A HYDROGEN BONDING STUDY OF THE HALOGEN SUBSTITUTED PHENOLS BY FAR INFRARED SPECTROSCOPY

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ABSTRACT

A HYDROGEN BONDING STUDY OF THE HALOGEN SUBSTITUTED PHENOLS BY FAR INFRARED SPECTROSCOPY

BY

Terry Steven Cox

Far infrared spectra in the 50-250 cm^{-1} region were obtained for solutions of the monohalophenols in cyclohexane. For each of the twelve compounds, assignment of the intermolecular hydrogen bond stretching frequency ν_σ was confirmed by the decrease in intensity of the broad band upon successive dilution of the halophenol in the solvent.

Correlation of the ν_σ values indicates that the predominant form of association is $O-H\cdots O$ hydrogen bonding, as opposed to $O-H\cdots X$ (X = halogen) bonding.

The data do not fit a simple harmonic oscillator approximation adequately; thus it is suggested that normal coordinate analysis be performed on the systems to predict force constants for the intermolecular hydrogen bonds.

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I. INTRODUCTION

The hydrogen bond is a molecular association important in many chemical and biological systems. For example, the fact that water is a liquid at room temperature and not a gas is a well known result of hydrogen bonding. Many biological molecules, including DNA, rely heavily on hydrogen bonding for their all-important spatial orientation.[1] According to Pimentel and McClellan[2], "a hydrogen bond exists between a functional group A-H and an atom or group of atoms B in the same or different molecule when a) there is evidence of bond formation (association or chelation), and b) there is evidence that this new bond linking A-H and B specifically involves the hydrogen atom already bonded to A". Hydrogen bonds are generally intermediate in "strength" between "chemical" bonds and van der Waals interactions, having bond enthalpies generally in the range from 1 to 10 kcal/mole. Hydrogen (H) bonds occur often in compounds containing electronegative atoms or areas of high electron density. Evidence for these bonds is usually manifest by molecular aggregation, causing changes in physical properties such as melting point, boiling point, viscosity, and apparent molecular weight. For example, it is well known that intermolecular hydrogen bonding in aliphatic alcohols causes them to have much higher boiling points than their corresponding aliphatic hydrocarbon analogs.

A comprehensive and clear discussion of H bonding is given by Pimentel and McClellan[2]; more recent works[3,4] serve to update the field.

Hydrogen bonding has been studied by numerous different methods; one of the most useful and widely accepted is vibrational spectroscopy, chiefly infrared but also Raman to some extent[5].

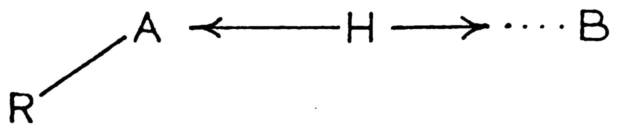
Figure 1 illustrates the vibrational modes of interest in the region of the H bond. Consider a molecule, RAH, hydrogen bonded to another molecule, B, through the H•••B bond. The most widely studied vibration is ν_s, the stretching mode of the A-H bond. The effect upon the frequency, intensity, and shape of the A-H stretching band when hydrogen bonding is introduced, A-H•••B, is measured. The ν_b bend and ν_t torsional modes are studied in a similar manner. Changes in the spectra of these vibrations upon the introduction of H bonding are indirectly correlated with the enthalpy of the hydrogen bond. The major portion of the present

Figure 1. Vibrational Spectroscopy of Hydrogen Bonded Systems

A——H Covalent Bond

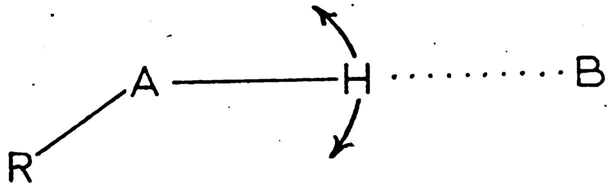
H···B Hydrogen Bond

ν_s



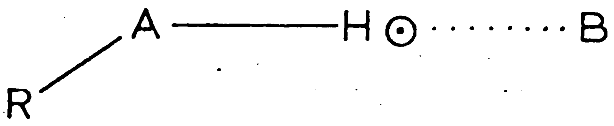
A—H stretch
(3500 – 2500 cm^{-1})

ν_b



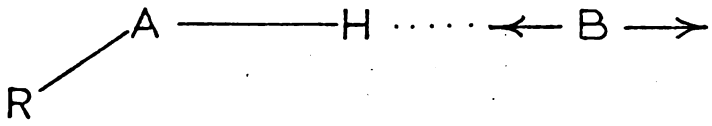
R—A—H bend (in-plane)
(1700–1000 cm^{-1})

ν_t



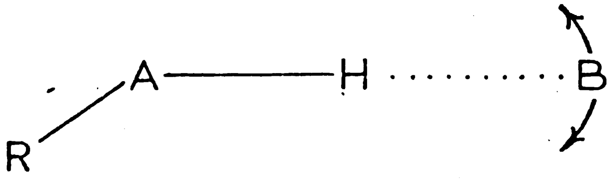
R—A—H torsion (out-of-plane)
(900– 300 cm^{-1})

ν_σ



A—H--B stretch
(250–50 cm^{-1})

ν_β



A—H--B bend
(below 50 cm^{-1})

literature deals with shifts in infrared absorptions (usually the ν_s mode) for compounds in which A above is an oxygen atom, i.e., alcohols[6], phenols[7], silanols[8], carbonyls[9], etc. Some work has also been reported for halogens[10], nitrogen[11] and sulfur[12] compounds. However, it should be noted that studies of the bonded A-H vibrational modes do not give direct information about the adjacent H···B bond.

The hydrogen bond vibrations ν_σ and ν_β are found in the infrared region below 250 cm^{-1}. This is a relatively inaccessible region of the electromagnetic spectrum, and instrumental limitations precluded extensive investigation of the stretch and bend of the H···B bond until the early 1960's. With the advent and development of Fourier transform far infrared spectrometers, investigation of hydrogen bonding, specifically via ν_σ has grown slowly.

Important contributions to the study of H bonding by infrared spectroscopy have been made by a number of researchers. Lake and Thompson[13] studied spectra of neat aliphatic alcohols between 50 and 400 cm^{-1}, using an interferometric spectrometer, and assigned bands due to the OH···O hydrogen bond stretch as well as the torsional modes of the monomers. Jakobsen et al.[14] have studied H bonding in carboxylic acids and alcohols in solid and liquid phases. Lattice vibrations are prominent in the far infrared spectra of the solids; nevertheless, these authors were able to assign the hydrogen bond stretching and twisting vibrations as well as the C-C torsion frequencies. Ginn and Wood[15] and Hall and Wood[16] studied the far infrared spectra of hydrogen bonded complexes of phenol with amines. Changes in ν_σ, the intermolecular hydrogen bond stretching frequency of the phenol-amine complex, were correlated with the strength of the H-bonded association. The more polar the environment, the greater the increase in ν_σ. The work of Hurley, et al.[17] concerning the hydrogen bond stretching frequencies of chlorophenols and anisoles established firm criteria for assigning absorptions due to intermolecular hydrogen bonding; the present work is an extension of that initiated by Hurley.

The general objective of this study was to utilize improved and advanced instrumental methods for the direct investigation of the vibrations of the hydrogen bond, and to evaluate the long term utility of far infrared spectroscopy as a H bond diagnostic technique. In addition, we hoped to obtain answers to certain questions specifically concerning the halophenols studied by Hurley.[18]

Hurley established three criteria for the assignment of hydrogen bonding ν_σ bonds in the far infrared. (The region is by no means devoid of other bands.)

1. The bands associated with hydrogen bond vibrations should be absent when a group incapable of hydrogen bonding is substituted for the hydrogen atom.
2. Hydrogen bond absorptions should be extremely weak in the Raman spectrum (due to a small polarizability change expected from a region of low electron density).
3. The far infrared absorptions due to hydrogen bonding should be broad and asymmetric (due to contributions of polymers with varying degree of association and due to transitions in upper vibrational states).

The above three criteria employed together serve to identify the bands due to hydrogen bonds with considerable certainty.

A fourth criterion which is often used to identify the presence of intermolecular bonding or other interactions is the behavior of the system upon dilution in a solvent. The intensity and shape of corresponding vibrational bands (either infrared absorption or Raman scattering) will change in relation to the proximity of solute molecules to one another. This criterion has not been used in far infrared studies, because the bands due to H bonding are weak to begin with, and previous instrumentation has not been sufficiently sensitive to monitor low concentrations. However, instrumental improvements have enabled the author to employ this technique in the investigation of the far infrared spectra of the halophenols in solution. Essentially, this investigation has extended the work of Hurley et al.;[17] the fourth criterion of dilution has been used to confirm band assignments and to obtain more meaningful frequencies, and from them somewhat more accurate information pertaining to hydrogen bond enthalpies. The simplified model proposed by Hurley to interpret the ν_σ absorptions of the monohalophenols, based on assumptions of fairly rigid molecules and decoupled motions, cannot adequately explain the more reliable experimental frequencies obtained in this work.

II. EXPERIMENTAL SECTION

Far infrared spectra in the 50 to 250 cm^{-1} region were obtained for phenol and the monohalophenols. Two different Fourier transform spectrometers were used in the course of this study and compared in terms of the quality of spectra obtained; the instrument producing more consistent spectra was chosen for all subsequent work.

Spectra were first obtained on a Block Industries Digilab FTS-16 far infrared interferometer, equipped with an on-line computer and x-y plotter. The instrument is capable of performing many fast scans to obtain sample and background interferograms, performing the Fourier transforms, ratioing sample against background spectra, and plotting the ratioed spectrum, all in a relatively short time. The instrument takes approximately 40 minutes to make 1000 scans each of sample and background with approximately 4 wavenumber resolution, compute the transforms, and plot the ratioed spectrum. The advantage of convenience was outweighed, however, by certain factors which led to unsatisfactory spectra.

a. The sensitivity of the triglycine sulfate detector in the 50-150 cm^{-1} range is fairly low, causing interference from background noise.

b. Total available light from the mercury vapor lamp is limited by the size of optics used.

c. The experimental set-up made removal of all traces of water vapor from the optical path difficult. (Many sharp bands exist in the region of interest due to the rotational spectrum of H_2O.)

More satisfactory spectra were obtained on a Beckman R.I.I.C. Model FS-720 Michelson interferometer. This instrument is equipped with a diamond window Golay detector and a high intensity mercury vapor light source. Mirror travel is controlled by a stepping motor and micrometer screw. Data are taken at precise intervals along each interferogram; each point is digitized and punched onto paper tape, and the information later punched on to computer cards. A CDC 6500 computer then performs a cosine transform of the interferogram and plots a spectrum. Sample data can be averaged and/or ratioed against background data to produce an effective double-beam spectrum.

Spectra obtained from the R.I.I.C. instrument were superior to those from the Digilab spectrometer, chiefly because of a better signal-to-noise ratio in the 50 to 150 cm^{-1} range. The more intense light source, larger optics, and more sensitive detector all contributed to the better spectra from the R.I.I.C. instrument. In addition, the entire interferometer, except for the sample compartment, was kept evacuated to eliminate water vapor bands. The sample compartment, in which experimental cells could be easily interchanged, was purged with dry nitrogen.

All spectra on both instruments were obtained using 12 micron Mylar beam splitters which have an efficiency peak at approximately 125 cm^{-1}.

Spectra of neat liquid halophenols were recorded using samples contained in polyethylene cells of 0.2 mm path length. Background spectra were taken of the empty polyethylene cells.

Spectra of phenol and halophenols in cyclohexane, carbon tetrachloride, and benzene solvents were recorded using an R.I.I.C. variable path length cell with high density polyethylene windows of approximately one inch diameter and approximately one mm thickness. Path lengths were varied according to the concentration of halophenol in the solvent in an attempt to keep the total number of solute molecules in the light path constant, regardless of concentration. Path lengths varied from 0.2 mm to 2 cm. Background spectra were recorded of the solvents alone in the same cell, using a path length appropriate for ratioing against sample spectra.

Water vapor was used to check the calibration of the instrument. Frequencies obtained were accurate to better than ±1 cm^{-1}. Resolution was chosen for most spectra at 4 cm^{-1} by limiting travel of the movable mirror.

Fluoro- and bromophenols and p-iodophenols were obtained from Aldrich Chemical Company; o-chlorophenol, o-iodophenol, and m-iodophenol were from Eastman Organic Chemicals; m- and p-chlorophenols, as well as phenol, were purchased from Matheson, Coleman and Bell. All solvents used were of spectral quality. All were obtained from Matheson, Coleman and Bell, except for cyclohexane which was obtained from J. T. Baker Chemicals.

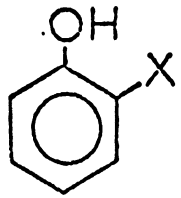
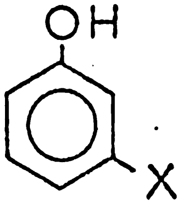
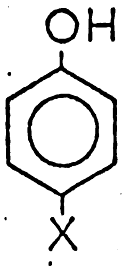
III. PREVIOUS RESEARCH

Hurley[18] investigated the spectra of the monohalophenols in the 50 to 250 cm^{-1} far infrared region. Using the three criteria mentioned earlier to assign the bands observed, he found, for each compound, one absorption due to intermolecular hydrogen bonding. Other bands in the spectrum could be attributed to so-called "X-sensitive" vibrations[19] which arise from normal modes involving the halogen atom, which alter the symmetry of the benzene ring and give rise to appreciable skeletal motion. Hurley's values attributed to the intermolecular hydrogen bond stretch, ν_σ, are shown in Table 1.

As noted in the table, Hurley's spectra were obtained under varying experimental conditions, depending upon the melting point of the sample. Spectra of those isomers which are liquids at room temperature were obtained from neat samples at ambient temperature. Isomers with melting points between 30 and 50 C were heated to obtain spectra of the melted samples. Those isomers melting above 50 C were dispersed in Nujol mulls and spectra taken.

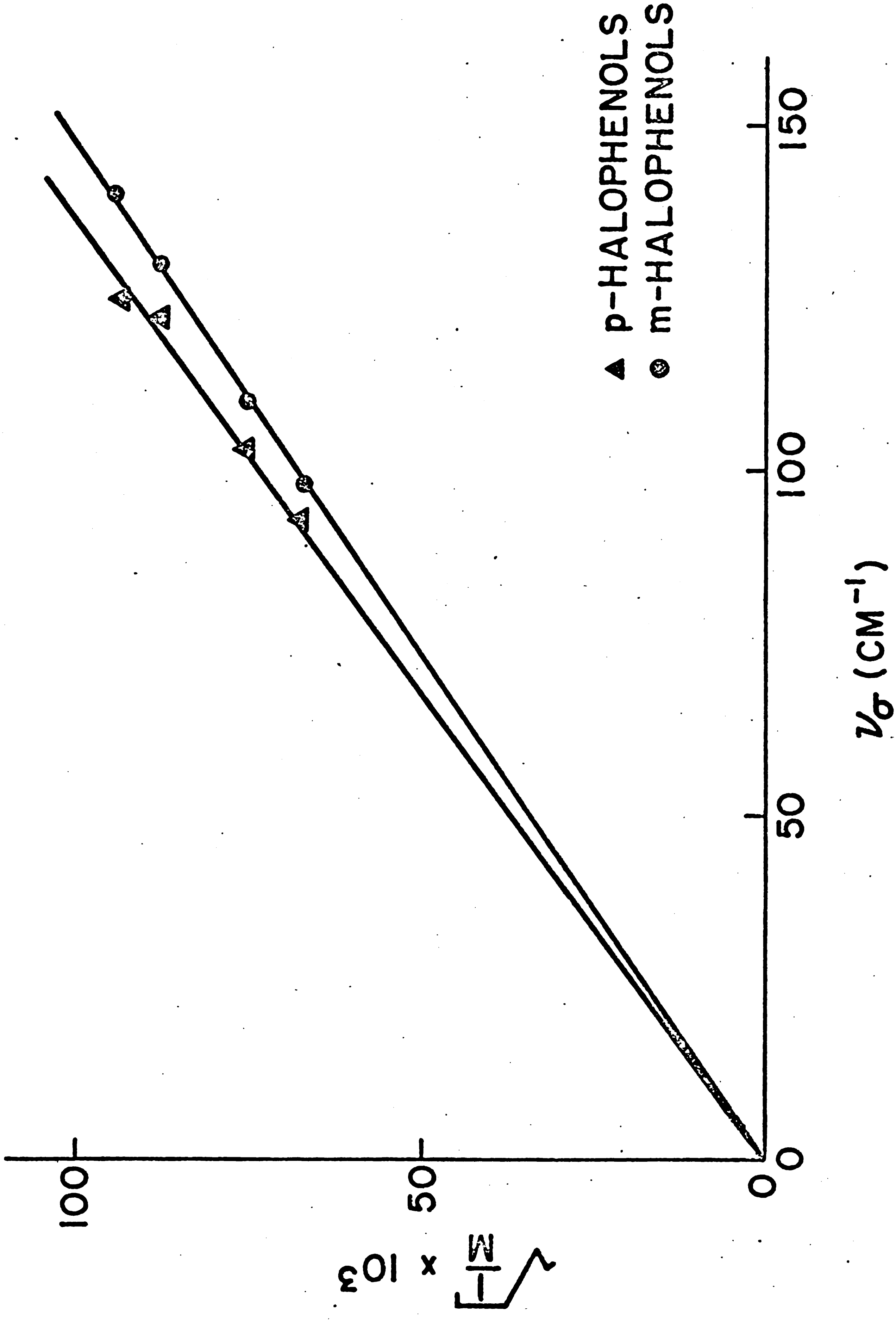
On the basis of his observed hydrogen bond stretching frequencies for the meta and para halophenols, Hurley[18] suggested a simplified model for calculating the force

Hydrogen Bond Stretching Frequencies

cm^{-1}	 ortho	 meta	 para
X = F fluorophenol	120 liquid	140 liquid	125 melt
X = Cl chlorophenol	84 liquid	130 melt	122 melt
X = Br bromophenol	85 liquid	110 melt	103 mull
X = I iodophenol	83 melt	96 mull	93 mull

constant of the hydrogen bond. He utilized a simple harmonic oscillator approximation with the assumption that since the frequency of the H-bond stretch was so much lower than all other vibrational motions of the molecule, these motions could be considered decoupled. With the additional assumption that the molecules were sufficiently rigid that the entire mass participated as a unit in the H-bond stretch, he could treat the ν_σ vibration as a stretching motion of a homonuclear diatomic molecule. Thus the equation $\nu = \frac{1}{2\pi}\sqrt{\frac{2k}{m}}$ was tested by a plot of ν versus $\sqrt{\frac{1}{m}}$ for the meta and para phenols. Here m is taken as the molecules weight, the monomeric species. Figure 2 shows that straight lines were obtained which passed through the origin. Force constants of 6.5 x 10^4 and 5.6 x 10^4 dynes/cm were calculated for the meta and para systems, respectively, from the slopes in the plot. The force constants obtained were not considered accurate, however, because of the numerous assumptions made in application of such a simplified model. The uncertainty of Hurley's results and the desire to repeat them under more uniform conditions led to the present study.

Figure 2. Plot of ν_{σ} (cm^{-1}) vs.
$\sqrt{\frac{1}{\mu}}$ for Meta- and Para- halophenols
(From Ref. 18)


▲ p-HALOPHENOLS
● m-HALOPHENOLS
$\sqrt{\frac{1}{M}} \times 10^3$
0
50
100
ν_σ (CM^{-1})
0
50
100
150

IV. RESULTS AND DISCUSSION

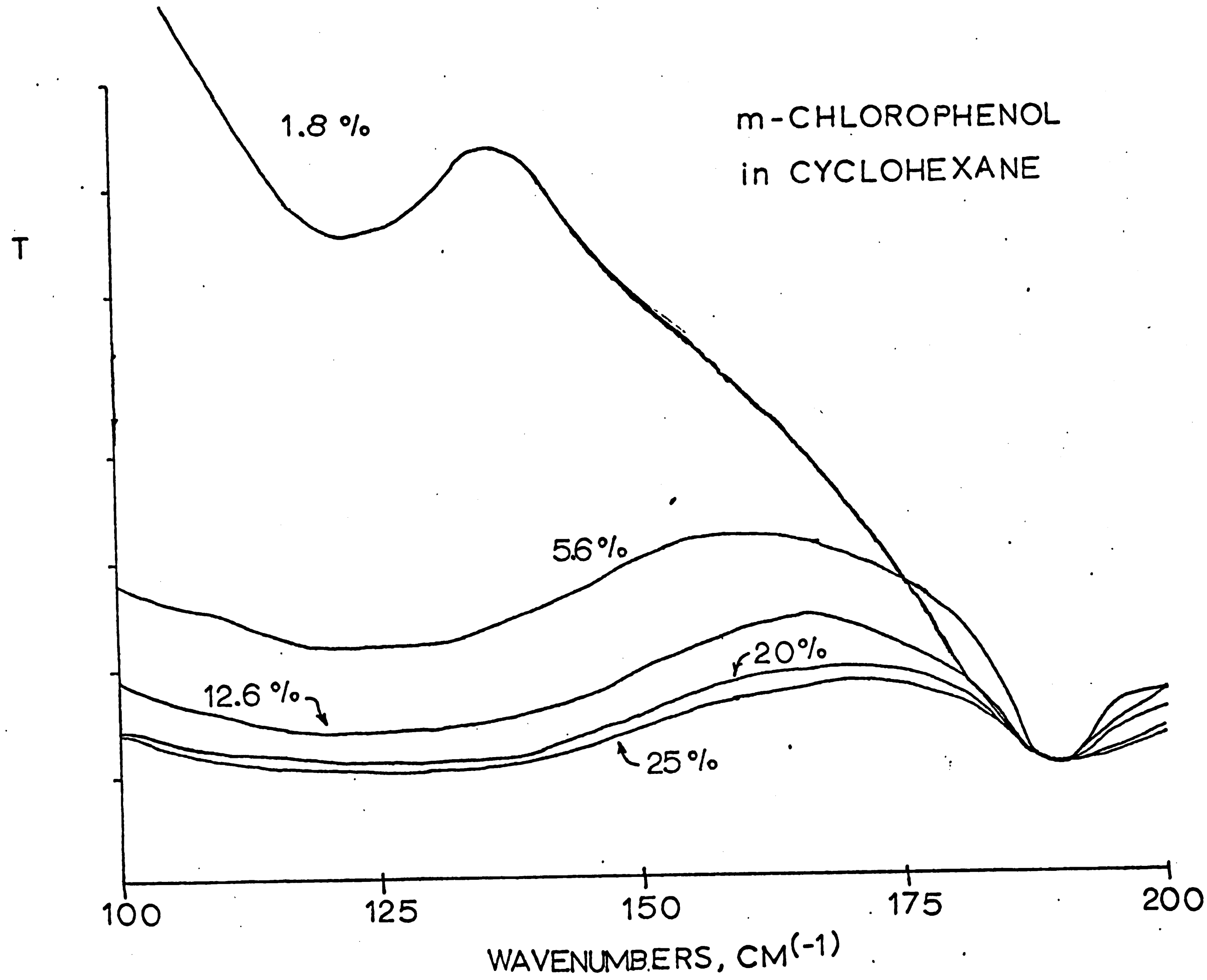
The far infrared spectra of the twelve mono-halophenols were recorded at varying concentrations in cyclohexane in order to subject all isomers to similar experimental conditions. Recent investigations have shown that cyclohexane is a good solvent to employ in studies involving hydrogen bonding.[22] It interacts with solutes of interest significantly less than benzene or carbon tetrachloride, and is conveniently transparent in the 50 to 250 cm^{-1} range. Sample cell thicknesses of up to 2 cm could be used without substantial loss of signal through the solvent. Trial spectra run in benzene and carbon tetrachloride were less satisfactory than in cyclohexane in the two respects mentioned above.

New values for ν_σ were determined, all based on dilute solutions in cyclohexane. Band shapes were typically broad (half widths 10-20 cm^{-1}), but narrowed and shifted slightly upon successive dilution, although the path length of the experimental cell was increased to maintain a nearly constant total amount of sample. Presumably, the decrease in concentration of higher polymeric species in dilute solution, leaving hydrogen bonded dimers chiefly present, contributed to this slight band narrowing. It should be noted, however, that the absorptions observed were still relatively broad, with half widths over 10 cm^{-1} in most cases.

The effect of dilution was also used as a criterion for confirming the existence of hydrogen bonds in the halophenols and substantiating Hurley's assignments. Those absorptions attributed to intermolecular H-bonds became less intense upon dilution, while bands attributed to internal motions (X-sensitive vibrations) remained strong. As mentioned above, the transparency of cyclohexane in the region of interest permits the long path lengths required to maintain the approximately constant total amount of solute under conditions of increasing dilution.

Figure 3 demonstrates the effect of dilution on the far infrared spectrum of meta-chlorophenol in cyclohexane. The band at 190 cm^{-1} is a chlorine-sensitive vibration; the broad band in the 125 cm^{-1} region is due to intermolecular H-bonding. The intensity of the X-sensitive band varied slightly among the experiments; the figure has been drawn by normalizing its peak absorbance. The extremely broad band at 25 mole percent narrowed with successive dilution to a band attributed chiefly to hydrogen bonded dimers at 1.8 mole %. The absorption maximum was easier to assign (123 cm^{-1}) because of this narrowing, even though the band was quite weak. The other halophenols were treated in the same manner; assignment of ν_σ for each compound was made

Figure 3. Far-Infrared Spectra of m-Chlorophenol at Various Concentrations in Cyclohexane (Mole Percents). Curves plotted normalized to absorption near 190 cm^{-1} (Transmittance in arbitrary units)


m-CHLOROPHENOL
in CYCLOHEXANE
T
1.8 %
5.6 %
12.6 %
20 %
25 %
100
125
150
175
200
WAVENUMBERS, CM(-1)

from the spectrum of the most dilute sample which yielded an easily detected absorption.

Table 2 shows the ν_σ values compiled in this study. As a result of more consistent techniques, these values must be considered more reliable than the frequencies reported by Hurley.[18]

If the ν_σ values for all twelve halophenols are now compared, some of the trends noted by Hurley and discussed in section III are still present.

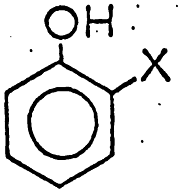
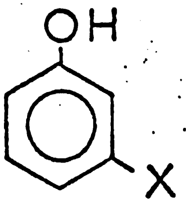
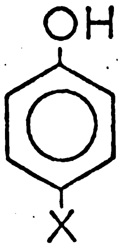
A. Meta- and Para-Halophenols

Hurley found for the meta- and para-halophenols a decrease in hydrogen bond stretching frequency accompanying the increase in molecular weight as heavier halogen atoms were substituted. This trend was explained in simple terms by an increase in the effective mass with appropriate normal coordinate involving the hydrogen bond stretch, thus "slowing" the vibration. Hurley's harmonic oscillator model was based upon this trend. The new data presented in Table 2 show a similar progression of high to low ν_σ values with increasing molecular mass, but the trend is now much less pronounced.

Also, it may be noted from Table 2 that for each halogen, the ν_σ frequency for the meta-isomer is higher than that for the corresponding para-halophenol. Such an effect is in agreement with the well-known differences in electronic structure between meta and para positions on a

Table 2. Hydrogen Bond Stretching Frequencies ν_σ for Dilute Solutions of the Monohalophenols in Cyclohexane

Hydrogen Bond Stretching Frequencies

cm^{-1}	 ortho	 meta	 para
X = F fluorophenol	105	125	112
X = Cl chlorophenol	80	123	113
X = Br bromophenol	(80) very weak	120	104
X = I iodophenol	75	114	101

phenol molecule.[21] One means of illustrating the differences between electronic environments in the meta and para positions is by discussing the acidity constants K_a for these isomers in water, which are listed in Table 3. One should note that the meta-substituted halophenols are significantly stronger acids than the corresponding para isomers. Greater acid strength indicates that a hydrogen can be abstracted more easily due to a lower electron density available at the oxygen atom. Thus, the electron withdrawing effect of the halogen is enhanced by inductive effects when it is at the meta position on the ring.[21] One would expect a phenol with a more protonic hydrogen to have a stronger electrostatic interaction with a given base, leading to a higher stretching frequency ν_σ. Thus, we see a correlation between greater acid strength and higher ν_σ for each metahalophenol when compared with its corresponding parahalophenol.

B. Orthohalophenols

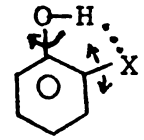
The frequency observed for the hydrogen bond stretch of orthofluorophenol seems in keeping with the trends noted and discussed in part A above. However, the remaining three orthohalophenols appear to have anomalously low ν_σ values. The reason suggested is that some <u>intra</u>molecular hydrogen bonding may be involved in ortho chloro, bromo, and iodophenol, with a concomitant decrease in the strength of the <u>inter</u>-molecular H-bond.

Table 3

Acidity Constants K_a for Halophenols in Water[20]

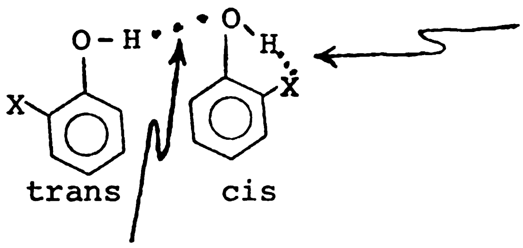
	F	Cl	Br	I
Meta	5.2×10^{-10}	16×10^{-10}	14×10^{-10}	13×10^{-10}
Para	1.1×10^{-10}	6.3×10^{-10}	5.6×10^{-10}	6.3×10^{-10}

The absorptions ν_σ which are observed in this work are necessarily the result of an intermolecular association. The presence of an intramolecular hydrogen bond would manifest itself in these systems primarily as a perturbation in the torsional vibration of the O-H group and as a change in the C-X wagging motion [see sketch below], since no additional vibrational degrees of freedom become available for a new far infrared absorption when an intramolecular hydrogen bond is formed. Such perturbations are found at higher frequencies than the spectral region under study, and were thus not observed in this work. Carlson and co-workers[22] have extensively studied the OH torsion in orthohalophenols. They have observed absorptions in the 300 to 400 cm^{-1} region and assigned them to ν_τ for OH. From a comparison of the observed frequencies with one another, and with torsional frequencies in non-hydrogen bonding situations, they have concluded[23] that in cyclohexane solutions the intramolecular hydrogen bond strength decreases in the order Cl > Br > I > F, with orthofluorophenol having almost <u>no</u> intramolecular interaction at all. The smaller size of the fluorine atom leads to a rather longer H•••X distance in <u>cis</u> orthofluorophenol than in the other <u>cis</u> H-bonding. Rather, in orthofluorophenol



the authors suggest a strong intermolecular dimerization of the trans-compound, which is not competing with cis isomers. Such a conclusion is in agreement with the ν_σ values observed in this work, and reported in Table 2.

The low hydrogen bond stretching frequencies observed for the intermolecular association in ortho- chloro, bromo, and iodophenol can thus be explained by the suggestion that electron density is shifted away from the oxygen atom, resulting in a weaker intermolecular bond, as depicted below.



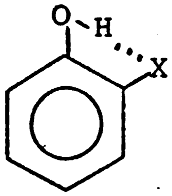
intramolecular H-bond draws electron density from the oxygen, leaving a lower base strength for the intermolecular H-bond with a second molecule.

intermolecular H-bond

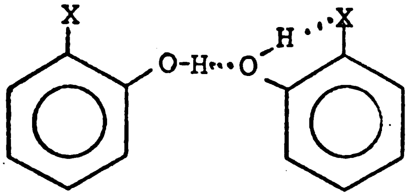
Allan and Reeves,[24] and Fateley[23] have discussed the occurrence of this type of cis-trans dimer at low concentrations in inert solvents. They have found that the cis isomer (intramolecularly H-bonded) is in greater abundance than the trans isomer in all orthohalophenols except orthofluorophenol. As noted above, our data agree with this conclusion. In addition, we find the ν_σ absorptions at equivalent concentrations to be substantially less intense for ortho- chloro, bromo, and iodophenol than the ν_σ bonds for orthofluorophenol and the halophenols substituted in the meta or para ring positions. These observations all suggest that the most abundant species for the heavier orthohalophenols at low concentrations in the cis isomer, with its intramolecular H-bond and the resultant absence of ν_σ in the far IR. The weak intermolecular H-bond absorption observed near 80 cm^{-1} for the Cl, Br, and I isomers is most likely due to interactions like (b) in Figure 4. Trans-trans interactions (c) are expected to be energetically less stable than (b), but trans-trans interactions might be an explanation for the extreme broadness of the ν_σ band for these isomers. In the case of orthofluorophenol, however, (c) is the expected H-bonded species at low concentrations, nearly to the exclusion of interactions of types (a) and (b).

Figure 4. Conformational Isomers of Orthohalophenols

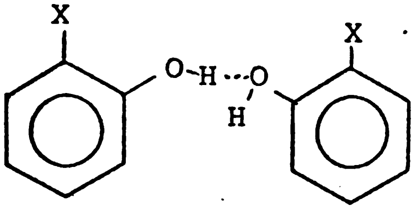
a. *cis*
b. *trans*-*cis*
c. *trans*-*trans*



a. cis



b. trans-cis

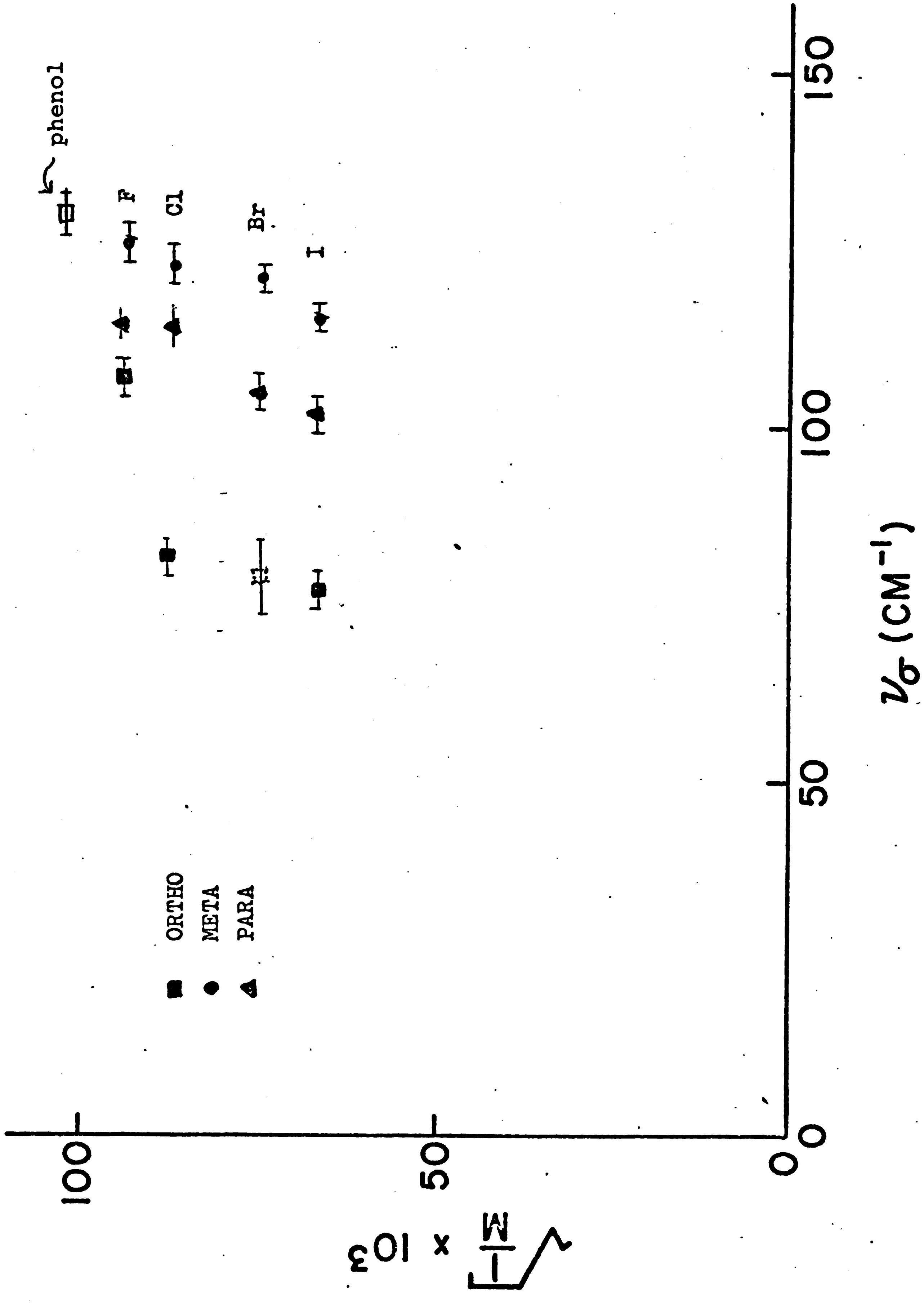


c. trans-trans

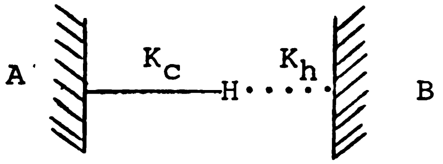
V. INTERPRETATION

A comparison of the ν_σ values reported by Hurley in Table 1 with the results of this work in Table 2 will show that the trends which have been discussed are present in both cases; however, certain differences appear. In general, absorptions observed in dilute solutions in this investigation are found at lower frequencies than those in the corresponding neat liquid spectra studied by Hurley. On the other hand, our dilute solution ν_σ values are generally higher than the absorptions observed by Hurley for mulls. As a result of the consistent conditions used in the present experiments, it may be suggested that Hurley's spectra should not be correlated in the manner shown in Figure 2. Absorptions such as ν_σ arising from intermolecular interactions are usually quite sensitive to phase and environment. To propose a model on the basis of a linear relationship derived from liquids, melts, and mulls may be an unwarranted presumption. It is our contention that the simple harmonic oscillator model suggested by Hurley is not adequate. Figure 5 is a plot of ν_σ versus $\sqrt{\frac{1}{m}}$ using the new data. Clearly, for none of the isomers

Figure 5. Plot of ν_J (cm^{-1}) vs. $\sqrt{\frac{1}{\eta}}$ for Halophenols in Cyclohexane


phenol
F
Cl
Br
I
■ ORTHO
● META
▲ PARA
$\sqrt{\frac{1}{M}} \times 10^3$
100
50
0
0
50
100
150
ν_σ (CM^{-1})

are the points fit by a straight line through the origin. The observation that the ν_σ values for each isomeric series now seem to fit straight lines which intercept the ν_σ axis between 60 and 90 cm^{-1}, leads to a new interpretation of the results. Hurley's simple harmonic oscillator model predicted a hydrogen bonded stretching frequency ν_σ of zero when the masses of the molecules approached infinity. This is not realistic, however, as some vibration would be observed for a hydrogen bonded to two infinitely heavy masses; the force constant K_c for the covalently bonded system A-H would have to be infinite compared with the force constant K_h for the hydrogen bonded H···B system in order for no motion to occur. In fact, a model which approximates reality should



take more of the bonds near the hydrogen into account, and, ideally, full normal coordinate analyses should be made.

The observations that the H-bond ν_σ values for the meta- and para-halophenols do not differ widely and that they can be related according to the mass of the molecule, bear on a question that has been raised; namely, is the intermolecular H-bond absorption due to O-H···O or O-H···X (X = halogen) hydrogen bonding? Most discussions in the literature assume that O-H···O bonding is involved,[26] but some (Ref. 3, p. 135) claim O-H···X bonding. Since intermolecular hydrogen bonding directly involving the halogen atom would necessarily involve electronegativity and size effects, the data presented here give better evidence for O-H···O bonding as the primary interaction. The fact that the ν_σ values for meta- and para- halophenols can be related nearly linearly with $\sqrt{\frac{1}{m}}$ for the molecule suggests that for each isomeric series the halogen's effect on the hydrogen bond is chiefly due to mass. In addition, the ν_σ value for phenol in cyclohexane, 130 cm^{-1}, which <u>must</u> be O-H···O hydrogen bonded, is fairly closely related by $\sqrt{\frac{1}{m}}$ to the metahalophenols. Evidence for O-H···O hydrogen bonding in preference to O-H···X bonding is substantiated by Whetsel[25] in investigations of ν(O-H) frequency shifts in dilute solutions of phenol in the presence of various proton acceptors.

In order to assign approximate force constants for hydrogen bonds in O-H···O systems, the common model used is the simple harmonic oscillator, relating ν_σ to $\sqrt{\frac{k}{\mu}}$, where *k* is the force constant and μ is the reduced mass of the system. Lake and Thompson[13] studied a series of aliphatic alcohols, observing their far infrared spectra. On the basis of the harmonic oscillator approximation and the assumption that the reduced mass should be chosen as the O-H···O portion of the system only, Lake and Thompson obtained hydrogen bond ofrce constants in the range between 0.6×10^4 and 1.36×10^4 dyne/cm for ethanol through n-heptanol. These values seem somewhat low; if the mass of the entire molecule is taken when calculating the reduced mass, the harmonic oscillator equation yields force constants ranging 1.6×10^4 to 9.3×10^4 dynes/cm. These values are more similar to those of H-bond force constants found by other methods,[4] but vary a great deal within the series, and seem too high for the long chain alcohols. It would seem reasonable to assume that the effect on the H-bond of mass drops off with increasing distance from the bonding site. Realistic H-bond force constants would then be obtained (2 to 5×10^4 dyne/cm) if only the first few carbon atoms were taken into account for determining effective reduced mass.

For the substituted phenols studied in this project, Figure 5 would indicate that the reduced mass to be used if one wishes to retain the simple harmonic oscillator model, is approximately the entire molecular system. If the compact size of a benzene ring and its proximity to the O-H···O bonding is compared with the effect of the first three carbon atoms in a straight chain aliphatic system, it is reasonable to consider the entire molecule in an approximation of force constants.

It is suggested that further analysis should not be made of the force constants of the systems discussed here, until a full normal coordinate analysis is developed. Such an analysis is beyond the scope of this project, but is suggested as a further project.

Without being quantitative, we suggest from our data that the force constants for the meta- and para- halophenols are actually lower than the 6.5 x 10^4 and 5.6 x 10^4 dyne/cm values reported by Hurley. This is indicated by the change in slope seen in Figure 4 as compared with Figure 2. Without a more accurate model, however, we cannot make definite conclusions.

VI. CONCLUSIONS

By creating a consistent environment of cyclohexane, we have assigned new values for the intermolecular hydrogen bond stretching frequencies ν_σ for the monohalophenols. The decrease in ν_σ intensity with decreasing concentration of the halophenol in solvent is added confirmation of the intermolecular nature of the absorption.

Due to the low intensity and broadness of ν_σ bonds, precise models of the system and force constants of the bonding are difficult to justify. Since the relationship between force constants and molecular mass is not known with any certainty, only order of magnitude estimates can be made. It is suggested that further work in this area be aimed toward a full understanding of the molecular species involved in the bonding, including the development of a full normal coordinate analysis on the data which are now available.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. J. D. Watson, Double Helix; Signet, 1969.
2. G. C. Pimentel and A. L. McClellan, The Hydrogen Bond; Freeman, San Francisco, 1960.
3. S. N. Vinogradov and R. H. Linell, Hydrogen Bonding; Van Nostrand Reinhold, 1971.
4. G. C. Pimentel and A. L. McClellan, "Hydrogen Bonding", in Annual Review of Physical Chemistry 22, 347 (1971).
5. L. J. Bellamy and R. J. Pace, Spectrochimica Acta 27A, 705 (1971).
6. M. Asselin and C. Sandorfỳ, J. Mol. Structure 8, 145 (1971).
7. A. W. Baker, H. O. Kerlinger, and A. T. Shulgin, Spectrochimica Acta 20, 1477 (1964).
8. T. Kagiya, Y. Sumida, T. Watanabe, and T. Tachi, Bull. Chem. Soc. Japan 44, 923 (1971).
9. B. A. Zadorozhnyi and I. K. Ishchenko, Optics and Spectroscopy 19, 306 (1965) Eng. Trans.
10. A. W. Baker and A. T. Shulgin, Can. J. Chem. 43, 650 (1965).
11. P. Combelas, F. Creuge, J. Lascombe, C. Quivoron, and M. Rey-Lafon, J. Chim. Phys. Physicochem. Biol. 66, 668 (1969).
12. N. Mori, S. Kaido, K. Suzuki, M. Nakamura, and Y. Tsuzuki, Bull. Chem. Soc. Jap. 44, 1858 (1971).
13. R. F. Lake and H. W. Thompson, Proc. Roy. Soc. 291A, 469 (1966).
14. R. J. Jakobsen, Y. Mikawa, and J. W. Brasch, Spectrochimica Acta 25A, 839 (1969).
15. S. G. W. Ginn and J. L. Wood, Spectrochimica Acta 23A, 611 (1967).

Bibliography (cont.)

16. A. Hall and J. L. Wood, Spectrochimica Acta 24A, 1109 (1968).

17. W. J. Hurley, I. D. Kuntz, Jr., and G. E. Leroi, J. Am. Chem. Soc. 88, 3199 (1966).

18. W. J. Hurley, "Far-Infrared and Raman Studies of Hydrogen Bonding", Ph.D. Dissertation, Princeton University, (1967).

19. D. H. Whitten, J. Chem. Soc. 1350 (1956).

20. R. T. Morrison and R. N. Boyd, Organic Chemistry, 2nd Ed., Allyn and Bacon, 1966.

21. L. P. Hammett, Physical Organic Chemistry, 2nd Ed., p. 354, McGraw-Hill, 1970.

22. G. L. Carlson, W. G. Fateley, and F. F. Bentley, Spectrochimica Acta 28A, 177 (1972).

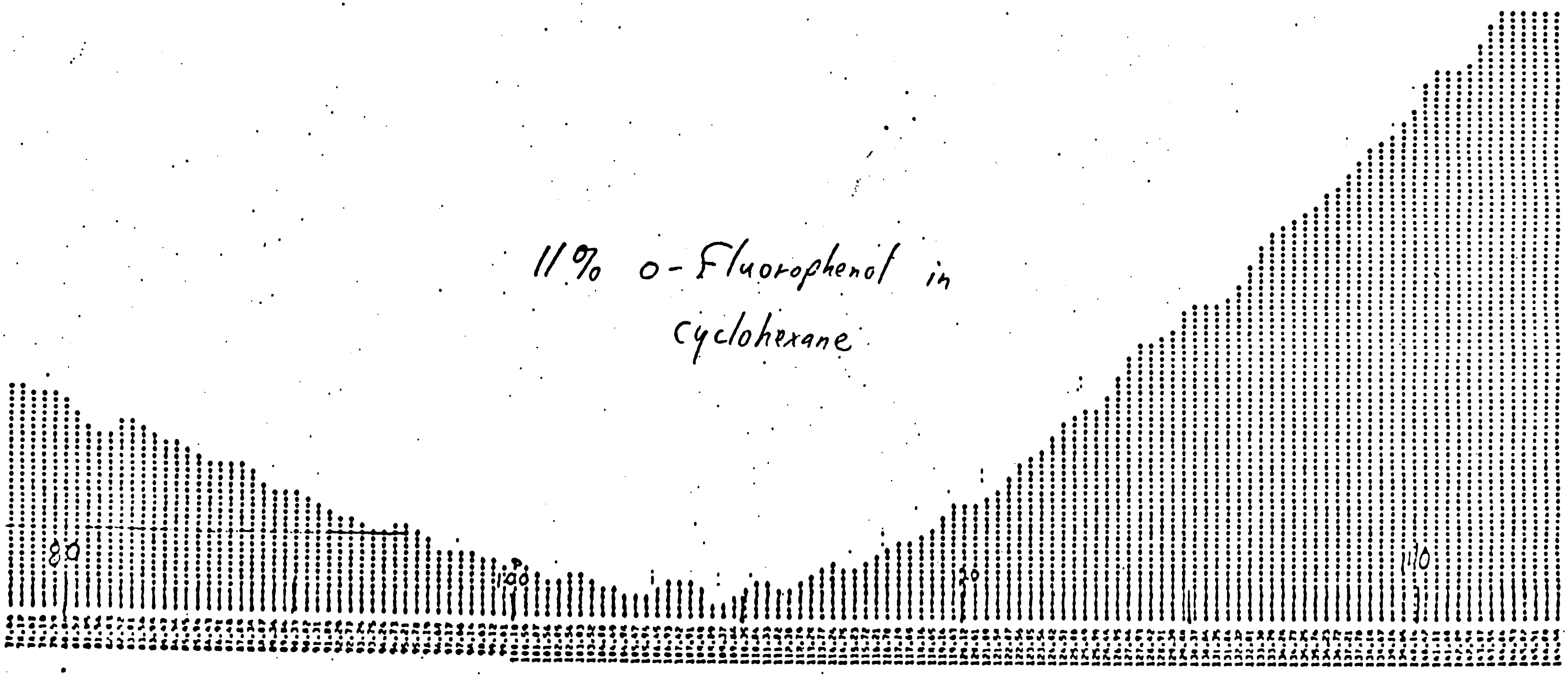
23. W. G. Fateley and G. L. Carlson, Paper No. 211, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland (1972).

24. E. A. Allan and L. W. Reeves, J. Phys. Chem. 67, 591 (1963).

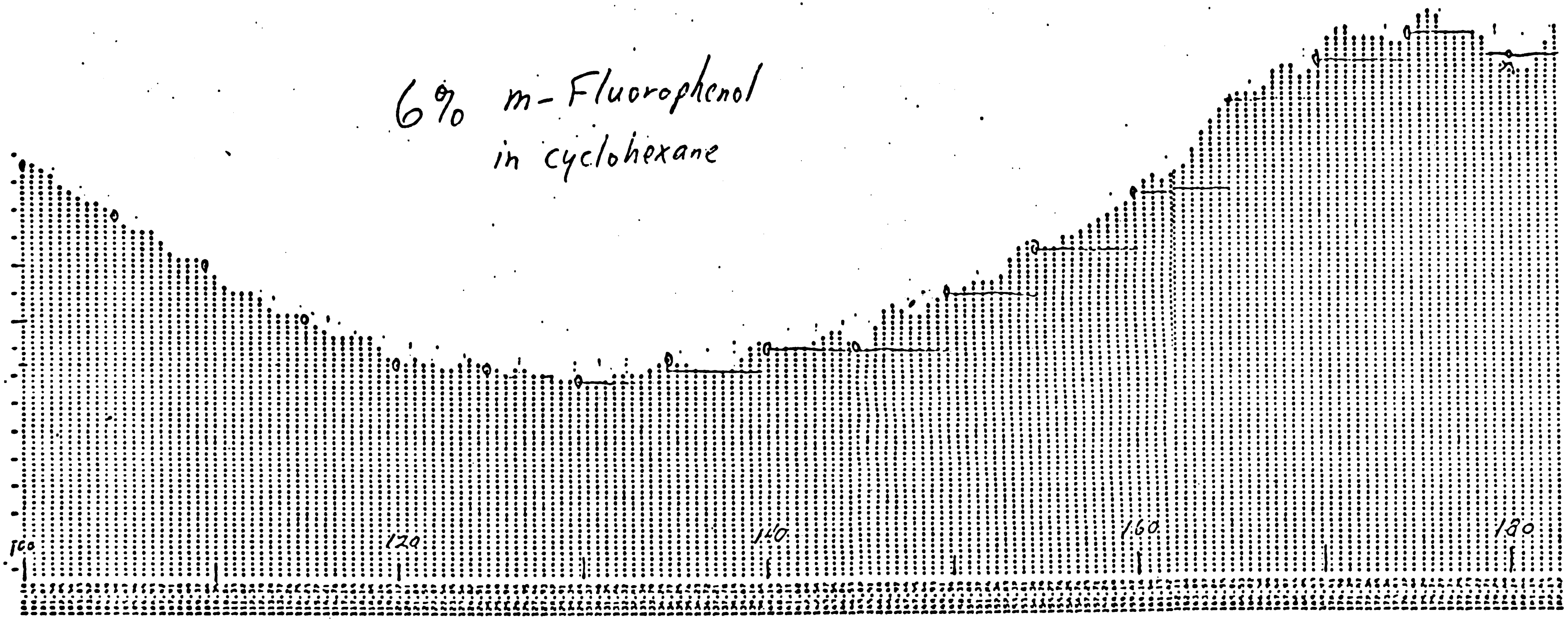
25. Kermit Whetsel, Private Communication to G. E. Leroi, April 20, 1972.

26. K. D. Möller and W. G. Rothschild, Far Infrared Spectroscopy, Ch. 6; Wiley, 1971.

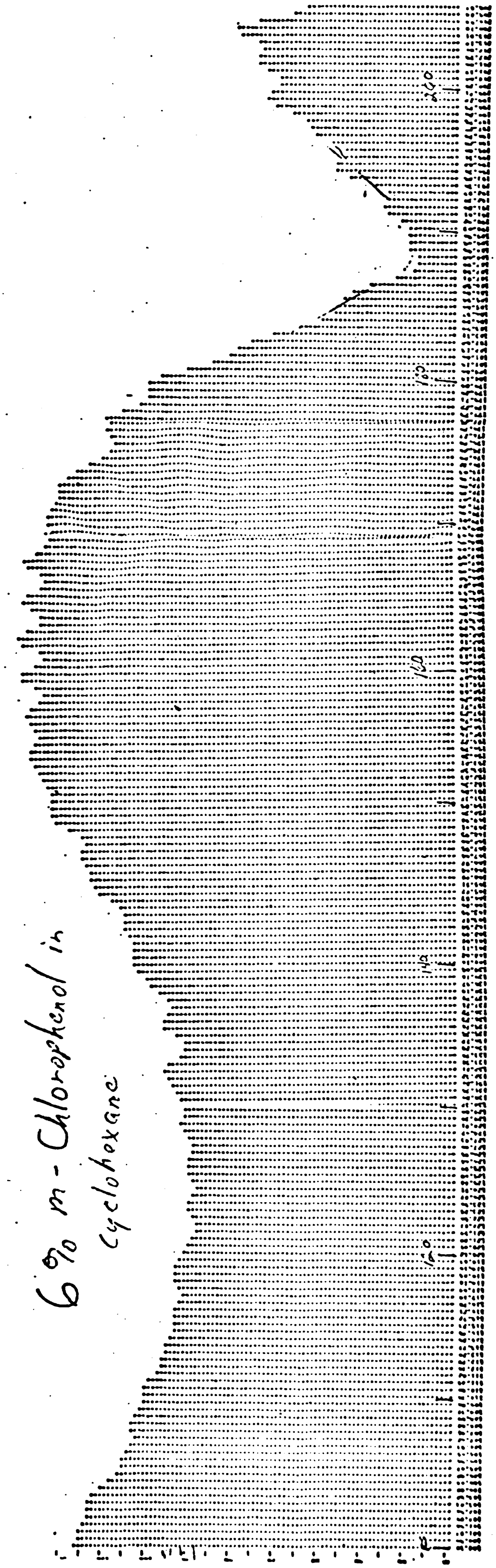
APPENDIX



11% o-Fluorophenol in cyclohexane

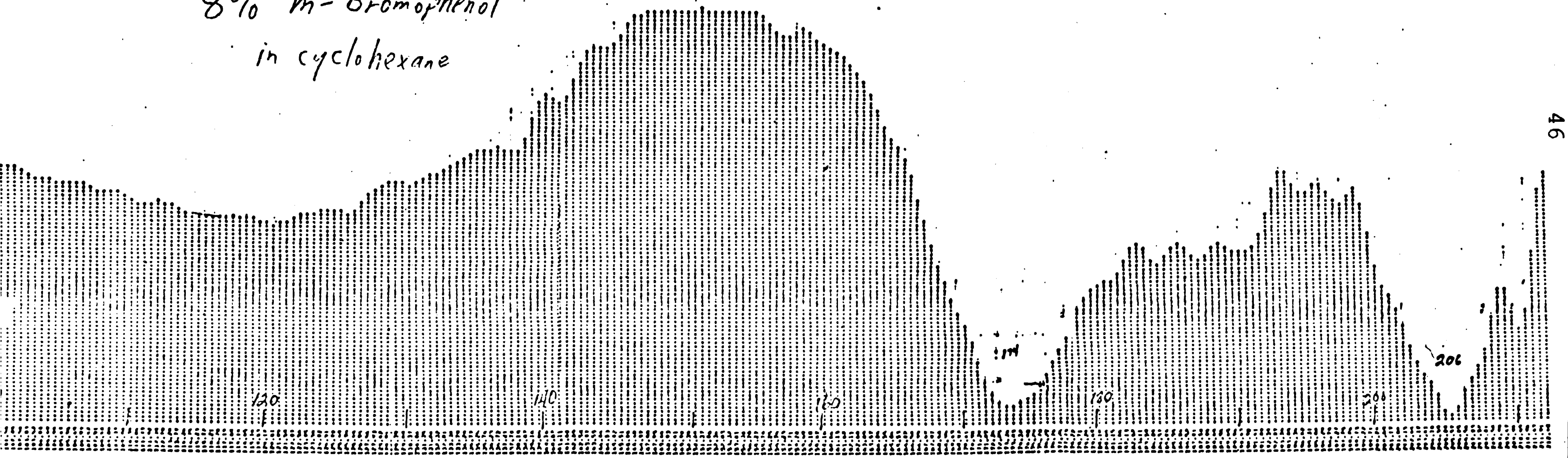


6% m-Fluorophenol
in cyclohexane

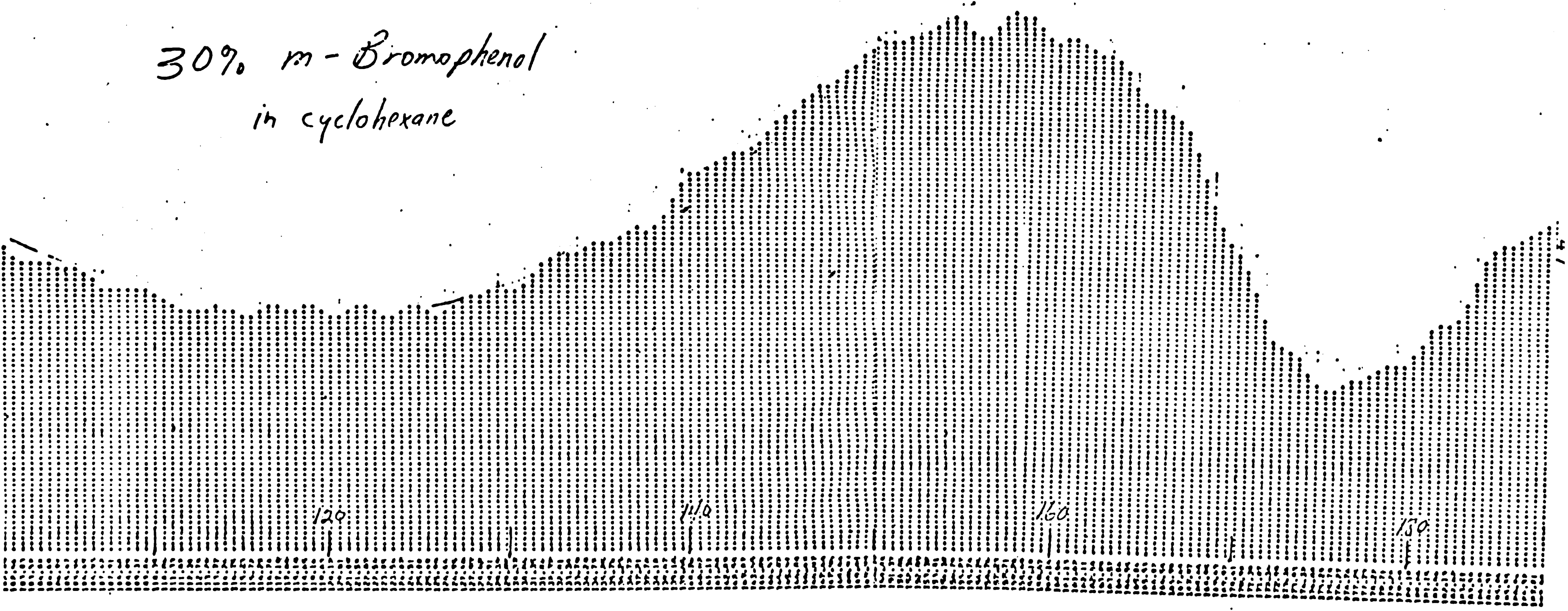


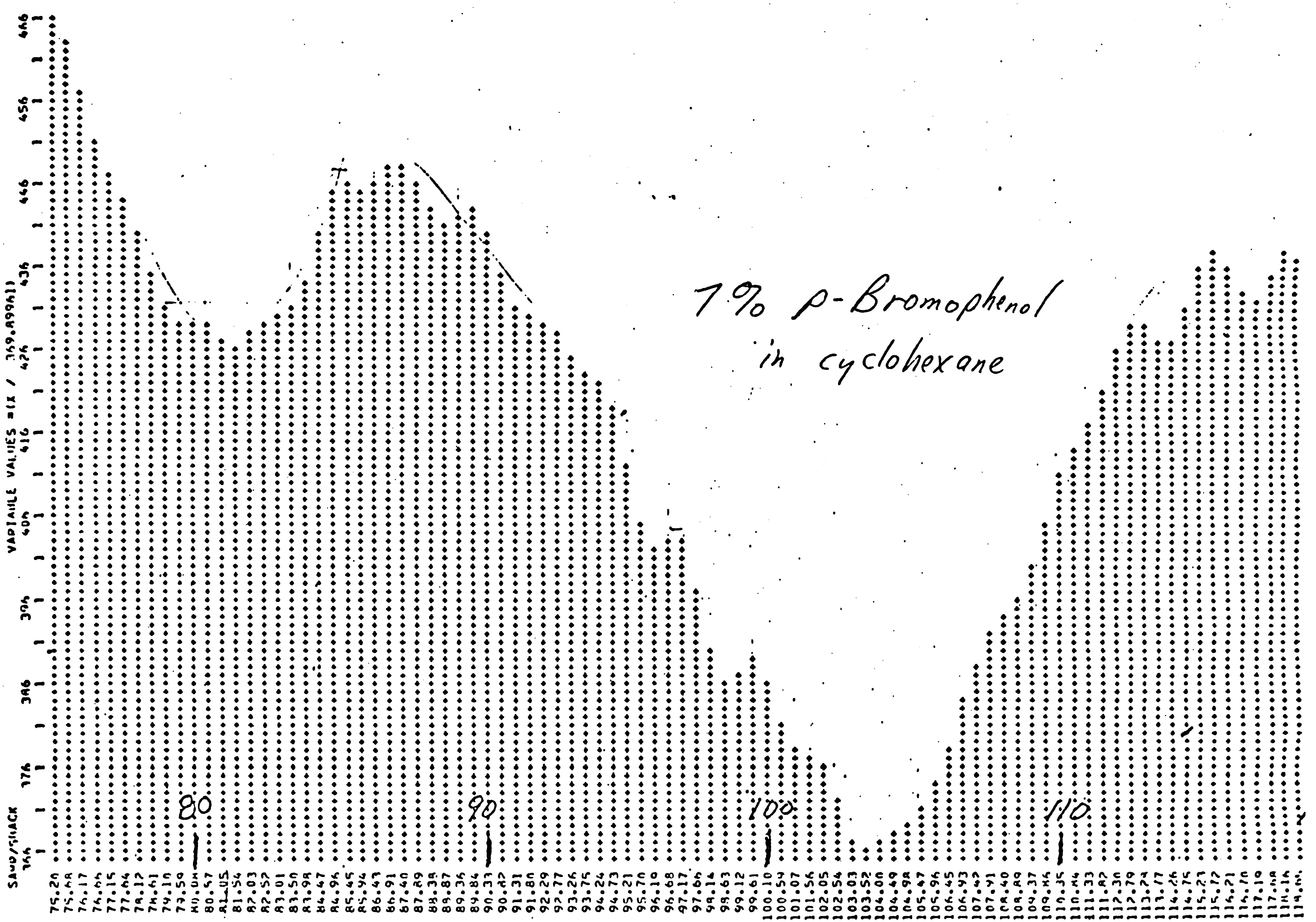
6% m-Chlorophenol in cyclohexane

8% m-Bromophenol
in cyclohexane



30% m-Bromophenol
in cyclohexane





7% p-Bromophenol
in cyclohexane

6% m-Iodophenol in cyclohexane