

FORCE CONSTANTS FOR 1, 3, 5 TRIMETHYL BENZENE

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INTRODUCTION

This paper presents the calculation of the valence force constants for the non-planar vibrations of the 1, 3, 5 trimethyl benzene molecule, namely, H , the methyl diagonal bending constant, h_m , the interaction constant between the methyl bendings, \bar{a}_o , the interaction constant between a methyl bending and an adjacent ortho hydrogen bending and lastly, \bar{a}_p , the interaction between a methyl bending and a para hydrogen bending. The values of the vibrational frequencies for the molecule are then deduced and compared with the assignments made by previous investigators from other considerations. For the purpose of this calculation, the results of the normal co-ordinate analysis of the non-planar vibrations of Benzene and its Deuterium derivatives (Miller and Crawford, 1946) have been utilised. The method of calculation is that given by the author (1953) in an earlier paper on the Force constants for the BF_3 molecule.

1, 3, 5 Trimethyl Benzene (commonly known as Mesitylene) belongs to the point group D_{3h} , if, as a first approximation, the CH_3 substituent is considered as a single atom, ignoring thereby the interactions within the methyl group, which affect the skeletal bending. The nine non-planar vibrations of 1, 3, 5 trimethyl benzene are divided into the two symmetry species as $3A_2'' + 3E''$, the latter being doubly degenerate. The vibrations of species A_2'' are infrared active and those of E'' are Raman active. One of the A_2'' fundamentals has not been recorded in infrared but only tentatively assigned (Pitzer and Scott, 1943) from Raman effect observations. Two weak Raman lines 145 cm.^{-1} and 182 cm.^{-1} are stated by Pitzer and Scott to have been observed by two different investigators. Of these, 182 cm.^{-1} has been assigned by Pitzer and Scott as one of the A_2'' fundamentals on the basis of the product rule analogous to that of Tellar and Redlich. The present calculations of the force constants of this molecule have led to the confirmation of this tentative assignment.

Pitzer and Scott have also suggested the frequency 439 cm.^{-1} as one of the E'' fundamentals of Mesitylene. In assigning the degenerate modes, it may be noted that certain frequencies should be either exactly or approximately the same as in Meta-Xylene (3, 5 dimethyl benzene). The three fundamentals 10, 16 and 17 (in Wilson's notation) of E'' species in 1, 3, 5 trimethyl benzene will be split up into $10a$, $16a$ and $17a$ of A_2 species and $10b$, $16b$ and $17b$ of B_2 species in case of (3, 5) *m*-Xylene. Here the degeneracy is removed, one component changing and the other remaining almost equal, i.e. $10a$, $16a$ and $17a$ in *m*-Xylene will be exactly same as 10, 16 and 17 of mesitylene. Pitzer and Scotts' assignment is based on this consideration. No line appears in the Mesitylene spectrum where No. 16 in Pitzer and Scotts' notation is expected. A very weak line is observed at 439 cm.^{-1} in the Raman spectrum of *m*-Xylene (assigned as $16a$). This is regarded by Pitzer and Scott (1943) as the corresponding frequency No. 16 in mesitylene. It is possible to compare this assignment with the value derived in these calculations from the force constants, but the author finds the agreement unsatisfactory.

A preliminary report of the results have been published in *Current Science* (Vol. 23, 115, 1954).

CALCULATIONS

Three types of non-planar valence force co-ordinates are used to construct the symmetry co-ordinates for the two species and they are schematically represented in Fig. 1.

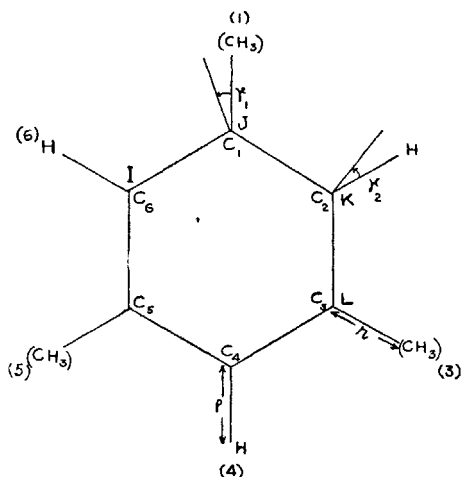


FIG. 1.

(1) The perpendicular displacement of the i -th CH_3 group defined by the two adjacent $\text{C}-\text{C}$ bonds is termed as $r\gamma_i$, where γ_i is the angle between $\text{C}-\text{CH}_3$ bond and the plane formed by C_1C_6 and C_1C_2 bonds of the molecule and r is the equilibrium distance of $\text{C}_{\text{arom}}-\text{C}_{\text{aliph}}$. (2) The corresponding perpendicular displacement of the i -th hydrogen atom is termed as $\rho\gamma_i$ where ρ is the equilibrium distance of $\text{C}-\text{H}$ bond length. (3) The non-planar ring bending deformations are regarded as torsions around $\text{C}-\text{C}$ bonds. The angle between the plane containing 6, 1, 2 carbon atoms and that containing 1, 2, 3 carbon atoms is termed as δ_1 . The corresponding internal co-ordinate is $R\delta_1$ where R is the equilibrium value of $\text{C}-\text{C}$ bond distance. The complete set of internal co-ordinates is $r\gamma_1, \rho\gamma_2, r\gamma_3, \rho\gamma_4, r\gamma_5, \rho\gamma_6, R\delta_1, R\delta_2, R\delta_3, R\delta_4, R\delta_5$ and $R\delta_6$. The symmetry co-ordinates are constructed with the above internal co-ordinates and are found to be just the same as those used in the case of 1, 3, 5 trifluoro benzene recently worked out by Ferguson (1953) and are given in Table I.

TABLE I

Species	Symmetry Co-ordinates
	$R_1 = 6^{-\frac{1}{2}} (r\gamma_1 + \rho\gamma_2 + r\gamma_3 + \rho\gamma_4 + r\gamma_5 + \rho\gamma_6)$
A_2''	$R_2 = 6^{-\frac{1}{2}} (r\gamma_1 - \rho\gamma_2 + r\gamma_3 - \rho\gamma_4 + r\gamma_5 - \rho\gamma_6)$
	$R_3 = R \times 6^{-\frac{1}{2}} (\delta_1 - \delta_2 + \delta_3 - \delta_4 + \delta_5 - \delta_6)$
	$R_{1a} = \frac{1}{2} (r\gamma_3 - \rho\gamma_2 - r\gamma_5 + \rho\gamma_6)$
	$R_{1b} = 12^{-\frac{1}{2}} (-2r\gamma_1 + \rho\gamma_2 + r\gamma_3 - 2\rho\gamma_4 + r\gamma_5 + \rho\gamma_6)$
E''	$R_{2a} = \frac{1}{2} (\rho\gamma_2 + r\gamma_3 - r\gamma_5 - \rho\gamma_6)$
	$R_{2b} = 12^{-\frac{1}{2}} (-2r\gamma_1 - \rho\gamma_2 + r\gamma_3 + 2\rho\gamma_4 + r\gamma_5 - \rho\gamma_6)$
	$R_{3a} = R \times 12^{-\frac{1}{2}} (-\delta_1 + 2\delta_2 - \delta_3 - \delta_4 + 2\delta_5 - \delta_6)$
	$R_{3b} = \frac{R}{2} (\delta_1 - \delta_3 + \delta_4 - \delta_6)$

P.E. Matrix

Table II gives the f matrix in terms of the valence force co-ordinates. In writing down this matrix, the notation of Miller and Crawford (1946) is retained for the ring deformation and the applicable hydrogen bending constants; o , m and p refer to ortho, meta and para relationship between the internal co-ordinates. The elements of the F matrix for the species A_2'' and E'' are given in Tables III and IV respectively.

TABLE II

	$r\gamma_1$	$r\gamma_3$	$r\gamma_5$	$\rho\gamma_2$	$\rho\gamma_4$	$\rho\gamma_6$	$R\delta_1$	$R\delta_2$	$R\delta_3$	$R\delta_4$	$R\delta_5$	$R\delta_6$
$r\gamma_1$	H	h_m	h_m	\bar{a}_o	\bar{a}_p	\bar{a}_o	$-\bar{c}_o$	$-\bar{c}_m$	$-\bar{c}_p$	$+\bar{c}_p$	$+\bar{c}_m$	$+\bar{c}_o$
$r\gamma_3$		H	h_m	\bar{a}_o	\bar{a}_o	\bar{a}_p	$+\bar{c}_m$	$+\bar{c}_o$	$-\bar{c}_o$	$-c_m$	$-\bar{c}_p$	$+\bar{c}_p$
$r\gamma_5$			H	\bar{a}_p	\bar{a}_o	\bar{a}_o	$-\bar{c}_p$	$+\bar{c}_p$	$+\bar{c}_m$	$+\bar{c}_o$	$-\bar{c}_o$	$-\bar{c}_m$
$\rho\gamma_2$				A	a_m	a_m	$+c_o$	$-c_o$	$-c_m$	$-c_p$	$+c_p$	$+c_m$
$\rho\gamma_4$					A	a_m	$+c_p$	$+c_m$	$+c_o$	$-c_o$	$-c_m$	$-c_p$
$\rho\gamma_6$						A	$-c_m$	$-c_p$	$+c_p$	$+c_m$	$+c_o$	$-c_o$
$R\delta_1$							B	b_o	b_m	b_p	b_m	b_o
$R\delta_2$								B	b_o	b_m	b_p	b_m
$R\delta_3$									B	b_o	b_m	b_p
$R\delta_4$										B	b_o	b_m
$R\delta_5$											B	b_o
$R\delta_6$												B

The table is symmetrical about the principal diagonal.

TABLE III

$$F_{11} = \frac{1}{2} A + a_m + \frac{1}{2} H + h_m + 2\bar{a}_o + \bar{a}_p$$

$$F_{12} = \frac{1}{2} H + h_m - \frac{1}{2} A - a_m$$

$$F_{13} = (c_o + c_p - c_m) - (\bar{c}_o + \bar{c}_p - \bar{c}_m)$$

$$F_{22} = \frac{1}{2} A + a_m + \frac{1}{2} H + h_m - 2\bar{a}_o - \bar{a}_p$$

$$F_{23} = -(c_o + c_p - c_m) + (\bar{c}_o + \bar{c}_p - \bar{c}_m)$$

$$F_{33} = B + 2b_m - 2b_o - b_p$$

TABLE IV

$$F_{11} = \frac{1}{2} (A - a_m + H - h_m - 2\bar{a}_o + 2\bar{a}_p)$$

$$F_{12} = \frac{1}{2} (H - h_m - A + a_m)$$

$$F_{13} = \frac{1}{2} \times 3^{\frac{1}{2}} (\bar{c}_o + c_o - \bar{c}_p + c_p)$$

$$F_{22} = \frac{1}{2} (A - a_m + H - h_m + 2\bar{a}_o - 2\bar{a}_p)$$

$$F_{23} = \frac{1}{2} \times 3^{\frac{1}{2}} (\bar{c}_o - c_o - \bar{c}_p + c_p)$$

$$F_{33} = B - b_o - b_m + b_p$$

The following assumptions are made in order to simplify the above matrix elements:—

(1) The forces involved in the distortion of the benzene ring are essentially the same in mesitylene as in benzene. Thus F_{33} of species A_2'' equals to Miller and Crawford's β and that of E'' to their θ . (2) The interaction between a CH_3 motion out of the plane and a non-planar ring deformation is equal to the interaction between a hydrogen motion out of the plane and a non-planar ring deformation, or in other words $\bar{c}_o = c_o$, $\bar{c}_m = c_m$, and $\bar{c}_p = c_p$. With the latter assumption F_{23} of species A_2'' and F_{13} of species E'' are equal to Miller and Crawford's (1946) η and ω respectively. F_{13} of species A_2'' and F_{23} of E'' are zero. These assumptions were also made by Ferguson to determine the force constants for 1, 3, 5 trifluoro benzene. Thus the constants A , a_m , η , β , θ and ω are carried over to this problem from benzene.

K.E. Matrix

The elements of the K.E. matrices are calculated by the method adopted by Wilson (1939). The vector expressions are obtained considering a unit vector perpendicular to the equilibrium plane of the molecule. These expressions are given in Table V.

TABLE V

$$\begin{aligned}
 {}^s R_{\delta_1}^I &= \frac{2V}{3}, & {}^s R_{\delta_1}^J &= -\frac{4V}{3}, & {}^s R_{\delta_1}^K &= \frac{4V}{3}, & {}^s R_{\delta_1}^L &= -\frac{2V}{3} \\
 {}^s r_{\gamma_{1,3,5}}^H &= V, & {}^s r_{\gamma_{2,4,6}}^{\text{CH}_3} &= V, & {}^s r_{\gamma_1}^{\text{C}_1} &= -V(1+2\rho_{\text{CH}_3}), & {}^s r_{\gamma_1}^{\text{C}_2} &= {}^s r_{\gamma_1}^{\text{C}_6} = \rho_{\text{H}} V
 \end{aligned}$$

Where V is unit vector perpendicular to the equilibrium plane of I , J , K (Fig. 1). The remaining expressions can be similarly written down.

With the help of these expressions, the matrix elements are derived. Tables VI and VII represent the G matrix elements for the species A_2'' and E'' respectively.

TABLE VI

$$\begin{aligned}
 G_{11} &= \frac{1}{2}(\mu_{\text{CH}_3} + \mu_{\text{H}}) + (\mu_{\text{C}})[1 + 4(\rho_{\text{H}} - \rho_{\text{CH}_3})^2] \\
 G_{12} &= \frac{1}{2}(\mu_{\text{CH}_3} - \mu_{\text{H}}) + 2\mu_{\text{C}}(\rho_{\text{CH}_3} - \rho_{\text{H}})[1 + 2(\rho_{\text{H}} + \rho_{\text{CH}_3})] \\
 G_{13} &= 8 \times 3^{\frac{1}{2}} \mu_{\text{C}}(\rho_{\text{H}} - \rho_{\text{CH}_3}) \\
 G_{22} &= \frac{1}{2}(\mu_{\text{CH}_3} + \mu_{\text{H}}) + \mu_{\text{C}}(1 + 2\rho_{\text{CH}_3} + 2\rho_{\text{H}})^2 \\
 G_{23} &= -4 \times 3^{\frac{1}{2}} \mu_{\text{C}}(2\rho_{\text{CH}_3} + 2\rho_{\text{H}} + 1) \\
 G_{33} &= 48\mu_{\text{C}}
 \end{aligned}$$

TABLE VII

$$\begin{aligned}
 G_{11} &= \frac{1}{2}[\mu_{\text{H}} + \mu_{\text{CH}_3} + \mu_{\text{C}} \{ (2\rho_{\text{CH}_3} + \rho_{\text{H}} + 1)^2 + (2\rho_{\text{H}} + \rho_{\text{CH}_3} + 1)^2 \}] \\
 G_{12} &= \frac{1}{2}[\mu_{\text{CH}_3} - \mu_{\text{H}} + \mu_{\text{C}}(5\rho_{\text{CH}_3}^2 + 4\rho_{\text{CH}_3} - 5\rho_{\text{H}}^2 - 4\rho_{\text{H}})] \\
 G_{13} &= 2\mu_{\text{C}}(3\rho_{\text{CH}_3} + 3\rho_{\text{H}} + 2) \\
 G_{22} &= \frac{1}{2}[\mu_{\text{CH}_3} + \mu_{\text{H}} + \mu_{\text{C}} \{ (1 + 2\rho_{\text{CH}_3} - \rho_{\text{H}})^2 + (1 + 2\rho_{\text{H}} - \rho_{\text{CH}_3})^2 \}] \\
 G_{23} &= 6\mu_{\text{C}}(\rho_{\text{CH}_3} - \rho_{\text{H}}) \\
 G_{33} &= 16\mu_{\text{C}}
 \end{aligned}$$

where μ 's are reciprocal atomic masses in atomic weight units.

$$\rho_{\text{H}} = \text{C—H/C—C} \quad \text{and} \quad \rho_{\text{CH}_3} = \text{C}_{\text{arom}}\text{—C}_{\text{aliph}}/\text{C—C}$$

DETERMINATION OF THE FORCE CONSTANTS

With the help of the above assumptions the F matrix of species A_2'' will involve only two unknown combinations of valence force constants, $\frac{1}{2}H+h_m$ and $2\bar{a}_o+\bar{a}_p$ and that of E'' will involve another two combinations $H-h_m$ and $2\bar{a}_o-2\bar{a}_p$. To determine these four combinations, only four frequencies, two of species A_2'' and two of E'' are required. The remaining fundamental for each species is then calculated. From the four combinations, the individual values of H , h_m , \bar{a}_o and \bar{a}_p are obtained.

Vibrations of species A_2''

Two of the fundamentals 690 cm.^{-1} and 840 cm.^{-1} are very definitely assigned, but the lowest infra-red active fundamental 182 cm.^{-1} is assigned by Pitzer and Scott on the basis of the product rule. Miller and Crawford's first set of constants for β and η of benzene led to imaginary force constants. The second set gave two sets of values for $\frac{1}{2}H+h_m$ and $2\bar{a}_o+\bar{a}_p$ because of the quadratic nature of the secular equation and they are given below.

	$\frac{1}{2}H+h_m$	$2\bar{a}_o+\bar{a}_p$
Set 1	0.340918	0.850213
Set 2	0.297849	0.03602

The calculations are repeated with both the sets to obtain the value of the third fundamental. With the first set a value so high as 1286 cm.^{-1} and with the second set, 179 cm.^{-1} which is in very close agreement with 182 cm.^{-1} is obtained. The first set of the constants is discarded, confirming the assignment of 182 cm.^{-1} as the third A_2'' fundamental, made by Pitzer and Scott.

Vibrations of species E''

Two of the fundamentals of species E'' , namely, 275 cm.^{-1} and 847 cm.^{-1} with Miller and Crawford's first set of constants for θ and ω have once again led to the imaginary values for the combinations $H-h_m$ and $2\bar{a}_o-2\bar{a}_p$. The second set of constants result in two sets of values as shown in the following table.

	$H-h_m$	$2\bar{a}_o-2\bar{a}_p$
Set 1	0.32016	-0.460656
Set 2	0.275677	-0.190547

With the first set of the above force constants a value 771 cm.^{-1} and with the second set a value 561 cm.^{-1} are obtained as the third fundamental of the E'' species. Neither of the values agrees with the value 439 cm.^{-1} suggested by Pitzer and Scott. A reinvestigation of the infra-red and Raman spectra of this molecule is desirable to establish this fundamental. From a comparison with the frequencies of 1, 3, 5 Trifluoro Benzene, it may be seen that 179 cm.^{-1} of A_2'' and 561 cm.^{-1} of E'' (mesitylene) calculated by the author compare well with the corresponding frequencies 214 cm.^{-1} of A_2'' and 595 cm.^{-1} of E'' (1, 3, 5 trifluoro benzene) observed by Nielsen (1950) and confirmed recently by Ferguson (1953).

In arriving at the individual values of the force constants the combinations which led to the fundamentals 179 cm.^{-1} of A_2'' and 561 cm.^{-1} of E'' are considered. These are given below.

$\frac{1}{2}H+h_m$	=	0.297849	H	=	0.382
$H-h_m$	=	0.275677	h_m	=	0.107
$2\bar{a}_o+\bar{a}_p$	=	0.03602	\bar{a}_o	=	-0.02
$2\bar{a}_o-2\bar{a}_p$	=	-0.190547	\bar{a}_p	=	0.076

The numerical values of the above force constants are to be finally multiplied by 10^5 and expressed in dynes/cm.

DISCUSSION OF THE RESULTS

The diagonal methyl wagging constant H is found to be 0.382 which is slightly greater than that of the corresponding Hydrogen constant $A = 0.378$ in benzene. This may imply that it is energetically more difficult to displace CH_3 group out of the plane than to displace a Hydrogen atom out of the plane of the benzene ring. F_{11} of species A_2'' refers to the dish-like symmetry co-ordinate representing bending of all the H and CH_3 atoms above and below the plane of the ring whereas F_{22} refers to puckered co-ordinate corresponding to a motion where CH_3 's and H's are displaced in the opposite sides of the ring. In case of benzene the energy required for the dish-like distortion must be less than that for the puckered displacement. But in this $F_{11} > F_{22}$. This may be attributed to the repulsive forces being predominant between hydrogen atoms and the CH_3 groups.

The following numerical values are used in the present calculations. $\text{C}-\text{C} = 1.39 \text{ \AA}$, $\text{C}-\text{H} = 1.08 \text{ \AA}$, $\text{C}_{\text{arom}}-\text{C}_{\text{aliph}} = 1.54 \text{ \AA}$, $\mu_{\text{H}} = 0.99206$, $\mu_{\text{C}} = 0.08326$, $\mu_{\text{CH}_3} = 0.066516$, $\rho_{\text{H}} = 0.7770$, $\rho_{\text{CH}_3} = 1.10791$.

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SUMMARY

Wilson's $F-G$ matrix method has been applied to the non-polar vibrations of 1, 3, 5 trimethyl benzene to determine the out-of-plane valence force constants. The value 182 cm.^{-1} assigned by Pitzer and Scott as the lowest A_2'' fundamental is confirmed from the present calculations. The assignment of 439 cm.^{-1} as one of the E'' fundamental appears doubtful, the calculated value being 561 cm.^{-1} .

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