOHEXADIENE-1,3. SAMPLE CALCULATION.

10--1.00--20.0---8-7-2--10-5-4-6-9-6-5-1

---8---8-----0.5

---9---9-----0.5

--10--10-----0.5

---7---7-----0.1

---6---6-----0.1

---5---5-----0.1

---4---5-----0.76

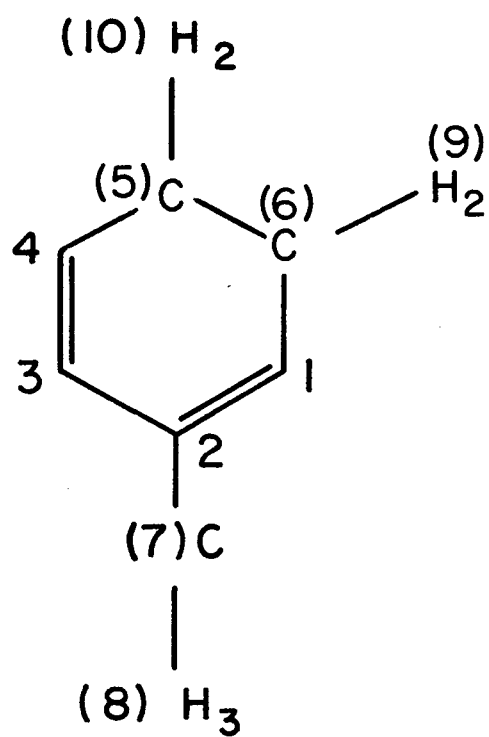
---5---6-----0.76

---1---6-----0.76

---2---7-----0.76

---5--10-----2.00

---6---9-----2.00



MU-35086

Fig. 20

---7---8-----2.00

---3---4-----1.00

---2---3-----1.00

---1---2-----1.00

blank

blank

2-METHYLCYCLOHEXADIENE-2,3. OVERLAP CALCULATION.

10-----20.0---8-7-2--10-5-4-6-9-6-5-1

---8---8-----0.5

---9---9-----0.5

--10--10-----0.5

---7---7-----0.1

---6---6-----0.1

---5---5-----0.1

---4---5-----0.76

---5---6-----0.76

---1---6-----0.76

---2---7-----0.76

---5---10-----2.00

---6---9-----2.00

---7---8-----2.00

---3---4-----1.00

---2---3-----1.00

---1---2-----1.00

blank

---4---5-----0.19

---5---6-----0.19

---1---6-----0.19

---2---7-----0.19

---5---10-----0.50

---6---9-----0.50

---7---8-----0.50

---3---4-----0.25

---2---3-----0.25

---1---2-----0.25

blank

blank

blank

The listing of the Fortran program is as follows:

```

$ID 400721,MU,20,LEVY
$IRJOB
$IBFTC MO
C HUCKEL MOLECULAR ORBITAL CALCULATION INCLUDING OVERLAP
C THIS PROGRAM REQUIRES THE SUBROUTINES HCLAG, MULT, METHYL, AND XEMERR
  DIMENSION H(41,41),U(41,41),ANAME(12),NUM(41),K(41),S(41,41),
  IC(41,41), IC(9), IH(9), ICPRM(9), ICOPRM(9), CHKRO(41), HP(41,41)
  COMMON IE, AH, AC, ACP, CONST, MCNTH, IDAY, IYEAR
  CALL SEIFPT(0,0,0,0)
  CALL METHYL
C THE STATEMENTS DOWN TO AND INCLUDING 3001 SET EVERYTHING IMPORTANT TO ZERO
101 DO 102 I=1, 41
  CHKRO(I) = 50.0
102 NUM(I) = I
  DO 3 I = 1,41
    DO 3 J = 1,41
      HP(I,J) = 0.0
      H(I,J) = 0.0
      ICARDS = 0
      DO 3001 I = 1,41
        DO 3001 J = 1,41
          IF(I-J) 5800, 5801, 5800
5800 S(I,J) = 0.0
      GO TO 3001
5801 S(I,J) = 1.00
3001 CONTINUE
C THE STATEMENTS DOWN TO 3009 READ AND PRINT THE INPUT MATRICES
  4 READ (2,5) (ANAME(I), I = 1, 12)
  5 FORMAT (12A6)
  6 READ(2,7) N,ALAM,N,ICRBIT,(IH(I),IC(I),ICPRM(I),ICOPRM(I),I=1,8)
  7 FORMAT(12,2F6.3, 16I2)
  8 IF(N) 15, 55, 15
  15 WRITE (3,16) (ANAME(I), I = 1,12)
801 WRITE (3,802)
802 FORMAT (1H0, 10X, 59HNON-ZERO ELEMENTS IN ORIGINAL H-MATRIX )
  9 READ (2,10) I, J, HCLD
 10 FORMAT (14, 14, F84.10)
 11 IF(I) 12,3002,12
 12 H(I, J) = HOLD
  HP(I,J) = HOLD
  H(J,I) = H(I,J)
  HP(J,I) = HOLD
1201 WRITE (3,1202) I, J, H(I, J)
1202 FORMAT(15X, 2HH(, 12, IH, ,12, 4H) = , F9.5)
 13 GO TO 9
3002 READ(2, 10) I, J, HCLD
  IF(HOLD.LT. 1.00E-05) GO TO 3029
  WRITE(3, 3003)

  ALAM = 0.0
  GO TO 3006

3003 FORMAT(1H0, 10X, 59HNON-ZERO OFF-DIAGONAL ELEMENTS IN ORIGINAL S-M
  MATRIX )
3004 READ (2,10) I, J, HOLD
3005 IF(I) 3006,14,3006

```

4000080

4000110

4000150

4000160

4000190

4000200

4000210

4000220

4000230

4000240

4000250

4000260

4000270

4000280

4000290

4000300

4000330

4000340

```

3006 S(I,J) = HOLD
S(J,I) = S(I,J)
3007 WRITE (3,3008) I, J, S(I,J)
ICARDS = ICARDS + 1
3008 FORMAT(15X, 2HS(,12,1H,,12,4H) = , F9.5)
3009 GO TO 3004
C THE STATEMENTS DOWN TO 3033 DO THE ACTUAL CALCULATION
14 CALL HDIAG (S, N, O, U, NR)
16 FORMAT (30H1 MOLECULAR ORBITAL CALCULATION OF , 12A6)
3010 WRITE (3,3011)
3011 FORMAT(1H0, 10X, 20HS(0) ELEMENTS )
3012 DO 3013 I=1,N
3013 WRITE (3,3014) I,1,S(I,1)
3014 FORMAT(15X, 2HS(, 12, 1H,,12, 4H) = , F9.5)
3015 DO 3016 I =1,N
3016 S(I,1) = S(I,1)*(-0.5)
3017 CALL MULT(U,S,C,N)
NFRD = N-1
3018 DO 3022 I = 1, NFRD
NIRD = I + 1
3019 DO 3022 J = NIRD , N
3020 HOLD = U(I,J)
3021 U(I,J) =U(J,I)
3022 U(J,I) = HOLD
3023 CALL MULT(C,U,S,N)
3024 CALL MULT(S,H,C,N)
3025 CALL MULT(C,S,H,N)
3029 CALL HDIAG(H,N,C,U,NR)
3033 CALL MULT (S,U,C,N)
18 WRITE (3,19)
19 FORMAT (1H0, 10X, 92HENERGY = ALPHA + (LAMBDA)(BETA). ALGEBRAICAL
11Y LARGEST LAMBDA CORRESPONDS TO LOWEST ENERGY. )
IF(ICARDS) 3034, 22, 3034
3034 WRITE (3,3035)
3035 FORMAT (1H0, 5X, 15HLOWEST ORBITALS )
C THE STATEMENTS TO 351 ORDER THE EIGENVECTORS IN ORDER OF INCREASING ENERGY
22 DO 23 I = 1,N
23 K(I) = I
231 ISTOP = N - 1
24 DO 24 I = 1, ISTOP
25 IST = I + 1
26 DO 24 J = IST, N
27 IF (H(I,I) - H(J,J)) 28, 34, 34
28 ATMP = H(I,I)
29 ITEMP = K(I)
30 H(I,I) = H(J,J)
31 K(I) = K(J)
32 H(J,J) = ATMP
33 K(J) = ITEMP
34 CONTINUE
35 NEND = 2*(N/2)
351 DO 45 I = 1, NEND, 2
C THE STATEMENTS TO 4512 WRITE OUT THE ENERGIES AND WAVE FUNCTIONS
36 WRITE (3,37)H(I,1), H(I+1, 1+1)
37 FORMAT (1H0, 9X, 10H LAMBDA = , F11.5, 35X, 9H LAMBDA = , F11.5)
38 DO 45 J = 1, N

```

4000350  
4000360  
4000370  
4000380  
4000390  
4000400  
4000430  
4000440  
4000450  
4000460  
4000470  
4000480  
4000490  
4000500  
4000510  
4000520  
4000530  
4000540  
4000550  
4000560  
4000570  
4000580  
4000590  
4000600  
4000610  
4000620  
4000650  
4000660  
4000670  
4000680  
4000690  
4000700  
4000710  
4000720  
4000730  
4000740  
4000750  
4000760  
4000770  
4000780  
4000790  
4000800  
4000810  
4000820  
4000830  
4000840  
4000850  
4000860

```

39 INDA = K(I) 4000870
40 INDB = K(I + 1) 4000880
41 RHOA = U(J, INDA)**2 4000890
42 RHOB = U(J, INDB)**2 4000900
43 WRITE (3,44)NUM(J), U(J,INDA), NUM(J), RHGA, NUM(J), U(J, 4000910
    1 INDB), NUM(J), RHGB 4000920
44 FORMAT (14X, 3H C( , 12, 2H)= , F8.5, 7X, 4HRHO( , 12, 2H)= ,F8.5, 4000930
    117X, 3H C( , 12, 2H)= , F8.5, 7X, 4HRHO( , 12, 2H)= , F8.5) 4000940
45 CONTINUE 4000950
46 IF(N-NEND) 47, 17, 47
47 WRITE (3,48)H(N,N) 4000970
48 FORMAT (1H0, 9X, 10H LAMBDA = , F11.5) 4000980
49 DO 51 J = 1, N 4000990
50 INDA = K(N) 4001000
501 RHOA = U(J, INDA)**2 4001010
51 WRITE (3,512)NUM(J), U(J, INDA), NUM(J), RHGA 4001020
512 FORMAT (14X, 3H C( , 12, 2H)= , F8.5, 7X, 4HRHO( , 12, 2H)= ,F8.5) 4001030
17 IF(ICARUS) 9001, 52, 9001
9001 WRITE(3,9002)
9002 FORMAT(1H0, 5X, 24HTRANSFORMED ORBITALS ) 4001040
4351 DO 4045 I = 1, NEND, 2 4001050
4036 WRITE (3,4037)H(I,I), H(I+1, I+1) 4001060
4037 FORMAT (1H0, 9X, 10H LAMBDA = , F11.5, 35X, 9HLAMBDA = , F11.5) 4001070
4038 DO 4045 J = 1, N 4001080
4039 INDA = K(I) 4001090
4040 INDB = K(I + 1) 4001100
4041 RHOA = C(J, INDA)**2 4001110
4042 RHOB = C(J, INDB)**2 4001120
4043 WRITE (3,4044)NUM(J), C(J,INDA), NUM(J), RHGA, NUM(J), C( 4001130
    1J, INDB), NUM(J), RHOB 4001140
4044 FORMAT (14X, 3H C( , 12, 2H)= , F8.5, 7X, 4HRHO( , 12, 2H)= ,F8.5, 4001150
    117X, 3H C( , 12, 2H)= , F8.5, 7X, 4HRHO( , 12, 2H)= , F8.5) 4001160
4045 CONTINUE 4001170
4046 IF (N-NEND) 4047, 52, 4047 4001180
4047 WRITE (3,4048)H(N,N) 4001190
4048 FORMAT (1H0, 9X, 10H LAMBDA = , F11.5) 4001200
4049 DO 4051 J = 1, N 4001210
4050 INDA = K(N) 4001220
4501 RHOA = C(J, INDA)**2 4001230
4051 WRITE (3,4512)NUM(J), C(J, INDA), NUM(J), RHGA 4001240
4512 FORMAT (14X, 3H C( , 12, 2H)= , F8.5, 7X, 4HRHO( , 12, 2H)= ,F8.5) 4001250
52 WRITE (3,53)NR
53 FORMAT (1H0, 10X, 28HNUMBER OF 2 BY 2 ROTATIONS = , I0)
C THE STATEMENTS NUMBERED 6000 CALCULATE THE COUPLING CONSTANTS
6001 TEST = 1.00E-05
6002 IF(Q.OT.TEST) GO TO 5900
6003 IF(IH(1)) 5900, 54, 5900
5900 WRITE (3, 5901)
5901 FORMAT(1H0,7777,10X, 78HTHE COUPLING CCKSTANTS LISTED BELOW ARE BA
    1SED ON THE FOLLOWING ASSUMPTIONS, )
5902 IF(Q.LT.TEST) GO TO 5905
5903 WRITE(3, 5904) C
5904 FORMAT(15X,3HQ =, F6.2)
5905 DO 5913 I = 1,8
5906 IF(IH(1)) 5907, 5914, 5907
5907 IF(ICUPRM(1)) 5908, 5911, 5908

```

```

5908 WRITE (3, 5909) IH(1), IH(1), IC(1), ICPRM(1), ICOPRM(1)
5909 FORMAT(15X, 2HA(, 12, 49H) IS DUE TO A METHYLENE GROUP (HYDROGENS N
      1UMBERED, 13, 17H, CARBON NUMBERED, 13, 21H) ATTACHED TO CARBONS,
      213, 4H AND, 13, 1H. )
5910 GO TO 5913
5911 WRITE(3, 5912) IH(1), IH(1), IC(1), ICPRM(1)
5912 FORMAT(15X, 2HA(, 12, 46H) IS DUE TO A METHYL GROUP (HYDROGENS NUMB
      IERED, 13, 17H, CARBON NUMBERED, 13, 20H) ATTACHED TO CARBON, 13,
      21H. )
5913 CONTINUE
5914 IF(IH(1)) 5600, 6004, 5600
5600 WRITE(3, 5915) MONTH, IDAY, IYEAR
5915 FORMAT(15X, 93HMEPHYL AND METHYLENE COUPLING CONSTANTS CALCULATED
      WITH THE FORMULAE IN SUBROUTINE METHYL CN ,12,1H/,12,1H/,12,1H. )
6004 DO 6039 I = 1,2
      DO 6040 J = 1,41
6040 CHKRG(I) = 50.0
      IF(IORBIT)6028, 6005, 6028
6005 NORR = N/2 - 1 + I
      GO TO 6006
6028 NORR = IORBIT - 1 + I
6006 INDA = K(NORR)
6007 IF(I - 1) 6011, 6008, 6011
6008 WRITE(3, 6009)
6009 FORMAT(1H0, 10X, 34HPOSITIVE ION COUPLING CONSTANTS )
6010 GO TO 6013
6011 WRITE(3, 6012)
6012 FORMAT(1H0, 10X, 34HNEGATIVE ION COUPLING CONSTANTS )
6013 DO 6031 I = 1,8
6014 IF(IH(1)) 6015, 6032, 6015
6015 IA = IH(1)
6016 IB = IC(1)
6017 ID = ICPRM(1)
6018 IE = ICOPRM(1)
6019 NUM(IA) = 0
      NUM(IB) = 0
6020 AH = C(IA, INDA)
6021 AC = C(IB, INDA)
6022 ACP = C(ID, INDA)
6023 IF(IE) 6024, 6025, 6024
6024 ACUP = C(IE, INDA)
6025 CALL METHYL
6026 WRITE(3, 6027) IA, CONST
6027 FORMAT(15X, 2HA(, 12, 4H) = , F8.3, 6H GAUSS )
6031 CONTINUE
6032 IF(Q.LT.TEST) GO TO 6039
6033 DO 6039 I = 1, N
6034 IF(NUM(I)) 6035, 6039, 6035
6035 DO 6036 J = 1, N
6036 IF((ABS(U(I, INDA)**2 - CHKRG(J))) .LT. TEST) GO TO 6039
6037 CHKRG(I) = U(I, INDA)**2
6038 CONST = ABS(CHKRG(I) * Q)
      WRITE(3, 6027) I, CONST
6039 CONTINUE
54 IF(ALAM.LT.TEST) GO TO 101
WRITE (3, 433) ALAM

```

```

      IF(C.NE.0.0) WRITE (3,434) Q
      CONTINUE
400 IF(IORBIT.EQ.0) IORBIT = N/2
402 CONTINUE
404 DO 407 I = 1,N
405 INDA = K(I)
406 DO 407 J = 1,N
407 C(J,I) = U(J,INDA)
408 DO 443 IORBIT = 1,2
      WRITE(3,435) IORBIT
      DO 460 I = 1,N
      DO 460 J = 1,N
460 H(I,J) = HP(I,J)
408 DO 409 I = 1,N
409 H(I,I) = H(I,I) + 2.0*ALAM*(C(I,IORBIT)**2)
410 CALL HDIAG(H,N,C,U,NR)
411 DO 412 I = 1,N
412 K(I) = I
413 DO 423 I = 1,ISTOP
414 IST = I + 1
415 DO 423 J = IST,N
416 IF(H(I,I) - H(J,J)) 417, 423, 423
417 ATEMP = H(I,I)
418 ITEMP = K(I)
419 H(I,I) = H(J,J)
420 K(I) = K(J)
421 H(J,J) = ATEMP
422 K(J) = ITEMP
423 CONTINUE
424 DO 427 I = 1,N
425 INDA = K(I)
426 DO 427 J = 1,N
427 S(J,I) = U(J,INDA)
428 DO 442 I = 1,N
429 RC = C(I,IORBIT)**2
430 JSTOP = IORBIT - 1
431 DO 432 J = 1,JSTOP
432 RO = RO + S(I,J)**2 - C(I,J)**2
433 FORMAT(1H0,////,10X,4HMCCLACHLAN SCF SPIN DENSITIES ASSUMING, //,
1 15X, 9HLMBOA = , F6.3)
434 FORMAT(15X, 4HQ = , F6.3)
435 FORMAT(1H0, 10X, 54HUNPAIRED ELECTRON IN ORBIT NUMBER , I2)
      ACUP = ABS(Q*RO)
436 IF(Q) 437, 440, 437
437 WRITE(3, 438) I, RO , I, ACUP
438 FORMAT(15X,4HRRG(, I2,4H) = , F8.5,10X,2H(, I2,4H) = , F8.5,6H GAUSS)
439 GO TO 442
440 WRITE(3, 441) I, RO
441 FORMAT(15X, 4HRRG(, I2, 4H) = , F8.5)
442 CONTINUE
443 IORBIT = IORBIT + 1
      GO TO 101
55 WRITE (3,56)
56 FORMAT (9HIFINISHED )
57 CALL EXIT
      END

```

400128C  
400129C  
400130C  
400131C

\$1BFTC MULT

```

SUBROUTINE MULT(A,B,C,N)
  DIMENSION A(41,41), B(41,41), C(41,41)
  DO 5 I=1,N
  DO 5 J=1,N
  C(I,J) = 0.0
  DO 5 L=1,N
  C(I,J) = C(I,J) + A(I,L)*B(L,J)
  RETURN
END

```

0010  
0040  
0050  
0060  
0070  
0080  
0090  
0100

\$1BFTC XEMERR

```

SUBROUTINE XEMERR(ERRNO)
  INTEGER ERRNO
  IF(30-ERRNO) 100, 1, 100
  1 CALL EXEM(71,1)
  GO TO 1000
100 CALL EXEM(71, 0)
1000 RETURN
END

```

\$1BFTC METHYL

```

SUBROUTINE METHYL
  COMMON IE, AH, AC, ACP, ACDP, CONST, MONTH, IDAY, IYEAR
  C STATEMENTS 6-8 GIVE DATE ON WHICH FORMULAS WERE LAST CHANGED
  6 MONTH = 12
  7 IDAY = 11
  8 IYEAR = 64
  1 IF(IE) 2, 4, 2
  C STATEMENT 2 IS THE FORMULA FOR CALCULATING A METHYLENE COUPLING CONSTANT
  2 CONST = ABS(327.0 * AH**2 + 161.0 * AC * AH + 19.8 * AC**2 +
  1(5.95 * AH + 1.46 * AC) * (ACP + ACDP) - 2.78*(ACP**2 + ACDP**2))
  3 GO TO 5
  C STATEMENT 4 IS THE FORMULA FOR CALCULATING A METHYL COUPLING CONSTANT
  4 CONST = ABS(219.8 * AH**2 + 13.17 * AC**2 + 107.7 * AH * AC +
  1 3.997 * AH * ACP + 0.973 * AC * ACP - 2.78*ACP**2)
  5 RETURN
END

```

```

SUBROUTINE HDIAG (H,N,IEGEN,U,NR)
C     MINDIS, FORTRAN II DIAGONALIZATION OF A REAL SYMMETRIC MATRIX BY
C     THE JACOBI METHOD.
C     MAY 19, 1959
C     CALLING SEQUENCE FOR DIAGONALIZATION
C     CALL HDIAG H, N, IEGEN, U, NR)
C     WHERE H IS THE ARRAY TO BE DIAGONALIZED.
C     N IS THE ORDER OF THE MATRIX, H.
C     IEGEN MUST BE SET UNEQUAL TO ZERO IF ONLY EIGENVALUES ARE
C     TO BE COMPUTED.
C     IEGEN MUST BE SET EQUAL TO ZERO IF EIGENVALUES AND EIGENVECTORS
C     ARE TO BE COMPUTED.
C     U IS THE UNITARY MATRIX USED FOR FORMATION OF THE EIGENVECTORS.
C     NR IS THE NUMBER OF ROTATIONS.
C     A DIMENSION STATEMENT MUST BE INSERTED IN THE SUBROUTINE.
C     DIMENSION H(N,N), U(N,N), X(N), IQ(N)
C     THE SUBROUTINE OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE
C     RIGHT OF THE MAIN DIAGONAL. THUS, ONLY A TRIANGULAR
C     SECTION NEED BE STORED IN THE ARRAY H.
C
C     DIMENSION H(41,41), U(41,41), X(41), IQ(41)
C     IF (N-1) 1000, 1000, 9
C     9 IF (IEGEN) 15, 10, 15
C     10 DO 14 I=1,N
C     DO 14 J=1,N
C     IF(I-J)12,11,12
C     11 U(I,J)=1.0
C     GO TO 14
C     12 U(I,J)=0.0
C     14 CONTINUE
C     15 NR = 0
C     SCAN FOR LARGEST OFF DIAGONAL ELEMENT IN EACH ROW
C     X(I) CONTAINS LARGEST ELEMENT IN ITH ROW
C     IQ(I) HOLDS SECOND SUBSCRIPT DEFINING POSITION OF ELEMENT
C     17 NM1=N-1
C     DO 30 I=1,NM1
C     X(I) = 0.0
C     IPL1=I+1
C     DO 30 J=IPL1,N
C     IF ( X(I) - ABS( H(I,J) ) ) 20,20,30
C     20 X(I)=ABS(H(I,J))
C     IQ(I)=J
C     30 CONTINUE

```

0010  
0020  
0030  
0040  
0050  
0060  
0070  
0080  
0090  
0100  
0110  
0120  
0130  
0140  
0150  
0160  
0170  
0180  
0190  
0200  
0210  
0220  
0230  
0240  
0250  
0260  
0270  
0280  
0310  
0320  
0330  
0340  
0350  
0360  
0370  
0380  
0390  
0400  
0410  
0420  
0430  
0440  
0450  
0460  
0470  
0480  
0490  
0500  
0510  
0520  
0530  
0540  
0550  
0560

|     |                                                                                                                                                            |      |
|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| C   | SET INDICATOR FOR SHUT-OFF, RAP=2**-27, NR=NO. OF ROTATIONS                                                                                                | 0570 |
|     | RAP=.745058059E-04                                                                                                                                         | 0580 |
|     | HDTEST=1.0E38                                                                                                                                              | 0590 |
| C   |                                                                                                                                                            | 0600 |
| C   | FIND MAXIMUM OF X(I) S FOR PIVOT ELEMENT AND                                                                                                               | 0610 |
| C   | TEST FOR END OF PROBLEM                                                                                                                                    | 0620 |
| C   |                                                                                                                                                            | 0630 |
| 40  | DO 70 I=1, NM1                                                                                                                                             | 0640 |
|     | IF (I-1) 60, 60, 45                                                                                                                                        | 0650 |
| 45  | IF (XMAX- X(I)) 60, 70, 70                                                                                                                                 | 0660 |
| 60  | XMAX=X(I)                                                                                                                                                  | 0670 |
|     | IPIV=I                                                                                                                                                     | 0680 |
|     | JPIV=IQ(I)                                                                                                                                                 | 0690 |
| 70  | CONTINUE                                                                                                                                                   | 0700 |
| C   |                                                                                                                                                            | 0710 |
| C   | IS MAX. X(I) EQUAL TO ZERO, IF LESS THAN HDTEST, REVISE HDTEST                                                                                             | 0720 |
|     | IF (XMAX) 1000, 1000, 80                                                                                                                                   | 0730 |
| 80  | IF (HDTEST) 90, 90, 85                                                                                                                                     | 0740 |
| 85  | IF (XMAX - HDTEST) 90, 90, 148                                                                                                                             | 0750 |
| 90  | HDIMIN = ABS( H(I, I) )                                                                                                                                    | 0760 |
|     | DO 110 I=2, N                                                                                                                                              | 0770 |
|     | IF (HDIMIN- ABS( H(I, I) )) 110, 110, 100                                                                                                                  | 0780 |
| 100 | HDIMIN=ABS(H(I, I))                                                                                                                                        | 0790 |
| 110 | CONTINUE                                                                                                                                                   | 0800 |
| C   |                                                                                                                                                            | 0810 |
|     | HDTEST=HDIMIN*RAP                                                                                                                                          | 0820 |
| C   |                                                                                                                                                            | 0830 |
| C   | RETURN IF MAX. H(I, J) LESS THAN (2**-27) ABS( H(K, K) - HIN)                                                                                              | 0840 |
|     | IF (HDTEST- XMAX) 148, 1000, 1000                                                                                                                          | 0850 |
| 148 | NR = NR+1                                                                                                                                                  | 0860 |
| C   |                                                                                                                                                            | 0870 |
| C   | COMPUTE TANGENT, SINE AND COSINE, H(I, I), H(J, J)                                                                                                         | 0880 |
| 150 | TANG=SIGN(2.0, (H(IPIV, IPIV)-H(JPIV, JPIV)))*H(IPIV, JPIV)/(ABS(H(IPIV, IPIV)-H(JPIV, JPIV))+SQRT((H(IPIV, IPIV)-H(JPIV, JPIV))**2+4.0*H(IPIV, JPIV)**2)) | 0890 |
|     | COSINE=1.0/SQRT(1.0+TANG**2)                                                                                                                               | 0900 |
|     | SINE=TANG*COSINE                                                                                                                                           | 0910 |
|     | HII=H(IPIV, IPIV)                                                                                                                                          | 0920 |
|     | H(IPIV, IPIV)=COSINE**2*(HII+TANG*(2.0*H(IPIV, JPIV)+TANG*H(JPIV, JPIV)))                                                                                  | 0930 |
|     | H(JPIV, JPIV)=COSINE**2*(H(JPIV, JPIV)-TANG*(2.0*H(IPIV, JPIV)-TANG*H(IPIV, JPIV)))                                                                        | 0940 |
|     | H(IPIV, JPIV)=0.0                                                                                                                                          | 0950 |
| C   |                                                                                                                                                            | 0960 |
| C   | PSEUDO RANK THE EIGENVALUES                                                                                                                                | 0970 |
| C   | ADJUST SINE AND COS FOR COMPUTATION OF H(IK) AND U(IK)                                                                                                     | 0980 |
|     | IF (H(IPIV, IPIV) - H(JPIV, JPIV)) 152, 153, 153                                                                                                           | 0990 |
| 152 | HTEMP = H(IPIV, IPIV)                                                                                                                                      | 1000 |
|     | H(IPIV, IPIV) = H(JPIV, JPIV)                                                                                                                              | 1010 |
|     | H(JPIV, JPIV) = HTEMP                                                                                                                                      | 1020 |
| C   | RECOMPUTE SINE AND COS                                                                                                                                     | 1030 |
|     | HTEMP = SIGN(1.0, -SINE) * COSINE                                                                                                                          | 1040 |
|     | COSINE = ABS(SINE)                                                                                                                                         | 1050 |
|     | SINE = HTEMP                                                                                                                                               | 1060 |
| 153 | CONTINUE                                                                                                                                                   | 1070 |
| C   |                                                                                                                                                            | 1080 |
|     |                                                                                                                                                            | 1090 |
|     |                                                                                                                                                            | 1100 |
|     |                                                                                                                                                            | 1110 |
|     |                                                                                                                                                            | 1120 |

|     |                                                      |      |
|-----|------------------------------------------------------|------|
| C   | INSPECT THE ICS BETWEEN I+1 AND N-1 TO DETERMINE     | 1130 |
| C   | WHETHER A NEW MAXIMUM VALUE SHOULD BE COMPUTED SINCE | 1140 |
| C   | THE PRESENT MAXIMUM IS IN THE I OR J ROW.            | 1150 |
| C   |                                                      | 1160 |
|     | DO 350 I=1,NM11                                      | 1170 |
|     | IF(I-IPIV)210,350,200                                | 1180 |
| 200 | IF(I-JPIV)210,350,210                                | 1190 |
| 210 | IF(IQ(I)-IPIV)230,240,230                            | 1200 |
| 230 | IF(IQ(I)-JPIV)350,240,350                            | 1210 |
| 240 | K=IQ(I)                                              | 1220 |
| 250 | HTEMP=H(I,K)                                         | 1230 |
|     | H(I,K)=0.0                                           | 1240 |
|     | IPL1=I+1                                             | 1250 |
|     | X(I) = 0.0                                           | 1260 |
| C   |                                                      | 1270 |
| C   | SEARCH IN DEPLETED ROW FOR NEW MAXIMUM               | 1280 |
| C   |                                                      | 1290 |
|     | DO 320 J=IPL1,N                                      | 1300 |
|     | IF ( X(I)- ABS( H(I,J) ) ) 300,300,320               | 1310 |
| 300 | X(I) = ABS(H(I,J))                                   | 1320 |
|     | IQ(I)=J                                              | 1330 |
| 320 | CONTINUE                                             | 1340 |
|     | H(I,K)=HTEMP                                         | 1350 |
| 350 | CONTINUE                                             | 1360 |
| C   |                                                      | 1370 |
|     | X(IPIV) = 0.0                                        | 1380 |
|     | X(JPIV) = 0.0                                        | 1390 |
| C   |                                                      | 1400 |
| C   | CHANGE THE OTHER ELEMENTS OF H                       | 1410 |
| C   |                                                      | 1420 |
|     | DO 530 I=1,N                                         | 1430 |
| C   |                                                      | 1440 |
|     | IF(I-IPIV)370,530,420                                | 1450 |
| 370 | HTEMP = H(I,IPIV)                                    | 1460 |
|     | H(I,IPIV) = COSINE*HTEMP + SINE*H(I,JPIV)            | 1470 |
|     | IF ( X(I) - ABS( H(I,IPIV) ) ) 380,390,390           | 1480 |
| 380 | X(I) = ABS(H(I,IPIV))                                | 1490 |
|     | IQ(I) = IPIV                                         | 1500 |
| 390 | H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)           | 1510 |
|     | IF ( X(I) - ABS( H(I,JPIV) ) ) 400,530,530           | 1520 |
| 400 | X(I) = ABS(H(I,JPIV))                                | 1530 |
|     | IQ(I) = JPIV                                         | 1540 |
|     | GO TO 530                                            | 1550 |
| C   |                                                      | 1560 |
| 420 | IF(I-JPIV)430,530,480                                | 1570 |
| 430 | HTEMP = H(IPIV,I)                                    | 1580 |
|     | H(IPIV,I) = COSINE*HTEMP + SINE*H(I,JPIV)            | 1590 |
|     | IF ( X(IPIV) - ABS( H(IPIV,I) ) ) 440,450,450        | 1600 |
| 440 | X(IPIV) = ABS(H(IPIV,I))                             | 1610 |
|     | IQ(IPIV) = I                                         | 1620 |
| 450 | H(I,JPIV) = -SINE*HTEMP + COSINE*H(I,JPIV)           | 1630 |
|     | IF ( X(I) - ABS( H(I,JPIV) ) ) 400,530,530           | 1640 |
| C   |                                                      | 1650 |
| 480 | HTEMP = H(IPIV,I)                                    | 1660 |
|     | H(IPIV,I) = COSINE*HTEMP + SINE*H(JPIV,I)            | 1670 |
|     | IF ( X(IPIV) - ABS( H(IPIV,I) ) ) 490,500,500        | 1680 |

|      |                                               |      |
|------|-----------------------------------------------|------|
| 490  | X(IPIV) = ABS(H(IPIV,1))                      | 1690 |
|      | IQ(IPIV) = 1                                  | 1700 |
| 500  | H(JPIV,1) = -SINE*HTEMP + CCSINE*H(JPIV,1)    | 1710 |
|      | IF ( X(JPIV) - ABS( H(JPIV,1)) ) > 10,530,530 | 1720 |
| 510  | X(JPIV) = ABS(H(JPIV,1))                      | 1730 |
|      | IQ(JPIV) = 1                                  | 1740 |
| 530  | CONTINUE                                      | 1750 |
| C    |                                               | 1760 |
| C    | TEST FOR COMPUTATION OF EIGENVECTORS          | 1770 |
| C    |                                               | 1780 |
|      | IF(IESEN)40,540,40                            | 1790 |
| 540  | DO 550 I=1,N                                  | 1800 |
|      | HTEMP=U(I,IPIV)                               | 1810 |
|      | U(I,IPIV)=CCSINE*HTEMP+SINE*U(I,JPIV)         | 1820 |
| 550  | U(I,JPIV)=-SINE*HTEMP+CCSINE*U(I,JPIV)        | 1830 |
|      | GO TO 40                                      | 1840 |
| 1000 | ND = N - 1                                    |      |
|      | DO 1001 I = 1,ND                              |      |
|      | NST = I + 1                                   |      |
|      | DO 1001 J = NST, N                            |      |
| 1001 | H(J,I) = H(I,J)                               |      |
|      | RETURN                                        |      |
|      | END                                           |      |

APPENDIX III

CALCULATIONS ON RADICAL CATIONS

Table XXI. Huckel Molecular Orbital Coefficients Neglecting Overlap for Radical Cations

| Radical Cation<br>$C_i$  | $i$       |         |         |         |         |         |        |        |         |         |
|--------------------------|-----------|---------|---------|---------|---------|---------|--------|--------|---------|---------|
|                          | 1         | 2       | 3       | 4       | 5       | 6       | 7      | 8      | 9       | 10      |
| 2,3 dimethyl butadiene   | -.59484   | -.33853 | .08374  | .15666  |         |         |        |        |         |         |
| Isoprene                 | .62503    | .36928  | -.09430 | -.17290 | -.33518 | -.56731 |        |        |         |         |
| 1,3 cyclohexadiene       | -.35303   | -.51963 | .14187  | .29194  |         |         |        |        |         |         |
| Toluene                  | a 0       | -.5000  | -.5000  | 0       | 0       | 0       |        |        |         |         |
|                          | b .52865  | .23764  | -.31500 | -.52084 | .21281  | .30423  |        |        |         |         |
|                          |           |         |         |         |         |         |        |        |         |         |
| o-xylene                 | a -.28999 | -.56546 | -.24715 | .10992  | .15162  |         |        |        |         |         |
|                          | b .41703  | -.06327 | -.47070 | .17723  | .26290  |         |        |        |         |         |
| m-xylene                 | a 0       | .48830  | .42189  | 0       | -.16288 | -.23883 |        |        |         |         |
|                          | b -.51267 | -.24151 | .28513  | .60526  | -.12515 | -.17356 |        |        |         |         |
| p-xylene                 | b -.50000 | 0       | 0       | 0       |         |         |        |        |         |         |
|                          | a .27218  | .49607  | -.17937 | -.27125 |         |         |        |        |         |         |
| Acenaphthene             | 0         | .40673  | .21864  | -.28914 | -.37416 | 0       | .11573 | .22306 |         |         |
| Pyracene                 | .24963    | .36743  | 0       | -.10031 | -.28643 |         |        |        |         |         |
| 9 methyl anthracene      | -.44987   | -.08705 | .30418  | .20476  | -.22494 | -.29181 | .11201 | .42220 | -.07977 | -.17986 |
| 9,10 dimethyl anthracene | -.21008   | -.28564 | .10734  | .43159  | -.07822 | -.18198 |        |        |         |         |

See Fig. 12 for numbering

a Antisymmetric orbital

b Symmetric orbital

Table XXII. McLachlan<sup>a</sup> SCF Spin Densities for Radical Cations

| Radical<br>Cation           | $\rho_i$ | i       |         |         |         |         |         |         |        |         |        |
|-----------------------------|----------|---------|---------|---------|---------|---------|---------|---------|--------|---------|--------|
|                             |          | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8      | 9       | 10     |
| 2,3 dimethyl<br>butadiene   |          | .43407  | .07868  | -.01449 | .00174  |         |         |         |        |         |        |
| Isoprene                    |          | .44555  | .11289  | -.01800 | .00416  | .06006  | .39534  |         |        |         |        |
| 1,3 cyclo-<br>hexadiene     |          | .11043  | .35451  | -.02037 | .05542  |         |         |         |        |         |        |
| Toluene                     | b        | -.03704 | .27314  | .26970  | -.00988 | -.01882 | -.01994 |         |        |         |        |
|                             | c        | .62725  | -.17014 | -.07484 | .58898  | .07809  | .19564  |         |        |         |        |
| o-xylene                    | b        | .06983  | .39687  | .07006  | -.02623 | -.01052 |         |         |        |         |        |
|                             | c        | .27468  | -.33664 | .40798  | .03728  | .11670  |         |         |        |         |        |
| m-xylene                    | b        | -.98475 | .47061  | .26783  | -.39368 | .02329  | .07749  |         |        |         |        |
|                             | c        | .35716  | .04903  | .08879  | .43637  | -.02721 | -.00738 |         |        |         |        |
| p-xylene <sup>3</sup>       | c        | .27263  | -.01966 | -.01151 | -.01409 |         |         |         |        |         |        |
|                             | b        | .05564  | -.00215 | .31373  | .06639  |         |         |         |        |         |        |
| Acenaphthene                |          | -.03566 | .20813  | .03333  | .08281  | .17130  | -.02691 | -.00462 | .04035 |         |        |
| Pyracene                    |          | .05874  | .16852  | -.02771 | -.00309 | .03968  |         |         |        |         |        |
| 9 methyl<br>anthracene      |          | .27247  | -.01977 | .10014  | .03112  | .04155  | .08914  | -.00820 | .23077 | -.00485 | .03366 |
| 9,10 dimethyl<br>anthracene |          | .03572  | .08774  | -.00994 | .24281  | -.00509 | .03523  |         |        |         |        |

a) Ref. 69.  $\lambda = 1.00$ ; b) Antisymmetric orbital; c) Symmetric orbital.

See Fig. 12 for numbering.

Table XXIII. Huckel Molecular Orbital Coefficients Including Overlap  
for Radical Cations .

| Radical<br>Cation<br>$C_i$  | i         |         |         |         |         |         |        |        |         |        |
|-----------------------------|-----------|---------|---------|---------|---------|---------|--------|--------|---------|--------|
|                             | 1         | 2       | 3       | 4       | 5       | 6       | 7      | 8      | 9       | 10     |
| 2,3 dimethyl<br>butadiene   | -.55488   | -.31372 | .08391  | .14773  |         |         |        |        |         |        |
| Isoprene                    | .58433    | .34384  | -.09540 | -.16420 | -.30950 | -.52596 |        |        |         |        |
| 1,3 cyclo-<br>hexadiene     | -.32988   | -.48209 | .14135  | .27740  |         |         |        |        |         |        |
| Toluene <sup>a</sup>        | a 0       | -.44721 | -.44721 | 0       | 0       | 0       |        |        |         |        |
|                             | b -.47004 | -.20854 | .28499  | .46143  | -.21123 | -.28196 |        |        |         |        |
|                             |           |         |         |         |         |         |        |        |         |        |
| o-xylene <sup>a</sup>       | a -.25988 | -.50512 | -.21677 | .11025  | .14121  |         |        |        |         |        |
|                             | b -.36876 | .06191  | .42028  | -.17431 | -.24276 |         |        |        |         |        |
| m-xylene <sup>a</sup>       | a 0       | .43890  | .37324  | 0       | -.15987 | -.21950 |        |        |         |        |
|                             | b .45080  | .21051  | -.25420 | -.54436 | .12691  | .16369  |        |        |         |        |
| p-xylene <sup>a</sup>       | a .44721  | 0       | 0       | 0       |         |         |        |        |         |        |
|                             | b -.24464 | -.44184 | .17517  | .24902  |         |         |        |        |         |        |
| Acenaphthene                | 0         | .37835  | .20073  | -.27185 | -.34496 | 0       | .11689 | .21313 |         |        |
| Pyrene                      | .23326    | .34089  | 0       | -.09995 | -.19615 |         |        |        |         |        |
| 9 methyl<br>anthracene      | -.42953   | -.08276 | .28968  | .19439  | -.21477 | -.27715 | .10796 | .40152 | -.08052 | .17251 |
| 9,10 dimethyl<br>anthracene | .20014    | .27150  | -.10332 | -.41167 | .07874  | .17476  |        |        |         |        |

<sup>a</sup>Antisymmetric orbital

<sup>b</sup>Symmetric orbital

REFERENCES

1. C. A. Coulson, Rev. Mod. Phys. 32, 169 (1960).
2. M. H. L. Pryce, Proc. Phys. Soc. A63, 25 (1950).
3. A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. 205A, 135 (1951).
4. B. Bleaney and K. W. H. Stevens, Rep. Prog. Phys. 16, 108 (1953).
5. G. E. Pake, Paramagnetic Resonance, (Benjamin, New York, 1962) Chap. 3.
6. A. J. Stone, Proc. Roy. Soc. 271A, 424 (1963).
7. H. A. Jahn and E. Teller, Proc. Roy. Soc. A161, 220 (1937).
8. A. J. Stone, Mol. Phys. 6, 509 (1963).
9. D. E. Ingram, Free Radicals as Studied by Electron Spin Resonance,  
(Butterworth Scientific Publications, London, 1958).
10. S. I. Weissman, J. Chem. Phys. 22, 1378 (1954).
11. E. Fermi, Z. Physik 60, 320 (1930).
12. R. G. Parr, Quantum Theory of Molecular Electronic Structure, (W. A.  
Benjamin, Inc., New York, 1963) p. 42.
13. H. M. McConnell, J. Chem. Phys. 24, 632, 764 (1956).
14. H. M. McConnell and H. H. Dearman, J. Chem. Phys. 28, 51 (1958).
15. H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 28, 107 (1958).
16. J. P. Colpa and J. R. Bolton, Mol. Phys. 6, 273 (1963).
17. G. Giacometti, P. L. Nardio and M. V. Pavan, Theoret. Chim. Acta. 1,  
404 (1963).
18. A. D. McLachlan, H. H. Dearman, and A. Lefebvre, J. Chem. Phys., 33,  
65 (1960).
19. M. Karplus and G. K. Fraenkel, J. Chem. Phys., 35, 1312 (1961).
20. S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, J. Chem.  
Phys., 21, 2227 (1953).

21. T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, J. Phys. Chem., 57, 504 (1953).
22. D. Lipkin, D. E. Paul, J. Townsend, and S. I. Weissman, Science, 117, 534 (1953).
23. G. K. Fraenkel and B. Segal, Ann. Rev. Phys. Chem. 10, 435 (1959).
24. R. Bersohn, *ibid.* 11, 369 (1960).
25. S. I. Weissman, *ibid.* 12, 151 (1961).
26. A. G. Shulman, *ibid.* 13, 325 (1962).
27. D. Kivelson and C. Thomson, *ibid.* 15, 197 (1964).
28. S. A. Al'tshuler and B. N. Kozyrev, Electron Paramagnetic Resonance, (Academic Press, New York, 1964).
29. A. Carrington, Quart. Rev. 17, 67 (1963).
30. D. E. Paul, D. Lipkin, S. I. Weissman, J. Am. Chem. Soc. 78, 116 (1956).
31. T. R. Tuttle and S. I. Weissman, *ibid.* 80, 5342 (1958).
32. H. W. Bowers and F. D. Greene, J. Am. Chem. Soc. 85, 2331 (1963).
33. D. H. Geske and A. H. Maki, J. Am. Chem. Soc., 82, 2671 (1960).
34. P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, J. Am. Chem. Soc. 85, 683 (1963).
35. E. W. Stone and A. H. Maki, J. Chem. Phys. 39, 1635 (1963).
36. L. H. Piette, P. Ludwig and R. N. Adams, J. Am. Chem. Soc. 84, 4212 (1962).
37. L. H. Piette, P. Ludwig and R. N. Adams, J. Am. Chem. Soc. 83, 3909 (1961).
38. C. A. Kraus, J. Chem. Ed. 30, 83 (1953).
39. W. L. Jolly, Progress. Inorg. Chem. 1, 235 (1959).
40. M. C. R. Symons, Quart. Rev. 13, 99 (1959).
41. G. Lepoutre and M. J. Sienko, Solutions Metal-Ammoniac: Propriétés Physico-Chimiques, (W. A. Benjamin, New York, 1964).

42. C. A. Kraus, J. Am. Chem. Soc. 30, 1323 (1908).
43. S. Freed and N. Sugarman, J. Chem. Phys. 11, 354 (1943).
44. R. A. Ogg, Phys. Rev. 69, 668 (1946).
45. R. A. Ogg, J. Chem. Phys. 14, 114 (1946).
46. E. Becker, R. H. Lindquist, B. J. Alder, J. Chem. Phys. 25, 971 (1956).
47. H. M. McConnell and C. H. Holm, J. Chem. Phys. 26, 1517 (1957).
48. J. V. Acrivos and K. S. Pitzer, J. Phys. Chem. 66, 1693 (1962).
49. M. Gold, W. L. Jolly and K. S. Pitzer, J. Am. Chem. Soc. 84, 2264 (1962).
50. H. A. Laitinen and C. H. Nyman, J. Am. Chem. Soc. 70, 3002 (1948).
51. G. S. Forbes and C. E. Norton, J. Am. Chem. Soc. 48, 2278 (1926).
52. L. R. Doyle, "The ESR Absorption of Two Solid-State Paramagnetic Centers", Lawrence Radiation Laboratory Report, UCRL-9602, March 1961.
53. A. J. Birch and H. Smith, Quart. Rev. 12, 17 (1958).
54. H. Smith, Chemistry in Non-Aqueous Ionizing Solvents, Part I, Vol. 2, (Interscience Publishers, New York, 1963).
55. N. Edelstein, "A Study of the Kinetics of the Reaction  $H + O_2$  by Paramagnetic Resonance", Lawrence Radiation Laboratory Report, UCRL-10108, April 1962.
56. F. R. Jensen and L. A. Smith, J. Am. Chem. Soc. 86, 956 (1964).
57. R. G. Parr and R. S. Mulliken, J. Chem. Phys. 18, 1338 (1950).
58. C. Sandorfy, Electronic Spectra and Quantum Chemistry, (Prentice-Hall Publishing Company, Inc., Englewood Cliffs, New Jersey, 1964).
59. H. L. Strauss, T. J. Katz, and G. K. Fraenkel, J. Am. Chem. Soc. 85, 2360 (1963).
60. A. Streitwieser, Molecular Orbital Theory, (John Wiley and Sons, Inc., New York, 1961).

61. O. Sovers and W. Kauzmann, J. Chem. Phys. 38, 813 (1963); O. Sovers, Thesis, Princeton University, 1961.
62. R. Hayes, Private communication.
63. J. R. Bolton, A. Carrington, and A. D. McLachlan, Mol. Phys. 5, 31 (1962).
64. J. P. Colpa and E. DeBoer, Mol. Phys. 7, 333 (1964).
65. R. S. Mulliken, C. H. Rieke and W. G. Brown, J. Am. Chem. Soc. 63, 41 (1941).
66. C. A. Coulson and V. A. Crawford, J. Chem. Soc. 1953, 2052.
67. P. Lowdin, J. Chem. Phys. 18, 365 (1950).
68. G. Goertzel and N. Tralli, Some Mathematical Methods of Physics, (McGraw-Hill, New York, 1960) Chapter 2.
69. A. D. McLachlan, Mol. Phys. 3, 233 (1960).
70. R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. 17, 1248 (1949).
71. D. G. Chesnut, J. Chem. Phys. 29, 43 (1958).
72. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 39, 2147 (1963).
73. R. J. Myers, unpublished results.
74. J. R. Bolton, J. Chem. Phys. 41, 2455 (1964).
75. J. R. Bolton and A. Carrington, J. Chem. Phys. 4, 497 (1961).
76. A. D. McLachlan, Mol. Phys. 2, 271 (1959).
77. E. DeBoer and S. I. Weissman, J. Am. Chem. Soc. 80, 4549 (1958).
78. M. C. R. Symons, J. Chem. Soc. 48, 277 (1959).
79. C. Heller and H. M. McConnell, J. Chem. Phys. 32, 1535 (1960).
80. E. W. Stone and A. H. Maki, J. Chem. Phys. 37, 1326 (1962).
81. P. H. Rieger and G. A. Fraenkel, J. Chem. Phys. 39, 609 (1963).
82. P. Ludwig, T. Layloff and R. N. Adams, J. Am. Chem. Soc. 86, 4568 (1964).

83. T. J. Katz and H. L. Strauss, J. Chem. Phys. 32, 1873 (1960).
84. E. W. Stone and A. H. Maki, J. Chem. Phys. 38, 1999 (1963).
85. SHARE writeup J6 XYP2 MOD available from the Math and Computing Group, Lawrence Radiation Laboratory, Berkeley, California.
86. D. F. Stevens, "LRL 7040 IBSYS Users' Manual", University of California, Lawrence Radiation Laboratory, Berkeley, California. November 1964.
87. A. Almenninger, O. Bastiansen, and M. Traettenberg, Acta. Chem. Scand. 12, 1221 (1958).
88. R. G. Lawler, J. R. Bolton, G. K. Fraenkel and T. H. Brown, J. Am. Chem. Soc. 86, 520 (1964).
89. H. L. Strauss, private communication.
90. R. W. Fessenden and S. Ogawa, J. Am. Chem. Soc. 86, 3591 (1964).
91. M. T. Jones, J. Chem. Phys. 38, 2892 (1963).
92. D. C. McCain, private communication.
93. T. H. Brown and M. Karplus, J. Chem. Phys. 39, 1115 (1963).
94. P. H. Rieger and G. K. Fraenkel, J. Chem. Phys. 37, 2811 (1962).

FIGURE CAPTIONS

1. Cell and Dewar for Electrolysis in Liquid Ammonia.
2. Diagram of Cell and Dewar for Electrolysis in Liquid Ammonia.
3. Experimental ESR Spectrum of 1,3-Butadiene.
4. Calculated ESR Spectrum of 1,3-Butadiene.
5. Bond Lengths and Angles of Methylene.
6. Experimental ESR Spectrum of 2,3-Dimethyl Butadiene.
7. Calculated ESR Spectrum of 2,3-Dimethyl Butadiene.
8. Experimental ESR Spectrum of 1,3-Cyclohexadiene.
9. Calculated ESR Spectrum of 1,3-Cyclohexadiene.
10. Experimental ESR Spectrum of Isoprene. Arrows indicate anomolous lines.
11. Calculated ESR Spectrum of Isoprene.
12. Numbering System for Molecular Orbital Calculations.
13. Experimental ESR Spectrum of 1,3,5-Cycloheptatriene.
14. Calculated ESR Spectrum of 1,3,5-Cycloheptatriene.
15. Numbering System for Cycloheptatriene.
16. Experimental ESR Spectrum of Monodeuterated 1,3,5-Cycloheptatriene.
17. Calculated ESR Spectra of the Four Possible Monodeuterated 1,3,5-Cycloheptatrienes.
18. Experimental ESR Spectrum of Nitrosobenzene.
19. Calculated ESR Spectrum of Nitrosobenzene.
20. Numbering System for 2-Methylcyclohexadiene.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.