THE USE OF INTERNAL-MOLECULAR POTENTIAL BARRIERS IN THE STUDY OF CHARGE TRANSFER INTERACTIONS

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CHAPTER I

INTRODUCTION

The Problem

Qualitative infrared evidence for the internal rotation of the methyl groups in crystalline hexamethylbenzene has been demonstrated by Leech, Powell and Sheppard (1). This evidence consists, in part, of the temperature dependence of the band contours of two vibrational modes which are usually associated with C-H bending. These two bands, located sharply around 1463 cm^{-1} and 1432 cm^{-1} at liquid nitrogen temperatures, were found to broaden with increasing temperatures, until at room temperature it became difficult to distinguish between the two bands.

These findings were interpreted as indicating that at lower temperatures the methyl groups are oriented in some manner, and at higher temperatures, after some initial energy requirement has been met, the methyl groups begin to rotate about their three-fold axis.

Earlier work by Thompson and Mann (2) with oriented crystals and polarized light have shown that these bands have different polarizations. The high frequency one is in the plane of the molecule, and the lower energy band is associated with a polarization out of the plane of the molecule. These results suggest that it might be possible to extend the work in reference (1) with oriented crystals and polarized light to arrive at more quantitative results.

By use of the above mentioned techniques this investigation attempts to 1) determine if the other methylbenzenes display similar splitting effects, 2) develop a method of estimating the energy requirements or as we will henceforth call them, barrier heights, mentioned above and 3) evaluate the changes that these barrier heights might undergo on complexation of the molecules involved in order to gain some insight into the intermolecular interactions involved. The methylbenzene derivatives: hexamethylbenzene (HMB), pentamethylbenzene (PMB) and p-tetramethylbenzene(durene) were especially chosen for this study because of their varying ability to form charge-transfer complexes.

Charge-Transfer Complexes

The term charge-transfer or molecular complex covers a wide variety of substances ranging from strong, primarily ionic complexes, to the extremely weak 'self-complexes'. There have been several attempts to explain the nature of the binding forces of molecular complexes, most offering little success. The most widely accepted theory is that of Mulliken (3,4,5), who postulates either a partial or nearly complete transfer of electrons from the 'donor' molecule to the 'acceptor' molecule, the amount of transfer being proportional to the strength of the intermolecular interaction. This electron transfer is accomplished by an overlapping of an unoccupied molecular orbital possessed by the acceptor. These two orbitals are usually the highest occupied and lowest unoccupied ones, but it has been shown that the symmetry of the two molecular orbitals is the more important factor in allowing the charge transfer interaction to take place (6).

There are several types of charge transfer donors and acceptors characterized by Mulliken (7): free radical, increvalent, σ and π. The free radical type possess only a single electron in its uppermost level, i.e. both donors and acceptors of this type possess an odd number of electrons. Increvalent donors possess an odd number of electrons, but donate a single electron to the interaction, while acceptors of this type have an even number of electrons but accept only a single electron during the complex formation. The σ and π donors and acceptors are characterized by possessing an even number of electrons and two electrons are partially transferred from the donor to the acceptor during the formation of the molecular complex. The σ and π designation refers to the type of molecular orbital involved in the complexation. It should be noted that σ donors are extremely rare whereas both types of acceptors are common.

In the complexes under study, the methylbenzenes were always the donor molecule. At this time the acceptors have been limited to the π type and the various acceptors used were: tetracyanoethylene (TCNE), chloranil (TCQ) and bromanil (TBQ). These acceptors are of differing strengths: i.e. they would form complexes of different stabilities with the same methylbenzene derivative.

In general, complex formation of this type takes place only in solution and it is difficult to form solid molecular complexes. All of the complexes in this study are obtainable with varying degrees of difficulty, in the solid state as oriented needle-like crystals.

Some of the most direct and successful investigations into charge transfer complexes have involved various spectroscopic techniques. Among these, is the absorption of ultraviolet and visible light. In the absorption spectra of molecular complexes at these frequencies, very intense bands are observed. These so called charge-transfer bands are characteristic of the molecular complexes, dependent on both the acceptor and the donor. In a simplified fashion, this absorption may be considered as 'causing the electron to jump from the donor to the acceptor' (6).

The effects of the reaction solvent on these band changes have been studied and it has been possible to classify three types of complexes (8). The first of these involves two neutral molecules where the excited state after the transfer is more polar than the ground state, so that changing to a more polar solvent will bring about a red shift in the charge-transfer band. All of the complexes in this study are of this type.

A reverse effect occurs with an ion pair where the complex is less polar. The third type involves a neutral and an ionic pair which yields unpredictable results. From these solvent studies it is postulated that solid complexes consist of either neutral or ionic molecules but not as both.

Polarization studies have been performed on a variety of charge-transfer systems, including the ones of interest to this study. Nakamoto (9) has shown that the charge-transfer absorption of the HMB-TCQ complex is primarily polarized in a direction perpendicular to the planes of the aromatic rings. This conclusion was made possible by x-ray work (10) which shows that the donor and acceptor molecules are alternately stacked so that all of their molecular planes are nearly perpendicular to the needle crystal axis. These statements as to polarization and crystal structure hold in general for methylbenzene π complexes (11).

Studies of the absolute intensities of charge-transfer absorption bands have led to some interesting results. Theory would predict an increase in the transition moment of the absorption with an increase in the stability of the complex due to the inhanced resonance interaction which should result. This increase in the transition moment should be observable by an increase in the extinction coefficient. In many of the cases studied this increase of absorption intensity has not been observed. An appropriate case in point would be the methylbenzene:iodine complexes. As methyl groups are added to the benzene ring in this series, the iodine complexes become stronger due to an increase in the donor strength, but at the same time the intensity of the charge-transfer band is decreased. Many systems show this effect; a notable exception, however, is the methylbenzene-TCQ complexes (6).

In order to explain these observations, Mulliken (12) suggested a concept called 'contact charge-transfer'. Basically this idea would allow charge-transfer absorption to occur on the collision of a donor with an acceptor during which no stable complex is formed. This concept explained the anomolous behavior of the complexes of the methylbenzenes with I_2 and TCQ. The transition moment of contact charge-transfer is assumed to be larger than in the case of the complex because the interaction takes place over a longer distance. For the iodine complex the symmetry requirements for charge-transfer are not as restrictive as they are for TCQ; i.e. there is no relative orientation of the donor and I_2 molecules which is much more favorable to contact charge-transfer than any other, hence at nearly every 'contact', charge-transfer could take place. For TCQ the molecular planes must be nearly parallel for the contact charge-transfer to take place, thus seriously limiting the number of 'contacts' which can result in charge-transfer. Therefore, as the stability of the I_2 complex increases, the contact charge-transfer which is an important contribution to the total absorption, decreases; while for TCQ the amount of contact interaction is not as important as is the molecular complex itself.

Vibrational spectroscopy has also proved to be an invaluable aid in the investigation of the charge-transfer phenomena. One use of this type of spectra depends on changes in intramolecular bond strengths, and therefore a shift in frequency of the fundamental vibration. According to the theory (7), when the donor gives up electrons from a bonding type orbital, the vibrational fundamentals are decreased in energy due to a weakening of the molecular bonding. Conversely, when the donor transfers electrons from an antibonding orbital the infrared absorption bands are shifted to higher frequencies due to a strengthening of the bonds. Sacrificial donors, i.e. one which loses electrons from a bonding orbital, are by far the most common π type.

In the same manner, charge-transfer induces vibrational shifts for the acceptor. Here, however, the shifts are determined by what type of orbital the electrons are transferred into, the most common case being transfer into an antibonding molecular orbital reducing the vibrational frequencies. Recently a comparison of band shifts for TCNE as a complete anion and an acceptor in a complex, enabled Stanley, et. al. (11) to make a semi-quantitative estimate of 5-10% charge-transfer for the HMB-TCNE system.

Another vibrational occurence associated with molecular complex formation is the activation of vibrational modes which are normally infrared inactive in the isolated molecules. An example of this is the activation of the Cl_2 stretching mode on complex formation with benzene

(13). A case more pertinent perhaps is the activation of the symmetric $C-CH_3$ stretching mode of HMB in the 2HMB-TCNE complex (14).

Ferguson and Matsen (15,16) and Ferguson (17) have developed selection rules which explain the activation of symmetric modes. Basically they contend that the modes are activated due to a change in the vertical ionization potential on vibration of the molecule. Some experimental support of this exists. An appropriate example is the vertical polarization of the activated C=C stretching mode of TCNE in the HMB-TCNE complex (11).

A further useful vibrational observation is the dichroic behavior of molecular vibrations in oriented crystals. This comes from the directional properties of the induced dipole associated with the vibration. This is useful for determining the orientation of molecules which compose the charge-transfer complex. Also the Ferguson-Matsen enhancement of modes along the axis of the charge-transfer interaction are observed even in solutions, and are helpful in determining orientations as long as the polarizations of the modes are known.

As has already been mentioned, the main purpose of this investigation was to determine the effect of complex formation on the barrier to methyl rotation in the methylbenzenes with a series of acceptors. There are two obvious contributions to this barrier. The first of these is the steric consideration. Second, is the contribution associated with a decrease in electron density connected with charge-transfer. With the study of different acceptors and donors it is found to be possible to differentiate between the effects of these contributions.

Past Experimental Studies of Barrier Heights

Recently, the evaluation of the barrier height to rotation in the pure methylbenzenes has drawn some interest. Until this time all of the quantitative experimental work on these barriers has been done by either neutron scattering or nuclear magnetic resonance. The only attempt to use infrared techniques was strictly qualitative in nature and has been cited (1).

Rush and Taylor (18) and Rush (19) were the first to make a quantitative estimate of barrier heights for methyl rotation on experimental grounds. They measured the energy-gain scattering of subthermal neutrons across a number of methylbenzenes. By plotting the intensity of the scattered neutrons against the energy gained upon scattering, they were able to obtain several peaks. In each case one of the peaks in the above plots was assigned to the $v = 1 \rightarrow v = 0$ transition of the torsional vibration of the methyl groups trapped below the barrier to rotation. Using these energies with a method of calculation analogous to what we will present here later, they were able to make a quantitative estimate of the potential barrier to rotation. Molecules studied include HMB, durene, prehnitene, mesitylene, hemimellitene and o-xylene.

Andrew (20) has studied the variation of nuclear magnetic resonance line width with temperature for HMB, mesitylene and the xylenes. He concluded that there exists some internal rotations of the methyl groups at all temperatures above 95°K, but no quantitative estimate of the barrier height associated with this rotation was offered.

Allen and Cowking (21,22) have measured the proton spin-lattice relaxation time for some methylbenzene derivatives over a temperature range of 2°K to 450°K. These relaxation times were used to calculate the correlation time by the method of Purcell and Pound (23). The correlation times were then used to calculate the potential barrier heights by assuming a simple activation energy relationship similar to the Arrhenius equation. This type of study was carried out with the compounds HMB, PMB and the three tetramethylbenzenes.

The quantitative results from the above methods for the compounds of interest to this study can be found listed in Table I. All of the previous workers agree that at lower temperatures the methyl groups are largely oscillating in a torsional manner, while at higher temperatures there appears to be enough energy available for some of the methyl groups to leave their potential well and rotate.

TABLE I

COLLECTED ESTIMATES OF BARRIERS TO METHYL ROTATION

Compound	V_o (Kcal/mole)	
	NS	NMR
HMB	1.07	1.6
PMB	----	2.2
durene	2.03	1.6

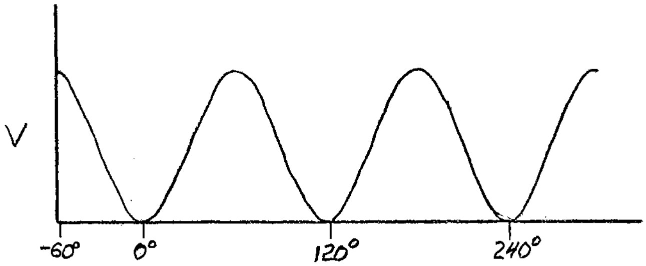

Figure 1. Potential Energy as a Function of the Angle of Torsion (8).

CHAPTER II

STATISTICAL APPROACH

A methyl group in the ground state of any of the methylbenzenes is vibrating in a torsional manner about the axis of the benzyl-methyl bond. The exact functional form of the potential well in which the methyl group oscillates is not known, as is indeed the case for virtually all torsional modes of vibration. Therefore, we must use the standard assumed potential function involving n identical potential minima,

$$V = \tfrac{1}{2}V_o\ (1 - \cos n\theta)$$

where θ is the angle of displacement from the equilibrium position, n equals three for the case under study because of the three-fold axis of the methyl group, and V_o is the barrier height to free rotation. See Figure 1 for potential diagram.

This assumption can be justified, intuitively at least, to the extent that the potential minima must be identical because hydrogen atoms on the methyl groups are indistinguishable. Whereas the curvature of the real and assumed functions are probably not identical, it can be said that the assumed function is the limiting case of small, higher order barriers.

As long as there is insufficient energy available for free rotation, the methyl group will remain in one of the quantized torsional states whose energy can be calculated by:

$$E_v = (v + \tfrac{1}{2})\, n \sqrt{\frac{V_o A_1 A_2}{A}}$$

where v is the vibrational quantum number, A_1 and A_2 are the rotational constants for the two parts of the molecule connected by the bond undergoing the torsional distortion, and A is the rotational constant for the entire molecule about the torsional axis (24).

It should be noted that since the potential wells are finite, there is only a finite number of allowed vibrational states. When an energy greater than V_o is available, the methyl groups can no longer occupy a torsional state, and they become rotors.

Because the moment of inertia of the rest of the molecule is so large compared to the methyl group, it is a good approximation to consider that only the methyl group is in motion with the onset of rotation. It then becomes obvious that the equation describing the states above the barrier is approximately that of a rigid rotor with but two degrees of freedom:

$$E_r = j^2 A_1$$

where j is the rotational quantum number and A_1 is the rotational constant for the methyl group about the appropriate axis. The above equation permits clockwise and counter-clockwise rotation as the two degrees of freedom but the axis of the rotor is not allowed to precess (25).

Since we will be primarily interested in population densities for these levels, it becomes necessary to consider the partition function for this type of system which is assumed to be:

$$Q = Q_v + Q_r$$

where Q_v is the partition function for the vibrational part of the system, and Q_r is the partition function for the rotational portion (26).

Since there are a finite number of vibrational states, this portion of the partition function is a finite series of the form:

$$Q_v = \sum_{v=o}^{L} G_v e^{-\frac{v E_v}{k T}}$$

where k is Boltzman's constant, T is the temperature, E_v is the vibrational spacing, L is the number of vibrational states allowed below the barrier, and G_v is the degeneracy of the torsional state, which is three for this case.

The expression for the rotational portion of the partition function is:

$$Q_r = \sum_{j=J}^{\infty} G_r e^{-\frac{j^2 A_1}{k T}}$$

where J is the lowest rotational quantum number above the barrier and G_r is the rotational degeneracy, which is in all cases of this type equal to two.

The calculation of Q_v is relatively straightforward, but the evaluation of Q_r is complicated by alternative methods of choosing J. The obvious (but not necessarily the correct one) would be to substitute the barrier height for a value of the rotational energy and solve for J directly. This yields:

$$J' = \sqrt{\frac{V_o}{A_1}}$$

An alternative method, believed to be more theoretically sound, was suggested by Pitzer (26). He suggested that since this type of rotor is not actually free, because the angular velocity oscillates as a cosine function, the spacing, which is dependent on the kinetic energy, might be more accurately defined by an initial j value determined thusly:

$$J = \sqrt{\frac{V_o}{2A_1}}$$

Of course when this expression is used in the split partition function, we must add back the energy above the zero point energy which was disregarded in determining the first j value above the barrier, i.e.:

$$\frac{V_o - E_v}{2}$$

and the total partition function becomes:

$$Q = \sum_{v=o}^{L} 3e^{-\frac{v\,E_v}{k\,T}} + \sum_{j=J}^{\infty} 2e^{\frac{E_v - 2j^2A_1 - V_o}{2\,k\,T}}$$

Since all of the appropriate partition functions can be evaluated, it is now possible to evaluate the probability of a given rotor being above the barrier:

$$P_a = \frac{Q_r}{Q}$$

or below the barrier:

$$P_b = \frac{Q_v}{Q}$$

For the purpose of this investigation, however, it is more meaningful to talk in terms of the probability of a given molecule having a certain minimum number of rotors. When these probabilities were calculated, the binomial distribution for a repeated trials experiment (27) was used. By using this function, the five point model for the development of the distribution function automatically became the model for the calculation. These points are:

I. There is a fixed number of repeated trials, in this case the number of methyl groups around the ring.

II. In each of these trials, one is concerned only with success or failure of each trial; for the problem under study, success is when the methyl group is above the barrier and failure is when the group is below the barrier.

III. The probability for the success must be the same for each trial; in this case the value is P_a.

IV. The trials must be independent. III and IV together eliminate any possibility of coupling; the validity of this assumption is discussed below.

V. Interest can only be shown in the total number of successes, not in their order; in this case, how many methyl groups are above the barrier but not which ones.

The assumption of no interaction between methyl groups is obviously inadequate, but we are forced to use this model for several reasons to get any leverage on these probabilities at all. First, there is no way to predict what effect a methyl rotor would have on the P_a of the other groups on the benzene ring. Second, the effect would certainly be different for different relative positions on the ring; i.e. a group across the ring from the rotor would be affected in a different manner than a neighbor to the rotor would. Since the information for a rigorous solution to this problem is not available, and since our experimental findings (which will be discussed thoroughly in a later chapter) tend to show that this calculation, although inexact, yields results which give some insight into the problem, we feel justified in using this simplified model.

The general equation for the binomial distribution for this case is:

$$1 = (P_a + P_b)^x$$

where x is the number of methyl groups on the benzene ring. On expansion this yields (x - 1) terms:

$$1 = P_b^x + \left\langle\begin{matrix}x\\1\end{matrix}\right\rangle P_a \, P_b^{(x-1)} + \ldots\ldots + \left\langle\begin{matrix}x\\y\end{matrix}\right\rangle P_a^y \, P_b^{(x-1)} + \ldots + P_a^x$$

where the coefficients are:

$$\left\langle\begin{matrix}x\\y\end{matrix}\right\rangle = \frac{x\,(x-1)\,(x-2)\,\ldots\,(x-y+1)}{y!}$$

Each term in the expansion has a physical meaning associated with it, i.e. P_b^x is the probability of a given molecule having no rotors at all. The second term $\left\langle\begin{matrix}x\\1\end{matrix}\right\rangle P_a^{(x-1)}$ is the probability of a molecule possessing a single rotor. To determine the probability of a molecule containing one or more rotors, (which will be designated as P_{1a}) one uses the equation:

$$P_{1a} = 1 - P_b^x$$

and similarly:

$$\begin{aligned} P_{2a} &= 1 - P_b^x - \binom{x}{1} Pa\ P_b^{(x-1)} \\ \cdot \quad &\quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ \cdot \quad &\quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ P_{xa} &= P_a^x \end{aligned}$$

It is possible to calculate the above series of probabilities using only a temperature, known atomic masses, known bond lengths, known bond angles and an assumed barrier height.

CHAPTER III

EXPERIMENTAL

As previously implied, a factor in the success of this investigation has been the ability to grow oriented crystals of the compounds and complexes studied. Such crystals could be obtained by recrystalizing stoichiometric amounts of the reactants on a polished NaCl window from a suitable solvent. It was found that best results were obtained when 0.5 millimoles of acceptor and the necessary amount of donor for the given complex were dissolved in 60 to 80 ml. of solvent contained in a standard 150 ml. beaker. Crystal growth was observed to be more uniform across the window when the NaCl platelet was suspended approximately 0.5 cm. above the bottom of the beaker. The rate of evaporation of the solvent during the recrystallization process was controlled by covering the mouth of the beaker to varying extent with a watch glass. The solvents used were diethyl-ether for the TCNE complexes and acetone for the TCQ and TBQ charge-transfer species. All solvents and compounds were reagent grade.

More difficulty was encountered in growing the solid complexes, as the number of methyl groups on the donor molecules decreased. Suitable samples of the durene complexes could only be grown at rates six to eight times faster than the HMB entities. Although the needle-like crystals are much shorter and narrower with rapid deposition, the actual spectra of these showed that the recrystalized complexes were ordered in the same manner as the more slowly grown crystals, although possibly not to the same degree. The necessity for the rapid growth technique arises from the high volatility of the complex constituents since the durene complexes are nearly as volatile as diethyl-ether.

The spectroscopic cell (Figure 2) consisted of a "cold finger" mounting for the window on which the complex was grown. This window was suspended in vacuum between two spectroscopic NaCl windows affixed to the outside of the cell. A large ground glass joint enabled the removal of the "cold finger" from the outside portion of the cell for ease in mounting and removing samples. When fully assembled the cell was completely sealed and possessed suitable valves so that it could be removed from the vacuum line and placed in the spectrometer with no change in internal pressure.

The high volatility of these complexes necessitated their being cooled at atmospheric pressure before the cell could be evacuated. This was accomplished by sweeping out the cell with dry nitrogen, then sealing the cell in such a manner that it contained an atmosphere of only dry nitrogen. The external optical windows were covered with saran wrap to prevent any damage to them from condensation. The "cold finger" was then cooled with liquid N_2 to a temperature well below that of the room. The vacuum line was then opened and the cell was evacuated. The saran wrap was removed after the danger of external condensation had passed. The above technique enables the spectra of these complexes to be taken at temperatures down to -180° C.

All temperatures were measured with an iron-constantan thermocouple and a Model 2745 Honeywell potentiometer. The thermocouple was implanted in a cavity (drilled for this purpose) in the base of the NaCl

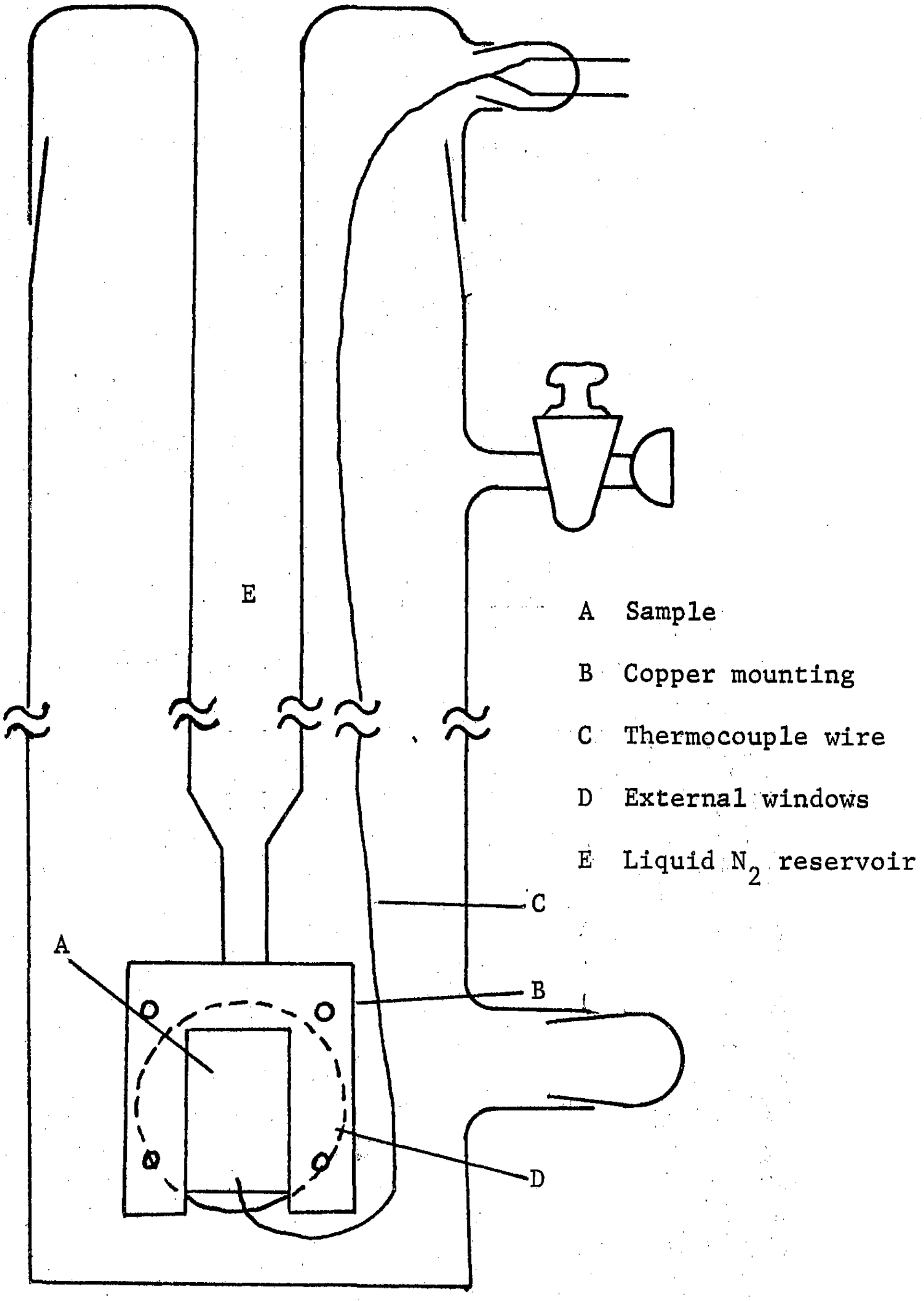

Figure 2. Schematic Cross Section of "Cold Finger" Cell

window upon which the sample was crystalized. The potentiometer was sufficiently sensitive to enable measurement of the temperature to within less than 1°C.

The temperature dependent studies were accomplished by allowing the liquid N_2 in the "cold finger" to evaporate entirely thus causing the temperature of the sample to rise. At intervals of 10°C. a small amount of liquid N_2 was introduced to the cold cell to stabilize the temperature and a spectra was taken between 1400 and 1500 cm^{-1}. During the period of the scan the temperature was not allowed to vary more than ± 1.5 degrees.

It was found that the observed temperature dependencies were completely reversible as to whether the sample was cooling or warming. The only difficulty of this nature was the loss of sample due to sublimation upon recooling once the temperature approached 20°C.; this loss was irreversible due to the tendency for these compounds to transfer to the glass and metal portions of the cold finger from the spectroscopic window since the former cool off much more rapidly than does the sample window when liquid N_2 is added.

During the course of the investigation a need was encountered for a method of studying PMB and durene at elevated temperatures. A cell (Figure 3) was constructed especially for this purpose. It consisted of a pair of NaCl windows separated by a standard teflon spacer held together under pressure by a screw clamp mounted on a 10 ohm ceramic resistor which was used as a source of heat. Temperature was again measured with an iron-constantan thermocouple embedded in the NaCl windows.

The spacer was used in an attempt to establish a closed system and

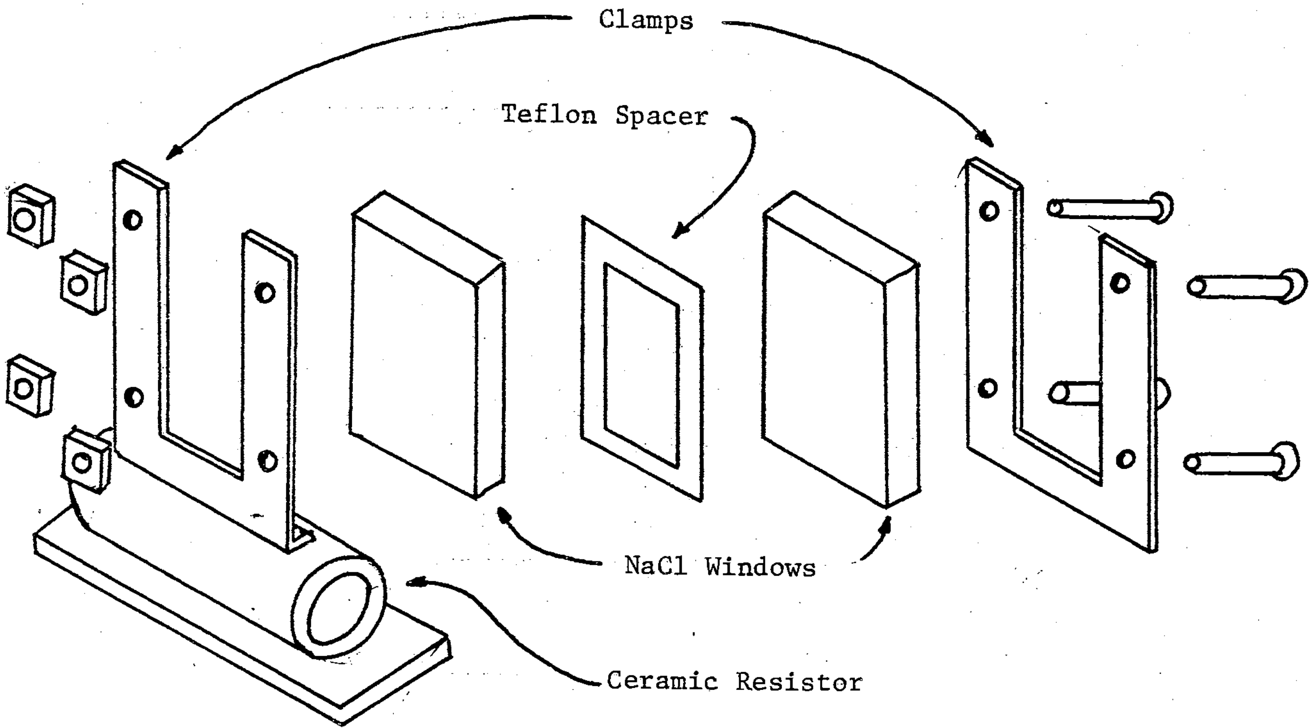

Figure 3. Exploded View of Heater Cell

keep these volatile compounds from subliming. This was only moderately successful since it was found that the samples could be maintained only for periods long enough to permit a single scan of the region of interest. The actual procedure was to heat the sample rapidly to the temperature desired, then scan between 1400 and 1500 cm.$^{-1}$ as quickly as possible. It should be noted that the odor of the vapors of these compounds could be detected during this entire process. Because of this imperfect seal and the toxicity of TCNE, no complexes were studied in this manner.

All spectra were taken with a Beckman IR-7 spectrometer with standard grating interchange and no modifications. Use was made of the polarization of the detected radiation which is inherent in the optics of the monochrometer. By changing the orientation of the crystal axis in the incident beam, the different polarizations of the molecular vibrations could be resolved due to the predominant polarization of the electric vector of the detected radiation in a horizontal manner with respect to the sample cavity of the spectrometer. Some representative examples of this effect are presented in Figure 4.

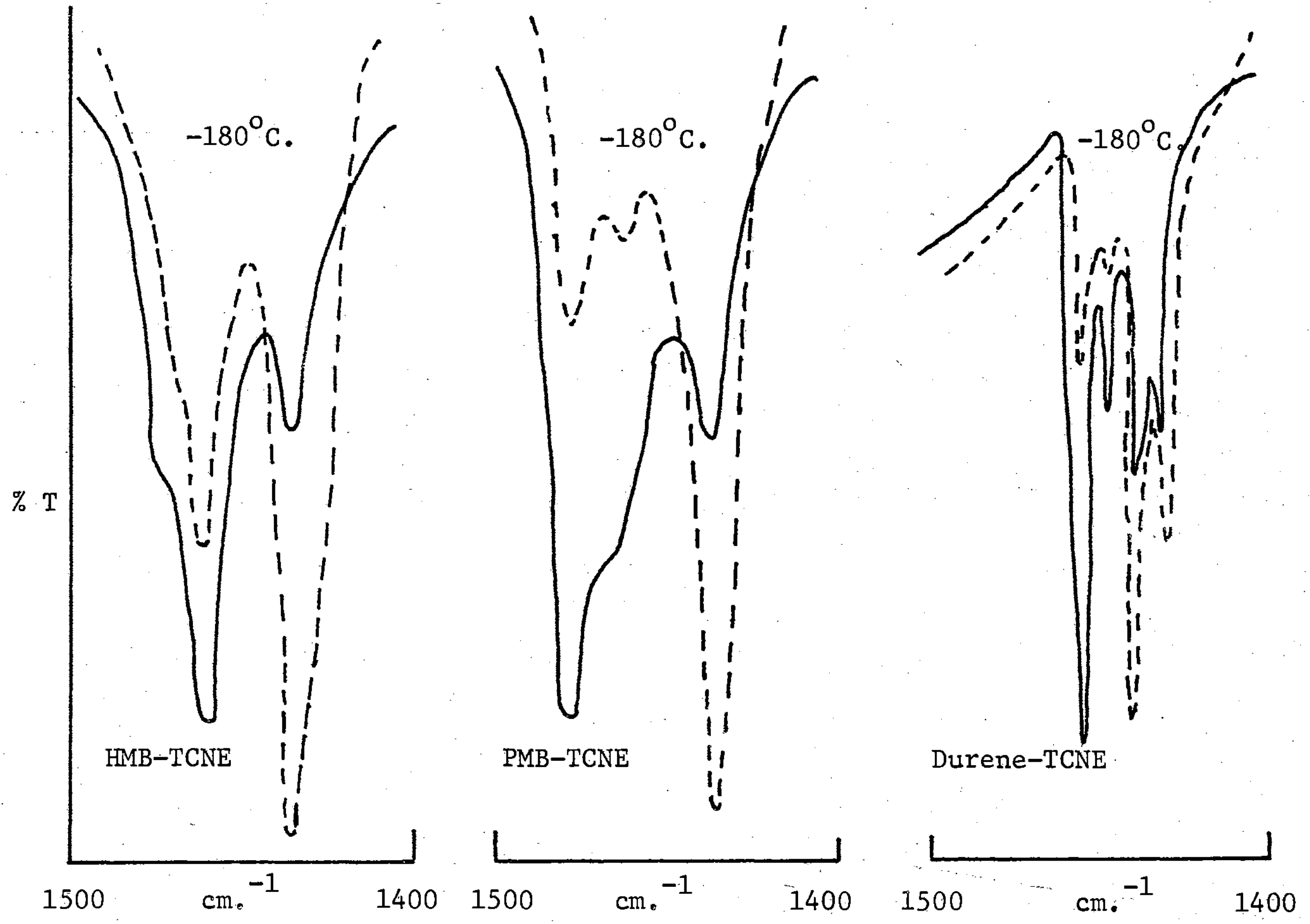

Figure 4. Example of Orientation Effects of Spectrometer. Solid Lines are Vertical Orientation of Crystals; Dotted Lines are Horizontal Orientation.

CHAPTER IV

RESULTS AND INTERPRETATIONS

General

The region of the spectrum between 1400 and 1500 cm.$^{-1}$ contains the absorptions which are associated with the methyl wagging modes of the methyl-benzene derivatives. In general there is a tendency for the in-plane and out-of-plane components of these absorptions to grow together as the temperature is increased from that of liquid N_2. Plots of the dependencies of these modes in general yielded an S-shaped curve.

An attempt to quantitatively relate these experimental curves to the barrier to methyl rotation was made in the following manner. A computer program was written (see Appendix), using the statistical approach of Chapter II as a basis, which would calculate all of the previously mentioned partition functions and probabilities at forty different temperatures with increments of 10°K. Calculations were made for HMB using the barrier heights found by Rush and Taylor (18), and Allen and Cowking (21) as a basis. Each of the alternative methods of evaluating the J value of the lowest state above the barrier was tried.

The results of these calculations were then compared with the experimental curve for HMB. It was found that of all the statistical parameters calculated the temperature dependence of P_{1a} (i.e. the probability of a given molecule possessing one or more rotors) most closely resembled the characteristics of the experimental plot in each of the four calculations. The temperature associated with the inflection points of each of the curves was chosen as the basis for comparison between the experimental and statistical curves.

One might be surprised that P_{1a} is the apparent statistical parameter of importance rather than one of the higher order probabilities such as P_{2a}, P_{3a}, etc. Such concern, however, is based on the assumption that there is no coupling between adjacent methyl groups around the benzene ring, while in fact it is believed that the interactions may be large enough so that, when one group rotates, all the groups of the molecule are perturbed to some extent. A possible useful analogy would be to consider the methyl groups as three toothed innerlocking pseudo-gears (31).

It should be noted that when the potential barrier of Rush and Taylor was used in the calculation, the experimental curve was more closely reproduced by using the obvious approach for evaluating the minimum J value above the barrier. Alternately when the value that Allen and Cowking found for the barrier was used, Pitzer's method (26) of evaluating the lowest J state yielded the best results. The latter approach was applied to this investigation for two reasons. First, the concept of the average kinetic energy determining the spacing of the rotational states associated with Pitzer's method was more appealing than the idea that the spacings are determined by the total energy of the rotor above equilibrium. Second, since Allen and Cowking deduced barriers from the temperature dependence of system parameters, as was done in this investigation, the results should be more nearly comparable.

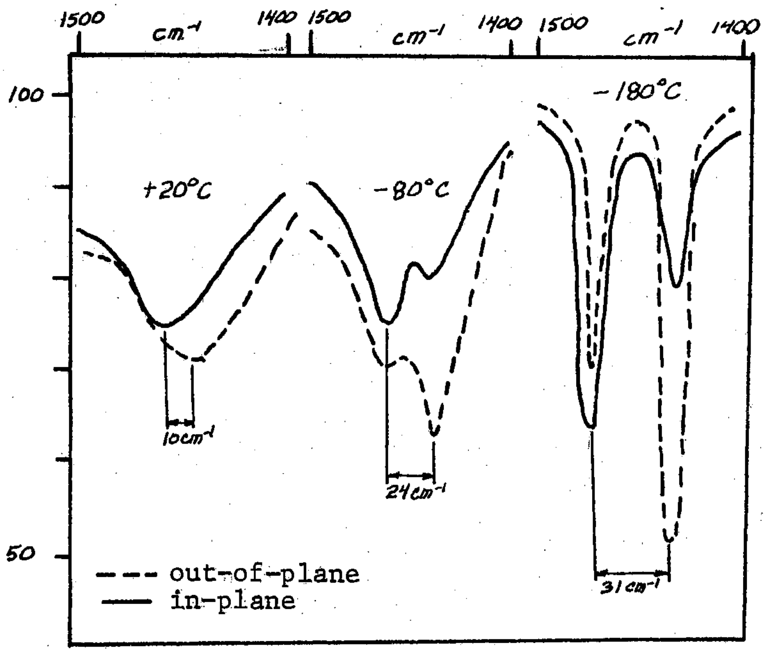

Figure 5. Temperature Dependence of HMB

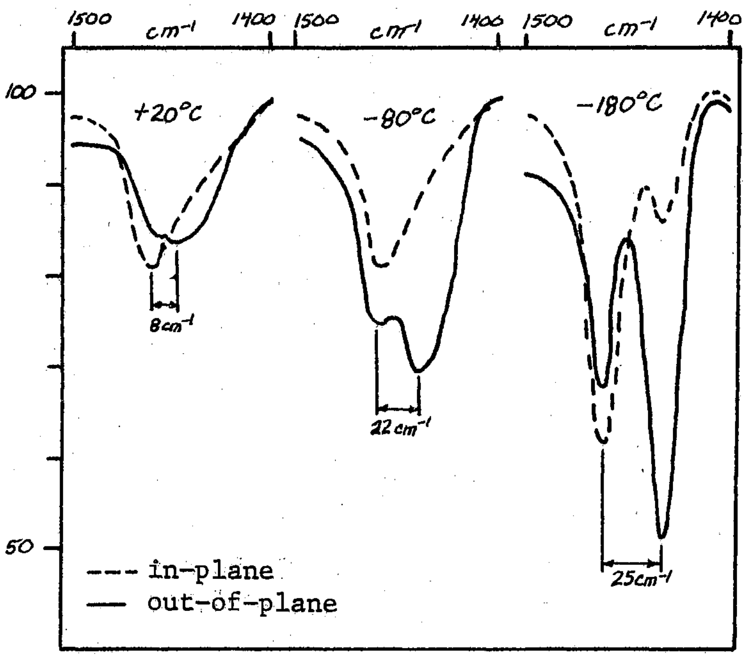

Figure 6. Temperature Dependence of HMB: TCNE

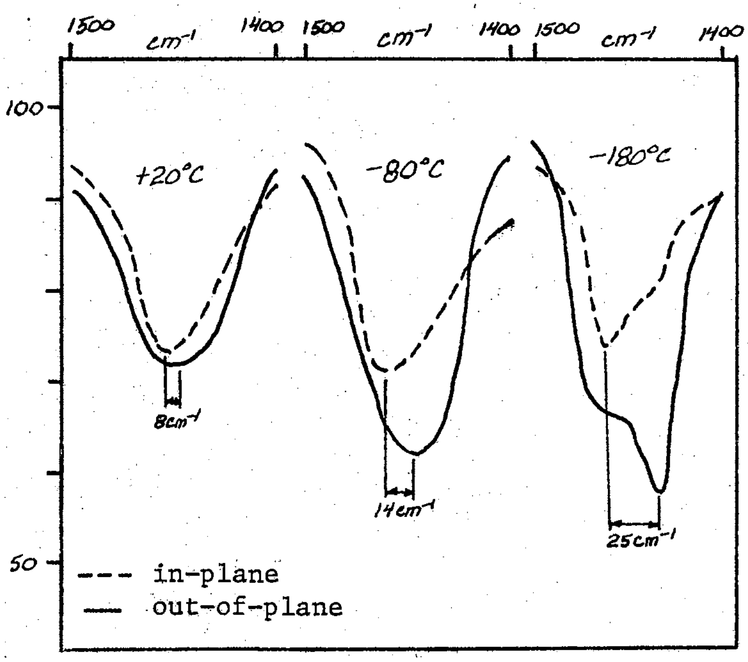

Figure 7. Temperature Dependence of 2HMB: TCNE

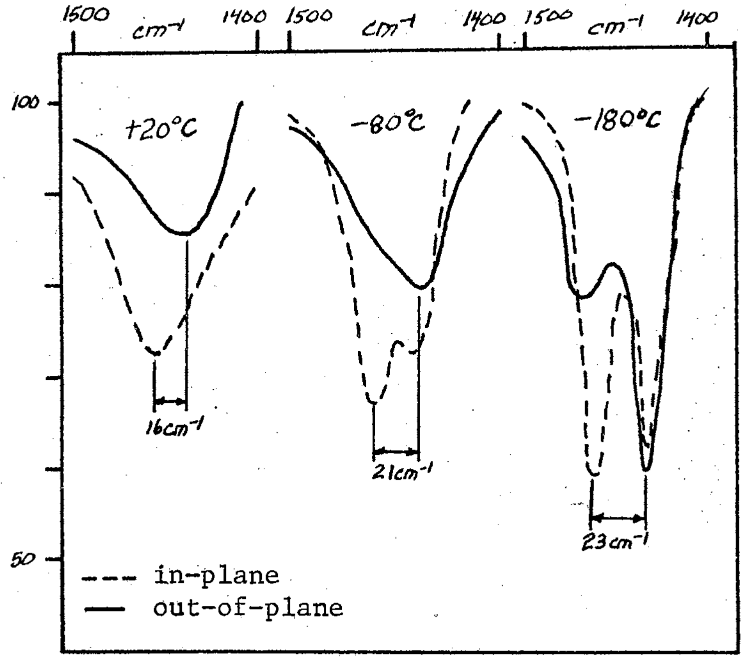

Figure 8. Temperature Dependence of HMB: TCQ

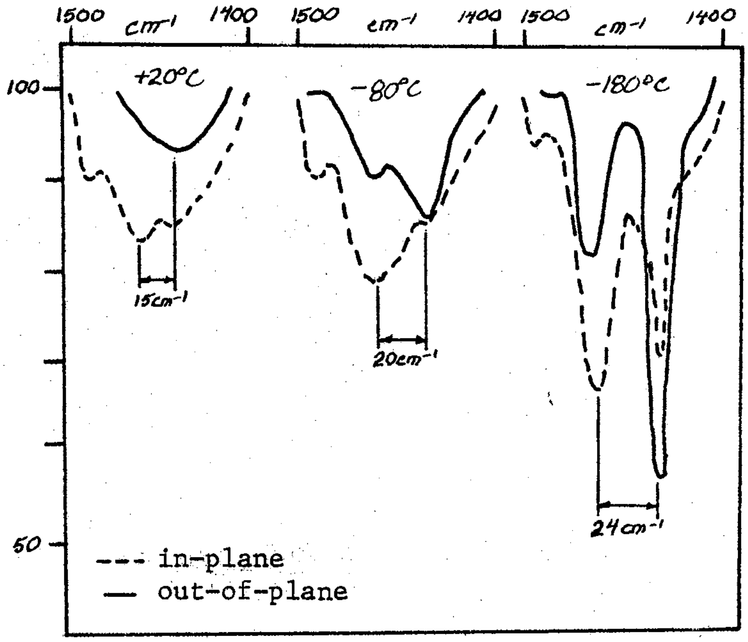

Figure 9. Temperature Dependence of HMB: TBQ

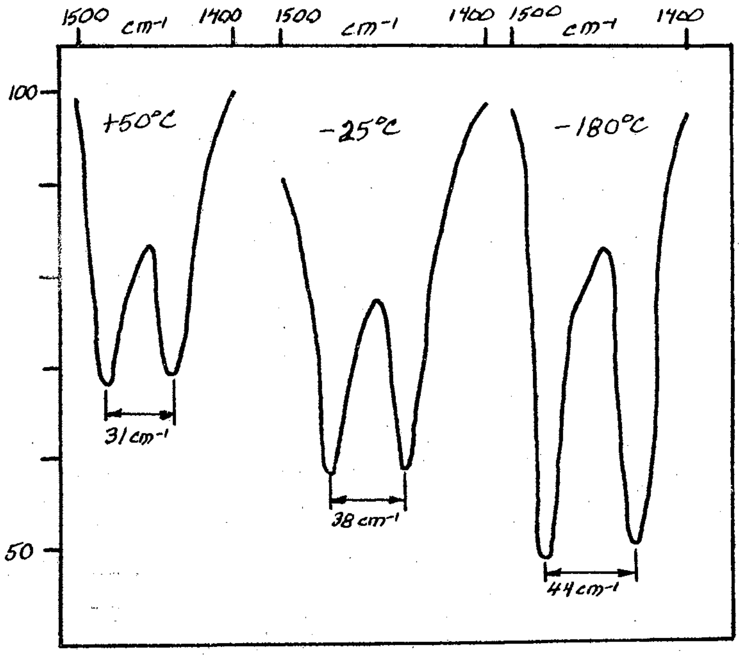

Figure 10. Temperature Dependence of Unoriented PMB

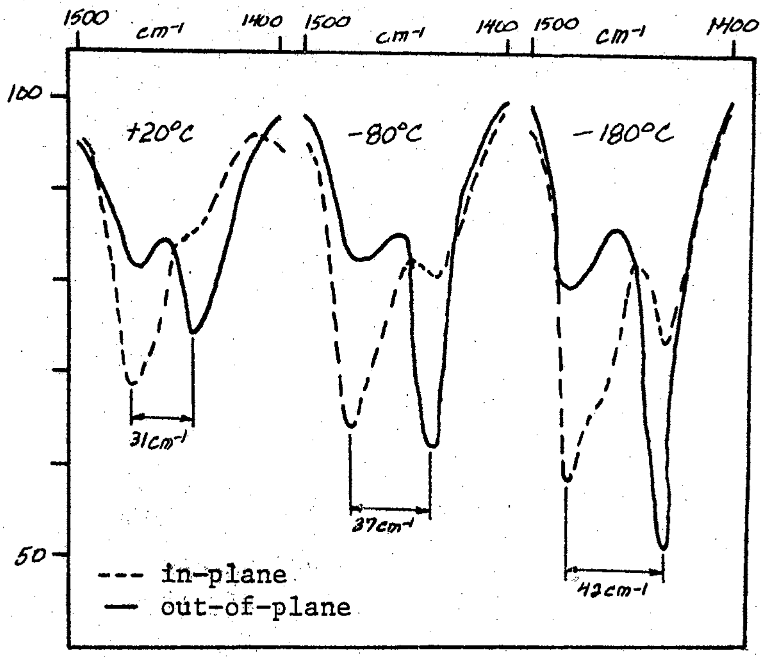

Figure 11. Temperature Dependence of PMB:
TCNE

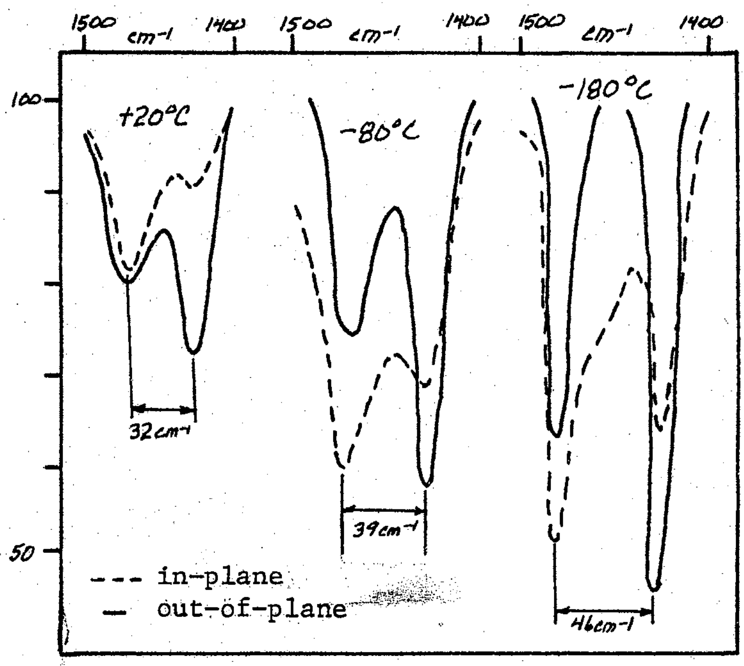

Figure 12. Temperature Dependence of 2PMB:
TCNE

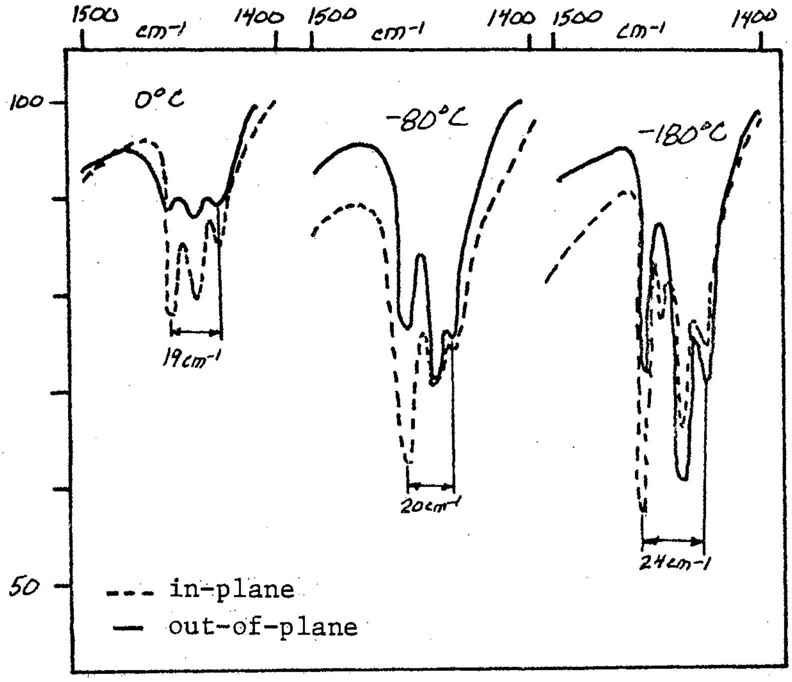

Figure 13. Temperature Dependence of Durene: TCNE

The method of this investigation would appear to be useful for studying changes in these barrier heights with environment even if the absolute potential barriers determined contain significant error. This is the purpose for which it was developed. However, the relative error encountered for pure HMB using the approach under study was at worst 0.5 Kcal./mole when compared to the neutron scattering data of Allen and Cowking, and only 0.05 Kcal./mole when compared to the NMR results. For this reason it is believed that the absolute barrier heights are of acceptable accuracy.

Figures 5 through 13 are representative spectra of each of the cases studied and show the character of the dependence which was measured.

Hexamethylbenzene

The interpretation of the HMB data was relatively straight forward since in pure HMB and each of the complexes studied only a single out-of-plane mode was found to be present, and positions of the in-plane modes were insensitive to temperature changes in each case. Thus, the analysis could be greatly simplified by simply following the lower frequency temperature dependence. Figures 14 and 15 are plots of the observed temperature effect on these low frequency band positions in each of the systems studied. The inflection points, apparent barrier heights and band frequencies at -180°C. are found in Table II.

Pentamethylbenzene

Treatment of the data for these systems was much more complex than the HMB interpretations. In the three cases studied: pure PMB,

TABLE II

TABULATED EXPERIMENTAL VALUES FOR HMB

	Inflection Points	Barrier Heights	In-Plane Modes	Out-of-Plane Modes
HMB	228°K.	1.55 Kcal.	1463 cm.$^{-1}$	1432 cm.$^{-1}$
HMB:TCNE	208°K.	1.25 Kcal.	1460 cm.$^{-1}$	1435 cm.$^{-1}$
2HMB:TCNE	163°K.	1.10 Kcal.	1462 cm.$^{-1}$	1438 cm.$^{-1}$
HMB:TCQ	220°K.	1.46 Kcal.	1462 cm.$^{-1}$	1437 cm.$^{-1}$
HMB:TBQ	208°K.	1.25 Kcal.	1459 cm.$^{-1}$	1427 cm.$^{-1}$

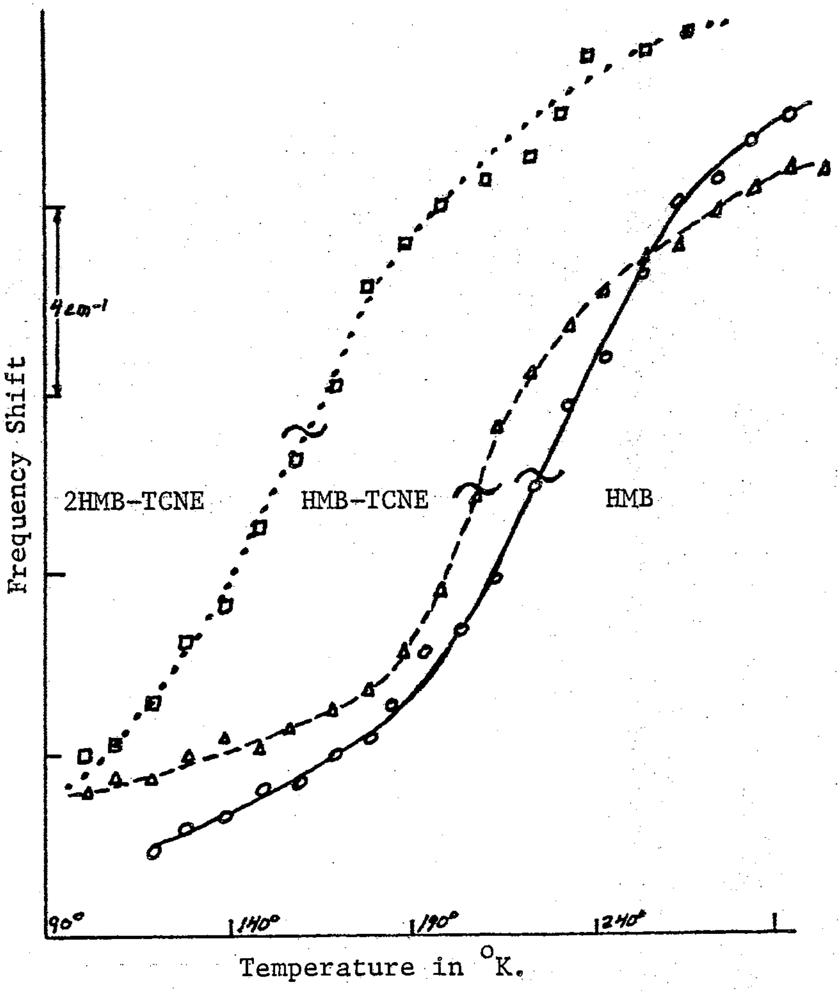

Figure 14. Temperature Dependent Spectral Shifts in HMB Complexes.

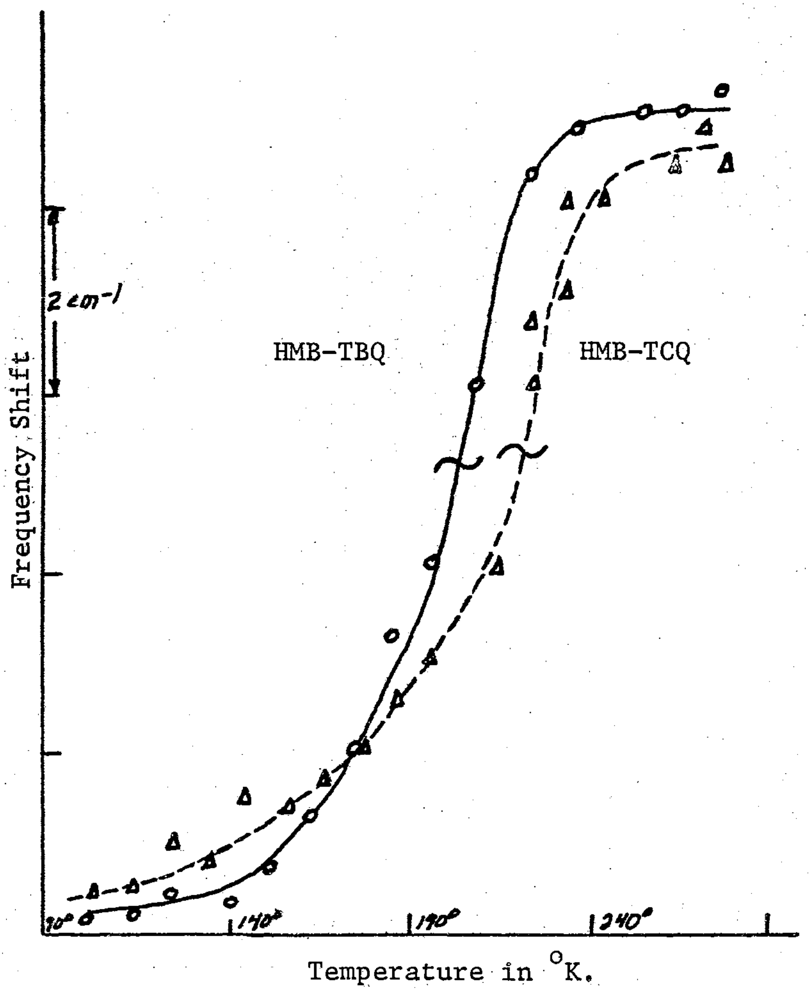

Figure 15. Temperature Dependent Spectral Shifts in HMB Complexes.

PBM-TCNE, and 2PMB-TCNE; each revealed a single band in either polarization. The complication results from the fact that both the in-plane and out-of-plane components displayed a temperature dependence in every case. When a simple temperature dependence plot of the splitting between polarizations was made, only the 2PMB-TCNE complex yielded an S-shaped curve, as PMB-TCNE appeared to have three inflection points and the pure PMB plot appeared linear when treated in this manner.

Since a difference plot between the two absorption peaks appeared inadequate, an alternative treatment was sought. When the isolated temperature dependence of each of the components were studied, the high frequency, in-plane mode yielded almost identical plots for each molecular entity studied, while the low frequency, out-of-plane mode resulted in three entirely different S-shaped curves for the three PMB environments (Figure 16). Because of this it was assumed that the temperature dependency of the in-plane modes may have been caused by something other than the onset of methyl rotation. It is not clear what the actual cause of this temperature dependency of the high frequency band might be, but one possibility is the onset of librations or rotations of the entire PMB molecule in its crystal lattice.

This suggestion is not unreasonable since both Andrew (20) and Rush and Taylor (18) report such motions occurring above 135°K. A barrier height for this type of motion of between 0.1 and 1.00 Kcal./mole gives a reasonable agreement with these observations when used in a statistical calculation.

Using the above assumption as a basis, the procedure was to match the inflection points of the temperature dependency of the low frequency band to the inflection points of the P_{1a} plots. This approach yielded

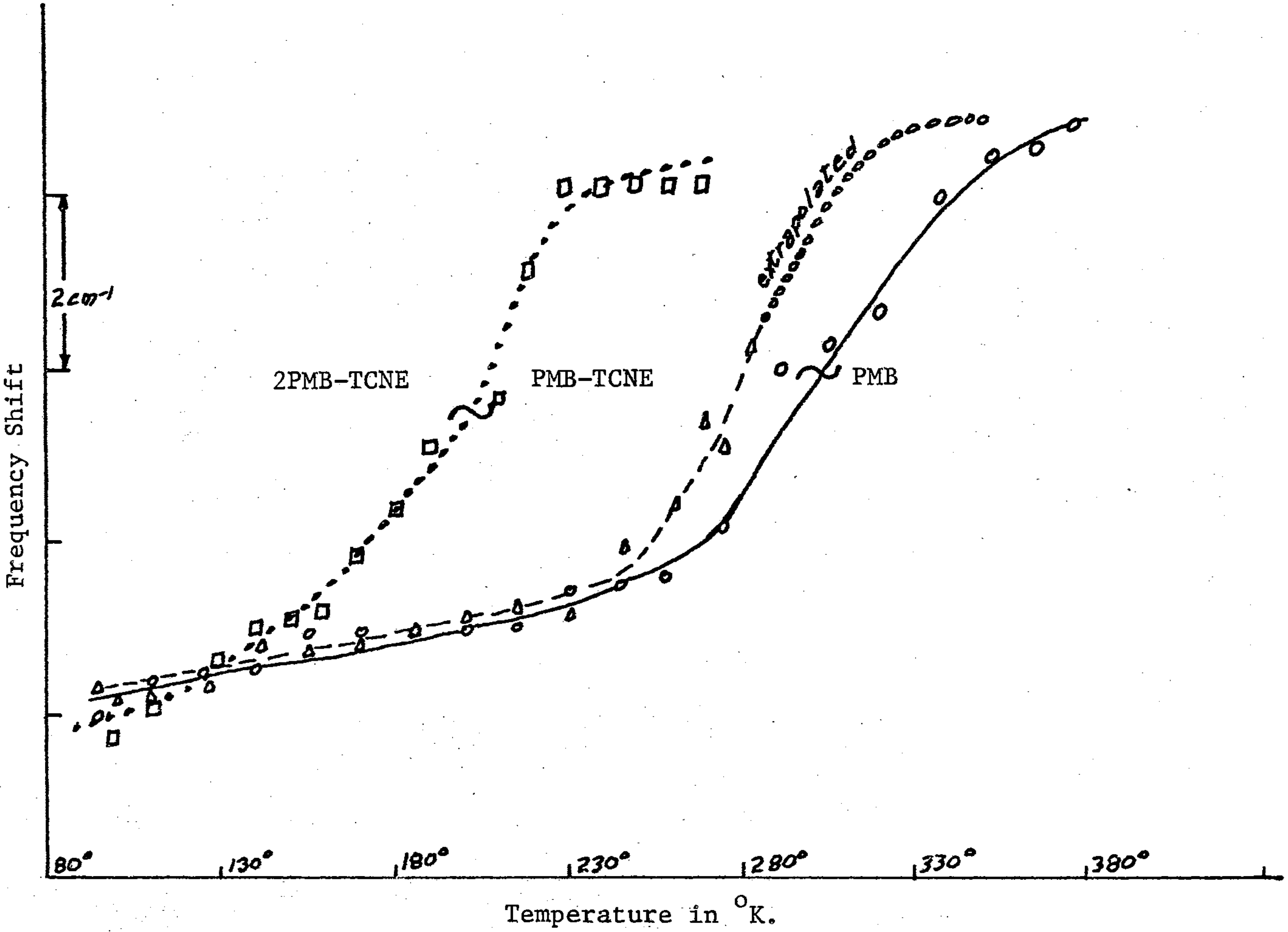

Figure 16. Temperature Dependent Spectral Shifts for PMB Complexes.

an estimated barrier of 2.06 Kcal./mole for pure PMB which compares reasonably with the value of 2.2 Kcal./mole presented by Allen and Cowking (22). Temperatures of inflection points, barriers, and band positions are listed in Table III.

It should be noted that the inflection point for the PMB-TCNE complex involved an extrapolation because studies above room temperature were considered unsafe due to the toxicity and volatility of the TCNE. The extrapolation was made on the basis that for both 2PMB-TCNE and pure PMB the S-shaped curve ranged over 6 cm.$^{-1}$ The same range was assumed with the PMB-TCNE complex and the top half of the "S" was extrapolated to closely resemble the other two curves in contour.

TABLE III

TABULATED EXPERIMENTAL VALUES FOR PMB

	Inflection Points	Barrier Heights	In-Plane Modes	Out-of-Plane Modes
PMB	308^{o}K.	2.06 Kcal.	1478 cm.$^{-1}$	1438 cm.$^{-1}$
PMB:TCNE	283^{o}K.	1.80 Kcal.	1478 cm.$^{-1}$	1436 cm.$^{-1}$
2PMB:TCNE	193^{o}K.	1.18 Kcal.	1480 cm.$^{-1}$	1434 cm.$^{-1}$

Durene

For pure durene there were two absorptions in the region of the spectrum under study, one in-plane and one out-of-plane. The high frequency band was not observed to shift in the temperature range between -180^{o}C. to 0^{o}C. although the low frequency band moved about 2 cm.$^{-1}$ over

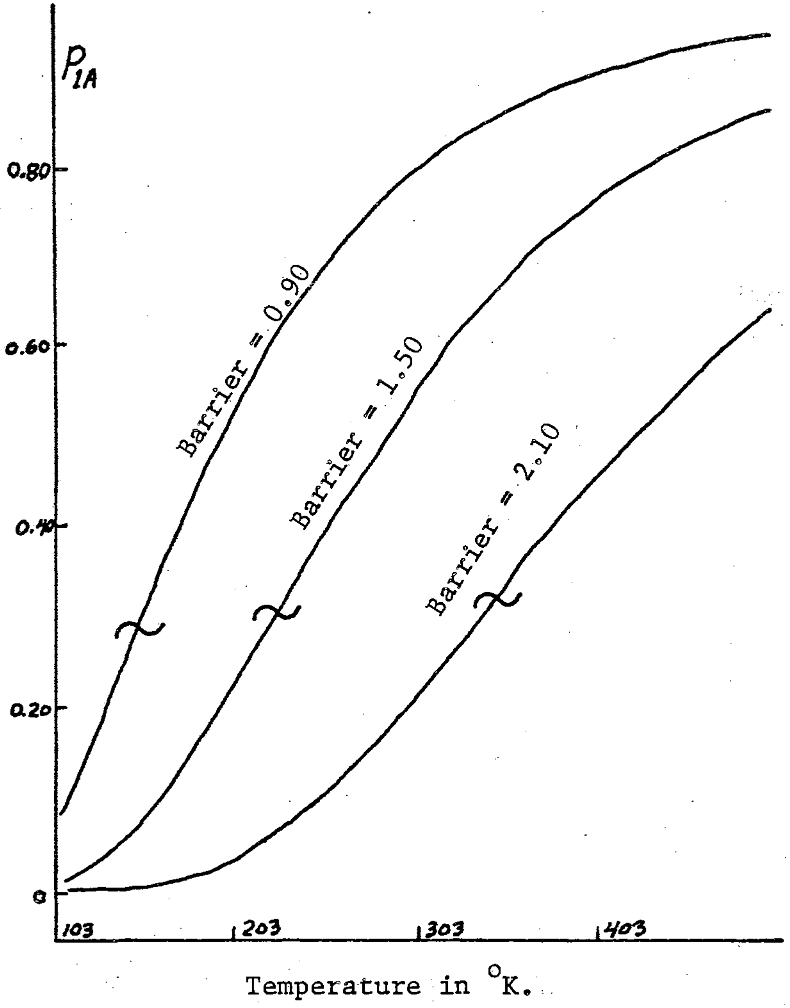

Figure 17. Some Sample Statistical Curves for PMB.

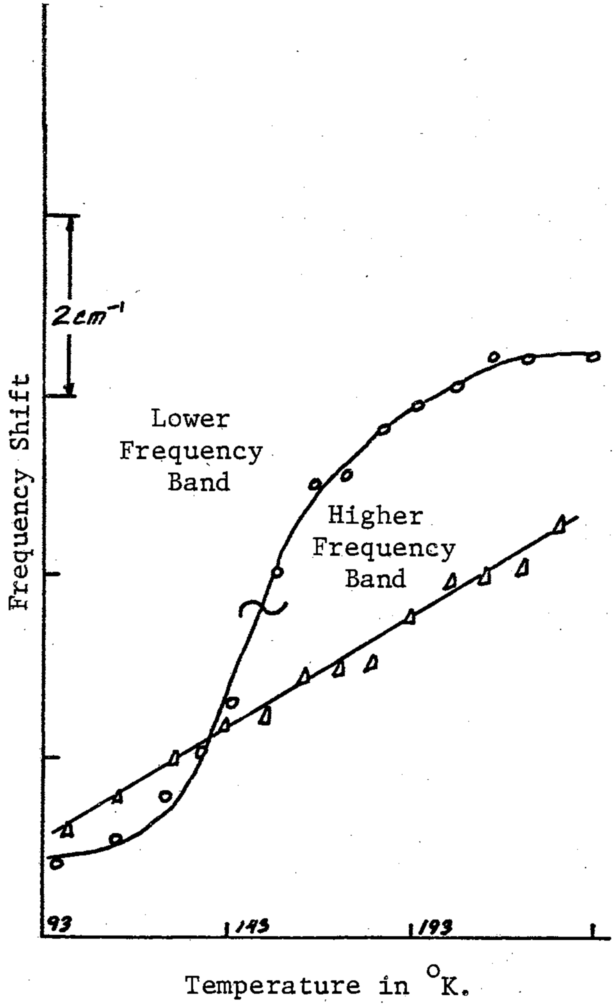

Figure 18. Temperature Dependent Spectral Shifts for Durene-TCNE.

these temperatures. This was not surprising in that a statistical calculation for durene using Allen and Cowking's (22) value of 1.60 Kcal/mole indicated an expected inflection point at 30°C. Attempts were made to study pure durene at higher temperatures, but the techniques employed were inadequate to cope with the relatively high volatility of this compound.

In the 1:1 complex with TCNE there were four bands in the region under study, two in-plane and two out-of-plane modes. The two high frequency, in-plane modes were not observed to be temperature dependent although the weaker of these two becomes unobservable at higher temperatures due to broadening of the two much more intense bands located on either side of it. Because of the static nature of the in-plane modes only the two out-of-plane vibrations were considered. Both of these were observed to be temperature dependent; plots of these dependencies revealed that the more intense higher frequency band moved in a linear fashion with temperature while the lower frequency of these two appeared to move in the expected S-shaped manner. When the inflection point of the latter curve at 153°C. was matched in a statistical manner the apparent barrier height was 0.80 Kcal/mole.

CHAPTER V

DISCUSSION OF RESULTS

The apparent potential barriers to methyl rotation as evaluated in the previous chapter seem to display certain definite trends. In every case studied, the barrier was lowered when a molecular complex was formed. Also the 2(donor)-TCNE complex in each case yielded a lower barrier than the simple 1:1 complex.

Throughout this discussion it should be remembered that the barrier to methyl rotation is not an absolute energy, but rather the difference between two absolute energies. This fact implies that a smaller experimental barrier does not necessarily mean a lower maximum on the potential curve for rotation, but might be the result of a higher minimum.

In attempting to understand the present results the logical starting point would be the molecular arrangements in the crystal lattice. Figure 17 is a schematic representation of the relative orientations of the molecules in pure HMB and a general methylbenzene-TCNE complex. In the complexes it has been shown that the donor and acceptor molecules are alternately stacked along the crystal axis in appropriate ratios; i.e., for the 1:1 case, donor-acceptor donor-acceptor; or for 2:1 complexes, donor-acceptor-donor-donor-acceptor-donor-etc. The pure methylbenzenes are presumed to be stacked in a similar manner except the molecular planes are parallel to the needle axis (11).

If steric interactions were dominant in the establishment of the

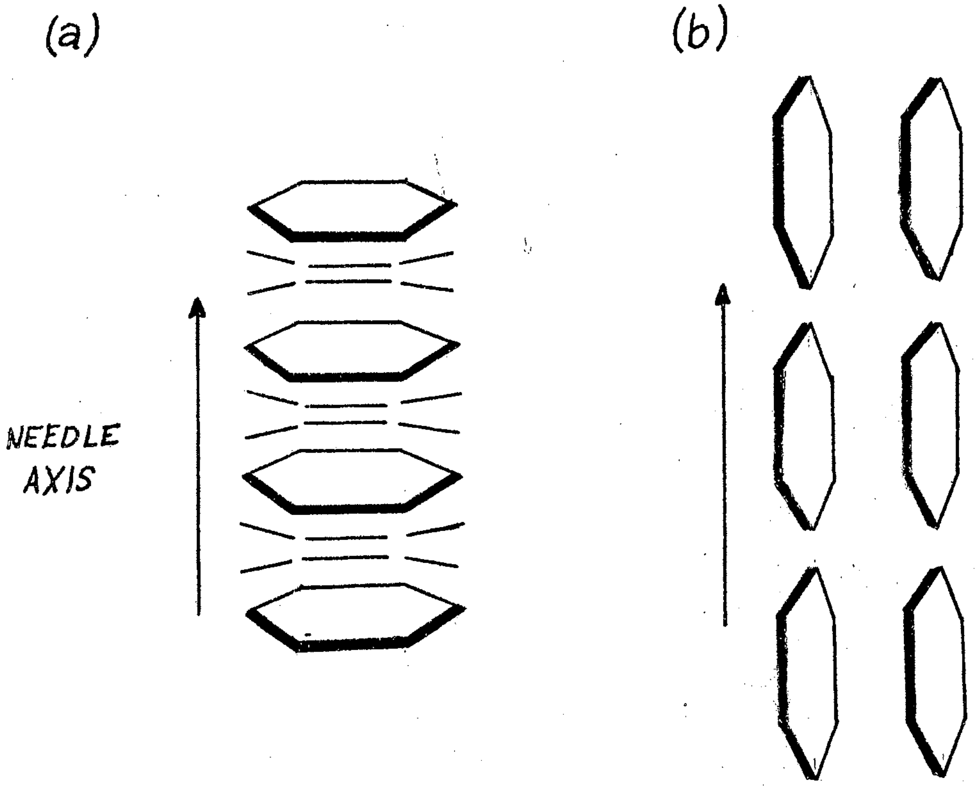

Figure 19. Stacking of Molecules Relative to the Crystal Needle Axis in the Solid State of (a) Methylbenzene-TCNE Complex, and (b) Pure Methylbenzene.

potential surface for rotation of the methyl groups, the maximum of the potential curve would obviously occur in the plane of the molecule, while the minimum should be out of the plane because of the relative distances involved. With this concept of the potential energy surface, the general lowering of the experimental barrier upon complexation can easily be explained as a result of the smaller intermolecular distances expected due to the charge transfer interactions, i.e., the absolute energy of the out-of-plane minimum is increased without necessarily effecting the absolute maximum.

The concept of steric interactions causing an increase in an absolute minimum is not original. Beaudet (28) evaluated the barrier to methyl rotation for a series of cis and trans isomers of propylene using microwave techniques. In each pair studied, the cis isomer yielded a lower barrier. In the equilibrium orientation of the methyl group, one of the methyl-hydrogens was found to be co-planar with the double bond and directed toward the functional group in the cis position. The lower barriers for the cis cases were explained as due to an increased steric interaction that raises the minimum when a larger group interchanges with the smaller hydrogen present in this position for the trans isomers.

This explanation is especially appealing when considering the ordering of the barrier reductions of the series of 1:1 complexes of HMB with TCNE, TCQ, and TBQ. The relative strengths of these acceptors are

$$\text{TCNE} > \text{TCQ} \geq \text{TBQ} \quad (6)$$

while the order of the lowering of the barrier heights was found to be

TCNE $\simeq$ TBQ > TCQ.

There is obviously no simple correlation between the acceptor strength and barrier height, i.e., induction effects alone will not explain the ordering observed. On the other hand, the stronger charge transfer interaction of TCNE would force the molecules to be stacked more closely together than in the other two cases. From this consideration alone we would expect a greater increase in the intermolecular steric interactions for this case and therefore the greatest increase in the potential minimum. The other members of this series, TCQ and TBQ, both have nearly the same acceptor strengths and should form a complex over nearly the same distance (6), but the bromine atoms of TBQ are larger than the chlorine atoms in TCQ causing a larger intermolecular steric interaction and the corresponding greater increase in the potential minimum.

However, this simple approach breaks down when comparing the reduction of the barrier heights in the 1:1 and 2:1 complexes of HMB and PMB with TCNE. With steric factors alone the larger reduction in the barrier for the 2:1 complexes would indicate a larger charge transfer interaction for these complexes. This is not the case, however, since the work of Youhne (29) tends to indicate less charge transfer in the 2:1 complexes. Youhne found the values of 1570 cm.$^{-1}$ with pure TCNE, 1560 cm.$^{-1}$ with HMB-TCNE, and 1570 cm.$^{-1}$ with 2HMB-TCNE for the absorption band associated with the C = C stretch of TCNE. Since TCNE is a sacrificial acceptor this data would indicate that there is more charge transfer taking place in the 1:1 complex. This band should be very sensitive to the magnitude of the charge transfer interaction since a

Huckle M.O. calculation by Penfold and Lipscomb (30) found the lowest unoccupied M.O. to be an antibonding orbital with five nodes located one in each nitrile group and one in the ethylene portion of the molecule.

The simple steric interpretation is further discredited by the frequencies of the out-of-plane bending mode of the hydrogen attached to the ring in PMB. These frequencies were found to be 865 $cm.^{-1}$ for PMB, 882 $cm.^{-1}$ for PMB-TCNE, and 875 $cm.^{-1}$ for 2PMB-TCNE. This ordering of frequencies tends to indicate the following order for the magnitude of the intermolecular interaction:

$$\text{PMB-TCNE} > \text{2PMB-TCNE} > \text{PMB}.$$

This agrees quite well with the amount of charge transfer found by observing the TCNE band shifts, but is not the ordering found for the barrier heights in these compounds. Since a simple steric or simple inductive effect is insufficient, a combination of these two explanations must be considered.

The inductive effect would be expected to mainly change the maximum of the potential energy curve; i.e., the greater the charge transfer the higher the absolute maximum. This is a result of hyperconjugation (31) caused by the electron withdrawal properties of the charge transfer interaction on the donor molecule. Hyperconjugation in the methyl benzenes would involve a shift in electron density from the carbon-hydrogen to the carbon-benzene bond region. This increases the bond order between the methyl group and the benzene ring which would tend to restrict methyl rotation. Also this increase in electron density between the methyl group and the ring would cause a shortening of this bond, drawing the adjacent methyl groups closer together, thereby further increasing the maximum of the potential curve due to increased in-plane steric interactions. This shift in electron density would increase as the extent of the charge transfer interaction increased.

This explanation for the expected induction effect on the barrier to methyl rotation tends to be confirmed by the work of Beaudet (28). Although the author did not discuss his data in this manner, an interesting correlation can be seen between the ordering of the evaluated barriers to methyl rotation and the electron withdrawing ability of the added functional groups in the trans-propylene isomers studied. As stronger electron withdrawing groups are substituted in the trans position with respect to the methyl group in propylene, the barrier to methyl rotation increases. Since substitution is trans in each case, there are no expected changes in steric interactions on the methyl group, and the barrier increases are indicative of a hyperconjugation effect on the methyl group bond order.

As a check on the presence of hyperconjugation in this study, the NMR spectra of HMB, HMB-TCNE, and HMB-TBQ were taken with a Varian A-60 spectrometer using tetrachloroethylene as a solvent.* Relative to HMB these showed a chemical shift of approximately 1.0 cps. down field for HMB-TCNE and a chemical shift of 0.3 cps. down field for HMB-TBQ. These shifts are what would be expected due to a decrease in the shielding of the protons caused by the decrease in electron density around the hydrogens associated with the hyperconjugation effect. The

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*We would like to thank Mr. William Dunn for his assistance in obtaining this data.

difference in shifts indicates a larger induction effect with the stronger acceptor. These conclusions do not consider the possibility of ring current effects, if these exist (32).

The combination of out-of-plane steric and hyperconjugation effect offers a satisfactory explanation of all the changes in barriers encountered in this investigation. When a simple 1:1 complex is formed, both the absolute minimum and the absolute maximum of the potential curve is increased, but for all acceptors studied the minimum (i.e., intermolecular effect) increases at a more rapid rate with respect to the extent of the charge transfer interaction than does the maximum (i.e, induction effect). This is evidenced by the net decrease in barrier height in each case. The fact that both TCNE and TBQ reduce the barrier height approximately the same amount is a result of two effects; first, a much smaller increase in the absolute maximum occurs with TBQ due to the weaker charge transfer interaction; secondly, as previously mentioned, the bulkier nature of TBQ causes a rise in the minimum to occur at larger intermolecular distances. This latter fact is further evidenced by comparison of steric effects of the comparable acceptors TCQ and TBQ stated earlier in this chapter.

The apparent barrier height is lower for the 2:1 complexes of TCNE than for the 1:1 cases, because in the latter complexes there is a much larger induction effect resulting from the charge transfer interaction. In both type of complexes, however, the out-of-plane steric interactions are increased to such an extent that the net effect of the lower barrier for the 2:1 complexes is mainly reflective of the smaller induction effect.

CHAPTER VI

SUMMARY

It was found that the temperature dependence of the methyl wagging modes of each of the methylbenzene derivatives could be used to obtain a reasonable estimate of the potential barrier to methyl rotation. This was achieved by matching the inflection point of a plot of this temperature dependence with the inflection point of the temperature dependence of the statistical parameter P_{1a} which was calculated with the aid of an assumed barrier height.

This technique was then extended to the study of changes of these barriers intrinsic with molecular complex formation. The barriers for these complexes were evaluated and tabulated. It was found that to adequately explain the changes in these barriers both the out-of-plane steric interactions and hyperconjugation effects must be considered. Of these 2 factors the intermolecular steric effects are larger in each case studied and increase at a faster rate than do the induction effects on the barrier as the strength of the charge transfer interaction increases.

This technique could be extended to the study of barrier changes in acceptor molecules, if such can be found which possess suitable rotating groups and appropriate temperature dependencies within their spectra. Other stable solid complexes of methyl benzenes with acceptors such as hexacyanobutadiene or tetracyanoquinodimethane (TCNO) might also provide interesting subjects for study.

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APPENDIX

SAMPLE STATISTICAL PROGRAM

```
$JOB    10106,442-42-1320,KP#026,TIME#20       KENNETH WILLIAMSON
C       ROTATIONAL STATE POPULATION STUDIES FOR PENTAMETHYLBENZENE   %PITZER<
C       BARRIER HEIGHT ASSUMED TO BE 2.00 KCAL
        DIMENSION T(40), Q(40), RPA(40), RPB(40), PA(40), PB(40),
       1    P1A(40), P2A(40), P3A(40), P4A(40), P5A(40), DPDT(40)
C       BA IS THE BARRIER HEIGHT IN KCAL
        BA=2.00
C       K IS THE BOLTZMAN CONSTANT
        REAL K
        K=1.38505E-16
C       BH IS THE METHYL  ROTATIONAL CONSTANT IN ERGS
        BH=1.0895E-15
C       T IS THE TEMPERATURE IN DEGREES KELVIN
        READ (5,1)T
      1 FORMAT (9X, 5F10.0<
C       VO IS THE BARRIER HEIGHT IN ERGS
        VO=BA*6.946E-14
C       A%I< ARE THE ROTATIONAL CONSTANTS USING REDUCED MOMENT OF INERTIA
        A1=BH
        A2=9.2455E-18
        A3=9.1677E-18
C       E IS THE VIBRATIONAL SPACING BELOW THE BARRIER
        E=3.0*SQRT(VO*A1*A2/A3)
        DO 7 I = 1,40
C       RPA IS THE ROTATIONAL PARTITION FUNCTION
        RPA(I)=0.0
C       J IS ROTATIONAL QUANTUM NUMBER,JMIN MUST BE ADJUSTED TO BARRIER
        DO 10 J=8,17
        Y=J
     10 RPA(I)=RPA(I)+2.0*EXP(( -2.0*Y*Y*BH + E - VO)/(2.0*K*T(I)))
C       RPB IS THE VIBRATIONAL PARTITION FUNCTION
        RPB(I)=3.0
C       L IS VIBRATIONAL QUANTUM NUMBER,LMAX MUST BE ADJUSTED TO BARRIER
        DO 11 L=1,3
        W=L
     11 RPB(I)=RPB(I)+3.0*EXP(-W*E/(K*T(I)))
C       Q IS THE TOTAL PARTITION FUNCTION
        Q(I) = RPA(I) + RPB(I)
C       PA IS THE PROBABILITY OF A GIVEN ROTOR ROTATING FREELY ABOVE THE BARRIER
        PA(I) = RPA(I)/Q(I)
C        PB IS THE PROB OF A GIVEN ROTOR BEING RESTRICTED BELOW THE BARRIER
        PB(I) = RPB(I)/Q(I)
C       P1A IS THE PROB OF ONE OR MORE ROTORS ON MOLECULE BEING ABOVE BARRIER
C       P2A, P3A, ETC. ARE THE PROBABLITIES FOR TWO OR MORE, THREE OR MORE, ETC.
C      1     BEING ABOVE THE BARRIER
        P1A(I) = 5.0*PA(I)*PB(I)**4 + 10.0*PA(I) **2*PB(I)**3 + 10.0*
       1   PA(I)**3*PB(I)**2 + 5.0* PA(I)**4*PB(I)**1 + PA(I)**5
        P2A(I) = 10.0*PA(I)**2*PB(I)**3 + 10.0*PA(I)**3*PB(I)**2 + 5.0*
       1     PA(I)**4*PB(I)**1 + PA(I)**5
        P3A(I) = 10.0*PA(I)**3*PB(I)**2 + 5.0*PA(I)**4*PB(I)**1 + PA(I)**5
        P4A(I) = 5.0*PA(I)**4*PB(I)**1 + PA(I)**5
        P5A(I) = PA(I)**5
      7 CONTINUE
        H=10.0
        A= 1.6000
        B=-0.8000
        C= 0.2286
        D=-2.8570E-02
        DO 12 I= 5,36
C       DPDT IS THE DIFFERENTIAL OF P1A WITH RESPECT TO TEMPERATURE


        DPDT(I)=A*(P1A(I+1)-P1A(I-1))/(2.0*H)+B*(P1A(I+2)-P1A(I-2))/
       1(4.0*H)+C*(P1A(I+3)-P1A(I-3))/(6.0*H)+D*(P1A(I+4)-P1A(I-4))/
       2(8.0*H)
     12 CONTINUE
        DPDT(1)= 0.0
        DPDT(2)=0.0
        DPDT(3)=0.0
        DPDT(4)=0.0
        DPDT(37)=0.0
        DPDT(38)=0.0
        DPDT(39)=0.0
        DPDT(40)=0.0
        WRITE (6,2)
      2 FORMAT (1X, 2H I, 10X, 2H T, 14X, 4H RPA, 10X, 4H RPB, 11X,
       1     2H Q, 12X, 3H PA, 12X, 3H PB<
        DO 3 I = 1,40
      3 WRITE (6,4) I, T(I), RPA(I), RPB(I), Q(I), PA(I), PB(I)
      4 FORMAT (2X, I2, 5X, F10.5, 5X, F10.5, 5X, F10.5, 5X, F10.5, 5X,
       1     F10.5, 5X, F10.5<
        WRITE (6,5)
      5 FORMAT (12X,4H P1A, 11X, 4H P2A, 11X, 4H P3A, 11X, 4H P4A, 11X,
       1      4H P5A, 11X, 5H DPDT<
        DO 9 I = 1,40
      9 WRITE (6,4) I, P1A(I), P2A(I), P3A(I), P4A(I), P5A(I), DPDT(I)
        STOP
        END
```

PROGRAM OUTPUT

```
          $ENTRY
  I          T                 RPA           RPB           Q            PA           PB
  1      103.00000          0.00057       3.24110       3.24168      0.00018      0.99982
  2      113.00000          0.00127       3.30974       3.31101      0.00038      0.99962
  3      123.00000          0.00247       3.38368       3.38615      0.00073      0.99927
  4      133.00000          0.00438       3.46196       3.46634      0.00126      0.99874
  5      143.00000          0.00719       3.54377       3.55096      0.00203      0.99797
  6      153.00000          0.01111       3.62839       3.63950      0.00305      0.99695
  7      163.00000          0.01633       3.71522       3.73155      0.00438      0.99562
  8      173.00000          0.02301       3.80374       3.82675      0.00601      0.99399
  9      183.00000          0.03131       3.89349       3.92480      0.00798      0.99202
 10      193.00000          0.04137       3.98408       4.02544      0.01028      0.98972
 11      203.00000          0.05327       4.07516       4.12844      0.01290      0.98710
 12      213.00000          0.06711       4.16646       4.23357      0.01585      0.98415
 13      223.00000          0.08296       4.25770       4.34066      0.01911      0.98089
 14      233.00000          0.10084       4.34868       4.44952      0.02266      0.97734
 15      243.00000          0.12078       4.43921       4.55999      0.02649      0.97351
 16      253.00000          0.14280       4.52912       4.67192      0.03057      0.96943
 17      263.00000          0.16689       4.61827       4.78516      0.03488      0.96512
 18      273.00000          0.19303       4.70656       4.89959      0.03940      0.96060
 19      283.00000          0.22119       4.79389       5.01507      0.04410      0.95590
 20      293.00000          0.25133       4.88017       5.13150      0.04898      0.95102
 21      303.00000          0.28342       4.96534       5.24876      0.05400      0.94600
 22      313.00000          0.31741       5.04935       5.36676      0.05914      0.94086
 23      323.00000          0.35324       5.13214       5.48539      0.06440      0.93560
 24      333.00000          0.39086       5.21370       5.60456      0.06974      0.93026
 25      343.00000          0.43020       5.29399       5.72419      0.07515      0.92485
 26      353.00000          0.47121       5.37300       5.84421      0.08063      0.91937
 27      363.00000          0.51382       5.45071       5.96453      0.08615      0.91385
 28      373.00000          0.55796       5.52712       6.08508      0.09169      0.90831
 29      383.00000          0.60358       5.60223       6.20581      0.09726      0.90274
 30      393.00000          0.65060       5.67604       6.32665      0.10284      0.89716




 31      403.00000          0.69897       5.74856       6.44753      0.10841      0.89159
 32      413.00000          0.74863       5.81979       6.56842      0.11397      0.88603
 33      423.00000          0.79950       5.88975       6.68925      0.11952      0.88048
 34      433.00000          0.85152       5.95845       6.80997      0.12504      0.87496
 35      443.00000          0.90464       6.02591       6.93056      0.13053      0.86947
 36      453.00000          0.95880       6.09214       7.05094      0.13598      0.86402
 37      463.00000          1.01394       6.15717       7.17111      0.14139      0.85861
 38      473.00000          1.07000       6.22100       7.29100      0.14676      0.85324
 39      483.00000          1.12693       6.28367       7.41060      0.15207      0.84793
 40      493.00000          1.18467       6.34518       7.52986      0.15733      0.84267
            P1A             P2A           P3A           P4A          P5A          DPDT
  1        0.00089          0.00000       0.00000       0.00000      0.00000      0.00000
  2        0.00191          0.00000       0.00000       0.00000      0.00000      0.00000
  3        0.00364          0.00001       0.00000       0.00000      0.00000      0.00000
  4        0.00630          0.00002       0.00000       0.00000      0.00000      0.00000
  5        0.01009          0.00004       0.00000       0.00000      0.00000      0.00044
  6        0.01517          0.00009       0.00000       0.00000      0.00000      0.00058
  7        0.02169          0.00019       0.00000       0.00000      0.00000      0.00073
  8        0.02971          0.00036       0.00000       0.00000      0.00000      0.00088
  9        0.03926          0.00063       0.00001       0.00000      0.00000      0.00103
 10        0.05034          0.00103       0.00001       0.00000      0.00000      0.00118
 11        0.06287          0.00162       0.00002       0.00000      0.00000      0.00132
 12        0.07679          0.00243       0.00004       0.00000      0.00000      0.00146
 13        0.09197          0.00351       0.00007       0.00000      0.00000      0.00158
 14        0.10829          0.00491       0.00011       0.00000      0.00000      0.00168
 15        0.12561          0.00665       0.00018       0.00000      0.00000      0.00178
 16        0.14377          0.00878       0.00027       0.00000      0.00000      0.00185
 17        0.16263          0.01134       0.00040       0.00001      0.00000      0.00192
 18        0.18206          0.01433       0.00058       0.00001      0.00000      0.00197
 19        0.20191          0.01779       0.00080       0.00002      0.00000      0.00200
 20        0.22205          0.02172       0.00109       0.00003      0.00000      0.00202
 21        0.24237          0.02613       0.00145       0.00004      0.00000      0.00204
 22        0.26275          0.03102       0.00189       0.00006      0.00000      0.00204
 23        0.28310          0.03638       0.00242       0.00008      0.00000      0.00203
 24        0.30334          0.04220       0.00305       0.00011      0.00000      0.00202
 25        0.32338          0.04846       0.00378       0.00015      0.00000      0.00199
 26        0.34317          0.05515       0.00463       0.00020      0.00000      0.00196
 27        0.36264          0.06223       0.00560       0.00026      0.00000      0.00193
 28        0.38175          0.06969       0.00669       0.00033      0.00001      0.00189
 29        0.40047          0.07750       0.00791       0.00041      0.00001      0.00185
 30        0.41875          0.08563       0.00927       0.00051      0.00001      0.00181
 31        0.43659          0.09406       0.01076       0.00063      0.00001      0.00176
 32        0.45395          0.10274       0.01239       0.00077      0.00002      0.00171
 33        0.47083          0.11167       0.01416       0.00092      0.00002      0.00166
 34        0.48721          0.12079       0.01607       0.00110      0.00003      0.00161
 35        0.50309          0.13010       0.01811       0.00130      0.00004      0.00156
 36        0.51848          0.13956       0.02029       0.00152      0.00005      0.00151
 37        0.53337          0.14915       0.02261       0.00177      0.00006      0.00000
 38        0.54776          0.15884       0.02506       0.00205      0.00007      0.00000
 39        0.56167          0.16862       0.02763       0.00235      0.00008      0.00000
 40        0.57510          0.17845       0.03033       0.00268      0.00010      0.00000

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****TOTAL COST:   $ 0.41          ****CARDS READ:     94          ****LINES PRINTED:     170
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VITA

Kenneth Michael Williamson

Candidate for the Degree of

Doctor of Philosophy

Thesis: THE USE OF INTERNAL-MOLECULAR POTENTIAL BARRIERS IN THE STUDY OF CHARGE TRANSFER INTERACTIONS

Major Field: Chemistry

Biographical:

Personal Data: Born in Marion, Ohio, April 12, 1942, the son of Kenneth O. and Florence P. Williamson.

Education: Attended public schools in Ohio, New York, Colorado and Oklahoma; graduated from Edison High School in Tulsa in 1960; received the Bachelor of Science degree with a major in chemistry from Oklahoma State University, Stillwater, Oklahoma, in May, 1965; completed the requirements for the Doctor of Philosophy degree in May, 1970.

Professional Experience: Graduate Teaching Assistant, Oklahoma State University, 1965 and 1968; Research Assistant, Oklahoma State University, 1966 and 1967; member of Phi Lambda Upsilon.