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THE POTENTIAL FUNCTION OF BENZENE

BY

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I. Introduction.

Few problems have attracted the interest of chemists more than the question of setting up a correct benzene formula. A brief survey of the formulas proposed is found e.g. in WITTIG¹. The final answer of chemistry is that the benzene molecule is plane and has a sixfold axis of symmetry (symmetry class D_{6h}). But as chemical constitution proofs are produced by means of substitution processes in which the molecule to be investigated is greatly disturbed, it is very desirable to obtain confirmation of the above-mentioned result by means of physical methods. The molecule to be investigated may by such methods be exposed to minimum disturbances (e.g. by irradiation of light) so that the aspects of the structure of the molecule obtained are exceedingly reliable.

Such a physical investigation, viz. a recording of the Raman spectra of benzene and completely or partly deuterated benzenes, was made in 1936—38 in the Chemical Laboratory of the University of Copenhagen^{2,3}. Indeed, similar investigations have been made by others,^{4,5} but a material as great and reliable as that provided by LANGSETH, LORD, and KLIT, has not been published from other quarters. In the present work I shall therefore in the main follow LANGSETH and LORD in their interpretation of the spectra observed. The result of their investigations was that the molecule of benzene has a sixfold axis of symmetry, the same result as that appearing from the chemical

¹ Stereochemie, 158—60. Leipzig 1930.

² LANGSETH and KLIT. D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XV, No. 13 (1938).

³ LANGSETH and LORD, D. Kgl. Danske Vidensk. Selskab, Math.-fys. Medd. XVI, No. 6 (1938).

⁴ REDLICH and STRICKS. Monatshefte f. Chem. 67, 213, 68, 47, 374 (1936).

INGOLD and collaborators. Nature 135, 1033 (1935); 139, 880 (1937). Journ. Chem. Soc. London 912 (1936).

properties of the molecule. Amongst other things this means that we now know for certain that the chemical bonds from carbon atom to carbon atom is the same throughout the whole benzene ring.

LANGSETH and LORD only in one part of their work tried to utilize the values of frequency found for a quantitative determination of the valence forces of the benzene molecule. In the present work it is intended to try to utilize the available material of figures to the utmost. Even though a complete description of the potential function for the vibrations thus cannot be obtained, we are approaching appreciably to such a description, so that a single characteristic feature of the conditions of force in the molecule may be adduced. But the calculations made are also otherwise of importance, for it has proved to be possible on the basis of some of the vibration frequencies found by LANGSETH and LORD to precalculate the magnitude of others. A comparison between calculated and observed values of frequency on the whole turns out as favourable as may be expected. As LANGSETH and LORD's interpretation of the spectra of deuterated benzenes could be carried through with the greatest certainty, the agreement mentioned means confirmation of the correctness of the method of calculation used in the present work.

II. Expression of Kinetic Energy and Potential Function. Definition of Symmetry Coordinates.

MANNEBACK and his collaborators^{1,2,3} were the first to take up the question of the calculation of the intramolecular forces in benzene on a broad basis. WILSON JUNR.⁴, indeed, about the same time had been occupied with the potential function for the vibrational degrees of freedom, but in his calculations had only deduced formulas applying to a so-called "valence force

¹ Ann. Soc. Scient. Brux. LIV, 230 (1934).

² Ann. Soc. Scient. Brux. LV, 129 (1935).

³ Ann. Soc. Scient. Brux. LV, 237 (1935).

⁴ Phys. Rev. 45, 706 (1934).

model". WILSON's work includes no numerical calculations. At these it is soon proved, as will appear from what follows, that the valence force system is very little suitable for a rendering of conditions of force in the benzene molecule. In MANNEBACK's paper¹ some of the constants of the general quadratic potential function were calculated, but it was published three years before LANGSETH and LORD's work, so that the problem could only be subjected to a very incomplete treatment. Furthermore, the calculations seem to have been made in an unnecessarily complicated way. Finally we shall have a use for expressions of the connexion between the force constants in the potential function and the frequencies of the partly deuterated benzenes. These are completely absent in MANNEBACK's paper. So I have had to make up my mind to start all the calculations afresh.

The general quadratic potential function for the vibrations of benzene must be formulated with regard to the grouping of the vibrations in symmetry classes. The potential is expressed as a function of certain so-called symmetry coordinates S_i , found in the same number and having the same symmetry qualities as the vibrations in the symmetry class to which they belong. Here, of course, LANGSETH and LORD's classification is followed (*loc. cit.*, Table I). Table I is a survey of the symmetry coordinates.

Table I.

Symmetry class	Elements of symmetry				Number of vibrations	Zero frequencies	Symmetry coordinates
	C_3^z	C_2^z	C_2^y	i			
A_{1g}	+	+	+	+	2	..	$S_1 S_2$
A_{2g}	+	+	-	+	1	R_z	S_4
A_{2u}	+	+	-	-	1	T_z	S_5
B_{1u}	+	-	+	-	2	..	$S_7 S_8$
B_{2g}	+	-	-	+	2	..	$S_9 S_{10}$
B_{2u}	+	-	-	-	2	..	$S_{11} S_{12}$
E_g^+	$\epsilon^{\pm 1}$	+	\pm	+	4	..	$S_{13} S_{14} S_{15} S_{16} S_{17} S_{18} S_{19} S_{20}$
E_u^+	$\epsilon^{\pm 1}$	+	\pm	-	2	..	$S_{21} S_{22} S_{23} S_{24}$
E_g^-	$\epsilon^{\pm 1}$	-	\pm	+	1	R_x, R_y	$S_{25} S_{26}$
E_u^-	$\epsilon^{\pm 1}$	-	\pm	-	3	T_x, T_y	$S_{27} S_{28} S_{29} S_{30} S_{31} S_{32}$

¹ Ann. Soc. Scient. Brux. LV, 237 (1935).

The four last symmetry classes include degenerate vibrations, hence two symmetry coordinates must be defined for each vibration. And consequently the potential function is rendered by the equation:

$$2V = a_1 S_1^2 + a_2 S_2^2 + a_3 S_1 S_2 + a_4 S_4^2 + a_5 S_5^2 + a_6 S_7 S_8 + a_7 S_7^2 + a_8 S_8^2 + a_9 S_9^2 + a_{10} S_{10}^2 + a_{11} S_9 S_{10} + a_{12} S_{12}^2 + a_{13} S_{11} S_{12} + a_{14} S_{11}^2 + a_{15} (S_{13}^2 + S_{17}^2) + a_{16} (S_{14}^2 + S_{18}^2) + a_{17} (S_{15}^2 + S_{19}^2) + a_{18} (S_{16}^2 + S_{20}^2) + a_{19} (S_{13} S_{14} + S_{17} S_{18}) + a_{20} (S_{13} S_{15} + S_{17} S_{19}) + a_{21} (S_{13} S_{16} + S_{17} S_{20}) + a_{22} (S_{14} S_{15} + S_{18} S_{19}) + a_{23} (S_{14} S_{16} + S_{18} S_{20}) + a_{24} (S_{15} S_{16} + S_{19} S_{20}) + a_{25} (S_{21}^2 + S_{23}^2) + a_{26} (S_{22}^2 + S_{24}^2) + a_{27} (S_{21} S_{22} + S_{23} S_{24}) + a_{28} (S_{27}^2 + S_{28}^2) + a_{29} (S_{29}^2 + S_{30}^2) + a_{30} (S_{31}^2 + S_{32}^2) + a_{31} (S_{27} S_{29} + S_{28} S_{30}) + a_{32} (S_{27} S_{31} + S_{28} S_{32}) + a_{33} (S_{29} S_{31} + S_{30} S_{32}) + a_{34} (S_{25}^2 + S_{26}^2).$$

The a 's are the so-called force constants, 34 of which thus being found in the complete potential function. It is the numerical values of these 34 constants I shall try to calculate.

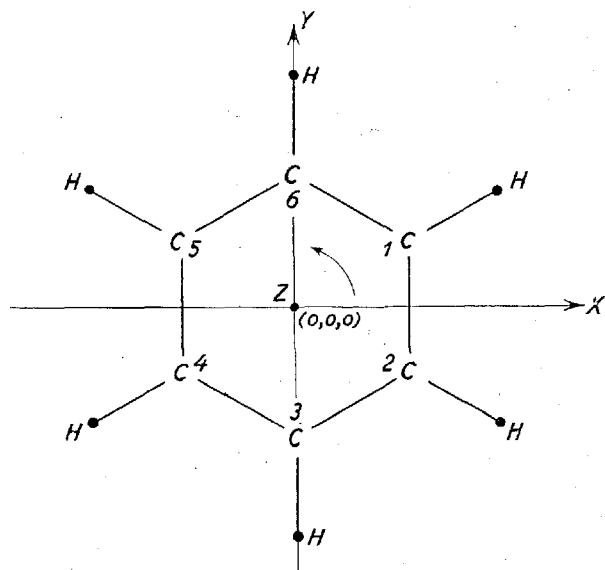


Fig. 1.

At the definition of the symmetry coordinates and the subsequent calculations the molecule is supposed to be placed in an orthogonal xyz coordinate system as shown in fig. 1.

The z -axis is perpendicular to the paper and has a positive direction towards the reader. The distance from $(0,0,0)$ to C is denoted by r ($= 1.40 \text{ \AA}^1$), the distance from $(0,0,0)$ to H is denoted by R ($= 2.48 \text{ \AA}^1$). The H and C atoms are numbered as shown in the drawing.

The components of the displacement of C atom no. j away from the position of equilibrium is denoted by

$$X_j, Y_j, Z_j \quad (j = 1, 2, 3, 4, 5, 6).$$

The components of the displacement of H atom no. j away from the position of equilibrium is denoted by

$$x_j, y_j, z_j \quad (j = 1, 2, 3, 4, 5, 6).$$

We define

$$U_j = X_j + iY_j \quad u_j = x_j + iy_j$$

$$U_j^* = X_j - iY_j \quad u_j^* = x_j - iy_j.$$

Inversely we have

$$X_j = \frac{1}{2} (U_j + U_j^*) \quad x_j = \frac{1}{2} (u_j + u_j^*)$$

$$Y_j = -\frac{i}{2} (U_j - U_j^*) \quad y_j = -\frac{i}{2} (u_j - u_j^*).$$

Because of the presence of the symmetry element C_3^Z it is further convenient to define the coordinates h_j and v_j , given by the equations

$$\begin{aligned} h_1 &= u_1 + u_3 + u_5 & h_2 &= u_2 + u_4 + u_6 \\ h_3 &= u_1 + \epsilon u_3 + \epsilon^2 u_5 & h_4 &= u_2 + \epsilon u_4 + \epsilon^2 u_6 \\ h_5 &= u_1 + \epsilon^2 u_3 + \epsilon u_5 & h_6 &= u_2 + \epsilon^2 u_4 + \epsilon u_6 \end{aligned}$$

$$\begin{aligned} v_1 &= z_1 + z_3 + z_5 & v_2 &= z_2 + z_4 + z_6 \\ v_3 &= z_1 + \epsilon z_3 + \epsilon^2 z_5 & v_4 &= z_2 + \epsilon z_4 + \epsilon^2 z_6 \\ v_3^* &= z_1 + \epsilon^2 z_3 + \epsilon z_5 & v_4^* &= z_2 + \epsilon^2 z_4 + \epsilon z_6 \end{aligned}$$

$$\epsilon = -\frac{1}{2} + \frac{i}{2} \sqrt{3}$$

¹ The distance $C-C = 1.40 \text{ \AA}$, the distance $C-H = 1.08 \text{ \AA}$.

and analogous definitions with capital letters instead of small letters.

Inversely we have

$$\begin{aligned} 3u_1 &= h_1 + h_3 + h_5 & 3u_2 &= h_2 + h_4 + h_6 \\ 3u_3 &= h_1 + \varepsilon^2 h_3 + \varepsilon h_5 & 3u_4 &= h_2 + \varepsilon^2 h_4 + \varepsilon h_6 \\ 3u_5 &= h_1 + \varepsilon h_3 + \varepsilon^2 h_5 & 3u_6 &= h_2 + \varepsilon h_4 + \varepsilon^2 h_6 \\ 3z_1 &= v_1 + v_3 + v_5^* & 3z_2 &= v_2 + v_4 + v_6^* \\ 3z_3 &= v_1 + \varepsilon^2 v_3 + \varepsilon v_5^* & 3z_4 &= v_2 + \varepsilon^2 v_4 + \varepsilon v_6^* \\ 3z_5 &= v_1 + \varepsilon v_3 + \varepsilon^2 v_5^* & 3z_6 &= v_2 + \varepsilon v_4 + \varepsilon^2 v_6^* \end{aligned}$$

An expression of the kinetic energy T of the molecule may now be drawn up, as

$$\begin{aligned} 2T &= \sum_1^6 m_H (\dot{x}_j^2 + \dot{y}_j^2 + \dot{z}_j^2) + \sum_1^6 m_c (\dot{X}_j^2 + \dot{Y}_j^2 + \dot{Z}_j^2) = \\ &= \frac{1}{3} m_H (\dot{h}_1 \dot{h}_1^* + \dot{h}_2 \dot{h}_2^* + \dot{h}_3 \dot{h}_3^* + \dot{h}_4 \dot{h}_4^* + \dot{h}_5 \dot{h}_5^* + \dot{h}_6 \dot{h}_6^* + \dot{v}_1^2 + 2\dot{v}_3 \dot{v}_3^* + \dot{v}_2^2 + 2\dot{v}_4 \dot{v}_4^*) \\ &+ \frac{1}{3} m_c (\dot{H}_1 \dot{H}_1^* + \dot{H}_2 \dot{H}_2^* + \dot{H}_3 \dot{H}_3^* + \dot{H}_4 \dot{H}_4^* + \dot{H}_5 \dot{H}_5^* + \dot{H}_6 \dot{H}_6^* + \dot{V}_1^2 + 2\dot{V}_3 \dot{V}_3^* + \dot{V}_2^2 + 2\dot{V}_4 \dot{V}_4^*) \end{aligned}$$

For the use of the coordinates h_j , v_j , H_j , and V_j for the definition of the symmetry coordinates it is further of importance to know how h_j , v_j , H_j , and V_j vary during those symmetry operations whose corresponding symmetry elements are found at the top of col. 2 in Table I.

By a rotation of 120° round the z -axis in the direction of the arrow we get

$$\begin{aligned} h_1 &\rightarrow \varepsilon h_1 & h_2 &\rightarrow \varepsilon h_2 & v_1 &\rightarrow v_1 & v_2 &\rightarrow v_2 \\ h_3 &\rightarrow h_3 & h_4 &\rightarrow h_4 & v_3 &\rightarrow \varepsilon^2 v_3 & v_4 &\rightarrow \varepsilon^2 v_4 \\ h_5 &\rightarrow \varepsilon^2 h_5 & h_6 &\rightarrow \varepsilon^2 h_6 & v_3^* &\rightarrow \varepsilon v_3^* & v_4^* &\rightarrow \varepsilon v_4^* \end{aligned}$$

and corresponding relations in capital letters.

By a rotation of 180° round the z -axis we get

$$\begin{aligned} h_1 &\leftrightarrow -h_2 & v_1 &\leftrightarrow v_2 \\ h_3 &\leftrightarrow -\varepsilon^2 h_4 & v_3 &\leftrightarrow \varepsilon^2 v_4 \\ h_5 &\leftrightarrow -\varepsilon h_6 & v_3^* &\leftrightarrow \varepsilon v_4^* \end{aligned}$$

By a rotation of 180° round the y -axis we get

$$\begin{aligned} h_1 &\leftrightarrow -h_1^* & h_2 &\rightarrow -h_2^* & v_1 &\rightarrow -v_1 & v_2 &\rightarrow -v_2 \\ h_3 &\rightarrow -\varepsilon^2 h_3^* & h_4 &\rightarrow -\varepsilon h_4^* & v_3 &\rightarrow -\varepsilon^2 v_3^* & v_4 &\rightarrow -\varepsilon v_4^* \\ h_5 &\rightarrow -\varepsilon h_5^* & h_6 &\rightarrow -\varepsilon^2 h_6^* & v_3^* &\rightarrow -\varepsilon v_3 & v_4^* &\rightarrow -\varepsilon^2 v_4 \end{aligned}$$

By inversion round (0,0,0) we finally get

$$\begin{aligned} h_1 &\leftrightarrow -h_2 & v_1 &\leftrightarrow -v_2 \\ h_3 &\leftrightarrow -\varepsilon^2 h_4 & v_3 &\leftrightarrow -\varepsilon^2 v_4 \\ h_5 &\leftrightarrow -\varepsilon h_6 & v_3^* &\leftrightarrow -\varepsilon v_4^* \end{aligned}$$

Corresponding relations are valid for capital letters.

Next, we may pass on to constructing the symmetry coordinates S_i .

In my doctor's thesis¹ I have had an opportunity to show how this is done in practice. With the symmetry class A_{1g} in benzene as an example I shall therefore only briefly state according to which criteria the symmetry coordinates S_1 and S_2 have been constructed. S_1 and S_2 are linear coordinate combinations which fulfil the following requirements:

(1) S_1 and S_2 must both be 0 at translational and rotational movements.

(2) As the vibrations in the A_{1g} class have the symmetry character $C_3^z(+)$, $C_2^z(+)$, $C_2^y(+)$, and $i(+)$ S_1 and S_2 must be invariant at the symmetry operations C_3^z , C_2^z , C_2^y , and $i(0,0,0)$.

(3) For vibrations in the A_{1g} class we have $(S_1, S_2) \neq (0,0)$, for vibrations in other symmetry classes $(S_1, S_2) = (0,0)$.

As appears, the symmetry coordinates may be selected in an infinite number of ways. The S_i chosen are rendered in Table II.

Table II.

$$\begin{aligned} S_1 &= i(\varepsilon^2 h_3 - \varepsilon h_3^* + \varepsilon^2 h_4 - \varepsilon h_4^*) \\ S_2 &= i(\varepsilon^2 H_3 - \varepsilon H_3^* + \varepsilon^2 H_4 - \varepsilon H_4^*) \\ S_4 &= \varepsilon^2 h_3 + \varepsilon h_3^* - \varepsilon h_4 - \varepsilon^2 h_4^* - \frac{R}{r}(\varepsilon^2 H_3 + \varepsilon H_3^* - \varepsilon H_4 - \varepsilon^2 H_4^*) \\ S_5 &= v_1 + v_2 - (V_1 + V_2) \\ S_7 &= i(\varepsilon h_3^* - \varepsilon^2 h_3 + \varepsilon^2 h_4^* - \varepsilon h_4) \\ S_8 &= i(\varepsilon H_3^* - \varepsilon^2 H_3 + \varepsilon^2 H_4^* - \varepsilon H_4) \end{aligned}$$

(To be continued)

¹ B. BAK, Det intramolek. Potential. København 1943.

Table II (continued).

$$\begin{aligned}
S_9 &= v_1 - v_2 \\
S_{10} &= V_1 - V_2 \\
S_{11} &= \varepsilon^2 h_3 + \varepsilon h_3^* + \varepsilon h_4 + \varepsilon^2 h_4^* \\
S_{12} &= \varepsilon^2 H_3 + \varepsilon H_3^* + \varepsilon H_4 + \varepsilon^2 H_4^* \\
S_{13} &= i(h_1 - h_1^* - h_2 + h_2^*) \\
S_{14} &= i(H_1 - H_1^* - H_2 + H_2^*) \\
S_{15} &= i(-\varepsilon h_5 + \varepsilon^2 h_5^* + \varepsilon^2 h_6 - \varepsilon h_6^*) \\
S_{16} &= i(-\varepsilon H_5 + \varepsilon^2 H_5^* + \varepsilon^2 H_6 - \varepsilon H_6^*) \\
S_{17} &= h_1 + h_1^* - (h_2 + h_2^*) \\
S_{18} &= H_1 + H_1^* - (H_2 + H_2^*) \\
S_{19} &= \varepsilon h_5 + \varepsilon^2 h_5^* - \varepsilon^2 h_6 - \varepsilon h_6^* \\
S_{20} &= \varepsilon H_5 + \varepsilon^2 H_5^* - \varepsilon^2 H_6 - \varepsilon H_6^* \\
S_{21} &= i(-\varepsilon^2 v_3 + \varepsilon v_3^* - \varepsilon v_4 + \varepsilon^2 v_4^*) \\
S_{22} &= i(-\varepsilon^2 V_3 + \varepsilon V_3^* - \varepsilon V_4 + \varepsilon^2 V_4^*) \\
S_{23} &= \varepsilon^2 v_3 + \varepsilon v_3^* + \varepsilon v_4 + \varepsilon^2 v_4^* \\
S_{24} &= \varepsilon^2 V_3 + \varepsilon V_3^* + \varepsilon V_4 + \varepsilon^2 V_4^* \\
S_{25} &= \frac{R}{r} (-\varepsilon^2 V_3 - \varepsilon V_3^* + \varepsilon V_4 + \varepsilon^2 V_4^*) + \varepsilon^2 v_3 + \varepsilon v_3^* - \varepsilon v_4 - \varepsilon^2 v_4^* \quad C_2^y(-) \\
S_{26} &= i \frac{R}{r} (\varepsilon^2 V_3 - \varepsilon V_3^* - \varepsilon V_4 + \varepsilon^2 V_4^*) - i(\varepsilon^2 v_3 - \varepsilon v_3^* - \varepsilon v_4 + \varepsilon^2 v_4^*) \quad C_2^y(+) \\
S_{27} &= h_1 + h_1^* + h_2 + h_2^* - (H_1 + H_1^* + H_2 + H_2^*) \quad C_2^y(-) \\
S_{28} &= i(-h_1 + h_1^* - h_2 + h_2^*) + i(H_1 - H_1^* + H_2 - H_2^*) \quad C_2^y(+) \\
S_{29} &= \varepsilon h_5 + \varepsilon^2 h_5^* + \varepsilon^2 h_6 + \varepsilon h_6^* \quad C_2^y(-) \\
S_{30} &= i(\varepsilon h_5 - \varepsilon^2 h_5^* + \varepsilon^2 h_6 - \varepsilon h_6^*) \quad C_2^y(+) \\
S_{31} &= \varepsilon H_5 + \varepsilon^2 H_5^* + \varepsilon^2 H_6 + \varepsilon H_6^* \quad C_2^y(-) \\
S_{32} &= i(\varepsilon H_5 - \varepsilon^2 H_5^* + \varepsilon^2 H_6 - \varepsilon H_6^*) \quad C_2^y(+)
\end{aligned}$$

Finally the possibilities of a translational and rotational movement away from the position of equilibrium are excluded by the equations

$$\begin{aligned}
m_H(h_1 - h_1^* + h_2 - h_2^*) + m_C(H_1 - H_1^* + H_2 - H_2^*) &= 0 \\
m_H(h_1 + h_1^* + h_2 + h_2^*) + m_C(H_1 + H_1^* + H_2 + H_2^*) &= 0 \\
m_H(v_1 + v_2) + m_C(V_1 + V_2) &= 0 \\
m_H R(-\varepsilon^2 v_3 - \varepsilon v_3^* + \varepsilon v_4 + \varepsilon^2 v_4^*) + m_C r(-\varepsilon^2 V_3 - \varepsilon V_3^* + \varepsilon V_4 + \varepsilon^2 V_4^*) &= 0 \\
m_H R(\varepsilon^2 v_3 - \varepsilon v_3^* - \varepsilon v_4 + \varepsilon^2 v_4^*) + m_C r(\varepsilon^2 V_3 - \varepsilon V_3^* - \varepsilon V_4 + \varepsilon^2 V_4^*) &= 0 \\
m_H R(\varepsilon^2 h_3 + \varepsilon h_3^* - \varepsilon h_4 - \varepsilon^2 h_4^*) + m_C r(\varepsilon^2 H_3 + \varepsilon H_3^* - \varepsilon H_4 - \varepsilon^2 H_4^*) &= 0
\end{aligned}$$

III. Drawing up and Solution of the Equations for the Vibrational Movements.

In what follows it is to be shown how this is done in the case of the vibrations in symmetry class A_{1g} . As regards the rest of the symmetry classes I shall content myself by stating in Table III the connexion between vibration frequencies and force constants.

The vibrations in the A_{1g} class contribute to the potential with the amount

$$2V = a_1 S_1^2 + a_2 S_2^2 + a_3 S_1 S_2.$$

The equations for the vibrational movements are drawn up by substitution in the formula

$$\frac{d}{dt} \left(\frac{\partial 2T}{\partial \dot{q}_K} \right) + \frac{\partial 2V}{\partial q_K} = 0.$$

For $q_k = S_1$ we derive $\frac{\partial 2V}{\partial S_1} = 2a_1 S_1 + a_3 S_2$ and from the expression for $2T$: $\frac{\partial 2T}{\partial \dot{S}_1} = \frac{m_H}{12} \dot{S}_1$.

Thus the equations for the movements are

$$\frac{m_H}{12} \ddot{S}_1 + 2a_1 S_1 + a_3 S_2 = 0$$

$$\frac{m_C}{12} \ddot{S}_2 + 2a_2 S_2 + a_3 S_1 = 0.$$

For harmonic vibrations we have $\ddot{S}_1 = -\omega^2 S_1$ and $\ddot{S}_2 = -\omega^2 S_2$, so that

$$\left(2a_1 - \frac{m_H}{12} \omega^2 \right) S_1 + a_3 S_2 = 0$$

$$a_3 S_1 + \left(2a_2 - \frac{m_C}{12} \omega^2 \right) S_2 = 0.$$

The equations have only solutions $\neq (0,0)$ for

$$\begin{vmatrix} 2a_1 - \frac{m_H}{12}z & a_3 \\ a_3 & 2a_2 - \frac{m_C}{12}z \end{vmatrix} = 0.$$

The roots of this quadratic equation in z are called z_1 and z_2 . We then have

$$z_1 + z_2 = 24 \left(\frac{a_2}{m_C} + \frac{a_1}{m_H} \right) (1) \quad z_1 z_2 = \frac{144}{m_C m_H} (4a_1 a_2 - a_3^2) (2).$$

The connexion between z_i and the frequency for the corresponding vibration ν_i is

$$z_i = 4\pi^2 \nu_i^2.$$

Table III shows the results of corresponding calculations in the other symmetry classes. In the first column the symmetry class is stated, in the second the designation of the frequency in close accordance with LANGSETH and LORD. The third column gives the derived relations between force constants and frequencies of vibration.

IV. Calculation of Some of the Force Constants of the Potential Function.

In what follows this calculation is to be carried through on the basis of frequency values from LANGSETH and LORD's work. As exclusively frequencies from the molecules C_6H_6 and C_6D_6 are used, the formulas of Table III are immediately applicable. The results are rendered in Table IV.

It appears from the Table that in the symmetry classes A_{1g} , B_{1u} , B_{2g} , and E_u^+ a calculation has been carried out from three constants on the basis of four frequencies.

Only in case theory and experiment completely cover one another it will be unimportant which three frequencies are used in the calculation. But here this is not so because of anharmonicity, and therefore I have, with the B_{2g} class as example, adopted the procedure of substituting the frequencies from

Table III.

Symmetry class	Frequency	Relations between frequencies and force constants
A_{1g}	$\nu_1 \nu_2$	$z_1 + z_2 = 24 \left(\frac{a_2}{m_C} + \frac{a_1}{m_H} \right) (1); \quad z_1 z_2 = \frac{144}{m_H m_C} (4a_1 a_2 - a_3^2) (2)$
A_{2g}	ν_3	$z_3 = 24 a_4 \frac{m_H R^2 + m_C r^2}{m_H m_C r^2} (3)$
A_{2u}	ν_{11}	$z_{11} = 6 a_5 \frac{m_H + m_C}{m_H m_C} (4)$
B_{1u}	$\nu_{12} \nu_{13}$	$z_{12} + z_{13} = 24 \left(\frac{a_8}{m_C} + \frac{a_7}{m_H} \right) (5); \quad z_{12} z_{13} = \frac{144}{m_H m_C} (4a_7 a_8 - a_6^2) (6)$
B_{2g}	$\nu_4 \nu_5$	$z_4 + z_5 = 6 \left(\frac{a_{10}}{m_C} + \frac{a_9}{m_H} \right) (7); \quad z_4 z_5 = \frac{9}{m_H m_C} (4a_9 a_{10} - a_{11}^2) (8)$
B_{2u}	$\nu_{14} \nu_{15}$	$z_{14} + z_{15} = 24 \left(\frac{a_{12}}{m_C} + \frac{a_{14}}{m_H} \right) (9); \quad z_{14} z_{15} = \frac{144}{m_H m_C} (4a_{12} a_{14} - a_{13}^2) (10)$
E_g^+	ν_6 ν_7 ν_8 ν_9	$\begin{vmatrix} 2a_{15} - \frac{m_H}{12}z & a_{19} & a_{20} & a_{21} \\ a_{19} & 2a_{16} - \frac{m_C}{12}z & a_{22} & a_{23} \\ a_{20} & a_{22} & 2a_{17} - \frac{m_H}{12}z & a_{24} \\ a_{21} & a_{23} & a_{24} & 2a_{18} - \frac{m_C}{12}z \end{vmatrix} = 0 \quad (11)$ <p>Roots: z_6, z_7, z_8, z_9</p>
E_u^+	$\nu_{16} \nu_{17}$	$z_{16} + z_{17} = 12 \left(\frac{a_{26}}{m_C} + \frac{a_{25}}{m_H} \right) (12); \quad z_{16} z_{17} = \frac{36}{m_C m_H} (4a_{25} a_{26} - a_{27}^2) (13)$
E_g^-	ν_{10}	$z_{10} = 12 a_{34} \frac{m_C r^2 + m_H R^2}{m_H m_C r^2} (14)$
E_u^-	ν_{18} ν_{19} ν_{20}	$\begin{vmatrix} 2a_{28} - \frac{m_H m_C}{12(m_H + m_C)}z & a_{31} & a_{32} \\ a_{31} & 2a_{29} - \frac{m_H}{12}z & a_{33} \\ a_{32} & a_{33} & 2a_{30} - \frac{m_C}{12}z \end{vmatrix} = 0 \quad (15)$ <p>Roots: z_{18}, z_{19}, z_{20}</p>

Table IV.

Symmetry class	Experimental material		Formula used	Calculated force constants; dyn per cm.	Frequencies calculated on the basis of force constants stated	
	C_6H_6 (cm^{-1})	C_6D_6 (cm^{-1})			C_6H_6	C_6D_6
A_{1g}	$\nu_1 = 992.5$ $\nu_2 = 3061.5$	945.2 2293.2	(1) (2)	$a_1 = 2.068 \cdot 10^4$ $a_2 = 5.678 \cdot 10^4$ $a_3 = \pm 4.519 \cdot 10^4$	$\nu_1 = 992.5$ $\nu_2 = 3061.2$	934.9 2296.5
A_{2g}	$\nu_3 = [1202]$		(3)	$a_4 = 0.2778 \cdot 10^4$		
A_{2u}	$\nu_{11} = 671$		(4)	$a_5 = 0.4083 \cdot 10^4$		
B_{1u}	$\nu_{12} = [1011.6]$ $\nu_{13} = [3055.1]$	[955.2] [2283.8]	(5) (6)	$a_6 = \pm 4.330 \cdot 10^4$ $a_7 = 2.078 \cdot 10^4$ $a_8 = 5.560 \cdot 10^4$	$\nu_{12} = 1013.0$ $\nu_{13} = 3051.8$	955.7 2283.3
B_{2g}	$\nu_4 = [664]$ $\nu_5 = [1048]$	[575] [856]	(7) (8)	$a_9 = 1.014 \cdot 10^4$ $a_{10} = 6.200 \cdot 10^4$ $a_{11} = \pm 1.698 \cdot 10^4$	$\nu_4 = 652.8$ $\nu_5 = 1065.1$	587 837
E_u^+	$\nu_{16} = 406$ $\nu_{17} = [845]$	350 [690]	(12) (13)	$a_{25} = 0.2757 \cdot 10^4$ $a_{26} = 1.859 \cdot 10^4$ $a_{27} = \pm 0.8375 \cdot 10^4$	$\nu_{16} = 404.8$ $\nu_{17} = 849.7$	351.1 689.5
E_g^-	$\nu_{10} = 849.7$		(14)	$a_{34} = 0.2809 \cdot 10^4$		

C_6H_6 and C_6D_6 in (7). In this way a_9 and a_{10} were determined. By substitution in (8) two different values of $(4a_9 \cdot a_{10} - a_{11}^2)$ were calculated. In the continued calculation a mean value was used. Thus the value for a_{11} of Table IV was found. Inversely we now by means of the values for a_9 , a_{10} , and a_{11} and the formulas (7) and (8) compute ν_4 and ν_5 in C_6H_6 and C_6D_6 . The results are rendered in col. 6 of Table IV together with results

obtained by using a similar procedure in other symmetry classes.

The experimental material in the classes A_{2g} , B_{1u} , B_{2g} , and E_u^+ is given in square brackets. The frequencies stated are not observed in the spectra of the C_6H_6 and the C_6D_6 molecules, but by considerations which will be discussed below, it is possible to determine their values approximately on the basis of the partly deuterated benzenes.

The frequencies in symmetry class B_{1u} given in square brackets deviate inconsiderably from those stated by LANGSETH and LORD, *loc. cit.* p. 75. The values given there have been obtained as the result of some calculations carried out on the basis of the valence force system (pp. 29—30). In these calculations it is assumed that the potential belonging to vibrations in the symmetry classes A_{1g} and B_{1u} may be described by using three constants, K , k , q . We have here used six constants, a_1 , a_2 , a_3 , a_6 , a_7 , and a_8 , and therefore, in order not to confuse two points of view, we must find another starting-point.

We shall first try to estimate the size of ν_{12} . The frequency is not Raman active in C_6H_6 and C_6D_6 , but in a number of deuterated benzenes it makes its appearance in the spectrum. The line is often displaced from its "normal" position, viz. in those deuterated benzenes in which it belongs to the same symmetry class as ν_1 . It is unperturbed in $o-C_6H_4D_2$ and $o-C_6H_2D_4$ only, and thus we may fairly well from the position of ν_{12} in these spectra—by extrapolation—infer the position of ν_{12} in C_6H_6 and C_6D_6 .

	C_6H_6	$o-C_6H_4D_2$	$o-C_6H_2D_4$	C_6D_6
Observed		992.8	974.0	
Extrapolated (1011.6)				955.2

These values only immaterially deviate from those found by LANGSETH and LORD. (1010 and 962.)

Next ν_{13} was calculated in the following way: Those vibrations which in C_6H_6 and C_6D_6 are grouped in two symmetry classes A_{1g} and B_{1u} , in sym-trideutero benzene belong to one symmetry class, A_1 . All the frequencies in this symmetry class

have been measured in the Raman spectrum of sym-trideutero-benzene. Hence we may calculate ν_{13} by means of TELLER's product rule¹

$$\frac{\nu_1 \nu_2 \nu_{12} \nu_{13} (C_6H_6)}{\nu_1 \nu_2 \nu_{12} \nu_{13} (s-C_6H_3D_3)} = 1.414 \quad \frac{\nu_1 \nu_2 \nu_{12} \nu_{13} (s-C_6H_3D_3)}{\nu_1 \nu_2 \nu_{12} \nu_{13} (C_6D_6)} = 1.414.$$

In these equations $\nu_{13}(C_6H_6)$ and $\nu_{13}(C_6D_6)$ are the only unknown quantities. They are calculated to be 3055.1 and 2283.8 cm^{-1} , respectively, in good agreement with LANGSETH and LORD, who record 3060 and 2290.

a_6 , a_7 , and a_8 then could be calculated in the way stated above. It is interesting to compare the numerical values of these constants with the numerical values of a_1 , a_2 , and a_3 . It is seen that these constants are really with good approximation equal in twos, so that the potential in the classes A_{1g} and B_{1u} may be described by means of three different constants as assumed and shown by LANGSETH and LORD.

The frequencies in the square brackets in the B_{2g} class are estimated values as in LANGSETH and LORD's paper. Only, in order not to confuse various points of view, the correction for anharmonicity has been omitted.

As for the frequencies in the E_u^+ class, reference may be made to the chapter on The Non-Planar Vibrations p.66 ff. in LANGSETH and LORD. For the frequencies in the A_{2g} class see *ibid.* pp. 65—66.

Thus it has proved possible to calculate 15 out of the 34 constants of the potential function. The reason why not all the 34 constants can be computed is a double one, viz. partly difficulties about the calculation which have not yet been overcome, partly lack of experimental material. Difficulties of the first category are found in the symmetry classes E_g^+ and E_u^- . In these classes respectively 10 and 6 constants enter. In C_6H_6 , C_6D_6 , and $s-C_6H_3D_3$ the available spectroscopically determined numerical material includes 31 frequencies, and in the spectra of the other deuterated benzenes there is also numerical material from which the values of the 16 constants mentioned depend. But so far I have not been able to overcome the dif-

¹ LANGSETH and LORD, *loc. cit.* pp. 14—17.

ficulties of a solution of the complicated equations (11) and (15)—that is to say, if these equations are to be utilized for the determination of the unknown force constants.

The lack of experimental material is felt particularly in the symmetry class B_{2u} ; for here the vibrations are neither active in the Raman spectrum nor in infrared absorption.

In what follows the reliability of the values of the force constants computed here is to be tried through a precalculation of vibration frequencies for the *partly* deuterated benzenes and a comparison with those determined experimentally. For three of the constants, a_4 , a_5 , and a_{34} , it is already now possible to carry out a test calculation. These constants were calculated by means of frequencies from the C_6H_6 spectrum. We may now by means of the values of the constants and the equations (3), (4), and (14) precalculate three of the vibration frequencies in the spectrum of C_6D_6 .

Calculated frequencies	Observed frequencies
$\nu_3 = 933$	924
$\nu_{11} = 492.5$	503
$\nu_{10} = 661.0$	663.5

The agreement must be designated as good.

V. Calculation of Vibration Frequencies in the Partly Deuterated Benzenes.

In the following considerations it is very useful to look at figs. 2 a and 2 b in LANGSETH and LORD (p. 14). Fig. 2 a is a survey of symmetry classes of the planar vibrations in C_6H_6 and deuterated benzenes. Fig. 2 b is a corresponding survey of the non-planar vibrations. The symmetry classes in the C_6H_6 and C_6D_6 molecules are stated against the symbol D_{6h} , the designation of the symmetry qualities of these molecules. The symmetry classes in $p-C_6H_4D_2$ (symmetry class V_h) are stated against V_h , etc. For the molecules with D_{6h} symmetry (C_6H_6 and C_6D_6) we have in the preceding section calculated numerical values for the force constants in the symmetry classes A_{1g} .

B_{1u} , and A_{2g} (planar vibrations), and B_{2g} , A_{2u} , E_u^+ , and E_g^- (non-planar vibrations). From fig. 2a it appears that it will be possible to precalculate the frequencies in the A_1' class in molecules with D_{3h} symmetry ($s\text{-}C_6H_3D_3$), because the A_1' class in D_{3h} molecules arises by a combination of the symmetry classes A_{1g} and B_{1u} in D_{6h} molecules. But the force constants in the A_{2g} class cannot be utilized for precalculations, as these must be combined with the force constants in either the B_{2u} or the E_g^+ class, which we do not know.

Matters are considerably more favourable in the case of the non-planar vibrations. Here the force constants in all the four symmetry classes of the D_{6h} molecules are known. It is evident from fig. 2b that a calculation of the frequencies for all non-planar vibrations in all partly deuterated benzenes is possible. Therefore we shall in what follows calculate the vibration frequencies for the A_1' class in $s\text{-}C_6H_3D_3$ and a selection of non-planar vibrations in deuterated benzenes specified below, everywhere comparing calculated and experimentally determined values.

1. Calculation of frequencies in $s\text{-}C_6H_3D_3$. The A_1' class.

The deuterium atoms being supposed to be placed in the positions 1, 3, and 5 (fig. 1), we have

$$\begin{aligned} 2T = & \frac{1}{3}m_H(\dot{h}_2\dot{h}_2^* + \dot{h}_4\dot{h}_4^* + \dot{h}_6\dot{h}_6^* + \dot{v}_2^2 + 2\dot{v}_4\dot{v}_4^*) \\ & + \frac{1}{3}m_D(\dot{h}_1\dot{h}_1^* + \dot{h}_3\dot{h}_3^* + \dot{h}_5\dot{h}_5^* + \dot{v}_1^2 + 2\dot{v}_3\dot{v}_3^*) \\ & + \frac{1}{3}m_C(\dot{H}_1\dot{H}_1^* + \dot{H}_2\dot{H}_2^* + \dot{H}_3\dot{H}_3^* + \dot{H}_4\dot{H}_4^* + \dot{H}_5\dot{H}_5^* \\ & + \dot{H}_6\dot{H}_6^* + \dot{V}_1^2 + 2\dot{V}_3\dot{V}_3^* + \dot{V}_2^2 + 2\dot{V}_4\dot{V}_4^*). \end{aligned}$$

The potential function is the sum of those contributions which in D_{6h} molecules are distributed to the classes A_{1g} and B_{1u} , thus

$$2V = a_1S_1^2 + a_2S_2^2 + a_3S_1S_2 + a_7S_7^2 + a_8S_8^2 + a_6S_7S_8$$

the a 's and the S 's of course having the same signification as above.

Next, it is easily inferred that

$$\frac{\partial 2T}{\partial \dot{S}_1} = \frac{m_H + m_D}{24} \dot{S}_1 + \frac{m_H - m_D}{24} \dot{S}_7$$

$$\frac{\partial 2T}{\partial \dot{S}_2} = \frac{m_C}{12} \dot{S}_2$$

$$\frac{\partial 2T}{\partial \dot{S}_7} = \frac{m_H - m_D}{24} \dot{S}_1 + \frac{m_H + m_D}{24} \dot{S}_7$$

$$\frac{\partial 2T}{\partial \dot{S}_8} = \frac{m_C}{12} \dot{S}_8.$$

The equations for the vibrational movements being drawn up as shown above, it is seen that the frequencies must be roots in the equation:

$$\begin{vmatrix} 2a_1 - \frac{m_H + m_D}{24}z & a_3 & \frac{m_D - m_H}{24}z & 0 \\ a_3 & 2a_2 - \frac{m_C}{12}z & 0 & 0 \\ \frac{m_D - m_H}{24}z & 0 & 2a_7 - \frac{m_H + m_D}{24}z & a_6 \\ 0 & 0 & a_6 & 2a_8 - \frac{m_C}{12}z \end{vmatrix} = 0.$$

From this the vibration frequencies may be computed. As for a_3 and a_6 , the sign of which is uncertain, it appears that only the squares of these enter. Below, calculated and observed (LANGSETH and LORD) frequencies are compared.

$s\text{-}C_6H_3D_3$. (A_1' class).

Calculated	Observed
$\nu_1 = 945.0$	956.6
$\nu_2 = 3058.2$	3055.1
$\nu_{12} = 1003.5$	1003.9
$\nu_{18} = 2290.5$	2283.8

The agreement must be called excellent. The vibrations here considered are planar, so-called valence vibrations (see figs. 1, 2, 12, and 13 in LANGSETH and LORD, p. 10). It is a common experience that particularly with vibrations of this type one obtains good agreement between experiment and calculation.

2. Calculation of frequencies in $s\text{-C}_6\text{H}_3\text{D}_3$. The A''_2 class.

The expression for $2T$ is the same as above. The expression for $A2V$ is

$$A2V = a_5 S_5^2 + a_9 S_9^2 + a_{10} S_{10}^2 + a_{11} S_9 S_{10}.$$

Further we have

$$\frac{\partial 2T}{\partial \dot{S}_5} = \frac{m_C(m_H + m_D)}{3N} \dot{S}_5 + \frac{m_C(m_D - m_H)}{3N} \dot{S}_9, \quad \frac{\partial 2T}{\partial \dot{S}_{10}} = \frac{m_C}{3} \dot{S}_{10}$$

$$\frac{\partial 2T}{\partial \dot{S}_9} = \frac{m_C(m_D - m_H)}{3N} \dot{S}_5 + \frac{2m_H m_D + m_C(m_H + m_D)}{3N} \dot{S}_9$$

$$N = 2m_C + m_H + m_D.$$

The determinant for the determination of the vibration frequencies here is

$$\begin{vmatrix} 2a_5 - \frac{m_C(m_H + m_D)}{3N}z & \frac{m_C(m_H - m_D)}{3N}z & 0 \\ \frac{m_C(m_H - m_D)}{3N}z & 2a_9 - \frac{2m_H m_D + m_C(m_H + m_D)}{3N} & a_{11} \\ 0 & a_{11} & 2a_{10} - \frac{m_C}{3}z \end{vmatrix} = 0$$

The unknown sign of a_{11} is of no importance for the value of the solution. We find

$s\text{-C}_6\text{H}_3\text{D}_3$. (A''_2 class).

Calculated	Observed
$\nu_4 = 666$	691
$\nu_5 = 964$	914
$\nu_{11} = 525$	533

The observed values originate from the infrared spectrum.¹—The vibrations are vibrations perpendicular to the plane of the benzene ring. Here the agreement between calculated and observed frequencies is considerably inferior to those for valence vibrations. The amplitude for non-planar vibrations is considerably greater than for valence vibrations. The anharmonicity therefore comes to play a great rôle, so that the assumption on which the calculations are made, viz. that it is sufficient to include square terms in the potential function, is less well fulfilled.

3. Calculation of frequencies in $s\text{-C}_6\text{H}_3\text{D}_3$. The E'' class.

The symmetry coordinates to be used are S_{23} , S_{24} , and S_{25} , originating from the symmetry classes E_u^+ and E_g^- in the D_{6h} molecules. Thus we have.

$$A2V = a_{25} S_{23}^2 + a_{26} S_{24}^2 + a_{27} S_{23} S_{24} + a_{34} S_{25}^2.$$

Finally it is inferred that

$$\frac{\partial 2T}{\partial \dot{S}_{23}} = \frac{1}{6N} [m_D(m_C r^2 + m_H R^2) + m_H(m_C r^2 + m_D R^2)] \dot{S}_{24} + \frac{1}{6N} (m_D m_C r^2 - m_H m_C r^2) \dot{S}_{25}$$

$$\frac{\partial 2T}{\partial \dot{S}_{25}} = \frac{1}{6N} [m_D(m_C r^2 + m_H R^2) - m_H(m_C r^2 + m_D R^2)] \dot{S}_{23} + \frac{1}{6N} (m_D m_C r^2 + m_H m_C r^2) \dot{S}_{25}$$

$$\frac{\partial 2T}{\partial \dot{S}_{24}} = \frac{m_C}{6} \dot{S}_{24}$$

$$N = 2m_C r^2 + (m_H + m_D) R^2.$$

After setting up the determinant, etc., as above, we get:

$s\text{-C}_6\text{H}_3\text{D}_3$. The E'' class.

Calculated frequencies	Observed frequencies ²
$\nu_{10} = 676$	712
$\nu_{17} = 848$	815
$\nu_{16} = 376$	373

¹ INGOLD, Nature 139, 880 (1937).

² LANGSETH and LORD, *loc. cit.*

The vibrations are non-planar vibrations. Considering this the agreement must be regarded as good.

4. Calculation of frequencies in $p\text{-C}_6\text{H}_4\text{D}_2$ and $p\text{-C}_6\text{HD}_{24}$.

The B_{3g} class.

The deuterium atoms in $p\text{-C}_6\text{H}_4\text{D}_2$ are supposed to be placed in the positions 3 and 6. We get

$$2T = \frac{1}{3} m_C (\dot{H}_1 \dot{H}_1^* + \dot{H}_2 \dot{H}_2^* + \dot{H}_3 \dot{H}_3^* + \dot{H}_4 \dot{H}_4^* + \dot{H}_5 \dot{H}_5^* + \dot{H}_6 \dot{H}_6^* + \\ + \dot{V}_1^2 + 2 \dot{V}_3 \dot{V}_3^* + \dot{V}_2^2 + 2 \dot{V}_4 \dot{V}_4^*) \\ + \frac{1}{3} m_H (\dot{h}_1 \dot{h}_1^* + \dot{h}_2 \dot{h}_2^* + \dot{h}_3 \dot{h}_3^* + \dot{h}_4 \dot{h}_4^* + \dot{h}_5 \dot{h}_5^* + \dot{h}_6 \dot{h}_6^* + \\ + \dot{v}_1^2 + 2 \dot{v}_3 \dot{v}_3^* + \dot{v}_2^2 + 2 \dot{v}_4 \dot{v}_4^*) \\ + \frac{m_D - m_H}{9} [(\dot{h}_1 + \varepsilon^2 \dot{h}_3 + \varepsilon \dot{h}_5)(\dot{h}_1^* + \varepsilon \dot{h}_3^* + \varepsilon^2 \dot{h}_5^*) + \\ + (\dot{h}_2 + \varepsilon \dot{h}_4 + \varepsilon^2 \dot{h}_6)(\dot{h}_2^* + \varepsilon^2 \dot{h}_4^* + \varepsilon \dot{h}_6^*) + (\dot{v}_1 + \varepsilon^2 \dot{v}_3 + \varepsilon \dot{v}_5)^2 + \\ + (\dot{v}_2 + \varepsilon \dot{v}_4 + \varepsilon^2 \dot{v}_6)^2].$$

$$\frac{\partial 2T}{\partial \dot{S}_9} = \frac{3 m_C r^2 (m_D - m_H)}{9 N} \dot{S}_{25} + \frac{3 m_H R^2 (m_H + 2 m_D) + 3 m_C r^2 (2 m_H + m_D)}{9 N} \dot{S}_{10}$$

$$\frac{\partial 2T}{\partial \dot{S}_{25}} = \frac{m_C r^2 (m_D - m_H)}{3 N} \dot{S}_9 + \frac{m_C r^2 (m_H + 2 m_D)}{6 N} \dot{S}_{25}, \quad \frac{\partial 2T}{\partial \dot{S}_{10}} = \frac{m_C}{3} \dot{S}_{10}.$$

$$N = 3 m_C r^2 + (m_H + 2 m_D) R^2.$$

$$A 2V = a_9 S_9^2 + a_{10} S_{10}^2 + a_{11} S_9 S_{10} + a_{24} S_{25}^2.$$

On the basis of this the frequencies are calculated in the below table.

$p\text{-C}_6\text{H}_4\text{D}_2$. The B_{3g} class.

Calculated frequencies	Observed frequencies
$\nu_5 = 1040$	966
$\nu_{10b} = 700$	738
$\nu_4 = 629$	634

These vibrations, too, are non-planar vibrations.

$p\text{-C}_6\text{H}_2\text{D}_4$. The B_{3g} class.

Calculated frequencies

Observed frequencies

$\nu_5 = 939$	927
$\nu_{10b} = 732$	765
$\nu_4 = 606$	605

The agreement is best for $p\text{-C}_6\text{H}_2\text{D}_4$, presumably because the molecule contains more deuterium atoms than $\text{C}_6\text{H}_4\text{D}_2$. Because of the greater mass the amplitudes of the deuterium atoms are smaller than those of the hydrogen atoms. The deviation of the vibrations from the harmonic mode of vibration therefore becomes smaller. (Compare the results with $o\text{-C}_6\text{H}_4\text{D}_2$ and $\text{C}_6\text{H}_2\text{D}_4$).

5. Calculation of frequencies in $o\text{-C}_6\text{H}_4\text{D}_2$ and $o\text{-C}_6\text{H}_2\text{D}_4$.

The B_2 class.

The deuterium atoms in $o\text{-C}_6\text{H}_4\text{D}_2$ are supposed to be placed in the positions 4 and 5. Thus we find

$$\frac{\partial 2T}{\partial \dot{S}_5} = \frac{m_H + 2 m_D}{9} \dot{A} + \frac{m_H - m_D}{18} \dot{S}_{23} + \frac{m_H - m_D}{18} \sqrt{3} \dot{H}$$

$$\frac{\partial 2T}{\partial \dot{S}_{23}} = \frac{m_H - m_D}{18} \dot{A} + \frac{m_D + 5 m_H}{36} \dot{S}_{23} + \frac{m_D - m_H}{36} \sqrt{3} \dot{H}$$

$$\frac{\partial 2T}{\partial \dot{S}_{26}} = \frac{r m_C}{6 R} \dot{K}, \quad \frac{\partial 2T}{\partial \dot{S}_{24}} = \frac{m_C}{6} \dot{S}_{24}.$$

$$A = \frac{1}{N} \left[m_C \left(\frac{R \sqrt{3}}{6 r} (m_H + m_D) + \frac{m_C r}{R \sqrt{3}} \right) S_5 + \frac{m_C r}{6 R} (m_H - m_D) S_{26} + \right. \\ \left. + \frac{m_D - m_H}{6} \left(\frac{R \sqrt{3} m_H}{3 r} + \frac{m_C r}{R \sqrt{3}} \right) S_{23} \right]$$

$$H = \frac{1}{N} \left[\frac{R m_C (m_D - m_H)}{3 r} S_5 - \frac{m_C r}{3 R \sqrt{3}} (2 m_H + m_D + 3 m_C) S_{26} + \right. \\ \left. + \frac{(m_H - m_D) R}{6 r} (m_H + m_C) S_{23} \right]$$

$$K = \frac{1}{N} \left[m_C \frac{m_D - m_H}{3} S_5 + \frac{\sqrt{3}}{18} (3 m_C (m_H + m_D) + m_H^2 + 5 m_H m_D) S_{26} + \frac{(m_H - m_D)(m_H + m_C)}{6} S_{23} \right]$$

$$N = \frac{R\sqrt{3}}{18r} [m_H^2 + 5 m_H m_D + 3 m_C (m_H + m_D)] + \frac{m_C r}{3\sqrt{3}R} (2 m_H + m_D + 3 m_C)$$

$$A2V = a_5 S_5^2 + a_{25} S_{23}^2 + a_{26} S_{24}^2 + a_{27} S_{23} S_{24} + a_{34} S_{26}^2.$$

By insertion of numerical values we calculate:

o-C₆H₄D₂. B₂ class.

Calculated frequencies	Observed frequencies ¹
$\nu_{10a} = 676$	782
$\nu_{11} = 571$	582
$\nu_{16b} = 369$	384
$\nu_{17b} = 841$	825

o-C₆H₂D₄. The B₂ class.

Calculated frequencies	Observed frequencies ¹
$\nu_{10a} = 684$	739
$\nu_{11} = 527$	—
$\nu_{16b} = 359$	369
$\nu_{17b} = 815$	778

VI. Estimate of the Error in the Force Constants.

It may be said at once about all the force constants that experimentally badly determined differences of frequency nowhere enter into the calculations. Hence there is practically no uncertainty originating from the measurement of the spectra as regards the numerical values. On the other hand it must

¹ LANGSETH and LORD, *loc. cit.*

be admitted that the values involve minor errors. For actually the equations (1)–(15) were deduced on the assumption that the vibrations were harmonic, this only being so where the amplitudes are small. This assumption is fulfilled best in the case of the planar valence vibrations, so that the constants a_1 , a_2 , a_3 , a_6 , a_7 , and a_8 , which describe the potential for these vibrations, are determined best. Hence it also appears that at the precalculation of the vibrations in *s*-C₆H₃D₃ (the A₁' class), where the values of these constants are used, we find values deviating at most 1 per cent. from those found experimentally.

On the other hand the constants describing changes of potential with non-planar vibrations are less well determined. The amplitudes here are so great that the vibrations become slightly anharmonic. Let us look at e. g. (14):

$$\nu_{10} = 4\pi^2 \nu_{10}^2 = 12 a_{34} \frac{m_C r^2 + m_H R^2}{m_H m_C r^2}.$$

ν_{10} is the frequency for one of the non-planar vibrations. As a rule a lower value for ν_{10} will be determined than the one which would appear if the vibration was harmonic. In rare cases, however, also a higher value. Of course it is not possible to give a common value for the error committed for all non-planar vibrations, because, as done here, we reckon with the observed frequency instead of the "harmonic" one, but in what follows, however, we shall, in accordance with ordinary spectroscopic experience,¹ reckon with an error of ± 2 per cent. in frequencies belonging to non-planar vibrations. As appears from (14), this involves that a_{34} is determined with an error of about ± 5 per cent. As for the constants a_4 ² and a_5 we obtain the same result.

For the constants a_9 , a_{10} , a_{11} , a_{25} , a_{26} , and a_{27} the connexion between frequencies and constants is more complicated. (7), (8), (12), (13). In what follows we shall assume that these constants, too, are exposed to an error of ± 5 per cent. The assumption of a possible error of ± 5 per cent. in the constants, corresponding to all non-planar vibrations, gives an unstrained

¹ Cf. LANGSETH and LORD, *loc. cit.* p. 81.

² a_4 belongs to a planar deformation vibration, but the remark on anharmonicity also applies here.

explanation of the deviations found between calculated and observed frequencies for the partly deuterated benzenes.

VII. The Intramolecular Forces.

It is now possible to calculate the forces acting on the individual atoms of the molecule when the atoms are removed from the position of equilibrium, to the same extent as we have above succeeded in establishing numerical values for the force constants in the potential function of benzene. With a view to the possibility of later treating the mechanism of reaction in processes in which benzene is involved, it should be noted that it is of the greatest importance to study those movements away from the position of equilibrium by which the numerically smallest forces become active. Among these movements we find all the non-planar vibrations, in which the amplitudes are great, i. e. there is a much greater chance to find a hydrogen atom outside the position of equilibrium perpendicular to the plane of the benzene ring than in this plane.

According to the above considerations the changes of potential by displacements of atoms perpendicular to the plane of the benzene ring are rendered by

$$\Delta 2V = a_5 S_5^2 + a_9 S_9^2 + a_{10} S_{10}^2 + a_{11} S_9 S_{10} + a_{25} (S_{21}^2 + S_{23}^2) + a_{26} (S_{22}^2 + S_{24}^2) + a_{27} (S_{21} S_{22} + S_{23} S_{24}) + a_{34} (S_{25}^2 + S_{26}^2).$$

Measured in dyne/cm. the numerical values of the force constants were determined as

$$\begin{array}{ll} a_5 = 0.408 \cdot 10^4 & a_9 = 1.01 \cdot 10^4 \\ a_{10} = 6.20 \cdot 10^4 & |a_{11}| = 1.70 \cdot 10^4 \\ a_{25} = 0.276 \cdot 10^4 & a_{26} = 1.86 \cdot 10^4 \\ |a_{27}| = 0.837 \cdot 10^4 & a_{34} = 0.281 \cdot 10^4. \end{array}$$

The values are supposed to involve an error of ± 5 per cent.

In order to learn about the forces active between the atoms of the benzene molecule on the basis of the above values, we shall examine a particularly simple movement away from the position of equilibrium. Supposing, by means which, indeed,

cannot be realized in practice, that the 11 atoms are kept in the position of equilibrium, while the 12th, *H*-atom no. 6 in fig. 1 (*H*(6)), is supposed to be displaced perpendicular to the plane of the benzene ring towards the reader. To this constellation applies

$$z_6 > 0 \quad x_6 = y_6 = 0$$

$$(x_j, y_j, z_j) = (0, 0, 0) \quad (j = 1, 2, 3, 4, 5)$$

$$X_j, Y_j, Z_j = (0, 0, 0) \quad (j = 1, 2, 3, 4, 5, 6)$$

By going through the expressions for S_1 , etc., we find under these circumstances

$$S_5 = z_6 \quad S_9 = -z_6 \quad S_{23} = 2z_6 \quad S_{25} = -2z_6$$

$$S_{10} = S_{21} = S_{22} = S_{24} = S_{26} = 0,$$

so that

$$\Delta 2V = a_5 S_5^2 + a_9 S_9^2 + a_{25} S_{23}^2 + a_{34} S_{25}^2.$$

On the basis of this we find

$$K_{H(6)} = -\frac{\partial V}{\partial z_6} = -z_6 (a_5 + a_9 + 4(a_{25} + a_{34}))$$

$$K_{H(1)} = -\frac{\partial V}{\partial z_1} = -z_6 (a_5 - a_9 + 2(a_{34} - a_{25})) = K_{H(5)}$$

$$K_{H(2)} = -\frac{\partial V}{\partial z_2} = -z_6 (a_5 + a_9 - 2(a_{34} + a_{25})) = K_{H(4)}$$

$$K_{H(3)} = -\frac{\partial V}{\partial z_3} = -z_6 (a_5 - a_9 + 4(a_{25} - a_{34}))$$

$$K_{C(6)} = -\frac{\partial V}{\partial Z_6} = -z_6 \left(-a_5 - 4 \frac{R}{r} a_{34} \right)$$

$$K_{C(1)} = -\frac{\partial V}{\partial Z_1} = -z_6 \left(-a_5 - 2 \frac{R}{r} a_{34} \right) = K_{C(5)}$$

$$K_{C(2)} = -\frac{\partial V}{\partial Z_2} = -z_6 \left(-a_5 + 2 \frac{R}{r} a_{34} \right) = K_{C(4)}$$

$$K_{C(3)} = -\frac{\partial V}{\partial Z_3} = -z_6 \left(-a_5 + 4 \frac{R}{r} a_{34} \right).$$

K denotes the force acting on the atom used as index.

By substitution of numerical values we find

$$\left. \begin{aligned} K_{H(1)} : K_{H(2)} : K_{H(3)} : K_{H(4)} : K_{H(5)} : K_{H(6)} : K_{C(1)} : K_{C(2)} : \\ : K_{C(3)} : K_{C(4)} : K_{C(5)} : K_{C(6)} = \\ 0.595 : -0.308 : 0.626 : -0.308 : 0.595 : -3.65 : 1.40 : -0.589 : \\ : -1.58 : -0.589 : 1.40 : 2.40. \end{aligned} \right\}$$

The result is illustrated in fig. 2, where the length of the arrows is proportional to the magnitude of the forces.

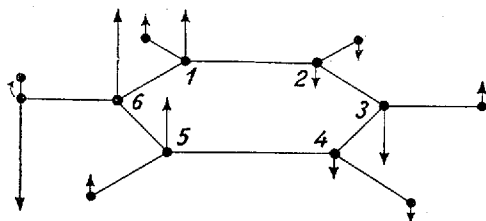


Fig. 2.

The force is of course greatest on the directly "attacked" hydrogen atom and its adjoining atom $C(6)$. But further it is seen that forces are active on all the other atoms as well. It is seen that the forces do not decrease the longer the atom is removed from $C(6)$ and $H(6)$, but that e.g. $K_{H(1)}$ and $K_{H(3)}$ are of very nearly the same magnitude and both nearly twice as great as $K_{H(2)}$. Or, in other words, the hydrogen atoms in *ortho* and *para* positions to the H atom subject to force are influenced fairly in the same way, while the hydrogen atoms in *meta* positions are only influenced by nearly half the force. Nearly the same rule (applying to the numerical values of the forces) may be set up as regards the carbon atoms.

A control calculation shows that these results in the main are independent of the error of ± 5 per cent. assumed in the values of the force constants.

The above considerations may be utilized in a discussion of the usefulness of WILSON's¹ potential function for benzene.

As mentioned, WILSON has not used the potential function

¹ Phys. Rev. 45, 706, (1935).

set up by him for numerical calculations. But it has been used to a limited extent by REDLICH and STRICKS¹ and LANGSETH and LORD². The question is whether it may also be applied to all the vibrations of benzene.

From personal information³ it is known that LANGSETH and LORD tried to carry through more extensive calculations on the basis of WILSON's potential function, but that the correspondence between calculated and observed frequencies often was so bad that they had to drop the matter. The reason why WILSON's potential system is applicable to a limited extent only is easily seen. Let us, as above, suppose $H(6)$ to be shifted from the position of equilibrium perpendicular to the plane of the benzene ring towards the reader. Fig. 3 represents the vertical plane through $C(6)$, $H(6)$ and the shifted $H(6)$ as placed in the horizontal plane of the benzene ring (1-2-3-4-5-6).

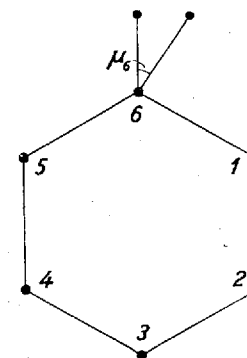


Fig. 3.

Moving $H(6)$ requires some work, as, according to WILSON,

(a) an angle μ_6 arises between the line $C(6)-H(6)$ and the plane defined by $C(6)$, $C(5)$, and $C(1)$. Thus we have

$$\Delta V = h(R-r)^2 \mu_6^2,$$

where h is a constant.

(b) The valences $C(5)-C(6)$ and $C(6)-C(1)$ make a torsional movement. For this is required the work

$$\Delta V = k_2(\varphi_{5,6}^2 + \varphi_{6,1}^2),$$

where k_2 is a constant and $\varphi_{5,6}$ is the angle by which the bond $C(5)-C(6)$ is twisted.

As appears, V only becomes a function of the rectangular coordinates with indices 1, 5, and 6. But this means that the force acting on the C and H atoms no. 2, 3, and 4 becomes zero. We have above had an opportunity of ascertaining that the effect

¹ Monatshefte, loc. cit.

² Loc. cit. p. 29.

³ From Professor LANGSETH.

of force on these atoms is as great as that on the atoms no. 1 and 5. WILSON in his potential function thus disregards the reciprocity of action between atoms which are not in the generally assumed structure formula connected with valence lines. Hence, WILSON's potential function is unsuitable for a rational treatment of the problems pointed out here.

This fundamental defect in WILSON's potential function must also be expected to appear at a consideration of the expressions for the connexion between force constants and vibration frequencies deduced by WILSON. According to WILSON

$$z_{11} = h \frac{m_C + m_H}{m_C m_H} \quad z_{10} = h \frac{m_C r^2 + m_H R^2}{m_H m_C r^2}.$$

In the present work it was deduced that

$$z_{11} = 6 a_5 \frac{m_C + m_H}{m_C m_H} \quad z_{10} = 12 a_{34} \frac{m_C r^2 + m_H R^2}{m_H m_C r^2}$$

WILSON uses *one* force constant, h , where *two* are used in the present work, viz. $6 a_5$ and $12 a_{34}$. This approximation can be applicable only if $6 a_5 = 12 a_{34}$. By substitution of the numerical values found here, it appears that $6 a_5 = 2.45$,¹ while $12 a_{34} = 3.37$.¹ Hence, it must be characterized as too rough an approximation to use one force constant only.

The results obtained in this paper seem to be of interest in another connexion. In treating problems of the electronic structure of molecules roughly two methods have crystallized out: the method of 'localized pairs' and the method of 'molecular orbitals'. It seems as if the above considerations represent a new means of deciding empirically which of the two methods should be used. In the case of the benzene molecule where a disturbance at one atom of the molecule produces a great effect on all the other atoms—independent of the distance from the atom attacked—the result is that benzene should be treated by means of the 'molecular orbitals' method, consistent with the views of E. HÜCKEL².

¹ Unity: 10^4 dyne/cm.

² E. HÜCKEL, Z. Physik **70**, 204 (1931); **72**, 310 (1931).

VIII. Summary.

(1) In the equations (1)–(15) the connexion is given between the vibration frequencies and the 34 force constants in the general quadratic potential function for C_6H_6 and isotopic molecules.

(2) On the basis of some of the experimental material from the RAMAN spectra of C_6H_6 and C_6D_6 and data from infrared absorption, numerical values are established for 15 of the force constants.

(3) The correctness of the deduced numerical values of the force constants is checked through a precalculation of frequencies from the Raman spectra of C_6D_6 , $s-C_6H_3D_3$, $p-C_6H_4D_2$, $p-C_6H_2D_4$, $o-C_6H_4D_2$, and $o-C_6H_2D_4$ and a comparison with the observed values. It is estimated that the differences between calculated and observed values which are bound to arise where the vibrations are anharmonic, may be explained on the assumption that the force constants involve an error of about 5 per cent.

(4) As only 15 of the necessary 34 constants can be calculated, only an imperfect picture of conditions of force can be drawn. Only by movements perpendicular to the plane of the benzene ring a complete description of the potential may be obtained. By a specified displacement of one of the atoms fairly equal forces appear on all the atoms. The considerations advanced make it possible to demonstrate a fundamental defect in WILSON's potential function.

The author wishes to offer his cordial thanks to Professor LANGSETH for helpful discussions on the subject.