AN INVESTIGATION OF THE FORCE FIELDS IN TRIBORINE TRIAMINE AND IN BENZENE

by
Shih-Chuan Chang

Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

1952

UMI Number: DP70084

UMI®

Dissertation Publishing

UMI DP70084

ProQuest®

ACKNOWLEDGEMENT

The author wishes to express his hearty appreciation to Dr. Robert A. Spurr for counsel and guidance without which this investigation would be impossible, to Dr. Shih-I Pai of the Institute of Fluid Dynamics and Applied Mathematics for advice in mathematics, and to all professors in this university from whom the author has received advanced instructions in physical science.

TABLE OF CONTENTS

INTRODUCTION

Various methods have been employed in the study of molecular structure:
dipole moments, Kerr effect, X-ray diffraction, electron diffraction, in-
frared absorption, and Raman scattering. Each method has its advantages
and disadvantages, and the kinds of information obtained from these vari-
ous methods are complementary to each other. Due to the limitation of the
magnitude of energy concerned, only vibrational and rotational spectra are
covered by the infrared region of spectra, with the rotational spectra ap-
pearing as fine structure of the near infrared spectra. This research
deals with the vibrational spectra only.

When a molecule is excited by a beam of electromagnetic radiation,
the nuclei of atoms in the molecule absorb energy and change their ampli-
tudes of vibration about the equilibrium position. The absorption fre-
quencies corresponding to the energy changes are the frequencies of change
in electric moment of the molecule. In addition, the incidental radiation
applies an electric field at the molecule, and thus polarizes the molecule.
This change in polarization gives rise to Raman frequencies. A study of
the symmetry properties of the normal vibrations will show that some of the
normal vibrations of the molecule involve a change in electric moment.
Others involve a change in polarization, while the rest of normal vibra-
tions do not alter these properties. Hence some of the normal frequencies
appear in the infrared spectrum, some in the Raman spectrum, and some are
inactive in both infrared and Raman spectra.

From the experimental data information about the arrangement of atoms
in the molecule and the electric fields between nuclei can be obtained by
mathematical analysis of the observed frequencies.

The investigation of force fields in a molecule consists of

(1) obtaining the infrared and Raman spectra of the purest compound

available;

(2) assignment of frequencies obtained to individual normal vibra-
tions;

(3) assuming a suitable force field, i.e., a potential energy func-
tion;

(4) with the assumed force field, setting up the secular equation
for the vibrational frequencies of the compound; and

(5) calculating the force constants with part of the experimental
data and using the rest of the data as a check of the adequacy
of the force field assumed.

In the case of the compounds investigated in this research the assign-
ment of frequencies has been extensively studied by other workers(15) and
is not here considered.

THEORY OF SMALL VIBRATIONS

A molecule consisting of n atoms will, in general, have $3n - 6$ de-
grees of vibrational freedom[1]; hence $3n - 6$ coordinates are required to
specify the vibrational state of the molecule. If the number $3n - 6$ is
represented by s, then there may be chosen a set of coordinates, q_i,
($i = 1, 2, 3, \ldots s$) which give the displacements of the atoms from their
equilibrium positions as a result of vibration. The potential energy, V,
may be expanded in the form of a Taylor series in terms of these coordi-
nates; for small vibrations, all terms beyond the quadratic may be neg-
lected.

$$V = V_o + \Sigma f_i' q_i + \frac{1}{2} \Sigma f_{ij} q_i q_j$$

where

$$f_i' = \left(\frac{\partial V}{\partial q_i}\right)_o \quad \text{and} \quad f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_o$$

[1]In case of linear molecules, the number of the degrees of freedom
is $3n - 5$.

The choice of standard energy level is arbitrary; thus V_0 may be assumed to have the value zero. The symbol f_i' represents the force between nuclei at their equilibrium positions and is also assumed to be zero, i.e., the potential function, plotted against a displacement, has zero slope at equilibrium. Hence, the potential energy function contains only the quadratic terms and can be written as $2V = \underline{q}'\underline{F}\underline{q}$, where $\underline{q}$ is the column matrix of coordinates, $\underline{q}'$ the transposed matrix of $\underline{q}$, a row matrix, and $\underline{F}$ the matrix of force constants f_{ij}. Similarly the kinetic energy function is $2T = \underline{\dot{q}}'\underline{G}^{-1}\underline{\dot{q}}$, where $\underline{\dot{q}}$ is the column matrix of $\dot{q}_i$, the time rate of change of q_i, $\underline{\dot{q}}'$ the transpose of $\underline{\dot{q}}$, and $\underline{G}^{-1}$ the matrix of masses of atoms in the molecule.

The Lagrangian equation of motion is

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$$

where L is the Lagrangian function, equal to T - V. Applying this equation to the potential energy and kinetic energy functions we have

$$\underline{G}^{-1}\underline{\ddot{q}} + \underline{F}\underline{q} = 0. \tag{I}$$

If the nuclei are treated as simple harmonic oscillators, i.e.,

$$q_i = Q_i \sin \sqrt{\lambda}\, t$$

where $\lambda = 4\pi^2\nu^2$, in which ν stands for frequency, equation I becomes

$$(\underline{F} - \underline{G}^{-1}\lambda)\underline{q} = 0.$$

Premultiplication by $\underline{G}$ gives

$$(\underline{G}\underline{F} - \lambda\underline{E})\underline{q} = 0$$

where $\underline{E}$ is the unit matrix, a matrix in which all diagonal members are unity and all other members are zero. For the non-trivial solutions, i.e., those for which the q_i's are not all equal to zero at the same time, the determinant $\|\underline{G}\underline{F} - \lambda\underline{E}\|$ must be zero. This is the so-called secular determinant.

It is clear that when the number of atoms in the molecule is large

the order of the determinant will be too high for convenient handling. A transformation of the matrices $\underline{G}$ and $\underline{F}$ with a suitable set of symmetry coordinates will change the determinant into several diagonal blocks. The value of the determinant is equal to the product of these blocks. Since the value of the determinant is zero, each block can be taken as a determinant having the value zero. Hence the original determinant of high order is resolved into several determinants of lower order, and the treatment is simplified.

The method of the calculation of symmetry coordinates has been fully treated by Nielsen and Berryman (2). Although a discussion of these methods is beyond the scope of this research, the operation of transformation (8) is a simple one. Suppose the symmetry coordinates have been obtained as $\underline{S} = \underline{C}\underline{q}$, $\underline{S}$ being the column matrix of symmetry coordinates, and $\underline{C}$ the transformation matrix. The $\underline{G}$ and $\underline{F}$ matrices in symmetry coordinates are $\underline{CGC}'$ and $\underline{CFC}'$, respectively, in which $\underline{C}'$ is the transposed matrix of $\underline{C}$.

A method for setting up the G matrix in symmetry coordinates, or any coordinates, is given by Wilson (30). James and Coolidge (16) give a formula for calculating the value of the determinant. By this method, using a trial-and-error procedure, the value is set equal to zero and the frequencies are found. Wilson (29) gives a method of developing the determinant into an equation. The scheme of finding the value of the determinant given by Frazer and Duncan (8) is preferred in this investigation for its clarity and ease of handling with a calculator.

FORCE FIELDS

The potential energy function in its most general form is

$$V = \sum_q \sum_i \left(\frac{\partial V}{\partial q_i}\right)_0 \Delta q_i + \frac{1}{2}\sum_q \sum_i \sum_j \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 \Delta q_i \Delta q_j$$

taking the arbitrary zero level at the equilibrium condition, the q_i being

the general coordinates. The simplest force fields assume that there are no forces in the bonds at the equilibrium position and no interactions between changes of coordinates, i.e., all first derivatives and second derivatives with i ≠ j vanish. Thus the simple valence force field assumes the form

$$2V = \sum_r \sum_i (\frac{\partial^2 V}{\partial r_i^2})_0 (\Delta r_i)^2 + \sum_\alpha \sum_i (\frac{\partial^2 V}{\partial \alpha_i^2})_0 (\Delta \alpha_i)^2$$

where r_i

$$2V = \sum_r \sum_i (\frac{\partial^2 V}{\partial r_i^2})_0 (\Delta r_i)^2 + \sum_P \sum_i (\frac{\partial^2 V}{\partial p_i^2})_0 (\Delta p_i)^2$$

e between bonds. Another simple force field is the central force field, of the form

$$2V = \sum_r \sum_i (\frac{\partial^2 V}{\partial r_i^2})_0 (\Delta r_i)^2 + \sum_P \sum_i (\frac{\partial^2 V}{\partial p_i^2})_0 (\Delta p_i)^2$$

where p_i is the distance between the unbonded atoms. These two force fields have been used by various investigators to calculate the vibrational frequencies of simple polyatomic molecules. Concerning the limitation of the application of these simple force fields, Linnett (18) concluded that the simple valence force field accounts for the vibrations of CH_4 fairly well, but not for CCl_4, while the simple central force field becomes more successful in going from hydride to halides, so far as the tetrahedral model is concerned. This suggests that the forces between the non-bonded halogen atoms are more important than those between the non-bonded hydrogen atoms, as would be expected. A further objection to the simple central force field is that it does not account for the bending vibrations of linear molecules since no interatomic distances change in such vibrations. Also it fails to account for the out-of-plane vibrations of planar molecules, e.g., H_2O. However, in the last case, the simple valence force field only accounts for such vibrations if some rather more complicated bending terms are included. The conclusion has been that we should base any improvements or refinements on fields of simple valence force field type rather than of those of the simple central force field type.

Various attempts have been made by investigators to improve these simple force fields (10) by introducing more terms into the potential energy function. However, the number of parameters, i.e., force constants which can be used is limited by the number of frequencies obtained experimentally, or their values cannot be obtained experimentally. Furthermore, the less the number of parameters used, the greater is the number of frequencies left to serve as a check of the force field assumed. Although in the case of some compounds, when isotopic molecules are available, additional experimental data can be obtained to allow the introduction of more terms, there is always present the question as to which cross-terms should be included or neglected.

For the out-of-plane vibrations of benzene, Bell (3) has successfully introduced torsion terms into the simple valence force field, and has suggested the application of this improved force field to the molecule of triborine triamine. The first part of this research carries out this suggestion.

Urey and Bradley (27) suggest a combination of valence force field and central force field

$$2V = 2\sum_{r}\sum_{i}(\frac{\partial V}{\partial r_i})_0 \Delta r_i + \sum_{r}\sum_{i}(\frac{\partial^2 V}{\partial r_i^2})_0(\Delta r_i)^2 + 2\sum_{p}\sum_{i}(\frac{\partial V}{\partial p_i})_0 \Delta p_i$$
$$+ \sum_{p}\sum_{i}(\frac{\partial^2 V}{\partial p_i^2})_0(\Delta p_i)^2 + 2\sum_{\alpha}\sum_{i}(\frac{\partial V}{\partial \alpha_i})_0 \Delta \alpha_i + \sum_{\alpha}\sum_{i}(\frac{\partial^2 V}{\partial \alpha_i^2})_0(\Delta \alpha_i)^2$$

with all symbols having the same meaning as before. It may be noted that although no cross-terms are introduced, all possible interaction terms are included after the non-bonded distances p_i are expressed in terms of the independent variables r_i and α_i. It is assumed that, in contrast to the concepts of the simple force fields, there are forces along the bonds and the non-bonded distances between atoms in the equilibrium position but

these forces balance each other and the resultant is zero around each atom at the equilibrium position. Mathematically speaking, the assumptions are: (1) In a plane section of the multi-dimensional space of coordinates, the potential energy of the system may not be a minimum at the origin, but at some point near the origin. For example, in the plane along the axis of coordinate Δr_i, the potential energy is minimum when $\frac{\partial V}{\partial r_i} = (\frac{\partial V}{\partial r_i})_0 + \frac{1}{2}(\frac{\partial^2 V}{\partial r_i^2})_0 \Delta r_i = 0$, i.e., at the point $\Delta r_i = -2(\frac{\partial V}{\partial r_i})_0 / (\frac{\partial^2 V}{\partial r_i^2})_0$. And (2) The individual first derivatives do not all vanish, though the coefficients of the first power terms of independent variables vanish. For example, in XY_4 type molecules, $(\frac{\partial V}{\partial r_i})_0 \neq 0$, $(\frac{\partial V}{\partial p_i})_0 \neq 0$, while $(\frac{\partial V}{\partial r_i})_0 + \sqrt{6}(\frac{\partial V}{\partial p_i})_0 = 0$, which is the equilibrium condition around the corner atom Y.

These assumptions reduce the number of parameters necessary and at the same time eliminate the difficulty of predicting the importance of individual cross-terms. It is advantageous that, as Simanouti (25) has shown, the force constants can be transferred from molecule to molecule, provided the electronic environment is the same in both molecules, i.e., they are of the same type, so far as the non-bonded distances are concerned.

As a further reduction of the number of force constants required, Urey and Bradley (27) and Heath and Linnett (19) assume a relation $V = a/p^n$, a being a constant and n a parameter. By differentiation of this equation the relation between $\partial V/\partial p_i$ and $\partial^2 V/\partial p_i^2$ can be found. The former workers find that the value of n may vary from 5 to 9 without any appreciable influence on the calculated results. The latter group prefers 4.5 as the value of n.

From the chemical viewpoint, this force field has the advantage of giving physical meaning to each force constant, and thus providing knowledge of the electric fields between both bonded and unbonded atoms. The second part of this research is devoted to applying this force field to the benzene

molecule with the intention that the force constants obtained may be used for the calculation of vibrational frequencies of other similar molecules, since all the previous applications of this force field have been confined to simpler molecules.

OUT-OF-PLANE HYDROGEN VIBRATIONS

IN TRIBORINE TRIAMINE.

Crawford and Edsall (5) have investigated the vibrational spectra of triborine triamine. The large discrepancy between the calculated and observed frequencies of the out-of-plane hydrogen vibrations was attributed to the interactions between hydrogen bonds attached in the meta positions, by analogy with a conclusion drawn by Lord and Andrews (17) in an investigation of benzene.

Bell (3) has suggested the use of a simple force field for the out-of-plane vibrations in triborine triamine. He had previously used a field of the same type for benzene. This calculation has been carried out in this research in the following way:

There are six out-of-plane normal vibrations in triborine triamine, three of which belong to symmetry group A" and three to symmetry group E"; as shown in the following figure:

$$A'' \qquad\qquad E''$$
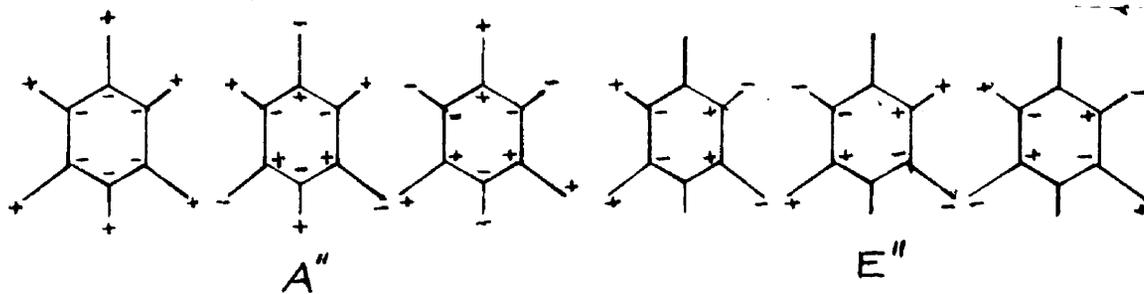
A study of these figures will show that four coordinates will suffice to describes the states of the system, when the two groups are treated separately. However, in each symmetry group, there are only three normal modes, i.e., three degrees of freedom, neglecting rotation and translation.

Hence, among these four coordinates, one is redundant, and is left in the calculation with the expectation that one root of the determinant will be zero.

The potential function assumed has the following form:

$$2V = \sum h_B (r\theta)^2 + \sum h_N (s\mu)^2 + \sum kc^2(\phi_R + \phi_H)^2 \qquad (I)$$

where h_B, h_N, and k are force constants and r and s are the internuclear distances of the B-H and the N-H bonds. The symbols, θ and μ represent the bending angle of these bonds. The quantities ϕ_R and ϕ_H are the angles of twist of the B-N bond due to ring distortion and hydrogen bending, respectively, and the quantity c is the distance from the center of the ring to the B-N bond. The bending angle is defined as the angle that X-H bond makes with the plane of the atom X and the neighboring two Y atoms, where X and Y may be either B or N. In terms of the out-of-plane displacement, the bending angle and the twist are expressed as follows: (4)

$$\mu = \frac{x-w}{r} + \frac{y+z-2w}{R}$$

$$c\phi = w-z + (R-r)x/r - (R-s)y/s - Rq'/r + Rq/s$$

where w, x, y, z, q' and q are the out-of-plane displacements of the corresponding atoms as indicated in the diagrams.

The calculation was carried out separately for the symmetry groups A" and E". External coordinates were used to represent the displacements.

For symmetry group A",
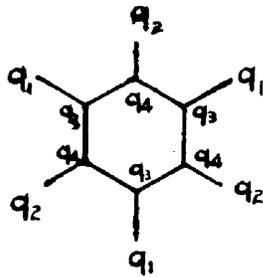
$$\theta = \frac{2(q_4 - q_3)}{R} + \frac{q_1 - q_3}{r}$$

$$r\theta = 2\alpha q_4 - (2\alpha + 1)q_3 + q_1$$

where $\quad \alpha = r/R$

$$\mu = \frac{2}{R}(q_3 - q_4) + (q_2 - q_4)/s$$

$$s\mu = q_2 + 2\beta q_3 - (2\beta + 1)q_4$$

where $\quad \beta = s/R$

$$\Phi = \frac{2}{c}(q_4 - q_3) - \frac{R}{rc}(q_1 - q_3) + \frac{R}{sc}(q_2 - q_4)$$

$$c\Phi = -q_1/\alpha + q_2/\beta + (1/\alpha - 2)q_3 + (2 - 1/\beta)q_4$$

Substitute $r\theta, s\mu$, and $c\Phi$ into (I);

$$\frac{2}{3}V = h_B\left\{q_1 - (2\alpha + 1)q_3 + 2\alpha q_4\right\}^2 + h_N\left\{q_2 + 2\beta q_3 - (2\beta + 1)q_4\right\}^2$$
$$+ 2k\left\{-q_1/\alpha + q_2/\beta + (1/\alpha - 2)q_3 + (2 - 1/\beta)q_4\right\}^2$$

Collect terms and put in matrix form;

$$2V = 3q'Eq$$

where $\underline{q}$ is the column matrix of the coordinates, q_1, q_2, q_3, and q_4, $\underline{q}'$ is the transposed matrix of $\underline{q}$, and

$$F = \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{12} & a_{22} & a_{23} & a_{24} \\ a_{13} & a_{23} & a_{33} & a_{34} \\ a_{14} & a_{24} & a_{34} & a_{44} \end{vmatrix}$$

$a_{11} = h_B + 2k/\alpha^2$

$a_{12} = -k2/\alpha\beta$

$a_{13} = -(2\alpha + 1)h_B - 2k(1/\alpha - 2)/\alpha$

$a_{14} = 2\alpha h_B + 2k(1/\beta - 2)/\alpha$

$a_{22} = h_N + 2k/\beta^2$

$a_{23} = 2\beta h_N + 2k(1/\alpha - 2)/\beta$

$a_{24} = -(1 + 2\beta)h_N - 2k(1/\beta - 2)/\beta$

$a_{33} = (1 + 2\alpha)^2 h_B + 4\beta^2 h_N + 2k(1/\alpha - 2)^2$

$a_{34} = -2\alpha(1 + 2\alpha)h_B - 2\beta(1 + 2\beta)h_N - 2(1/\alpha - 2)(1/\beta - 2)k$

$a_{44} = 4\alpha^2 h_B + (1 + 2\beta)^2 h_N + 2(2 - 1/\beta)^2 k$

The kinetic energy, T, has the form:

$$\frac{2}{3}T = m_H \dot{q}_1^2 + m_H \dot{q}_2^2 + m_B \dot{q}_3^2 + m_N \dot{q}_4^2$$

$$G^{-1} = \begin{vmatrix} m_H & & & \\ & m_H & & \\ & & m_B & \\ & & & m_N \end{vmatrix}$$

The secular determinant is

$$\|F - \lambda G^{-1}\| = \begin{Vmatrix} a_{11} - m_H\lambda & a_{12} & a_{13} & a_{14} \\ a_{12} & a_{22} - m_H\lambda & a_{23} & a_{24} \\ a_{13} & a_{23} & a_{33} - m_B\lambda & a_{34} \\ a_{14} & a_{24} & a_{34} & a_{44} - m_N\lambda \end{Vmatrix} = 0.$$

$\lambda = 4\pi^2 c^2 A \nu^2 = 5.889 \times 10^{-2} \times \nu^2$,

$c = $ velocity of light,

$A = \frac{1}{16}$ of the mass of O^{16} atom,

$\nu = $ frequency of the vibration.

The numerical values of constants used in this calculation are:

r, internuclear distances between B and H atoms $= 1.20$ Å

s, internuclear distances between N and H atoms $= 1.02$ Å

R, internuclear distances between N and B atoms $= 1.44$ Å

$\alpha = r/R = 0.833$

$\beta = s/R = 0.709$

$m_H = 1.008$

$m_B = 10.820$

$m_N = 14.008$

Put these into the secular determinant;

$a_{11} = h_B + 2.880k$ $\qquad$ $a_{22} = h_N + 3.987k$

$a_{12} = -3.388k$ $\qquad$ $a_{23} = 1.416 h_N - 2.259k$

$a_{13} = -2.666 h_B + 1.920k$ $\qquad$ $a_{24} = -2.416 h_N + 1.661k$

$a_{14} = 1.666 h_B - 1.411k$

$a_{33} = 7.111 h_B + 2.005 h_N + 1.280k$

$a_{34} = -4.441 h_B + 3.421 h_N - .941k$

$a_{44} = 2.775 h_B + 5.837 h_N + .691k$

For symmetry group E'',
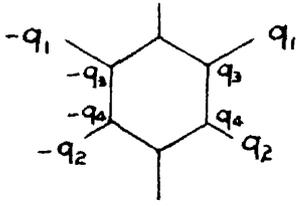
$$\theta = \frac{1}{r}(q_1 - q_3) + \frac{1}{R}(q_4 - 2q_3)$$

$$r\theta = q_1 - (1+2\alpha)q_3 + \alpha q_4 \qquad\qquad \alpha = r/R$$

$$s\mu = q_2 + \beta q_3 - (1+2\beta)q_4 \qquad\qquad \beta = s/R$$

$$c\phi_{3-4} = Rq_1/r - Rq_2/s - (R-r)q_3/r + (R-s)q_4/s$$

$$= q_1/\alpha - q_2/\beta + (1 - 1/\alpha)q_3 + (1/\beta - 1)q_4$$

$$c\phi_{0-4} = Rq_2/s - q_3 - q_4 - (R-s)q_4/s$$

$$= q_2/\beta - q_3 - q_4/\beta$$

$$c\phi_{0-3} = -q_1/\alpha + q_3/\alpha + q_4$$

$$2V = h_B\sum_2 (r\theta)^2 + h_N\sum_2 (s\mu)^2 + k\sum_6 (c\phi)^2$$

$$V = h_B\left\{q_1 - (1+2\alpha)q_3 + \alpha q_4\right\}^2 + h_N\left\{q_2 + \beta q_3 - (1+2\beta)q_4\right\}^2$$

$$+ k\left\{q_1/\alpha - q_2/\beta + (1 - 1/\alpha)q_3 - (1 - 1/\beta)q_4\right\}^2$$

$$+ k\left\{q_2/\alpha - q_3 - q_4/\beta\right\}^2 + k\left\{-q_1/\alpha + q_3/\alpha + q_4\right\}^2$$

Collect terms and put into matrix form,

$$V = 2q'Eq$$

where q is the column matrix of coordinates, q' is the transposed matrix of q, and

$$E = \begin{vmatrix} b_{11} & b_{12} & b_{13} & b_{14} \\ b_{12} & b_{22} & b_{23} & b_{24} \\ b_{13} & b_{23} & b_{33} & b_{34} \\ b_{14} & b_{24} & b_{34} & b_{44} \end{vmatrix}$$

$$b_{11} = h_B + 2k/\alpha^2$$

$$b_{12} = -k/\alpha\beta$$

$$b_{13} = -(1+2\alpha)h_B + (1 - 2/\alpha)k/\alpha$$

$$b_{14} = \alpha h_B - (2 - 1/\beta)k/\alpha$$

$$b_{22} = h_N + 2k/\beta^2$$

$$b_{23} = \beta h_N + (1/\alpha - 2)k/\beta$$

$$b_{24} = -(1+2\beta)h_N + (1 - 2/\beta)k/\beta$$

$$b_{33} = (1+2\alpha)^2 h_B + \beta^2 h_N + 2(1 - 1/\alpha + 1/\alpha^2)k$$

$$b_{34} = -\alpha(1+2\alpha)h_B - \beta(1+2\beta)h_N - (1 - 2/\alpha - 2/\beta + 1/\alpha\beta)k$$

$$b_{44} = \alpha^2 h_B + (1+2\beta)^2 h_N + 2(1 - 1/\beta + 1/\beta^2)k$$

The kinetic energy has the form:

$$\frac{2}{3}T = m_H \dot{q}_1^2 + m_H \dot{q}_2^2 + m_B \dot{q}_3^2 + m_N \dot{q}_4^2$$

$$\underline{G}^{-1} = \begin{vmatrix} m_H & & & \\ & m_H & & \\ & & m_B & \\ & & & m_N \end{vmatrix}$$

The secular determinant is

$$\| \underline{E} - \underline{G}^{-1}\lambda \| = \begin{Vmatrix} b_{11} - m_H\lambda & b_{12} & b_{13} & b_{14} \\ b_{12} & b_{22} - m_H\lambda & b_{23} & b_{24} \\ b_{13} & b_{23} & b_{33} - m_B\lambda & b_{34} \\ b_{14} & b_{24} & b_{34} & b_{44} - m_N\lambda \end{Vmatrix} = 0.$$

Put the values of α and β into it;

$$b_{11} = h_B + 2.880k$$
$$b_{12} = -1.694k$$
$$b_{13} = -2.667h_B - 1.680k$$
$$b_{14} = 0.833h_B - 0.706k$$
$$b_{22} = h_N + 3.986k$$
$$b_{23} = 0.708h_N - 1.130k$$
$$b_{24} = -2.417h_N - 2.574k$$
$$b_{33} = 7.111h_B + 0.502h_N + 2.480k$$
$$b_{34} = -2.222h_B - 1.712h_N + 2.530k$$
$$b_{44} = 0.694h_B + 5.842h_N + 3.162k$$

Note:-- If it is desired to remove the redundant coordinate, it
can be readily done by matrix transformation by use of the conditions
of conservation of linear and angular momentum for A" and B", res-
pectively. The new matrices are $\underline{L}'\underline{F}\underline{L}$ and $\underline{L}'\underline{G}^{-1}\underline{L}$, where $\underline{L}'$ is the
transposed matrix of $\underline{L}$ and

$$\underline{L} = \begin{vmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ -\dfrac{m_H}{m_N} & -\dfrac{m_H}{m_N} & -\dfrac{m_B}{m_N} & \end{vmatrix} \qquad \text{for A"},$$

$$= \begin{vmatrix} 1 & & & \\ & 1 & & \\ & & 1 & \\ -(1+\alpha)m_H/m_N & -(1+\beta)m_H/m_N & -m_B/m_N & \end{vmatrix} \qquad \text{for B"}.$$

A trial-and-error method was used to evaluate the values of the force constants. The evaluation was started with a set of arbitrarily assumed values. Using these values and one frequency of the vibrations belonging to the determinant, the value of the determinant was found, which is at first usually quite different from the correct value zero. Then two of the force constants were assumed to be correct, and the value of the third one was adjusted to make the determinant vanish.

In the next step this force constant was assumed to be correct, and another force constant was adjusted in the same fashion to fit another frequency. After three steps are completed, a new set of force constants are obtained. A second cycle of trials serves to readjust the force constants a second time. This process was repeated until a set of force constants was obtained which fit all three frequencies simultaneously, i.e., when any one of the frequencies is put into the determinant, the determinant vanishes.

Table I gives the results of this evaluation and explains the method in detail.

A knowledge of the force constants from various sources, e.g., Crawford and Edsall's calculation (5), a table of force constants of various bonds (11), etc., will give a good set of values to begin with, and thus save labor, since the process of trial and error might give divergent results if the assumed set is too far from the correct values.

With the knowledge of the nature of the vibration it is not difficult to find which frequency should be chosen to adjust a particular force constant. For example, the vibration of the frequency 1070 cm.$^{-1}$ involves mainly the N-H bending, and should be used to adjust the force constant h_N. On the other hand, after several trials it will be plain which frequency is sensitive to the value of one particular force constant. It follows that

TABLE I.* EVALUATION OF FORCE CONSTANTS FOR TRIBORINE TRIAMINE.

Symmetry group	Frequency used	$h_B \times 10^{-4}$	$h_N \times 10^{-4}$	$kh \times 10^{-4}$	Value of determinant
E"	288	2.00	2.00	0.00	1227.
				0.20	148.6
				0.30	9.99
				0.40	-102.5
	1070	2.00	2.00	0.30	44288.
			3.70		-1641.
	798	2.00	3.70	0.30	-689.
	288	2.00	3.70	0.28	1.93
	1070	2.00	3.70	0.28	649.
			3.72		-0.42
	798	2.00	3.72	0.28	-690.
		2.10			55.2
		2.09			2.38
	288	2.09	3.72	0.28	.004
	1070	2.09	3.72	0.28	-553.
			3.70		71.1
			3.71		-176.7
	798	2.09	3.70	0.28	16.4
		2.20			815.
	288	2.09	3.70	0.28	-5.33
A"	415	2.09	3.70	0.28	-448.8
				0.14	624.
				0.22	7.43
	622	2.09	3.70	0.22	1287.
		2.30			1818.
		1.54			-104.6
		1.57			45.0
	1098	1.56	3.70	0.22	1133.
			3.30		20150.
			3.72		173.9
	622	1.56	3.72	0.22	-50.2
	288	1.56	3.72	0.22	14.53

Final results:

	h_B	BRL value	h_N	BRL value	k	BRL value
A"	1.56	1.58037	3.72	3.71177	0.22	0.22285
E"	2.09	2.09651	3.70	3.70103	0.28	0.27975
Average	1.83		3.71		0.25	

* All force constants are in dyne/cm.

this frequency should be used to adjust this particular force constant.

Theoretically the value of the determinant should be zero when the correct values of the force constants are used. But it seldom becomes zero in actual calculation due to the limited number of significant figures used. Therefore the set of force constants that gives the value of the determinant closest to zero is the most suitable set.

The trial-and-error process was carried out to the second decimal place of the largest force constant in this research, since the frequencies are experimentally determined to three significant figures. The author is indebted to the Computing Division of the Ballistics Research Laboratory, Aberdeen Proving Ground, Maryland, for checking the evaluation of the force constants. Their results are included in Table I as a comparison.

Two different sets of force constants were obtained from the frequencies of symmetry groups A" and E". The average values of the constants are listed in Table III in comparison with those of benzene and ethylene. The frequencies calculated from these average values are listed in Table II.

TABLE II.

Observed frequency cm^{-1}	Calculated frequency (5) cm^{-1}	% Deviation	Calculated frequency cm^{-1} (this research)	% Deviation this research)
1098	1278	16.4	1117	1.7
622	756	21.6	661	6.3
415	403	2.9	437	5.3
1070	1086	1.5	1054	1.5
798	790	1.0	753	5.6
288	283	1.7	270	6.3
		Mean 7.5		Mean 4.5

The satisfactory agreement obtained between the calculated frequencies and the observed frequencies renders unnecessary Crawford and Edsall's assumption of interactions between hydrogen bonds attached in the meta positions. Their lack of success in predicting the frequencies of the

·out-of-plane vibrations may be laid to neglect of the influence of the hydro-

gen atoms on the twisting of the carbon-carbon bonds. When this effect is

included, as has been done in this research, the agreement between calcu-

lated and observed values is satisfactory.

TABLE III. FORCE CONSTANTS FOR TRIBORINE TRIAMINE, BENZENE, AND ETHYLENE.

Type of constant	Value
B - H bending, h_B	1.83×10^4 dyne/cm
N - H bending, h_N	3.71×10^4 dyne/cm
B - N twisting, k'	0.39×10^{-12} dyne-cm
benzene C - C twisting [3]	0.77×10^{-12} dyne-cm
ethylene C - C twisting [3]	1.7×10^{-12} dyne-cm

$$k' = kc^2$$

The value of the twisting force constant obtained by Crawford and

Edsall (5) without introduction of ϕH in the potential function corres-

ponds to 1.6×10^{-12} dyne-cm for k'. The value given here of $0.39 \times$

10^{-12} dyne-cm is more reasonable, since one would expect the ring bonds

in triborine triamine to have less resistance to twisting than those in

benzene and ethylene.

If it is assumed that k' varies linearly with double-bond character

for different bonds, the double-bond character of the B - N bond in triborine

triamine is 39/77 x 1/2 or 28 percent, taking that of benzene as 50 percent.

This assumption can be tested by calculating the double-bond character of

benzene by the use of the ethylene twisting constant. The value obtained

is 45 percent. Since the double-bond character in benzene is known to be

50 percent, the agreement is good. The double-bond character of a bond can

also be estimated by the empirical formula of Pauling (23). The B-N dis-

tance in triborine triamine has been measured in two investigations (2, 26)

by electron diffraction as $1.47 \pm 0.07A$ and $1.44 \pm 0.02A$. These values in-

-serted in the formula give 27 percent and 40 percent, respectively, for the

double-bond character of the B - N bond, and the first value is in agreement with the value given above. It appears, therefore, that the B - N bond in triborine triamine has a 28 percent double-bond character.

SYMMETRY PROPERTIES OF BENZENE

Considerations of the Raman and infrared spectra of benzene, deutero-benzenes, and substituted benzenes indicate that the benzene molecule is planar and hexagonal, with all atoms symmetrically placed. Considerable work has been done on benzene spectra. Probably the most comprehensive work is that of Ingold and coworkers (15). Other work involves fluorescence the Raman effect, and the near infrared spectrum (24, 17, 1, 7). For previous references see Herzberg (13). The point group of this model, i.e., the set of symmetry operations of the benzene molecule, is D_{6h}. This group consists of twelve classes (13, 30), namely, E or identity; C_2 rotation by π about the six-fold axis; C_3 rotation by $\pm 2\pi/3$ about the six-fold axis; C_6 rotation by $\pi/3$ about the six-fold axis; C_2' rotation by π about axes P, Q, R, as shown in the following figure; C_2'' rotation by π about axes T, U, V; i inversion through the center of symmetry; σ_h reflection through the plane of symmetry in the plane of the molecule; S_6 rotatory reflection about the six-fold axis by $\pm\pi/3$, S_3 rotatory-reflection about the six-fold axis by $\pm 2\pi/3$; σ_v'' reflection through planes D, F, G; σ_v' reflection through planes A, B, C.

If a symmetry operation is denoted by R and a normal coordinate by Q_k, there are three possibilities when a symmetry operation R is applied to Q_k:
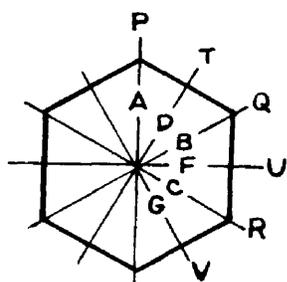
$$RQ_k \rightarrow Q_k \qquad (Q_k \text{ is symmetric to R}) \qquad (1)$$

$$RQ_k \rightarrow -Q_k \qquad (Q_k \text{ is antisymmetric to R}) \qquad (2)$$

$$RQ_k \rightarrow R_{nk}Q_n \qquad (\text{degenerate}) \qquad (3)$$

The summation is over all the Q_n with the same frequency, i.e., over all the degenerate normal vibrations in the same class. When translations and rotations are eliminated, (1), (2), and (3) give the irreducible representations of the types of symmetry allowed in the molecule. The symmetry operations allowed for benzene molecule and their characters, i.e., the sum of the diagonal coefficients R_{kk} of the irreducible representation matrices, are given in Table IV.

TABLE IV.   SYMMETRY CHARACTERS OF POINT GROUP D_{6h}

Symmetry class R =	E	C_2	C_3	C_6	C_2'	C_2''	i	σ_h	S_6	S_3	σ_v''	σ_v'
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E_{2g}	2	2	-1	-1	0	0	2	2	-1	-1	0	0
E_{1g}	2	-2	-1	1	0	0	2	-2	-1	1	0	0
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
E_{2u}	2	2	-1	-1	0	0	-2	-2	1	1	0	0
E_{1u}	2	-2	-1	1	0	0	-2	2	1	-1	0	0
h_j	1	1	2	2	3	3	1	1	2	2	3	3
x_j'	36	0	0	0	-4	0	0	12	0	0	0	4

The symbol h_j is the number of operations in each class and the character x_j' is obtained from the operations on coordinates other than normal coordinates in the same way as x_j is obtained from normal coordinates. The values for x_j' shown in Table IV were obtained by Wilson (30) from 36 external coordinates.

The number of normal vibrations in the ith class may be calculated from the following formula:

$$n_i = (1/N) \sum_j h_j x_j^{(i)} x_j'$$

where N is the total number of operations, $x_j^{(i)}$ is the value of x_j in the ith class. Applied to the benzene molecule, the result is

$$2A_{1g} + A_{2g} + 2B_{2g} + 4E_{2g} + E_{1g} + A_{2u} + 2B_{1u} + 2B_{2u} + 2E_{2u} + 3E_{1u}$$

The same result can be obtained by the method of counting the number of sets of equivalent atoms in each element of symmetry (14). This result shows there are 20 different fundamental frequencies, of which 10 are degenerate. Therefore the secular determinant may be factored by the use of symmetry into four linear factors, of which two are equal (A_{2g}, A_{2u}, $E_{1g}(2)$), six quadratic factors of which two are equal (A_{1g}, B_{2g}, B_{1u} $E_{2u}(2)$), two equal cubic factors ($E_{1u}(2)$), and two equal quartic factors ($E_{2g}(2)$). The modes of normal vibration determined from these considerations are shown in Figure 1.

The symmetry coordinates required to factor the secular determinant may be derived by the method given by Nielsen and Berryman (22). Different sets of symmetry coordinates (13,30) may be calculated. The set which was used in this research is taken from the work of Crawford and Miller and is shown in Table VII.
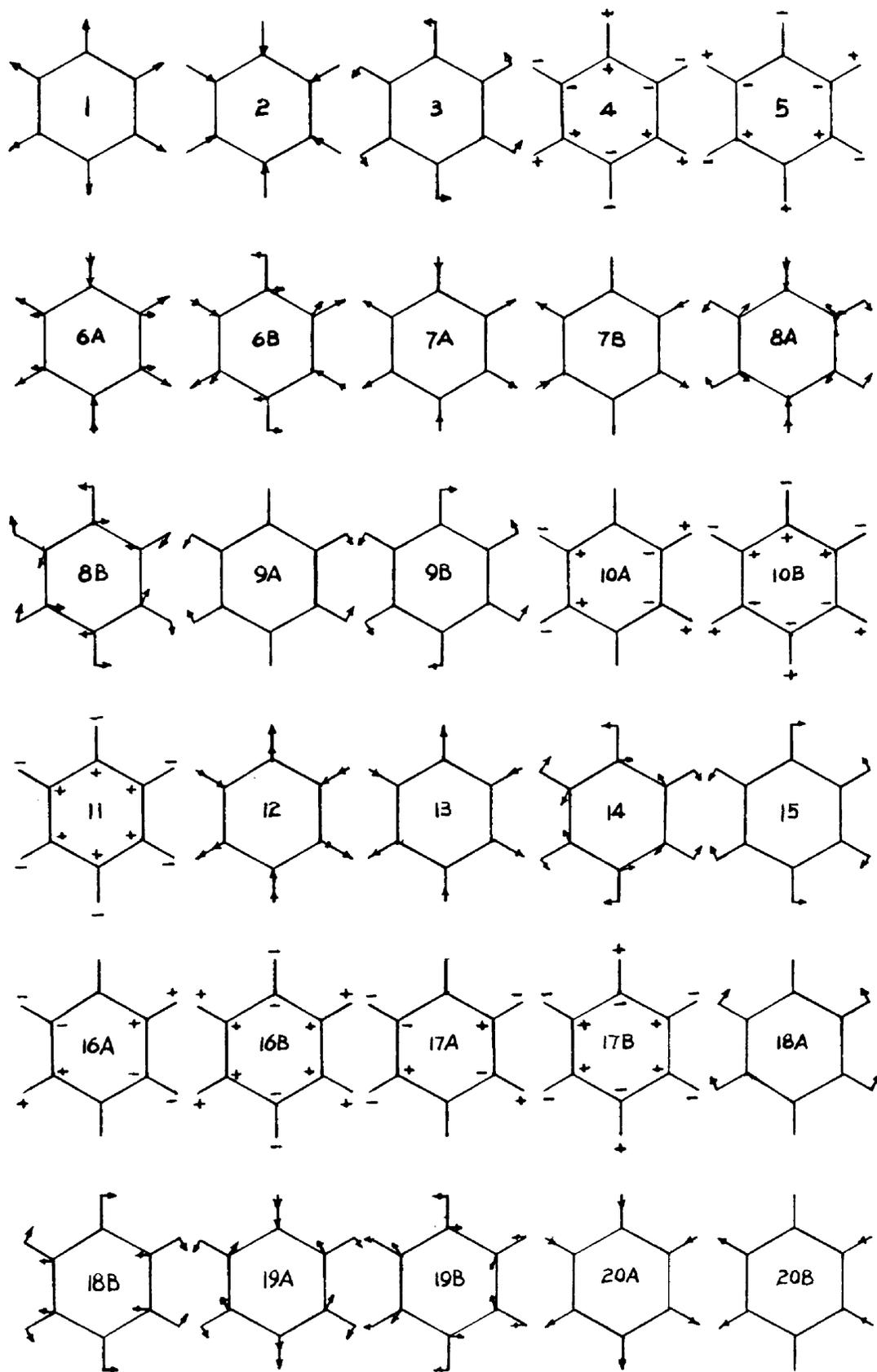
Fig. 1

Calculation of F Matrices.

Of the 30 normal modes of vibration shown in Figure 1, 21 are planar, in which all atoms move in the plane of the molecule, and 9 are out-of-plane, in which all atoms vibrate in the direction perpendicular to the plane of the molecule. These two groups of vibrations are usually treated separately. This research deals with planar vibrations.

The potential energy function was assumed as follows:

$$
\begin{aligned}
2V = &\ 2F_s' \sum_6 R_o \Delta R_i + F_s \sum_6 (\Delta R_i)^2 + 2f_s' \sum_6 r_o \Delta r_i + f_s \sum_6 (\Delta r_i)^2 \\
&+ 2F_b' \sum_6 R_o^2 \Delta \alpha_i + F_b \sum_6 (R_o \Delta \alpha_i)^2 + 2f_b' \sum_6 r_o^2 \Delta \theta_i + f_b \sum_6 (r_o \Delta \theta_i)^2 \\
&+ 2f_m' \sum_6 p_o(\Delta p_{i,+} + \Delta p_{i,-}) + f_m \sum_6 \{(\Delta p_{i,+})^2 + (\Delta p_{i,-})^2\} \\
&+ 2f_p' \sum_6 d_o \Delta d_i + f_p \sum_6 (\Delta d_i)^2 + 2F_m' \sum_6 P_o \Delta P_i + F_m \sum_6 (\Delta P_i)^2 \\
&+ F_p' \sum_6 D_o \Delta D_o + F_p \sum_6 (\Delta D_i)^2 / 2
\end{aligned}
$$

The coordinates were defined as follows, the symbols in parantheses being the corresponding force constants:

r_i (f_s', f_s), distance C_i-H_i;
R_i (F_s', F_s), distance C_i-C_{i-1};
θ_i (f_b', f_b), angle $C_{i-1}\hat{C}_i H_i$;
α_i (F_b', F_b), angle $C_{i-1}C_i C_{i+1}$;
$p_{i,\pm}$ (f_m', f_m), nonbonded distance $C_{i\pm 1}$-H_i;
d_i (f_p', f_p), nonbonded distance $H_i H_{i-1}$;
P_i (F_m', F_m), nonbonded distance C_{i-1}-C_{i+1};
D_i (F_p', F_p), nonbonded distance C_{i-1}-C_{i+2}.
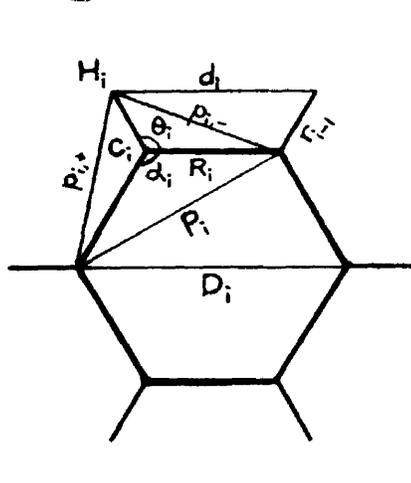
~The nonbonded distances p, d, P, and D were taken as dependent variables and expressed in terms of the independent variables r, R, Θ, and α :

$$p_0 \Delta p_{i,-} = R_0(1 + p/2)\Delta R_{i-1} + R_0(p + 1/2)\Delta r_i + \frac{\sqrt{3}}{2} R_0 r_0 \Delta \theta_i$$
$$+ \frac{1}{2p_0^2}\left\{\frac{3}{4} r_0^2 (\Delta R_{i-1})^2 + \frac{3}{4} R_0^2 (\Delta r_i)^2 - \frac{1}{2} R_0 r_0 (R_0^2 + r_0^2 + \frac{5}{2} R_0 r_0)(\Delta \theta_i)^2\right.$$
$$- \frac{3}{2} R_0 r_0 \Delta R_{i-1}\Delta r_i + \sqrt{3} r_0 (r_0^2 + \frac{1}{2} R_0 r_0)\Delta R_{i-1}\Delta \theta_i$$
$$\left. + \sqrt{3} R_0 (R_0^2 + \frac{1}{2} R_0 r_0)\Delta r_i \Delta \theta_i\right\}$$

$$P_0 \Delta P_i = \frac{R_0}{2}\left\{3\Delta R_i + 3\Delta R_{i-1} + \sqrt{3} R_0 \Delta \alpha_i\right\}$$
$$+ \frac{R_0^2}{2P_0^2}\left\{\frac{3}{4}(\Delta R_i)^2 + \frac{3}{4}(\Delta R_{i-1})^2 - \frac{9}{4}(R_0 \Delta \alpha_i)^2 - \frac{3}{2}\Delta R_i \Delta R_{i-1} + \frac{3\sqrt{3}}{2}\Delta R_i R_0 \Delta \alpha_i\right.$$
$$\left. + \frac{3\sqrt{3}}{2}\Delta R_{i-1} R_0 \Delta \alpha_i\right\}$$

$$d_0 \Delta d_i = \frac{d_0}{2}\left\{\Delta r_i + \Delta r_{i+1} + 2\Delta R_i + \sqrt{3} r_0 (-\Delta\theta_i + \Delta\theta_{i+1} - \Delta\alpha_i)\right\}$$
$$+ \frac{3}{8}(\Delta r_i)^2 + \frac{3}{8}(\Delta r_{i+1})^2 - \frac{3}{4}\Delta r_i \Delta r_{i+1} + \frac{\sqrt{3}}{4}(d_0 + R_0)(\Delta r_{i+1}\Delta\theta_{i+1} - \Delta r_{i-1}\Delta\theta_{i+1} - \Delta r_i \Delta\alpha_i)$$
$$+ \frac{\sqrt{3}}{4} r_0 (\Delta r_i \Delta\theta_{i+1} - \Delta r_{i+1}\Delta\theta_i - \Delta r_{i+1}\Delta\alpha_i) + \frac{1}{4} r_0^2 (\Delta\theta_i \Delta\theta_{i+1} + \Delta\theta_{i+1}\Delta\alpha_i)$$
$$- \frac{1}{4} r_0 (R_0 + r_0/2)\left[(\Delta\theta_i)^2 + (\Delta\theta_{i+1})^2 + (\Delta\alpha_i)^2 + 2\Delta\theta_i \Delta\alpha_i\right]$$

$$D_0 \Delta D_i = R_0 \left\{\Delta R_{i+1} + \Delta R_{i-1} + 2\Delta R_i + \sqrt{3} R_0 (\Delta\alpha_i + \Delta\alpha_{i+1})\right\}$$
$$+ \frac{3}{8}(\Delta R_{i-1})^2 + \frac{3}{8}(\Delta R_{i+1})^2 - \frac{3}{4}\Delta R_{i-1}\Delta R_{i+1}$$
$$+ \frac{3\sqrt{3}}{4} R_0 (\Delta R_{i-1}\Delta\alpha_i + \Delta R_{i+1}\Delta\alpha_{i+1}) + \frac{\sqrt{3}}{4}(\Delta R_{i-1}\Delta\alpha_{i+1} + \Delta R_{i+1}\Delta\alpha_i)$$
$$- \frac{3}{8} R_0^2\left[(\Delta\alpha_i)^2 + (\Delta\alpha_{i+1})^2\right] - \frac{1}{4} R_0^2 \Delta\alpha_i \Delta\alpha_{i+1}$$

The calculation of these expressions is carried out in Appendices I and II. When these expressions are put in, the potential energy function in matrix form is given on next page. The quantities $\underline{R}$, $\underline{r}$, $\underline{\theta}$, and $\underline{\alpha}$ are the column matrices of individual species of coordinates, e.g.,

$$\underline{R} = \begin{vmatrix} \Delta R_1 \\ \Delta R_2 \\ \Delta R_3 \\ \Delta R_4 \\ \Delta R_5 \\ \Delta R_6 \end{vmatrix}$$

E is the unit matrix and the leading rows of $\underline{M_i}$'s are given in Table V.

$$2V = 2F_s' R_o \underline{e}\,\underline{R} + 2f_s' r_o \underline{e}\,\underline{r} + 2f_b' r_o^2 \underline{e}\,\underline{\theta} + 2F_b' R_o^2 \underline{e}\,\underline{\alpha}$$

$$+ 2f_m' R_o \left\{ 2(p + \tfrac{1}{2}) \underline{e}\,\underline{r} + (2+p)\underline{e}\,\underline{R} - \tfrac{\sqrt{3}}{2} r_o \underline{e}\,\underline{\alpha} \right\}$$

$$+ f_P' d_o \left\{ 2\underline{e}\,\underline{r} + 2\underline{e}\,\underline{R} - \sqrt{3}\, r_o \underline{e}\,\underline{\alpha} \right\}$$

$$+ 3F_m' R_o \left\{ 2\underline{e}\,\underline{R} + \tfrac{1}{\sqrt{3}} R_o \underline{e}\,\underline{\alpha} \right\}$$

$$+ 2F_P' R_o \left\{ 2\underline{e}\,\underline{R} + \sqrt{3}\,R_o \underline{e}\,\underline{\alpha} \right\}$$

$$+ f_s' \underline{r}'\underline{E}\,\underline{r} + F_s \underline{R}'\underline{E}\,\underline{R} + F_b R_o^2 \underline{\alpha}'\underline{E}\,\underline{\alpha} + f_b r_o^2 \underline{\theta}'\underline{E}\,\underline{\theta}$$

$$+ \sigma f_m' \left\{ a_1 \underline{R}'\underline{E}\,\underline{R} + b_1 \underline{r}'\underline{E}\,\underline{r} + c_1 r_o^2 \underline{\theta}'\underline{E}\,\underline{\theta} + d_1 R_o^2 \underline{\alpha}'\underline{E}\,\underline{\alpha} \right.$$
$$+ 2e_1 \underline{R}'\underline{M}_8 \underline{r} + 2f_1 \underline{R}'\underline{M}_9 r_o \underline{\theta} + 2g_1 \underline{R}'\underline{E}\,\underline{\alpha}\, R_o$$
$$\left. + 2k_1 \underline{r}'\underline{E}\, R_o \underline{\alpha} + 2p_1 r_o \underline{\theta}'\underline{E}\, R_o \underline{\alpha} \right\}$$

$$+ \sigma f_m \left\{ a_2 \underline{R}'\underline{E}\,\underline{R} + b_2 \underline{r}'\underline{E}\,\underline{r} + c_2 r_o^2 \underline{\theta}'\underline{E}\,\underline{\theta} + d_2 R_o^2 \underline{\alpha}'\underline{E}\,\underline{\alpha} \right.$$
$$+ 2e_2 \underline{R}'\underline{M}_8 \underline{r} + 2f_2 r_o \underline{R}'\underline{M}_9 \underline{\theta} + 2g_2 R_o \underline{R}'\underline{E}\,\underline{\alpha}$$
$$\left. + 2k_2 R_o \underline{r}'\underline{E}\,\underline{\alpha} + 2p_2 R_o r_o \underline{\theta}'\underline{E}\,\underline{\alpha} \right\}$$

$$+ f_P' \left\{ b_3 \underline{r}'\underline{M}_2 \underline{r} + c_3 r_o^2 \underline{\theta}'\underline{M}_7 \underline{\theta} + d_3 R_o^2 \underline{\alpha}'\underline{E}\,\underline{\alpha} \right.$$
$$\left. + 2h_3 r_o \underline{r}'\underline{M}_{10}\underline{\theta} + 2k_3 R_o \underline{r}'\underline{M}_{12}\underline{\alpha} + 2p_3 R_o r_o \underline{\theta}'\underline{M}_{13}\underline{\alpha} \right\}$$

$$+ f_P \left\{ a_4 \underline{R}'\underline{E}\,\underline{R} + b_4 \underline{r}'\underline{M}_1 \underline{r} + c_4 r_o^2 \underline{\theta}'\underline{M}_2 \underline{\theta} + d_4 R_o^2 \underline{\alpha}'\underline{E}\,\underline{\alpha} \right.$$
$$+ 2e_4 \underline{R}'\underline{M}_8 \underline{r} + 2f_4 r_o \underline{R}'\underline{M}_9 \underline{\theta} + 2g_4 R_o \underline{R}'\underline{E}\,\underline{\alpha}$$
$$\left. + 2h_4 r_o \underline{r}'\underline{M}_{10}\underline{\theta} + 2k_4 R_o \underline{r}'\underline{M}_8'\underline{\alpha} + 2p_4 R_o r_o \underline{\theta}'\underline{M}_9'\underline{\alpha} \right\}$$

$$+ \epsilon F_m' \left\{ a_5 \underline{R}'\underline{M}_2 \underline{R} + d_5 R_o^2 \underline{\alpha}'\underline{E}\,\underline{\alpha} + 2g_5 R_o \underline{R}'\underline{M}_8 \underline{\alpha} \right\}$$

$$+ \epsilon F_m \left\{ a_6 \underline{R}'\underline{M}_1 \underline{R} + d_6 R_o^2 \underline{\alpha}'\underline{E}\,\underline{\alpha} + 2g_6 R_o \underline{R}'\underline{M}_8 \underline{\alpha} \right\}$$

$$+ F_P' \left\{ a_7 \underline{R}'\underline{M}_6 \underline{R} + d_7 R_o^2 \underline{\alpha}'\underline{M}_3 \underline{\alpha} + 2g_7 R_o \underline{R}'\underline{M}_{11}\underline{\alpha} \right\}$$

$$+ F_P \left\{ a_8 \underline{R}'\underline{M}_5 \underline{R} + d_8 R_o^2 \underline{\alpha}'\underline{M}_1 \underline{\alpha} + 2g_8 R_o \underline{R}'\underline{M}_{11}\underline{\alpha} \right\} \qquad (II)$$

$$\underline{e} = | 1, 1, 1, 1, 1, 1 |$$
$$\sigma = R_o^2 / p_o^2 = (1 + p + p^2)^{-1} = 0.4200$$
$$\epsilon = R_o^2 / P_o^2 = 1/3$$

TABLE V. Leading rows of submatrices $\underline{M}$.

$M_1 = (1, 1/2, -, -, -, 1/2)$

$M_2 = (1, -1/2, -, -, -, -1/2)$

$M_3 = (3, 1/2, -, -, -, 1/2)$

$M_4 = (3, 1, -, -, -, 1)$

$M_5 = (3, 2, 1/2, -, 1/2, 2)$

$M_6 = (1, -, -1/2, -, -1/2, -)$

$M_7 = (2+\rho, -\rho/2, -, -, -, -\rho/2)$

$M_8 = (1, 1, -, -, -, -)$

$M_9 = (1, -1, -, -, -, -)$

$M_{10} = (-, 1, -, -, -, -1)$

$M_{11} = (3, 3, 1, -, -, 1)$

$M_{12} = (2+\rho, -, -, -, -, \rho)$

$M_{13} = (2+\rho, -, -, -, -, -\rho)$

$M_{14} = (2+\rho, \rho/2, -, -, -, \rho/2)$

The rest of the matrices can be readily obtained by permuting the members in the leading rows. For example, $\underline{M}_8$ is shown in Table V as $\underline{M}_8 =$ (1, 1, -, -, -, -) which means

$$\underline{M}_8 = \begin{vmatrix} 1 & 1 & & & & \\ & 1 & 1 & & & \\ & & 1 & 1 & & \\ & & & 1 & 1 & \\ & & & & 1 & 1 \\ 1 & & & & & 1 \end{vmatrix} .$$

The geometrical coefficients a, b, c, ...s are given in Table VI. It may be noted here that in the summation

$$\sum_6 (\Delta R_i + \Delta R_{i-1} + \Delta R_{i+1}) = \sum_6 3\Delta R_i$$

$$\sum_6 \left\{ (\Delta R_i)^2 + (\Delta R_{i-1})^2 + (\Delta R_{i+1})^2 \right\} = \sum_6 3(\Delta R_i)^2$$

$$\sum_6 \Delta R_i \Delta R_{i-1} = \sum_6 \Delta R_i \Delta R_{i+1} \neq \sum_6 \Delta R_{i-1} \Delta R_{i+1}.$$

By assumption of this force field the coefficients of the linear terms, which represent the equilibrium conditions, must vanish. There-fore,

$$F_s' + (2+\rho)f_m' + (1+\rho)f_p' + 3F_m' + 2F_p' = 0$$

$$\rho f_s' + (2\rho+1)f_m' + (1+\rho)f_p' = 0 \tag{III}$$

$$f_b' = 0 \qquad \rho = r_o/R_o$$

Thus, Equation (II) has the following form, after collecting terms and simplifying:

$$2V = \underline{R}'\left\{\left[F_s + \sigma(a_1 f_m' + a_2 f_m)\right]\underline{E} + \frac{a_5}{3}F_m'\underline{M}_2 + \frac{a_6}{3}F_m\underline{M}_1 \right.$$
$$\left. + a_7 F_p'\underline{M}_6 + a_8 F_p\underline{M}_5\right\}\underline{R}$$
$$+ \underline{r}'\left\{\left[f_s + \sigma b_1 f_m' + \sigma b_2 f_m\right]\underline{E} + b_3 f_p'\underline{M}_2 + b_4 f_p\underline{M}_1\right\}\underline{r}$$
$$+ r_0\underline{\theta}'\left\{\left[f_b + \sigma c_1 f_m' + \sigma c_2 f_m\right]\underline{E} + c_3 f_p'\underline{M}_7 + c_4 f_p\underline{M}_2\right\}r_0\underline{\theta}$$
$$+ R_0\underline{\alpha}'\left\{\left[F_b + \sigma d_1 f_m' + \sigma d_2 f_m\right]\underline{E} + \left[d_3 f_p' + d_4 f_p + \frac{d_5}{3}F_m' + \frac{d_6}{3}F_m\right]\underline{E}\right.$$
$$\left. + d_7 F_p'\underline{M}_3 + d_8 F_p\underline{M}_1\right\}R_0\underline{\alpha}$$
$$+ 2\underline{R}'\left\{\sigma e_1 f_m' + \sigma e_2 f_m + e_4 f_p\right\}\underline{M}_8\,\underline{r}$$
$$+ 2\underline{R}'\left\{\sigma f_1 f_m' + \sigma f_2 f_m + f_4 f_p\right\}\underline{M}_9 r_0\underline{\theta}$$
$$+ 2\underline{R}'\left\{\left[\sigma g_1 f_m' + \sigma g_2 f_m + g_4 f_p\right]\underline{E} + \frac{1}{3}\left[g_5 F_m' + g_6 F_m\right]\underline{M}_8\right.$$
$$\left. + \left[g_7 F_p' + g_8 F_p\right]\underline{M}_{11}\right\}R_0\underline{\alpha}$$
$$+ 2\underline{r}'\left\{h_3 f_p' + h_4 f_p\right\}\underline{M}_{10} r_0\underline{\theta}$$
$$+ 2\underline{r}'\left\{\left[\sigma k_1 f_m' + \sigma k_2 f_m\right]\underline{E} + k_3 f_p'\underline{M}_{12} + k_4 f_p\underline{M}_8'\right\}R_0\underline{\alpha}$$
$$+ 2 r_0\underline{\theta}'\left\{\left[\sigma p_1 f_m' + \sigma p_2 f_m\right]\underline{E} + p_3 f_p'\underline{M}_{13} + p_4 f_p\underline{M}_9'\right\}R_0\underline{\alpha} \qquad (IV)$$

Crawford and Miller define the angle for C-H bending as the angle between C-H bond and the bisector of the C-C-C angle, which is different from the angle θ as shown in Figure 2.
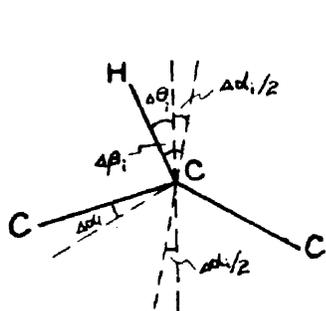
$$\Delta\theta_i = \Delta\beta_i - \Delta\alpha_i/2$$
$$r_0\Delta\theta_i = r_0\Delta\beta - \frac{r_0}{2}R_0\Delta\alpha_i$$
$$r_0\underline{\theta} = \underline{E}\,\beta\,r_0 - \frac{r_0}{2}R_0\underline{E}\,\underline{\alpha}$$

In order to utilize their symmetry coordinates, it is necessary to change θ into β. If the potential matrix is divided into submatrices, $\underline{A}$, $\underline{B}$, $\underline{C}$, ...$\underline{P}$,

$$2V = \left| \underline{R}, \; \underline{r}, \; \underline{\theta}, \; \underline{\alpha}' \right| \left\| \begin{matrix} \underline{A} & \underline{M} & \underline{F} & \underline{G} \\ \underline{M}' & \underline{B} & \underline{H} & \underline{K} \\ \underline{F}' & \underline{H}' & \underline{C} & \underline{P} \\ \underline{G}' & \underline{K}' & \underline{P}' & \underline{D} \end{matrix} \right\| \left\| \begin{matrix} \underline{R} \\ \underline{r} \\ \underline{\theta} \\ \underline{\alpha} \end{matrix} \right\|$$

$$= \left| \underline{R}', \; \underline{r}', \; \underline{\beta}', \; \underline{\alpha}' \right| \left\| \begin{matrix} \underline{E} & & & \\ & \underline{E} & & \\ & & \underline{E} & \\ & & -\tfrac{\ell}{2}\underline{E} & \underline{E} \end{matrix} \right\| \left\| \begin{matrix} \underline{A} & \underline{M} & \underline{F} & \underline{G} \\ \underline{M}' & \underline{B} & \underline{H} & \underline{K} \\ \underline{F}' & \underline{H}' & \underline{C} & \underline{P} \\ \underline{G}' & \underline{K}' & \underline{P}' & \underline{D} \end{matrix} \right\| \left\| \begin{matrix} \underline{E} & & & \\ & \underline{E} & & \\ & & \underline{E} & -\tfrac{\ell}{2}\underline{E} \\ & & & \underline{E} \end{matrix} \right\| \left\| \begin{matrix} \underline{R} \\ \underline{r} \\ \underline{\beta} \\ \underline{\alpha} \end{matrix} \right\|$$

$$2V = \left| \underline{R}', \; \underline{r}', \; \underline{\beta}', \; \underline{\alpha}' \right| \left\| \begin{matrix} \underline{A} & \underline{M} & \underline{F} & \underline{G}^* \\ \underline{M}' & \underline{B} & \underline{H} & \underline{K}^* \\ \underline{F}' & \underline{H}' & \underline{C} & \underline{P}^* \\ \underline{G}^* & \underline{K}^* & \underline{P}^{*\,'} & \underline{D}^* \end{matrix} \right\| \left\| \begin{matrix} \underline{R} \\ \underline{r} \\ \underline{\beta} \\ \underline{\alpha} \end{matrix} \right\|$$

$$\underline{G}^* = \underline{G} - \tfrac{\ell}{2}\underline{E}$$
$$= \left[\tfrac{\sigma}{2} g_1 f_m' + \tfrac{\sigma}{2} g_2 f_m + \tfrac{1}{2} g_4 f_p + g_5 F_m' + \tfrac{1}{3} g_6 F_m \right] \underline{M}_8 + \left[g_7 F_p' + g_8 F_p \right] \underline{M}_{11}$$

$$\underline{K}^* = \underline{K} - \tfrac{\ell}{2}\underline{H}$$
$$= (\sigma k_1 f_m' + \sigma k_2 f_m) \underline{E} + k_3 f_p' \underline{M}_{14} + k_4 f_p \underline{M}_1$$

$$\underline{P}^* = \underline{P} - \tfrac{\ell}{2}\underline{C}$$
$$= -\tfrac{\ell}{2} f_b \underline{E} - \tfrac{\ell}{8} f_p' \underline{M}_{10} + \tfrac{1}{2} p_4 f_p \underline{M}_{10}$$

$$\underline{D}^* = \underline{D} + \tfrac{\ell^2}{4}\underline{C} - \tfrac{\ell}{2}\underline{P} - \tfrac{\ell}{2}\underline{P}'$$
$$= \left[F_b + \tfrac{\ell^2}{4} f_b + \tfrac{d_5}{3} F_m' + \tfrac{1}{3} d_6 F_m + \tfrac{1}{2}\sigma d_1 f_m' + \tfrac{1}{2} d_2 f_m \right] \underline{E}$$
$$- \tfrac{\ell}{8} f_p' \underline{M}_7 + \tfrac{1}{2} d_4 f_p \underline{M}_1 + d_7 F_p' \underline{M}_3 + d_8 F_p \underline{M}_1$$

Therefore, the final form of potential energy function in terms of β is:

$$2V = \underline{R}'\{[F_s + \sigma a_1 f_m' + \sigma a_2 f_m + a_4 f_p]\underline{E} + \tfrac{1}{3}a_5 F_m'\underline{M}_2 + \tfrac{1}{3}a_6 F_m\underline{M}_1$$

$$+ a_7 F_p'\underline{M}_6 + a_8 F_p\underline{M}_5\}\underline{R}$$

$$+\underline{r}'\{[f_s + \sigma b_1 f_m' + \sigma b_2 f_m]\underline{E} + b_3 f_p'\underline{M}_2 + b_4 f_p\underline{M}_1\}\underline{r}$$

$$+r_0\underline{\beta}'\{[f_b + \sigma c_1 f_m' + \sigma c_2 f_m]\underline{E} + c_3 f_p'\underline{M}_7 + c_4 f_p\underline{M}_2\}r_0\underline{\beta}$$

$$+R_0\underline{\alpha}'\{[F_b + \tfrac{\beta^2}{4}f_b + \tfrac{\sigma}{2}d_1 f_m' + \tfrac{\sigma}{2}d_2 f_m + \tfrac{1}{3}d_5 F_m' + \tfrac{1}{3}d_6 F_m]\underline{E}$$

$$- \tfrac{\beta}{8}f_p'\underline{M}_7 + \tfrac{1}{2}d_4 f_p\underline{M}_1 + d_7 F_p'\underline{M}_3 + d_8 F_p\underline{M}_1\}R_0\underline{\alpha}$$

$$+2\underline{R}'\{\sigma e_1 f_m' + \sigma e_2 f_m + e_4 f_p\}\underline{M}_8\underline{r}$$

$$+2\underline{R}'\{\sigma f_1 f_m' + \sigma f_2 f_m + f_4 f_p\}\underline{M}_9 r_0\underline{\beta}$$

$$+2\underline{R}'\{[\tfrac{\sigma}{2}g_1 f_m' + \tfrac{\sigma}{2}g_2 f_m + \tfrac{1}{2}g_4 f_p + \tfrac{1}{3}g_5 F_m' + \tfrac{1}{3}g_6 F]\underline{M}_8$$

$$+ [g_7 F_p' + g_8 F_p]\underline{M}_{11}\}R_0\underline{\alpha}$$

$$+2\underline{r}'\{h_3 f_p' + h_4 f_p\}\underline{M}_{10} r_0\underline{\beta}$$

$$+2\underline{r}'\{[\sigma k_1 f_m' + \sigma k_2 f_m]\underline{E} + k_3 f_p'\underline{M}_{14} + k_4 f_p\underline{M}_1\}R_0\underline{\alpha}$$

$$+2r_0\underline{\beta}'\{-\tfrac{\beta}{2}f_b\underline{E} - \tfrac{\beta}{8}f_p'\underline{M}_{10} + \tfrac{1}{2}P_4 f_p\underline{M}_{10}\}R_0\underline{\alpha} \qquad (V)$$

The set of symmetry coordinates used to factor the potential matrix is listed in Table VII, which has the characteristic that each symmetry coordinate involves only one internal coordinate. Hence, in each row of the transformation matrix only six members are nonvanishing and the rest are null. From the fundamental principal of matrix operation, in the operation $\underline{F}$ = $\underline{S}\ \underline{V}\ \underline{S}'$, $F_{ij} = \sum_m \sum_n S_{im} V_{mn} S_{jn}$. Since part of row $\underline{S}_i$ and column $\underline{S}_j$ are null, one may ignore the corresponding part of matrix $\underline{V}$. Thus, the operation of premultiplication by a matrix 1x24 and postmultiplication by a matrix 24x1 of a matrix 24x24 is simplified to an operation of premultiplication by a matrix 1x6 and postmultiplication by a matrix 6x1 of a matrix 6x6. For example, the internal coordinate involved in the symmetry coordinate S_1 is $\underline{R}$. Then, $F_{11} = \sum_{24} \sum_{24} S_{1m} V_{mn} S_{1n} = \sum_6 \sum_6 S_{1R} V_{RR} S_{1R}$. So in the calculation of F_{11}, the only part concerned is the first term of Equation V.

The factorization is further simplified by another principle of matrix operation. Since $\underline{S}_i (\underline{M}_i + \underline{M}_j)\ \underline{S}_j' = \underline{S}_i \underline{M}_i \underline{S}_j' + \underline{S}_i \underline{M}_j \underline{S}_j'$, each component matrix in individual term of Equation V can be treated separately. For example, to find F_{11} one may calculate $\underline{S}_1\ \underline{E}\ \underline{S}_1'$, $\underline{S}_1\ \underline{M}_1\ \underline{S}_1'$, $\underline{S}_1\ \underline{M}_2\ \underline{S}_1'$, $\underline{S}_1\ \underline{M}_5\ \underline{S}_1'$, and $\underline{S}_1\ \underline{M}_6\ \underline{S}_1'$ separately. The calculation was carried out and the results are listed in the columns $\underline{S}_i \underline{M}\ \underline{S}_j'$ under their corresponding force constant symbols. Each of these products multiplied by its corresponding geometrical coefficient contributes one term to the expression for F_{11}.

$$\therefore \quad F_{1,1} = [F_S + \sigma a_1 f_m' + \sigma a_2 f_m + a_4 f_p] \underline{S}_1 \underline{E} \underline{S}_1'$$
$$+ \tfrac{1}{3} a_5 F_m' \underline{S}_1 \underline{M}_2 \underline{S}_1' + \tfrac{1}{3} a_6 F_m \underline{S}_1 \underline{M}_1 \underline{S}_1'$$
$$+ a_7 F_p' \underline{S}_1 \underline{M}_6 \underline{S}_1' + a_8 F_p \underline{S}_1 \underline{M}_5 \underline{S}_1'$$

The coefficients for individual force constants are listed along under SCGC, symmetry coordinate geometrical coefficient, in Table VIII.

Among the 23 symmetry coordinates used there are two redundant coordinates which represent rotation. These redundant coordinates were eliminated

by another transformation operation. The transformation matrix L has the form

$$\begin{vmatrix} 1 & & \\ & 1/\sqrt{2} & 1/\sqrt{2} \\ & 1 & \\ & -1/\sqrt{2} & 1/\sqrt{2} \end{vmatrix}$$

and

$$L'E_{2u}L = \begin{vmatrix} 1 & & & \\ & 1/\sqrt{2} & & -1/\sqrt{2} \\ & & 1 & \\ & 1/\sqrt{2} & & 1/\sqrt{2} \end{vmatrix} \begin{vmatrix} c & f & h & p \\ f & a & e & g \\ h & e & b & k \\ p & g & k & d \end{vmatrix} \begin{vmatrix} 1 & & & \\ & 1/\sqrt{2} & & 1/\sqrt{2} \\ & & 1 & \\ & -1/\sqrt{2} & & 1/\sqrt{2} \end{vmatrix}$$

$$= \begin{vmatrix} c & (f-p)/\sqrt{2} & h & (f+p)/\sqrt{2} \\ (f-p)/\sqrt{2} & (a-2g+d)/2 & (e-k)/\sqrt{2} & (a-d)/\sqrt{2} \\ h & (e-k)/\sqrt{2} & b & (e+k)/\sqrt{2} \\ (f+p)/\sqrt{2} & (a-d)/\sqrt{2} & (e+k)/\sqrt{2} & (a+2g+d)/2 \end{vmatrix}$$

$F_{i,j}$	F_s	f_s	F_b	f_b	f'_m	f_m
18,18				1	σc_1	σc_2
18,19					$\sigma f_1/\sqrt{2}$	$\sigma f_2/\sqrt{2}$
18,20						
19,19	$1/2$		$1/2$	$p^2/8$	A^*	B^*
19,20					$\sqrt{\tfrac{3}{8}}\,\sigma(1-p)$	$\sqrt{\tfrac{3}{2}}\sigma(p+\tfrac{1}{2})(1+p)$
20,20		1			σb_1	σb_2

$F_{i,j}$	f'_p	f_p	F'_m	F_m	F'_p	F_p
18,18	$c_3(2+p/2)$	$c_4/2$				
18,19	$\sqrt{3}p/8\sqrt{2}$	$\frac{f_4}{\sqrt{2}}-\sqrt{\tfrac{3}{8}}p_4$				
18,20	$-\sqrt{3}h_3$	$-\sqrt{3}h_4$				
19,19	$-\tfrac{p}{8}(1+p/4)$	$(1+3p/4)/2$	-1	$1/2$	-1	0
19,20	$-\tfrac{1}{\sqrt{2}}(2+\tfrac{3}{2}p)k_3$	$\sqrt{\tfrac{3}{8}}(1+3p/4)$				
20,20	$b_3/2$	$3b_4/2$				

$$^* \quad A = \tfrac{\sigma p}{16}(10p^2+13p+2) \qquad B = \tfrac{\sigma}{16}(16+28p+13p^2)$$

TABLE VI.   Geometrical Coefficients.

	f'_m 1	f_m 2	f'_p 3	f_p 4	F'_m 5	F_m 6	F'_p 7	F_p 8
a	$\frac{3}{2}\rho^2$ .9056	$2(1+\rho/2)^2$ 3.8558		1	3/2	9/2	3/4	1/2
b	3/2	$2(\rho+1/2)^2$ 3.2614	3/2	1/2	-9/4	3/4		
c	$-\frac{2}{3}(1+\rho/2)(\rho+1/2)$ -4.5640	3/2	$-1/2\rho$ -.6435	3/2	$3\sqrt{3}/4$	$3\sqrt{3}/4$		
d	$-\rho(1+\rho/2)(\rho+1/2)$ -1.3777	$3\rho^2/4$ .4528	$-\frac{\rho}{2}(1+\rho/2)$ -.5394	$3\rho^2/4$ .4528	-9/4	3/4	-1/4	3/2
e	$-3\rho/4$ -.5828	$(\rho+1/2)(\rho/2+1)$ 1.7731		1/2				
f	$-\frac{\sqrt{3}}{2}\rho(\rho+1/2)$ -.8593	$-\frac{\sqrt{3}}{2}(1+\rho/2)$ -1.2024		$-\sqrt{3}/2$				
g	$-\frac{\sqrt{3}}{2}\rho^2(\rho+1/2)$ -.6677	$-\frac{\sqrt{3}}{2}\rho(1+\rho/2)$ -.9343		$-\sqrt{3}\rho/2$ -.6729	$3\sqrt{3}/4$	$3\sqrt{3}/4$	$\sqrt{3}/8$	$\sqrt{3}/4$
h			$\sqrt{3}/4$	$\sqrt{3}/4$				
k	$-\frac{\sqrt{3}}{2}(1+\rho/2)$ -1.2024	$-\frac{\sqrt{3}}{2}\rho(\rho+1/2)$ -.8593	$-\sqrt{3}/4$	$-\sqrt{3}\rho/4$ -.3364				
p	$-(1+\rho/2)(\rho+1/2)$ -1.7731	$3\rho/4$ .5828	$-1/4$	$3\rho/4$ .5828				

TABLE VII.   Symmetry Coordinates of Benzene.

Class	Symmetry coordinate	Nonvanishing members of transformation matrix						Normalizing factor	Internal coordinates
A_{1g}	S_1	1	1	1	1	1	1	$6^{-1/2}$	$\underline{R}$
	S_2	1	1	1	1	1	1	$6^{-1/2}$	$\underline{r}$
A_{2g}	S_3	1	1	1	1	1	1	$6^{-1/2}$	$r_0\underline{\beta}$
B_{1u}	S_{12}	-1	1	-1	1	-1	1	$6^{-1/2}$	$R_0\underline{\alpha}$
	S_{13}	-1	1	-1	1	-1	1	$6^{-1/2}$	$\underline{r}$
B_{2u}	S_{14}	-1	1	-1	1	-1	1	$6^{-1/2}$	$\underline{R}$
	S_{15}	-1	1	-1	1	-1	1	$6^{-1/2}$	$r_0\underline{\beta}$
E_{1ga}	S_{6a}	-2	1	1	-2	1	1	$12^{-1/2}$	$R_0\underline{\alpha}$
	S_{7a}	-2	1	1	-2	1	1	$12^{-1/2}$	$\underline{r}$
	S_{8a}	-1	2	-1	-1	2	-1	$12^{-1/2}$	$\underline{R}$
	S_{9a}	0	-1	1	0	-1	1	$1/2$	$r_0\underline{\beta}$
E_{1gb}	S_{6b}	0	-1	1	0	-1	1	$1/2$	$R_0\underline{\alpha}$
	S_{7b}	0	-1	1	0	-1	1	$1/2$	$\underline{r}$
	S_{8b}	-1	0	1	-1	0	1	$1/2$	$\underline{R}$
	S_{9b}	2	-1	-1	2	-1	-1	$12^{-1/2}$	$r_0\underline{\beta}$
E_{2ua}	S_{18a}	0	1	1	0	-1	-1	$1/2$	$r_0\underline{\beta}$
	S_{19a}	-1	0	1	1	0	-1	$1/2$	$\underline{R}$
	S_{20a}	-2	-1	1	2	1	-1	$12^{-1/2}$	$\underline{r}$
	S_{ra}	-2	-1	1	2	1	-1	$12^{-1/2}$	$R_0\underline{\alpha}$
E_{2ub}	S_{18b}	2	1	-1	-2	-1	1	$12^{-1/2}$	$r_0\underline{\beta}$
	S_{19b}	1	2	1	-1	-2	-1	$12^{-1/2}$	$\underline{R}$
	S_{20b}	0	1	1	0	-1	-1	$1/2$	$\underline{r}$
	S_{rb}	0	1	1	0	-1	-1	$1/2$	$R_0\underline{\alpha}$

Example: $S_1 = (1, 1, 1, 1, 1, 1)\underline{R}$

TABLE VIII. Members of F Matrix.

Class	F_{ij}	Internal coordinates involved	F_s S_iMS_j'	F_s SCGC	f_s S_iMS_j'	f_s SCGC	F_b S_iMS_j'	F_b SCGC	f_b S_iMS_j'	f_b SCGC	f_m' S_iMS_j'	f_m' SCGC	f_m S_iMS_j'	f_m SCGC	f_P' S_iMS_j'	f_P' SCGC	f_P S_iMS_j'	f_P SCGC	F_m' S_iMS_j'	F_m' SCGC	F_m S_iMS_j'	F_m SCGC	F_P' S_iMS_j'	F_P' SCGC	F_P S_iMS_j'	F_P SCGC	F_{ij}	Class
A_{1g}	$F_{1,1}$	RR	1	1							1	σa_1	1	σa_2			1	a_4	0	—	2	$2a_6/3$	0	—	8	$8a_8$	$F_{1,1}$	A_{1g}
	$F_{1,2}$	Rr									2	$2\sigma e_1$	2	$2\sigma e_2$			2	$2e_4$									$F_{1,2}$	
	$F_{2,2}$	rr			1	1					1	σb_1	1	σb_2	0	—	2	$2b_4$									$F_{2,2}$	
A_{2g}	$F_{3,3}$	$\beta\beta$					1	1			1	σc_1	1	σc_2	2	$2C_3$	0	—									$F_{3,3}$	A_{2g}
B_{1u}	$F_{12,12}$	$\alpha\alpha$					1	1	1	$\rho^2/4$	1	$\sigma d_1/2$	1	$\sigma d_2/2$	$2(1+\rho)$	$-\frac{\rho}{\sqrt6}(1+\rho)$	0	—	1	$d_5/3$	1	$d_6/3$	2	$2d_7$	0	—	$F_{12,12}$	B_{1u}
	$F_{12,13}$	αr			1	1					1	σk_1	1	σk_2	2	$2k_3$	0	—									$F_{12,13}$	
	$F_{13,13}$	rr			1	1					1	σb_1	1	σb_2	2	$2b_3$	0	—									$F_{13,13}$	
B_{2u}	$F_{14,14}$	RR	1	1							1	σa_1	1	σa_2			1	a_4	2	$2a_5/3$	0	—	0	—	0	—	$F_{14,14}$	B_{2u}
	$F_{14,15}$	$R\beta$									2	$2\sigma f_1$	2	$2\sigma f_2$			2	$2f_4$									$F_{14,15}$	
	$F_{15,15}$	$\beta\beta$							1	1	1	σc_1	1	σc_2	$2(1+\rho)$	$2(1+\rho)C_3$	2	$2C_4$									$F_{15,15}$	
E_{1g}	$F_{6,6}$	$\alpha\alpha$							1	$\rho^2/4$	1	$\sigma d_1/2$	1	$\sigma d_2/2$	$2+\frac23\rho$	$-\frac{\rho}{6}(2+\frac23\rho)$	1/2	$d_4/4$	1	$d_5/3$	1	$d_6/3$	5/2	$5d_7/2$	1/2	$d_8/2$	$F_{6,6}$	E_{1g}
	$F_{6,7}$	αr									1	σk_1	1	σk_2	$2+\frac\rho2$	$(2+\frac\rho6)k_3$	1/2	$k_4/2$									$F_{6,7}$	
	$F_{6,8}$	αR									1	$\sigma g_1/2$	1	$\sigma g_2/2$			1	$g_4/2$	1	$g_5/3$	1	$g_6/3$	1	g_7	1	g_8	$F_{6,8}$	
	$F_{6,9}$	$\alpha\beta$							0	—					$-\sqrt3$	$\sqrt3\rho/8$	$-\sqrt3$	$-\sqrt3 p_4/2$									$F_{6,9}$	
	$F_{7,7}$	rr			1	1					1	σb_1	1	σb_2	3/2	$3b_3/2$	1/2	$b_4/2$									$F_{7,7}$	
	$F_{7,8}$	rR									1	σe_1	1	σe_2			1	e_4									$F_{7,8}$	
	$F_{7,9}$	$r\beta$													$\sqrt3$	$\sqrt3 h_3$	$-\sqrt3$	$\sqrt3 h_4$									$F_{7,9}$	
	$F_{8,8}$	RR	1	1							1	σa_1	1	σa_2			1	a_4	3/2	$a_5/2$	1/2	$a_6/6$	3/2	$3a_7/2$	1/2	$a_8/2$	$F_{8,8}$	
	$F_{8,9}$	$R\beta$									$-\sqrt3$	$-\sqrt3\sigma f_1$	$-\sqrt3$	$-\sqrt3\sigma f_2$			$-\sqrt3$	$-\sqrt3 f_4$									$F_{8,9}$	
	$F_{9,9}$	$\beta\beta$							1	1	1	σc_1	1	σc_2	$2+\frac32\rho$	$(2+\frac32\rho)C_3$	3/2	$3C_4/2$									$F_{9,9}$	
E_{2u}	$F_{18,18}$	$\beta\beta$							1	1	1	σc_1	1	σc_2	$2+\frac\rho2$	$(2+\frac\rho6)C_3$	1/2	$C_4/2$									$F_{18,18}$	E_{2u}
	$F_{18,19}$	βR									1	σf_1	1	σf_2			1	f_4									$F_{18,19}$	
	$F_{18,20}$	βr													$-\sqrt3$	$-\sqrt3 h_3$	$-\sqrt3$	$-\sqrt3 h_4$									$F_{18,20}$	
	$F_{18,r}$	$\beta\alpha$							0	—					$\sqrt3$	$-\sqrt3\rho/8$	$\sqrt3$	$\sqrt3 p_4/2$									$F_{18,r}$	
	$F_{19,19}$	RR	1	1							1	σa_1	1	σa_2			1	a_4	1/2	$a_5/6$	3/2	$a_6/2$	3/2	$3a_7/2$	9/2	$9a_8/2$	$F_{19,19}$	
	$F_{19,20}$	Rr									$\sqrt3$	$\sqrt3\sigma e_1$	$\sqrt3$	$\sqrt3\sigma e_2$			$\sqrt3$	$\sqrt3 e_4$									$F_{19,20}$	
	$F_{19,r}$	$R\alpha$									$\sqrt3$	$\sqrt3\sigma g_1/2$	$\sqrt3$	$\sqrt3\sigma g_2/2$			$\sqrt3$	$\sqrt3 g_4/2$	$\sqrt3$	$g_5/\sqrt3$	$\sqrt3$	$g_6/\sqrt3$	$3\sqrt3$	$3\sqrt3 g_7$	$3\sqrt3$	$3\sqrt3 g_8$	$F_{19,r}$	
	$F_{20,20}$	rr			1	1					1	σb_1	1	σb_2	1/2	$b_3/2$	3/2	$3b_4/2$									$F_{20,20}$	
	$F_{20,r}$	$r\alpha$									1	σk_1	1	σk_2	$2+\frac32\rho$	$(2+\frac32\rho)k_3$	3/2	$3k_4/2$									$F_{20,r}$	
	$F_{r,r}$	$\alpha\alpha$							1	$\rho^2/4$	1	$\sigma d_1/2$	1	$\sigma d_2/2$	$2+\frac\rho2$	$-\frac{\rho}{6}(2+\frac\rho2)$	3/2	$3d_4/4$	1	$d_5/3$	1	$d_6/3$	7/2	$7d_7/2$	3/2	$3d_8/2$	$F_{r,r}$	

SCGC = Symmetry coordinate geometrical coefficient

$$\rho = r_0/R_0 = 0.7770$$
$$\sigma = (1+\rho+\rho^2)^{-1} = 0.4200$$

Example: $F_{12} = 2\sigma e_1 f_m' + 2\sigma e_2 f_m + 2e_4 f_P$.

The final form of the F matrix given is Table IX and Table X lists the numerical values of the coefficients of the force constants which are involved in the members of the F matrix. Table XI gives the reciprocal of the dynamic matrix, G matrix, while the numerical values of its members are given in Table XII.

TABLE IX.   F Matrix.

$$\underline{F} = \begin{vmatrix} \underline{F}(A_{1g}) & & & & & & & \\ & \underline{F}(A_{2g}) & & & & & & \\ & & \underline{F}(B_{1u}) & & & & & \\ & & & \underline{F}(B_{2u}) & & & & \\ & & & & \underline{F}(E_{1ga}) & & & \\ & & & & & \underline{F}(E_{1gb}) & & \\ & & & & & & \underline{F}(E_{2ua}) & \\ & & & & & & & \underline{F}(E_{2ub}) \end{vmatrix}$$

$$\underline{F}(A_{1g}) = \begin{vmatrix} F_{1,1} & F_{1,2} \\ F_{1,2} & F_{2,2} \end{vmatrix}$$

$$\underline{F}(A_{2g}) = F_{3,3}$$

$$\underline{F}(B_{1u}) = \begin{vmatrix} F_{12,12} & F_{12,13} \\ F_{12,13} & F_{13,13} \end{vmatrix}$$

$$\underline{F}(B_{2u}) = \begin{vmatrix} F_{14,14} & F_{14,15} \\ F_{14,15} & F_{15,15} \end{vmatrix}$$

$$\underline{F}(E_{1gb}) = \underline{F}(E_{1ga}) = \begin{vmatrix} F_{6,6} & F_{6,7} & F_{6,8} & F_{6,9} \\ F_{6,7} & F_{7,7} & F_{7,8} & F_{7,9} \\ F_{6,8} & F_{7,8} & F_{8,8} & F_{8,9} \\ F_{6,9} & F_{7,9} & F_{8,9} & F_{9,9} \end{vmatrix}$$

$$\underline{F}(E_{2ua}) = \underline{F}(E_{2ub}) = \begin{vmatrix} F_{18,18} & F_{18,19} & F_{18,20} \\ F_{18,19} & F_{19,19} & F_{19,20} \\ F_{18,20} & F_{19,20} & F_{20,20} \end{vmatrix}$$

TABLE X.   Numerical Value of SCFC.

Number
of F   SCFC of Force constant
matrix

	F_s	f_s	F_b	f_b	f_m'	f_m	f_p'	f_p	F_m'	F_m	F_p'	F_p

Class A_{1g}

$F_{1,1}$	1				.3804	1.6196		1				
$F_{1,2}$					-.4396	1.4895		1				
$F_{2,2}$		1			.6301	1.3699		1				

Class A_{2g}

$F_{3,3}$			1	-1.9171	.6301	-1.2870						

Class B_{1u}

$F_{12,12}$			1	.1509	-.2893	.0951	-.3452			-3/4	1/4	-1/2
$F_{12,13}$				-.5051	-.3609	-.3660						
$F_{13,13}$		1			.6301	1.3699	3					

Class B_{2u}

$F_{14,14}$	1				.3804	1.6196		1	1			
$F_{14,15}$					-.7219	-1.0101		-1.7320				
$F_{15,15}$		1			-1.9171	.6301	-2.2870	3				

Class B_{1g}

$F_{6,6}$			1	.1509	-.2893	.0951	-.3074	.1132	-3/4	1/4	-.6250	3/4
$F_{6,7}$				-.5051	-.3609	-1.0342	-.1182					
$F_{6,8}$				-.1402	-.1962		-.3364	$\sqrt{3}/4$	$\sqrt{3}/4$	.2165	$\sqrt{3}/4$	
$F_{6,9}$						.1682	-.3047					
$F_{7,7}$		1			.6301	1.3699	2.2500	.2500				
$F_{7,8}$				-.2448	.7448		.5000					
$F_{7,9}$						.7500	.7500					
$F_{8,8}$	1				.3804	1.6196	1	3/4	3/4	1.1250	1/4	
$F_{8,9}$				.6251	.3748		1.5000					
$F_{9,9}$		1		-1.9171	.6301	-2.2870	2.2500					

Class E_{2u}

$F_{18,18}$			1	-1.9171	.6301	-1.5370	.7500					
$F_{18,19}$				-.2552	-.3571	.1190	-.3692					
$F_{18,20}$						-.7500	-.7500					
$F_{19,19}$	1/2	1/2	.0755	.2854	1.1972	-.1159	1.2525		-1	1/2	-1	
$F_{19,20}$				.0374	1.1674	.3692	.3692					
$F_{20,20}$		1			.6301	1.3699	.7500	.7500				

TABLE XI. G Matrix.

$$\underline{G} = \begin{vmatrix} \underline{G}(A_{1g}) & & & & & & & \\ & \underline{G}(A_{2g}) & & & & & & \\ & & \underline{G}(B_{1u}) & & & & & \\ & & & \underline{G}(B_{2u}) & & & & \\ & & & & \underline{G}(E_{1ga}) & & & \\ & & & & & \underline{G}(E_{1gb}) & & \\ & & & & & & \underline{G}(E_{2ua}) & \\ & & & & & & & \underline{G}(E_{2ub}) \end{vmatrix}$$

$$\underline{G}(A_{1g}) = \begin{vmatrix} 1/M & -1/M \\ -1/M & 1/M + 1/m \end{vmatrix}$$

$$\underline{G}(A_{2g}) = (\rho + 1)^2/M + 1/m$$

$$\underline{G}(B_{1u}) = \begin{vmatrix} 12/M & 12^{1/2}/M \\ 12^{1/2}/M & 1/M + 1/m \end{vmatrix}$$

$$\underline{G}(B_{2u}) = \begin{vmatrix} 3/M & -3^{1/2}/M \\ -3^{1/2}/M & 1/M + 1/m \end{vmatrix}$$

$$\underline{G}(E_{1ga}) = \underline{G}(E_{1gb}) = \begin{vmatrix} 15/2M & 27^{\frac{1}{2}}/2M & -27^{\frac{1}{2}}/2M & -3^{\frac{1}{2}}(5\rho+2)/4M \\ 27^{\frac{1}{2}}/2M & 1/M + 1/m & -1/2M & -3\rho/4M \\ -27^{\frac{1}{2}}/2M & -1/2M & 5/2M & 3(\rho+2)/4M \\ -3^{\frac{1}{2}}(5\rho+2)/4M & -3/4M & 3(\rho+2)/4M & (5\rho^2 + 4\rho+8)/8M + 1/m \end{vmatrix}$$

$$\underline{G}(E_{2ua}) = \underline{G}(E_{2ub}) = \begin{vmatrix} (9\rho^2 + 12\rho+8)/8M + 1/m & -6^{\frac{1}{2}}(3\rho+2)/4M & 3\rho/4M \\ -6^{\frac{1}{2}}(3\rho+2)/4M & 3/M & -6^{\frac{1}{2}}/2M \\ 3\rho/4M & -6^{\frac{1}{2}}/2M & 1/M + 1/m \end{vmatrix}$$

M = mass of C atom

m = mass of H or D atom

$\rho = r_0/R_0$

Table XII.   Numerical Values of Members of G Matrix.

$$\underline{G}(A_{1g}) = \begin{vmatrix} .0833 & -.0833 \\ -.0833 & 1.0753* \end{vmatrix}$$

$$\underline{G}(A_{2g}) = 1.2550*$$

$$\underline{G}(B_{1u}) = \begin{vmatrix} .9992 & .2884 \\ .2884 & 1.0753* \end{vmatrix}$$

$$\underline{G}(B_{2u}) = \begin{vmatrix} .2498 & -.1442 \\ -.1442 & 1.0753* \end{vmatrix}$$

$$\underline{G}(E_{1ga}) = \underline{G}(E_{1gb}) = \begin{vmatrix} .6245 & .2163 & -.2163 & -.2122 \\ .2163 & 1.0753* & -.0416 & -.0485 \\ -.2163 & -.0416 & .2082 & .1734 \\ -.2122 & -.0485 & .1734 & 1.1391* \end{vmatrix}$$

$$\underline{G}(E_{2ua}) = \underline{G}(E_{2ub}) = \begin{vmatrix} 1.2289* & -.2208 & .0485 \\ -.2208 & .2498 & -.1020 \\ .0485 & -.1020 & 1.0753* \end{vmatrix}$$

*   For C_6D_6 the number 0.4960 is to be deducted from the values of these members.

EVALUATION OF FORCE CONSTANTS

From the calculations of the previous chapter, it may be seen that there are 16 force constants in the potential energy function of planar vibrations, but that only 12 appear in the symmetry coordinate F matrix. In all there are 14 different force constants to be evaluated, namely, f'_s, f_s, F'_s, F_s, f'_m, f_m, f'_p, f_p, F'_m, F_m, F'_p, F_p, f_b, and F_b. The equilibrium condition gives two equations relating some of the constants (Eq. III, p. 23). Therefore 12 frequencies are required to calculate the remaining constants.

Of the 21 planar vibrations of benzene, classes E_{1g} and E_{2u} are double degenerate and classes B_{1g}, B_{1u} and A_{2g} are inactive in both infrared and Raman spectra. Various investigators have calculated the inactive frequencies from the product rule or from the force constants obtained from the active frequencies by the use of force fields different from the one used in this investigation. It was felt preferable not to use these calculated values of inactive frequencies for the calculation of force constants for a new force field. Thus, benzene spectra give only 9 frequencies. Additional data must be obtained before the determinants can be solved for all force constants; these data are obtained from the spectra of hexadeuterobenzene.

If the frequencies were put into the determinants and the determinants were developed, there would be a set of equations containing 12 unknown to the 4th power, which are too complicated for a rigorous algebraic solution. The trial-and-error method which had been used conveniently in the triborine triamine case is to be preferred.

Before starting the calculation, a literature survey was made to obtain as much information as possible from previous work. Heath and Linnett (19) assume that the Lennard-Jones relation for the repulsive

force between molecules of an inert gas can be applied to the repulsive force between nonbonded atoms. The relation is $V = aq^{-12} - bq^{-6}$. Furthermore, they argue that the contribution of the second term to the values of derivatives of V is small as compared to the first term and can be neglected. If this assumption can be accepted, then

$$\frac{1}{q_0}\left(\frac{\partial V}{\partial q}\right)_0 = \frac{1}{13}\left(\frac{\partial^2 V}{\partial q^2}\right)_0$$

or

$$f'_k = f_k/13$$

It is interesting to note that, although this relation has not been used in Simanouti's work (25), the force constants given by him fit fairly well into the relation, as shown in Table XIII.

Table XIII**

k	f_{k*}	$- f_k/13$	f'_{k*}
H-H	0.1	-.008	-0.0
F-F	1.35	-.104	-0.3
$Cl-Cl$	0.65	-.05	-0.1
Br-Br	0.5	-.038	-0.1
C-H	0.4	-.031	-0.05
C-F	1.3	-.1	-0.1
C-Cl	0.6	-.046	-0.1
C-Br	0.5	-.038	-0.1
H-Cl	0.8	-.062	-0.05
Cl-Br	0.55	-.042	-0.1

* taken from reference 14.
** all quantities are in 10^5 dyne/cm.

Although one can not take the thirteen-fold relation in magnitude very seriously, since Simanouti's data for f'_k give only one significant figure, it would be safe to assume that f_k is greater and f'_k is smaller than zero.

An inspection of Table X will reveal that, with a set of assumed nonbonded force constants, frequencies of class A_{1g} can be used to adjust the values of f_s and F_s, and that frequencies of class E_{2u} will then be suitable for the adjustment of f_b and F_b. As a first approximation, f'_m, f'_p, F'_m, and

F'_p were assumed to be zero, f_p, F_m, and F_p were given the values of 0.07, 0.07, and 0.06, respectively (all figures are in units of 10^5 dyne/cm.), and the five frequencies were used to adjust f_s, F_s, f_b, F_b, and f_m, since they are the five largest.

After several cycles of trial and error, it was found that the frequencies were conveniently fitted by the five force constants with the exception of $^{V}19$, a hybrid of C-C stretching and C-C bending. A drastic change in the value of $F_{19,19}$ would not greatly improve the agrement. In order to fit this frequency the value of $F_{18,19}$ would have to be greater than zero, which contradicts to the predicted value of force constants based on the above-mentioned assumption. This point was confirmed by another series of calculations, shown in Table XVII, series 26-44.

In this series of calculations a somewhat different scheme was employed. Benzene and hexadeuterobenzene give six experimentally observed fundamentals in the symmetry class E_{2u}. As Crawford and Miller point out, one of the six equations obtained by inserting the frequencies into the determinants cannot be used for the evaluation of force constants, because of dependency among the six equations. However there are six members in the F matrix block of class E_{2u}. A value for one of the six members will have to be assumed. One can predict that the value of $F_{18,20}$ is small, and with an assumed value of $F_{18,20}$ one can use the five frequencies to adjust the other five members.

The results given in series 26-44 show that the value of $F_{18,20}$ is rather unimportant compared to the other five members, and that a positive value for $F_{18,19}$ fits the frequency better.

Crawford and Miller (6) have given a positive value for $F_{18,19}$, though they obtain this positive value by assuming $F_{18,20}$ and $F_{19,20}$ to be zero. The disagreements between their values for the members of the F matrix and

and the signs of these members predicted by the above reasoning are listed in Table XIV for comparison.

Table XIV

Class	Member of F matrix	C & M symbol	C & M value	Sign predicted
A_{1g}	$F_{1,2}$	ξ_1	-0.420	-
B_{2u}	$F_{14,15}$	μ_2	1.30 (or -0.203)	-
B_{1u}	$F_{12,13}$	γ_2	0.106	- small
E_{2u}	$F_{18,19}$	μ_4	1.40	-
	$F_{18,20}$	τ_4	0*	- small
	$F_{19,20}$	ξ_4	0*	-
E_{1g}	$F_{6,7}$	γ_3	0*	-
	$F_{6,8}$	χ_3	0.181	-
	$F_{6,9}$	π_3	0.241	- small
	$F_{7,8}$	ξ_3	0*	-
	$F_{7,9}$	τ_3	0*	- small
	$F_{8,9}$	μ_3	0	-

* assumed to be zero.

Since Crawford and Miller assume that some members are zero, it is not surprising that there are some disagreements in classes E_{1g} and E_{2u}. However, there are four frequencies in class A_{1g}, two from benzene spectra and two from hexadeuterobenzene spectra. Discounting one for the dependency, there should be enough information to solve for the values of all three members in the block concerned. One would expect the solution to be unique, and that no two valid sets of values can be obtained. But in the actual numerical approximation several points have to be considered.

First, in the normal coordinate treatment of molecular vibrations it is usually assumed that the vibrators can be treated as harmonic oscillators, and unless in the case where the anharmonicity data are complete, the correction for anharmonicity is ignored. Secondly, when the frequencies of isotopic molecule are used, the product rule is assumed to be exact. Thirdly,

the errors in experimental data are uncertain. And lastly, since the precision of experimental data limits the number of significant figures in the force constants calculated from them, one can not expect exact fit from the force constants. For instance, three significant figures are usually given for large force constants, such as C-H stretching and C-C stretching constants, but for smaller force constants, only one significant figure is given. Due to this limitation one would be satisfied when the agreement between the calculated frequencies and the observed data turns out to be within 1%, even in the case of the frequency which has been used to calculate the force constants. In other words, one may always expect some disagreement between calculated and observed frequencies.

There are, therefore, four factors which influence the value of force constants; namely, the anharmonicity of molecular vibrations, the agreement between product rule and the experimentally observed frequencies of isotopic molecules, the experimental error and the error in numerical approximation. Since no distinction can be made between the last two factors, it seems to be proper to combine them together and call it combined error.

The individual influence of these factors on the values of members in F matrix block of class A_{2g} had been studied by a rigorous algebraic analysis, the results of which are shown in Table XV. For the anharmonicity, the definition by Herzberg for diatomic molecules was used, i.e. $\gamma = W_e$ (1-2x_e) where W_e is the corrected frequency, and x is the percentage of anharmonicity and γ is the observed frequency. In columns I and II, combined errors of 1 and 0.5% were introduced respectively, but the difference between the predictions of the product rule and the actually observed frequencies had not been removed. In order to show the effect the extreme case

where the error in the benzene frequencies is taken to be positive and that in deuterobenzene frequencies negative was used. Column III shows the result of the calculation with no combined error in C-H or C-D stretching vibration, but an assumed error of 0.4% in C-C stretching frequencies. In column IV it was assumed there is no error in the frequencies, but the anharmonicity of C-H vibration was assumed to be 2.5% and the anharmonicity in C-D vibration of hexadeuterobenzene was obtained by the use of product rule. In columns V and VI, a small error was assumed along with the anharmonicity which is treated in the same way as in the calculation in column IV.

It may be seen from the results of these calculations:

(1) In the extreme case where the combined error in benzene frequencies is positive and that in hexadeuterobenzene is negative, the value of $F_{1,2}$ can shift from -0.420 to 1.3704;

(2) The values of $F_{1,1}$ and $F_{2,2}$ remain almost constant; and

(3) The consideration of anharmonicity in C-H vibration and C-D vibration increases the value of $F_{1,2}$.

Table XV.

	I	II	III	IV	V	VI	C & M value
$x_{C-H}\ (C_6H_6)$	---	---	---	.025	.025	.025	
$z_{C-C}(C_6H_6)$	.01	.005	.004	---	.005	.005	
$z_{C-H}(C_6H_6)$	.01	.005	---	---	.005	.0006	
$z_{C-C}(C_6D_6)$	-.01	-.005	-.004	---	-.005	-.005	
$z_{C-D}(C_6D_6)$	-.01	-.005	---	---	-.005	-.0006	
$y_{C-C}\ (C_6H_6)$	1.0201	1.0100	1.0080	1.0000	1.0100	1.0100	
$y_{C-H}\ (C_6H_6)$	1.0201	1.0100	1.0000	1.1080	1.1191	1.1093	
$y_{C-C}\ (C_6D_6)$	.9801	.9900	.9920	1.0000	.9900	.9900	
$y_{C-D}\ (C_6D_6)$	.9801	.9900	1.0000	1.0933	1.0824	1.0920	
$F_{1,1}*$	7.8212	7.6286	7.8031	7.6384	7.6369	7.6320	7.83
$F_{1,2}*$	1.3704	.3765	-.3482	-.0967	.8808	.1121	-.420
$F_{2,2}*$	5.3943	5.1980	5.0198	5.6218	5.8357	5.6667	5.00

z_i = assumed combined factor in ith vibration.

$$y = (1 - z)^2/(1 - 2x)^2$$

$$\left(\frac{\lambda_{C-C}\,\lambda_{C-H}\,y_{C-C}\,y_{C-H}}{\|G\|}\right)_{C_6H_6} = \left(\frac{\lambda_{C-C}\,\lambda_{C-D}\,y_{C-C}\,y_{C-D}}{\|G\|}\right)_{C_6D_6}$$

* All in 10^5 dyne/cm.

Since the results shown in Table XV prove that the combined error, which can not be avoided in numerical approximation, has a large influence on the value of $F_{1,2}$, it would be advisable not to use frequencies in class A_{1g} to ascertain the value of force constant. Unfortunately the large number of members in other blocks makes a rigorous algebraic analysis impossible. However, it is interesting to introduce the anharomonicity to the frequencies in other classes to investigate the effect.

Little work has been done on the anharmonicity in benzene vibration. Ellis [7] has recorded some absorption bands of benzene in near infrared region. Based on his data the following calculation was made on the assumption that these bands are all C-H stretching vibration.

Table XVI.

n	wavelength	frequency cm^{-1}	1st difference cm^{-1}	2nd difference cm^{-1}
0		----		
1		3080	3080	
2	1.66	6024	2944	-136
3	1.145	8734	2710	-234
4	0.885	11300	2566	-144

$$\text{average } -171$$
$$x_e = 2.54\%$$

If the fundamental 3099 cm^{-1} is taken as the first frequency of the series, x_e, the anharmonicity would have a value of 2.64%. The assignment of the bands as the C-H stretching vibrations is by no means certain. The introduction of anharmonicity is only for the purpose of studying its effect on the value of force constants. Hence, the actual value of x_e used in the calculation is rather unimportant because one would not intend to use the calculated force constants for other purposes. In the following calculation the average value of 2.6% for x_e was used[1] for the C-H vibration in class E_{2u}. The anharmonicity in all other types of vibration was assumed to be negligible. The results obtained from the calculation of classes E_{2u} and E_{1g} are listed in Table XVII, serial No. 46-70. The effect of anharmonicity in these two classes is not so prominent as that in class A_{2g}, possibly because the anharmonicity of other vibrations than the C-H stretching vibration cannot be ignored in these classes. But, roughly speaking, the general trend is the consideration of anharmonicity increases the calculated values of the off-diagonal members of the F matrix.

---

[1]Ellis (7) and Barnes and Fulweilergive the corresponding value of x_e as 1.9 and 1.8% respectively, on the basis of the same assumption that had been made for the calculation of Table XVI. Although the numerical value is somewhat different from that used in this research, it has no effect on the conclusion reached in this research.

Since the complete anharmonicity data are not available, precise value of force constants, especially those for the nonbonded distances, cannot be obtained. A set of approximate force constants was therefore calculated by the use of some of the inactive frequencies obtained by Wilson by consideration of product rule. Table XVIII shows the value of force constants and the calculated frequencies of benzene and hexadeuterobenzene.

TABLE XVII. Evaluation of members of F matrix.
Class E_{2u}

Serial No.	$F_{18,18}$	$F_{18,19}$	$F_{18,20}$	$F_{19,19}$	$F_{19,20}$	$F_{20,20}$	D ($V18$)	D ($V19$)	D ($V20$)
		Member of F matrix					Value of determinant		
1	.8667	-.0557	-.0230	4.1194	.1589	5.1358	-.0845	-.4688	-1.0741
2	.6667	"	"	4.2194	"	"	-.3791		
3	.4667	"	"	"	"	"	-.6395		
4	.8667	"	"	"	"	"	-.1180	-.5646	
5	.7667	"	"	4.1694	"	"	-.2581	-.3070	
6	.6667	"	"	4.0194	"	"	-.5475		
7	1.0667	"	"	"	"	"	-.0336	1.0135	
8	.7667	"	"	4.2194	"	"	-.2489		
9	.9667	"	"	"	"	"	.0123	-.8297	
10	.9167	"	"	"	"	"	-.9531		
11	1.0793	-.0628	"	3.9734	.1822	5.1632	.0119	-1.0376	
12	"	"	"	4.2234	"	"	.1527		
13	.9793	"	"	"	"	"	.0211	-.8537	
14	.7793	"	"	4.1234	"	"	-.2633		
15	.8793	"	"	"	"	"	-.1433		
16	.9793	"	"	"	"	"	-.8220		
17	"	"	"	4.0734	"	"	-.4287		
18	.9919	-.0699	"	4.0823	.2056	5.1106	-.0367		
19	.8793	-.0628	"	4.0734	.1822	5.02032	-.1571		
20	.9793			"		"	-.0423		
21	1.0093					"		-.8878	
22	.9793			3.5734		"	-.2656		
23	1.1793			3.5734		"	-.1581	-.8479	-1.7787
24	1.3793			"		"	-.0507	-1.8799	
25	.8793			4.5734		"	.0050	-.7755	
26	.8000	.2140	.0750	4.0000	-.6000	5.60000	.0380	.4946	14.4942
27	"	"	"	"	"	5.40000	.0352	.4801	9.8368
28	"	"	"	5.0000	"	5.00000	.2469	-.0063	1.0320
29	.7000	.2140	"	"	"	"	.0479	.1769	1.0143
30	"	"	"	5.3000	"	4.9500	.0723	.0068	.0533
3						C_6D_6	-.0850	-.1182	.9181
31	"	.4000	"	"	"	4.9500	.1737	.3023	-.1130
32	.6000	"	"	"	"	"	-.0562	.4492	-.1488
33	"	"	"	6.3000	"	"	-.0727	-.1987	.4398
34	"	"	"	6.0000	"	"	-.0683	-.0506	-.0766
						C_6D_6	-.1569	-.1657	1.0555
35	.7000	.2140	"	5.300	-.3000	4.9500	.0797	-.0910	-1.9893
36	.6600	"	"	5.4500	"	4.9600	-.0130	-.0922	-1.4157
37	"	"	"	5.6000	"	5.0400	-.0010	-.2226	-.2988
38	"	"	"	5.4500	"	5.0200	-.0091	-.1321	-.3726
39	"	"	"	5.3000	"	"	-.0172	-.0421	-.4465
						C_6D_6	-.1232	-.1768	.3610
40	"	.1020	"	"	"	5.0200	-.0358	-.2586	-.3631
41	"	"	"	5.0000	"	5.0500	-.1360	-.0811	.1728
42	.7100	"	"	"	"	"	-.0301	-.1629	.1848
43	.7300	"	"	4.7000	"	"	-.0292	-.0358	.0555
						C_6D_6	-.0969	-.1262	.4676
44	"	"	0	"	"	5.0500	-.0384	-.0701	-.2937
						C_6D_6	-.0976	-.1478	.3558
45	1.000	-.1994	-.0328	4.9000	.6577	6.100	.1623	1.7718	-1.4273
						C_6D_6	-.0157	.8287	-.1185

48

TABLE XVII. (Continued)

Serial No.	F_{18,18}	F_{18,19}	F_{18,20}	F_{19,19}	F_{19,20}	F_{20,20}	D (V18)	D (V19)	D (V20)
46	.9900	-.1994	-.0328	4.9000	.6577	6.1100	.1347	1.7957	-1.1358
47	.9500	"	"	4.500	"	6.5000	-.1955	1.6330	10.8737
48	.9700	-.1994	-.0328	3.500	"	6.200	-.7018	1.2554	1.0288
49	.9500	-.1994	-.0328	4.500	"	5.8575	-.1723	-1.4320	
50	1.2000	-.2142	-.0750	4.200	.6169	5.8600	.0319	-2.0657	.1150
51	"	"	"	3.900	"	"	-.1745	-2.0051	-.0660
						C_6D_6 5.8600	.0066	-.6465	-.2194
52	"	0	"	"	"	5.8600	.1897	-1.3779	-.0950
53	"	-.1071	"	"	"	"	.0095	-1.6620	-.0810
54	"	"	"	"	0	"	-.0061	-1.4715	
55	"	"	"	4.2000	0	"		-1.7586	
56	"	-.2142	"	6.1000	.6169	"		-2.1952	
57	"	.2142	.0750	3.9000	-.6169	"		-1.2028	
58	"	.4284	.1500	"	-1.2338	"		-.3041	
59	"	"	"	3.0000	"	"	-.4734	-.2375	13.9757
60	.6000	"	"	"	"	3.0000	.0126	1.4585	-80.
61	"	"	"	"	-.6169	5.0000	-.0044	2.0596	16.2422
62	1.2000	"	"	"	"	5.8600			8.4669
63	.6000	"	"	2.5000	"	5.6000	.0048	2.4	
64	.870	-.1995	-.0328	6.140	.6577	5.86	.6282	-2.1682	
65	1.0000	-.1994	-.0328	6.600	"	"	1.0709	-2.2257	
66	.870	-.1994	"	5.60	"	5.86	.0896	-1.7617	
67	"	"	"	5.20	"	"	-.0537	-1.5831	
68	"	"	"	5.00	"	"	-.1253	-1.4874	
69	.700	"	"	5.20	"	"	-.5373	-1.3262	-8.6124
70	1.2000	"	"	4.20	"	5.8575	.0670	-2.0158	-8.6051

Serial Nos. 45-70 with 2.6% anharmonicity in C-H vibration.

TABLE XVII. (Continued)

Serial No.	Member of F matrix									Value of determinant			
	$F_{6,6}$	$F_{6,7}$	$F_{6,8}$	$F_{6,9}$	$F_{7,7}$	$F_{7,8}$	$F_{7,9}$	$F_{8,8}$	$F_{9,9}$	$D(\nu_6)$	$D(\nu_7)$	$D(\nu_8)$	$D(\nu_9)$
Class E_{1g}													
71	.5310	-.05	-.05	-.0068	5.1682	.1169	.0230	7.6132	.6994	-.1321	-8.633		
72	"	"	"	"	5.0682	"	"	"	"	"	.6725		
73	"	"	"	"	5.0782	"	"	"	"		1.9088		
74	"	"	"	"	"	"	"	7.7132	"		1.9748		
75	"	"	"	"	"	"	"	7.4132	"		-.20	1.7761	
76	"	"	"	"	5.0782	"	"	7.0132	"		-.0949	1.5117	
77	"	"	"	"	"	"	"	6.7067	"	.1029		1.0057	
78	.6310	"	"	"	"	"	"	"	"	.0194	-.4995		
79	"	"	"	"	5.1682	"	"	"	"		1.9521		
80	"	"	"	"	5.0962	"	"	"	"		1.4571		
81	"	"	"	"	5.1682	"	"	7.0963	"		9.4535		
82	"	"	"	"	5.0782	"	"	"	"		-.5910		
83	"	"	"	"	5.0835	"	"	"	"			1.7540	
84	"	"	"	"	"	"	"	7.6132	"		-14.10		
85	"	"	"	"	5.0782	"	"	4.9568	"		-.0553		
86	.5310	"	"	"	6.2046	"	"	4.9516	"		-.0909		
87	.4838	-.0644	-.0581	"	5.0802	.1467	.0230	7.8268	1.0476		-1.6		
88	.6595	-.1041	-.0797	-.0067	5.1075	.2286	.0229	7.3808	1.0924			.3106	-2.5163
89	.6600	-.1087	-.08755	-.0145	5.0547	.2538	.0492	7.5262	1.0951			.1907	-2.7136
2.6% anharmonicity in C-H vibrations													
90	.6400	-.1418	-.0311	-.0505	5.8600	.4469	.0750	7.6800	1.1000	-.0111	-19.28		
91	"	"	"	"	5.7000	"	"	"	"		1.5419		
92	"	"	"	"	5.7500	"	"	"	"		-5.4240		
93	"	"	"	"	5.7100	"	"	"	"		.3021	4.1994	
94	"	"	"	"	"	"	"	6.7000	"			3.7266	
95	"	"	"	"	"	"	"	6.0000	"			3.38	
96	"	"	"	"	"	"	"	7.6800	"				.3352
97	.6400	-.1418	-.0311	-.0505	5.7100	.4469	.0750	7.6800	1.3000				.0774

TABLE XVIII.   FORCE CONSTANTS OF BENZENE AND THE CALCULATED FREQUENCIES.

Force Constants

	10^5 dyne/cm.
C-H stretching, f_s'	0.07
f_s	5.47
C-C stretching, F_s'	0.60
F_s	7.94
C-C-C bending, F_b	0.33
H-C-C bending, f_b	0.87
C-H nonbonded distance, f_m'	-0.06
f_m	-0.33
H-H nonbonded distance, f_p'	0.05
f_p	0.04
C-C nonbonded distance, meta, F_m'	0.74
F_m	0.48
C-C nonbonded distance, para, F_p'	-1.37
F_p	-0.26

Calculated Frequencies

Class	Frequency number	C_6H_6 Calculated frequency cm.$^{-1}$	C_6H_6 Assigned frequency cm.$^{-1}$	% Diff.	C_6D_6 Calculated frequency cm.$^{-1}$	C_6D_6 Assigned frequency cm.$^{-1}$	% Diff.
A_{1g}	1	995	(992)	0.3	939	(943)	-0.4
	2	3066	3062	0.1	2298	2293	0.2
A_{2g}	3	1232	1326		958	1037	
B_{1u}	12	1018	(1010)	0.8	961	(963)	-0.2
	13	3096	3060	1.2	2320	2290	1.4
B_{2u}	14	1853	1648		1800	1571	
	15	1145	1110		810	825	
E_{1g}	6	622	(606)	2.6	573	(577)	-0.1
	7	3081	3047	1.1	2257	2265	-0.3
	8	1600	(1596)	0.3	1542	1552	-0.6
	9	1128	1178	-4.3	843	867	-2.8
E_{2u}	18	1012	(1037)	-2.5	795	(813)	-2.2
	19	1499	(1485)	0.9	1316	(1333)	-1.1
	20	3072	(3080)	-0.3	2279	(2294)	-0.5

( )--- Used to evaluate force constants.

DISCUSSION

Anharmonicity and Force Constants.

The calculation of force constants serves for two purposes, namely, the reproduction of the observed frequencies by calculation and the knowledge of the forces among atoms in the molecule concerned. Chemists are interested in the latter rather than the former in seeking an understanding of the nature of bonds. From the calculation of force constants of benzene in the previous chapter it may be seen that the anharmonicity in vibrations has a large influence on the values of the off-diagonal members of the F matrix, so that the influence is prominent and cannot be ignored on the value of those force constants representing the forces between non-bonded atoms. A set of force constants calculated from the observed frequencies without consideration of anharmonicity will not give a real picture of the forces among the atoms. Therefore, evaluation of the force constants for the nonbonded distances would have to await complete anharmonicity data for benzene vibrations.

Urey-Bradley Force Field.

This force field is a combination of the valence force field and the central force field, or rather a valence force field with further interpretation of the valence force constants. It may be seen from a comparison of Equations I and III that the coefficients of various terms in Equation IV are equivalent to ordinary valence force constants, though in this force field they are interpreted as linear combinations of force constants, instead of considering them individually as the force constants of any bond or the interactions between coordinates. Treated in the manner, the force constants are independent to surroundings if intermolecular forces are neglected. Therefore one can expect to be able to transfer these force

constants from molecule to molecule, and to use them as representative of the forces among atoms. It seems proper to say that these force constants should be used for the correlation of force constants with bond lengths and the nature of chemical bonds, while the ordinary valence force constants should be used in the comparison of bond energies of various bonds, since the rupture of bonds are accompanied by changes in nonbonded distances.

Furthermore, it is assumed that the forces among atoms are not zero in the equilibrium position. Since the nuclear charge and the electronic cloud do not vanish when nucleus are at their equilibrium positions, it is more reasonable to assume forces do exist there.

Physical Meaning of Negative Force Constant.

In the valence force field the first derivatives of potential energy are assumed to be zero, while the second derivatives must be positive. Otherwise the frequency would be imaginary and the compound would be unstable. In the calculations of this research some of the force constants acquire negative values. The sign of the first derivative indicates whether the force is a repulsive or an attractive force. The negative values of second derivatives are puzzling at first sight. However these force constants represent the forces in nonbonded distances and the nonbonded distances are dependent variables. None of these distances can be changed without some variation in one of the independent coordinates. For instance, one cannot change the distance between two C atoms occupying meta positions without producing some change in one C-C bond or in the angle between these two C-C bonds. Therefore a change in the nonbonded distance not only produces a force with respect to this distance change, but also with respect to changes in other bonds or angles, and the sum of potential energy changes is greater than zero. It would imply instability if the sum of potential energy

changes were negative, i.e., if the linear combination of force constants in Equation III had a negative value.

CONCLUSIONS

1. The introduction of the influence of hydrogen displacements on the N-B twisting in triborine triamine improves the agreement between the calculated and observed frequencies of out-of-plane hydrogen vibrations, and the twisting force constant thus obtained is more reasonable.

2. If the twisting force constant varies linearly with double-bond character, the double-bond character of B-N bond in triborine triamine is 28 percent, taking that of benzene as 50 percent. A double-bond character of 27 percent is calculated from considerations of bond lengths.

3. The anharmonicity in benzene vibrations has a large influence on the value of the force constants for the nonbonded distances. A precise solution of the secular determinant would have to await complete anharmonicity data for benzene vibrations. A more thorough study of benzene vibrations in the near infrared region is indicated.

4. Ordinary valence force constants may be used for the comparison of bond energies of different bonds in different molecules. However, the force constants obtained by the use of the Urey-Bradley field, which are independent of surroundings, are more suitable for the purpose of correlating force constants with bond lengths and for studying the nature of bonds.

5. Negative values for second derivatives in the potential energy function suggested by Urey and Bradley are explained.

Calculation of Δp

$$p_i^2 = R_i^2 + r_i^2 - 2R_i r_i \cos\theta_i \qquad .$$

$$p_i \frac{\partial p_i}{\partial R_i} = R_i - r_i \cos\theta_i \qquad\qquad p_0\left(\frac{\partial p_i}{\partial R_i}\right)_0 = R_0 + r_0/2$$

since $\qquad\qquad \theta_0 = 2\pi/3$.

Similarly, $\qquad\qquad\qquad\qquad p_0\left(\frac{\partial p_i}{\partial r_i}\right)_0 = r_0 + R_0/2$.

$$p_i \frac{\partial p_i}{\partial \theta_i} = R_i r_i \sin\theta_i \qquad\qquad p_0\left(\frac{\partial p_i}{\partial \theta_i}\right)_0 = \frac{\sqrt{3}}{2} R_0 r_0$$

$$\left(\frac{\partial p_i}{\partial R_i}\right)^2 + p_i \frac{\partial^2 p_i}{\partial R_i^2} = 1 \qquad\qquad p_0\left(\frac{\partial^2 p_i}{\partial R_i^2}\right)_0 = 3r_0^2/4p_0^2$$

since $\qquad\qquad p_0^2 = R_0^2 + r_0^2 + R_0 r_0 .$

Similarly, $\qquad\qquad\qquad\qquad p_0\left(\frac{\partial^2 p_i}{\partial r_i^2}\right)_0 = 3R_0^2/4p_0^2$.

$$\left(\frac{\partial p_i}{\partial \theta_i}\right)^2 + p_i \frac{\partial^2 p_i}{\partial \theta_i^2} = R_i r_i \cos\theta_i , \qquad p_0\left(\frac{\partial^2 p_i}{\partial \theta_i^2}\right)_0 = -\frac{R_0 r_0}{2p_0^2}\left[R_0^2 + r_0^2 + \frac{5}{2}R_0 r_0\right]$$

$$\frac{\partial p_i}{\partial R_i}\frac{\partial p_i}{\partial r_i} + p_i \frac{\partial^2 p_i}{\partial R_i \partial r_i} = -\cos\theta_i , \qquad p_0\left(\frac{\partial^2 p_i}{\partial R_i \partial r_i}\right)_0 = -3R_0 r_0/4p_0^2$$

$$\frac{\partial p_i}{\partial R_i}\frac{\partial p_i}{\partial \theta_i} + p_i \frac{\partial^2 p_i}{\partial R_i \partial \theta_i} = r_i \sin\theta_i , \qquad p_0\left(\frac{\partial^2 p_i}{\partial R_i \partial \theta_i}\right)_0 = \frac{\sqrt{3}\, r_0}{2p_0^2}\left[r_0^2 + R_0 r_0/2\right]$$

$$\frac{\partial p_i}{\partial r_i}\frac{\partial p_i}{\partial \theta_i} + p_i \frac{\partial^2 p_i}{\partial r_i \partial \theta_i} = R_i \sin\theta_i , \qquad p_0\left(\frac{\partial^2 p_i}{\partial r_i \partial \theta_i}\right)_0 = \frac{\sqrt{3}\, R_0}{2p_0^2}\left[R_0^2 + R_0 r_0/2\right]$$

$$\Delta p_i = \left(\frac{\partial p_i}{\partial R_i}\right)_0 \Delta R_i + \left(\frac{\partial p_i}{\partial r_i}\right)_0 \Delta r_i + \left(\frac{\partial p_i}{\partial \theta_i}\right)_0 \Delta\theta_i$$

$$+ \frac{1}{2}\left(\frac{\partial^2 p_i}{\partial R_i^2}\right)_0 (\Delta R_i)^2 + \frac{1}{2}\left(\frac{\partial^2 p_i}{\partial r_i^2}\right)_0 (\Delta r_i)^2 + \frac{1}{2}\left(\frac{\partial^2 p_i}{\partial \theta_i^2}\right)_0 (\Delta\theta_i)^2$$

$$+ \left(\frac{\partial^2 p_i}{\partial R_i \partial r_i}\right)_0 \Delta R_i \Delta r_i + \left(\frac{\partial^2 p_i}{\partial r_i \partial \theta_i}\right)_0 \Delta r_i \Delta\theta_i + \left(\frac{\partial^2 p_i}{\partial R_i \partial \theta_i}\right)_0 \Delta R_i \Delta\theta_i$$

$$\therefore \quad p_0 \Delta p_i = R_0(1 + p/2)\Delta R_i + R_0(p + 1/2)\Delta r_i + \frac{\sqrt{3}}{2}R_0 r_0 \Delta\theta_i$$

$$+ \frac{1}{2p_0^2}\left[\frac{3}{4}r_0^2(\Delta R_i)^2 + \frac{3}{4}R_0^2(\Delta r_i)^2 - \frac{R_0 r_0}{2}(R_0^2 + r_0^2 + \frac{5}{2}R_0 r_0)(\Delta\theta_i)^2\right.$$

$$-\frac{3}{2}R_0 r_0 \Delta R_i \Delta r_i + \sqrt{3}\, r_0(r_0^2 + R_0 r_0/2)\Delta R_i \Delta\theta_i$$

$$\left. + \sqrt{3}\, R_0^2(R_0 + r_0/2)\Delta r_i \Delta\theta_i\right]$$

APPENDIX II

CALCULATION OF ΔD
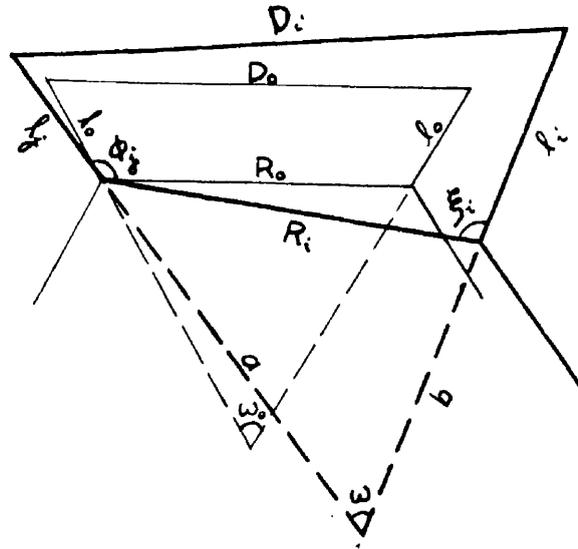
$$D_i^2 = (l_j + a)^2 + (l_i + b)^2 - 2(l_j + a)(l_i + b)\cos\omega$$

$$\frac{a}{\sin(\pi - \xi_i)} = \frac{b}{\sin(\pi - \phi_j)} = \frac{R_i}{\sin\omega}$$

$$\frac{a}{\sin\xi_i} = \frac{b}{\sin\phi_j} = \frac{R_i}{\sin\omega}$$

$$a = AR_i \qquad\qquad b = BR_i$$

where
$$A = \frac{\sin\xi_i}{\sin\omega} \qquad\qquad B = \frac{\sin\phi_j}{\sin\omega}$$

$$D_i^2 = (l_j + R_i A)^2 + (l_i + R_i B)^2 - 2(l_j + R_i A)(l_i + R_i B)\cos\omega$$

$$= l_j^2 + l_i^2 - 2l_i l_j \cos\omega + 2R_i\{l_j A + l_i B - (l_i A + l_j B)\cos\omega\}$$
$$+ R_i^2\{A^2 + B^2 - 2AB\cos\omega\} \qquad\qquad (I)$$

$$
\left.
\begin{aligned}
D_i &= D_0 + \Delta D_i & \omega &= \omega_0 + \Delta\omega \\
l_i &= l_0 + \Delta l_i & &= \xi_i - (\pi - \phi_j) \\
l_j &= l_0 + \Delta l_j & &= \xi_i + \phi_j - \pi \\
R_i &= R_0 + \Delta R_i & \Delta\omega &= \Delta\xi_i + \Delta\phi_j \\
\xi_i &= \xi_0 + \Delta\xi_i & \xi_0 &= \phi_0 = 2\omega_0 = \frac{2}{3}\pi \\
\phi_j &= \phi_0 + \Delta\phi_j & D_0 &= R_0 + l_0
\end{aligned}
\right\} \qquad (II)
$$

$$A^2 + B^2 - 2AB\cos\omega = \sin^{-2}\omega\left\{\sin^2\phi_j + \sin^2\xi_i - 2\sin\phi_j\sin\xi_i\cos\omega\right\}$$

$$= \sin^{-2}\omega\left\{\sin^2\phi_j + \sin^2\xi_i + 2\sin\phi_j\sin\xi_i\cos(\phi_j+\xi_i)\right\}$$

$$= \sin^{-2}\omega\left\{\sin^2\phi_j + \sin^2\xi_i + 2\sin\phi_j\sin\xi_i\cos\phi_j\sin \right.$$
$$\left. -2\sin^2\phi_j\sin^2\xi_i\right\}$$

$$= \sin^{-2}\omega\left(\sin\phi_j\cos\xi_i + \cos\phi_j\sin\xi_i\right)^2$$

$$= \sin^{-2}\omega\,\sin^2(\phi_j+\xi_i)$$

$$= 1 \tag{III}$$

$$\sin\phi_j = \sin(\phi_0 + \Delta\phi_j)$$

$$= \sin\phi_0\cos\Delta\phi_j + \cos\phi_0\sin\Delta\phi_j$$

$$= \frac{1}{2}\left\{\sqrt{3} - \Delta\phi_j - \frac{\sqrt{3}}{2}(\Delta\phi_j)^2\right\}$$

NEGLECTING TERMS HIGHER THAN QUADRATIC. SIMILARLY,

$$\sin\xi_i = \frac{1}{2}\left\{\sqrt{3} - \Delta\xi_i - \frac{\sqrt{3}}{2}(\Delta\xi_i)^2\right\}$$

$$\sin\omega = \frac{1}{2}\left\{\sqrt{3} + \Delta\phi_j + \Delta\xi_i - \frac{\sqrt{3}}{2}(\Delta\phi_j + \Delta\xi_i)^2\right\}$$

HENCE,

$$A = \frac{\sin\xi_i}{\sin\omega} = 1 - \frac{1}{\sqrt{3}}\Delta\xi_i - \frac{2}{\sqrt{3}}\Delta\phi_j + \frac{5}{6}(\Delta\xi_i)^2 + \frac{2}{3}(\Delta\phi_j)^2$$
$$+ 2\Delta\xi_i\Delta\phi_j$$

$$\left.\begin{array}{l} B = \dfrac{\sin\phi_j}{\sin\omega} = 1 - \dfrac{1}{\sqrt{3}}\Delta\phi_j - \dfrac{2}{\sqrt{3}}\Delta\xi_i + \dfrac{5}{6}(\Delta\phi_j)^2 \\[2mm] \qquad\qquad + \dfrac{2}{3}(\Delta\xi_i)^2 + 2\Delta\xi_i\Delta\phi_j \\[3mm] \cos\omega = \dfrac{1}{2}\left\{1 - \sqrt{3}(\Delta\phi_j + \Delta\xi_i) - \dfrac{1}{2}(\Delta\phi_j + \Delta\xi_i)^2\right\} \end{array}\right\} \tag{IV}$$

PUT (II), (III), AND (IV) INTO (I), AND COLLECT TERMS

$$(\Delta D_i)^2 + 2D_0\Delta D_i = H$$

SOLVE. AND DEVELOP

$$D_0\Delta D_i = \frac{H}{2} - \frac{H^2}{8D_0^2}$$

where

$$\frac{1}{2}H = \frac{1}{2}\left\{ D_0\left[\Delta l_j + \Delta l_i + 2\Delta R_i + \sqrt{3}\,l_0\,(\Delta\phi_j + \Delta\xi_i)\right] \right.$$
$$+ (\Delta l_j)^2 + (\Delta l_i)^2 + (\Delta R_i)^2 - \Delta l_i\,\Delta l_j + \Delta R_i\,(\Delta l_i + \Delta l_j)$$
$$+ \sqrt{3}\,D_0\,(\Delta l_i\,\Delta\phi_j + \Delta l_i\,\Delta\xi_i) + \sqrt{3}\,l_0\,(\Delta l_i\,\Delta\phi_j + \Delta l_j\,\Delta\xi_i)$$
$$+ \sqrt{3}\,l_0\,\Delta R_i\,(\Delta\phi_j + \Delta\xi_i) - \frac{1}{2}\,l_0(R_0 - l_0)\left[(\Delta\phi_j)^2 + (\Delta\xi_i)^2\right]$$
$$\left. + l_0^2\,\Delta\phi_j\,\Delta\xi_i \right\}$$

and

$$\frac{H^2}{8D_0^2} = \frac{1}{8}\left\{ (\Delta l_j)^2 + (\Delta l_i)^2 + 2\Delta l_i\,\Delta l_j + 4(\Delta R_i)^2 \right.$$
$$+ 3l_0^2\left[(\Delta\phi_j)^2 + (\Delta\xi_i)^2 + 2\Delta\phi_j\,\Delta\xi_i\right]$$
$$+ 4\Delta R_i\,(\Delta l_i + \Delta l_j) + 2\sqrt{3}\,l_0(\Delta l_i + \Delta l_j)(\Delta\phi_j + \Delta\xi_i)$$
$$\left. + 4\sqrt{3}\,l_0\,\Delta R_i\,(\Delta\phi_j + \Delta\xi_i) \right\}.$$

$$\therefore \quad D_0\,\Delta D_i = \frac{D_0}{2}\left\{ \Delta l_i + \Delta l_j + 2\Delta R_i + \sqrt{3}\,l_0(\Delta\phi_j + \Delta\xi_i) \right\}$$
$$+ \frac{3}{8}(\Delta l_i)^2 + \frac{3}{8}(\Delta l_j)^2 - \frac{3}{4}\Delta l_i\,\Delta l_j$$
$$+ (D_0 + R_0)\frac{\sqrt{3}}{4}(\Delta l_i\,\Delta\phi_j + \Delta l_i\,\Delta\xi_i)$$
$$+ \frac{\sqrt{3}}{4}\,l_0\,(\Delta l_i\,\Delta\phi_j + \Delta l_j\,\Delta\xi_i)$$
$$- \frac{1}{4}\,l_0(R_0 + \frac{1}{2}l_0)\left[(\Delta\phi_j)^2 + (\Delta\xi_i)^2\right] - \frac{1}{4}\,l_0^2\,\Delta\phi_j\,\Delta\xi_i \quad {}^{*}$$

For Δd_i, the variation of the nonbonded distance between H_i and H_{i-1}, $D_i = d_i$, $R_i = R_i$, $l_j = r_i$, $l_j = r_{i-1}$, $\xi_i = \pi - \theta_{i-1} - \alpha_{i-1}$, and $\phi_j = \theta_i$.

$$d_0\,\Delta d_i = \frac{d_0}{2}\left\{ \Delta r_i + \Delta r_{i+1} + 2\Delta R_i + \sqrt{3}\,r_0\,(\Delta\theta_i + \Delta\theta_{i+1} - \Delta\alpha_{i-1}) \right\}$$
$$+ \frac{3}{8}(\Delta r_i)^2 + \frac{3}{8}(\Delta r_{i+1})^2 - \frac{3}{4}(\Delta r_i)(\Delta r_{i+1})$$
$$+ \frac{\sqrt{3}}{4}(d_0 + R_0)(\Delta r_i\,\Delta\theta_{i+1} + \Delta r_{i+1}\,\Delta\theta_{i+1} - \Delta r_i\,\Delta\alpha_i)$$
$$+ \frac{\sqrt{3}}{4}\,r_0\,(\Delta r_{i+1}\,\Delta\theta_i + \Delta r_i\,\Delta\theta_{i+1} - \Delta r_{i+1}\,\Delta\alpha_i)$$
$$- \frac{1}{4}\,r_0(R_0 + \frac{r_0}{2})\left[(\Delta\theta_i)^2 + (\Delta\theta_{i+1})^2 + (\Delta\alpha_i)^2 + 2\Delta\theta_i\,\Delta\alpha_i\right]$$
$$+ \frac{1}{4}\,r_0^2(\Delta\theta_i\,\Delta\theta_{i+1} + \Delta\theta_{i+1}\,\Delta\alpha_i)$$

* This result can be readily verified by a Taylor's expansion of ΔD_i, while $D_i^2 = [l_i\sin\xi_i - l_j\sin\phi_j]^2 + [R_i - l_i\cos\xi_i - l_j\cos\phi_j]^2$.

For ΔD_i, the variation of the nonbonded distance between C_{i+1} and C_{i-2}, $D_i = D_j$, $D_0 = 2R_0$, $R_0 = l_0$, $l_i = R_{i-1}$, $l_j = R_{i+1}$, $\xi_i = \alpha_i$, and $\phi_j = \alpha_{i+1}$.

$$D_0 \Delta D_i = R_0 \left[\Delta R_{i-1} + 2\Delta R_i + \Delta R_{i+1} + \sqrt{3}\, R_0 (\Delta\alpha_{i+1} + \Delta\alpha_i) \right]$$

$$+ \frac{3}{8}(\Delta R_{i-1})^2 + \frac{3}{8}(\Delta R_{i+1})^2 - \frac{3}{4}\Delta R_{i-1}\Delta R_{i+1}$$

$$+ \frac{3\sqrt{3}}{4} R_0 (\Delta R_{i-1}\Delta\alpha_i + \Delta R_{i+1}\Delta\alpha_{i+1})$$

$$+ \frac{\sqrt{5}}{4} R_0 (\Delta R_{i-1}\Delta\alpha_{i+1} + \Delta R_{i+1}\Delta\alpha_i)$$

$$- \frac{3}{8} R_0^2 \left[(\Delta\alpha_i)^2 + (\Delta\alpha_{i+1})^2 \right] - \frac{1}{4} R_0^2 \Delta\alpha_i \Delta\alpha_{i+1} \quad .$$

Out-of-Plane Hydrogen Vibrations in Triborine Triamine

Robert A. Spurr and Shih-Chuan Chang
*Department of Chemistry, University of Maryland,
College Park, Maryland*
(Received February 8, 1951)

CRAWFORD and Edsall[1] have investigated the infrared and Raman spectra of triborine triamine. The discrepancy between the calculated and observed frequencies of the out-of-plane hydrogen vibrations was attributed to the interactions between hydrogen bonds attached in the meta positions. Bell[2] has suggested the use of a simple potential function for the out-of-plane vibrations in triborine triamine, which he has applied successfully to benzene. We have carried out the calculations and have obtained satisfactory agreement with the observed frequencies, as is shown in Table I.

The potential function assumed has the following form:

$$2V = \Sigma h_B r^2 \lambda^2 + \Sigma h_N s^2 \mu^2 + \Sigma k'(\phi_R + \phi_H)^2,$$

where h_B is the bending force constant for the B−H bond, r is the internuclear distance, and λ is the angle which the bond makes with the plane of the ring. The symbols h_N, s, and μ denote the corresponding quantities for the N−H bond. The constant k' expresses a resistance to twisting of the B−N bond. The quantities ϕ_R and ϕ_H represent the twist of the B−N bond due to ring distortion and hydrogen bending, respectively.[3] This potential function differs from that assumed by Crawford and Edsall[1] by the introduction of ϕ_H. The fairly satisfactory agreement obtained by this potential function renders unnecessary the assumption of interactions between hydrogen bonds attached in the meta positions.

The force constants were fitted to the three A'' frequencies and

TABLE I.

Observed frequency[1] cm⁻¹	Calculated frequency[1] cm⁻¹	% Deviation	Calculated frequency cm⁻¹ (this research)	% Deviation (this research)
1098	1278	16.4	1117	1.7
622	756	21.6	661	6.3
415	403	2.9	437	5.3
1070	1086	1.5	1054	1.5
798	790	1.0	753	5.6
288	283	1.7	270	6.3
		Mean 7.5		Mean 4.5

TABLE II. Force constants for triborine triamine, benzene, and ethylene.

Type of constant	Value
B−H bending, h_B	1.83×10^4 dyne/cm
N−H bending, h_N	3.71×10^4 dyne/cm
B−N twisting, k'	0.39×10^{-12} dyne-cm
benzene C−C twisting[2]	0.77×10^{-12} dyne-cm
ethylene C−C twisting[2]	1.7×10^{-12} dyne-cm

also to the three E'' frequencies. For the calculation of the frequencies in Table I, average values of the constants were used. These are given in Table II, together with the constants corresponding to k' for benzene and ethylene. The value of the twisting force constant obtained by Crawford and Edsall[1] without introduction of ϕ_H in the potential function corresponds to 1.6×10^{-12} dyne-cm for k'. The value given here of 0.39×10^{-12} dyne-cm is more reasonable, since one would expect the ring bonds in triborine triamine to have less resistance to twisting than those in benzene and ethylene.

If it is assumed that k' varies linearly with double-bond character for different bonds, the double-bond character of the B−N bond in triborine triamine is $39/77 \times 1/2$ or 28 percent, taking that of benzene as 50 percent. This assumption can be tested by calculating the double-bond character of benzene by the use of the ethylene twisting constant. The value obtained is 45 percent. The double-bond character of a bond can also be estimated by the empirical formula of Pauling.[4] The B−N distance in triborine triamine has been measured in two investigations[5,6] by electron diffraction as 1.47±0.07A and 1.44±0.02A. These values inserted in the formula give 27 percent and 40 percent, respectively, for the double-bond character of the B−N bond, in rough agreement with the value given above.

[1] B. L. Crawford and J. T. Edsall, J. Chem. Phys. 7, 223 (1939).
[2] R. P. Bell, Trans. Faraday Soc. 41, 293 (1945).
[3] Bell, Thompson, and Vago, Proc. Roy. Soc. (London) A192, 498 (1948).
[4] L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1940), p. 175.
[5] A. Stock and R. Wierl, Z. anorg. u. allgem. Chem. 203, 228 (1931).
[6] S. H. Bauer, J. Am. Chem. Soc. 60, 524 (1938).

BIBLIOGRAPHY

1. Barnes, J. and W. H. Fulweiler, *Phys. Rev.* 32, 618 (1928).

2. Baurr, S. H., *J. Am. Chem. Soc.* 60, 524 (1938).

3. Bell, R. P., *Trans. Faraday Soc.* 41, 293 (1945).

4. Bell, R. P., H. W. Thompson, and E. E. Vago, *Proc. Royal Soc.* (London) A 192, 498 (1948).

5. Crawford, B. L. and J. T. Edsall, *J. Chem. Phys.* 7, 223 (1939).

6. Crawford, B. L. and F. A. Miller, *J. Chem. Phys.* 17, 249 (1949).

7. Ellis, J. W., *J. Am. Chem. Soc.* 49, 347 (1927); *Phys. Rev.* 33, 29 (1929).

8. Frazer, R. A., W. J. Duncan, and A. R. Collar, Elementary Matrices. MacMillan Co., New York (1947) p. 27.

9. ibid, p. 106.

10. Herzberg, G., Infrared and Raman Spectra. D. van Nostrand Co., New York (1949) p. 186.

11. Ibid, p. 193.

12. Ibid, p. 363.

13. Ibid, p. 116.

14. Ibid, p. 138.

15. Ingold, C. K. et al., *J. Chem. Soc.* (London) 1946, 222-333.

16. James, H. M., and A. S. Coolidge, *J. Chem. Phys.* 1, 834 (1933).

17. Kohlrausch, K. W. F., Der Smekel-Raman-Effekt. Verlag von Julius Springer. Berlin. (1931).

18. Linnett, J. W., *Quart. Rev.* 1, 73 (1947).

19. Linnett, J. W., and D. F. Heath, *Trans. Faraday Soc.* 44, 561, 873, 878, 884 (1948).

20. Lord, R. C., and D. H. Andrews, *J. Phys. Chem.* 41, 149 (1937).

21. Mair, R. D. et al., *J. Chem. Phys.* 17, 1236 (1949).

22. Nielsen, J. R. and L. H. Berryman, *J. Chem. Phys.* 17, 659 (1949).

23. Pauling, L., Nature of the Chemical Bond. Cornell University Press. Ithaca, New York. (1940). p. 175.

24. Shull, H., J. Chem. Phys. 17, 295 (1949).

25. Simanouti, T. et al., J. Chem. Phys. 17, 245, 734, 848, 1102 (1949);
    Bull. I. P. C. R. (Japan) 21, 825 (1942); 23, 133 (1944).

26. Stock, A., and R. Wierl, Z. Anorg. n. Allgen. Chem. 203, 228 (1931).

27. Urey, H. C., and C. A. Bradley, Phys. Rev. 38, 1969 (1931).

28. Wilson, E. B., J. Chem. Phys. 9, 76 (1941).

29. Wilson, E. B., J. Chem. Phys. 7, 1047 (1939).

30. Wilson, E. B., Phys. Rev. 45, 706 (1934).

VITA

Shih-Chuan Cheng, born on December 30, 1925 in Nanking, China. National Central University, Nanking, China, 1933-1935. National Institute of Technology, Chungking, China, 1935-1938. Purdue University, Indiana, 1947-1950. University of Maryland, 1950-1952. Assistant chemical engineer, chemical engineer of the 10th Arsenal, Chungking, China, 1938-1946. Chemical engineer of the 60th Arsenal, Nanking, China, 1946-1947. B.S. 1938. M.S. in Ch. E. 1949. Ph.D 1952.