NUCLEAR MAGNETIC RESONANCE
STUDY OF
HINDERED ROTATION
IN
3-ARYL SUBSTITUTED HYDANTOINS

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ABSTRACT

The subject of this work is a study of hindered rotation in some 3-aryl substituted hydantoins by nuclear magnetic resonance (NMR) total line shape analysis. The compounds were prepared from suitable aromatic isocyanates by condensation with amino acids. In these compounds the C-5 substituents and in certain cases the ortho-substituent protons are magnetically non-equivalent and show a chemical shift difference, except when there is rapid rotation about the aryl C-N bond. This magnetic non-equivalence disappears on heating.

The kinetic and thermodynamic parameters for rotation of the aryl group have been evaluated through complete line-shape analysis of the temperature dependent spectra by using a non-linear regression method. Evidence has been found that aryl group substituents exhibit small electronic effects on the activation parameters for rotation. The influence of a buttressing substituent on the activation parameters has been investigated, as well as the influence of substituents in the C-5 position.
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INTRODUCTION

During the last twenty years, high resolution nuclear magnetic resonance has become one of the most important techniques for studying rate processes, especially those which occur in systems that are in thermodynamic equilibrium. When these processes have rate constants of the same order of magnitude as the total linewidth (in cycles per second) of the NMR spectra of a magnetic nucleus (roughly $10^{-1}$ - $10^{-5}$ sec$^{-1}$), they may give rise to significant changes in the shape of NMR signals. Indeed, "... if the average lifetimes of a number of species in equilibrium exceed an upper limit, the NMR spectrum will show them as individual entities. Conversely, if the lifetimes are short with respect to the NMR scale, one will obtain a single spectrum. The phenomena that can be observed during the transition from one extreme to the other, and their interpretation, are the realm of the method called DYNAMIC NUCLEAR MAGNETIC RESONANCE". ¹

DNMR has been used to measure kinetic parameters in many types of chemical and physical processes. This technique may be applied to processes with activation energies extending from 20-25 kcal per mole down to 5-6 kcal per mole.¹ Such rate processes as proton
transfer, and rotation around sterically crowded single bonds or partial double bonds have activation energies falling within this range.

Restricted Aryl Group Rotation in Amides:

Until recently the only data available on hindered rotation of aryl groups in amides were concerned solely with acyclic amides.

Siddall and Prohaska,² and later Mislow et al.,³ and Sutherland et al.,⁴ studied the NMR spectra of some N-benzyl-N-(o-tolyl) amides. The spectrum of the benzylic methylenic protons of these compounds shows an AB quartet at sufficiently low temperatures. The appearance of this quartet was originally attributed to slow inversion of the nitrogen atom,² since the benzylic methylenic protons must be diastereotopic if the configuration at nitrogen is pyramidal. Mislow,³ on the other hand, suggested that hindered rotation about the aryl-nitrogen bond is a plausible explanation of the observed non-equivalence. This hypothesis is reasonable in view of the fact that the barrier to nitrogen inversion in formamide is only about 1 kcal per mole while the activation energy obtained from the collapse of the AB quartet in the case of such amide is about 20 kcal per mole.
This explanation is now generally accepted.

The origin of the magnetic non-equivalence of the methylene protons and the temperature dependence of their spectra based on the slow rotation model may be seen from the following figures, which represent an approximation to the ground state configurations.

\[ \begin{align*}
\text{A} & \quad \leftrightarrow \quad \text{B} \\
\text{R} & \quad \text{H} & \quad \text{C} & \quad \text{N} & \quad \text{C} & \quad \text{R}' \\
\text{H}_a & \quad \text{C} & \quad \text{N} & \quad \text{C} & \quad \text{R}' \\
\text{X} & \quad \text{1} & \quad \text{2} & \quad \text{3} \\
\end{align*} \]

Interconversion of the enantiomeric isomers, A and B, interchanges the environments of the methylene protons and affects the spectrum arising from these protons if the rate of interconversion is sufficiently rapid. If \( R \) is a group which does not undergo spin-spin interaction with the methylene group, these protons give rise to an AB quartet at low rates of interconversion. When the rate of interconversion is fast on the NMR time scale, the quartet collapses to a singlet through time averaging of the environments of the methylene protons.

Hund\(^5\) and Huang\(^6\) later reached the following conclusion following a more extensive study of the same type of compounds:
a) The exchange process which results in the AB quartet of the benzylic methylenic protons being temperature dependent is not simply rotation around the C-N bond, but involves a competing process in which amide isomerization occurs.

b) A small electronic effect due to the substituent on the aryl ring is observable. This appears to act on the barrier of rotation of the C-N bond of the amide group and affects the process of rotation about the aryl C-N bond only indirectly.

c) A buttressing effect between a group on the 3 position and a 2-methyl substituent is observable.

Since the interpretation of rotation around the aryl C-N bond should be more straightforward in the case of N-aryl cyclic amides, in which the complication of amide isomerization is absent, it is surprising that until recently the only work reported on these systems was that of Mislow et al.,\(^3\) on compound (I).
These workers measured a $\Delta G^+$ of 17.3 kcal per mole at $73^\circ$ for this compound. They used the coalescence point method which, although not as reliable as the complete shape line analysis method, is nevertheless qualitatively valid.

In the hope of obtaining a clearer insight into the mechanism of rotation, Fehlner 7 investigated a series of 3-aryl-6-sulfamoyl-7-chloro-2,3-dihydro-4(1H)-quinazolinones (II) and hydantoins (III), by line shape analysis and equilibration methods.

![Chemical structures II and III](image)

His results for the quinazolinone series confirmed the importance of the steric interaction between the ortho substituent group and the carbonyl group in the 4 position. The results further emphasized the steric influence of any $R_1$ and $R_2$ substituent bulkier than a hydrogen atom. He found that when the $R_3$ substituent is bulkier than a hydrogen atom, this group exercises
a buttressing effect. Unlike Hund and Huang, he found that the electronic effect of the substituents was not important in the quinazolinone series.

In his investigation of restricted rotation around the C-N bond in 3-aryl hydantoins, Fehlner arrived at the same general conclusion about the effects of aryl group substituents, except when a chlorine atom was in the ortho position. The barrier to rotation is higher when a chlorine atom is present than when the substituent in the ortho position is a methyl group. Since a chlorine atom is less bulky than a methyl group, the higher barrier to rotation might be attributed solely to an electronic effect rather than a normal steric effect.

Icli, also working in this laboratory, prepared a series of 1-aryl substituted hydantoins (IV). In the course of his work, he discovered that a chlorine atom in the ortho position on 1-aryl hydantoins gives rise to a smaller rather than larger barrier of rotation relative to a methyl group in the same position.
This could be due to the fact that during rotation the ortho chlorine in the 3-aryl substituted hydantoin is obliged to pass an electronegative oxygen atom, thereby giving rise to a stronger interaction than when the substituent is a methyl group. In contrast, in 1-aryl substituted hydantoins the group in the ortho position does not interact with the oxygen atom in the preferred transition state for rotation, but rather with the substituents in the 5 position, as shown below (V).  

![Diagram](image)

**Present Investigation**

The purpose of the work presented in this thesis was:

a) To determine whether through-space electronic effects, mesomeric effects, and buttressing effects influence the barrier of rotation in the 3-aryl substituted hydantoins.

b) To check Fehlner's observations that a chlorine atom
can give rise to a larger barrier of rotation than a methyl group in this type of compound.

c) To determine the magnitude of the influence of substituents in positions other than ortho, especially the 5 position, and to rationalize their influences.

d) To obtain further information on the effect of the thiocarbonyl group versus the carbonyl group on the magnitude of the barrier of rotation.

The reasons behind the choice of 3-aryl substituted hydantoins for this study are the following:

i) Hydantoins, being cyclic amides, have a system which is made easier to interpretate than acyclic compounds because of the prearrangement of the substituents that the aryl ring must pass in its rotation.

ii) Since hydantoins are planar, problems associated with ring inversion are expected to be absent.

iii) The synthesis of hydantoins is relatively easy.
Stereochemistry and Spectra of Hydantoins

Consider the stereochemistry in the conformational ground state of a hydantoin in which the hydrogen atom has been replaced by an unsymmetrically substituted aryl group in position 3, as in VI.

Because of steric interaction between the ortho substituents on the aryl group and the carbonyl oxygen atoms of the heterocyclic moiety, the two rings cannot be co-planar in the ground state for internal rotation around the aryl C-N bond. A large dihedral angle is to be expected. For convenience in representing the stereochemistry of these molecules a dihedral angle of 90° is assumed.

If the aryl ring and the hydantoin ring are not co-planar, four different isomers must be considered. These are represented in simplified form as follows, the molecule being viewed along the aryl C-N axis from the heterocyclic end.
If \( R_1 \) and \( R_2 \) are identical then isomers A and D are identical, as are isomers B and C. Isomers A and C (or B and D) will form an enantiomeric pair, with identical NMR spectra under normal conditions. Thus these isomers cannot be distinguished by the NMR method using achiral media.

However, since these molecules lack a plane of symmetry, \( R_1 \) and \( R_2 \) are diastereotopic. Provided that their magnetic environments are sufficiently different to produce a chemical shift difference, these two substituents should be distinguishable.
If \( R_1 = R_2 = H \) an AB quartet is expected from these protons in the conformational ground state of the molecule. This type of spectrum has been reported earlier for conformers such as hydantoins. Chemical shift and \( \gamma \)eminal coupling constants within the range of 3.6-4.9 \( \delta \) and 16.0-12.0 Hz, respectively, have been observed.

If rotation around the C-N aryl bond occurs, corresponding to interconversion between isomers A and B (or C and D), the environments of \( R_1 \) and \( R_2 \) undergo enantiomeric interchange (provided that \( R_1 = R_2 \)). If rotation around the same axis is rapid on the NMR timescale, the AB quartet arising from the geminal protons on C-5 will collapse to a singlet. At intermediate rates of rotation partial collapse of the AB quartet is expected. Such behaviour has been reported earlier. The temperature dependence of such a spectrum arising from the geminal protons in the 5 position of 3-\( \alpha \)-naphthyl-1-methylhydantoin (pyridine solution) is illustrated by means of computer simulation in Figure 1, using data of Fehlner.

If \( R_1 = R_2 = \text{CH}_3 \) these groups are expected to give rise to two peaks of equal intensity under condition of slow rotation about the C-N bond. Spin-spin coupling between the protons of the geminal methyl groups is expected to be too small for the fine structure to be resolvable although some line broadening may be detected. Under condition of fast rotation the two methyl lines are
expected to collapse to a single, time averaged line. Such behaviour has been observed in a number of cases. The temperature dependence of the 5,5-dimethyl signals of 3-(o-bromophenyl)-5,5-dimethylhydantoin is illustrated in Figure 2. Data for the computer simulation are taken from the work of Fehlner. 7

When $R_1 \neq R_2$ the rotational isomers are diastereomers. All four isomers (configurational and rotational) are distinct, but the members of the pairs A and C, and B and D are enantiomeric and are, therefore, not normally distinguishable by the NMR method. Since A and B or (C and D) are diasteromers, they are expected to differ in all their physical properties, including their NMR spectra. Thus $R_1$ in A is expected to differ in chemical shift from $R_1$ in B. The same is true for $R_2$ in the same isomers. Since diastereomers have different free energies the concentration of the two forms A and B (or C and D) are expected to be different at equilibrium. The spectrum of an equilibrium mixture of such diastereomeric rotational isomers is, therefore, expected to be the sum of the spectra of the two distinguishable diastereomers, of unequal intensity. In principle, all lines in the overall spectrum should show splitting resulting from the contribution of the two forms, but in practice the chemical shifts may not be great enough for all splitting to be resolvable.
Figure 1: Computer Simulated Spectra of the C-5 Protons of 3-α-naphthyl-l-methylhydantoin in Pyridine at Various Temperatures.
Figure 2: Computer Simulated Spectra of the C-5 Methyl Group of 3-(o-bromophenyl)-5,5-dimethylhydantoin in 2-chloropyridine at Various Temperatures.
Figure 2: (Continued)
At high rates of rotation, a time averaged spectrum is expected, the chemical shifts of the nuclei reflecting the average environment in the two diastereomers. The time averaged lines will not be equidistant between the corresponding line positions of the individual isomers of rotation, but will appear at frequencies weighted according to the relative populations of the two species. Such behaviour has been reported by Fehlner,⁷ and has been observed in the present investigation.

When \( R_1 = H, R_2 = CH_3 \) the spectrum arising from the C-5 substituents at low rates of rotation consists of two sometimes overlapping methyl doublets and two methine quartets. At high rates of rotation the pair of methyl doublets collapses to a single doublet and the pair of methine quartets collapses to a single quartet. Several such cases have been reported by Fehlner.⁷ This case is illustrated in Figure 3 for the C-5 methyl signal of 3-(o-chlorophenyl)-5-methylhydantoin. Data for the computer simulation were obtained by Fehlner.⁷

If spin coupling between \( R_1 \) and \( R_2 \) is absent the spectra are less complicated. When \( R_1 = H, R_2 = C_6H_5 \), the spectrum of \( R_1 \) consists of two singlets of unequal intensity under condition of slow rotation, and a time averaged singlet if rotation is fast.

The spectrum of the ortho substituent, \( R_3 \) on the
aryl group may also be dependent on the rate of rotation about the C-N bond. If $R_1 = R_2$, the magnetic environments of $R_3$ in the pair of rotamers are identical. Thus if $R_3 = CH_3$, a single signal is seen under all conditions. However if $R_1 \neq R_2$, the environments of $R_3$ in the two rotamers are different. If $R_3 = CH_3$ two lines of unequal intensity will be seen under conditions of slow rotation and a single time averaged line under fast rotation. This case is illustrated for the ortho-methyl spectrum of 3-(o-tolyl)-5-methylhydantoin (VII) in Figure 4. Data for the computer simulation were obtained in the present investigation.

The prediction of the appearance of the spectra of 3-aryl hydantoins outlined above are based on the stereochemistry of these molecules. Experimentally determined spectra may not be in accord with prediction for the following reasons:

a) The chemical shift differences may be too small for the signals arising from nuclei in different environments to be resolved. Degeneracy of this type may sometimes be resolved by choice of a more suitable solvent.

b) The rate of rotation may be fast at the lowest temperature attainable, with the result that the time averaged spectrum is always seen. This situation may be difficult to distinguish from that in a).

When $R_1 = H$, $R_2 = CH_3$, and $R_3 = OCH_3$ in the present
Figure 3: Computer Simulated Spectra of the C-5 Methyl Groups of 3-(o-chlorophenyl)-5-methylhydantoin in Pyridine at Various Temperatures.
Figure 3: (Continued)
Figure 4: Computer Simulated Spectra of the ortho-methyl Group of 3-o-tolyl-5-methylhydantoin (VII) in DMSO-d$_6$ at Various Temperatures.
investigation (compound (XXIII)) no splitting was seen. It is difficult to establish which of these factors is responsible for the failure to observe splitting in this case.

c) The rate of rotation may be so slow at the highest attainable temperature that collapse of the spectrum is not observed. Examples of highly hindered 3-aryl-2-thiohydantoins, which have this property, have been reported by Fehlner\textsuperscript{7} and confirmed by this investigation.

Following a review of the types of spectra to be expected for various classes of substituted hydantoins, it was decided that 5-phenyl hydantoins ($R_1 = \text{H}, R_2 = \text{C}_6\text{H}_5$) should provide the most suitable spectra for the present investigation. Consequently most of the compounds prepared were of this type. In this series uncomplicated 5-methylene signals may be used to obtain rate constants for interconversion of rotational isomers. In addition, the ortho methyl signals from those compounds with $R_3 = \text{CH}_3$ may be used for the same purpose.
Theory and Calculation of Spectra

Collapse of a pair of singlets to a singlet peak.

The equations for the collapse of a pair of singlets to a singlet peak, as depicted in Figures 2 and 4, have been derived from the Bloch equations\textsuperscript{11,12,13} by Gütowsky and Holm.\textsuperscript{14} The equation for the intensity, \( I \), at any point, \( \omega \), is:

\[
I = k \frac{(1 + \tau/T_2)P_2 + QR}{P^2 + R^2}
\]

where

\[
1/\tau = \frac{\tau_A + \tau_B}{\tau_A \tau_B}
\]

and:

\[
P = \tau((1/T_2)^2 - (1/2(\omega_A + \omega_B) - \omega)^2 - 1/4(\omega_A - \omega_B)^2 + 1/T_2
\]

\[
Q = \tau(1/2(\omega_A + \omega_B) - \omega - 1/2(p_A - p_B)(\omega_A - \omega_B))
\]

\[
R = (1/2(\omega_A + \omega_B) - \omega)(1 + 2\tau/T_2) + 1/2(p_A - p_B)(\omega_A - \omega_B)
\]

Parameter \( k \) is a scaling factor to allow for the adjustment of the intensity to that of the experimental value. Parameters \( p_A \) and \( p_B \) are the populations of the two
rotamers and are equal to $\tau_A/(\tau_A + \tau_B)$ and $\tau_B/(\tau_A + \tau_B)$, respectively. Parameters $\tau_A$ and $\tau_B$ are the lifetimes of the two rotamers in seconds, while $\omega_A$ and $\omega_B$ are their chemical shifts in radians/sec. The transverse relaxation time $T_2$ is related to the linewidth, $W$, (in Hz) by the equation:

$$T_2 = \frac{1}{\pi W}$$

When possible, $W$ is measured from the half height of the peaks in a nonexchanging system.

In practice, $W$ includes all contributions to the linewidth due to inhomogeneity of the magnetic field and other factors such as viscosity, drifting, unresolved long range coupling, etc.

Another formulation of the line shape method applicable to this case is based on a density matrix method and does not contain the assumption of equal transverse relaxation times for exchanging sites, which is inherent in the Gutowsky-Holm equation as it is normally used.
Comparison of Spectra

When the experimental spectra have been obtained, theoretical spectra must be fitted to them.

Until recently, the experimental and theoretical spectra were plotted together and compared visually. Corrections were made to the parameters and the process was repeated until an acceptable fit was found, using subjective criteria. This procedure involved a large amount of time and the final values of the parameters were somewhat dependent on the skill and patience of the operator. Today this comparison is made by a computer, which compares the spectra point by point and then adjusts the parameters accordingly, until the best fit based on non-subjective criteria is obtained.

This can be done by use of a non-linear least square analysis programme, such as that devised by Marquardt, which is based on the maximum neighborhood method. This programme, in combination with the subroutines containing the line shape equations for the system being considered, allows accurate fitting, and gives standard error analysis for the parameters involved. A listing of this programme is contained in the Appendix.

The output of this programme can be used to plot the experimental and theoretical spectra calculated by the fitting procedure. Two examples of the validity of
this programme can be seen in Figures 5, and 6, which show superimposed the experimental spectra and the spectra simulated by using the parameter values calculated by the computer.
Figure 5: Experimental (—) and Theoretical (...) Spectra for 3-o-toly1-5-methylhydantoin (VII) in DMSO-d$_6$ at Various Temperatures. Mean lifetimes are shown.
Figure 6: Experimental (—) and Theoretical (..) Spectra for 3-(2,3-dimethylphenyl)-5-methylhydantoin (IX) in DMSO-d$_6$ at Various Temperatures. Mean Lifetimes are Shown.
Calculation of Thermodynamic Parameters

After the rate constants or mean lifetimes have been obtained at a number of different temperatures, one can find the activation energy by means of the Arrhenius equation:

\[ k = A e^{-E_a/RT} \]

where:
- \( k \) = reaction rate constant
- \( A \) = frequency factor
- \( E_a \) = activation energy
- \( R \) = gas constant
- \( T \) = absolute temperature

By plotting \( \ln k \) versus \( 1/T \), one can determine the activation energy \( E_a \) from the slope, and the frequency factor \( A \) from the intercept of the best fit straight line.

The above equation assumes that \( E_a \) and \( A \) are independent of the temperature, which can only be an approximation. Experience has shown this approximation to be a good one.

At the present time the tendency is to obtain Eyring parameters. This is done by equating the Arrhenius equation,

\[ k = k_b (kT/h)e^{-\Delta G/RT} \]

that can be rewritten as:
\[ k = \frac{k_b K T}{h e^{-\Delta H^\ddagger / R T}} e^{(\Delta S^\ddagger / R)} \]

**where:**

- \( k \) = rate constant
- \( K \) = transmission coefficient
- \( k_b \) = Boltzmann's constant
- \( h \) = Planck's constant
- \( \Delta G^\ddagger \) = free energy of activation
- \( \Delta S^\ddagger \) = entropy of activation
- \( \Delta H^\ddagger \) = enthalpy of activation
- \( R \) = gas constant
- \( T \) = absolute temperature

The transmission coefficient, \( K \), is assumed to be equal to one. Other values have been tried, but they give unrealistic results.

It is possible to calculate \( \Delta S^\ddagger \) and \( \Delta H^\ddagger \) from the temperature independent activation energy \( E_a \) obtained from the Arrhenius plot. This is done by equating:

\[
\begin{align*}
\Delta H^\ddagger &= E_a - RT \\
\Delta G^\ddagger &= 2.303RT(10.3191 + \log T + \log t) \\
\Delta S^\ddagger &= (\Delta H^\ddagger - \Delta G^\ddagger) / T
\end{align*}
\]

A programme, ACTPAR, has been written to find the best straight line for the plot of \( \ln k \) versus \( 1/T \) through the use of a linear regression method. A listing of ACTPAR is contained in the Appendix.
Alternative Method for Calculating $\Delta G^*$ of Activation

The method of the maximum separation of peaks$^{16}$ is, or better was, a widely used method to calculate thermodynamic parameters for an exchanging AB system. It is much simpler than the complete line shape analysis, but can unfortunately introduce errors of large magnitude (10-30%), as Gutowsky et al. have shown.$^{17}$ According to this method the rate equation can be expressed as,

$$k = \frac{\pi (\nu_{AB}^2 - 6J_{AB}^2)^{1/2}}{\sqrt{2}}$$

where

$k = $ rate constant

$\nu_{AB} =$ maximum difference in chemical shift between A and B

$J_{AB} =$ coupling constant

When $J$ is zero this expression reduces to

$$k = \frac{\pi \nu_{AB}}{\sqrt{2}}$$

Once $k$ is known, one can obtain $\Delta G^*$ by substituting $k$ into the Eyring equation.
Measurement of Spectra

All spectra of hydantoins used for kinetic studies were taken in deuterated dimethylsulfoxide. By using DMSO-d$_6$, it was possible to prepare concentrated solutions (0.25–0.50 mole/l) in order to maximize the signal-to-noise ratio. Further DMSO-d$_6$ did not interfere with any hydantoin absorption. In the case of ortho-methoxy hydantoins, DMSO-d$_6$ and pyridine were used as solvents since it was necessary to lower the temperature below the DMSO-d$_6$ freezing point.

The internal standard used was tetramethyilsilane. It was possible to maintain the lock on tetramethyilsilane up to a temperature of 150$^\circ$.

The spectra were taken on a Varian HA-100 spectrometer using the standard variable temperature equipment. Using methanol and ethylene glycol, the temperature was determined after each run by comparing the peak separation obtained by locking on the C-H peak and measuring the chemical shift of the hydroxyl proton. Care was taken to ensure that the temperature had first come to equilibrium.

Spectra of the protons under study were taken at an interval of 8–10$^\circ$ degrees over the range of temperature where collapse of the spectrum was observed.

Care was taken to minimize the drift, to maximize the homogeneity, and above all to avoid saturation of the peaks.
Fitting of the Spectra

The theoretical spectra were fitted to the experimental spectra by use of a non-linear least squares regression programme. Different type of subprogrammes were available to cope with different kinds of systems, for example NLIN AB for the collapse of an AB quartet, and NLIN GH for the collapse of two singlets to one singlet.

The spectra were entered into the computer as data pair corresponding to intensity and position. These were obtained by estimating a suitable baseline and measuring the intensity of the peaks at different frequencies. Since a typical spectrum may have three data pairs for each Hz, and an average of ten spectra are required for each case, it is evident that this process is time consuming if the spectra are measured manually and the data pairs are punched on computer cards.

Colebrook et al.\textsuperscript{18} prepared the programmes LINDI and TAPGH to overcome this problem. By using a combination of the Hewlett-Packard F-3B line follower and the H-P 2114B computer, these programmes allow one to digitalize directly from the spectrum.

The computer drives the X-axis sweep of the recorder through an 8 bit digital-to-analogue converter, while the line follower head follows the spectral trace,
which must be recorded in black ink. A voltage proportional to the spectrum intensity is supplied to the analogue-to-digital converter from the Y-axis slide wire. The computer moves the recorder arm across the spectrum in 250 increments, storing a digitalized intensity for each spectrum. Before the run is started the line-follower is adjusted successively to the left and right limits of the portion of the spectrum to be scanned. On output the computer calculates the frequencies corresponding to different intensities.

The main programme is written in FORTRAN, whereas the subroutines, which drive the recorder, affect digitalization, and provide a variable delay to control the scanning rate, are written in Assembler. Since a line follower cannot cope with steep curves, there is a provision in the programme for interrupting the sweep through the switch register of the computer, so that the spectrum can be scanned at any point and time under operator control. There is also a provision to abort a scan through the computer switch register. The computer outputs up to 251 (the number is selectable) baseline corrected intensity-frequency data pairs on the teletypewriter and also punches them on a paper tape. A listing of these programmes is included in the Appendix.

Another FORTRAN programme has been written for the
2114B to process the paper tape at a later stage. This programme writes the digital information on magnetic tape together with the required control parameters for the non-linear regression programme used for fitting a computed to a digitalized spectrum. The operator must type in the original estimates for the parameters and specify which parameters are to be held constant and which ones are to be varied. The data on the magnetic tape are then processed on the CDC 6400 computer.

If the system consists of two singlets collapsing to one singlet, six parameters are needed to describe the line shape and intensity. They are $v_A$ and $v_B$, the chemical shifts in Hz; $\tau_A$ and $\tau_B$, the lifetimes of the two species in seconds; $k$, a scaling factor; and $W$ the linewidth in Hz. Although all six parameters can be varied, it is desirable to hold the linewidth constant since the programme has difficulty distinguishing between some of the parameters, particularly between the linewidth and the lifetimes. Usually the linewidth was estimated from the linewidth of the low temperature spectrum where broadening due to exchange was minimal.

An accurate linewidth is necessary mainly when one is dealing with spectra having a slow exchange rate. It is desirable to check the linewidth at low temperature with a standard reference compound (e.g. methylene chloride) so as to minimize the error due to viscosity broadening.
At higher temperatures, and consequently faster exchange rates, variation in the linewidth has a very small effect on the other parameters.

When the value of $W$ has been determined, initial estimates must be made for the other parameters. The values for $v_A$ and $v_B$ can be estimated from the spectrum at low temperature, but the values for the lifetimes $\tau_A$ and $\tau_B$, as well as for the scaling factor $k$, must be based on previous experience. However initial estimates in error by approximately 100% did not have a significant effect upon the final values of the other parameters.

Once the initial values of the parameters have been determined, a theoretical spectrum based upon these parameters is calculated using the line shape equation provided in the NLIN GH subroutine. A point by point comparison of the experimental and calculated spectra, followed by the regression procedure, provides new values for those parameters not held constant. These new values become initial values and the procedure is repeated until the change in the parameters being calculated satisfies special convergence limits. At this time the final values of the parameters are printed and a graphic display of the experimental and calculated point is printed. Standard errors for the calculated parameters are also provided.

Among the parameters that could vary during the fitting procedure are the chemical shifts $v_A$ and $v_B$. 
Figures 7, 8, and 9 show the variation of the calculated values of the chemical shift difference as a function of temperature. At temperatures near coalescence there was some difficulty in calculating the parameters. Therefore in cases where scattering was observed the low temperature curve was extrapolated as indicated. This temperature dependence results, in part from small changes in the proton environments within the molecule. The aryl ring and the hydantoin ring may alter their average orientation with respect to each other. Probably the main cause of scatter in the chemical shift differences is due to the lack of sensitivity of the computer to these parameters in the fitting procedure when there is considerable exchange broadening.

The effect of the variation of the chemical shift with temperature on the precision of the fitting procedure has been shown to be quite pronounced at temperatures near and above the coalescent temperature by Huang$^6$ and Bentz.$^9$ If the variation of the chemical shift with temperature is not too great, an average or an extrapolated value for the chemical shift may be used in the fitting procedure. However, it is incorrect to assume that the values of the chemical shift differences obtained near or above coalescence have the same validity as those obtained at lower temperature.
Figure 7: Temperature Dependence of the Chemical Shift Difference of the ortho-methyl Protons in the 3-(2-methylphenyl)-5-phenylhydantoin (VIII).
Figure 8: Temperature Dependence of the Chemical Shift Difference of the ortho-methyl Protons in the 3-(2-methylphenyl)-5-methylhydantoin (VII).
Figure 9: Temperature Dependence of the Chemical Shift Difference of the ortho-methyl Protons in the 3-(4-chloro-2-methylphenyl)-5-phenylhydantoin (XIII).
Actpar

This programme calculates Arrhenius and Eyring activation parameters and 90% confidence intervals from input values of mean lifetimes, calculated by the NLIN programme, and temperature. It uses a linear regression method to fit the Arrhenius equation in logarithmic form to the input data, i.e. the equation is in the form:

\[ \ln(1/\tau) = \ln A - \frac{E_a}{RT} \]

the independent variable being \((1/\tau)\) and the dependent variable being \(\ln(1/\tau)\). Error analysis is given at each stage of the calculation, i.e. following the regression calculations, following the Eyring calculations, following the Arrhenius calculations.

The programme uses a previously prepared look-up table to find Student's \(T\) values for use in calculating 90% confidence intervals. Standard errors and 90% confidence limits in the Arrhenius and Eyring parameters are based on the regression errors in the slope and intercept of the regression line. Eyring parameters are calculated (with 90% confidence limits) at a temperature specified by the user.

The regression method and confidence interval calculations employed are based on P.D. Lark, B.R. Craven,

The computer print-out is designed so that the user can easily recognize any experimental point which poorly fits the regression line. Included in the print-out are the data required for the preparation of an Arrhenius plot.

Calculation:

The Arrhenius equation has the form,

\[ k = A \exp\left(\frac{-E_a}{RT}\right) \]

where:
- \( k \) = rate constant (1/sec.)
- \( A \) = frequency factor
- \( E_a \) = Arrhenius activation energy (cal.)
- \( R \) = gas constant (1.987 cal.deg.\(^{-1}\)mole\(^{-1}\))
- \( T \) = absolute temperature

The programme returns the value of \( A \) and \( E_a \).

The Eyring equations have the form,

\[ \Delta H^* = E_a - RT \]
\[ \Delta G^* = RT(ln(k_b/h) + lnT - lnk) \]
\[ \Delta S = (\Delta H^* - \Delta G^*)/T \]
where:

\( \Delta G^\ddagger = \) free energy of activation

\( \Delta S^\ddagger = \) entropy of activation

\( \Delta H^\ddagger = \) enthalpy of activation

\( k_b = \) Boltzmann's constant \((1.38 \times 10^{-16} \text{erg/deg.})\)

\( h = \) Planck's constant \((6.625 \times 10^{-27} \text{erg/deg.})\)

\( \Delta S^\ddagger \) may also be expressed in the form,

\[
\Delta S^\ddagger = R(\ln A - \ln(k_b/h) - \ln T - 1.0)
\]
DATA and RESULTS

The data and the results for the hydantoins are presented for each individual compound. The kinetic data are presented in a table followed by the Arrhenius plot for that compound. The standard errors for the lifetimes are obtained from the non-linear least squares programme. They are an indication of the sensitivity of the line shape fits to changes in the lifetime parameter. When chemical shifts have been held constant they are followed by the letter c. During the line shape calculation, the chemical shift was held constant when the computer returned obviously incorrect values if the chemical shift was allowed to vary. Sometimes the value of the chemical shift was extrapolated from values at lower temperatures.

The Arrhenius plots have been arranged for convenient display rather than for purposes of comparison.

The tables of thermodynamic data follow the Arrhenius plots. All the values are given for $25^\circ$, except for the activation energies which are temperature independent.

Confidence limits for the activation energies $E_a$ are also given; they are a measure of the quality of fit of the experimental points to the straight line calculated through a linear least squares programme.
Table I: Lifetimes, Rotational Rates, and Chemical Shift Differences for 3-o-tolyl-5-methylhydantoin (VII) in DMSO-d$_6$ Solution at Various Temperatures, Calculated with a Linewidth of 1.0 Hz.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec.$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tau A, Collapse of the ortho-methyl Signal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.5</td>
<td>0.719</td>
<td>0.023</td>
<td>1.380</td>
<td>3.5</td>
</tr>
<tr>
<td>59.0</td>
<td>0.475</td>
<td>0.030</td>
<td>2.105</td>
<td>3.5</td>
</tr>
<tr>
<td>63.5</td>
<td>0.474</td>
<td>0.025</td>
<td>2.109</td>
<td>3.5</td>
</tr>
<tr>
<td>68.0</td>
<td>0.324</td>
<td>0.031</td>
<td>3.086</td>
<td>3.5</td>
</tr>
<tr>
<td>72.5</td>
<td>0.207</td>
<td>0.004</td>
<td>4.870</td>
<td>3.5</td>
</tr>
<tr>
<td>80.0</td>
<td>0.141</td>
<td>0.012</td>
<td>7.092</td>
<td>3.5</td>
</tr>
<tr>
<td>85.5</td>
<td>0.149</td>
<td>0.012</td>
<td>6.710</td>
<td>3.5</td>
</tr>
<tr>
<td>Tau B, Collapse of the ortho-methyl Signal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.5</td>
<td>0.718</td>
<td>0.019</td>
<td>1.301</td>
<td>3.5</td>
</tr>
<tr>
<td>59.0</td>
<td>0.473</td>
<td>0.023</td>
<td>2.107</td>
<td>3.5</td>
</tr>
<tr>
<td>63.5</td>
<td>0.470</td>
<td>0.022</td>
<td>2.110</td>
<td>3.5</td>
</tr>
<tr>
<td>68.0</td>
<td>0.322</td>
<td>0.025</td>
<td>3.091</td>
<td>3.5</td>
</tr>
<tr>
<td>72.5</td>
<td>0.200</td>
<td>0.003</td>
<td>4.950</td>
<td>3.5</td>
</tr>
<tr>
<td>80.0</td>
<td>0.143</td>
<td>0.013</td>
<td>7.097</td>
<td>3.5</td>
</tr>
<tr>
<td>85.5</td>
<td>0.147</td>
<td>0.011</td>
<td>6.920</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table II: Lifetimes, Rotational Rates, and Chemical Shift Differences for 3-o-tolyl-5-phenylhydantoin(VIII) in DMSC-d$_6$ Solution at Various Temperatures, Calculated with a Linewidth of 1.0 Hz.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec.$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tau A, Collapse of the ortho-methyl Signal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>2.520</td>
<td>0.012</td>
<td>0.395</td>
<td>14.3</td>
</tr>
<tr>
<td>27.0</td>
<td>1.610</td>
<td>0.009</td>
<td>0.619</td>
<td>14.3</td>
</tr>
<tr>
<td>44.0</td>
<td>1.100</td>
<td>0.003</td>
<td>0.902</td>
<td>14.3</td>
</tr>
<tr>
<td>75.0</td>
<td>0.078</td>
<td>0.011</td>
<td>12.770</td>
<td>14.3</td>
</tr>
<tr>
<td>87.0</td>
<td>0.040</td>
<td>0.023</td>
<td>24.870</td>
<td>14.3</td>
</tr>
<tr>
<td>94.0</td>
<td>0.028</td>
<td>0.012</td>
<td>34.850</td>
<td>14.3</td>
</tr>
<tr>
<td>98.0</td>
<td>0.013</td>
<td>0.007</td>
<td>76.920</td>
<td>14.3</td>
</tr>
<tr>
<td>103.0</td>
<td>0.028</td>
<td>0.013</td>
<td>38.080</td>
<td>14.3</td>
</tr>
<tr>
<td>107.0</td>
<td>0.017</td>
<td>0.003</td>
<td>57.47</td>
<td>14.3</td>
</tr>
<tr>
<td>Tau B, Collapse of the ortho-methyl Signal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>1.520</td>
<td>0.013</td>
<td>0.657</td>
<td>14.3</td>
</tr>
<tr>
<td>27.0</td>
<td>1.060</td>
<td>0.010</td>
<td>0.940</td>
<td>14.3</td>
</tr>
<tr>
<td>44.0</td>
<td>0.780</td>
<td>0.029</td>
<td>1.280</td>
<td>14.3</td>
</tr>
<tr>
<td>75.0</td>
<td>0.160</td>
<td>0.012</td>
<td>9.400</td>
<td>14.3</td>
</tr>
<tr>
<td>87.0</td>
<td>0.060</td>
<td>0.025</td>
<td>16.666</td>
<td>14.3</td>
</tr>
<tr>
<td>94.0</td>
<td>0.041</td>
<td>0.010</td>
<td>24.390</td>
<td>14.3</td>
</tr>
<tr>
<td>98.0</td>
<td>0.015</td>
<td>0.008</td>
<td>66.666</td>
<td>14.3</td>
</tr>
<tr>
<td>103.0</td>
<td>0.053</td>
<td>0.002</td>
<td>18.650</td>
<td>14.3</td>
</tr>
<tr>
<td>107.0</td>
<td>0.028</td>
<td>0.003</td>
<td>35.460</td>
<td>14.3</td>
</tr>
</tbody>
</table>
Table III: Lifetimes, Rotational Rates, and Chemical Shift Differences for 3-(2,3-dimethylphenyl)-5-methylhydantoin (IX) in DMSO-d$_6$ Solution at Various Temperatures, Calculated with a Linewidth of 1.0 Hz.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec.$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.0</td>
<td>0.534</td>
<td>0.012</td>
<td>1.872</td>
<td>3.7</td>
</tr>
<tr>
<td>103.0</td>
<td>0.320</td>
<td>0.009</td>
<td>3.125</td>
<td>3.7</td>
</tr>
<tr>
<td>110.0</td>
<td>0.274</td>
<td>0.003</td>
<td>3.649</td>
<td>3.7</td>
</tr>
<tr>
<td>114.0</td>
<td>0.209</td>
<td>0.055</td>
<td>4.784</td>
<td>3.8</td>
</tr>
<tr>
<td>118.0</td>
<td>0.153</td>
<td>0.013</td>
<td>6.535</td>
<td>3.9</td>
</tr>
<tr>
<td>123.0</td>
<td>0.121</td>
<td>0.017</td>
<td>8.264</td>
<td>3.9</td>
</tr>
<tr>
<td>126.0</td>
<td>0.117</td>
<td>0.014</td>
<td>8.547</td>
<td>3.9</td>
</tr>
<tr>
<td>129.0</td>
<td>0.128</td>
<td>0.013</td>
<td>7.812</td>
<td>3.9</td>
</tr>
</tbody>
</table>

**Tau A, Collapse of the ortho-methyl Signal**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec.$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.0</td>
<td>0.450</td>
<td>0.033</td>
<td>2.220</td>
<td>3.7</td>
</tr>
<tr>
<td>103.0</td>
<td>0.277</td>
<td>0.022</td>
<td>3.610</td>
<td>3.7</td>
</tr>
<tr>
<td>110.0</td>
<td>0.238</td>
<td>0.011</td>
<td>4.200</td>
<td>3.7</td>
</tr>
<tr>
<td>114.0</td>
<td>0.186</td>
<td>0.003</td>
<td>5.370</td>
<td>3.8</td>
</tr>
<tr>
<td>118.0</td>
<td>0.136</td>
<td>0.011</td>
<td>7.240</td>
<td>3.9</td>
</tr>
<tr>
<td>123.0</td>
<td>0.109</td>
<td>0.013</td>
<td>9.170</td>
<td>3.9</td>
</tr>
<tr>
<td>126.0</td>
<td>0.103</td>
<td>0.004</td>
<td>9.680</td>
<td>3.9</td>
</tr>
<tr>
<td>129.0</td>
<td>0.102</td>
<td>0.013</td>
<td>9.800</td>
<td>3.9</td>
</tr>
</tbody>
</table>

**Tau B, Collapse of the ortho-methyl Signal**
Table IV: Lifetimes, Rotational Rates, and Chemical Shift Differences for 3-(2-methyl-4-nitrophenyl)-5-methylhydantoin (X) in DMSO-d₆ Solution at Various Temperatures, Calculated with a Linewidth of 1.0 Hz.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec⁻¹)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.5</td>
<td>0.331</td>
<td>0.012</td>
<td>3.020</td>
<td>3.9c</td>
</tr>
<tr>
<td>41.5</td>
<td>0.271</td>
<td>0.007</td>
<td>3.690</td>
<td>3.9</td>
</tr>
<tr>
<td>45.5</td>
<td>0.249</td>
<td>0.006</td>
<td>4.010</td>
<td>3.9</td>
</tr>
<tr>
<td>50.0</td>
<td>0.199</td>
<td>0.007</td>
<td>5.020</td>
<td>3.9</td>
</tr>
<tr>
<td>55.0</td>
<td>0.173</td>
<td>0.004</td>
<td>5.780</td>
<td>3.9</td>
</tr>
<tr>
<td>59.0</td>
<td>0.133</td>
<td>0.003</td>
<td>7.510</td>
<td>3.9</td>
</tr>
<tr>
<td>63.5</td>
<td>0.113</td>
<td>0.004</td>
<td>8.840</td>
<td>3.9</td>
</tr>
<tr>
<td>68.0</td>
<td>0.079</td>
<td>0.005</td>
<td>12.590</td>
<td>3.9</td>
</tr>
<tr>
<td>73.0</td>
<td>0.067</td>
<td>0.001</td>
<td>14.880</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Tau A, Collapse of the ortho-methyl Signal

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec⁻¹)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.5</td>
<td>0.294</td>
<td>0.014</td>
<td>3.400</td>
<td>3.9</td>
</tr>
<tr>
<td>41.5</td>
<td>0.228</td>
<td>0.008</td>
<td>4.380</td>
<td>3.9</td>
</tr>
<tr>
<td>45.5</td>
<td>0.201</td>
<td>0.007</td>
<td>4.970</td>
<td>3.9</td>
</tr>
<tr>
<td>50.0</td>
<td>0.177</td>
<td>0.008</td>
<td>5.640</td>
<td>3.9</td>
</tr>
<tr>
<td>55.0</td>
<td>0.134</td>
<td>0.005</td>
<td>7.460</td>
<td>3.9</td>
</tr>
<tr>
<td>59.0</td>
<td>0.110</td>
<td>0.004</td>
<td>9.090</td>
<td>3.9</td>
</tr>
<tr>
<td>63.5</td>
<td>0.083</td>
<td>0.006</td>
<td>11.970</td>
<td>3.9</td>
</tr>
<tr>
<td>68.0</td>
<td>0.065</td>
<td>0.006</td>
<td>15.220</td>
<td>3.9</td>
</tr>
<tr>
<td>73.0</td>
<td>0.051</td>
<td>0.001</td>
<td>19.490</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Tau B, Collapse of the meta-methyl Signal
Table V: Lifetimes, Rotational Rates, and Chemical Shift Differences for 3-(2-methyl-4-nitrophenyl)-5-methyl-2-thiohydantoin (XI) in DMSO-d$_6$ Solution at Various Temperatures, Calculated with a Linewidth of 1.0 Hz.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec.$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.0</td>
<td>0.430</td>
<td>0.002</td>
<td>2.322</td>
<td>5.2</td>
</tr>
<tr>
<td>75.0</td>
<td>0.398</td>
<td>0.003</td>
<td>2.512</td>
<td>5.3</td>
</tr>
<tr>
<td>84.0</td>
<td>0.353</td>
<td>0.021</td>
<td>2.830</td>
<td>5.5</td>
</tr>
<tr>
<td>93.0</td>
<td>0.130</td>
<td>0.013</td>
<td>7.640</td>
<td>5.4</td>
</tr>
<tr>
<td>103.0</td>
<td>0.116</td>
<td>0.011</td>
<td>8.550</td>
<td>5.7</td>
</tr>
<tr>
<td>110.0</td>
<td>0.114</td>
<td>0.019</td>
<td>8.740</td>
<td>5.3</td>
</tr>
<tr>
<td>117.0</td>
<td>0.051</td>
<td>0.003</td>
<td>19.560</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Tau A, Collapse of the ortho-methyl Signal

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec.$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.0</td>
<td>0.353</td>
<td>0.002</td>
<td>2.830</td>
<td>5.2</td>
</tr>
<tr>
<td>75.0</td>
<td>0.339</td>
<td>0.009</td>
<td>2.940</td>
<td>5.3</td>
</tr>
<tr>
<td>84.0</td>
<td>0.312</td>
<td>0.002</td>
<td>3.200</td>
<td>5.5</td>
</tr>
<tr>
<td>93.0</td>
<td>0.096</td>
<td>0.015</td>
<td>10.330</td>
<td>5.4</td>
</tr>
<tr>
<td>103.0</td>
<td>0.087</td>
<td>0.009</td>
<td>11.507</td>
<td>5.7</td>
</tr>
<tr>
<td>110.0</td>
<td>0.088</td>
<td>0.017</td>
<td>11.261</td>
<td>5.3</td>
</tr>
<tr>
<td>117.0</td>
<td>0.051</td>
<td>0.003</td>
<td>19.305</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Table VI: Lifetimes, Rotational Rates, and Chemical Shift Differences for 3-(4-chloro-2-methylphenyl)-5-methylhydantoin (XII) in DMSO-d₆ Solution at Various Temperatures, Calculated with a Line-width of 1.0 Hz.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec⁻¹)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.0</td>
<td>0.380</td>
<td>0.002</td>
<td>2.630</td>
<td>3.6</td>
</tr>
<tr>
<td>63.0</td>
<td>0.264</td>
<td>0.007</td>
<td>3.780</td>
<td>3.7</td>
</tr>
<tr>
<td>68.0</td>
<td>0.192</td>
<td>0.015</td>
<td>5.200</td>
<td>3.4</td>
</tr>
<tr>
<td>72.0</td>
<td>0.157</td>
<td>0.021</td>
<td>6.360</td>
<td>3.6</td>
</tr>
<tr>
<td>78.0</td>
<td>0.101</td>
<td>0.019</td>
<td>9.900</td>
<td>3.6</td>
</tr>
<tr>
<td>82.0</td>
<td>0.100</td>
<td>0.011</td>
<td>9.990</td>
<td>3.6</td>
</tr>
<tr>
<td>87.0</td>
<td>0.072</td>
<td>0.002</td>
<td>13.720</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Tau A, Collapse of the ortho-methyl Signal

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec⁻¹)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.0</td>
<td>0.302</td>
<td>0.002</td>
<td>3.310</td>
<td>3.6</td>
</tr>
<tr>
<td>63.0</td>
<td>0.239</td>
<td>0.006</td>
<td>4.180</td>
<td>3.7</td>
</tr>
<tr>
<td>68.0</td>
<td>0.189</td>
<td>0.023</td>
<td>5.200</td>
<td>3.4</td>
</tr>
<tr>
<td>72.0</td>
<td>0.138</td>
<td>0.019</td>
<td>7.240</td>
<td>3.6</td>
</tr>
<tr>
<td>78.0</td>
<td>0.100</td>
<td>0.017</td>
<td>9.910</td>
<td>3.6</td>
</tr>
<tr>
<td>82.0</td>
<td>0.079</td>
<td>0.009</td>
<td>12.56</td>
<td>3.6</td>
</tr>
<tr>
<td>87.0</td>
<td>0.056</td>
<td>0.002</td>
<td>17.62</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Tau B, Collapse of the ortho-methyl Signal
Table VII: Lifetimes, Rotational Rates, and Chemical Shift Differences for 3-(4-chloro-2-methylphenyl)-5-phenylhydantoin (XIII) in DMSO-d$_6$ Solution at Various Temperatures, Calculated with a Line-width of 1.2 Hz.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec.$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tau A, Collapse of the ortho-methyl Signal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.0</td>
<td>2.460</td>
<td>0.003</td>
<td>0.405</td>
<td>14.3</td>
</tr>
<tr>
<td>57.0</td>
<td>0.955</td>
<td>0.025</td>
<td>1.046</td>
<td>14.3</td>
</tr>
<tr>
<td>65.0</td>
<td>0.440</td>
<td>0.015</td>
<td>2.242</td>
<td>14.3</td>
</tr>
<tr>
<td>75.0</td>
<td>0.227</td>
<td>0.009</td>
<td>4.400</td>
<td>14.3</td>
</tr>
<tr>
<td>84.0</td>
<td>0.095</td>
<td>0.003</td>
<td>10.510</td>
<td>14.3</td>
</tr>
<tr>
<td>89.0</td>
<td>0.075</td>
<td>0.002</td>
<td>12.570</td>
<td>14.3</td>
</tr>
<tr>
<td>Tau B, Collapse of the ortho-methyl Signal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.0</td>
<td>1.710</td>
<td>0.003</td>
<td>0.583</td>
<td>14.3</td>
</tr>
<tr>
<td>57.0</td>
<td>0.723</td>
<td>0.023</td>
<td>1.380</td>
<td>14.3</td>
</tr>
<tr>
<td>65.0</td>
<td>0.342</td>
<td>0.017</td>
<td>2.920</td>
<td>14.3</td>
</tr>
<tr>
<td>75.0</td>
<td>0.173</td>
<td>0.009</td>
<td>5.750</td>
<td>14.3</td>
</tr>
<tr>
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<td>0.072</td>
<td>0.003</td>
<td>13.860</td>
<td>14.3</td>
</tr>
<tr>
<td>89.0</td>
<td>0.053</td>
<td>0.002</td>
<td>15.840</td>
<td>14.3</td>
</tr>
</tbody>
</table>
Table VIII: Lifetimes, Rotational Rates, and Chemical Shift Difference for 3-(2-chlorophenyl)-5-phenylhydantoin (XIV) in DMSO-d$_6$ Solution at Various Temperatures, Calculated with a Linewidth of 1.6 Hz.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.0</td>
<td>3.780</td>
<td>0.002</td>
<td>0.264</td>
<td>7.5c</td>
</tr>
<tr>
<td>75.0</td>
<td>1.920</td>
<td>0.015</td>
<td>0.520</td>
<td>7.5</td>
</tr>
<tr>
<td>119.0</td>
<td>0.237</td>
<td>0.013</td>
<td>4.219</td>
<td>7.5</td>
</tr>
<tr>
<td>128.0</td>
<td>0.160</td>
<td>0.027</td>
<td>6.230</td>
<td>7.5</td>
</tr>
<tr>
<td>134.0</td>
<td>0.113</td>
<td>0.003</td>
<td>8.840</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Tau A, Collapse of the C-5 Proton Signal

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lifetime (sec.)</th>
<th>Standard Error</th>
<th>Rate Constant (sec$^{-1}$)</th>
<th>Chemical Shift Difference (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.0</td>
<td>4.030</td>
<td>0.002</td>
<td>0.248</td>
<td>7.5</td>
</tr>
<tr>
<td>75.0</td>
<td>2.210</td>
<td>0.013</td>
<td>0.452</td>
<td>7.5</td>
</tr>
<tr>
<td>119.0</td>
<td>0.228</td>
<td>0.011</td>
<td>4.380</td>
<td>7.5</td>
</tr>
<tr>
<td>128.0</td>
<td>0.144</td>
<td>0.028</td>
<td>6.940</td>
<td>7.5</td>
</tr>
<tr>
<td>134.0</td>
<td>0.097</td>
<td>0.001</td>
<td>10.230</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Tau B, Collapse of the C-5 Proton Signal
Figure 10: Arrhenius Plots for 3-(2-methylphenyl)-5-methylhydantoin (VII) in DMSO-d₆ Solution. 
Tau A = 0, Tau B = x.
Figure 11: Arrhenius Plots for 3-(2-methylphenyl)-5-phenylhydantoin (VIII) in DMSO-d₆ Solution.
Tau A = 0, Tau B = x.
Figure 12: Arrhenius Plots for 3-(2,3-dimethylphenyl)-5-methylhydantoin (IX) in DMSO-d₆ Solution. Tau A = 0, Tau B = x.
Figure 13: Arrhenius Plots for 3-(2-methyl-4-nitrophenyl)-5-methylhydantoin (X) in DMSO-d₆ Solution.
Tau A = 0, Tau B = x.
Figure 14: Arrhenius Plots for 3-(2-methyl-4-nitrophenyl)-5-methyl-2-thiohydantoin (XI) in DMSO-d6 Solution. Tau A = 0, Tau B = x.
Figure 15: Arrhenius Plots for 3-(4-chloro-2-methylphenyl)-5-methylhydantoin (XII) in DMSO-d$_6$ Solution. Tau A = 0, Tau = x.
Figure 16: Arrhenius Plots for \(3-(4\text{-chloro-2-methylphenyl})-5\text{-phenylhydantoin (XIII)}\) in DMSO-\(d_6\) Solution. Tau A = 0, Tau B = x.
Figure 17: Arrhenius Plots for 3-(2-chlorophenyl)-5-phenylhydantoin (XIV) in DMSO-d$_6$ Solution.
Tau A = 0, Tau B = x.
Table IX: Kinetic and Thermodynamic Parameters for Rotation Around the C-N Aryl Bond for Some 3-Aryl Substituted Hydantoins in DMSO-d$_6$ Solution.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$ (kcal/mole)</th>
<th>$\Delta H^\ddagger(25^\circ)$ (kcal/mole)</th>
<th>$\Delta G^\ddagger(25^\circ)$ (kcal/mole)</th>
<th>$\Delta S^\ddagger(25^\circ)$ (e.u.)</th>
<th>$K$ (25$^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIII</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_A$</td>
<td>12.5 ± 0.7</td>
<td>12.4 ± 0.7</td>
<td>18.0 ± 0.1</td>
<td>- 22.0 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>$\tau_B$</td>
<td>11.9 ± 0.7</td>
<td>11.7 ± 0.7</td>
<td>17.8 ± 0.1</td>
<td>- 22.9 ± 2.0</td>
<td>0.61</td>
</tr>
<tr>
<td>XIII</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_A$</td>
<td>13.0 ± 0.8</td>
<td>12.4 ± 0.8</td>
<td>18.4 ± 0.1</td>
<td>- 20.0 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>$\tau_B$</td>
<td>12.6 ± 0.5</td>
<td>12.4 ± 0.5</td>
<td>18.2 ± 0.1</td>
<td>- 21.0 ± 2.0</td>
<td>0.70</td>
</tr>
</tbody>
</table>
Table X: Kinetic and Thermodynamic Parameters for Rotation Around the C-N Aryl Bond for Some 3-Aryl substituted Hydantoins in DMSO-$d_6$ Solution.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$ (kcal/mole)</th>
<th>$\Delta H^\ddagger$ (25°) (kcal/mole)</th>
<th>$\Delta G^\ddagger$ (25°) (kcal/mole)</th>
<th>$\Delta S^\ddagger$ (25°) (e.u.)</th>
<th>$K$ (25°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$</td>
<td>8.5 ± 0.8</td>
<td>7.0 ± 0.7</td>
<td>17.1 ± 0.1</td>
<td>- 31.8 ± 2.0</td>
<td>0.90</td>
</tr>
<tr>
<td>$\tau_A$</td>
<td>9.1 ± 0.7</td>
<td>8.5 ± 0.8</td>
<td>17.0 ± 0.1</td>
<td>- 28.3 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>$\tau_B$</td>
<td>10.5 ± 0.8</td>
<td>9.9 ± 0.7</td>
<td>18.3 ± 0.1</td>
<td>- 28.1 ± 2.1</td>
<td></td>
</tr>
<tr>
<td>$XI$</td>
<td>10.4 ± 0.7</td>
<td>9.7 ± 0.9</td>
<td>18.2 ± 0.1</td>
<td>- 28.0 ± 2.2</td>
<td></td>
</tr>
</tbody>
</table>
Table XI: Kinetic and Thermodynamic Parameters for Rotation Around the C-N Aryl Bond for Some 3-Aryl Substituted Hydantoins in DMSO-d$_6$ Solution.

![Chemical Structure](image)

VII, $R = H$

XII, $R = Cl$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$ (kcal/mole)</th>
<th>$\Delta H^\circ$ (25°) (kcal/mole)</th>
<th>$\Delta G^\circ$ (25°) (kcal/mole)</th>
<th>$\Delta S^\circ$ (25°) (e.u.)</th>
<th>$K$ (25°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII $\tau_A$</td>
<td>11.7 ± 0.9</td>
<td>11.1 ± 0.9</td>
<td>18.0 ± 0.1</td>
<td>- 24.7 ± 2.0</td>
<td>1.00</td>
</tr>
<tr>
<td>VII $\tau_B$</td>
<td>11.7 ± 0.9</td>
<td>11.1 ± 0.9</td>
<td>18.0 ± 0.1</td>
<td>- 23.0 ± 2.0</td>
<td>1.00</td>
</tr>
<tr>
<td>XII $\tau_A$</td>
<td>13.7 ± 0.8</td>
<td>13.1 ± 0.7</td>
<td>18.2 ± 0.1</td>
<td>- 17.1 ± 2.0</td>
<td>1.00</td>
</tr>
<tr>
<td>XII $\tau_B$</td>
<td>14.2 ± 0.4</td>
<td>13.6 ± 0.4</td>
<td>18.2 ± 0.1</td>
<td>- 15.3 ± 2.0</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table XII: Kinetic and Thermodynamic Parameters for Rotation Around the C-N Aryl Bond for Some 3-Aryl Substituted Hydantoins in DMSO-d$_6$ Solution.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$ (kcal/mole)</th>
<th>$\Delta H^\ddagger(25^\circ)$ (kcal/mole)</th>
<th>$\Delta G^\ddagger(25^\circ)$ (kcal/mole)</th>
<th>$\Delta S^\ddagger(25^\circ)$ (e.u.)</th>
<th>$K$ (25°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIV $\tau_A$</td>
<td>13.4 ± 0.5</td>
<td>12.8 ± 0.5</td>
<td>19.8 ± 0.1</td>
<td>-23.3 ± 2.0</td>
<td>1.35</td>
</tr>
<tr>
<td>$\tau_B$</td>
<td>14.3 ± 0.7</td>
<td>13.7 ± 0.7</td>
<td>19.9 ± 0.1</td>
<td>-21.2 ± 2.0</td>
<td></td>
</tr>
<tr>
<td>IX $\tau_A$</td>
<td>11.7 ± 0.8</td>
<td>11.1 ± 0.8</td>
<td>19.2 ± 0.1</td>
<td>-27.4 ± 2.0</td>
<td>0.85</td>
</tr>
<tr>
<td>$\tau_B$</td>
<td>11.6 ± 0.8</td>
<td>11.1 ± 0.8</td>
<td>19.1 ± 0.1</td>
<td>-27.1 ± 2.0</td>
<td></td>
</tr>
</tbody>
</table>
DISCUSSION

Stereochemistry of the Hetero Ring

The decision to study 3-aryl substituted hydantoins was made in the hope that this would be a simpler system to interpret than other N-aryl substituted amide systems, because of the fact that hydantoins are assumed to be planar or near planar molecules. Therefore, problems associated with the heterocyclic ring inversion are expected to be absent. Further, being cyclic amides, hydantoins have a system which is easier to interpret than acyclic compounds because of the prearrangement of the substituents that the aryl ring must pass during rotation.

Indirect spectroscopic evidence of the planarity of the hydantoin is discussed in a paper by van der Helm et al. Through x-ray spectroscopy this group found rhodanine, a molecule very similar to the hydantoin molecule, to be planar. A more recent x-ray crystallographic study of 2-thiohydantoin has shown that this molecule is also planar. In addition substituents on the aryl
ring must pass a carbonyl or thionyl group during rotation, and the difference between the transition states and the ground states depend upon the primary effects due to the nature or size of these groups.

Secondary effects on the barrier of rotation could arise because of different groups in the 1 and 5 positions. Since in all cases the 1 position was unsubstituted, the effect of a substituent on this position can be ignored in this study. It was expected that the substituents on the 5 position would cause little buttressing effect since they are not coplanar with the C-4 carbonyl group. Further the carbonyl group, having a partial double bond, would be resistant to bending by the C-5 substituents. It is possible that while the C-5 substituents do not evidently affect the transition state they can affect the ground states of the interconvertible rotamers. Fehlner found indeed that the equilibrium constants of some hydantoins do differ, although slightly, from unity, as can be seen in Table XIII.

The degree of planarity of the hydantoin molecule is enhanced by two factors. Since the ring is five membered it will be much flatter than a six membered ring, and the partial double bond character of the C-N bond caused by the amide resonance would help to constrain the ring.

It can be seen that eight electrons, four from the
Table XIII: Kinetic and Thermodynamic Parameters for Rotation Around the C-N Aryl Bond for some 3-Aryl Substituted Hydantoins in DMSO-d₆ Solution.\(^7\)

![Chemical Structure](image)

XXX, \(R_1 = CF_3\), \(R_2 = H\)
XXXI, \(R_1 = CH_3\), \(R_2 = CH_3\)
XXXII, \(R_1 = Cl\), \(R_2 = H\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_a) (kcal/mole)</th>
<th>(\Delta H^* (25^\circ)) (kcal/mole)</th>
<th>(\Delta G^* (25^\circ)) (kcal/mole)</th>
<th>(\Delta S^* (25^\circ)) (c.u.)</th>
<th>(K (25^\circ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXX (\tau_A)</td>
<td>16.4 ± 0.9†</td>
<td>15.8</td>
<td>20.80</td>
<td>-16.7</td>
<td>1.01</td>
</tr>
<tr>
<td>(\tau_B)</td>
<td>16.9 ± 0.9†</td>
<td>16.3</td>
<td>20.80</td>
<td>-15.0</td>
<td></td>
</tr>
<tr>
<td>XXXI</td>
<td>14.7 ± 0.7†</td>
<td>14.1</td>
<td>16.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XXXII (\tau_A)</td>
<td>15.0 ± 0.6†</td>
<td>14.4</td>
<td>19.33</td>
<td>-17.5</td>
<td>1.18</td>
</tr>
<tr>
<td>(\tau_B)</td>
<td>19.23</td>
<td>-16.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

§ 2-Chloropyrydine Solution
† Standard Deviation
two nitrogens, four from the two carbonyl groups, contribute to the different resonance forms of the hetero ring.

![Resonance forms of a hetero ring](image)

It is probable that the canonical forms II, III, and IV make a significant contribution to the electronic structure of hydantoins. This assumption is supported by the work of Corey, who found that the resonance form shown below is a major contributor to the structure of 2,5-diketopiperazine, a molecule very similar to hydantoin.

![Structure of 2,5-diketopiperazine](image)
Relative Influence of Carbonyl and Thiocarbonyl Groups

A comparison of the kinetic data for the compounds X and XI, shows that the $\Delta G^+$ value for the thiohydantoin

\[
\begin{array}{c}
\text{O}_2 \text{N} \\
\text{CH}_3
\end{array}
\]

\[X, X = O\]

\[\text{XI}, X = S\]

is larger than the corresponding parameter for the hydantoin, (18.3 ± 0.13 kcal/mole versus 17.1 ± 0.12 kcal/mole). This enhancement of the $\Delta G^+$ value when the oxygen atom in the 2 position is substituted by a sulphur atom, had already been observed by Fehlner\(^7\) for 3-α-naphthyl-5-methylhydantoin.

\[
\begin{array}{c}
\text{CH}_3
\end{array}
\]

3-α-naphthyl-5-methylhydantoin $X = O$

3-α-naphthyl-5-methyl-2-thiohydantoin $X = S$

He found that while the $\Delta G^*$ value for the thiohydantoin was 25.5 ± 0.1 kcal/mole, it was only 18.3 ± 0.1 kcal/mole for the corresponding hydantoin. This effect can be explained as follows.
Because of its greater size, sulphur tends to be less electronegative (2.5) than oxygen (3.5).\textsuperscript{23} Therefore one might expect a decrease of the dipole moment in compounds where the oxygen of the carbonyl group is substituted by sulphur. However, this is not the case. Mautner et al.\textsuperscript{24,25,26} have shown that the dipole moment of the thiocarboxyl group is always greater than the corresponding carbonyl analogue. They attribute this to a greater contribution of the ionic form \( \overset{+}{C} = S \) in the thiocarboxyl group than the \( \overset{+}{C} = O \) form in the carbonyl group. This is confirmed by infrared data.\textsuperscript{27,28}

The greater single bond character in the thiocarboxyl group is reflected in the bond length of this group. While the carbonyl length is only about 77\% of the length of the single C-O bond, the thiocarboxyl bond length is about 88\% of the analogous C-S bond.\textsuperscript{29} It has been suggested that the greater contribution of the ionic form in the thiocarboxyl group can be due to the ability of the 3d orbitals of sulphur to accept electrons and stabilize the C-S state.\textsuperscript{30} As a consequence of the greater length of the C-S bond, a stronger steric interaction occurs between the sulphur atom and the groups in the ortho positions in the transition state during the rotational process, which causes a larger barrier of rotation than in the corresponding carbonyl compound. It has been suggested,\textsuperscript{31} that in the 3-aryl-2-thiohydantoins the more
bulky ortho substituent must pass the carbonyl oxygen atom in the transition state for rotation rather than the more bulky sulphur atom, i.e. the preferred transition state is 2 rather than 1.

This hypothesis, although quite plausible does not appear to be adequate to explain the large difference in the effect on the rotational barrier when sulphur is substituted in the 2 position, e.g. about 7 kcal/mole in the case of 3-α-naphthyl-5-methylhydantoin and about 1.3 kcal/mole in the case of compound X.

From a consideration of the data accumulated so far, it is evident that more information is needed in order that the nature of the rotational barrier in thiohydantoins can be understood.

Relative Influence of the Chlorine Atom and the Methyl Group

It has been commonly observed,32,33 that a methyl group exerts a steric effect greater than that of a chlorine atom, for example in restricting internal rotation
in hindered biphenyls.\textsuperscript{32} This order is consistent with the size of these groups as determined by x-ray crystallographic measurements of van der Waals radii.\textsuperscript{34}

Nevertheless, the $\Delta G^\ddagger$ of rotation around the C-N bond was found in the case of 3-(2-chlorophenyl)-5-phenylhydantoin (XIV) to be $19.8 \pm 0.1$ kcal/mole compared to only $18.0 \pm 0.1$ kcal/mole for 3-(2-methylphenyl)-5-phenylhydantoin (VIII), or about 2 kcal/mole greater. Therefore, if the chlorine atom is less bulky than the methyl group,

the difference in the value of $\Delta G^\ddagger$ must be due to electronic effects.

For the investigation of the electronic effects on the barrier of rotation of hydantoins, the following compounds were prepared in an attempt to distinguish between field effects and resonance effects:

\begin{align*}
\text{VII, } R &= \text{ H} \\
\text{X, } R &= \text{ NO}_2 \\
\text{XII, } R &= \text{ Cl}^2
\end{align*}
Their free energies of activation for rotation are:

VII, \hspace{1cm} 18.0 \pm 0.1 \text{ kcal/mole}
X, \hspace{1cm} 17.1 \pm 0.1 \text{ kcal/mole}
XII, \hspace{1cm} 18.2 \pm 0.1 \text{ kcal/mole}

Since both the nitro group and the chlorine atom are electron withdrawing, one might expect them to influence the barrier of rotation in the same way. However, this is not the case. While the nitro group lowers the barrier of rotation by about 1 kcal/mole, the chlorine atom either does not affect it, or affects it only slightly, 0.2 kcal/mole.

To explain this, one must consider the fact that while the nitro group and the chlorine atom have the same field effect, their resonance behaviour is completely different. Under the term field effects one includes the different effects due to a polar substituent:

a) The influence through space by the electric dipole field created by a polar substituent.

b) The polarization of a \( \pi \) system by an electrostatic charge due to the polar substituent, or inductoelectronic effect.\(^{35}\)

c) The inductive effect transmitted through the \( \sigma \) bonds.

Under the name of resonance effects one considers:

a) The mesomeric effect.

b) Mutual conjugation between the substituent and the reaction center through an intervening conjugated system.
Further, one must consider the fact that while the field effects due to a substituent in the para position on the aryl ring can operate in both the transition state and ground state, the resonance effects due to the same substituent can operate only in the transition state, since only in this state are the phenyl ring and the hydantoin ring coplanar and their mutual conjugation is possible. However, this resonance must not be confused with the amide resonance of the hydantoin ring. Since the hydantoin ring is planar, the amide resonance is present both in the ground and in the transition state for rotation.

If one considers the transition state of the para nitro compound, one can see that because of the presence of the nitro group the following resonance hybrids are possible.
This makes the lone pair of electrons of the nitrogen atom in the 3 position less free to participate in the amide resonance with the carbonyl in the 2 position, thereby favoring a larger contribution of the resonance form $\alpha$ at the expense of $\beta$.

\[ \begin{align*}
\alpha \quad & \quad \beta
\end{align*} \]

It follows that the carbonyl groups in the 2 and 4 position will have more double bond character and the C=O bond will be shorter than in the unsubstituted compound. Being shorter, the carbonyls will interact less with the methyl group in the ortho position and consequently the energy of the transition state will be lowered. Further, the aryl C-N bond will be shorter.

However, the chlorine atom produces a resonance condition that makes the carbon atom attached to the nitrogen in the 3 position more negative, which could probably disfavor the conjugation of electrons with the phenyl ring, making them freer to participate in the amide resonance.
As evidence of this one can see that while the cyclization of the hydantoic acid, which involves the participation of the electron pair on the nitrogen in the 3 position, is possible and facile when the substituent on the para position is a chlorine atom, it becomes very difficult or impossible when the substituent is a nitro group.
Thus it follows that when the substituent is a chlorine atom the resonance form $\beta$ will be enhanced, with consequent lengthening of the carbonyl bonds and raising of the energy of the transition state relative to the nitro substituted compound.

When only field effects are involved, the nitro group and the chlorine atom exhibit similar behaviour since they are both electron withdrawing groups. When they are in the para position, they tend to make the aryl carbon atom attached to the nitrogen in the 3 position more positive, which alters the $\pi$ system of the amide resonance in the hydantoin ring by an inductoelectronic effect. The electrons of the nitrogen in the 3 position are now less free and tend to be more attracted to this atom. Consequently the carbonyl bond in the 2 position will be shorter and the energy of the transition state lowered, since the interaction of the carbonyl and the substituent on the aryl ring will be less than in the case of an unsubstituted compound.

In contrast to the resonance effects, the inductoelectronic effect can alter the ground state as well. Since it interferes with the amide resonance of the hydantoin ring, one can suggest that it raises the energy of the ground state slightly, although this has still to be proved.
It is interesting to note that Spaargaren and coworkers investigated the electronic effects on the barrier of rotation of the amide C-N bond in several N,N-dimethylbenzamides and obtained similar results.\textsuperscript{36} They prepared among others, the following compounds:

\begin{center}
\[\text{XV, } R = \text{H}\]
\[\text{XVI, } R = \text{NO}_2\]
\[\text{XVII, } R = \text{Br}_2\]
\[\text{XVIII, } R = \text{F}\]
\end{center}

The resonance effects of a nitro group and of a halogen atom on the rotational barrier in the N,N-dimethylbenzamides should be similar but opposite to the resonance effects in the case of the corresponding hydantoins. This is due to the fact that while in the hydantoins the barrier of rotation is increased by a group which lengthens the C=O bond in the 2 position, in the N,N-dimethylbenzamides the barrier of rotation is increased by each group which increases the double bond character of the C-N bond.

If one considers a N,N-dimethylbenzamide with a halogen atom in the \textit{para} position, it can be seen that due to this atom the following resonance is possible:
This resonance causes the C-N bond to have less double bond character and consequently raises the energy of the ground state, thereby lowering the barrier of rotation. In the case of the nitro substituent the opposite is true. In this case the resonance condition is more likely to be the following:
The nitro group enhances the double bond character of the C-N bond, lowering the energy of the ground state and consequently raising the barrier of rotation.

The experimental results by Spaargaren et al.\textsuperscript{36}, obtained by total line shape analysis, confirm this hypothesis as shown below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Free Energy of Activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>XV</td>
<td>15.67 kcal/mole</td>
</tr>
<tr>
<td>XVI</td>
<td>16.35 kcal/mole</td>
</tr>
<tr>
<td>XVII</td>
<td>15.58 kcal/mole</td>
</tr>
<tr>
<td>XVIII</td>
<td>15.54 kcal/mole</td>
</tr>
</tbody>
</table>

Field and Resonance Contribution to the Barrier of Rotation of 3-Aryl Substituted Hydantoins.

After determining the \( \Delta G^\dagger \) values of different hydantoins an attempt was made to determine what percentage of the variation in \( \Delta G^\dagger \) was due to field effects and what percentage was due to the resonance effects, since only these two phenomena must be taken into account when considering the influence of a substituent removed by at least three carbon atoms from the center of reaction.\textsuperscript{37}

According to Swain and Lupton,\textsuperscript{38} the effect of a substituent is given by a constant \( \sigma \), which is a combination of the constants \( F \), due to the field, and \( R \), due to the
resonance:

\[ \sigma = r^F + r^R \]

where F and R are different for each substituent, (Cl, H, NO₂), and \( r^f \) and \( r^r \) are empirical sensitivities or weighting factors independent of substituents but different for each system. It follows that the free energy of rotation \( \Delta G^\ddagger \) can be obtained simply by:

\[ \Delta G^\ddagger = -2.303RT(r^R + f^F) + \Delta G^\circ \]

If the temperature is considered a constant equal to 298°, one can rewrite the above equation as:

\[ \Delta G^\ddagger = r^R + f^F + \Delta G^\circ \]

This equation was used in this work for determining the constant \( r \) and \( f \) for this type of rotation. Unfortunately the series of hydantoins studied so far was too small to give reliable results. The only conclusion possible was that while the chorine atom in the ortho position exerts a greater interaction with the carbonyl in the 2 position than a methyl group, the chlorine atom in the para position tends to have little or no effect on the barrier of rotation because the resonance effects and the field effects cancel each other since F and R for the chlorine atom have opposite sign.
Buttressing Effect

The effective size of the ortho substituent on the aryl ring may be increased by preventing it from bending backwards in the transition state by putting another substituent in the meta position. The existence of this effect, known as the buttressing effect, has been previously confirmed particularly in the work of Adams.\textsuperscript{39} Fehlner,\textsuperscript{7} in his work on some cyclic amides of the type shown below, found that while compound XIX has a $\Delta G^\ddagger$ of rotation of 16.3 kcal/mole and a $\Delta S^\ddagger$ of -31.4 ± 2 e.u.,

![Chemical Structure](image)

compound XX has a $\Delta G^\ddagger$ and a $\Delta S^\ddagger$ values of 18.4 kcal/mole and -21.5 ± 2 e.u. respectively. Fehlner suggested that the less negative value of $\Delta S^\ddagger$ in compound XX is probably caused by a decrease in the rocking motion of the aryl ring in the ground state.

To check if the buttressing effect would have any influence on the barrier of rotation of the 3-aryl substituted hydantoins, compound IX was prepared. The $\Delta G^\ddagger$
and $\Delta S^*$ of this compound were found to be 19.1 kcal/mole and $-27 \pm 2$ e.u. respectively, versus a $\Delta S^*$ of 18.0 kcal/mole and a $\Delta S^*$ of $-24 \pm 2$ e.u. for compound VII, the corresponding compound without any meta substituent on the aryl ring.

![Chemical Structure](image)

While the $\Delta G^*$ of compound IX is greater than that of compound VII, as expected, the $\Delta S^*$ of compound IX is more negative in contrast to Fehlner's results with compounds XX and XIX. As an explanation the following hypothesis is given.

In the case of Fehlner's compound XX, the less negative value of $\Delta S^*$ is probably caused by a decrease in the activation volume in the transition state. In the transition state of compound XIX the ortho methyl group is bent backwards, while in the transition state of compound XX the ortho methyl cannot bend backwards, but probably bends out of the normal plane because of the presence of the chlorine atom in the meta position. Hence the entropy of the transition state of compound XX is increased relative to that of compound XIX. In the ground state the meta-chloro group has little effect,
as one can see from the equilibrium constants (k = 1.18
for XIX, k = 1.16 for XX), which indicate that the methyl
group is not bent out of its normal position in compound XX.
Therefore the entropy of activation in compound XX is
less negative than in compound XIX. This is not true in
the case of compound IX. In this compound the meta methyl
group, which is bulkier than a chlorine atom, probably
interacts with the ortho methyl group in the ground state
as well as in the transition state. This interaction is
reflected in the equilibrium constants of compounds VII
and IX (K = 0.85 for IX, k = 1.0 for VII). Because of
this interaction the ortho methyl group in compound IX
is probably bent out of its normal plane and the entropy
of both the ground and transition state is raised, with
the result that ΔS° in compound IX is not less negative
than in compound VII. Indeed, since the limits of experimental
accuracy are ± 2 e.u. in the ΔS° measurements, it could
be concluded from the results that ΔS° of compound IX is
equal to that of compound VII.

Finally, the meta-substituent could induce some change
in the ΔC° of rotation through electronic effects. However,
this is not the case when a methyl group is involved,
since it is in the meta position, the electronic effect
should be minimal. The field factor F for such a group is
small, 0.0052, while the resonance factor R is 0.141, and the
constants f and r cannot be greater than unity for
similar systems.
Effect of the Substituent in the 5 Position

The following compounds were prepared to see if a different substituent in the 5 position could influence the barrier of rotation.

\[
\text{VII, } R = \text{CH}_3 \\
\text{VIII, } R = \text{C}_6\text{H}_5
\]

\[
\text{XII, } R = \text{CH}_3 \\
\text{XIII, } R = \text{C}_6\text{H}_5
\]

Their free energies and equilibrium constants are shown below.

Table XV: Free Energies of Rotation and Equilibrium Constants of Some Hydantoins.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^\dagger$ kcal/mole</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tau A, Tau B</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>18.0 18.1</td>
<td>1.00</td>
</tr>
<tr>
<td>VIII</td>
<td>18.0 17.8</td>
<td>0.61</td>
</tr>
<tr>
<td>XII</td>
<td>18.2 18.2</td>
<td>1.00</td>
</tr>
<tr>
<td>XIII</td>
<td>18.4 18.2</td>
<td>0.70</td>
</tr>
</tbody>
</table>
As one can see from Table XV the substitution of the methyl group in the 5 position with the more bulky phenyl ring does not change the free energy of activation. Indeed, all the values of the free energies of activation are identical within experimental error. This seems to exclude any steric effect of the substituent in the 5 position in the transition state. However, since the equilibrium constants diminish with the substitution of a phenyl ring with a methyl group in the 5 position, one must consider the possibility of some interaction between the two phenyl rings in the ground state. This interaction could be electronic and/or steric.

Since the phenyl ring in the 5 position is not coplanar with the hydantoin ring, one can exclude any mesomeric interaction between these two moieties. It is possible to rationalize the effect of the phenyl ring in the 5 position on the ground state by looking at the Dreiding models of compounds VIII and XIII. Since the aryl ring attached to the nitrogen in the 3 position rotates, the ortho methyl group will sometimes be cisoid and sometimes transoid with respect to the aryl ring in the 5 position, as shown in the next page.
When the 5-phenyl and the methyl groups are transoid they do not interfere with each other. However, this is not true when the two groups are cisoid to each other. In such a case the ortho methyl group interferes with the phenyl ring in the 5 position. Consequently the transoid isomer has a longer lifetime than the cisoid isomer, and the equilibrium constants for the compounds VIII and XIII are less than unity. This interference between the C-5 phenyl and the ortho methyl group is probably a steric one, since the methyl moiety has a small field factor ($F = -0.052$). However, more data are needed to confirm the hypothesis given above.
Entropy of Activation

Large negative entropies of activation in the rotational process of hydantoins were previously reported in the work of Fehlner.\textsuperscript{7} Although the entropy values are not as trustworthy as the values for the free energies,\textsuperscript{1} they have been confirmed by other methods.\textsuperscript{7,40} In this work the entropy values can be considered accurate to within a range of ± 2 e.u. An explanation for the entropies being negative can be deduced from the fact that, while the aryl ring has a rocking motion in the ground state, this rocking motion must be absent or restricted in the transition state. In addition to this, since the molecular volume in the transition state must be less than in the ground state, the entropy of activation must be negative.

![Ground state and transition state diagram](image)

Furthermore, on considering Table XVI, it is interesting to note that while the nitro-substituted hydantoin has a larger negative entropy of activation than the unsubstituted compound, the chlorine-substituted hydantoin possesses
slightly less negative entropies of activation than the unsubstituted compound. Evidently both the nitro group and the chlorine atom must affect the rocking motion of the aryl ring attached to the nitrogen in the 3 position.
Table XVI: Free Energies and Entropies of Activation of Some Hydantoins.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^\ddagger$ (kcal/mole)</th>
<th>$\Delta S^\ddagger$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_A$ 18.0 ± 0.1</td>
<td>- 23.7 ± 2</td>
</tr>
<tr>
<td>VII</td>
<td>$\tau_B$ 18.0 ± 0.1</td>
<td>- 23.0 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\tau_A$ 18.2 ± 0.1</td>
<td>- 17.1 ± 2</td>
</tr>
<tr>
<td>XII</td>
<td>$\tau_B$ 18.2 ± 0.1</td>
<td>- 15.3 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\tau_A$ 18.0 ± 0.1</td>
<td>- 22.0 ± 2</td>
</tr>
<tr>
<td>VIII</td>
<td>$\tau_B$ 17.8 ± 0.1</td>
<td>- 22.9 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\tau_A$ 18.4 ± 0.1</td>
<td>- 20.0 ± 2</td>
</tr>
<tr>
<td>XIII</td>
<td>$\tau_B$ 18.2 ± 0.1</td>
<td>- 21.0 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\tau_A$ 17.1 ± 0.1</td>
<td>- 30.6 ± 2</td>
</tr>
<tr>
<td>X</td>
<td>$\tau_B$ 17.0 ± 0.1</td>
<td>- 28.3 ± 2</td>
</tr>
</tbody>
</table>
Since the nitro group and the chlorine atom can interfere with the rocking motion of the aryl ring by means of their field and/or resonance phenomena, it is better to separate these two effects and determine how each influences the ground and/or the transition state of rotation of hydantoins.

Because both the chlorine atom and the nitro group have the same field effects, and since the field effects act in both the ground and the transition state in the same direction one can ignore their influence on the entropies of activation.

In contrast to the field effects however, the resonance effects can be taken into account only in the transition state. If one considers the resonance due to the nitro group, which is shown below, it is evident that this resonance tends to create a partial double bond between the nitrogen in the 3 position and the carbon attached to this atom. Because of this double bond, the rocking motion of the aryl ring in the transition
state is hindered to a larger extent than in the unsubstituted compound. It follows that the entropy of activation of the nitro-substituted compound in the transition state is less than the entropy of the unsubstituted one. In the case of the chlorine atom the opposite is true. Conjugation between the electrons on the nitrogen in the 3 position and the aryl ring is not favored, since it would place a negative charge on the aryl carbon atom, as shown above. Thus the rocking motion of the aryl ring is increased slightly relative to that in the corresponding unsubstituted hydantoin, and consequently the entropy of the transition state is also increased. This results in para-chloro substituted hydantoins having slightly less negative entropies of activation than the corresponding unsubstituted ones, as shown in Table XVI.
SUMMARY

A study of the hindered rotation of a series of 3-aryl substituted hydantoins has led to the following conclusions:
I) Electronic effects cannot be disregarded in predicting the $\Delta G^\ddagger$ and $\Delta S^\ddagger$ of activation.
II) The substituents in the 5 position can affect the equilibrium constants of rotation, although they do not significantly affect the $\Delta G^\ddagger$ of rotation.
III) The ortho-methyl group is probably bent backwards in the transition state.
IV) A chlorine atom, although slightly smaller than a methyl group, presents a larger barrier of rotation in the hydantoins.
V) A sulphur atom causes a larger barrier of rotation than an oxygen atom when it is in the 2 position.
EXPERIMENTAL SECTION

Preparation of Arylisocyanates

The procedure described below was followed for the preparation of 4-methoxy-2-methylphenylisocyanate, 4-chloro-2-methylphenylisocyanate, and 2,3-dimethyl-phenylisocyanate. All the other isocyanates were available commercially.

4-Methoxy-2-methylphenylisocyanate. The procedure followed is an adaptation of that used by Schriner, Horne, and Cox.\textsuperscript{11}

Ethyl acetate (100 ml), freshly distilled and dried over anhydrous magnesium sulphate, was saturated with phosgene at room temperature. The phosgene had been previously purified by bubbling it through sulphuric acid. A solution of 15.0 g (0.0109 mole) of 4-methoxy-2-methyl-aniline in 250 ml of dry ethyl acetate was added dropwise. Towards the end of the addition, the solution was heated gently to break the lumps of 4-methoxy-2-methylaniline hydrochloride which had formed. After the aniline had been added, the stream of phosgene was continued until the solid had all dissolved. The unreacted phosgene was trapped by passing it through a 20\% NaOH solution. The ethyl acetate solvent was removed by vacuum distillation
at room temperature, and the isocyanate was distilled at 105-107° under 5-7 mm of pressure. It was then used for the preparation of the corresponding hydantoin without further purification. The yield of the isocyanate was 8.0 g or 44%; ir (liquid film, cm⁻¹) large strong band at 2260 (NCO).⁴²

4-Chloro-2-methylphenylisocyanate. This compound was prepared by the method described above. Starting material: 4-chloro-2-methylaniline (50.0 g, 0.354 mole). The isocyanate was distilled at 105° under 1 mm of pressure and was then used without further purification. The yield of isocyanate was 50.0 g or 85%; ir (liquid film, cm⁻¹) large strong band at 2260 (NCO).⁴²

2-Methyl-4-nitrophenylisocyanate. This compound was prepared by the method described above. Starting material: 2-methyl-4-nitroaniline (10.0 g, 0.066 mole). The isocyanate was distilled at 115-117° under 1 mm of pressure. It was then used for the preparation of the corresponding hydantoin without further purification. The yield of the isocyanate was 11.8 g or 85%; ir (KBr, cm⁻¹) large strong band at 2260 (NCO).⁴²

2,3-Dimethylphenylisocyanate. This compound was prepared by the method described above. Starting
material: 2,3-dimethylaniline (50.0 g, 0.41 mole).
The isocyanate was distilled at 75°C under 1 mm of vacuum. It was then used without further purification for the preparation of the corresponding hydantoin. The yield of the isocyanate was 50.0 g or 83%; ir (liquid film, cm⁻¹) large strong band at 2260 (NCO).
Preparation of Arylisothiocyanates

2-Methyl-4-nitrophenylisothiocyanate. The method followed was that of Coghill and Johnson. 43 2-Methyl-4-nitroaniline (20.0 g, 0.131 mole) was dissolved in 300 ml of dry ethyl acetate, to which 40.0 g of thio- phosgene was added. The reaction mixture was then heated under reflux until the hydrochloride went into solution. The solvent was evaporated and 50 ml of hot toluene was added. The isothiocyanate crystallized out on cooling. It was then used without further purification. The yield of the isothiocyanate was 14.0 g or 55%; mp 81-83°; ir (KBr, cm⁻¹) large strong band at 2075 (NCS). 42

4-Methoxy-2-methylphenylisothiocyanate. This compound was prepared by the method described above. Starting material: 4-methoxy-2-methylaniline (25.0 g 0.182 mole). The isothiocyanate was distilled at 128-132° under 1 mm vacuum. It was then used without further purification. The yield of the isothiocyanate was 27.0 g or 87%; ir (liquid film, cm⁻¹) large strong band at 2095 (NCS). 42

2-Isothiocyanatobiphenyl. This compound was prepared by the method described above. Starting material: 2-aminobiphenyl (25.0 g, 0.148 mole). The isothiocyanate
was distilled at 165° under 1 mm vacuum. It was then used without further purification. The yield of the iso-thiocyanate was 25.0 g or 80%; ir (liquid film, cm⁻¹) large strong band at 2100 (NCS).⁴²
Preparation of 3-Aryl Hydantoins

3-(2-Methoxyphenyl)-5,5-dimethylhydantoin (XXI). The procedure used was that of Behr and Clarcke. 44 2-Methylalanine (1.0 g, 0.0097 mole) was dissolved in 40 ml of 0.5 N NaOH solution. To this solution 2-methoxyphenylisocyanate (2.0 g, 0.0136 mole) was added and the mixture was stirred at room temperature for two hours. After having been filtered, the mixture was acidified to pH 5 and the resulting white precipitate was collected by filtration. This white precipitate was dissolved in 20 ml of hot water and 5 ml of 12 N HCl. The solution was then refluxed for two hours, filtered, cooled, and neutralized with sodium carbonate. The hydantoin precipitate was collected by filtration. It was crystallized from 95% ethanol and water. The yield of the hydantoin was 0.130 g or 8.9%; mp 161-163°; nmr (CDCl₃, δ) 1.3 (6H, singlet, C-5 methyl protons), 3.2 (3H, singlet, o-methoxy protons), 5.5 (1H, broad singlet, NH proton), 6.0 (4H, multiplet, phenyl protons); ir (KBr, cm⁻¹) 1715 (CO), 1770 (CO), 3210 (NH). 42

3-(4-Methoxy-2-methylphenyl)-5-methylhydantoin (XXII). This compound was prepared by the method described above. Starting material: DL-alanine (1.0 g, 0.0112 mole), and
4-methoxy-2-methylphenylisocyanate (2.3 g, 0.0134 mole).
The yield of the hydantoin after crystallization from 90% ethanol and water was 0.1 g or 5.3%; mp 146-147°; nmr (DMSO-d₆, δ) 1.35 (3H, doublet, C-5 protons), 2.1 (3H, doublet, o-methyl protons), 3.8 (3H, singlet, p-methoxy protons), 7.2 (3H, multiplet, phenyl protons): ir (KBr, cm⁻¹) 1715 (CO), 1775 (CO), 3300 (NH).

3-(2-Methylphenyl)-5-methylhydantoin (VII). This compound was prepared by the method described above. Starting material: DL-alanine (1.0 g, 0.0112 mole), and o-tolylisocyanate (2.0 g, 0.015 mole). The compound was crystallized from 95% ethanol and water. The yield was 1.2 g or 44%; mp 124-126°; nmr (DMSO-d₆, δ) 1.35 (3H, doublet, C-5 methyl protons), 2.1 (3H, doublet, o-methyl protons), 7.3 (4H, multiplet, phenyl protons); ir (KBr, cm⁻¹) 1715 (CO), 1775 (CO), 3250 (NH).

3-(2-Methoxyphenyl)-5-phenylhydantoin (XXIII). This compound was prepared by the method described above. Starting material: DL-alanine (2.0 g, 0.0224 mole), and 2-methoxyphenylisocyanate (4.0 g, 0.0278 mole). The compound was crystallized from 95% ethanol and water. The yield of the hydantoin was 1.17 g or 24%; mp 146-147°; nmr (DMSO-d₆, δ) 1.3 (3H, doublet, C-5 methyl protons), 3.2
(3H, singlet, o-methoxy protons), 6.1 (4H, multiplet, phenyl protons); ir (KBr, cm⁻¹) 1710 (CO), 1775 (CO), 3200 (NH).

3-(2-Methylphenyl)-5-phenylhydantoin (VIII). This compound was prepared by the method described above. Starting material: phenylglycine (3.44 g, 0.0228 mole), and o-tolylisocyanate (3.6 g, 0.0270 mole). The product was crystallized in 95% ethanol and water. The yield was 1.5 g or 25%; mp 197-199°; nmr (DMSO-d₆, δ) 2.1 (3H, doublet, o-methyl protons), 5.4 (1H, doublet, C-5 proton), 7.4 (9H, multiplet, phenyl protons); ir (KBr, cm⁻¹) 1715 (CO), 1775 (CO), 3200 (NH).

3-(4-Chloro-2-methylphenyl)-5-methylhydantoin (XII). This compound was prepared by the method described above. Starting material: DL-alanine (2.0 g, 0.0224 mole), and 4-chloro-2-methylphenylisocyanate (4.5 g, 0.0270 mole). The yield of the hydantoin was 1.0 g or 18.5%; mp 148-150°; nmr (DMSO-d₆, δ) 1.2 (3H, doublet, C-5 protons), 2.0 (3H, doublet, o-methyl protons), 7.1 (3H, multiplet, phenyl protons), 8.3 (1H, broad singlet, NH proton); ir (KBr, cm⁻¹) 1715 (CO), 1775 (CO), 3200 (NH).

3-(4-Chloro-2-methylphenyl)hydantoin (XXIV). This
compound was prepared by the method described above. Starting material: glycine (2.0 g, 0.0268 mole), and 4-chloro-2-methylphenylisocyanate (5.0 g, 0.0304 mole). The compound was crystallized from 95% ethanol and water. The yield of the hydantoin was 0.5 g or 8.3%; mp 108-110\(^\circ\); nmr (DMSO-\textsubscript{d}\textsubscript{6}, 6) 2.10 (3H, doublet, \(\alpha\)-methyl protons), 4.0 (2H, singlet, C-5 protons), 7.2 (3H, multiplet, phenyl protons); ir (KBr, cm\textsuperscript{-1}) 1715 (CO), 1775 (CO), 3280 (NH).

3-(4-Chloro-2-methylphenyl)-5-phenylhydantoin (XIII).
This compound was prepared by the method described above. Starting material: phenylglycine (3.0 g, 0.0199 mole), and 4-chloro-2-methylphenylisocyanate (5.0 g, 0.0304 mole). The product was crystallized from 95% ethanol and water. The yield of the hydantoin was 0.5 g or 8.4%; mp 155-157\(^\circ\); nmr (DMSO-\textsubscript{d}\textsubscript{6}, 6) 2.2 (3H, doublet, \(\alpha\)-methyl protons), 5.5 (1H, doublet, C-5 proton), 7.5 (8H, multiplet, phenyl protons); ir (KBr, cm\textsuperscript{-1}) 1715 (CO), 1770 (CO), 3280 (NH).

3-(4-Chloro-2-methylphenyl)-5,5-dimethylhydantoin (XXV).
This compound was prepared by the method described above. Starting material: 2-methylalanine (2.0 g, 0.0199 mole), and 4-chloro-2-methylphenylisocyanate (4.2 g, 0.025 mole). The product was crystallized from 95% ethanol and water. The yield of the hydantoin was 0.1 g or 2.1%; mp 184-186\(^\circ\);
nmr (DMSO-d$_6$, $\delta$) 1.4 (6H, singlet, C-5 protons), 2.1 (3H, singlet, $\alpha$-methyl protons), 7.4 (3H, multiplet, phenyl protons); ir (KBr, cm$^{-1}$) 1720 (CO), 1775 (CO), 3210 (NH).

3-(2-Methoxyphenyl)hydantoin (XXIX). This compound was prepared by the method described above. Starting material: glycine (2.0 g, 0.0268 mole), and 2-methoxyphenylisocyanate (4.0 g, 0.0278 mole). The product was crystallized from 95% ethanol and water. The yield of the hydantoin was 3.2 g or 60%; mp 170-171$^\circ$; nmr (DMSO-d$_6$, $\delta$) 3.75 (3H, singlet, $\alpha$-methoxy protons), 4.15 (2H, singlet, C-5 protons), 7.2 (4H, multiplet, phenyl protons), 8.2 (1H, broad singlet, NH proton); ir (KBr, cm$^{-1}$) 1710 (CO), 1770 (CO), 3300 (NH).

3-(2,3-Dimethylphenyl)-5-methylhydantoin (IX). This compound was prepared by the method described above. Starting material: DL-alanine (2.0 g, 0.0228 mole), and 2,3-dimethylphenylisocyanate (4.0 g, 0.0227 mole). The product was crystallized from 95% ethanol and water. The yield of the hydantoin was 1.4 g or 28%; mp 148-150$^\circ$; nmr (DMSO-d$_6$, $\delta$) 1.4 (3H, doublet, C-5 methyl protons), 2.3 (3H, doublet, $\alpha$-methyl protons), 2.0 (3H, singlet, m-methyl protons), 7.2 (3H, multiplet, phenyl protons); ir (KBr, cm$^{-1}$) 1710 (CO), 1770 (CO), 3220 (NH).
3-(2,3-Dimethylphenyl)hydantoin (XXVI). This compound was prepared by the method described above. Starting material: glycine (2.0 g, 0.0268 mole), and 2,3-dimethylphenylisocyanate (4.5 g, 0.0304 mole). The product was crystallized from 95% ethanol and water. The yield of the hydantoin was 1.0 g or 18.3%; mp 131-133°; nmr (DMSO-d₆, δ) 2.0 (3H, singlet, o-methyl protons), 2.3 (3H, singlet, m-methyl protons), 4.2 (2H, singlet, C-5 protons), 7.3 (3H, multiplet, phenyl protons), 8.3 (1H, broad singlet, NH proton); ir (KBr, cm⁻¹) 1715 (CO), 1770 (CO), 3300 (NH).

3-(2-Chlorophenyl)-5-phenylhydantoin (XIV). This compound was prepared by the method described above. Starting material: phenylglycine (1.7 g, 0.0112 mole), and 2-chlorophenylisocyanate (1.8 g, 0.0112 mole). The product was crystallized from 95% ethanol and water. The yield of the hydantoin was 0.41 g or 27%; mp 163-165°; nmr (DMSO-d₆, δ) 4.3 (1H, doublet, C-5 proton), 6.7 (4H, multiplet, phenyl protons); ir (KBr, cm⁻¹) 1720 (CO), 1780 (CO), 3280 (NH).

3-(2-Methyl-4-nitrophenyl)-5-methylhydantoin (X). This compound was prepared according the method of Wheeler et al. A mixture of 3-(2-methyl-4-nitrophenyl)-5-methyl-2-thiohydantoin
(2.5 g, 0.01 mole) and chloroacetic acid (0.95 g, 0.01 mole) was refluxed in 10 ml of distilled water. The hydantoin crystallized out on cooling. It was recrystallized from 95% ethanol and water. The yield of the hydantoin was 0.10 g or 4.4%; mp 166-168\(^\circ\); nmr (DMSO-d\(_6\), \(\delta\)) 1.4 (3H, doublet, C-5 methyl protons), 2.2 (3H, doublet, o-methyl-protons), 4.5 (1H, quartet, C-5 proton); ir (KBr, cm\(^{-1}\)) 1705 (CO), 1760 (CO), 3240 (NH).
Preparation of 3-Aryl Thiohydantoins

3-(2-Methyl-4-nitrophenyl)-5-methyl-2-thiohydantoin (XI).
The procedure followed was that of Pujari and Root.\textsuperscript{46}
DL-alanine (2.5 g, 0.027 mole) was dissolved in 2 ml of water and 1.0 g of NaOH was added. To this solution, a solution of 2-methyl-4-nitrophenylisothiocyanate (4.8 g, 0.025 mole) in 20 ml of absolute alcohol was added dropwise. The resulting solution was refluxed for two hours, when 25 ml of 6 N HCl was then added. The thiohydantoin precipitated and was recrystallized from 95% ethanol and water. The yield of the thiohydantoin was 5.1 g or 90%; mp 209-210°; nmr (DMSO-d\textsubscript{6}, δ) 1.5 (3H, doublet, C-5 methyl protons), 2.3 (3H, doublet, o-methyl protons), 7.3 (4H, multiplet, phenyl protons); ir (KBr, cm\textsuperscript{-1}) 1190 (CS), 3400 (NH).

3-(4-Methoxy-2-methylphenyl)-5-methyl-2-thiohydantoin (XXVII).
This compound was prepared by the method described above.
Starting material: DL-alanine (2.4 g, 0.027 mole), and 4-methoxy-2-methylphenylisocyanate (4.8 g, 0.027 mole).
The yield of the thiohydantoin was 4.7 g or 70%; mp 145-147°; nmr (DMSO-d\textsubscript{6}, δ) 1.4 (3H, doublet, C-5 methyl protons), 2.1 (3H, singlet, o-methyl protons) 3.8 (3H, singlet, p-methoxy protons), 7.0 (3H, multiplet, phenyl protons); ir (KBr, cm\textsuperscript{-1}) 1190 (CS), 1720 CO, 3300 (NH).
3-(2-Biphenyl)-5-methyl-2-thiohydantoin (XXVIII).
This compound was prepared by the method described above.
Starting material: DL-alanine (2.4 g, 0.027 mole), and
2-isothiocyanatobiphenyl (4.8 g, 0.022 mole). The compound
was crystallized from 95% ethanol and water. The yield
of the thiohydantoin was 5.0 g or 78%; mp 142-144°C; nmr
(DMSO-d$_6$, δ) 1.8 (3H, quartet, C-5 methyl protons), 5.0
(9H, multiplet, phenyl protons); ir (KBr, cm$^{-1}$) 1720 (CO),
3250 (NH).
Spectra of Hydantoins and Thiohydantoins

Infrared and NMR spectra were taken of the following compounds:

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<tr>
<th>Formula</th>
<th>Substituents</th>
<th>Compound Label</th>
</tr>
</thead>
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<td>$R_1 = H, R_2 = CH_3$</td>
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</tr>
<tr>
<td></td>
<td>$R_1 = H, R_2 = H$</td>
<td>XXIX</td>
</tr>
<tr>
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<td>XXI</td>
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<tr>
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</tbody>
</table>
NMR Spectra

The experimental conditions have been described previously. The absorptions in the NMR spectra of hydantoins and thiohydantoins agree quite well with data reported by Corral and Orazi,\textsuperscript{47} and Fehlner.\textsuperscript{7} Two examples of hydantoin spectra are illustrated in Figures 18 and 19. In DMSO-$d_6$ solution, the C-5 methyl group absorbs between $\delta$ 1.25 and $\delta$ 1.55, while the methyl group in the ortho position absorbs between $\delta$ 1.35 and $\delta$ 2.30. The hydrogen atom in the 5 position absorbs between $\delta$ 3.55 and $\delta$ 5.52. In the 5 methyl-substituted compounds the C-5 proton absorbs from $\delta$ 4.3 to $\delta$ 4.4, while in the corresponding 5 phenyl compounds the same proton absorbs, probably because of the deshielding due to the phenyl ring, between $\delta$ 5.3 and $\delta$ 5.4. The phenyl peaks are generally very complicated; they absorb between $\delta$ 4.8 and $\delta$ 7.2. The NH proton absorbs over a wide range and is broadened by the quadrupole relaxation of the nitrogen atom. The magnitude of the coupling constant between the C-5 methyl and the C-5 proton in the 5 methyl-substituted hydantoins varies from a minimum of 6.5 Hz for compound VII to a maximum of 12 Hz for compound XXVIII. All the spectra recorded during this work are easily reproducible.
Taken at 60 MHz in DMSO-d$_6$ solution at room temperature.

Figure 18: NMR spectrum of 3-(2-methylphenyl)-5-phenyldieneton (VIII).
Figure 19: NMR Spectrum of 3-(4-chloro-2-methylphenyl)-5-methylhydantoin (XII) Taken at 60 MHz in DMSO-d$_6$ Solution at Room Temperature.
Infrared Spectra

All the infrared spectra of hydantoins and thiohydantoins in this work were taken through potassium bromide disks on a Perkin-Elmer 457 infrared spectrometer.

The infrared spectra of a number of substituted hydantoins have already been well discussed in a paper by Elliot and Natarajan.\textsuperscript{48} Those of 3-phenyl hydantoins have been discussed by Saifer,\textsuperscript{49} and Epp.\textsuperscript{50,51} Their results agree very well with each other.

Two modes of vibration are very easily recognized in the infrared spectra of hydantoins and thiohydantoins. One is the N-H stretching mode, which varies from 3180 cm\textsuperscript{-1} to 3300 cm\textsuperscript{-1} for the hydantoins, and from 3250 cm\textsuperscript{-1} to 3400 cm\textsuperscript{-1} in the case of the corresponding thiohydantoins. The second important mode of vibration is the carbonyl stretching mode. This mode gives rise to two bands in hydantoins. The first is a moderate intensity absorption band between 1760 cm\textsuperscript{-1} and 1780 cm\textsuperscript{-1}, while the second is a very strong broad band between 1705 cm\textsuperscript{-1} and 1720 cm\textsuperscript{-1}. It has been suggested that this latter band may be a doublet.\textsuperscript{48} In the thiohydantoins there is only one carbonyl stretching band, found between 1720 cm\textsuperscript{-1} and 1740 cm\textsuperscript{-1}. The assignment of the C=S stretching vibration to the absorption between 1400 cm\textsuperscript{-1} and 1425 cm\textsuperscript{-1} was given by Kimmel and Saifer.\textsuperscript{49} In contrast, Epp\textsuperscript{51} assigned
the same stretching mode to the absorption around 1200 cm\(^{-1}\).
Both bands are present in all the thiohydantoin{s, but while Kimmel and Salfer did not give any explanation for their assignment, Epp pointed out that on opening the hydantoin ring, the band between 1400 cm\(^{-1}\) and 1425 cm\(^{-1}\) does not shift, while that around 1200 cm\(^{-1}\) does shift. Further, Mecke\(^{52}\) calculated that in the case of thiolactams, the ratio \(\nu(C=O)/\nu(C=S)\) would be approximately 1.5, so that \(\nu(C=S)\) would be about \((1800-1500)/1.5\) or \(1200-1050\) cm\(^{-1}\). Since Mecke's experimental values confirmed his calculations, (see Table XVII), it is considered reasonable to identify the absorption between 1195-1185 cm\(^{-1}\) in the thiohydantoin{s as the C=S stretching mode.}
Table XVII: Infrared Frequencies of Some Carbonyl and Thiocarbonyl Compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stretching Mode</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiopyrrolidone</td>
<td>( \nu(C=S) )</td>
<td>1115 cm(^{-1})</td>
</tr>
<tr>
<td>Pyrrolidone</td>
<td>( \nu(C=O) )</td>
<td>1706 cm(^{-1})</td>
</tr>
<tr>
<td>Thiopiperidone</td>
<td>( \nu(C=S) )</td>
<td>1112 cm(^{-1})</td>
</tr>
<tr>
<td>Piperidone</td>
<td>( \nu(C=O) )</td>
<td>1672 cm(^{-1})</td>
</tr>
<tr>
<td>Thiocaprolactam XI</td>
<td>( \nu(C=S) )</td>
<td>1117 cm(^{-1})</td>
</tr>
<tr>
<td>Caprolactam X</td>
<td>( \nu(C=O) )</td>
<td>1669 cm(^{-1})</td>
</tr>
<tr>
<td>XXVII</td>
<td>( \nu(C=S) )</td>
<td>1190 cm(^{-1})</td>
</tr>
<tr>
<td>XXII</td>
<td>( \nu(C=O) )</td>
<td>1760 cm(^{-1})</td>
</tr>
</tbody>
</table>
Mass Spectra

The spectra recorded in Tables XVIII, XIX, XX, and XXI were taken on a Hitachi Perkin-Elmer RMU-7 spectrometer. The direct introduction of the sample was used in all cases.

Up to the present time there is only one publication in the literature dealing with the mass spectra of thiohydantoins. The spectrum of 3-phenylthiohydantoin has been reported by a group of Russian chemists. The major fragments have been assigned to the following ions: \( \phi \text{NCS}^+ (m/e 135), \phi \text{NCO}^+ (m/e 119), \phi \text{NCH}^+ (m/e 104), \phi \text{NH}_2^+ (m/e 93), \phi^+ (m/e 77) \). More work has been done on the mass spectra of the hydantoins.7,54,55

The mode of decomposition for 3-(2-methoxyphenyl)-hydantoin (XXIX) seems to fit the mode of decomposition of hydantoins, as previously described.7,54,55
Since the ion $\text{CH}_2\text{-NH}$-CO (m/e 57) is abundant in the case of this hydantoin, it is probable that the isocyanate can also be lost as a neutral fragment. This seems to be confirmed by the work of Djerassi, and Coutts.
Furthermore, Djerassi showed by isotopic labelling that the C-4 carbonyl group was preferentially (> 90%) expelled in the isocyanate extrusion. This decomposition process proceeds further, yielding an ion of lower mass: \[ \text{HN–CH}_2 \] m/e 29 → \[ \text{HN≡CH}^+ \] m/e 28

The same ion could also be formed by a different process: \[ \text{OCH}_3 \]

In the mass spectrum of the 3-(2-biphenyl)-5-methyl-2-thiohydantoin (XXVIII), in addition to the usual ions; there occurs an ion at m/e 238 which could be derived from a different fragmentation pattern.
The ion at m/e 253 could possibly arise through the following sequence.  

In the same spectrum one of the most intense absorptions appears at m/e 152, accompanied by another intense absorption at m/e 151. Since it has already been pointed out that the C-N aryl bond can be broken, a possible explanation for the production of these ions is that the following sequence occurs,
The very intense peak at m/e 221 could have been formed in the following manner:

However, this has yet to be proved.
The very intense peak at m/e 221 could have been formed in the following manner,

However, this has yet to be proved.
Table XVIII: Mass Spectrum of 3-(2-methoxyphenyl)hydantoin (XIX) in Terms of % of Base Peak.

<table>
<thead>
<tr>
<th>M/e</th>
<th>% Base Peak</th>
<th>M/e</th>
<th>% Base Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>206</td>
<td>9.9</td>
<td>104</td>
<td>6.8</td>
</tr>
<tr>
<td>205</td>
<td>6.8</td>
<td>81</td>
<td>6.2</td>
</tr>
<tr>
<td>190</td>
<td>13.2</td>
<td>77</td>
<td>4.0</td>
</tr>
<tr>
<td>189</td>
<td>4.1</td>
<td>76</td>
<td>5.4</td>
</tr>
<tr>
<td>188</td>
<td>32.0</td>
<td>70</td>
<td>4.4</td>
</tr>
<tr>
<td>167</td>
<td>6.8</td>
<td>66</td>
<td>4.3</td>
</tr>
<tr>
<td>155</td>
<td>4.8</td>
<td>65</td>
<td>5.4</td>
</tr>
<tr>
<td>151</td>
<td>10.6</td>
<td>57</td>
<td>8.1</td>
</tr>
<tr>
<td>150</td>
<td>14.9</td>
<td>56</td>
<td>5.8</td>
</tr>
<tr>
<td>149</td>
<td>100.0</td>
<td>55</td>
<td>5.8</td>
</tr>
<tr>
<td>141</td>
<td>13.6</td>
<td>45</td>
<td>3.9</td>
</tr>
<tr>
<td>125</td>
<td>5.6</td>
<td>41</td>
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<tr>
<td>123</td>
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<td>29</td>
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</tr>
<tr>
<td>105</td>
<td>4.0</td>
<td>28</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Table XIX: Mass Spectrum of 3-(2-methylphenyl)-5-phenylhydantoin (VIII) in Terms of % of Base Peak.

<table>
<thead>
<tr>
<th>M/e</th>
<th>% Base Peak</th>
<th>M/e</th>
<th>% Base Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>267</td>
<td>9.1</td>
<td>106</td>
<td>62.3</td>
</tr>
<tr>
<td>266</td>
<td>39.7</td>
<td>105</td>
<td>68.8</td>
</tr>
<tr>
<td>194</td>
<td>5.3</td>
<td>104</td>
<td>80.1</td>
</tr>
<tr>
<td>189</td>
<td>9.6</td>
<td>103</td>
<td>5.9</td>
</tr>
<tr>
<td>169</td>
<td>4.3</td>
<td>92</td>
<td>5.3</td>
</tr>
<tr>
<td>167</td>
<td>9.1</td>
<td>91</td>
<td>24.7</td>
</tr>
<tr>
<td>160</td>
<td>3.7</td>
<td>90</td>
<td>9.6</td>
</tr>
<tr>
<td>156</td>
<td>4.3</td>
<td>89</td>
<td>12.3</td>
</tr>
<tr>
<td>155</td>
<td>12.9</td>
<td>83</td>
<td>7.5</td>
</tr>
<tr>
<td>154</td>
<td>4.3</td>
<td>79</td>
<td>10.7</td>
</tr>
<tr>
<td>149</td>
<td>24.2</td>
<td>78</td>
<td>32.2</td>
</tr>
<tr>
<td>142</td>
<td>6.4</td>
<td>77</td>
<td>43.0</td>
</tr>
<tr>
<td>141</td>
<td>36.5</td>
<td>76</td>
<td>16.6</td>
</tr>
<tr>
<td>134</td>
<td>20.9</td>
<td>75</td>
<td>4.3</td>
</tr>
<tr>
<td>133</td>
<td>100.0</td>
<td>74</td>
<td>4.3</td>
</tr>
<tr>
<td>132</td>
<td>23.6</td>
<td>71</td>
<td>9.6</td>
</tr>
<tr>
<td>128</td>
<td>4.3</td>
<td>70</td>
<td>13.9</td>
</tr>
<tr>
<td>119</td>
<td>5.3</td>
<td>69</td>
<td>9.1</td>
</tr>
<tr>
<td>118</td>
<td>11.3</td>
<td>65</td>
<td>11.8</td>
</tr>
<tr>
<td>117</td>
<td>11.3</td>
<td>57</td>
<td>27.4</td>
</tr>
<tr>
<td>115</td>
<td>6.4</td>
<td>55</td>
<td>20.4</td>
</tr>
<tr>
<td>112</td>
<td>4.3</td>
<td>52</td>
<td>12.9</td>
</tr>
<tr>
<td>107</td>
<td>8.0</td>
<td>51</td>
<td>25.8</td>
</tr>
</tbody>
</table>
Table XX: Mass Spectrum of 3-(2-biphenyl)-5-methyl-2-thiohydantoin (XXVIII) in Terms of % of Base Peak.

<table>
<thead>
<tr>
<th>M/e</th>
<th>% Base Peak</th>
<th>M/e</th>
<th>% Base Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>22.0</td>
<td>179</td>
<td>10.6</td>
</tr>
<tr>
<td>282</td>
<td>100.0</td>
<td>178</td>
<td>36.0</td>
</tr>
<tr>
<td>279</td>
<td>11.3</td>
<td>177</td>
<td>12.2</td>
</tr>
<tr>
<td>253</td>
<td>4.6</td>
<td>169</td>
<td>5.0</td>
</tr>
<tr>
<td>249</td>
<td>5.8</td>
<td>168</td>
<td>4.9</td>
</tr>
<tr>
<td>238</td>
<td>4.2</td>
<td>167</td>
<td>23.6</td>
</tr>
<tr>
<td>223</td>
<td>6.6</td>
<td>166</td>
<td>4.4</td>
</tr>
<tr>
<td>222</td>
<td>6.6</td>
<td>155</td>
<td>7.3</td>
</tr>
<tr>
<td>221</td>
<td>32.0</td>
<td>154</td>
<td>4.5</td>
</tr>
<tr>
<td>212</td>
<td>4.6</td>
<td>153</td>
<td>4.4</td>
</tr>
<tr>
<td>210</td>
<td>20.0</td>
<td>152</td>
<td>19.3</td>
</tr>
<tr>
<td>205</td>
<td>8.6</td>
<td>151</td>
<td>12.4</td>
</tr>
<tr>
<td>197</td>
<td>6.2</td>
<td>150</td>
<td>12.6</td>
</tr>
<tr>
<td>196</td>
<td>1.7</td>
<td>139</td>
<td>4.0</td>
</tr>
<tr>
<td>195</td>
<td>5.7</td>
<td>127</td>
<td>15.3</td>
</tr>
<tr>
<td>184</td>
<td>4.0</td>
<td>85</td>
<td>8.6</td>
</tr>
<tr>
<td>181</td>
<td>9.0</td>
<td>77</td>
<td>6.0</td>
</tr>
<tr>
<td>180</td>
<td>16.0</td>
<td>76</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Table XXI: Mass Spectrum of 3-(2-methyl-4-nitrophenyl)-5-methylhydantoin (X) in Terms of % of Base Peak.

<table>
<thead>
<tr>
<th>M/e</th>
<th>% Base Peak</th>
<th>M/e</th>
<th>% Base Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>252</td>
<td>15.5</td>
<td>120</td>
<td>4.8</td>
</tr>
<tr>
<td>251</td>
<td>100.0</td>
<td>117</td>
<td>6.2</td>
</tr>
<tr>
<td>222</td>
<td>2.8</td>
<td>105</td>
<td>5.0</td>
</tr>
<tr>
<td>180</td>
<td>4.8</td>
<td>104</td>
<td>19.7</td>
</tr>
<tr>
<td>179</td>
<td>46.6</td>
<td>103</td>
<td>4.8</td>
</tr>
<tr>
<td>178</td>
<td>46.6</td>
<td>90</td>
<td>3.6</td>
</tr>
<tr>
<td>175</td>
<td>11.5</td>
<td>89</td>
<td>19.7</td>
</tr>
<tr>
<td>162</td>
<td>7.6</td>
<td>78</td>
<td>8.6</td>
</tr>
<tr>
<td>149</td>
<td>39.5</td>
<td>77</td>
<td>26.8</td>
</tr>
<tr>
<td>148</td>
<td>18.5</td>
<td>76</td>
<td>8.1</td>
</tr>
<tr>
<td>141</td>
<td>27.6</td>
<td>71</td>
<td>3.9</td>
</tr>
<tr>
<td>133</td>
<td>6.2</td>
<td>70</td>
<td>24.0</td>
</tr>
<tr>
<td>132</td>
<td>8.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


APPENDIX
LISTINGS OF
AND
DIRECTIONS FOR THE USE OF
THE COMPUTER PROGRAMS UTILIZED
IN THIS RESEARCH PROJECT
LINDI

This programme digitalizes NMR spectra and transfers them to paper tape, which is later used as input in the TAPGH programme. (See also Fitting of the Spectra section).
FTN,B

PROGRAM LINDI
COMMON IDEN(35), KY(256), IZ(4), X(4)
WRITE(2,100)
100 FORMAT("LINE FOLLOWER DIGITIZATION OF NMR SPECTRA")
CALL RESET
WRITE(2,101)
101 FORMAT("ENTER VALUES IN FREE FIELD FORMAT"/
"TO AROB: SET SWITCH 15"/
"FOR MANUAL SCAN: SET SWITCH 0"/
"NOTE: YES = 1, NO = 0")/
2 "PREPARE LINE FOLLOWER")
M1=1
PAUSE
2 WRITE(2,102)
102 FORMAT("ENTER IDENTIFICATION")
CALL RESET
READ(1,103) IDEN
103 FORMAT(35A2)
3 WRITE(2,104)
104 FORMAT("ENTER POINTS/HZ")
READ(1,*) PPHZ
WRITE(2,105)
105 FORMAT("ADJUST SENSOR TO LEFT FREQUENCY LIMIT")
CALL PLOT(0,0)
PAUSE
WRITE(2,106)
106 FORMAT("ADJUST SENSOR TO RIGHT FREQUENCY LIMIT")
CALL PLOT(250,0)
PAUSE
CALL PLOT(0,0)
WRITE(2,107)
107 FORMAT("ENTER LEFT FREQUENCY LIMIT")
READ(1,*) FL
WRITE(2,108)
108 FORMAT("ENTER RIGHT FREQUENCY LIMIT")
READ(1,*) FR
HZPT=(FR-FL)/250.0
AHZ=ABS(HZPT)
AMULT=1.0/(AHZ*PPHZ)
MULT=AMULT + 0.5
IF (MULT-1)4.5
4 MULT=1
AMULT=1.0
5 CONTINUE
NPT=250/MULT+1
PPCS=1.0/(AHZ*FLOAT(MULT))
FREQI=HZPT*FLOAT(MLT)
10 WRITE(2,109)
109 FORMAT("SET SENSOR ON BASE LINE")
CALL RESET
PAUSE
IVAL=0
MDEL=M1
CALL DIG3(MDEL,IVAL)
NBASE=IVAL
WRITE(2,110)
110 FORMAT("SET SENSOR ON CURVE")
PAUSE
WRITE(2,110)
117 FORMAT("ENTER SCAN RATE: 1 = FAST, 10 = SLOW")
READ(1,*)IDEL
MDEL=IDEL
DEL=0.1*FLOAT(IDEL)
DO 12 I=1,251
J=I-1
CALL PLOT(J,0)
IF (ISSW(0))20,21
20 CALL DHALT
21 CONTINUE
CALL DIG3(MDEL,IVAL)
KY(I)=IVAL
IF (ISSW(15))22,12
22 CALL PLOT(0,0)
GO TO 10
12 CONTINUE
CALL PLOT(0,0)
WRITE(2,111)
111 FORMAT("REPEAT SCAN ?")
READ(1,*)IR
IF (IR)10,13,10
13 CONTINUE
DO 14 I=1,251
KY(I)=KY(I)-NBASE
14 CONTINUE
IF (ISSW(15))50,15
15 WRITE(2,130)
130 FORMAT("PAPER TAPE REQUIRED ?")
READ(1,*)IPT
IF (IPT)60,61,60
60 CALL LEADR(2,10)
61 WRITE(2,113)IDEN
113 FORMAT(//35A2/)
   WRITE(2,122)NPT
122 FORMAT(14X,"NUMBER OF POINTS = ",I3)
   WRITE(2,114)FL,FR
114 FORMAT("
12)
   WRITE(2,115)PHZ,PPCS
115 FORMAT(9X,"POINTS/HZ: REQUESTED = ",F5.2,5X,"RECORDED = ",F5.2)
   WRITE(2,116)IDEL,DEL
116 FORMAT("\nDELAY FACTOR PER POINT SCANNED = ",I2,5X,"DELAY (SEC) = "
1,F5.1/
   WRITE(2,118)
118 FORMAT("\nINTEN. FREQ. INTEN. FREQ. INTEN. FREQ. INTEN. FREQ.
1 FREQ./")
   FREQ=FL
   N=1
   I=1
40 IY=KY(N)
   IY(I)=IY
   IZ(I)=FREQ
   FREQ=FREQ + FREQI
   I=I+1
   N=N+MULT
   IF (251-N)44,42
42 CONTINUE
   IF (4-I)44,40
44 CONTINUE
   NNN=I-1
   IF (ISSW(15))50,45
45 CONTINUE
   WRITE(2,121)(IZ(I),X(I),I=1,NNN)
121 FORMAT(3(15,F8.2,4X)(15,F8.2))
   I=1
   IF (251-N)25,40
25 CONTINUE
   IF (IPT)49,50,49
49 CALL LEADR(2,10)
50 WRITE(2,119)
119 FORMAT(//"NEXT CASE")/
   PAUSE
   GO TO 2
END
END$
This programme transfers the digitalized NMR spectra from the paper tape to the magnetic tape, which is later used as input for both the NLIN GH and the PUNNLIN programmes. (See also Fitting of the Spectra section).
PROGRAM TAPGH
   COMMON IB(6), B(6), IDEN(35), X(256), KY(256), KKY(4), XX(4)
   K0 = 0
   K1 = 1
   K6 = 6
   FK8 = 0.0
   WRITE(2, 100)
100 FORMAT("""PREPARE INPUT TAPE FOR NLINGH"""", """"USE FREE FIELD FORMAT FOR
   RI INPUT"", """"NOTE: YES = 1, NO = 0"""", """"TO ABORT: SET SWITCH 15"""")
   WRITE(2, 101)
101 FORMAT("""CAUTION"", """"CAUTION"", """"DO NOT PROCEED UNTIL DATA TAPE IS MOU
   NTED"""")
   PAUSE
   WRITE(2, 102)
102 FORMAT("""PARAMETER IDENTIFICATION:"", """"B(1) = TAU(A)"", """"B(2) = TAU(B"
   1)"", """"B(3) = SHIFT(A)"", """"B(4) = SHIFT(B)"", """"B(5) = SCALING FACTOR"
   2"", """"B(6) = LINE WIDTH"""")
   2 WRITE(2, 103)
103 FORMAT("""ENTER SPECTRUM NUMBER"""")
   CALL RESET
   WRITE(2, 104)
104 FORMAT("""ENTER NUMBER OF FIXED PARAMETERS"""")
   READ(1,*) KP
   IF (KP) 5, 3, 5
   5 WRITE(2, 105)
105 FORMAT("""ENTER SUBSCRIPTS OF FIXED PARAMETERS"""")
   DO 6 I = 1, KP
      READ(1,*) IB(I)
   6 CONTINUE
   3 WRITE(2, 106)
106 FORMAT("""ENTER TAU(A)"""")
   READ(1,*) B(1)
   WRITE(2, 107)
107 FORMAT("""ENTER TAU(B)"""")
   READ(1,*) B(2)
   WRITE(2, 108)
108 FORMAT("""ENTER SHIFT(A)"""")
   READ(1,*) B(3)
   WRITE(2, 109)
109 FORMAT("""ENTER SHIFT(B)"""")
   READ(1,*) B(4)
   WRITE(2, 110)
110 FORMAT("""ENTER SCALING FACTOR"""")
READ(1,*)B(5)
WRITE(2,111)
111 FORMAT("ENTER LINE WIDTH")
READ(1,*)B(6)
IF (ISSW(15))2,7
7 READ(5,120)IDEN
120 FORMAT(35A2)
READ(5,122)NPT
122 FORMAT(33X,13,4/)
N=1
NC=NPT
NN=4
8 READ(5,121)KXY(I),XX(I), I=1,NN
121 FORMAT(3(I5,F8.2,4X)(I5,F8.2))
DO 9 I=1,NN
KXY(I)=KXY(I)
XX(I)=XX(I)
N=N+1
9 CONTINUE
NC=NC-NN
IF (NC-4)11,10,10
10 NN=4
GO TO 12
11 NN=NC
12 CONTINUE
IF (NPT-N)13,8,8
13 WRITE(2,133)IDEN
133 FORMAT("IDENTIFICATION:"//35A2/)
WRITE(2,135)
135 FORMAT("TRANSFER TO MAGNETIC TAPE ?")
READ(1,*)IT
IF (IT)26,29,26
26 MAX=KXY(I)
DO 45 I=2,NPT
IF (MAX-KXY(I))40,45
40 MAX=KXY(I)
45 CONTINUE
SPRD=MAX
SPRD=0.011*SPRD
WRITE(7,140)NPT,K6,KP,K1,K1,K0
140 FORMAT(12I3)
WRITE(7,140)K0,K1,K1,K0,K0,K0
WRITE(7,145)K0,SPRD
IF (KP)30,31,30
30 WRITE(7,140)IB(I), I=1,KP,K0,K0,K0,K0,K0,K0,K0
31 WRITE(7,142)(FK0,I=1,8)
142 FORMAT(6F10.0)
   WRITE(7,143)(BI,I=1,6)
143 FORMAT(6F10.4)
   DO 27 I=1,NPT
   Y=FLOAT(KY(I))/100.0
   WRITE(7,145)Y,X(I)
145 FORMAT(2F10.3)
27 CONTINUE
   WRITE(7,146)NRUN,IDENT
146 FORMAT(13,35A2)
   WRITE(2,150)
150 FORMAT("IS ANOTHER DATA SET TO FOLLOW ?")
   READ(1,*)IS
   IF(IS)29,28,29
28 WRITE(7,140)(KO,I=1,6)
   END FILE 7
   REWIND 7
   WRITE(2,151)
151 FORMAT("TAPE PREPARATION COMPLETE")
29 WRITE(2,152)
152 FORMAT("NEXT CASE")
   PAUSE
   GO TO 2
END
END$
NLIN GH

In the output of this programme, the computer first plots the experimental spectrum and the spectrum calculated from the initial guesses for the parameters. It then fits the spectra showing the changes in the parameters for each iteration. When the best fit is found, another plot of the experimental and the final calculated spectra, as well as a tabular output of the points, is given. Finally, an error analysis of the fit is printed. (See also Fitting of the Spectra section).
PROGRAM NLIN(INPUT, OUTPUT, TAPE3, TAPE5, TAPE6=OUTPUT)

CDC 6400 VERSION. OCTOBER 1971
TAPES IS USED FOR DATA INPUT

MODIFIED VERSION. APRIL 1971
PREPARED FOR MAGNETIC TAPE INPUT.
RESTRICTED TO TWO DATA VALUES; IN (2F10.0) FORMAT.
CARD INPUT MAY BE USED, BUT FORMAT CARD (ITEM 7) MUST BE OMITTED.
TO RE-CONVERT TO ORIGINAL VERSION OF NLIN, INSERT AFTER CARD 1250
READ(5,902)(FMT(I), I=1,12)
REPLACE CARD 1280 WITH
56 READ(5,FMT)Y(I), (X(I,L), L=1,M)
REMOVE CARD 1281

NONLINEAR LEAST SQUARES
BY D. W. MARQUARDT
PROGRAMMED BY T. BAUMEISTER III,
J. ANN SHELDON AND RUBY M. STANLEY
IRKT=1 MEANS USE UPPER A MATRIX
IRKT=2 MEANS USE TAPE 3

DIMENSION FMT(18), PRNT(5), SPRNT(5)
DIMENSION BS(50), DB(50), BA(50), G(50), W(51), IB(49), SA(50), P(50), A(50)
  10, 51), B(50)
DIMENSION X(500,1), Y(500)
DIMENSION CONS(25)
DATA IBCH/1H /*ICCH/1HO/*IPCH/1HP/*IXCH/1HX/*IYCH/1HY/

-------------------------------------------------------------
MAX NO OF PARAMETERS IS K=50
MAX NO OF IND VARS IS M=10
MAX NO OF OBSERVATIONS IS N=500
IWHER =-1 MEANS DO ANY SPECIAL INITIALIZING FOR CASE
C
IWHER = 0 MEANS START NEW CASE OR END RUN
IWHER = 1 MEANS GET P S AND F
IWHER GREATER THAN 1 MEANS GET F ONLY

SET ITERATION LIMIT
ITLIM=50

NPRNT=0
650 IWHER = 0
652 GO TO 4
653 IWHER = IWHER
IF (IWHER *.GE. 0) GO TO 654
IF (IWHER *.EQ. 0) GO TO 660
651 CONTINUE

CODING FOR CASE INITIALIZING GOES HERE

CALL SUBZ(Y,X,B,PRNT,NPRNT,N)

IF (IBOUT *.EQ. 0) GO TO 652
GO TO 650
654 CONTINUE

CODING TO MAKE F GOES HERE
F IS Y HAT (I)
NPRNT IS THE NO. OF OTHER WORDS TO BE PRINTED
THE WORDS TO BE PRINTED ARE IN PRNT(1)...PRNT(5)

CALL FCODE(Y,X,B,PRNT,F,I,RES)

IF (IWHER *.NE. 1) GO TO 652
656 IF (IFSS2 *.NE. 0) GO TO 652
658 CONTINUE

CODING TO MAKE DF/DB GOES HERE
MAKE K OF THEM, CALL THEM P(J)
C THEY ARE MADE FROM X(I,L) AND B(J)
C
C ********************************************
CALL PCODE(P,X,R,PRNT,F,L)
C
C ********************************************
GO TO 652

660 STOP 111
C THIS IS THE END OF THE MAIN ROUTINE
C
C
4 IWHER = IWHER
C = 0
IF (IWHER.LT.0) GO TO 59
IF (IWHER.EQ.0) GO TO 10
C
8 GO TO (75,304,606,620), IWHER
C READ FIRST CARD OF NEXT CASE

10 ITCT=0
IBOUT=0
K1 = 1
K2 = 1
IISS = 0
READ (5,900) N,K,IP,M,IFP,NCONS
NTILDA=N*NCONS
XNT=NTILDA
IF (N.LE.0) GO TO 20
READ (5,900) IWS1,IWS2,IWS3,IWS4,IWS5,IWS6
IFSS1=2
IF (IWS5.EQ.0) GO TO 210
PAUSE 5

210 CONTINUE
WRITE (6,932)

211 GO TO 21
C END OF LAST PROBLEM

20 GO TO ( 19, 17),IBKT
17 REWIND 3
19 IWHERE=0
   GO TO 653
21 IF (IFP .LE. 0) GO TO 22
23 CONTINUE
   READ (5,930) YMN,SPRD
22 IF (IP .LE. 0) GOTO 30
24 READ (5,900) (IB(I), I = 1,IP)
   DO 26 I = 1,IP
   IF (IB(I) .GT. 0) GOTO 26
25 WRITE (6,926)
212 CONTINUE
   IBOUT=1
26 CONTINUE
30 READ (5,931) FF,T,E,TAU, XL, GAMCR, DEL, ZETA
C DUB IN INPUT CONSTANTS IF NOT SUPPLIED
C ( XL IS CHECKED IN FIRST ITERATION )
31 IF (FF .GT. 0.) GOTO 34
32 FF=4.
34 IF (E .GT. 0.) GOTO 37
36 E=.00005
37 IF (TAU .GT. 0.) GOTO 39
38 TAU=.001
39 IF (T .GT. 0.) GOTO 42
40 T=2.
42 IF (K .GT. 25) GOTO 46
44 IBKT=1
   GO TO 50
46 IBKT=2
   REWIND 3
50 IF (GAMCR .GT. 0.) GOTO 52
51 GAMCR = 45.
52 IF (DEL .GT. 0.) GOTO 55
DEL=.00001
55 IF (ZETA*GT.*0.) GO TO 53
ZETA=.1E-30
53 XRDB = 1.
54 CONTINUE
C READ IN INITIAL B GUESSES 7 TO THE CARD
   READ (5,901) (B(I),I=1,K)
   DO 56 I=1,N
56 READ(5,950)Y(I),(X(I,L),L=1,M)
950 FORMAT(2F10.0)
   IWMER=-1
   GO TO 653
59 IBKA=1
C
C ********************************************
C START THE CALCULATION OF THE PTP MATRIX
58 WRITE (6,907)N,K,IP,M,IFP,GAMCR,DEL,FF,TE,TAU,XL,ZETA
213 GO TO 61
60 CONTINUE
   IF (IWS5*NE.*0.) GO TO 61
   IWS3=IWS3+1
   IWS3=MAX0(IWS3,0)
61 DO 62 I=1,K
   G(I) =0.
62 DO 62 J=1,K
   A(I,J)=0.
60 CONTINUE
   GO TO (63,69,69),IBKA
63 IF (IWS5*EQ.*0.)GO TO 630
630 IFSS3=IWS3
   IFSS2=IWS2
   GO TO 70
64 IFSS3=0
66 GO TO (70,65), IFSS2
65 IFSS2=0
   GO TO 70
69  CONTINUE
70  WRITE (6,908) ITCT,(B(J),J=1,K)
214 CONTINUE
   IF (IFSS3.EQ.0) GO TO 73
71  IF (IFP.LE.0) GO TO 68
67  WS = YMN+SPRD
   WRITE( 6,906)YMN,WS
258 CONTINUE
   GO TO 73
68  WRITE( 6,910)
259 CONTINUE
73  I=1
   PHI=0.,
   PHIN=0.,
   ICONS=1
   IF (IFSS2.EQ.0) GO TO 57
   GO TO 600
72  IF (IFSS2.EQ.1) GO TO 602
   C     THIS IS THE ANALYTICAL P S ROUTINE
57  IWHER=1
   C     GET P S AND F
   GO TO 653
75  IF (IP.LE.0) GO TO 80
76  DO 77 II=1,IP
   IWS=IB(II)
77  P(IWS)=0.
   GO TO 80
   C     THIS IS THE ESTIMATED P S ROUTINE
600 CONTINUE
602 IWHER=3
GO TO 653

606 RWS=RES
FSAVE=F
DO 607 II=1,NPRNT
607 SPRNT(II)=PRNT(II)
J=1

608 IF (IP.LE.0) GO TO 618

610 DO 612 II=1,IP
IF ((J-IB(II)).EQ.0) GO TO 621

612 CONTINUE

618 DBW=B(J)*DEL
TWS=B(J)
B(J)=B(J)+DBW
WHERE=4
GO TO 653

620 B(J)=TWS
P(J)=-(RES-RWS)/DBW
GO TO 622

621 P(J)=0.
622 J=J+1
IF ((J-K).LE.0) GO TO 608

624 RES=RWS
F=FSAVE
DO 625 II=1,NPRNT

625 PRNT(II)=SPRNT(II)

END OF ESTIMATED P S ROUTINE

C NOW, USE THE P S TO MAKE PARTIALS MATRIX

80 DO 82 JJ=1,K
G(JJ)=G(JJ)+RES*P(JJ)
DO 82 II=JJ,K
A(II*JJ)=A(II*JJ)+P(II)*P(JJ)
82 A(JJ*II)=A(II*JJ)
IF (IFP .LE. 0) GO TO 318
800 IF (IFSS3 .EQ. 0 .OR. I .GT. N) GO TO 314
     PLOTTING Y(I)*F
     802 IO = (Y(I)-YMN)*100./SPRD
     IPP = (F-YMN)*100./SPRD
     IF (IO.EQ.IPP) GO TO 808
     IF (IO.GT.IPP) GO TO 812
     Y(I) OUT FIRST
     804 IP1=IOCH
     IP2=IPCH
     I1=IO
     I2=IPP
     GO TO 816
     ONLY ONE CHARACTER
     808 IP1=IYCH
     IP2=I8CH
     I1=IO
     I2=IPP
     GO TO 816
     F OUT FIRST
     812 IP1=IPCH
     IP2=I0CH
     I1=IPP
     I2=IO
     ZERO PLOTS IN THE LEFT HAND COLUMN, SO I1 IS ITS
     OWN BLANK COUNTER
     OVERFLOWS PLOT X IN COLUMN 102
     UNDERFLOWS ALSO PLOT X IN COLUMN ZERO
     816 IF (I2 .LE. 101) GO TO 819
     817 I2=101
     IP2=IXCH
     IF (I1.LT.101) GO TO 819
     818 I1=101
IP1=IXCH
IP2=IBCH
GO TO 825
819 IF (I1*GE.0) GO TO 825
822 I1=0
  IP1=IXCH
  IF (I2*GT.0) GO TO 825
823 I2=1
  IP2=IBCH
825 I1M1=I1
  I1M2=I2-I1-1
  IF (I1M1*GT.0) GO TO 832
820 IF (I1M2*GT.0) GO TO 828
824 WRITE (6,928)IP1,IP2
215 CONTINUE
  GO TO 844
828 WRITE (6,928)IP1,(IBCH,II=1,I1M2),IP2
216 CONTINUE
  GO TO 844
832 IF (I1M2*GT.0) GO TO 840
836 WRITE (6,928) (IBCH,II=1,11M1),IP1,IP2
217 CONTINUE
  GO TO 844
840 WRITE (6,928) (IBCH,II=1,11M1),IP1,(IBCH,II=1,11M2),IP2
218 CONTINUE
844 GO TO 314
318 WS=RES
  IF (IFSS3.EQ.0.OR.I,GT.N) GO TO 314
308 IF (NPRNT,GT.0) GO TO 312
310 WRITE (6,925)Y(I),F,WS
219 CONTINUE
  GO TO 314
312 WRITE (6,925)Y(I),F,WS,(PRNT(JJ),JJ=1,NPRNT)
220 CONTINUE
314 WS=RES
    PHI=PHI+WS*WS
    IF (I.GT.N) GO TO 313
    PHIN=PHIN+WS*WS
    GO TO 315
313 CONS(Icons)=RES
    Icons=Icons+1
315 I=I+1
    IF (I.LE.NTILDA) GO TO 72
84 IF (IP.LE.0) GO TO 88
77 DO 87 JJ=1,IP
    IWS=IB(JJ)
    DO 86 II=1,K
        A(IWS,II)=0.
86 A(II,IWS)=0.
87 A(IWS,IWS)=1.
88 GO TO (90,704,703),IBKA
C SAVE SQUARE ROOTS OF DIAGONAL ELEMENTS
90 DO 92 I=1,K
92 SA(I)=SQRT(A(I,I))
    DO 106 I=1,K
    DO 100 J=1,K
        WS = SA(I)*SA(J)
    IF (WS.GT.0.) GOTO 98
96 A(I,J) =0.
    GO TO 100
98 A(I,J)=A(I,J)/WS
100 CONTINUE
    IF(SA(I).GT.0.) GOTO 104
102 G(I)=0.
    GO TO 106
104 G(I)=G(I)/SA(I)
106 CONTINUE
   DO 110 I=1,K
110   A(I,I)=1.
120   PHIZ=PHI
   C
   WE NOW HAVE PHI ZERO
   GO TO (1132,1130),IBKT
1130 WRITE (3)A
   REWIND 3
   GO TO 1134
1132 DO 1133 II=1,K
1133 A(III*JJ)=A(II*JJ)
   C
   ........................................................................
1134 CONTINUE
   IF (ITCT.NE.0) GO TO 163
   C
   FIRST ITERATION
150 IF(XL.GT.0.) GOTO 154
152 XL=0.01
154 DO 161 J=1,K
161 BS(J)=B(J)
   C
   BS(J) CORRESPONDS TO PHIZ
163 IBK1=1
   WS=N-K+IP
   ITCT=ITCT+1
   IF (ITCT.GT.ITAL) GO TO 1800
   SE=SRT(PHIP/WS)
   IF (IFSS3.GT.0) GO TO 165
162 IF (IFSS2.EQ.0) GO TO 168
167 WRITE (6,911)PHIZ,SE,XLL,GAMMA,XL
221 CONTINUE
   GO TO 169
168 WRITE (6,912)PHIZ,SE,XLL,GAMMA,XL
222 CONTINUE
   GO TO 169
165 IF (NCONS.EQ.0) GO TO 166
   WRITE (6,938) (JJ,CONS(JJ),JJ=1,NCONS)
166 WRITE (6,939)
111 DO 114 I=1,K
   WRITE (6,937) I, (A(I,J),J=1,K)
114 CONTINUE
   IF (IFSS2.EQ.0) GO TO 1661
   WRITE (6,903) PHIZ,SE,XL
223 CONTINUE
   GO TO 169
1661 WRITE (6,909)PHIZ,SE,XL
224 CONTINUE
169 GO TO 200
164 PHIL=PHI

C     WE NOW HAVE PHI LAMBDA
   DO 170 J=1,K
   IF (ABS(DB(J))/(ABS(B(J))*TAU)).GE.E) GO TO 172
170 CONTINUE
   WRITE (6,923)
225 CONTINUE
   GO TO 700
172 IF (IWS5.EQ.0) GO TO 1720
1720 IF (IWS4.EQ.0) GO TO 173
   IF (IWS4.EQ.1) GO TO 171
   IWS4=IWS4-1
   GO TO 173
171 WRITE (6,924)
226 CONTINUE
   GO TO 700
173 XKDB = 1.
   IF (PHIL.GT.PHIZ) GO TO 190
174 XLS=XL
    DO 176 J=1,K
    BA(J)=B(J)
176  B(J)=BS(J)
    IF (XL.GT.*.00000001) GO TO 175
175  DO 1176 J=1,K
    B(J)=BA(J)
1176 BS(J)=B(J)
    GO TO 60
177 PHL4=PHI
    WE NOW HAVE PHI(LAMBDA/10)
    IF (PHL4.GT.*PHIZ) GOTO 184
182  DO 183 J=1,K
183   BS(J)=B(J)
    GO TO 60
184  XLS=XL
    DO 186 J=1,K
    BS(J)=BA(J)
186   B(J)=BA(J)
    GO TO 60
190   IBK1=4
    XLS=XL
    XL=XL/10.*
    DO 185 J=1,K
185   B(J)=BS(J)
    GO TO 200
187   IF (PHI.LE.*PHIZ) GOTO 196
191  XL=XLS
    IBK1=3
192  XL=XL#10.*
195  DO 193 J=1,K
193  B(J)=BS(J)
     GO TO 200
194  PHIT4=PHI
     C    WE NOW HAVE PHI(10*LAMBDA)
180  IF (PHIT4.GT.PHIZ) GO TO 198
196  DO 197 J=1,K
197  BS(J)=B(J)
     GO TO 60
198  IF (GAMMA.GE.GAMCR) GO TO 192
199  XKDB = XKDB/2.
     DO 1199 J=1,K
     IF (ABS(DB(J))/(ABS(B(J))+TAU)).GE.E) GO TO 195
1199  CONTINUE
     DO 1200 J=1,K
1200  B(J)=BS(J)
     WRITE (6,934)
     227  CONTINUE
     GO TO 700
     C
     C  ******************************************
     C   SET UP FOR MATRIX INVERSION
     C
     200  GO TO (1102,1100),IBKT
     1100  READ (3)A
     REWIND 3
     GO TO 1104
     1102  DO 1103 II=1,K
     III=II*25
     DO 1103 JJ=1,K
1103  A(II+JJ)=A(III+JJ)
     1104  DO 202 I=1,K
     202  A(I,I)=A(I,I)+XL
     C  GET INVERSE OF A AND SOLVE FOR DB (J)'S
IBKM=1

C

C THIS IS THE MATRIX INVERSION ROUTINE

C K IS THE SIZE OF THE MATRIX

404 CALL GJR(A,K,ZETA,MSING)
GO TO (415,650), MSING
415 GO TO (416,710), IBKM

C END OF MATRIX INVERSION, SOLVE FOR DB(J)

416 DO 420 I=1,K
DB(I)=0.
420 DO 421 J=1,K
DB(I)=A(I,J)*G(J)*DB(I)
421 DB(I)=XKDB*DB(I)
XLL=0.
DTG = 0.
GTG = 0.
DO 250 J=1,K
XLL=XLL+DB(J)*DB(J)
250 DB(J)=DB(J)/SA(J)
KIP=K-IP
IF (KIP.EQ.1) GO TO 1257
CGAM=DTG/SQRT(XLL*GTG)
JGAM = 1
IF(CGAM.GT.0.0) GO TO 253
251 CGAM = ABS(CGAM)
JGAM = 2
253 GAMMA = 57.2957795*(1.5707288+CGAM*(-0.2121144+CGAM*(0.074261
1-CGAM*0.187293)))*SQRT(1.-CGAM)
GO TO (257,255), JGAM
255 GAMMA = 180.*-GAMMA
IF (XL.LT.1.0) GO TO 257
1255 WRITE (6,922) XL,GAMMA
228 CONTINUE
   GO TO 700
1257 GAMMA=0.
257 XLL=SQR(XLL)
   IBK2=1
   GO TO 300
252 IF (IFSS3.EQ.0) GO TO 256
254 WRITE (6,904) (DR(J),J=1,K)
229 CONTINUE
   WRITE (6,905) PHI,XL,GAMMA,XLL
230 CONTINUE
256 GO TO (164,177,194,187),IBK1

C
C ...........................................................................
C
C CALCULATE PHI

300 I=1
   PHI=0.,
   PHIN=0.,
   IWHER=2
   IF (IWS5.EQ.0) GO TO 653
   GO TO 653
304 PHI=PHI+(RES**2)
   IF (I*GT.N) GO TO 305
   PHIN=PHIN+RES*RES
305 I=I+1
   IF (I.LE.NTILDA) GO TO 302
316 IISS = 1
   K1 = K2
   GO TO 999

C
C
C THIS IS THE CONFIDENCE LIMIT CALCULATION

700 DO 702 J=1,K
702 R(J)=BS(J)
C WRITE (6,933)N,K,IP,M,FF,T,TAU
231 CONTINUE
IBKA=2
NTILDA=N
C THIS WILL PRINT THE Y,YHAT,DELTA Y
ITCT=ITCT+1
IFSS3=1
GO TO 61
704 IF (IFP.LE.0) GO TO 703
705 IBKA=3
IFP=0
GO TO 61
703 IF (NCONS.EQ.0) GO TO 706
C WRITE (6,938) (JJ,CONS(JJ),JJ=1,NCONS)
706 WS=N*K+IP
SE=SQR(THI/WS)
PHIZ=PHI
IF (IFSS2.EQ.0) GO TO 709
707 WRITE (6,903)PHIZ,SE,XL
C NOW WE HAVE MATRIX A
708 GO TO (1122,1120),IBKT
232 CONTINUE
GO TO 708
709 WRITE(6,909)PHIZ,SE,XL
C NOW WE HAVE MATRIX A
708 GO TO (1122,1120),IBKT
1120 WRITE (3)A
REWIND 3
GO TO 1124
1122 DO 1123 II=1,K
III=II*25
DO 1123 JJ=1,K
1123 A(III, JJ)=A(II, JJ)
1124 IBKM=2
GO TO 404

C
C  NOW WE HAVE C = A INVERSE

710 DO 711 J=1,K
   IF (A(J,J)*LT.0) GO TO 713
711 SA(J)=SQRT(A(J,J))
   GO TO 715
713 IBOUT=1
715 KST=-4
   WRITE (6,916)
234 KST=KST+5
   KEND=KST+4
   IF (KEND*LT.K) GO TO 719
   KEND=K
719 DO 712 I=1,K
712 WRITE (6,918)I,(A(I,J), J=KST,KEND)
   IF (KEND*LT.K) GO TO 234
   IF (IBOUT*EQ.0) GO TO 717
   WRITE (6,936)
   GO TO 650
717 DO 718 I=1,K
   DO 718 J=1,K
   WS=SA(I)*SA(J)
   IF (WS*GT.0) GO TO 716
714 A(I,J)=0,
   GO TO 718
716 A(I,J)=A(I,J)/WS
718 CONTINUE
   DO 720 J=1,K
A(J,J)=1.
WRITE (6,917)
CONTINUE
KST=9
KST=KST+10
KEND=KST+9
IF (KEND.LT.K) GO TO 722
KEND=K
DO 724 I=1,K
WRITE (6,935) I,(A(I,J),J=KST,KEND)
IF (KEND.LT.K) GO TO 721
C
GET T*SE*SQRT(C(I,I))
DO 726 J=1,K
SA(J)= SE*SA(J)
GO TO (1112,1110)*IBKT
READ (3) A
REWIND 3
GO TO 1114
DO 1113 II=1,K
III=II+25
DO 1113 JJ=1,K
A(II, JJ)=A(III, JJ)
CONTINUE
WRITE (6,919)
CONTINUE
WS=K=IP
DO 750 J=1,K
IF (IP.LE.0) GO TO 743
DO 742 I=1,IP
IF (J.EQ.IB(I)) GO TO 746
CONTINUE
HJTD=SQRT(WS*FF)*SA(J)
STE=SA(J)
OPL=BS(J)=SA(J)+T
OPL=BS(J)+SA(J)*T
SPL=BS(J)+HJTD
WRITE(6,927)J,STE,OPL,OPL,SPL,SPU
SPU=BS(J)+HJTD
239 CONTINUE
GO TO 750
746 WRITE(6,913)J
240 CONTINUE
750 CONTINUE
C  NONLINEAR CONFIDENCE LIMIT
   IF (IWS6.EQ.1) GO TO 650
   WS=K*IP
   WSL=N*K*IP
   PKN=WS/WSL
   PC=PHIZ*(1+FF*PKN)
   WRITE(6,920)PC
241 CONTINUE
WRITE(6,921)
242 CONTINUE
IFSS3=1
K1 = 1
999 DO 790 J = K1,K
   K2 = J
   IF(IISS.EQ.1) GO TO 998
   IISS = 0
   GO TO (252,780,704,762,766,772)*IBK2
998 IBKP=1
   DO 752 JJ=1,K
   752 BJ(JJ)=BS(JJ)
   IF (IP.LE.0) GO TO 758
754 DO 756 JJ=1,IP
   IF (J.EQ.IB(JJ)) GO TO 787
756 CONTINUE
758 DD=-1,
    IBKN=1
760 D=DD
    B(J)=BS(J)+D*SA(J)
    IBK2=4
    GO TO 300
762 PHI1=PHI
    IF (PHI1*GE.*PC) GO TO 770
764 D=D+DE
    IF (D/DD,GE.*5.*) GO TO 788
765 B(J)=BS(J)+D*SA(J)
    IBK2=5
    GO TO 300
766 PHID=PHI
    IF (PHID*LT.*PC) GO TO 764
    IF (PHID*GE.*PC) GO TO 778
770 D=D/2.
    IF (D/DD,LE.*.001) GO TO 788
771 B(J)=BS(J)+D*SA(J)
    IBK2=6
    GO TO 300
772 PHID=PHI
    IF (PHID*GT.*PC) GO TO 770
778 XK1=PHIZ/D+PHI1/(1.-D)+PHID/(D*(D-1.))
    XK2=-((PHIZ*(1.+D))/D/(1.-D)*PHI1+PHID/(D*(D-1.)))
    XK3=PHIZ=PC
    BC = (SQR(T(XK2*XK2-4.*XK1*XK3)-XK2)/(2.*XK1)
    GO TO (779,784), IBKN
779 B(J)=BS(J)+SA(J)*BC
    GO TO 781
784 B(J)=BS(J)+SA(J)*BC
781 IBK2=2
GO TO 300
780 GO TO (782,786),IBKN
782 IBKN=2
    DD=1.
    BL=BL(J)
    PL=PHI
    GO TO 760
786 BU=BU(J)
    PU=PHI
    GO TO (783,795,785,789),IBKP
783 WRITE (6,918) J, BL, PL, BU, PU
243 CONTINUE
    GO TO 790
795 WRITE (6,915) J, BU, PU
244 CONTINUE
    GO TO 790
785 WRITE (6,918) J, BL, PL
245 CONTINUE
    GO TO 790
787 WRITE (6,913) J
246 CONTINUE
    GO TO 790
789 WRITE (6,914) J
247 CONTINUE
    GO TO 790
788 GO TO (791,792),IBKN
C       DELETE LOWER PRINT
791 IBKP=2
    GO TO 780
792 GO TO (793,794),IBKP
C       DELETE UPPER PRINT
793 IBKP=3
    GO TO 780
C

794  IBKP=4
    GO TO 780
790  CONTINUE
    GO TO 10
1800  WRITE(6,1850)
    GO TO 10
C

------------------------------------------------------------------------
900  FORMAT (25I3)
901  FORMAT (7F10.0)
902  FORMAT (18A4)
903  FORMAT (/13X,4H PHI 14X,4H S E 9X,7H LAMBDA 6X,
    1 25H ESTIMATED PARTIALS USED /5X,2E18,8, E13,3 )
904  FORMAT(/12H INCREMENTS 5E18,8/(12X,5E18,8) )
905  FORMAT (13X,4H PHI 10X,7H LAMBDA 6X,7H GAMMA 6X, 7H LENGTH /
    1 5X, E18,8, 3E13,3)
906  FORMAT(1X,1E9,2,86X,1E9,2 /1X,1H+ 99X,1H+ )
907  FORMAT( SH1N = I3,5X,5H K = I3,5X,5H P = I3,5X,5H M = I3,5X,
    1 7H IFP = I3,5X,13H GAMMA CRIT = E10,3,5X,6H DEL = E10,3/6H FF =
    2E10,3,5X,5H T = E10,3,5X,5H E = E10,3,5X,7H TAU = E10,3,5X,6H XL =
    3 E10,3 , 4X, 7HZETA = E10,3 )
908  FORMAT (/2H (I3,13H) PARAMETERS 5E18,8/(18X,5E18,8))
909  FORMAT (/13X,4H PHI 14X,4H S E 9X,7H LAMBDA 6X,
    1 25H ANALYTIC PARTIALS USED /5X,2E18,8, E13,3)
910  FORMAT(1H /5X,9X,4H OBS 13X,5H PRED 13X,5H DIFF )
911  FORMAT (/13X,4H PHI 14X,4H S E 11X,7H LENGTH 6X, 7H GAMMA 6X,
    1 7H LAMBDA 6X, 25H ESTIMATED PARTIALS USED /5X,2E18,8, 3E13,3)
912  FORMAT (/13X,4H PHI 14X,4H S E 11X,7H LENGTH 6X, 7H GAMMA 6X,
    1 7H LAMBDA 6X, 25H ANALYTIC PARTIALS USED /5X,2E18,8, 3E13,3)
913  FORMAT(2X,I3,20H PARAMETER NOT USED )
914  FORMAT(2X,I3,12H NONE FOUND )
915  FORMAT(2X,I3,36X,2E18,8 )
916  FORMAT(1H /13H PTP INVERSE )
917 FORMAT(1H /30H PARAMETER CORRELATION MATRIX )
918 FORMAT( 2X,13,5E18.8)
919 FORMAT( 1H /1H / 13X,4H STD 17X, 16H ONE = PARAMETER 21X ,
1 14H SUPPORT PLANE / 3X, 2H B 7X,6H ERROR 12X, 6H LOWER 12X,
2 6H UPPER 12X, 6H LOWER 12X, 6H UPPER )
920 FORMAT( 1H /1H /30H NONLINEAR CONFIDENCE LIMITS / /
1 16H PHI CRITICAL = E15.8 )
921 FORMAT(1H / 6H PARA 6X,8H LOWER B 8X,10H LOWER PHI 10X,8H UPPER B
1 8X,10H UPPER PHI )
922 FORMAT (1H1,60X,17HGAMMA LAMBDA TEST 6X,2E13.3)
923 FORMAT (1H1,90X,12HEPSILON TEST )
924 FORMAT (1H1,90X,10HFORCE OFF )
925 FORMAT (5X,6E18.8/59X,2E18.8)
926 FORMAT ( 40H BAD DATA* SUBSCRIPTS FOR UNUSED RS = 0 / / / )
927 FORMAT(2X,13,5E18.8 )
928 FORMAT(1H , 110A1 )
929 FORMAT(10A1)
930 FORMAT (7F10.0)
931 FORMAT (8F10.0)
932 FORMAT(1H1)
933 FORMAT(5HON = .I3,5X,5H K = .I3,5X,5H P = .I3,5X,5H M = .I3,5X,
1 6H FF = .E10.3,5X,5H T = .E10.3,
25X,5H E = .E10.3,5X,7H TAU = .E10.3/)
934 FORMAT (1H1,80X,18HGAMMA EPSILON TEST )
935 FORMAT (3X,15,2X,10F10.4)
936 FORMAT (27H0 NEGATIVE DIAGONAL ELEMENT )
937 FORMAT (3X,15,2X,10F10.4/(10X,10F10.4))
938 FORMAT (1H /25H CONSTRAINT RESIDUALS * * *(3X,15,33X,E18.8))
939 FORMAT (1H /23H PTP CORRELATION MATRIX )
1850 FORMAT(//41H ITERATION LIMIT EXCEEDED, RUN TERMINATED)
END
SUBROUTINE GJR(A,N,EPS,MSING)
C GAUSS-JORDAN-RUTISHAUSER MATRIX INVERSION WITH DOUBLE PIVOTING.
DIMENSION A(50,50), B(50), C(50), P(50), Q(50)
INTEGER P, Q
MSING=1
DO 10 K=1,N
C DETERMINATION OF THE PIVOT ELEMENT
  PIVOT=0.
  DO 20 I=K,N
    DO 20 J=K,N
      IF(ABS(A(I,J))=ABS(PIVOT)) 20, 20, 30
    30 PIVOT=A(I,J)
    P(K)=I
    Q(K)=J
  20 CONTINUE
  IF(ABS(PIVOT)-EPS)< 40, 40, 50
C EXCHANGE OF THE PIVOTAL ROW WITH THE KTH ROW
  50 IF(P(K)=K) 60, 60, 60
  60 DO 70 J=1,N
    L=P(K)
    Z=A(L,J)
    A(L,J)=A(K,J)
  70 A(K,J)=Z
C EXCHANGE OF THE PIVOTAL COLUMN WITH THE KTH COLUMN
  80 IF(Q(K)=K) 85, 85, 85
  85 DO 100 I=1,N
    L=Q(K)
    Z=A(I,L)
    A(I,L)=A(I,K)
  100 A(I,K)=Z
  90 CONTINUE
C JORDAN STEP
  DO 110 J=1,N
    IF(130,J,K) 120, 120, 130
  120 B(J)=1./PIVOT
C(J) = 1.
GO TO 140
130 B(J) = -A(K,J)/PIVOT
C(J) = A(J,K)
140 A(K,J) = 0.
110 A(J,K) = 0.
DO 10 I = 1,N
DO 10 J = 1,N
10 A(I,J) = A(I,J) + C(I)*B(J)
C
REORDERING THE MATRIX
DO 155 M = 1,N
K = N - M + 1
IF (P(K) = K) 160, 170, 160
160 DO 180 I = 1,N
L = P(K)
Z = A(I,L)
A(I,L) = A(I,K)
180 A(I,K) = Z
170 IF (Q(K) = K) 190, 155, 190
190 DO 150 J = 1,N
L = Q(K)
Z = A(L,J)
A(L,J) = A(K,J)
150 A(K,J) = Z
155 CONTINUE
151 RETURN
40 PRINT 45,P(K),Q(K),PIVOT
45 FORMAT(16H0 SINGULAR MATRIX 3H I=I3, 3H J=I3, 7H PIVOT=E16.8/)
MSING = 2
GO TO 151
END
SUBROUTINE SUBZ(Y,X,B,PRNT,NPRNT,N)
C
CDC 6400. OCTOBER 1971
DIMENSION Y(500), X(500,1), B(50), PRNT(5), IDEN(7)
READ (5,800) NRUN, IDEN
WRITE (6,801) NRUN, IDEN
WRITE (6,802) NPRINT=1
800 FORMAT(I3,7A10)
801 FORMAT(9H NLIN GH // I4H RUN NUMBER = I3,5X,7A10///)
802 FORMAT(25H PARAMETER IDENTIFICATION///5X,12H B(1) = TAU/5X,12H B(12) = TAU/5X,11H B(3) = ANU/5X,11H B(4) = RNU/5X,22H B(5) = SCALIN
2G FACTOR/5X,18H B(6) = LINE WIDTH///)
RETURN
END
SUBROUTINE FCODE(Y, X, B, PRNT, F, I, RES)
DIMENSION Y(500), X(500,1), B(50), PRNT(5)
PI=3.1415927
TPI=6.2831853
RIT=PI*B(6)
TOR=(B(1)*B(2))/(B(1)+B(2))
DELP=(B(1)-B(2))/(B(1)+B(2))
SNU=0.5*(B(3)+B(4))
DNU=0.5*(B(3)-B(4))
DLGNU=SNU-X(I,1)
P=TOR*(RIT*RIT-TPI*TPI*(DLGNU*DLGNU-DNU*DNU))*RIT
Q=TOR*TPI*(DLGNU*DELP*DNU)
R=TPI*(DLGNU*(1.0+2.0*TOR*RIT)+DELP*DNU)
F=B(5)*(P*(1.0+TOR*RIT)+Q*R)/(P*P*R*R)
RES=Y(I,1)-F
PRNT(1)=X(I,1)
RETURN
END
SUBROUTINE PCODE(P, X, B, PRNT, F, I)
DIMENSION P(50), X(500,1), B(50), PRNT(5)
RETURN
END
PUNNLIN

This programme uses the output of TAPGH as input to punch the cards which are later used as input for STACKGH.
PROGRAM PUNNLIN((OUTPUT,PUNCH,TAPE5,TAPE61=OUTPUT,TAPE62=PUNCH)
C
C PUNCHES NLIN DATA CARDS FOR UP TO 8 PARAMETERS
C PROGRAM IS DESIGNED FOR MAGNETIC TAPE INPUT
C FORMAT IS SUITABLE FOR PLOTTING PROGRAMS
DIMENSION b(10),iden(18),ib(10)
DIMENSION y(200),x(200)
WRITE(61,200)
200 FORMAT(16H PROGRAM PUNNLIN///)
1 READ(5,900)n,k,ip,m,ifp,ncons
WRITE(61,900)n,k,ip,m,ifp,ncons
WRITE(62,900)n,k,ip,m,ifp,ncons
900 FORMAT(25I3)
IF (N.EQ.0) GO TO 15
READ(5,900)ISW1,ISW2,ISW3,ISW4,ISW5,ISW6
WRITE(61,900)ISW1,ISW2,ISW3,ISW4,ISW5,ISW6
WRITE(62,900)ISW1,ISW2,ISW3,ISW4,ISW5,ISW6
READ(5,930)ymn,sprd
WRITE(61,930)ymn,sprd
WRITE(62,930)ymn,sprd
930 FORMAT(7F10.3)
IF (IP.EQ.0) GO TO 3
READ(5,900)(ib(i),i=1,ip)
WRITE(61,900)(ib(i),i=1,ip)
WRITE(62,900)(ib(i),i=1,ip)
3 READ(5,931)ff,te,tau,ql,ga,del,zeta
WRITE(61,931)ff,te,tau,ql,ga,del,zeta
WRITE(62,931)ff,te,tau,ql,ga,del,zeta
931 FORMAT(8F10.3)
READ(5,930)(bi(i),i=1,k)
WRITE(61,930)(bi(i),i=1,k)
WRITE(62,930)(bi(i),i=1,k)
DO 10 i=1,n
READ(5,100)y(i),x(i)
WRITE (61, 100) Y(I), X(I)
WRITE (62, 100) Y(I), X(I)
100 FORMAT (2F10.3)
10 CONTINUE
   READ (5, 101) NRUN, IDEN
   WRITE (61, 101) NRUN, IDEN
   WRITE (62, 101) NRUN, IDEN
101 FORMAT (I3, 14A4)
   GO TO 1
15 STOP 1
   REWIND 5
END
STACK GH

This programme stacks outputs from NLIN GH. Plots of the digitalized spectra are superimposed on the theoretical spectra (smooth curves) calculated from the best fit values of the line shape parameters. The sets of spectra are separated vertically on the plot. The heights and vertical placing of the spectra are calculated automatically.

The original sets of data cards containing the digitalized spectra are used.

Input cards are prepared as follows:

Item 1  Format(I3,18A4)

NSETS Number of sets of spectra to be stacked on each plot. A zero value for NSETS will terminate the run.

IDEN Alphanumeric identification. This is printed on the plot output.

Item 2  Format(3F10.0)

FR 1 Low frequency limit of plot.

FR 2 High frequency limit of plot.

SCALE Plotting scale in mm/Hz.

Item 3  Format(I3,7X,F10.0)

NDATA Number of data pair of digitalized spectrum.

TEMP Temperature of measurement. This is printed on the plot.
Item 4  Format(6F10.0)
        B(1)  Mean lifetime on site A (sec.).
        B(2)  Mean lifetime on site B (sec.).
        B(3)  Chemical shift on site A (Hz).
        B(4)  Chemical shift on site B (Hz).
        B(5)  Scaling factor.
        B(6)  Natural linewidth (Hz).

Item 5  Format(2F10.0)

SPECYL  Y co-ordinate of point in experimental spectrum
SPECXL  X co-ordinate of point in experimental spectrum.

Any number of runs may be stacked one after another.
Each run produces a separate plot. The job is terminated
by a blank card following the last data set.

Items 3, 4, and 5 are repeated for each set of spectra,
i.e. the total number of sets of spectra comprising 3, 4,
and 5 = NSETS for each run.
PROGRAM STACKGH(INPUT, OUTPUT, TAPE3, TAPE60=INPUT, TAPE61=OUTPUT)
C CDC 3300 FORTRAN, FEBRUARY 1971
C CDC 6400 FORTRAN, MAY 1972
C THIS PROGRAM STACKS OUTPUTS FROM NLINGH
C A PLOT OF THE DIGITIZED SPECTRUM IS SUPERIMPOSED ON THE SPECTRUM
C CALCULATED FROM THE BEST FIT PARAMETERS
C B(1) = MEAN LIFETIME IN SECONDS ON SITE A
C B(2) = MEAN LIFETIME IN SECONDS ON SITE B
C B(3) = CHEMICAL SHIFT IN HZ ON SITE A
C B(4) = CHEMICAL SHIFT IN HZ ON SITE B
C B(5) = SCALING FACTOR
C B(6) = LINE WIDTH IN HZ
C
DIMENSION IDEN(7), Y(3000), B(6), KRAY(14), SPECX(200), SPECY(200)
WRITE(61, 200)
200 FORMAT(16H1) PROGRAM STACKGH///
1 READ(60, 201) NSETS, IDEN
201 FORMAT(13, 7A10)
IF (NSETS.EQ.0) GO TO 50
NPLOT = 0
SETS=NSETS
HEIGHT=200.0/SETS
RISE=HEIGHT/25.4
BASE=-RISE
READ(60, 203) FX1, FR2, SCALE
203 FORMAT(3F10.0)
WRITE(61, 204) IDEN
204 FORMAT(10X, 7A10///)
WRITE(61, 206) FR1, FR2, SCALE, HEIGHT
206 FORMAT(20H PLOTTING PARAMETERS/// 5X, 18H FREQUENCY RANGE = *F8.2*4H T
10 *F8.2*3H HZ/5X, 9H SCALE = *F6.2*6H MM/HZ, 5X, 10H HEIGHT = *F6.2*3
2H M4)
DENS=100.0
XMAX=SCALE*(FR2-FR1)/25.4
NPOINT=DENS*XMAX+0.5
IF (NPOINT.GT.3000) NPOINT=3000
STEP=(FR2-FR1)/NPOINT

C
DRAW AXES AND TICK MARKS
LY=XMAX+6.0
YL=(FR2-FR1)*FLOAT(LY)/XMAX
YLOW=FR1-DENS*STEP*1.5
CALL SAXES(3+10+LY+1.0,10+0+YL+0.0,YLOW+0.0,YLOW)
YT=FR1
CALL PLOTXY(9.9,YT+0.0)
CALL PLOTXY(10.0,YT+1.0)
30 YT=YT+5.0
YLM=YL+YL
IF (YT.GT.FR2) GO TO 35
CALL PLOTXY(10.0,YT+1.0)
CALL PLOTXY(9.95,YT+1.0)
CALL PLOTXY(10.0,YT+1.0)
YT=YT+5.0
IF (YT.GT.FR2) GO TO 35
CALL PLOTXY(10.0,YT+1.0)
CALL PLOTXY(9.9,YT+1.0)
CALL PLOTXY(10.0,YT+1.0)
GO TO 30
35 CONTINUE

C
PROCESS SETS OF SPECTRA
DO 45 II=1,NSETS
NPLPT=NPLPT+1
BASE=BASE+RISE
READ(50,210)NUDATA,TEMP
210 FORMAT(I3,7X,F10.0)
WRITE(61,211)NPLT,TEMP
211 FORMAT(/'I3,T4X,14HTEMPERATURE = ',F5.1//)
READ(60,202)B(1),B(2),B(3),B(4),B(5),B(6)
202 FORMAT(6F10.0)
WRITE(61,205)B(1),B(2),B(3),B(4),B(5),B(6)
205 FORMAT(/'3H CALCULATION PARAMETERS/'5X,32HMAN LIFETIME ON SITE A (1SEC) = ',F8.4,5X,32HMAN LIFETIME ON SITE B (SEC) = ',F8.4,5X,32HCMCHEMICAL SHIFT ON SITE A (HZ) = ',F8.2,5X,32HCMCHEMICAL SHIFT ON SITE B (HZ) = ',F8.2,5X,32HLINEWIDTH (HZ) = ',F8.2//)
DO 10 I=1,NDATA
10 READ(60,207)SPECY(I),SPECX(I)
207 FORMAT(2F10.0)
WRITE(61,208)
208 FORMAT(/'3H DIGITIZED SPECTRUM/'5X,9HINTENSITY,5X,9HFREQUENCY//)
DO 15 I=1,NDATA
15 WRITE(61,209)SPECY(I),SPECX(I)
209 FORMAT(3X,F10.3,5X,F10.3)

C
calculate theoretical spectrum
PI=3.1415927
TPI=6.2831853
RIT=PI*B(6)
TOR=(B(1)+B(2))/(B(1)+B(2))
DELP=(B(1)-B(2))/(B(1)+B(2))
SNU=0.5*(B(3)+R(4))
DNU=0.5*(B(3)-R(4))
FREQ=FRI*STEP
DO 20 I=1,NPOINT
FREQ=FREQ+STEP
DLGNU=SNU-FREQ
PU=TOR*(RIT*RIT-TPI*TPI)*((DLGNU*DLGNU-DNU*DNU))**RIT
QU=TOR*TPI*(DLGNU*DELP*DNU)
RU = TPI * (ULGNUM * (1.0 + 2.0*TUR*RIT) + DELP*DNUM)  
FU = (PU * (1.0 + TOR*RIT) + QU*RU) / (PU*PU + RU*RU)  
20    Y(I) = FU*H(B)

C

SCALE BOTH SPECTRA TO CALCULATED HEIGHT
YMAX = Y(I)
DO 21 I = 2, NPPOINT
IF (YMAX*GT Y(I)) GO TO 21
YMAX = Y(I)
21    CONTINUE
FACTOR = HEIGHT / (25.4 * YMAX)
DO 28 I = 1, NPPOINT
28    Y(I) = Y(I) * FACTOR
DO 29 I = 1, NDATA
29      SPECY(I) = SPECY(I) * FACTOR

C

PLOT THE SPECTRA
ENCOD(60*110*KRAY(1)) TEMP, B(1), B(2)
110    FORMAT (F6.1, B6.2, 8X, F6.4, 6H SEC., 8X, F6.4, 6H SEC., 8X)
XP1 = 8.95 - BASE
XP2 = 9.30 - BASE
XP3 = 9.60 - BASE
X = XP1
YYY = 9.85 - Y(NPOINT) - BASE
CALL PLOTXY (YYY, X, 0, 0)
DO 24 I = 2, NPPOINT
J = NPPOINT + 1
X = X + STEP
YYY = 9.85 - Y(J) - BASE
24    CALL PLOTXY (YYY, X, 1, 0)
Y2 = YLOW + YL*(FLOAT(LY) - 0.6)/FLOAT(LY)
Y3 = YLOW + 0.1*YL/FLOAT(LY)
XSUM = FR1 + FR2

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DO 40 I=1,NDATA
XX=XSUM-SPECX(I)
YSPEC=Y5-SPECY(I)-BASE
40 CALL PLOTXY(YSPEC,XX,0,Y)
CALL PLOTXY(XP1,FR2,0,Y)
CALL LABEL(11*13,KRAY(1))
CALL PLOTXY(XP2,FR2,0,Y)
CALL LABEL(11*13,KRAY(3))
CALL PLOTXY(XP3,FR2,0,Y)
CALL LABEL(11*13,KRAY(5))
C
C PROCESS NEXT PAIR OF SPECTRA
45 CONTINUE
CALL PLOTXY(0,0,YLOW,0,Y)
WRITE(61,100)
100 FORMAT(//'SUMMARY OF PLOT CALCULATIONS//)
WRITE(61,102)NPOINT
102 FORMAT(9X*28H NUMBER OF POINTS PLOTTED = ,I4)
WRITE(61,105)LY
105 FORMAT(37H LENGTH OF FREQUENCY AXIS (INCHES) = ,I3)
WRITE(61,106)YL
106 FORMAT(3X*34H LENGTH OF FREQUENCY AXIS IN HZ = ,F7.2)
WRITE(61,107)FR1,X
107 FORMAT(10X,27H FREQUENCY RANGE PLOTTED = ,F7.2,4H TO ,F7.2,3H HZ//
1//)
END FILE 3
C
C START NEXT CASE
GO TO 1
50 CONTINUE
END FILE 3
REWIND 3
STOP 1
END
ACTPAR

This programme calculates Arrhenius and Eyring activation parameters and 90% confidence intervals from inputted lifetimes and temperatures. It uses a linear regression method to fit the Arrhenius equation in logarithmic form to the input data, i.e. the equation is in the form

$$\ln \left( \frac{1}{\tau} \right) = \ln (A) - \frac{E_a}{RT}$$

the independent variable being $\ln(T)$ and the dependent variable being $\ln(1/\tau)$. Error analysis is given at each stage of the calculation, i.e. following the regression calculations, following the Arrhenius calculations, and following the Eyring calculations. The Eyring parameters are calculated (with 90% confidence limits) at a temperature specified by the user.

Data cards are prepared as follows:

<table>
<thead>
<tr>
<th>Item</th>
<th>Format</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Format(I3,7A10)</td>
<td>Run number. Any non-zero number will do.</td>
</tr>
<tr>
<td>NRUN</td>
<td></td>
<td>A zero value for NRUN will terminate the job.</td>
</tr>
<tr>
<td>IDEN</td>
<td></td>
<td>Alphanumeric identification.</td>
</tr>
<tr>
<td>2</td>
<td>Format(Fl0,0)</td>
<td>Temperature ($^\circ K$) at which the Eyring parameters are to be calculated.</td>
</tr>
</tbody>
</table>
Item 3  Format(2F10.0)
TC(I)  Temperature of measurement in °C.
TAU(I)  Mean lifetime in seconds.
Item 4  Blank card.†

Data sets (Items 1-4) may be stacked one after another.
The run is terminated by an additional blank card.§

† ACTPAR does its own counting of data cards. This card
signals the end of the experimental data set.

§ This means that there will be two blank cards at the
end of the complete data deck.
PROGRAM ACTPAR(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)

SIR GEORGE WILLIAMS UNIVERSITY. NOVEMBER, 1971.

FORTRAN IV FOR CDC 6400.

CALCULATION OF ARRHENIUS AND EYRING ACTIVATION PARAMETERS USING
LINEAR REGRESSION ANALYSIS.

LINEAR REGRESSION ANALYSIS BASED ON
LARK, CRAVEN, AND BOSWORTH, "THE HANDLING OF CHEMICAL DATA".
CONFIDENCE LIMITS ARE BASED ON SLOPE AND INTERCEPT OF ARRHENIUS LINE
K = A*EXP(-EACT/RT)

DIMENSION IDEN(7),TAU(50),TC(50),TK(50),TR(50),REXP(50),RFIT(50),
1HEXP(50),SEXp(50),SFIT(50),GEXP(50),GFIT(50)
DIMENSION ALKE(50),ALKR(50)
GK=1.98646E-3
BK=1.38049E-16
PK=6.6254E-27
RKH=BK/PK
ALNR=ALOG(RKH)

1 READ(5,100)NRUN,IDEN
100 FORMAT(I3,7A10)
   IF (NRUN.EQ.0) STOP 1
   WRITE(6,101)
101 FORMAT(15H1PROGRAM ACTPAR:///1X,15(1H*),* ARRHENIUS AND EYRING ACT
   IVATION PARAMETERS AND 90 PERCENT CONFIDENCE INTERVALS */15(1H*)//
2/)
   READ(5,102)TEMP
102 FORMAT(F10.0)
   I=1
2 READ(5,103)TC(I),TAU(I)
103 FORMAT(2F10.0)
IF (TAU(I) .EQ. 0.0 .AND. TC(I) .EQ. 0.0) GO TO 3
I=I+1
GO TO 2
3 NDATA=I-1

C
WRITE OUT EXPERIMENTAL DATA
WRITE(6,105)NRUN,IDEN
105 FORMAT(* CASE NUMBER *,I3,1X,7A10,/**/
WRITE(6,106)
106 FORMAT(/1X,6(1H*),* EXPERIMENTAL LIFETIMES, RATE CONSTANTS, AND TE
1MPERATURES *,6(1H*)/**/
WRITE(6,110)
110 FORMAT(5X,*POINT*,5X,*LIFETIME*,5X,*RATE CONSTANT*,5X,*DEGREES C.*,5X
1,*DEGREES K,*/15X,* (SECONDS)*,5X,*(1/SECOND)*/*
DO 4 I=1,NDATA
TK(I)=TC(I)+273.16
REXP(I)=1.0/TAU(I)
TR(I)=1000.0/TK(I)
WRITE(6,111)I,TAU(I),REXP(I),TC(I),TK(I)
4 CONTINUE

C
LINEAR REGRESSION CALCULATIONS
WRITE(6,120)
120 FORMAT(/1X,21(1H*),** LINEAR REGRESSION TO ARRHENIUS EQUATION **,
120(1H*)/**)
SUMX=SUMY=SUMXX=SUMYY=SUMXY=0.0
DO 6 I=1,NDATA
ALKE(I)=ALOG(REXP(I))
SUMX=SUMX+1.0/TK(I)
SUMY=SUMY+ALKE(I)
SUMXX=SUMXX+1.0/TK(I)**2
SUMXY=SUMXY+(ALOG(REXP(I)))/TK(I)
SUMYY=SUMYY*(ALOG(REXP(I))**2
6 CONTINUE
NF=NDATA-2
FN=NF
PN=NDATA
XAV=SUMX/PN
YAV=SUMY/PN
CSUMXX=SUMXX-PN*(XAV**2)
CSUMYY=SUMYY-PN*(YAV**2)
CSUMXY=SUMXY-PN*XAV*YAV
SLOPE=CSUMXY/CSUMXX
YINT=YAV-SLOPE*XAV
EACT=-GK*SLOPE
A = EXP(YINT)

ARRHENIUS PARAMETER CONFIDENCE INTERVAL CALCULATIONS
DSUMYY=CSUMYY-SLOPE*CSUMXY
STERR2=DSUMYY/FN
STERR=SQRT(STERR2)
ERSLOPE=STERR/SQRT(CSUMXX)
W1=SUMXX/(PN*CSUMXX)
ERINT=STERR/SQRT(W1)
EACTERR=GK*ERSLOPE
WRITE(6,121)
121 FORMAT(/* COMPARISON OF EXPERIMENTAL AND REGRESSION VALUES OF LN(RATE CONSTANT)*//5X*POINT*5X*LN(KEXP)*5X*LN(KFIT)*5X*DIFFERENCE 2NCE*5X*DEGREES C*/)
DO 20 I=1,NDATA
ALKR(I)=YINT+SLOPE/TK(I)
DY=ALKE(I)-ALKR(I)
RY=DY/STERR
WRITE(6,122)I,ALKE(I),ALKR(I),DY,RY,TC(I)
122 FORMAT(6X,I2,5X,F8.3,5X,F8.3,6X,F8.3,8X,F8.2,7X,F8.1)
20 CONTINUE
    WRITE(6,123)
123  FORMAT(///1X,4('1H*'),* STANDARD LINEAR REGRESSION ERRORS *,5(1H*)//
         1/)
    WRITE(6,124)STERR
124  FORMAT(5X,* STANDARD ERROR IN REGRESSION = *,F8.3/)
    WRITE(6,125)ERINT
125  FORMAT(5X,* STANDARD ERROR IN INTERCEPT = *,F8.3/)
    WRITE(6,126)ERSLOPE
126  FORMAT(10X,* STANDARD ERROR IN SLOPE = *,F8.3/)
    ST=0.0
    CALL STUDENT(NF,ST)
C 90 PERCENT CONFIDENCE INTERVAL IN LN(K) AT A CHOSEN TEMPERATURE
C W2=1.0/PN*(1.0/TEMP*XAV)**2)/CSUMXX
C ERR=STERR*SQRT(W2)
C CIY=ST*ERRY
C 90 PERCENT CONFIDENCE INTERVAL IN SLOPE
C CISLOPE=ST*ERSLOPE
C 90 PERCENT CONFIDENCE INTERVAL IN INTERCEPT
C CIYINT=ST*ERINT
C LOGA=YINT/2.303
C LOGIA=CIYINT/2.303
C 90 PERCENT CONFIDENCE INTERVAL IN ACTIVATION ENERGY
C CIE=6K*CISLOPE
C ELO=EA CT=CIE
C EHI=EA CT+CIE
C YINTHI=YINT+CIYINT
C YINTL0=YINT-CIYINT
C ALO=EXP(YINTL0)
C AHI=EXP(YINTHI)
    WRITE(6,130)
130  FORMAT(///1X,38('1H*'),* ARRHENIUS ACTIVATION PARAMETERS *,38('1H*')//
         1* ACTIVATION PARAMETERS AND STANDARD ERRORS*//*)
WRITE(6,134)EACT,EACTER
134 FORMAT(5X,**ACTIVATION ENERGY = **F7.3,5X,**STANDARD ERROR = **F6.3)
WRITE(6,135)YINT,ERINT
135 FORMAT(8X,**NATURAL LOG(A) = **F7.3,5X,**STANDARD ERROR = **F6.3/)
WRITE(6,136)
136 FORMAT(/** ACTIVATION PARAMETERS AND CONFIDENCE LIMITS*/)
WRITE(6,131)ACT,CIE,ELO,EHI
131 FORMAT(5X,**ACTIVATION ENERGY = **F7.3,3X,**(OR=)**F6.3,5X,
1*LOWER LIMIT = **F7.3,3X,**UPPER LIMIT = **F7.3,2X,**KCAL/MOLE*)
WRITE(6,132)A,ALO,AIM
132 FORMAT(6X,**FREQUENCY FACTOR = **E10.4,5X,**LOWER LIMIT = **E10.4,
13X,**UPPER LIMIT = **E10.4)
WRITE(6,137)YINT,CIYINT
137 FORMAT(8X,**NATURAL LOG(A) = **F7.3,3X,**(OR=)**F6.3)
WRITE(6,133)CLOGA,CLOGIA
133 FORMAT(9X,**COMMON LOG(A) = **F7.3,3X,**(OR=)**F6.3)

C
CALCULATE EYRING PARAMETERS
WRITE(6,140)
140 FORMAT(///1X,31(1H*),** EYRING ACTIVATION PARAMETERS **31(1H*)//)
WRITE(6,141)
141 FORMAT(5X,**POINT**8X,**ENTHALPY**10X,**------ENTROPY (E.U.)------**,110X,**FREE ENERGY (KCAL/MOLE)**/17X,**(KCAL/MOLE)**9X,**EXP.**6X,
2*FIT**5X,**DIFF.**11X,**EXP.**5X,**FIT**5X,**DIFF.*)
DO 14 I=1,NDATA
HEXP(I)=EACT-GK*TK(I)
GEXP(I)=(GK*TK(I))*((ALNR+ALOG(TK(I))=ALOG(REXP(I))))
SEXP(I)=1000.0*(HEXP(I)-GEXP(I))/TK(I)
RFIT(I)=A*EXP(SLOPE/TK(I))
GFI(T(I)=(GK*TK(I))*((ALNR+ALOG(TK(I))=ALOG(RFIT(I))))
SFI(T(I)=1000.0*GK*(YINT-ALNR+ALOG(TK(I)))-1.0)
DIFFS=SEXP(I)-SFI(T(I)

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DIFFG=GEXP(I)-GFIT(I)
WRITE(6,141)I,HEXP(I),SEXPI(I),SFIT(I),DIFFS,GEXP(I),GFIT(I),DIFFG
141 CONTINUE

C CALCULATE EYRING PARAMETERS FOR A SPECIFIC TEMPERATURE
WRITE(6,150)TEMP
150 FORMAT(8X{/* EYRING ACTIVATION PARAMETERS CALCULATED FOR *F5.1,*/
1* DEG.*K.*//34X,*(+OR-)*,6X,*INTERVAL*,6X,*LOWER*,8X,*UPPER*/)
YTEMP=YINT+SLOPE/TEMP
YLO=YTEMP-CIY
YHI=YTEMP+CIY

C 90 PERCENT CONFIDENCE INTERVAL IN FREE ENERGY
RTEMP=A*EXP(SLOPE/TEMP)
GT=(GK*TEMP)*(ALNR+ALOG(TEMP)-ALOG(RTEMP))
GLO=(GK*TEMP)*(ALNR+ALOG(TEMP)-YHI)
GHI=(GK*TEMP)*(ALNR+ALOG(TEMP)-YLO)
GERR=GHI-GLO
GERR2=GERR/2.0

C 90 PERCENT CONFIDENCE INTERVAL IN ENTHALPY
HT=EMCT+GK*TEMP
HLO=EL0-GK*TEMP
HHI=EH1-GK*TEMP
HERR=HHI-HLO
HERR2=HERR/2.0

C 90 PERCENT CONFIDENCE INTERVAL IN ENTROPY
STD=1000.0*GK*(YINT-ALNR-ALOG(TEMP)-1.0)
SLO=1000.0*GK*(YINTLO-ALNR-ALOG(TEMP)-1.0)
SHI=1000.0*GK*(YINTHI-ALNR-ALOG(TEMP)-1.0)
SERR=SHI-SLO
SERR2=SERR/2.0
WRITE(6,151)HT,HERR2,HERR,HLO,HHI
151 FORMAT(8X,*ENTHALPY = *F7.3*4(6X,F7.3),2X,*KCAL/MOLE*/)

WRITE(6,152) STD,SERR2,SERR,SLO,SHI
152 FORMAT(9X,*ENTROPY = *F6.2*4(7X,F6.2),3X,**E*U,*)
WRITE(6,153) GT,GERR2,GERR,GLO,SHI
153 FORMAT(5X,*FREE ENERGY = *F7.3*4(6X,F7.3),2X,*KCAL/MOLE*)
WRITE(6,154) RTEMP,TEMP
154 FORMAT(/3X,*RATE CONSTANT =,E10.4,* (1/SEC) AT *,F5.1,  
1* DEGREES K,*)
CLT=1.0/RTEMP
WRITE(6,155) CLT,TEMP
155 FORMAT(8X,*LIFETIME =,E10.4,* (SEC) AT *,F5.1,  
1* DEGREES K,*)
C
C CALCULATE DATA FOR PLOTTING
WRITE(6,160)
160 FORMAT(/4(1H*),* DATA FOR PREPARATION OF ARRHENIUS PLOT *,4(1H*)  
1//5X,*POINT*,5X,*LN(KEXP)*,5X,*LN(KFIT)*,5X,*1000/T*  
DO 60 I=1,NDATA
WRITE(6,161) I,ALKE(I),ALKR(I),TR(I)
161 FORMAT(6X,I2,5X,F8.3,5X,F8.3,4X,F8.3)
60 CONTINUE
WRITE(6,199)
199 FORMAT(/2(1X,110(1H*))  
C
C START NEXT CASE
GO TO 1
END
SUBROUTINE STUDENT(NF,VAL)

C STUDENTS T VALUES FOR 90 PERCENT CONFIDENCE LIMITS
DIMENSION T(48)
T(1)=6.314
T(2)=2.920
T(3)=2.353
T(4)=2.132
\[ T(5) = 2.015 \]
\[ T(6) = 1.943 \]
\[ T(7) = 1.895 \]
\[ T(8) = 1.860 \]
\[ T(9) = 1.833 \]
\[ T(10) = 1.812 \]
\[ T(11) = 1.796 \]
\[ T(12) = 1.782 \]
\[ T(13) = 1.771 \]
\[ T(14) = 1.761 \]
\[ T(15) = 1.753 \]
\[ T(16) = 1.746 \]
\[ T(17) = 1.740 \]
\[ T(18) = 1.734 \]
\[ T(19) = 1.729 \]
\[ T(20) = 1.725 \]
\[ T(21) = 1.721 \]
\[ T(22) = 1.717 \]
\[ T(23) = 1.714 \]
\[ T(24) = 1.711 \]
\[ T(25) = 1.708 \]
\[ T(26) = 1.706 \]
\[ T(27) = 1.703 \]
\[ T(28) = 1.701 \]
\[ T(29) = 1.70 \]
\[ T(30) = 1.70 \]

DO 1 I = 31, 35

1 CONTINUE

DO 2 I = 36, 48

2 CONTINUE

VAL = T(NF)
RETURN
END
This programme will supply listings of source programmes suitable for theses.

Cards are prepared as follows:

Item 1  Format(I2)
        NUM     The number of copies of programme required.
        The run terminates if NUM is zero.
Item 2  Card deck to be listed.
Item 3  An end of deck card with 9999 punched in columns 77-80. This card signals the end of the deck to be listed.
Item 4  A blank card to terminate the run.†

† Items 1 through 3 may be repeated for more than one deck.
PROGRAM TLIST(INPUT,OUTPUT,TAPE60=INPUT,TAPE61=OUTPUT)
DIMENSION LINE(19,900)
1 READ(60,900)NUM
   IF (NUM.EQ.0) GO TO 10
   ICT=0
   NN=1
2 READ(60,901)(LINE(I,NN),I=1,19),ISTOP
   IF (ISTOP.EQ.9999) GO TO 3
   ICT=ICT+1
   NN=NN-1
   GO TO 2
3 CONTINUE
   IX=1
4 J=1
5 ICT2=1
   WRITE(61,903)
   WRITE(61,904)
   WRITE(61,904)
   WRITE(61,904)
   WRITE(61,905)(LINE(I,J),I=1,19)
   ICT2=ICT2+1
   J=J+1
6 WRITE(61,905)(LINE(I,J),I=1,19)
   ICT2=ICT2+1
   J=J+1
   IF (J.GT.ICT) GO TO 7
   IF (ICT2.GT.33) GO TO 5
   GO TO 6
7 IX=IX+1
   IF (IX.LE.NUM) GO TO 4
   GO TO 1
900 FORMAT(I2)
901 FORMAT(19A4,I4)
903 FORMAT(1H1)
904 FORMAT(1H--)
905 FORMAT(12X,19A4)
10 STOP 1
END