FOREWORD

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This report covers work conducted from July 1960 to July 1961.

ABSTRACT

As the first step in making assignments of the low-frequency vibrations of para-substituted benzene compounds, complete vibrational assignments of several representative compounds have been started.

While assignments have been made for many monosubstituted benzenes, there is need for a complete assignment of a monosubstituted benzene with an electron-attracting substituent. To fill this need, an assignment of benzonitrile has been made. Attempts to prepare benzonitrile-d_5 were unsuccessful, but are being continued. To confirm the previous assignment of phenol, a sample of phenol-2,4,6-d_3 was prepared. A complete vibrational assignment of this molecule has been made. Attempts to prepare phenol-d_5 are in progress.

The assignments of p-cresol and deuterated p-cresols has been carried almost to completion.

Using the vibrational assignments mentioned above as a foundation, the low-frequency vibrations of 28 para-substituted benzene compounds have been assigned as completely as possible. It has been shown that certain of the low-frequency vibrations are sensitive to the nature of the substituent.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Freeman F. Bentley

FREEMAN F. BENTLEY
Chief, Analytical Branch
Physics Laboratory
Directorate of Materials and Processes

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INVESTIGATION OF THE INFRARED ABSORPTION SPECTRA OF SELECTED AROMATIC COMPOUNDS

by

R. J. Jakobsen

INTRODUCTION

Vibrations of substituted benzene compounds occurring in the low-frequency (below 650 cm^{-1}) spectral region involve either motion of the entire benzene ring or considerable motion of the bond joining the ring and the substituent. Such vibrations are apt to be sensitive not only to the mass of the substituent, but also to the nature or type of the substituent. If the factors affecting this sensitivity to the nature of the substituent can be established, the far-infrared spectral region can prove extremely useful to chemists. Not only will the analytical or organic chemist have a better means of identifying benzene substitution, but the physical chemist will have improved methods for studying the molecular structure and physical and chemical constants of benzene derivatives. The long-range objective of this research program is to gain the maximum information about the sensitivity of long-wavelength (low frequency) infrared absorption for characterization of substitutents on aromatic rings and about the use of low-frequency infrared absorption bands for determination of molecular structure.

The vibrational spectrum of benzene has been assigned rather completely by Ingold and coworkers(1,2) and Mair and Hornig(3). However, it was only with the aid of several deutero-benzenes that Ingold could make such a complete assignment. Normal coordinate analyses of benzene, leading to force constant values and accurate descriptions of the vibrational modes, have been made by many workers, among whom are Miller and Crawford(4), Crawford and Miller(5), Whiffen(6), Califano and Crawford(7), and Albrecht(8). With the aid of this knowledge of the frequencies and vibrational modes of benzene, it was conceivable that the assignment of the frequencies and vibrational modes of substituted benzenes could be readily established. However, this has not proved to be the case.

Most of the research done on the vibrational spectra of substituted benzene compounds has been in the 4000 to 650 cm^{-1} region of the spectrum. Until recently, only the work on Raman spectra of benzene derivatives by Kohlrausch and coworkers(9) included any real attempt to make assignments in the low-frequency region. These assignments were made without the benefit of infrared data and are correspondingly incomplete. Recently, Wilcox, Stephenson, and Coburn(10), using mainly Kohlrausch's Raman data and the halobenzene assignments of Whiffen(11), attempted to assign the low-frequency vibrations of a series of monosubstituted benzenes and to correlate these frequencies with physical properties of the compounds. Using Raman data obtained from the literature or experimentally, along with infrared data obtained experimentally, assignments were made at Battelle(12) for the low-frequency vibrations of para-substituted phenols. Both the work on monosubstituted benzenes and that on para-substituted phenols demonstrated clearly the need for accurate assignment of the

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low-frequency vibrations and that these assignments needed to be based on complete vibrational assignments of representative compounds.

However, a review of the literature reveals that only in the past few years have any appreciable number of substituted benzene assignments been made, and those that have been made often disagree with one another in some aspects of the assignments. Much of the disagreement stems from the assignment of vibrational modes to frequencies. Very little work has been done using deuterated benzenes either to confirm frequency assignments or to help define the modes of vibration.

Pitzer and Scott(13) assigned the frequencies of toluene and p-xylene. The assignment of p-xylene has been revised by Battelle(12) on the basis of the infrared spectra below 500 cm^{-1} which were not obtained by Pitzer and Scott. Assignments for toluene have been made by Wilmshurst and Bernstein(14), Randle and Whiffen(15), and Fuson, Garrigou-Lagrange, and Josien(16). All four of these literature references of toluene disagree on the assignment for toluene. Wilmshurst and Bernstein also assigned toluene-α-d_3 and Fuson, Garrigou-Lagrange, and Josien assigned toluene α-d_3 and toluene-d_8. The halobenzenes were assigned by Whiffen(11) without the benefit of deuterated halobenzenes, but the halobenzenes themselves were used as isotopes of one another. Benzaldehyde and p-chlorobenzaldehyde were assigned by Padhye and Vladkar(17). Narasimham, Nielsen, and Theimer(18) assigned the frequencies of benzotrifluoride.

Other than the assignment of toluene-d_8(16), the only work done on ring-deuterated monosubstituted benzenes was the assignment of pentadeutero fluorobenzene by Steele, Lippincott, and Xavier(19). A value series of assignments are those made by J. C. Evans(20,21,22) on aniline, aniline-ND, aniline-ND_2, ethynylbenzene, ethynylbenzene-d, phenol, and phenol-OD. Phenol has also been assigned by Battelle(12) and by Green(23). For monosubstituted benzene compounds with electron-attracting substituents, assignments have been made on nitrobenzene(10,24); phenyl isothiocyanate and phenyl isocyanate(10,25); benzene sulphonyl chloride, benzene sulphonyl fluoride, and methyl benzene sulphonate(26); benzonitrile(27); and alkali metal benzoates(24).

While the number of assignments of monosubstituted benzene derivatives may appear to be large, it must be emphasized that assignments conflict; few of the assignments are supported by assignments of deuterated compounds, and few of them do much to elucidate the modes of the low-frequency vibrations. These data are needed to make accurate assignments of the low-frequency vibrations of a series of monosubstituted benzenes. Accurate assignments (both symmetry class and mode) of corresponding vibrations must be made if the factors affecting the sensitivity of the vibrations to the nature of the substituent are to be established.

For parasubstituted benzene derivatives, there have been even fewer vibrational assignments. Most of the work has been on parasubstituted halobenzenes.(28,29,30) Other assignments include p-xylene(12,13), p-chlorobenzaldehyde(17), p-nitroaniline(31), and p-chlorobenzotrifluoride(32). The only other work on parasubstituted benzenes has been the assignment of p-cresol and the tentative assignment of hydroquinone made at Battelle.(12) The only studies of deuterated compounds have been the assignment of the infrared-active vibrations of p-dichlorobenzene-d_4 by Saëki.(33)

Randle and Whiffen have observed that six vibrations of monosubstituted benzene derivatives are sensitive to the mass and nature of the substituent. The number of substituent-sensitive vibrations is not known for para-substituted benzene compounds, but work in this laboratory(12) indicates that nine vibrations are substituent sensitive.

The present research program was designed to study the sensitivity of low-frequency infrared absorption to the nature of benzene substituents by:

(1) Making vibrational assignments of representative mono- and para-substituted benzene derivatives.

(2) Preparing suitable deuterated benzene compounds to confirm the vibrational assignments made in Item (1) and to help define the modes of vibration better.

(3) Using the data obtained in Items (1) and (2) to aid in assigning the low-frequency vibrations of para-substituted benzenes.

VIBRATIONAL ASSIGNMENTS OF INDIVIDUAL MOLECULES

Benzonitrile

In the past year several assignments(10,24,25,26,27) of monosubstituted benzene compounds with electron attracting substituents have been made. While these assignments have not been substantiated by the use of deuterated isotopes, and the modes of the low-frequency vibrations are still in doubt, they are of some use in establishing the effects of electron-attracting substituents on low-frequency vibrations. However, the assignment of benzonitrile(27) conflicts with the other assignments of monosubstituted benzenes with electron-attracting substituents. This assignment of benzonitrile made by Bak and Nielsen(27) was made by analogy with the assignment of pyridine. They obtained infrared data (to 400 cm^{-1}) on liquid benzonitrile and used literature values(34) for the low-frequency infrared results and the Raman spectra(35,36). Battelle has made assignments for benzonitrile by comparison with the assignments of other monosubstituted benzenes, especially phenyl acetylene(21). These assignments are also based on infrared vapor band contours (to 240 cm^{-1}), Raman polarization data, and use of the inequality rule(37).

Benzonitrile has been shown by microwave data(38) to have a planar symmetrical structure and undoubtedly possesses C_{2v} symmetry. The 33 normal vibrations are distributed as follows: $(12a_1 + 11b_2)$ in-plane and $(3a_2 + 7b_1)$ out-of-plane vibrations. The a_1 modes will give polarized Raman bands and A-type vapor infrared bands. The b_1 and b_2 modes will give C-type vapor infrared bands, respectively, and depolarized Raman bands. The a_2 bands will be depolarized in the Raman spectra and should be inactive in the infrared spectra.

Table 1 gives the assignment of the fundamental vibrations of benzonitrile along with the designations of the modes of vibration. The previous vibrational assignments of monosubstituted benzenes(2,15) have shown that 24 vibrations are almost insensitive to the nature and mass of the substituent and may be easily identified. This is the case for benzonitrile, although the b_1 CH deformation at 989 cm^{-1} was not observed and was

TABLE 1. FUNDAMENTAL FREQUENCIES OF BENZONITRILE

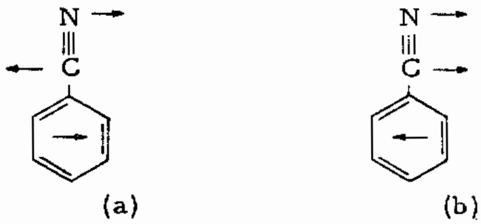
Symmetry Class	Infrared		Raman,	Mode
	Vapor	Liquid	Liquid	
a_1	3081 ms	3080 sh		CH stretch
		3062 mw	3068 w,p	CH stretch
		3042 sh		CH stretch
	2240 m	2232 s	2229 vs,p	C≡N stretch
		1599 m	1599 vs,dp	CC stretch
	1490 s,A	1494 s		CC stretch
	1190 mw,A	1194 mw	1191 mw,p	X-sensitive (C-CN stretch?)
	1177 w	1179 mw	1177 mw,p	CH deformation
	1028 ms,A	1027 m	1027 w,p	CH deformation
		1002 w	1001 s,p	CC stretch
			769 mw,p	X-sensitive (CC stretch?)
		462 w	461 mw,p	X-sensitive (CC deformation?)
b_2			3072 m	CH stretch
		3027 w		CH stretch
	1585 m	1584 w		CC stretch
	1443 m	1448 s		CC stretch
		1337 mw		CC stretch
	1287 m,B	1289 mw		CH deformation
		1163 mw	1161 w,dp	CH deformation
	1072 m,B	1070 mw		CH deformation
		629 w	629 w,?	CC deformation
		381 m	380 w,dp	X-sensitive (C≡N deformation?)
		(271)		X-sensitive (C-CN deformation?)
b_1		(989)		CH deformation
	923 ms,C	927 m		CH deformation
	753 s,C	760 vs		CH deformation
	685 s,C	686 s		CC deformation
	543 s,C	550 s	548 mw,dp	X-sensitive (CC deformation?)
			172 mw,dp	X-sensitive (C≡N deformation?)
			172 mw,dp	X-sensitive (C-CN deformation?)
a_2	978 vw			CH deformation
	848 w			CH deformation
	401 vw?			CC deformation

Note: A, B, C = type of vapor band contour; p = polarized; dp = depolarized; vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder; X-sensitive = modes probably sensitive to the nature and mass of the substituent and the exact mode of the vibration is uncertain.

assigned from consideration of the overtones and combination bands in the 1650 to 2000 cm^{-1} region(39).

Four of the nine remaining unassigned fundamentals are in the a_1 symmetry class. The C≡N stretching vibration is obviously the strong polarized Raman and infrared band at 2232 cm^{-1}. The other three a_1 modes are readily assigned to the polarized Raman bands at 1191, 769, and 461 cm^{-1}. The exact nature of the modes of these three vibrations is uncertain. However, the band at 1191 cm^{-1} must contain much stretching motion of the C-C band between the ring and the substituent because it falls near the frequencies assigned to carbon-carbon stretching vibrations(12,13,14,15). The two modes at 769 and 461 cm^{-1} are probably mixtures of ring carbon stretching modes and an in-plane ring deformation similar to the 606 cm^{-1} vibration of benzene.

Two of the unassigned modes are in the b_2 class and should approximate an in-plane -C≡N deformation and an in-plane C_{ar}-CN deformation as shown below as (a) and (b), respectively.



One of these modes can be assigned to the infrared and Raman band at 381 cm^{-1}. Hidalgo(40) has shown that an in-plane mode falls near this frequency for both aliphatic and aromatic nitriles.

Two alternatives are possible for the assignment of the second mode. One alternative consists of assigning the second mode to a frequency in the 500 cm^{-1} region. This mode has been assigned to 516 cm^{-1} in phenyl acetylene(21) and should fall near this region for benzonitrile since the spectra of these two compounds show a close similarity. This assumes that the assignment of phenyl acetylene is correct, at least insofar as this mode is concerned. However, no absorption band of reasonable intensity has been observed in this spectral region for benzonitrile. While not apparent in the spectra of liquid benzonitrile, a weak band has been observed in the vapor spectra at 551 cm^{-1}. In the liquid spectra this band is obscured by the strong b_1 ring deformation at 550 cm^{-1}, but in the vapor spectra the ring deformation falls at 543 cm^{-1} and the 551 cm^{-1} band can be observed. This 551 cm^{-1} frequency could be the unassigned b_2 mode.

The second alternative is the assignment of an unobserved band at 271 cm^{-1} to this b_2 mode. Joshi(41) reports such a band at 271 cm^{-1} calculated from ultraviolet data. Since the other bands Joshi calculated from UV data agree with observed vibrational frequencies, the 271 cm^{-1} vibration could be real. The 551 cm^{-1} frequency could then be assigned as the first overtone of the 271 cm^{-1} vibration (271 + 271 = 542, $b_2 \times b_2 = a_1$). From intensity considerations the 551 cm^{-1} is more likely to be an overtone or combination band and this fact plus Joshi's data makes us prefer this assignment rather than assigning the 551 cm^{-1} band as a fundamental.

The last two unassigned modes are in the b_1 class. One must be assigned to the Raman band at 172 cm^{-1}. No unassigned band was observed that could be attributed to the second mode. Evans(21) experienced the same difficulty with phenyl acetylene and assigned the second b_1 mode to 353 cm^{-1}, coincident with the lowest b_2 mode. The same assignment could be applied here, but the intensity of the 380 cm^{-1} band in benzonitrile is not as great as the 353 cm^{-1} band in phenyl acetylene, and it is unlikely that two modes exist at 380 cm^{-1}. Instead, from intensity considerations, the second b_1 mode is assigned as coincident with the other b_1 mode at 172 cm^{-1}. A very weak Raman band has been observed at 162 cm^{-1} as a shoulder on the 172 cm^{-1} Raman band. If this is a real band, it may be the second b_1 mode, but additional spectra are needed to prove this point.

Table 2 shows a comparison between the assignments of phenyl acetylene and the assignments of benzonitrile, made both in this laboratory and by Bak and Nielsen(27). The assignment for benzonitrile made by Battelle and the assignment of phenyl acetylene made by Evans(21) show a remarkable similarity except for the two bands mentioned previously.

The differences between this laboratory's assignment of benzonitrile and the assignment made by Bak and Nielson(27) are substantial. Battelle had the benefit of vapor band contours and Raman polarization data, which often dictated the placement of frequencies in symmetry classes and caused some of the differences between the two assignments. Application of the inequality rule(37) to C_6H_5CN, C_6H_6, and C_6H_5D(2) aided in reaching unambiguous choices for many vibrations of the b_2 and a_2 classes (such as 1337, 1289, and 848 cm^{-1}). This also brought about differences between the two assignments.

Bak and Nielsen(27) assigned frequencies at 673 and 700 cm^{-1} to fundamentals. However, both of these appear as very weak shoulders on the side of the strong 686 cm^{-1} ring deformation. Intensity considerations ruled out Battelle's assigning these bands as fundamentals. The low-frequency assignments made by Bak and Nielsen(27) were partly based on infrared data taken from the literature(34). No bands were observed in this laboratory at 313, 266, or 208 cm^{-1}. While it is possible to assign one of these as a fundamental (as we have done), it is difficult to visualize three such fundamentals.

Attempts are still in progress to prepare benzonitrile-d_5, for use in substantiating this laboratory's assignment and especially to get information on the two unobserved low-frequency fundamentals.

The fact that there are two unobserved fundamentals is of real interest and is becoming a major concern. For not only do these unobserved bands represent the only differences between the assignment of phenyl acetylene and benzonitrile, but assignments made for other aromatic compounds (to be described later in the report) indicate that this is not the only case of such behavior. Two possible explanations are available, neither of which is really acceptable.

One explanation would consider the possible intensities of the vibrations involved. There are four modes involving bending (either in- or out-of-plane) of the C-CN bond or the -C≡N bond. Two of these have been observed and assigned (381 and 172 cm^{-1}). Following this explanation, we must postulate that the other two vibrations are of such low intensity that they cannot be observed. From this standpoint, it would be interesting to be able to assign definitely the two observed frequencies to symmetry classes

TABLE 2. COMPARISON OF THE ASSIGNMENTS OF PHENYL ACETYLENE AND BENZONITRILE

Symmetry Class	Frequency, cm^{-1}(a)		
	$C_6H_5C\equiv CH$(21)	$C_6H_5C\equiv N$	$C_6H_5C\equiv N$(27)
a_1	3068	3080	--
	3059	3062	--
	3035	3042	--
	2118	2232	2217
	1599	1599	1597
	1488	1494	1490
	1194	1194	1192
	1178	1179	1178
	1029	1027	1070
	1001	1002	1026
	763	769	1000
	467	462	547
b_2	3100	3072	--
	3084	3027	--
	1573	1584	1579
	1443	1448	1447
	1332	1337	1353, 1389
	1284	1289	1190
	1160	1163	1162
	1070	1070	1070
	621	624	673
	515	381	313
	353	271	266
b_1	984	989	972
	918	927	843
	756	760	757
	691	686	686
	531	550	460
	353	172	208
	165	172	170
92	971	978	926
	842	848	700
	--	401	385

(a) Frequencies are taken from the liquid spectra.

(to be certain whether they are in- or out-of-plane vibrations). However, Raman depolarization data are of no help here because both classes will give depolarized Raman lines, and infrared vapor band contours are of no help because the 380 vibration is not observed in the vapor spectra and Battelle's instrument cannot reach 172 cm^{-1}. It is conceivable that the effective dipole moment for in- and out-of-plane bending could be vastly different and one of these moments could be very small leading to bands of low intensity. However, this is not considered likely. Especially, since Steele and Whiffen(42) have shown that the effective dipole moments are approximately equal in the case of p-difluorobenzene for in- and out-of-plane C-F bending. Since the $-C{\equiv}N$ band lies on the symmetry axis, it can almost be treated as a point mass group and can approximate the p-difluorobenzene case insofar as ring-substituent bending is concerned.

The other explanation for the nonappearance of two fundamentals would be that the in-plane mode (such as δC-CN) is accidentally degenerate with the out-of-plane mode (δC-CN). This implies similar force constants for both in- and out-of-plane bending. Nyquist and Potts(43) treat this possibility for $\equiv$C-H deformations of acetylene compounds. They conclude that the in- and out-of-plane vibrations will be degenerate for alkyl acetylenes. For molecules with a planar group attached to the triply bonded carbon ($C_6H_5-C{\equiv}CH$), the degeneracy will be split and two vibrations are observed. Following this line of reasoning, separate frequencies should be observed for the in- and out-of-plane modes of benzonitrile which involve the $C-C{\equiv}N$ bond.

It is possible that the degeneracy exists between either the two in-plane modes (see Structures (a) and (b), page 5) involving the $C-C{\equiv}N$ bonds or the out-of-plane modes involving this bond. If this is true, the two in-plane modes must be vastly different from Structures (a) and (b), and the true description of the modes is not known.

Phenol and Phenol-2,4,6-d_3

The vibrational spectra of phenol have been assigned in this laboratory(12) and by Green(23). Both phenol and phenol-OD have been assigned by Evans(22). These assignments of phenol agree very well except for minor points:

(1) A reversal of the assignment of symmetry classes for the out-of-plane CH bending vibrations at 978 and 958 cm^{-1}. The strongest of the two vibrations is most likely the b_1 vibration, since a_2 vibrations are forbidden in the infrared and should be weak if they appear at all. A study of other monosubstituted benzenes revealed this to be the case. Therefore, the assignment made at Battelle has been changed to agree with the assignments of Evans and Green.

(2) The highest in-plane CH bending vibration has been assigned by Evans and Green to 1292 or 1313 cm^{-1} and by Battelle to 1178 cm^{-1}. This vibration would be expected to fall near 1290 cm^{-1} (as in the case of mono-deuterobenzene), but no vibration was observed in this region. However, Evans(44) has observed that this band can be seen only with a spectrometer equipped with a grating. Therefore, the assignment made at Battelle was gladly changed to agree with his.

The various assignments of all other frequencies agree very well, even the low-frequency substituent-sensitive vibrations. Battelle has attempted to label the vibrations with an approximate mode such as in-plane ring deformation or substituent-ring bending mode. Evans(22) reports the same behavior for the 410 cm^{-1} vibration of phenol that Battelle has reported for both phenol and para-substituted phenols; the band shifts drastically (51 cm^{-1}) on change of physical state. Therefore, this behavior is consistent with the description of the vibrational mode, namely ring-substituent in-plane bending. The assignment of phenol by Evans(22) has added definite support to Battelle's assignment(12) of the broad band, found in the gas spectra of phenol, below 320 cm^{-1} to the OH torsional vibration. In liquid and solid phenol, the broad band centering near 650 cm^{-1} has been assigned to the OH torsional or out-of-plane bending mode. However, in the free molecule (phenol vapor), no band was observed near this frequency, but a strong band was observed below 320 cm^{-1} and a weak doublet was seen at 575 cm^{-1}. The exact center of the 320 cm^{-1} vibration was not observed due to the limits of Battelle's CsBr prism. This band near 320 cm^{-1} was assigned as the OH torsional vibration or hindered rotation of the OH group around the C-O axis. The doublet near 575 cm^{-1} was assigned as the first overtone of this vibration.

Evans, assuming that the torsional mode was a pure mode not interacting with any other, calculated the height of the barrier hindering internal rotation about the C-O bond and the frequency of the torsional mode. The calculated value of the frequency was 307 cm^{-1}. In order to prove this point, the low-frequency vapor spectra of phenol was obtained on the Perkin-Elmer Model 102 spectrometer at the Aeronautical Systems Division. The exact center of this torsional vibration was observed at 308 cm^{-1}, in very good agreement with the value calculated by Evans. A similar band (305 cm^{-1}) was observed in the spectra of phenol-2,4,6-d_3 vapor but not in the spectra of dilute solutions (in CS_2) of phenol-OD.

As further confirmation of the assignment of phenol and as a means of elucidating the modes of vibration, a sample of ring-deuterated phenol has been prepared. This deuterated phenol was prepared by heating (130 C), for 24 to 48 hours, two parts by weight of phenol with four parts by weight of D_2O and one part by weight of D_2SO_4. This process was repeated several times and, after the fourth exchange, no change was observed in the infrared spectrum of the product even though an appreciable C-H stretching vibration was still observed. A high-resolution nuclear-magnetic-resonance (NMR) spectrum of the compound showed only one peak in the aromatic proton region, indicating that at no place on the benzene ring were there two adjacent protons present. Electronic integration of the peak areas showed that almost exactly two aromatic protons remained for each hydroxy proton. By comparison with the NMR spectrum of phenol, it was observed that the chemical shift of the aromatic proton peak was the same as the chemical shift of the protons meta to the OH group of phenol. This would also follow from chemical reasoning, since the positions ortho and para to the OH group of phenol would be more active and would more easily exchange with deuterium. Therefore, it was concluded that this compound was phenol-2,4,6-d_3.

Complete infrared spectra (both vapor and solution) have been obtained on this deuterated compound. After the infrared spectra were obtained, the remaining sample was sent to Monsanto Research Corporation in order to obtain the Raman spectrum of this compound. However, there was not enough sample to obtain a good spectrum and only a few of the stronger bands were observed. Raman data are needed to complete the assignment. Recently this laboratory has attempted to prepare a larger sample of phenol-2,4,6-d_3, but NMR data indicates that the deuteration has proceeded past the

TABLE 3. VIBRATIONAL DATA FOR PHENOL-2,4,6-d_3

Frequencies, cm^{-1}				Assignment	
Infrared			Raman		
Solution	Vapor		Solution		
	3657				
3605 sh	3648			Monomer	a_1 fundamental, OH stretch
	3638				
3498 sh				End group	
3344 va,br				Polymer	
3062 W	3070				a_1 and b_2 fundamentals CH stretch
	3055				
2302 W					a_1 and b_2 fundamentals CD stretch
2285 W	2286				
2272 W	2268				
1587 sh					a_1 fundamental, CC stretch
1579 vs	1583				b_2 fundamental, CC stretch
1470 vw	1463				
1450 vs	1446				a_1 fundamental, CC stretch
1410 w	1420	B			b_2 fundamental, CC stretch
	1408				
	1330				b_2 fundamental OH deformation and CC stretch
1349	1322			Polymer	
	1317				
1326	1311				
	1307			Monomer	
1281 vw					b_2 fundamental, CH deformation
1239 s	1240				a_1 fundamental, C-OH stretch
1225 vs				Polymer	b_2 fundamental OH deformation and CC stretch
1193 sh				End group	
	1180	A			
	1172			Monomer	
	1163				
1132 w	1125				b_2 fundamental, CH deformation
	1085	A			
1077 ms	1078		1082		a_1 fundamental, CD deformation
	1069				
1045 w	1043				b_2 fundamental, CD deformation
1030 vw	1033				
963 w			964 m		a_1 fundamental, CC stretch
	925	C			
917 ms	917				b_1 fundamental, CD deformation
	909				
	903				
889 vw					
	856	C			
847 m	848		848 w		b_1 fundamental, CH deformation
	840				

TABLE 3. (Continued)

Frequencies, cm^{-1}			
Infrared		Raman	
Solution	Vapor	Solution	Assignment
830 mw	823		a_1 fundamental, CD deformation
808 vw	808		
797	794		a_1 fundamental, CC stretch
	782		
	769		a_2 fundamental, CD deformation
770 ms			
	762		
	697		
685 ms	684 } C		b_1 fundamental, CC deformation
	670		
631 vw			
602 w	596		b_2 fundamental, CC deformation
572 w	585		2 OH, a_1
	567		
552 ms	550 C		b_1 fundamental, CD deformation
517			a_1 fundamental, CC deformation
489 vw			
467 s	466		b_1 fundamental, CC deformation
455 sh	452		
	402		a_2 fundamental, CC deformation
	391		
390 w	381		b_2 fundamental, C-OH deformation
650			Polymer } b_1 fundamental, OH deformation
312	305		Monomer
		(240)	b_1 fundamental, C-OH deformation

TABLE 4. COMPARISON OF THE ASSIGNMENTS OF PHENOL AND PHENOL-2,4,6-d_3

Symmetry Class	Frequencies, cm^{-1}		Description (For Phenol-2,4,6-d_3)
	Phenol	Phenol-2,4,6-d_3	
a_1	3350	3345	OH stretch
	3070	3062	CH stretch
	3061	2302	CD stretch
	3020	2285	CD stretch
	1604	1587	CC stretch
	1500	1450	CC stretch
	1259	1239	C-OH stretch
	1168	1077	CD deformation
	1000	963	CC stretch
	1025	830	CD deformation
	812	797	CC stretch
	531	517	CC deformation
b_2	3050	3055	CH stretch
	3044	2272	CD stretch
	1597	1579	CC stretch
	1474	1410	CC stretch
	1362	1349	CC stretch and OH deformation
	1292	1281	CH deformation
	1228	1225	OH deformation and CC stretch
	1152	1132	CH deformation
	1072	1045	CD deformation
	618	602	CC deformation
	410	390	C-OH deformation
b_1	978	917	CD deformation
	888	847	CH deformation
	690	685	CC deformation
	752	552	CD deformation
	508	467	CC deformation
	242	(240)	C-OH deformation
a_2	958	(930)	CH deformation
	828	770	CD deformation
	410	402	CC deformation

stage of replacing three of the ring hydrogen atoms with deuterium. Since phenol-d_5 would be even more desirable (from a vibrational analysis standpoint) the deuteration is being continued in the hopes of preparing this pentadeutero compound.

The vibrational data already obtained for phenol-2,4,6-d_3 are shown in Table 3. All the overtone and combination bands between 3000 and 1600 cm^{-1} have been omitted. A few of the bands falling between 1600 and 200 cm^{-1} do not show any assignment. Some of these have been assigned as overtones and combination bands. However, no obvious assignment as overtones or combination bands can be made for several observed frequencies. Among these are the bands at 889, 631, 489, and 455 cm^{-1}. Since these are all very weak bands, it is possible that they arise from an impurity such as a phenol deuterated to a different degree than phenol-2,4,6-d_3.

The assigned fundamentals of the deuterated phenol are listed by symmetry class in Table 4 where they are compared to the fundamentals of phenol. The symmetry of the deuterated phenol is the same as that of the parent phenol and therefore the number of vibrations in each symmetry class and the type of vapor band contours will be the same as for phenol. These assignments can be made with a reasonable degree of certainty by use of the vapor spectra band contours, comparison with the assignments of the parent phenol, and by comparison with assignments for other deuterated benzene compounds(2,19). However, better Raman spectra are needed to clear up some of the questions raised by application of the product rule.

The Redlich-Teller product rule(45,46) can be used to substantiate vibrational assignments; it takes the following form:

$$\prod_{k=1}^{3N-6} \frac{\omega_k'}{\omega_k} = \prod_{i=1}^{3N} \left(\frac{m_i}{m_i'}\right)^{1/2} \left(\frac{M'}{M}\right)^{3/2} \left(\frac{I_x' I_y' I_z'}{I_x I_y I_z}\right)^{1/2} ,$$

where the primes indicate the isotopically substituted molecule; ω_k = the k normal frequencies of the molecule in question (or the k normal frequencies of a particular symmetry class); m = the masses of the representative atoms that are transformed into one another by the symmetry operations permitted by the molecule); M = the total mass of the molecules; and I_x, I_y, I_z = the moments of inertia about the x, y, and z axis, respectively. Of course, the smaller the number of vibrations in a given symmetry dose, the more valuable the product rule is as a check on the vibrational assignment.

Applying the product rule to the frequencies of phenol and phenol-2,4,6-d_3 gave the results listed in Table 5.

TABLE 5. REDLICH-TELLER PRODUCT RATIOS FOR PHENOL AND PHENOL-2,4,6-d_3

Symmetry Class	Calculated Values	Observed Values
a_1	0.361	0.366
b_2	0.742	0.712
a_2	1.00	0.887
b_1	0.515	0.594

The lack of agreement between calculated and observed values for the a_2 class is not surprising since the 930 cm^{-1} assignment was not actually observed, but was assigned from combination bands in the 1600 to 2000 cm^{-1} region. The observed product ratios for the b_1 and b_2 classes are not as close to the calculated values as desired. However, several bands in these symmetry classes do not give distinctive vapor band contours. Better Raman spectra might show the need for a reversal of the assignments of these bands or the appearance of new bands which would more closely satisfy the product rule conditions.

p-Cresol and Deuterated p-Cresols

The vibrational spectrum of p-cresol has previously been assigned at Battelle.(12) Recent work on p-cresol has not changed this assignment appreciably except for consideration of the CH_3 and OH torsional modes. However, this recent work has clarified several doubtful points concerning the assignment of p-cresol and led to assignments of the deuterated p-cresols.

Since the assignment of p-cresol, several deuterated p-cresols have been prepared and the vibrational spectra of these compounds has been analyzed.

The deuterated compounds were prepared in several ways. In one method, three grams of p-cresol, 3 grams of a 5 per cent platinum-on-carbon catalyst, and 9 milliliters of D_2O were shaken together for 48 hours at 130 C. After the partially deuterated p-cresol was extracted with CCl_4, the entire process was repeated several times. The final product gave an infrared spectrum in which the CH and CD stretching vibrations were of nearly equal intensity. The NMR spectrum of this compound showed a strong single peak in the aromatic proton region overlying what appeared to be a weak quartet, this quartet being undeuterated p-cresol. The single peak showed that these were no adjacent protons on the benzene ring. Integration of the peak area indicated that approximately two protons remained in the aromatic ring per three protons of the methyl. The single peak also showed that both protons had to be either adjacent to the carbon atom with the OH group attached to it or adjacent to the ring carbon atom with the CH_3 group attached to it. Consideration of the chemistry involved indicated that the protons had to be meta to the OH group. The structure was then assigned as p-cresol-2,6-d_2 (considering the phenolic carbon in the one position). The purity was calculated to be better than 95 per cent, with less than 5 per cent of the original p-cresol remaining.

The p-cresol-d_4 was prepared by shaking 2 milliliters of p-cresol with 4 milliliters of D_2O and 1 milliliter of D_2SO_4 at 130 C for 24 to 48 hours. The deuterated p-cresol was extracted with CCl_4; fresh D_2O and D_2SO_4 were added to it and the mixture was again shaken at 130 C. This process was repeated three times. After the third time no aromatic CH stretching vibration was apparent in the infrared spectrum of the compound, and the NMR spectrum indicated that at least 92 per cent of the ring protons had exchanged with deuterium.

Deuteration of the hydroxy proton of p-cresol was accomplished by simple exchange at room temperature, with ethanol-d. The procedure of Tryon, Brown, and Kharasch(47) was followed. Rough quantitative NMR measurements indicated better than 90 per cent exchange.

Complete infrared and Raman data (the Raman data by E. R. Lippincott at the University of Maryland and by the Monsanto Research Corporation) have been obtained for p-cresol-OD and p-cresol-2,6-d_2. At the present time, only infrared data have been obtained on p-cresol-d_4. After the infrared spectra were obtained, the remaining sample was too small to permit obtaining good Raman spectra. The preparation of larger amounts of p-cresol-d_4 is now in progress.

The symmetry of the deuterated compounds remains the same as that of p-cresol (C_{2v}) if the substituent groups are again treated as point mass groups. Thus, there are 42 normal vibrations divided among the symmetry classes as follows: ($14a_1 + 14b_2$) planar + ($4a_2 + 10b_1$) nonplanar. The a_2 class is infrared inactive; all other classes are active in both the infrared and Raman. The only polarized Raman frequencies will fall in the a_1 class. The a_1, b_2, and b_1 classes will give Types A, B, and C band contours, respectively.

The assignment of the deuterated p-cresols was made consistent with vapor-band contours, the inequality rule, the Redlich-Teller product rule, and where possible, with Raman polarization data and the assignment of the deuterium isotopes of benzene. The assigned frequencies of the deuterated compounds are listed in Table 6 along with the revised assignments for p-cresol.

None of the assigned frequencies of p-cresol have been changed from the previous assignment(12) except for the assignment of the torsional OH vibration. Vapor spectra of p-cresol obtained at the Aeronautical Systems Division showed a strong vibration at 295 cm^{-1} and a weak doublet near 555 cm^{-1}. Similar to the vibration at 308 cm^{-1} in phenol, this vibration has to be assigned to the OH torsional mode of the monomer with the 555 cm^{-1} doublet being the overtone of this vibration. It is not observed in the spectra of liquid p-cresol, but a broad vibration near 630 cm^{-1} was observed which is the OH torsional mode of the polymer. Again this parallels the spectra of phenol. Similar vibrations were observed for p-cresol-2,6-d_2 (623 cm^{-1}, 291 cm^{-1}) and p-cresol-d_4 (620 cm^{-1}, 290 cm^{-1}). For p-cresol-OD there was no vibration observed at 630 cm^{-1} (as expected), but the polymer OD torsional vibration was seen near 470 cm^{-1}. The monomer OD torsional vibration is expected to lie at a frequency beyond the range of our spectrometer.

Although the methyl torsional vibration has not been observed, substantiation for its previous assignment to the 125 to 25 cm^{-1} range comes from the work of Fately(48). He assigned the torsional vibration to this frequency range for a large number of aliphatic methyl compounds and predicts the same range for aromatic methyl compounds.

For p-cresol, there is some doubt whether the a_2 CH deformation should be assigned to the Raman band at 823 cm^{-1} or the infrared band at 805 cm^{-1} The 805 cm^{-1} infrared band is seen as a strong sharp band in dilute CS_2 solutions, but for liquid p-cresol this band shifts and it is seen only as a shoulder on the low-frequency side of the strong 818 cm^{-1} band. In acetone or pyridine solutions, this band is seen as a shoulder on the high-frequency side of the 818 cm^{-1} band. This shifting in solution indicates an OH vibration and the possibility that this band was an overtone of the 430 cm^{-1} C-OH deformation. This point was checked by obtaining the solution spectra of other para-substituted phenols. For these compounds, a vibration was seen in the 800 cm^{-1} region (which shifted on going from liquid to solution), if the C-OH deformation was above 400 cm^{-1}. For those phenols where the C-OH deformation was below 400 cm^{-1}, no bands were observed in the 800 cm^{-1} region. This indicates that not only

TABLE 6. FUNDAMENTAL FREQUENCIES OF p-CRESOL AND DEUTERATED p-CRESOLS

Symmetry Class	Frequencies, cm^{-1}				Description
	p-Cresol	p-Cresol-2,6-d_2	p-Cresol-d_4	p-Cresol-OD	
a_1	3594	3592	3593	2655	Monomer } OH stretch
	3472	3477	3480	2590	End group } or
	3350	3345	3353	2480	Polymer } OD stretch
	3070	3032	2266	3070	CH or CD stretch
	3060	2277	2258	3060	CH or CD stretch
	2919	2924	2919	2922	CH_3 stretch
	1618	1608	1588	1616	CC stretch
	1515	1467	1410	1510	CC stretch
	1379	1379	1379	1374	CH_3 deformation
	1251	1244	1212	1255	X-sensitive (CX stretch)
	1212	1201	1121	1217	X-sensitive (CX stretch)
	1170	1060	946	1168	CH or CD deformation
	1015	922	815	1012	CH or CD deformation
	842	826	790	844	CC stretch
	738	707	689	732	X-sensitive (CC stretch)
	468	462	453	460	X-sensitive (CC deformation)
b_2	3038	3051	2249	3038	CH or CD stretch
	3032	2265	2249	3032	CH or CD stretch
	2950	2943	2948	2946	CH_3 stretch
	1600	1591	1576	1595	CC stretch
	1464	1463	1458	1450	CH_3 deformation
	1439	1409	1410	1421	CC stretch
	1361	1351	1320	1354	CC stretch
	1290	1275	1045	1279	CH or CD deformation
	1235	1235	1212	1002	Polymer } OH or
	1192	1200	1200	968	End group } OD deformation
	1170	1172	--	--	Monomer }
	1114	1109	1108	1110	CH_3 rock
	1102	884	879	1099	CH or CD deformation
	642	637	(619)	644	CC deformation
	430	433	403	425	X-sensitive (CX deformation)
	340	329	322	337	X-sensitive (CX deformation)

TABLE 6. (Continued)

Symmetry Class	Frequencies, cm^{-1}				Description
	p-Cresol	p-Cresol-2,6-d_2	p-Cresol-d_4	p-Cresol-OD	
b_1	2931	2930	(2930)	2918	CH_3 stretch
	1458	1463	1448	1450	CH_3 deformation
	1038	1038	1045	1038	CH_3 rock
	928	822		925	CH or CD deformation
	818	760	701	812	CH or CD deformation
	700	673	(578)	698	CC deformation
	508	468	432	506	CC deformation
	340	329	322	337	X-sensitive (CX deformation)
	~630	~623	~620	470	Polymer } OH or OD
	295	291	290	--	Monomer } deformation
	161	179	--	--	X-sensitive (CX deformation)
a_2	952	856	(790)	(950)	CH or CD deformation
	823	723	(688)	824	CH or CD deformation
	416	386	372	(412)	CC deformation
	<300	--	--	--	CH_3 torsion

is this band (800 cm^{-1} region) an overtone of the C-OH deformation (400 cm^{-1} region) but its appearance must be due to Fermi resonance with another fundamental, probably the CC stretching vibration at 842 cm^{-1}. The 823 cm^{-1} Raman band must, therefore, be the CH deformation.

Another question arose over whether the infrared bands at 464 cm^{-1} and 333 cm^{-1} were derived from the same vibrations as the Raman bands at the corresponding frequencies. This question arose because these frequencies are seen in the infrared spectra of liquid p-cresol but not in the spectra of p-cresol vapor. The absence of these bands in the gas phase strongly indicate a vibration connected with the OH group. This leads to an explanation of the 464 cm^{-1} infrared band. The O-H···O stretching vibration of a hydrogen-bonded polymer would be expected to fall in the 200 to 250 cm^{-1} range(49). These frequencies are beyond the range of this laboratory's spectrometer, but overtones of this vibration would be expected in the 400 to 500 cm^{-1} range, which could be observed. Therefore, the 464 cm^{-1} infrared band is assigned to the first overtone of the O-H···O stretching vibration (which would fall near 232 cm^{-1}) and is different from the 468 cm^{-1} Raman band which is an in-plane CC deformation. This assignment is supported by the disappearance of the infrared band in the vapor spectra. This is because the 464 cm^{-1} band is an overtone of the O-H···O stretching vibration for polymers and, in the gas state, p-cresol exists mainly as a monomer which, of course, would not have any O-H···O vibrations.

The 333 cm^{-1} infrared band can also be explained as an overtone and different from the 340 cm^{-1} Raman band which is assigned as a ring substituent in-plane bending vibration. The infrared band must be the overtone of the 161 cm^{-1} frequency which has been assigned to an out-of-plane ring-substituent bending mode. However, the 161 cm^{-1} frequency must be essentially a ring-OH bending mode in order to explain the absence of a band at 333 cm^{-1} in the vapor spectra. As has been reported previously(12), the 430 cm^{-1} is mainly an in-plane C-OH bending vibration which shifts in going from liquid to solution to vapor. The 161 cm^{-1} vibration must be the corresponding out-of-plane mode also shifting with change of state. This means the 333 cm^{-1} overtone would also shift and in the vapor spectra would fall under the OH torsional mode at 295 cm^{-1}.

Assignment of the 430 cm^{-1} frequency and the 161 cm^{-1} frequency to the in- and out-of-plane C-OH bending modes leaves only the 340 cm^{-1} frequency for the assignment of both the in- and out-of-plane $C-CH_3$ bending modes. However, if there is free rotation of the methyl group about the $C-CH_3$ bond, such degeneracy would not be unreasonable.

Redlich-Teller product ratios have been calculated for the three deuterated p-cresols, and in Table 7 the calculated and observed values are compared. The calculated and observed product ratios agree fairly well except for the b_1 class of p-cresol-2,6-d_2. Here the observed ratio is too large, as compared with the calculated ratio. It is likely that the discrepancy arises from the rise of the lowest ring substituent bending mode from 161 to 179 cm^{-1} upon deuteration of the aromatic ring. Of great interest here will be the value (obtained from the Raman spectra) of the same mode in p-cresol-d_4.

TABLE 7. REDLICH-TELLER PRODUCT RATIOS FOR p-CRESOL

Symmetry	p-Cresol-2,6-d_2		p-Cresol-d_4		p-Cresol-OD	
Class	Calculated	Observed	Calculated	Observed	Calculated	Observed
a_1	0.505	0.526	0.255	0.248	0.718	0.705
b_2	0.530	0.544	0.263	0.289	0.711	0.716
b_1	0.722	0.784	0.561	0.534	0.718	0.752
a_2	0.714	0.732	0.510	0.619	1.030	0.976

The assignment of the 30 benzenelike fundamentals (excluding internal vibrations of the substituent groups) of p-cresol can also be checked by application of the inequality rule.(37) This rule considers two molecules, such as RX and RY where the mass of the substituent X is greater than that of the substituent Y. Then in any given symmetry class of RX containing "a" modes associated with the RX group, the jth highest frequency has between the jth and (j + a)th highest frequencies of the equivalent symmetry class of RY.

Table 8 lists the assigned benzenelike frequencies of p-cresol (RX) and of phenol (RY) and toluene (RY). This table serves to illustrate the application of the inequality rule, for any frequency of p-cresol lies below the corresponding frequency of phenol or toluene, but above the next lowest frequency. Virtually all of the frequencies of p-cresol fall between or very near the boundaries set up by the inequality rule. Application of the inequality rule to the frequencies of p-cresol did not indicate any need for a change in the assignment.

Summary of Vibrational Assignments

The assignment of several mono- or disubstituted benzene compounds (supported by assignments of deuterated compounds) has either been completed or is in progress and will soon be completed. These assignments will be the foundation on which to base the assignment of the low-frequency vibrations of para-substituted benzenes.

While several normal coordinate analyses have been made for benzene(4,5,6,7,8) no one has been successful in using the benzene force constants to predict the frequencies of substituted benzenes. Recently, Albrecht(50) made a normal coordinate analysis for the in-plane vibrations of a model para-substituted benzene compound. Assuming a ring-substituent bond distance of 1.4 A and a substituent mass of 20, he adopted the benzene force field(8) without change and was able to calculate the in-plane frequencies of the model compound. These calculated frequencies are listed in Table 9 along with the assignment of the in-plane frequencies of p-cresol and p-xylene made at Battelle(12) and the in-plane frequencies of p-difluorobenzene assigned by Stojiljkovich and Whiffen(30).

Albrecht found that the cross terms in the potential energy function were small and therefore could be neglected. He could then calculate the fractional potential energy distribution for each coordinate and identify the modes of vibration. The modes of

TABLE 8. BENZENELIKE FREQUENCIES OF PHENOL, p-CRESOL, AND TOLUENE

Symmetry Class	Frequencies, cm^{-1}		
	Phenol	p-Cresol	Toluene(14, 16)
a_1	3070	3070	3087
	3061	3060	3063
	3050	1618	3055
	1604	1515	1605
	1500	1251	1494
	1253	1212	1208
	1168	1170	1175
	1025	1015	1030
	999	842	1003
	812	738	784
	531	468	521
b_2	3044	3038	3039
	3020	3032	3029
	1597	1600	1586
	1474	1939	1494
	1362	1361	1331
	1292	1290	1312
	1152	1102	1154
	1072	642	1080
	618	430	623
	410	340	344
b_1	978	928	978
	888	818	893
	752	700	728
	690	508	695
	508	340	464
	242	161	217
a_2	958	952	964
	828	823	843
	410	416	408

TABLE 9. COMPARISON OF CALCULATED AND OBSERVED IN-PLANE FREQUENCIES OF PARA-SUBSTITUTED BENZENES

Symmetry Class		Frequencies, cm^{-1}, and Description of Mode							
		Calculated(50) $m_x = 20$		p-Xylene $m_x = 15$		p-Cresol $m_x = 15, 17$		p-Difluorobenzene(30) $m_x = 19$	
C_{2v}	V_h	C-X = 1.4 A		C-X = 1.5 A		C-X = 1.5, 1.35 A		C-X = 1.3 A	
a_1	a_g	3063	νCH	3054	νCH	3070	νCH	3084	νCH
		1676	νCH	1618	νCC	1618	νCC	1617	νCC
		1286	βCH	1205	νCX	1212	νCX	1245	βCH
		1126	βCH	1183	βCH	1170	βCH	1142	νCC
		806	νCC	829	νCC	842	νCC	858	αCCC
		399	αCCC	460	αCCC	468	αCCC	451	νCX
b_2	b_{3g}	3043	νCH	3030	νCH	3038	νCH	3084	νCH
		1587	νCC	1581	νCC	1600	νCC	1617	νCC
		1304	βCH	1313	βCH	1290	βCH	1285	βCH
		650	αCCC	644	αCCC	642	αCCC	635	αCCC
		424	βCX	313	βCX	430	βCX	427	βCX
a_1	b_{μ}	3071	νCH	3050	νCH	3060	νCH	3050	νCH
		1566	βCH, νCC	1517	νCC	1515	νCC	1511	νCC
		1276	βCH	1226	νCX	1251	νCX	1212	νCC
		1026	νCC	1022	βCH	1015	βCH	1012	βCH
		638	νCX	742	νCC	738	νCC	737	νCX
b_2	$b_{2\mu}$	3179	νCH	3020	νCH	3032	νCH	3080	νCH
		1407	νCC	1455	νCC	1439	νCC	1437	νCC
		1285	νCC	1340	νCC	1361	νCC	1285	νCC
		1092	βCH	1118	βCH	1102	βCH	1085	βCH
		332	βCX	232	βCX	340	βCX	350	βCX

Note: νCH or νCX = stretching vibration, βCH or βCX = in-plane bending vibration, νCC = carbon-carbon stretching vibration, αCCC = in-plane ring deformation.

vibration for each assigned frequency are also listed in Table 9 as are the assigned modes for p-cresol, p-xylene, and p-difluorobenzene.

The agreement between the calculated and the assigned frequencies is remarkably good, especially since the mass of the substituents and the ring-substituent bond distances of the assigned compounds are different from those used for the calculated frequencies.

Although the agreement between calculated and assigned frequencies is very good for the compounds listed, it must be remembered that none of the compounds contain electron-attracting substituents. Such compounds can be expected to show larger deviations if the work with monosubstituted benzenes with electron-attracting substituents holds for disubstitution.

The agreement between the calculated and the assigned modes of vibration is not so good as the agreement for the frequencies. Most of the disagreement on modes of vibration falls in the symmetry classes corresponding to the a_1 class for compounds of C_{2v} symmetry. Albrecht points out that, in this class, there is a great deal of mixing between modes of different kinds, and if one mode is slightly dominant in one molecule, it may easily give way to another mode if a different molecule. Such is often the case here. Deuteration studies of p-cresol and p-xylene has shown that the vibration near 1020 cm^{-1} must contain appreciable CH motion and not be a ring mode as Albrecht shows for his model compound. Since the ring-substituent stretching modes, the ring-breathing modes, and the in-plane ring deformation all show considerable mixing of modes, the dominant mode for a given frequency could easily vary from compound to compound. Albrecht's calculations produce too many modes containing appreciable CH bending motion and it is felt that at least one of these modes (in the 1200 cm^{-1} region) must in reality contain much ring-substituent stretching motion as borne out by the studies of deuterated p-cresol.

LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED BENZENES

Results

The ultimate aim of this program is to determine the sensitivity of low-frequency infrared absorption for determining the nature of substituents on benzene rings. In order to do this, correct assignments must be made for these low-frequency vibrations, for it is only the changes with substituents of corresponding vibrations that can indicate the potential of the low-frequency spectral region. Thus, it becomes extremely important for the assignment of the low-frequency vibrations to be correct. Correct assignments, however, are often difficult to make and all possible information should be used. It is for this reason that complete vibrational assignments must be used to aid in the assignment of the low-frequency vibrations of substituted benzenes in general.

While the vibrational assignments of representative compounds have not been completed, it was felt that the assignment of para-substituted benzenes in general should be started. A series of 28 para-substituted benzenes were selected as being representative of types of benzene compounds. These compounds are the 28 compounds that can be formed using the following seven substituents: $-NH_2$, $-OH$, $-CH_3$, $-Cl$, $-Br$, $-CN$, and $-NO_2$. These give substituents that are electron donors, electron attractors, halogens, and alkyl groups.

Infreared spectra, from 650 to 300 cm^{-1}, were obtained for all 28 compounds. Most of these compounds are solids at room temperature and were run as solids in Nujol. A few of the compounds are liquids at room temperature and were run as such. Raman data for these compounds have been obtained from the literature.(9) The needed Raman depolarization data were available for only a few of the compounds. All vibrational assignments of related benzene compounds, those made at Battelle(12) and those taken from the literature(11,13-33,37), were used to aid in the assignments.

Tentative assignments have been made for some of the low-frequency vibrations of the 28 para-disubstituted benzene compounds, and these assignments are listed in Tables 10 through 16. While there are a total of four ring-substituent bending modes (two in-plane and two out-of-plane), an attempt has been made to assign only two (one in-plane and one out-of-plane) for any given series of para-substituted benzenes. Within any given series, the fact that one of the two substituents remains constant means that one in-plane and one out-of-plane bending mode will also tend to remain constant.

While there are still gaps in the assignments and some of the assignments are uncertain, in general the assignments are more reliable than the assignments made previously(12) for para-substituted phenols. The use of many classes of para-substituted benzene compounds has made it easier to observe trends in corresponding vibrations.

Even though the vibrational assignment of representative benzene compounds has not yet been completed, the data already acquired have been invaluable in making the assignment of the low-frequency vibrations of para-substituted benzenes in general.

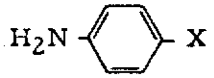
Conclusions and Discussion

Considering each vibration separately, the highest out-of-plane ring deformation is relatively constant in position (622 to 650 cm^{-1}) and thus easy to assign. It is of medium intensity in the Raman spectra and weak or unobserved in the infrared spectra.

The lowest out-of-plane ring deformation (lowest in Tables 10 through 16) appears as a strong infrared band in the 479 to 517 cm^{-1} range as long as the substituents are not electron attracting ($-CN$, $-NO_2$). When one or both of the substituents is a cyano group, the vibration gains intensity and shifts to higher frequencies (541 to 561 cm^{-1}) probably due to Fermi resonance with one of the out-of-plane ring substituent bending modes. When one or both of the substituents is the nitro group, this vibration loses intensity and falls in the 464 to 497 cm^{-1} range.

The strong Raman, weak infrared band in the 471 to 215 cm^{-1} range is relatively easy to assign when Raman polarization data are available. The in-plane ring deformation is the only polarized Raman vibration falling in this frequency range. Polarization data are available for almost all the substituted phenols and toluenes. When polarization

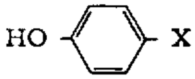
TABLE 10. LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED ANILINES



	Frequency, cm^{-1}						
Vibrations[a]	X = NH_2	OH	CH_3	Cl	Br	CN	NO_2
ϕCC	646	648	643	637	629	--	631
ϕCC	517	512	505	507	504	485	491
αCCC	465	467	464	379	289	421	--
$\beta PhNH_2$,X	354	345	410	403	394	404	402
$\gamma PhNH_2$,X	335	--	334	318	--	--	--

(a) ϕCC = out-of-plane ring deformation, αCCC = in-plane ring deformation, βPhX = in-plane ring deformation, γPhX = out-of-plane ring deformation.

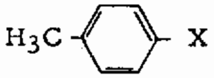
TABLE 11. LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED PHENOLS



	Frequency, cm^{-1}						
Vibrations[a]	X = NH_2	OH	CH_3	Cl	Br	CN	NO_2
ϕCC	648	648	642	634	632	650	630
ϕCC	512	517	508	504	504	483	497
αCCC	467	471	468	382	290	421	376
βPhOH,X	360	371	430	434	443	412	414
γPhOH,X	--	322	340	331	319	--	--

(a) ϕCC = out-of-plane ring deformation, αCCC = in-plane ring deformation, βPhX = in-plane ring deformation, γPhX = out-of-plane ring deformation.

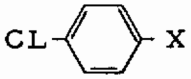
TABLE 12. LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED TOLUENES



	Frequency, cm^{-1}						
Vibrations(a)	X = NH_2	OH	CH_3	Cl	Br	CN	NO_2
ϕCC	644	644	643	635	632	648	638
ϕCC	505	504	483	485	479	--	468
αCCC	464	468	457	377	291	410	362
$\beta PhCH_3$,X	334	340	313	304	364	346	--
$\gamma PhCH_3$,X	166	161	--	--	--	161	--

(a) ϕCC = out-of-plane ring deformation, α CCC = in-plane ring deformation, βPhX = in-plane ring deformation, γPhX = out-of-plane ring deformation.

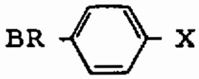
TABLE 13. LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED CHLOROBENZENES



	Frequency, cm^{-1}						
Vibrations(a)	X = NH_2	OH	CH_3	Cl	Br	CN	NO_2
ϕCC	637	634	635	627	624	640	629
ϕCC	507	504	485	485	479	--	470
αCCC	379	382	377	331	261	349	389
βPhCl,X	318	--	--	299	284	302	313
γPhCl,X	--	--	--	--	--	--	--

(a) ϕCC = out-of-plane ring deformation, α CCC = in-plane ring deformation, βPhX = in-plane ring deformation, γPhX = out-of-plane ring deformation.

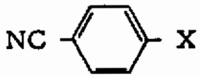
TABLE 14. LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED BROMOBENZENES



Vibrations(a)	Frequency, cm^{-1}						
	X = NH$_2$	OH	CH$_3$	Cl	Br	CN	NO$_2$
ϕCC	629	632	632	624	624	636	622
ϕCC	504	504	479	479	473	--	464
αCCC	289	290	291	261	215	262	256
βPhBr,X	--	--	242	220	272	--	203
γPhBr,X	--	--	--	--	--	--	--

(a) ϕCC = out-of-plane ring deformation, αCCC = in-plane ring deformation, βPhX = in-plane ring deformation, γPhX = out-of-plane ring deformation.

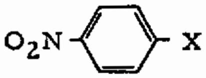
TABLE 15. LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED BENZONITRILES



Vibrations(a)	Frequency, cm^{-1}						
	X = NH$_2$	OH	CH$_3$	Cl	Br	CN	NO$_2$
ϕCC	--	650	648	640	636	645	644
ϕCC	547	546	548	542	544	561	541
αCCC	485	483	441	442	434	415	--
βPhCN,X	421	421	410	349	--	362	334
γPhCN,X	--	158	--	146	--	136	147

(a) ϕCC = out-of-plane ring deformation, αCCC = in-plane ring deformation, βPhX = in-plane ring deformation, γPhX = out-of-plane ring deformation.

TABLE 16. LOW-FREQUENCY VIBRATIONS OF PARA-SUBSTITUTED NITROBENZENES



		Frequency, cm^{-1}					
Vibrations[a]	X = NH_2	OH	CH_3	Cl	Br	CN	NO_2
ϕCC	631	630	638	629	622	644	--
ϕCC	491	497	468	470	464	--	--
αCCC	--	376	362	389	256	250	--
$\beta PhNO_2$,X	--	250	226	272	270	233	--
$\gamma PhNO_2$,X	--	--	--	--	--	168	--

(a) ϕCC = out-of-plane ring deformation, αCCC = in-plane ring deformation, βPhX = in-plane ring deformation, γPhX = out-of-plane ring deformation.

data are not available, this band is assigned as the strongest Raman band following the general pattern of the phenols and toluenes for this vibration.

The ring-substituent bending modes are much more difficult to assign. Good values have been determined for the in-plane bending mode of substituted phenols by observing frequency shifts with change of state. For substituted anilines a similar behavior pattern has been observed. The in-plane ring-substituent bending mode for the other substituted benzenes has been assigned mainly on the basis of the assignment of this mode in monosubstituted benzenes.

The out-of-plane ring-substituent bending mode has been assigned by analogy with other assignments on para-substituted benzenes. In Tables 10 through 16, the designation of the last two modes in each table is not meant to imply bending modes of the ring and a particular substituent. These are only ring-substituent bending modes that are relatively constant in frequency for each particular class of compounds, but could involve motion of both substituents.

In Table 17 are listed the frequency ranges of three vibrations for the various classes of compounds studied. These three vibrations have been assigned as substituent sensitive modes, with the highest frequency mode being a mixture of ring-substituent stretching motion and ring deformation. The two lower frequency modes are in- and out-of-plane ring substituent bending modes, respectively. This table emphasizes the sensitivity of low-frequency infrared absorption to the nature of the substituent and establishes the analytical value of the far-infrared spectral region. For by the use of these three frequencies (one in the conventional infrared region and two in the low-frequency region) the nature of the substituents on benzene rings can be determined.

TABLE 17. FREQUENCIES OF CERTAIN SUBSTITUENT-SENSITIVE VIBRATIONS OF PARA-SUBSTITUTED BENZENES

Para-Substituted Compounds	Frequencies, cm^{-1}		
	νCX, αCCC, νCC	βCX	γCX
Anilines	1263-1314	345-410	318-335
Phenols	1253-1282	300-443	319-340
Toluenes	1200-1216	314-364	161-170
Chlorobenzenes	1081-1091	284-318	--
Bromobenzenes	1063-1070	203-272	--
Benzonitriles	1172-1221	334-421	136-158
Nitrobenzenes	1107-1116	226-272	--

RECOMMENDATIONS FOR FUTURE WORK

The following points are recommendations for a profitable extension of the present work:

(1) Extend the analytical study by assigning the low-frequency vibrations of para-substituted benzenes with different substituents such as $-OCH_3$, $-C_2H_3$, -F, $-CH=CH_2$, $-C\equiv CH$, and -COOH.

(2) Extend the analytical program to selected meta- and ortho-substituted benzene derivatives.

(3) Complete all assignments of individual compounds that have already been started.

(4) Extend the theoretical program by gaining more information about the modes of vibration. This can be accomplished by (a) preparation and assignment of more deuterated compounds such as the deuterated monohalobenzenes and (b) preparation and assignment of other isotopic benzenes such as chlorobenzene-Cl^{35} and chlorobenzene-Cl^{36} and benzene compounds substituted with nitrogen isotopes.

PUBLICATIONS AND TALKS RESULTING FROM THIS WORK

The following talks have resulted from work under this contract [AF 33(616)-7162] and under Contract No. AF 33(616)-6190:

"The Vibrational Spectra of Para-Substituted Phenols", Jakobsen, R. J., and Brewer, E. J., The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (March, 1960).

"The Vibrational Spectra of Para-Substituted Benzenes", Jakobsen, R. J., The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (March, 1961).

Papers submitted (or to be submitted) for publication which resulted from work under these two contracts include:

"The Vibrational Spectra of Para-Substituted Phenols", Jakobsen, R. J., and Brewer, E. J., Applied Spectroscopy, in press.

"The CsBr Spectra of Para-Substituted Benzene Compounds", Jakobsen, R. J., Applied Spectroscopy, to be submitted.

"The Vibrational Spectra of Deuterated Phenols", Jakobsen, R. J., Spectrochimica Acta, to be submitted.

"The Vibrational Spectra of p-Cresol", Jakobsen, R. J., Journal of Chemical Physics, to be submitted.

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