



This is to certify that the

thesis entitled

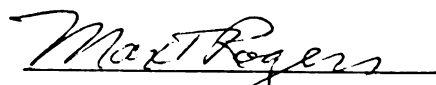
**ESR STUDIES OF ALICYCLIC
RADICALS IN ADAMANTANE**

presented by

JOHN CHOO WANG SONG

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in CHEMISTRY


Major professor

Date 9th September, 1977

ESR STUDIES OF ALICYCLIC
RADICALS IN ADAMANTANE

By

John Choo Wang Song

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1977

6-107905

ABSTRACT

ESR STUDIES OF ALICYCLIC RADICALS IN ADAMANTANE

By

John Choo Wang Song

Solid solutions of a number of alicyclic compounds have been irradiated in solid solution in adamantane. The ESR spectra of the cyclic radicals produced are mostly isotropic and have been studied over as wide a temperature range as possible. These have been analyzed and the ESR parameters interpreted and compared with other information in the literature. The electronic and geometrical structures of the radicals have been deduced, as far as possible, from the nuclear hyperfine splittings and g values. Radicals studied include hydrocarbon radicals (cyclopentyl, cyclopentenyl), substituted hydrocarbon radicals (1-hydroxycyclopentyl, 1-cyclobutanecarboxylic acid, 1-cyclopentanecarboxylic acid, 1-cyclohexanecarboxylic acid, 1-cycloheptanecarboxylic acid) and cyclic ketone radicals (2-cyclopentanonyl, 2-cycloheptanonyl). Some heterocyclic oxygen and sulfur radicals (2-tetrahydrofuranyl, 2-tetrahydrothiophenyl, 2-tetrahydropyranyl, 2-tetrahydrothiopyranyl, 1,4-dioxanyl) and nitrogen radicals (1-pyrrolidinyl, 2-piperidinyl) have also been investigated. Some radicals were also found to give isotropic ESR spectra in the pure crystalline precursor and were included in this work (1-cyclohexanecarboxylic acid radical in

cyclohexanecarboxylic acid, 1-cyclopentanecarboxylic acid radical in cyclopentanecarboxylic acid, 1-cyclobutanecarboxylic acid radical in cyclobutanecarboxylic acid).

Ring inversion in cyclic radicals can at present be studied only by ESR and one objective of this work was to obtain the barriers restricting ring inversion in cyclic radicals. Temperature dependent ESR spectra were observed for several of the radicals and values of E_a , the energy barrier restricting inversion, were evaluated for 2-tetrahydrofuranyl, 2-tetrahydrothiophenyl, 1-pyrrolidinyl, 2-tetrahydropyranyl and 1,4-dioxanyl, among the heterocyclic radicals, and also for 1-cyclopentanecarboxylic acid radical both in adamantane and in the self matrix, for 1-cyclohexanecarboxylic acid radical in the self matrix, and for 2-cycloheptanonyl radical in adamantane. The values have been compared with values reported in the literature for radicals and with the barriers to inversion in comparable undamaged cyclic molecules as determined from NMR. The effects on ring inversion of introducing one and two sp^2 centers into the rings have been determined.

A computer program has been written for determining nuclear exchange rates from nuclear hyperfine splitting parameters and line-widths. The program requires the experimental relative intensities of second-derivative Gaussian lines within the region of temperature where the ring inversion rates are comparable to the inverse of the nuclear hyperfine splittings.

TO

My Mother,

who has been critically ill
during the course of this work

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor M.T. Rogers for allowing the author freedom to pursue this subject, and for his infinite patience and guidance. The author wishes to thank sincerely Dr. R.V. Lloyd, without whose help this work could not have begun. Thanks are due to Dr. William Waller for his assistance in mathematics and computer programming. The author also wishes to extend thanks to Dr. J.Y. Lee for discussion, Dr. Henry Luke for his assistance with the X-ray unit, and Kathy and Mark Uebersax in Food Science, Michigan State University, for their assistance with γ -irradiation. Mr. Wayne Burkhardt has been instrumental in keeping the ESR spectrometer operating throughout the course of this research.

TABLE OF CONTENTS

	Page
DEDICATION	ii
ACKNOWLEDGEMENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF STRUCTURAL FORMULAE	xiii
INTRODUCTION	1
HISTORICAL SURVEY	6
I. Cyclic Organic Radicals	6
II. Rates of Conformational Change from ESR Spectroscopy	9
THEORY	16
I. Analysis of ESR Spectra	16
II. Interpretation of Hyperfine Interaction Constants	21
(a) α -Proton Hyperfine Interactions	21
(b) β -Proton Hyperfine Interactions	27
(c) γ -Proton Hyperfine Splittings	30
(d) Fluorine Hyperfine Interactions	30
(e) Chlorine Hyperfine Interactions	32
(f) Carbon-13 Hyperfine Interactions	34
(g) Nitrogen-14 Hyperfine Interactions	36
III. Exchange Rates from ESR Linewidths	39
EXPERIMENTAL	42
I. Instrumentation	42
II. Chemicals	43
III. Sample Preparation and Handling	44
IV. Irradiation	46
V. Analysis of Data	46

	Page
RESULTS	48
I. Cyclic Carboxylic Acids	48
A. Cyclopentanecarboxylic Acid in Adamantane	48
B. Cyclopentanecarboxylic Acid	58
C. Cyclohexanecarboxylic Acid	61
D. Cyclobutanecarboxylic Acid	67
E. Cycloheptanecarboxylic Acid in Adamantane	67
F. Cyclopropanecarboxylic Acid in Adamantane	71
II. Cyclic Ketones	71
A. Cyclopentanone in Adamantane	71
B. Cycloheptanone in Adamantane	73
III. Heterocyclic Oxygen Compounds	79
A. Tetrahydrofuran in Adamantane	79
B. Tetrahydropyran in Adamantane	83
C. Dioxane in Adamantane	87
IV. Heterocyclic Sulfur Compounds	92
A. Tetrahydrothiophene in Adamantane	92
B. Pentamethylene Sulfide in Adamantane	99
V. Heterocyclic Nitrogen Compounds	99
A. Pyrrolidine in Adamantane	99
B. Piperidine in Adamantane	102
VI. Other Alicyclic Compounds	107
A. Cyclopentyl Chloride in Adamantane	107
B. Cyclopentyl Bromide in Adamantane	109
C. Cyclopentane in Adamantane	109
D. Cyclopentanol in Adamantane	109
E. 1,2-Dichlorotetrafluorocyclobutene in Adamantane	109
DISCUSSION	116
I. Some Properties of the Adamantane Matrix	116
II. ESR Parameters for Cyclic Radicals	118
III. Alicyclic Carboxylic Acid Radicals	132
IV. Cyclic Ketone Radicals	137
V. Heteroalicyclic Radicals	139
(a) Five-membered Rings	139
(b) Six-membered Rings	143
VI. Other Radicals	145
(a) Cyclopentenyl and Cyclopentyl Radicals	145
(b) 1-Hydroxy-1-cyclopentyl Radical	147
(c) The Radical from 1,2-Dichlorotetrafluorocyclobutene	147
SUMMARY	149
REFERENCES	151

LIST OF TABLES

Table		Page
1	Representative α - and β -proton hyperfine interactions for aliphatic radicals in the pure liquid phase or in solution	24
2	Representative α - and β -proton hyperfine interactions for some alicyclic radicals in the pure liquid phase or in solution	25
3	Representative ^{19}F isotropic hyperfine splittings	31
4	Representative chlorine isotropic hyperfine splittings	35
5	Representative ^{13}C isotropic hyperfine splittings	37
6	Representative ^{14}N isotropic hyperfine splittings	38
7	Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 1-cyclopentanecarboxylic acid radical in adamantane	54
8	Experimental relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 1-cyclopentanecarboxylic acid radical in adamantane	55
9	Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 1-cyclohexanecarboxylic acid radical in the self-matrix	64
10	Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 1-cyclohexanecarboxylic acid radical in the self matrix	64
11	Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 2-cycloheptanonyl radical in adamantane	76
12	Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 2-cycloheptanonyl radical in adamantane	76

Table		Page
13	Spin orientations for 2-tetrahydropyranyl radical under conditions of slow and fast ring inversion	84
14	Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 2-tetrahydropyranyl radical in adamantane	88
15	Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 2-tetrahydropyranyl radical in adamantane	88
16	Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 1-pyrrolidinyl radical in adamantane	103
17	Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 2-pyrrolidinyl radical in adamantane	103
18	Some sets of ESR parameters giving calculated spectra in good agreement with the observed spectra for the radical in irradiated $\text{c-C}_4\text{F}_4\text{Cl}_2$	115
19	ESR parameters in solid matrices obtained in this work and in related literature studies	119
20	Dihedral angles for β protons for radicals in some ideal conformations	123
21	Conformation of cyclic radicals from proton hyperfine interactions	124
22	Activation energies, E_a , and frequency factors, $(1/\tau)_0$, for ring inversion in some alicyclic radicals	127
23	Kinetic parameters for ring inversion in some alicyclic compounds obtained from dynamic NMR	129

LIST OF FIGURES

Figure		Page
1	Potential energy relationships among the conformations of cyclohexane	11
2	Interaction of electron and nuclear dipoles in a magnetic field H , where r is the separation between the dipoles and θ is the angle between H and the electron-nucleus direction	18
3	Spin polarization in a π -electron radical with an α -hydrogen substituent	22
4	Dihedral angles for a π -electron radical with the odd electron in a $2p_z$ orbital on carbon, approximately planar arrangement of bonds to that carbon, and two β hydrogens (view along $C_\alpha - C_\beta$ bond showing dihedral angles θ_1, θ_2 for H_{β_1}, H_{β_2})	28
5	Hyperconjugation (left) by overlap for a β -CH ₃ three-hydrogen atom MO of the same symmetry as the odd-electron orbital of a π -electron radical resulting in net positive spin density on the β hydrogens (right)	29
6	(a) Geometry of the trifluoromethyl radical from ESR data, $a(F_\alpha) = 144$ G and $\phi \approx 19^\circ$, (b) Transfer of negative spin directly from fluorine to carbon in π -electron radicals leaving positive spin density on fluorine	33
7	ESR spectra of 1-cyclopentanecarboxylic acid radical in adamantane	49
8	Nuclear spin states for the four protons in 1-cyclopentanecarboxylic acid radical	51
9	Field positions and intensities for the lines in the ESR spectrum of 1-cyclopentanecarboxylic acid radical in adamantane (the numbers designate the spin states in Figure 8): (a) fast exchange region, (b) slow exchange region	52

Figure		Page
10	Calculated values of relative intensity $[F(\omega)]$ versus $\log(1/\tau)$ for 1-cyclopentanecarboxylic acid radical (second line relative to outer invariant line) in adamantane	56
11	Plot of $\log(1/\tau)$ versus $1/T^\circ K$ for 1-cyclopentanecarboxylic acid radical in adamantane	57
12	ESR spectra of 1-cyclopentanecarboxylic acid radical in the self matrix	59
13	Field positions and intensities of the lines in the ESR spectrum of 1-cyclopentanecarboxylic acid radical in the self matrix: (a) fast exchange region, (b) slow exchange region	60
14	ESR spectra of 1-cyclohexanecarboxylic acid radical in the self matrix	62
15	Calculated values of the relative intensities of the second line to the invariant outer line, $[F(\omega)]$, versus $\log(1/\tau)$ for 1-cyclohexanecarboxylic acid radical	65
16	Plot of $\log(1/\tau)$ versus $1/T^\circ K$ for 1-cyclohexanecarboxylic acid radical in the self matrix	66
17	ESR spectra of 1-cyclobutanecarboxylic acid radical: (a) in polycrystalline 1-cyclobutanecarboxylic acid, (b) and (c) in adamantane	68
18	ESR spectra of 1-cycloheptanecarboxylic acid radical in adamantane	69
19	ESR spectra of 2-cyclopentanonyl radical in adamantane	72
20	ESR spectra of 2-cycloheptanonyl radical in adamantane (lines indicated by inverted triangles). The remaining lines arise from a second, unidentified radical	74
21	Calculated relative intensities for the second line relative to the invariant outer line versus $\log(1/\tau)$ for 2-cycloheptanonyl radical in adamantane	77

Figure		Page
22	Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 2-cycloheptanonyl radical in adamantane	78
23	ESR spectra of 2-tetrahydrofuranyl radical in adamantane	80
24	Calculated values of relative intensities $[F(\omega)]$ versus $\log(1/\tau)$ for 2-tetrahydrofuranyl radical in adamantane	81
25	Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 2-tetrahydrofuranyl radical in adamantane	82
26	ESR spectra of 2-tetrahydropyranyl radical in adamantane	85
27	Field positions and intensities for lines in the spectrum of 2-tetrahydropyranyl radical in adamantane. The numbers refer to the nuclear spin states of Table 15	86
28	Calculated values of the relative intensities of the lines indicated by arrows in Figure 26, $F(\omega)$, versus $\log(1/\tau)$ for 2-tetrahydropyranyl radical in adamantane	89
29	Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 2-tetrahydropyranyl radical in adamantane	90
30	ESR spectra of 1,4-dioxanyl radical in adamantane	91
31	Calculated values of relative intensity, $F(\omega)$, versus $\log(1/\tau)$ for 1,4-dioxanyl radical in adamantane	93
32	Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 1,4-dioxanyl radical in adamantane	94
33	ESR spectra of 2-tetrahydrothiophenyl radical in adamantane	95
34	Calculated values of the relative intensities, $F(\omega)$, of the lines indicated by arrows in Figure 33 versus $\log(1/\tau)$ for 2-tetrahydrothiophenyl radical in adamantane	97
35	Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 2-tetrahydrothiophenyl radical in adamantane	98

Figure		Page
36	ESR spectrum of 2-tetrahydrothiopyranyl radical in adamantane at -92°C	100
37	ESR spectra of 1-pyrrolidinyl radical in adamantane. Lines used for measurement of relative intensity are indicated by arrows	101
38	Calculated values of the relative intensities, $F(\omega)$, of lines indicated by arrows in Figure 37 versus $\log(1/\tau)$ for 1-pyrrolidinyl radical in adamantane	104
39	Plot of $\log(1/\tau)$ versus $1/T^{\circ}\text{K}$ for 1-pyrrolidinyl radical in adamantane	105
40	ESR spectrum of 2-piperidinyl radical in adamantane at 25°C	106
41	ESR spectrum of cyclopentenyl radical from a sample of cyclopentyl chloride in adamantane irradiated at room temperature	108
42	ESR spectrum of cyclopentenyl radical from a sample of cyclopentyl bromide in adamantane irradiated at room temperature	108
43	ESR spectrum of cyclopentyl radical in adamantane: (a) -121°C , rapid ring inversion, (b) -187°C , slow ring inversion	110
44	ESR spectrum of the 1-hydroxycyclopentyl radical in adamantane at 25°C . The line positions of the quartet are indicated below while the remaining lines are attributed to other radicals	111
45	(a) ESR spectrum at -60°C of radical produced by irradiation of 1,2-dichlorotetrafluorocyclobutene in adamantane, (b), (c), (d) simulated spectra using the parameters of Table 18(b), (c) and (d), respectively	112

LIST OF STRUCTURAL FORMULAE

Formula		Page
I	Cyclopentenyl radical	8
II, III	Cyclohexyl radical-equivalent chair forms	12
IV, V	2-Cyclohexanonyl radical-equivalent half-chair forms	12
VI	1,4-Dioxanyl radical	14
VII	4-Piperidiny radical (protonated form)	14
VIII	Morpholiny radical	14
IX, X	Cyclohexenyl radical-equivalent forms	15
XI	1-Cyclopentanecarboxylic acid radical-envelope forms and half-chair forms	50
XII	1-Cyclohexanecarboxylic acid	62
XIII	1-Cyclobutanecarboxylic acid radical: (a) planar, (b) puckered	71
XIV	1-Cycloheptanecarboxylic acid radical: (a) chair, (b) twisted-chair	71
XV	1-Cycloheptanecarboxylic acid radical-unsymmetrical twisted-chair conformations	71
XVI	2-Cyclopentanonyl radical	74
XVII	2-Cycloheptanonyl radical-equivalent twist-chair forms	76
XVIII(a)	2-Tetrahydrofuranyl radical	84
(b)	2-Tetrahydropyranyl radical	84
XIX	2-Tetrahydrothiophenyl radical-equivalent half-chair forms	97
XX	2-Tetrahydrothiopyranyl radical-equivalent twist-chair forms	100

Formula		Page
XXI	1-Pyrrolidinyl radical-equivalent half-chair forms	100
XXII	2-Piperidinyl radical-equivalent chair forms	108
XXIII	Cyclopentyl radical	114
XXIV	1-Hydroxycyclopentyl radical	114
XXV	1,2-Dichlorotetrafluorocyclobutene-anion or cation radical	114
XXVI	1,2-Dichlorotrifluorocyclobutene radical	114
XXVII	Adamantane	117
XXVIII	2-Methyltetrahydrofuranyl radical	131
XXIX	2-Methyltetrahydrothiophenyl radical	131
XXX	Cycloheptanone ketyl	136
XXXI	1,2-Dichlorotetrafluorocyclobutene radical anion	148
XXXII	2,2,3,3,4,4-Hexafluorocyclobutanone ketyl	148

INTRODUCTION

Chemists have been interested in magnetic resonance spectroscopy because of the variety of information of chemical interest which can be obtained from it. Nuclear magnetic resonance spectroscopy (NMR) has been particularly useful for the study of diamagnetic materials while electron spin resonance spectroscopy (ESR) requires the presence of unpaired electrons and so has been important in the study of paramagnetic substances. Since the discovery of ESR by Zavoisky,¹ it has been applied by chemists to many areas of chemistry including the study of inorganic radicals,² transition metal ions,³ organic radicals,⁴ and paramagnetic systems of biological origin.⁵ Although most organic and inorganic compounds are diamagnetic, a variety of free radicals may be obtained from them by chemical oxidation or reduction, or by irradiation with UV-visible light, γ -rays, X-rays or electrons.

Chemical information which may be obtained from a study of the ESR spectra of radicals includes identification of the radical species, electronic and geometrical structures of these species, and kinetic parameters such as rates of conformational changes. From rates of exchange measured as a function of temperature it is possible to obtain energy barriers restricting conformational changes and the accompanying entropy changes.

Samples for ESR investigation may be single crystals, Polycrystalline powders, solutions or gases. ESR spectra of gases

have only been interpreted for diatomic radicals and are generally too complex to be useful. The most information is obtained from the anisotropic spectra of single crystals studied as a function of orientation since both isotropic and anisotropic nuclear hyperfine interactions are obtained.⁶⁻⁹ Polycrystalline spectra are a superposition of single crystal spectra for all orientations; while they are often difficult to interpret, methods have been developed for obtaining ESR parameters from powder spectra.²

Although most information is obtained from single crystal ESR studies, single crystals are often hard to obtain and analysis of the spectra can be complicated. Lines in solids are usually broad and line shape analysis may be difficult where there are overlapping lines and unresolved hyperfine structure. As a result, there are relatively few studies of conformational changes, which depend on line shape analysis, in single crystals or powders.

Solution ESR spectra are simpler since only isotropic hyperfine interactions are observed if the tumbling rate of the radicals is large enough to completely average out the anisotropic hyperfine interactions. Radicals are often too short-lived in solution for ESR study but a number of techniques have been developed for obtaining good spectra in solution. Fessenden and Schuler¹⁰ generated steady-state concentrations of radicals inside the ESR cavity with a pulsed high energy electron beam and obtained excellent isotropic spectra of a variety of hydrocarbon radicals. Norman and co-workers¹¹

used a rapid flow system in which two or more reactants are mixed in the ESR cavity to produce the desired radical. Kochi and Krusic¹² generated the desired steady-state concentration of radicals by UV-irradiation of a mixture of t-butyl peroxide with the precursor.

It is also possible to obtain isotropic ESR spectra of radicals in solids by various matrix isolation techniques since radical recombination is often slow in solids, particularly at low temperatures. Thus, Bennett and co-workers¹³ devised an ingenious rotating cryostat in which free radicals, generated chemically, are deposited on a cold rotating drum with an inert matrix such as camphane or xenon. By mixing the vapor of an appropriate organic halide with sodium vapor and co-depositing the mixture on the drum, a variety of radicals were made and the ESR spectra obtained. Within a certain temperature range, characteristic of the matrix, it was found that the radicals tumbled freely enough to give isotropic spectra but recombined slowly enough that good ESR spectra could be obtained. Other solid matrices which have since been used to trap radicals include germanium tetrachloride,¹⁴ sulfur hexafluoride,¹⁵ and various substances, such as urea, which form stable inclusion compounds.¹⁶

In the course of an attempt to prepare adamantyl radicals by irradiation of adamantane, Wood and Lloyd¹⁷ discovered that adamantane provided a useful solid matrix for obtaining isotropic spectra of organic free radicals. Adamantane ($C_{10}H_{18}$) is a tricyclic hydrocarbon which is not easily damaged by high energy radiation. It is a "plastic" crystal, sublimates even at room temperature, undergoes a change

of crystal structure from tetragonal to cubic at 208°C,^{18,19} and forms solid solutions with many organic compounds. When a solid solution of an appropriate precursor in adamantane is irradiated the adamantane does not appear to suffer radiation damage and the radicals obtained are those from damage to the precursor molecule. Within a temperature range from that corresponding to onset of rapid tumbling of the radicals (usually -60 to -80°C) to the temperature at which rapid decomposition of the radicals occurs, the ESR spectra of the radicals produced are isotropic. It is believed that the radicals are in substitutional rather than interstitial sites.¹⁷ Adamantane therefore provides an excellent medium for the study of conformational changes in radicals since a wide temperature range can be covered (as much as -160° to +80°C using the Varian Temperature Controller), line widths tend to be reasonably narrow (2-5G) and interactions between the radical and host crystal are small.¹⁷ Where the radicals are stable at room temperature the solid solution of precursor in adamantane can be irradiated at room temperature, otherwise irradiation is carried out at low temperatures. In either case the ESR spectra are followed as a function of temperature and at each temperature the microwave power and the modulation amplitude are varied to separate, as far as possible, lines arising from different radicals. Below the transition temperature of adamantane (208°K) the lines tend to broaden and the spectra become those of a polycrystalline material; these are sometimes difficult to interpret and have been analyzed in this work only when the anisotropic splittings are small. Studies of conformational changes in radicals trapped in an adamantane matrix have been reported²⁰⁻²²

from various laboratories but no systematic study of a series of compounds using exact lineshape analysis methods has been made. In the present investigation a series of alicyclic hydrocarbons and saturated heterocyclic compounds have been dissolved in adamantane, irradiated with X-rays or γ rays, and the ESR spectra obtained over a temperature range. Where the spectra show the effects of ring motions, detailed line shape analyses have been made and the barriers to ring inversion estimated. The results have been interpreted and compared with those for the diamagnetic precursors as well as with those for other radicals which are reported in the literature.

HISTORICAL SURVEY

I. Cyclic Organic Radicals

The ESR spectra of the alicyclic radicals, such as the cyclopentyl and cyclohexyl radicals, obtained by loss of a hydrogen atom (or other group) from the corresponding saturated hydrocarbon (or substituted hydrocarbon), were first observed after high energy irradiation of polycrystalline solids²³⁻²⁶ at 77°K but the resolution was not very good. The first high-resolution isotropic ESR spectra of the cyclic radicals from cyclopropyl through cycloheptyl were obtained by electron irradiation of both liquid and polycrystalline solid precursors.^{10,27} Cyclopentyl and cyclohexyl radicals have also been obtained by reaction of sodium with the corresponding halide²⁸ and by irradiation of the iodides.²⁹ Cyclopentyl radical has been prepared in a cyclopentane-neohexane glass³⁰ and in a solid adamantane matrix.²⁰ Cyclohexyl radical was observed in an adamantane matrix²¹ and in a clathrate-hydrate matrix.³¹

A number of hydrocarbon radicals with one or more substituents have been found to be stable and their ESR spectra observed. The series 1-hydroxycyclobutyl, 1-hydroxycyclopentyl, 1-hydroxycyclohexyl and 1-hydroxycyclooctyl was reported by Corvaja et al.³² and 3-aminocyclopentyl and 4-aminocyclohexyl by Norman et al.³³ A particularly interesting series of 1-carboxy radicals is obtained by irradiation of the salts of the cyclic acids,^{34,35} the solid acids themselves,³³⁻³⁸ or the 1,1-dicarboxylic acids;³⁹ many are stable even at room temperature.

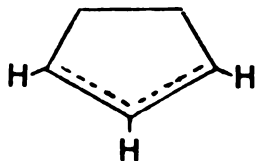
Irradiation of the cyclic halides appears to result in loss of the halogen except in the case of fluorocarbon halides which often give fluorine substituted cyclic radicals.¹⁰ A series of 1-substituted cyclopentyl radicals was prepared by U.V. irradiation of 1,1'-azobis (1-X-cyclopentanes),⁴⁰ where X = CN, CNO, CH₃, OH and H.

The heterocyclic radicals obtained by loss of a hydrogen atom (or other group) from saturated heterocyclic compounds containing oxygen, nitrogen or sulfur atoms have been extensively studied by ESR and have been produced by a variety of techniques.⁴¹ The most stable radical is usually the one with the odd electron on the carbon adjacent to the heteroatom although other radicals are sometimes also observed.

The 2-tetrahydrofuranyl radical has been obtained from tetrahydrofuran (THF) by reduction with Ti³⁺ in a chemical flow system,^{11,33} by radiolysis with high energy electrons at low temperature,⁴¹ by UV photolysis in the presence of di-t-butylperoxide (DTBP),^{42,43} and by irradiation in an adamantane matrix.²⁰ When 2-methyltetrahydrofuran is irradiated in an adamantane matrix more than one radical is obtained and their correct identification is still the subject of argument.^{44,45} Dioxane yields only the dioxanyl radical.^{11,32,33,42,43} Tetrahydrothiophene gives the 2-tetrahydrothiophenyl radical⁴³ and thiodioxane the corresponding thiodioxanyl radical.³² The nitrogen heterocycles give more complex products since there is a hydrogen, or other group, on nitrogen which may be lost or damaged in addition to the expected ring damage.⁴¹

The abstraction of a hydrogen atom with hydroxyl radical derived from the interaction of Ti^{3+} ion and hydrogen peroxide in aqueous solution in a flow system has been used to generate a large number of cyclic radicals.^{11,33,46,47} Abstraction of a hydrogen atom with t-butoxyl radical derived from the photolysis of di-t-butyl peroxide in a solution of the precursor alone, or mixed with isopentane,¹² has been widely used to produce cyclic radicals.^{32,42,43,48} Abstraction of a hydrogen atom from an alcohol or ether by photolysis in the presence of a ketone has also been used.⁴⁹ The cyclic radicals from $\text{C}_3\text{H}_5\cdot$ through $\text{C}_6\text{H}_{11}\cdot$ were prepared³⁸ by photooxidation of the carboxylic acids in the presence of Ce(IV) . Irradiation of the precursor in a solid adamantane matrix has been employed recently in a number of laboratories to produce both heterocyclic radicals^{20,44,45,50-52} and radicals from cyclic ketones.^{22,53}

In a number of cases more than one hydrogen atom is lost and a cyclic allylic-type radical results. Thus, irradiation of cyclopentane or a cyclopentyl halide in adamantane has been found in the present work to give as one of the products an allylic radical which could be I or a more complex radical containing the grouping $-\text{CH}_2-\text{CH}=\dot{\text{C}}\text{H}-\text{CH}-\text{CH}_2-$. An allylic radical formed as a radiation



I

product of cycloheptane in thiourea³⁴ and the authors suggested that it was not cycloheptenyl but a complex radical resulting from reactions of the original radiation products. Allylic radicals have been observed as products of the irradiation of unsaturated compounds and the proton hyperfine splittings for these,^{10,25,55-59} and the related cyclohexadienyl type radicals,^{61,61} are well characterized. A number of cycloalkenyl radicals were produced by γ irradiation of cyclic olefins in adamantane and the very well resolved ESR spectra provided proton hyperfine splittings for protons in various ring positions.⁶² A study of substituted cyclohexenyl radicals in adamantane has also been made.⁶³ Analogous heterocyclic radicals have been identified in γ -irradiated furoic acid and thiophene-2-carboxylic acid.⁶⁴ The oxidation of cyclic α -diketones has yielded a series of cycloalkane-semidiones,⁶⁵ and the reduction of cyclic ketones a series of cyclic ketyls,⁶⁶ in both of which the odd electron is on oxygen, and ring inversion in these has been studied by ESR.

II. Rates of Conformational Change from ESR Spectroscopy

The different possible ring conformations for common ring systems, their relative energies and the rates of interconversion between them have been extensively investigated and the subject is dealt with in modern organic chemistry textbooks⁶⁷ and monographs.⁶⁸ Barriers hindering interconversion between conformers have been determined by NMR for a number of ring compounds and the subject has been reviewed.⁶⁹ The NMR method does not give experimental barriers

when these are smaller than about 5 kcal/mole but microwave and infrared spectroscopy are useful for the study of lower barriers.⁷⁰

The ESR spectra of a number of cyclic radicals show lineshape changes with change of temperature and these can be used to determine rates of interconversion between conformers in the range 10^5 - 10^9 Hz and barriers below about 10 kcal/mole. Linewidth effects in ESR spectroscopy, and their application in studying conformation changes, have been reviewed.⁷¹⁻⁷³ A detailed study of cyclohexyl radical includes a mathematical treatment for the case of Gaussian lineshapes.²⁷ Ring motions in the 2-cyclohexanonyl radical have also been studied by ESR and details of the analysis of the spectra given.²²

The most stable form of cyclohexane itself is the chair form in which the angle strains, torsional strains and Van der Waals strains are minima. Conversion from one chair form to the equivalent one requires that the molecule go through less stable conformations and the energy relationships among these are shown in Fig. 1. The activation parameters for the chair-chair interconversion have been measured by NMR spectroscopy⁶⁹ and are $\Delta H^\ddagger = 9.1 \pm 0.5$ kcal/mole, $\Delta G^\ddagger = 10.6$ kcal/mole at -67°C , and $\Delta S^\ddagger = -5.8 \pm 0.4$ eu. In cyclohexyl radical the three atoms bonded to the ring carbon atom bearing the odd electron must be almost planar since the carbon-13 hyperfine splitting⁷⁴ is only about 41 G, the same within experimental error as observed in the planar methyl radical. The inversion barrier determined from the ESR spectra of cyclohexyl radical in a solid

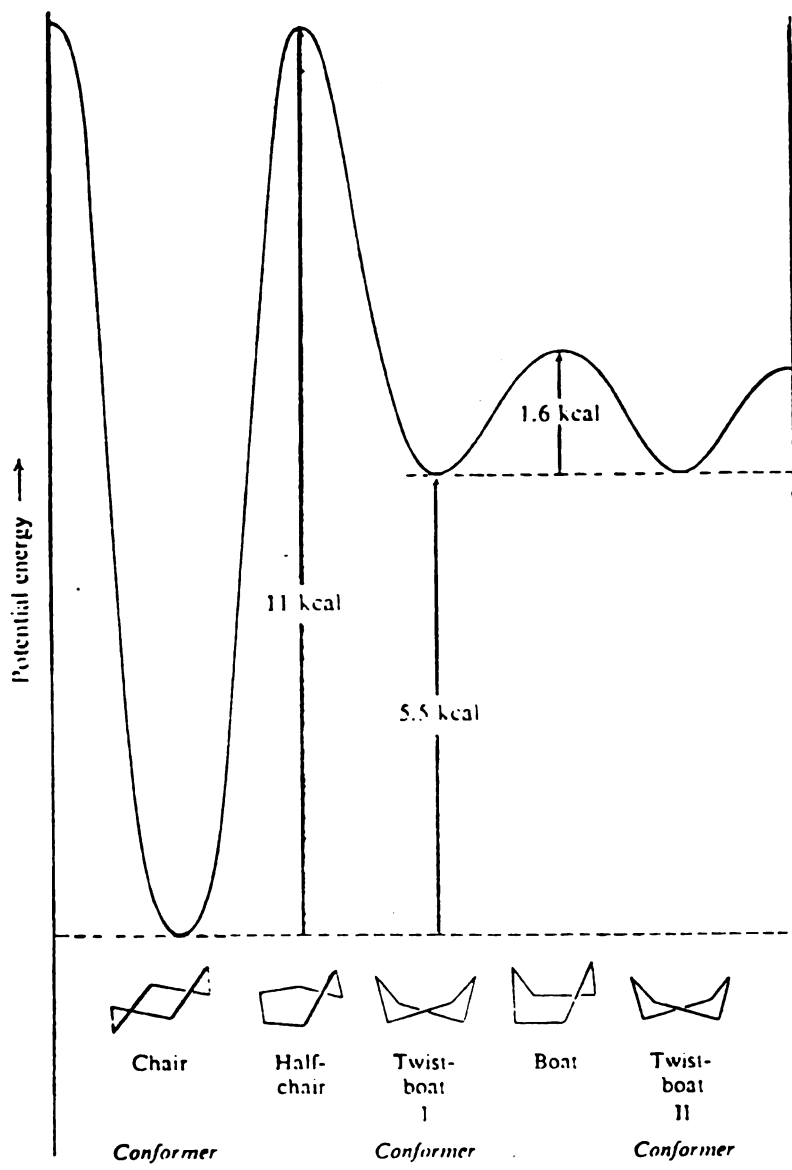
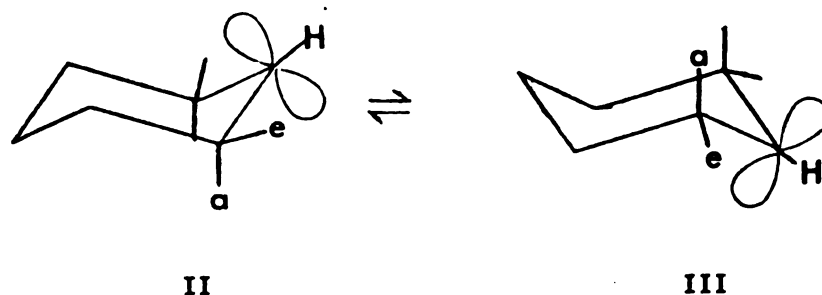
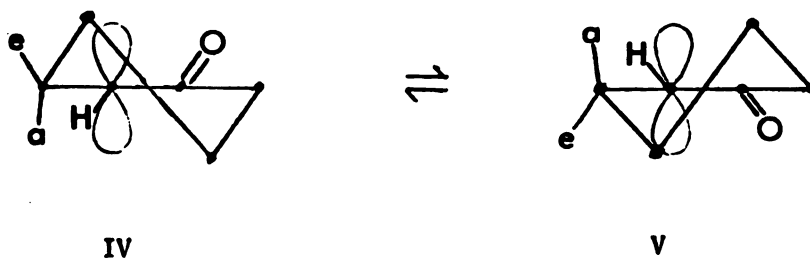


Figure 1. Potential energy relationships among the conformations of cyclohexane.

cyclohexane matrix²⁷ is $E_a = 4.9 \pm 0.5$ kcal/mole. This must correspond to a chair-chair inversion (II-III) modified by the introduction of an sp^2 center at one carbon in the ring and is considerably smaller than



the barrier in cyclohexane itself. The introduction of a second sp^2 center into the ring in 2-cyclohexanonyl radical (IV,V) lowers the observed inversion barrier further^{22,53} to 3.7 ± 0.1 kcal/mole. The



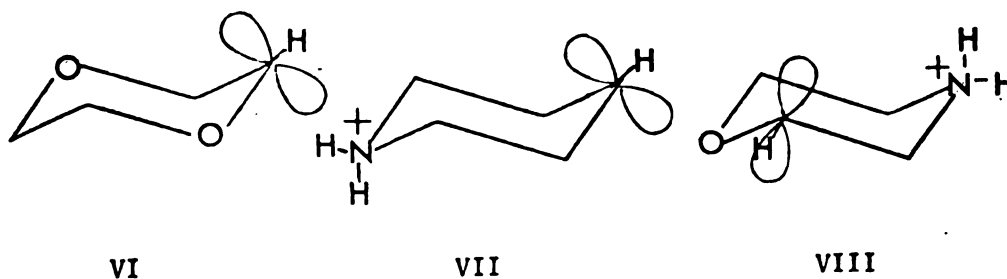
barrier for cyclohexene determined from NMR data⁶⁹ is 5.4 kcal/mole, rather similar to that found for cyclohexyl radical. The situation is quite different in the five-membered saturated ring series.

Cyclopentane undergoes rapid pseudorotation which is hindered by only

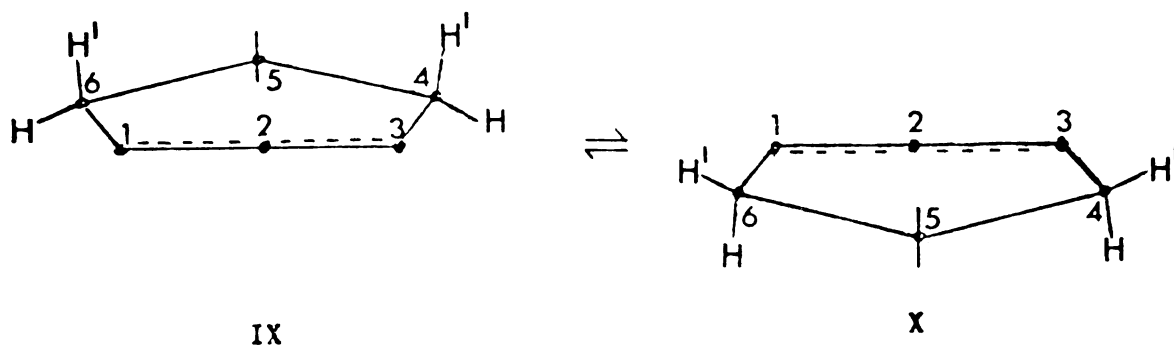
a small barrier.^{70,75,76} The barriers to interconversion between the different stable conformers of cyclopentane, tetrahydrofuran and tetrahydrothiophene are too small to measure by NMR.

When the radicals obtained by abstraction of a hydrogen atom are studied by ESR, linewidth changes are observed and from these it is possible to estimate barriers hindering interconversion between ring conformers. For cyclopentyl radical the barrier in a clathrate-hydrate matrix was estimated to be 2.7 ± 0.2 kcal/mole while in adamantane it was 2.8 ± 0.3 kcal/mole. The corresponding barriers for the 2-tetrahydrofuranyl radical in a clathrate-hydrate and in adamantane are 2.1 ± 0.2 kcal/mole and 2.4 ± 0.4 kcal/mole, respectively.^{20,31} Not many substituted radicals have been studied but 1-cyclobutane-carboxylic acid radical shows a transformation between ring conformations hindered by a barrier of 1.5 kcal/mole in the γ -irradiated sodium salt of cyclobutane-1-carboxylic acid³⁵ whereas the same radical (but possibly with a proton on the carboxyl group) in 1,1-cyclobutanecarboxylic acid shows a barrier to ring inversion of only about 0.06 kcal/mole.³⁹ The barrier to ring inversion for 1-cyclopentane carboxylic acid radical in the sodium salt of cyclopentane-1-carboxylic acid has been reported as 0.37 kcal/mole³⁵ whereas for the same radical (possibly with a proton on the carboxyl group) in 1,1-cyclopentanecarboxylic acid the value is $E_a = 3.70 \pm 0.05$ kcal/mole.³⁹ Leung and Hunt mention in a footnote to their article³⁷ on irradiated cyclohexanecarboxylic acid that the spectra indicated

an interconversion barrier of 4.9 kcal/mole for 1-cyclohexane carboxylic acid radical. Gilbert et al.³³ report barriers for ring inversion in three heterocyclic radicals obtained by Ti^{3+} reduction of precursors in aqueous acid solution, the values for the radicals from dioxane (VI), piperidine (VII) and morpholine (VIII) being 6.74 ± 0.7 kcal/mole, 7.27 ± 0.6 kcal/mole and 9.25 ± 0.9 kcal/mole, respectively. Pratt and co-workers^{22,53} have measured the barrier to inversion in 2-cyclo-



hexanonyl radical (IV,V), $\Delta H^\ddagger = 3.7 \pm 0.1$ kcal/mole, and several other substituted cyclohexanonyl radicals in adamantane. Gilbert and Trenwith³³ report a much higher value for the barrier in 2-cyclohexanonyl radical in acid solution ($\Delta H^\ddagger = 5.44 \pm 0.5$ kcal/mole). Cyclohexenyl radical⁶³ in adamantane inverts between two equivalent conformation (IX, X) and the barrier is reported as 6.81 ± 0.58 kcal/mole (C_5 is above or below the plane formed by the other five carbon atoms but H,H' differ in IX and X).⁶³



Although ring inversion barriers have now been measured for a dozen or so radicals, it is difficult to draw any conclusion from the results since some values are for the liquid phase while others are for radicals in a variety of solid matrices. Also, the analysis of the spectra to provide the inversion rates has differed and various approximation methods have been employed.

THEORY

I. Analysis of ESR Spectra⁷⁷⁻⁷⁹

The energy W of a magnetic dipole $\bar{\mu}$ in a magnetic field $\bar{H}$ is given classically by the expression

$$W = - \bar{\mu} \cdot \bar{H} = - \mu H \cos \theta \quad (1)$$

where θ is the angle between $\bar{\mu}$ and $\bar{H}$. Electron and nuclear magnetic moments are, however, quantized and the allowed energies W_i are the solutions of the Schrödinger equation

$$\hat{H} \psi_i = W_i \psi_i \quad (2)$$

where $\hat{H}$ is the spin Hamiltonian operator and ψ_i are the spin eigenfunctions.

For a single electron in a magnetic field $\bar{H}$, the spin Hamiltonian may be written $\hat{H} = g\beta\hat{S}_z$, where $\hat{S}_z$ is the operator for the z component of the spin and z is the direction of quantization H . The spin eigenfunctions for the electron are $|\alpha\rangle$ and $|\beta\rangle$ and the energy of transition between these two allowed spin states

$$\Delta\omega = g\beta H = h\nu \quad (3)$$

is the general resonance condition. The spectroscopic splitting factor g is 2.0023 for the free electron but is altered when spin-orbit coupling becomes significant; the Bohr magneton $\beta = \hbar e/2mc = 9.273 \times 10^{-21}$ erg G⁻¹.

If a magnetic nucleus of spin I interacts with an electron in an oriented radical (in a single crystal, for example), a more general spin Hamiltonian

$$\hat{H} = \beta \bar{H} \cdot \bar{g} \cdot \bar{S} + \bar{S} \cdot \bar{T} \cdot \bar{I} - g_N \beta_N \bar{H} \cdot \bar{I} \quad (4)$$

may be necessary to give experimental energy states and transitions in agreement with observations. The first term is the Zeeman energy term describing the interaction of the odd electron of spin $\bar{S}$ with the applied magnetic field, $\bar{g}$ is a second rank tensor and the Zeeman energy in a field of 3000 G is about 9 GHz. The second term describes the interaction of the odd electron with a nucleus of spin $\bar{I}$. The hyperfine interaction tensor $\bar{T}$ is a second rank tensor and hyperfine energies for protons in organic radicals usually fall in the range 0-50 G. This term may be written

$$\bar{S} \cdot \bar{T} \cdot \bar{I} = a \bar{S} \cdot \bar{I} - g \beta g_N \beta_N \left[\frac{\bar{I} \cdot \bar{S}}{r^3} - \frac{3(\bar{I} \cdot \bar{r})(\bar{S} \cdot \bar{r})}{r^5} \right], \quad (5)$$

where the isotropic hyperfine interaction a arises from the Fermi contact interaction and may be written

$$a = 8\pi/3 [g \beta g_N \beta_N |\psi_0|^2] \quad , \quad (6)$$

ψ_0 is the electron wavefunction evaluated at $r = 0$, r is the electron-nucleus distance and g_N, β_N are the nuclear g factor and nuclear magneton, respectively. The second term on the right-hand side of Equation (5) is the electron dipole-nuclear dipole interaction term which may also be written as a second rank tensor $\bar{T}'$, which must be traceless. If $\bar{T}$

is diagonalized, a is obtained from the sum of the diagonal elements

$$a = 1/3(T_{xx} + T_{yy} + T_{zz}) \quad (7)$$

and the diagonal elements of $\bar{T}'$ are given by

$$T'_{ii} = T_{ii} - a. \quad (8)$$

When the radicals are able to tumble freely the dipole-dipole interaction is averaged to zero. This may be seen by averaging the dipole-dipole energy

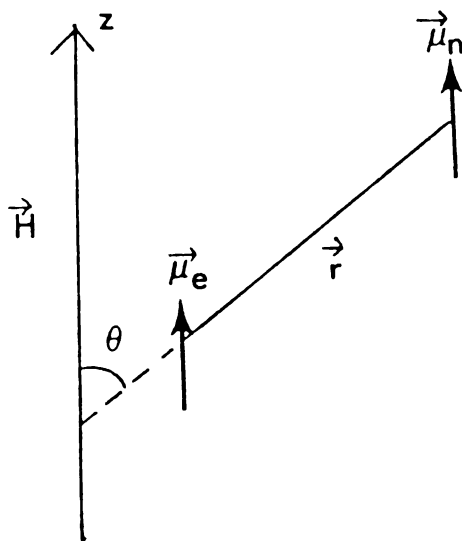


Fig. 2. Interaction of electron and nuclear dipoles in a magnetic field H , where r is the separation between the dipoles and θ is the angle between H and the electron-nucleus direction.

$$W = [(1 - 3\cos^2\theta)/r^3] \mu_{Nz}\mu_{ez} \quad (9)$$

over the surface of a sphere; then $\langle \cos^2\theta \rangle = 1/3$ and $W = 0$. Hence, in solution, or in a solid where the radicals have sufficient motional freedom, only the Fermi contact term a is found experimentally. In a single crystal the dipolar tensor $\bar{T}'$ is also found but ESR spectra must be obtained by rotating the crystal about three axes and taking spectra every few degrees.

The Fermi contact term a is related to the s character of the odd electron orbital while the dipolar tensor $\bar{T}'$ depends on the magnitude and direction of the p (or d) character of the odd electron orbital. Values of $\bar{T}'_2$ lead to estimates of the fraction of an odd electron in outer np (or nd) orbitals of atoms in molecules since $\bar{T}'_2$ for occupancy by a single electron has been computed for various atoms from the wave functions.

The final term in Equation (4) is the nuclear Zeeman term. The energy of interaction of a proton with a field of 3200 G is 5.26 G so this term is often small compared to the hyperfine interaction and may then be neglected.

Solutions of the Schrodinger equation for radicals for which the spin Hamiltonian of Equation (4) is appropriate may be rather complex. However, the second and third terms are small compared to the first term in the magnetic fields commonly employed and we may then write

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad (10)$$

where

$$\hat{H}_0 = g\beta H S_z + a S_z I_z + g_N \beta_N H I_z \quad (11)$$

is the unperturbed Hamiltonian with z the direction of quantization,
and

$$\hat{H}' = (\mathbf{a}/2)(\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) = (\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y) \mathbf{a} \quad (12)$$

is the perturbation term - the off-diagonal matrix elements.

Second-order perturbation theory then gives the approximate
wave functions ψ_n and energy states E_n :

$$\begin{aligned} \psi_n &= \phi_n - \sum_{m \neq n} \frac{\langle m | \hat{H}' | n \rangle}{\epsilon_m - \epsilon_n} \phi_m \\ E_n &= \epsilon_n + \langle n | \hat{H}' | n \rangle - \sum_{m \neq n} \frac{\langle m | \hat{H}' | n \rangle \langle n | \hat{H}' | m \rangle}{\epsilon_m - \epsilon_n} \end{aligned} \quad (13)$$

where the basis functions ϕ_m are eigenfunctions of $\hat{H}_0$ with zero-order
energy values ϵ_m .

II. Interpretation of Hyperfine Interaction Constants

Hyperfine interaction constants are directly related to the electronic and geometric structures of radicals. ESR data for a variety of organic radicals have been reported and nuclear hyperfine splittings found to depend on the type of radical (σ - or π -radical), the particular nucleus studied and its location relative to the odd-electron center(s).⁷⁷⁻⁷⁹

In the following sections present knowledge concerning radicals of the type studied in this thesis, in which the odd electron is centered on a carbon atom, is reviewed and the interpretation of hyperfine interactions discussed for α -, β - and γ -hydrogens, α - and β -fluorines, α - and β -chlorines, carbon-13 when it is the odd electron site, and nitrogen-14. The calculation of radical structures and of hyperfine interactions by CNDO/INDO methods is also reviewed briefly.

(a) α -Proton Hyperfine Interactions

A detailed study of α -proton hyperfine interactions was first made for the radical $\text{H}-\dot{\text{C}}(\text{COOH})_2$ in irradiated single crystals of malonic acid.⁸⁰ The diagonalized tensor for the α -proton was found to be $\bar{\mathbf{T}}(\text{H}_\alpha) = [\mathbf{T}_{xx}, \mathbf{T}_{yy}, \mathbf{T}_{zz}] = [-32.5, -21.7, -10.3]\text{G}$, the isotropic interaction $a(\text{H}_\alpha) = -1/3[32.5 + 21.7 + 10.3] = -21.5\text{ G}$ and the anisotropic portion of the interaction $\bar{\mathbf{T}}'(\text{H}_\alpha) = [-11.0, -0.2, +11.2]\text{G}$. Some approximate calculations⁸⁰⁻⁸² showed that the odd electron is almost 100% in a $2p_z$ orbital on the central carbon atom (the z axis is taken normal to the plane of the radical) and that the radical is planar. This type of radical is often called a π -electron radical even when not strictly planar. Although it might be expected that the isotropic

splitting would be zero, since the 2p orbital has a nodal plane through the proton, an appreciable spin density is observed and this must arise from odd electron density which has been transferred to the s orbitals of hydrogen. The sign of the interaction is negative which means that the net odd electron density on hydrogen has a spin opposite to that of the odd electron. This has been explained⁸⁰ as resulting from spin polarization and the mechanism is illustrated in Fig. 3. The spin

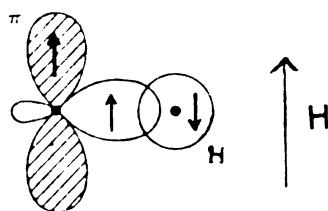


Figure 3. Spin polarization in a π -electron radical with an α -hydrogen substituent.

orientation of the odd electron in the $2p_z$ orbital on carbon is taken as positive. The electron of the bonding pair of the C-H bond which may be assigned to carbon tends to have the same spin by the Hund rule. The other bonding electron, which may be assigned to hydrogen, therefore tends to have a negative spin by the Pauli exclusion principle. The excess negative spin is small, the fraction of an odd electron on hydrogen with negative spin usually being about 23/508, or 0.04, since the observed α proton hyperfine splitting is about -23 G for many π -electron radicals and the hydrogen atom itself shows a hfs of 508 G. The abbreviation hfs = hyperfine splitting is used extensively in the literature and occasionally in this work.

McConnell⁸¹ suggested that as the fraction of odd electron ρ_{π} in the $2p_z$ orbital of a π -electron radical decreased, the α -proton hyperfine splitting $a(H_{\alpha})$ would decrease according to the semi-empirical rule:

$$a(H_{\alpha}) = Q_H \rho_{\pi} \quad , \quad (14)$$

where Q_H is a constant for a series of related radicals and is usually assigned a value of about -23 G for simple aliphatic radicals. Values of Q_H for various series of organic radicals have been estimated by combining experimental observations with MO theory.⁷⁷⁻⁷⁸ The observed α -proton hyperfine interactions for a number of cyclic radicals are given in Tables 1 and 2. The values are generally more positive than -23 G indicating that odd electron density has been transferred from carbon to the more electronegative atoms O or S. However, no single value of Q_H can be used for all these since radicals in which the $\dot{C}$ -H group lies between two oxygen atoms may even show a positive α -hydrogen splitting.

The dipolar contribution to the α -proton hyperfine splitting tensor of a $\dot{C}$ -H radical from the interaction of an odd electron in a $2p_z$ orbital of the carbon atom with the electron distribution on hydrogen has been calculated⁸² and the tensor components found to be [+15.3, -1.8, -13.9] G along the C-H direction, the perpendicular to the radical plane, and the perpendicular to C-H in the plane, respectively. These values give good agreement with the experimental values for malonic acid radical⁸⁰ and various from π -electron radicals of the same type.

Table 1. Representative α - and β -proton hyperfine interactions for aliphatic radicals in the pure liquid phase or in solution.^b

Radical	$a(H_\alpha)^a$	$a(H_\beta)$
$\cdot \text{CH}_2\text{CH}_3$	-22.38	26.87
$\cdot \text{C}(\text{CH}_3)_3$	-	22.72
$\cdot \text{CHFCH}_3$	-17.31	24.48
$\cdot \text{CF}_2\text{CH}_3$	-	13.99
$\cdot \text{CF}_2\text{H}$	(+)22.2	-
$\cdot \text{CH}_2\text{Cl}$	-22	-
$\cdot \text{CCl}_2\text{CH}_3$	-	19.7
$\cdot \text{CH}_2\text{OH}$	-17.4	-
$\cdot \text{CH}(\text{OH})\text{CH}_3$	-15.4	22.2
$\cdot \text{CH}(\text{COOH})\text{CH}_3$	-20.18	24.98
$\text{C}_2\text{H}_5 - \text{N} - \dot{\text{C}}\text{H} - \text{CH}_3$	-14.6	20.0
$\text{C}_2\text{H}_5 - \dot{\text{N}} - \text{CH}_2 - \text{CH}_3$	-14.27	36.90

^aValues are in Gauss.

^bAll values are from Reference 73 except the last two which are from References 17 and 113, respectively.

Table 2. Representative α - and β -proton hyperfine interactions for some alicyclic radicals in the pure liquid phase or in solution.

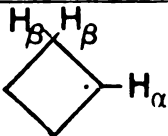
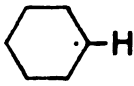
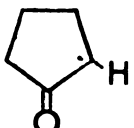
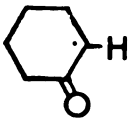
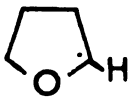
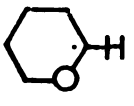
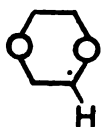
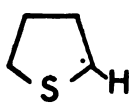
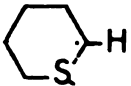
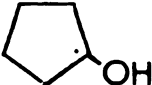
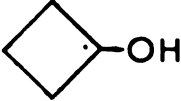
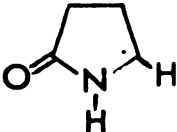
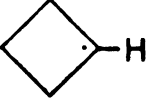
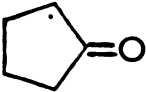
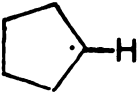
Radical	$a(H_\alpha)^a$	$a(H_\beta)$	Reference ^b
	21.20	36.66 ^c	10
	21.48	35.16	10
	21.15	23	10
	21.8	24.7	10
	18.0	38.1	33
	17.4	33.0	22(33)
	13.60	28.06	11(42,43)
	16.07	24.41	101
	17.1	23.6	42(43)
	16.9	26.1	43

Table 2 (continued)

Radical	$a(H_\alpha)$	$a(H_\beta)$	Reference
	18.5	22.5	48
		27.0	32 (40)
		27.6	32
	16.3	29.1	47
	$a(H_\gamma)$ Values		
	1.12		
	0.53		
	1.90		
	0.71		

^aValues are in Gauss.

^bWhere additional references are given in parentheses the values obtained are similar but are not given.

^cAll radicals are either planar or are inverting rapidly to give only an averaged value of $a(H_\beta)$.

(b) β -Proton Hyperfine Interactions

Isotropic β -proton hyperfine interactions, $a(H_\beta)$, in π -electron radicals have been shown to depend on the dihedral angle θ between the direction of the $2p_z$ orbital of the odd electron and the projection of the $C-H_\beta$ bond direction onto a plane normal to the $C_\alpha-C_\beta$ bond (Figure 4). Equation (15), where ρ_α is the

$$a(H_\beta) = Q_{CCH}^H \rho_\alpha \cos^2 \theta, \quad (15)$$

fraction of an odd electron in the $2p_z$ orbital of the α carbon and Q_{CCH}^H is a constant characteristic of the $\dot{C}$ -C-H system, has a quantum mechanical basis.⁷⁸ The constant Q_{CCH}^H has been assigned the value 58.6 G from a study of $CH_3\dot{C}$ radicals.¹¹

The empirical relationship⁷⁷

$$a(H_\beta) = B_o + B \cos^2 \theta \quad (16)$$

is also often used with B_o in the range 0-4 G and B in the range 40-50 G; the value of B depends on ρ_α . In this work we will use Equation 16 along with the value $B_o = 0$ so that $a(H_\beta) = B \cos^2 \theta = \rho_\alpha Q_{CCH}^H \cos^2 \theta$. When there is free rotation about the $C_\alpha-C_\beta$ bond, as is often the case with $CH_3\dot{C}$ radicals, $\langle \cos^2 \theta \rangle = 1/2$ and $a(H_\beta) = B/2$.

If the radical is not planar at the radical center, it has been found that B is altered and appears to decrease with increasing deviation from planarity.¹²¹

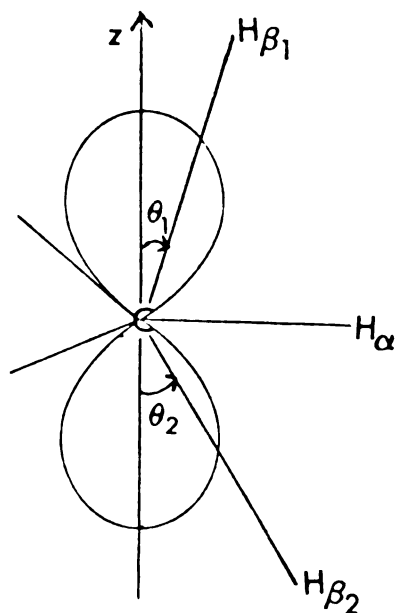


Figure 4. Dihedral angles for a π -electron radical with the odd electron in a $2p_z$ orbital on carbon, approximately planar arrangement of bonds to that carbon, and two β hydrogens (view along $C_\alpha - C_\beta$ bond showing dihedral angles θ_1 , θ_2 for H_{β_1} , H_{β_2} ; these are measured from the $\pm z$ axes as shown).

The relationship of Equation (16) has been widely employed in interpreting the β -proton hyperfine splittings of simple π -electron radicals, and of cyclic radicals, in terms of structure (Tables 1 and 2). Thus, in cyclohexyl radical with $a(H_{\beta_1}) = 39.4$ G for two β protons and $a(H_{\beta_2}) = 5.3$ G for two β protons, the values $\theta_1 = -22^\circ$, $\theta_2 = 82^\circ$ and $B_0 = 4.5$ G were obtained using Equation (16) along with the value $\frac{1}{2}B + B_0 = 24.7$ G for the β -proton splitting in isopropyl radical. The radical is presumed to be nearly planar at the odd-electron carbon because of the large α -proton hyperfine interaction $a(H_\alpha) = 21.3$ G and the small value of $a(^{13}\text{C})$ (41.3 G)⁷⁴ observed for that carbon atom. However, the values are consistent with either the chair or twisted boat forms for the radical.

It is surprising that $a(H_\beta)$, with maximum observed values as high as +50 G, may be much larger than $a(H_\alpha)$, which is typically smaller than about -24 G (in absolute magnitude). Both the high values and the positive sign have been attributed to hyperconjugation⁷⁹⁻⁸³ (Figure 5) which provides direct transfer of negative spin from the β hydrogens into the $2p_z$ orbital of the odd electron; this leaves

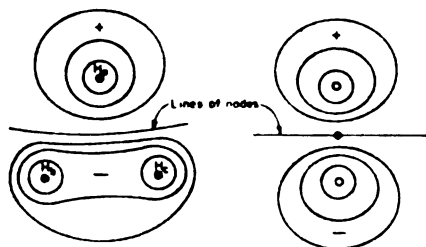


Figure 5. Hyperconjugation (left) by overlap for a β -CH₃ three-hydrogen atom MO of the same symmetry as the odd-electron orbital of a π -electron radical resulting in net positive spin density on the β hydrogens (right).

net positive spin density in the $1s$ orbitals of the β hydrogens and should be a maximum for dihedral angle $\theta = 0^\circ$ and a minimum for $\theta = 90^\circ$, as observed.

Anisotropic hyperfine interactions for β hydrogens are small since the electron nucleus distance r of Equations (5) and (9) is large.

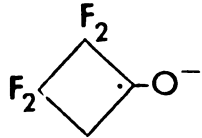
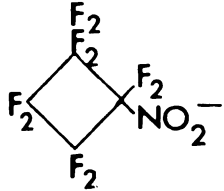
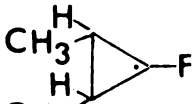
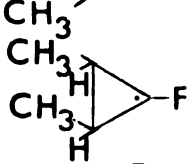
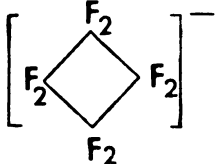
(c) γ -Proton Hyperfine Splittings

Hyperfine interactions with γ protons of cyclic radicals are small but are sometimes observed and a few values are listed in Table 2.

(d) Fluorine Hyperfine Interactions

Information concerning α - and β -fluorine hyperfine interactions has been obtained from both single crystal⁸⁴⁻⁸⁶ and solution^{10,87} studies and some typical values are given in Table 3. It has been shown that π -electron radicals with one or more α fluorine substituents are not planar^{10,88} so that the odd electron is in an sp^n hybrid orbital rather than a pure p orbital. McConnell's rule, Equation (14), therefore does not apply for isotropic α -fluorine hyperfine interactions, but instead a large positive splitting is observed which increases with the angle ϕ by which the $C-F_\alpha$ bonds are bent from the plane normal to the odd electron orbital (Figure 6a). The angle of bending is known approximately for the fluorine-substituted methyl radicals from the observed values of $a(^{13}C)$. (See Equation 17 in the next section).

Table 3. Representative ^{19}F isotropic hyperfine splittings.^a

Radical	$a(\text{F}_\alpha)^b$	$a(\text{F}_\beta)$
$\cdot \text{CF}_3$	142.4	
$\cdot \text{CHF}_2$	84.2	
$\cdot \text{CH}_2\text{F}$	64.3	
$\cdot \text{CF}_2\text{CF}_3$	84.9	11.2
$\cdot \text{CF}(\text{CF}_3)_2$	67.4	19.2
$\cdot \text{C}(\text{CF}_3)_3$	--	17.9
$\cdot \text{CFCF}_2$	84.6	10.5
$\cdot \text{CH}_3\text{OCF}_2\dot{\text{C}}\text{Cl}_2$		21.1
	82.9	$a(\text{F}_\gamma) = 37.33$
	93.3	3.06
	77.6	$a(\text{H}_\beta) = 15.6$
	74.8	$a(\text{H}_\beta) = 5.5$
	147.7	

^aAll values are from Reference 87 except the last three which are from References 116 and 117.

^bAll values are in Gauss.

These results have been interpreted^{10,84} as resulting from direct overlap of the p orbitals on fluorine with the odd-electron orbital and transfer of negative spin from fluorine to carbon by this direct mechanism. The interaction would be similar to that illustrated in Fig. 5 but with the lone pairs of the $2p_z$ orbitals of fluorine, rather than the pseudo- π orbitals of the $-\text{CH}_2$ or $-\text{CH}_3$ groups, donating negative spin density into the odd-electron orbital (Figure 6b).

Isotropic β -fluorine hyperfine splittings vary from 0-70 G and appear to depend on the dihedral angle between the odd-electron orbital and the C-F_β bond according to an empirical relationship of the type of Equation (16). If B_0 is taken to be zero and $B = 76$ G. then, for a freely rotating $\beta\text{-CF}_3$ group, $a(\text{F}_\beta) = 38$ G.

Both α - and β -fluorine hyperfine interactions show considerable anisotropy; for α -fluorines⁸⁵ $T^1[\text{F}_\alpha] \cong [120, -60, -60\text{G}]$ and for β -fluorines⁸⁶ it varies from zero to a maximum of $T^1[\text{F}_\beta] \cong [+54, -17, -17\text{G}]$. The large net positive spin density in the 2p orbitals of the β fluorines leads to an appreciable anisotropic hyperfine interaction.

e) Chlorine Hyperfine Interactions

Chlorine hyperfine interactions behave qualitatively in a manner similar to the corresponding fluorine interactions but are much smaller because of the smaller magnetic moment of chlorine. The ESR spectra of chloro-radicals are more complex because two chlorine isotopes of different magnetic moment are present, each with spin $I = 3/2$

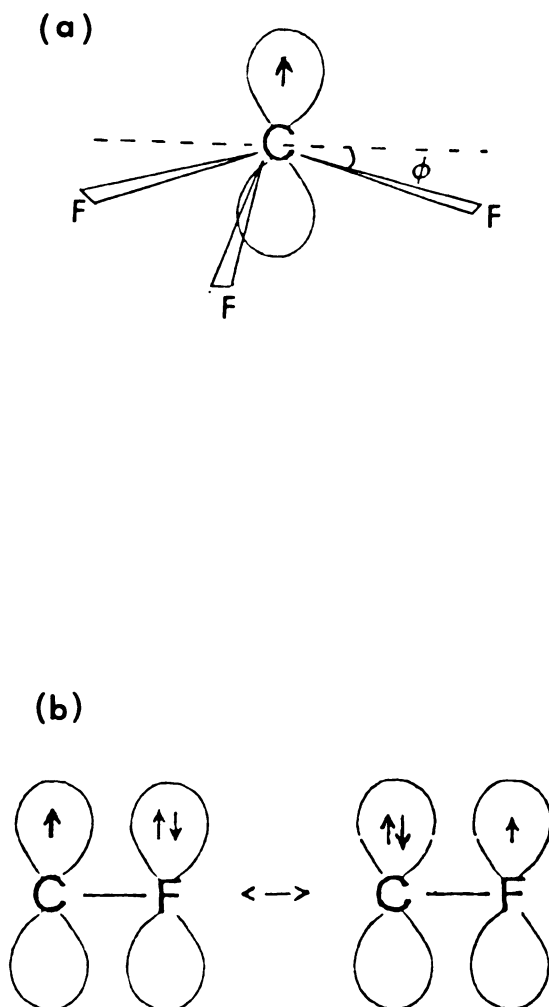


Figure 6. (a) Geometry of the trifluoromethyl radical from ESR data, $a(F_{\alpha}) = 144 \text{ G}$ and $\phi \cong 19^\circ$, (b) Transfer of negative spin directly from fluorine to carbon in π -electron radicals leaving positive spin density on fluorine.

and a large nuclear quadrupole moment. Some typical values of $a(\text{Cl}_\alpha)$ and $a(\text{Cl}_\beta)$ are given in Table 4.

f) Carbon-13 Hyperfine Interactions

If the radical precursor is enriched with ^{13}C at the radical site, or if a sufficiently good signal-to-noise ratio can be obtained so that ^{13}C -satellites are observable, the ^{13}C hyperfine splittings may be obtained for the carbon bearing the odd electron. The isotropic ^{13}C interaction for a planar π -electron radical should be zero since the carbon nucleus is at a node of the $2p_z$ electron orbital. However, even in the planar $\cdot\text{CH}_3$ radical it is found¹⁰ that $a(^{13}\text{C}) = 39 \text{ G}$. This is in excellent agreement with the value calculated by MO theory for a vibrating $\cdot\text{CH}_3$ radical.⁸⁹ When the odd-electron orbital acquires some s character and the radical becomes non-planar the Karplus-Schrader equation⁸⁹

$$a(^{13}\text{C}) = K_0 + K_2[2\tan^2\phi] \quad (17)$$

relates the observed splitting to the angle ϕ (Figure 5) by which the radical is bent from the plane. It is found theoretically⁸⁹ that for $\cdot\text{CH}_3$ $K_0 \approx 40\text{G}$, while Hartree-Fock theory gives $K_2 = a_0(^{13}\text{C}) = 1110\text{G}$ for the odd electron in a pure 2s orbital.⁹⁰ The value $a(^{13}\text{C}) = 272\text{G}$ observed¹⁰ for $\cdot\text{CF}_3$ thus leads to $\phi = 17^\circ$, not far from the value expected for sp^3 hybridization of the orbitals of carbon. The fractional s character of the odd electron orbital may be estimated from the relationship

Table 4. Representative chlorine isotropic hyperfine splittings.^a

Radical	$a(\text{Cl}_\alpha)$	$a(\text{Cl}_\beta)$
. CHCl_2	3.5	
. CH_2Cl	2.8	
. CHClCOOH	3.7	
. CClFCONH_2	3.0	
. CCl_3	6.25	
. $\text{CCl}_2\text{CF}_2\text{OCH}_3$	4.0	
. $\text{ClCH}_2\dot{\text{C}}(\text{CH}_3)_2$		19.5(³⁵ Cl) 16.2(³⁷ Cl)
. CFCI_2	10.5	
. $\text{CH}_2\text{COCH}_2\text{Cl}$		$a(\text{Cl}_\gamma) = 0.42$
. $\text{CH}(\text{CH}_2\text{Cl})_2$		$a = 14.2$
$\text{HCIC} \cdots \text{CH} \cdots \text{CH}_2$	1.2	

^a All values are from Reference 87.

$$\rho_{2s} = a(^{13}\text{C})/a_o(^{13}\text{C}). \quad (18)$$

The anisotropic ^{13}C interaction for the carbon bearing the odd electron is approximately of the form

$$\bar{\mathbf{T}}'(^{13}\text{C}) = [2B, -B, -B] \quad (19)$$

with near axial symmetry. The value $2B_o(^{13}\text{C}) = 65 \text{ G}$ has been calculated from Hartree-Fock theory for an electron in a pure 2p orbital on carbon.⁹⁰ The observed maximum anisotropic hyperfine interaction $2B(^{13}\text{C})$ may thus be used to estimate the fraction of an odd electron in the $2p_\pi$ orbital from the relationship

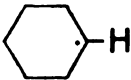
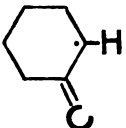
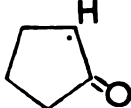
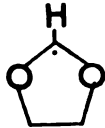
$$\rho_{2p} = 2B/2B_o. \quad (20)$$

It is found, however, that an empirical value of $2B_o(^{13}\text{C}) = 45 \text{ G}$ gives more reasonable p densities than the Hartree-Fock value which appears to be too high. Some typical ^{13}C hyperfine splittings are shown in Table 5.

g) Nitrogen-14 Hyperfine Interactions

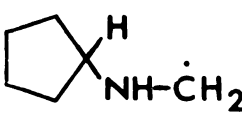
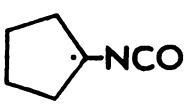
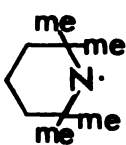
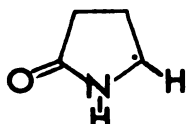
Isotropic hyperfine interactions for a nitrogen atom on which the odd electron is centered vary from 0-16 G. The nitrogen-14 nucleus with $I = 1$ has a rather small magnetic moment and an appreciable electric quadrupole moment. An α -nitrogen substituent gives a small isotropic splitting and $a(^{14}\text{N}_\alpha)$ varies from 0-6 G for these. The anisotropic hyperfine interaction for a nitrogen bearing the odd electron is of the form of Equation (19), with approximate axial

Table 5. Representative ^{13}C isotropic hyperfine splittings.

Radical	$a(^{13}\text{C}_\alpha)^a$	$a(^{13}\text{C}_\beta)$	Reference
$\cdot \text{CH}_3$	38.34		74
$\cdot \text{CHFCONH}_2$	40.0		85
$\cdot \text{CH}_2\text{F}$	54.8		10
$\cdot \text{CF}_2\text{COO}$	79		85
$\cdot \text{CF}_2\text{CONH}_2$	88.2		85
$\cdot \text{CHF}_2$	148.8		10
$\cdot \text{CF}_3$	271.6		10
	41.3		74
$\cdot \text{CH}_2\text{CH}_3$	+39.07	-13.57	74
	(+)26.6	$a(^{13}\text{CH}_2) = (-)10.7$ $a(^{13}\text{C}=\text{O}) = (-)14.0$	53
	(+)26.7		53
	(+)103.0		101

^aValues in Gauss.

Table 6. Representative ^{14}N isotropic hyperfine splittings.

Radical	$a(^{14}\text{N})^a$	Reference
$\text{CH}_3 - \dot{\text{C}}\text{H} - \text{NH}_2$	4.9	17
$\text{CH}_3 - \underset{\text{CH}_3}{\underset{ }{\text{N}}} - \dot{\text{C}}\text{H}_2$	7.03	17
	5.77	17
	4.2	17
	14.66	b
	1.75	c
$(\text{CH}_3)_2\dot{\text{N}}\text{H}^+$	19.28	113
$(\text{CH}_3)_2\dot{\text{N}}$	14.78	113

^aAll values are in Gauss; me = methyl.^bJ.R. Roberts and K.U. Ingold, J. Amer. Chem. Soc. 95, 3228 (1973).^cH. Taniguchi and Y. Kirino, J. Amer. Chem. Soc. 99, 3625 (1977).

symmetry and $2B(^{14}\text{N}) = 35 \text{ G}.$ ⁹⁰ Some typical observed nitrogen hyperfine splittings are shown in Table 6.

III. Exchange Rates from ESR Line widths

Rates of ring inversion motions may be obtained from a study of the ESR linewidths when the rate of exchange of nuclei with different hyperfine coupling constants Δa is of the same order of magnitude as $1/\Delta a$. The necessary relationship between exchange rate and linewidth is obtained by solution of the Bloch equations modified to include nuclear spin exchange. This has been done for Lorentzian lineshapes and the theory is given in several textbooks.⁷⁷⁻⁷⁹ In many cases the lines of the ESR spectrum are broadened by unresolved hyperfine interactions and this appears to be true for the cyclic radicals studied in this work. The lineshapes are then more nearly Gaussian and Ogawa and Fessenden²⁷ modified the Bloch equations by substituting an empirical term $\sigma^2 t$ for $1/T_2$. Writing $G(t) = G_1(t) + iG_2(t)$ for the total magnetization, the rate of change of the in-phase and out-of-phase components of magnetization are

$$\left(\frac{d}{dt}\right)G_1(t) = [i(\omega_0 + \omega h_1) - \sigma^2 t - 1/\tau] G_1(t) + G_2(t)/\tau \quad (21)$$

$$\left(\frac{d}{dt}\right)G_2(t) = [i(\omega_0 + \omega h_2) - \sigma^2 t - 1/\tau] G_2(t) + G_1(t)/\tau, \quad (22)$$

where τ is the correlation time for the exchange, ωh_1 and ωh_2 are the isotropic hyperfine interactions for the spins at sites 1 and 2, respectively, and $\omega_0 = \gamma_e H_0$. The solutions to Equations (21) and (22) are

$$G_1(t) = C_1 Z_1(t) + C_2 Z_2(t) \quad (23)$$

$$G_2(t) = D_1 \tilde{Z}_1(t) + D_2 \tilde{Z}_2(t), \quad (24)$$

where $Z_1(t) = \exp[-\sigma^2 t^2/2 + (n_1 + \gamma + i\Delta/2)t] \quad (25)$

$$Z_2(t) = \exp[-\sigma^2 t^2/2 + (n_1 - \gamma + i\Delta/2)t] \quad (26)$$

$$\tilde{Z}_1(t) = \exp[-\sigma^2 t^2/2 + (n_2 + \gamma - i\Delta/2)t] \quad (27)$$

$$\tilde{Z}_2(t) = \exp[-\sigma^2 t^2/2 + (n_2 - \gamma - i\Delta/2)t] \quad (28)$$

$$D_1 = \tau(\gamma + i\Delta/2)C_1 \quad (29)$$

$$D_2 = \tau(-\gamma + i\Delta/2)C_2 \quad (30)$$

$$n_1 = i(\omega_0 + h_1) - 1/\tau \quad (31)$$

$$n_2 = i(\omega_0 + h_2) - 1/\tau \quad (32)$$

$$\Delta = \omega h_2 - \omega h_1 \quad (33)$$

$$\gamma = \sqrt{T^{-2} - (\Delta/2)^2} \quad (34)$$

The line shape is given by⁹¹

$$I(\omega) = \text{Real} \left\{ \int_0^\infty G(t) e^{-i\omega t} dt \right\} \quad (35)$$

and the second derivative of the absorption, which is commonly recorded in this work, is then given by⁹²

$$\frac{\partial^2 I(\omega)}{\partial \omega^2} = -\frac{1}{\sigma^3} \text{Real} \left\{ \sum_{\pm} B_{\pm} [-\xi_{\pm} + (1 + \xi_{\pm}^2) e^{\xi_{\pm}^2/2} ((2\pi)^{1/2} [1 - \Phi(\xi_{\pm})]) \right\}, \quad (36)$$

where

$$\xi_{\pm} = Y_{\pm} + i \frac{(\omega - \omega_m)}{\sigma} \quad (37)$$

$$Y_{\pm} = [\alpha \pm \sqrt{\alpha^2 - 1}] a \quad (38)$$

$$\alpha = 2/\tau\Delta \quad (39)$$

$$a = \Delta/2\sigma \quad (40)$$

$$\Delta = \omega h_2 - \omega h_1 \quad (41)$$

$$\omega_m = (\omega h_1 + \omega h_2)/2 + \omega_0 \quad (42)$$

Certain lines of each spectrum are invariant to exchange of the nuclei and it is convenient to measure the intensities of the lines which are dependent on exchange rate relative to one of the invariant lines (for which $\tau \rightarrow \infty$). Thus, we measure

$$F(\omega) = (\partial^2 I / \partial \omega^2) / (\partial^2 I / \partial \omega^2)_{\tau \rightarrow \infty} \quad (43)$$

and use these ratios, $F(\omega)$, to obtain the correlation times, τ , using either a graph²⁷ or a computer program written by W. G. Waller.⁹² Details of the calculations and a listing of the computer program are given in Appendix I.

A measure of the barrier restricting the exchange may be obtained from measurement of τ at different temperatures. The Eyring equation

$$\begin{aligned} r = (1/\tau) &= (kT/h) \exp(-\Delta G^\ddagger/RT) \\ &= (kT/h) e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}, \end{aligned}$$

$$\text{or, } \ln(1/\tau) = \ln(kT/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/R(1/T), \quad (44)$$

permits the calculation of the enthalpy, entropy and free energy of activation for exchange from a plot of $\ln(1/\tau)$ versus $1/T^\circ\text{K}$. The rate r of a conformation change is inversely proportional to the lifetime τ of the conformation.^{67,68} The Arrhenius equation

$$\ln(1/\tau) = E_a/RT + \ln(1/\tau)_0 \quad (45)$$

is also often used in discussing conformational changes and the energy barriers E_a and frequency factors $(1/\tau)_0$ are obtained from plots of $\ln(1/\tau)$ versus reciprocal absolute temperature.

EXPERIMENTAL

I. Instrumentation

Preliminary ESR spectra were recorded using a Varian E-4 X-band spectrometer equipped with an E-257 Variable Temperature Accessory.

More precise measurements were carried out with a Varian V-4502 X-band spectrometer system including V-4560 100kHz Field Modulation and Control Unit, Mark I Fieldial regulation, 12" electromagnet, V-4531 Multi-purpose rectangular cavity, and V-4540 Variable Temperature Accessory.

Both first and second derivatives of the absorption were recorded, the latter by an arrangement for detecting at double the modulation frequency of 40 Hz. Second derivative curves are more convenient to analyze because of their resemblance to the absorption curve and were used in most cases.

Sample temperatures were measured by placing a copper-constantan thermocouple in the cavity close to the sample and were read on a Trendicator 400 Electronic Temperature Meter. The error in temperatures measured in this way is estimated to be $\pm 2^{\circ}\text{C}$.

Magnetic field calibration was carried out with a small NMR spectrometer using a doped water sample. The tunable marginal oscillator covered the range 12.2-21.2 MHz and proton markers were placed on the ESR spectra at various field intervals. The proton resonance frequencies were read directly on a Monsanto Model 1515A Counter-Timer to ± 1 kHz. All spectra were recorded on 11"x17" chart paper using a Moseley Autograf Model 7000A X-Y recorder with the magnetic field increasing from left to right. In this thesis all are second-derivative spectra.

Klystron frequencies were measured directly to ± 0.1 MHz with a Hewlett-Packard Model 5245L Electronic Counter equipped with a Hewlett-Packard Model 5255A Frequency Converter covering the range 3-12.4 GHz.

Periodic checks on the performance of the spectrometer system and on the precision of measurement were made with standard Varian samples having the values $g = 2.0028$ (strong pitch) and $g = 2.0037$ (DPPH powder).

II. Chemicals

Adamantane, $C_{10}H_{16}$, purissimum (99+%) from Aldrich Chemical Co., Milwaukee, Wis., was used as a matrix in most of the ESR work and impurities which might give interfering radicals must be removed as far as possible.¹⁷ For this purpose the adamantane was dissolved in spectrograde n-heptane (Mallinckrodt Chemical Works, St. Louis, Mo.), treated with activated charcoal (Nuchar-C 190-N, West Virginia Pulp and Paper Co., New York, N. Y.), filtered, and n-heptane removed with a vacuum pump until most of the adamantane had crystallized out. The mother liquor was removed by filtration and the white crystalline powder dried. This process was repeated three or more times until a sample X-irradiated at room temperature gave very little background signal even at high microwave power. Such weak background signals become negligible relative to the stronger signals obtainable with most of the radicals studied even at much lower microwave power. Deuterioadamantane, $C_{10}D_{16}$ (Merck of Canada, Ltd., Montreal, Canada)

was used as a matrix in certain experiments to reduce line broadening. It was used as received.

Most of the radical precursors used were obtained from the Aldrich Chemical Co. These include cycloheptanone, cyclobutanone, cyclobutanecarboxylic acid, cyclohexanecarboxylic acid, cyclopentanecarboxylic acid, cyclopentanol, cyclopentylamine, cyclopentyl chloride, cyclopentyl bromide, tetrahydrothiophene, pentamethylene sulfide, tetrahydropyran, pyrrole and pyrrolidine. Cyclopropanecarboxylic acid was from Pfaltz and Bauer, Stamford, Conn.) and 1,2-dichlorotetrafluorocyclobutene from PCR, Inc., Gainesville, Florida.

III. Sample Preparation and Handling

Radical precursors were incorporated into adamantane by dissolving ~0.5 g purified adamantane in the liquid precursor, with the aid of heat where necessary, then removing excess liquid by evaporation. Where the liquids were not very volatile, the solution was rapidly frozen with liquid nitrogen to incorporate as much precursor as possible into the solid and the solid then allowed to warm to room temperature. Excess liquid was removed by suction filtration and the crystals dried under vacuum.

The white, fluffy powders were made into a cylindrical pellet 3 mm in diameter and ~1 cm in length in a KBr pellet press using a special tungsten carbide brushing (Strehlinger Co., Lansing, Mich.) and a hardened steel plunger which had been chrome plated. Where necessary the oxygen trapped in the pellet was removed by pressing the pellet while evacuating the die.

Solid precursors were cosublimed with adamantane, which sometimes results in the precursor molecules being incorporated into the adamantane,¹⁷ or were melted together with adamantane. These methods did not lead to the observation of any suitable ESR signals with any of the solid precursors tried in this work and it is assumed that none were incorporated into the adamantane.

In several cases pure crystalline solids were irradiated ("neat" samples). Where these were liquids at room temperature, they were sealed in quartz tubes (3 mm ID, 4 mm OD) after dissolved oxygen had been removed by repeated freeze-pump-thaw cycles.

Samples which had been irradiated at room temperature were transferred directly to the ESR cavity and spectra taken at room temperature. The sample temperature was then slowly lowered using the variable temperature control system and spectra were taken at intervals down to the lowest accessible temperature (about -190°C). Samples irradiated at 77°K were transferred to the cold ESR cavity as rapidly as possible to prevent warmup and initial spectra taken at as low a temperature as feasible, usually close to 77°K. The sample was then warmed slowly and spectral changes followed as a function of temperature. In most cases several cycles of warming and cooling were followed by ESR in order to separate reversible from irreversible changes and to aid in analyzing the often very complex changes occurring.

When it appeared from the spectra that more than one radical was present, power saturation studies were carried out. In many cases the lines of some radicals saturate more readily than

those of others and the changes in the spectrum with microwave power level assist in assigning the spectra.

IV. Irradiation

X-irradiations were carried out with a GE XRD-1 X-ray generator operating at 20-40 kV and 10 ma with a chromium target tube.

γ -Irradiations used the ^{60}Co gamma irradiator housed in the Food and Human Nutrition Building. Where the radicals studied were stable in the solid matrix at room temperature, X-irradiation at room temperature for 30-120 minutes was normally used. Where the radicals studied were not stable at room temperature, or where neat liquids were to be irradiated in the polycrystalline state, γ irradiation was carried out at 77°K. Small vials (1 dram) or sealed quartz tubes (3 mm ID) were placed in a Dewar filled with liquid nitrogen and irradiated for 3-5 hours at a dose rate of about 0.3 Mrad/hr (3×10^7 erg gm⁻¹ hr⁻¹).

V. Analysis of Data

Radical g values were calculated from the measured magnetic field H_0 at the center of the spectrum and the measured Klystron frequency ν using the equation

$$g = h\nu/\beta H_0$$

with $\beta = 9.27 \times 10^{-21}$ erg gauss⁻¹ and $h = 6.6262 \times 10^{-27}$ erg sec.

Magnetic fields were computed from the observed proton magnetic resonance frequencies using the relation

$$H(\text{gauss}) = 2\pi\nu/\gamma_p = 2.348682 \times 10^{-4} \nu(\text{Hz})$$

based on the value $\gamma_p = 2.6751965 \times 10^4 \text{ rad sec}^{-1} \text{ gauss}^{-1}$ for the magnetogyric ratio of the proton.

Correlation times for ring inversion τ were calculated from the intensities of those lines which varied with temperature, relative to those (usually the outer ones) which did not, by use of the computer program ESREX4 written for the CDC-6500 computer (see Section III of THEORY, above, and Appendix I of this thesis). The data input to this program include the measured Klystron frequency $\omega_0 = 2\pi\nu_0$ and the hyperfine coupling constants $\omega h_1, \omega h_2 \text{ RAD/SEC....}$ for the spectral lines employed, along with their relative peak heights in second-derivative presentation. Measured hyperfine splittings ΔG were converted to frequency units RAD/SEC for the program using the measured g value and the relationship

$$\Delta \text{ RAD/SEC} = (2\pi\beta/h) \Delta (g/g_e) ,$$

where $g_e = 2.00232$ is the g value of the free electron.

The program ESRCON1, which simulates isotropic ESR spectra, was also used in this work. Estimated hyperfine interactions for up to five different groups of nuclei may be input and the simulated ESR spectrum displayed on a Calcomp plotter. Some preliminary spectral simulations were done using the Tektronix 4010 during the early stages of this research.

RESULTS

I. Cyclic Carboxylic AcidsA. Cyclopentanecarboxylic Acid in Adamantane

A solid solution of cyclopentanecarboxylic acid (CPCA) in adamantane was X-irradiated at room temperature. The ESR spectrum at 25°C [Figure 7(a)] is a quintet with relative line intensities approximately 1:4:6:4:1 and $a(H_{\beta}) = 31.5$ G. On lowering the temperature the intensities of the inner lines change relative to the two outer lines, which are invariant in intensity. Selective broadening of lines 2 and 4 as the temperature is lowered [Fig. 7(b) - (e)] corresponds to intermediate rates of exchange. At -109°C the second and fourth lines have disappeared and a triplet with relative intensities 1:4:1 remains [Figure 7(e)]. On cooling further the lines broaden and seven-line spectra [Fig. 7(f) - (h)] appear with $a(H_{\beta_1}) = 22.1$ G and $a(H_{\beta_2}) = 41.0$ G; these are presumably powder spectra since the lines are broad, as would be expected when the tumbling rate of the radicals becomes small and the adamantane matrix changes to its low-temperature structure. The resolution remains good even at the lowest temperatures since β -proton splittings are nearly isotropic.

These spectra are similar qualitatively to those observed for cyclohexyl radical, and first interpreted in detail by Ogawa and Fessenden,²⁷ and are accounted for it the only stable radical produced is the 1-cyclopentanecarboxylic acid radical (XI) with two "axial" and two "Equatorial" β protons and either the "envelope" or "half-chair" conformation (XI, top and bottom). Then, at low temperature where ring inversion is slow, the seven-line spectrum corresponding

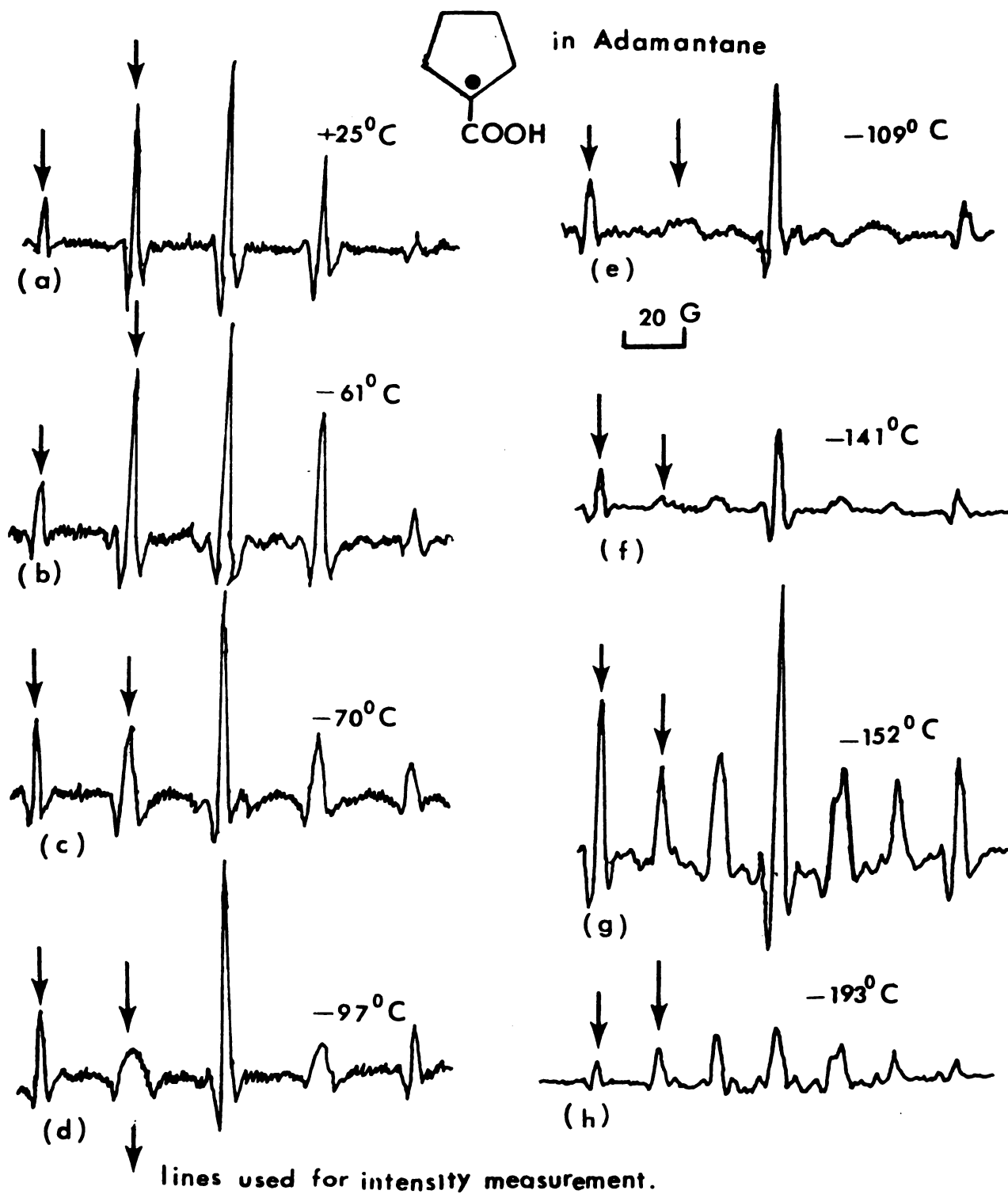
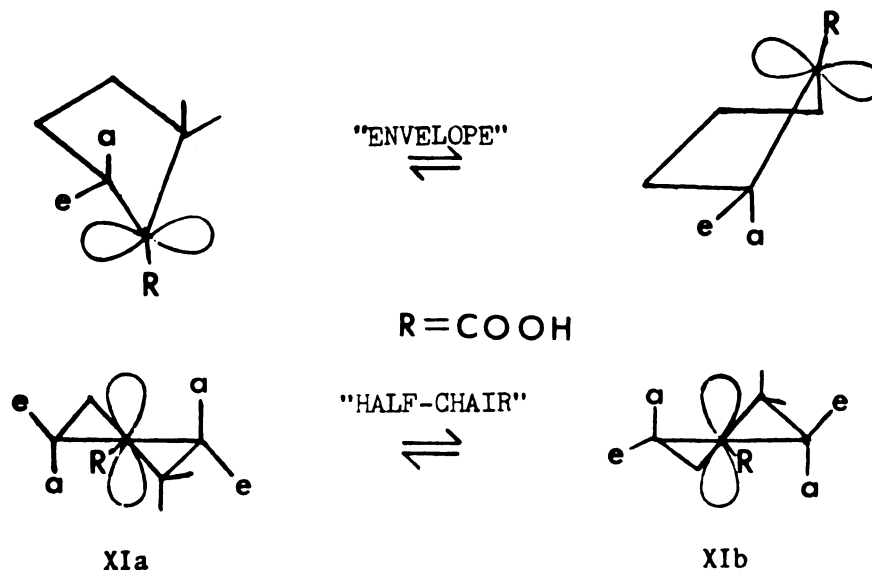
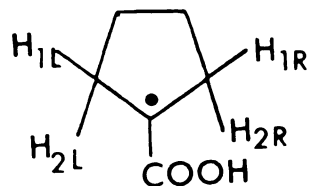


Figure 7. ESR spectra of 1-cyclopentanecarboxylic acid radical in adamantane.



to a partially overlapping triplet of triplets with $a(H_{\beta_1}) = 22.1$ G and $a(H_{\beta_2}) = 41.0$ G, is obtained. On warming to room temperature, ring inversion becomes rapid and the four β protons become equivalent giving a 1:4:6:4:1 quintet with $\langle a(H_{\beta}) \rangle = 1/2 [a(H_{\beta_1}) + a(H_{\beta_2})] = 31.5$ G. At intermediate temperatures exchange of protons β_1 and β_2 by ring inversion leads to a mixing of spin states and changes in intensity of the three inner lines relative to the two outer lines. The nuclear spin orientations possible for four protons are shown in Figure 8 and the lines in the ESR spectrum when an odd electron interacts with two protons with $a = 21$ G and two with $a = 42$ G are shown in Figure 9. The spectrum of Figure 7(h) corresponds to the stick diagram of Figure 9(b) with seven lines with relative intensities 1:2:3:4:3:2:1. The diagram of Figure 9(a), corresponding to rapid exchange of the two pairs of protons, shows how such rapid exchange leads to a narrow five-line quintet with $\langle a \rangle = (21+42)/2 = 31.5$ G and relative intensities 1:4:6:4:1. In the intermediate portion of Figure 9 the dotted lines



	L R*	L R	L R	L R
	1**	2	3	4
H ₁	- -	- -	- -	- -
H ₂	- -	- +	+ -	+ +
	5	6	7	8
H ₁	- +	- +	- +	- +
H ₂	- -	- +	+ -	+ +
	9	10	11	12
H ₁	+ -	+ -	+ -	+ -
H ₂	- -	- +	+ -	+ +
	13	14	15	16
H ₁	+ +	+ +	+ +	+ +
H ₂	- -	- +	+ -	+ +

* L and R indicate left and right hand hydrogens on the diagram at the top.

**There are sixteen combinations of the nuclear spin quantum numbers for the four β protons, labeled 1-16 above; $m_I = \pm 1/2$ are designated by + or -.

Figure 8. Nuclear spin orientations of the four β protons of 1-cyclopentanecarboxylic acid radical.

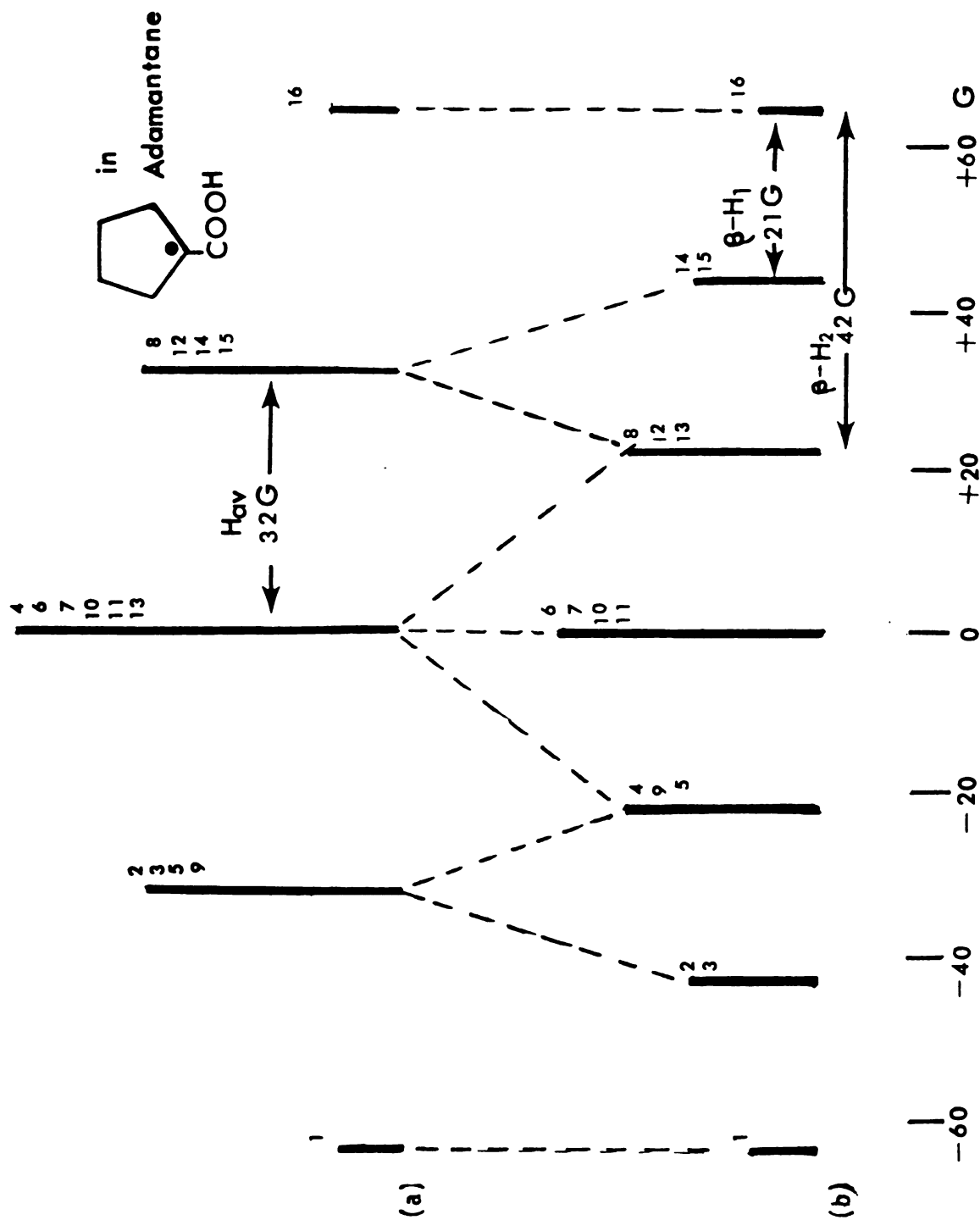


Figure 9. Field positions and intensities for the lines in the ESR spectrum of 1-cyclopentanecarboxylic acid radical in adamantane (the numbers designate the spin orientations in Figure 8): (a) fast exchange region, (b) slow exchange region.

indicate that the line intensities are changing with exchange rate but with the two outer lines invariant in intensity. In this intermediate region relative intensities of inner to outer lines may be used to obtain correlation times τ according to Equation (43) using the theory of Section III.

Values of $\log(1/\tau)$ as a function of the ratio of the intensity of line 2 to line 1 for 1-cyclopentanecarboxylic acid radical (indicated by arrows in Figure 7) were computed by use of the computer program ESREX4 (Appendix B) and are given in Table 7. The experimental values of the relative intensity of line 2 to line 1 ($F(\omega)$) are shown in Table 8 at various temperatures and are plotted versus $\log(1/\tau)$ in Figure 10. Values of $\log(1/\tau)$ at various temperatures are plotted versus $1/T^\circ\text{K}$ in Figure 11 and the parameters of the Arrhenius rate equation, Equation 45, $E_a = 1.43$ kcal/mole and $(1/\tau)_0 = 1.25 \times 10^{10} \text{ sec}^{-1}$, were obtained from the slope and intercept of the best straight line through the experimental points.

Using $B_0 = 0.0$ G, $B = 44$ G and $\theta_1 + \theta_2 = 60^\circ$ in Equation 16, the experimental values of $a(H_{\beta_1})$ and $a(H_{\beta_2})$ for the 1-cyclopentanecarboxylic acid radical lead to the values 45° and 15° for the dihedral angles between the 2p orbital of the odd electron and "axial" and "equatorial" β protons. These values are somewhat closer to the values of the dihedral angles (10° and 50°) for the half-chair conformation than they are to the "ideal" values for the envelope conformation (-10° and 70°). For this reason the conformations of the cyclic five-membered ring radicals have been drawn as half-chair forms in most of this work.

Table 7. Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 1-cyclopentanecarboxylic acid radical in adamantane.^{a,b}

$\log_{10}(1/\tau)$	$F(\omega)$
+11.0	1.99
10.5	1.97
10.0	1.87
9.5	1.68
9.0	1.17
8.5	0.42
8.0	0.00
7.5	0.28
7.0	0.66
6.5	0.88
6.0	0.96
5.5	0.99

^a $F(\omega)$ is defined by Equation 43 and is the ratio of the intensity of the given line to one of the outer invariant lines in the second-derivative spectrum.

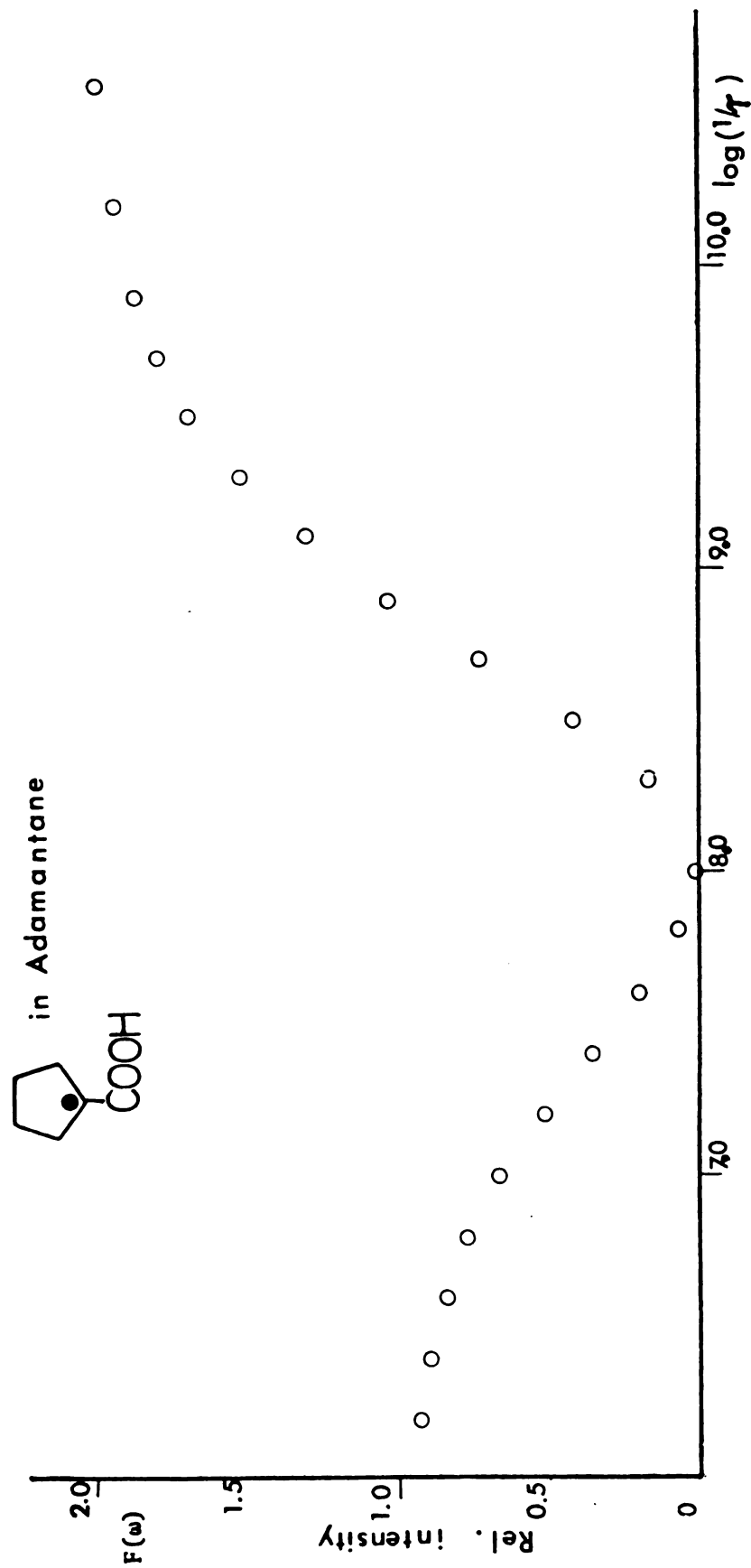
^bThe rate of inversion is $1/\tau$ where τ is the correlation time for exchange (Equations 21 and 22).

Table 8. Experimental relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 1-cyclopentanecarboxylic acid radical in adamantane.^{a,b}

$T^{\circ}\text{C}$	$1/T^{\circ}\text{K}(\times 10^3)$	$F(\omega)$	$\log(1/\tau)$
+11	3.52	1.88	9.97
-11	3.82	2.00	10.80
-65	4.81	0.74	8.72
-81	5.21	0.29	8.40
-100	5.78	0.17	8.28
-121	6.58	0.00	8.00
-141	7.58	0.13	7.70
-152	8.26	0.26	7.53
-161	8.93	0.43	7.31
-171	9.80	0.63	7.04

^aThe values of $1/\tau$ are taken from Figure 10.

^bThe lines used to obtain $F(\omega)$ are indicated by arrows in Figure 7.



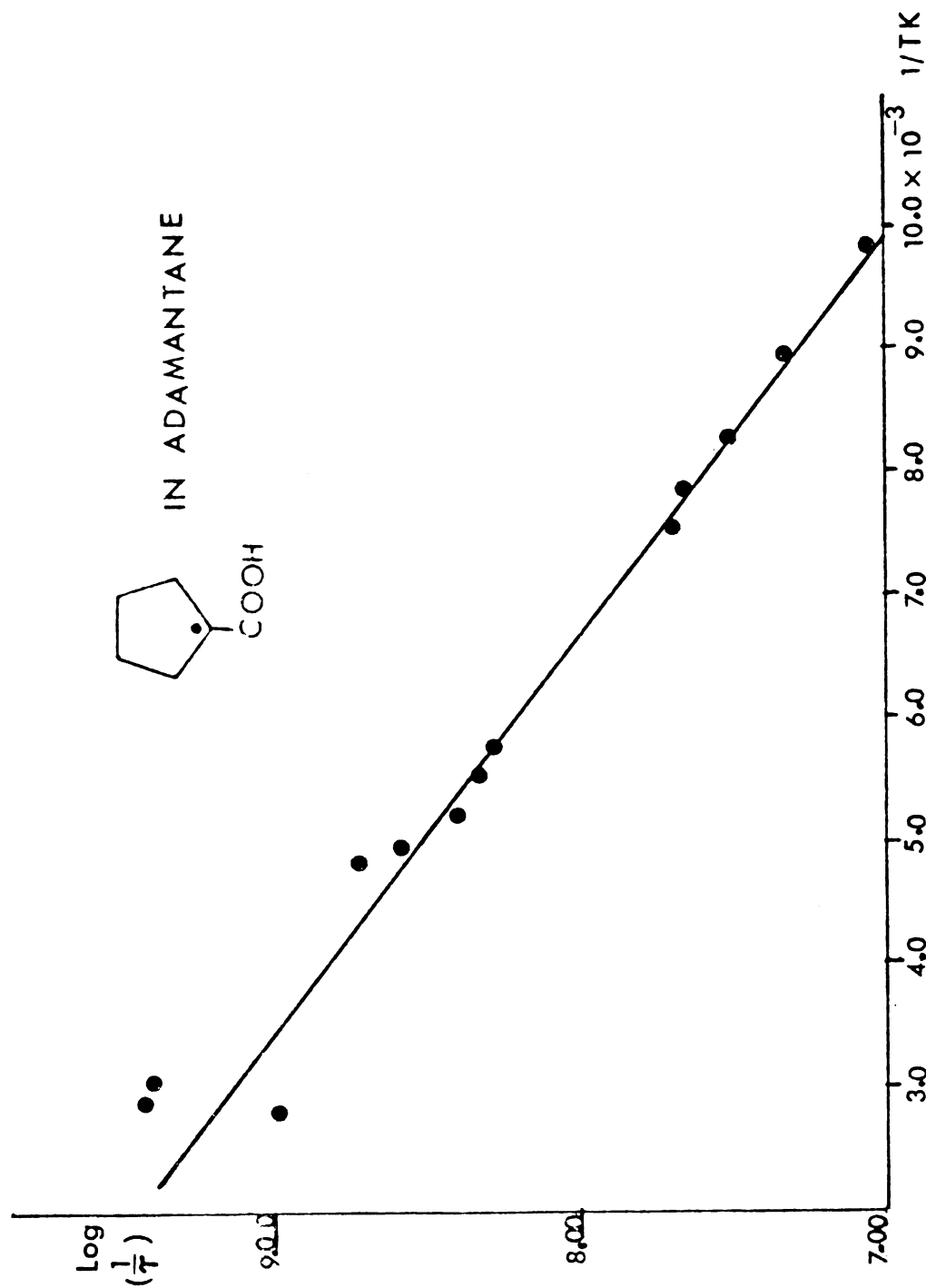


Figure 11. Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 1-cyclopentanecarboxylic acid radical in adamantane.

B. Cyclopentanecarboxylic Acid

When neat CPCA was γ -irradiated, the spectra were again characteristic of a nonplanar 1-cyclopentanecarboxylic acid radical which is undergoing a hindered ring motion but with different ESR parameters than for the same radical in adamantane. At -36°C the spectrum [Figure 12(c)] is a triplet of triplets indicating that there are two protons with $a(\text{H}_{\beta_1}) = 28.3 \text{ G}$ and two with $a(\text{H}_{\beta_2}) = 34.0 \text{ G}$. The line positions and relative intensities are in agreement with the stick diagram of Fig. 13(b). When the temperature is raised to 0°C [Figure 12(a)] the spectrum has become a quintet with relative intensities approaching 1:4:6:4:1 indicating that rapid inversion of the ring between the rigid conformations stable at -36°C is averaging the β proton splittings. The result of such a process would be an average splitting $\langle a(\text{H}_{\beta}) \rangle = (28.3 + 34.0)/2 = 31.3 \text{ G}$, as observed. In the intermediate temperature range [Fig. 12(b) for -9°C] the outer lines remain invariant but the inner lines change in position and intensity as a result of the ring inversion process. The dotted lines of Figure 13 show the results of averaging the two sets of β protons leading, at high temperatures, to the quintet of Figures 12(a) and 13(a).

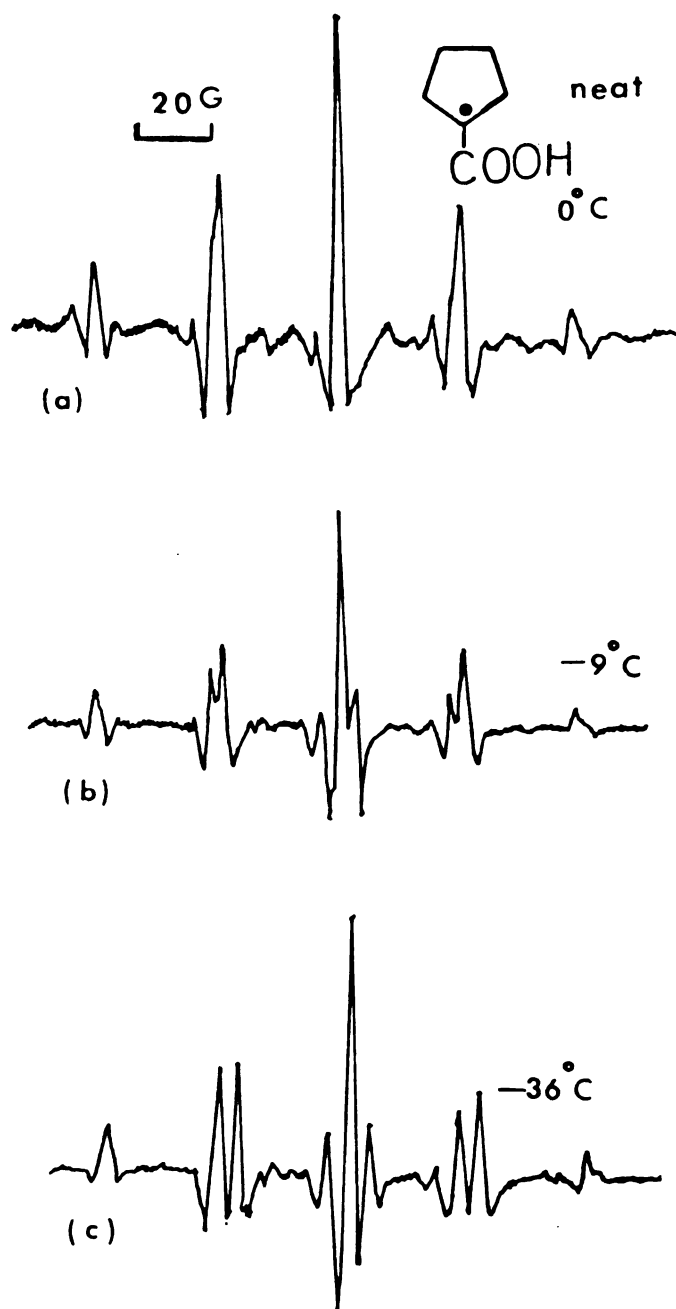


Figure 12. ESR spectra of 1-cyclopentanecarboxylic acid radical in the self matrix.

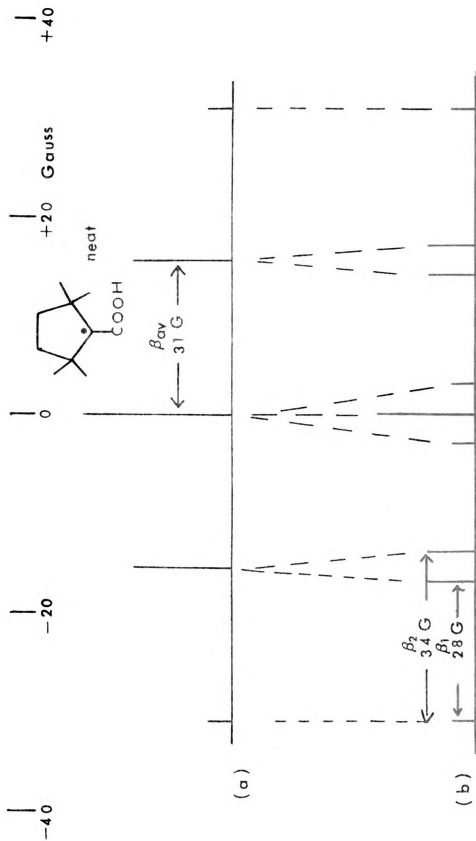
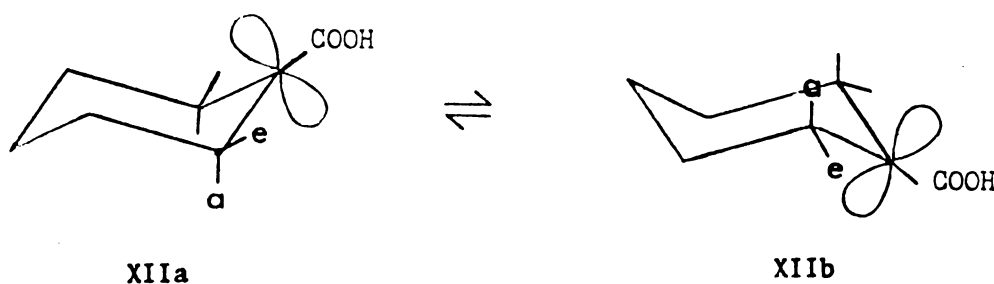


Figure 13. Field positions and intensities of the lines in the ESR spectrum of 1-cyclopentanecarboxylic acid radical in the self matrix: (a) fast exchange region, (b) slow exchange region.

The dihedral angles calculated from Equation 16 for the two sets of β protons of the CPCA radical in the pure CPCA matrix are 34° and 26° , respectively. The stable conformation in CPCA is thus different from that in adamantane.

C. Cyclohexanecarboxylic Acid

Pure solid polycrystalline cyclohexanecarboxylic acid (CHCA) was γ -irradiated and the ESR spectra observed at various temperatures [Figure (14)]. At $+9^\circ\text{C}$ a quintet with $a(\text{H}_\beta) = 21.1$ G and relative intensities 1:4:6:4:1 was observed [Figure 14(a)]. This quintet persists on cooling until about -50°C when it begins to change to a triplet. At -60°C a triplet with relative intensities 1:4:1 and $a(\text{H}_\beta) = 42.1$ G is obtained [Figure 14(b)] and this remains until about -90°C when a more complex spectrum appears. These spectra indicate that the only radical formed is cyclohexanecarboxylic acid radical (XII). The low-temperature spectrum [Figure 14(c)]



is presumably a powder spectrum since the tumbling of impurity species in adamantane has usually slowed in this temperature range to the point where anisotropic interactions are broadening the lines.

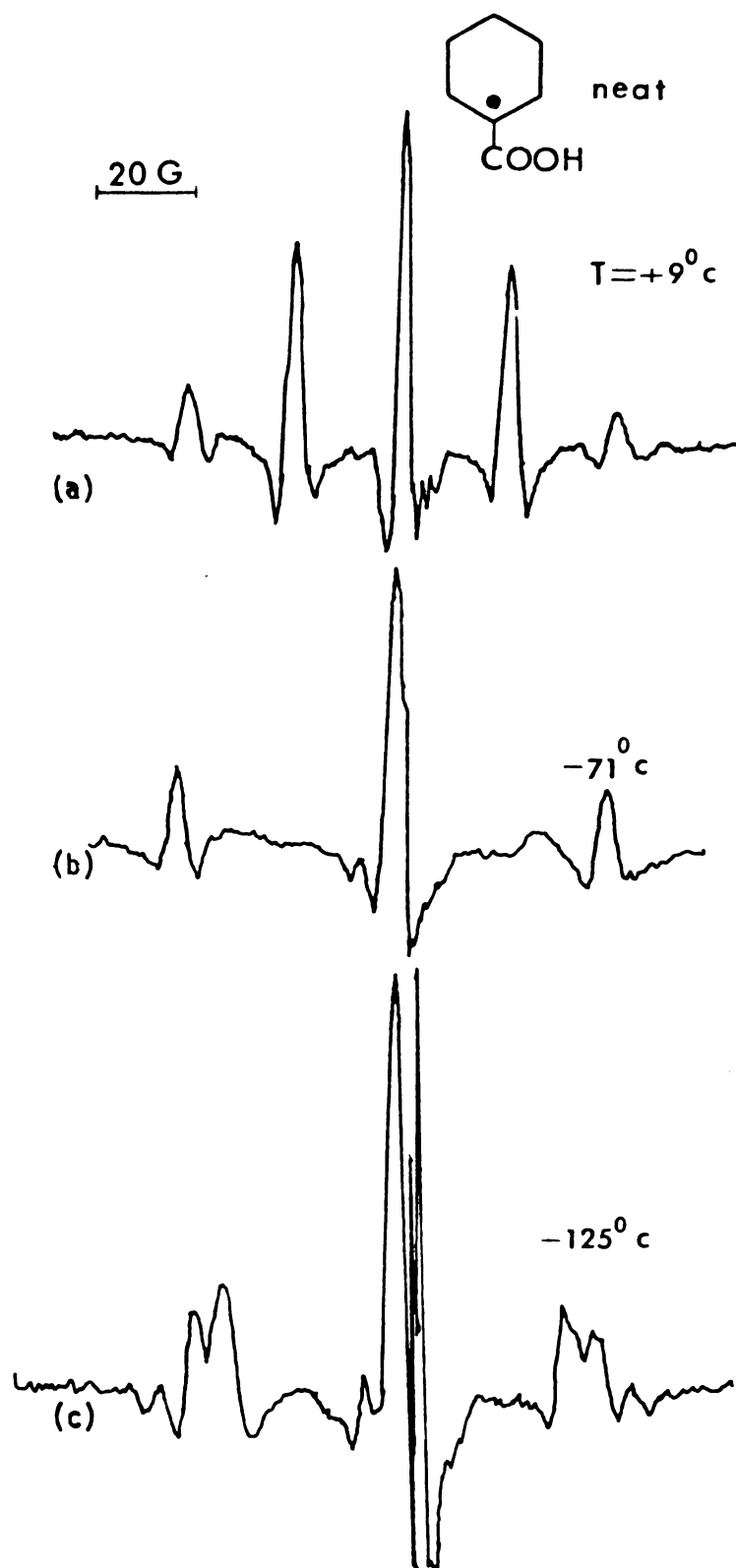


Figure 14. ESR spectra of 1-cyclohexanecarboxylic acid radical in the self matrix.

The spectra are thus qualitatively similar to those observed for cyclohexyl radical²⁻ and those described in detail above for 1-cyclopentanecarboxyl radical and are consistent with a slow inter-conversion of radical XII between equivalent chair forms below -60° leading to hyperfine splittings $a(H_{\beta_1}) = 37$ G for two axial β -protons and $a(H_{\beta_2}) = 5.0$ G for two equatorial β protons. Above -50°C inter-conversion is rapid enough so that only an average is observed with $\langle a(H_{\beta}) \rangle = 1/2[a(H_{\beta_1}) + a(H_{\beta_2})] = 21.0$ G and a five-line quintet of relative intensities 1:4:6:4:1 is observed. At intermediate temperatures the spectral changes are as indicated in the correlation diagram of Figure 9. The same set of spin states as was used in discussing CPCA radical [Figure (8)] may be used also for CHCA radical.

The intensity of the next outer lines (lines 2 and 4 of Figure 14(a)), which vary with temperature, were measured relative to the invariant outer lines and the ratios $F(\omega)$ at various temperatures are given in Table 10. The computer program ESREX4 was used to obtain values of $\log(1/\tau)$ as a function of $F(\omega)$ and the calculated values for cyclohexanecarboxylic acid radical in CHCA matrix are given in Table 9 and also plotted graphically in Figure 15. Values of $\log(1/\tau)$ corresponding to the observed values of $F(\omega)$ at various temperatures are given in Table 10 and are plotted graphically versus reciprocal temperature in Figure 16. The slope and intercept of the best straight line through the points of Figure 16 lead to the values $E_a = 3.7$ kcal/mole and $(1/\tau)_0 = 1.7 \times 10^{12}$ for the barrier to the ring inversion process and the frequency factor, respectively.

Table 9. Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 1-cyclohexanecarboxylic acid radical in the self-matrix.

$\text{Log}_{10}(1/\tau)$	$F(\omega)$
+11.0	1.98
10.5	1.95
10.0	1.84
9.5	1.55
9.0	0.93
8.5	0.21
8.0	0.12
7.0	0.81
6.0	0.98

Table 10. Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 1-cyclohexanecarboxylic acid radical in the self matrix.^a

$T^{\circ}\text{C}$	$1/T^{\circ}\text{K}(\times 10^3)$	$F(\omega)$	$\log(1/\tau)$
+22	3.39	1.73	9.75
+ 9	3.55	1.68	9.65
0	3.66	1.57	9.55
-11	3.82	1.17	9.18
-26	4.05	0.88	8.98
-39	4.27	0.38	8.65
-56	4.61	0.23	8.53
-71	4.95	0.0	

^aThe values of $\log(1/\tau)$ are taken from Figure 15.

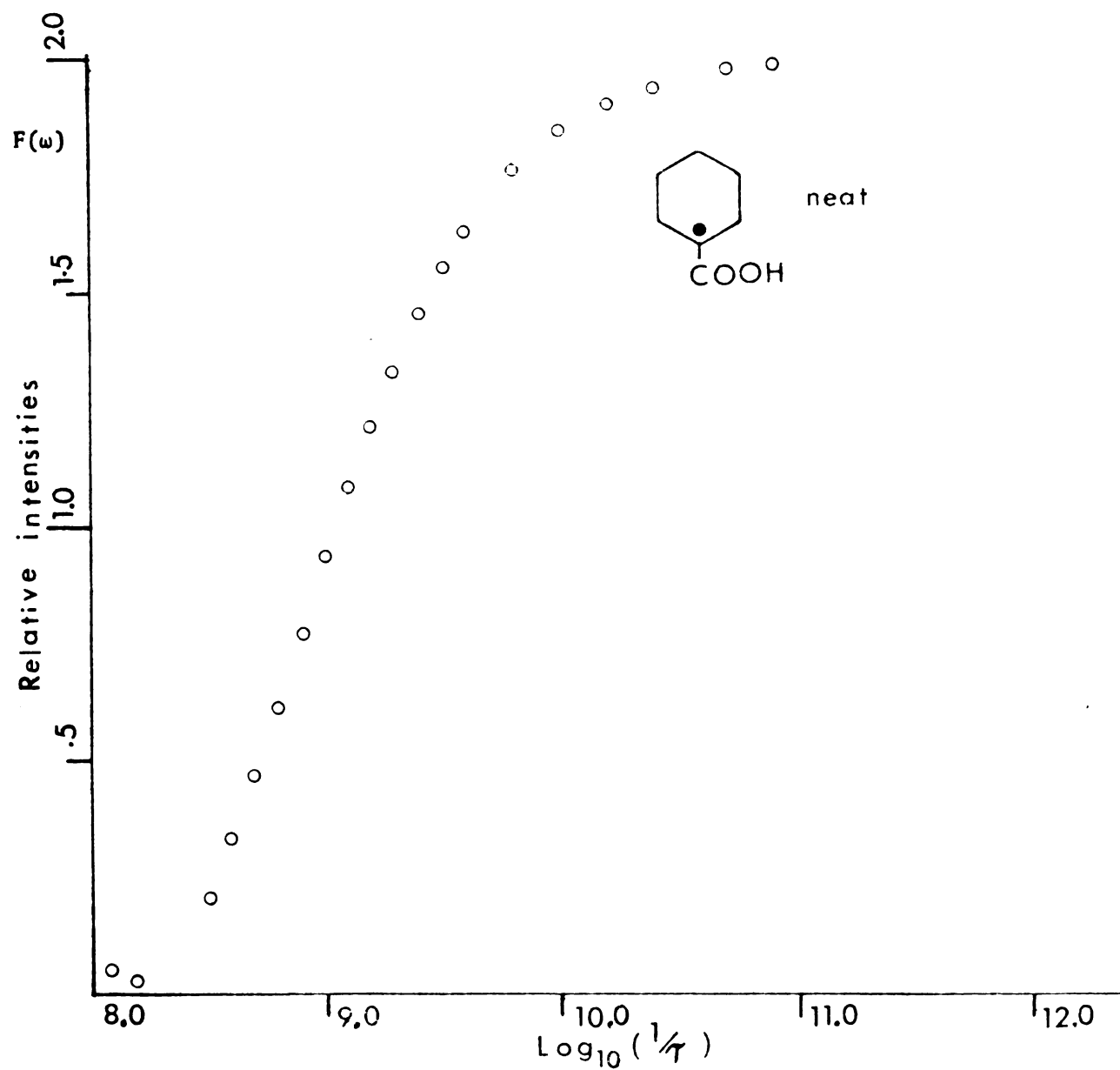


Figure 15. Calculated values of the relative intensity of the second line to the invariant outer line $[F(\omega)]$ versus $\log(1/\tau)$ for 1-cyclohexanecarboxylic acid radical.

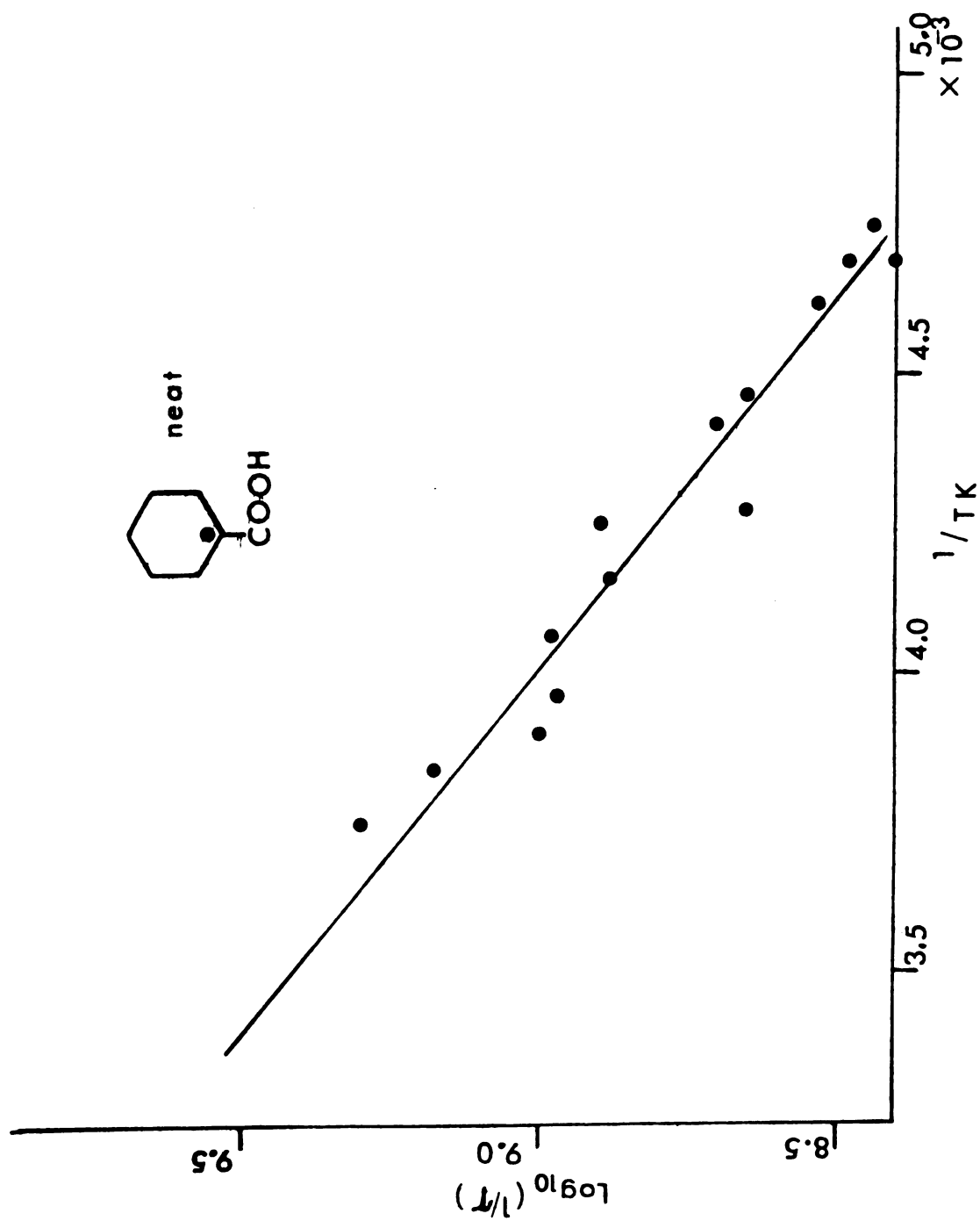


Figure 16. Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 1-cyclohexanecarboxylic acid radical in the self matrix.

D. Cyclobutanecarboxylic Acid

A solid solution of cyclobutanecarboxylic acid in adamantane was γ -irradiated at room temperature. The ESR spectrum consisted of a rather weak quintet with $a(H_\beta) = 31.8$ G [Figure 17(a)].

Better spectra were obtained when cyclobutanecarboxylic acid was irradiated as the pure crystalline solid at 77°K. The spectrum on warming to -15°C [Figure 17(b)] consists of a strong quintet with $a(H_\beta) = 32.9$ G and relative intensities about 1:2.5:3.8:2.5:1 indicating that the 1-cyclobutanecarboxyl radical XIII, with four equivalent β protons, has been produced. There are also two or three additional, weaker lines present of unknown origin. Radical XIII decomposes above about -8°C while below -40°C the lines broaden and the spectrum becomes characteristic of a powder [Figure 17(c)]. No temperature dependence of the isotropic spectrum, which would be indicative of a measurable ring inversion process, is observed between -8° and -40°C.

E. Cycloheptanecarboxylic Acid in Adamantane

A solid solution of cycloheptanecarboxylic acid in adamantane was γ -irradiated at 77°K. The spectrum at 25°C [Figure 18(a)] can be considered to be made up of the superposition of two multiplets - a quintet with relative intensities 1:4:6:4:1 and $a(H) = 13.4$ G, and a triplet of triplets with $a(H_1) = 17.9$ G, $a(H_2) = 22.5$ G. Both multiplets have the same g value but they appear to arise from different radicals. The quintet disappears on cooling to -56°C [Figure 18(b)].

The triplet of triplets persists over a wide temperature range (-60° to +60°C) with relative intensities and splitting parameters

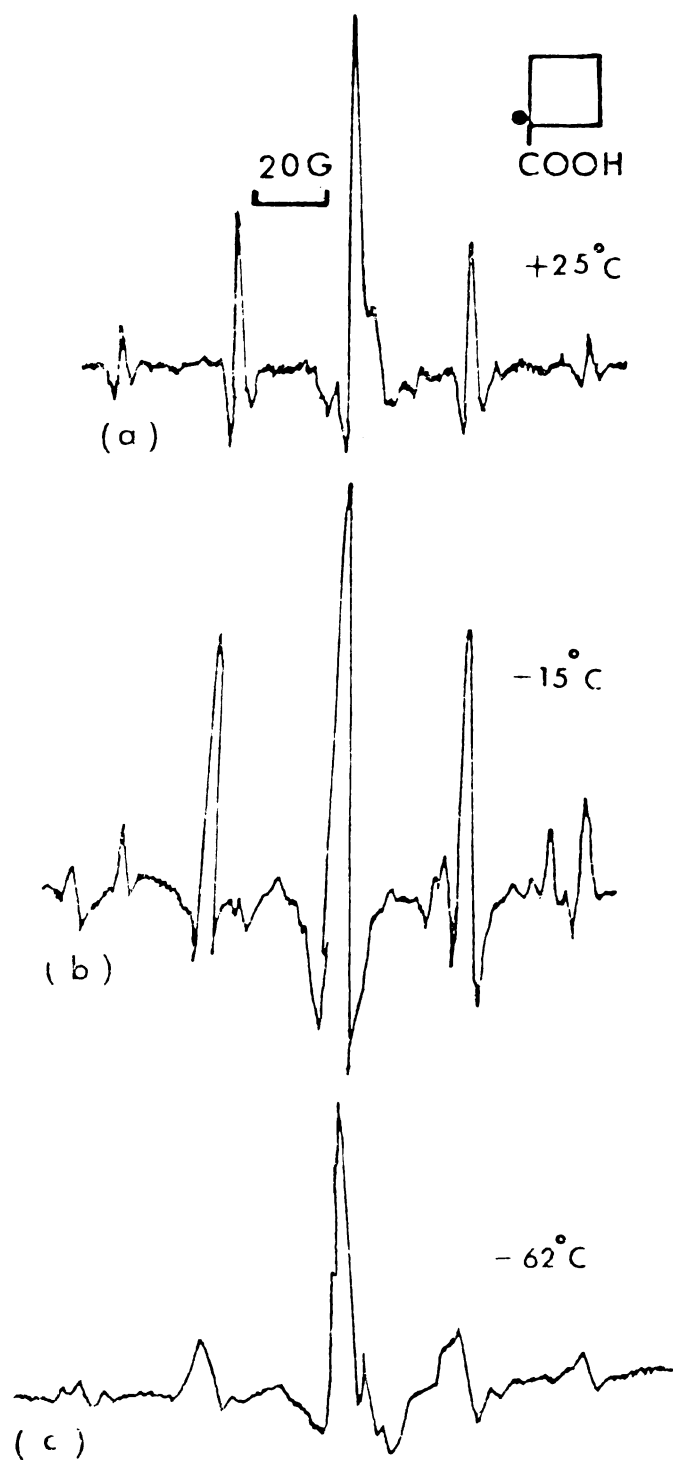


Figure 17. ESR spectra of 1-cyclobutanecarboxylic acid radical:
(a) in polycrystalline 1-cyclobutanecarboxylic acid,
(b) and (c) in adamantane.

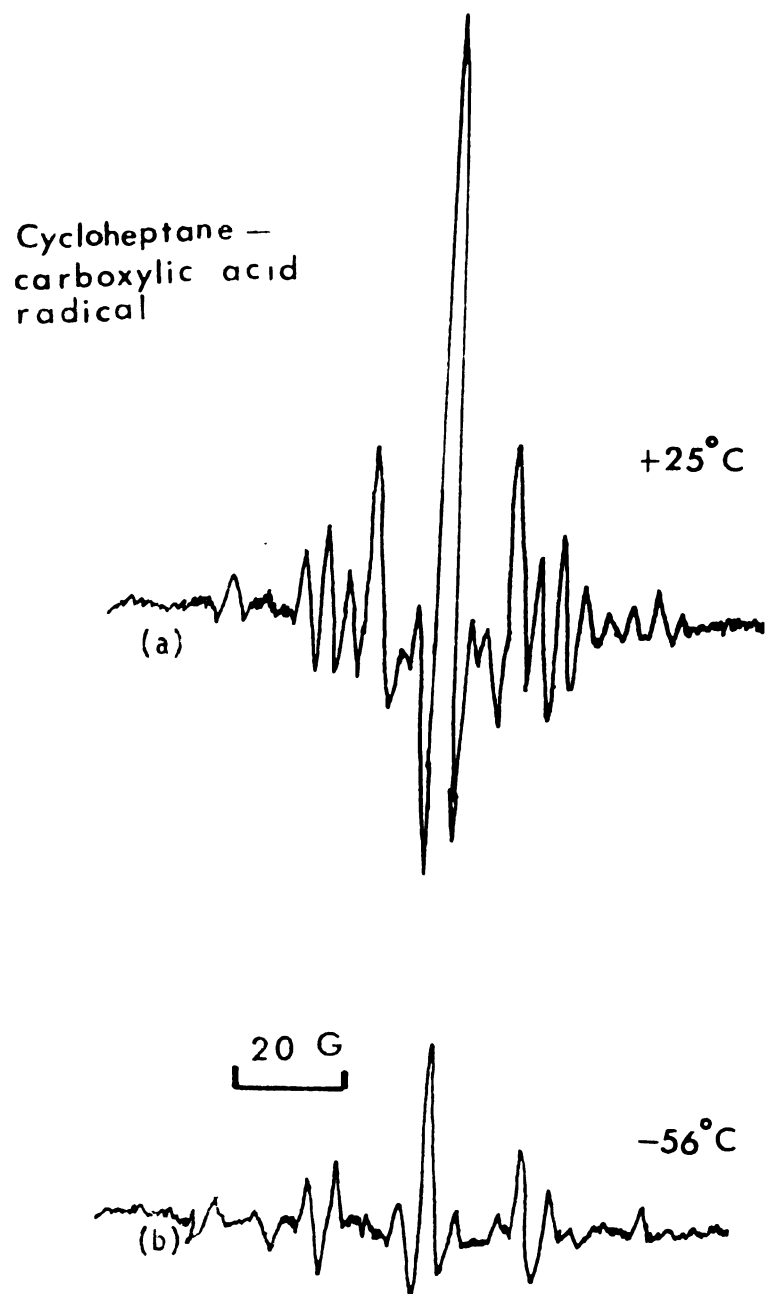
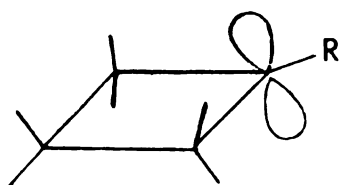
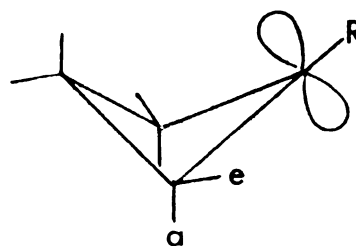


Figure 18. ESR spectra of 1-cycloheptanecarboxylic acid radical in adamantane.



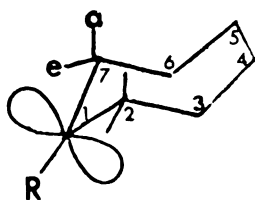
Planar

or

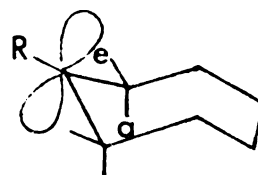


Puckered

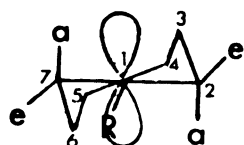
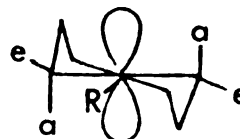
XIII



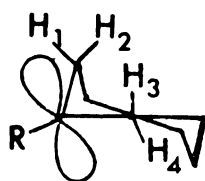
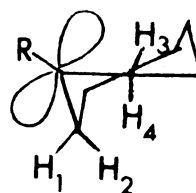
Chair



XIV(a)

Twist-chair
(symmetrical)

XIV(b)

Twist-chair
(unsymmetrical)

XV

Some Structural Formulae for Cyclic Carboxylic Acid Radicals ($R = \text{COOH}$)
Transformation among the twist-chair forms of the seven-membered ring (XIV(b), XV) can occur by a process of pseudorotation in which the C_2 axis moves around the ring one carbon atom at a time.

almost unchanged and might be assigned to an 2-cycloheptanecarboxylic acid radical, XIV (chair) or XV (symmetrical or unsymmetrical twist-chair), in a rigid conformation with two pairs of nonequivalent β protons. The quintet, however, is not spectrum which would result from rapid interconversion between two nonplanar forms such as XIV or XV, since the hyperfine interaction of 13.4 G is much smaller than the average of the triplet splittings, and the triplet of triplets never coalesces into the quintet. The origin of these lines remains unexplained.

Pure cycloheptanecarboxylic acid was also γ irradiated at 77°K. In the range -90°C to -120°C four broad lines were observed with $a(H_1) = 25$ G, $a(H_2) = 61$ G and $g = 2.0036$. Above -90°C the radical disappeared. There is not sufficient information available at present to interpret this spectrum but it is presumably a powder pattern since isotropic proton hyperfine splittings as large as 61 G are not observed in cyclic radicals.

F. Cyclopropanecarboxylic Acid in Adamantane

A sample γ irradiated at 77°K showed no ESR spectrum and it is possible that the acid did not enter the adamantane matrix. When the pure acid was irradiated at 77°K complex ESR spectra were obtained which could not be interpreted.

II. Cyclic Ketones

A. Cyclopentanone in Adamantane

The spectra of solid solutions of cyclopentanone in adamantane γ -irradiated at 77°K are shown at two temperatures in Figure 19. The spectrum at -24°C is a doublet of triplets with each line further

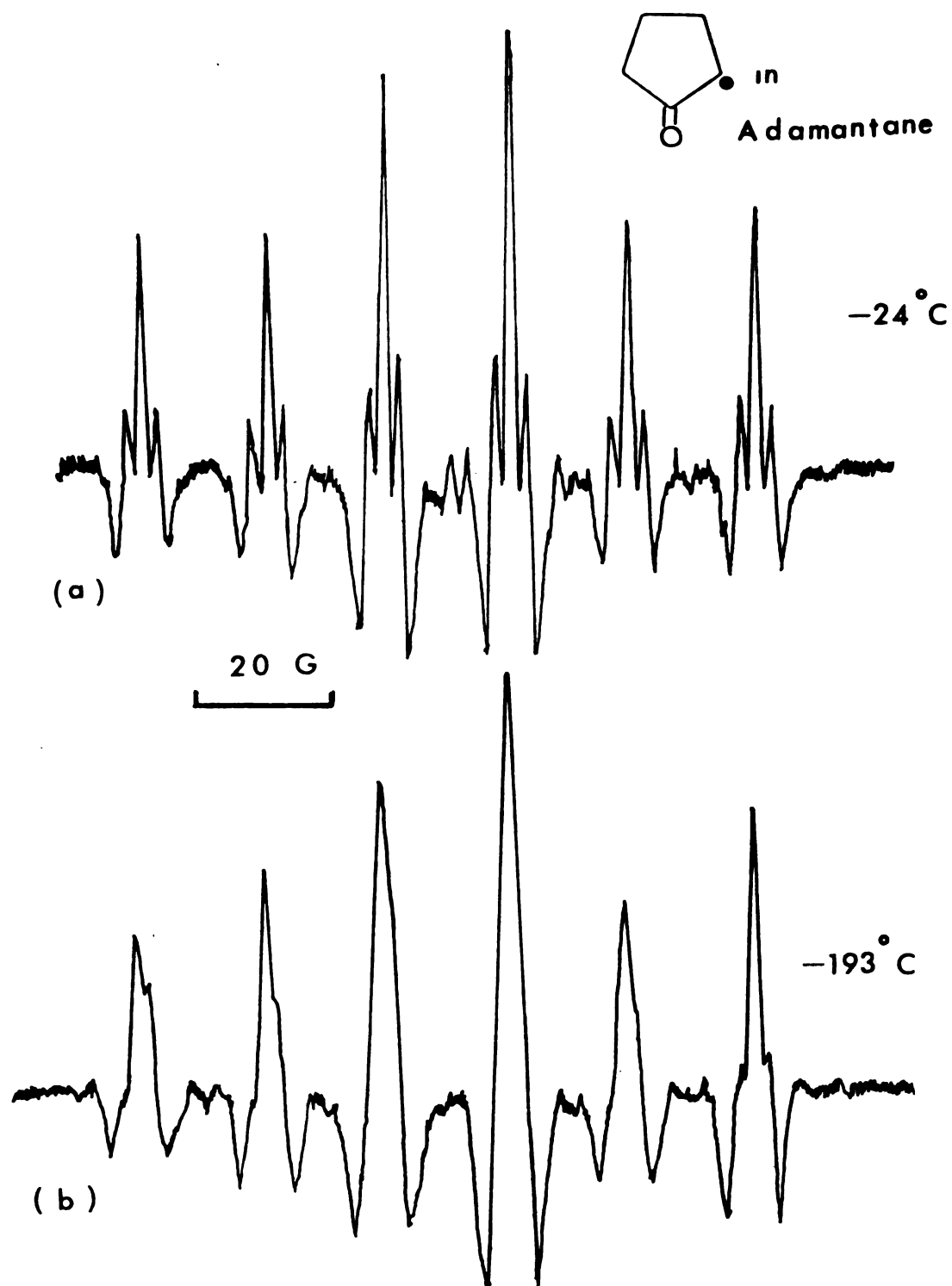
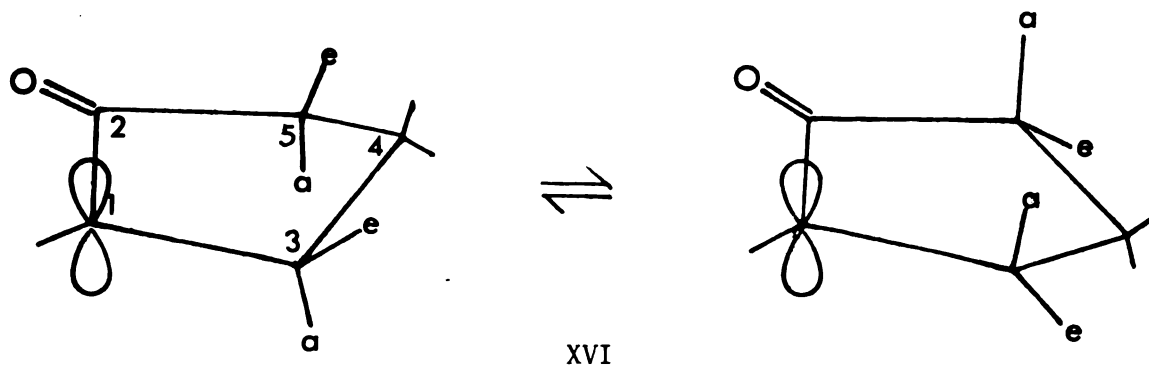


Figure 19. ESR spectra of 2-cyclopentanonyl radical in adamantane.

split into a triplet. This spectrum persists to low temperatures although lines 1,3,5 become broadened relative to lines 2,4,6 at -193°C [Figure 19(b)]. The spectra indicate that the only stable radical produced is the 2-cyclopentanonyl radical, XVI, and



that it is either planar, or is undergoing rapid inversion even at the lowest temperature, since the spectrum at -193°C is still a doublet of triplets. The small additional splitting of 2.2 G observed above -60° is apparently from two equivalent γ protons. The ESR parameters observed are $g = 2.0046$, $a(\text{H}_{\alpha}) = 18.5 \text{ G}$, $a(\text{H}_{\beta}) = 36.0 \text{ G}$ (two equivalent β protons), $a(\text{H}_{\gamma}) = 2.2 \text{ G}$ (two equivalent γ protons). No changes were observed in the spectra which would indicate that ring inversion is occurring at a rate measurable by ESR.

B. Cycloheptanone in Adamantane

A sample was x-irradiated at room temperature for two hours and spectra recorded immediately following irradiation, first at room temperature then at a series of lower temperatures [Figure 20]. Although lines from a second radical are present at all temperatures, a doublet of triplets attributable to the 2-cycloheptanonyl radical

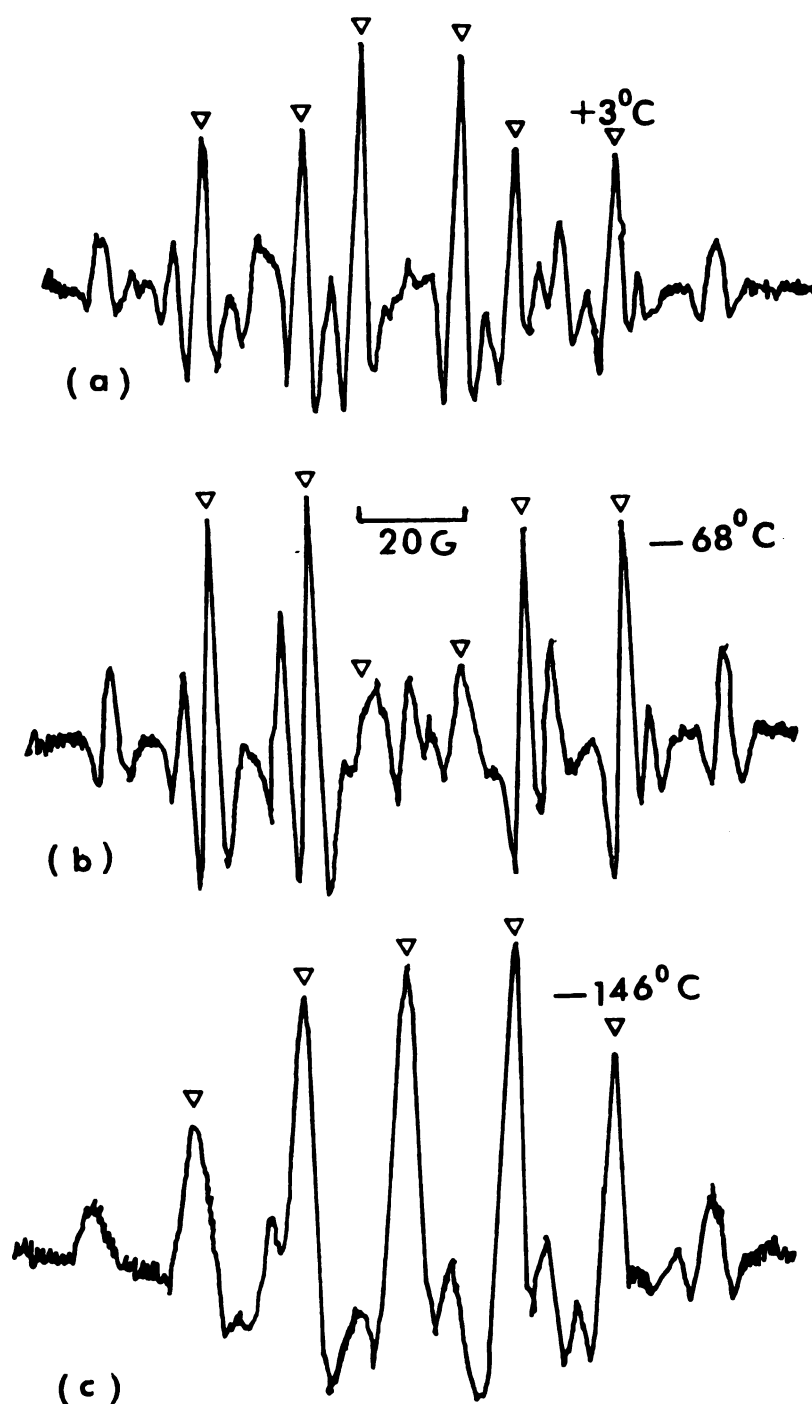
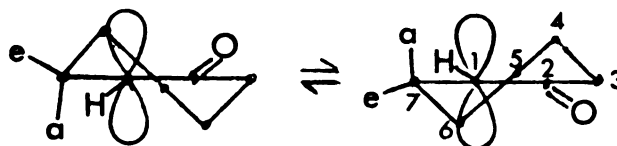


Figure 20. ESR spectra of 2-cycloheptanonyl radical in adamantane (lines indicated by inverted triangles). The remaining lines arise from a second, unidentified radical.

XVII can be identified at +3°C and these six lines are indicated by



XVII

small arrows in Figure 20(a) and (b). The ESR parameters at +3°C are $a(H_{\alpha}) = 18.5$ G, $a(H_{\beta}) = 28.8$ G (two equivalent β protons) and $g = 2.0042 \pm 0.0002$. As the temperature is lowered the two central lines broaden and decrease in intensity [Figure 20(b)] until the coalescence temperature of -88°C is reached. At lower temperatures the two β protons appear to become equivalent and the five line spectrum at -146°C can be assigned ESR parameters $a(H_{\alpha}) = a(H_{\beta_1}) = 19.1$ G and $a(H_{\beta_2}) = 38.2$ G. These values would predict a high-temperature average splitting for the β protons after they become equivalent of $\langle a(H_{\beta}) \rangle = \frac{19.1 + 38.2}{2} = 28.65$ G in agreement with the observed value of 28.8 G. The radical is very stable at room temperature.

Values of the relative intensities of one of the inner lines (lines 3 and 4) to one of the outer lines for 2-cycloheptanonyl radical were calculated as functions of $\log(1/\tau)$ using the program ESREX4 and are given in Table 11 and plotted graphically in Figure 21. Values of $\log(1/\tau)$ at the temperatures at which relative intensities could be measured are listed in Table 12 and plotted versus $1/T^{\circ}\text{K}$ in Figure 22. From this Arrhenius plot the activation energy for the ring

Table 11. Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 2-cycloheptanonyl radical in adamantane.

Log $(1/\tau)$	$F(\omega)$
+11.0	1.99
10.5	1.97
10.0	1.91
9.5	1.73
9.0	1.28
8.5	0.54
8.0	0.0
7.5	0.35
7.0	0.71
6.5	0.90
6.0	0.97

Table 12. Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 2-cycloheptanonyl radical in adamantane.

T°C	$1/T^{\circ}\text{K}(\times 10^3)$	$F(\omega)$	$\log(1/\tau)$
+68	2.93	1.66	9.34
+40	3.19	1.62	9.30
+ 3	3.62	1.53	9.21
-16	3.89	1.47	9.18
-37	4.24	1.26	8.99
-45	4.39	0.79	8.66
-55	4.59	0.52	8.48
-68	4.88	0.32	8.34
-79	5.15	0.27	8.30
-88	5.41	0.0	

^aThe values of $\log(1/\tau)$ are from Figure 21.

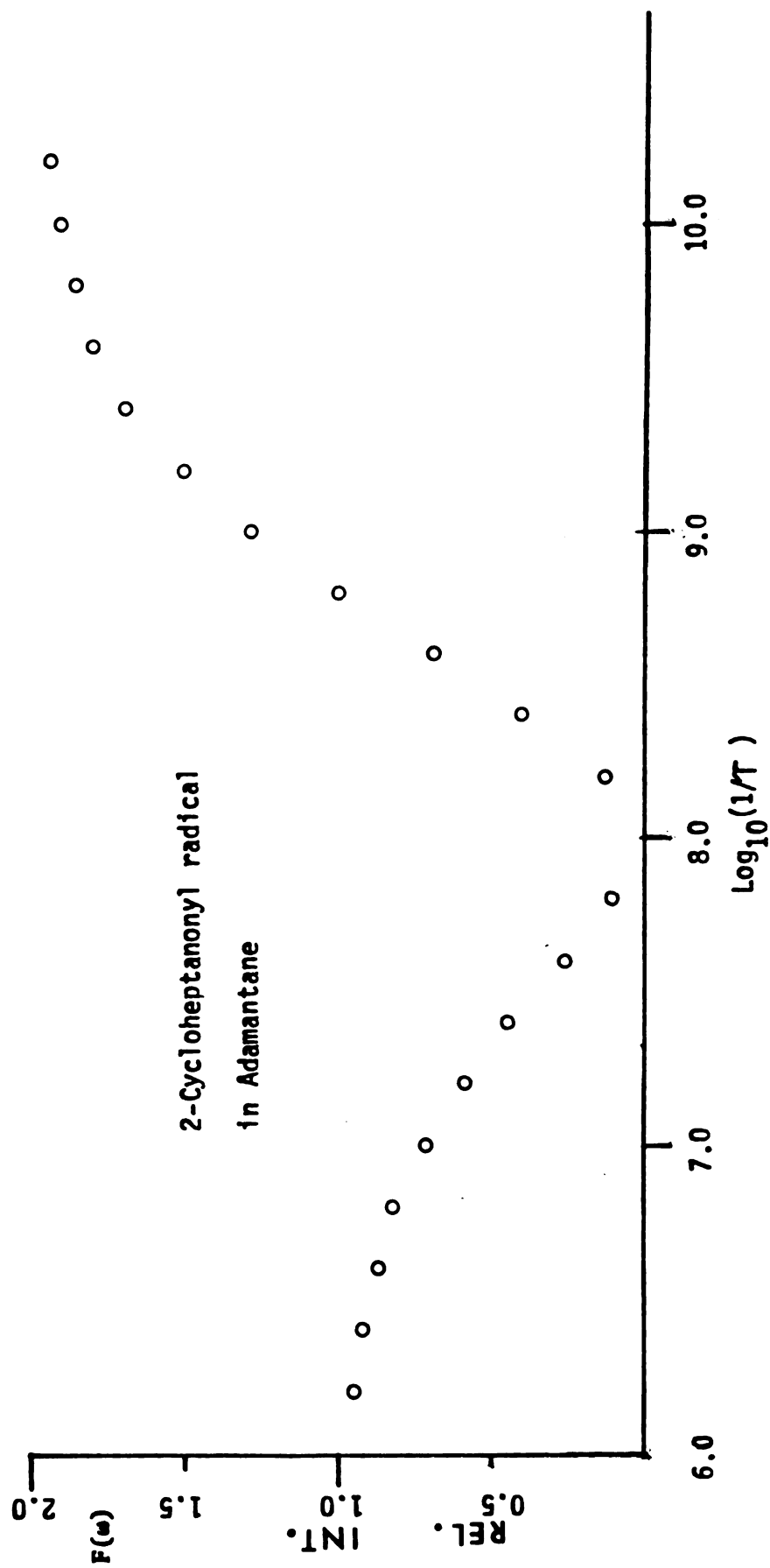


Figure 21. Calculated relative intensities for the second line relative to the invariant outer line versus $\log(1/\tau)$ for 2-cycloheptanonyl radical in adamantane.

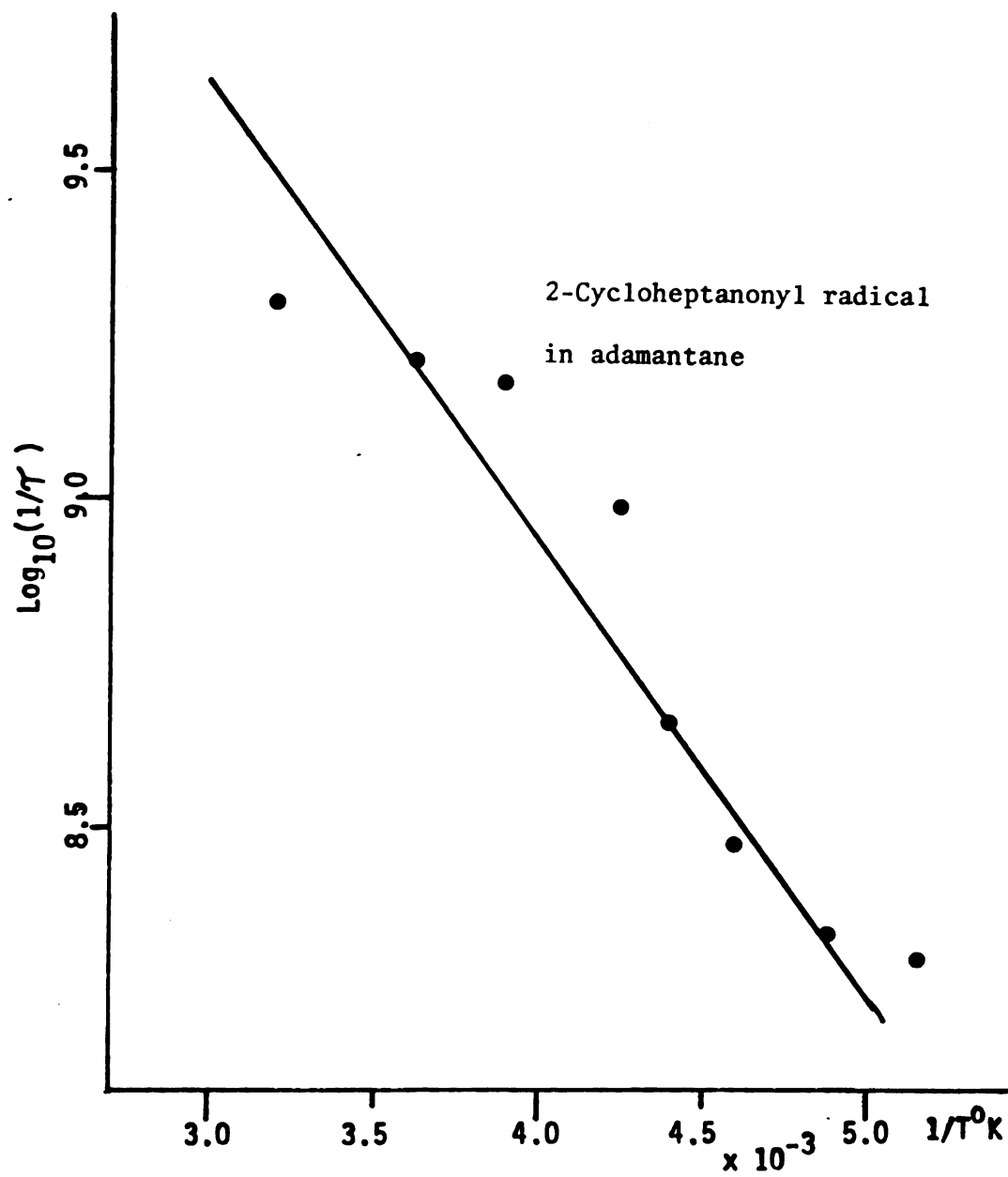


Figure 22. Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 2-cycloheptanonyl radical in adamantane.

inversion process is found to be $E_a = 3.2$ kcal/mole and the frequency factor $(1/\tau)_0 = 5.5 \times 10^{11}$.

The coalescence temperature for 2-cycloheptanonyl radical (185°K) is slightly lower than that observed for 2-cyclohexanonyl radical²² (198°K) which implies that the activation energy for ring inversion should be lower for 2-cycloheptanonyl radical as is found ($E_a = 3.2$ kcal/mole for 2-cycloheptanonyl radical and $E_a = \Delta H^\ddagger + RT = 3.70 + 0.60 = 4.30$ kcal/mole for 2-cyclohexanonyl radical.²²)

III. Heterocyclic Oxygen Compounds

A. Tetrahydrofuran in Adamantane

Tetrahydrofuran (THF) in adamantane was γ -irradiated at 77°K for three hours and ESR spectra taken at a series of temperatures up to -10°C where it becomes unstable (Figure 23). The spectrum is a doublet of triplets which indicates that the radical is the 2-tetrahydrofuranyl radical XVIII (a) and the ESR parameters at -71°C are $a(H_\alpha) = 13.6$ G and $a(H_\beta) = 27.7$ G (two equivalent β protons). At lower temperatures the two β protons become nonequivalent with $a(H_{\beta_1}) = 18.0$ G and $a(H_{\beta_2}) = 37.3$ G.

The intensity of line 3 relative to line 2 was measured at various temperatures down to -193°C which is approximately the coalescence temperature. The values of $\log (1/\tau)$ versus relative intensity are plotted in Figure 24 and values from this graph used for the Arrhenius plot of Figure 25. The slope and intercept of the straight line of Figure 25 lead to the values $E_a = 2.2 \pm 0.5$ kcal/mole and $(1/\tau)_0 = 6.9 \times 10^{13}$ for the ring inversion process.

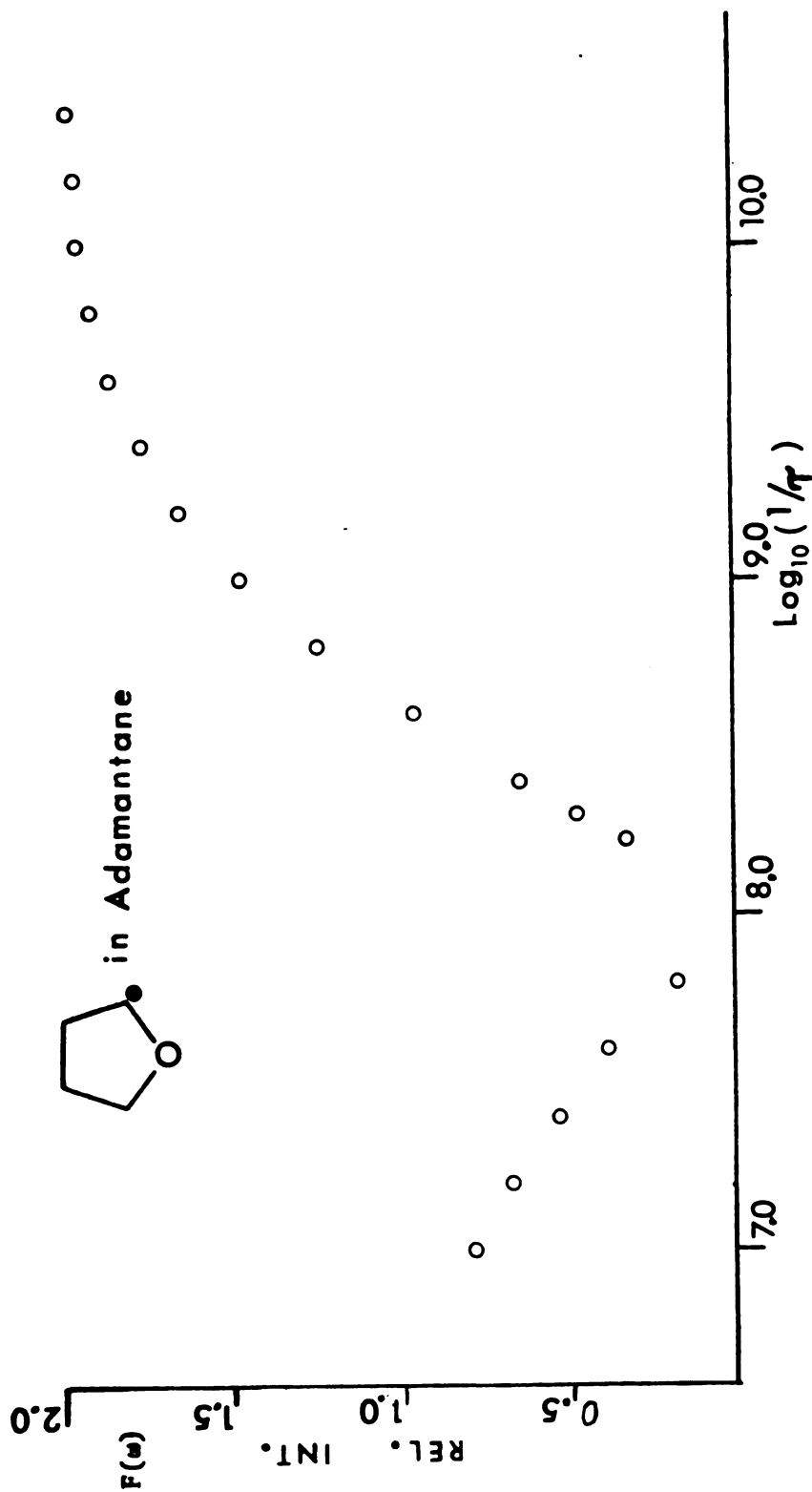


Figure 24. Calculated values of relative intensities $[F(\omega)]$ versus $\log(1/\tau)$ for 2-tetrahydrofuran-2-yl radical in adamantane.

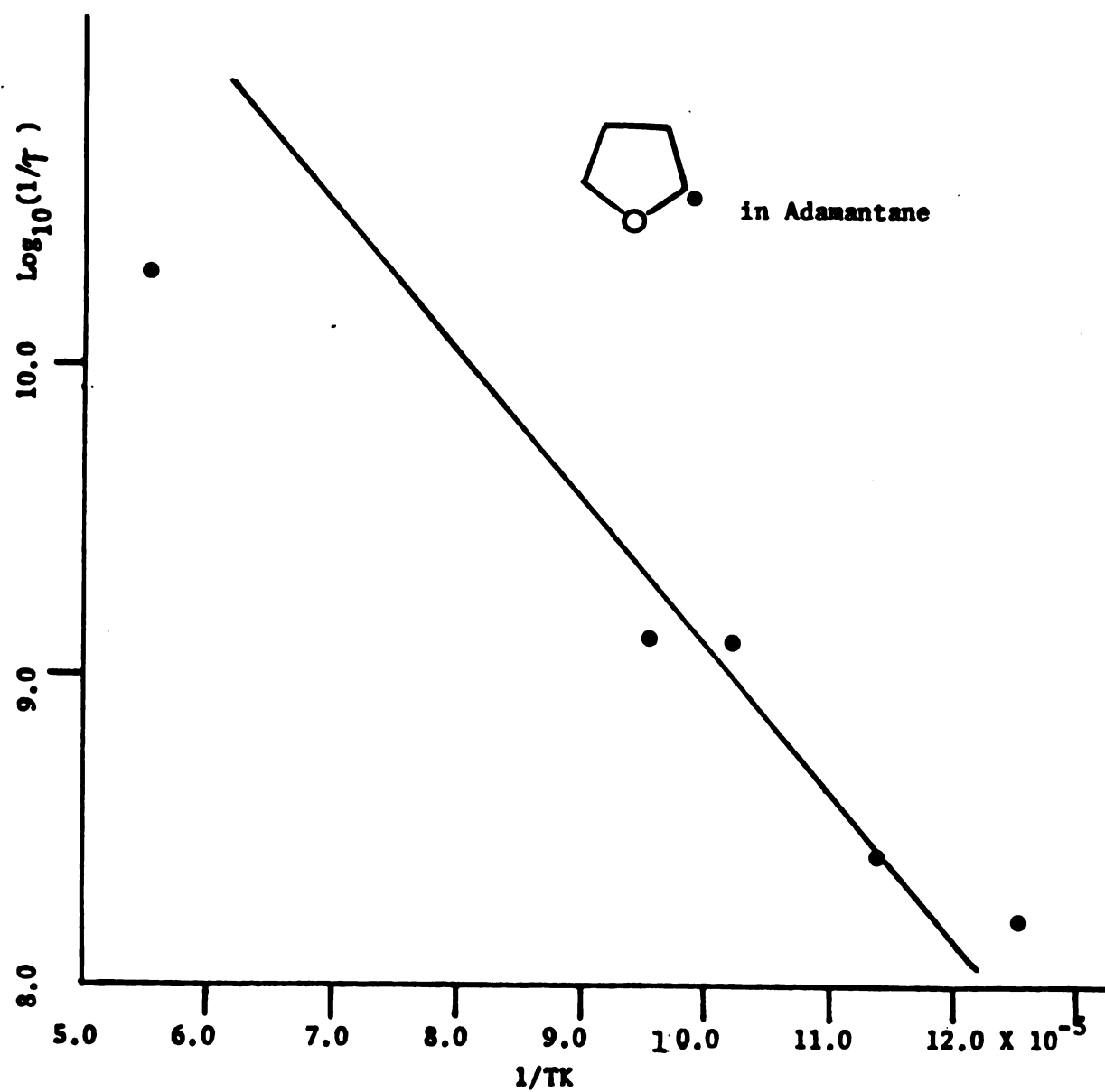
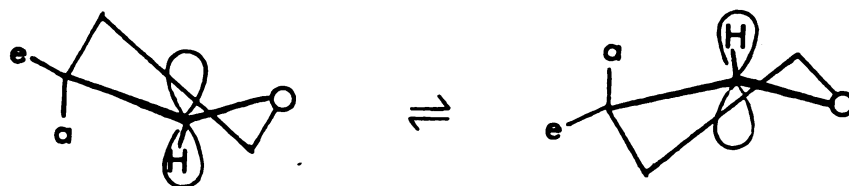


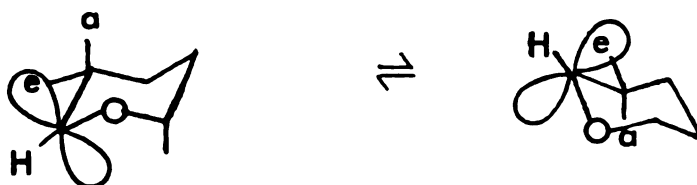
Figure 25. Plot of $\log(1/\tau)$ versus $1/T^{\circ}\text{K}$ for 2-tetrahydrofuranyl radical in adamantane.

B. Tetrahydropyran in Adamantane

A solid solution of tetrahydropyran in adamantane was γ -irradiated at 77°K and the ESR spectra collected at various temperatures. At very low temperatures the spectrum consists of eight lines of equal intensity [Figure 26(c)]. This is accounted for if the radical produced is the expected 2-tetrahydropyranyl radical XVIII (b) with a rigid conformation so that the β protons are not equivalent. The ESR



XVIII(a) 2-Tetrahydrofuryl radical



XVIII(b) 2-Tetrahydropyranyl radical

parameters are $a(H_\alpha) = 16.1$ G, $a(H_{\beta_1}) = 40.0$ G and $a(H_{\beta_2}) = 5.0$ G.

On warming, four of the lines broaden and their peak heights become smaller as shown in Figure 26(b) taken at -90°C . At -11°C they have disappeared and only four lines of equal intensity remain [Figure 26(a)] with $a(H_\alpha) = 16.1$ G and $a(H_{\beta_1}) + a(H_{\beta_2}) = 45$ G.

The spectrum analysis may be carried out in the usual way by writing the nuclear spin orientations for three nonequivalent protons H_α , $H_{\beta_1} = H_a$, and $H_{\beta_2} = H_e$ where H_a , H_e indicate "axial" and "equatorial" type β protons [Table 13]. The corresponding stick plot for the spectra of 2-tetrahydropyranyl radical are shown in Figure 27.

Table 13. Spin orientations for 2-tetrahydropyranyl radical under conditions of slow and fast ring inversion.

Spin State	H_α	H_a	H_e	$(H - H_e)^*_{\text{Low Temp.}}$	$(H - H_e)^{**}_{\text{High Temp.}}$
1	-	-	-	$-\frac{1}{2}(a_\alpha + a_a + a_e)$	$(-a_\alpha/2) - a_{\text{av.}}$
2	-	-	+	$-\frac{1}{2}(a_\alpha + a_a - a_e)$	$-a_\alpha/2$
3	-	+	-	$-\frac{1}{2}(a_\alpha - a_a + a_e)$	$-a_\alpha/2$
4	-	+	+	$-\frac{1}{2}(a_\alpha - a_a - a_e)$	$(-a_\alpha/2) + a_{\text{av.}}$
5	+	-	-	$+\frac{1}{2}(a_\alpha - a_a - a_e)$	$(+a_\alpha/2) - a_{\text{av.}}$
6	+	-	+	$+\frac{1}{2}(a_\alpha - a_a + a_e)$	$+a_\alpha/2$
7	+	+	-	$+\frac{1}{2}(a_\alpha + a_a - a_e)$	$+a_\alpha/2$
8	+	+	+	$+\frac{1}{2}(a_\alpha + a_a + a_e)$	$(+a_\alpha/2) + a_{\text{av.}}$

* $H = H_e + m_a a_a + m_e a_e$ to first order, where H_e is the magnetic field at the center of the spectrum in Gauss, a_α is the α -proton hyperfine splitting, a_a and a_e are axial and equatorial hfs, respectively, m_a, m_e are the proton spin quantum numbers, and + indicates $m = +\frac{1}{2}$, - indicates $m = -\frac{1}{2}$.

** $a_{\text{av.}} = (a_a + a_e)/2$.

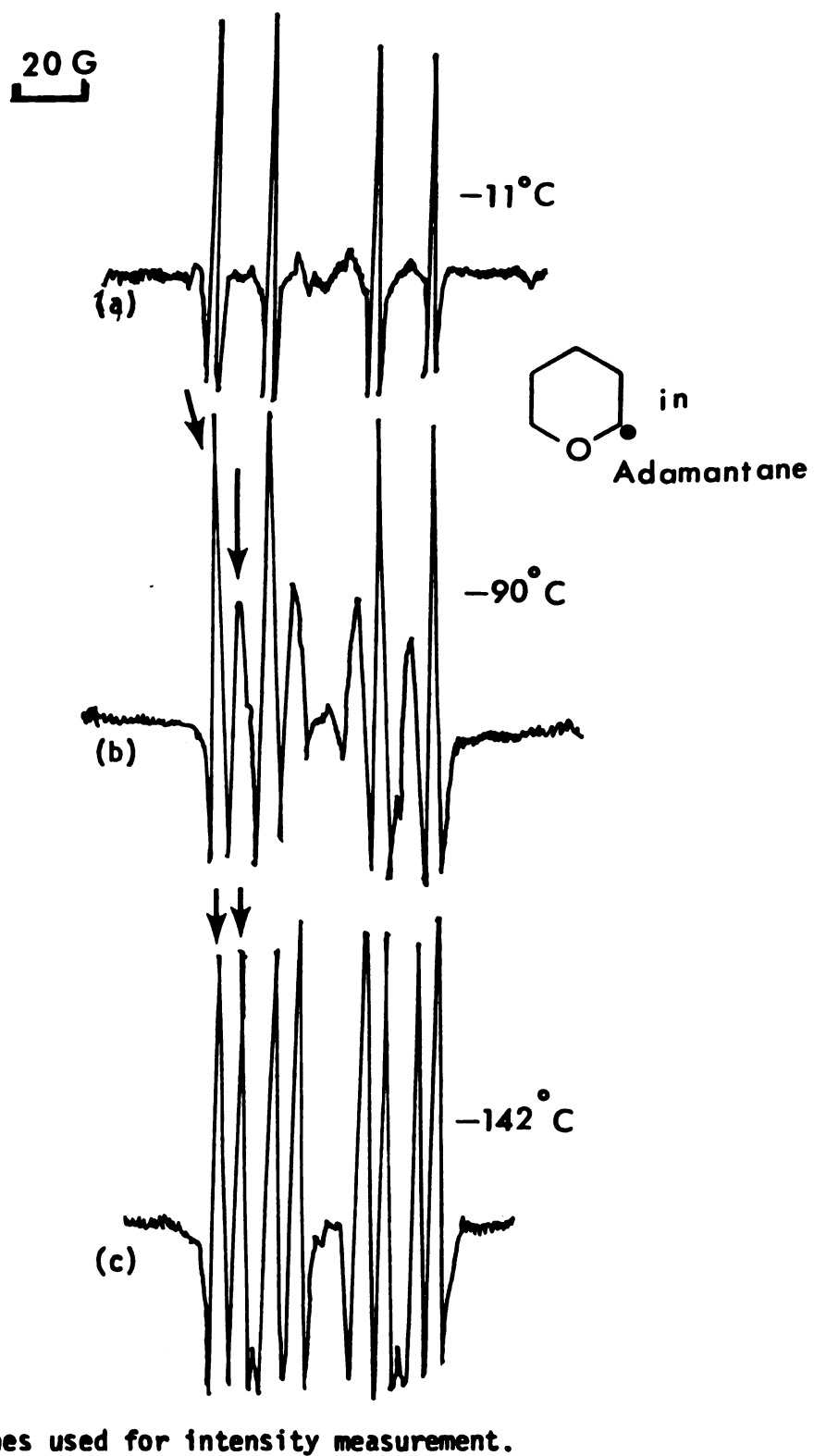


Figure 26. ESR spectra of 2-tetrahydropyranyl radical in adamantane.

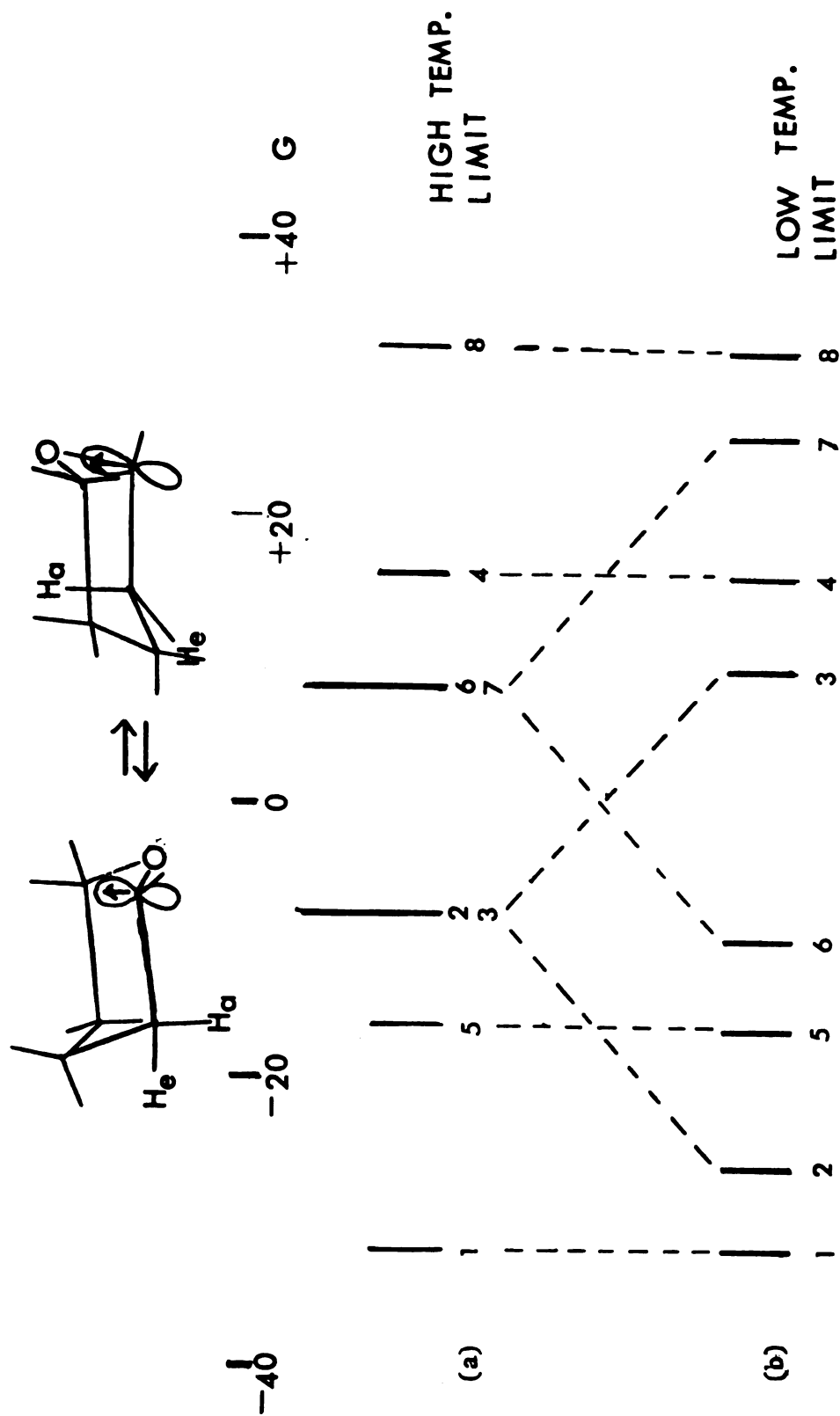


Figure 27. Field positions and intensities for lines in the spectrum of 2-tetrahydropyranyl radical in adamantane. The numbers refer to the nuclear spin states of Table 13.

Exchange of H_a and H_e by ring inversion would interchange spin states 2 and 3 and 6 and 7 of Figure 27 and lead to the changes in spectra with temperature observed with the eight line calculated spectrum of Figure 27 corresponding to the observed spectrum at -142°C of Figure 26. The high temperature triplet of triplets of Figure 27(a) should be observed when ring inversion is sufficiently rapid to make the two β protons equivalent. However, the radicals decay before a high enough temperature can be reached and the spectrum of Figure 26(a) taken at -11°C corresponds to the intermediate region of Figure 27, where lines 2, 3, 6, 7 are sufficiently broadened by inversion to be unobservable. Values of $\log (1/\tau)$ versus relative peak intensity for 2-tetrahydropyranyl radical were obtained using program ESREX4 (Table 14 and Figure 28). The values of $\log (1/\tau)$ obtained using this graph plus the experimental intensities at different temperatures are given in Table 15 and are plotted graphically in Figure 29. The activation energy for ring inversion is $E_a = 3.7$ kcal/mole and the frequency factor $(1/\tau)_0 = 3.9 \times 10^{11} \text{ sec}^{-1}$ from the slope and intercept of Figure 29.

C. Dioxane in Adamantane

A solid solution of dioxane in adamantane was γ irradiated at 77°K and the ESR spectra studied over a range of temperatures up to about 0°C where decay of the radical becomes rapid. At -82° [Figure 30(c)] eight lines of approximately equal intensity were observed characteristic of a radical with three different proton splittings. The 1,4-dioxanyl radical VI appears to be the only radical

Table 14. Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 2-tetrahydropyranyl radical in adamantane.

$\text{Log}_{10}(1/\tau)$	$F(\omega)$
+9.0	0.50
8.6	0.09
8.2	0.01
7.8	0.17
7.4	0.47
7.0	0.73
6.6	0.88
6.2	0.95
5.8	0.98
5.4	0.99

Table 15. Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 2-tetrahydropyranyl radical in adamantane.^{a,b}

$T^{\circ}\text{C}$	$1/T^{\circ}\text{K}(\times 10^3)$	$F(\omega)$	$\log(1/\tau)$
-58	4.65	0.00	8.20
-68	4.88	0.38	7.52
-75	5.05	0.43	7.46
-85	5.32	0.56	7.29
-94	5.59	0.69	7.09
-102	5.85	0.80	6.88
-109	6.10	0.82	6.66
-120	6.54	0.96	6.05
-131	7.04	1.00	5.70

^aValues of $F(\omega)$ are from Figure 26 plus some spectra not illustrated.

^bValues of $\log(1/\tau)$ are from Figure 28.

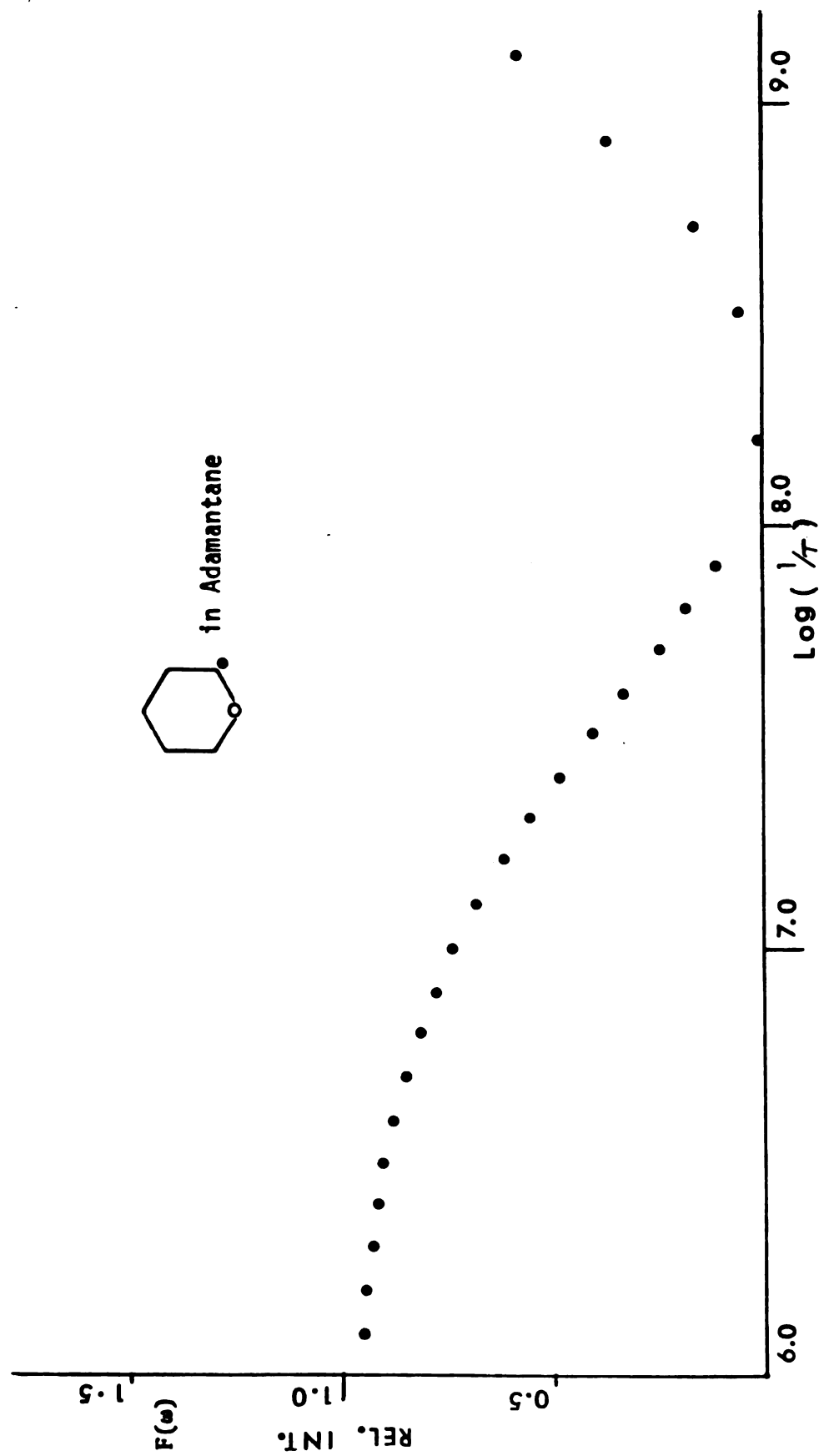


Figure 28. Calculated values of the relative intensities of the lines indicated by arrows in Figure 26, $F(\omega)$, versus $\log(1/\tau)$ for 2-tetrahydropyranyl radical in adamantane.

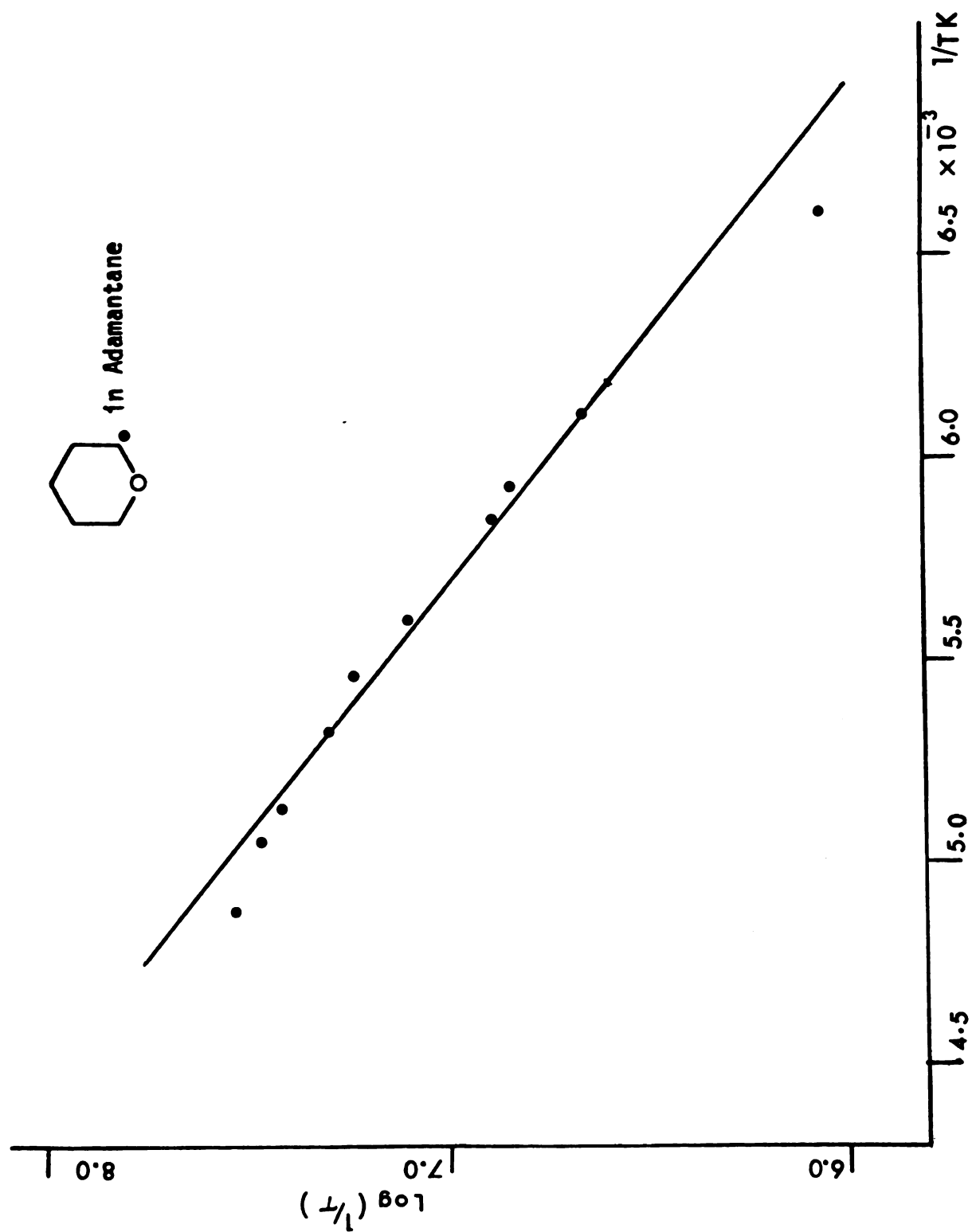


Figure 29. Plot of $\log(1/\tau)$ versus $1/T^{\circ}\text{K}$ for 2-tetrahydropyranyl radical in adamantane.

1, 4 DIOXANE IN ADAMANTANE

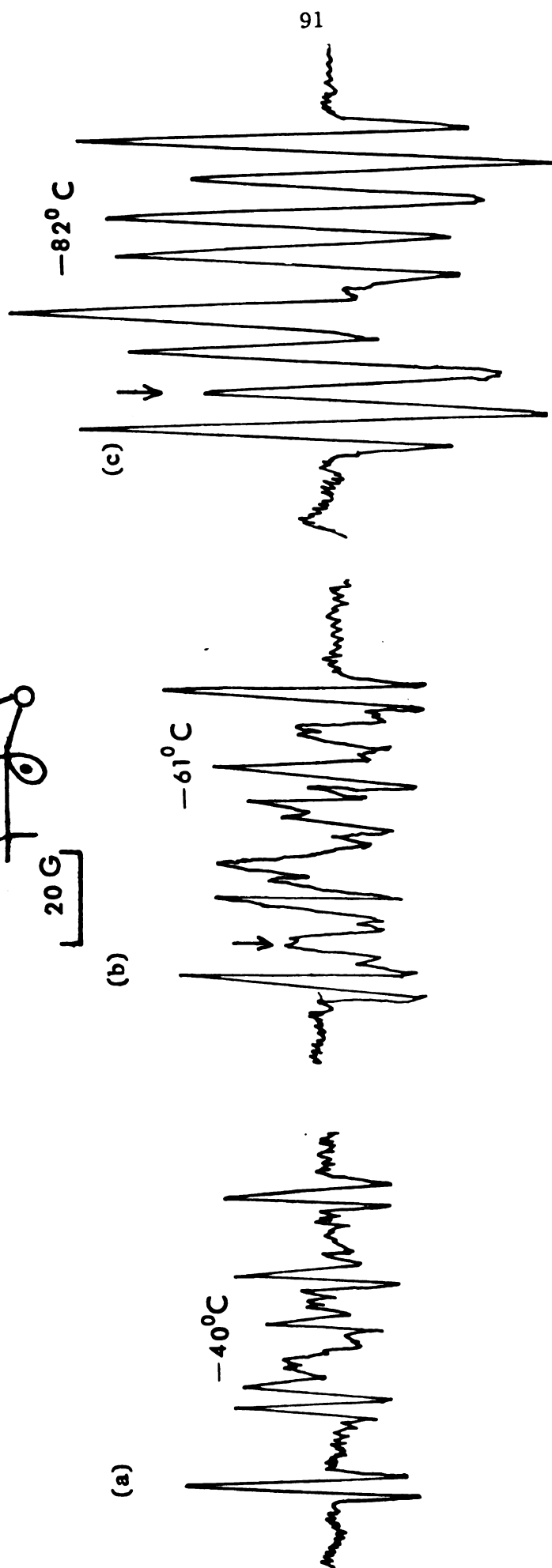
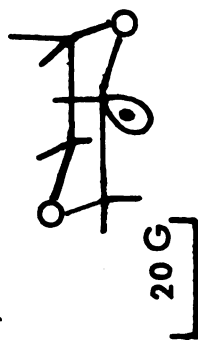


Figure 30. ESR spectra of 1,4-dioxanyl radical in adamantane (a) at -40°C , (b) at -61°C , and (c) at -82°C .

present and the hyperfine splittings may be assigned to one α proton, $a(H_\alpha) = 17.3$ G and two unequal β protons, $a(H_{\beta_1}) = 8.9$ G and $a(H_{\beta_2}) = 39.5$ G; the g value is 2.0034.

On warming the intensities of lines 2 and 4 decrease while lines 1 and 3 remain invariant (Figure 27). At -40°C the spectrum is approaching the high-temperature limit [Figure 27(a)] with the β protons equivalent. The temperature dependence of the spectrum was analyzed as described above for 2-tetrahydropyranyl radical using the ratio of the intensity of line 2 to line 1. Calculated values of the relative intensities versus $\log(1/\tau)$ for the 2-dioxanyl radical were obtained using ESREX4 and are plotted in Figure 31. Values of $\log(1/\tau)$ at measured temperatures were then plotted versus $1/T^\circ\text{K}$ in Figure 32 from which $E_a = 3.7$ kcal/mole and $(1/\tau)_0 = 6.5 \times 10^{10}$ for the ring inversion process.

IV. Heterocyclic Sulfur Compounds

A. Tetrahydrothiophene in Adamantane

A sample was X-irradiated at room temperature and ESR spectra recorded from room temperature, where the radical is reasonably stable, down to -188°C . The room temperature spectrum [Figure 33(a)] is a triplet of triplets (plus some weaker unidentified lines) indicating that the principal radical is the 2-tetrahydrothiophenyl radical XIX; the hyperfine splittings $a(H_\alpha) = 16.0$ G and $a(H_\beta) = 25.5$ G (two equivalent

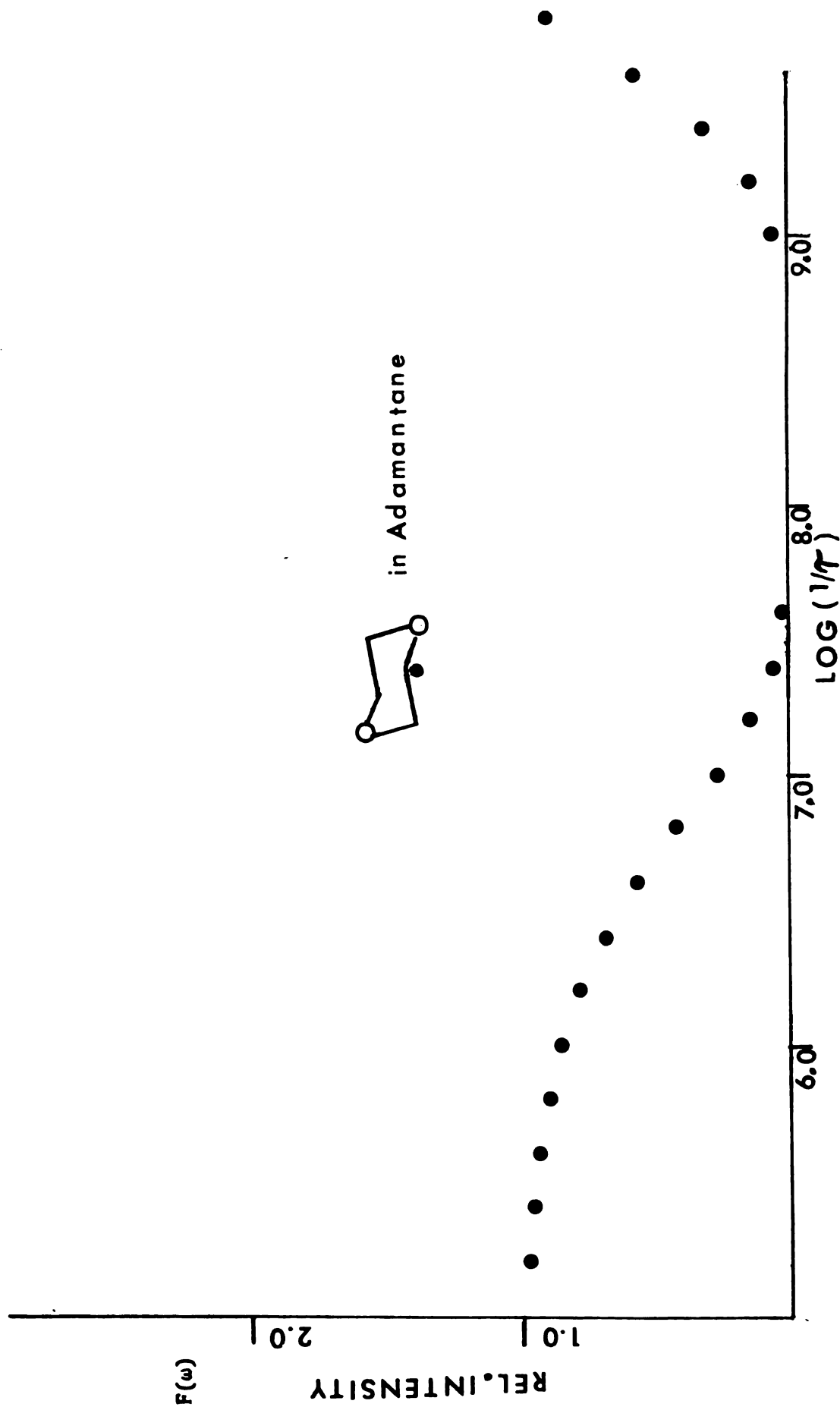


Figure 31. Calculated values of relative intensity, $F(\omega)$, versus $\log(1/\tau)$ for 1,4-dioxany radical in adamantane.

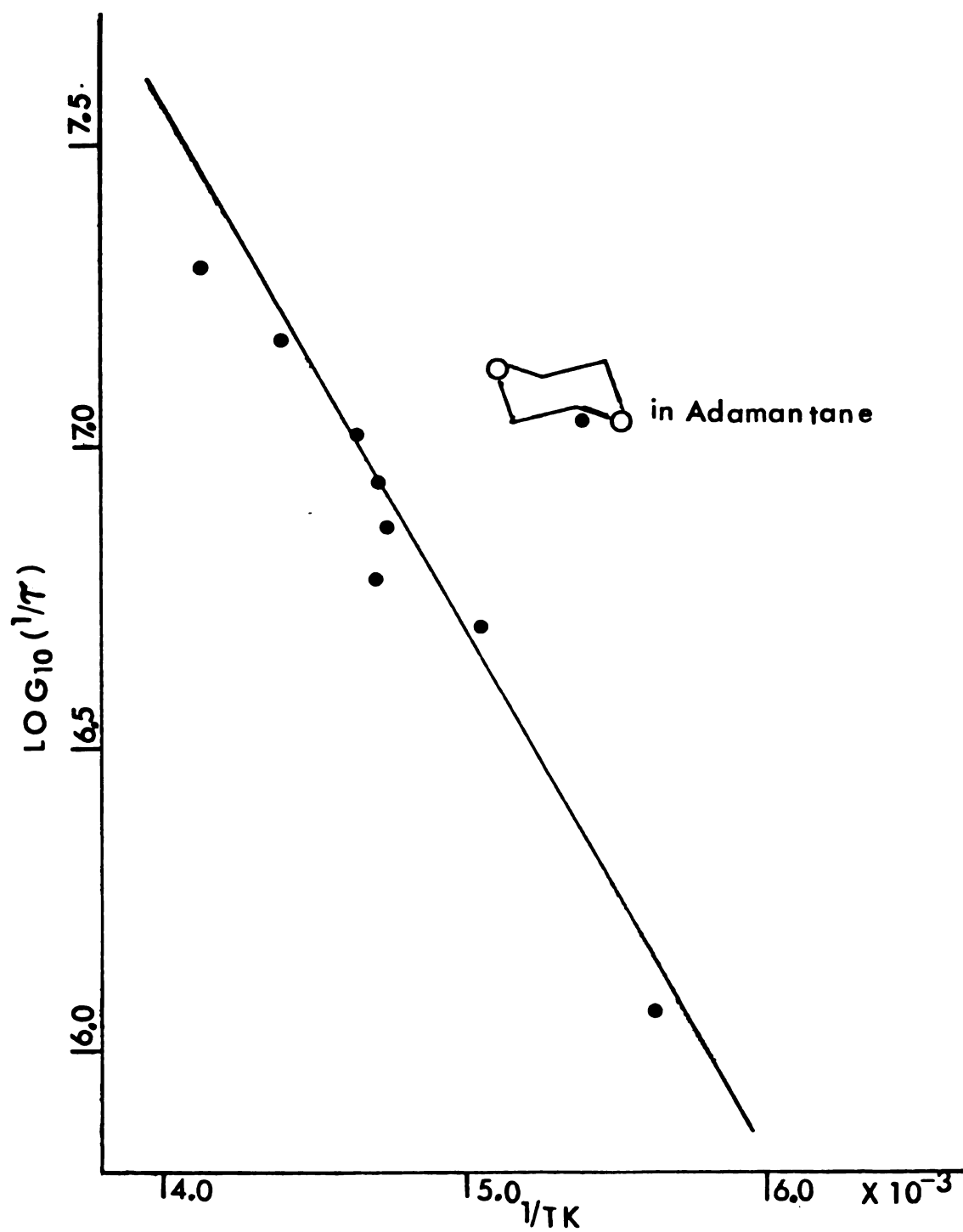


Figure 32. Plot of $\log(1/\tau)$ versus $1/T$ for 1,4-dioxanyl radical in adamantane.

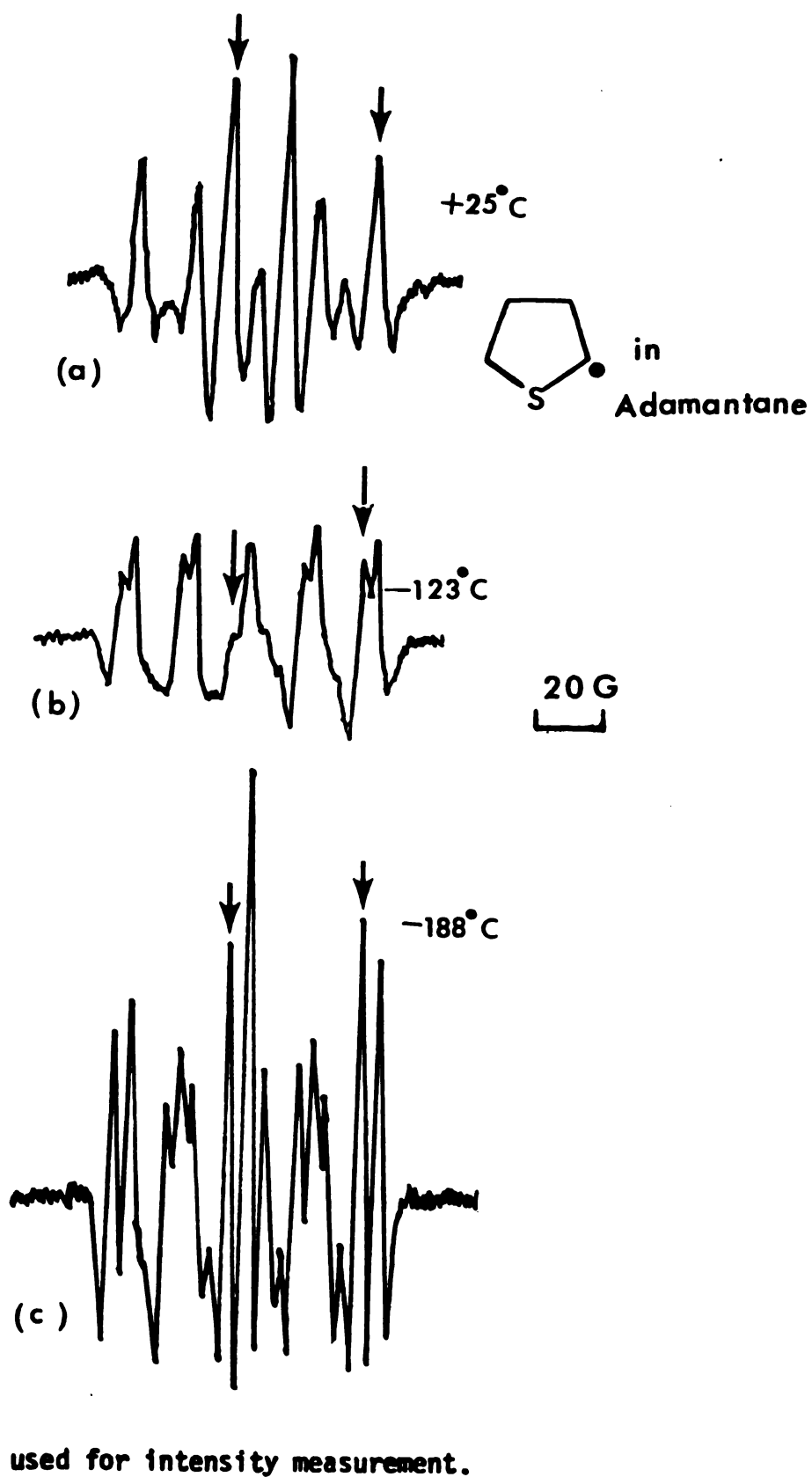
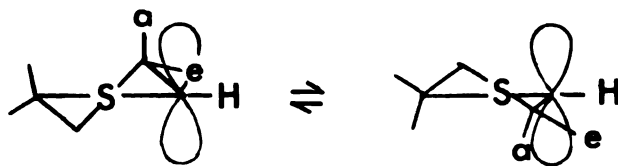


Figure 33. ESR spectra of 2-tetrahydrothiophenyl radical in adamantane.



XIX

protons), are consistent with this assignment. On lowering the temperature the two central lines decrease in intensity, vanishing at the coalescence temperature, -104°C . At lower temperatures the β protons become nonequivalent with $a(\text{H}_{\beta_1}) = 37.4 \text{ G}$, $a(\text{H}_{\beta_2}) = 19.0 \text{ G}$, $a(\text{H}_{\gamma}) = 4.8 \text{ G}$ and $a(\text{H}_{\alpha}) = 15.0 \text{ G}$ at -171°C . (Figure 33(c)). At intermediate temperatures the ratio of intensities of one of the central lines to one of the outer lines was measured. Calculated values of this ratio were plotted versus $\log (1/\tau)$ [Figure 34] and values of $\log (1/\tau)$ corresponding to the observed relative intensities were then plotted versus $1/T^{\circ}\text{K}$ [Figure 35]. The slope and intercept of the best straight line of the Arrhenius plot [Figure 35] leads to the activation energy for ring inversion, $E_a = 2.7 \pm 0.5 \text{ kcal/mole}$, and the frequency factor, $(1/\tau)_0 = 9.8 \times 10^{11} \text{ sec}^{-1}$.

A sample of tetrahydrothiophene was distilled three times, degassed and sealed under vacuum in a quartz tube. After γ -irradiation at liquid nitrogen temperature, ESR spectra were taken at various higher temperatures. At -102°C only very broad lines were observed and above -80°C these vanished so no radical products could be identified.

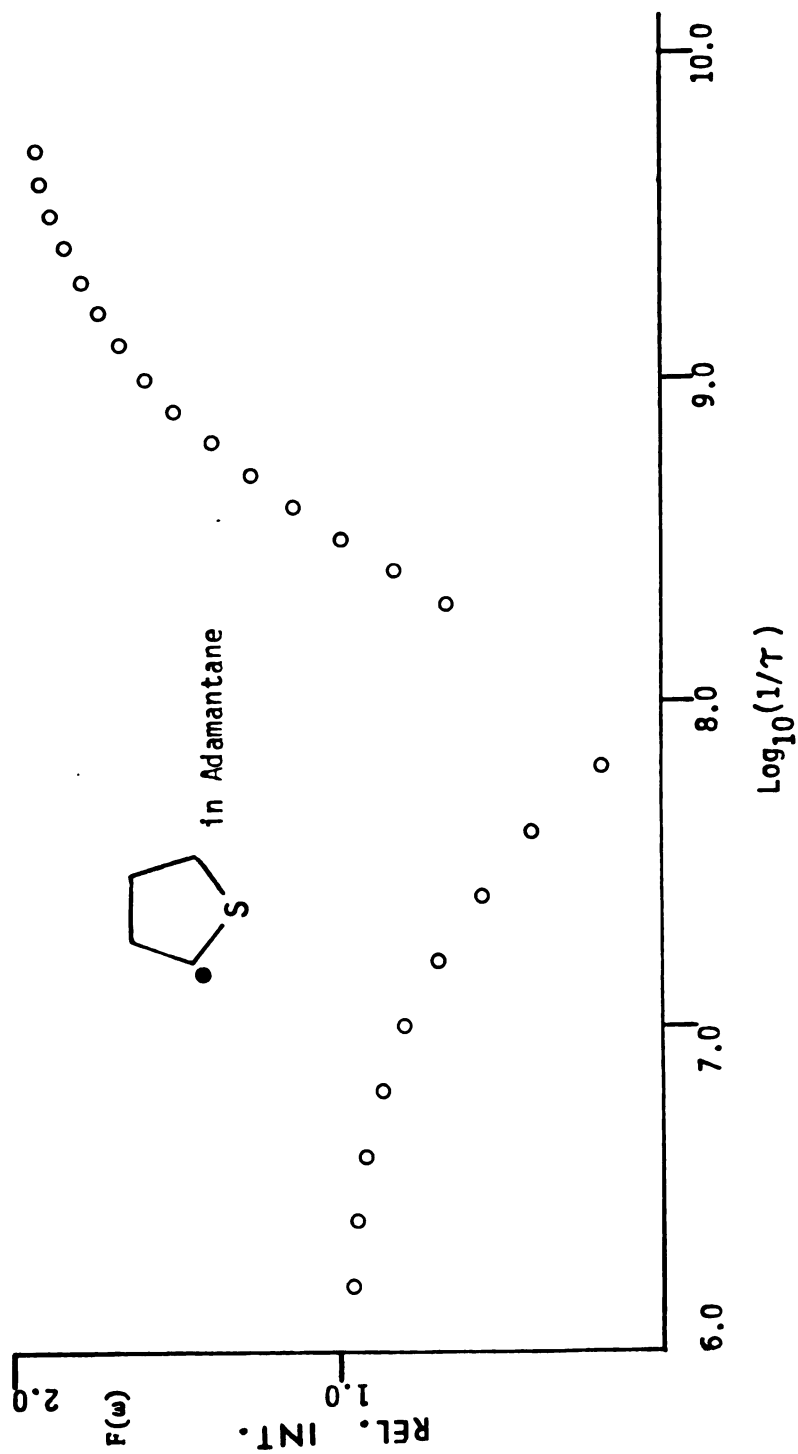


Figure 34. Calculated values of the relative intensities, $F(\omega)$ of the lines indicated by arrows in Figure 33 versus $\log(1/\tau)$ for 2-tetrahydrothiophenyl radical in adamantane.

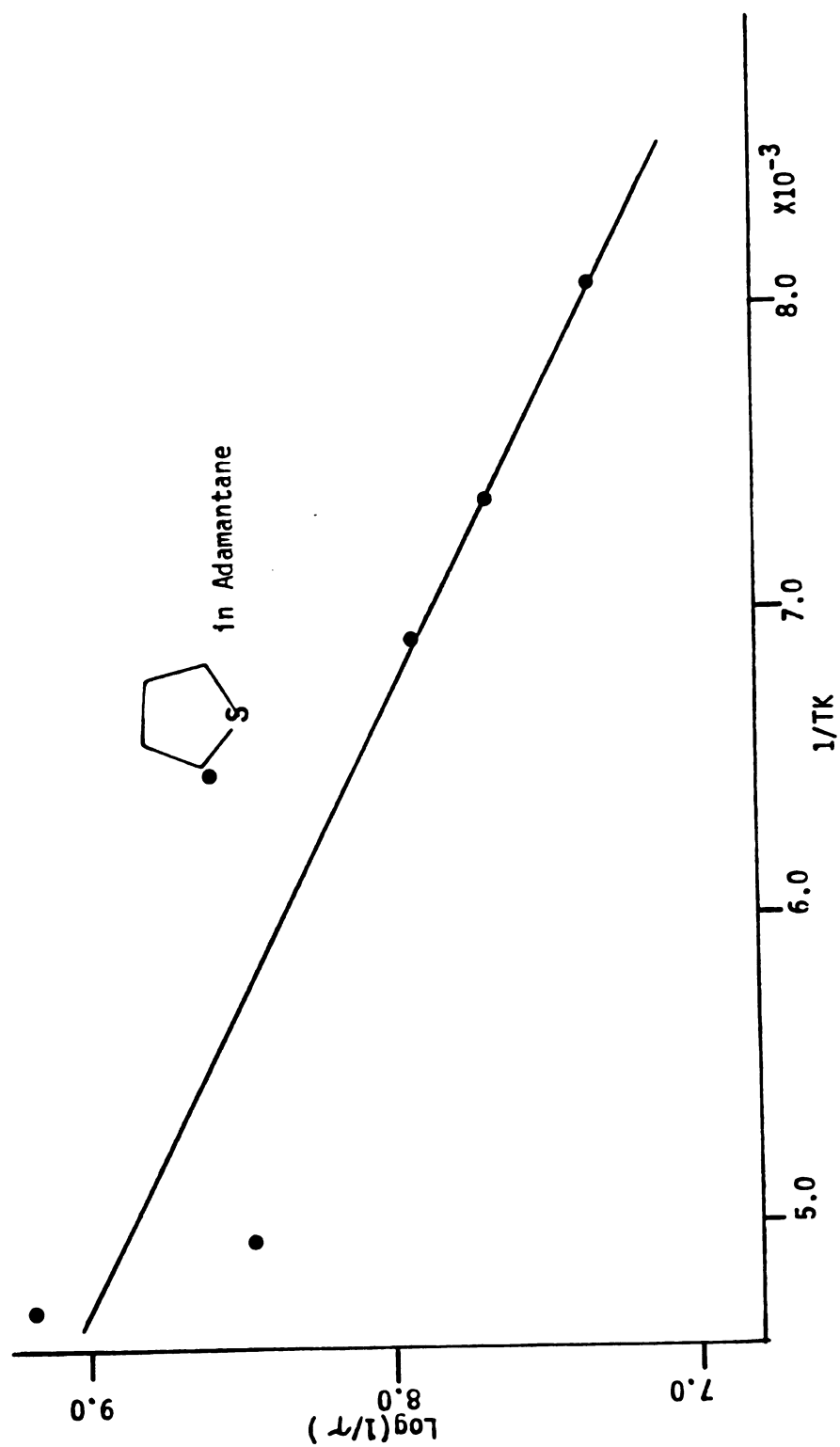
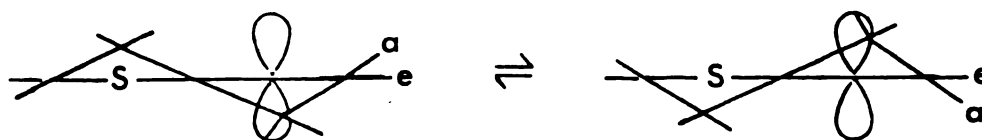


Figure 35. Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 2-tetrahydrothiophenyl radical in adamantane.

B. Pentamethylene sulfide in adamantane

A sample was γ -irradiated at 77°K and spectra recorded while the sample was warming up. At -92°C an eight line spectrum characteristic of the 2-tetrahydrothiopyranyl radical XX was obtained [Figure 36] along with several unidentified lines. The ESR parameters



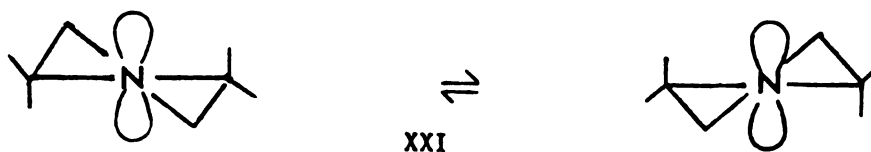
XX

from this spectrum are $a(H_{\beta_1}) = 4.2$ G, $a(H_{\beta_2}) = 42.8$ G, $a(H_{\alpha}) = 18.1$ G and $g = 2.0042 \pm 0.0002$. The radicals recombine rapidly above -80°C and have disappeared at -60°C. They are much less stable than the 2-tetrahydrothiophenyl radicals (XIX) and spectra showing temperature dependence of line intensities could not be obtained.

V. Heterocyclic Nitrogen Compounds

A. Pyrrolidine in adamantane

A sample was γ -irradiated at 77°K and ESR spectra recorded while gradually warming to room temperature. The spectra at various temperatures between -190°C and -32°C are shown in Figure 37 and all appear to arise from the 10pyrrolidinyl radical XXI. At higher temperatures (-32°) the four β protons are equivalent with



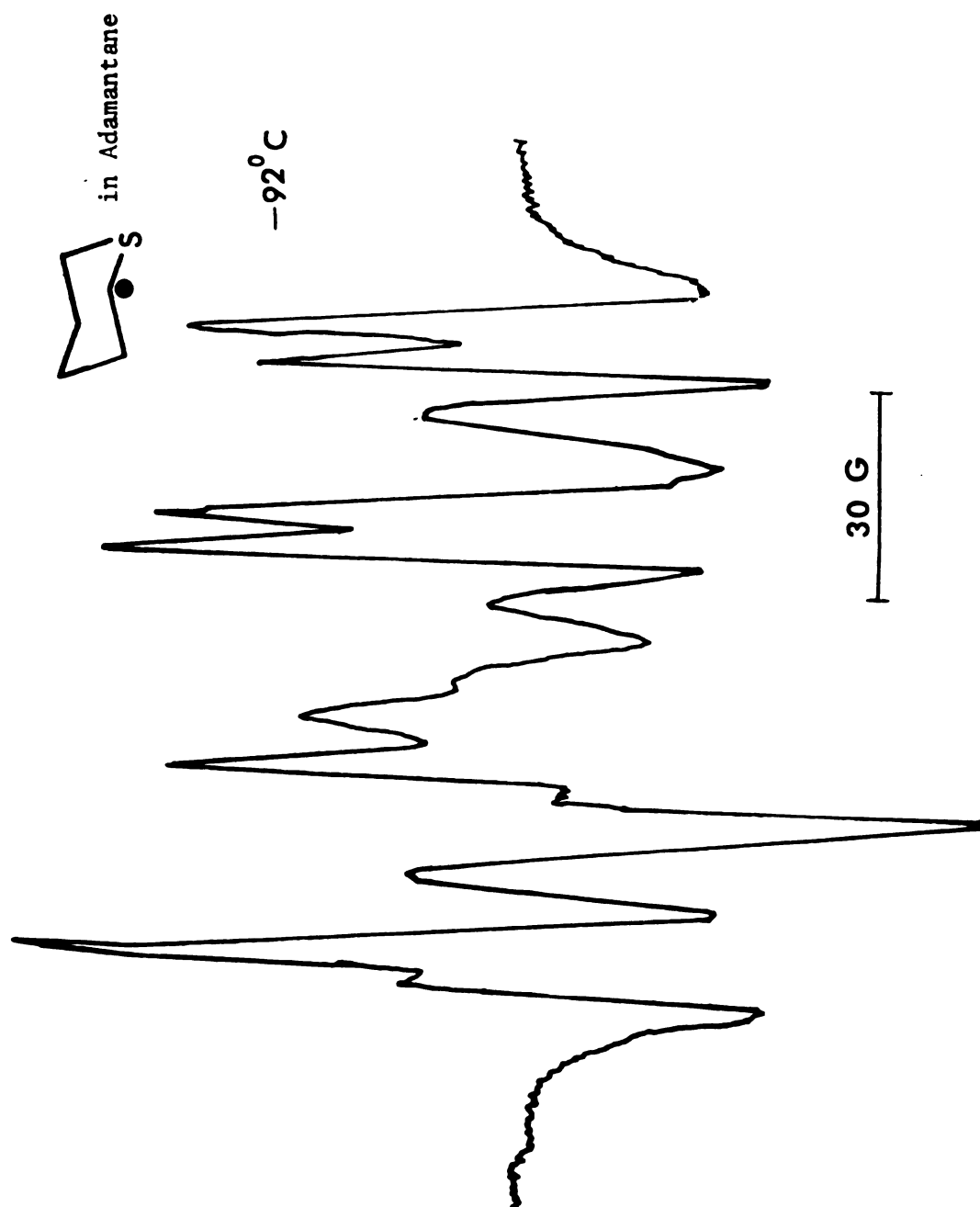


Figure 36. ESR spectrum of 2-tetrahydrothiopyranyl radical in adamantane at -92°C .

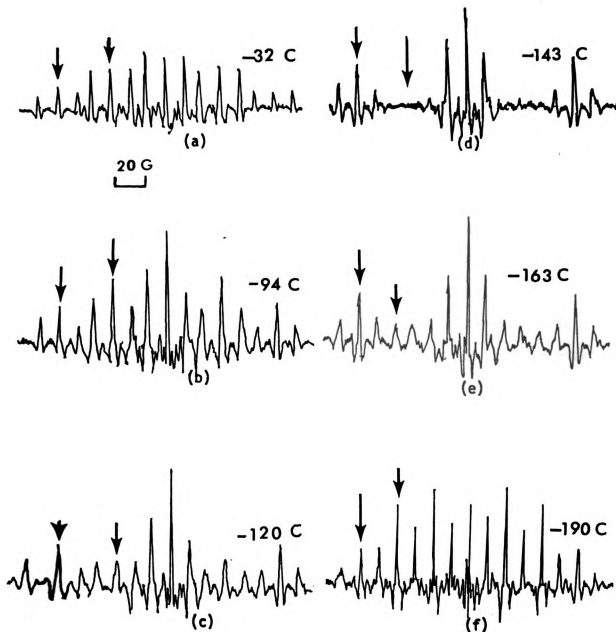


Figure 37. ESR spectra of 1-pyrrolidinyl radical in adamantane. Lines used for measurement of relative intensity are indicated by arrows.

$a(H_\beta) = 40.1$ G, $a(^{14}\text{N}) = 14.5$ G and $g = 2.0048$. At very low temperatures (below -173°K) the β protons appear to become nonequivalent with two having $a(H_{\beta_1}) = 27.0$ G and two $a(H_{\beta_2}) = 54.2$ G since these parameters, along with the value $a(^{14}\text{N}) = 13.5$ G, account for the positions of the lines of Figure 37(f).

The temperature dependence of the spectra has been employed to study the ring motion. The intensity of the central line of the next-to-outer triplet relative to the central line of the outer triplet was measured at each temperature (the $m_I = \pm 1$ lines of the nitrogen triplets change intensity relative to the $m_I = 0$ line and so could not be used) and values are given in Table 16 along with the calculated values of $\log(1/\tau)$ corresponding to the measured relative intensities. The calculated values of $\log(1/\tau)$ for various relative intensities were calculated by use of ESREX4 and are given in Table 17 and plotted graphically in Figure 38. An Arrhenius plot $\log(1/\tau_c)$ versus $1/T^\circ\text{K}$ is shown in Figure 39 and leads to an activation energy for ring inversion, $E_a = 2.9$ kcal/mole, and $(1/\tau)_0 = 6.5 \times 10^{12} \text{ sec}^{-1}$.

This radical (XXI) is stable to -10°C . A sample of pyrrolidine in adamantane irradiated at 25°C gives the spectrum of another radical.

B. Piperidine in Adamantane

A sample was X-irradiated at room temperature and the spectrum recorded immediately [Figure 40]. The basic spectrum, neglecting some unidentified lines, is a doublet of doublets resulting from two different splittings by single protons each line of which is further split by interaction with ^{14}N into triplets. By analogy

Table 16. Calculated values of relative intensities $F(\omega)$ versus $\log(1/\tau)$ for 1-pyrrolidinyl radical in adamantane.

$\log_{10}(1/\tau)$	$F(\omega)$
+11.0	1.98
10.5	1.94
10.0	1.82
9.5	1.49
9.0	0.83
8.5	0.16
8.0	0.04
7.5	0.37
7.0	0.72
6.5	0.90
6.0	0.97
5.5	0.99

Table 17. Experimental values of relative intensities $F(\omega)$ at various temperatures and the corresponding calculated values of $\log(1/\tau)$ for 2-pyrrolidinyl radical in adamantane.^{a,b}

$T^{\circ}\text{C}$	$1/T^{\circ}\text{K}(\times 10^3)$	$F(\omega)$	$\log(1/\tau)$
-51	4.50	1.80	10.0
-94	5.59	1.29	9.32
-110	6.13	0.86	9.04
-120	6.54	0.38	8.70
-132	7.09	0.20	8.41
-143	7.69	0.0	8.00
-163	9.10	0.35	7.41
-173	10.00	0.55	7.21

^aValues of $F(\omega)$ are from Figure 37.

^bValues of $\log(1/\tau)$ are from Figure 38.

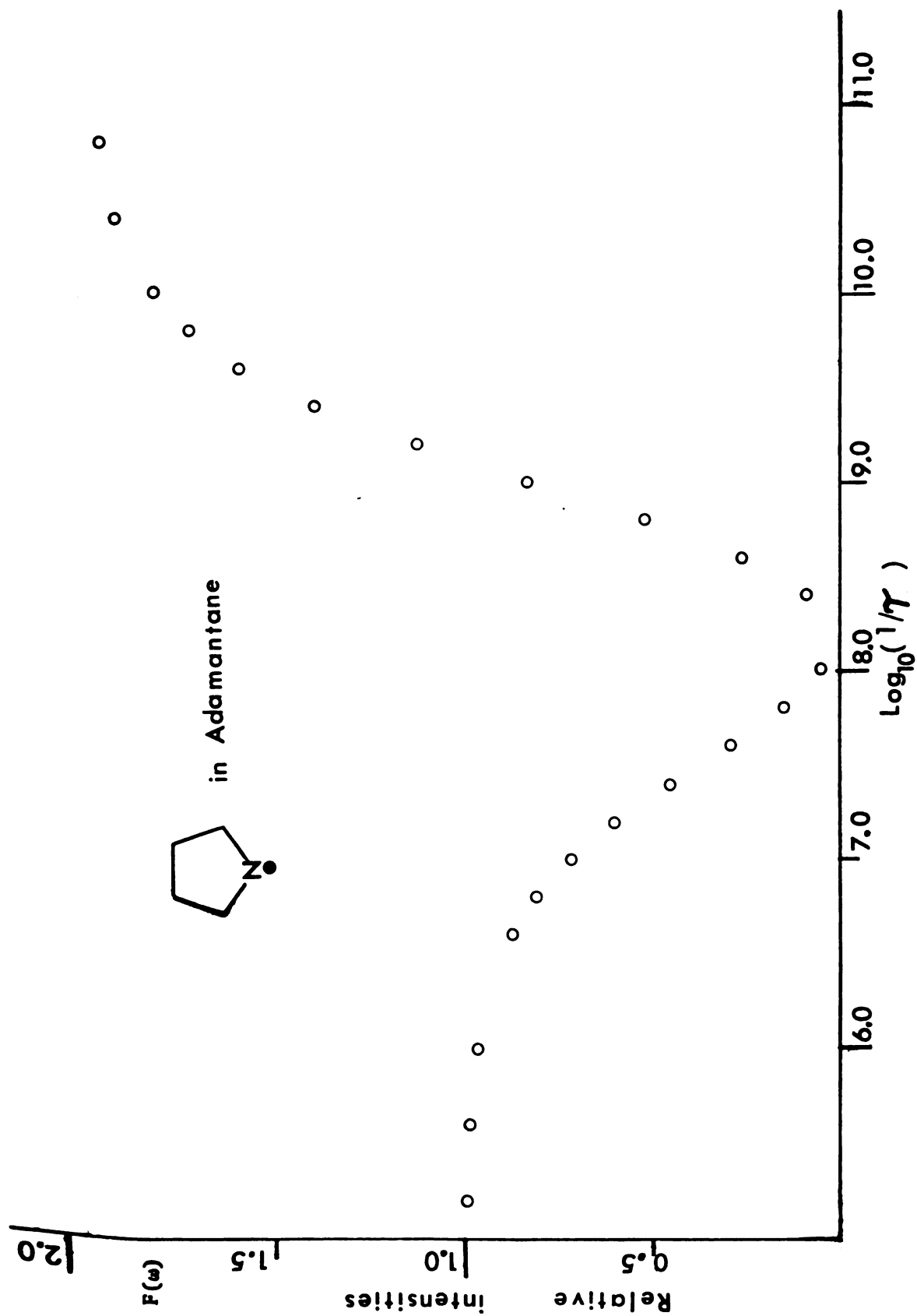


Figure 38. Calculated values of the relative intensities, $F(\omega)$, of lines indicated by arrows in Figure 37 versus $\log(1/\tau)$ for 1-pyrrolidiny radical in adamantane.

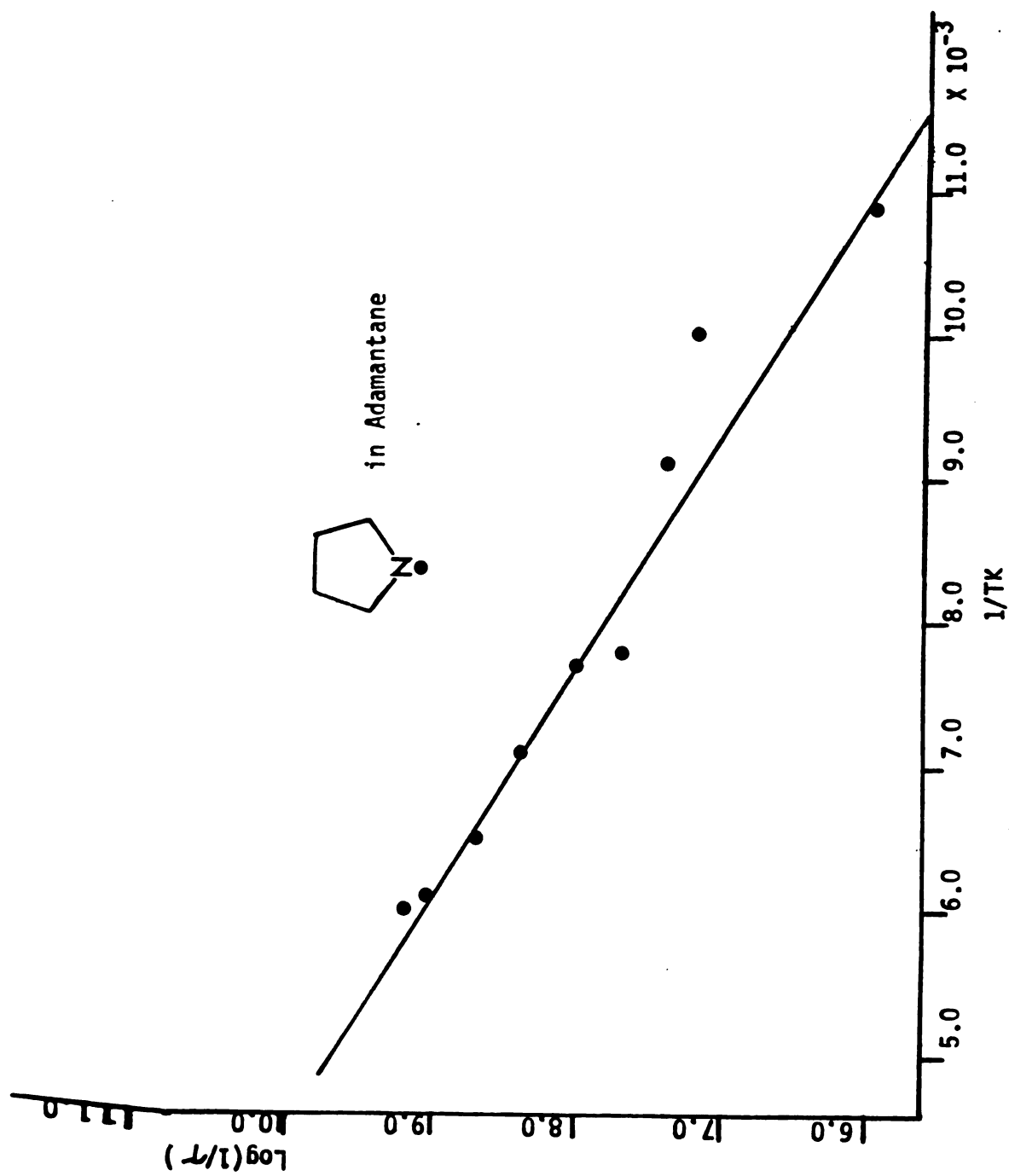


Figure 39. Plot of $\log(1/\tau)$ versus $1/T^\circ\text{K}$ for 1-pyrrolidinyl radical in adamantane.

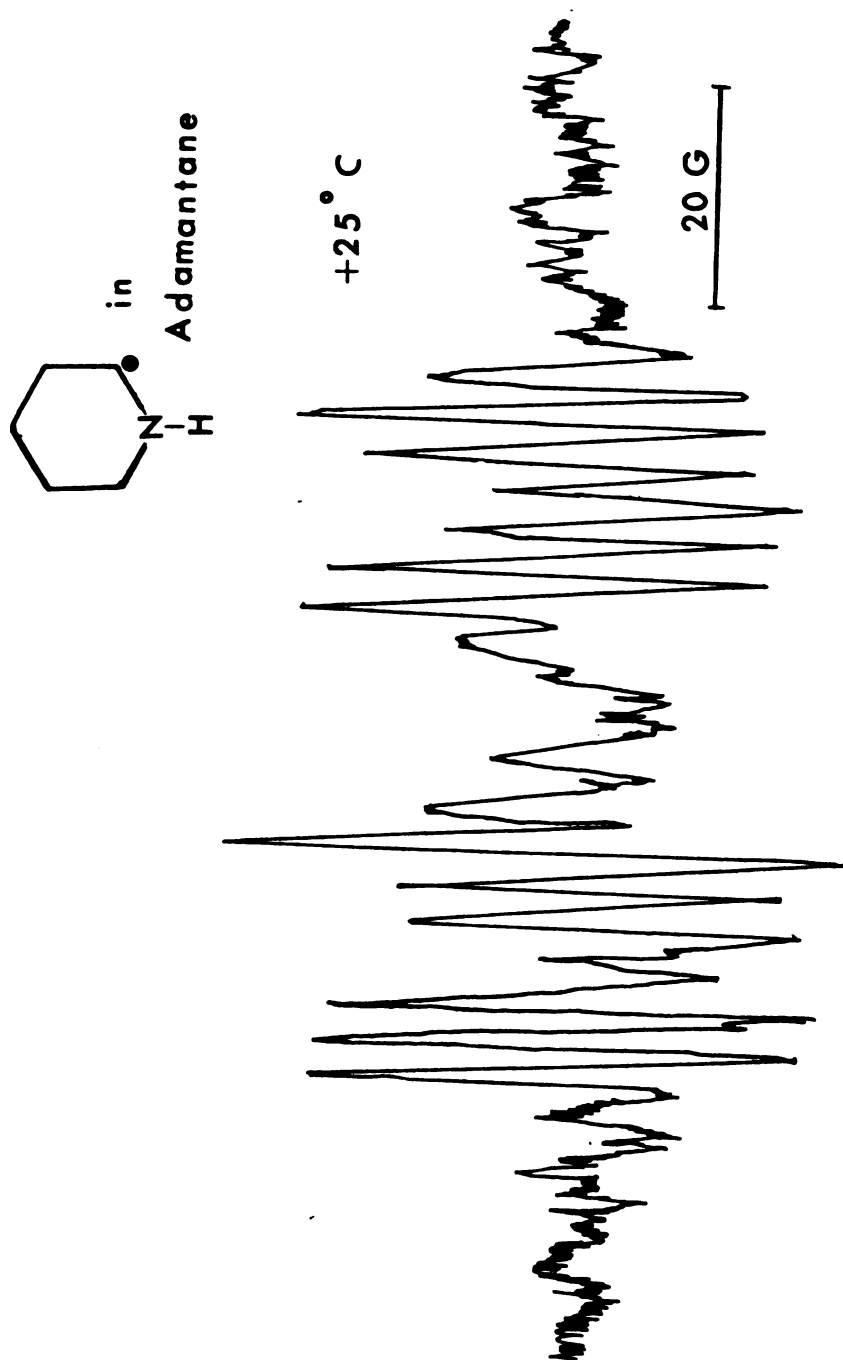
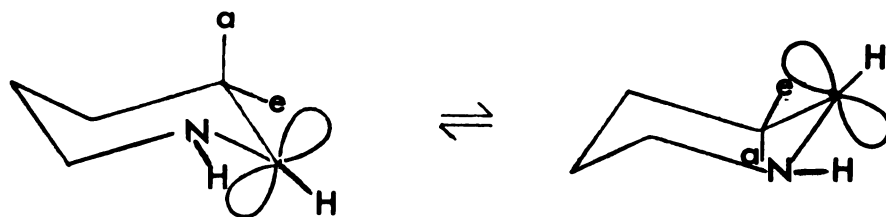


Figure 40. ESR spectrum of 2-piperidinyl radical in adamantane at 25°C.

with the temperature-dependent spectra of the 2-tetrahydropyranyl radical [Figure 27 and Table 13] this spectrum can be assigned to the 2-piperidiny radical XXII in an intermediate temperature region



XXII

where the ring motion leads to low intensities for certain lines. The ESR parameters $a(H_\alpha) = 13.7$ G, $a(^{14}\text{N}) = 3.4$ G, $a(H_{\beta_1}) + a(H_{\beta_2}) = 41.9$ G and $g = 2.0030$ were obtained on this assumption. Microwave saturation studies indicate that lines from a second radical are present and the activation energy for ring inversion could not be obtained because of overlapping lines.

VI. Other Alicyclic Compounds

A. Cyclopentyl Chloride in Adamantane

A sample of cyclopentyl chloride in adamantane was X-irradiated at room temperature and the spectrum recorded immediately [Figure 41]. It may be analyzed as a quintet of triplets each line of which shows a small doublet splitting and the ESR parameters $a(H_1) = 2.7$ G, $a(H_2) = 14.3$ G (two equivalent protons), $a(H_3) = 22.2$ G (four equivalent protons) and $g = 2.0029$ indicate that the radical is the cyclopentenyl radical I.

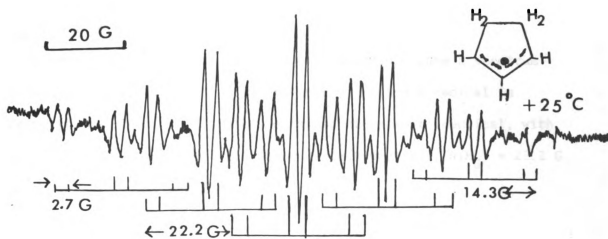


Figure 41. ESR spectrum of cyclopentenyl radical from a sample of cyclopentyl chloride in adamantane irradiated at room temperature.

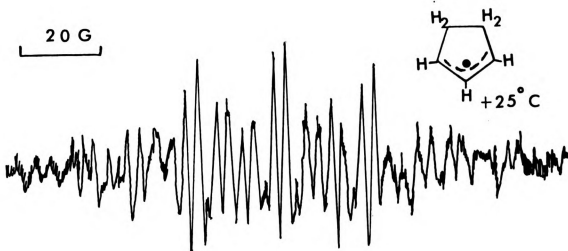


Figure 42. ESR spectrum of cyclopentenyl radical from a sample of cyclopentyl bromide in adamantane irradiated at room temperature.

B. Cyclopentyl Bromide in Adamantane

A sample X-irradiated at room temperature gave a spectrum [Figure 42] very similar to that of the cyclopentenyl radical in Figure 41, and the ESR parameters obtained are almost identical, with $a(H_1) = 2.7$ G, $a(H_2) = 14.5$ G (two equivalent protons), $a(H_3) = 22.2$ G (four equivalent protons) and $g = 2.0027$.

C. Cyclopentane in Adamantane

A sample irradiated at 77°K gave the spectrum shown in Figure 43(a) at -121°C. This is a doublet of quintets characteristic of cyclopentane radical (XXIII) in the region of fast ring inversion with $a(H_\alpha) = 21.42$ G, $a(H_\beta) = 35.6$ G, and $g = 2.0031$. At -187°K the spectrum changed to that of Figure 43(b) indicating that ring inversion is slow with $E_a = 2.2$ kcal/mole and $(1/\tau)_0 = 1.46 \times 10^{12} \text{ sec}^{-1}$ found as above with $a(H_\alpha) = 21.1$ G, $a(H_{\beta 1}) = 25.2$ G and $a(H_{\beta 2}) = 45.6$ G.

D. Cyclopentanol in Adamantane

A sample X-irradiated at room temperature gave a complex room temperature ESR spectrum which must arise from two or more radicals (Figure 44). The values $a(H_\beta) = 27.6$ G (four equivalent protons) and $g = 2.0033$ indicates that one of the products is radical XXIV undergoing rapid inversion at room temperature. The low-temperature spectra could not be interpreted so no information concerning the ring inversion process could be obtained for 1-hydroxycyclopentyl radical.

E. 1,2-Dichlorotetrafluorocyclobutene in Adamantane

A sample was γ -irradiated at 77°K and the spectra observed at various temperatures. At -50°C the spectrum of Figure 45(a) was obtained and analysis of the spectrum by computer simulation using ESR was

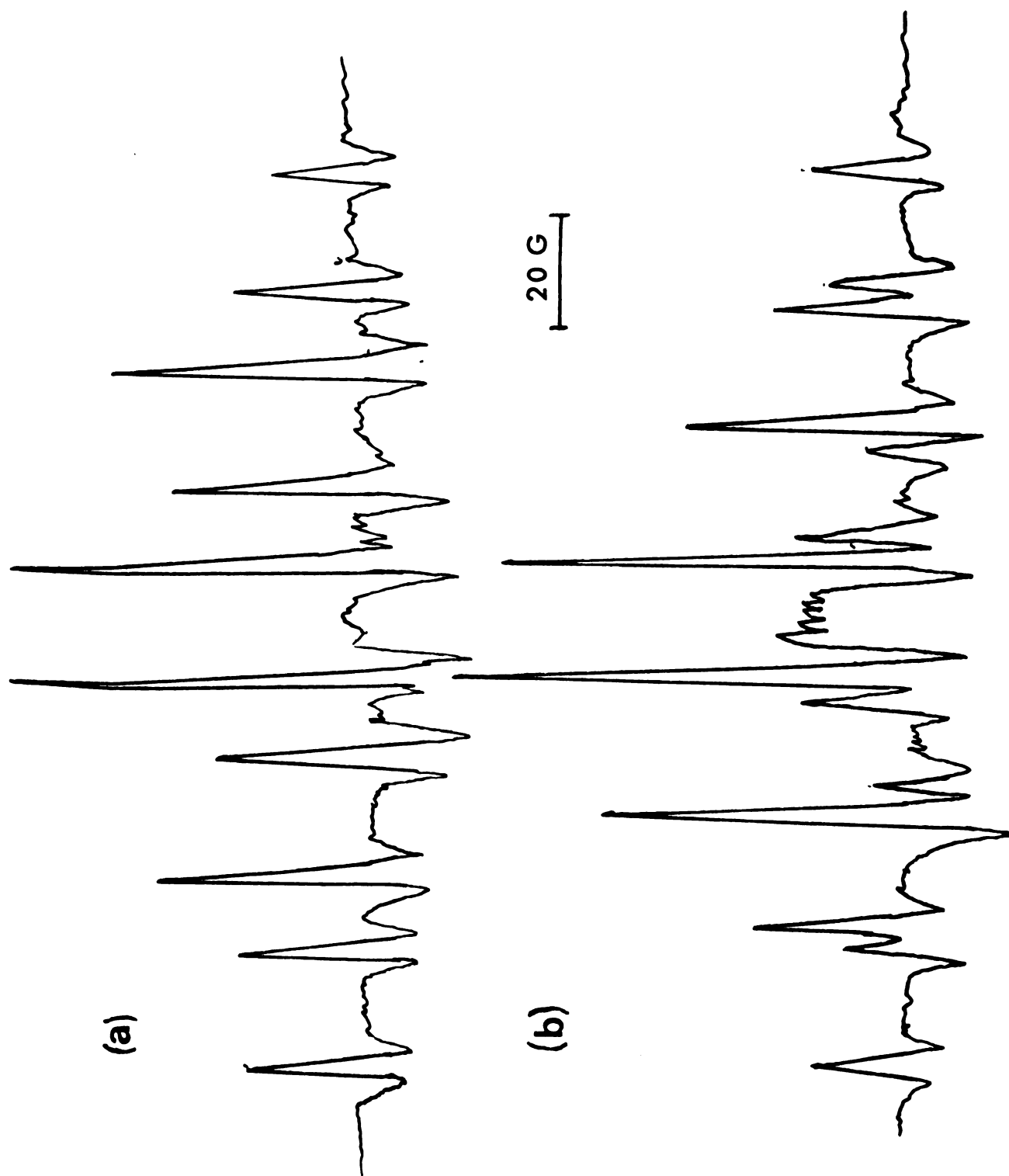


Figure 43. ESR spectrum of cyclopentyl radical in adamantane: (a) -121°C, rapid ring inversion, (b) -187°C, slow ring inversion.

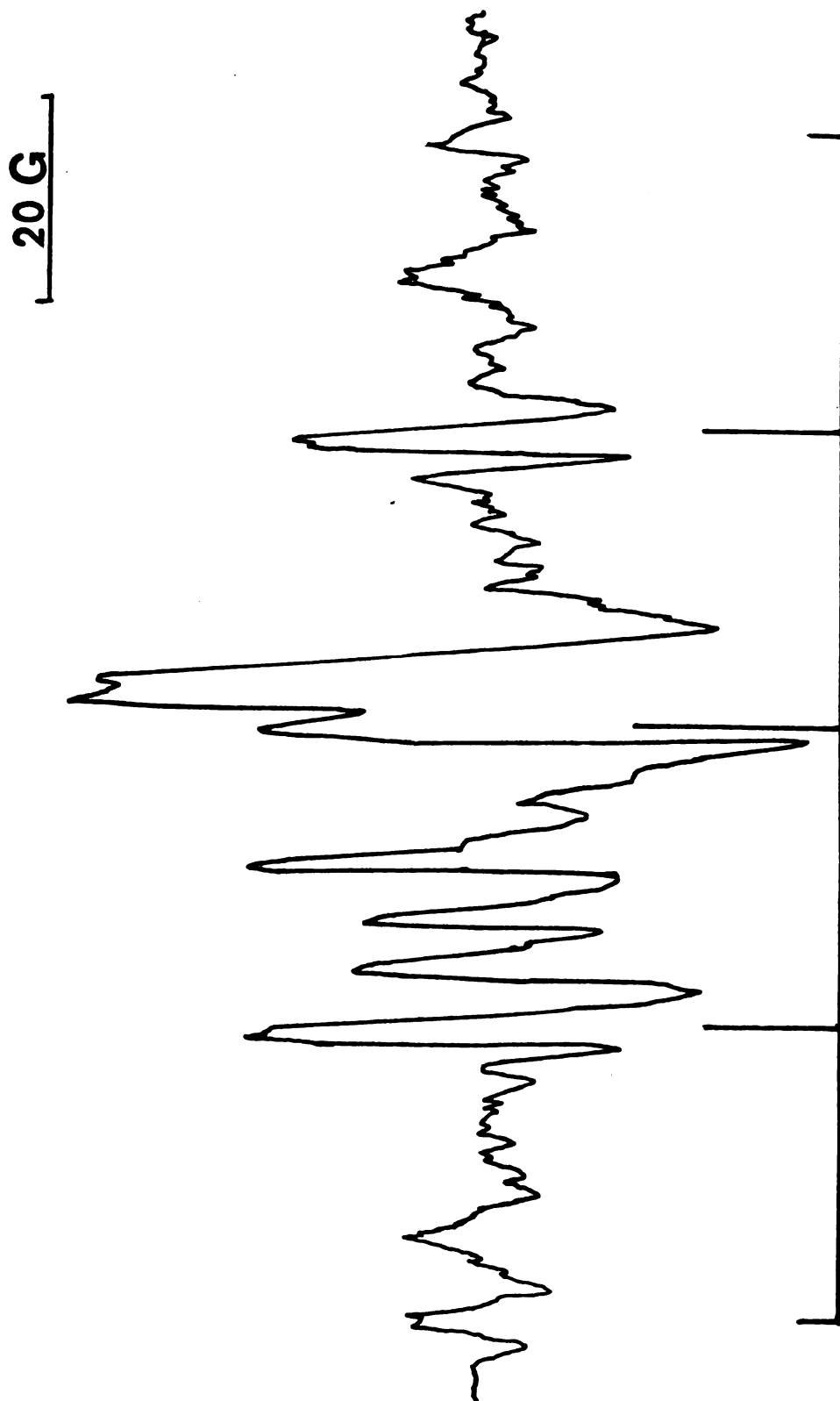


Figure 44. ESR spectrum of the 1-hydroxycyclopentyl radical in adamantane at 25°C. The line positions of the quintet are indicated below while the remaining lines are attributed to other radicals.

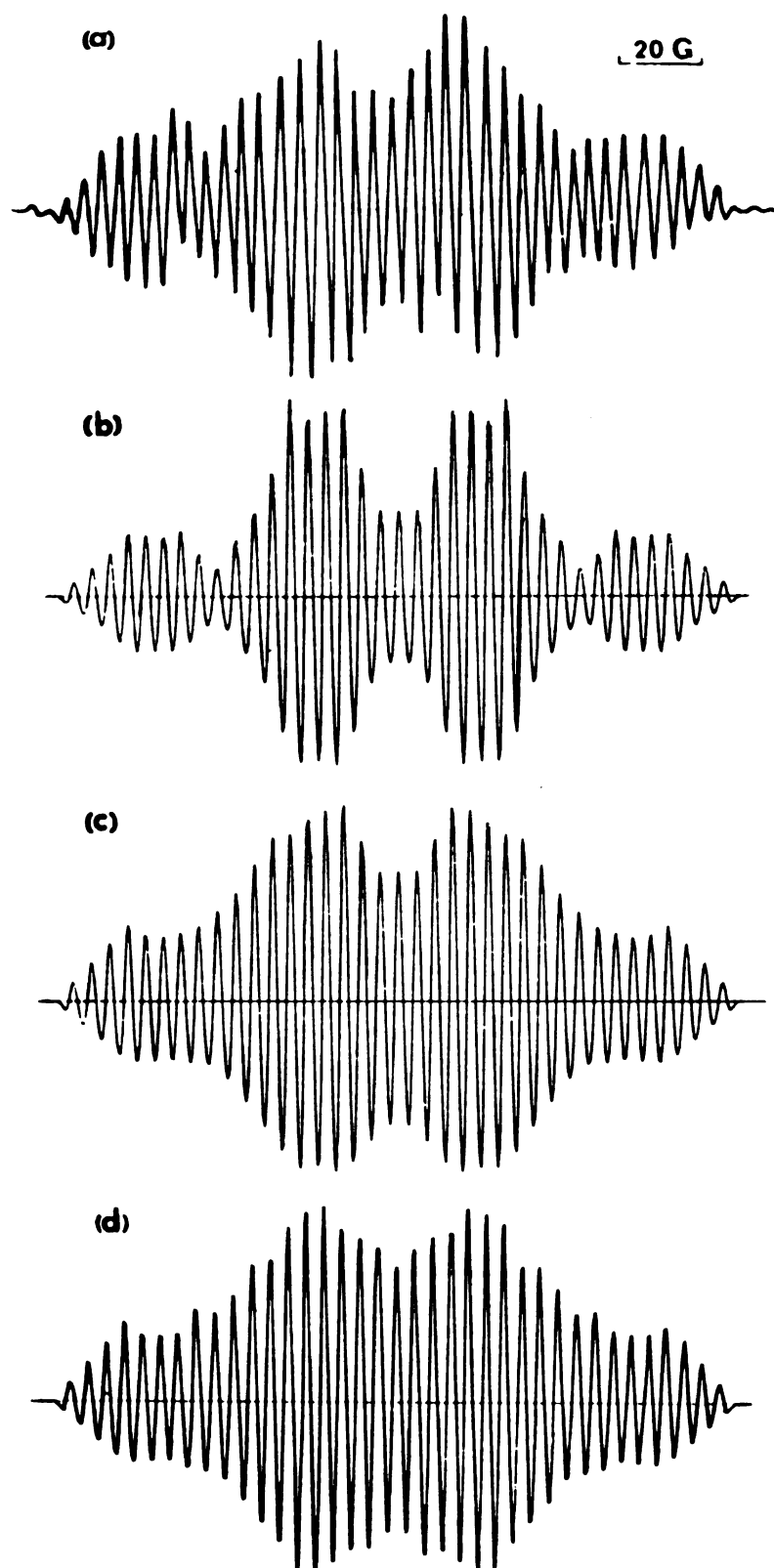
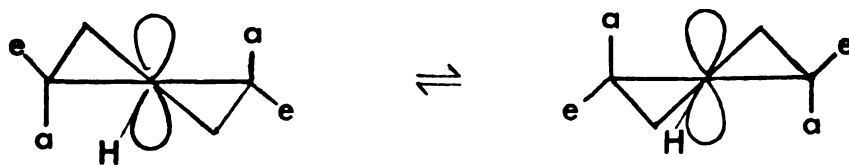
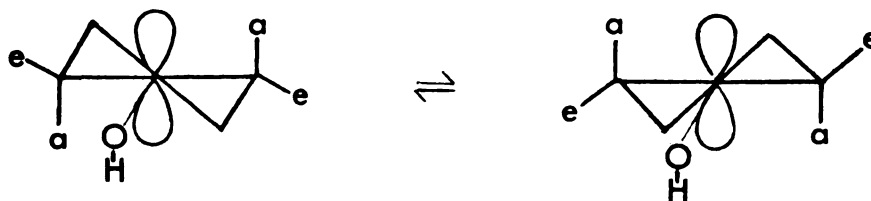


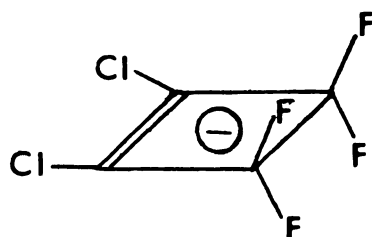
Figure 45. (a) ESR spectrum at -60°C of radical produced by irradiation of 1,2-dichlorotetrafluorocyclobutene in adamantane, (b), (c), (d) simulated spectra using the parameters of Table 18(b), (c) and (d), respectively.



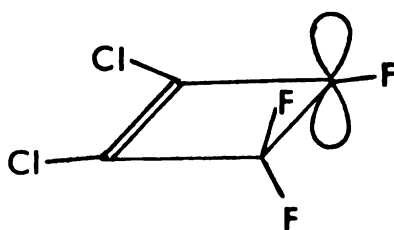
XXIII



XXIV



XXV



XXVI

Some Structural Formulae for Cyclic Radicals and Radical Ions

attempted. The observed relative intensities of the outer four low-field and high-field lines are nearly 1:2:3:4 and suggest strongly that these are part of a septet arising from two equivalent chlorine atoms with $a(\text{Cl}) = 4.1 \text{ G}$ and predicted relative intensities 1:2:3:4:3:2:1. The fluorine hyperfine splittings cannot all be equal, nor are there two pairs, since the overall pattern suggests a quartet rather than a quintet. We have therefore considered several cases for spectrum simulation. These include (a) three equivalent fluorines and two different chlorines, (b) two equivalent fluorines and two nonequivalent fluorines plus two equivalent chlorines, (c) four nonequivalent fluorines and two equivalent chlorines, (d) three fluorines of one kind and one of another plus two equivalent chlorines and (e) three different fluorines and two different chlorines. ESR parameters giving the best overall fit of calculated to observed spectra are given in Table 18 (b), (c) and (d) for each of the above cases (based on structure XXV) and simulated spectra obtained with these parameters are shown in Figure 45(b)-(d). All agree within experimental error with the experimental spectrum of Figure 45(a). The sets (a) and (e) of Table 18 correspond to a radical $\text{c-C}_4\text{F}_3\text{Cl}_2$ (XXVI) formed by loss of one fluorine while the other sets are for a radical cation or anion $\text{c-C}_4\text{F}_4\text{Cl}_2$ (XXV). Although the latter reproduce the experimental spectrum better, it is possible to obtain a similar fit by allowing the relative intensities in cases (a) and (e) to deviate from the theoretical values. Since internal motions in the radical could cause such deviations, XXV must be considered a possible structure.

Table 18. Some sets of ESR parameters giving calculated spectra in good agreement with the observed spectra for the radical in irradiated $\text{c-C}_4\text{F}_4\text{Cl}_2$.

Case*	$a(\text{F}_1)$	$a(\text{F}_2)$	$a(\text{F}_3)$	$a(\text{F}_4)$	$a(\text{Cl}_1)$	$a(\text{Cl}_2)$
(a)	$36.9(3)^\dagger$				4.1(1)	8.2(1)
(b)	40.0(1)	32.6(2)	15.8(1)		4.1(2)	
(c)	40.0(1)	36.6(1)	28.6(1)	15.8(1)	4.1(2)	
(d)	36.4(3)	11.7(1)			4.1(2)	
(e)	69.7(1)	28.7(1)	12.4(1)		4.1(1)	8.2(1)

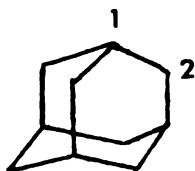
* The four cases correspond to those in the text and the first three to simulated spectra in Figure 45.

[†] All values in Gauss. Numbers in parenthesis after each hyperfine splitting are the numbers of equivalent atoms with that value of a .

DISCUSSION

I. Some Properties of the Adamantane Matrix

Adamantane (XXVII) has been shown to provide a rigid, nonpolar matrix with spherical holes so the radicals, which substitute for adamantane molecules, can rotate freely and give isotropic ESR spectra. The radicals tend to be stable for several hours at room temperature and spectra can be obtained over a wide temperature range.¹⁷ In order



XXVII

to obtain isotropic spectra with good signal-to-noise ratio the precursor must dissolve sufficient adamantane and the radicals produced must be able to rotate freely in the holes. There is apparently a maximum size molecule that can be accommodated in the matrix. In this work it has been found that 1-cyclopentanecarboxylic acid radical gives excellent spectra but 1-cyclohexanecarboxylic acid radical is apparently too large to rotate freely and only anisotropic spectra are obtained.

With straight chain radicals six or seven carbon atoms is often the upper limit for radicals which can be accommodated.¹⁷ There is also a lower limit, since small radicals can diffuse and recombine, and this may explain our failure to observe radicals from 1,2-dichloroethane. In other cases, particularly highly polar molecules such as 2-pyrrolidone,

piperazine, pyrrole and 2,4-pentanedione, the precursor does not appear to dissolve any adamantane.

Adamantane itself yields 2-adamantyl radicals on irradiation^{95,96} but not 1-adamantyl or any other radicals. If impure adamantane is used the impurities give ESR spectra and these have often been mistaken for adamantyl radicals.⁹⁷ Where the radical precursors employed yield radicals of greater stability than 2-adamantyl, the 2-adamantyl radicals disappear, probably by abstracting a hydrogen atom from the precursor, and only the spectrum of the radicals from the precursor are observed. However, 2-adamantyl would not normally be observed in this research since it gives only a broad doublet which would be almost completely discriminated against in the second-derivative presentation used here.

Hydrogen atoms appear to be produced from both adamantane and the precursor molecules on irradiation. They diffuse readily and transfer the radiation damage. Larger groups do not appear to be lost probably because of the cage effect. Thus, C-C and C-N bonds are not usually broken and groups such as carboxyl (in cyclopentanecarboxylic acid) are retained. While chlorine and bromine are lost from the cyclopentyl halides, this may be the result of splitting out HCl or HBr from the radical first produced (by loss of one hydrogen) followed by diffusion of the small molecule out of the cage.

The unusual stability of most radicals observed here must result from the slowness of diffusion out of the cage of neighboring adamantane molecules and also stability of the radical with respect to 2-adamantyl radical which could always be produced by hydrogen abstraction

if it were favored. 1-Cyclopentanecarboxylic acid radical was found to be particularly stable, disappearing only at 75°C in adamantane (but 5°C in the pure acid matrix). Several radicals could be studied up to 50-80°C and disappeared only slowly even at these elevated temperatures. On the other hand the radical from 2-pentamethylene sulfide disappears even at -60°C and may be an example of a radical which is less stable than 2-adamantyl and so is labile in the adamantane matrix. Where the odd electron can be delocalized over several atoms, as in the cyclic carboxylic acid radicals, the radicals may be more stable.

When the precursor itself forms plastic crystals, freely rotating radicals may sometimes be obtained on irradiation of the pure solid at temperatures above the transition point at which free rotation of the molecules occurs. In the present investigation isotropic spectra for the radicals from cyclobutanecarboxylic acid, cyclopentanecarboxylic acid and cyclohexanecarboxylic acid were obtained by irradiation of the pure solids.

II. ESR Parameters for Cyclic Radicals

Sixteen alicyclic radicals, which have been produced in this investigation by γ -irradiation of alicyclic compounds in an adamantane matrix, are listed in Table 19. Where the β proton hyperfine interactions show a temperature dependence, the values are given at both the lowest and highest temperatures attained. Dihedral angles expected for β protons for various "ideal" conformations are given in Table 20 and the preferred conformations of the radicals studied, based on the observed values of $a(H_\beta)$, are listed in Table 21. Table 22 summarizes the experimental values of the barriers to ring inversion determined in this work.

Table 19. ESR parameters in solid matrices obtained in this work and in related literature studies.

Radical	$a(H_\alpha)$ Gauss ^a		$a(H_\alpha)$	g^b	Matrix ^d	Reference
	$a(H_{\beta_1}), a(H_{\beta_2})$	$\langle a(H_\beta) \rangle$	$a(\text{other})$			
Carboxylic Acid Radicals						
1-Cyclopentanecarboxylic acid	22.1 (-193°C)	31.5(+25°C)	-	2.0037	A	This work
	41.0					
	22.5 (-196°C)	31.8 (R.T.)			CPCANA	35
	42.1					
	21.6 (4.2-77°K)				CPDCA	39
1-Cyclohexanecarboxylic acid	42.3					
	28.3 (-36°C)	31.3(0°C)			N	This work
	34.0					
	42.1 (-60°C)	21.1(+0°C)		2.0032	CHCA	This work
	37 5	($\beta_1 + \beta_2$) (-120°C)	20.9(30°C)	2.0029	CHCA	37
1-Cyclobutanecarboxylic acid		32.9(-15°C)			N	This work
		31.8(R.T.)		2.0049	A	This work
	37-40 (4°K)	31.9(25°C)	$a(^{13}\text{C}) = 38^c$		CBDCA	39
	20-25	32.0(27°C)			CBCANA	35
1-Cyclopropanecarboxylic acid		24.1(25°C)	$a(^{13}\text{C}) = 49^c$		CPDCA	39

Table 19 (continued)

Radical	$a(H_\beta)$ Gauss ^a		$a(H_\alpha)$	b^b	Matrix ^d	Reference
	$a(H_{\beta_1}), a(H_{\beta_2})$	$\langle a(H_\beta) \rangle$	$a(\text{other})$			
1-Cycloheptanecarboxylic acid	17.9 22.5	(25°C)		2.0036	A	This work
2-Alkanonyl Radicals						
2-Cyclopentanonyl			36.0(-24°C) 36.1(-18°C) 37.0 38.1(19°C)	2.0046 2.0047	A A Sol'n Sol'n	This work 22 32 33
2-Cyclohexanonyl	20.4 44.1	(143°K)	18.2		A	22
2-Cycloheptanonyl	≈19.1 ≈38.2	(146°C)	28.8(+3°C) 18.5	2.0042	A	This work
2-Cyclobutanonyl			35.6(220°K) 19.0		A	22
Heteroalicyclic Radicals						
2-Tetrahydrofuran-2-yl	18.0 37.3	(-193°C)	27.7(-71°C) 13.6	2.0034	A	This work
	19 38	(-196°C)	28.5(-13°C) 13		A	41

Table 19 (continued)

Radical	a(H _α) Gauss ^a		a(H _α)		g ^b	Matrix	Reference
	a(H _β ₁), a(H _β ₂)	<a(H _β)>	a(other)				
2-Tetrahydropyranyl	40.0 5.0 (-142°C)	β ₁ +β ₂ =45 (-11°C)	16.1	2.0029	A		This work
	40.8 6.6 (-100°C)		15.9		Frozen Sol'n		32
1,4-Dioxanyl	39.5 8.9 (-82°C)	-	17.3	2.0034	A		This work
	38.75 8.4 (-88°C)	22.7 (R.T.)	17.38 (R.T.)		Sol'n		98
2-Tetrahydrothiophenyl	19.0 4.8 (-188°C)	25.5 (R.T.)	16.0	2.0044	A		This work
	41.8 13.5 (-196°C)		16.0		A		44
2-Tetrahydrothiopyranyl	4.2 42.8 (-92°C)		18.1	2.0042	A		This work
1-Pyrrolidiny1	27.0 54.2 (-173°C)	40.1 (-32°C)	a(¹⁴ N)=14.0	2.0048	A		This work
		39 (R.T.)	a(¹⁴ N)=14.4		A		52

Table 19 (continued)

Radical	$a(H_\beta)$ Gauss ^a		$a(H_\alpha)$	^b g	Matrix	Reference
	$a(H_{\beta_1}), a(H_{\beta_2})$	$\langle a(H_\beta) \rangle$	$a(\text{other})$			
2-Piperidinyl	(40.0) ^c	$\beta_1 + \beta_2 = 41.9$	13.7 $a(^{14}\text{N}) = 3.4$	2.0030	A	This work
Other Radicals						
1-Hydroxy-1-cyclopentyl		27.6 (25°C)		2.0033	A	This work
Cyclopentyl	22.8 (-196°C) 45.7		22.8			29(25)
		35.6 (-60°C)	22.1	2.0032	A	This work
Cyclopentenyl		22.2 (25°C)	2.7 14.3	2.0029	A	This work
		21.6	3.1 14.0		A	62

^aValues of a in this work are in Gauss and have probable errors ± 0.5 G in most cases.

^bValues of g have probable errors ± 0.0003 except for 1-cyclobutanecarboxylic acid radical where it is ± 0.0006 .

^cValues of $a(^{13}\text{C})$ are from Reference 113.

^dA = adamantane, N = neat, CPCA = cyclopentanecarboxylic acid, CHCA = cyclohexanecarboxylic acid, CBDCA = cyclobutanedicarboxylic acid, CPDCA = cyclopentanedicarboxylic acid, CPCANa = sodium salt of cyclopentanecarboxylic acid.

^eValue from Reference 122.

Table 20. Dihedral Angles for β Protons for Radicals in Some Ideal Conformations

Conformation	θ_1	θ_2	Comment	Reference
Four-membered Rings (one sp^2 center)				
Planar	24.7°	24.7°		
Puckered	31.5°	17.3°	Puckering angle $\eta = 10^\circ$	120
Puckered	38.4°	10.4°	Puckering angle $\eta = 20^\circ$	120
Five-membered Rings (one sp^2 center)				
Planar	30	30		
Envelope (C_s)	60	0		33
Twist-chair (C_2)	50	10	Ref.33 gives $70^\circ, -10^\circ$	33
Five-membered Rings (two sp^2 centers)				
Planar	30	30		
Envelope (C_s)	60	0	Puckering angle $\eta = 30^\circ$	120
Six-membered Rings (one sp^2 center)				
Chair	90	-30		
Boat	90	-30		
Twist-boat	60	0		
Six-membered Rings (two sp^2 centers)				
Half-chair	45°	15°		33
Seven-membered Rings (one sp^2 center)				
Chair or boat	90°	-30°		
Twist-chair (symmetrical)	75°	-15°		32
Twist-chair (unsymmetrical)	(60	-60		32
	90	-30		
Seven-membered Rings (two sp^2 centers)				
Chair	90°	-30°	If C_4, C_5 of XIVA are sp^2	104

Table 21. Conformations of Cyclic Radicals from Proton Hyperfine Interactions.^a

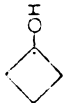
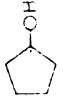
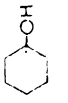
Radical	Matrix ^b	$a(H_1)$	ρ_1	$a(H_1), a(H_2)$ $a(H_3)$	$\frac{a(H_1)}{a(H_2)}$	θ_1, θ_2 $\langle \theta \rangle$	Probable Preferred Conformation	Reference
	Sol'n	21.2	0.94	$\langle \theta \rangle = 36.66$		$\langle \theta \rangle = 24.7^\circ$ (48.9)	Rapidly inverting puckered	10
	A	21.1	0.94	25.2, 45.6 (-18.7°) 35.6 (-60°)	0.55	15°, 15°	Half-chair	This work
	A	21.15	0.94	5.0, 40.0	0.12	-10°, 70°	Distorted chair	This work
	CHCl ₃ C ₆ H ₆ /C ₆ H ₁₄	21.4 21.0	0.95 0.95	21.4, 28.9 21.0, 31.4	0.74 0.67	24°, 36° 20°, 40°	Twist-chair with large torsional motions	13 25
	Sol'n			$\langle \theta \rangle = 27.6$		(36.8)		32
	A			$\langle \theta \rangle = 27.6$		(76.8)		This work
	C ₆ H ₁₁ (OH)			10.0, 36.1 (-196°)	0.24	1°, 50°	Distorted chair	32, 99
	A	19.0	0.81	$\langle \theta \rangle = 35.6$		(47.5)	Planar	22
	A	18.5	0.82	$\langle \theta \rangle = 36.0$		(48.0)	Rapidly inverting envelope	This work
	A	18.1	0.75	20.4, 44.1	0.46	11°, 49°	Half-chair	22
	A	18.5	0.82	19.1, 38.2	0.50	13°, 47°	Distorted half-chair?	This work

Table 21 (continued)

Radical	Matrix	$\alpha(H_a)$	ρ_a	$\alpha(H_{\beta_1}), \alpha(H_{\beta_2})$ $\langle \alpha(H_{\beta}) \rangle$	$\frac{\alpha(H_{\beta_1})}{\alpha(H_{\beta_2})}$	θ_1, θ_2 $\langle \theta \rangle$	B	Probable Preferred Conformation	Reference
	CBDA			22.6, 38.5 (4°K)	0.59	5°, 40°	38.8	Puckered, ^c $\eta = 20$	39
	A			22.1, 41.0	0.54	15°, 45°	44.0	Half-chair	This work
	CPDA			28.3, 34.0	0.83	25°, 35°	41.4	Flattened twist-chair	This work
	Self	21.1		5.0, 37.0 (-60°)	0.14	-9°, 69°	37.9	Distorted chair	This work
	A			17.9, 22.5 (-56°)	0.80	25°, 35°	27.4	Distorted twist-chair	This work
	Sol'n			2.08, 7.02	0.30	3°, 57°		Chair	66
	A	13.6	0.60	18.0, 37.3 (-193°) 27.7 (-71°)	0.48	12°, 48°	39.0	Half-chair	This work
	A	16.1	0.72	5.0, 40.0 (-142°) $\theta_1 + \theta_2 = 45.0$ (-11°)	0.13	-10°, 70°	41.2	Distorted chair or twist-boat	This work
	A	17.3	0.77	8.9, 39.5 (-82°)	0.23	-2°, 62°	39.5	Distorted chair	This work
	A	16.0	0.71	19.0, 37.4 (-171°) 25.5 (25°)	0.59	13°, 47°	39.4	Half-chair	This work
	A	18.1	0.80	4.2, 42.8 (-92°)	0.10	-13°, 73°	45.0	Chair	This work
	Sol'n	17.5	0.78	9.5, 35.5	0.27	1°, 59°	35.5	Distorted chair	48
	A	$\alpha(^{14}N) = 14.5$	0.84	27.0, 54.2 (-173°)	0.50	13°, 47°	57	Half-chair	This work

Table 21 (continued)

Radical	Matrix	$a(H_a)$	ρ_a	$a(H_{B1}), a(H_{B2})$ $\langle a(H_B) \rangle$	$\frac{a(H_{B1})}{a(H_{B2})}$	θ_1, θ_2 $\langle \theta \rangle$	B	Probable Preferred Conformation	Reference
	A	13.7	0.61	$\langle \theta \rangle = 21$	0.025	$-18^\circ, 78^\circ$	44.2	Chair	This work ^d
	A	$H_1 = 2.7$ $H_2 = 14.3$	-0.12 0.64	$\langle \theta \rangle = 22.2$				Planar	This work

^aThe calculated quantities in this table were obtained as follows: (1) $\rho_a = a(H_a)/22.5$; $\cos^2 \theta_2 = a(H_{B1})/a(H_{B2})$; θ_1, θ_2 and B from the equation $B \cos^2 \theta = a(H_B)$ and the assumption $\theta_1 + \theta_2 = 60^\circ$. Where only $\langle a(H_B) \rangle$ is available, values of θ_1, θ_2, B are estimates taken from a graph of values of $\langle a(H_B) \rangle$ versus $\theta; \theta_1, \theta_2$ are defined as in Figure 4.

^bMatrices are A = adamantane; Sol'n = solution or liquid phase, DTBA = 1,1-cyclobutanedicarboxylic acid; Self = precursor neat; CPCA = cyclopentanedicarboxylic acid; CHBr = cyclohexyl bromide solid; $C_{14}H_{14}OH$ = cycloheptane; $C_{11}H_{11}OH$ = cyclopentanol.

^cAngle of puckering η is as defined in Reference 120.

^dThe values of θ_1, θ_2 and B were obtained using our data and the value $a(H_{B1}) = 40$ G from Reference 122.

Table 22. Activation energies, E_a , and frequency factors, $(1/\tau)_0$, for ring inversion in some alicyclic radicals.

Radical	Matrix ^a	E_a (kcal/mole)	$(1/\tau)_0 \text{ sec}^{-1}$	Reference
Cyclopentyl	A	2.7 ± 0.2	2.5×10^{12}	20
	A	2.2 ± 0.5	1.5×10^{12}	This work
2-Tetrahydrofuran-1-yl	A	2.2 ± 0.5	6.9×10^{13}	This work
	A	2.4	1.6×10^{13}	20
	CH	2.1 ± 0.2	1×10^{13}	41
2-Tetrahydrothiophen-1-yl	A	2.7 ± 0.5	9.8×10^{11}	This work
1-Pyrrolidin-1-yl	A	2.9 ± 0.5	6.5×10^{12}	This work
1-Cyclopentane-carboxylic acid	A	1.4 ± 0.2	1.3×10^{10}	This work
	CPDA	3.7	-	39
	CPCANa	0.37	0.5×10^9	35
Cyclohexyl	A	4.9 ± 0.5	1.0×10^{13}	This work
2-Tetrahydropyran-1-yl	A	3.7 ± 0.5	3.9×10^{11}	This work
1,4-Dioxan-1-yl	A	3.7 ± 0.5	6.5×10^{10}	This work
	Sol'n	7.64 ± 0.7	-	98
2-Cyclohexanone-1-yl	A	3.70 ± 0.7 ($\Delta H^\ddagger$)	-	22
	Sol'n	5.45	-	33

Table 22. (continued)

Radical	Matrix ^a	E _a (kcal/mole)	(1/τ) ₀ sec ⁻¹	Reference
Cyclohexenyl	A	6.81 ± 0.6 (ΔH [‡])	-	63
1-Cyclohexane-carboxylic acid	CHCA	3.7 ± 0.5	1.7 × 10 ¹²	This work
	CHCA	3.4	7 × 10 ¹¹	37
2-Cycloheptanonyl	A	3.2 ± 0.5	5.5 × 10 ¹¹	This work
1-Cyclobutane-carboxylic acid	CBCANa	1.5	3 × 10 ⁹	35
	CBDCA	0.06	-	39

^a A = adamantane, CH = clathrate hydrate, CPDA = cyclopentanedicarboxylic acid, CPCANa = cyclopentane-carboxylic acid sodium salt, CHCA = cyclohexanedicarboxylic acid, CBCANa = sodium salt of cyclobutane-carboxylic acid, CBDCA = cyclobutanedicarboxylic acid.

Table 23. Kinetic parameters for ring inversion in some alicyclic compounds obtained from dynamic NMR.*

Compounds	$\Delta G^\ddagger$ (kcal/mole)	$\Delta H^\ddagger$ (kcal/mole)
Cyclohexane	10.1 10.3 10.25	11.5 $\pm$ 2 9.1 $\pm$ 0.5 10.71 $\pm$ 0.04
Fluorocyclohexane	10.14	9.87 $\pm$ 0.1
Cyclohexanol	11.7 $\pm$ 1	-
Cyclohexanone-3,3,4,4,5,5-d ₅	4.1 $\pm$ 0.1	-
Cyclohexene-d ₆	5.4	-
Tetrahydropyran	10.3	-
Tetrahydrothiopyran	9.4	-
Piperidine	10.4	14.1
Cycloheptene	5.0	-
Cycloheptene oxide	7.7	-
Cyclooctane-d ₁₄	8.1	7.4
1,4-Dioxane-d ₆	9.7	-

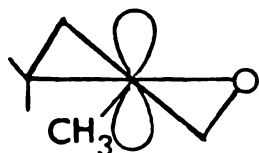
* This table is from Reference 69.

Barriers to ring inversion in molecules found by NMR are given in Table 23. Matrix effects are generally small and are difficult to evaluate accurately since they are often of the same order of magnitude as the experimental errors in the hyperfine splitting constants, which are of the order of ± 0.5 G on the average. However, the 1-cyclopentane-carboxyl radical has a conformation less distorted from planar by about 10° in the self matrix than in adamantane (Table 19).

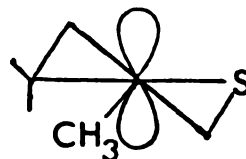
The hyperfine splittings for α -hydrogens varied from 13.6 in 2-tetrahydrofuranyl radical to 18.5 in 2-cycloheptanonyl and 2-cyclopentanonyl radicals. These values are considerably lower than that observed in the planar π -electron methyl radical (23 G) or in cyclic hydrocarbon radicals such as cyclohexyl (21.15 G). Several factors may contribute to the decrease - the cyclic radicals may not be planar at the trivalent carbon atom, electronegative heteroatoms or substituent groups may decrease the odd electron density on the trivalent carbon atom and delocalization of the odd electron onto substituents or heteroatoms with π electrons may become possible. If the McConnell equation [Equation 15] is applied the spin densities on trivalent carbon may be estimated in these radicals and range from 0.8 in the 2-cycloalkanonyl radicals to 0.6 in 2-tetrahydrofuranyl radical.

The hyperfine splittings for the β -hydrogens of cyclic radicals depend on ring conformation and the dihedral angles between the axis of the p orbital containing the odd electron and the $-C-H_\beta$ bonds can be obtained from the data using Equation 16. The constants

B and B_0 of this equation are not known too well for cyclic radicals because the dihedral angles cannot be measured experimentally. In this work $B_0 = 0$ is assumed, along with the relationship $\theta_1 + \theta_2 = 60^\circ$, and values of B and θ_1, θ_2 are obtained from the experimental values of $a(H_{\beta_1})$ and $a(H_{\beta_2})$. These results will be discussed below. For the simplest π -electron radical with a freely rotating β -methyl group $a(H_{\beta}) = 26.87$ G and Equation 16 would give $B\langle\cos^2\theta\rangle = \frac{B}{2} = 26.87$ G or $B = 53.74$ G. It has been shown¹¹ that delocalization of the odd electron, which decreases the odd electron density in the $2p_{\pi}$ orbital of the trivalent carbon, leads to lower values of B . Thus, for the radicals XXVIII and XXIX the β -methyl hyperfine splittings⁴⁴ are



XXVIII



XXIX

19.0-19.5 G and $B = 38$ -39. In the radicals studied here values of B are generally in the range 40-48 G or, if Equation 15 is employed along with the value $B = 58$ G¹¹, $\rho_{\alpha} \approx 0.7 - 0.8$ for these radicals. $a(^{14}\text{N})$ is smaller, usually in the range 1.7-5.7 G (Table 6).

Nitrogen hyperfine splittings, when they can be resolved, are useful in assigning radical structures. When the odd electron is centered on a nitrogen atom in a π -electron radical, $a(^{14}\text{N}) \approx 14.0$ -15.0 G, whereas if the odd electron is centered on an adjacent carbon atom $a(^{14}\text{N})$ is smaller, usually in the range 1.7-5.7 G (Table 6).

The measured isotropic g values given in Table 19 are generally somewhat larger than the free spin value (2.0023). This is attributed to spin-orbit interaction and values of $\Delta g = (g_{\text{obs}} - 2.0023)$ become larger when delocalization of the odd electron onto neighboring atoms, particularly heavier atoms, becomes more important. Thus, for planar π -radicals the successive substitution of hydrogen by an atom with an unshared pair of electrons, at positions where the spin density is appreciable, cause a progressive increase in the g -factor.⁹⁴ The g -factors are often useful in the identification of radicals. For example, the values $\Delta g = 0.0025$ for the radical from irradiated pyrrolidine and $\Delta g = 0.0007$ for the radical from piperidine indicate that the odd electron is centered on nitrogen in the former case but carbon in the latter case. The very large value $\Delta g = 0.0025$ for 2-cyclohexanonyl radical has been shown⁵³ to result from extensive delocalization of the odd electron onto oxygen - 25% as estimated from the ^{17}O hyperfine interaction. In otherwise similar radicals Δg should be larger when delocalization is onto a heavier atom; $\Delta g = 0.0021$ for 2-tetrahydrothiophenyl radical compared to $\Delta g = 0.0011$ for 2-tetrahydrofuranyl radical. However, an opposing decrease in g occurs when the odd electron orbital acquires s character and the radical becomes nonplanar.¹¹

III. Alicyclic Carboxylic Acid Radicals

1-Cyclopentanecarboxylic acid radical (XI) at -193°C gives an ESR spectrum (Figure 7(h)) which can be analyzed as a triplet of triplets with hyperfine splittings of 22 and 41 G. It is reasonable to assign these to two nonequivalent pairs of β protons corresponding

to a cyclopentane ring frozen in a single conformation on the ESR time scale. The room temperature quintet can then be assigned to four equivalent β protons resulting from rapid exchange between two equivalent conformations and the fact that the quintet splitting (31.3 G) is just the average of the two low-temperature splittings tends to confirm this interpretation.

It will be assumed here that the radical at low temperature has either the "envelope" or "half-chair" conformation⁶⁸ and that exchange between the two equivalent conformers XIa and XIb occurs at room temperature. The dihedral angles θ_1 , θ_2 between the direction of the odd electron 2p orbital on carbon and the β -C-H bonds may then be calculated from Equation 16. The simultaneous equations

$$\begin{aligned} B \cos^2 \theta_1 &= 22.0 \text{ G} \\ B \cos^2 \theta_2 &= 41.0 \text{ G} \\ \theta_1 + \theta_2 &= 60^\circ \end{aligned}$$

lead to

$$\theta_1 = 45^\circ, \theta_2 = 15^\circ, B = 44 \text{ G (Figure 4)}.$$

Gilbert and Trenwith³³ have shown that for cyclic five-membered ring radicals in solution the ESR data are in better agreement with the C_2 ("half-chair") conformations than with the C_s ("envelope") conformations. Assuming no distortion from tetrahedral angles or from the ideal symmetry, the calculated values of θ_1 and θ_2 are 10° and 50° for the C_2 radical and -10° and 70° for the C_s radical. Our data agree better with the C_2 conformations for the 1-cyclopentanecarboxylic acid radical although the probable errors in such a calculation are rather large.

When pure cyclopentanecarboxylic acid was irradiated at 77°K the overall behavior of the spectra was similar but the hyperfine splitting constants at low temperature were more nearly equal with $a(H_{\beta_1}) = 28.3$ G, $a(H_{\beta_2}) = 34.0$ G, and (at 0°C) $\langle a(H_{\beta}) \rangle = 31.1$ G. From these one obtains $\theta_1 = 34^\circ$, $\theta_2 = 26^\circ$ and $B = 41$ G by use of Equation 16. These values are much closer to the values $\theta_1 = \theta_2 = 30^\circ$ expected for a planar radical than are the parameters for the same radical in adamantane. The molecule is thus less twisted from planar in the self matrix. Also, the assumption that $\theta_1 + \theta_2 = 60^\circ$ may not be correct for cyclopentane derivatives but the H-C-H angles do not appear to have been determined precisely, the usual assumption being that they are tetrahedral.

The energy barrier restricting ring inversion in 1-cyclopentanecarboxylic acid radical (XIa $\rightleftharpoons$ XIb) is found to be $E_a = 1.43$ kcal/mole in adamantane. This is less than that found for cyclopentyl radical itself,³¹ also in adamantane, $E_a = 2.7$ kcal/mole. In cyclopentane it has been estimated that the planar and puckered forms differ in energy by 5-6 kcal/mole^{75,76} but there are no definite energy minima and maxima (such as XIa, XIb) since the puckering can move around the ring by pseudorotation with a change in internal energy of the molecule of the order of RT (0.6 kcal/mole at 25°C).

The 1-cyclohexanecarboxylic acid radical appears to not be produced in adamantane, possibly because of the steric factor. However, it is observed in the self matrix with low-temperature splittings $a(H_{\beta_1}) = 37$ G, $a(H_{\beta_2}) = 5$ G and high-temperature (+9°C) splitting

$\langle a(H_\beta) \rangle = 21.1$ G. These values lead to dihedral angles (Figure 4) $\theta_1 = 69^\circ$, $\theta_2 = -9^\circ$ and $B = 39$ G. The conformational change is presumably a chair $\rightleftharpoons$ chair inversion as in cyclohexane itself (XIIa $\rightleftharpoons$ XIIb).

The energy barrier restricting ring inversion is found to be $E_a = 3.7$ kcal/mole which is somewhat less than in cyclohexyl radical where $E_a = 4.9$ kcal/mole.²⁷ The "coalescence" temperature (at which the high-temperature quintet splits into the low-temperature triplet of triplets) is also lower (-60°) for 1-cyclohexanecarboxylic acid radical than for cyclohexyl radical ($\approx 25^\circ\text{C}$).

The decrease in inversion barrier in going from cyclopentyl to 1-cyclopentanecarboxyl and from cyclohexyl to 1-cyclohexanecarboxyl may result from delocalization of the odd electron onto the carboxyl groups of the acid radicals with resultant partial double bond character in the $\dot{\text{C}}\text{-COOH}$ carbon-carbon bond. This would tend to make the acid radicals planar at the trivalent carbon whereas the hydrocarbon radicals are believed to be nonplanar. Thus, the chair $\rightleftharpoons$ chair interconversion in cyclohexyl radical would be accompanied by an inversion whereas in 1-cyclohexanecarboxyl it would not. At present the only carbon-13 splitting which has been reported for any of these radicals is the value $a(^{13}\text{C}) = 41$ G for cyclohexyl⁷⁴ and this suggests that the radical is bent a few degrees from planarity. If K_o is taken to have a value midway between that found for planar methyl radical (38 G)¹⁰ and that calculated for a hypothetical planar tertiary radical (27 G),¹⁰³ the use of Equation 17 would lead to $\theta = 3.4^\circ$ for the bending from planarity in cyclohexyl.

For 1-cyclobutanecarboxylic acid radical (XIII) only an average β -hydrogen splitting, $\langle a(H_\beta) \rangle = 31.8$ G, could be observed and no conditions could be found which would give further splitting of the lines corresponding to freezing out one ring conformation. The same radical in the single crystal matrix^{35,39} 1,1-cyclobutanedicarboxylic acid gave $\langle a(H_\beta) \rangle = 32$ G at 300°C and at low temperature one ring conformation was frozen out so that $a(H_{\beta_1}) = 36.4$ and $a(H_{\beta_2}) = 27.8$ G at 77°K. Apparently even at the lowest temperatures accessible in adamantane the ring inversion remains rapid on the ESR time scale.

The results for γ -irradiated cycloheptanecarboxylic acid in adamantane are rather difficult to interpret since several radicals are produced but it does appear from the spectra that the 1-cycloheptanecarboxylic acid radical (XIV,XV) is one of the products and that it is in a rigid conformation at all temperatures employed in this work. Ohmae *et al.*²⁵ found a similar result for the cycloheptyl radical in irradiated solid cycloheptane with two different β proton hyperfine splittings, $a(H_{\beta_1}) = 24$ and $a(H_{\beta_2}) = 20$ G, at -196°C. However, in the liquid at -6°C only a single β hyperfine interaction, $a(H_\beta) = 24.7$ G, is found.¹⁰ Also, the cycloheptanone ketyl (XXX) is observed⁶⁶ in a single conformation between -40° and +88°C in dimethoxymethane solution with $a(H_{\beta_1}) = 7.02$ G and $a(H_{\beta_2}) = 2.08$ G. These results are surprising since cycloheptyl derivatives appear to interconvert rapidly on the NMR time scale with values of $E_a < 5$ kcal/mole.¹⁰⁴ The radical structures are undoubtedly more rigid and show that introduction



XXX

of sp^2 centers makes 5- and 7-membered rings less flexible.

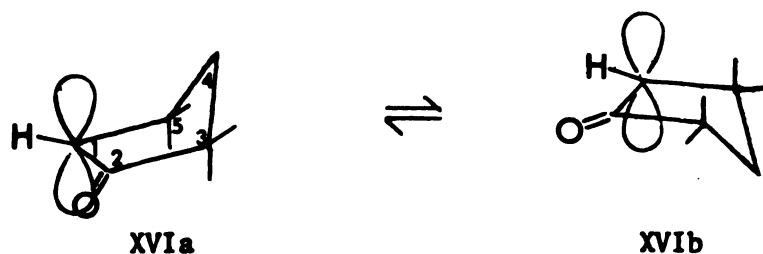
The rather low values of the β proton hyperfine splittings found for 1-cycloheptanecarboxylic acid radical, as well as for the other cycloheptyl radicals reported in the literature, have not been explained satisfactorily. It appears that for these radicals either the value of B is smaller than in other cyclic radicals or the spin density on the α -carbon is smaller. If we assume the former, and use $B = 27.4$ along with the observed β splittings of 17.9 and 22.5 G for 1-cycloheptanecarboxyl, the values $\theta_1 = 25^\circ$, $\theta_2 = 35^\circ$ are obtained. These are approximately the values to be expected if the radical has the chair conformation XIV with the radical center in the 1-position. The twist-chair forms (XV) which are favored in theoretical calculations on cycloheptane itself¹⁰⁵ lead to quite different angles with the radical center in the 1-position and do not appear to be the stable forms for the radicals ($\theta_1 = 75^\circ$, $\theta_2 = -15^\circ$ for symmetrical twist-chair).

IV. Cyclic Ketone Radicals

The 2-cyclohexanonyl radical (IV, V) in adamantane has been studied^{22,53} and the activation parameters for ring inversion between two half-chair forms found to be $\Delta H^\ddagger = 3.70$ kcal/mole, $E_a = \Delta H^\ddagger + RT = 4.3$ kcal/mole and $\Delta G^\ddagger = 4.39$ kcal/mole. NMR studies of cyclohexanone¹⁰⁶ lead to $\Delta G^\ddagger = 5.2$ kcal/mole for the ring inversion process in that molecules compared to $\Delta G^\ddagger = 10.6$ kcal/mole in cyclohexane. Pratt *et al.*²² conclude that the introduction of one sp^2 center into cyclohexane, as in cyclohexanone or cyclohexyl radical ($E_a = 4.9$ kcal/mole¹⁰) lowers the barrier by about one-half. Introduction of a second sp^2 center in 2-cyclohexanonyl radical produces an additional lowering

of only about 1 kcal/mole and this is attributed⁵³ to the allylic-type resonance in the radical which gives the C_1-C_2 bond about 15% double-bond character and so tends to make atoms 1-2-3-6 of the ring coplanar and give a structure already halfway through the conformational change of cyclohexanone.

It is not surprising then that 2-cyclopentanonyl radical XVI interconverts rapidly on the ESR time scale even at the lowest temperatures studied here and that the two β protons remain equivalent. Cyclopentanone has been shown¹⁰⁷ by refined force field calculations to exist in the half-chair form with an angle of twist of the C_3-C_4 bond out of the $C_5-C_1-C_2$ plane of about 24° . The barrier to inversion must be less than 5 kcal/mole since it has not been detected by NMR. An additional sp^2 center, plus the contribution of allylic resonance (XVIa $\rightleftharpoons$ XVIb), will tend to make $C_3-C_2-C_1-C_5$ coplanar and so give a



ground state conformation already halfway through the conformational change accompanying the inversion of cyclopentanone. The radical would then either be planar or have the envelope conformation XI with C_4 at the "tip of the flap" and a low barrier to inversion of C_4 .

The β proton hyperfine interaction $\langle a(H_\beta) \rangle = 36.0$ G is comparable to the averaged values found in the rapidly interconverting cyclobutyl (36.6 G), cyclopentyl (35.2 G) and 2-cyclohexanonyl (33.0) radicals.

The ESR spectra of 2-cycloheptanonyl radical in adamantane show temperature dependence which indicates a ring inversion process. The coalescence temperature for transformation from two nonequivalent β protons to two equivalent ones occurs at a lower temperature (-99°C) than the corresponding change in 2-cyclohexanonyl (-72°) indicating a lower barrier to inversion ($E_a = 3.2$ kcal/mole versus $E_a = 4.3$ kcal/mole) for 2-cycloheptanonyl. The most probable structure for cycloheptanone is a half-twist-chair form with the carbonyl group at C_2 and the odd electron on C_1 . The carbon atoms carrying the odd electron and the carbonyl group, and those on either side (7,1,2,3, of XVII) will tend to be coplanar. The remaining three can then take either equivalent conformation of XVII and the inversion barrier observed will correspond to this change.¹⁰⁸ However, because of the flexibility of the cycloheptane ring it may be possible to go from one form to the other via low-energy paths of the type giving rise to pseudorotation and so have a barrier lower than that in 2-cyclohexanonyl but averaging the H_{β} splittings in a complex manner.

The observed values of $a(\text{H}_{\beta})$ lead to the values $\theta_1 = 46^{\circ}$, $\theta_2 = 14^{\circ}$ and $B = 39$ G (using Equation 16) for the dihedral angles of the rigid conformation at low temperatures. Lown⁶⁶ reported $\theta_1 = 57^{\circ}$, $\theta_2 = 3^{\circ}$ for cycloheptyl ketyl but no inversion even at $+88^{\circ}\text{C}$.

The 2-cycloalkanonyl radicals with 5, 6 and 7-membered rings are all very stable in adamantane even at room temperature.

V. Heteroalicyclic Radicals

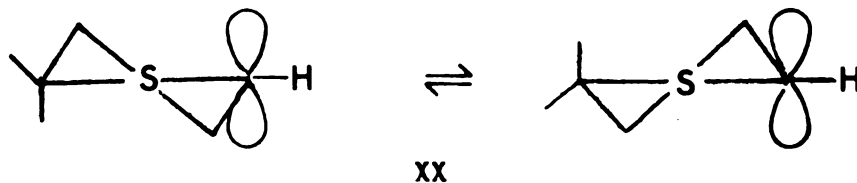
(a) Five-membered Rings

The ESR spectra of the 2-tetrahydrofuranlyl and 2-tetrahydrothiophenyl radicals, XVIII(a) and XIX, both show temperature dependence

indicative of ring inversion processes. The barriers hindering inversion are 2.2 kcal/mole and 2.7 kcal/mole, respectively. Previous measurements of the barrier for 2-tetrahydrofuranyl gave 2.1 kcal/mole in a clathrate-hydrate matrix³¹ and 2.4 kcal/mole in adamantane²⁰ in good agreement with the results of the present study.

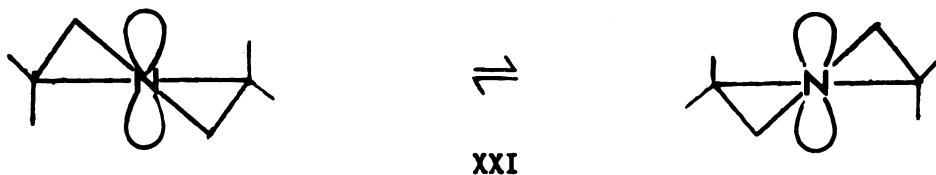
Tetrahydrofuran, like cyclopentane, undergoes pseudorotation with only a small barrier; both are able to invert by a low-energy path which does not involve going through the high central barrier of the planar configuration.¹⁰⁹ However, with the introduction of a radical center apparently two equivalent conformations exist which interconvert only by passage over a substantial barrier (2.1 kcal/mole). It seems likely that these are the two half-chair conformations XVIII(a) suggested for cyclopentanone,¹¹⁰ which also has one sp^2 carbon in the ring. The barrier in cyclopentyl radical (2.7 kcal/mole²⁰) is slightly higher than that in 2-tetrahydrofuranyl as might be expected from the larger repulsions when oxygen is replaced by a methylene group.

Inversion in 2-tetrahydrothiophenyl radical XX would similarly involve the transformation by passage through an intermediate form of



higher energy. In view of the expected greater delocalization of the odd electron onto sulfur, it is surprising that the barrier in 2-tetrahydrothiophenyl (2.7 kcal/mole) is larger than those for 2-tetrahydrofuranlyl or cyclopentyl; however, it must be noted that the errors are of the same order as the differences being considered.

Irradiation of pyrrolidine in adamantane leads to formation of the radical XXI by loss of the NH proton rather than to the expected radical by loss of an α proton. With the odd electron centered on nitrogen, the 1-pyrrolidinyl radical might have either the envelope or the twist-chair structure but the height of the barrier to inversion (2.0 kcal/mole) is only slightly higher than the values for the other five-membered ring radicals discussed above so the structures are probably similar. Inversion could then be attributed to the transformation



by analogy with cyclopentanone.¹¹⁰

The α proton hyperfine interactions in the 2-tetrahydrofuranlyl and 2-tetrahydrothiophenyl radicals, 13.6 G and 16.0 G, are much smaller than observed²⁰ for cyclopentyl (23 G in a clathrate-hydrate matrix). This indicates that the odd electron population of the α carbon ρ_α is smaller in the heterocyclic radicals. The latter may be estimated,

along with the β splittings, using Equations 15 and 16 with the empirical constants found by Shiga et al. for cyclic radicals: $\rho_\alpha = a(H_\alpha)/22.5$ and $a(H_\beta) = 50 \rho_\alpha \cos^2 \theta$. These lead to the values $\rho_\alpha = 0.60$ and 0.71 and $\langle a(H_\beta) \rangle = 50 \rho_\alpha (3/4) = 22.5$ and 26.6 (if θ is taken as 30°) for 2-tetrahydrofuranyl and 2-tetrahydrothiophenyl, respectively, to compare with the observed $\langle a(H_\beta) \rangle = 27.7$ and 25.5 , respectively.

The higher apparent spin density on the α -carbon of 2-tetrahydrothiophenyl, despite the general belief that delocalization onto sulfur should be greater than onto oxygen, has been explained by Biddles et al.⁴³ They suggest that the oxygen radicals deviate more from planarity at the trivalent carbon and so have smaller α -proton splittings despite a larger spin density on the radical center. It has been shown^{11,111} that increased bending at the radical center, and the accompanying increase in s character of the odd electron orbital, leads to more positive values of $a(H_\alpha)$. Since the values of $a(H_\alpha)$ observed for the cyclic radicals studied in this work are all presumably negative, the result would be smaller numerical values for oxygen radicals than for sulfur radicals with equal spin density on C_α . This would explain the discrepancy between the calculated and observed values of $\langle a(H_\beta) \rangle$ noted above since, if ρ_α for the oxygen radical is actually larger than calculated from the $a(H_\alpha)$ value, the calculated value of $\langle a(H_\beta) \rangle$ would also be larger.

It is found for nitrogen containing radicals that a relationship of the type of Equation 14 holds so that $a(^{14}\text{N}) \approx Q_N^N \rho_N$ with $Q_N^N \approx 19.0$.^{112,113} The observed value $a(^{14}\text{N}) = 14.5$ G for 1-pyrrolidinyl

radical thus indicates an odd electron spin density of about 0.76 on nitrogen. The β proton splittings appear to depend on the dihedral angle θ through a relationship of the type of Equation 16 but with a larger value of the constant B. Thus, if we choose $B_0 = 0$ and $B = 57$ the observed values $a(H_\beta) = 27.0$ and 54.2 at low temperature give the values $\theta_1 = 13^\circ$, $\theta_2 = 47^\circ$. These are reasonable angles since the corresponding values for cyclopentyl and for 1-cyclopentanecarboxyl radicals are essentially the same. For the aliphatic radical $(CH_3-CH_2)_2\dot{N}$ the values $a(^{14}N) = 14.3$ and $a(H_\beta) = 36.9$ were observed¹¹³ with the latter value attributed to a conformational preference corresponding to $\langle\theta\rangle = 35^\circ$.

(b) Six-membered Rings

The four heteroalicyclic compounds with six-membered rings studied were tetrahydropyran, 1,4-dioxane, pentamethylene sulfide and piperidine. When irradiated in the adamantane matrix all gave cyclic radicals in which an α proton had been abstracted. The stable conformation for all these radicals is assumed to be the chair form and ring inversion involving a chair $\rightleftharpoons$ chair transformation is expected and is observed for the oxygen radicals. The radical from tetrahydrothiopyran is unstable above -80°C so temperature-dependent ESR spectra in the region of coalescence could not be obtained. In the case of piperidine, more than one radical was produced and overlapping lines from the different spectra made it impossible to obtain the barrier for ring inversion.

The barrier restricting ring inversion in 2-tetrahydropyranyl radical was found to be 3.7 kcal/mole and in 1,4-dioxanyl radical to also be 3.7 kcal/mole. These values are somewhat lower than the value $E_a = 4.9$ kcal/mole reported for cyclohexyl radical¹⁰ as might be expected from the replacement of a methylene group in the ring by one or two oxygens. The higher barrier $\Delta F^\ddagger = 10.5$ kcal/mole found by NMR for ring inversion in cyclohexane compared to the values $\Delta F^\ddagger = 10.3$ kcal/mole and $\Delta F^\ddagger = 9.7$ kcal/mole for tetrahydropyran and 1,4-dioxane are in qualitative agreement with this explanation and there is various evidence that a lone pair is smaller than a hydrogen.¹¹⁴ Recently Gaze and Gilbert⁹⁸ have measured the barrier in 1,4-dioxanyl radical prepared by photolytic decomposition of di-*t*-butyl peroxide in the presence of dioxane. They obtain a value $E_a = 7.64$ kcal/mole, which is about double that reported here and represents an unusually large effect of the matrix. The introduction of an sp^2 center into cyclohexane reduces the inversion barrier from $E_a = \Delta H^\ddagger + RT \approx 11.4$ kcal/mole to $E_a = 4.9$ kcal/mole in cyclohexyl whereas the reduction appears to be somewhat larger in the two heterocyclic radicals but any differences are not larger than the combined experimental errors of the two numbers (± 1 kcal/mole). The degree of bending at the radical center was found to be small (zero $\pm 10^\circ$) in an INDO study of 1,4-dioxanyl.⁹⁸ It is probable that the lowered barriers on introducing an sp^2 center are a result of the lower torsional energy of sp^2 - sp^3 relative to sp^3 - sp^3 bonds and that the changes on introducing a hetero-atom into the ring are related to the changes in these torsional energies.¹⁰⁷

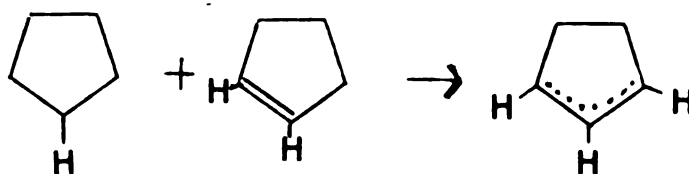
VI. Other Radicals

(a) Cyclopentenyl and Cyclopentyl Radicals

The cyclopentenyl radical (I), produced by irradiation of both cyclopentyl chloride and cyclopentyl bromide, is very stable in adamantane at room temperature. The hyperfine splitting parameters for the radical ($a(H_{\alpha_1}) = 14.3$ G, $a(H_{\alpha_2}) = 2.7$ G and $\langle a(H_{\beta}) \rangle = 22.2$ G) are similar to those observed for the same radical produced by irradiation of cyclopentene in adamantane⁶² ($a(H_{\alpha_1}) = 14.0$, $a(H_{\alpha_2}) = 3.1$ and $\langle a(H_{\beta}) \rangle = 21.6$ G) and are typical of allylic radicals.¹¹⁵

When cyclopentyl bromide is γ irradiated at -196°C the product is the cyclopentyl radical²⁹ (XXIII) which is frozen into a single conformation at that temperature with two β protons and one α proton giving $a(H_{\alpha}) = a(H_{\beta_1}) = 22.8$ G and $a(H_{\beta_2}) = 45.7$ G. In the adamantane matrix the cyclopentyl radical does not appear to be a stable product. Irradiation of cyclopentane itself at -196°C , however, was found to give only the cyclopentyl radical.²⁵ In this investigation it was found that cyclopentane in adamantane gave the cyclopentyl radical when γ irradiated at 77°K and allowed to warm to -60°C . The spectrum at this temperature was a doublet of quintets indicating that rapid ring inversion is averaging the β splittings and $\langle a(H_{\beta}) \rangle = 35.6$ G, $a(H_{\alpha}) = 22.1$ G. When the matrix warms to room temperature the spectrum changes to that of cyclopentenyl radical. The mechanism of this change is not clear but it seems unlikely that either hydrogen atoms from the initial radiation damage or the adamantyl radicals of the matrix

abstract the additional two protons from the ring since this would require two additional hydrogen abstraction reactions; it also seems unlikely that H_2 is lost from cyclopentyl. Helcke and Fantechi⁵⁴ suggested that cycloheptenyl radical was formed in irradiated cycloheptane (in thiourea matrix) as a result of abstraction of a hydrogen from cycloheptene by the first-formed cycloheptyl radical; the cycloheptene would be one radiolysis product of cycloheptane at low temperature and would not be detected by ESR. By analogy the reaction



might be the source of cyclopentenyl radical at higher temperatures in irradiated cyclopentane in adamantane.

The cyclopentenyl radical is probably planar since the π system extending over three of the ring carbons would tend to favor the conformation in which the other two carbons are in the same plane. However, the observed average value of $a(H_\beta)$ could arise from a planar radical for which $a(H_\beta) \approx 0.6(50)(3/4) = 22.5$ G, since $\rho_\alpha \approx 14.3/23$ and $\theta = 30^\circ$, or from a rapidly inverting radical with $\theta_1 = 20^\circ$, $\theta_2 = 40^\circ$ and $\langle a(H_\beta) \rangle = (26.4 + 17.6)/2 = 22.0$ G.

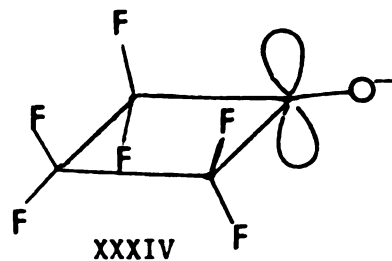
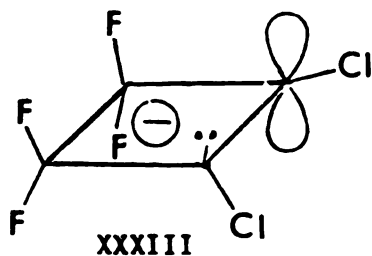
(b) 1-Hydroxy-1-cyclopentyl Radical

Irradiation of cyclopentanol in adamantane leads to formation of the 1-OH-cyclopentyl radical for which the four β protons are equivalent and $\langle a(H_\beta) \rangle = 27.6$ G. The same radical in toluene solution was produced by UV irradiation of 1,1'-azobis (1-hydroxycyclopentane) and $\langle a(H_\beta) \rangle = 27.0$ observed,⁴⁰ and also by UV irradiation of di-*t*-butyl peroxide, cyclopentanol and iso-octane mixtures with $\langle a(H_\beta) \rangle = 28.0$ reported.³² The radical appears to be rapidly interconverting between half-chair forms at room temperature.

(c) The Radical from 1,2-Dichlorotetrafluorocyclobutene

While the structure of this radical cannot be deduced with certainty from the ESR spectrum, the loss of a fluorine to give radical XXVI appears to be most probable. Irradiation of 1-fluoro-1-bromo-2,3-dimethylcyclopropane gives the 1-fluoro-2,3-*cis*-dimethylcyclopropyl radical¹¹⁶ with $a(F_\alpha) = 77.6$ G which is comparable to other α fluorine splittings in aliphatic radicals (Table 3). Also, the splittings for β protons on the same side of the ring as the odd electron are larger than those on the opposite side. Since typical β -fluorine splittings for such radicals are in the range 20-40 G¹¹⁸ and α -chlorine splittings in the range 4-10 G¹¹⁸ the hyperfine splittings estimated for structure XXVI are reasonable. On the other hand, formation of a radical anion with the odd electron in a higher molecular orbital would probably lead to larger values of $a(F)$ than observed since the radical anion of perfluorocyclobutane shows eight equivalent fluorines with $a(F) = 147.7$ G. Addition of the odd electron at the double bond to give

radical XXXIII is also not likely since the ketyl of perfluorocyclo-



butanone (XXXIV) shows large β and γ hyperfine splittings¹¹⁸ $a(F_\beta) = 82$ G, $a(F_\gamma) = 35$ G, and two fluorines with $a(F) = 82$ G would give an ESR spectrum with much greater spread than observed.

SUMMARY

Solid solutions of sixteen cyclic compounds in adamantane have been irradiated and the ESR spectra studied over the temperature range 77°K-300°K. The cyclic radicals produced have been identified from the ESR spectra and the nuclear hyperfine interaction constants and g values measured. In the case of ten radicals the temperature dependence of the spectra has permitted the rate of ring inversion to be studied as a function of temperature and the constants E_a and $(1/\tau)_0$ of the Arrhenius equation determined. The significance of the hyperfine interactions, g values and energy barriers restricting ring inversion, has been studied.

Barriers to ring inversion in six-membered rings are reduced by about 50% in going from the values measured by NMR in the undamaged molecule to the radical. Energy barriers in five-membered cyclic radicals are smaller than in the corresponding six-membered ring radicals but no NMR results are available for the undamaged molecules. The only seven-membered ring radical which could be studied, 2-cycloheptanonyl, shows a barrier to inversion slightly smaller than the six-membered radical 2-cyclohexanonyl but much larger than 2-cyclopentanonyl, which is too small to be measured by ESR in the adamantane matrix.

Various characteristics of the radiation chemistry of cyclic compounds in adamantane have been discussed along with the effects of the matrix on hyperfine splittings and inversion barriers.

A computer program ESREX4 has been written for calculating the rates of exchange of equivalent nuclei in radicals from the ESR parameters and the relative intensities of second-derivative Gaussian lines in the ESR spectrum.

References

1. E. Zavoisky, Doctoral Dissertation, Moscow, FIAN, 1944; J. Phys. U.S.S.R. 9, 245 (1945).
2. P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, New York (1967).
3. A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Oxford University Press, New York (1970).
4. J. K. Kochi, editor, "Free Radicals", Vols. 1 and 2, Wiley-Interscience, New York (1972); S. Y. Psezhetskii, et al., "EPR of Free Radicals in Radiation Chemistry", Wiley, New York (1974).
5. H. M. Swartz, J. R. Bolton and D. C. Borg, editors, "Biological Applications of Electron Spin Resonance", Wiley-Interscience (1972).
6. R. F. Picone, Ph. D. Thesis, Michigan State University (1973).
7. R. C. Schoening, Ph.D. Thesis, Michigan State University (1973).
8. J. R. Shock, Ph.D. Thesis, Michigan State University (1973).
9. W. G. Waller, Ph.D. Thesis, Michigan State University (1973).
10. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 39, 2147 (1963); J. Chem. Phys. 43, 2704 (1965).
11. W. T. Dixon and R. O. C. Norman, J. Chem. Soc. 4850 (1964); A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, Chem. Commun. 23, 1353 (1969); J. Chem. Soc. A 124 (1971).
12. J. K. Kochi and P. J. Krusic, Chemical Society Special Publication No. 24, London (1970); P. J. Krusic and J. K. Kochi, J. Amer. Chem. Soc. 90, 7155 (1968).
13. J. E. Bennett, "Molecular Spectroscopy", Proceedings of the 4th Conference on the Spectroscopy, Institute of Petroleum Chemistry, London (1968).
14. J. Roncin and R. Debuyst, J. Chem. Phys. 51, 577 (1969).
15. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 45, 1845 (1966).
16. O. H. Griffith, J. Chem. Phys. 41, 1093 (1964); 42, 2644, 2651 (1965).
17. D. E. Wood and R. V. Lloyd, J. Chem. Phys. 52, 3840 (1970); 53, 3932 (1970).
18. C. E. Nordman and D. L. Schmitkons, Acta Cryst. 18, 764 (1965).
19. J. Donohue and S. H. Goodman, Acta Cryst. 22, 352 (1967).
20. A. P. Kuleshov and V. I. Trofimov, Zh. Strukt. Khim. 14, 866 (1973).

21. L. Bonazzola, N. Leray and R. Marx, Chem. Phys. Lett. 24, 88 (1974).
22. H. F. Walter, Ph. D. Thesis, University of Pittsburgh (1975); D. M. Camaioni, H. F. Walter, J. E. Jordan and D. W. Pratt, J. Amer. Chem. Soc. 95, 7978 (1973).
23. B. Smaller and M. S. Matheson, J. Chem. Phys. 28, 1169 (1958).
24. N. Ia. Cherniak, N. N. Bubnov, L. S. Poliak, In. D. Tsvetkov and V. V. Voevodski, Opt. i Spektr. 6, 360 (1959); G. M. Zhidomirov and N. N. Bubnov, Opt. i Spektr. 12, 245 (1962).
25. T. Ohmae, S. I. Ohnishi, K. Kuwata, H. Sakurai and I. Nitta, Bull. Chem. Soc. Japan 40, 226 (1967).
26. N. Ya. Buben, Yu. N. Motin, A. I. Pristupa and V. N. Shamshev, Dokl. Akad. Nauk. SSSR. 152, 352 (1963).
27. S. Ogawa and R. W. Fessenden, J. Chem. Phys. 41, 994 (1964).
28. J. E. Bennett and A. Thomas, Nature, 195, 995 (1962).
29. P. B. Ayscough and C. Thomson, Trans. Faraday Soc. 58, 1477 (1962).
30. C. Fauquenot, J. P. Dodelet and P. Claes, Bull. Soc. Chim. Belges 80, 315 (1971).
31. A. L. Blyumenfel'd and V. I. Trofimov, Zh. Struktr. Khim. 14, 230 (1973).
32. C. Corvaja, M. Brustolon and G. Giacometti, Z. Phys. Chem. 66, 279 (1969); C. Corvaja, G. Giacometti and M. Brustolon, Z. Phys. Chem. 82, 272 (1972); C. Corvaja, G. Giacometti and G. Sartori, J. Chem. Soc. Faraday II, 709 (1973).
33. B. C. Gilbert, R. O. C. Norman and M. Trenwith, J. Chem. Soc. Perkin II, 1033 (1974); B. C. Gilbert and M. Trenwith, J. Chem. Soc. Perkin II, 1083 (1975).
34. Yu. D. Tsvetkov, J. R. Rowlands and D. H. Whiffen, J. Chem. Soc. 810 (1964).
35. G. M. Zhidomirov and Yu. D. Tsvetkov, Opt. i Spektr. 8, 34 (1963).
36. M. Kikuchi, N. Leray and J. Roncin, Chem. Phys. Lett. 34, 395 (1975).
37. P. M. K. Leung and J. W. Hunt, J. Phys. Chem. 71, 3177 (1967).
38. D. Grestorex and T. J. Kemp, Trans. Faraday Soc. 67, 1576 (1971).
39. L. R. Dalton and A. L. Kwiram, J. Amer. Chem. Soc. 94, 6930 (1972); T. N. Margulis, L. R. Dalton and A. L. Kwiram, Nature (Phys. Sci.) 242, 82 (1973); B. H. Robinson, L. A. Dalton, A. H. Beth and L. R. Dalton, Chem. Phys. 18, 321 (1976).

40. P. Smith, D. W. House and L. B. Gilman, J. Phys. Chem. 77, 2249 (1973).
41. V. I. Trofimov and I. I. Chkheidze, Khim. Vysik. Energ. 1, 324 (1967); 6, 185 (1972); Dokl. Akad. Nauk SSSR 198, 354 (1971).
42. A. Hudson and K. D. J. Root, Tetrahedron 25, 5311 (1969).
43. I. Biddles, A. Hudson and J. T. Wiffen, Tetrahedron, 28, 867 (1972).
44. B. C. Dismukes and J. E. Willard, J. Phys. Chem. 80, 1435 (1976).
45. A. C. Ling and L. Kevan, J. Phys. Chem. 80, 592 (1976).
46. H. Taniguchi, J. Phys. Chem. 74, 3143 (1970).
47. T. Shiga, A. Boukhors and P. Douzou, J. Phys. Chem. 71, 4264 (1967).
48. E. A. C. Lucken and B. Poncioni, Helv. Chim. Acta 55, 2673 (1972).
49. H. Zeldes and R. Livingstone, J. Chem. Phys. 45, 1946 (1966).
50. D. L. Winters and A. C. Ling, Can. J. Chem. 54, 1971 (1976).
51. R. E. Linder and A. C. Ling, Can. J. Chem. 50, 3982 (1972).
52. D. W. Pratt, I. I. Dillon, R. V. Lloyd and D. E. Wood, J. Phys. Chem. 75, 3486 (1971).
53. D. M. Camaioni and D. W. Pratt, J. Amer. Chem. Soc. 94, 9258 (1972); D. M. Camaioni, H. F. Walter and D. W. Pratt, J. Amer. Chem. Soc. 95, 4057 (1973).
54. G. A. Helcké and R. Fantechi, Mol. Phys. 18, 1 (1970).
55. S. I. Ohnishi and I. Nitta, J. Chem. Phys. 39, 2848 (1963).
56. S. Arai, S. Shida, K. Yamaguchi and Z. Kuri, J. Chem. Phys. 37, 1885 (1962).
57. C. Heller and T. Cole, J. Chem. Phys. 37, 243 (1962).
58. T. Shida and W. H. Hamill, J. Amer. Chem. Soc. 88, 5371 (1966).
59. P. B. Ayscough and H. E. Evans, Trans. Faraday Soc. 60, 801 (1964).
60. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 38, 773 (1963); D. H. Whiffen, Mol. Phys. 6, 223 (1963).
61. D. E. Wood and H. M. McConnell, J. Chem. Phys. 37, 1150 (1962); M. B. Kim and D. E. Wood, J. Amer. Chem. Soc. 97, 1004 (1975).

62. D. R. Gee and J. K. S. Wan, Can. J. Chem. 49, 20 (1971).
63. N. M. deTannoux, M. S. Thesis, University of Pittsburgh (1975).
64. R. J. Cook, J. R. Rowlands and D. H. Whiffen, Mol. Phys. 7, 57 (1964); B. Eda, R. J. Cook and D. H. Whiffen, Trans. Faraday Soc. 60, 1497 (1964).
65. G. A. Russell, G. R. Underwood and D. C. Lini, J. Amer. Chem. Soc. 89, 6636 (1967); G. A. Russell and E. T. Storm, J. Amer. Chem. Soc. 86, 744 (1964).
66. J. W. Lown, Can. J. Chem. 43, 2571, 3294 (1965).
67. R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston (1966).
68. E. L. Eliel, N. L. Allinger, S. I. Angyal and G. M. Morrison, "Conformational Analysis," Interscience, New York (1965).
69. F. A. L. Anet and R. Anet, in "Dynamic NMR Spectroscopy," L. M. Jackman and F. A. Cotton, Editors, Academic Press, New York (1975).
70. W. D. Gwinn and A. S. Gaylord, International Review of Science, Physical Chemistry Series Two, Vol. 3, "Spectroscopy," Butterworths (1976).
71. P. D. Sullivan and J. R. Bolton, "Advances in Magnetic Resonance," 4, 39 (1970).
72. A. Hudson and G. R. Luckhurst, Chem. Rev. 69, 191 (1969).
73. J. K. Kochi, in "Advances in Free Radical Chemistry," 5, 189 (1975).
74. R. W. Fessenden, J. Phys. Chem. 71, 74 (1967).
75. K. S. Pitzer and W. E. Donath, J. Amer. Chem. Soc. 81, 3213 (1959).
76. L. A. Carrier, G. J. Jiang, W. B. Person and J. N. Willis, Jr., J. Chem. Phys. 56, 1440 (1972).
77. J. E. Wertz and J. R. Bolton, "Electron Spin Resonance," McGraw-Hill, New York (1972).
78. P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen, London (1967); N. M. Atherton, "Electron Spin Resonance," Ellis Horwood, London (1973).
79. A. Carrington and A. D. McLachlan, Introduction to Magnetic Resonance, Harper & Row, New York (1967).

80. T. Cole, C. Heller, and H. M. McConnell, Proc. Natl. Acad. Sci. U. S. 45, 525 (1959); H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, J. Amer. Chem. Soc. 82, 766 (1960).
81. H. M. McConnell, J. Chem. Phys. 24, 764 (1956); H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 28, 107 (1958).
82. H. M. McConnell and J. Strathdee, Mol. Phys. 2, 129 (1959).
83. A. Horsfield, J. R. Morton and D. H. Whiffen, Mol. Phys. 4, 425 (1961); Trans. Faraday Soc. 57, 1657 (1961).
84. M. T. Rogers and D. H. Whiffen, J. Chem. Phys. 40, 2662 (1964).
85. M. T. Rogers and L. D. Kispert, J. Chem. Phys. 55, 2360 (1971).
86. L. D. Kispert and M. T. Rogers, J. Chem. Phys. 54, 3326 (1971).
87. A. Hudson and K. D. J. Root, in "Advances in Magnetic Resonance, Vol. 5, J. Waugh, editor, Academic Press, New York (1971).
88. J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).
89. D. M. Schrader and M. Karplus, J. Chem. Phys. 40, 1593 (1964).
90. See Reference 78, Appendix III.
91. A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, New York (1961).
92. Apparently Ogawa and Fessenden (Ref. 27) obtained exact solutions of the modified Bloch equations but they never explicitly say so and do not give the solutions but only the final result which involves peak intensities at line centers. The complete solutions used here were obtained by W. G. Waller and are given in Appendix I.
93. Program ESREX4 written by W. G. Waller and Choo Song (1976); See Appendix A of this thesis.
94. H. M. McConnell and R. E. Robertson, J. Phys. Chem., 61, 1018 (1957).
95. J. R. Ferrell, G. R. Holdren, Jr., R. V. Lloyd and D. E. Wood, Chem. Phys. Letters, 9, 343 (1971).
96. R. V. Lloyd and M. T. Rogers, Chem. Phys. Letters, 17, 428 (1972).
97. L. Bonazzola and R. Marx, Chem. Phys. Letters, 8, 413 (1970); W. G. Filby and K. Günther, Chem. Phys. Letters, 14, 440 (1972).

98. C. Gaze and B. C. Gilbert, J. Chem. Soc. Perkin II, 754 (1977).
99. T. Ohmae, S. I. Ohnishi, H. Sakurai and I. Nitta, J. Chem. Phys. 42, 4053 (1965).
100. A. Faucitano, A. Buttafava and F.F. Martinotti, J. Chem. Soc. Perkin II, 1017 (1976).
101. A. L. J. Beckwith and P. K. Tindal, Aust. J. Chem. 24, 2099 (1971).
102. J.C. Watson, Ph.D. Thesis, Michigan State University (1970).
103. D. E. Wood, L. F. Williams, R. F. Sprecher and W. A. Latham, J. Amer. Chem. Soc. 94, 6241 (1972).
104. E. S. Glazer, R. Knorr, C. Ganter and J. D. Roberts, J. Amer. Chem. Soc. 94, 6026 (1972).
105. J. B. Hendrickson, J. Amer. Chem. Soc. 89, 7047 (1967).
106. F. R. Jensen and B. H. Beck, J. Amer. Chem. Soc. 90, 1066 (1968).
107. N. L. Allinger, M. T. Tribble and M. A. Miller, Tetrahedron, 28, 1173 (1972).
108. E. S. Glazer, R. Knorr, C. Ganter and J. D. Roberts, J. Amer. Chem. Soc., 94, 6026 (1972).
109. G. S. Engerholm, A. C. Luntz, W. D. Gwinn and D. O. Harris, J. Chem. Phys. 50, 2446 (1969).
110. F. J. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, J. Amer. Chem. Soc. 81, 4915 (1959).
111. J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970); J. Chem. Phys. 48, 4802 (1968).
112. J. C. M. Henning, J. Chem. Phys. 44, 2139 (1966).
113. W. C. Danen and R. C. Rickard, J. Amer. Chem. Soc. 94, 3254 (1972); W. C. Danen and T. T. Kensler, J. Amer. Chem. Soc. 92, 5235 (1970).
114. H. Booth, Progress in Nuclear Magnetic Resonance Spectroscopy, 5, 149 (1969).
115. P. J. Krusic, P. Meakin and B. E. Smart, J. Amer. Chem. Soc. 96, 6211 (1974); 90 7157 (1968).

116. T. Kawamura, M. Tsumura and T. Yonezawa, J. Chem. Soc. Comm. 373 (1977).
117. M. Shiotani and F. Williams, J. Amer. Chem. Soc. 98, 4006 (1977).
118. A. J. Bowles, A. Hudson and R. A. Jackson, Chem. Phys. Letters 5, 552 (1970); A. Hudson and K. D. J. Root, Advances in Magnetic Resonance, 5, 1 (1971).
119. M. Kikuchi, N. Leray and J. Roncin, Chem. Phys. Letters 34, 395 (1975).
120. G. M. Zhidomirov, I. A. Abronin, I. D. Micheikin and N. V. Chuvylkin, J. Magnetic Resonance, 17, 161 (1975); J. Strukt. Chem. 16, 16 (1975).
121. T. Kawamura, M. Matsunaga and T. Yonezawa, J. Amer. Chem. Soc. 97, 3234 (1975).
122. V. I. Trofimov, I. I. Chkheidze, and A. L. Blyumenfel'd, High Energy Chem. 6, 166 (1972).

APPENDIX A
SOLUTION TO MODIFIED BLOCH EQUATIONS

For ring inversion in cyclohexyl radical, the following modified Bloch equations must be solved.

$$\frac{d}{dt} G_1(t) = \{i(\omega_0 + \omega_{h_1}) - \sigma^2 t - \tau^{-1}\} G_1(t) + \tau^{-1} G_2(t) \quad (A-1)$$

$$\frac{d}{dt} G_2(t) = \{i(\omega_0 + \omega_{h_2}) - \sigma^2 t - \tau^{-1}\} G_2(t) + \tau^{-1} G_1(t) \quad (A-2)$$

As $t \rightarrow \infty$ in (A-1) the equation is dominated by the $-\sigma^2 t G_1(t)$ term if the $\tau^{-1} G_2(t)$ cross term is ignored. The asymptotic equation $G_1'(t) = -\sigma^2 t G_1(t)$ has the solution $G_1(t) = K e^{\frac{-\sigma^2 t^2}{2}}$.

We factor out the asymptotic behavior by setting

$$G_1(t) = e^{\frac{-\sigma^2 t^2}{2}} Q_1(t); \quad G_2(t) = e^{\frac{-\sigma^2 t^2}{2}} Q_2(t) \quad (A-3)$$

Then (A-1) becomes

$$\begin{aligned} \left(\frac{-\sigma^2}{2} 2t\right) e^{\frac{-\sigma^2 t^2}{2}} Q_1(t) + e^{\frac{-\sigma^2 t^2}{2}} Q_1'(t) = \\ \{i(\omega_0 + \omega_{h_1}) - \sigma^2 t - \tau^{-1}\} e^{\frac{-\sigma^2 t^2}{2}} Q_1(t) + \tau^{-1} e^{\frac{-\sigma^2 t^2}{2}} Q_2(t) \end{aligned}$$

or

$$Q_1'(t) = \{i(\omega_0 + \omega_{h_1}) - \tau^{-1}\}Q_1(t) + \tau^{-1}Q_2(t) \quad (\text{A-4})$$

and by symmetry:

$$Q_2'(t) = \{i(\omega_0 + \omega_{h_2}) - \tau^{-1}\}Q_2(t) + \tau^{-1}Q_1(t) \quad (\text{A-5})$$

$$\text{Let } \eta_1 = i(\omega_0 + \omega_{h_1}) - \tau^{-1} \text{ and } \eta_2 = i(\omega_0 + \omega_{h_2}) - \tau^{-1} \quad (\text{A-6})$$

Disregarding the cross term in (A-4) the solution is $Q_1(t) = e^{\eta_1 t}$
so we factor this out of (A-4) and (A-5) by setting

$$Q_1(t) = e^{\eta_1 t} R_1(t); \quad Q_2(t) = e^{\eta_2 t} R_2(t) \quad (\text{A-7})$$

Equations (A-4), (A-5) become

$$\eta_1 e^{\eta_1 t} R_1(t) + e^{\eta_1 t} R_1'(t) = \eta_1 e^{\eta_1 t} R_1(t) + \tau^{-1} e^{\eta_2 t} R_2(t);$$

similarly for (A-5) or

$$e^{\eta_1 t} R_1'(t) = \tau^{-1} e^{\eta_2 t} R_2(t) \quad (\text{A-8})$$

$$e^{\eta_2 t} R_2'(t) = \tau^{-1} e^{\eta_1 t} R_1(t) \quad (\text{A-9})$$

or

$$R_2(t) = \tau e^{(\eta_1 - \eta_2)t} R_1'(t) \quad (\text{A-10})$$

$$R_1(t) = \tau e^{(\eta_2 - \eta_1)t} R_2'(t) \quad (\text{A-11})$$

From (A-6) we have $\eta_1 - \eta_2 = i(\omega_{h_1} - \omega_{h_2})$.

To agree with Fessenden's notation, let $\Delta = \omega_{h_2} - \omega_{h_1}$, then
we have

$$R_2(t) = \tau e^{-i\Delta t} R_1'(t) \quad (A-12)$$

$$R_1(t) = \tau e^{+i\Delta t} R_2'(t) \quad (A-13)$$

Differentiating Eq. (A-12) gives: $R_2'(t) = \tau(-i\Delta)e^{-i\Delta t} R_1'(t) + \tau e^{-i\Delta t} R_1''(t)$ and substituting Eq. (A-13) for $R_2'(t)$ gives

$$\tau^{-1} e^{-i\Delta t} R_1(t) = -i\tau\Delta e^{-i\Delta t} R_1'(t) + \tau e^{-i\Delta t} R_1''(t) \quad (A-14)$$

or

$$R_1(t) + i\tau^2\Delta R_1'(t) - \tau^2 R_1''(t) = 0 \quad (A-15)$$

Setting $R_1(t) = K e^{pt}$ produces

$$K e^{pt} + i\tau^2\Delta p K e^{pt} - \tau^2 p^2 K e^{pt} = 0 \quad (A-16)$$

or

$$1 + i\tau^2\Delta p - \tau^2 p^2 = 0 \quad (A-17)$$

or

$$p^2 - i\Delta p - \tau^{-2} = 0 \quad (A-18)$$

So

$$p = \frac{i\Delta + \sqrt{-\Delta^2 + 4\tau^{-2}}}{2} \quad (A-19)$$

$$\text{Let } \gamma = \frac{\sqrt{4\tau^{-2} - \Delta^2}}{2} = \sqrt{\tau^{-2} - \left(\frac{\Delta}{2}\right)^2} \quad (A-20)$$

Then

$$R_1(t) = C_1 e^{(\gamma + \frac{i\Delta}{2})t} + C_2 e^{(-\gamma + \frac{i\Delta}{2})t} \quad (A-21)$$

From Eq. (A-12) we have

$$R_2(t) = \tau e^{-i\Delta t} \left\{ \left(\gamma + \frac{i\Delta}{2} \right) C_1 e^{(\gamma + \frac{i\Delta}{2})t} + \left(-\gamma + \frac{i\Delta}{2} \right) C_2 e^{(-\gamma + \frac{i\Delta}{2})t} \right\} \quad (A-22)$$

or

$$R_2(t) = \tau \left\{ \left(\gamma + \frac{i\Delta}{2} \right) C_1 e^{(\gamma - \frac{i\Delta}{2})t} + \left(-\gamma + \frac{i\Delta}{2} \right) C_2 e^{(-\gamma - \frac{i\Delta}{2})t} \right\} \quad (A-23)$$

or

$$R_2(t) = D_1 e^{(\gamma - \frac{i\Delta}{2})t} + D_2 e^{(-\gamma - \frac{i\Delta}{2})t} \quad (A-24)$$

when

$$D_1 = \tau \left(\gamma + \frac{i\Delta}{2} \right) C_1; \quad D_2 = \tau \left(-\gamma + \frac{i\Delta}{2} \right) C_2 \quad (A-25)$$

Thus

$$G_1(t) = e^{-\frac{\sigma^2 t^2}{2}} Q_1(t) = e^{-\frac{\sigma^2 t^2}{2}} e^{\eta_1 t} R_1(t) \quad (A-26)$$

$$= e^{-\frac{\sigma^2 t^2}{2}} e^{\eta_1 t} \left[C_1 e^{(\gamma + \frac{i\Delta}{2})t} + C_2 e^{(-\gamma + \frac{i\Delta}{2})t} \right] \quad (A-27)$$

$$= C_1 Z_1(t) + C_2 Z_2(t), \quad (A-28)$$

where

$$Z_1(t) = e^{-\frac{\sigma^2}{2} t^2 + (\eta_1 + \gamma + \frac{i\Delta}{2})t}; \quad (A-29)$$

$$Z_2(t) = e^{-\frac{\sigma^2}{2} t^2 + (\eta_1 - \gamma + \frac{i\Delta}{2})t}$$

Likewise

$$G_2(t) = e^{-\frac{\sigma^2 t^2}{2}} Q_2(t) = e^{-\frac{\sigma^2 t^2}{2}} e^{\eta_2 t} R_2(t) \quad (A-30)$$

$$= e^{-\frac{\sigma^2 t^2}{2}} e^{\eta_2 t} \left[D_1 e^{(\gamma - \frac{i\Delta}{2})t} + D_2 e^{(-\gamma - \frac{i\Delta}{2})t} \right] \quad (A-31)$$

$$= D_1 \tilde{Z}_1(t) + D_2 \tilde{Z}_2(t) \quad (A-32)$$

where

$$\begin{aligned} \tilde{Z}_1(t) &= e^{-\frac{\sigma^2}{2} t^2 + (\eta_2 + \gamma - \frac{i\Delta}{2})t}; \\ \tilde{Z}_2(t) &= e^{-\frac{\sigma^2}{2} t^2 + (\eta_2 - \gamma - \frac{i\Delta}{2})t} \end{aligned} \quad (A-33)$$

The line shape is given by

$$I(\omega) = \text{Real}\{\int_0^\infty G(t) e^{-i\omega t} dt\}, \quad (A-34)$$

where

$$G(t) = G_1(t) + G_2(t) \quad (A-35)$$

So

$$I(\omega) = I_1(\omega) + I_2(\omega),$$

where

$$I_1(\omega) = \text{Real}\{\int_0^\infty G_1(t) e^{-i\omega t} dt\} \quad (A-36)$$

and

$$I_2(\omega) = \text{Real}\{\int_0^\infty G_2(t) e^{-i\omega t} dt\} \quad (A-37)$$

$$\begin{aligned} I_1(\omega) &= \text{Real}\{C_1 \int_0^\infty e^{-\frac{\sigma^2}{2} t^2 + (\eta_1 + \gamma + \frac{i\Delta}{2} - i\omega)t} dt + \\ &\quad C_2 \int_0^\infty e^{-\frac{\sigma^2}{2} t^2 + (\eta_1 - \gamma + \frac{i\Delta}{2} - i\omega)t} dt\} \end{aligned} \quad (A-38)$$

$$I_2(\omega) = \text{Real}\{D_1 \int_0^\infty e^{-\frac{\sigma^2}{2} t^2 + (\eta_2 + \gamma - \frac{i\Delta}{2} - i\omega)t} dt + D_2 \int_0^\infty e^{-\frac{\sigma^2}{2} t^2 + (\eta_2 - \gamma - \frac{i\Delta}{2} - i\omega)t} dt\} \quad (\text{A-39})$$

Now

$$\begin{aligned} \eta_1 + \frac{i\Delta}{2} - i\omega &= i(\omega_0 + \omega_{h_1}) - \tau^{-1} + i\left(\frac{\omega_{h_2} - \omega_{h_1}}{2}\right) - i\omega \\ &= i\left(\omega_0 + \frac{\omega_{h_1} + \omega_{h_2}}{2} - \omega\right) - \tau^{-1} \\ &= i(\omega_m - \omega) - \tau^{-1} \end{aligned} \quad (\text{A-40})$$

where $\omega_m = \frac{1}{2}(\omega_{h_1} + \omega_{h_2}) + \omega_0$ defined by Fessenden (A-41)

$$\begin{aligned} \eta_2 - \frac{i\Delta}{2} - i\omega &= i(\omega_0 + \omega_{h_2}) - \tau^{-1} - i\left(\frac{\omega_{h_2} - \omega_{h_1}}{2}\right) - i\omega \\ &= i\left(\omega_0 + \frac{\omega_{h_1} + \omega_{h_2}}{2} - \omega\right) - \tau^{-1} \\ &= i(\omega_m - \omega) - \tau^{-1} \end{aligned} \quad (\text{A-42})$$

Because Eq. (A-39) is the same as Eq. (A-41) the integrals of $I_1(\omega)$ are the same as those in $I_2(\omega)$. So we combine (A-38) and (A-39) into

$$I(\omega) = \text{Real}\{[C_1 + D_1] \int_0^\infty e^{V_+} dt + [C_2 + D_2] \int_0^\infty e^{V_-} dt\}, \quad (\text{A-43})$$

where

$$V_{\pm} = -\frac{\sigma^2}{2} t^2 + \{-\tau^{-1} \pm \gamma + i(\omega_m - \omega)\}t \quad (\text{A-44})$$

Here

$$\gamma = \sqrt{\frac{1}{\tau^2} - \left(\frac{\Delta}{2}\right)^2} = \left(\frac{\Delta}{2}\right) \sqrt{\left(\frac{2}{\tau\Delta}\right)^2 - 1} = \left(\frac{\Delta}{2}\right) \sqrt{\alpha^2 - 1} \quad (\text{A-45})$$

where

$$\alpha = 2/\tau\Delta \quad \text{as defined by Fessenden.} \quad (\text{A-46})$$

Since $\tau^{-1} = (\frac{\Delta}{2})\alpha$ we can write $V_{\pm}$ as

$$V_{\pm} = -\frac{\sigma^2}{2} t^2 + \left\{ \left(\frac{\Delta}{2} \right) [-\alpha \pm \sqrt{\alpha^2 - 1}] + i(\omega_m - \omega) \right\} t \quad (\text{A-47})$$

$$= -\frac{(\sigma t)^2}{2} + \left\{ [-\alpha \pm \sqrt{\alpha^2 - 1}]a + i\frac{(\omega_m - \omega)}{\sigma} \right\} (\sigma t) \quad (\text{A-48})$$

where

$$a = \Delta/2\sigma \quad \text{as defined in Fessenden.} \quad (\text{A-49})$$

So

$$V_{\pm} = -\frac{1}{2} [(\sigma t)^2 + 2\{[\alpha \mp \sqrt{\alpha^2 - 1}]a - i\frac{(\omega_m - \omega)}{\sigma}\}(\sigma t)] \quad (\text{A-50})$$

$$= -\frac{1}{2} [(\sigma t) + \xi_{\pm}]^2 + \frac{1}{2} \xi_{\pm}^2 \quad (\text{A-51})$$

where

$$\xi_{\pm} = [\alpha \mp \sqrt{\alpha^2 - 1}]a + i\frac{(\omega - \omega_m)}{\sigma} \quad (\text{A-52})$$

So

$$J_{\pm} = \int_0^{\infty} e^{V_{\pm}} dt = e^{\frac{1}{2} \xi_{\pm}^2} \int_0^{\infty} e^{-\frac{1}{2} [(\sigma t) + \xi_{\pm}]^2} dt. \quad (\text{A-53})$$

Let $t' = \sigma t + \xi_{\pm}$, then $dt' = \sigma dt \Rightarrow dt = \frac{1}{\sigma} dt'$, and $t \Big|_0^{\infty} \Rightarrow t' \Big|_{\xi_{\pm}}^{\infty}$

$$J_{\pm} = e^{\frac{1}{2} \xi_{\pm}^2} \int_{\xi_{\pm}}^{\infty} e^{-\frac{1}{2} t'^2} \frac{1}{\sigma} dt' = \frac{\sqrt{2\pi}}{\sigma} e^{\frac{1}{2} \xi_{\pm}^2} [1 - \Phi(\xi_{\pm})], \quad (\text{A-54})$$

where $\Phi(x)$ is the standard error function $\frac{1}{\sqrt{2\pi}} \int_{-\infty}^x e^{-\frac{1}{2} u^2} du$. (A-55)

[Note that the error function has a complex argument.]

To evaluate C_1, C_2, D_1 and D_2 we set the following initial conditions:

$$G_1(0) = 1 \Rightarrow C_1 + C_2 = 1 \quad (\text{A-56})$$

$$G_2(0) = 1 \Rightarrow D_1 + D_2 = 1 \quad (\text{A-57})$$

which from Eq. (A-25) gives

$$\tau(\gamma + \frac{i\Delta}{2})C_1 + \tau(-\gamma + \frac{i\Delta}{2})(1 - C_1) = 1 \quad (\text{A-58})$$

or

$$C_1\{\tau(\gamma + \frac{i\Delta}{2}) - \tau(-\gamma + \frac{i\Delta}{2})\} + \tau(-\gamma + \frac{i\Delta}{2}) = 1 \quad (\text{A-59})$$

or

$$C_1 = \frac{1 + \tau(\gamma - \frac{i\Delta}{2})}{2\tau\gamma} = \frac{1}{2\tau\gamma} + \frac{1}{2} - \frac{i\Delta}{4\gamma} \quad (\text{A-60})$$

But from Eqs. (A-45), (A-46),

$$\tau\gamma = (\frac{\tau\Delta}{2})\sqrt{\alpha^2 - 1} = \frac{\sqrt{\alpha^2 - 1}}{\alpha} \quad (\text{A-61})$$

and

$$\frac{i\Delta}{4\gamma} = \frac{i\Delta}{4(\frac{\Delta}{2})\sqrt{\alpha^2 - 1}} - \frac{i}{2\sqrt{\alpha^2 - 1}} \quad (\text{A-62})$$

So,

$$C_1 = \frac{1}{2}(\frac{\alpha}{\sqrt{\alpha^2 - 1}}) + \frac{1}{2} - \frac{1}{2}(\frac{i}{\sqrt{\alpha^2 - 1}}) = \frac{1}{2}\left[1 + \frac{\alpha - i}{\sqrt{\alpha^2 - 1}}\right] \quad (\text{A-63})$$

Thus,

$$C_2 = \frac{1}{2}\left[1 - \frac{\alpha - i}{\sqrt{\alpha^2 - 1}}\right] \quad (\text{A-64})$$

Now

$$\begin{aligned} D_1 &= \tau(\gamma + \frac{i\Delta}{2})C_1 = (\frac{\sqrt{\alpha^2 - 1}}{\alpha} + \frac{i}{\alpha})C_1 \\ &= \frac{1}{\alpha}(\sqrt{\alpha^2 - 1} + i)(\frac{1}{2})(1 + \frac{\alpha - i}{\sqrt{\alpha^2 - 1}}) \end{aligned} \quad (\text{A-65})$$

or

$$D_1 = \frac{1}{2\alpha} (\sqrt{\alpha^2 - 1} + i + (\alpha - i) + i \frac{(\alpha - i)}{\sqrt{\alpha^2 - 1}})$$

$$= \frac{1}{2\alpha} (\sqrt{\alpha^2 - 1} + \alpha + \frac{1}{\sqrt{\alpha^2 - 1}} + i \frac{\alpha}{\sqrt{\alpha^2 - 1}}) \quad (A-66)$$

$$= \frac{1}{2\alpha} (\frac{\alpha^2}{\sqrt{\alpha^2 - 1}} + \alpha + \frac{i\alpha}{\sqrt{\alpha^2 - 1}}) \quad (A-67)$$

So,

$$D_1 + C_1 = \frac{1}{2\alpha} (\frac{\alpha^2}{\sqrt{\alpha^2 - 1}} + \alpha + \alpha + \frac{\alpha^2}{\sqrt{\alpha^2 - 1}} + \frac{i\alpha}{\sqrt{\alpha^2 - 1}} - \frac{i\alpha}{\sqrt{\alpha^2 - 1}}) \quad (A-68)$$

or

$$D_1 + C_1 = \frac{1}{\alpha} (\frac{\alpha^2}{\sqrt{\alpha^2 - 1}} + \alpha) = 1 + \frac{\alpha}{\sqrt{\alpha^2 - 1}} \quad (A-69)$$

Since $(D_1 + C_1) + (D_2 + C_2) = 2$ we have

$$D_2 + C_2 = 1 - \frac{\alpha}{\sqrt{\alpha^2 - 1}} \quad (A-70)$$

Using Eqs. (A-69), (A-70), (A-54) in (A-43) gives

$$I(\omega) = \text{Real}\{ (1 + \frac{\alpha}{\sqrt{\alpha^2 - 1}})]_+ + (1 - \frac{\alpha}{\sqrt{\alpha^2 - 1}})]_- \} \quad (A-71)$$

$$= \frac{\sqrt{2\pi}}{\sigma} \text{Real}\{ \sum_{\pm} B_{\pm} e^{\frac{1}{2}\xi_{\pm}^2} [1 - \phi(\xi_{\pm})] \} \quad (A-72)$$

when

$$B_{\pm} = 1 \pm \frac{\alpha}{\sqrt{\alpha^2 - 1}} \text{ as defined by Fessenden ;} \quad (A-73)$$

and from (A-52)

$$\xi_{\pm} = Y_{\pm} + i \frac{(\omega - \omega_m)}{\sigma}, \quad (\text{A-74})$$

where

$$Y_{\pm} = [\alpha \mp \sqrt{\alpha^2 - 1}]a \quad \text{as defined by Fessenden} \quad (\text{A-75})$$

and

$$\alpha = 2/\tau\Delta; \quad a = \Delta/2\sigma; \quad \Delta = \omega_{h_2} - \omega_{h_1};$$

$$\omega_m = \frac{1}{2}(\omega_{h_1} + \omega_{h_2}) + \omega_0. \quad (\text{A-76})$$

Let

$$\tilde{I}(\omega) = \frac{\sqrt{2\pi}}{\sigma} \left\{ \sum_{\pm} B_{\pm} e^{\frac{1}{2}\xi_{\pm}^2} \pm \left[1 - \phi(\xi_{\pm}) \right] \right\}. \quad (\text{A-77})$$

Then

$$I(\omega) = \text{Real}\{\tilde{I}(\omega)\}, \quad (\text{A-78})$$

$$\frac{\partial I(\omega)}{\partial \omega} = \text{Real}\left\{\frac{\partial \tilde{I}(\omega)}{\partial \omega}\right\} \quad \frac{\partial^2 I(\omega)}{\partial \omega^2} = \text{Real}\left\{\frac{\partial^2 \tilde{I}(\omega)}{\partial \omega^2}\right\}.$$

We see from (A-74) that

$$\frac{\partial \xi_{\pm}}{\partial \omega} = \frac{i}{\sigma} \quad (\text{A-79})$$

and from (A-55) that

$$\frac{\partial \phi(x)}{\partial x} = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2} \quad (\text{A-80})$$

So

$$\frac{\partial \tilde{I}(\omega)}{\partial \omega} = \frac{\sqrt{2\pi}}{\sigma} \left\{ \sum_{\pm} B_{\pm} \left\{ e^{\frac{1}{2}\xi_{\pm}^2} \left(\frac{i}{\sigma} \right) [1 - \phi(\xi_{\pm})] + e^{\frac{1}{2}\xi_{\pm}^2} \left[-\frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}\xi_{\pm}^2} \left(\frac{i}{\sigma} \right) \right] \right\} \right\} \quad (A-81)$$

$$= \frac{\sqrt{2\pi}}{\sigma} \left\{ \sum_{\pm} B_{\pm} \left(\frac{i}{\sigma} \right) \left\{ \xi_{\pm} e^{\frac{1}{2}\xi_{\pm}^2} [1 - \phi(\xi_{\pm})] - \frac{1}{\sqrt{2\pi}} \right\} \right\} \quad (A-82)$$

$$= \frac{i\xi_{\pm}}{\sigma} \frac{\sqrt{2\pi}}{\sigma} \left\{ \sum_{\pm} B_{\pm} e^{\frac{1}{2}\xi_{\pm}^2} [1 - \phi(\xi_{\pm})] \right\} - \frac{\sqrt{2\pi}}{\sigma} \left\{ \sum_{\pm} B_{\pm} \left(\frac{i}{\sqrt{2\pi} \sigma} \right) \right\} \quad (A-83)$$

or

$$\frac{\partial \tilde{I}(\omega)}{\partial \omega} = \frac{i\xi_{\pm}}{\sigma} \tilde{I}(\omega) - \frac{\sqrt{2\pi}}{\sigma} \sum_{\pm} B_{\pm} \left(\frac{i}{\sqrt{2\pi} \sigma} \right). \quad (A-84)$$

Thus,

$$\frac{\partial^2 \tilde{I}(\omega)}{\partial \omega^2} = \left(\frac{i}{\sigma} \right) \left(\frac{i}{\sigma} \right) \tilde{I}(\omega) + \frac{i\xi_{\pm}}{\sigma} \left\{ \frac{i\xi_{\pm}}{\sigma} \tilde{I}(\omega) - \frac{\sqrt{2\pi}}{\sigma} \sum_{\pm} B_{\pm} \left(\frac{i}{\sqrt{2\pi} \sigma} \right) \right\} \quad (A-85)$$

$$= \left(-\frac{1}{\sigma^2} - \frac{\xi_{\pm}^2}{\sigma^2} \right) \tilde{I}(\omega) - \frac{\sqrt{2\pi}}{\sigma} \sum_{\pm} B_{\pm} \left(\frac{-\xi_{\pm}}{\sqrt{2\pi} \sigma^2} \right) \quad (A-86)$$

$$= \frac{1}{\sigma^2} \frac{\sqrt{2\pi}}{\sigma} \left\{ \sum_{\pm} B_{\pm} \left[\frac{\xi_{\pm}}{\sqrt{2\pi}} - (1 + \xi_{\pm}^2) e^{\frac{1}{2}\xi_{\pm}^2} [1 - \phi(\xi_{\pm})] \right] \right\}. \quad (A-87)$$

Finally,

$$\frac{\partial^2 I(\omega)}{\partial \omega^2} = \frac{-1}{\sigma^3} \text{Real} \left\{ \sum_{\pm} B_{\pm} \left[-\xi_{\pm} + (1 + \xi_{\pm}^2) e^{\frac{1}{2}\xi_{\pm}^2} \underbrace{\left\{ \sqrt{2\pi} [1 - \phi(\xi_{\pm})] \right\}}_{\text{Fessenden's erf}(\xi_{\pm})} \right] \right\}. \quad (A-88)$$

We have

$$\phi(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^z e^{-\frac{1}{2}t^2} dt. \quad (A-89)$$

From the "Handbook of Mathematical Functions", edited by M. Abramowitz and I.A. Stegun (1967), referred to as [A], there is defined (p. 297)

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt ; \quad (\text{A-90})$$

let $t = \frac{t'}{\sqrt{2}}$ then $dt = \frac{dt'}{\sqrt{2}}$ and $t \Big|_0^z \rightarrow \frac{t'}{\sqrt{2}} \Big|_0^z \rightarrow t' \Big|_0^{\sqrt{2} z}$ so

$$\operatorname{erf}(z) = 2 \frac{1}{\sqrt{2\pi}} \int_0^{\sqrt{2} z} e^{-\frac{1}{2} t'^2} dt' = 2\{\Phi(\sqrt{2} z) - \Phi(0)\}$$

or

$$\operatorname{erf}(z) = 2\Phi(\sqrt{2} z) - 1 . \quad (\text{A-91})$$

Also [A] defines

$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) \quad (\text{A-92})$$

and

$$\omega(z) = e^{-z^2} \operatorname{erfc}(-iz) . \quad (\text{A-93})$$

We then have

$$\operatorname{erfc}(z) = 2 - 2\Phi(\sqrt{2} z) \quad (\text{A-94})$$

and

$$\omega(z) = 2e^{-z^2} [1 - \Phi(-\sqrt{2} iz)] . \quad (\text{A-95})$$

So

$$\Phi(-\sqrt{2} iz) = 1 - \frac{1}{2} e^{z^2} \omega(z) \quad (\text{A-96})$$

or

$$\Phi(z) = 1 - \frac{1}{2} e^{-\frac{1}{2} z^2} \omega\left(\frac{iz}{\sqrt{2}}\right) . \quad (\text{A-97})$$

Thus,

$$e^{\frac{1}{2} z^2} (1 - \Phi(z)) = \frac{1}{2} \omega\left(\frac{iz}{\sqrt{2}}\right) . \quad (\text{A-98})$$

Using (A-98) in (A-88) gives

$$\frac{\partial^2 I(\omega)}{\partial \omega^2} = \frac{-1}{\sigma^3} \operatorname{Real} \left\{ \sum_{+} B_{+} [-\xi_{+} + (1 + \xi_{+}^2)^{\sqrt{\pi}/2} \omega(\frac{i\xi_{+}}{\sqrt{2}})] \right\}. \quad (\text{A-99})$$

According to formula 7.1.8 on p. 297 of [A]

$$\omega(z) = \sum_{n=0}^{\infty} \frac{(iz)^n}{\Gamma(\frac{n}{2} + 1)} \quad (\text{A-100})$$

Since $\Gamma(\frac{1}{2}) = \sqrt{\pi}$, we can expand this as

$$\omega(z) = \sum_{k=0}^{\infty} \left\{ \frac{(-z^2)^k}{k!} + \frac{(iz)(-z^2)^k}{(K + \frac{1}{2})(K - \frac{1}{2}) - (\frac{3}{2})(\frac{1}{2})\sqrt{\pi}} \right\}. \quad (\text{A-101})$$

On the bottom of p. 328, we have the approximations :

For $z = x + iy$, if $x > 3.9$ or $y > 3$ then

$$\omega(z) = iz \left(\frac{0.4613135}{z^2 - 0.1901635} + \frac{0.09999216}{z^2 - 1.7844927} + \frac{0.002883894}{z^2 - 5.5253437} \right) + \epsilon(z) \quad (\text{A-102})$$

where $|\epsilon(z)| < 2 \times 10^{-6}$.

If $x > 6$ or $y > 6$ then

$$\omega(z) = iz \left(\frac{0.5124242}{z^2 - 0.2752551} + \frac{0.05776536}{z^2 - 2.724745} \right) + \eta(z) \quad (\text{A-103})$$

where $|\eta(z)| < 1 \times 10^{-6}$.

Also we have the identity (from bottom of p. 325 of [A])

$$\begin{aligned} \omega(-x + iy) &= \overline{\omega(x + iy)} \omega(x - iy) \\ &= ze^{y^2 - x^2} (\cos 2xy + i \sin 2xy) - \overline{\omega(x + iy)} \end{aligned} \quad (\text{A-104})$$

Eq. (A-104) also gives

$$\omega(-x - iy) = \overline{\omega(x - iy)} = 2e^{y^2 - x^2} (\cos 2xy - i \sin 2xy) - \omega(x + iy). \quad (\text{A-105})$$

If $\text{Im}(\xi_{\pm}) = 0$ and $\text{Re}(\xi_{\pm}) > 6$, then

$$\begin{aligned} \omega\left(\frac{i\xi_{\pm}}{\sqrt{2}}\right) &= i \left[\frac{i\xi_{\pm}}{\sqrt{2}} \right] \left(\frac{.5124242}{\left[\frac{i\xi_{\pm}}{\sqrt{2}} \right]^2} + \frac{.05176536}{\left[\frac{i\xi_{\pm}}{\sqrt{2}} \right]^2} \right) \\ &\quad - .02752551 \left[\frac{i\xi_{\pm}}{\sqrt{2}} \right] - 2.724745 \end{aligned} \quad (\text{A-106})$$

$$= \frac{\xi_{\pm}}{\sqrt{2}} \left(\frac{.5124242}{\left(\frac{\xi_{\pm}^2}{2} \right) + .02752551} + \frac{.05176536}{\left(\frac{\xi_{\pm}^2}{2} \right) + 2.724745} \right).$$

APPENDIX B

PROGRAM ESREX4

```

PROGRAM ESREX4 (OUTPUT=65,TAPE6=OUTPUT)
REAL INT,NOEXCH
WH1=4.43917E8
WH2=8.03276E8
WG=5.727130E10
TAU=1.00E30
SIGMA=5.9E935E7
W=WG+WH1
INT=F(W,WG,WH1,WH2,TAU,SIGMA)
NOEXCH=INT
WRITE(6,105) W,NOEXCH
105 FORMAT(///,10X,*W=*,E15.7,/,10X,*NOEXCH (THE INTENSITY AT TAU
C=1.0E30 SEC/RAD)=*,E15.7,/)
ALOG=-11.0
ELOG=2.3025851*ALOG
TAU=EXP(ELOG)
WRITE(6,101) TAU
101 FORMAT(1H1,///,5X,*CORRELATION TIME FOR JUMPING (SEC/RAD) TAU=*,
E10.4)
WRITE(6,102)
102 FORMAT(///,15X,*TAU (SEC/RAD)*,5X,*LOG OF TAU*,15X,*INTENSITY*,
C15X,*RELATIVE INTENSITY (INT/INTENSITY AT NO EXCHANGE)*,/)
1 W=WG+WH2
ELOG=2.3025851*ALOG
TAU=EXP(ELOG)
INT=F(W,WG,WH1,WH2,TAU,SIGMA)
RELINT=INT/NOEXCH
WRITE(6,103) TAU,INT,RELINT
103 FORMAT(10X,E15.7,27X,E15.7,15X,F10.3,*(AT W1)*,/)
W=WG+((WH1+WH2)/2.0)
INT=F(W,WG,WH1,WH2,TAU,SIGMA)
RELINT=INT/NOEXCH
WRITE(6,104) TAU,INT,RELINT
104 FORMAT(10X,E15.7,27X,E15.7,15X,F10.3,*(AT WM)*,/)
W=WG+WH1
INT=F(W,WG,WH1,WH2,TAU,SIGMA)
RELINT=INT/NOEXCH
WRITE(6,106) TAU,ALOG,INT,RELINT
106 FORMAT(10X,E15.7,5X,F7.2,15X,E15.7,15X,F10.3,*(AT W2)*,///)
ALOG=ALOG+0.10
IF (ALOG.GT. -5.0) GO TO 200
GO TO 1
200 CONTINUE
END
REAL FUNCTION F(W,WG,WH1,WH2,TAU,SIGMA)
IMPLICIT COMPLEX (Z)
ZSQRT2 = CMPLX(0.0, (1.0/SQRT(2.0)))
ZPI2 = (1.2533141373155,0.0)
C ZPI2 = SQRT(PI/2.0)
DELTA = WH2-WH1
ALPHA = 2.0/(TAU*DELTA)
A = DELTA/(2.0*SIGMA)
WM = 0.5*(WH1+WH2)+WG
DIF = (W-WM)/SIGMA
ZALPHA = CMPLX(ALPHA,0.0)
ZA = CMPLX(A,0.0)
ZDIF = CMPLX(0.0,DIF)
ZU = CSQRT(ZALPHA**2-(1.0,0.0))
ZYP = (ZALPHA-ZU)*ZA
ZYM = (ZALPHA+ZU)*ZA
ZUU = ZALPHA/ZU
ZBP = (1.0,0.0) + ZUU
ZBM = (1.0,0.0) - ZUU
ZXIP = ZYP+ZDIF
ZXIM = ZYM+ZDIF
ZARGP = ZSQRT2*ZXIP
ZARGM = ZSQRT2*ZXIM
ZWP = ZW(ZARGP)
ZWM = ZW(ZARGM)
ZADUP = ZPI2*((1.0,0.0) + ZXIP*ZXIP)*ZWP
ZADDM = ZPI2*((1.0,0.0) + ZXIM*ZXIM)*ZWM
ZTOTP = ZBP*(-ZXIP+ZADDP)
ZTOTM = ZBM*(-ZXIM+ZADDM)
ZM = ZTOTP+ZTOTM
F = REAL(ZM)
100 FORMAT(/,W,WG,WH1,WH2,TAU=*,E18.10,/,SIGMA,WM,DELTA,DIF=*,
E18.10)
102 FORMAT(*ZU,ZUU=*,E18.10,/,*ZYP,ZYM=*,E18.10,/,*ZARGP,ZWP=*,
E18.10,/,*ZARGM,ZWM=*,E18.10)
101 FORMAT(*ZXIP,M=*,E20.10,/,*ZADDP,M=*,E20.10,/,
1 *ZBP,M=*,E20.10,/,*ZTOTP,M=*,E20.10,/,*ZA,ZM=*,E20.10)

```

```

      RETURN
      END
      COMPLEX FUNCTION ZW(Z)
      IMPLICIT COMPLEX (A-H,J-W,Z),INTEGER (I),REAL (X,Y)
      COMMON /ZW/ INDEX,ITEFM,XMAX
      DATA INDEX/0/
C THIS ROUTINE CALCULATES THE W FUNCTION WHICH IS RELATED TO THE ERF OF
C FUNCTION AS FOLLOWS:  $W(Z) = \exp(-Z^2) * (1.0 - \text{ERF}(-iZ))$ , WHERE
C  $\text{ERF}(Z) = (2.0/\text{SQRT}(\pi)) * \text{INTEGRAL FROM } 0 \text{ TO } Z \text{ OF THE FUNCTION}$ 
C  $\exp(-t^2)$ . THE DEFINITION AND RELATIONS USED TO CALCULATE  $W(Z)$  ARE
C FOUND IN "HANDBOOK OF MATHEMATICAL FUNCTIONS" BY M. ABRAMOWITZ AND
C I.A. STEGUN (1964), P. 297 AND BOTTOM OF PP. 327 AND 32A.
C
      X = REAL(Z) $ Y = AIMAG(Z)
      IFLAG = 0
      IF(X.GE.0.0) GO TO 10
      IFLAG = IFLAG+1 $ X = -X
      10 IF(Y.GE.0.0) GO TO 20
      IFLAG = IFLAG+2 $ Y = -Y
C IFLAG = (0,1,2,3) IF ( (X POS.,Y POS.) , (X NEG.,Y POS.) , (X POS.,
C Y NEG.) , (X NEG.,Y NEG.) )
C AT THIS POINT BOTH X AND Y ARE POSITIVE
      20 IF(INDEX.EQ.0) GO TO 25
      GO TO (60,40,30) INDEX
      25 IF((X.GT.6.0).OR.(Y.GT.6.0)) 30,4)
      30 Q = Z*Z
      A1 = (0.5124242,0.0)/(Q-(0.2752551,0.0))
      A2 = (0.05176536,0.0)/(Q-(2.724745,0.0))
      ZW = (0.0,1.0)*Z*(A1+A2)
      GO TO 100
      40 IF((X.GT.3.9).OR.(Y.GT.3.0)) 50,60
      50 Q = Z*Z
      A1 = (0.4613135,0.0)/(Q-(0.1901635,0.0))
      A2 = (0.09999216,0.0)/(Q-(1.7844927,0.0))
      A3 = (0.00288389,0.0)/(Q-(5.5253437,0.0))
      ZW = (0.0,1.0)*Z*(A1+A2+A3)
      GO TO 100
      60 Q = -Z*Z
      T1 = (1.0,0.0)
      T2 = (0.0,1.12837916709551)*Z
C T2 = I*Z/(0.5*SQRT(PI))
      K1 = (0.0,0.0) $ K2 = (0.5,0.0)
      ZW = T1+T2
      ITEFM = 1 $ XMAX = -1.0
      65 K1 = K1+(1.0,0.0) $ K2 = K2+(1.0,0.0)
      T1 = 0*T1/K1
      T2 = 0*T2/K2
      ADD = T1+T2
      ZW = ZW+ADD
      ITERM = ITEFM+1
      XPEM2 = REAL(ADD)**2+AIMAG(ADD)**2
      XPEM = SQRT(XPEM2)
      XMAX = AMAX1(XMAX,XPEM)
      IF(XPEM2.LT.1.0E-26) 100,65
      100 IF(IFLAG.EQ.0) RETURN
      IF(IFLAG.EQ.1) 105,110
      105 ZW = CONJG(ZW)
      RETURN
      110 XX = 2.0*EXP(Y*Y-X*X)
      XR = XX*COS(2.0*X*Y)
      XI = XX*SIN(2.0*X*Y)
      IF(IFLAG.EQ.2) 115,120
      115 ZW = CMPLX(XR,XI)-CONJG(ZW)
      RETURN
      120 ZW = CMPLX(XR,-XI)-ZW
      RETURN
      END
      COMPLEX FUNCTION CNORMAL(Z)
      IMPLICIT COMPLEX (A-Z)
C THIS ROUTINE CALCULATES THE STANDARD NORMAL DISTRIBUTION FUNCTION FOR
C COMPLEX ARGUMENTS. CNORMAL(Z) IS (1.0/SQRT(2.0*PI)) TIMES THE
C INTEGRAL FROM MINUS INFINITY TO Z OF THE FUNCTION  $\exp(-u^2/2.0)$ .
C THE EXPANSION FOR THE ERF FUNCTION IS GIVEN IN
C "HANDBOOK OF MATHEMATICAL FUNCTIONS" BY M. ABRAMOWITZ AND I.A. STEGUN,
C P.297 (1964).
      Q = -(0.5,0.0)*Z*Z
      U = Z/(2.5066282746,0.0)
      S = U
      N = (0.0,0.0) $ M = (1.0,0.0)
      10 N = N+(1.0,0.0) $ M = M+(2.0,0.0)
      U = 0*U/N

      T = U/M
      S = S+T
      IF((REAL(T)**2+AIMAG(T)**2).LT.1.0E-26) 15,10
      15 CNORMAL = S+(0.5,0.0)
      RETURN
      END

```