Carbon-13 Nuclear Magnetic Resonance (NMR) Relaxation of Alkyl Chains in the 5CB

by

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CARBON-13 NUCLEAR MAGNETIC RESONANCE (NMR)

RELAXATION OF ALKYL CHAINS IN THE 5CB

BY

ABDELMONEM ALI HRESHA

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

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To My Father

I would like to dedicate this thesis to my father who passed away on Dec. 16, 1992.

May Allah grant him paradise ameen.

Abstract

In the present study; Carbon-13 nuclear magnetic resonance proton decoupled relaxation of the alkyl chains has been considered in the 5CB, and the results has been compared to deuterium relaxation in alkyl chains. In this work a previous model that worked well has been extended for the aromatic core. The following improvements has been introduced:

1. Experimental order parameters is used for the individual positions.
2. The formulas for correlation times in terms of one or more diffusion time(s) are found and evaluated.
3. The diffusion times are fitted to the experimental ^{13}C results.

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CHAPTER 1

Introduction

1.1 The History of NMR spectroscopy

The development of magnetic resonance spectroscopy ranks among the most important advances in chemical physics during the past four decades. The principal ideas behind magnetic resonance are common to both electron spin resonance (E.S.R) and nuclear magnetic resonance (N.M.R), but there are differences in the magnitudes and signs of the magnetic interactions involved, which naturally lead to divergence in the experimental techniques employed [CMD].

The history of NMR spectroscopy is a classic example of the development of an original discovery in one branch of science leading to a routine technique used in all branches of chemical science [LOF]. The first NMR signals were independently observed by two groups of physicists in 1945; Bloch, Hanser and Packard at Stanford University detected a signal from the protons of water, and Purcell, Torrey and Pound at Harvard University observed a signal from the protons in paraffin wax. Bloch and Purcell were jointly awarded the Nobel Prize for physics in 1952 for this discovery. In 1949 and 1950, a number of investigators noted that nuclei of the same species absorbed energy at different frequencies and so the phenomenon of the chemical shift was discovered. Since that time, the development of NMR techniques has been rapid. The first commercial high resolution proton NMR spectrometer was produced in 1953 and such CW (Continuous Wave) proton spectrometers were an integral part of most research and teaching laboratory for

many years.

The greater problems associated with ^{13}C NMR, mainly due to the much lower sensitivity of this nucleus in natural abundance compared with protons, were not satisfactory overcome until the introduction of commercial FT (Fourier transformation) spectrometers about 1970 [LOF]. Now, however, FT spectrometers are an essential part of most modern laboratories and with this technique the NMR signals of almost any nucleus with magnetic moment can be detected routinely, and the relaxation behavior of the spins studied.

1.1.1 The Discovery of Liquid Crystals

The discovery of liquid crystals dates back to one hundred years ago. The term ' liquid crystal' implies a state intermediate between the liquid and crystalline states, partaking somewhat of the properties of both. This description is especially apt for NMR spectra but, in many cases not for NMR relaxation [CHN] . As will be considered below, we are concerned here with the class of liquid crystal referred to as 'thermotropic': organic molecules which display a mesogenic phase or phases between their solid and liquid phases.

Let us limit ourselves to simple NMR interactions, specifically interactions which either do not involve interactions between spins, that is to quadrupole interactions and chemical shifts, or else interactions between but two spins, namely dipole-dipole interaction. The study of NMR relaxation provides, in principle, a powerful means of studying the molecular dynamics of liquid crystal [DON,EMS]. In particular, with NMR the experimentalist has the unique ability to observe the dynamical behavior of individual atomic sites in a molecule [SHM].

To interpret these observation requires theories which explain not only the general but also the detailed features of the molecular dynamics involved. One

powerful test of the validity of NMR theories of relaxation in a liquid crystal is to compare deuterium relaxation with the carbon-13 relaxation of a carbon bound to the equivalent proton in an undeuterated molecule [VLD].

In the present study We consider carbon-13 nuclear magnetic resonance proton decoupled relaxation of the alkyl chains in the 5CB, and compare the results to deuterium relaxation in alkyl chains. We extend a previous model that worked well for the aromatic core, and introduce the following changes:

1. Experimental order parameters is used for the individual positions.
2. The formulas for correlation times in terms of one or more diffusion time(s) are found and evaluated.
3. The diffusion times are fitted to the experimental ^{13}C results.

To show that the results are plausible, the model is then used to predict something else; specifically the deuterium relaxation times and/or the high field ^{13}C relaxation times.

1.2 Nuclear Spin Relaxation

There are a large number of published papers concerned with nuclear spin relaxation in liquid crystalline samples [WAD]. The majority of these observe the decay of a perturbed proton magnetization and most observe only the total magnetization arising from all protons. these experiments yield just one relaxation time, which is difficult, if not impossible to relate to the details of molecular motion in the liquid crystalline phase [LUK]. The molecules forming liquid crystal phases are almost invariably non-rigid and of low symmetry. As a consequence, describing their detailed motion is a formidable task requiring, in general, numerous time dependent angular correlation functions. Nuclear spin relaxation studies

can provide a useful test of theories of motion if relaxation data related to several different sites in a molecule can measured a different temperatures and at different nuclear resonance frequencies.

The most general methods of studying nuclear spin relaxation at several sites in a mesogen are to use either deuterium [LIN] or carbon-13 resonance [CHA,FGE,HUT]. For the latter it is essential to decouple all the protons whilst observing the carbon resonances, but available experimental methods can lead to extensive sample heating. As a consequence carbon-13 NMR is difficult to apply to the study of relaxation in liquid crystalline samples where temperature stability is essential. The method does resolve several locations on the core, but resolution of the chain deteriates for long chains. However, deuteron magnetic resonance is an excellent method for investigating relaxation phenomena provided that suitably deuteriated mesogens can be synthesized. The spectra comprise well separated doublets from the chain, but the aromatic core locations are not well resolved, arising from the nuclear electric quadrupole interaction and spin relaxation is dominated by the fluctuations in time of the laboratory components of this interaction and is entirely intramolecular in origin. The site selectivity of the spectra is demonstrated in figure 1.1 by the deuteron NMR spectrum of the nematogen 4-n-pentyl-d_{11}-4'-cyano-2,3,5,6-d_4-biphenyl (5CB-d_{15}) whose structure and nuclear labeling are shown in figures 1.2 and 1.3. We will use this selectivity to allow a re-interpretation of the alkyl carbon-13 spectra in the nematic phase. The spectra 5CB is shown in figure 2.1.

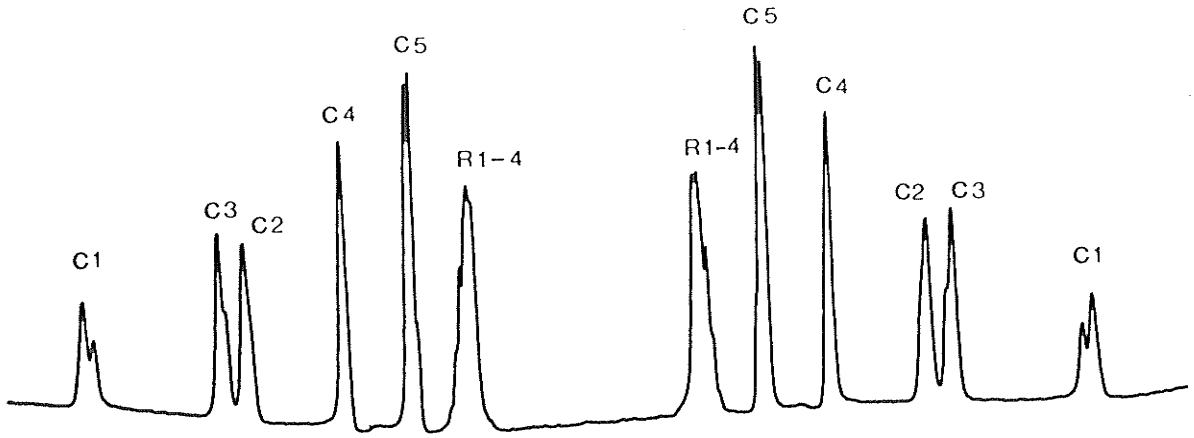

Figure 1.1: **30.7 MH_Z deuteron NMR spectrum of 4-n-pentyl -d_{11}-4'-cyano-2,3, 5,6- d_4-biphenyl (5CB-d_{15}) in the nematic phase. The peaks are labelled with their assignment using the numbering of figures 1.2 and 1.3 (from [TUR]).**

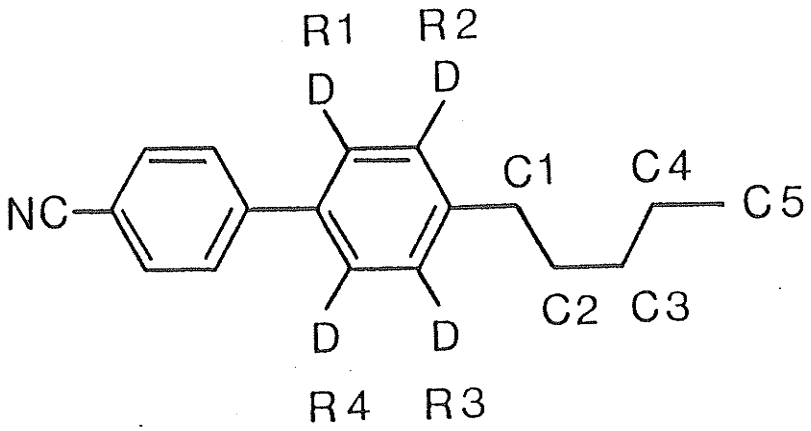

Figure 1.2: **molecule of 5CB-d_{15} showing the atomic labelling (from [TUR]).**

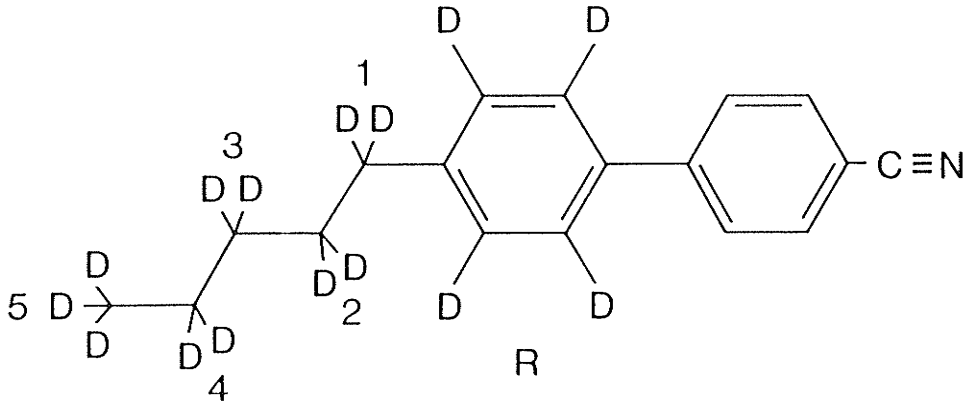

Figure 1.3: **The molecule 4-n-pentyl-$d_1$1-4'-cyanobiphenyl-d_4 showing the nuclear labelling of the deuterons used (from [BEC]).**

CHAPTER 2

CHAPTER 2

Theory

In the conventional experiment a π pulse is used to invert the spins and the recovery observed with a $\pi/2$ pulse. For the case of Carbon-13 it is assumed that appropriate proton decoupling is used. For the case considered here the recovery is indeed exponential and follows:

$$M_z(t) = M_0(1 - 2\ e^{-t/T_{1Z}}) \tag{2.1}$$

We desire to calculate T_{1Z}. For the case of quadrupolar spins T_{1Q} can also be measured, but the experimental aspects of this determination will not concern us.

The primary source of both deuterium and carbon-13 relaxation is the modulation of the appropriate interaction by molecular angular fluctuations(AFs) [DON].

The carbon-13 Zeeman spin-lattice relaxation rate ($R_{1ZC} = T_{1ZC}^{-1}$) due to AFs modulations of the dipole-dipole interaction of the carbon-13 with a single directly bonded proton is

$$R_{1ZC} = A_{CH}[J_0(\omega_C - \omega_H) + 3J_1(\omega_C) + 6J_2(\omega_C + \omega_H] \tag{2.2}$$

where ω_C is the ^{13}C resonance frequency, ω_H is the ^1H resonance frequency, and

$$A_{CH} = \frac{1}{2}\ (\gamma_C\ \gamma_H\ \hbar\ /\ r_{CH}^3)^2$$

where γ_C and γ_H are the ^{13}C and ^1H gyromagnetic ratios, respectively, $\hbar$ is Planck's constant divided by 2π, and r_{CH} is the $^{13}C{-}^1H$ bond length [VOD,ABR].

If a sample's directory is parallel to the magnetic field then the deuterium

Zeeman (R_{1ZD}) and the deuterium quadrupole (R_{1QD}) spin lattice relaxation

$$R_{1ZD} = A_D[J_1(\omega_0) + 4J_2(2\omega_0)] \tag{2.3}$$

$$R_{1QD} = 3A_D J_1(\omega_0) \tag{2.4}$$

where the spectral densities $J_p(\omega)$ are defined later in this chapter, ω_0 is the ^2D resonance frequency, and

$$A_D = (3\pi^2/2)(e^2qQ/h)^2$$

where e^2qQ/h is the quadrupole coupling constant [DRY]. One of the advantages of deuterium relaxation is that R_{1ZD} and R_{1QD} can be measured simultaneously [VOD] and so equations 2.3 and 2.4 are easily solved to yield $J_1(\omega_0)$ and $J_2(2\omega_0)$, providing only that A_D is known.

In the case where the carbon is not directly bonded to a proton, there is still dipole-dipole relaxation with neighboring protons but it is necessary to include an additional relaxation contribution due to chemical shift anisotropy [LEW]. The ^{13}C spin-lattice relaxation due to chemical shift anisotropy is

$$R_{1ZCSA} = A_{CSA} J_{1CSA}(\omega_c) \tag{2.5}$$

with

$$A_{CSA} = \frac{3}{2}(\omega_C \sigma_{ZZ})^2$$

where σ_{ZZ} is the component of the shielding tensor along the director, and the "CSA" subscript indicates that the spectral density differs slightly from those used in equations 2.2, 2.3, 2.4.

We consider first Dong's theory [DRY] for rod-like mesogens for the special case where the long molecular axis and the para-axes of the rings coincide with the principal axis. The molecular dynamics are assumed to be adequately described by

treating the molecule as a symmetric top with rotational diffusion constants $D_{||}$ and $D_{\perp}$ about the long molecular axis, and with internal ring rotation uncorrelated to molecular tumbling and described by a rotational diffusion constant D_R for rotation about the para-axis.

If internal ring rotation is ignored then the correlation time for the overall molecular motion is

$$\tau_{pq}^{-1} = (D_{||} - D_{\perp})q^2 + (D_{\perp}/\beta_{pq}^2) \tag{2.6}$$

where the β_{pq}^2 are functions of the order parameter $< P_2 >$ which is given by Nordio and Segre [NOR]. Internal ring rotation can be included by adding a term in D_R so that equation 2.6 becomes

$$\tau_{pq}^{-1} = (D_{\perp}/\beta_{pq}^2) + (D_{||} - D_{\perp})q^2 + D_R(1 - \delta_{q0}) \tag{2.7}$$

with δ_{q0} the Kronecker delta.

For the case of an alkyl chain equation 2.6 or 2.7 will only be of interest if interaction between aromatic protons and chain carbon occur. We expect the carbon of the chain closest to the core to have a set of τ_{pq}^{-1} similar to equation 2.6. As carbon at an infinite distance along the chain would have the isotropic result:

$$\tau_{pq}^{-1} = (D_i/6) \tag{2.8}$$

where (i) is equal the carbon number. In chapter three four different models have been used to analysis the data which are the following:

For model A and B:

$$T(IA, IB) = DPAR * (1 + (IB - 1) * *2)$$

Where DPAR = D_i, and D_i is the diffusion constant characteristic of the spin. T(IA,IB) = τ_{pq}^{-1}, and (IB - 1) ** 2 = q^2. By changing these variables I got the following model:

$$\tau_{pq}^{-1} = D_i(1 + q^2)$$

For model C:

$$T(IA, IB) = DPAR$$

which will change to

$$\tau_{pq}^{-1} = D_i$$

For model D:

$$T(IA, IB) = DPAR/B(IA, IB) + DPAR * QQ$$

where B(IA,IB) = B_{pq}, and B_{pq} is the rotation matrices; which will change to

$$\tau_{pq}^{-1} = D_i/B_{pq} + D_i q^2$$

For model E:

$$T(IA, IB) = DPAR/B(IA, IB) + DPAR * QQ + DPAR$$

which will change to

$$\tau_{pq}^{-1} = D_i/B_{pq} + D_i q^2 + D_i$$

The spectral densities can be written as

$$\begin{aligned} J_p(\omega) &= f_0 \ \kappa(p,0)\tau_{p0}/(1+\omega^2\tau_{p0}^2) + \\ &\quad f_1 \ \kappa(p,1)\tau_{p1}/(1+\omega^2\tau_{p1}^2) + \\ &\quad f_2 \ \kappa(p,2)\tau_{p2}/(1+\omega^2\tau_{p2}^2) \end{aligned} \tag{2.9}$$

with

$$\begin{aligned} \kappa(p,q) &= < [D_{pq}^2(\Omega_0)]^2 > \\ &\quad - | < D_{pq}^2(\Omega_0 > |^2 \delta_{p0}\delta_{q0} \end{aligned} \tag{2.10}$$

where the $D_{pq}^2\Omega_0$ are Wigner rotation matrices written as functions of the Euler angles Ω_0 which transform from the molecular to the director frame. The κ(p,q)

are given by Freed [FRD] as functions of $< P_2 >=< D^2_{00}(\Omega_0) >$ and $< P_4 >=< D^4_{00}(\Omega_0) >$.

For both quadrupole and dipole-dipole interactions the f_n are given by

$$f_0 = [d^2_{00}(\beta_{1F})]^2 = (3\cos^2\beta_{1F} - 1)^2/4$$

$$f_1 = [d^2_{10}(\beta_{1F})]^2 = (3\sin^2 2\beta_{1F})/8$$

$$f_2 = [d^2_{20}(\beta_{1F})]^2 = (3\sin^4\beta_{1F})/8 \tag{2.11}$$

where β_{1F} is the angle between the local symmetry interaction (for dipole-dipole and quadrupole interactions, the C-H and C-D bond, respectively) and the para-axis of the ring. For chemical shift anisotropy the f_n are given by

$$f_0 = 1, \quad f_1 = 0, \quad \text{and} \quad f_2 = (1/6)(\frac{\sigma_{xx} - \sigma_{yy}}{\sigma_{zz}})^2 \tag{2.12}$$

where σ_{xx} and σ_{yy} are the components of the shielding tensor perpendicular to the director [WIT].

Relaxation can occur not only from modulations arising from angular fluctuations (AFs) but also from order director fluctuations ODF) which can modulate any of the interactions considered above [DON,ABR,WIT,DGY]. The ODF contributions to the ^{13}C dipole-dipole and^{13}C chemical shift anisotropy can be approximated with

$$R^{ODF}_{1ZC} = A_{CH} J^{ODF}_1 \tag{2.13}$$

$$R^{ODF}_{1ZCSA} = A_{CSA} J^{ODF}_1 \tag{2.14}$$

with

$$J^{ODF}_1 = \frac{3kT < P_2 >^2}{4\sqrt{2}\pi\sqrt{\omega_0}K(D + K/\eta)^{1/2}} f_0 \tag{2.15}$$

where k is Boltzmann's constant, K is the average elastic constant, D is the translation diffusion constant, and η is the rotational viscosity. As can be seen from

equation 2.11, the ODF contribution to the dipole-dipole relaxation of a protonated carbon with a bond angle of 70.5° with the director is much smaller than the AFs contribution, while from equation 2.12 it can be seen that the ODF and AFs contributions to the chemical shift are similar [LEW]. There are corrections to equations 2.13 and 2.14 due to the high frequency cutoff [DON,FRD] and a cross term between ODF and AFs [DON,FRD], but both of these corrections are small in the present situation. In practice ODF does not appear to be an important source of relaxation in alkyle chains.

2.1 The Carbon-13 Chemical Shifts and Spin Lattice Relaxation Times

The carbon-13 chemical shifts and spin lattice relaxation times have been measured for all of the resolved resonances in the nematic and isotropic phases of 4-cyano-4'-n-pentylbiphenyl (5CB) [PEE]. The spectra 5CB is shown in figure 2.1. The chemical shift assignments for the aromatic carbons in both phases and the alkyle carbons in the isotropic phase follow from the results for 5CB [BOC], with the sequence along the chain being C9, C11, C10, C12, C13, etc. In the nematic phase of 5CB the relaxation times suggest that C10 and C11 order is reversed; this is reasonable, and the carbons closer to the aromatic core should be more highly ordered in the nematic phase and thus the C10 line should be shifted more than the C11 line at the phase transition. Because C10 shifts curve the most, C10 must have biggest order parameter,and so must really be next to core and thus is really C9. The assignment of the alkyl line with the largest chemical shift as being due to C9 is questionable for the nematic phase, and this assignment will be reconsidered in this work. For the alkyl chain, the resonances of the terminal carbon and the next to terminal carbon are both well resolved in this series, but

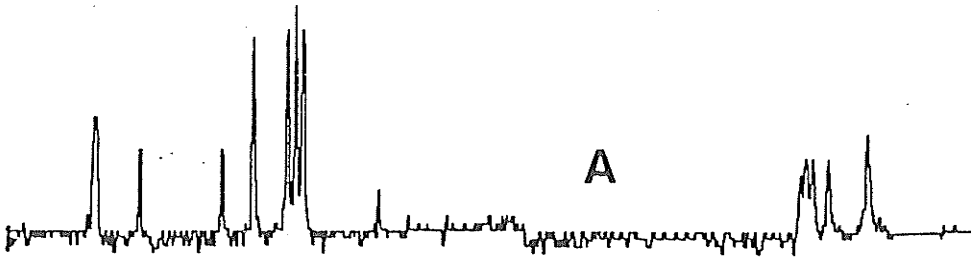

Figure 2.1: **Carbon-13 Fourier transform NMR spectra recorded on the Bruker SXP-4-100 spectrometer. (A) is a spectrum of nematic 5CB at 27.6 ^{o}C. The spectral width is 5200 Hz. The baseline spectra have been corrected to remove instrumental distortions (from [PEE]).**

there is significant overlap for the other carbons in the chain so that the physical significance of the results for these lines is questionable.

The alkyl spin-lattice relaxation times (T_1's) for 5CB are reproduced in table 2.1, along with the activation energies shown in figure 2.2.

The solid lines give the least squares fit of a straight line to ln (T_1) as a function of 1000/T, so that the slopes provide a graphical representation of the activation energies. It is difficult to compare the relaxation times along the middle of the chains, especially as line overlap obscures the situation. The results for C9 and for the last carbon of the chain can perhaps be rationalized by noting that the longer relaxation time corresponds in the present case to faster random motions. The final carbon of the pentyl chain can be regarded as independent from the rest of the molecule. The magnitude of the even-odd effect for the next to last carbon appears to be inconsistent with the behaviour of both C9 and of the last carbon of the chain. The chemical shifts as a function of temperature are given in table 2.2,

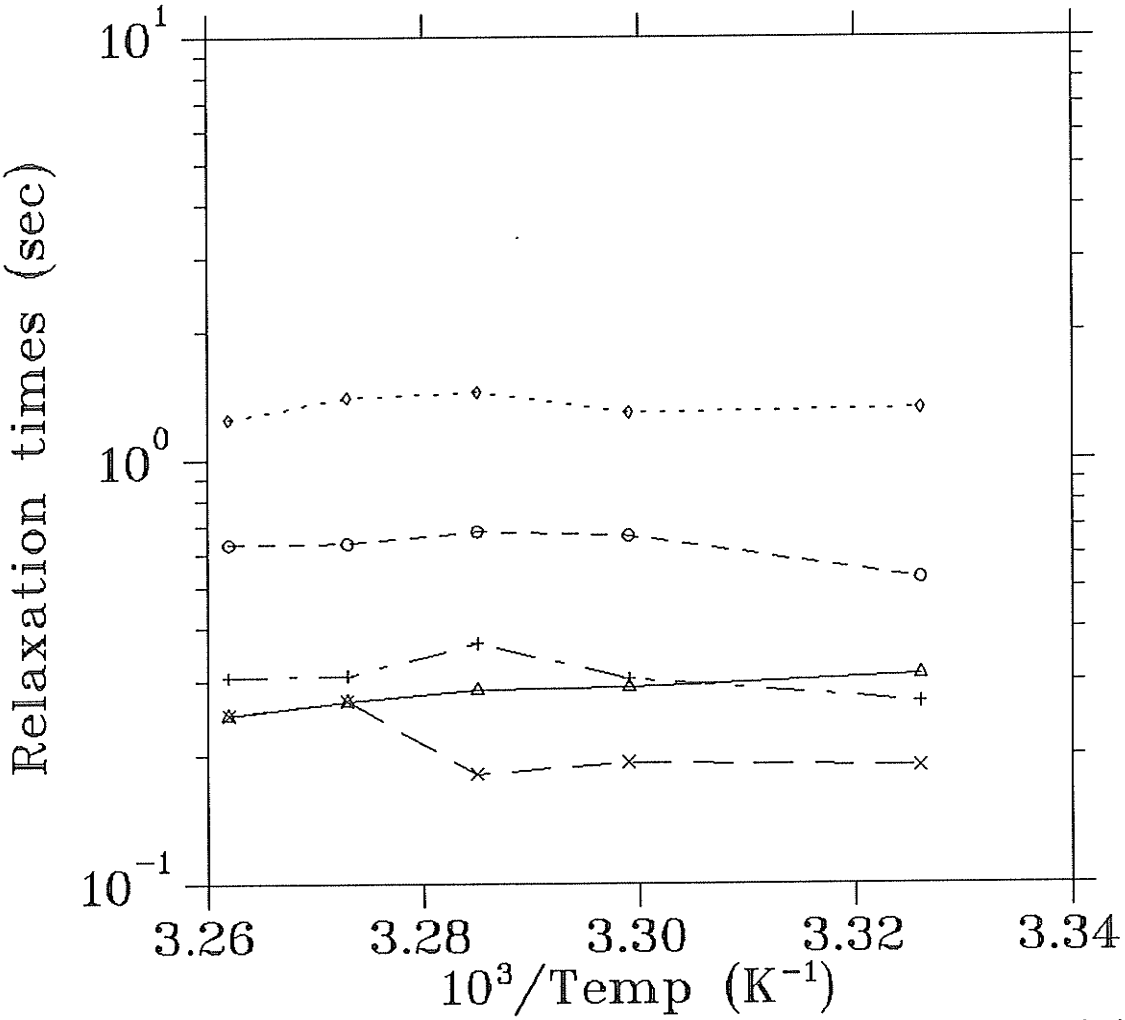

Figure 2.2: **The temperature dependence of C9 (Δ), C10 (×), C11 (+), C12 (○), and C13 (◇) alkyl relaxation times of 5CB (from [PEE]).**

Table 2.1: **Experimental relaxation times in 5CB, with T_1 (sec) as a function of temperature. (Activation energies in KJ/moles)**

Temp.	pentyl chain (Nematic) [sec]				
^0C	C9	C10	C11	C12	C13
33.4	0.249	0.249	0.306	0.633	1.248
32.4	0.269	0.269	0.309	0.637	1.399
31.3	0.286	0.181	0.368	0.679	1.445
30.0	0.289	0.193	0.304	0.663	1.291
27.5	0.311	0.189	0.268	0.527	1.319
E_a	-26.6	42.4	19.9	22.7	10.2
	±3.8	±19.0	±14.3	±10.9	±8.9

and for 5CB in figure 2.3.

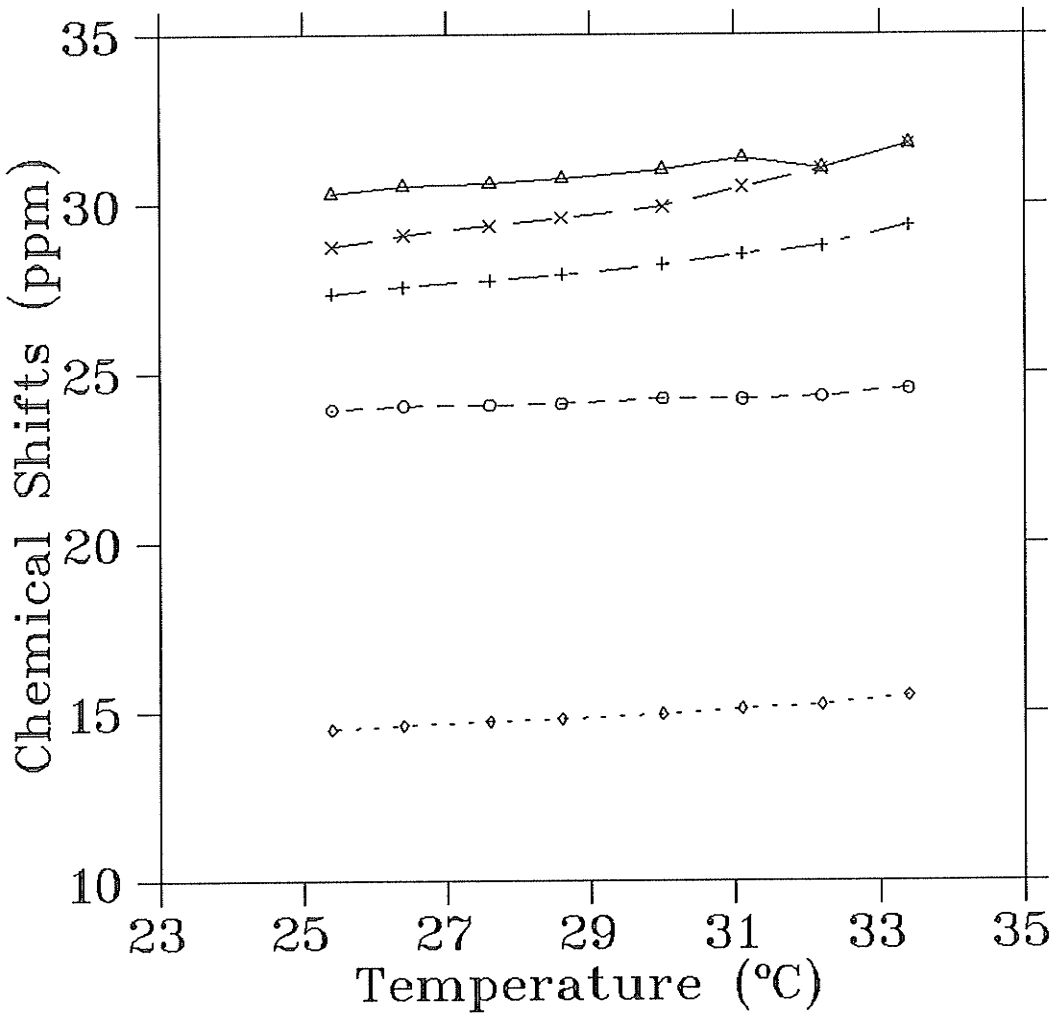

Figure 2.3: **The temperature dependence of the alkyl carbon-13 line positions in 5CB. Chemical shifts are given with respect to TMS. The Symbols used are C9 (Δ), C10 (×), C11 (+), C12 (○), and C13 (◇) (from [PEE]).**

Table 2.2: **Experimental chemical shifts (ppm with respect to TMS) for 5CB as a function of temperature.**

Temp.	pentyl chain (Nematic) [ppm]				
^0C	C9	C10	C11	C12	C13
33.4	31.770	31.770	29.352	24.525	15.462
32.2	31.039	31.039	28.751	24.307	15.180
31.1	31.349	30.498	28.502	24.229	15.075
30.0	31.008	29.919	28.205	24.241	14.915
28.6	30.744	29.588	27.896	24.093	14.786
27.6	30.610	29.357	27.709	24.053	14.710
26.4	30.522	29.069	27.549	24.033	14.589
25.4	30.303	28.727	27.334	23.916	14.470

CHAPTER 3

CHAPTER 3

Analysis

In this chapter various programs and different models would be analysed. Some of these models will work and some not. To simplify the comparison with deuterium relaxation times and to eliminate a possible source of confusion we will introduce a reduced relaxation time for the carbon-13 relaxation times. We have given the relaxation rates R_{1ZC} for one attached proton, and for N attached protons the theoretical rate simply multiplied by N [ABR]; no such complication exists for the R_{1ZD} of deuterium relaxation. Possible confusion has been avoided by defining reduced carbon-13 relaxation times T_1/N, and calculate these theoretically as $1/R_{1ZC}$.

3.1 MODEL A

The values of relaxation times T_1 of the temperature 30.0 °C which are shown in table 2.1 for C9, C10, C11, C12, and C13 are 0.289, 0.193, 0.304, 0.663, and 1.291 respectively. The first four carbon C9, C10, C11,and C12 should be multiplied by 2 and the last carbon C13 should be multiplied by 3; This is explained in figure 1.3. Therefore the values of C9, C10, C11, C12, and C13 would become 0.578, 0.386, 0.608, 1.326, and 3.878 respectively. From appendix A.1 the program ABD5.FOR is used to analysis the data ABD5.DAT shown in appendix A.2. This program is using the following model:-

$$T(IA, IB) = DPAR * (1 + (IB - 1) * *2)$$

Table 3.1: **ABD5.DAT**

carbon number	TDEG ^oC	DPAR $[s^{-1}]$	ADF	BETA	P_2	P_4	RBOND [cm]
C9	30.0	4.300	0.000	70.500	0.125	0.000	1.101
C10	30.0	2.900	0.000	70.500	0.082	0.000	1.101
C11	30.0	4.500	0.000	70.500	0.089	0.000	1.101
C12	30.0	9.985	0.000	70.500	0.057	0.000	1.101
C13	30.0	29.200	0.000	70.500	0.042	0.000	1.101

$$\tau_{pq}^{-1} = D_i(1 + q^2)$$

The values of the order parameters P_2 are taken from P.A.Beckmann's paper [BTL]. In order to get the above values of the relaxation times T_1, the program has been run several times by changing the values of DPAR's each time. The values of the relaxation times are same as to the data to 4 figures; This is shown in appendix A.3. The values of the spectral densities are shown in table 3.2

This model will work only if We change the assignment of C9 to C10; And by comparing the spectral densities results with R. Y. Dong's spectral densities [DYR,NGR] it has been found that by plotting the two graphs of Dong's results versus our results, each of these two graphs is a straight line. These are shown in figures 3.1, and 3.2, and table 3.3.

By plotting Model A's spectral densities versus the carbon number from table 3.3, We got a straight line, that is shown in figure 3.3. The values of the relaxation rates R are almost the same as the values of P. A. Beckmann's relaxation rates, this is shown in table 3.4.

Table 3.2: **The output of the program ABD5.FOR**

Carbon number	Spectral density $[s^{-1}]$	Relaxation times [sec]	Relaxation rates $[s^{-1}]$
C9	8.92	0.574	42.93
C10	13.17	0.388	64.10
C11	8.39	0.604	40.84
C12	3.81	1.317	18.72
C13	1.30	3.841	6.42

Table 3.3: **Calculated Model A's spectral densities versus Dong's spectral densities**

Carbon number	Model A spectral densities $[s^{-1}]$	Dong(1) spec. densities $[s^{-1}]$	Dong(2) spec. densities $[s^{-1}]$
C9	13.17	32.20	26.75
C10	8.92	18.50	14.91
C11	8.39	14.80	12.43
C12	3.81	8.10	6.75
C13	1.30	3.70	2.85

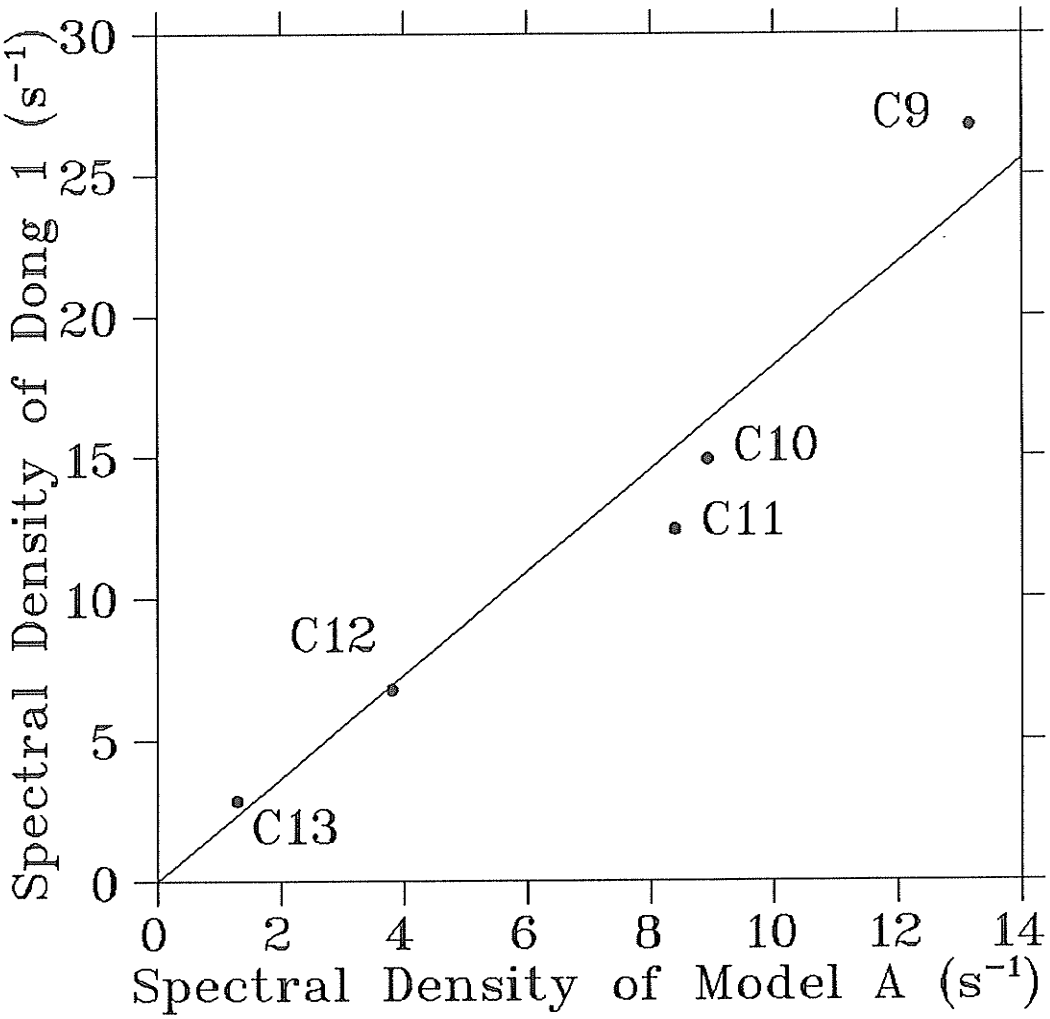

Figure 3.1: **Dong1 results vs. Model A results**

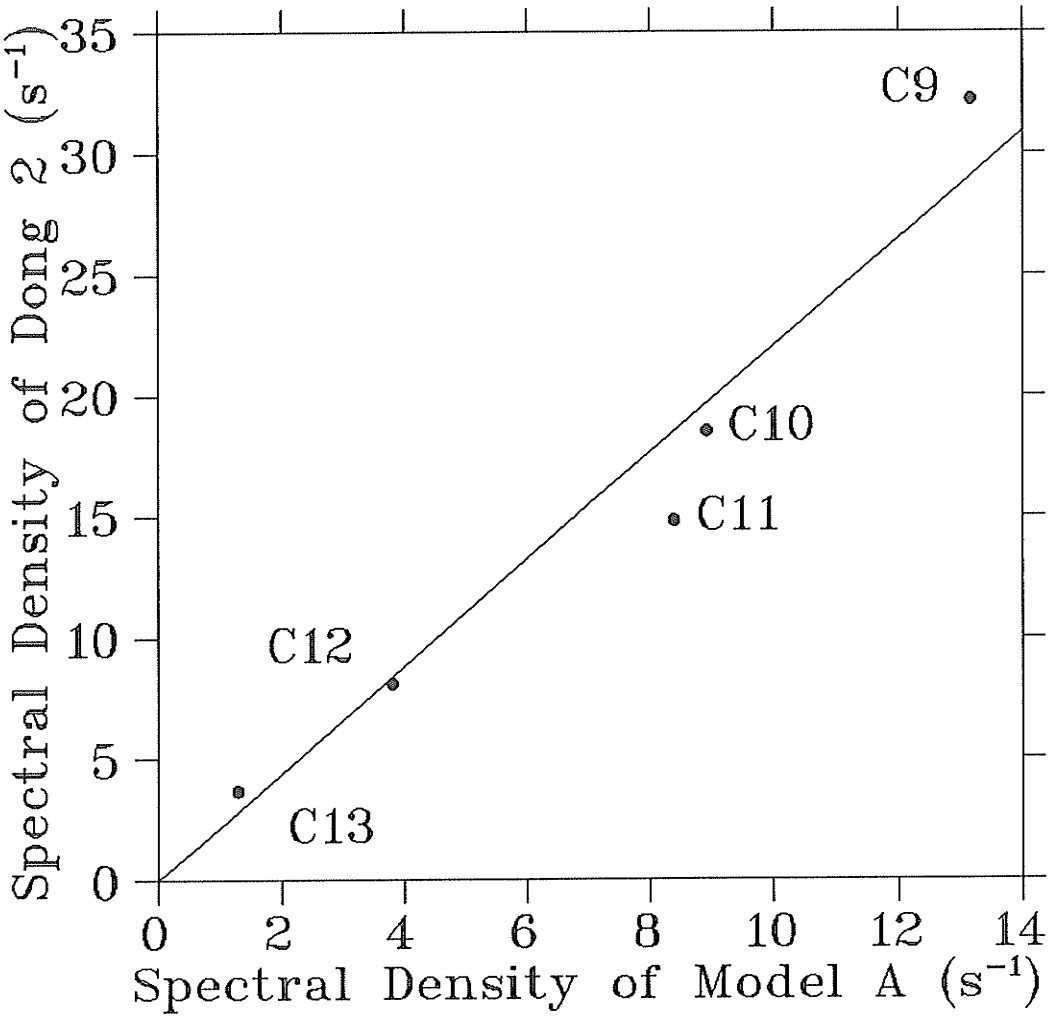

Figure 3.2: **Dong2 results vs. Model A results**

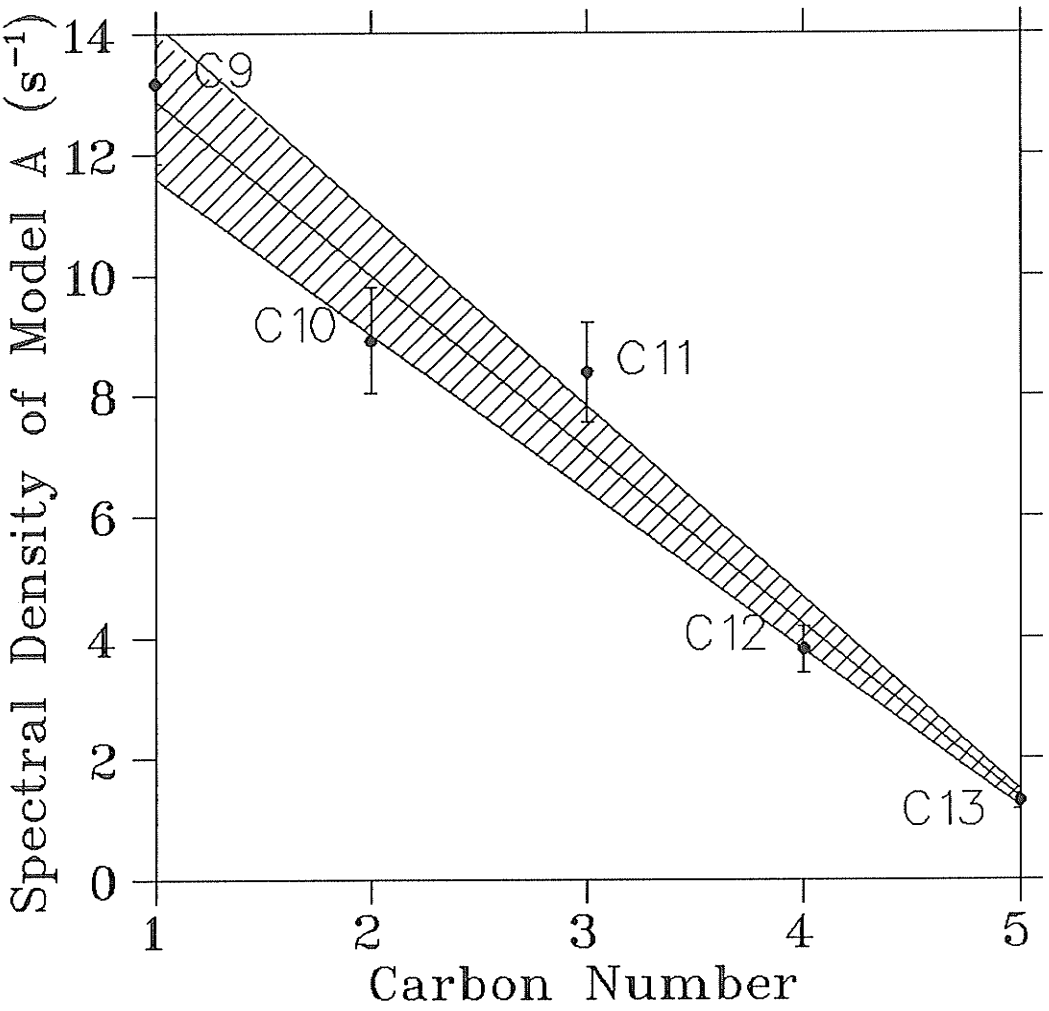

Figure 3.3: **Model A results vs. Carbon Number**

Table 3.4: **Calculated Model A's relaxation rates versus Beckmann's relaxation rates**

Carbon number	Model A relax. rates $[s^{-1}]$	Beckmann relax. rates $[s^{-1}]$
C9	64.10	63.34
C10	42.93	41.09
C11	40.84	35.25
C12	18.72	18.45
C13	6.42	6.35

So from the above analysis We conclude that this model works only if We interchange the first two carbon C9 and C10.

3.2 MODEL B

The average values of relaxation times T_1 for the first two temperatures 33.4 °C and 32.4 °C which are shown in table 2.1 for C9, C10, C11, C12, and C13 are 0.259, 0.259, 0.308, 0.635, and 1.324 respectively. The first four carbon C9, C10, C11,and C12 should be multiplied by 2 and the last carbon C13 should be multiplied by 3; This is explained in figure 1.3. Therefore the values of C9, C10, C11, C12, and C13 would become 0.5i8, 0.518, 0.615, 1.270, and 3.971 respectively. From appendix A.1 the program ABD5.FOR is used to analyse the data HRE5.DAT shown in appendix B.2. This program is using the following model:-

$$T(IA, IB) = DPAR * (1 + (IB - 1) * *2)$$

$$\tau_{pq}^{-1} = D_i(1 + q^2)$$

Table 3.5: **HRE5.DAT**

carbon number	TDEG ^oC	DPAR $[s^{-1}]$	ADF	BETA	P_2	P_4	RBOND [cm]
C9	34.8	3.830	0.000	70.500	0.214	0.000	1.101
C10	34.8	3.862	0.000	70.500	0.148	0.000	1.101
C11	34.8	4.589	0.000	70.500	0.159	0.000	1.101
C12	34.8	9.580	0.000	70.500	0.107	0.000	1.101
C13	34.8	30.100	0.000	70.500	0.078	0.000	1.101

The values of the order parameters P_2 are taken from R. Y. Dong's paper [LJS]. In order to get the above values of the relaxation times T_1, the program has been run several times by changing the values of DPAR's each time. The values of the relaxation times are same as to the data to 4 figures; This is shown in appendix B.3. The values of the spectral densities are shown in table 3.6

This model will not work because by comparing the spectral densities results with R. Y. Dong's spectral densities [DYR,NGR] it has been found that by plotting a graph of Dong's results versus our results, this graph is not a straight line. These are shown in figures 3.4, and 3.5, and table 3.7.

By plotting Model B's spectral densities versus the carbon number from table 3.7, We got a smooth curve that is shown in figure 3.6.

The values of the relaxation rates R are different from the values of P. A. Beckmann's relaxation rates; This is shown in table 3.8.

So from the above analysis We conclude that this model works only if the first carbon C9 has been ignored. This argument is true because from the figures 3.4,

Table 3.6: **The output of the program HRE5.FOR**

Carbon number	Spectral density $[s^{-1}]$	Relaxation times [sec]	Relaxation rates $[s^{-1}]$
C9	10.13	0.518	47.42
C10	9.96	0.518	67.59
C11	8.40	0.615	39.98
C12	4.01	1.271	19.34
C13	1.27	3.974	6.19

Table 3.7: **Calculated Model B's spectral densities versus Dong's spectral densities**

Carbon number	Model B spectral densities $[s^{-1}]$	Dong(1) spec. densities $[s^{-1}]$	Dong(2) spec. densities $[s^{-1}]$
C9	10.13	32.20	26.75
C10	9.96	18.50	14.91
C11	8.40	14.80	12.43
C12	4.01	8.10	6.75
C13	1.27	3.70	2.85

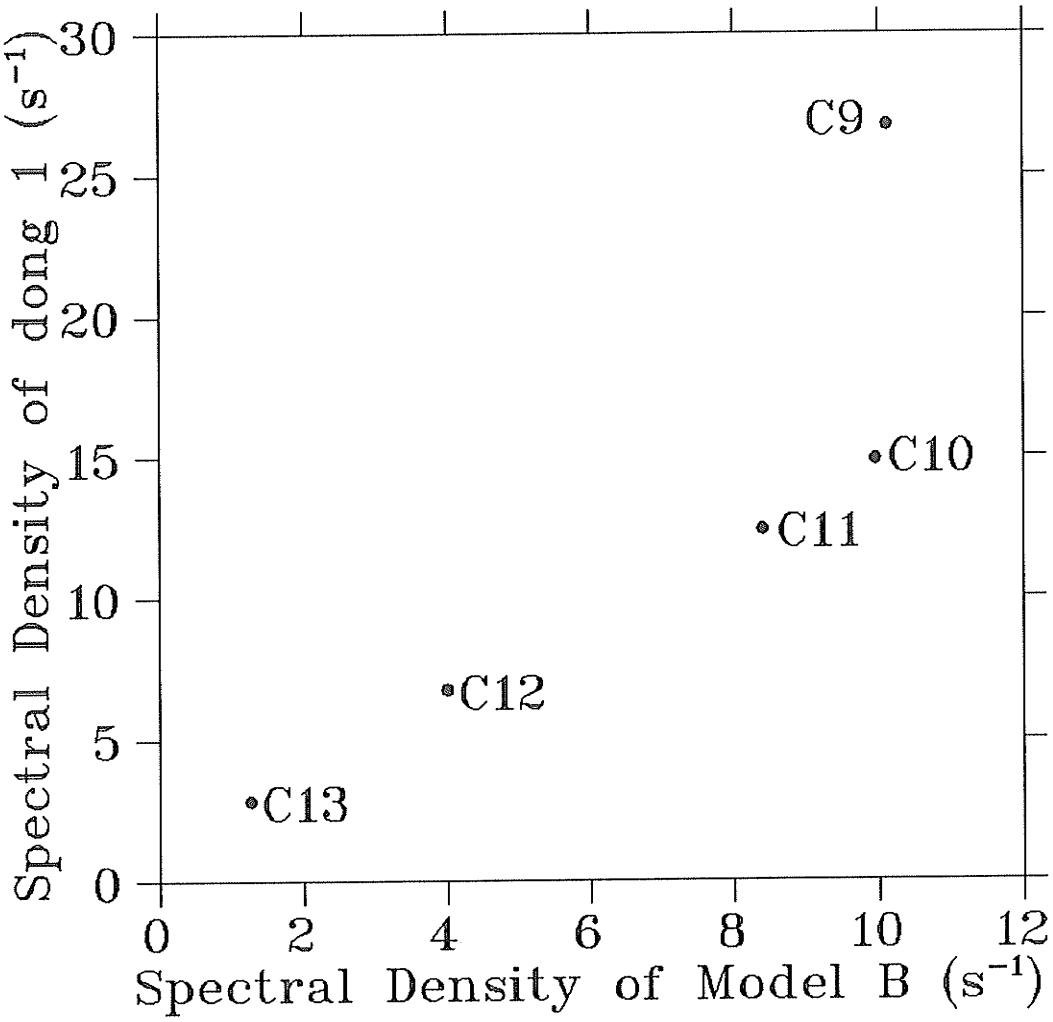

Figure 3.4: **Dong1 results vs. Model B results**

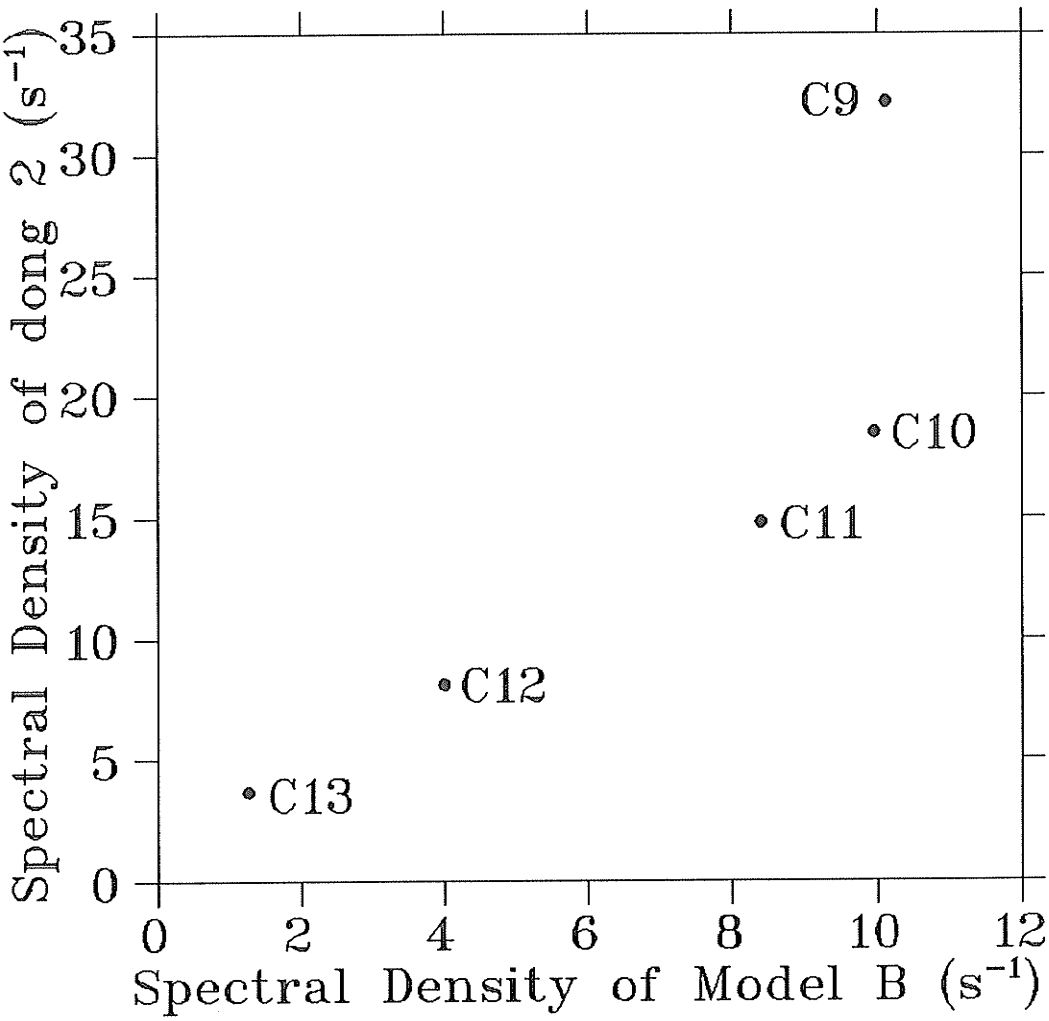

Figure 3.5: **Dong2 results vs. Model B results**

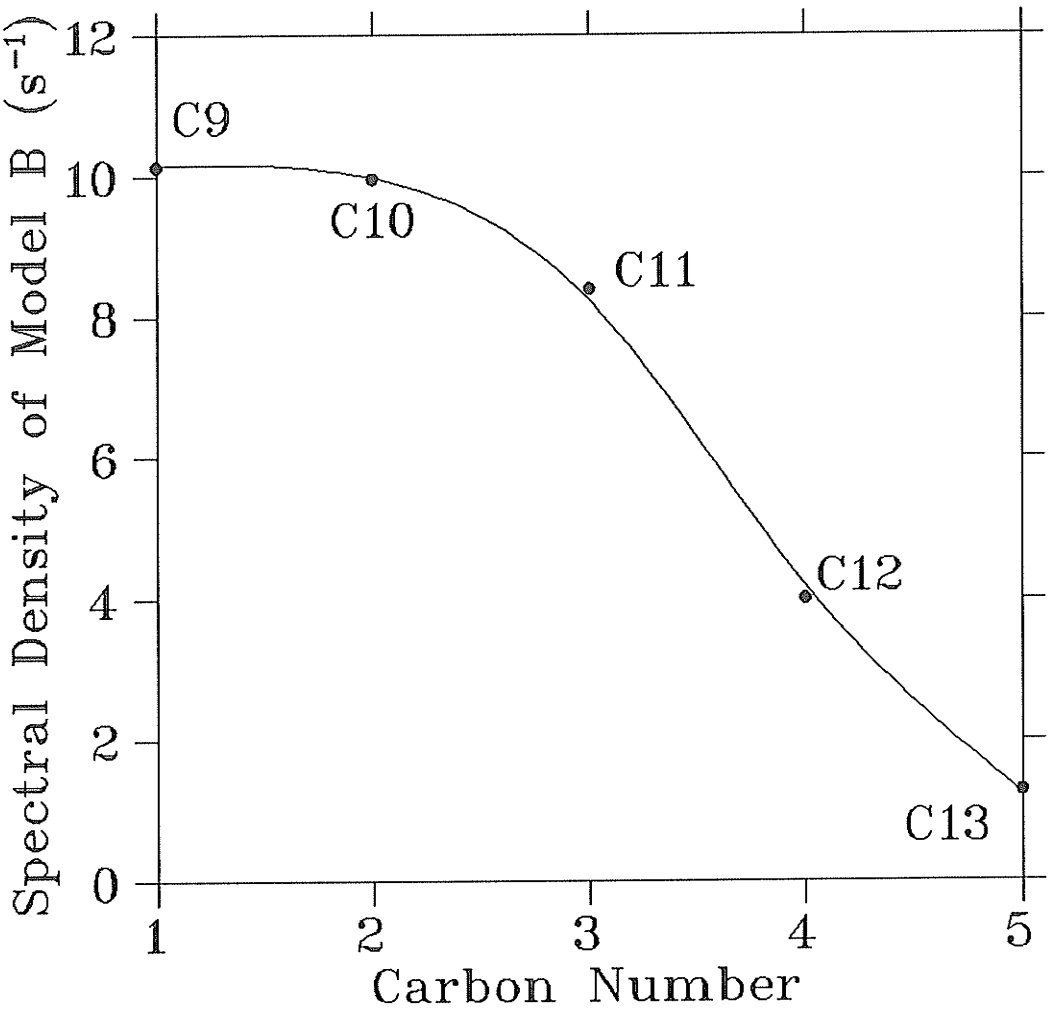

Figure 3.6: **Model B results vs. Carbon Number**

Table 3.8: **Calculated Model B's relaxation rates versus Beckmann's relaxation rates**

Carbon number	Model B relax. rates $[s^{-1}]$	Beckmann relax. rates $[s^{-1}]$
C9	47.42	73.25
C10	47.59	38.36
C11	39.98	28.72
C12	19.34	18.10
C13	6.19	6.12

and 3.5 if We ignore the first carbon C9, then the two graphs would be a straight line.

3.3 MODEL C

The values of relaxation times T_1 of the temperature 30.0 °C which are shown in table 2.1 for C9, C10, C11, C12, and C13 are 0.289, 0.193, 0.304, 0.663, and 1.291 respectively. The first four carbon C9, C10, C11, and C12 should be multiplied by 2 and the last carbon C13 should be multiplied by 3; This is explained in figure 1.3. Therefore the values of C9, C10, C11, C12, and C13 would become 0.578, 0.386, 0.608, 1.326, and 3.878 respectively. From appendix C.1 the program ABD7.FOR is used to analysis the data ABD7.DAT shown in appendix C.2. This program is using the following model:-

$$T(IA, IB) = DPAR$$

$$\tau_{pq}^{-1} = D_i$$

Table 3.9: **ABD7.DAT**

carbon number	TDEG ^oC	DPAR $[s^{-1}]$	ADF	BETA	P_2	P_4	RBOND [cm]
C9	30.0	12.000	0.000	70.500	0.214	0.000	1.101
C10	30.0	7.990	0.000	70.500	0.148	0.000	1.101
C11	30.0	12.500	0.000	70.500	0.159	0.000	1.101
C12	30.0	27.300	0.000	70.500	0.107	0.000	1.101
C13	30.0	79.200	0.000	70.500	0.078	0.000	1.101

The values of the order parameters P_2 are taken from R. Y. Dong's paper [LJS]. In order to get the above values of the relaxation times T_1, the program has been run several times by changing the values of DPAR's each time. The values of the relaxation times are same as to the data to 4 figures; This is shown in appendix C.3. The values of the spectral densities are shown in table 3.10

This model will not work because by comparing the spectral densities results with R. Y. Dong's spectral densities [DYR,NGR] it has been found that by plotting a graph of Dong's results versus our results , this graph is not a straight line. These are shown in figures 3.7, and 3.8, and table 3.11.

By plotting Model C's spectral densities versus the carbon number from table 3.11, We did not get a straight line that is shown in figure 3.9. The values of the relaxation rates R are almost the same as the values of P. A. Beckmann's relaxation rates except the first carbon C9; This is shown in table 3.12.

So from the above analysis WE conclude that this model works only if the first carbon C9 has been ignored. This argument is true because from the figures 3.7,

Table 3.10: **The output of the program ABD7.FOR**

Carbon number	Spectral density $[s^{-1}]$	Relaxation times [sec]	Relaxation rates $[s^{-1}]$
C9	6.58	0.575	34.31
C10	9.99	0.386	46.07
C11	6.41	0.603	32.60
C12	2.98	1.328	15.59
C13	1.04	3.871	5.40

Table 3.11: **Calculated Model C's spectral densities versus Dong's spectral densities**

Carbon number	Model C spectral densities $[s^{-1}]$	Dong(1) spec. densities $[s^{-1}]$	Dong(2) spec. densities $[s^{-1}]$
C9	6.58	32.20	26.75
C10	9.99	18.50	14.91
C11	6.41	14.80	12.43
C12	2.98	8.10	6.75
C13	1.04	3.70	2.85

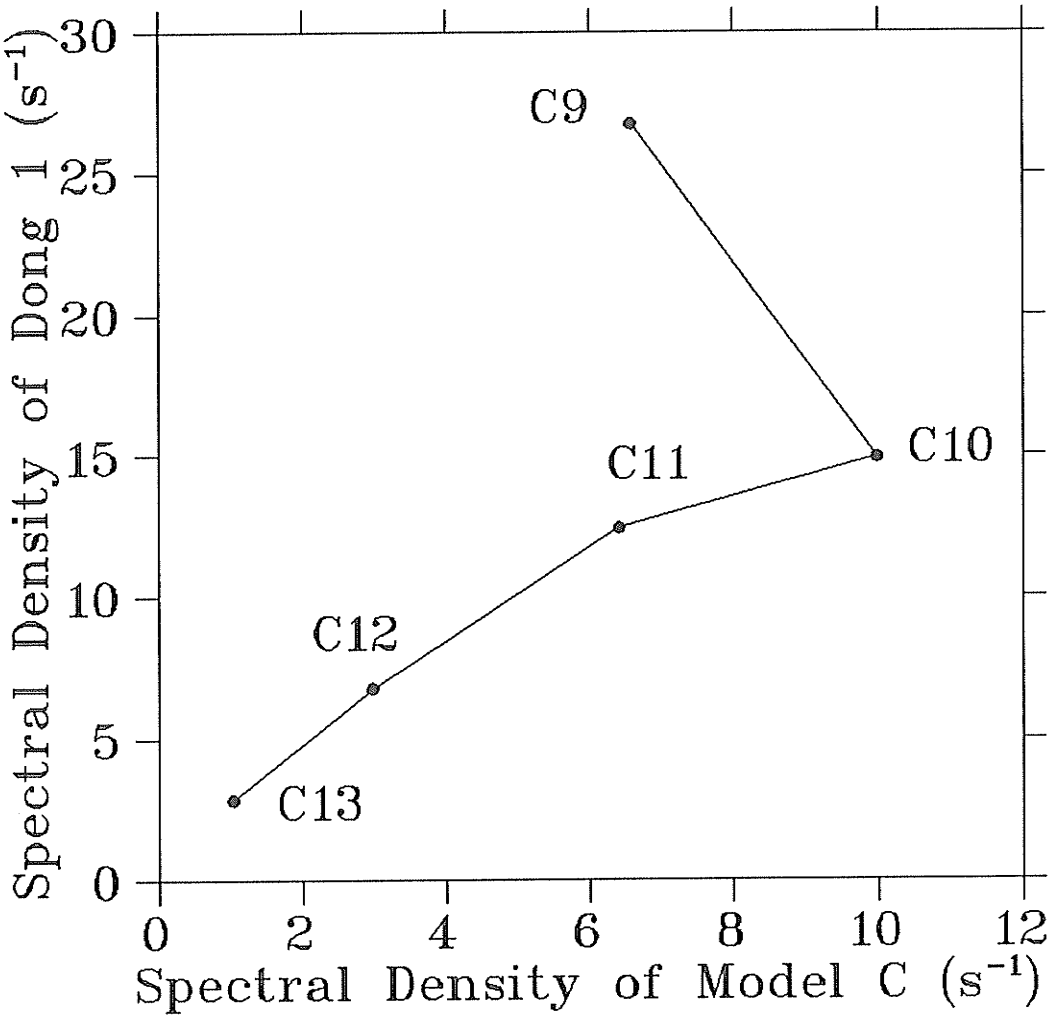

Figure 3.7: **Dong1 results vs. Model C results**

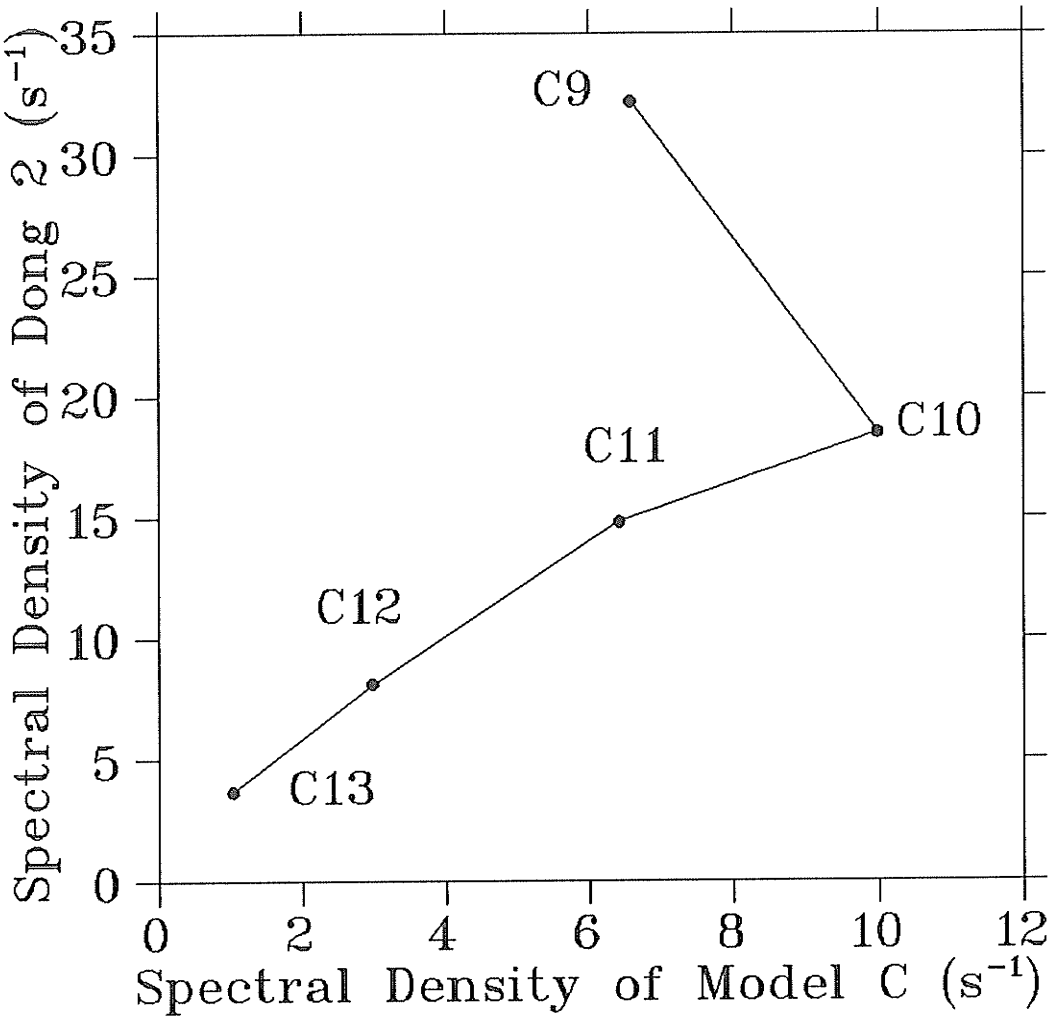

Figure 3.8: **Dong2 results vs. Model C results**

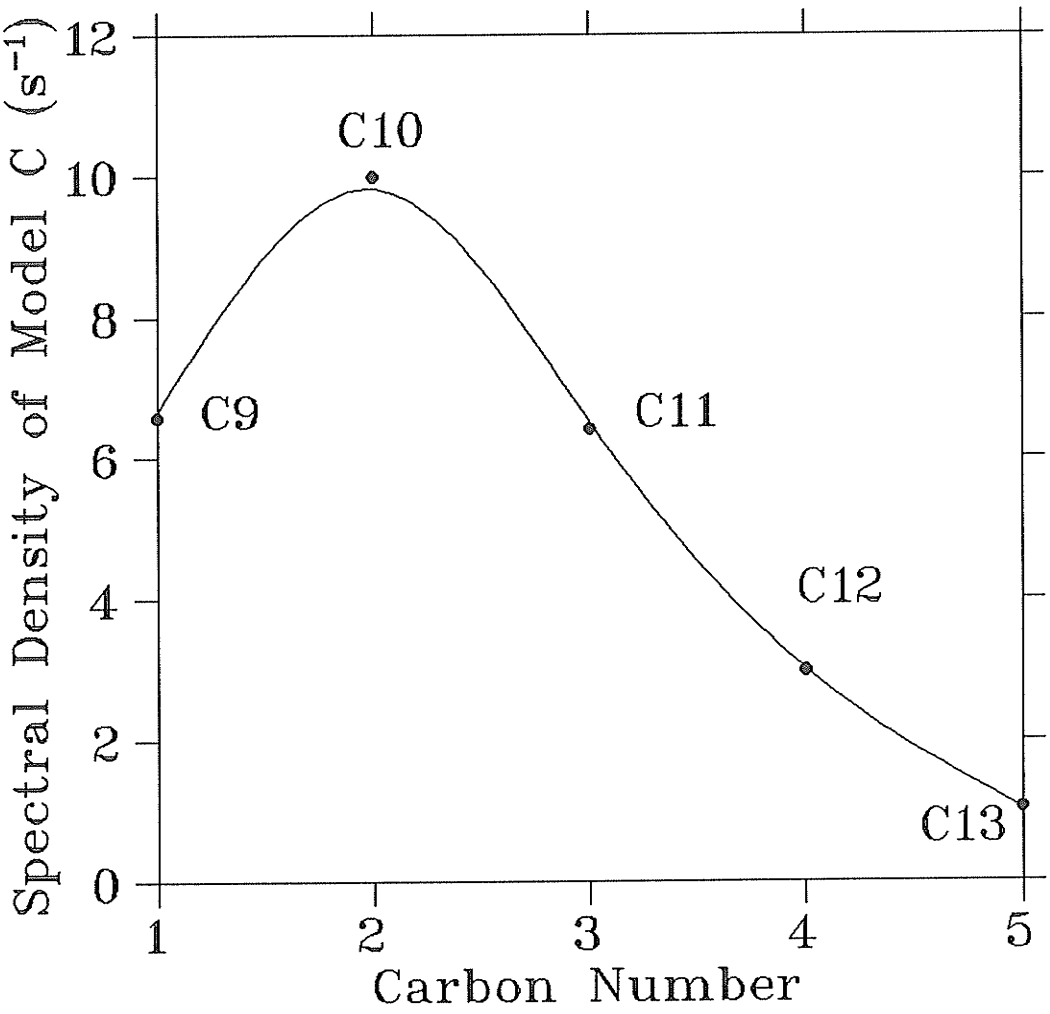

Figure 3.9: **Model C results vs. Carbon Number**

Table 3.12: **Calculated Model C's relaxation rates versus Beckmann's relaxation rates**

Carbon number	Model C relax. rates $[s^{-1}]$	Beckmann relax. rates $[s^{-1}]$
C9	34.31	63.34
C10	46.07	41.09
C11	32.60	35.25
C12	15.59	18.45
C13	5.40	6.35

and 3.8 if We ignore the first carbon C9, then my two graphs would be a straight line.

3.4 MODEL D

The values of relaxation times T_1 of the temperature 27.5 °C which are shown in table 2.1 for C9, C10, C11, C12, and C13 are 0.311, 0.189, 0.268, 0.527, and 1.319 respectively. The first four carbon C9, C10, C11,and C12 should be multiplied by 2 and the last carbon C13 should be multiplied by 3; This is explained in figure 1.3. Therefore the values of C9, C10, C11, C12, and C13 would become 0.622, 0.378, 0.536, 1.054, and 3.957 respectively. From appendix D.1 the program JDTLA0.FOR is used to analysis the data JDTLA0.DAT shown in appendix D.2. This program is using the following model:-

$$T(IA, IB) = DPAR/B(IA, IB) + DPAR * QQ$$

$$\tau_{pq}^{-1} = D_i/B_{pq} + D_i q^2$$

Table 3.13: **JDTLA0.DAT**

carbon number	TDEG ^oC	DPAR $[s^{-1}]$	ADF	BETA	P_2	P_4	RBOND [cm]
C9	27.5	1.272	0.000	70.500	0.214	0.000	1.101
C10	27.5	0.664	0.000	70.500	0.148	0.000	1.101
C11	27.5	1.061	0.000	70.500	0.159	0.000	1.101
C12	27.5	2.232	0.000	70.500	0.107	0.000	1.101
C13	27.5	8.543	0.000	70.500	0.078	0.000	1.101

The values of the order parameters P_2 are taken from R. Y. Dong's paper [LJS]. In order to get the above values of the relaxation times T_1, the program has been run several times by changing the values of DPAR's each time. The values of the relaxation times are same as to the data to 4 figures; This is shown in appendix D.3. The values of the spectral densities are shown in table 3.14

This model will not work because by comparing the spectral densities results with R. Y. Dong's spectral densities [DYR,NGR] it has been found that by plotting a graph of Dong's results versus our results , this graph is not a straight line. These are shown in figures 3.10, and 3.11, and table 3.15.

By plotting Model D's spectral densities versus the carbon number from table 3.14, We did not get a smooth curve that is shown in figure 3.12. The values of the relaxation rates R are different from the values of P. A. Beckmann's relaxation rates, this is shown in table 3.16.

So from the above analysis We conclude that this model works only if the first carbon C9 has been ignored. This argument is true because from the figures 3.10, and 3.11 if We ignore the first carbon C9, then the two graphs would be a straight

Table 3.14: **The output of the program JDTLA0.FOR**

Carbon number	Spectral density $[s^{-1}]$	Relaxation times [sec]	Relaxation rates $[s^{-1}]$
C9	7.90	0.622	43.84
C10	15.44	0.378	82.57
C11	9.63	0.536	51.83
C12	4.64	1.054	24.35
C13	1.22	3.957	6.32

Table 3.15: **Calculated Model D's spectral densities versus Dong's spectral densities**

Carbon number	Model D spectral densities $[s^{-1}]$	Dong(1) spec. densities $[s^{-1}]$	Dong(2) spec. densities $[s^{-1}]$
C9	7.90	32.20	26.75
C10	15.44	18.50	14.91
C11	9.63	14.80	12.43
C12	4.64	8.10	6.75
C13	1.22	3.70	2.85

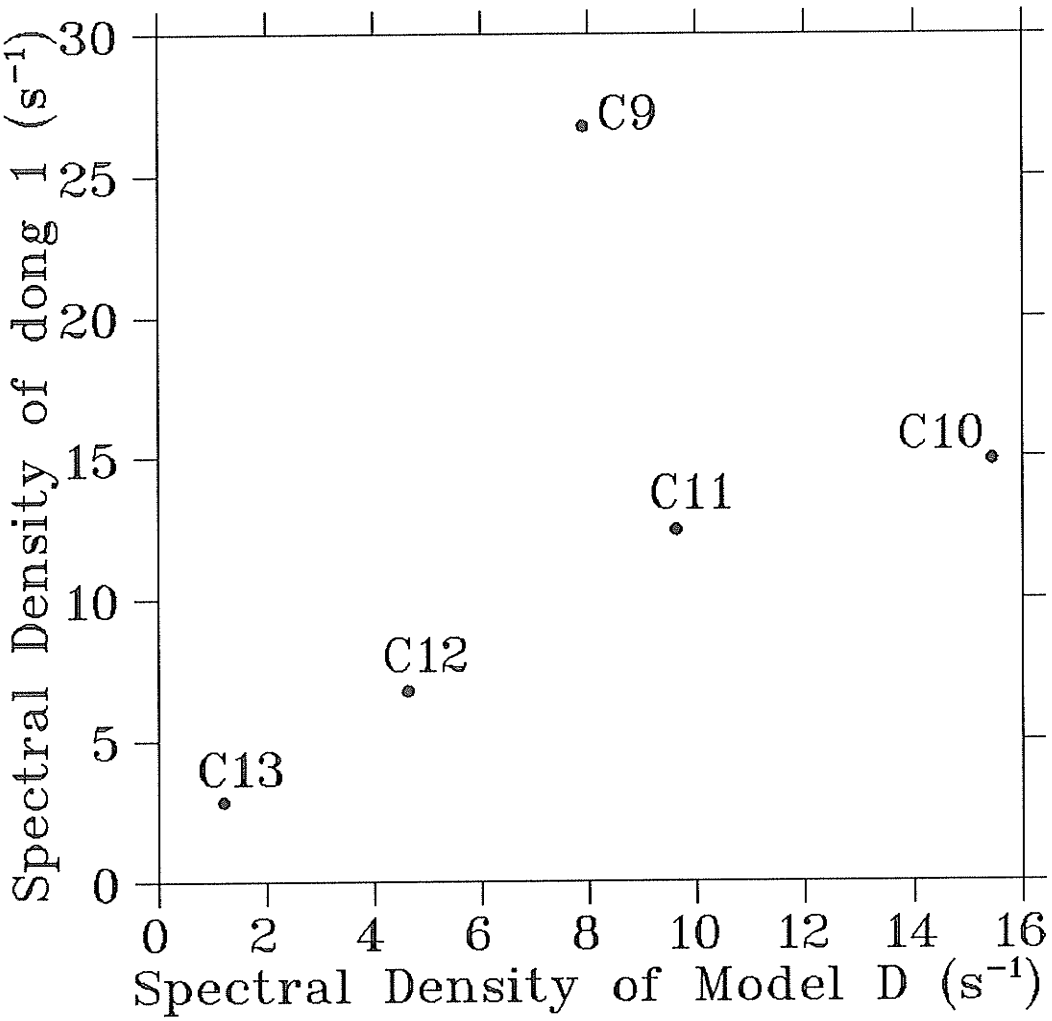

Figure 3.10: **Dong1 results vs. Model D results**

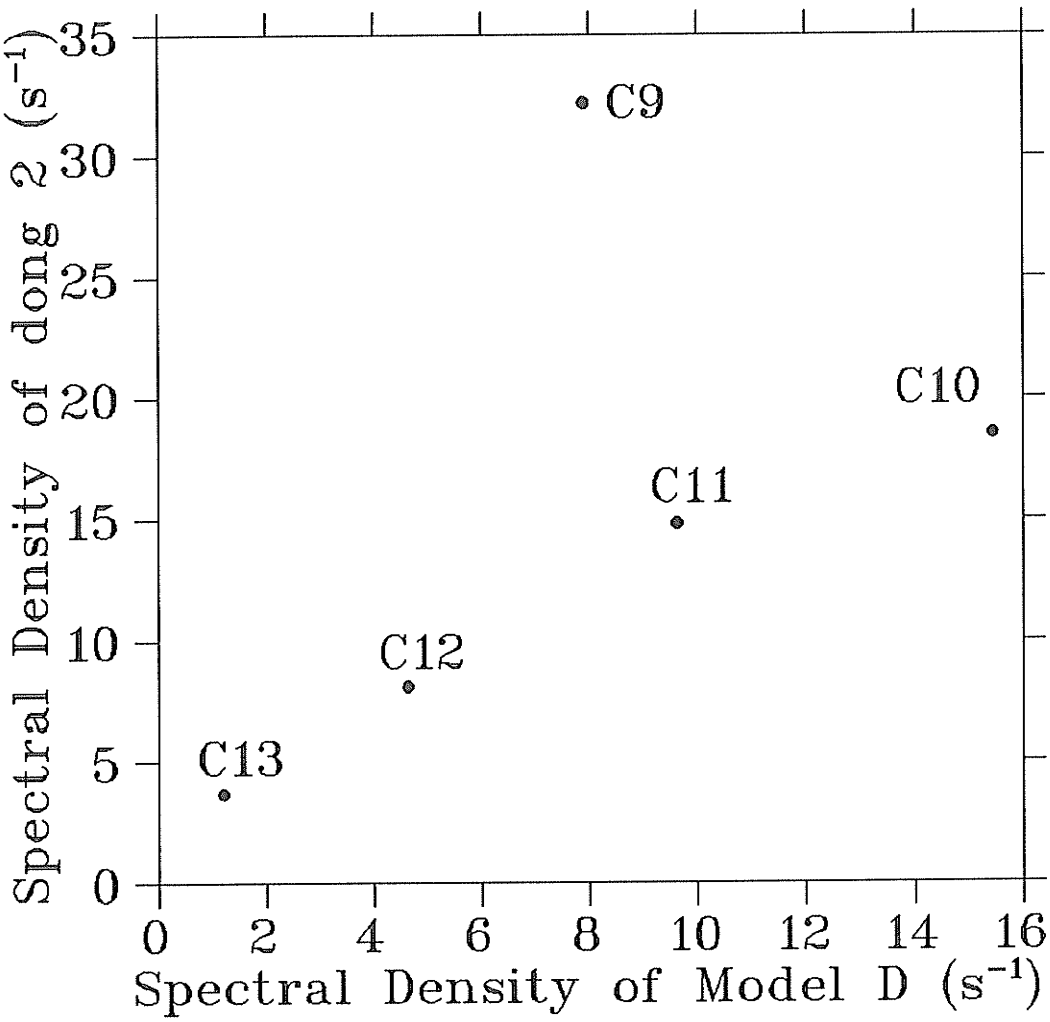

Figure 3.11: **Dong2 results vs. Model D results**

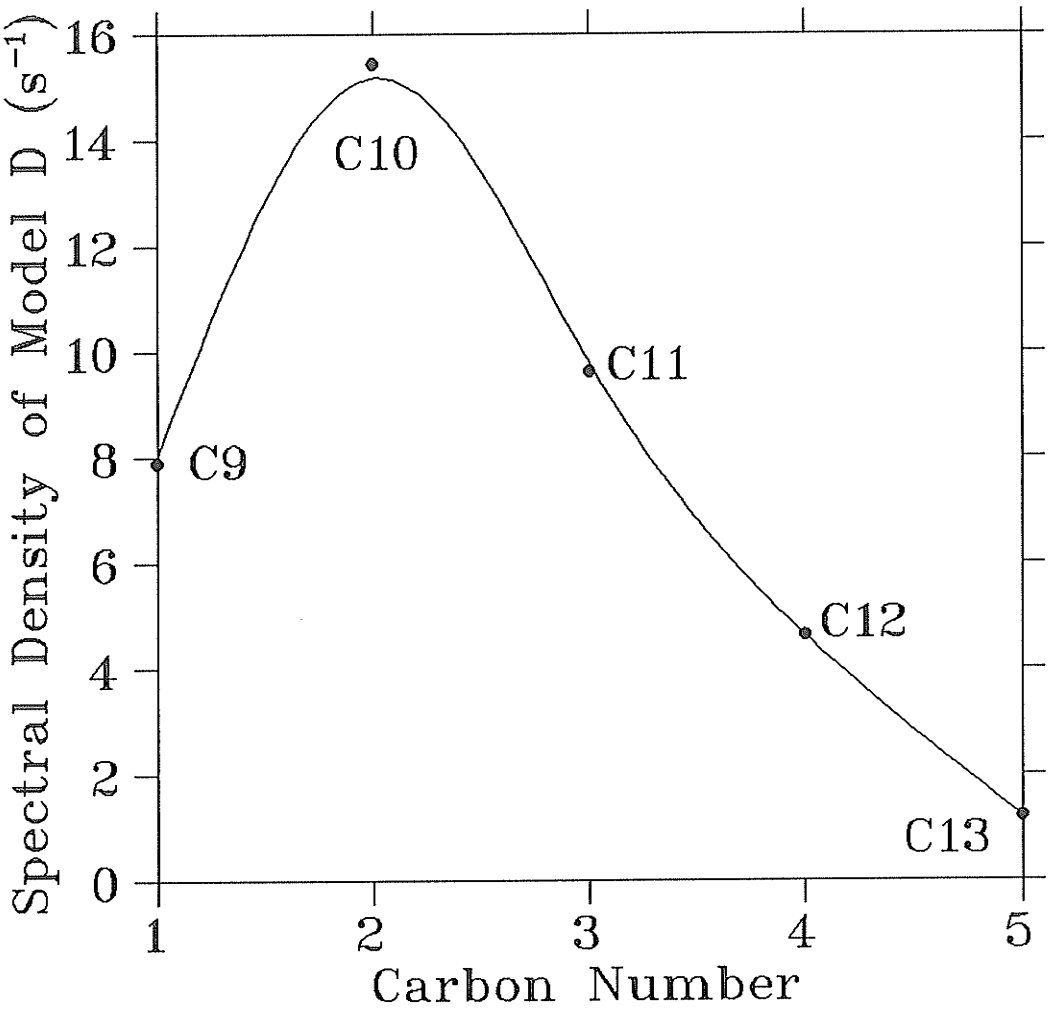

Figure 3.12: **Model D results vs. Carbon Number**

Table 3.16: **Calculated Model D's relaxation rates versus Beckmann's relaxation rates**

Carbon number	Model D relax. rates $[s^{-1}]$	Beckmann relax. rates $[s^{-1}]$
C9	43.84	64.65
C10	82.57	40.45
C11	51.83	31.20
C12	24.35	18.71
C13	6.32	6.09

line.

3.5 MODEL E

The values of relaxation times T_1 of the temperature 31.3 °C which are shown in table 2.1 for C9, C10, C11, C12, and C13 are 0.286, 0.181, 0.368, 0.679, and 1.445 respectively. The first four carbon C9, C10, C11,and C12 should be multiplied by 2 and the last carbon C13 should be multiplied by 3; This is explained in figure 1.3. Therefore the values of C9, C10, C11, C12, and C13 would become 0.572, 0.362, 0.736, 1.358, and 4.335 respectively. From appendix D.1 the program JDTLA3.FOR is used to analysis the data JDTLA3.DAT shown in appendix E.1. This program is using the following model:-

$$T(IA, IB) = DPAR/B(IA, IB) + DPAR * QQ + DPAR$$

$$\tau_{pq}^{-1} = D_i/B_{pq} + D_i q^2 + D_i$$

Table 3.17: **JDTLA3.DAT**

carbon number	TDEG ^oC	DPAR $[s^{-1}]$	ADF	BETA	P_2	P_4	RBOND [cm]
C9	31.3	1.143	0.000	70.500	0.125	0.000	1.101
C10	31.3	0.614	0.000	70.500	0.082	0.000	1.101
C11	31.3	1.515	0.000	70.500	0.089	0.000	1.101
C12	31.3	2.890	0.000	70.500	0.057	0.000	1.101
C13	31.3	8.340	0.000	70.500	0.042	0.000	1.101

The values of the order parameters P_2 are taken from P.A.Beckmann's paper [LJS]. In order to get the above values of the relaxation times T_1, the program has been run several times changing the values of DPAR's each time. The values of the relaxation times are same as to the data to 4 figures; This is shown in appendix E.2. The values of the spectral densities are shown in table 3.18

This model will not work because by comparing the spectral densities results with R. Y. Dong's spectral densities [DYR,NGR] it has been found that by plotting a graph of Dong's results versus our results, this graph is not a straight line. These are shown in figures 3.13, and 3.14, and table 3.19.

By plotting Model E's spectral densities versus the carbon number from table 3.18, We did not get a smooth curve that is shown in figure 3.15. The values of the relaxation rates R are different from the values of P. A. Beckmann's relaxation rates, this is shown in table 3.20.

So from the above analysis We conclude that this model works only if the first carbon C9 has been ignored. This argument is true because from the figures 3.13, and 3.14 if We ignore the first carbon C9, then the two graphs would be a straight

Table 3.18: **The output of the program JDTLA3.FOR**

Carbon number	Spectral density $[s^{-1}]$	Relaxation times [sec]	Relaxation rates $[s^{-1}]$
C9	9.02	0.572	47.73
C10	16.98	0.362	87.96
C11	6.87	0.736	35.73
C12	3.63	1.358	18.61
C13	1.12	4.336	5.74

Table 3.19: **Calculated Model E's spectral densities versus Dong's spectral densities**

Carbon number	Model E spectral densities $[s^{-1}]$	Dong(1) spec. densities $[s^{-1}]$	Dong(2) spec. densities $[s^{-1}]$
C9	9.02	32.20	26.75
C10	16.98	18.50	14.91
C11	6.87	14.80	12.43
C12	3.63	8.10	6.75
C13	1.12	3.70	2.85

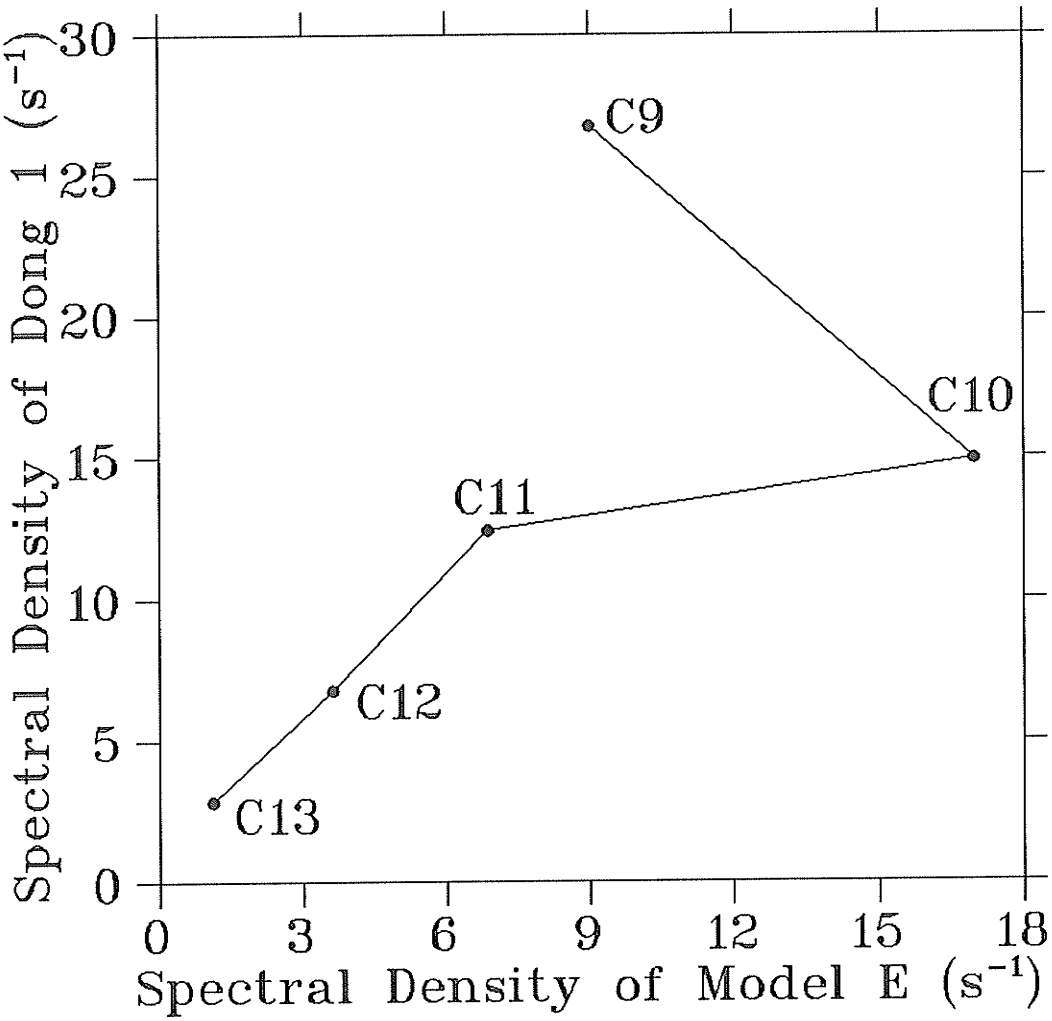

Figure 3.13: **Dong1 results vs. Model E results**

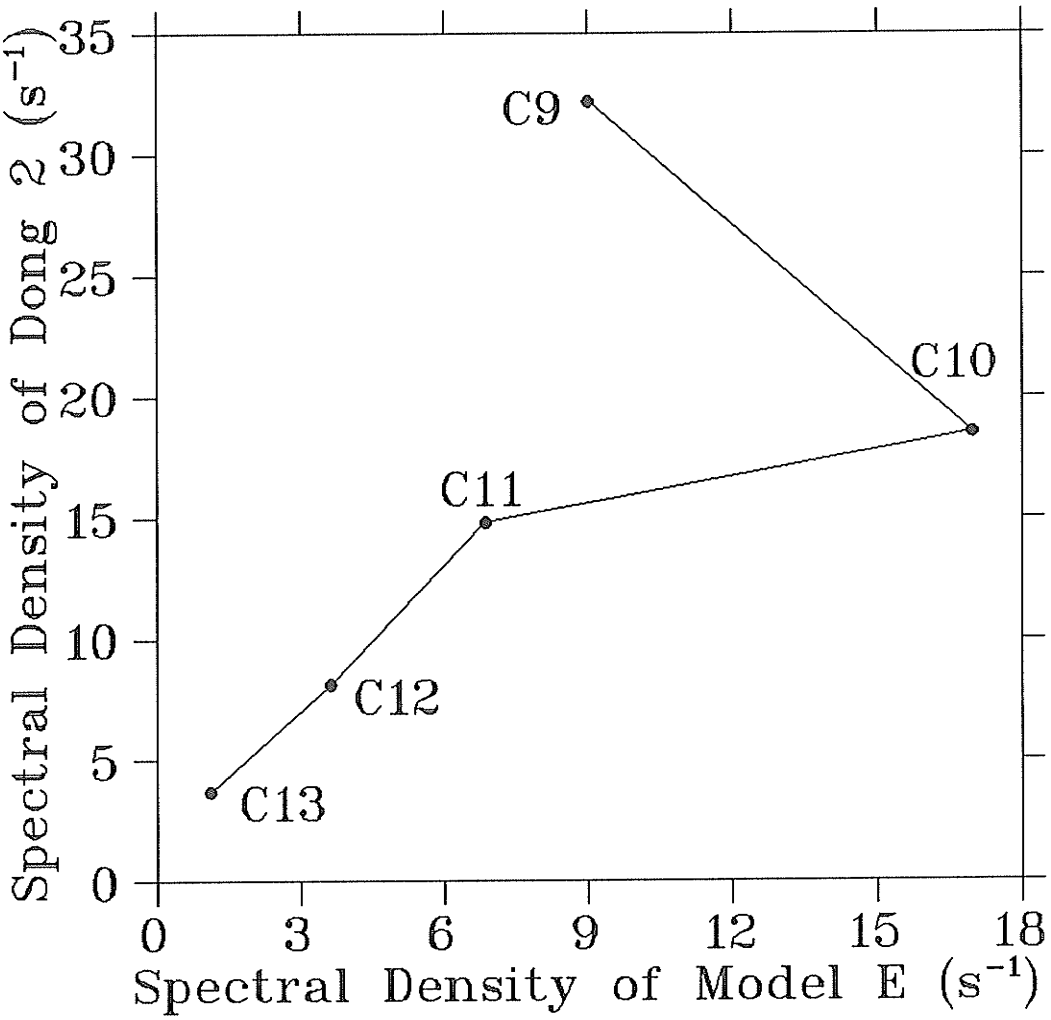

Figure 3.14: **Dong2 results vs. Model E results**

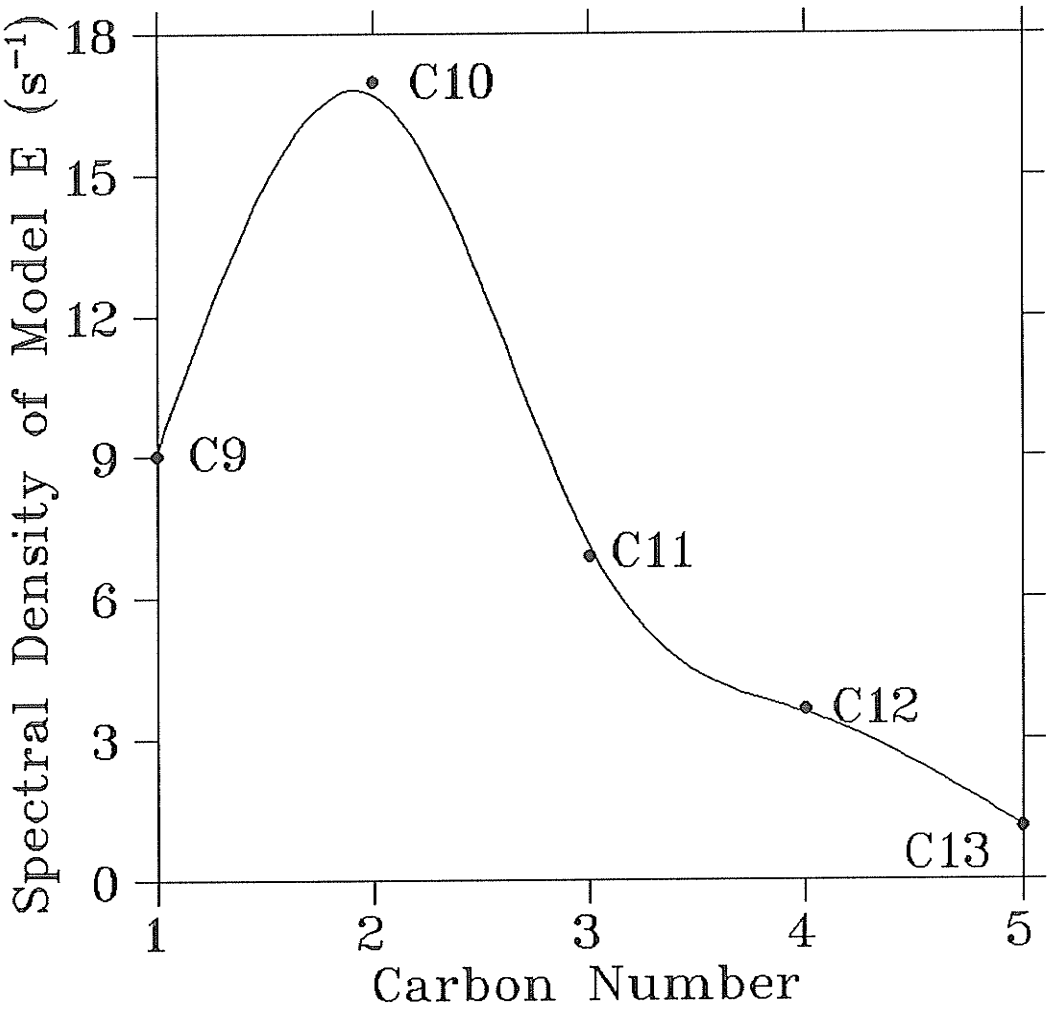

Figure 3.15: **Model E results vs. Carbon Number**

Table 3.20: **Calculated Model E's relaxation rates versus Beckmann's relaxation rates**

Carbon number	Model E relax. rates $[s^{-1}]$	Beckmann relax. rates $[s^{-1}]$
C9	47.73	67.95
C10	87.96	36.82
C11	35.73	29.26
C12	18.61	17.90
C13	5.74	6.85

line.

CHAPTER 4

CHAPTER 4

Conclusion

We consider carbon-13 nuclear magnetic resonance proton decoupled relaxation of the alkyl chains in the 5CB, and compare the results to deuterium relaxation in alkyl chains. We extend a previous model that worked well for the aromatic core, and the following changes has been introduced:

1. Experimental order parameters was used for the individual positions.
2. The formulas for correlation times in terms of one or more diffusion time(s) are found and evaluated.
3. The diffusion times are fitted to the experimental ^{13}C results.

The best model that fits the data is model A which is the following:-

$$T(IA, IB) = DPAR * (1 + (IB - 1) * *2)$$

$$\tau_{pq}^{-1} = D_i(1 + q^2)$$

P. A. Beckmann's order parameters have been used in this model, by running the program several times the values of relaxation times are same as to the data to four digits. But the values of the spectral densities would only agree with Dong's spectral densities when We interchange the assignment of the first two carbon C9 and C10. This argument is true because of the following observations:

1. It is to be observed that from figure 2.3 the line labelled as C10 shows the greatest change in chemical shifts with temperature. This requires that this

line has the greatest order parameter, which suggests that the line C10 in fact corresponds to C9 on the carbon chain (closest to the core).

2. It is also to be observed that from figure 2.2 the line of carbon C10 shows more curvature. Therefore the assignment of C9 has to be changed to the assignment of C10. By changing these two assignments We have got the following results:-

   (a) The values of the calculated relaxation times are the same as to the experimental relaxation times.

   (b) By plotting Dong's spectral densities with ours, these graphs are straight line. These are shown in figures 3.1, and 3.2.

   (c) The values of the relaxation rates R are almost the same as the values of P. A. Beckmann's relaxation rates, this is shown in table 3.4.

   (d) By plotting Model A's spectral densities versus the carbon number from table 3.3, We got a straight line, that is shown in figure 3.3.

   Model B uses the same model as in A, but the relaxation times and the order parameters are different from model A. This model works only if the first carbon C9 has been ignored. This argument is true because from the figures 3.6, 3.4, and 3.5 if We ignore the first carbon C9, then the three graphs would be a straight line.

   In model C; different model has been used which is the following:

$$T(IA, IB) = DPAR$$

$$\tau_{pq}^{-1} = D_i$$

   this model also works only if the first carbon C9 is ignored. This argument is true because from the figures 3.9, 3.7, and 3.8 if We ignore the first carbon

C9, then the three graphs would be a straight line.

The models D and E are also different from the above models:

$$T(IA, IB) = DPAR/B(IA, IB) + DPAR * QQ$$

$$\tau_{pq}^{-1} = D_i/B_{pq} + D_i q^2$$

$$T(IA, IB) = DPAR/B(IA, IB) + DPAR * QQ + DPAR$$

$$\tau_{pq}^{-1} = D_i/B_{pq} + D_i q^2 + D_i$$

These two models have almost the same discussion and conclusion as the models B and C.

APPENDICES

APPENDIX A

ABD5 Program

A.1 ABD5.FOR

```
C     ABD5.F0R MARCH. 11, 1993
C     T(IA,IB)=T(IA,IB)*(1+(IB-1)**2)
C     BETA=70.5 RBOND=1.101
C     MEANT FOR 5CB,6CB,7CB,8CB MODEL WITH
C     P2,P4=F(TNI-T), D=D(T,DEG K)
C
C     ABD5.FOR USES MOD OF R.Y.DONG,MCLC,141,349-359(86)
C     AND R.Y.DONG,JCP,88,3762-3969(88). BASED
C     ON JDONGB. HANDLES ODF, BUT NOT (YET)
C     VALID FOR C1 ( ETC.) .
C     FINDS J1,J2,J3 AND QUAD T1Z,Y1Q AND
C     CARBON-13 T1 FOR AROMATIC RING.
C
C     R = R1Z(Q), R1Q, R2(Q), R1C(DD)(C-H)
C     NP = 0(FULL), 1(PARTIAL), 2(LIMITED-NO EXT NAR)
C
      REAL*4 J(6),K(3,3),B(3,3),T(3,3),F(3,3),R(4),RI(4)
```

```
      REAL*4 W(6)/0.,96.4E6,192.9E6,423.3E6,142.2E6,707.7E6/
      REAL*4 POW(5,6),A(3)/0.5E12,1.8E10,0.0/
      REAL*4 EA(3),AD(3)
      LOGICAL*1 TITLE(78)
      REAL*4 JODF
      READ(5,998) NP,(TITLE(IO),IO=1,78)
  998 FORMAT(I2,78A1)
      WRITE(6,999) (TITLE(IO),IO=1,78)
  999 FORMAT(' HRESHA',' ',78A1,/)
      DO 995 IA=1,6
      READ(5,996) (POW(IO,IA),IO=1,5)
  995 WRITE(6,997) (POW(IO,IA),IO=1,5)
  996 FORMAT(' ',5E13.6)
  997 FORMAT(' ',5E13.6)
C     READ IN DIFFUSION CONSTANTS
      READ(5,930) AD(1),EA(1)
  930 FORMAT(2E10.3)
      WRITE(6,935) AD(1),EA(1)
  935 FORMAT(' D ',2E11.3)
C     READ IN NEXT PARAMETER SET
  900 WRITE(6,901)
  901 FORMAT(' ')
      READ(5,101) TDEG,DPAR,ADF,BETA,P2,P4,RBOND
```

```
  101  FORMAT(4E11.3,3F7.3)
       IF(P2.LE.0.0) GO TO 910
       TK = 1000.0 / (TDEG + 273.15)
       DPAR = DPAR*1.0E+09
       WRITE(6,202) TDEG,DPAR,ADF,BETA,P2,P4,RBOND

  202  FORMAT(' T,Dll,ADF,BETA,P2,P4,R:',/,' ',4E11.3,3F7.3)
       JODF = ADF * ( 4./256. ) / A(1)
       A(3) = A(2) / (RBOND**6 )
       TDEG = 1000.0 / ( TDEG + 273.15 )
       BETA = BETA * 0.0174533
       WRITE(6,203) JODF
  203  FORMAT(' JODF=',E13.5)
C      D0,D1,D2 = D00, 2*D10, 2*D20
       D0 = ((3.0*((COS(BETA))**2)-1.0)**2)*0.25
       D1 = 3.0*((SIN(2.0*BETA))**2)*0.25
       D2 = 3.0*((SIN(BETA))**4)*0.25
       WRITE(6,205) A(1),A(2),A(3),D0,D1,D2,TDEG
  205  FORMAT(' A , D:',6E14.6,' 1000/T ',F6.3)
       IC = 0
       DO 500 IA=1,3
       DO 500 IB=1,3
       IF(IA.GT.IB) GO TO 500
```

```
      IC = IC + 1
      B(IA,IB) = POW(1,IC)
      DO 510 ID=2,5
  510 B(IA,IB) = B(IA,IB) + POW(ID,IC)*(P2**(ID-1))
  500 CONTINUE
      B(2,1) = B(1,2)
      B(3,1) = B(1,3)
      B(3,2) = B(2,3)
C     FIND FREED KAPPA ELEMAENTS
      K(1,1) = 0.2 + (2./7.)*P2 + (18./35.)*P4 - P2**2
      K(1,2) = 0.2 + (1./7.)*P2 - (12./35.)*P4
      K(1,3) = 0.2 - (2./7.)*P2 + ( 3./35.)*P4
      K(2,2) = 0.2 + (1./14.)*P2 + (8./35.)*P4
      K(2,3) = 0.2 - (1./7.)*P2 - ( 2./35.)*P4
      K(3,3) = 0.2 + (2./7.)*P2 + ( 1./70.)*P4
      K(2,1) = K(1,2)
      K(3,1) = K(1,3)
      K(3,2) = K(2,3)
C     FIND "CORRELATION TIMES"
      DO 20 IA=1,3
      DO 20 IB=1,3
      T(IA,IB)=DPAR
      T(IA,IB)=T(IA,IB)*(1+(IB-1)**2)
```

```
20      T(IA,IB) = 1.0 / T(IA,IB)
        IF(NP.NE.0) GO TO 950
        WRITE(6,208) B(1,1),B(1,2),B(1,3),B(2,2),B(2,3),B(3,3)
208     FORMAT(' BETA:',/,' ',6E11.4)
        WRITE(6,210) ((K(IA,IB),IB=1,3),IA=1,3)
210     FORMAT(' K ',/,(' ',3E15.5))
        WRITE(6,220) ((T(IA,IB),IB=1,3),IA=1,3)
220     FORMAT(' T ',/,(' ',3E15.5))


950     CONTINUE
C       TRY EXTREME NARROWING
        IF(NP.EQ.2) GO TO 301
        DO 30 IA=1,3
        DO 30 IB=1,3
30      F(IA,IB) = T(IA,IB)
        DO 35 IA=1,3
        J(IA) = (D0*K(IA,1)*F(IA,1) + D1*K(IA,2)*F(IA,2)
1       + D2*K(IA,3)*F(IA,3) )
        IF(IA.EQ.2) J(IA) = J(IA) + JODF
35      J(IA+3) = J(IA)
        NGOTO = 1
        GO TO 400
301     CONTINUE
```

```
C       J FOR BOTH RON'S D AND OUR C13
        DO 47 IB=1,2
        DO 45 IC=1,3
        DO 40 IA=1,3
        ID = IC + 3*(IB-1)
40      F(IC,IA) = T(IC,IA)/(1.+(W(ID)*T(IC,IA))**2)
45      J(ID) = (D0*K(IC,1)*F(IC,1) + D1*K(IC,2)*F(IC,2)
1       + D2*K(IC,3)*F(IC,3) )
        IF(ID.EQ.2.OR.ID.EQ.5) J(ID) = J(ID) + JODF
47      CONTINUE
        NGOTO = 2
        GO TO 400
302     CONTINUE
        GO TO 900
400     CONTINUE
        R(1) = J(2) + 4.*J(3)
        R(2) = 3.*J(2)
        R(3) = ( 3.*J(1) + 3.*J(2) + 2.*J(3) )*0.5
        R(4) = J(4) + 3.*J(5) + 6.*J(6)
        R(1) = A(1)*R(1)
        R(2) = A(1)*R(2)
        R(3) = A(1)*R(3)
        R(4) = A(3)*R(4)
```

```
      DO 420 IA=1,4
  420 RI(IA) = 1.0 / R(IA)
      WRITE(6,230) (J(IO),IO=1,6),(R(IO),IO=1,4),(RI(IO),IO=1,4)
  230 FORMAT(' J',6E11.4,/,' R',4E11.4,/,' T',4E11.4)
      GO TO (301,302),NGOTO
C
  910 STOP
      END
```

A.2 ABD5.DAT

```
01 ABD5 , 11-4 BETA , RONS JCP,88,3962 5CB FIG.3
0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
4.862E+11 1.802E+00
30.000 4.300 0.000 70.500 0.125 0.000 1.101
30.000 2.900 0.000 70.500 0.082 0.000 1.101
30.000 4.550 0.000 70.500 0.089 0.000 1.101
30.000 9.985 0.000 70.500 0.057 0.000 1.101
30.000 29.200 0.000 70.500 0.042 0.000 1.101
0.000
```

A.3 ABD5.OUT

JDONGB ABD5 , 11-4 BETA , RONS JCP,88,3962 5CB FIG.3

0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
D 0.486E+12 0.180E+01

T,Dll,ADF,BETA,P2,P4,R:
0.300E+02 0.430E+10 0.000E+00 0.705E+02 0.125 0.000 1.101
JODF= 0.00000E+00
A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00
0.297032E+00 0.592172E+00 1000/T 3.299
J 0.1772E-10 0.1785E-10 0.1702E-10 0.1772E-10 0.1785E-10 0.1702E-10
R 0.4296E+02 0.2677E+02 0.3518E+02 0.1752E+01
T 0.2328E-01 0.3736E-01 0.2842E-01 0.5708E+00
J 0.1772E-10 **0.1784E-10** 0.1700E-10 0.1765E-10 0.1784E-10 0.1686E-10
R **0.4293E+02** 0.2676E+02 0.3517E+02 0.1741E+01
T 0.2329E-01 0.3736E-01 0.2843E-01 **0.5744E+00**

T,Dll,ADF,BETA,P2,P4,R:
0.300E+02 0.290E+10 0.000E+00 0.705E+02 0.082 0.000 1.101
JODF= 0.00000E+00
A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00
0.297032E+00 0.592172E+00 1000/T 3.299
J 0.2633E-10 0.2632E-10 0.2551E-10 0.2633E-10 0.2632E-10 0.2551E-10
R 0.6419E+02 0.3948E+02 0.5225E+02 0.2611E+01

T 0.1558E-01 0.2533E-01 0.1914E-01 0.3830E+00

J 0.2633E-10 **0.2631E-10** 0.2547E-10 0.2610E-10 0.2629E-10 0.2497E-10

R **0.6410E+02** 0.3946E+02 0.5222E+02 0.2575E+01

T 0.1560E-01 0.2534E-01 0.1915E-01 **0.3884E+00**

T,Dll,ADF,BETA,P2,P4,R:

0.300E+02 0.455E+10 0.000E+00 0.705E+02 0.089 0.000 1.101

JODF= 0.00000E+00

A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00

0.297032E+00 0.592172E+00 1000/T 3.299

J 0.1678E-10 0.1679E-10 0.1623E-10 0.1678E-10 0.1679E-10 0.1623E-10

R 0.4086E+02 0.2519E+02 0.3330E+02 0.1663E+01

T 0.2447E-01 0.3971E-01 0.3003E-01 0.6014E+00

J 0.1678E-10 **0.1679E-10** 0.1622E-10 0.1672E-10 0.1678E-10 0.1609E-10

R **0.4084E+02** 0.2518E+02 0.3329E+02 0.1653E+01

T 0.2449E-01 0.3971E-01 0.3004E-01 **0.6049E+00**

T,Dll,ADF,BETA,P2,P4,R:

0.300E+02 0.998E+10 0.000E+00 0.705E+02 0.057 0.000 1.101

JODF= 0.00000E+00

A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00

0.297032E+00 0.592172E+00 1000/T 3.299

J 0.7639E-11 0.7621E-11 0.7458E-11 0.7639E-11 0.7621E-11 0.7458E-11

R 0.1873E+02 0.1143E+02 0.1517E+02 0.7604E+00

T 0.5340E-01 0.8748E-01 0.6590E-01 0.1315E+01

J 0.7639E-11 **0.7620E-11** 0.7457E-11 0.7633E-11 0.7620E-11 0.7443E-11

R **0.1872E+02** 0.1143E+02 0.1517E+02 0.7594E+00

T 0.5341E-01 0.8749E-01 0.6591E-01 **0.1317E+01**

T,Dll,ADF,BETA,P2,P4,R:

0.300E+02 0.292E+11 0.000E+00 0.705E+02 0.042 0.000 1.101

JODF= 0.00000E+00

A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00

0.297032E+00 0.592172E+00 1000/T 3.299

J 0.2608E-11 0.2601E-11 0.2560E-11 0.2608E-11 0.2601E-11 0.2560E-11

R 0.6420E+01 0.3901E+01 0.5187E+01 0.2604E+00

T 0.1558E+00 0.2563E+00 0.1928E+00 0.3840E+01

J 0.2608E-11 **0.2601E-11** 0.2560E-11 0.2608E-11 0.2601E-11 0.2559E-11

R **0.6420E+01** 0.3901E+01 0.5187E+01 0.2604E+00

T 0.1558E+00 0.2563E+00 0.1928E+00 **0.3841E+01**

APPENDIX B

HRE5 Program

B.1 HRE5.DAT

```
01 HRE5 , 11-4 BETA , RONS JCP,88,3962 5CB FIG.3
0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
4.862E+11 1.802E+00
34.800 3.830 0.000 70.500 0.214 0.000 1.101
34.800 3.862 0.000 70.500 0.148 0.000 1.101
34.800 4.589 0.000 70.500 0.159 0.000 1.101
34.800 9.580 0.000 70.500 0.107 0.000 1.101
34.800 30.100 0.000 70.500 0.078 0.000 1.101
0.000
```

B.2 HRE5.OUT

HRESHA HRE5 , 11-4 BETA , RONS JCP,88,3962 5CB FIG.3

0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
D 0.486E+12 0.180E+01

T,Dll,ADF,BETA,P2,P4,R:
0.348E+02 0.383E+10 0.000E+00 0.705E+02 0.214 0.000 1.101
JODF= 0.00000E+00
A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00
0.297032E+00 0.592172E+00 1000/T 3.247
J 0.1946E-10 0.2026E-10 0.1866E-10 0.1946E-10 0.2026E-10 0.1866E-10
R 0.4745E+02 0.3039E+02 0.3912E+02 0.1942E+01
T 0.2107E-01 0.3291E-01 0.2556E-01 0.5148E+00
J 0.1946E-10 **0.2025E-10** 0.1865E-10 0.1936E-10 0.2025E-10 0.1846E-10
R **0.4742E+02** 0.3038E+02 0.3911E+02 0.1929E+01
T 0.2109E-01 0.3292E-01 0.2557E-01 **0.5185E+00**

T,Dll,ADF,BETA,P2,P4,R:
0.348E+02 0.386E+10 0.000E+00 0.705E+02 0.148 0.000 1.101
JODF= 0.00000E+00
A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00
0.297032E+00 0.592172E+00 1000/T 3.247
J 0.1966E-10 0.1993E-10 0.1883E-10 0.1966E-10 0.1993E-10 0.1883E-10
R 0.4763E+02 0.2989E+02 0.3911E+02 0.1945E+01

T 0.2100E-01 0.3346E-01 0.2557E-01 0.5142E+00

J 0.1966E-10 **0.1992E-10** 0.1882E-10 0.1956E-10 0.1992E-10 0.1862E-10

R **0.4759E+02** 0.2988E+02 0.3910E+02 0.1930E+01

T 0.2101E-01 0.3346E-01 0.2558E-01 **0.5181E+00**

T,Dll,ADF,BETA,P2,P4,R:

0.348E+02 0.459E+10 0.000E+00 0.705E+02 0.159 0.000 1.101

JODF= 0.00000E+00

A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00

0.297032E+00 0.592172E+00 1000/T 3.247

J 0.1651E-10 0.1679E-10 0.1580E-10 0.1651E-10 0.1679E-10 0.1580E-10

R 0.4000E+02 0.2519E+02 0.3288E+02 0.1634E+01

T 0.2500E-01 0.3970E-01 0.3041E-01 0.6119E+00

J 0.1651E-10 **0.1679E-10** 0.1579E-10 0.1645E-10 0.1679E-10 0.1568E-10

R **0.3998E+02** 0.2518E+02 0.3287E+02 0.1626E+01

T 0.2501E-01 0.3971E-01 0.3042E-01 **0.6151E+00**

T,Dll,ADF,BETA,P2,P4,R:

0.348E+02 0.958E+10 0.000E+00 0.705E+02 0.107 0.000 1.101

JODF= 0.00000E+00

A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00

0.297032E+00 0.592172E+00 1000/T 3.247

J 0.7966E-11 0.7992E-11 0.7674E-11 0.7966E-11 0.7992E-11 0.7674E-11

R 0.1934E+02 0.1199E+02 0.1581E+02 0.7881E+00

T 0.5170E-01 0.8341E-01 0.6327E-01 0.1269E+01

J 0.7966E-11 **0.7992E-11** 0.7672E-11 0.7960E-11 0.7992E-11 0.7658E-11

R **0.1934E+02** 0.1199E+02 0.1581E+02 0.7871E+00

T 0.5170E-01 0.8342E-01 0.6327E-01 **0.1271E+01**

T,Dll,ADF,BETA,P2,P4,R:

0.348E+02 0.301E+11 0.000E+00 0.705E+02 0.078 0.000 1.101

JODF= 0.00000E+00

A , D: 0.500000E+12 0.180000E+11 0.101053E+11 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.247

J 0.2537E-11 0.2535E-11 0.2461E-11 0.2537E-11 0.2535E-11 0.2461E-11

R 0.6189E+01 0.3802E+01 0.5034E+01 0.2517E+00

T 0.1616E+00 0.2630E+00 0.1987E+00 0.3974E+01

J 0.2537E-11 **0.2535E-11** 0.2461E-11 0.2537E-11 0.2535E-11 0.2460E-11

R **0.6188E+01** 0.3802E+01 0.5034E+01 0.2516E+00

T 0.1616E+00 0.2630E+00 0.1987E+00 **0.3974E+01**

APPENDIX C

ABD7 Program

C.1 ABD7.FOR

```
C     ABD7.F0R MAR. 3, 1993
C     CHANGING A_D FROM 5.0E11 TO 4.18E11
C     TEMPERATURE = 30.0 °C
C     BETA=70.5 RBOND=1.101
C     MEANT FOR 5CB,6CB,7CB,8CB MODEL WITH
C     P2,P4=F(TNI-T), D=D(T,DEG K)
C
C     ABD7.FOR USES MOD OF R.Y.DONG,MCLC,141,349-359(86)
C     AND R.Y.DONG,JCP,88,3762-3969(88). BASED
C     ON JDONGB. HANDLES ODF, BUT NOT (YET)
C     VALID FOR C1 ( ETC.) .
C     FINDS J1,J2,J3 AND QUAD T1Z,Y1Q AND
C     CARBON-13 T1 FOR AROMATIC RING.
C
C     R = R1Z(Q), R1Q, R2(Q), R1C(DD)(C-H)
C     NP = 0(FULL), 1(PARTIAL), 2(LIMITED-NO EXT NAR)
C
```

```
      REAL*4 J(6),K(3,3),B(3,3),T(3,3),F(3,3),R(4),RI(4)
      REAL*4 W(3)/23.51E8,7.89E8,39.29E8/
      REAL*4 AJ(6)
      REAL*4 POW(5,6),A(3)/4.18E11,1.8E10,0.0/
      REAL*4 EA(3),AD(3)
      LOGICAL*1 TITLE(78)
      REAL*4 JODF
      READ(5,998) NP,(TITLE(IO),IO=1,78)
  998 FORMAT(I2,78A1)
      WRITE(6,999) (TITLE(IO),IO=1,78)
  999 FORMAT(' HRESHA',' ',78A1,/)
      DO 995 IA=1,6
      READ(5,996) (POW(IO,IA),IO=1,5)
  995 WRITE(6,997) (POW(IO,IA),IO=1,5)
  996 FORMAT(' ',5E13.6)
  997 FORMAT(' ',5E13.6)
C     READ IN DIFFUSION CONSTANTS
      READ(5,930) AD(1),EA(1)
  930 FORMAT(2E10.3)
      WRITE(6,935) AD(1),EA(1)
  935 FORMAT(' D ',2E11.3)
C     READ IN NEXT PARAMETER SET
  900 WRITE(6,901)
```

```
  901  FORMAT(' ')
       READ(5,101) TDEG,DPAR,ADF,BETA,P2,P4,RBOND
  101  FORMAT(4E11.3,3F7.3)
       IF(P2.LE.0.0) GO TO 910
       TK = 1000.0 / (TDEG + 273.15)
       DPAR = DPAR*1.0E+09
       WRITE(6,202) TDEG,DPAR,ADF,BETA,P2,P4,RBOND


  202  FORMAT(' T,Dll,ADF,BETA,P2,P4,R:',/,' ',4E11.3,3F7.3)
       JODF = ADF * ( 4./256. ) / A(1)
       A(3) = A(2) / (RBOND**6 )
       TDEG = 1000.0 / ( TDEG + 273.15 )
       BETA = BETA * 0.0174533
       WRITE(6,203) JODF
  203  FORMAT(' JODF=',E13.5)
C      D0,D1,D2 = D00, 2*D10, 2*D20
       D0 = ((3.0*((COS(BETA))**2)-1.0)**2)*0.25
       D1 = 3.0*((SIN(2.0*BETA))**2)*0.25
       D2 = 3.0*((SIN(BETA))**4)*0.25
       WRITE(6,205) A(1),A(2),A(3),D0,D1,D2,TDEG
  205  FORMAT(' A , D:',6E14.6,' 1000/T ',F6.3)
       IC = 0
       DO 500 IA=1,3
```

```
      DO 500 IB=1,3
      IF(IA.GT.IB) GO TO 500
      IC = IC + 1
      B(IA,IB) = POW(1,IC)
      DO 510 ID=2,5
  510 B(IA,IB) = B(IA,IB) + POW(ID,IC)*(P2**(ID-1))
  500 CONTINUE
      B(2,1) = B(1,2)
      B(3,1) = B(1,3)
      B(3,2) = B(2,3)
C     FIND FREED KAPPA ELEMAENTS
      K(1,1) = 0.2 + (2./7.)*P2 + (18./35.)*P4 - P2**2
      K(1,2) = 0.2 + (1./7.)*P2 - (12./35.)*P4
      K(1,3) = 0.2 - (2./7.)*P2 + ( 3./35.)*P4
      K(2,2) = 0.2 + (1./14.)*P2 + (8./35.)*P4
      K(2,3) = 0.2 - (1./7.)*P2 - ( 2./35.)*P4
      K(3,3) = 0.2 + (2./7.)*P2 + ( 1./70.)*P4
      K(2,1) = K(1,2)
      K(3,1) = K(1,3)
      K(3,2) = K(2,3)
C     FIND "CORRELATION TIMES"
      DO 20 IA=1,3
      DO 20 IB=1,3
```

```
      T(IA,IB)=DPAR
   20 T(IA,IB) = 1.0 / T(IA,IB)
      IF(NP.NE.0) GO TO 950
      WRITE(6,208) B(1,1),B(1,2),B(1,3),B(2,2),B(2,3),B(3,3)
  208 FORMAT(' BETA:',/,' ',6E11.4)
      WRITE(6,210) ((K(IA,IB),IB=1,3),IA=1,3)
  210 FORMAT(' K ',/,(' ',3E15.5))
      WRITE(6,220) ((T(IA,IB),IB=1,3),IA=1,3)
  220 FORMAT(' T ',/,(' ',3E15.5))

  950 CONTINUE
C     TRY EXTREME NARROWING
      IF(NP.EQ.2) GO TO 301
      DO 30 IA=1,3
      DO 30 IB=1,3
   30 F(IA,IB) = T(IA,IB)
      DO 35 IA=1,3
      J(IA) = (D0*K(IA,1)*F(IA,1) + D1*K(IA,2)*F(IA,2)
     1 + D2*K(IA,3)*F(IA,3) )
      IF(IA.EQ.2) J(IA) = J(IA) + JODF
   35 J(IA+3) = J(IA)
      NGOTO = 1
      GO TO 400
  301 CONTINUE
```

```
C       J FOR BOTH RON'S D AND OUR C13
        DO 47 IB=1,2
        DO 45 IC=1,3
        DO 40 IA=1,3
        ID = IC + 3*(IB-1)
   40   F(IC,IA) = T(IC,IA)/(1.+(W(ID)*T(IC,IA))**2)
   45   J(ID) = (D0*K(IC,1)*F(IC,1) + D1*K(IC,2)*F(IC,2)
        1 + D2*K(IC,3)*F(IC,3) )
        IF(ID.EQ.2.OR.ID.EQ.5) J(ID) = J(ID) + JODF
   47   CONTINUE
        NGOTO = 2
        GO TO 400
  302   CONTINUE
        GO TO 900
  400   CONTINUE
        R(1) = J(2) + 4.*J(3)
        R(2) = 3.*J(2)
        R(3) = ( 3.*J(1) + 3.*J(2) + 2.*J(3) )*0.5
        R(4) = J(4) + 3.*J(5) + 6.*J(6)
        R(1) = A(1)*R(1)
        R(2) = A(1)*R(2)
        R(3) = A(1)*R(3)
        R(4) = A(3)*R(4)
```

```
      DO 419 IA=1,3
  419 AJ(IA)=J(IA)*A(1)
      WRITE(6,231) (AJ(IO),IO=1,3)
  231 FORMAT(' AJ=',3F12.4)
      DO 420 IA=1,4
  420 RI(IA) = 1.0 / R(IA)
      WRITE(6,230) (J(IO),IO=1,6),(R(IO),IO=1,4),(RI(IO),IO=1,4)
  230 FORMAT(' J',6E11.4,/,' R',4E11.4,/,' T',4E11.4)
      GO TO (301,302),NGOTO
C
      910 STOP
      END
```

C.2 ABD7.DAT

```
01 ABD7 , 11-4 BETA , RONS JCP,88,3962 5CB FIG.3
0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
4.862E+11 1.802E+00
30.000 12.000 0.000 70.500 0.214 0.000 1.101
30.000 7.990 0.000 70.500 0.148 0.000 1.101
30.000 12.500 0.000 70.500 0.159 0.000 1.101
30.000 27.300 0.000 70.500 0.107 0.000 1.101
30.000 79.200 0.000 70.000 0.078 0.000 1.101
0.000
```

C.3 ABD7.OUT

HRESHA ABD7 , 11-4 BETA , RONS JCP,88,3962 5CB FIG.3

0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
D 0.486E+12 0.180E+01

T,Dll,ADF,BETA,P2,P4,R:
0.300E+02 0.120E+11 0.000E+00 0.705E+02 0.214 0.000 1.101
JODF= 0.00000E+00
A , D: 0.418000E+12 0.180000E+11 0.101053E+11 0.110796E+00
0.297032E+00 0.592172E+00 1000/T 3.299
AJ= 6.0810 6.6122 7.6756
J 0.1455E-10 0.1582E-10 0.1836E-10 0.1455E-10 0.1582E-10 0.1836E-10
R 0.3731E+02 0.1984E+02 0.2672E+02 0.1740E+01
T 0.2680E-01 0.5041E-01 0.3743E-01 0.5747E+00
AJ= 5.8562 **6.5837** 6.9324
J 0.1401E-10 0.1575E-10 0.1658E-10 0.1455E-10 0.1582E-10 0.1836E-10
R **0.3431E+02** 0.1975E+02 0.2559E+02 0.1740E+01
T 0.2914E-01 0.5063E-01 0.3907E-01 **0.5747E+00**

T,Dll,ADF,BETA,P2,P4,R:
0.300E+02 0.799E+10 0.000E+00 0.705E+02 0.148 0.000 1.101
JODF= 0.00000E+00
A , D: 0.418000E+12 0.180000E+11 0.101053E+11 0.110796E+00
0.297032E+00 0.592172E+00 1000/T 3.299

AJ= 9.5998 10.0949 11.1994

J 0.2297E-10 0.2415E-10 0.2679E-10 0.2297E-10 0.2415E-10 0.2679E-10

R 0.5489E+02 0.3028E+02 0.4074E+02 0.2589E+01

T 0.1822E-01 0.3302E-01 0.2455E-01 0.3863E+00

AJ= 8.8349 **9.9974** 9.0187

J 0.2114E-10 0.2392E-10 0.2158E-10 0.2297E-10 0.2415E-10 0.2679E-10

R **0.4607E+02** 0.2999E+02 0.3727E+02 0.2589E+01

T 0.2171E-01 0.3334E-01 0.2683E-01 **0.3863E+00**

T,Dll,ADF,BETA,P2,P4,R:

0.300E+02 0.125E+11 0.000E+00 0.705E+02 0.159 0.000 1.101

JODF= 0.00000E+00

A , D: 0.418000E+12 0.180000E+11 0.101053E+11 0.110796E+00

0.297032E+00 0.592172E+00 1000/T 3.299

AJ= 6.0887 6.4352 7.1937

J 0.1457E-10 0.1540E-10 0.1721E-10 0.1457E-10 0.1540E-10 0.1721E-10

R 0.3521E+02 0.1931E+02 0.2598E+02 0.1657E+01

T 0.2840E-01 0.5180E-01 0.3849E-01 0.6034E+00

AJ= 5.8807 **6.4096** 6.5468

J 0.1407E-10 0.1533E-10 0.1566E-10 0.1457E-10 0.1540E-10 0.1721E-10

R **0.3260E+02** 0.1923E+02 0.2498E+02 0.1657E+01

T 0.3068E-01 0.5201E-01 0.4003E-01 **0.6034E+00**

T,Dll,ADF,BETA,P2,P4,R:

0.300E+02 0.273E+11 0.000E+00 0.705E+02 0.107 0.000 1.101

JODF= 0.00000E+00

A , D: 0.418000E+12 0.180000E+11 0.101053E+11 0.110796E+00

0.297032E+00 0.592172E+00 1000/T 3.299

AJ= 2.8870 2.9844 3.2181

J 0.6907E-11 0.7140E-11 0.7699E-11 0.6907E-11 0.7140E-11 0.7699E-11

R 0.1586E+02 0.8953E+01 0.1203E+02 0.7530E+00

T 0.6306E-01 0.1117E+00 0.8316E-01 0.1328E+01

AJ= 2.8658 **2.9819** 3.1528

J 0.6856E-11 0.7134E-11 0.7543E-11 0.6907E-11 0.7140E-11 0.7699E-11

R **0.1559E+02** 0.8946E+01 0.1192E+02 0.7530E+00

T 0.6413E-01 0.1118E+00 0.8386E-01 **0.1328E+01**

T,Dll,ADF,BETA,P2,P4,R:

0.300E+02 0.792E+11 0.000E+00 0.700E+02 0.078 0.000 1.101

JODF= 0.00000E+00

A , D: 0.418000E+12 0.180000E+11 0.101053E+11 0.105322E+00

0.309881E+00 0.584797E+00 1000/T 3.299

AJ= 1.0140 1.0365 1.0937

J 0.2426E-11 0.2480E-11 0.2617E-11 0.2426E-11 0.2480E-11 0.2617E-11

R 0.5411E+01 0.3109E+01 0.4169E+01 0.2583E+00

T 0.1848E+00 0.3216E+00 0.2398E+00 0.3871E+01

AJ= 1.0131 **1.0364** 1.0910

J 0.2424E-11 0.2479E-11 0.2610E-11 0.2426E-11 0.2480E-11 0.2617E-11

R **0.5401E+01** 0.3109E+01 0.4165E+01 0.2583E+00

T 0.1852E+00 0.3216E+00 0.2401E+00 **0.3871E+01**

APPENDIX D

JDTLA0 program

D.1 JDTLA0.FOR

```
C     jdtlaa.for Mar. 06, 1993
C     based on JDONGD.FOR MEANT FOR 5CB tail carbons
C
C     USES MOD OF R.Y.DONG,MCLC,141,349-359(86) AND
C     R.Y.DONG,JCP,88,3762-3969(88).
C
C     FINDS J1,J2,J3 AND QUAD T1Z,Y1Q AND
C     CARBON-13 T1 FOR Tail (?)
C
C     R = R1Z(Q), R1Q, R2(Q), R1C(DD)(C-H)
C     NP = 0(FULL), 1(PARTIAL), 2(limited)
C
      REAL*4 J(9),K(3,3),B(3,3),T(3,3),F(3,3),R(5),RI(5)
      REAL*4 W(9),jodf,ja(3),con/6.28319e+06/
      REAL*4 POW(5,6),A(3)/0.5E12,1.8E10,0.0/
C
      LOGICAL*1 TITLE(78)
```

```
C
      w(1) = 0.0
      w(2) = 15. * con
      w(3) = 30.2 * con
      w(4) = ( 90. - 26.3 ) * con
      w(5) = ( 26.3 ) * con
      w(6) = ( 90. + 26.3 ) * con
      w(7) = ( 500. - 125.6 ) * con
      w(8) = ( 125.6 ) * con
      w(9) = ( 500. + 125.6 ) * con
      READ(5,998) NP, model,(TITLE(IO),IO=1,78)
998   FORMAT(2I5,78A1)
      WRITE(6,999) np,model,(TITLE(IO),IO=1,78)
999   FORMAT(' jdtlaa 13jan93 ',2I5,' ',78A1,/)
C
      DO 995 IA=1,6
      READ(5,996) (POW(IO,IA),IO=1,5)
995   WRITE(6,997) (POW(IO,IA),IO=1,5)
996   FORMAT(5E13.6)
997   FORMAT(' ',5E13.6)
C     READ IN NEXT PARAMETER SET
900   WRITE(6,901)
901   FORMAT(' ')
```

```
      READ(5,101) TDEG,DPAR,ADF,BETA,P2,P4,RBOND
  101 FORMAT(4F8.3,3F6.3)
      IF(RBOND.LE.0.0) GO TO 910
C
      WRITE(6,202) TDEG,DPAR,ADF,BETA,P2,P4,RBOND

  202 FORMAT(' T,dif,ADF,BETA,P2,P4, R:',/,' ',6F9.3,3F7.3)
      jodf = ADF * ( 4./256. ) / A(1)
      A(3) = A(2) / (RBOND**6 )
      TDEG = 1000.0 / ( TDEG + 273.15 )
      BETA = BETA * 0.0174533
      DPAR = DPAR * 1.0E+09
      write(6,203) jodf,A(1),a(2),a(3),BETA,DPAR
  203 format(' jodf,a1,a2,a3,beta,dpar= ',/,' ',6e12.4)
C     D0,D1,D2 = D00, 2*D10, 2*D20
      D0 = ((3.0*((COS(BETA))**2)-1.0)**2)*0.25
      D1 = 3.0*((SIN(2.0*BETA))**2)*0.25
      D2 = 3.0*((SIN(BETA))**4)*0.25
      WRITE(6,205) D0,D1,D2,TDEG
  205 FORMAT(' d0,d1,d2= ',3E14.6,' 1000/T ',F6.3)
C     find nordio and segre beta
      IC = 0
      DO 500 IA=1,3
```

```
      DO 500 IB=1,3
      IF(IA.GT.IB) GO TO 500
      IC = IC + 1
      B(IA,IB) = POW(1,IC)
      DO 510 ID=2,5
  510 B(IA,IB) = B(IA,IB) + POW(ID,IC)*(P2**(ID-1))
  500 CONTINUE
      B(2,1) = B(1,2)
      B(3,1) = B(1,3)
      B(3,2) = B(2,3)
C     FIND FREED KAPPA ELEMAENTS
      K(1,1) = 0.2 + (2./7.)*P2 + (18./35.)*P4 - P2**2
      K(1,2) = 0.2 + (1./7.)*P2 - (12./35.)*P4
      K(1,3) = 0.2 - (2./7.)*P2 + ( 3./35.)*P4
      K(2,2) = 0.2 + (1./14.)*P2 + (8./35.)*P4
      K(2,3) = 0.2 - (1./7.)*P2 - ( 2./35.)*P4
      K(3,3) = 0.2 + (2./7.)*P2 + ( 1./70.)*P4
      K(2,1) = K(1,2)
      K(3,1) = K(1,3)
      K(3,2) = K(2,3)
C     FIND "CORRELATION TIMES"
      DO 20 IA=1,3
      DO 20 IB=1,3
```

```
      if(model.eq.1) t(ia,ib) = dpar
      if(model.eq.2) t(ia,ib) = dpar*float((1+(ib-1)**2))
      if(model.eq.1.or.model.eq.2) go to 20
      QQ = FLOAT( (IB-1)**2 )
      T(IA,IB) = DPAR/B(IA,IB) + (DPAR)*QQ
      IF(IB.EQ.0) GO TO 20
      T(IA,IB) = T(IA,IB) + DPAR

20    T(IA,IB) = 1.0 / T(IA,IB)
      IF(NP.NE.0) GO TO 950
      WRITE(6,208) B(1,1),B(1,2),B(1,3),B(2,2),B(2,3),B(3,3)
208   FORMAT(' BETA:',/,' ',6E11.4)
      WRITE(6,210) ((K(IA,IB),IB=1,3),IA=1,3)
210   FORMAT(' K ',/,(' ',3E15.5))
      WRITE(6,220) ((T(IA,IB),IB=1,3),IA=1,3)
220   FORMAT(' T ',/,(' ',3E15.5))
950   CONTINUE
C     TRY EXTREME NARROWING
      DO 30 IA=1,3
      DO 30 IB=1,3
30    F(IA,IB) = T(IA,IB)
      DO 35 IA=1,3
      J(IA) = (D0*K(IA,1)*F(IA,1) + D1*K(IA,2)*F(IA,2)
```

```
     1      + D2*K(IA,3)*F(IA,3) )
            IF(IA.EQ.2) J(IA) = J(IA) + JODF
            j(ia+6) = j(ia)
    35      J(IA+3) = J(IA)
            NGOTO = 1
            GO TO 400
   301      CONTINUE
C           J FOR BOTH RON'S D AND OUR C13s
            DO 47 IB=1,3
            DO 45 IC=1,3
            DO 40 IA=1,3
            ID = IC + 3*(IB-1)
    40      F(IC,IA) = T(IC,IA)/(1.+(W(ID)*T(IC,IA))**2)
    45      J(ID) = (D0*K(IC,1)*F(IC,1) + D1*K(IC,2)*F(IC,2)
     1      + D2*K(IC,3)*F(IC,3) )
            IF(ID.EQ.2.OR.ID.EQ.5) J(ID) = J(ID) + JODF
    47      CONTINUE
            NGOTO = 2
            GO TO 400
   302      CONTINUE
            GO TO 900
   400      CONTINUE
            R(1) = J(2) + 4.*J(3)
```

```
      R(2) = 3.*J(2)
      R(3) = ( 3.*J(1) + 3.*J(2) + 2.*J(3) )*0.5
      R(4) = J(4) + 3.*J(5) + 6.*J(6)
      R(5) = J(7) + 3.*J(8) + 6.*J(9)
      R(1) = A(1)*R(1)
      R(2) = A(1)*R(2)
      R(3) = A(1)*R(3)
      R(4) = A(3)*R(4)
      R(5) = A(3)*R(5)
      Do 419 ia=1,3

419   ja(ia) = j(ia)*a(1)
      DO 420 IA=1,5
420   RI(IA) = 1.0 / R(IA)
      write(6,229) (ja(io),io=1,3)
229   format(' ja',3e11.4)
      WRITE(6,230) (J(IO),IO=1,9),(R(IO),IO=1,5),(RI(IO),IO=1,5)
230   FORMAT(' J ',3E11.4,/,' ',6e11.4,/,' R ',5E11.4,/,' T ',5E11.4)

      GO TO (301,302),NGOTO
910   STOP
      END
```

D.2 JDTLA0.DAT

```
999 0 jan 17 1993
0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
27.500 1.272 0.000 70.500 0.214 0.000 1.101
27.500 0.664 0.000 70.500 0.148 0.000 1.101
27.500 1.061 0.000 70.500 0.159 0.000 1.101
27.500 2.232 0.000 70.500 0.107 0.000 1.101
27.500 8.543 0.000 70.500 0.078 0.000 1.101
```

D.3 JDTLA0.OUT

jdtlaa 13jan93 999 0 jan 17 1993

0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01

T,dif,ADF,BETA,P2,P4,R:
27.500 1.272 0.000 70.500 0.214 0.000 1.101
jodf,a1,a2,a3,beta,dpar=
0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.1272E+10
d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.326
ja 0.7502E+01 0.7904E+01 0.8986E+01
J 0.1500E-10 0.1581E-10 0.1797E-10
0.1500E-10 0.1581E-10 0.1797E-10 0.1500E-10 0.1581E-10 0.1797E-10
R 0.4385E+02 0.2371E+02 0.3210E+02 0.1721E+01 0.1721E+01
T 0.2281E-01 0.4217E-01 0.3116E-01 0.5812E+00 0.5812E+00
ja 0.7502E+01 **0.7904E+01** 0.8984E+01
J 0.1500E-10 0.1581E-10 0.1797E-10
0.1498E-10 0.1580E-10 0.1791E-10 0.1433E-10 0.1573E-10 0.1626E-10
R **0.4384E+02** 0.2371E+02 0.3209E+02 0.1716E+01 0.1607E+01
T 0.2281E-01 0.4218E-01 0.3116E-01 0.5827E+00 **0.6221E+00**

T,dif,ADF,BETA,P2,P4,R:
27.500 0.664 0.000 70.500 0.148 0.000 1.101
jodf,a1,a2,a3,beta,dpar=
0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.6640E+09

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.326

ja 0.1500E+02 0.1544E+02 0.1680E+02

J 0.2999E-10 0.3088E-10 0.3360E-10

0.2999E-10 0.3088E-10 0.3360E-10 0.2999E-10 0.3088E-10 0.3360E-10

R 0.8263E+02 0.4632E+02 0.6245E+02 0.3276E+01 0.3276E+01

T 0.1210E-01 0.2159E-01 0.1601E-01 0.3052E+00 0.3052E+00

ja 0.1500E+02 **0.1544E+02** 0.1678E+02

J 0.2999E-10 0.3087E-10 0.3356E-10

0.2985E-10 0.3086E-10 0.3314E-10 0.2572E-10 0.3034E-10 0.2414E-10

R **0.8257E+02** 0.4631E+02 0.6243E+02 0.3246E+01 0.2644E+01

T 0.1211E-01 0.2159E-01 0.1602E-01 0.3080E+00 **0.3783E+00**

T,dif,ADF,BETA,P2,P4,R:

27.500 1.061 0.000 70.500 0.159 0.000 1.101

jodf,a1,a2,a3,beta,dpar=

0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.1061E+10

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.326

ja 0.9326E+01 0.9634E+01 0.1055E+02

J 0.1865E-10 0.1927E-10 0.2111E-10

0.1865E-10 0.1927E-10 0.2111E-10 0.1865E-10 0.1927E-10 0.2111E-10

R 0.5185E+02 0.2890E+02 0.3899E+02 0.2052E+01 0.2052E+01

T 0.1929E-01 0.3460E-01 0.2565E-01 0.4872E+00 0.4872E+00

ja 0.9326E+01 **0.9633E+01** 0.1055E+02

J 0.1865E-10 0.1927E-10 0.2110E-10

0.1861E-10 0.1926E-10 0.2100E-10 0.1749E-10 0.1913E-10 0.1829E-10

R **0.5183E+02** 0.2890E+02 0.3899E+02 0.2045E+01 0.1866E+01

T 0.1929E-01 0.3460E-01 0.2565E-01 0.4890E+00 **0.5360E+00**

T,dif,ADF,BETA,P2,P4,R:

27.500 2.232 0.000 70.500 0.107 0.000 1.101

jodf,a1,a2,a3,beta,dpar=

0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.2232E+10

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.326

ja 0.4559E+01 0.4643E+01 0.4927E+01

J 0.9119E-11 0.9287E-11 0.9853E-11

0.9119E-11 0.9287E-11 0.9853E-11 0.9119E-11 0.9287E-11 0.9853E-11

R 0.2435E+02 0.1393E+02 0.1873E+02 0.9711E+00 0.9711E+00

T 0.4107E-01 0.7179E-01 0.5339E-01 0.1030E+01 0.1030E+01

ja 0.4559E+01 **0.4643E+01** 0.4926E+01

J 0.9119E-11 0.9287E-11 0.9853E-11

0.9115E-11 0.9286E-11 0.9841E-11 0.8986E-11 0.9272E-11 0.9511E-11

R **0.2435E+02** 0.1393E+02 0.1873E+02 0.9703E+00 0.9486E+00

T 0.4107E-01 0.7179E-01 0.5339E-01 0.1031E+01 **0.1054E+01**

T,dif,ADF,BETA,P2,P4,R:

27.500 8.543 0.000 70.500 0.078 0.000 1.101

jodf,a1,a2,a3,beta,dpar=

0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.8543E+10

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.326

ja 0.1208E+01 0.1222E+01 0.1275E+01

J 0.2415E-11 0.2444E-11 0.2550E-11

0.2415E-11 0.2444E-11 0.2550E-11 0.2415E-11 0.2444E-11 0.2550E-11

R 0.6322E+01 0.3666E+01 0.4920E+01 0.2531E+00 0.2531E+00

T 0.1582E+00 0.2728E+00 0.2033E+00 0.3951E+01 0.3951E+01

ja 0.1208E+01 **0.1222E+01** 0.1275E+01

J 0.2415E-11 0.2444E-11 0.2550E-11

0.2415E-11 0.2444E-11 0.2550E-11 0.2413E-11 0.2444E-11 0.2544E-11

R **0.6322E+01** 0.3666E+01 0.4920E+01 0.2531E+00 0.2527E+00

T 0.1582E+00 0.2728E+00 0.2033E+00 0.3951E+01 **0.3957E+01**

APPENDIX E

JDTLA3 program

E.1 JDTLA3.DAT

```
999 3 jan 17 1993
0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01
31.300 1.143 0.000 70.500 0.125 0.000 1.101
31.300 0.614 0.000 70.500 0.082 0.000 1.101
31.300 1.515 0.000 70.500 0.089 0.000 1.101
31.300 2.890 0.000 70.500 0.057 0.000 1.101
31.300 9.340 0.000 70.500 0.042 0.000 1.101
```

E.2 JDTLA3.OUT

jdtlaa 13jan93 999 3 jan 17 1993

0.166275E+00 0.596980E-01 0.892276E-01-0.589343E+00 0.273903E+00
0.166416E+00 0.187291E-02 0.112825E+00-0.497358E+00 0.215632E+00
0.165870E+00-0.106399E+00 0.360264E-01-0.606901E-01-0.349307E-01
0.165719E+00-0.197752E-01 0.264281E-01-0.300436E+00 0.128263E+00
0.166058E+00-0.632585E-01 0.411946E-01-0.173258E+00 0.291278E-01
0.166195E+00 0.101228E+00 0.536315E-01-0.126492E+00 0.553662E-01

T,dif,ADF,BETA,P2,P4,R:
31.300 1.143 0.000 70.500 0.125 0.000 1.101
jodf,a1,a2,a3,beta,dpar=
0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.1143E+10
d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.285
ja 0.8822E+01 0.9025E+01 0.9680E+01
J 0.1764E-10 0.1805E-10 0.1936E-10
0.1764E-10 0.1805E-10 0.1936E-10 0.1764E-10 0.1805E-10 0.1936E-10
R 0.4774E+02 0.2708E+02 0.3645E+02 0.1899E+01 0.1899E+01
T 0.2094E-01 0.3693E-01 0.2743E-01 0.5265E+00 0.5265E+00
ja 0.8822E+01 **0.9024E+01** 0.9677E+01
J 0.1764E-10 0.1805E-10 0.1935E-10
0.1762E-10 0.1805E-10 0.1927E-10 0.1670E-10 0.1794E-10 0.1706E-10
R **0.4773E+02** 0.2707E+02 0.3645E+02 0.1893E+01 0.1747E+01
T 0.2095E-01 0.3694E-01 0.2744E-01 0.5282E+00 **0.5724E+00**

T,dif,ADF,BETA,P2,P4,R:
31.300 0.614 0.000 70.500 0.082 0.000 1.101
jodf,a1,a2,a3,beta,dpar=
0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.6140E+09

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.285

ja 0.1677E+02 0.1699E+02 0.1776E+02

J 0.3355E-10 0.3397E-10 0.3553E-10

0.3355E-10 0.3397E-10 0.3553E-10 0.3355E-10 0.3397E-10 0.3553E-10

R 0.8804E+02 0.5096E+02 0.6840E+02 0.3523E+01 0.3523E+01

T 0.1136E-01 0.1962E-01 0.1462E-01 0.2838E+00 0.2838E+00

ja 0.1677E+02 **0.1698E+02** 0.1774E+02

J 0.3355E-10 0.3396E-10 0.3549E-10

0.3336E-10 0.3394E-10 0.3494E-10 0.2824E-10 0.3328E-10 0.2418E-10

R **0.8796E+02** 0.5095E+02 0.6838E+02 0.3485E+01 0.2760E+01

T 0.1137E-01 0.1963E-01 0.1463E-01 0.2870E+00 **0.3623E+00**

T,dif,ADF,BETA,P2,P4,R:

31.300 1.515 0.000 70.500 0.089 0.000 1.101

jodf,a1,a2,a3,beta,dpar=

0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.1515E+10

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.285

ja 0.6776E+01 0.6872E+01 0.7215E+01

J 0.1355E-10 0.1374E-10 0.1443E-10

0.1355E-10 0.1374E-10 0.1443E-10 0.1355E-10 0.1374E-10 0.1443E-10

R 0.3573E+02 0.2062E+02 0.2769E+02 0.1429E+01 0.1429E+01

T 0.2798E-01 0.4850E-01 0.3612E-01 0.7000E+00 0.7000E+00

ja 0.6776E+01 **0.6872E+01** 0.7214E+01

J 0.1355E-10 0.1374E-10 0.1443E-10

0.1354E-10 0.1374E-10 0.1439E-10 0.1314E-10 0.1370E-10 0.1338E-10

R **0.3573E+02** 0.2062E+02 0.2769E+02 0.1426E+01 0.1359E+01

T 0.2799E-01 0.4851E-01 0.3612E-01 0.7013E+00 **0.7357E+00**

T,dif,ADF,BETA,P2,P4,R:

31.300 2.890 0.000 70.500 0.057 0.000 1.101

jodf,a1,a2,a3,beta,dpar=

0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.2890E+10

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.285

ja 0.3603E+01 0.3632E+01 0.3745E+01

J 0.7207E-11 0.7264E-11 0.7490E-11

0.7207E-11 0.7264E-11 0.7490E-11 0.7207E-11 0.7264E-11 0.7490E-11

R 0.1861E+02 0.1090E+02 0.1460E+02 0.7471E+00 0.7471E+00

T 0.5373E-01 0.9178E-01 0.6850E-01 0.1338E+01 0.1338E+01

ja 0.3603E+01 **0.3632E+01** 0.3745E+01

J 0.7207E-11 0.7263E-11 0.7489E-11

0.7205E-11 0.7263E-11 0.7484E-11 0.7145E-11 0.7257E-11 0.7327E-11

R **0.1861E+02** 0.1090E+02 0.1460E+02 0.7468E+00 0.7365E+00

T 0.5373E-01 0.9178E-01 0.6851E-01 0.1339E+01 **0.1358E+01**

T,dif,ADF,BETA,P2,P4,R:

31.300 9.340 0.000 70.500 0.042 0.000 1.101

jodf,a1,a2,a3,beta,dpar=

0.0000E+00 0.5000E+12 0.1800E+11 0.1011E+11 0.1230E+01 0.9340E+10

d0,d1,d2= 0.110796E+00 0.297032E+00 0.592172E+00 1000/T 3.285

ja 0.1122E+01 0.1128E+01 0.1154E+01

J 0.2244E-11 0.2256E-11 0.2307E-11

0.2244E-11 0.2256E-11 0.2307E-11 0.2244E-11 0.2256E-11 0.2307E-11

R 0.5743E+01 0.3384E+01 0.4529E+01 0.2310E+00 0.2310E+00

T 0.1741E+00 0.2955E+00 0.2208E+00 0.4330E+01 0.4330E+01

ja 0.1122E+01 **0.1128E+01** 0.1154E+01

J 0.2244E-11 0.2256E-11 0.2307E-11

0.2244E-11 0.2256E-11 0.2307E-11 0.2242E-11 0.2256E-11 0.2302E-11

R **0.5743E+01** 0.3384E+01 0.4529E+01 0.2310E+00 0.2306E+00

T 0.1741E+00 0.2955E+00 0.2208E+00 0.4330E+01 **0.4336E+01**

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