

ELECTRONIC EFFECT OF SUBSTITUENTS UPON OUT-OF-PLANE C-H VIBRATIONS OF AROMATIC COMPOUNDS

BY

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ABSTRACT

An experimental and theoretical study of the infrared spectra of aromatic compounds has been made in order to evaluate the effect of the electrophilic substituent upon some of the vibrations of the aromatic nucleus. In this paper, particular attention is paid to the out-of-plane C-H bending vibrations between 820 cm^{-1} and 950 cm^{-1} . Eleven carboxyl-substituted benzenes are investigated systematically.

The spectra of these compounds show positive shift in frequency and pronounced decrease in intensity. Theoretical considerations and discussions are made between C-H out-of-plane bending vibrations and the force constants using the simplified potential functions. Steric hindrance or hydrogen bonding by the effect of the electrophilic substituents is suggested.

1. Introduction

In general, it has been known that the out-of-plane CH bending vibrations of substituted benzenes are primarily determined by the number and the positions of substituents on the ring rather than by the nature of the substituents (1). However, it has been observed that there are many spectral anomalies (2). The factors which determine the out-of-plane CH bending vibrations are masses of the substituents (3), the effects of the substituents upon π -electron densities of the aromatic nucleus, and the steric hindrance.

While it is very interesting to know the correlations between the molecular structure and its property, because the electronic effects of the substituents upon π -electron densities of the aromatic nucleus are the important factors of the chemical reactivity.

Among many substituents, carboxyl group is one of the typical electrophilic substituents. The present paper deals systematically with the infrared spectra of eleven carboxyl-substituted benzenes. The spectra of carboxyl-substituted benzenes fall outside of characteristic frequency range.

The purpose of the present paper is to discuss these spectral anomalies. First, the experimental results are given, comparing them with the spectra of the nucleophilic substituted benzenes which have methyl groups. Next, the theoretical considerations of the simplified potential function are given and the correlations between the π -electron density of the benzene nucleus and force constants are discussed.

2. Experiments and results

The spectra were recorded on a Shimadzu Type 275 infrared spectrophotometer, using a sodium chloride prism. The spectra of the compounds were obtained as mulls in mineral oil.

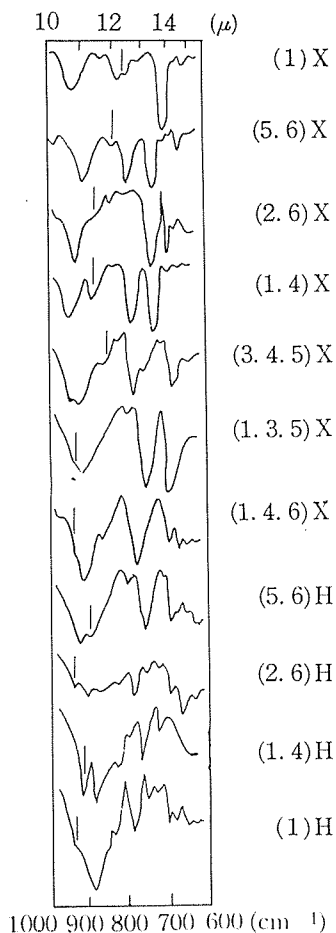


Fig. 1. Out-of-plane C-H bending frequencies for carboxyl-substituted benzenes.

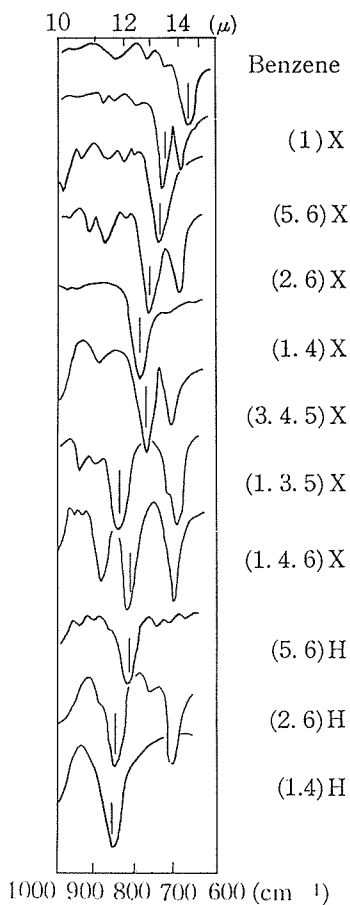


Fig. 2. Out-of-plane C-H bending frequencies for methyl-substituted benzenes.

Most of the compounds studied were supplied by members of the Petrochemical Department of Research Center of Maruzen Oil Company. These compounds were used without further purification unless their purities were rather doubtful. If purifications were necessary, the standard method of recrystallization was used.

The spectra of all aromatic carboxylic acids fall in the range between 820 cm^{-1} and 950 cm^{-1} , but the spectra of all aromatic compounds with methyl-substituents have the CH out-of-plane bending vibrations in the range between 720 cm^{-1} and 870 cm^{-1} (Figs. 1~2). The marked decreases in the spectral intensities with the shifts to higher frequencies are apparently observed.

The positive shifts in frequencies are about 90 cm^{-1} to the corresponding aromatic compounds with methyl substituents. The data summarized in Table I show that the increases in frequencies are caused by the electrophilic substituents.

Table I. Frequencies of carboxyl- and methyl-substituted benzenes ("a" bands)

Type	Methyl-substituted benzenes	Carboxyl-substituted benzenes
(1) X*	728 cm^{-1}	808 cm^{-1}
(5.6) X	742	831
(2.6) X	769	886
(1.4) X	794	882
(3.4.5) X	766	843
(1.3.5) X	835	926
(1.4.6) X	806	862
(5.6) H**	804	893
(2.6) H	848	943
(1.4) H	867	925
(1) H	864	940

* (1) X denotes the monosubstituted compound and X denotes COOH substituent, and so on.

** (5.6) H denotes the 1.2.3.4- tetrasubstituted benzenes and H denotes hydrogen.

3. Theoretical considerations and discussions

At first, some assumptions concerning carbon atoms of the benzene ring and the substituents have been made in order to simplify the calculations. Then, the potential and kinetic energy functions are constructed.

Next, the appropriate force constants are assumed and F and G matrices can be obtained. It is easy to construct a secular equation $|GF - \lambda E| = 0$.

Using this equation, the force constants are determined by the method of least squares. Then the distributions of the potential energies are calculated and the types of vibrations are determined by L -matrix.

(i) Potential energy function and kinetic energy function

Since the method of simplified calculations is used, it is assumed that carbon atoms of the benzene ring and the substituents are fixed in the plane determined by the benzene ring. These assumptions are natural because their vibrations are relatively small and so have little effects upon the CH out-of-plane vibrations. Then it is only necessary to consider the displacements of hydrogen atoms.

The kinetic energy function (T) and the potential energy function (V) are assumed as :

$$2T = \sum m\dot{z}_i^2 = \sum \frac{1}{m} p_i^2, \quad (1)$$

where z_i is the displacement of hydrogen atom H_i perpendicular to the plane determined by benzene ring, dot denotes differentiation with respect to time, p_i is the momentum conjugate to z_i ; and

$$2V = \sum A^{(i)}z_i^2 + 2\sum B^{(i)}z_i z_{i+1} + 2\sum C^{(i)}z_i z_{i+2} + 2\sum D^{(i)}z_i z_{i+3}, \quad (2)$$

where $A^{(i)}$, $B^{(i)}$, $C^{(i)}$ and $D^{(i)}$ are force constants.

In order to construct the potential energy function, it is necessary to define the force constants clearly. Nine force constants A_0 , B_0 , C_0 , D , a_0 , a_m , a_p , b and C_1 have been assumed (4). Among them, A_0 , B_0 , C_0 and D are those when benzene has no substituents.

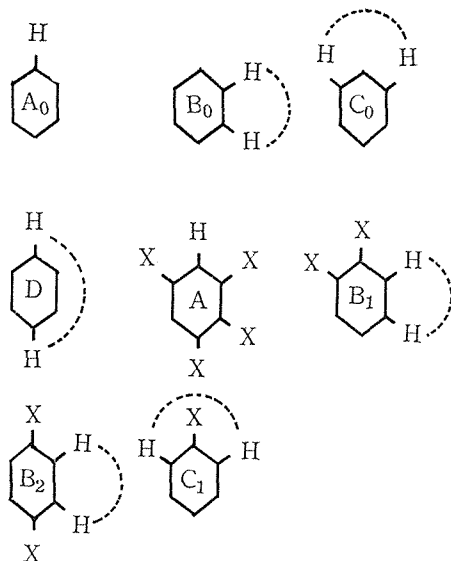


Fig. 3. Force constants (where $X=\text{COOH}$).

When some substituents are introduced, it is assumed that the effects of substituents upon force constants of C-H bending vibration are additive. Then the effects of ortho-, meta- and para-substituents upon A_0 are a_o , A_m and a_p , respectively. For example,

$$A = A_0 + 2a_o + a_m + a_p.$$

Also, the effect of the substituents upon B_0 is assumed to be b . Since the carboxyl substituent has meta-orientation, B can be written as follows:

$$B_1 = B_0 + b, \quad B_2 = B_0 + 2b.$$

(ii) F -matrix and G -matrix

F - and G -matrices are the expressions for the potential and kinetic energy functions. It is apparent that G -matrix is a diagonal one and each element of the matrix is the reciprocal of the mass of hydrogen atom. F -matrix can be constructed using nine force constants. The results are shown in Appendix A.

It is necessary to consider the symmetry of molecules and the symmetry coordinates. For this problem the group theory is very convenient in practice. The symmetry of benzene molecule is that of the group D_{6h} which consists of the following operations, E , $2C_6$, $2C_3$, C_2 , $3C_2'$, $3C_2''$, i , $2S_6$, $2S_3$, σ_h , $3\sigma_d$ and $3\sigma_v$.

As subgroups of D_{6h} , there are C_{2v} , C_{2v}^* , C_s , V_h and D_{3h} . Each of them represents the symmetry of substituted benzene. This is done in Appendix B. It is possible to set up the symmetry coordinates from their character tables. Then, the symmetry coordinates are combined properly, taking the omissions of coordinates and orthogonality into consideration. The results are shown in Appendix C.

F -matrices are reconstructed by these normal coordinates (see, Appendices A & C). The results are as follows:

(1) Benzene

S_1	S_2	S_3	S_4	S_5	S_6
$A_0 + 2B_0 + 2C_0 + D$					
	$A_0 + B_0 - C_0 - D$				
		$A_0 + B_0 - C_0 - D$			
			$A_0 - B_0 - C_0 + D$		
				$A_0 - B_0 - C_0 + D$	
					$A_0 - 2B_0 + 2C_0 - D$

(2) Mono-substituted benzene

S_7	S_8	Z_4	S_9	S_{10}
$A_0 + a_0 + C_1$	$B_0 + b + D$	$\sqrt{2} C_0$		
	$A_0 + a_m + C_0$	$\sqrt{2} B_0$		
		$A_0 + a_p$		
			$A_0 + a_0 - C_1$	$B_0 + b - D$
				$A_0 + a_m - C_0$

(3) 5,6-disubstituted benzene

S_{11}	S_{12}	S_{13}	S_{14}
$A_0 + a_m + a_p + B_0$	$B_0 + b + C_0$		
	$A_0 + a_0 + a_m + D$		
		$A_0 + a_m + a_p - B_0$	$B_0 + b - C_0$
			$A_0 + a_0 + a_m - D$

(4) 2,6-disubstituted benzene

S_8	Z_4	Z_1	S_{10}
$A_0 + a_0 + a_p + C_0$	$\sqrt{2} (B_0 + b)$	$\sqrt{2} C_1$	
	$A_0 + 2a_m$	D	
		$A_0 + 2a_0$	
			$A_0 + a_0 + a_p - C_0$

(5) 1,4-disubstituted benzene

S_{15}	S_2	S_{16}	S_4
$(A_0 + a_0 + a_m) + (B_0 + 2b) + C_1 + D$			
	$(A_0 + a_0 + a_m) + (B_0 + 2b) - C_1 - D$		
		$(A_0 + a_0 + a_m) - (B_0 + 2b) + C_1 - D$	
			$(A_0 + a_0 + a_m) - (B_0 + 2b) - C_1 + D$

(6) 3,4,5-trisubstituted benzene

S_7	Z_1	S_9
$A_0 + a_0 + a_m + a_p + C_0$	$\sqrt{2} (B_0 + b)$	
	$A_0 + 2a_m + a_p$	
		$A_0 + a_0 + a_m + a_p - C_0$

(7) 1,3,5-trisubstituted benzene

S_{17}	S_9	S_{18}
$A_0 + 2a_0 + a_p + 2C_1$		
	$A_0 + 2a_0 + a_p - C_1$	
		$A_0 + 2a_0 + a_p - C_1$

(8) 1.4.6-trisubstituted benzene

Z_2	Z_3	Z_5
$A_0 + a_0 + 2a_m$	$B_0 + 2b$	D
	$A_0 + a_0 + a_m + a_p$	C_1
		$A_0 + 2a_0 + a_m$

(9) 1.2.3.4-tetrasubstituted benzene

S_{19}	S_{20}
$A_0 + a_0 + 2a_m + a_p + (B_0 + 2b)$	
	$A_0 + a_0 + 2a_m + a_p - (B_0 + 2b)$

(10) 1.3.4.5-tetrasubstituted benzene

S_7	S_9
$A_0 + 2a_0 + a_m + a_p + C_1$	
	$A_0 + 2a_0 + a_m + a_p - C_1$

(11) 2.3.5.6-tetrasubstituted benzene

S_{12}	S_{14}
$A_0 + 2a_0 + 2a_m + D$	
	$A_0 + 2a_0 + 2a_m - D$

(12) 2.3.4.5.6-pentasubstituted benzene

Z_1
$A_0 + 2a_0 + 2a_m + a_p$

Using the secular equation $|GF - \lambda E| = 0$, the nine force constants have been calculated by the method of least squares and the frequencies have also been obtained from the following equation:

$$\nu_i = \frac{1}{2\pi c} \sqrt{\lambda_i}, \quad (3)$$

where ν_i is the frequency and c is the velocity of light.

(iii) Consideration on the types of vibrations

The types of vibrations are determined by L -matrix whose definition is

$$R = LQ, \quad (4)$$

where Q is a matrix of the normal coordinate and R an internal one. Then, the potential energy is expressed as:

$$2V = \tilde{Q} \tilde{F} L Q = \tilde{Q} A Q, \quad (5)$$

where \tilde{Q} means the transposed matrix of Q , and A is a diagonal one whose element is an eigenvalue λ_a .

From (5) we have

$$\left. \begin{aligned} \tilde{F} L &= A, \\ \lambda_a &= \sum_{i,j} \tilde{L}_{ai} F_{ij} L_{ja} = \sum_{i,j} F_{ij} L_{ia} L_{ja}. \end{aligned} \right\} \quad (6)$$

An eigenvalue λ_a expresses the potential energy when the vibration belonging to λ_a is not reduced. Therefore, the distribution of the potential energy can be obtained by calculating the value of $F_{ij} L_{ia} L_{ja}$. It is also possible to investigate

which coordinate contributes mainly to the vibration, because the value $F_{ii}L_{ia}^2$ is remarkably larger than $F_{ij}L_{ia}L_{ja}$ ($i \neq j$).

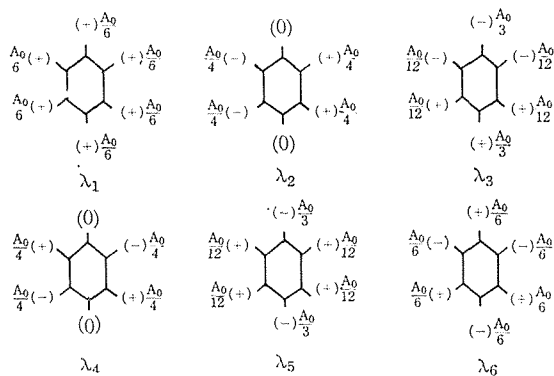
It is necessary to get L -matrix in order to determine the types of vibrations. The formula $Q=L^{-1}R$ is shown in Appendix C. L^{-1} is the orthogonal matrix. L can be obtained as a transposed one of L^{-1} .

(iv) Discussion

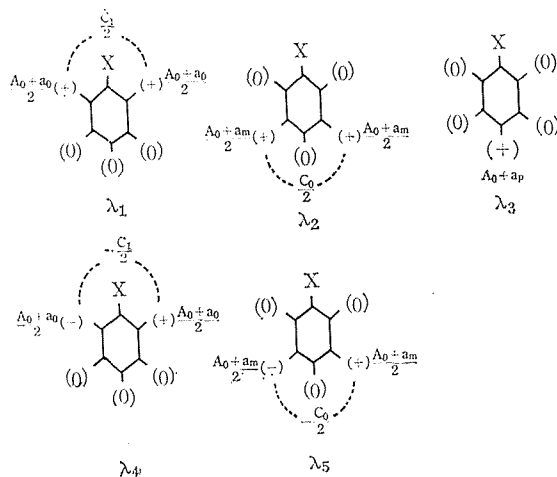
The types of the vibrations are summarized in Fig. 4.

The type of the out-of-plane C-H bending vibrations of substituted benzenes were elucidated throughly from Fig. 4. Furthermore, the contributions of the CH vibrations to the potential energy have become clear. In order to evaluate

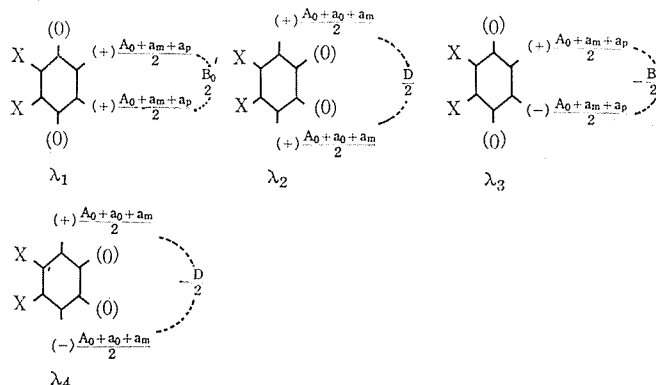
(1) Benzene ($\lambda_1, \lambda_2=\lambda_3, \lambda_4=\lambda_5, \lambda_6$)



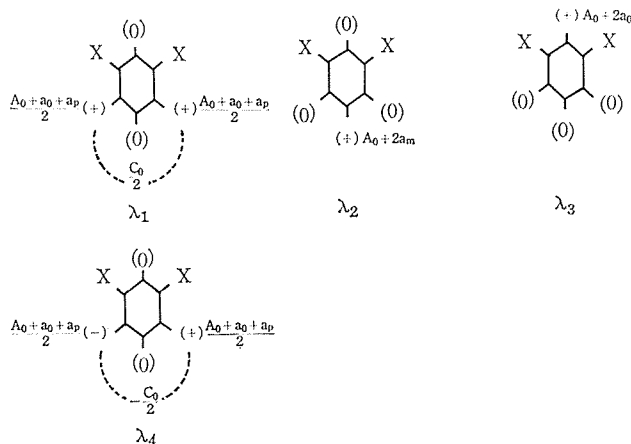
(2) (1) X ($\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5$)



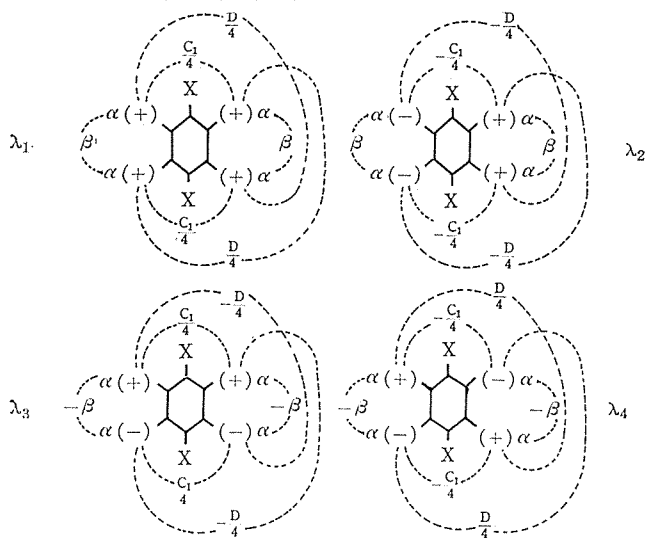
(3) (5.6) X ($\lambda_1, \lambda_2, \lambda_3, \lambda_4$)



(4) (2.6) X ($\lambda_1, \lambda_2, \lambda_3, \lambda_4$)



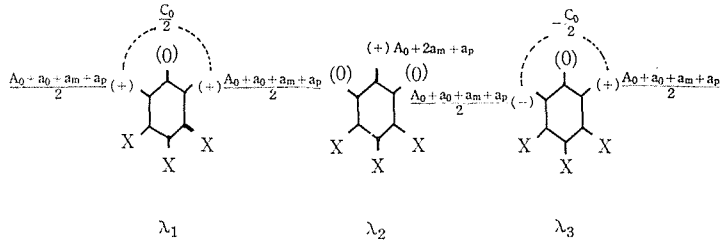
(5) (1.4) X ($\lambda_1, \lambda_2, \lambda_3, \lambda_4$)



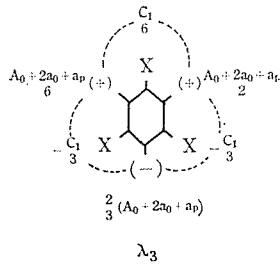
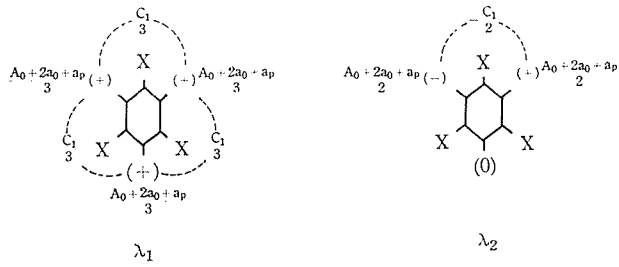
$$\alpha = \frac{A_0 + a_0 + a_m}{4}$$

$$\beta = \frac{B_0 + 2b}{4}$$

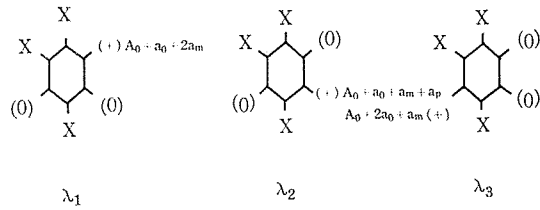
(6) (3.4.5) X ($\lambda_1, \lambda_2, \lambda_3$)



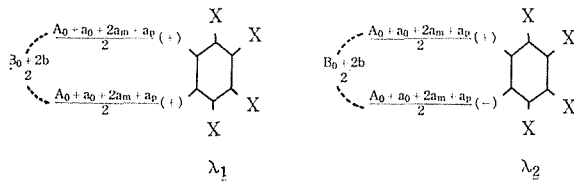
(7) (1.3.5) X ($\lambda_1, \lambda_2 = \lambda_3$)



(8) (1.4.6) X ($\lambda_1, \lambda_2, \lambda_3$)



(9) (5.6) H ($\lambda_1 \neq \lambda_2$)



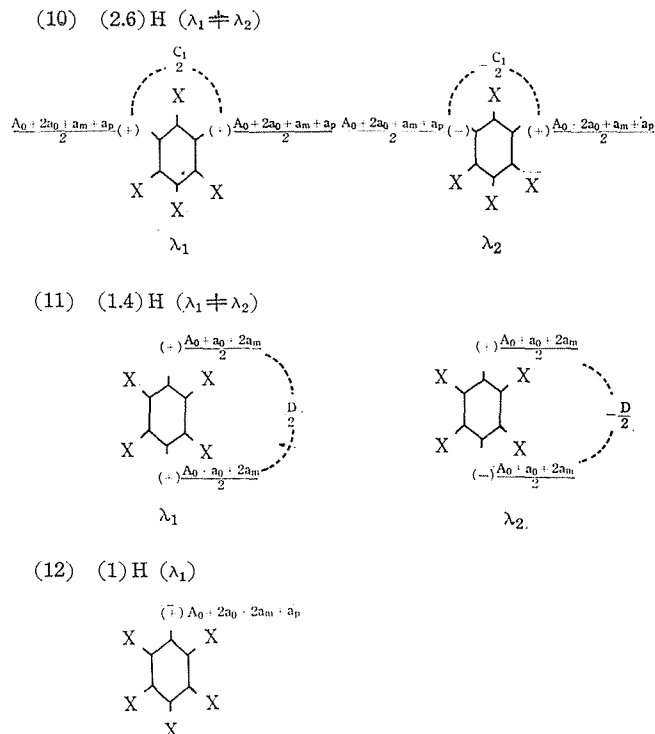


Fig. 4. Types of vibration.

the potential energy at every position, it was tried to summarize them. The potential energies were composed of all force constants, but it was found that they decidedly depended on the constants of A_0 , a_0 , a_m and a_p . Then, the effects of the other force constants upon the potential energy vanished.

The calculated force constants are shown in Table II.

Table II. Force constants (10^5 dyne cm^{-1})

$A :$ 0.474	$a_0 :$ 0.018	$b :$ 0.023
$B_0 :$ -0.076	$a_m :$ 0.005	$c_1 :$ 0.0
$C_0 :$ -0.023	$a_p :$ 0.006	
$D :$ -0.007		

It is said that carboxyl substituent is meta-orientation. The force constant at meta-position must be the lowest and the force constant at ortho-position is nearly equal to that at para-position. Our results were $a_0 > a_p > a_m$. The inequality was consistent with the theory of meta-orientation (5).

The depletion of π -electron densities of the aromatic nucleus by electrophilic substituent must lead to increased force constants. It was found that a_0 was three times as large as a_p . It was suggested that the hydrogen bonding or the steric hindrance at adjacent one is remarkably large. In this paper, the asymmetry of carboxyl substituent is not taken into account, and so it affects the values of the force constants a little.

The calculated frequencies of CH out-of-plane bending vibrations from these force constants are compared with the observed ones in Table III.

Table III. Comparison with experimental values.

Type	Observed	Calculated
Benzene	675	673
	849	849
	975	976
	995	994
(1) X	808	747
(5.6) X	831	782
(2.6) X	886	824
(1.4) X	882	880
(3.4.5) X	843	831
(1.3.5) X	926	932
(1.4.6) X	862	891
(5.6) H	893	897
(2.6) H	943	937
(1.4) H	925	930
(1) H	940	941

The coincidence between the observed and calculated values is satisfactory. The assignments of the carboxylic-substituted benzenes are not completed. We used all the frequencies of benzene and adopted only "a" bands in other cases. The frequencies of mono- and para-carboxyl-substituted benzenes are by 80 cm^{-1} higher than the corresponding methyl ones and the intensities of the formers are extremely lower than the latters. We applied these experimental facts to other polysubstituted ones.

It must be useful to assign the other bands from these calculations. The C-O-H out-of-plane vibrations are so broad and strong that CH bending vibrations except "a" band are hindered. Now, we have been preparing the deuterated ones to obtain the full spectra in this region.

It is very interesting that the spectra of carboxyl-substituted benzenes with water of crystallization are extremely varied.

Acknowledgment

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Appendix A.

F-matrices (Symmetry matrices)

(1) Benzene

	Z_1	Z_2	Z_3	Z_4	Z_5	Z_6
Z_1	A_0	B_0	C_0	D	C_0	B_0
Z_2		A_0	B_0	C_0	D	C_0
Z_3			A_0	B_0	C_0	D
Z_4				A_0	B_0	C_0
Z_5					A_0	B_0
Z_6						A_0

(2) Mono-substituted benzene

	Z_2	Z_3	Z_4	Z_5	Z_6
Z_2	$A_0 + a_0$	$B_0 + b$	C_0	D	C_1
Z_3		$A_0 + a_m$	B_0	C_0	D
Z_4			$A_0 + a_p$	B_0	C_0
Z_5				$A_0 + a_m$	$B_0 + b$
Z_6					$A_0 + a_0$

(3) 5,6-disubstituted benzene

	Z_1	Z_2	Z_3	Z_4
Z_1	$A_0 + a_0 + a_m$	$B_0 + b$	C_0	D
Z_2		$A_0 + a_m + a_p$	B_0	C_0
Z_3			$A_0 + a_m + a_p$	$B_0 + b$
Z_4				$A_0 + a_0 + a_m$

(4) 2,6-disubstituted benzene

	Z_1	Z_3	Z_4	Z_5
Z_1	$A_0 + 2a_0$	C_1	D	C_1
Z_3		$A_0 + a_0 + a_p$	$B_0 + b$	C_0
Z_4			$A_0 + 2a_m$	$B_0 + b$
Z_5				$A_0 + a_0 + a_p$

(5) 1,4-disubstituted benzene

	Z_2	Z_3	Z_5	Z_6
Z_2	$A_0 + a_0 + a_m$	$B_0 + 2b$	D	C_1
Z_3		$A_0 + a_0 + a_m$	C_1	D
Z_5			$A_0 + a_0 + a_m$	$B_0 + 2b$
Z_6				$A_0 + a_0 + a_m$

(6) 3,4,5-trisubstituted benzene

	Z_1	Z_2	Z_6
Z_1	$A_0 + 2a_m + a_p$	$B_0 + b$	$B_0 + b$
Z_2		$A_0 + a_0 + a_m + a_p$	C_0
Z_6			$A_0 + a_0 + a_m + a_p$

(7) 1.3.5-trisubstituted benzene

	Z_2	Z_4	Z_6
Z_2	$A_0 + 2a_0 + a_p$	C_1	C_1
Z_4		$A_0 + 2a_0 + a_p$	C_1
Z_6			$A_0 + 2a_0 + a_p$

(8) 1.4.6-trisubstituted benzene

	Z_2	Z_3	Z_5
Z_2	$A_0 + a_0 + 2a_m$	$B_0 + 2b$	D
Z_3		$A_0 + a_0 + a_m + a_p$	C_1
Z_5			$A_0 + 2a_0 + a_m$

(9) 1.2.3.4-tetrasubstituted benzene

	Z_5	Z_6
Z_5	$A_0 + a_0 + 2a_m + a_p$	$B_0 + 2b$
Z_6		$A_0 + a_0 + 2a_m + a_p$

(10) 1.3.4.5-tetrasubstituted benzene

	Z_2	Z_6
Z_2	$A_0 + 2a_0 + a_m + a_p$	C_1
Z_6		$A_0 + 2a_0 + a_m + a_p$

(11) 2.3.5.6-tetrasubstituted benzene

	Z_1	Z_4
Z_1	$A_0 + 2a_0 + 2a_m$	D
Z_4		$A_0 + 2a_0 + 2a_m$

(12) 2.3.4.5.6-pentasubstituted benzene

	Z_1
	$A_0 + 2a_0 + 2a_m + a_p$

Appendix B.

Symmetry considerations

Symmetry group D_{6h} of benzene consists of the following twenty-four elements:

$$E, 2C_6, 2C_3, C_2, 3C_2', 3C_2'', i, 2S_3, 2S_6, \sigma_h, 3\sigma_d, 3\sigma_v,$$

where

$$2C_6 = \{1C_6, 2C_6\}, 2C_3 = \{1C_3, 2C_3\}, 3C_2' = \{1C_2', 2C_2', 3C_2'\}, 3C_2'' = \{1C_2'', 2C_2'', 3C_2''\},$$

$$2S_3 = \{1S_3, 2S_3\}, 2S_6 = \{1S_6, 2S_6\}, 3\sigma_d = \{1\sigma_d, 2\sigma_d, 3\sigma_d\}, 3\sigma_v = \{1\sigma_v, 2\sigma_v, 3\sigma_v\}.$$

Symmetry operations $2C_6$, $2C_3$ and C_2 have sixfold, threefold and twofold axis which will be regarded as the Z -axis of cartesian coordinates. Each element of $3C_2'$ and $3C_2''$ has twofold axis which lies in the plane of benzene ring (Fig. 5). $3\sigma_d$ and $3\sigma_v$ are the reflections with respect to the planes which contain the Z -axis. The intersection of this plane with the X - Y plane is shown in Fig. 5.

The operation σ_h is the reflection with respect to the X - Y plane. $2S_3$ and $2S_6$ are defined

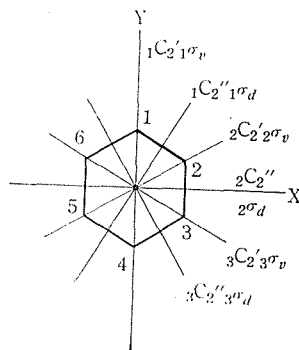


Fig. 5. Symmetry operations.

as the follows :

$${}_1S_3 = \sigma_h \cdot {}_1C_3, \quad {}_1S_6 = \sigma_h \cdot {}_1C_6.$$

The operation "i" is the reflection to the center of symmetry. E is an identical operation.

Fig. 6 shows the symmetrical displacement when the element of D_{6h} operates benzene. It is impossible to understand the change of sign by Fig. 6. This is shown in Table IV.

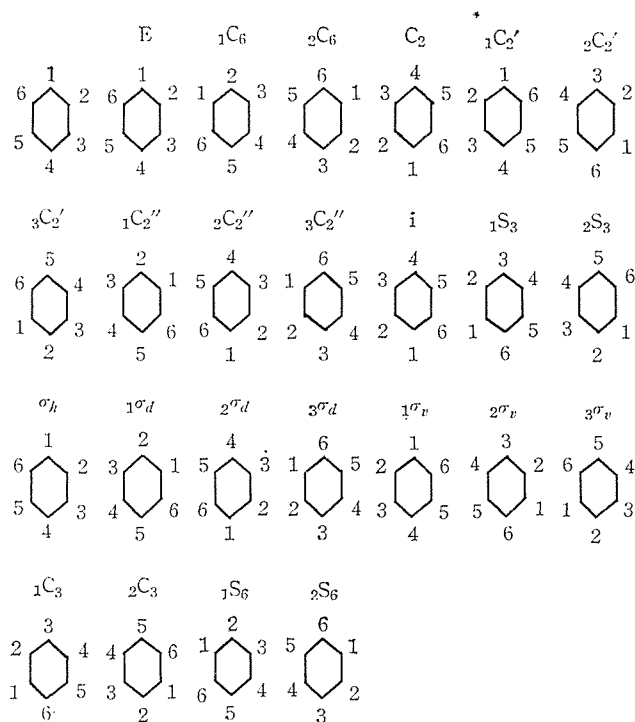


Fig. 6.

Table IV. Sign of the coordinate.

<i>R</i>	<i>E</i>	${}_1C_6$	${}_2C_6$	${}_1C_3$	${}_2C_3$	C_2	${}_1C_2'$	${}_2C_2'$	${}_3C_2'$	${}_1C_2''$	${}_2C_2''$	${}_3C_2''$	<i>i</i>
RZ_1	Z_1	Z_6	Z_2	Z_5	Z_3	Z_4	$-Z_1$	$-Z_3$	$-Z_5$	$-Z_2$	$-Z_4$	$-Z_6$	$-Z_4$
<i>R</i>	${}_1S_3$	${}_2S_3$	${}_1S_6$	${}_2S_6$	σ_h	${}_1\sigma_d$	${}_2\sigma_d$	${}_3\sigma_d$	${}_1\sigma_v$	${}_2\sigma_v$	${}_3\sigma_v$		
RZ_1	$-Z_5$	$-Z_3$	$-Z_6$	$-Z_2$	$-Z_1$	Z_2	Z_4	Z_6	Z_1	Z_3	Z_5		

Symmetries of substituted benzenes are expressed as subgroups of D_{6h} . It is shown in Table V.

Table V. Symmetry groups of substituted benzenes.

Benzene	(1) X	(5, 6) X	(2, 6) X	(1, 4) X	(3, 4, 5) X	(1, 3, 5) X	(1, 4, 6) X	(5, 6) H	(2, 6) H	(1, 4) H	(1) H
D_{6h}	C_{2v}	C_{2v}^*	C_{2v}	V_h	C_{2v}	D_{3h}	C_s	C_{2v}^*	D_{3h}	V_h	C_{2v}

Elements of symmetry groups are given in Table VI.

Table VI. Elements of the symmetry groups.

	Elements							
C_{2v}	E	${}_1C_2'$	${}_1\sigma_v$	σ_h				
C_{2v}^*	E	${}_2C_2''$	${}_2\sigma_d$	σ_h				
V_h	E	${}_1C_2'$	${}_2C_2''$	C_2	i	${}_2\sigma_d$	${}_1\sigma_v$	σ_h
C_s	E	σ_h						
D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$		

Symmetry coordinates are obtained according to the formula $\sum_{R \in G} \chi_R^{(\gamma)} R Z_1$.
 $(\chi_R^{(\gamma)})$: character of species γ .)

Appendix C.

Normal coordinates and L^{-1} -matrices

(1) Benzene

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} & 1/\sqrt{6} \\ 0 & 1/2 & 1/2 & 0 & -1/2 & -1/2 \\ -2/\sqrt{12} & -1/\sqrt{12} & 1/\sqrt{12} & 2/\sqrt{12} & 1/\sqrt{12} & -1/\sqrt{12} \\ 0 & -1/2 & 1/2 & 0 & -1/2 & 1/2 \\ -2/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} & -2/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} \\ 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} & 1/\sqrt{6} & -1/\sqrt{6} \end{pmatrix} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \\ Z_5 \\ Z_6 \end{pmatrix}$$

(2) Mono-substituted benzene

$$\begin{pmatrix} S_7 \\ S_8 \\ Z_4 \\ S_9 \\ S_{10} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} & 0 \end{pmatrix} \begin{pmatrix} Z_2 \\ Z_3 \\ Z_4 \\ Z_5 \\ Z_6 \end{pmatrix}$$

(3) 5,6-disubstituted benzene

$$\begin{pmatrix} S_{11} \\ S_{12} \\ S_{13} \\ S_{14} \end{pmatrix} = \begin{pmatrix} 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \\ Z_4 \end{pmatrix}$$

(4) 2,6-disubstituted benzene

$$\begin{pmatrix} S_8 \\ Z_4 \\ Z_1 \\ S_{10} \end{pmatrix} = \begin{pmatrix} 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} Z_1 \\ Z_3 \\ Z_4 \\ Z_5 \end{pmatrix}$$

(5) 1,4-disubstituted benzene

$$\begin{pmatrix} S_{15} \\ S_2 \\ S_{16} \\ S_4 \end{pmatrix} = \begin{pmatrix} 1/2 & 1/2 & 1/2 & 1/2 \\ 1/2 & 1/2 & -1/2 & -1/2 \\ 1/2 & -1/2 & -1/2 & 1/2 \\ -1/2 & 1/2 & -1/2 & 1/2 \end{pmatrix} \begin{pmatrix} Z_2 \\ Z_3 \\ Z_5 \\ Z_6 \end{pmatrix}$$

(6) 3,4,5-trisubstituted benzene

$$\begin{pmatrix} S_7 \\ Z_1 \\ S_9 \end{pmatrix} = \begin{pmatrix} 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_6 \end{pmatrix}$$

(7) 1,3,5-trisubstituted benzene

$$\begin{pmatrix} S_{17} \\ S_9 \\ S_{18} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 1/\sqrt{2} & 0 & -1/\sqrt{2} \\ 1/\sqrt{6} & -2/\sqrt{6} & 1/\sqrt{6} \end{pmatrix} \begin{pmatrix} Z_2 \\ Z_4 \\ Z_6 \end{pmatrix}$$

(8) 1,4,6-trisubstituted benzene

$$\begin{pmatrix} Z_2 \\ Z_3 \\ Z_5 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ & 1 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} Z_2 \\ Z_3 \\ Z_5 \end{pmatrix}$$

(9) 1,2,3,4-tetrasubstituted benzene

$$\begin{pmatrix} S_{14} \\ S_{20} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} Z_5 \\ Z_6 \end{pmatrix}$$

(10) 1,3,4,5-tetrasubstituted benzene

$$\begin{pmatrix} S_7 \\ S_9 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} Z_2 \\ Z_6 \end{pmatrix}$$

(11) 2,3,5,6-tetrasubstituted benzene

$$\begin{pmatrix} S_{12} \\ S_{14} \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} Z_1 \\ Z_4 \end{pmatrix}$$

(12) 2,3,4,5,6-pentasubstituted benzene

$$\{Z_1\} = \{Z_1\}$$