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STEVEN S, James Floyd, Jr., 1951-
MICROWAVE SPECTROSCOPIC STRUCTURAL STUDIES
OF CIS-AZOMETHANE, METHYLISOCYANIDE-BORANE,
AND ETHYLISOCYANIDE-BORANE.

Rice University, Ph.D., 1977
Chemistry, physical

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MICROWAVE SPECTROSCOPIC STRUCTURAL STUDIES
OF CIS-AZOMETHANE, METHYLISOCYANIDE-BORANE,
AND t-BUTYLISOCYANIDE-BORANE

by

JAMES F. STEVENS, JR.

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

THESIS DIRECTOR'S SIGNATURE:

Robert F. Curl

HOUSTON, TEXAS

MAY, 1977
MICROWAVE SPECTROSCOPIC STRUCTURAL STUDIES
OF Cis-AZOMETHANE, METHYLISOCYANIDE-BORANE,
AND t-BUTYLISOCYANIDE-BORANE

by

JAMES F. STEVENS, JR.

ABSTRACT

The microwave spectra of the ground states of cis-
azomethane, d₆-cis-azomethane, methylisocyanide-borane, and
t-butylisocyanide-borane in the 26.5 - 40 GHz region are
reported. In addition the microwave spectrum of the first
excited torsional state of d₆-cis-azomethane in this region
is also reported.

For cis-azomethane and d₆-cis-azomethane both R-branch
and Q-branch transitions have been assigned. For the first
excited torsional state of d₆-cis-azomethane only Q-branch
transitions have been assigned.

Fine structure due to internal rotation was observed in
transitions belonging to the ground torsional state of cis-
azomethane and the first excited state of the d₆ species.
Analysis of these splittings gives a barrier to internal
rotation of 1329 ± 50 cal/mole for the normal species and
1624 ± 50 cal/mole for the d₆ species. Relative intensity
measurements of the ground state and first excited torsional
state of the deuterated species indicates a value of 1656 ±
50 cal/mole for the barrier to internal rotation.

The inertial defects of the ground state moments of
inertia are consistent with a structure in which the heavy
atoms are contained in the same plane. By assuming a N=N bond length of 1.254 Å, a C-H bond length of 1.085 Å, and a H-C-H bond angle of 109.5° the remaining structural parameters were found to be 1.485 Å and 119.4° for the N-C bond length, and the N=N-C angle respectively.

An analysis of the Stark effect of cis-azomethane and d₆-cis-azomethane indicates dipole moments of 3.20 ± 0.09D and 3.33 ± 0.09D for the normal and deuterated species respectively.

The molecular complexes methylisocyanide-borane and t-butylishocyanide-borane have been prepared and their microwave spectra in the region 26.5 - 40 GHz have been observed.

Using the rotational constants of the 14 isotopic species of methylisocyanide-borane prepared an rₛ heavy atom structure has been determined to be r(C-N) = 1.416 ± 0.004 Å, r(N≡C) = 1.155 ± 0.006 Å, and r(CB) = 1.566 ± 0.004 Å. Assuming r(CH) = 1.100 ± 0.015 Å and r(BH = 1.220 ± 0.020 Å, /HCN and /HBC can be evaluated by isotopic substitution as 109.0 ± 0.5° and 105.7 ± 0.6°. The dipole moment was found to be 6.73 ± 0.07D and the barrier to internal rotation estimated to be less than 4.2 cal/mol.

Analysis of the rotational constants of the four isotopic species of t-butylishocyanide-borane prepared gives a rₛ value of 1.568 ± 0.005 Å for r(CB).
ACKNOWLEDGMENTS

I wish to thank my thesis advisor, Professor Robert F. Curl, Jr., whose help and friendship have aided me more than can be expressed by this acknowledgement.

I would also like to acknowledge Dr. John Bevan whose idea it was to synthesize the isocyanide-borane complexes. All work in Part II was done in collaboration with him and part of this work (methylisocyanide-borane) has appeared in an altered form as a publication co-authored by him, Professor Curl, R. A. Geanangel, and M. Grace Hu.

I gratefully thank the Robert A. Welch Foundation for their financial support of both myself and this work.

No acknowledgement would be complete without a thank you for my wife Sandy who has made my life and work much easier with her love and help.
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<th>PART II-B - t-Butylisocyanide-Borane.</th>
<th>Page</th>
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<tr>
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PART I.

cis-Azomethane
PART I
INTRODUCTION

The most stable isomer of all known acyclic azoalkanes, with the exception of perfluoroazomethane\textsuperscript{1}, is the trans configuration. The difference in ground state energy of 7 - 8 kcal/mole\textsuperscript{2} between the trans and cis isomer of acyclic azoalkanes was such that it was not until 1964\textsuperscript{3} that an acyclic cis-azoalkane, cis-azomethane, was isolated. This first cis-azoalkane was formed photochemically by irradiation the trans isomer in solution. It was not for another ten years that chemical synthesis of cis-trans mixtures were reported\textsuperscript{4,5}.

Structural studies of cis-azoalkanes have been few due to their recent availability and thus far structural studies have been reported for only the cyclic azoalkanes 2,3-diazabicyclo(2.2.1)hep-2-ene\textsuperscript{6}, 2,3-diazabicyclo(2.2.2)oct-2-ene\textsuperscript{7}, 7,8-diazapentacyclo(4.2.2.0\textsuperscript{2}.0\textsuperscript{3}.9.0\textsuperscript{4}.10)dec-7-ene\textsuperscript{7}, and 7,8-diazatricyclo(4.2.2.0\textsuperscript{2}.5)dec-7-ene\textsuperscript{7} in addition to the previously mentioned cis-perfluoroazomethane\textsuperscript{1}. Structural parameters of these molecules are shown in Figure I-1.

Interest in the structural parameters of cis-azoalkanes has arisen for two reasons. Firstly, a prediction has been made that the N=N-C angle should be much larger than the 120° expected from simple valence theory due to steric interactions of the alkane groups\textsuperscript{8}. This prediction
rises from an empirical correlation between R=N=N bond angle and the predicted\(^1\)\((n,\pi^*)\) excitation energy which indicated a C=N=N angle of 131° in cis-azo-2-methyl-2-propane. Thus experimental determination of these bond angles becomes of great interest. The second reason for interest in the structures of cis-azo compounds is closely related to the first and is the evidence\(^9\) which shows that the ring strain energy of five membered cyclic azoalkanes is less than that of similar six membered cyclic azoalkanes, a result opposite to that found in carbocyclic compounds. Again, if the C=N=N angle is larger than the C-C=C angle, this trend is explained, but not in terms of steric repulsion.

It was felt that a structural investigation of cis-azomethane would be a worthwhile first step in explaining these observations. Toward this end an investigation of the microwave spectrum of cis-azomethane was undertaken with a view toward obtaining structural information.

An important additional point of interest in the microwave spectrometric study of cis-azomethane is the effects of internal rotation of the methyl groups. This interest arises because of the possibility that the top-top interactions would be large enough to cause an analyzable effect upon the rotational spectrum of cis-azomethane. In previous two top molecules studied by microwave spectroscopy these interactions have either not been found or the coupling effects could not be analyzed. The proximity
of the two tops in cis-azomethane caused speculation that these interactions might be very large and that the effects of top-top coupling might be analyzed.

Experimental

The initial sample of cis-azomethane was prepared from trans-azomethane obtained from Merck, Sharp, and Dohme. No additional purification steps were carried out on the trans-azomethane as the sample as obtained had no observable spectrum in the microwave region scanned. The trans-to-cis conversion was accomplished by the irradiation of trans-azomethane frozen at liquid nitrogen temperature with the unfiltered output of a 450 watt Hanovia ultraviolet lamp for approximately 45 minutes. Upon comparison of the uv spectra before and after irradiation it was possible to see an additional absorption band due to the cis-azomethane. Unfortunately the percentage of conversion could not be determined as the molar extinction coefficients for neither molecule were available. Qualitatively it would appear that the percentage of conversion was rather small as diminution in the trans-azomethane absorption peak was undetectable. Further irradiation did not appear to increase the percentage of cis-azomethane.

The microwave spectrum of this mixture of cis- and trans-azomethane was recorded using a Hewlett-Packard 8460A MRR Spectrometer. Although initial work used a static sample charge, in later observations the sample
was flowed through the stark cell in order to eliminate absorption lines arising from the formation of N-methylene, N'-methyl hydrazine (Figure I-2) via a 1 → 3 sigmatropic shift.

\[
\begin{align*}
\text{H}_2\text{C} &= \text{N} - \text{N} \equiv \text{CH}_3 \\
\end{align*}
\]

Figure I-2

The time consuming nature of the preparation for a comparatively short scanning time possible with the amount of cis-azomethane produced necessitated a new synthetic approach. 2,3-dimethyl, 7,7-spiroethylene, 2,3-diaza-bicyclo(2.2.1)hept-5-ene (I) was obtained from Professor P. S. Engel and was pyrolyzed directly into the Stark cell of the microwave spectrometer. This pyrolysis (Figure I-3) was carried out by allowing I to vaporize at room temperature and pass through approximately two feet of heated \( \frac{1}{2} \)" glass tubing filled with glass helices.

\[
\begin{align*}
\text{I} &\rightarrow \text{N} \equiv \text{N} \equiv \text{CH}_3 + \text{CH}_3 \\
\end{align*}
\]

Figure I-3
It was found that a temperature of 230°C was sufficient to give a spectrum 2 to 3 times as intense as the one obtained from the irradiated trans-azomethane sample without introducing extraneous transitions. Extraneous transitions were observed when the temperature was raised to 320°C. The pressure at the end of the Stark cell closest to the vacuum pump was kept at pressures between 10 and 100 mtorr depending upon whether a high or low resolution scan was desired. No measurement of the pressure at the end of the Stark cell into which the sample was being introduced was made.

All d₆-cis-azomethane was prepared by the pyrolysis of d₆-I and was carried out in all regards as in the normal species. d₆-I was synthesized by the reduction of the precursor of I (2,3-dicarbomethoxy, 7,7-spiroethylene, 2,3-diazabicyclo(2.2.1)hept-5-ene) with LiAIH₄ instead of LiAIH₄.

Assignment of the Spectrum

The ground state spectrum in the 26.5 - 40 GHz region has been assigned for both cis-azomethane and d₆-cis-azomethane. In addition a Q-branch assignment has been made for the first excited torsional state of the deuterated species.

The normal species assignment was accomplished in the following manner. As can be seen in Figure I-4 the fast scan spectrum is dominated by three Q-branch transi-
### TABLE I-1
Transition Frequencies (MHz) of the Ground State of cis-Azomethane

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed ν* of A₁A₁ Species</th>
<th>Obs.-Calc.</th>
<th>Δν (A₁A₁-EE) Obs.</th>
<th>Δν (EE-A₁E) Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2₁,₂ - 1₀,₁</td>
<td>31487.10</td>
<td>.00</td>
<td>1.78</td>
<td>1.90</td>
</tr>
<tr>
<td>3₂,₂ - 3₁,₃</td>
<td>36279.40</td>
<td>.08</td>
<td>7.50</td>
<td>7.60</td>
</tr>
<tr>
<td>3₂,₁ - 3₁,₂</td>
<td>27250.38</td>
<td>-.02</td>
<td>2.43</td>
<td>2.43</td>
</tr>
<tr>
<td>4₂,₃ - 4₁,₄</td>
<td>39825.60</td>
<td>-.05</td>
<td>7.79</td>
<td>7.71</td>
</tr>
<tr>
<td>6₁,₅ - 6₀,₆</td>
<td>35599.90</td>
<td>.03</td>
<td>10.72</td>
<td>10.32</td>
</tr>
<tr>
<td>6₂,₄ - 6₁,₅</td>
<td>27044.26</td>
<td>.06</td>
<td>4.62</td>
<td>4.45</td>
</tr>
<tr>
<td>7₂,₅ - 7₁,₆</td>
<td>30042.95</td>
<td>-.06</td>
<td>6.31</td>
<td>6.36</td>
</tr>
<tr>
<td>8₂,₆ - 8₁,₇</td>
<td>35050.98</td>
<td>.04</td>
<td>8.77</td>
<td>8.82</td>
</tr>
<tr>
<td>9₃,₆ - 9₂,₇</td>
<td>39116.51</td>
<td>.02</td>
<td>4.21</td>
<td>4.33</td>
</tr>
</tbody>
</table>

**A₁A₁** | **EE** | **A₁E** | **ν** ± 0.10 MHz |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16285.08</td>
<td>16283.40</td>
<td>16281.59</td>
</tr>
<tr>
<td>B</td>
<td>6739.07</td>
<td>6738.50</td>
<td>6737.94</td>
</tr>
<tr>
<td>C</td>
<td>5067.31</td>
<td>5067.30</td>
<td>5067.27</td>
</tr>
<tr>
<td>K</td>
<td>-.0702</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔE</td>
<td>9.9 x 10⁻⁹**</td>
<td>δJ = -2.2 x 10⁻³</td>
<td></td>
</tr>
<tr>
<td>ΔJK</td>
<td>3.4 x 10⁻⁸</td>
<td>δK = -6.0 x 10⁻⁴</td>
<td></td>
</tr>
</tbody>
</table>

**While use of these centrifugal distortion constants allows the observed spectrum to be fitted well it should be noted that the probable errors in the constants are larger than the constants themselves.**
tions, which were soon assigned with the aid of a spectrum predicted from an assumed structure and some experimentation with assignments. The three transitions were found to be of the family $J_{2, J-2} + J_{1, J-1}$ with $J=6,7,8$. Using the resulting (A-C) and $\kappa$ the remaining Q-branch transitions with sufficient intensity in the 26.5 - 40 GHz region were soon measured and assigned.

In a slow scan most transitions were found to consist of a symmetrical internal rotation triplet as has been found in several previous cases $^1, ^2, ^3$ involving molecules with two equivalent internal rotors in which the barrier to internal rotation was sufficiently high enough to cause the $A_1E$ and $E A_1$ symmetry states (see section on internal rotation) to be essentially degenerate. A trace of a typical slow scan is shown in Figure I-5. As can be seen in the figure some transitions have further, smaller, splittings which are probably due to nuclear quadrupole structure arising from the two $^{14}N$ nuclei. Those transitions for which triplets were not observed were predicted to have unresolvably small internal rotation splittings.

The strongest R-branch transition in the 26.5 - 40 GHz region, $^{2}_{1, 2} + ^1_{0, 1}$, was readily assigned since it was the only strong line with the correct Stark effect within one GHz of the frequency predicted from an assumed structure. In addition it was possible to predict from the splittings of the Q-branch transitions the internal rotation splitting of this transition to be approximately 1.6 MHz while
TABLE I-2
Transition Frequencies (MHz) of the Ground Torsional State of d₆-cis-Azomethane

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed Frequency*</th>
<th>Obs. - Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3₁,₃ - 2₀,₂</td>
<td>32995.74</td>
<td>0.003</td>
</tr>
<tr>
<td>4₀,₄ - 3₁,₃</td>
<td>31783.66</td>
<td>0.001</td>
</tr>
<tr>
<td>3₂,₂ - 3₁,₃</td>
<td>27605.03</td>
<td>-0.079</td>
</tr>
<tr>
<td>5₃,₂ - 5₂,₃</td>
<td>37153.62</td>
<td>0.065</td>
</tr>
<tr>
<td>6₃,₃ - 6₂,₄</td>
<td>35263.10</td>
<td>-0.071</td>
</tr>
<tr>
<td>6₂,₅ - 6₁,₆</td>
<td>37067.18</td>
<td>0.099</td>
</tr>
<tr>
<td>7₃,₄ - 7₂,₅</td>
<td>33184.79</td>
<td>0.055</td>
</tr>
<tr>
<td>7₁,₆ - 7₀,₇</td>
<td>32328.21</td>
<td>-0.093</td>
</tr>
<tr>
<td>8₃,₅ - 8₂,₆</td>
<td>31362.64</td>
<td>-0.041</td>
</tr>
<tr>
<td>9₃,₆ - 9₂,₇</td>
<td>30273.66</td>
<td>0.046</td>
</tr>
<tr>
<td>9₂,₇ - 9₁,₈</td>
<td>30215.53</td>
<td>0.069</td>
</tr>
<tr>
<td>1₀₃,₇ - 1₀₂,₈</td>
<td>30326.60</td>
<td>-0.005</td>
</tr>
<tr>
<td>1₂₃,₉ - 1₂₂,₁₀</td>
<td>34931.18</td>
<td>-0.015</td>
</tr>
<tr>
<td>1₁₃,₈ - 1₁₂,₉</td>
<td>31818.68</td>
<td>-0.009</td>
</tr>
</tbody>
</table>

Standard Deviation = 0.087

A = 12741.781
B = 5344.901
C = 4158.977
Δₜₜ = -0.00332
Δₖₜ = 0.01235
Δₗ = -0.01149
δₚ = -0.00371
δₗ = -0.00021

* ± 0.05 MHz

** While use of these centrifugal distortion constants allows the observed spectrum to be fitted well it should be noted that the probable errors in the constants are larger than the constants themselves.
the experimental splitting was 1.7 MHz, well within experimental error.

It was found that each set of triplet components could be fit with a simple rigid rotor plus quartic centrifugal distortion Hamiltonian. The results of this fit are shown in Table I-1. As was expected, the C rotational constant was found to be independent of internal rotation state. The centrifugal distortion constants are not well enough defined by the lines fitted to note any real dependence on internal rotation state. The broad scan spectrum of d₆-cis-azomethane is shown in Figure I-6. Again it is dominated by Q-branches.

The ground and first excited torsional states of d₆-cis-azomethane were assigned and fit in the same manner as the normal species with some small differences. Perhaps the major difference was that the initial Q-branch assignment was made for the family \( J_{3, J-3} + J_{2, J-2} \)' with \( J=10,11,12 \). The ground state of the deuterated species shows no internal rotation splittings because the torsional moments of inertia are approximately doubled as a result of the substitution of deuterium for hydrogen in the methyl groups. This result was expected on the basis of predictions using the barrier to internal rotation determined by analysis of the normal species spectrum. The results of the fitting with rotational and centrifugal distortion constants of the observed transitions are shown in Table I-2.
MICROWAVE SPECTRUM OF CIS-AZOMETHANE

FIGURE I-4
$8_{1.7} - 8_{2.6}$

8.8 MHz

1.2 MHz

FIGURE I-5
Only Q-branch transitions of the first excited torsional state of deuterated cis-azomethane were assigned due to the predicted low intensity of the R-branch transitions in this microwave region. The Q-branch transitions, however, are sufficient for internal rotation analysis and present an interesting feature. In two of the high J transitions it was possible to see quartets instead of triplets due to the splitting of the A₁E and EA₂ symmetry species. However, in most of the transitions it was impossible to resolve the A₁E-EA₂ or the larger A₁A₂-EE internal rotation splittings. This was due to a combination of the rather low intensity of the transitions caused by the Boltzmann factor for excited states and the predicted smallness of the internal rotation splittings. A fit of the observed transitions with (A-C) and κ is shown in Table I-3.

An attempt was made to observe in natural abundance the species in which a ¹³C atom was substituted for a ¹²C nucleus, but an assignment was not found primarily because the weak signals approached the sensitivity limit of the spectrometer.

Structure

It was found that, with no assumptions, the analysis of the rotational constants derived from the assignments and fittings of the two ground vibrational state microwave spectra of cis-azomethane and d₆-cis-azomethane
### Table I-3
Transition Frequencies (MHz) of the First Excited Torsional State of $d_6$-cis-Azomethane

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed $\nu$ of A A Species</th>
<th>$\Delta\nu(A_1A_2=EE)$</th>
<th>$\Delta\nu(A_1A_2-A_1E)$</th>
<th>$\Delta\nu(A_1A_2-EA_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>obs-calc.</td>
<td>obs</td>
<td>calc</td>
<td>obs</td>
</tr>
<tr>
<td>$6_{3,3} - 6_{2,4}$</td>
<td>34602.69</td>
<td>-.932</td>
<td>0</td>
<td>+085</td>
</tr>
<tr>
<td>$7_{3,4} - 7_{2,5}$</td>
<td>33537.37</td>
<td>-.689</td>
<td>0</td>
<td>+.185</td>
</tr>
<tr>
<td>$8_{3,5} - 8_{2,6}$</td>
<td>31686.72</td>
<td>.423</td>
<td>0</td>
<td>+.109</td>
</tr>
<tr>
<td>$9_{3,6} - 9_{2,7}$</td>
<td>30514.96</td>
<td>1.143</td>
<td>0</td>
<td>-.439</td>
</tr>
<tr>
<td>$10_{3,7} - 10_{2,8}$</td>
<td>30428.80</td>
<td>.738</td>
<td>-1.55</td>
<td>-1.51</td>
</tr>
<tr>
<td>$11_{3,8} - 11_{2,9}$</td>
<td>31730.11</td>
<td>-.323</td>
<td>-3.49</td>
<td>-3.097</td>
</tr>
<tr>
<td>$12_{3,9} - 12_{2,10}$</td>
<td>34611.17</td>
<td>-.121</td>
<td>-4.95</td>
<td>0.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\Delta v (A_1A_2)$</th>
<th>$EE$</th>
<th>$A_1E$</th>
<th>$EA_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A - C) in MHz</td>
<td>8615.9827</td>
<td>8616.3884</td>
<td>8616.7137</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>-.72934</td>
<td>-.72929</td>
<td>-.72926</td>
</tr>
<tr>
<td>Standard Dev.</td>
<td>.84</td>
<td>.75</td>
<td>.74</td>
</tr>
</tbody>
</table>
yielded two conclusions about the structure of cis-azomethane. Using three reasonable assumptions about the structure a complete structure of cis-azomethane can be derived.

The most obvious conclusion which may be drawn from the experimental facts is that the four heavy atoms of the molecule are all in a plane. This can be shown by considering the apparent inertial defect $\Delta$.

\[
\Delta = I_c - I_a - I_b \quad \text{Eq. I-1.}
\]

\[
\Delta = \Delta' - n m_h (r_{hh})^2 \quad \text{Eq. I-2.}
\]

Equation I-1 defines the inertial defect, $\Delta$, in terms of the moments of inertia $I_a$, $I_b$, and $I_c$. Equation I-2 shows the form the inertial defect is expected to take for a molecule in which the only nonplanar atoms are $n$ pairs of equivalent hydrogen atoms which are separated by a distance of $r_{hh}$. The mass of one hydrogen atom is represented by $m_h$, while $\Delta'$ is a small contribution to the inertial defect due to vibrations and is generally of the order of 0.1 - 0.3 amu-$\text{Å}^2$ for light rigid molecules. It is possible to calculate the value of $\Delta$ if the methyl group hydrogens are the only out of plane atoms. For the normal species this calculation yields $\approx 6.38$ amu-$\text{Å}^2$ while for the $d_5$-cis-azomethane species the calculated inertial defect is $\approx 12.76$ amu-$\text{Å}^2$. The corresponding experimental values of 6.287 and 12.700 amu-$\text{Å}^2$ are
thus quite consistent with a planar heavy atom skeleton.

The second conclusion is drawn from the internal rotation splittings of the ground vibrational state of cis-azomethane and is that the methyl group symmetry axes meet the N-N bond at an angle of 126 $\pm$ 2°. This result comes from the use of the following equation.

$$\theta = 90 + \arctan\left(\frac{\Delta A/\Delta B}{\sqrt{B/A}}\right)$$  \hspace{1cm} \text{Eq. I-3.}

In this equation, the source of which shall be shown in the section of this thesis dealing with the barrier to internal rotation, \(\theta\) is the angle referred to above, while \(\Delta A\) and \(\Delta B\) are the differences in the corresponding rotational constants of the AA and the EE internal rotation symmetry states. It should be stressed that this angle of 126° is not the N=N-C bond angle since it is well known that methyl group symmetry axes are often non-colinear with the bond formed between the methyl group carbon and its bonding partner.

In order to form additional conclusions regarding the structure it was found necessary to assume the methyl group structure and one of the heavy atom structural parameters.

The assumed methyl group structure was picked in the following way. The H-C-H angle was assumed to be 109.5° and the bond length was chosen so that the difference in
inertial defects of the deuterated and normal species of \textit{cis}-azomethane was matched. Equation I-4 shows the proper relationship.

\begin{equation}
  r_{C-H} = \left(\frac{(\Delta_d - \Delta_h)}{8\Delta \text{msin}^2(109.5/2)}\right)^{\frac{1}{2}} \quad \text{Eq. I-4.}
\end{equation}

The $r_s$ C-H bond length calculated was 1.085 Å. This assumed structure appeared reasonable and was used without further modification.

Although there are only three other parameters, $r(N=N)$, $r(C-N)$, and $\angle{CNN}$, and four independent moments of inertia from the normal and $d_6$ species, the four moments of inertia do not well determine the three structural parameters. Thus, the final step was to assume a value for one of the heavy atom bonding parameters. The idea of assuming the C-N-N bond angle was rejected immediately since there were no known measurements of this angle in non-cyclic azoalkane compounds. Using an assumed value for the N-C bond length was also rejected since this appears to vary among those \textit{cis}-azoalkane compounds for which the structures are known. However, it was found upon examination of the structures known for \textit{cis}-azoalkane compounds (shown in figure I-1) that the N=N bond length appeared to be relatively constant. This distance varies from 1.247 to 1.260 Å in the known cases. It should also be noted that the smallest value of this parameter is 1.247 Å for \textit{trans}-azomethane\textsuperscript{1} was determined to be 1.254 Å by different
experimenters\textsuperscript{14} using the same techniques of electron
diffraction. This reduces the range of $N=\overline{N}$ bond lengths
to 0.007 Å even though three methods of structural determin-
ation (X-ray crystallography, electron diffraction, and
microwave spectroscopy) are involved. Since a comparison
of the structures of cis- and trans-2-butene\textsuperscript{15} showed,
within experimental error, no difference in $\text{C}=\text{C}$ double
bond lengths it was felt that the assumption that the
$N=\overline{N}$ bond length of cis-azomethane was the same as that
found in trans-azomethane, i.e., $r(\text{N}=\overline{\text{N}}) = 1.254$ Å, was the
most reasonable assumption possible at this time.

A fit of the remaining parameters to the observed
rotational constants using the outlined assumptions
yielded values of 1.484 Å and 119.45° for the $\text{C}-\text{N}$ bond
length and the $\text{C}-\overline{\text{N}}=\overline{\text{N}}$ angle, respectively, for the normal
species. The corresponding values obtained for $d_6$-cis-
azomethane are 1.487 Å and 119.30°.

The values derived for the $\text{C}-\text{N}-\overline{\text{N}}$ bond angle and
the angle made by the methyl axes with the NN bond result
in a methyl tilt of about 6.6° which is the largest yet
found by microwave spectroscopy.

That is thought to be the best structure which can
be proposed from the experimental data is shown in Figure
I-7.
Dipole Moment

The effect of an applied electric field on the frequency of a rotational transition (Stark effect) has long been recognized as an accurate method for measuring molecular dipole moments. In order to determine the dipole moment of cis-azomethane a measurement of the Stark effects of the $J_{2,1} - l_{0,1}$ of the normal species and $J_{3,1} - 2_{0,1}$ of the $d_6$ species transitions were made. The Stark cell was calibrated by measurement of the Stark effect of the $J_{2,0} - l_0$ transition of propyne for which the dipole moment has been determined to be $0.7840 \text{ D}^{16}$.

A least squares fit to the frequency measurements of the $|M| = 0,1$ components of this transition at five different voltages yielded a value of $3.20 \pm 0.09 \text{ D}$ for the dipole moment of the normal species. A similar measurement of the $|M| = 0,1,2$ components of the $d_6$ species transition gave a dipole moment of $3.33 \pm 0.09 \text{ D}$. The uncertainties shown are 95% confidence intervals calculated assuming only the frequency measurements of propyne, cis-azomethane, and $d_6$-cis-azomethane were liable to error, ignoring any error due to inaccuracies of voltage readings.

Barrier to Internal Rotation

Microwave spectroscopy has been used in a wide variety of molecules to determine the nature of the potential function which hinders the free rotation about single bonds. For the most part the internal rotators
studied have been methyl groups and the method of analysis used the principal axis method (PAM), developed by Wilson, Lin, and Kilb and systematized by Herschbach.

The model used most often is one of a single rigid symmetric top attached to a rigid frame of any symmetry. For this model there are four degrees of freedom, three for overall rotation and one for the hindered rotation of the symmetric top about an axis co-linear with its symmetry axis.

The potential function is usually assumed to be of the form

\[ V(\alpha) = \frac{V_3}{2} \left(1 - \cos 3\alpha\right) \]  

Eq. I-5.

where \( \alpha \) is the variable representing the angle of rotation of the 3-fold symmetric top about its symmetry axis and ranges from 0 to 2\( \pi \).

The Hamiltonian for this model is given by

\[ H = H_r + F(p-P)^2 + V(\alpha) \]  

Eq. I-6.

(See Table I-4 for notation.)

Without the cross term \(-2FPp\) in equation I-6, the Hamiltonian is separable into two parts, overall rotation and internal rotation. The eigenvalues for both problems have been extensively tabulated.

The overall rotation portion of the Hamiltonian would just be the rigid rotor Hamiltonian, \( H_r \), with the
Table I-4

Notation Used in the Internal Rotation Problem

g = x, y, z refers to the principal axes of inertia fixed in the framework part of the molecule

$I_g$ = principal moments of inertia in the entire molecule.

$I_\alpha$ = moment of inertia of the internal top about its symmetry axis

$\lambda_g$ = direction cosines between the top axis and the principal axes

$rI_\alpha$ = reduced moment of inertia for internal rotation where $r = 1 - \sum g^2 I_\alpha/I_g$

$P^g_\alpha$ = components of the total angular momentum along the principal axis.

$p$ = total angular momentum of the internal top along its symmetry axis.

$P = \sum g^g P^g_\alpha I_\alpha/I_g$

$v$ = the principal torsional quantum number for the harmonic oscillator (infinite barrier) limit.

$\sigma$ = an index which gives the symmetry or periodicity of the torsional wave function. For a three fold barrier $\sigma = 0$ for the A species, $\sigma = \pm 1$ for the E species.

$H_\tau = (\hbar^2/2)(P_x^2/I_x + P_y^2/I_y + P_z^2/I_z)$, which is the usual Hamiltonian for a rigid rotor.

$F = \hbar^2/2rI_\alpha$

For the two top problem an additional term is needed. This term $q$ is defined as follows:

$q = - \sum g^g g^1 g^2 I_\alpha/I_g$
addition of $FP^2$ which would cause no qualitative change since it is quadratic in the $P_g$ as is $H_r$.

The remaining portion of equation 1-6 (corresponding to internal rotation) if the cross term is neglected is

$$FP^2 + \frac{1}{2} V_3 (1 - \cos 3\alpha).$$

The eigenvalues of this type of problem are well known and the boundary conditions of invariance as $\alpha \rightarrow \alpha + 2\pi$ is satisfied by two types of Mathieu functions. The first type of Mathieu function which satisfies this equation has a period of $2\pi/3$ in $\alpha$ and transforms according to the $A$ species under the symmetry group $C_3$. The second type of Mathieu equation has a period of $2\pi$ in $\alpha$ and belongs to the $E$ species. The consequence of this is that for high barrier each torsional level $v$ has two sublevels, a nondegenerate level of symmetry $A$ ($\sigma = 0$) and a doubly degenerate level with symmetry $E$ ($\sigma = \pm 1$). The splitting of the degeneracy of the two sublevels can be thought of as arising from "tunneling" through the potential barrier. This "tunneling" splitting itself would not cause any observable effects in the rotational spectrum, if it were not for the cross term of $-2FPp$ which couples overall and internal rotation and has effects which differ for the $A$ and $E$ sublevels of a given torsional level.

The coupling terms which cause the observable effects of internal rotation on the rotational spectrum can be
treated by perturbation theory. The procedure chosen by Herschbach was to apply successive Van Vleck transformations to reduce the matrix elements which are non diagonal in \( V \) \(-2\mathbf{F}^2\mathbf{p} \) to an order high enough to be neglected\(^{19} \).

The result of these transformations is that the original Hamiltonian can now be factored into smaller rotational matrices, \( H_{V\sigma} \), one for each torsional state. The form of these transformed Hamiltonians is

\[
H_{V\sigma} = H_{\mathbf{R}} + F \sum_n W_{v\sigma}^{(n)} p^n .
\]

Eq. I-7

In equation I-7, \( H_{V\sigma} \) is the effective Hamiltonian for the torsional state specified by \( v\sigma \). The term \( H_{\mathbf{R}} \) is still the rigid rotor Hamiltonian as given in Table I-4, so that the \( W \)'s include both the coupling term and that in \( P^2 \). The dimensionless perturbation coefficients \( W_{v\sigma}^{(n)} \) depend only on \( V_3/F \) for a potential barrier of the form of equation I-5 and in theory could be calculated using \( n^{th} \) order perturbation theory. Herschbach's major contribution to this problem was the development of a more practical method of evaluation for these perturbation coefficients which are now tabulated for a wide range of \( V_3/F \) values.

Certain facts about the \( W_{v\sigma}^{(n)} \) are of interest. Firstly, the zeroth order coefficient \( W_{v\sigma}^{(0)} \) is the pure torsion energy which is an eigenvalue of the Mathieu functions and as stated before does not contribute to the rotational
transition frequencies. Secondly, symmetry requires that the odd order perturbation terms are zero for the A levels.

Once the matrix representing $H_{\nu\sigma}$ for an individual J value and torsional state $\nu\sigma$, has been found, it is necessary to diagonalize it in the rotational quantum number $K$ in order to predict the rotational energy levels. While it is possible to do this by direct numerical methods, Herschbach outlined a number of approximations which eliminated the need for direct diagonalization for most applications.

The approximation used most often is to ignore all but the second order perturbation terms. Using this approximation the total perturbation of the pure rotational Hamiltonian is

$$FW_{\nu}^{(2)}(\alpha P_x + \beta P_y + \gamma P_z)^2.$$  \hspace{1cm} \text{Eq. I-8.}$$

Since this perturbation is purely quadratic in the angular momentum components, it is possible to absorb them into the rigid rotor terms shown in Table I-4. The result is a change in the effective rotational constants. For example, the rotational constant of $P_x^2$ now becomes

$$A = \hbar^2/2I_x + F\alpha^2W_{\nu\sigma}^{(2)}.$$  \hspace{1cm} \text{Eq. I-9.}$$
Since the perturbation terms are different for the A and E sublevels, it is now possible to use the differences in the rotational constants of the rotational transitions associated with the A and E torsional sublevels to determine the value of \( \Delta W_{VA}^{(2)} - \Delta W_{VE}^{(2)} \) and from that the value of \( V_3 \).

The necessary equations are

\[
\Delta A = A_{VA} - A_{VE} = F_{VA}^{(2)} \left[ \Delta W_{VA}^{(2)} - \Delta W_{VE}^{(2)} \right]. \quad \text{Eq. I-10a}
\]

\[
\Delta B = B_{VA} - B_{VE} = F_{SB}^{(2)} \left[ \Delta W_{VA}^{(2)} - \Delta W_{VE}^{(2)} \right]. \quad \text{Eq. I-10b}
\]

\[
\Delta C = C_{VA} - C_{VE} = F_{SV}^{(2)} \left[ \Delta W_{VA}^{(2)} - \Delta W_{VE}^{(2)} \right]. \quad \text{Eq. I-10c}
\]

As shown by Herschbach, it is only slightly more complicated to include perturbation terms of orders other than two, but for most cases the effect of these additional terms may be neglected in comparison to the second order terms. For the sake of brevity a discussion of the inclusion of these terms will not be included here.

Although all of the previous discussion on internal rotation has dealt with the problem of a single internal rotor, Pierce showed that the results and tabulated perturbation coefficients of Herschbach can be used without a great deal of trouble to determine the effects of two equivalent symmetric tops capable of internal rotation on the rotational spectrum of a molecule. The
kinetic energy is given by

\[ H^r + F[(p_1 - P_1)^2 + (p_2 - P_2)^2] + F'[p_1 - P_1 + (p_2 - P_2)]. \quad \text{Eq. I-11.} \]

In equation I-11, \( H^r \) is the same quantity defined in Table I-4, while \((p_1 - P_1)\) and \((p_2 - P_2)\) are the angular momenta of tops 1 and 2 relative to the framework. \( F \) and \( F' \) are the rotational constants for internal rotation and are defined as

\[ F_+ = F + F' = \hbar^2/[2I_\alpha (r + q)] \quad \text{Eq. I-12.} \]

The Fourier expansion of the potential energy for tops with threefold symmetry is now given as

\[ V(\alpha_1, \alpha_2) = V_0 = \frac{1}{2} V_3 (2 - \cos3\alpha_1 - \cos3\alpha_2) \]
\[ + V_3'\cos3\alpha_1 \cos3\alpha_2 + V_3''\sin3\alpha_2 \sin3\alpha_1 \]
\[ + \text{terms in } 3n\alpha_1, 3n\alpha_2; \ n = 2,3,... \quad \text{Eq. I-13.} \]

In order to make full use of Herschbach's methods and tables, Pierce chose as the zeroth order Hamiltonian

\[ H^{(0)} = H^r + F(p_1^2 + p_2^2) + \frac{1}{2} V_3* (2 - \cos3\alpha_1 - \cos3\alpha_2) \quad \text{Eq. I-14.} \]

where \( V_3* = V_3 - 2V_3' \).
As his perturbation Hamiltonian, Pierce chose

\[ H^{(1)} = 2F_+ P_+^2 + 2F_- P_-^2 - 4F_+ P_+ P_- - 4F_- P_+ P_- 
+ F'(p_1 p_2 + p_2 p_1) + V_3'(1 - \cos 3\alpha_1)(1 - \cos 3\alpha_2) 
+ V_3'' \sin 3\alpha_1 \sin 3\alpha_2 . \tag{Eq. I-15} \]

where \( P_+ = \frac{1}{2}(p_1 + p_2) \) and \( P_- = \frac{1}{2}(p_1 - p_2) \).

The procedure followed by Pierce was much the same as Herschbach's in that the final result of several Van Vleck transformations was an effective rotational Hamiltonian of the form

\[ H_{VV} = H_r + F \sum_n \left[ \hat{W}_{VV}^{(+n)} P_+^{(n)} + \hat{W}_{VV}^{(-n)} P_-^{(n)} \right], \quad n = 0, 1, 2, \ldots \tag{Eq. I-16} \]

Unfortunately, this effective rotational Hamiltonian is good only for states for which \( v = v' \) due to the nature of the assumptions used by Pierce in his transformations. Since it is necessary to measure more than one torsional state in order to determine \( V_3, V_3', \) and \( V_3'' \), this Hamiltonian is often not particularly useful in that in most molecules the only state with \( v = v' \) which is low enough in energy to assign is the \( v = v' = 0 \) state. This torsional state often has no observable internal rotation splittings for the barriers encountered in many molecules. Another method of determining the barrier parameters was tried for cis-azomethane and will be described later.
Before detailing the method of calculation used, it is necessary to discuss certain symmetry considerations. As previously noted for the one top problem where the top has a symmetry axis of order 3, the two torsional sublevels transform as the different species of the group formed by the direct product of two simple groups. In order for two tops to be equivalent, the entire molecule must be either of $C_2V$ or $C_2$ symmetry. If the molecule has $C_2V$ symmetry as does cis-azomethane then the symmetries of the torsional states will be the symmetry species of $C_3V \times C_3V$. If the molecule has $C_2$ symmetry, such as dimethylamine, the torsional sublevels will be of the symmetry species $C_3V \times C_3$.

These groups are most logically discussed as the nuclear permutation-inversion groups introduced by Longuet-Higgins\textsuperscript{20}. $C_3V \times C_3V$ is shown in Table I-5 along with the permutation-inversion notation used to describe the operations.

The application of the symmetry principles to the most common problems associated with the rotation-internal torsion levels of molecules with two equivalent methyl groups have been worked out by Myers and Wilson\textsuperscript{21}. The two most important problems to be dealt with are the selection rules and the statistical weights of individual torsional sublevels.

As shown by Myers and Wilson the electric dipole transitions allowed are as follows:
Table I-5

Character Table and Definition of Symmetry Operations of the Group $C_{3v} \times C_{3v}$

<table>
<thead>
<tr>
<th>EE</th>
<th>$2C_{3}^-$</th>
<th>$3C_{2x}$</th>
<th>$2C^+$</th>
<th>$4C_{3}^{+}C_{3}^{-}$</th>
<th>$6C_{2x}^{+}C_{3}^{-}$</th>
<th>$3C_{2z}$</th>
<th>$6C_{2z}C_{3}^{-}$</th>
<th>$9C_{2z}C_{2x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1}A_{1}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{1}A_{2}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{1}E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2}A_{1}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2}A_{1}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2}E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td>$EA_{1}$</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$EA_{2}$</td>
<td>2</td>
<td>2</td>
<td>-2</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>EE</td>
<td>4</td>
<td>-2</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The clearest method of seeing the effects of the nine symmetry operations on cis-azomethane is to show the permutations of the six hydrogen nuclei and two nitrogen nuclei caused by each operation. Using the labeling shown below and standard permutation notation the results are as follows:

![Azomethane Structure](image)

$EE: \ (\alpha) (\beta) (A) (B) (C) (D) (E) (F) (G) \quad C_{3}^{-}: \ (\alpha) (\beta) (ABC) (EGF)$

$C_{2x}: (\alpha \beta) (AE) (BF) (CG) \quad C_{3}^{+}: (\alpha) (\beta) (ABC) (EFG)$

$C_{3}^{+}C_{3}^{-}: (\alpha) (\beta) (ACB) (E) (F) (G) \quad C_{3}^{+}C_{2x}: (\alpha \beta) (AFCEBG)$

$C_{2z}: (\alpha \beta) (AE) (BG) (CF) \quad C_{2z}C_{3}^{-}: (\alpha) (\beta) (AGCEBF)$

$C_{2z}C_{2x}: (\alpha) (\beta) (A) (E) (GF) (BC) \quad C_{2z}C_{2x}: (\alpha) (\beta) (AGCEBF)$
Each torsional level \( vv' \) is made up of four sublevels, although often the EA and AE sublevels are nearly degenerate causing the rotational transitions to be split into triplets instead of quartets. The symmetry species of sublevels depends only upon the torsional state involved.

For the irreducible representations \( A_1A_2, EE, A_1E, \) and \( EA_1 \).

For the (0,1) state (the + state in which the vibration having both rotors are rotating in the same direction is excited) the sublevels are \( A_1A_2, EE, A_1E, \) and \( EA_2 \). For the (1,0) state (the - state corresponding to the rotors in opposite directions) the sublevels have symmetries of \( A_2A_1, EE, A_2E, \) and \( EA_1 \). The statistical weights for the cases involved in this work are shown in Table I-6 and were worked out by the methods of Myers and Wilson using the results of Table I-5.

The first approach to calculating the barrier to internal rotation was to assume that all top-top interactions were zero and to use the method proposed by Herschbach in equation I-10. As explained in the section on the assignment of the spectrum, the rotational transitions of each torsional sublevel were fitted to a normal rigid rotor Hamiltonian with the addition of quartic centrifugal distortion parameters. By using the ratio of \( A_{A_1A_1 - A_{EE}} \)
Table I-6

Statistical Weights of Torsional Sublevels
Observed in this Investigation

<table>
<thead>
<tr>
<th>Symmetry of Torsional Sublevel</th>
<th>Statistical Weight of Rotational Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ee-oo</td>
</tr>
<tr>
<td>Ground State of the Normal Species</td>
<td></td>
</tr>
<tr>
<td>$A_1A_1$</td>
<td>78</td>
</tr>
<tr>
<td>EE</td>
<td>144</td>
</tr>
<tr>
<td>$A_1E$</td>
<td>42</td>
</tr>
<tr>
<td>$EA_1$</td>
<td>36</td>
</tr>
<tr>
<td>Ground State of the $d_6$ Species</td>
<td></td>
</tr>
<tr>
<td>$A_1A_1$</td>
<td>561</td>
</tr>
<tr>
<td>$A_1E$</td>
<td>600</td>
</tr>
<tr>
<td>$EA_1$</td>
<td>576</td>
</tr>
<tr>
<td>EE</td>
<td>1584</td>
</tr>
<tr>
<td>(0,1) State of the $d_6$ Species</td>
<td></td>
</tr>
<tr>
<td>$A_1A_2$</td>
<td>561</td>
</tr>
<tr>
<td>$A_1E$</td>
<td>600</td>
</tr>
<tr>
<td>$EA_2$</td>
<td>576</td>
</tr>
<tr>
<td>EE</td>
<td>1584</td>
</tr>
<tr>
<td>(1,0) State of the $d_6$ Species</td>
<td></td>
</tr>
<tr>
<td>$A_2A_1$</td>
<td>528</td>
</tr>
<tr>
<td>$A_2E$</td>
<td>552</td>
</tr>
<tr>
<td>$EA_1$</td>
<td>576</td>
</tr>
<tr>
<td>EE</td>
<td>1584</td>
</tr>
</tbody>
</table>
to $B_{A_1A_1} - B_{EE}$ for the ground state of the normal species it was possible to determine the direction cosines of the two tops' symmetry axes to the principal axes of the mole. Once this was accomplished the value of $A_{A_1A_1} - A_{EE}$ was inserted into equation I-10a along with the calculated value of $F = 170453.95$ MHz. The resulting value of $W_{0A}^{(2)} - W_{0E}^{(2)}$ was used with Herschbach's tables to give a $V_3$ of 1329 cal/mole.

A similar calculation was performed on the first excited state of $d_6$-cis-azomethane using an $F$ of 88634.31 MHz and the direction cosine derived from the normal species. This calculation yielded a value of $V_3$ of 1624 cal/mole.

The errors in these numbers are hard to determine since it is likely that it is simplicity of the model used that probably causes the most of discrepancy between the two calculated $V_3$'s. The estimated experimental error in $\Delta A$ and $\Delta B$ corresponds to $\pm 50$ cal/mole.

There is an additional observation giving yet another value for $V_3$. The relative intensities of an excited torsional state (0,1) can be related by the following equations

$$\frac{I_{\text{ex}}}{I_{\text{grnd}}} = \left(\frac{g_{\text{ex}}}{g_{\text{grnd}}}\right) e^{-\Delta E/kT} \quad \text{Eq. I-17.}$$

$$\Delta b = \frac{4\Delta E}{9F} \quad \text{Eq. I-18.}$$

where the $g$'s are the degeneracies of the two torsional states and can be found in Table I-5. The $\Delta b$ is related
to $V_3/F$ and has been tabulated by Herschbach. Using the experimental value of 0.57 for $I_{ex}/I_{grnd}$ at 25°C yields a value of $V_3$ of 1656 cal/mole.

Although apparent barriers for totally deuterated tops 50 cal/mole larger than those found for the normal species' top are not uncommon, the difference of 300 cal/mole in this case seems too large to ascribe to a combination of experimental error and isotope effect. In order to determine if the experimental data could be made consistent, an attempt to fit the three pieces of data using top-top interactions of the type $V_3' \cos 3\alpha_1 \cos 3\alpha_2$ and $V_3'' \sin 3\alpha_1 \sin 3\alpha_2$ was made.

The method used was as follows. Using the experimental data and several equations, it was possible to determine the energy difference between (1) the sublevels of the ground torsional state of the normal species, (2) the ground and first excited state of $d_6$-cis-azomethane, and (3) the sublevels of the first excited torsional state of $d_6$-cis-azomethane. Equation I-7 was used to determine the second energy differences, while the following equation along with equation I-10 was used for the remaining two energy differences.

$$ [W^{(2)}_{VAA} - W^{(2)}_{VEE}] = -\frac{1}{2} \left( \frac{2\pi}{3} \right)^2 \frac{E_{AA} - E_{EE}}{F} \quad \text{Eq. I-19.} $$

The approach was to try to match these three energy differences by using a computer program designed to set
up the matrix approximating the Hamiltonian for internal rotation using the free rotor functions \( \exp(i m_1 \alpha_1) \exp(i m_2 \alpha_2) \) as basis functions. It was found necessary to use 17 of these functions in order to have truncation errors less than 1% of the energy differences between \( A_1A_2 \) and \( EA_2 \) levels of the first excited torsional state of \( d_6 \)-cis-azomethane, while for the same degree of accuracy for the \( A_1A_1 - EA_1 \) splitting of the ground state of normal cis-azomethane only 13 basis functions were needed. By making use of the symmetries of different torsional sublevels' Hamiltonians, it was possible in the case of the AA levels to reduce the size of the 17 basis function matrix from \( 289 \times 289 \) to approximately one-fourth of this size. A similar symmetry transformation allowed the AE and EA matrices to be reduced to about one-half of the untransformed matrix's size, but no reduction in size was possible for the matrix representing the EE torsional sublevel.

Due to the non-linear dependence of the observed quantities on the potential function parameters, it is necessary to carry out a search of many points to fix \( V_3', V_3'', \) and \( V_3''' \). Even though the matrices, which must be diagonalized to obtain the torsional sublevel energies, can be reduced in size, they are still large enough for the computation of a single point to be fairly expensive (\( \approx \$25.00 \)). After a number of combinations of \( V_3', V_3'', \) and \( V_3''' \) did not produce energy levels and splittings resembling the observed, the attempt to find barrier
parameters which would reproduce the experimental energy
difference was given up due to prohibitive expense.
Table I-7 shows the results for the various combinations
of barrier parameters chosen.

A similar attempt was made using the same program as
above to reproduce the experimental data by using a Van
der Waal's steric attraction-repulsion potential (an exp-6
function) and the experimental structure. This was done by
doing a Fourier decomposition of the potential function
produced by allowing the methyl groups to turn and calcul-
ating the change in energy as the hydrogens moved past
each other. It was hoped that by combining these inter-
action terms with the sort of barrier found in the one-
top problem, such as propylene, the torsional sublevel
splittings might be reproduced. It was found, however,
that the resulting potential function appeared to favor an
equilibrium position in which one methyl hydrogen eclipsed
the N=N bond while the corresponding hydrogen of the second
methyl group was in the same plane, but 180° away. If this
was the proper equilibrium position, the ground state of
the normal species would not be a triplet, but either a
sextet or octet.

An additional discouraging aspect of this attempt
was the trial of a Leonard-Jones 12-6 potential function.
The interaction terms produced with this potential function
were so different from that of the Van der Waal's function
that further work in this direction was deemed futile.
### Table I-7

Results of Different Combinations of Barrier Parameters

<table>
<thead>
<tr>
<th>$V_3$</th>
<th>$V_3'$</th>
<th>$V_3''$</th>
<th>SH*</th>
<th>SD**</th>
<th>$\Delta^+ \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-700</td>
<td>0</td>
<td>0</td>
<td>-293</td>
<td>59</td>
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</tr>
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<td>0</td>
<td>-138</td>
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<td>-3.4138</td>
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<tr>
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<td>0</td>
<td>-84</td>
<td>10</td>
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<tr>
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<td>0</td>
<td>+200</td>
<td>-301</td>
<td>79</td>
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<td>-408</td>
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<td>-1200</td>
<td>500</td>
<td>-500</td>
<td>-207</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental Values | -428.17 | 40.13 | -3.4935 |

* $A_1A_1 - EA_1$ energy (MHz) difference of ground torsional state of normal species.

** $A_1A_1 - EA_1$ energy (MHz) difference of first excited torsional state of $d_6$ species.

$^+ \quad$ Difference in energy (MHz) of ground and first excited torsional state of $d_6$ species.
PART I
DISCUSSION OF RESULTS

The structure determined for cis-azomethane appears to be consistent with the structural parameters reported at present for cis-azoalkanes. The N=N-C bond angle of 119.4° is quite close to the 120° angle expected from simple valence theory and is about 3° smaller than the value predicted by Baird and Swenson\textsuperscript{22} of 122° using molecular orbital methods.

The methyl tilt of about 6.6° is large compared to the tilts found in previous molecules. The tilt of 3.3° found in methanol\textsuperscript{25} was formerly the largest tilt found by microwave spectroscopic investigations. The severe steric crowding of the two methyl groups would appear to be the cause of this methyl tilt.

A comparison of the barriers to internal rotation, $V_3$, determined to be $\approx 1330$ cal/mole for the normal species and $\approx 1625$ cal/mole for the first excited torsional state of $d_6$-cis-azomethane is difficult since the large discrepancy between the deuterated and normal species barrier height must be due top-top interactions not accounted for in the simple model used. Further work on this problem needs to be done such as a microwave study of both the singly deuterated species to determine the equilibrium position of the methyl groups. A study of the tri-deuterated species is also indicated in order to gain more insight on the
apparent deuterium isotope effect on the barrier to internal rotation.
PART II.

Methylisocyanide-Borane

and

t-Butylisocyanide-Borane
PART II
INTRODUCTION

The nature of the bonding between donor-acceptor complexes in which boron acts as an electron acceptor has been a subject of interest for some time and many of these complexes have been studied by microwave spectroscopy\(^1,12\). Most of these studies have involved complexes in which second row atoms act as electron donors to the vacant orbitals of boron.

In attempting to explain the trends in donor-acceptor bond lengths and relative strengths of the coordinate bonds two hypotheses have been put forth. The first explanation\(^13\) was that the enhancement of the strength of the coordinate bond between boron and second row donor atoms when borane, but not BF\(_3\), was the acceptor (as opposed to the similar acceptor power with first row donors) was that the vacant \(d_\pi\) orbitals of the second row donors overlapped the \(H_3\) group orbital of \(\pi\) symmetry. The 'back donation' of electrons from the borane group, forming a \(d_\pi-p_\pi\) bond component in addition to the classical \(\sigma\) bond gives added strength to borane complexes not available to complexes in which BF\(_3\) is the electron acceptor due to the electron withdrawing power of the fluorine atoms.

The second explanation, given by Rudolph and Parry\(^14\), for the greater strength of second row donor complexes with borane, as opposed to BF\(_3\), was that the second row...
donors studied had been highly polarizable ligands, i.e., phosphines or sulfides for which an alternative hypothesis offered a better explanation of the observed facts. This hypothesis, briefly explained, is that the overall bonding strengths of polarizable ligands such as phosphine were "strongly dependent upon the field strength of the positive center". Further, it was noted that for the field strength to become appreciable it was necessary for the donor-acceptor nuclei to have "unusually short bond distances". Thus it was concluded that the close approach of the separate segments of the complexes forced rearrangement of the normally planar BX$_3$ molecule into a tetrahedral structure. Since the rearrangement energy for BF$_3$ was estimated to be about three times that of BH$_3$ this model clearly predicted the preference of second row donors, such as phosphines and sulfides, for borane.

As has been pointed out by previous authors$^{3,12,14,15}$ both models fail in certain major predictions. The 'back donation' model incorrectly predicts that F$_3$PBH$_3$ should have a stronger P-B$^\pi$ bond than F$_2$PBH$_3$ since the additional electron withdrawing power of the added fluorine would make the phosphorus in F$_3$PBH$_3$ a better electron acceptor.

The objection to the Rudolph and Parry model of phosphine-borane bond formation is that in order to explain the relative energy differences of F$_2$HPBH$_3$ and F$_3$PBH$_3$ it was necessary to postulate an internal 'hydrogen bond' between the protonic hydrogen and the two fluorines.
This assumed hydrogen bond would have two effects. Firstly, the F-P-F and H-P-F angles would decrease allowing the borane group to come closer without increasing the deformation energy. The second effect would be to reduce the effective positive charge of the hydrogen, releasing bonding electrons toward phosphorus and loosening the lone pair electrons to give a stronger P-B bond. However, the subsequent structural determination of F₂HPBH₃ showed no evidence of an internal hydrogen bond and no apparent change in the B-B-F angle from that found in F₃PBH₃.

Thus, no model yet proposed comes close to fully explaining the nature of electron donor-acceptor complexes in which boron acts as an acceptor. However, a study of the structures of a wider variety of boron adducts might enable investigators to see a pattern which would enable the formation of a predictive model. Toward this end it was observed that only two complexes in which a carbon atom acted as an electron donor to boron had ever been prepared. Of the two observed complexes, t-butylioscyanide-trimethylborane¹⁶ and borane carbonyl⁹ only the latter has been the subject of a structural investigation. In order to increase the range of usable data on carbon-borane complexes two previously unknown adducts, methyl isocyanide-borane (Figure II-1) and t-butylioscyanide-borane (Figure II-2) were prepared and their microwave spectra investigated. From these microwave studies a complete structure was determined for methylisocyanide-borane, while only the
C-B bond length was determined for t-butyliosocyanide-borane.
PART II-A
Methylisocyanide-Borane

Experimental

Although the common species of methylisocyanide-borane was initially observed using a flow system in which the two components were flowed through the absorption cell of the microwave spectrometer it was soon found that in a static system mixing the components at a total pressure of 1 - 2 torr gave a strong signal and reduced consumption of the diborane and methylisocyanide markedly. In the static system the spectrum gradually weakened over several hours. This was easily overcome by the mixing of new samples every one to two hours.

The methylisocyanide was prepared by heating methyl-iodide and silver cyanide in a 1:2 molar ratio in a sealed tube, evacuated of air, for four hours at 80°C\textsuperscript{17,18}. The methylisocyanide was removed from the resulting black tar-like mass by vacuum distillation.

The \(^{13}\text{CH}_3\text{NC}\) and \(\text{CD}_3\text{NC}\) isotopic species were prepared using the method just described by heating \(^{13}\text{CH}_3\) (10 atom % \(^{13}\text{C}\)) and \(\text{CD}_3\) (99 atom % D)\textsuperscript{19} with silver cyanide to give the corresponding isotopically substituted methylisocyanide.

The \(\text{CH}_3\text{^{15}NC}\) and \(\text{CH}_3\text{N}^{13}\text{C}\) species were prepared by reacting \(\text{KC}^{15}\text{N}\) (97.1 atom % \(^{15}\text{N}\)) and \(\text{K}^{13}\text{CN}\) (95.0 atom % \(^{13}\text{C}\)) with an approximately five fold excess aqueous
solution of silver nitrate. The isotopically substituted silver cyanide precipitate was washed, dried, and then reacted with methyl iodide in the same manner as above.

The diborane and d₆-diborane were obtained from Professor R. A. Geanangel and Mrs. M. Grace Hu, both of the University of Houston chemistry department. I am informed that the diborane was prepared by the method of Nöth and Beyer²⁰, while the d₆-diborane was prepared by a modification of the method of Davis, Brown, Hopman, and Kibby²¹.

All of the microwave spectra were recorded in the R-band (26.5 - 40 GHz) using a Hewlett-Packard Model 8460A MRR spectrometer with 33.3 KHz stark modulation. Frequency measurements were made at pressures in the range of 5 - 40 mtorr using a small d.c. offset voltage (∼ 40 V) to move the K ≠ 0 components with a fast first order stark effect out of the frequency area of the K=0 components which have only a comparatively slow second order stark effect. All frequency measurements were made at room temperature since cooling the stark cell did not improve the signal to noise ratio measurably. The lines were relatively broad, but no nuclear quadrupole effects could be resolved. Due to the broadness of the lines the frequency measurements are accurate only to about ± .2 MHz as opposed to the usual accuracy of ± .05 MHz.
Assignment of the Spectra

A low resolution spectrum of the common isotopic species of methylisocyanide-borane is shown in Figure II-3. As expected the spectrum is that of a symmetric rotor with the \( J \to J+1 \) transitions given by the expression \( \nu_{J,J+1} = 2B(J,J+1) \), with the observed absorption lines assigned to the \( J4 \to 3, J5 \to 4 \) transitions. The relative intensities of the \( \text{CH}_3\text{NC} - {^{10}\text{BH}}_3 \) transitions to those of the more prevalent \( \text{CH}_3\text{NC} - {^{11}\text{BH}}_3 \) agree with the relative abundances of the boron isotopes (\( {^{10}\text{B}} = 19.6\%, \ {^{11}\text{B}} = 80.4\% \)). Even in the fast scan depicted in Figure II-3 at least two series of transitions due to low frequency vibrations are apparent on the high frequency side of the ground state transitions. A high resolution scan (Figure II-4) shows a series of transitions to the low frequency side of the ground state \( m=0 \) line. These transitions which correspond to increasing \( m \) values are associated with the internal rotation of the complex and, as will be explained in the section on the barrier to internal rotation, were assigned in the same manner used for methylsilyl-acetylene\(^{22}\).

The ground state \( K=0, m=0 \) transition frequencies for the fourteen different isotopic species are given in Table II-1 and the corresponding rotational constants calculated using the above expression for the transition frequencies are listed in Table II-2.

The frequencies of a number of \( m \) components associated with internal rotation for the \( ^{12}\text{CH}_3{^{14}}\text{N}{^{12}}\text{C} - {^{11}}\text{BH} \) and
Table II-1

Symmetric Top Rotational Transition Frequencies* (MHz) of Methylisocyanide–Borane in the Ground State. m=0,K=0

<table>
<thead>
<tr>
<th>Isotopic Species</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J4 + 3</td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3 )</td>
<td>27673.90</td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{10}\text{BH}_3 )</td>
<td>28602.25</td>
</tr>
<tr>
<td>( ^{13}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3 )</td>
<td>26964.35</td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{15}\text{N}^{12}\text{C}^{11}\text{BH}_3 )</td>
<td>27616.01</td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{15}\text{N}^{12}\text{C}^{10}\text{BH}_3 )</td>
<td>28449.01</td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{14}\text{N}^{13}\text{C}^{11}\text{BH}_3 )</td>
<td>27607.84</td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{14}\text{N}^{13}\text{C}^{10}\text{BH}_3 )</td>
<td>28521.76</td>
</tr>
<tr>
<td>( ^{12}\text{CD}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3 )</td>
<td></td>
</tr>
<tr>
<td>( ^{12}\text{CD}_3^{14}\text{N}^{12}\text{C}^{10}\text{BH}_3 )</td>
<td></td>
</tr>
<tr>
<td>( ^{12}\text{CD}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3 )</td>
<td></td>
</tr>
<tr>
<td>( ^{12}\text{CD}_3^{14}\text{N}^{12}\text{C}^{10}\text{BD}_3 )</td>
<td></td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BD}_3 )</td>
<td></td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{10}\text{BD}_3 )</td>
<td></td>
</tr>
<tr>
<td>( ^{12}\text{CH}_3^{14}\text{N}^{13}\text{C}^{11}\text{BD}_3 )</td>
<td></td>
</tr>
</tbody>
</table>

* Estimated accuracy of frequency measurement ± 0.2 MHz.
Table II-2

Ground State Rotational Constants (MHz) and Moments of Inertia (amuÅ²) of Methylisocyanide-Borane

<table>
<thead>
<tr>
<th>Isotopic Species</th>
<th>Rotational Constant*</th>
<th>Moment of Inertia**</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$</td>
<td>3459.24</td>
<td>146.095</td>
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<tr>
<td>$^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{10}\text{BH}_3$</td>
<td>3575.28</td>
<td>141.353</td>
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<td>$^{13}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$</td>
<td>3370.73</td>
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<tr>
<td>$^{12}\text{CH}_3^{15}\text{N}^{12}\text{C}^{11}\text{BH}_3$</td>
<td>3452.00</td>
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<td>$^{12}\text{CH}_3^{15}\text{N}^{12}\text{C}^{10}\text{BH}_3$</td>
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<td>3041.51</td>
<td>166.160</td>
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</table>

* ± 0.05 MHz.

** ± 0.002 amuÅ².


\[ ^{12}\text{CD}_3^{14}\text{N}^{12}\text{C} - ^{11}\text{BH}_3 \] isotopic species are given in Table II-3.

The frequencies of the most prominent satellite series, associated with the heavy atom bending vibration of the complex, are given in Table II-4 for the \[ ^{12}\text{CH}_3^{14}\text{N}^{12}\text{C} - ^{11}\text{BH}_3 \] isotopic species.

**Molecular Structure**

The analysis of the rotational spectrum of a molecule gives the moments of inertia of the molecule. By observing the spectra of several isotopic species of the same molecule the differences in the moments of inertia can be used to give accurate values for the center of mass coordinates of each isotopically substituted atom.

Since the pattern of transitions for all isotopic species of methylisocyanide-borane indicates the complex is a symmetric top the relationship between the change of moment of inertia and the parent isotopic species on-axis z coordinate of the substituted atom is given by one of Kraitchman's equations\(^\text{2}^3\) as:

\[
|z| = (\Delta I/M)^{\frac{1}{2}}
\]

Eq. II-1.

In the above equation \(\Delta I\) is the change of the moment of inertia (in amu-Å\(^2\)) upon isotopic substitution and \(M\) is the reduced mass (amu) defined as:
Table II-3

Transition Frequencies* (MHz) of the Ground State Components of Internal Rotation for $^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$ and $^{12}\text{CD}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$ Isotopic Species

<table>
<thead>
<tr>
<th></th>
<th>$^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$</th>
<th>$^{12}\text{CD}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$</th>
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</thead>
<tbody>
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<td>J4 + 3</td>
<td>J5 + 4</td>
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<td>5</td>
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<td>6</td>
<td>27609.21</td>
<td>34511.31</td>
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</table>

* $\pm$ 0.2 MHz.
Table II-4

Rotational Transition Frequencies* and Constants**(MHz) for the First Five Quanta of the Low Frequency Bending Vibration of $^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$

<table>
<thead>
<tr>
<th>Quantum Number</th>
<th>Transitions</th>
<th>Rotational Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J4 + 3$</td>
<td>$J5 + 4$</td>
</tr>
<tr>
<td>0</td>
<td>27673.70</td>
<td>34591.95</td>
</tr>
<tr>
<td>1</td>
<td>27757.85</td>
<td>34697.37</td>
</tr>
<tr>
<td>2</td>
<td>27843.15</td>
<td>34803.32</td>
</tr>
<tr>
<td>3</td>
<td>27928.35</td>
<td>34910.71</td>
</tr>
<tr>
<td>4</td>
<td>28014.21</td>
<td>35016.90</td>
</tr>
<tr>
<td>5</td>
<td>28100.73</td>
<td>35124.94</td>
</tr>
</tbody>
</table>

* $\pm 0.4$ MHz.

** $\pm 0.09$ MHz.

† Unresolved $m=0,1$; $K=0$ components of internal rotation.
\[ M = M\Delta m / (M + \Delta m) \quad \text{Eq. II-2.} \]

In equation II-2 \( M \) is the mass of the parent isotopic species and \( \Delta m \) the change of mass upon isotopic substitution.

The \( r_s \) molecular \( z \) coordinates derived from equation II-1 using the observed changes in the moment of inertia are shown in Table II-5. The on-axis bond lengths in the molecule were calculated from the \( z \) coordinates of adjacent atoms and are given in Table II-6. The large number of isotopic species observed overdetermines the molecular structure and thus allows some bond lengths to be determined using more than one set of data. As can be seen in Table II-6 the variations are qll within experimental error.

The error limits of the on-axis bond lengths were calculated in the following manner. The error in the frequency of a particular transition was estimated by examining both the broadness of the transition and the range of deviation over several measurements. This error was divided by \( 2(J+1) \) to give the error in the rotational constant. The error in the rotational constant was easily converted to the error in the moment of inertia since

\[ I = 505377/B \quad \text{Eq. II-3.} \]

Where \( I \) is the moment of inertia measured in amu-Å²
Table II-5

$z_z$ Coordinates (Å) of Methylisocyanide–Borane

<table>
<thead>
<tr>
<th>Atom</th>
<th>$^{12}$CH$_3^{14}$N$^{12}$C$^{11}$BH</th>
<th>$^{12}$CH$_3^{14}$N$^{12}$C$^{10}$BH$_3$</th>
<th>$^{12}$CH$_3^{14}$N$^{12}$C$^{11}$BD$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>$-2.162 \pm 0.001^+$</td>
<td>$-2.202 \pm 0.001$</td>
<td>$-2.033 \pm 0.001$</td>
</tr>
<tr>
<td>C$_1$</td>
<td>$-0.0596 \pm 0.003$</td>
<td>$-0.636 \pm 0.003$</td>
<td>$-0.465 \pm 0.003$</td>
</tr>
<tr>
<td>N</td>
<td>$+0.559 \pm 0.003$</td>
<td>$+0.519 \pm 0.003$</td>
<td>---</td>
</tr>
<tr>
<td>C$_2$</td>
<td>$+1.975 \pm 0.001$</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$^+$ Calculated from errors in rotational constants.
Table II-6

$r$, Structural Parameters (Å)
För Methylisocyanide-Borane

<table>
<thead>
<tr>
<th>Parent Isotopic Species</th>
<th>$^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3$</th>
<th>$^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{10}\text{BH}_3$</th>
<th>$^{12}\text{CH}_3^{14}\text{N}^{12}\text{C}^{11}\text{BD}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r(\text{BC}_1)$</td>
<td>$1.566 \pm 0.004$</td>
<td>$1.565 \pm 0.004$</td>
<td>$1.568 \pm 0.004$</td>
</tr>
<tr>
<td>$r(\text{C}_1\text{N})$</td>
<td>$1.155 \pm 0.006$</td>
<td>$1.155 \pm 0.006$</td>
<td>---</td>
</tr>
<tr>
<td>$r(\text{C}_2\text{N})$</td>
<td>$1.416 \pm 0.004$</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
and $B$ is the rotational constant measured in MHz. The combined error of the two moments of inertia used to calculate $\Delta I$ in equation II-1 was then used to calculate the error in the $z$ coordinate of the isotopically substituted atom. A simple addition of the errors in the two coordinates of adjacent atoms was taken as the final error in bond length.

The coordinates of the off-axis borane and methyl hydrogens could not be determined from the experimental data using Kraitchman's equations since no species with a singly substituted hydrogen were studied. Mono and di-deuterated substitutions were not attempted because of expected difficulties in interpreting the resulting asymmetric rotor spectra arising from the great number of vibrational satellites and the internal rotation structure. Since the borane $H-B$ bond parameters are not as of yet well characterized an attempt was made to evaluate the coordinate of both the borane and methyl hydrogens using the symmetrically substituted isotopic species $\text{CH}_3\text{NC-BH}_3$, $\text{CH}_3\text{NC-BD}_3$, and $\text{CH}_3\text{NC-BD}_3$. If either the methyl or borane hydrogens are substituted the change of moment of inertia is given by

$$\Delta I = Mz_H^2 + 3(m_D - m_H)\rho_H^{2/2} \quad \text{Eq. II-4.}$$

where $z_H$ is the on axis hydrogen coordinate, $M$ is the same quantity defined in equation II-2, and $\rho_H$ is the
distance from the axis to the proton. The first term on this expression is approximately nine times larger than the second term with the result that any small error in $z_H$ causes four times that error in $\rho_H$. The on-axis coordinate, $z_H$, can be determined within about $\pm \ 0.01 \ \text{Å}$ by double substitution giving an error of $\pm \ 0.04 \ \text{Å}$ in $\rho_H$, which is unsatisfactory.

If, however, reasonable values are assumed for $r(B-H)^{10}$ and $r(C-H)^{26}$, it is possible to estimate $\angle HB_1$ and $\angle HC_2N$ with some confidence. Using the assumed values of $r(B-H) = 1.220 \ \text{Å}$ and $r(C-H) = 1.100 \ \text{Å}$, $\angle HBC_1$ and $\angle HC_2N$ were found to be $105.7 \pm 6^\circ$ and $109.0 \pm 0.5^\circ$ respectively. From these values $\angle HBH$ and $\angle HCH$ were calculated to be $113.0 \pm 0.6^\circ$ and $110.0 \pm 0.5^\circ$. The best structure derived from experimental data and assumptions is shown in Table II-7.

**Internal Rotation**

The theory of the interactions between internal rotation and nontorsional vibrations which account for the observable internal rotation effects in the rotational spectrum for two tops capable of internal rotation about a common symmetry axis was first developed by Kivelson$^{25}$ to interpret the microwave spectrum of methylsilane. Eight years after Kivelson's initial paper Kirtman$^{26}$ formalized the theory. Kirchoff and Lide$^{22}$ used Kirtman's theory (with an assumption about the magnitude of the ratio of the internal rotation constants F and G) to place an
Table II-7
Molecular Structure of Methylisocyanide-Borane

\[ r(BC_1) = 1.566 \pm 0.004 \text{ Å}, \quad r(C_1N) = 1.155 \pm 0.006 \text{ Å} \]

\[ r(NC_2) = 1.416 \pm 0.004 \text{ Å}, \]

\[ (r(BH) = 1.220 \pm 0.020 \text{ Å})^+, \quad (r(CH) = 1.100 \pm 0.015 \text{ Å})^+ \]

\[ \langle HCN \rangle = 109.0 \pm 0.5^\circ, \quad \langle HBC \rangle = 105.7 \pm 0.6^\circ \]

\[ \langle HBH \rangle = 113.0 \pm 0.5^\circ, \quad \langle HCH \rangle = 110.0 \pm 0.6^\circ \]

\[ ^+ \text{ Assumed molecular parameters.} \]
upper limit to the barrier to internal rotation of 3 cal/mole for the molecule methylsilylacetylene.

Without going into the theoretical justifications, it has been shown that for a symmetric top molecule with two internal rotors and \( K=0 \) the frequency of the individual internal rotation component denoted by the quantum number \( m \) is given by

\[
v_{J,J+1} = 2(J+1)(B+Gm^2 + C/(4m^2 - 9) - D_J(J+1)^2) \quad \text{Eq. II-5.}
\]

The expression for the \( K \neq 0 \) components is more complicated and is not easily utilized since the assignment of these transitions is extremely difficult. In the present case only the \( K=0 \) components were assigned and analyzed. Further the centrifugal distortion term \( D_J(J+1)^2 \) was eliminated from equation II-5 since the error in the term was found to be larger than the term itself, indicating almost no discernable centrifugal distortion. The results of the least squares fit of the experimental data shown in Table II-4 to the modified equation II-5 are given in Table II-8.

In order to evaluate the barrier to internal rotation, \( V_3 \), in light of the now determined \( C \) and \( G \) constants the relationships

\[
C = 9sF/8 - 81s^2G/128 \quad \text{Eq. II-6.}
\]

\[
s = 4V_3/9(A_1 + A_2) \quad \text{Eq. II-7.}
\]
Table II-8

Rotational Constants (MHz)
for Methylisocyanide-Borane Assuming a
Small Barrier to Internal Rotation

<table>
<thead>
<tr>
<th></th>
<th>$^{12}$CH$_3^{14}$N$^{12}$C$^{11}$BH$_3$</th>
<th>$^{12}$CH$_3^{14}$N$^{12}$C$^{11}$BH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>3459.26 + 0.01</td>
<td>3094.75 + 0.01</td>
</tr>
<tr>
<td>$C$</td>
<td>-0.094 + 0.078</td>
<td>-0.149 + 0.053</td>
</tr>
<tr>
<td>$G$</td>
<td>-0.2245 + 0.0005</td>
<td>-0.1775 _ 0.0015</td>
</tr>
</tbody>
</table>

From fitting the expression

$$\nu = 2(J + 1)[B + Gm^2 + C/(4m^2 - 9)]$$

to the frequencies in Table II-3
are needed. In equation II-7 the terms $A_1$ and $A_2$ are the rotational constants for the two tops and were evaluated from the structure given in Table II-7 to be 156,040 MHz and 122,368 MHz for the methyl and borane groups respectively. The rotational constant of the deuterated methyl group was evaluated to be 78,020 MHz. An obvious difficulty in solving for $s$, and from that $V_3$, is that equation II-6 has two unknowns $s$ and $F$. $F$ is a molecular constant which describes the coupling of the two tops, the value of which depends upon the normal vibrations, geometry, and vibrational state of the molecule. The enormous difficulty of calculating a value for $F$ has caused it to be treated, in general, as an empirical parameter. Previously $^2$5 $F$ has been determined by assigning and analyzing several excited torsional states, but in this case it was not possible to assign any excited torsional states so approximations were necessary.

The same approximations used in the analysis of the microwave spectrum of methylisilylacetylene by Kirchoff and Lide were picked as the best available. The first approximation used was that the ratio of the $F$ of the normal species to $F_D$ of the CD$_3$NC-BH$_3$ species was greater than 1.0. This appears reasonable since this ratio was between 1.1 and 1.4 in all cases in which it was reported. Upon insertion of $F/F_D > 1.0$ into

$$ s^2 = \frac{128(.822(F_{CD}/F_D)-C)}{81 \ G_D((G/G_D) - (F/0.822 \ F_D))} \quad \text{Eq. II-8.} $$
an upper limit to \( s \) of 5.25 is found. The next approximation made was to assume that \( |F/G| > 10 \), which also appears reasonable since this ratio is of the order of 50 - 100 for all symmetric tops studied. This gave \( F \leq -2.245 \) since \( G \) had already been determined. This value of \( F \) and the observed value of \( C \) allowed equation II-6 to be solved for \( s \). Since equation II-6 is quadratic in \( s \) two values of \( s \) are derived. Of the two values, 17.74 and .037, only the smaller of the two was less than the upper limit of 5.25 found by application of the \( F/F_D > 1.0 \) approximation. The new value of \( s \) lead to an upper limit to the barrier to internal rotation of 4.2 cal/mole.

**Dipole Moment**

The effect of an applied electric field on the frequency of a rotational transition (Stark effect) has long been recognized as an accurate method for measuring molecular dipole moments. In order to determine the dipole moment of methylisocyanide-borane a measurement of the Stark effect of the \( K=0, m=3 \) internal rotation component of the ground state \( J4 \neq 3, M=1,2 \) and \( J5 \neq 4, M=3 \) transitions. It was necessary to use the \( m=3 \) internal rotation component of the transitions due to the overlap of the \( m=0,1,2 \) components and the small intensity of the \( m > 3 \) components. The stark cell constant was determined by the measurement of the frequency shifts of the \( J2 \neq 1, K=0 \) transition of the ground vibrational state of methyl-
acetylene for which the dipole moment has been measured to be 0.7840 D\textsuperscript{27}. The final value of the dipole moment of methylisocyanide was determined to be 6.73 ± 0.07 D. Table II-2 shows the results.

**Low Frequency Bending Vibration**

Figure II-5 shows a plot of the difference in rotational constants, (B\textsubscript{V} - B\textsubscript{0}), against the vibrational quantum number V. For the first five quanta the plot is linear indicating an almost harmonic oscillation.

Both the large number of unidentified and possibly overlapping vibrational satellites and the internal rotation components cause relative intensity measurements to be very difficult. However, relative intensity measurements of the first four vibrational states of the most prominent satellite series were attempted and gave intensity ratios of 100:72.2:48.8:26.9. This yields an estimate of 186 ± 23 cm\textsuperscript{-1} for the fundamental frequency of the vibration.
### Table II-9
Dipole Moment of Methylisocyanide-Borane

<table>
<thead>
<tr>
<th>Transition*</th>
<th>m</th>
<th>M</th>
<th>Dipole Moment (Debyes)</th>
<th>Estimated Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>J4 → 3</td>
<td>3</td>
<td>1</td>
<td>6.74</td>
<td>± 0.28</td>
</tr>
<tr>
<td>J4 → 3</td>
<td>3</td>
<td>2</td>
<td>6.69</td>
<td>± 0.16</td>
</tr>
<tr>
<td>J5 → 4</td>
<td>3</td>
<td>3</td>
<td>6.75</td>
<td>± 0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.73</td>
<td>± 0.07</td>
</tr>
</tbody>
</table>

* Stark cell calibrated using the J2 → 1, K=0, in the vibrational ground state of $^{12}_{\text{CH}}^{12}_{\text{C}}$ for which $\mu = 0.7840$ D. (J. S. Muenter, V. W. Laurie, *J. Chem. Phys.* 45, 855 (1966)).

† 95% confidence limit
FIGURE II-5
PART II-B

t-Butylisocyanide-Borane

Experimental

The t-butylisocyanide-borane complex was formed in the same manner as the methylisocyanide-borane complex with the substitution of t-butylisocyanide for methylisocyanide.

The t-butylisocyanide was initially prepared in the same manner as the methylisocyanide, i.e., placing t-butyl iodide and silver cyanide in a 1:2 molar ratio in a sealed tube, evacuated of air, for periods of time ranging from 15 minutes to 12 hours at room temperature and then removing the t-butylisocyanide by vacuum distillation. This method of preparation was unsatisfactory because large amounts of impurities (t-butylcyanide and hydrogen cyanide) were not removed in the vacuum distillation process. It was found that the generation of these impurities was eliminated by reacting the t-butyl iodide with the silver cyanide in ethyl ether while keeping the reaction at \( \approx -10^\circ C \) for 48 hours. The solid mass of reacted silver cyanide was separated from the ether and dissolved in a saturated aqueous KCN solution. The layer of t-butylisocyanide was removed from the aqueous layer by pipette and used without further purification.

The \(^{13}\text{C}\) enriched t-butylisocyanide was prepared from 90 atom % potassium cyanide in the same manner used for
$^{13}\text{C}$ enriched methylisocyanide.

Other experimental aspects of this work were identical to those of the methylisocyanide-borane work and will not be elaborated upon here.

**Assignment of the Spectra**

The general appearance of the microwave spectrum of t-butlyisocyanide-borane (Figure II-6) is much like that of methylisocyanide-borane in that it is a symmetric top spectrum, fitting the $\nu_{J,J+1} = 2B(J+1)$ expression fairly well for the $J_{10} \leftrightarrow 9$, $J_{11} \leftrightarrow 10$, $J_{12} \leftrightarrow 11$, and $J_{13} \leftrightarrow 12$ transitions observed. Again there is an obvious series of transitions due to low frequency vibrations which progressed to the high frequency side of the ground state transitions.

There are, however, some important differences in the spectrum of this molecule and that of methylisocyanide-borane. The substitution of methyl groups for hydrogen atoms causes the internal rotation splittings to collapse and the transitions due to higher vibrational states to move much closer in frequency to the ground vibrational state rotational transitions. The overlapping of rotational transitions due to several series of vibrational modes causes a near continuum of absorption at frequencies above the ground state transitions for over 500 MHz even at moderately low pressures. The transition frequencies of the ground states of the four observed species are given in Table II-10 while the rotational constants and
Table II-10
Symmetric Top Rotational Transition
Frequencies\(^{\dagger}\) (MHz) of t-Butylisocyanide-Borane
in the Ground State. \(m=0, K=0\)

<table>
<thead>
<tr>
<th>Isotopic Species</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J10-9</td>
</tr>
<tr>
<td>((^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3)</td>
<td>28482.21</td>
</tr>
<tr>
<td>((^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{12}\text{C}^{10}\text{BH}_3)</td>
<td>---</td>
</tr>
<tr>
<td>((^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{13}\text{C}^{11}\text{BH}_3)</td>
<td>28258.05</td>
</tr>
<tr>
<td>((^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{13}\text{C}^{10}\text{BH}_3)</td>
<td>29114.80</td>
</tr>
</tbody>
</table>

\(^{\dagger}\)Estimated accuracy of measurement \(\pm 0.5\) MHz

Table II-11
Ground State Rotational Constants (MHz)
and Moments of Inertia (amu-Å\(^2\))
of t-Butylisocyanide-Borane

<table>
<thead>
<tr>
<th>Isotopic Species</th>
<th>Rotational Constant</th>
<th>Moment of Inertia</th>
</tr>
</thead>
<tbody>
<tr>
<td>((^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{12}\text{C}^{11}\text{BH}_3)</td>
<td>1424.109 (\pm 0.002)</td>
<td>354.8724 (\pm 0.0003)</td>
</tr>
<tr>
<td>((^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{14}\text{C}^{10}\text{BH}_3)</td>
<td>1468.148 (\pm 0.002)</td>
<td>344.2276 (\pm 0.0003)</td>
</tr>
<tr>
<td>((^{12}\text{CH}_3)_3^{14}\text{C}^{13}\text{N}^{13}\text{C}^{11}\text{BH}_3)</td>
<td>1412.93 (\pm 0.02)</td>
<td>357.680 (\pm 0.003)</td>
</tr>
<tr>
<td>((^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{13}\text{C}^{10}\text{BH}_3)</td>
<td>1455.72 (\pm 0.02)</td>
<td>347.166 (\pm 0.003)</td>
</tr>
</tbody>
</table>
moments of inertia are given in Table II-11.

**Molecular Structure**

Using the same methods as outlined in the previous discussion on the evaluation to the structure of methylisocyanide-borane it was possible to determine the $r_s$ coordinates of the boron atom and the carbon atom bonded to the boron atom using two different sets of data. These results are shown in Table II-12. The two values determined for the B-C bond length, while not in as close agreement as the three values found for methylisocyanide-borane, are within experimental error and the difference can be attributed to the lack of resolution caused by the collapse of the internal rotation states.

Further isotopic substitutions were not made for two reasons. In the first place it was felt that the closeness of the nitrogen atom to the center of mass ($\approx 0.5$ Å), coupled with the relative largeness of the uncertainties of the other moments of inertia would make the measurement uninformative. Secondly, it was felt that additional isotopic substitutions, while aesthetically pleasing, would not yield information worth the additional expense and time.
Table II-12

$r_s$ Coordinates and Structural Parameters of t-Butylisocyanide-Borane (Å)

<table>
<thead>
<tr>
<th></th>
<th>$(^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{12}\text{C}^{-11}\text{BH}_3$</th>
<th>$(^{12}\text{CH}_3)_3^{12}\text{C}^{14}\text{N}^{12}\text{C}^{-10}\text{BH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_x (B)$</td>
<td>$3.2518 \pm 0.0001$</td>
<td>$3.2855 \pm 0.0001$</td>
</tr>
<tr>
<td>$Z_s (C)$</td>
<td>$1.682 \pm 0.005$</td>
<td>$1.721 \pm 0.005$</td>
</tr>
<tr>
<td>$r_s (B-C)$</td>
<td>$1.570 \pm 0.005$</td>
<td>$1.565 \pm 0.005$</td>
</tr>
</tbody>
</table>
PART II
DISCUSSION OF RESULTS

The molecular structure of methylisocyanide-borane may be compared with the isolated components of the complex and with related borane complexes.

The $r(\text{N}=\text{C}_1)$ distance is shortened by .011 Å with respect to methylisocyanide$^{24}$. A similar shortening has been observed in x-ray crystallographic measurements of methylcyanide-BX$_3$ (X=F,Cl) complexes$^{28,29}$ and has been associated with an observed increase in the force constant of this bond on complex formation$^{30,31}$. This indicates some methylisocyanide complexes may show an increase of the $\nu_{\text{N}=\text{C}}$ stretching frequency on complex formation similar to that found for the $\nu_{\text{C} = \text{N}}$ stretching frequencies of certain methyl cyanide complexes$^{32}$. In contrast, the CN and OC bond lengths in trimethylamine-borane$^7$ and borane carbonyl$^{10}$ are both lengthened by .032 Å and .003 Å respectively. It is also interesting to note that $r(\text{C}_2-\text{N})$ in methylisocyanide-borane is shortened by .008 Å compared with methylisocyanide$^{24}$.

The $r(\text{B}-\text{C}_1)$ distance is observed to be .029 Å longer than in borane carbonyl$^{10}$ while $\angle \text{H-B-H} = 113.0 \pm .5^\circ$, although not as reliably determined, compares reasonably closely with corresponding values of 113.3° observed in trimethylamine-borane$^7$ and the recently redetermined value of 114.5° in borane carbonyl.
Since only one parameter of the t-butylisocyanide-borane complex, i.e., the C-B bond length, was determined only a comparison with methylisocyanide-borane is possible. The average \( r(\text{B-C}) \) for the two parent species of t-butylisocyanide-borane is 1.568 Å and agrees within experimental error with the \( r(\text{B-C}) \) of 1.566 Å determined for methylisocyanide-borane. This result contrasts with the \( N-F \) distances observed\(^{33} \) in the hydrogen bonded complexes t-butylcyanide-HF and methylcyanide-HF in which the additional methyl groups significantly shortened the \( N-F \) bond length.

The dipole moment of methylisocyanide-borane of 6.73 \( \pm 0.07 \) D compares with 4.84 \( \pm 1 \) D and 1.795 \( \pm 0.01 \) D observed in trimethylamine-borane\(^{7} \) and borance carbonyl\(^{9} \) and the corresponding values of 3.83 \( \pm 0.06 \) D, 0.612 \( \pm 0.003 \) D, and 0.112 \( \pm 0.005 \) D found in methylisocyanide\(^{34} \), trimethylamine\(^{35} \), and carbon monoxide\(^{36} \). No dipole measurement for t-butylisocyanide-borane was possible due to the proximity of excited vibrational state transitions to the ground state transitions and the high \( J \) values of the transitions observed in the \( R \)-band.

As was expected methylisocyanide-borane is almost a free internal rotator, the upper limit to the barrier to internal rotation being estimated as 4.2 cal/mole.

An interesting aspect of this work was an attempt to displace carbon monoxide from borane carbonyl with methylisocyanide. Isocyanides are thought to be stronger \( \sigma \) donors toward metal ions than is carbon monoxide, but
comparison of IR stretching frequency shifts of metal carbonyls and metal isocyanides indicate similar π donor abilities. Thus one would expect isocyanide-borane complexes to be more stable than borane carbonyl.

However, it was observed that upon mixing methylisocyanide with borane carbonyl the rate of weakening of the borane carbonyl transition appeared to be no different from that of static dissociation. It was expected that the large amount of methylisocyanide introduced would have reduced the intensity of the observed line significantly, but since there is no prediction that equilibrium is established this observation does not provide information on relative bond strengths.

While the fact that the C–B bond length in borane carbonyl bond is .029 Å shorter than the same parameter in the isocyanide complexes would appear to indicate that the borane carbonyl bond is relatively stronger it must be noted that extensive studies⁴ of phosphine–borane complexes show no correlation between bond strength and bond length.

Another intriguing feature of the comparison of borane carbonyl and methylisocyanide–borane is the greater dipole moment enhancement in the latter case (2.90 D vs 1.683 D). If, as has been speculated², the stability of borane carbonyl is due to 'back donation' of electrons to unfilled \( d_{\pi} \) orbitals of carbon monoxide (which would decrease charge separation and dipole moment),
this difference in dipole moment enhancement would indicate that the cause of the longer C-B bond length in isocyanide-borane complexes is due to a much smaller amount of 'back donation' and hence a smaller π bond supplement to the classical σ bond.
REFERENCES TO PART I


10. S. F. Nelson, private communication to P. S. Engel.


REFERENCES TO PART II


19. All isotopically enriched samples purchased from Merck, Sharpe, and Dohme, Montreal Canada.
The following programs were used to calculate the internal rotation energy levels.
UNREDUCED HAMILTONIAN FOR ALL LEVELS OF $A_h A_v$, $E_E$, $A_v E$, AND $E_v A$ SPECIES.

```fortran
TEST:PROC OPTIONS(MAIN);
DPT RANGE(A:HO:2) FLOAT DEC VALUE(FLOAT DEC(16));
DPT RANGE(1:IN) FIXED BIN VALUE(FIXED BIN(31,0));
DCL H(169,169),HI(169),D(169),EI(169),E2D(169);
DCL (VCYTFSS,EMOUSS,EGRTS) ENTRY OPTIONS(FORTRAN NOMAP);
I99=169;
Iu=0; I1=1; I2=2; I3=3; I4=4;
I1=1; I8=12; I7=11;
N0=620; FJU=Q4; 0;
F1=166857*0; F2=166857*0; F12=-1159*3; CONV1=10489*6;
I7=153; L3=26; I63=143;
V3=2356*6; V3=4540*01; V6=640*7;
V6=490*5; VS=482*5; VC36=1698*2; VS36=-966*3;
L1=13; L2=13;
V=V*CONV1; V3=V3*CONV1; VS=V5*CONV1; VC=VC*CONV1; V6=V6*CONV1;
V6=V6*CONV1; VS6=VS6*CONV1; VC36=VC36*CONV1; VS36=VS36*CONV1;
D=0*31;
D1=I=11 TO I99;
D1=I=11 TO I99;
I1=J=10 TO I99;
END; END;
DO J1=10 TO IJ1;
DO J2=11 TO 11;
IF J1=10 E J2=11 THEN GOTO MV: ELSE:
MMA1=I3*(L1/12)+J1;
MMA2=I3*(L2/12)+J2;
MN=I3*(L1/12)+J1;
MN=I3*(L2/12)+J2;
I=1;
D1=M1=M4=M1 TO MMA1 BY I3;
D1=M2=M4=M2 TO MMA2 BY I3;
AM1=M1=AM2=M2;
H(I,1)=F1*A41*AM1+F2*AM2+K1*F12*AM1*AM2+V;
I=11;
END; END;
I=11;
DO M1=11 TO I9;
DO M2=11 TO 19;
H(I,1)=V3/TW0; H(I+11,1)=V3/TW0;
I=11;
END;
I=1+11;
END;
I=11;
DO M1=11 TO I9;
DO M2=11 TO 17;
H(I+12,1)=V6/TW0; H(I+12,1)=V6/TW0;
I=1+11;
END;
I=1+12;
```
END;
DO I=11 TO I72;
H(I+I+L2)=V3/TWO; H(I+L2,I)=V3/TWO;
END;
I=11;
DO M1=I1 TO I8;
DO M2=I1 TO I8;
H(I+I+L2+11)=(VC+V3)/FOUR; H(I+L2+11,I)=(VC+V3)/FOUR;
I=I+I1;
END;
I=I+I1;
END;
I=11;
DO M1=I1 TO I8;
DO M2=I1 TO I7;
H(I+I+L2+12)=(VC36+VS36)/FOUR; H(I+L2+12,I)=(VC36+VS36)/FOUR;
I=I+I1;
END;
I=I+I2;
END;
I=I2;
DO M1=I1 TO I8;
DO M2=I1 TO I3;
H(I+I+L2+11)=(VC+V3)/FOUR; H(I+L2+11,I)=(VC+V3)/FOUR;
I=I+I1;
END;
I=I+I1;
END;
I=13;
DO M1=I1 TO I8;
DO M2=I1 TO I7;
H(I+I+L2+12)=(VC36+VS36)/FOUR; H(I+L2+12,I)=(VC36+VS36)/FOUR;
I=I+I1;
END;
I=I+I2;
END;
DO I=I1 TO I63;
H(I+I+L3)=V6/TWO; H(I+L3,I)=V6/TWO;
END;
I=11;
DO M1=I1 TO I7;
DO M2=I1 TO I3;
H(I+I+L3+11)=(VC36+VS36)/FOUR; H(I+L3+11,I)=(VC36+VS36)/FOUR;
I=I+I1;
END;
I=I+I1;
END;
I=I1;
DO M1=I1 TO I7;
DO M2=I1 TO I7;
H(I+I+L3+12)=(VC6+VS6)/FOUR; H(I+L3+12,I)=(VC6+VS6)/FOUR;
I=I+I1;
END;
I=I+I2;
END;
I=I2;
DO M1=I1 TO I7;
   DO M2=I1 TO I8;
      H(I1+L3*I1)=(VC36+VS36)/FOUR; H(I1+L3=I1,I)=(VC36+VS36)/FOUR;
      I=I+11;
   END;
   I=I+11;
END;
I=I3;
DO M1=I1 TO I7;
   DO M2=I1 TO I7;
      H(I1+L3+I2)=(VC6+VS6)/FOUR; H(I1+L3=I2,I)=(VC6+VS6)/FOUR;
      I=I+11;
   END;
   I=I+12;
END;
CALL VCVTFS(H1,I99,I99,H1);
CALL EHOUSS(H1,I99,CI,ED,E2D);
CALL EGRTIS(DI,E2D,I99,I1,IC,IER);
PUT SKIP LIST(*ERROR PARAMETER= *IER);
DI(I2)=0.0;
PUT SKIP(2) LIST(DI(I1),DI(I2));
BY:END:END;
END TEST;
REAL*8 HAA(H1,H1), HI(J321), DI(B1), LD(B1), E2D(B1), M, S, S1, S2
I99=81
MMX=25
00 1 I=1, I99
00 1 J=1, I99
HAA(I,J)=0.0
I=0
J=0
M1=2*MMX-1
DO J=1, MMX, 1
M1=M1X=1
DO J=M1X+1, MMX, 1
MMX=M1X=M1
IF (H1.EQ.0. AND M1P.LT.0) GO TO 2
IF (IABS(M1P).LT.IABS(M1)) GO TO 2
I=I+1
J=0
M2X=1, MMX, 1
M2=M2X=1
DO J=M2X+1, MMX, 1
M2P=M2P=M1X=M1
IF (M2.EQ.0. AND M2P.LT.0) GO TO 2
IF (IABS(M2P).LT.IABS(M2)) GO TO 2
J=J+1
S1=4.00000
IF (M1.EQ.0. AND M1P.EQ.0) S1=S1+4.0000000
IF (M1P.EQ.0) S1=S1+4.0000000
S2=4.00000
IF (M2.EQ.0. AND M2P.EQ.0) S2=S2+4.0000000
IF (M2P.EQ.0) S2=S2+4.0000000
S=DSQRT(S1)*DSQRT(S2)
HAA(I,J)=(H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)
1+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)+H(M1,M1P,M2,M2P)
C U T I N U E
CALL VCVTF (HAA, I99, I99, HI)
CALL EHOUSS (H1, I99, DI, ED, E2D)
CALL ECHRTS (DI, E2D, I99, 1, 0, 1, ER)
901 FORMAT (' ENERGY FOR ', 2*H1, ' BY ', 2*H1, ' MATRIX= ', E10.20)
WRITE (6,901) I, J, DI(I)
STOP
END

REduced Hamiltonian for A1 A1 Species.
REDELE HAA(72,72), HI(2592), J(72), ED(72), E2D(72), HS, S1, S2
199=72
MMX=25
DO 1 J=1,199
DO 1 J=1,199
HAA(I,J)=0.0
I=0
J=0
MMX2=2*MMX-1
DO 2 M1X=1,MMX,3
M1=M1X-1
DO 2 M2PX=1,MMX,3
M2P=M2PX-1
IF(M1+M1P.EQ.0) GO TO 2
IF(M1.EQ.0 .AND. M1P.LT.0) GO TO 2
IF(IABS(M1P)*LT.IABS(M1)) GO TO 2
I=I+1
J=0
DO 2 M2X=1,MMX,3
M2=M2X-1
DO 2 M2PX=1,MMX,3
M2P=M2PX-1
IF(M2+M2P.EQ.0) GO TO 2
IF(M2.EQ.0 .AND. M2P.LT.0) GO TO 2
IF(IABS(M2P)*LT.IABS(M2)) GO TO 2
J=J+1
S1=4.00000
IF(M1.EQ.M1P) S1=S1+4.00000
IF(M1.EQ.0 .AND. M1P.EQ.0) S1=S1+4.00000000
IF(M1.EQ.M1P) S1=S1+4.0000000000
S2=4.000000
IF(M2.EQ.M2P) S2=S2+4.00000000
IF(M2.EQ.0 .AND. M2P.EQ.0) S2=S2+4.0000000000
IF(M2.EQ.M2P) S2=S2+4.00000000
S=SQRT(S1)*SQRT(S2)
HAA(I,J)=(H(M1,M1P,M2,M2P) + H(M1,M1P,M2,M2P))
1+H(M1,M1P,M2,M2P) + H(M1,M1P,M2P,M2P) + H(M1,M1P,M2P,M2P)
1+H(M1,M1P,M2P,M2) + H(M1,MP,M2,M2P) + H(M1,MP,M2P,M2)
1+H(M1P,M1,M2,2P) + H(M1P,M1,M2P,M2) + H(M1P,M1,M2P,M2) + H(M1P,M1,M2P,M2)
CONTINUE
CALL VCVTFS(HAA,199,199,HI)
CALL EHOUSS(H1,199,DO,E2D)
CALL EQRTIS(D1,E2D,199,1,1,IER)
FORMAT('ENERGY FOR ',I4,' BY ',I4,' MATRIX= ',E30.20)
WRITE(6,901) I,J,DI(1)
STOP
END
REAL*8 H,S1,S2,HAA(136,136),HI(9316),DI(136),E2D(136),ED(136)
199=136
MMX=25
MPX=23
I=0
MMX2=2*MMX+1
MPX2=2*MPX+3
DO 2 MIX=1,MMX2,3
M1=MIX-MMX+1
DO 2 MIP=1,MPX2,3
MIP=M1*FX-MPX=3
MPL1=M1+M1P
IF(MPL1.EQ.0) GO TO 2
IF(MPL1.GT.0) GO TO 2
I=I+1
J=0
DO 2 M2X=1,MMX2,3
M2=M2X-MMX+1
DO 2 M2PX=1,MPX2,3
M2P=M2PX-MPX=3
MPL2=M2+M2P
IF(MPL2.EQ.0) GO TO 2
IF(MPL2.GT.0) GO TO 2
J=J+1
S1=1.0D0
S2=1.0D0
IF(MPL1.EQ.0) S1=DSQRT(2.0D0)
IF(MPL2.EQ.0) S2=DSQRT(2.0D0)
S=2*S1*S2
HAA(I,J)=(H(M1,M1P,M2,M2P)+H(-MIP,-M1,M2,M2P))S
H(M1,M1P,M2,M2P)+H(-MIP,-M1,M2,M2P))/S
2 CONTINUE
CALL VCVTFS(HAA,199,199,HI)
CALL EHOUSS(HI,199,DI,ED,E2D)
CALL EQRT15(DI,E2D,199,1.0,IER)
FORMAT(' ENERGY FOR ',I4,' BY ',I4,' MATRIX= ',E30.20)
WRITE(6,901) I,J,DI(1)
STOP
END
REDUCED HAMILTONIAN FOR EA_1 SPECIES.

RFAL*8 H,S,S1,S2,HAA(91,91),H1(4186),DI(91),E2D(91),ED(91)

1=91
MM1X=19
MPX=17
I=3
MM2X=2*MMX-1
MPXXX=2*MPX+3
DO 2 M1X=1,MMX2,3
M1=M1X=MM1X
DO 2 M1PX=M1X-2,3
M1P=M1PX-MPX=3
MPL1=M1+M1P
IF(MPL1.GT.0) GO TO 2
I=I+1
J=0
DO 2 M2X=1,MMX2,3
M2=M2X-MM1X+1
DO 2 M2PX=M2X-2,3
M2P=M2PX-MPX=3
MPL2=M2+M2P
IF(MPL2.GT.0) GO TO 2
J=J+1
S1=1.000
S2=1.000
IF(MPL1.EQ.0) S1=DSQRT(2.000)
IF(MPL2.EQ.0) S2=DSQRT(2.000)
S=2*S1*S2
HAA(I,J)=(H(M1,M1P,M2,=M2P)+H(M1P=M1,M2,=M2P)
1+H(M1,M1P,M2P=M2)+H(M1P=M1,M2P=M2))/S
2
CONTINUE
CALL VCVTS(HAA,199,199,H1)
CALL EHOUSS(H1,199,DI,ED,E2D)
CALL EORTIS(DI,E2D,199,10,IER)
901 FORMAT(' ENERGY FOR ',I4,' BY',I4,' MATRIX=',E30.20)
WRITE(6,901) I,J,DI(1)
STOP
END
SUBROUTINE TO CALCULATE HAMILTONIAN MATRIX ELEMENTS.

REAL FUNCTION H=8(M1,M1P,M2,M2P)
REAL*3 F1,F12,V3,V6,V6C,VSC,V36,V36C,V36S,V6S,C,AM1,AM1P
AM1=M1
AM1P=M2P
F1=166.8571,000
F12=-1159.300
V=0
V3=1025.000
V6=400.000
V6C=225.000
V6S=0
V36C=0
V36S=0
C=10449.600
V=VC3
V3=V3*C
V6=V6*C
VC=VC*C
VS=VS*C
V36C=V36*C
V36S=V36*C
V6S=V6S*C
I=ABS(M1-M2)
J=ABS(M1P-M2P)
IF(I.EQ.0) GO TO 8
IF(J.EQ.0) GO TO 8
IS=(M1-M2)/I
JS=(M1P-M2P)/J
IF(IS.EQ.JS) VS=VS
IF(IS.EQ.JS) V6S=V6S
IF(IS.EQ.JS) V36S=V36S
H=0.0
IF(I.EQ.0) GO TO 1
IF(I.EQ.3) GO TO 3
IF(I.EQ.6) GO TO 6
GO TO 7
1 H=(AM1*AM1+AM1P*AM1P)*F12+V
IF(IABS(J).EQ.0) H=V3/2.0
IF(IABS(J).EQ.6) H=V6/2.0
GO TO 7
3 H=V3/2.0
IF(J.EQ.3) H=(VC+V5)/4.0
IF(J.EQ.6) H=(V36+V36S)/4.0
GO TO 7
9 H=V6/2.0
IF(J.EQ.3) H=(VC30+V36S)/4.0
IF(J.EQ.6) H=(VC6+V6S)/4.0
7 RETURN
END