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Marvin Margoshes
Iowa State College

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INFRARED SPECTRA
OF SOME AROMATIC COMPOUNDS

by

Marvin Margoshes

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Head of Major Department

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Dean of Graduate College

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TABLE OF CONTENTS

ABSTRACT

A study was made of the effect of substituent groups on the infrared spectra of aromatic compounds. Particular attention was devoted to the out-of-plane vibrations which give rise to strong absorption bands between 650 and 900 cm^{-1} with frequencies characteristic of the number and position of substituent groups. Most substituent groups were found to affect the spectra in a manner dependent upon the mass of the atom attached to the ring, but nitro and carboxyl groups and salts and esters of carboxyl groups had the effect of abnormally light groups. In addition, these same groups sometimes caused a new absorption band to appear in this region. Possible reasons for the effect of these groups are discussed, and a hydrogen bond between an electronegative atom of the substituent group and a hydrogen atom ortho to the group is found to be the most probable cause of the effect.

Spectra in the region of the in-plane hydrogen bending vibrations and the C-H stretching vibrations were also studied in an effort to provide confirmation for the hydrogen bond hypothesis. No confirmation was found, but it is shown that the data do not disprove the hypothesis.

A method was developed for the determination of the ratio of phenyl to para-tolyl groups in tetra-arylsilanes and hexa-aryldisilanes.

Study of the spectra of benzyl chloride and phenyl acetate in the liquid and solid states showed the presence of at least two rotational isomers in benzyl chloride but no such isomerism in phenyl acetate.

Study of the region between 15 and 25 microns indicated that it should be possible, for certain symmetries of substitution, to find

correlations between the nature of the substituents and the frequency of absorption bands.

INTRODUCTION

The absorption spectrum between 2 and 25 microns is one of the most useful physical properties of a chemical compound. Except for stereoisomers that are mirror images of one another, no two compounds are known that have identical absorption spectra over this region. If the spectrum of an unknown material matches that of a sample of known composition, the unknown is positively identified. The concentration of a compound in solution may be determined by measuring the intensity of absorption at some particular wavelength and comparing this with the absorption of a series of standards of known composition. In the majority of cases the absorption will follow Beer's law. Analysis by infrared spectroscopy of hydrocarbon mixtures with as many as ten components has been reported,[1] and analysis of even more complex mixtures is possible by a combination of data from infrared, Raman, and mass spectra.

Determination of the exact nature of the ground and excited states of the absorbing molecule is possible only for the most simple compounds. If the electronic energy of the ground state of the molecule is known as a function of the position of the atomic nuclei with respect to the center of mass of the molecule, it is possible to use this potential function in the Schrödinger equation. Solution of this equation will lead to certain energy levels with spacings corresponding to the observed infrared and Raman frequencies. If the exact potential function is not known, a good approximation may be made by assuming that the potential function is that of an harmonic oscillator. With reasonable values for the constants involved, solution of the equation will again lead to energy levels with spacings corresponding to the energy of photons of infrared radiation emitted or absorbed by that substance.

Since the use of the potential function of an harmonic oscillator in the Schrödinger equation leads to a reasonable solution, it would appear to be possible to treat the molecule as a system of vibrating masses according to the methods of classical physics. In fact, this is the method that has been applied to many compounds with considerable success. The molecule is considered to be composed of a system of point masses (the atomic nuclei) with the bonds between the masses having different resistances to deformation in the orthogonal directions. For the case of a diatomic molecule the differential equation for the harmonic oscillator is $-kx = ud^2x/dt^2$, where k is equal to the change in the bond strength per unit change of internuclear distance at the equilibrium internuclear distance, x is the change of internuclear distance, and u is the reduced mass of the system: $m_1m_2/(m_1 + m_2)$. Solution of this equation leads to the equation: $\nu = \frac{1}{2\pi} \sqrt{k/u}$, where ν is the frequency of vibration. These calculated frequencies correspond to the observed infrared frequencies if a reasonable value of k is used. Several methods of estimating the value of k have been described, such as Badger's rule.[2]

Classically, a vibrating system will absorb or emit light of the frequency of the vibration if the vibration causes a periodic change of dipole moment. The selection rules in quantum mechanics that determine whether or not a particular transition between the ground and excited states will cause absorption or emission of light also involve the change in dipole moment, though there are other requirements as well. As in the treatment of the frequency of vibration, most compounds are too complex to permit an exact quantum-mechanical treatment of absorption intensities, so that it is necessary to use the classical selection rule that the vibration must involve a change in dipole moment for absorption of light to occur.

As the number of atoms in the molecule increases, even the comparatively simple classical treatment of the vibrations of the molecule becomes difficult, particularly if the molecule is of low symmetry. The practical difficulties involved in solving the complex equations of a many-body problem make it necessary to assume certain simplifications, the reliability of the results then depending on the validity of the assumptions. If, however, the system is of a high symmetry, the symmetry considerations may require certain relationships between the force constants that will simplify the problem considerably, making solution of the equations possible.

The value of infrared spectra is increased considerably by the fortunate circumstance that many groups of atoms vibrate with almost exactly the same frequency regardless of the nature of the rest of the molecule. For example, if the molecule includes C-H groups, there will be an infrared absorption band at about 3000 cm^{-1}, with little change in frequency resulting from the environment of the group. The reason for these characteristic group frequencies is that the normal vibrations of the molecule are very similar in certain cases to vibrations involving only particular groups, with little contribution from the rest of the molecule. In the case of C-H groups, a particular vibration may involve motion of more than one hydrogen atom but there will be little motion of, for example, oxygen or halogen atoms. These characteristic group frequencies are useful for the indication of the presence of particular functional groups, particularly since the vibrational groups often correspond to the functional groups of interest to the chemist. By means of the characteristic group vibrations it is often possible to make some estimate of the structure of a compound even though no spectrum of an authentic sample is available for comparison. The slight changes in the frequency of vibration of the functional group can also give important information about the environment of the group. An example is the shift of OH and NH stretching vibrations to lower frequency when the group is involved in a hydrogen bond.

The availability of commercial infrared spectrophotometers in the last decade has made possible the collection of spectra of a large number of compounds, providing data for empirical correlation of spectra with structure. Observed characteristic absorption frequencies have been collected in the form of charts by Thompson,[3] Barnes, Gore, Stafford, and Williams,[4] Randall and others,[5] and Colthup.[6] Although these charts are useful as a means of indicating where to expect characteristic absorption bands for the various functional groups, an understanding of the theory of vibrational spectra is essential for correct interpretation of infrared spectra.

In spite of the relative complexity of aromatic compounds (the simplest compound in this series, benzene, has twelve atoms, 30 vibrational degrees of freedom), their infrared spectra have received considerable attention. The most complete work of assignment of infrared and Raman bands to vibrations of an aromatic molecule has been done by Ingold and his group[7] on benzene. Less complete work on the spectrum of benzene has been done by Miller and Crawford[8] and by Crawford and Parr,[9] among others. The lower symmetry of the substituted benzenes makes assignment of their vibrations more difficult than for benzene, but some work has been done on individual molecules. The assignments previously made in the case of benzene can serve as a useful guide to the vibrations of the substituted benzenes. For example, Pitzer and Scott[10] have made assignments of the vibrations of toluene and some other methyl substituted benzenes by comparison with the spectrum of benzene rather than by a complete vibrational analysis. Plyler[11] has studied the spectra of twelve substituted benzenes in the 15 to 40 micron region and has made assignments based largely on those of Pitzer and Scott.[10] Similarly, Depaigne-Delay and Lecomte[12] have studied a series of substituted benzenes from 5 to 8 microns and have made tentative assignments based on symmetry considerations. Bell, Thompson, and Vago[13] and Cole and Thompson[14] have considered some of the out-of-plane vibrations of substituted benzenes, basing their assignments of vibrational frequencies and amplitudes on a simplified normal coordinate treatment with two force constants. One of the conditions that they placed on their results was that they should agree with the results of Pitzer and Scott.[10]

Other studies of the spectra of aromatic compounds have been designed to find the characteristic frequencies of vibration without necessarily assigning the frequencies to particular vibrations. Some of these studies will be mentioned later, but at the present time mention should be made of a discussion of the spectra of hydrocarbons by McMurry and Thornton[15] as well as a study by Cannon and Sutherland[16] of the spectra of a number of aromatic compounds including many condensed ring compounds. At the time of writing, no general study has appeared of the effect of the nature of the substituent groups on the frequency of the vibrations of the benzene nucleus, attention having been restricted to the effect of changing the position of substitution.

The present study of the spectra of aromatic compounds was prompted by the observation of certain anomalies while performing routine analyses. As first observed by Barnes, Liddell, and Williams,[17] the frequency of absorption bands in the region from 675 to 900 cm^{-1} (11 to 15 microns) in the spectra of aromatic compounds is determined largely by the number and position of substituents on the ring and is relatively independent of the nature of the substituents. However, it was observed that many aromatic carboxylic acids and nitro compounds did not have the expected spectra in this region. It appeared worthwhile to investigate the extent of the deviations, to correlate the frequencies of the absorption bands with the nature of the substituents, and, if possible, to find some explanation for whatever shifts were observed.

At about the same time as the present investigation was started, a large number of aromatic silicon and tin compounds became available for study. The literature on the spectra of aromatic silanes was very sparse; the few correlations that had been made were based on a relatively small number of compounds. No data had been found in the literature on the spectra of aromatic stannanes. For the above reasons, many aromatic silanes and stannanes were included in this study.

EXPERIMENTAL

Most of the spectra were recorded on a Baird Associates Model B infrared spectrophotometer[18] using a sodium chloride prism from 2 to 16 microns and a potassium bromide prism from 12 to 26 microns. The spectra in the 3 to 4 micron region of some of these compounds were recorded on a Perkin-Elmer Model 112 spectrophotometer using a calcium fluoride prism. Wavelength calibration of both instruments was done by scanning the spectra of polystyrene, carbon dioxide vapor, and Eastman Kodak Technical grade 1,2,4-trichlorobenzene. The wavelengths of the absorption bands of these compounds have been measured accurately at the National Bureau of Standards.[19]

The spectra of all solids were obtained with the sample in the form of a mineral oil slurry and occasionally in solution. The spectra of liquids were obtained using the pure liquid in 0.1 mm. cells and thinner capillary cells of unknown path length. Most of the compounds studied were either commercially available or were supplied by members of the Chemistry Department of Iowa State College, and were used without further purification unless there was reason to doubt their purity. If purification was necessary, standard methods of distillation and recrystallization were used.

EFFECT OF THE NATURE OF THE SUBSTITUENTS ON THE OUT-OF-PLANE C-H BENDING VIBRATIONS

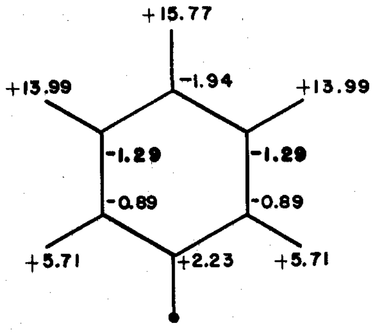
Infrared absorption bands in the 11 to 15 micron region have been used for several years to determine the arrangement of substituents on the benzene ring. Barnes, Liddell, and Williams[17] appear to have been the first to observe that the frequencies of the absorption bands in this region are determined, within limits, by the number and position of substituents on the ring rather than by the nature of the substituents. Whiffen and Thompson[20] and Thompson and Torkington[21] improved and extended the correlations. The observed absorption frequencies for various types of substitution have been collected in charts by Thompson,[3] Barnes, Gore, Stafford, and Williams,[4] and Colthup.[6] Colthup[6] extended the correlations to include non-benzene aromatic systems, such as the naphthalenes and pyridines, by pointing out that the number of adjacent hydrogen atoms appears to be the factor controlling the frequency of the bands. For example, the same band structure between 675 and 900 cm^{-1} is shown by pyridine as by a typical mono-substituted benzene. The relation between absorption frequency and the number of adjacent hydrogen atoms has been shown in graphic form in a recent article by Crawford.[22]

The origin of the absorption bands in the 11 to 15 micron region has received some theoretical treatment. Pitzer and Scott,[10] from analysis of the spectra of toluene and other methyl substituted benzenes, assigned the bands to out-of-plane vibrations of the hydrogen atoms on the ring, the atoms moving above and below the plane of the ring. A normal coordinate treatment by Miller and Crawford[8] confirmed the assignments of Pitzer and Scott.[10] Bell, Thompson, and Vago[13] calculated the frequency of some of the absorption bands, assuming that the substituents did not participate in the vibration. Their treatment used only two force constants. Later, Cole and Thompson[14] obtained slightly better agreement with experimentally observed frequencies by repeating the calculations with a revised value for one of the force constants. The nature of the vibrations in all of these assignments was essentially the same, differing only in detail. The form of the vibrations for some types of substitution, as calculated by Cole and Thompson,[14] is shown in Figure 1 (+ indicates motion above the plane of the paper, - indicates motion below the plane of the paper; the numbers indicate relative amplitudes of motion).

While examining the spectra of a large number of aromatic compounds it became evident that the frequency of the bands between 11 and 15 microns did not always correspond to what would be expected from the arrangement of the substituents, particularly if one or more of the substituents was a nitro or carboxyl group. The same effect has been noted by Flett[23] for the substituted benzoic acids, though he did not investigate the matter very thoroughly nor did he propose any explanation for the anomalies.

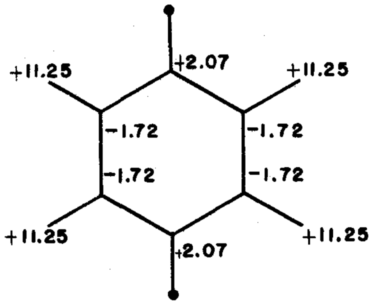
Effect of the Mass of the Substituents

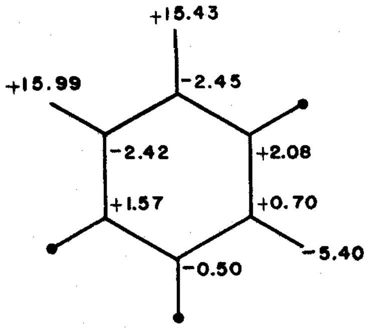
The effect of the mass of the substituent groups on the frequency of the benzene ring vibrations is best studied in the monosubstituted benzenes in order to avoid steric effects and the complication of having two groups change at once. When the effect of changing the mass of the



Monosubstituted benzenes
723 cm^{-1}

Para-disubstituted benzenes
837 cm^{-1}





1,2,4-Trisubstituted benzenes
830 cm^{-1}

Figure 1. Form of some out-of-plane vibrations of substituted benzenes.

From data of Cole, A. R. H. and H. W. Thompson, Trans. Faraday Soc. 46, 103 (1950).

substituents in monosubstituted benzenes is established, it may be possible to extend the correlations to more complex cases.

Colthup[6] indicated strong absorption bands for monosubstituted benzenes at 680 to 720 cm^{-1} (13.9 to 14.8 microns) and 725 to 775 cm^{-1} (12.9 to 13.8 microns). No correlation was found between the mass of the substituent group and the position of the lower frequency band, but the higher frequency band showed a definite shift to lower frequency with increasing mass of the atom attached to the ring, as shown in Figure 2. This graph is a plot of frequency vs. mass of the substituent atom for a group of compounds of the type (phenyl) $_nM$, where n is the valence of the substituent atom, M. Although most substituent groups affect the frequency of the absorption band in a manner dependent on the mass of the atom attached to the ring, there are some striking exceptions. For example, since the frequency of this vibration in toluene is 728 cm^{-1}, the methyl group acts as though it were very heavy. Similarly, in benzoic acid the vibration is at 807 cm^{-1}, so the carboxyl group acts as though it were much lighter than the actual mass of the carbon atom. The general trend towards lower frequency with increasing mass of the substituent can be readily understood. In deuterobenzene it is probable that the vibration involves some motion of the deuterium atom, increasing the energy of the vibration. As the substituent atom becomes heavier it moves less and less in the vibration so that the energy of the vibration decreases.

An attempt was made to correlate the frequency of the 12 micron band of para-disubstituted benzenes with the sum of the masses of the two substituent atoms. Most of the points fell close to a smooth curve

Key to Figure 2

The compounds represented are (1) deuterobenzene,[a] (2) tetraphenylmethane, (3) diphenyl ether, (4) fluorobenzene, (5) tetraphenylsilane, (6) triphenylphosphine, (7) diphenylsulfide, (8) chlorobenzene, (9) tetraphenylgermane, (10) bromobenzene, (11) tetraphenyltin, (12) triphenylstibine, (13) iodobenzene, (14) diphenylmercury, (15) tetraphenyllead, (16) triphenylbismuthine.

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[a] Tiers, G. V. D. and J. H. Tiers, J. Chem. Phys. 20, 761 (1952).

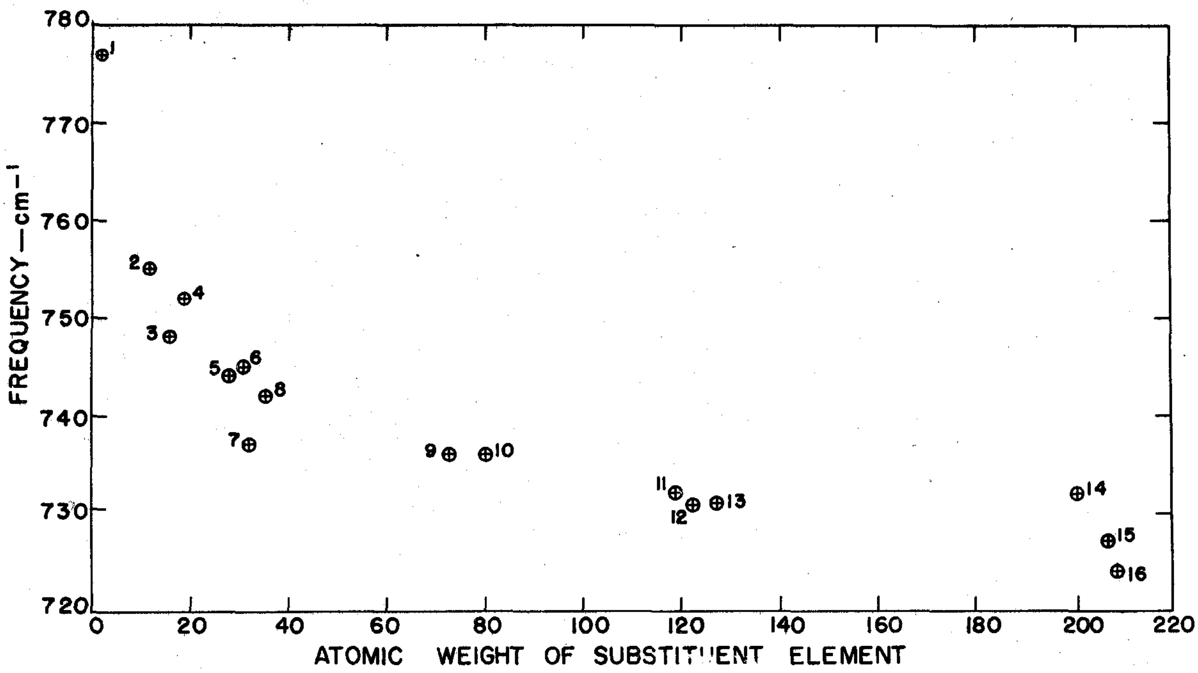


Figure 2. Frequency of the C-H bending vibration vs. atomic weight of substituent atom for monosubstituted benzenes.

See opposite page for key.

of about the same shape as that in Figure 2, but there were some abnormally large deviations, particularly for para-deuterotoluene. An alternative method of assigning to each group a characteristic band shift gave more satisfactory results. The characteristic band shifts were determined from the spectra of the monosubstituted benzenes by subtracting a base frequency from the frequency of the absorption band of the compound. The exact frequency used for the base was immaterial, since use of a different base frequency would merely displace the resultant curve by a constant value. A base frequency of 727 cm^{-1} was chosen to give the lowest possible shifts for all groups without the confusion of having negative shifts for some groups. In a few cases the monosubstituted benzene had more than one absorption band in this region; the value that was then chosen was the one that would give the best agreement in the para-disubstituted benzenes. Table 1 lists the values used for the groups for which data was available. Figure 3 is a plot of the frequency of the 12 micron band of para-disubstituted benzenes *vs.* the sum of the band shifts caused by each of the substituents in monosubstituted benzenes. A straight line could be drawn through the points with only a minor amount of scattering of the points about the line. This type of plot permitted the correlation of data of the substituted toluenes, benzoic acids, and nitrobenzenes as well as of those compounds that would fit on a curve such as is shown in Figure 2. The slope of the line in Figure 3 is less than unity, showing that each substituent produces less of a shift in the para-disubstituted benzenes than in the monosubstituted benzenes.

Table 1. Characteristic Band Shifts for Various Substituent Groups

Compound	Group	Frequency (cm^{-1})	Shift (cm^{-1})
Deuterobenzene	-d	778	51[a]
Triphenylmethane	-CH	762	35
Trans-stilbene	-C=	767	40
Toluene	$-CH_3$	728	1
Ethylbenzene	$-C_2H_5$	747	20
t-Butylbenzene	$-C(CH_3)_3$	764	37
Benzyl alcohol	$-CH_2OH$	736	9
Benzyl chloride	$-CH_2Cl$	768	41
Benzotrichloride	$-CCl_3$	805	78
Benzonitrile	-CN	763	36
Acetophenone	-COR	763	36
Benzaldehyde	-CHO	748	21
Benzoyl chloride	-COCl	779	52
Benzoic acid	-COOH	808	81
Sodium benzoate	-COONa	820	93
Ethyl benzoate	-COOR	809	82
Tetraphenylmethane	-C	755	28
Benzamide	$-CONH_2$	771	44
Aniline	$-NH_2$	755	28
Aniline hydrochloride	$-NH_3^+$	741	14
Tetraphenylhydrazine	-NN-	747	20
Dimethyl aniline	$-N(CH_3)_2$	753	26
Nitrobenzene	$-NO_2$	794	67
Anisole	$-OCH_3$	758	31
Phenol	-OH	753	26
Phenyl acetate	-OOCR	752	25
Fluorobenzene	-F	752	25
Tetraphenylsilane	-Si	744	17
Triphenylphosphine	-P	745	18
Diphenylsulfide	-S	738	11
Sodiumbenzenesulfonate	$-SO_3Na$	754	27
Benzenesulfonylchloride	$-SO_2Cl$	757	30
Chlorobenzene	-Cl	742	15
Bromobenzene	-Br	737	10
Tetraphenylstannane	-Sn	732	5
Triphenylstibine	-Sb	731	4
Tetraphenyllead	-Pb	728	1
Iodobenzene	-I	731	4
Diphenylmercury	-Hg	733	6
Triphenylbismuthine	-Bi	731	4

[a] In addition to the above values, from a comparison of several compounds the values of 9 for the CH_2 group (except where otherwise noted) and 36 for the phenyl group were chosen as giving the best fit for the data.

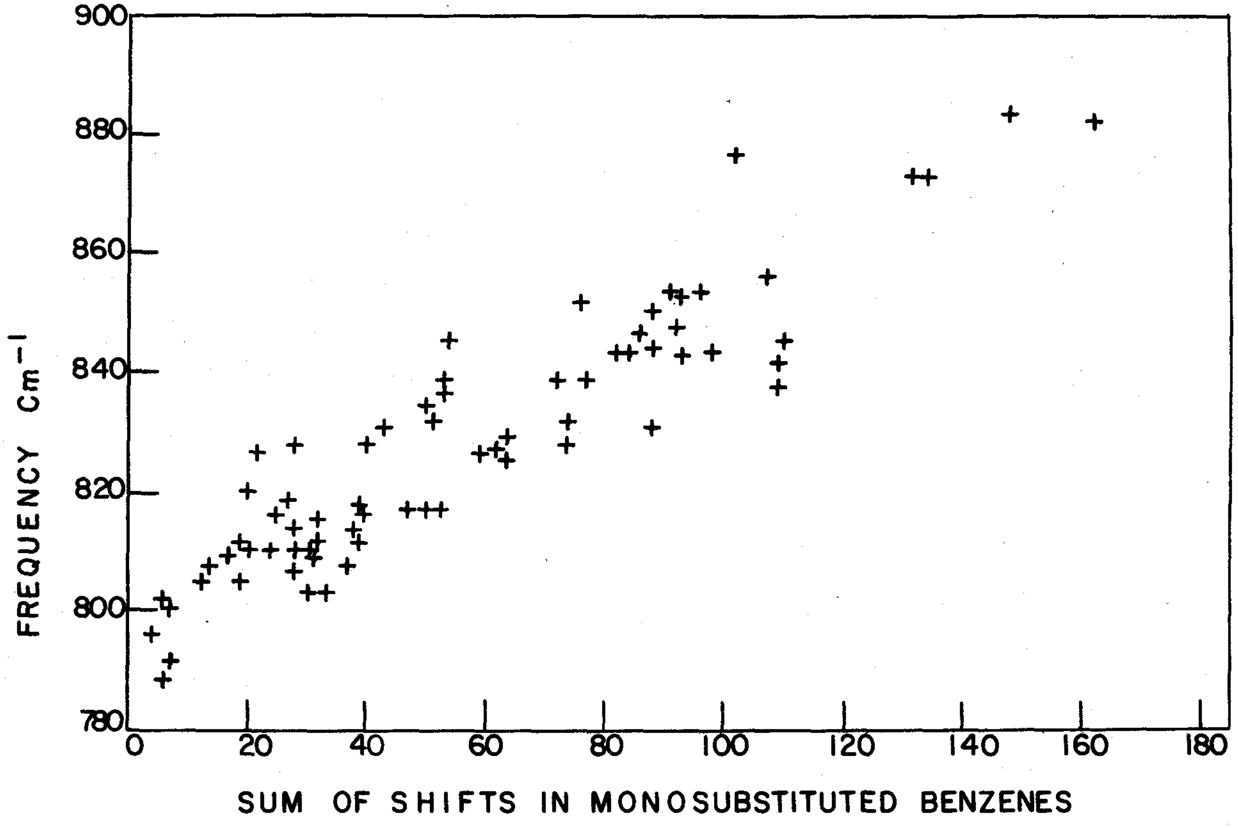


Figure 3. Variation of the frequency of the 12 micron band of para-disubstituted benzenes as a function of the sum of the shifts caused by the substituents in monosubstituted benzenes.

Similar correlations to the correlation of Figure 3 can be shown for certain bands of meta-disubstituted benzenes. Colthup[6] listed two strong bands at 675 to 730 cm^{-1} (13.7 to 14.8 microns) and 750 to 810 cm^{-1} (12.3 to 13.3 microns) and a moderately strong band at 850 to 900 cm^{-1} (11.1 to 11.8 microns) for meta-disubstituted benzenes. The band at the lowest frequency appeared to be relatively unaffected by changes in the substituents, as was the lower frequency band in this region of monosubstituted benzenes, but the other two bands shifted regularly with changes in the substituent groups. Shown in Figures 4 and 5 are the observed frequencies of these bands as a function of the sum of the shifts caused by the two substituents in monosubstituted benzenes. The same general trends that were found for the para-disubstituted benzenes appear in the corresponding graph for the meta-disubstituted benzenes, but with somewhat more scattering of points, particularly for the 850 to 900 cm^{-1} band. In several cases it was not possible to choose one band as the out-of-plane hydrogen bending vibration. The vertical lines in Figures 4 and 5 connect points which were found for an individual compound.

As in the other disubstituted benzenes, a correlation was found for the ortho-disubstituted benzenes between the frequency of an absorption band in this same general region and the sum of the shifts produced by the two substituent groups in the monosubstituted benzenes. Ortho-disubstituted benzenes have one strong absorption band in this region, listed by Colthup[6] as being between 730 and 770 cm^{-1} (13.0 to 13.7 microns). Figure 6 shows the correlation between the nature of the substituents and the frequency of this absorption band in the ortho-disubstituted benzenes. The scattering of points is considerably greater

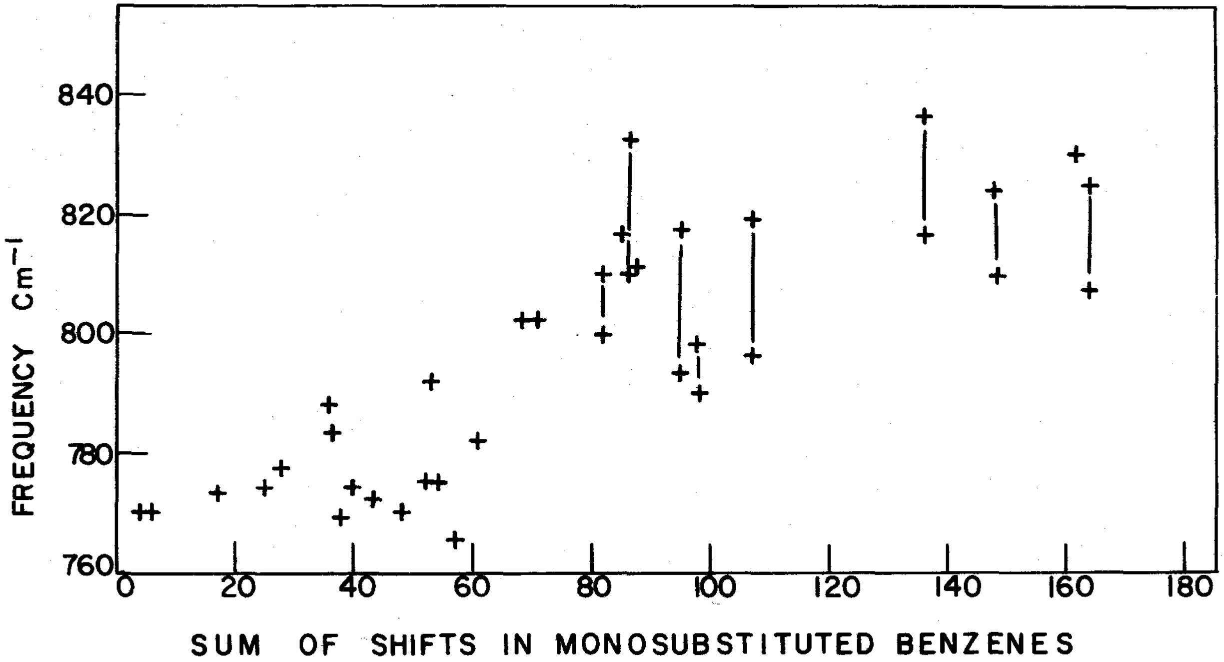


Figure 4. Variation of the frequency of the 12 to 13 micron band of meta-disubstituted benzenes as the substituents are changed.

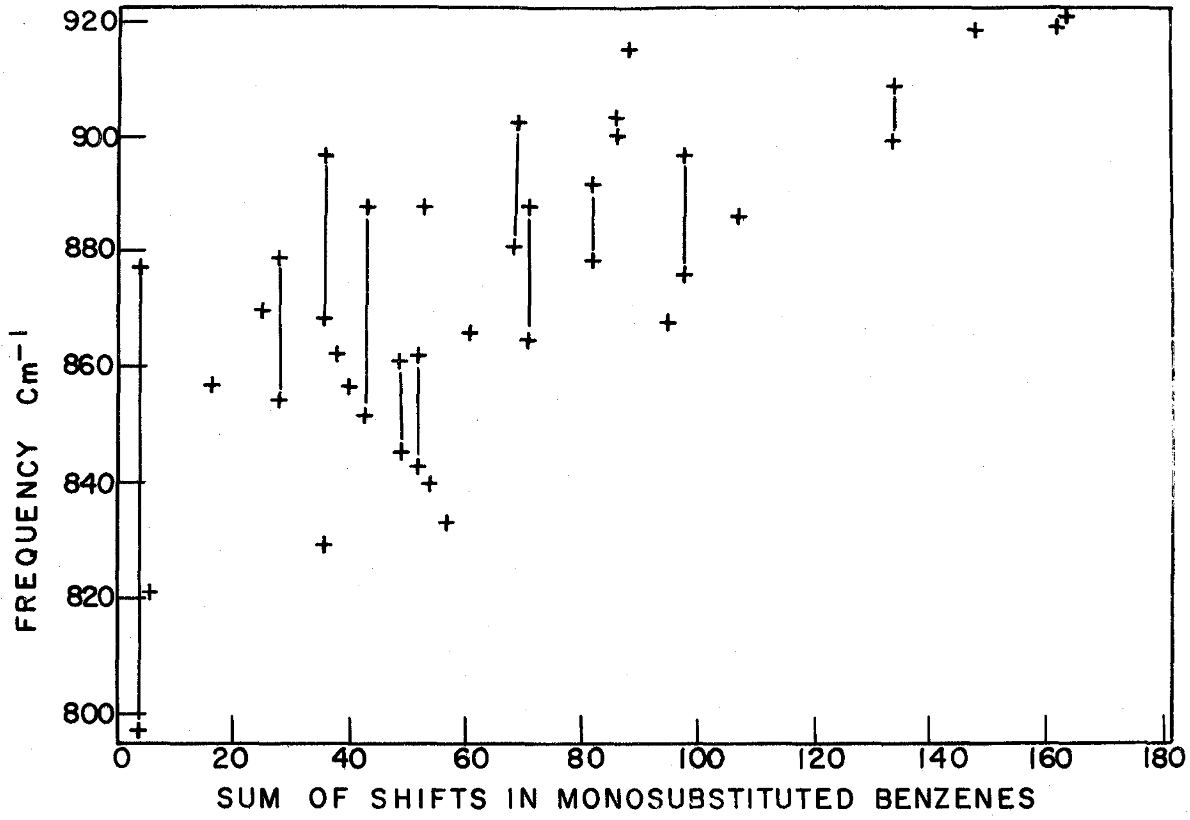


Figure 5. Frequency of the 11 to 12 micron band in meta-disubstituted benzenes vs. sum of band shifts caused by the substituents in monosubstituted benzenes. Vertical lines connect points found for individual compounds when choice of a particular absorption band could not be made.

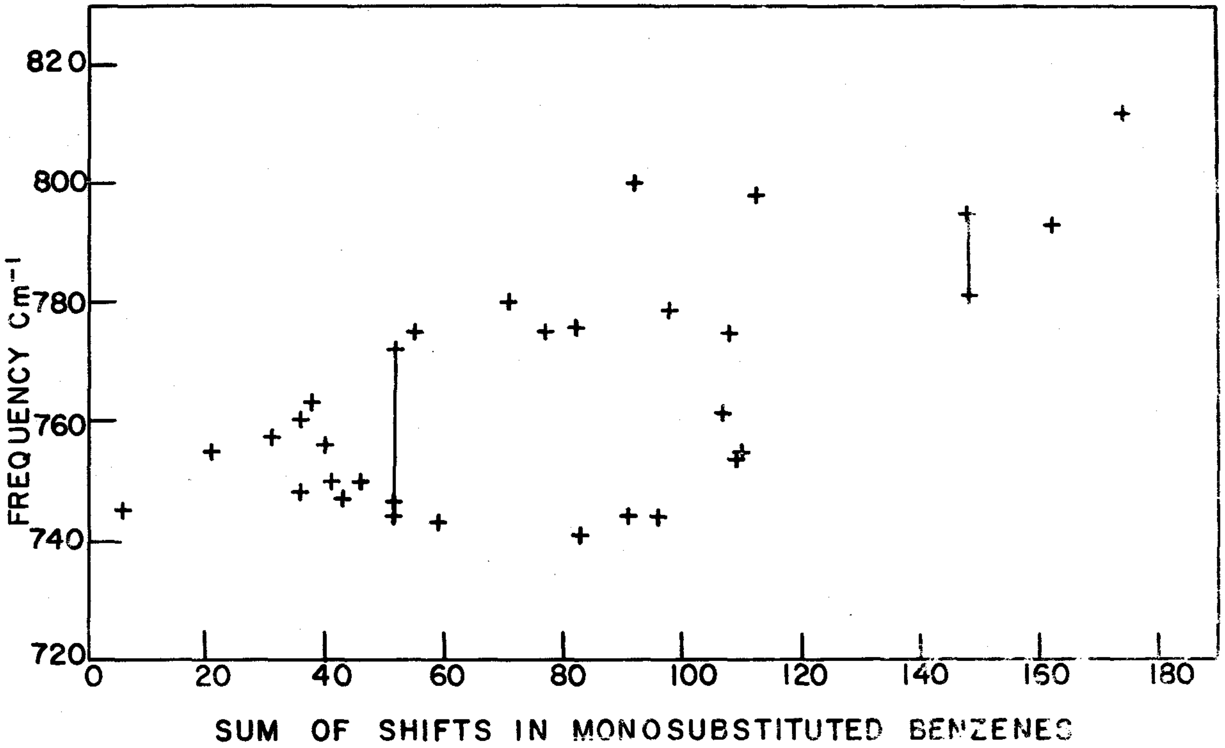


Figure 6. Variation of the frequency of the 13 to 14 micron band of meta-disubstituted benzenes as the substituents are changed.

than was found for the meta- or para-disubstituted benzenes, perhaps because of steric interactions between the substituents. The curve appears to be split into two parts through a portion of its range, most, though not all, of the points on the lower branch being for ortho-substituted benzoic acids or esters.

Not enough data have been collected on trisubstituted benzenes to demonstrate similar trends but it is likely that such trends exist. Except in the case of symmetrical trisubstitution, steric effects must be considered, as will be discussed later.

Part of the scattering of the points in Figures 3, 4, 5, and 6 probably arose from the method used for determining the spectra. Spectra of solids were obtained in the form of mineral oil slurries, and of liquids in the form of thin films between salt plates. Some of the data taken from the literature[14, 20, 24, 25] was from solution spectra. The exact frequency of a vibration depends, in part, on the nature of the medium surrounding the molecule. Ideally, all spectra should be determined with the compound in the form of a vapor, but this is not always possible. Neither is it possible to use a single solvent for all compounds, so that the effect of the surrounding medium would be the same for all. Kirkwood[26] has suggested that if there is a simple electrostatic interaction between the vibrating group and the solvent the frequency shift should be proportional to $(D-1)/(2D + 1)$, where D is the static value of the dielectric constant of the solvent. It is possible that the scattering of the points in Figures 3, 4, 5, and 6 could be reduced by obtaining the spectra of all the compounds in solution and correcting for the effect of the solvent by this equation or some other applicable relationship.

Extra Absorption Bands Found in Certain Compounds

In addition to the absorption bands expected, aromatic nitro compounds, carboxylic acids, and salts and esters of carboxylic acids sometimes showed an additional strong absorption band in the region of the out-of-plane hydrogen bending vibrations. This extra band appeared for certain substituents and certain symmetries of substitution only. Of the various symmetries of substitution studied, an extra band appeared only for para-disubstitution and 1,2,4-trisubstitution, and only when one of the substituents was a nitro or carboxyl group or an ester or salt of a carboxyl group. Figure 7 shows the spectra from 11.5 to 14 microns of some para-disubstituted benzenes. The lower compounds all have a nitro or carboxyl group as one of the substituents and there is a band just above 13 microns that does not appear in the normal compounds shown at the top of the figure. It is apparent that this extra band cannot be caused by a vibration of one of the substituents, since these are different in the three compounds shown and because these same substituents do not cause absorption in this region in other compounds. The absorption frequency must correspond to some vibration of the ring, but the type of vibration is not known. Mann and Thompson[27] have studied the infrared spectrum of a single crystal of para-nitroaniline using polarized light and found that the bands at 755 and 840 cm^{-1} (13.25 and 11.90 microns) both have the dichroism that would be expected for out-of-plane deformations of the benzene ring. This suggests, but does not prove, that the extra band may also be an out-of-plane hydrogen bending vibration.

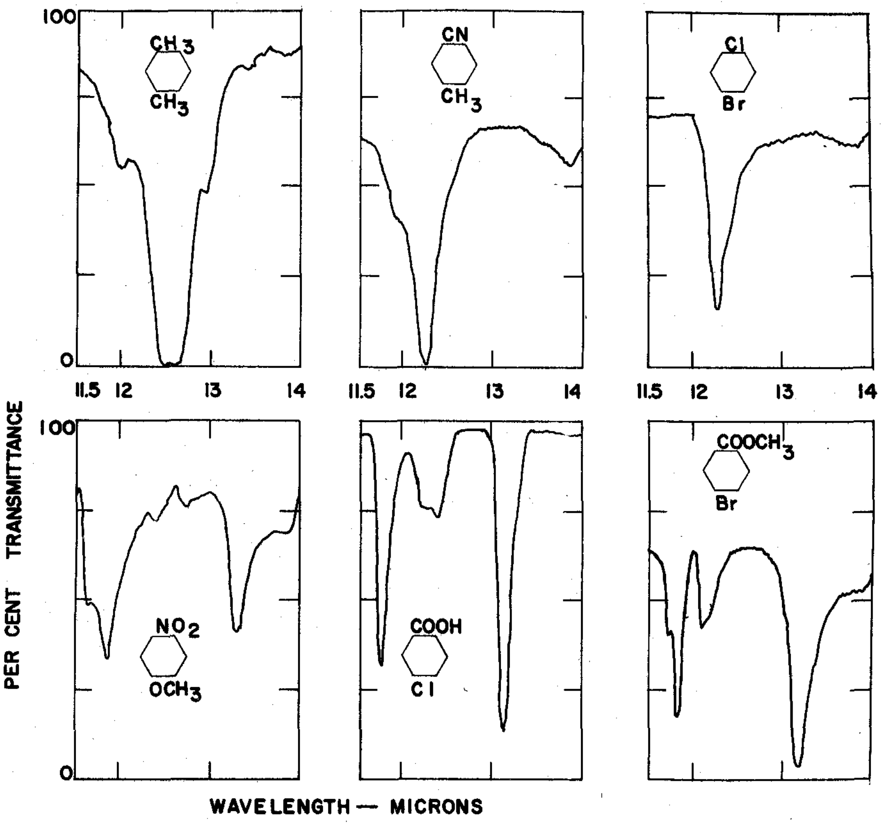


Figure 7. Spectra from 11.5 to 14 microns of some para-disubstituted benzenes.

The 1,2,4-trisubstituted also had an extra band at about 13 microns and, strangely, it appeared whether the other two substituents were in the 2,4-, 2,5-, or 3,4-positions, with the nitro or carboxyl group in the number 1 position. It is rather strange that this extra band should appear only in these few cases and that it should then be present regardless of the exact arrangement of substituents. In both the para-disubstituted and 1,2,4-trisubstituted compounds the band was not observed if more than one of the substituents was a nitro or carboxyl group.

Evidence Indicating Hydrogen Bond Interactions between Substituent Groups and Ring Hydrogen Atoms

In addition to the introduction of a new absorption band into this region of the spectrum, nitro and carboxyl groups and salts and esters of carboxyl groups were also found to cause abnormally large shifts of the out-of-plane hydrogen bending vibrations to higher frequencies. These groups act as though they are extremely light, causing even greater shifts than deuterium, lightest of all the substituents, as is shown by the data of Table 1 and Figures 3, 4, 5, and 6. Figure 7 also shows this shift in the case of a few para-disubstituted benzenes. The effect of these groups is, however, most striking in the monosubstituted benzenes. Figure 8 shows the normal band pattern in this region for monosubstituted benzenes. There is a strong absorption band between 680 and 720 cm^{-1} (13.9 to 14.8 microns) and another of about the same intensity between 725 and 775 cm^{-1} (12.9 to 13.8 microns). Figure 9 shows the changes caused by certain substituents. The lower

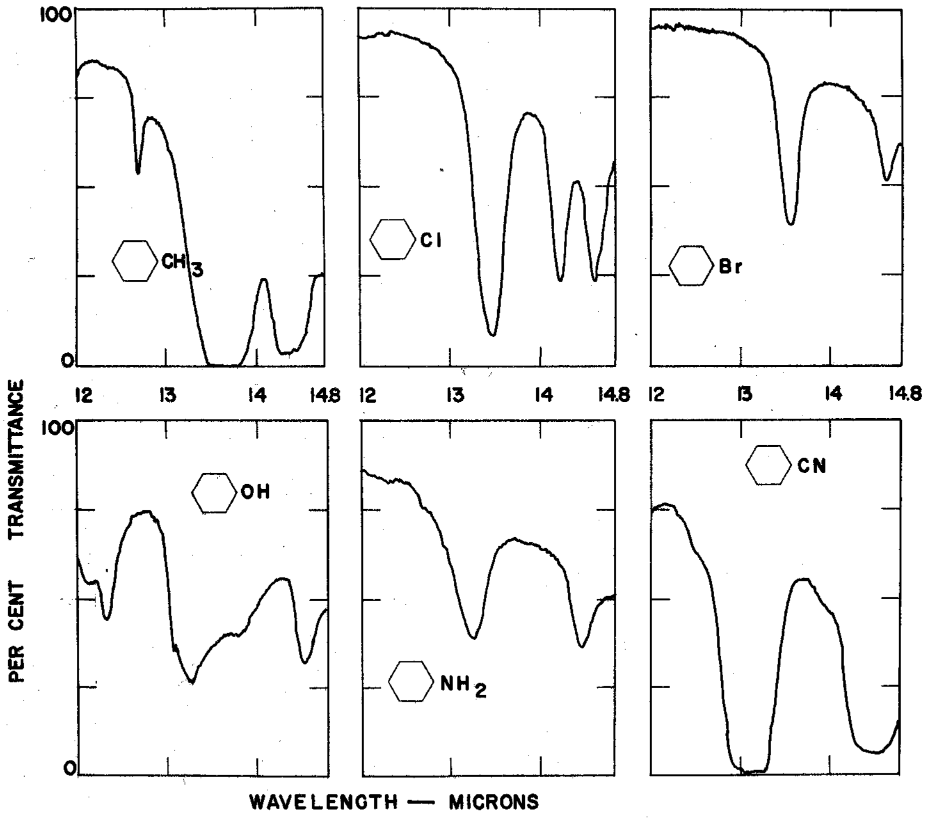


Figure 8. Spectra from 12 to 14.8 microns of some normal monosubstituted benzenes.

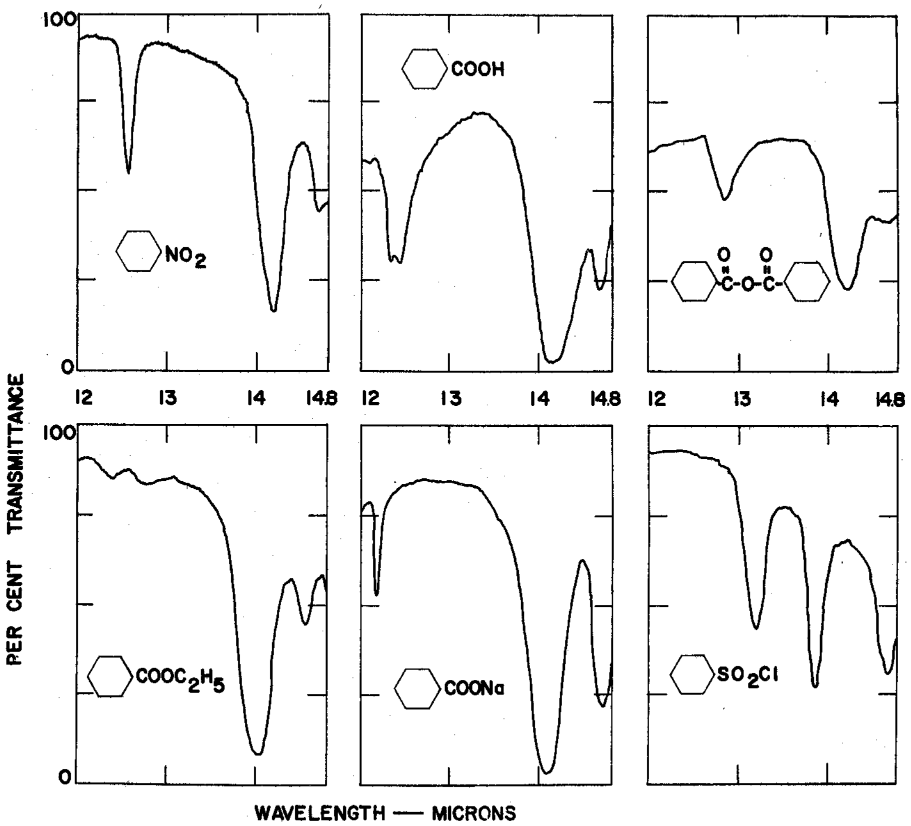


Figure 9. Spectra from 12 to 14.8 microns of some monosubstituted benzenes with anomalous band patterns.

frequency vibration is apparently unaffected, but the higher frequency band is displaced well above 775 cm^{-1} and appears with much lower intensity. The decrease in intensity is most striking in ethyl benzoate, where the higher frequency vibration has nearly disappeared. The spectrum of benzene sulfonyl chloride has also been included in this group, although it is normal except for an extra band at about 13.9 microns that is apparently caused by a vibration of the SO_2Cl group. The spectrum of this compound will be discussed in more detail later.

As further indication of the shifts in frequency caused by the groups mentioned above, Table 2 lists the frequency of the 12 micron band in several para-disubstituted benzenes. For the substituted toluenes and dihalobenzenes the characteristic absorption band is between 800 and 820 cm^{-1}; in each of the compounds in which one of the substituents is a nitro or carboxyl group the band is displaced to 840 to 855 cm^{-1}; if both of the substituents are nitro or carboxyl groups, there is an additional displacement to about 880 cm^{-1}.

In other cases, band shifts may be observed even if the same substituents are arranged in similar ways. An example of this is the pair of isomers 2,4- and 2,5-dimethylbenzoic acid. Both are 1,2,4-trisubstituted, yet 2,4-dimethylbenzoic acid has its characteristic band at 841 cm^{-1} and the 2,5-acid has its band at 822 cm^{-1}. This cannot be a steric effect because the adjacent substituents are the same in both compounds. In the compounds in which the carboxyl group is replaced by a triphenylstannyl group the band is at 819 cm^{-1} in the 2,4-dimethyl compound and at 817 cm^{-1} in the 2,5-dimethyl compound.

Table 2. C-H Bending Frequencies for Para-substituted Benzenes

Compound	Frequency (cm^{-1})
p-Fluorotoluene	818[a]
p-Chlorotoluene	809[a]
p-Bromotoluene	803[a]
p-Iodotoluene	800[a]
p-Dichlorobenzene	820[a]
p-Dibromobenzene	811[a]
p-Chlorobromobenzene	816[a]
p-Tolunitrile	814
p-Chloroiodobenzene	811[a]
p-Xylene	794[b]
p-Nitrobromobenzene	839
p-Nitroaniline	842
p-Toluic Acid	843
p-Aminobenzoic Acid	841
p-Hydroxybenzoic Acid	856
p-Chlorobenzoic Acid	853
p-Bromobenzoic Acid	853
p-Dinitrobenzene	874
Terephthalic Acid	882

[a] Data from A. R. H. Cole and H. W. Thompson, Trans. Faraday Soc. 46, 103 (1950).

[b] American Petroleum Institute Research Project 44. Carnegie Institute of Technology. Catalog of Infrared Spectral Data. Serial No. 312.

Examples of the effect of steric interactions on the frequency of the out-of-plane hydrogen bending vibrations in ortho-disubstituted benzenes are discussed later in this section.

As was mentioned previously, the bands in this region correspond to the out-of-plane C-H bending vibrations of the aromatic nucleus. Some of the factors that might affect the frequency of these vibrations, in addition to the mass effect already discussed, are (1) changes in the bending force constants brought about by differences in the electron distribution as the resonance structure is affected by the substituent, (2) coupling with some other vibration of the molecule, and (3) interaction of hydrogen atoms on the ring with suitably oriented atoms of the substituent group.

If the observed frequency changes are caused by a change of the resonance structure of the ring affecting the bending force constants, the spectra of benzonitrile, nitrobenzene, and benzoic acid should be similar in the 675 to 900 cm^{-1} region since, as is shown by the meta-directing property of the group and the large dipole moment of benzonitrile, a nitrile group affects the resonance structure of the ring in the same manner and to about the same extent as a nitro or carboxyl group. Figures 8 and 9 show that the frequency and intensity of the C-H bending vibrations are entirely different for benzonitrile than for benzoic acid or nitrobenzene. Similarly, for para-disubstituted benzenes, Figure 7 and the data of Table 2 show that the frequency of the C-H bending vibration in para-tolunitrile is much lower than the frequencies for para-substituted nitrobenzenes or benzoic acids. Further evidence against any pronounced effect of resonance becomes apparent from an examination of

Figure 2. If resonance affected the bending force constants to any appreciable extent, the frequencies for such diverse compounds as tetraphenyl lead, where there is little resonance interaction between the ring and the substituents, and the halobenzenes, where there is a good deal of such interaction, should not follow the same relationship.

Coupling of the C-H bending vibrations with some other vibration of the molecule might also account for the observed changes in frequency of the absorption bands. Both nitro and carboxyl groups vibrate at frequencies somewhat below 650 cm^{-1}, and these vibrations might couple with the C-H bending vibrations. It is important to note that the band between 680 and 720 cm^{-1} in monosubstituted benzenes does not exhibit a significant frequency change in nitrobenzene or benzoic acid even though this band would be more likely to couple with the vibration of the nitro or carboxyl group, being of more nearly the same frequency. Both the 680 to 720 cm^{-1} band and the one at the higher frequency are in the same symmetry class.[10] In this same connection it is interesting to look for evidence of coupling between the C-H bending vibrations of the separate rings in condensed ring compounds. The spectrum of naphthalene[28] in the vapor phase shows no discernible splitting of the band at 779 cm^{-1}. Examination of the spectra of other polynuclear aromatics shows that, as a general rule, there appears to be no strong coupling between the vibrations of the various rings, even though such interactions might be expected.

The effect of a nitro or carboxyl group on the C-H bending frequencies can be most simply explained by the interaction of a ring hydrogen atom with a suitably oriented electronegative atom or group, i.e., the formation of a hydrogen bond. Hydrogen stretching vibrations are known to move to lower frequencies when a hydrogen bond is formed. This change in frequency can be explained by considering that less energy is required to move a proton along the line between two attractive centers than is needed to move the proton the same distance away from one attractive center. In contrast, for a bending vibration such as is involved here, more energy is needed to move the proton out of the line between two attractive centers than is required simply for the bending of a single bond. Hydrogen bonding should cause the bending vibrations to occur at higher frequencies than in the unbonded case, in agreement with the experimentally observed change in frequency.

A study of the crystal structures of some aromatic nitro compounds and carboxylic acids lends support to this interpretation of the effect of nitro and carboxyl groups. When an electronegative atom is forced by the geometry of the system to lie close to a ring hydrogen atom, an attractive force of the type usually called hydrogen bonding may be expected. The crystal structure of diethyl terephthalate was determined through X-ray methods by Bailey.[29] The distance between the carbonyl oxygen atom and the carbon atom closest to it on the ring was found to be 2.85 ± 0.05 angstroms, and for the other oxygen atom the distance of approach to the closest ring carbon atom is only 2.69 ± 0.05 angstroms. Assuming a normal bond angle and distance for the ring hydrogen, the O-H distance in the latter case is about 2.2 angstroms. The C-O-C bond angle found by Bailey is 117°, which suggests an SP^2 configuration for the oxygen atom, so that the ring hydrogen atom is probably located within the region occupied by the unshared pair of electrons of the oxygen atom. The interatomic distances and angles are similar to those found in catechol, where there is known to be a hydrogen bond.[30] The effect of resonance in a carboxylic acid is to place a partial positive charge on the ortho carbon atom, weakening the C-H bond, and to place a partial negative charge on the oxygen atom, which would strengthen a hydrogen bond.

The X-ray structure of para-dinitrobenzene was completed most recently by Abrahams.[31] From the position of the atoms in the crystal lattice the distance between the oxygen atoms of the nitro group and the ortho carbon atoms was found to be 2.71 ± 0.03 angstroms, a short enough distance for the formation of a moderately strong hydrogen bond.

Figure 9 shows that the sulfone group in benzenesulfonylchloride does not have an appreciable effect on the frequency of the C-H bending vibrations, even though the oxygen atoms appear to be favorably oriented for formation of a hydrogen bond. The structure of bisphenylsulfonylsulfide[32] shows that for a sulfone group attached to a benzene ring the carbon to oxygen distance is about 3.0 angstroms, apparently too large a distance for formation of a hydrogen bond.

The data for only one acid and one nitro compound are discussed here. The interatomic distances should be about the same in other aromatic compounds with these substituents unless steric factors cause rotation of the group out of the plane of the ring, the increased interatomic distances then inhibiting hydrogen bonding. Francel[33] has determined the orientation of the nitro group with respect to the plane of the ring, by the use of polarized infrared light, and has determined the frequency of the out-of-plane C-H bending vibrations for four nitrobenzenes. In ortho-nitrophenol and ortho-nitroaniline the nitro group is in the plane of the ring and the C-H bending frequencies are 748 and 747 cm^{-1}, respectively, while in ortho-chloro and ortho-bromonitrobenzene the nitro group is rotated out of the plane of the ring and the C-H bending frequencies are 732 and 731 cm^{-1}, respectively. In the corresponding carboxylic acids the carboxyl group is in the plane of the ring in salicylic acid[34] (762 cm^{-1}) and may be assumed to be in the plane of the ring in anthranilic acid (755 cm^{-1}) and rotated out of the plane of the ring in ortho-chloro and ortho-bromobenzoic acid (744 cm^{-1} for both). In all cases the effect of steric factors causing rotation of the group out of the plane of the ring is to shift the C-H bending frequencies in the direction expected if a hydrogen bond is being broken.

The carbon to oxygen distance in aromatic aldehydes, ketones, or acyl halides should be about the same as the carbonyl oxygen to carbon distance in diethyl terephthalate, about 2.85 angstroms. The hydrogen bond in these compounds would then be weaker than in nitrobenzene or benzoic acid though stronger than in benzenesulfonylchloride. In benzaldehyde there is a band at 13.38 microns (748 cm^{-1}) and in benzoylchloride, at 12.88 microns (777 cm^{-1}). Apparently, the frequency of the band is little affected until the carbon to oxygen distance is less than about 2.8 angstroms. In benzoylchloride, the chlorine atom probably comes close enough to the ortho hydrogen atom to form a hydrogen bond, though this bond does not appear to be so strong as that in benzoic acid or nitrobenzene.

This hydrogen bond interaction provides an explanation of the small frequency change of the 680 to 720 cm^{-1} band in monosubstituted benzenes compared to the pronounced displacement of the 725 to 775 cm^{-1} band. According to the results of Pitzer and Scott,[10] the higher frequency vibration can be treated as an out-of-plane displacement of the hydrogen atoms only, since the motions of the carbon atoms are small compared to those of the hydrogen atoms. The lower frequency band, however, corresponds to a vibration in which the motions of the carbon atoms are nearly as great as those of the hydrogen atoms. Since, to a first approximation, only the motions of the hydrogen atoms are disturbed by the proposed hydrogen bond, the higher frequency band should be affected more than the lower frequency band.

The difference in frequency of the C-H bending vibration in 2,4- and 2,5-dimethylbenzoic acid discussed earlier can be explained similarly. From the assignments of Cole and Thompson[14] (see Figure 1) it is known that the amplitude of the bonded hydrogen atom in 2,4-dimethylbenzoic acid is nearly 16 units, while in 2,5-dimethylbenzoic acid the vibrational amplitude of the bonded hydrogen atom is 5.4 units. Therefore, the C-H bending vibration in the 2,4-dimethyl acid should have a higher frequency than in the 2,5-dimethyl acid, in agreement with the observed frequencies of 822 cm^{-1} for the 2,5-acid and 841 cm^{-1} for the 2,4-acid. It is interesting to note that the form of the vibration is such that most of the energy is in the vibration of the two adjacent hydrogen atoms, in agreement with the observation[6] that the frequencies of the absorption bands in this region are determined principally by the number of adjacent hydrogen atoms.

Additional evidence for this hydrogen bond hypothesis is found in the spectra of phenylacetic acid, diphenylacetic acid, and triphenylacetic acid, shown in the 13 to 14 micron region in Figure 10. It is seen that phenylacetic acid has a single absorption band at 13.27 microns (754 cm^{-1}), diphenylacetic acid has two absorption bands at 13.32 and 13.63 microns (750 and 734 cm^{-1}) of about equal intensity, and triphenylacetic acid has two absorption bands at 13.13 and 13.60 microns (761 and 735 cm^{-1}) with the latter about twice as strong as the former. Fisher-Hirschfelder-Taylor models of these compounds indicate that steric factors prevent the formation of more than one C-H-O hydrogen bond, so that the spectra may be interpreted as follows: The single band in the spectrum of phenylacetic acid is due to vibrations of the hydrogen atoms on the ring as affected by hydrogen bonding, and the two bands of about equal intensity in the spectrum of diphenylacetic acid are attributed to the C-H bending vibrations of the unbonded ring (13.63 microns) and the bonded ring (13.32 microns). A similar argument applies to triphenylacetic acid. Both the intensities and frequencies of the absorption bands can be interpreted in this way.

In all three of these compounds the carbonyl stretching vibration is at 1700 cm^{-1}. In methyltriphenylacetate the carbonyl stretching vibration is at 1725 cm^{-1} and the C-H bending bands are at 748 and 760 cm^{-1}. In triphenylsilylcarboxylic acid and triphenylgermanylcarboxylic acid the carbonyl stretching vibration is at a somewhat lower frequency, 1650 cm^{-1}, and in both of these compounds the C-H bending vibration is not split into two frequencies, there being single bands at 742 and 737 cm^{-1}, respectively. In the methyl esters of these two acids the carbonyl stretching vibration has shifted to 1690 cm^{-1} and the C-H bending vibration is split into two bands at 740 and 752 cm^{-1} for the

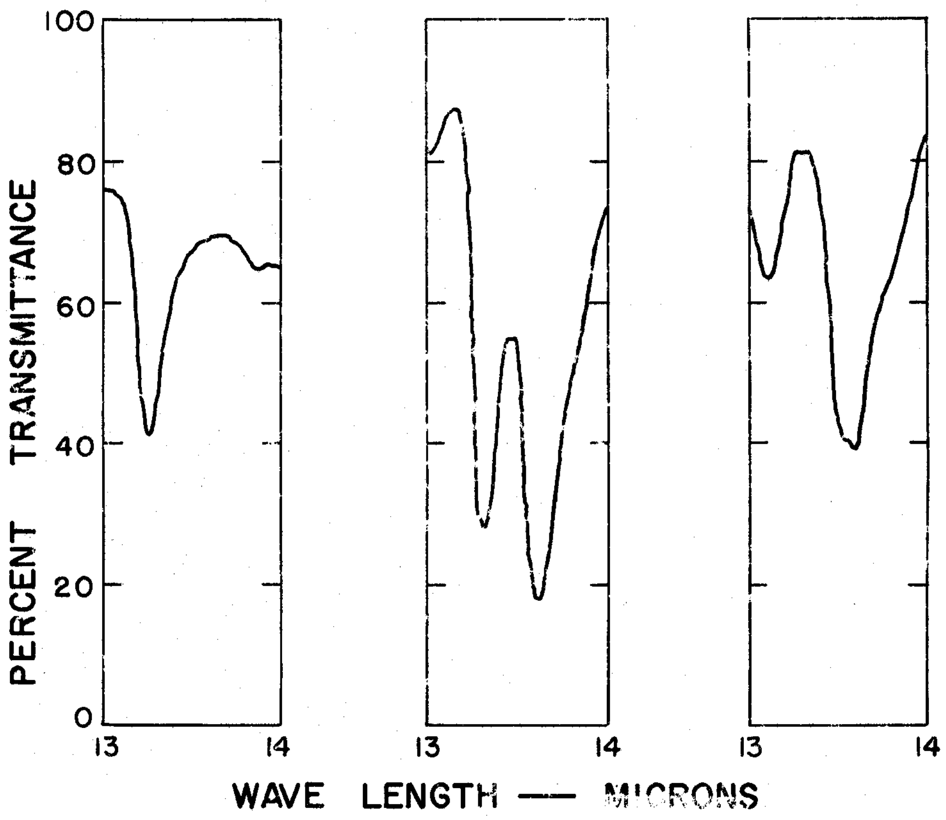


Figure 10. Spectra from 13 to 14 microns of (from left to right) phenylacetic acid, diphenylacetic acid, and triphenyl acetic acid as mineral oil slurries.

silicon compound and 733 and 747 cm^{-1} for the germanium compound. In both cases the lower frequency band is about twice as intense as the higher frequency band, just as in triphenylacetic acid. There is, then, a close relation between the frequency of the carbonyl stretching vibration and splitting of the C-H bending vibration, indicating that the carbonyl group is concerned with the forces responsible for the splitting of the C-H bending vibration. This data is relatively easy to interpret on the basis of the hydrogen bond hypothesis, but would probably be more difficult to explain in any other way.

Besides oxygen, other electronegative atoms, such as fluorine and chlorine, can also act as acceptor atoms in the formation of hydrogen bonds. A hydrogen bond may, therefore, be present in compounds such as benzotrifluoride and benzotrichloride in which there is a favorable spatial configuration. The infrared spectra of these compounds indicate that such a bond is formed, though it is not so strong as the bond in benzoic acid or nitrobenzene. The 728 cm^{-1} band of toluene has shifted to 770 cm^{-1} in benzotrifluoride[35] and to 805 cm^{-1} in benzotrichloride. Some of this shift, though perhaps not all, appears to be due to hydrogen bonding. The difference in frequency between benzotrifluoride and benzotrichloride is probably caused by the larger orbitals of chlorine as compared to fluorine, enabling the chlorine atom to form a stronger hydrogen bond.

It should be emphasized that the data discussed here do not provide proof that the proposed hydrogen bond actually exists. The hypothesis merely provides a convenient way of explaining certain band shifts in a simple and consistent manner. A particular weakness of the proposal is that it fails to explain why a methyl group acts as though its mass were about the same as that of lead or bismuth, even though there may be some connection between the apparently large mass of the methyl group and the apparently small masses of nitro and carboxyl groups.

THE C-H STRETCHING VIBRATIONS

If the hydrogen bond proposed as a cause of the changes in the frequency of the out-of-plane hydrogen bending vibrations actually exists, it might have some effect on the C-H stretching vibrations as well. The effect may be a general shift in the frequency of all of the C-H stretching bands or, more likely, some of the bands may shift and others remain at the normal frequencies. In this study no attempt was made to evaluate all of the factors involved in determining the frequencies of the C-H stretching vibrations. Only enough data were collected to determine whether or not the presence of nitro or carboxyl groups would cause any gross changes in the C-H stretching vibrations in aromatic compounds.

It has been known for some time that the frequencies of C-H stretching vibrations near 3000 cm^{-1} are different for aromatic and aliphatic compounds.[36] Thus, the C-H stretching vibrations have been found to be near 2900 cm^{-1} for saturated hydrocarbons, near 3080 cm^{-1} for olefins and aromatic compounds, and near 3300 cm^{-1} for acetylenes. Most of the study of the C-H stretching vibrations has been done on hydrocarbons, so little is known of the effect of various substituents on the frequency and intensity of the C-H stretching vibrations. Fox and Martin[37] noted differences in the spectra of benzene, phenol, and various aromatic alcohols but did not attempt a complete study of the factors causing the differences. Barchewitz and Chabal[38] also noticed differences in the C-H stretching vibrations of monosubstituted benzenes, but did not report any further investigation. They did not report the form of the compound for which the spectra were recorded, whether in solution or as a pure compound, and the frequency values published by them are in poor agreement with the values obtained in this study. In particular, they listed only one frequency for each compound while, in reality, the band structure in this region is quite complex.

Table 3 lists the frequencies of the bands in this region for several monosubstituted benzenes in carbon tetrachloride solution. The spectra were obtained on a Perkin-Elmer Model 112 spectrophotometer using a calcium fluoride prism. The precision of the frequency measurements was somewhat dependent on how well the position of the absorption maximum could be determined in the broader bands, but the probable maximum error in frequency was about 5 cm^{-1}.

The most nearly characteristic feature of the C-H stretching frequencies of these monosubstituted benzenes was a strong band near 3060 cm^{-1}. However, in phenol, fluorobenzene, and phenylboric acid there was no strong absorption band closer to this frequency than 3045 or 3050 cm^{-1}. However, the important fact, from the point of view of this study, was that there was no particular change in this frequency in the case of benzoic acid or nitrobenzene. Thus, there was no general shift of the C-H stretching frequency when a nitro or carboxyl group was attached to the ring. There was another strong band in this region, in the case of nitrobenzene and benzoic acid, that might have been a C-H stretching frequency affected by hydrogen bonding. This band was at 2890 cm^{-1} in benzoic acid and 2865 cm^{-1} in nitrobenzene,

Table 3. Absorption Bands near 3000 cm^{-1} of Some Monosubstituted Benzenes

Compound	Absorption Frequencies (cm^{-1})^{a}				
Benzene		3067			3033
Fluorobenzene				3049	
Chlorobenzene		3065			3024
Bromobenzene		3065			3018, 3007
Iodobenzene			3057		3012, 2997
Tetraphenylmethane	3084	3067			3034
Phenyl Ether			3062		3038
Triphenylstibine			3056		3021, 3004, 2995
Triphenylphosphine			3057		3016, 3006
Diphenylmercury	3081	3069			3034
Triphenylsilane			3057		3015
Benzonitrile			3061		3033
Phenol	3081			3046	
Benzotrichloride			3062		3033
Benzoic Anhydride		3067		3049	3038
Benzoic Acid		3067			3017, 2967, 2890
Nitrobenzene		3070			3035, 2925, 2865
Phenylboric Acid				3045	3033

[a] Strong bands are underlined.

and it was nearly as strong as the band near 3060 cm^{-1} in both cases. Bands near 2870 cm^{-1} are more nearly typical of aliphatic than of aromatic compounds.

In order to determine whether the band at 2865 cm^{-1} was due to a C-H stretching vibration, deuterated nitrobenzene was prepared. Nitrobenzene was chosen rather than benzoic acid because it would be somewhat easier to prepare and because the absorption bands of nitrobenzene in this region were sharper than those of benzoic acid, which overlapped considerably even in solution. Deuterated benzene was prepared by the exchange between D_2SO_4 and benzene.[39] Sulfur trioxide was prepared by distillation from fuming sulfuric acid and was collected in a flask cooled in an ice bath. Heavy water was added to this to prepare heavy sulfuric acid, and the concentration of this acid was checked by density measurements. About 50 mole per cent D_2SO_4 was mixed with a small quantity of benzene and allowed to stand several days, the process being repeated three times. This gave a small quantity of partially deuterated benzene, the ratio of hydrogen to deuterium being about 3:1, based on the infrared spectrum. This benzene was nitrated according to the method of Fieser.[40] It has been shown[41] that in this procedure there will be only a negligible loss of deuterium through exchange and that there is no preferential replacement of either hydrogen or deuterium by the nitro group. Approximately 150 mg. of partially deuterated nitrobenzene was obtained by this method, in fractions of 100 and 50 mg. each. The larger fraction was dissolved in 1 ml. of carbon tetrachloride and its spectrum recorded with the Baird infrared spectrophotometer and with the Perkin-Elmer

Model 112 spectrophotometer, using a 0.8 mm. cell. These spectra were compared with those of a sample of normal nitrobenzene recorded under the same conditions.

As would be expected, the band at 3067 cm^{-1} decreased in intensity in proportion to the amount of hydrogen replaced by deuterium, and a new band appeared at 2299 cm^{-1}. The band at 2865 cm^{-1} did not decrease in intensity correspondingly, there being only a slight change in intensity that could be ascribed to errors in weighing the sample, adding the solvent, and measuring the transmittancy. This demonstrated that the band at 2865 cm^{-1} is not caused by a vibration involving the hydrogen atoms, but rather appears to be an overtone of the N-O stretching vibration at about 1530 cm^{-1}. The band at 2890 cm^{-1} in benzoic acid is, similarly, probably an overtone of the carbonyl stretching vibration.

There are some weaker bands in the spectrum of nitrobenzene in this region that did decrease in intensity in the partially deuterated compound. One is at 3035 cm^{-1} in nitrobenzene and it corresponds to a band at 2277 cm^{-1} in the deuterated compound. This is a normal C-H stretching vibration, analogous to the band at 3033 cm^{-1} in benzene. Another band appears at 2925 cm^{-1} in nitrobenzene and it also became less intense in the deuterated compound. However, its intensity is only about one fourth of that of the band at 3070 cm^{-1}, and no C-D stretching vibration was found that would correspond to it in the deuterated compound. It is apparently not a C-H stretching absorption band, but some combination or overtone frequency. No other bands appear at a frequency high enough to be caused by C-H stretching vibrations.

The above data indicate that C-H stretching vibrations are not affected by nitro and carboxyl groups in the way that a hydrogen bond would normally be expected to affect them. As will be discussed in the following section, the in-plane hydrogen bending vibrations are also unaffected by the presence of nitro and carboxyl groups. Thus, aside from the disturbance of the out-of-plane vibrations, there is no indication of the presence of a hydrogen bond between nitro or carboxyl groups and hydrogen atoms on the benzene ring. The fact that the in-plane bending and the stretching vibrations do not shift in the presence of nitro or carboxyl groups is not inconsistent, however, with the hydrogen bond proposed here, as will be discussed in the section on the in-plane bending vibrations.

IN-PLANE VIBRATIONS OF THE HYDROGEN ATOMS

In the region between 8.5 and 10.5 microns, particularly from 9 to 10 microns, there are usually several moderately strong, sharp absorption bands in the spectra of aromatic compounds. Pitzer and Scott[10] have assigned the vibrations at 1030 and 1070 cm^{-1} (9.71 and 9.35 microns) in toluene to vibrations of the hydrogen atoms in the plane of the ring. Cole and Thompson[14] assigned a band at 1065 cm^{-1} in monosubstituted benzenes to an out-of-plane vibration, but their calculations were based on the assumption that the vibration would be out-of-plane. In addition, as is shown below, these bands were not found to be affected by changes in the substituent in the same way as were the out-of-plane vibrations between 11 and 15 microns. The assignments made by Pitzer and Scott are, thus, more likely to be correct.

The present study has shown that these bands occur at frequencies characteristic of the element attached to the benzene ring in monosubstituted benzenes and that they are useful for the identification of groups such as phenyl-silicon, phenyl-tin, etc. Table 4 lists the frequencies and relative intensities of the bands in this region for monosubstituted benzenes with a number of different substituent atoms. Most of the listings are averages based on several compounds with phenyl groups attached to the particular element, though some are based on single compounds. These bands are relatively insensitive to changes in the molecule, provided that the element attached to the ring is not changed. In the 11 to 15 micron region toluene and benzoic acid have

Table 4. Band Frequencies near 1000 cm^{-1} for Monosubstituted Benzenes with Various Substituent Elements

Substituent Elements	Absorption Bands*
Nitrogen	1029 (w), 1070 (w)
Carbon	1000 (w), 1030 (m), 1075 (m) (these intensities vary widely)
Oxygen	1023 (m), 1073 (m)
Halogens	1000 (m), 1020 (s), 1070 (s)
Sulfur	997 (m), 1022 (m), 1070 (m)
Phosphorus	1024 (m), 1090 (s)
Arsenic	1025 (m), 1075 (m)
Antimony	996 (m), 1018 (w), 1067 (m)
Bismuth	990 (s), 1010 (w), 1050 (w)
Silicon	998 (w), 1030 (w), 1110 (s)
Germanium	997 (w), 1025 (w), 1090 (s)
Tin	997 (m), 1022 (w), 1075 (s)
Lead	995 (s), 1015 (m), 1056 (w)
Mercury	997 (m), 1018 (m), 1064 (w)

*(s) = strong, (m) = moderate, (w) = weak.

quite different band structures, but in the 8.5 to 10.5 micron region the spectra of the two compounds are nearly superimposable. The same is true for nitrobenzene, tetraphenylhydrazine, and aniline.

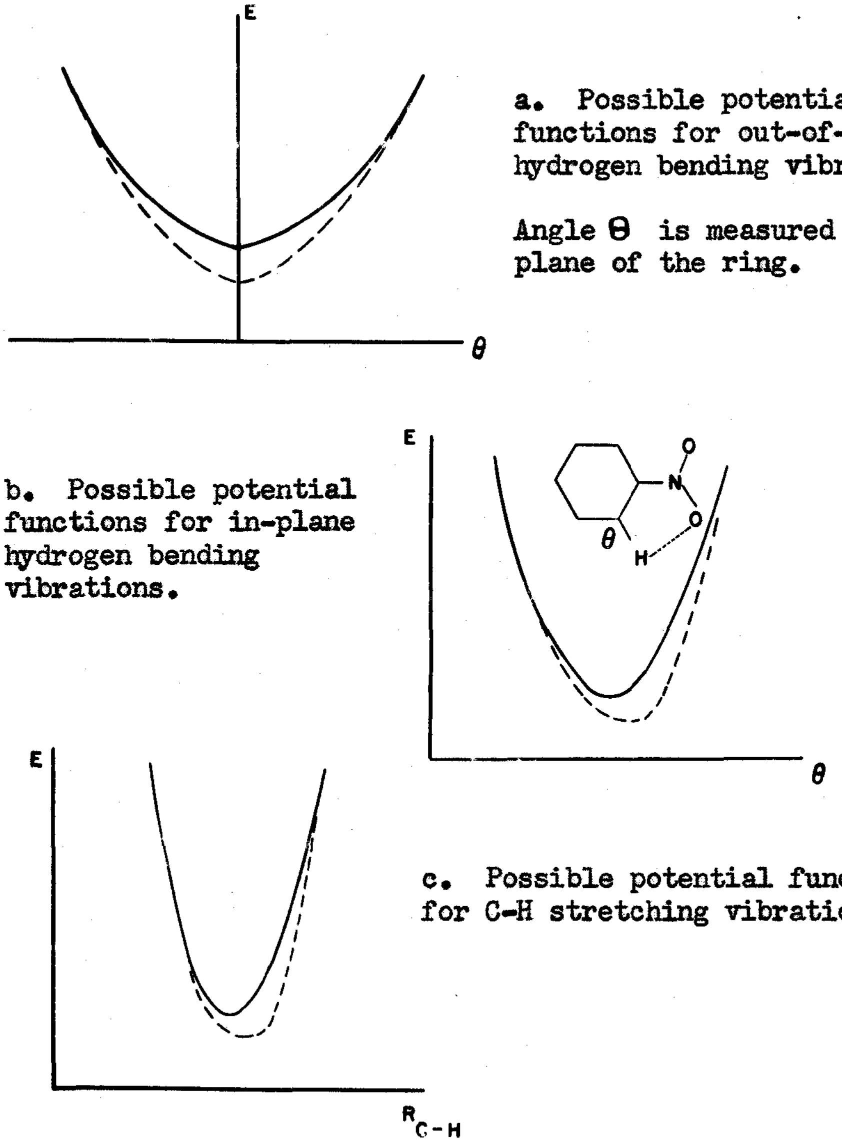
The band pattern is often closely similar for several different elements attached to a phenyl group. There does not seem to be any systematic variation along the rows or columns of the periodic table, although certain similarities can be found. While phenyl groups attached to silicon, germanium, or tin have similar band patterns, phenyl groups attached to carbon or lead have different band patterns than phenyl groups attached to one of the first three elements mentioned. Similarly, if the substituent atom is carbon, nitrogen, or oxygen, the band patterns are similar, but fluorobenzene has a different pattern. All of the halobenzenes have about the same band pattern in this region.

Some other groups have strong absorption bands in this region, occasionally interfering with the bands of the phenyl group. The groups that cause the most serious interference are the Si-O group of siloxanes and the sulfoxide group. Because of the possibility of interference from other groups, it is often better to look for the absence of a band rather than its presence as an indication of the structure of the compound.

As was mentioned in the previous section, the failure of the C-H stretching and in-plane bending vibrations to change measurably in frequency in the presence of a nitro or carboxyl group does not disprove the hydrogen bond hypothesis used to explain the shifts of the out-of-plane C-H bending vibrations. In order to understand why this is so, it will be necessary to consider the potential functions for the three vibrations with normal substituents and with hydrogen bonding substituents as shown in Figures 11a, b, and c. In these diagrams the C-H group adjacent to the substituent is considered separately, but closely similar potential functions would apply to the molecule as a whole.

Figure 11a shows a possible potential function for the out-of-plane vibration. The solid line is the potential function when the substituent is a halogen or some other non-hydrogen bonding substituent; the dotted line is the potential function when there is a hydrogen bond. In the presence of a nitro or carboxyl group the C-H group will be stabilized with the hydrogen atom in the plane of the ring, with more energy required for motion out of the plane of the ring than if there were no hydrogen bond. When the hydrogen atom moves far enough out of the plane of the ring, the hydrogen bond becomes very weak, and the two potential functions merge. The effect of the hydrogen bond on the out-of-plane vibrations is thus to increase the slope of the potential function at the equilibrium internuclear distance, increasing the spacing between the vibrational energy levels and causing the absorption bands to occur at higher frequencies, in agreement with the observed frequency changes.

The situation is different for the in-plane bending vibrations. Figure 11b shows the possible shape of the potential function for this type of vibration for the case of no hydrogen bond (solid line) and a hydrogen bond of the type proposed (dashed line). Because of the hydrogen bond, the hydrogen atom is probably moved slightly from its normal position toward the oxygen atom of the nitro or carboxyl group.



a. Possible potential functions for out-of-plane hydrogen bending vibrations.

Angle θ is measured from plane of the ring.

b. Possible potential functions for in-plane hydrogen bending vibrations.

c. Possible potential functions for C-H stretching vibrations.

Figure 11. Possible potential functions for some vibrations of substituted benzenes. The solid line is for the case of no hydrogen bond; the dotted line, for the case of a hydrogen bond involving the ring hydrogen atoms.

For very large distances from the oxygen atom the two potential functions again merge. The net effect is to displace the equilibrium internuclear distance, effecting only a slight change in the shape of the potential function. The in-plane bending vibrations should then move only slightly to lower frequency.

Figure 11c shows the shape of the potential function for the C-H stretching vibrations with and without a hydrogen bond. The equilibrium internuclear distance would be increased slightly by the hydrogen bond and the two potential functions would merge as the hydrogen atom moved away from the oxygen atom. As in the in-plane bending vibrations, the effect would be only a very slight change in the absorption frequencies, perhaps too slight to measure.

Although study of the in-plane bending and stretching vibrations fails to provide confirmation of the hydrogen bond hypothesis, neither is the hypothesis disproved. All of the observations can be adequately explained by the proposed hydrogen bond, and there is no evidence available to disprove its existence conclusively.

FUNCTIONAL GROUP ANALYSIS OF ARYLSILANES

The recent preparation by Gilman and Wu[42] of a series of hexa-aryldisilanes containing phenyl and para-tolyl groups made necessary the development of some method of checking the structures of these compounds. The similar tetra-arylsilanes were also available. All para-tolylsilanes have an absorption band at 12.5 microns and all phenylsilanes absorb at 13.5 and 14.3 microns, with little variation in wavelength. The relative intensities of the bands due to phenyl and para-tolyl groups were observed to vary in proportion to the relative concentrations of the two groups. Various investigators have found that the intensity of an absorption band is often directly proportional to the concentration of the group responsible for the band, and this proportionality has been used for the determination of the concentrations of various functional groups. Integrated intensities over the entire absorption band must often be used; but if the shape of the absorption band does not vary too widely, it is possible to use the more simple technique of measuring only the peak intensity. For example, a recent study by Jones and others[43] of the carbonyl stretching bands in steroids has shown that the integrated intensity is characteristic of the particular type of carbonyl group involved (ketone, acid, etc.) and that the peak intensity is sometimes also related to the group concentration. Intensities are more sensitive than frequencies to variations in the structure of the molecule, but this can be satisfactorily taken into account.

In devising a functional group analysis for the arylsilanes, an attempt was made to relate the relative numbers of para-tolyl and phenyl groups to the ratio of the intensities of the 12.5 micron band to the 13.5 micron and 14.3 micron bands. In both cases there was some correlation between the intensity ratio and the ratio of group concentrations, but with considerable scattering of the points. Considerable success was attained by using the sum of the peak intensities of the 13.5 and 14.3 micron bands, rather than the individual peak intensities, and plotting the ratio of this sum to the peak intensity of the 12.5 micron band against the ratio of phenyl to para-tolyl groups in the sample. The analytical curve is shown in Figure 12.

The method of sample preparation simply involved dissolution of a small amount of the sample in carbon disulfide, the amount of sample being adjusted if necessary so that the peak transmission of the strongest band of the three used was about 20 per cent. Since this was an internal standard method, it was not necessary to weigh the sample. A 0.4 mm. cell was used. The peak value of T_o/T was determined for each of the bands at 12.5, 13.5 and 14.3 microns, and the ratio of the sum of the intensities of the 13.5 and 14.3 micron bands to the intensity of the 12.5 micron band plotted against the ratio of phenyl to para-tolyl groups in the compound. The compounds represented in Figure 12 include all possible tetra-arylsilanes and hexa-aryldisilanes with phenyl and para-tolyl groups as substituents. They are triphenyl-p-tolylsilane, diphenyldi-p-tolylsilane, phenyltri-p-tolylsilane, pentaphenyl-p-tolyldisilane, tetraphenyl-1,1-di-p-tolyldisilane, tetraphenyl-1,2-di-p-tolyldisilane, 1,1,1-triphenyltri-p-tolyldisilane, 1,1,2-triphenyltri-p-tolyldisilane, 1,1-diphenyltetra-p-tolyldisilane, 1,2-diphenyltetra-p-tolyldisilane, and phenylpenta-p-tolyldisilane,

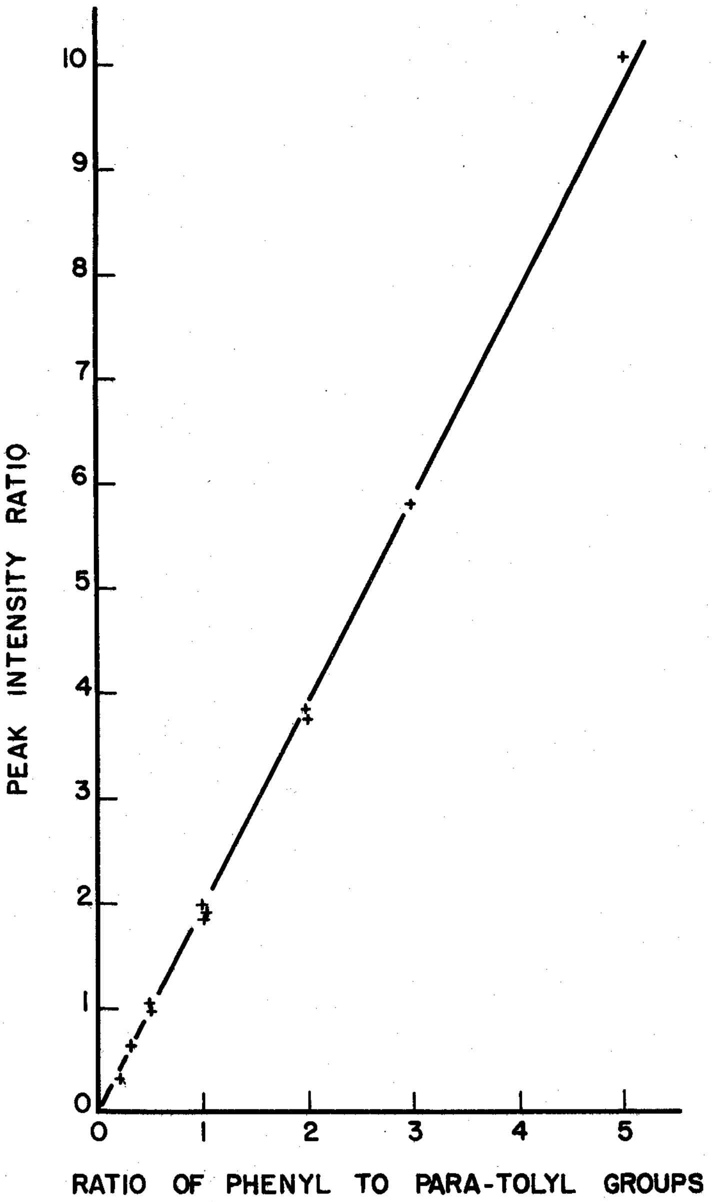


Figure 12. Analytical curve for functional group analysis of tetra-arylsilanes and hexa-aryldisilanes containing phenyl and para-tolyl groups.

eleven compounds in all. The points in Figure 12 lie almost exactly on a straight line passing through the origin, indicating that the precision of this method of functional group analysis is limited only by the errors in determining the peak absorption intensities.

In order to determine the effect of other groups on this functional group analysis, the spectra of diphenyl-p-tolylchlorosilane and phenyldi-p-tolylchlorosilane were measured in carbon disulfide solution. The three peak intensities were measured as before and the intensity ratio calculated. For both compounds the points fell considerably below the straight line of Figure 12; but if the two points were connected by a straight line, the extension of the line passed through the origin. Thus, a different analytical curve must be used if even this slight change in molecular structure is made.

The fact that the sum of two band intensities must be used for the phenyl group, rather than the intensity of a particular band, can be understood from the fact that both vibrations are in the same symmetry class,[10] so that there is probably some resonance, or coupling, between the vibrations. Since this type of interaction involves mixing of the wave functions corresponding to the two excited states, and since these wave functions determine the intensities of the bands, it is natural that there is some mixing of intensity of the two bands. No other example is known of the use of a sum of two band intensities in a functional group analysis, though this technique would seem to be applicable to other groups as well, particularly methyl and methylene groups where the C-H stretching vibrations are split by coupling.

THE REGION FROM 15 TO 26 MICRONS

Aside from the study of some individual molecules, very little has been done to correlate the structure of aromatic compounds with their spectra between 15 and 26 microns. Plyler[11] has studied the spectra of twelve substituted benzenes between 15 and 40 microns, assigning frequencies to the various vibrations largely on the basis of the work of Pitzer and Scott,[10] on the methyl benzenes. Plyler noted that there was at least one band in this region that shifted regularly with change of mass of the substituent for the series of halobenzenes and that toluene could be included in the series if the methyl group were assigned a mass slightly less than that of fluorine. The present study has confirmed and extended Plyler's observation.

The relative simplicity of the spectra in this region, compared to the usual complexity of the 2 to 15 micron region, suggests that interpretation of the spectra should be comparatively simple if the proper correlations can be established. A special advantage is that few groups absorb in this region of the spectrum; in particular, aliphatic groups do not seem to have any strong absorption bands in this region. Especially in the silanes, aliphatic groups obscure the characteristic bands of the aromatic groups in the 675 to 900 cm^{-1} region.

Many aromatic compounds have only one strong absorption band in this region, though some have two or three, the exact number of bands and their exact frequencies often changing from the solid or pure liquid to a solution. The frequency of the band is sensitive to the mass of the atom or atoms attached to the ring, with some variation for various groups having the same atom attached to the ring. For monosubstituted benzenes in which the substituent atom is carbon the variation is fairly large, ranging from 493 cm^{-1} for triphenylmethane to 583 cm^{-1} for triphenylcarbinol. For heavier substituent atoms the variation is less. The intensities of the band or bands also vary, but they are usually fairly strong and rather broad.

The compounds in the series tetraphenylmethane, tetraphenylsilane, tetraphenylgermane, tetraphenylstannane, and tetraphenylplumbane all have similar spectra. In the form of mineral oil slurries, these compounds have two bands in this region, quite close together, with the splitting decreasing as the mass of the central atom increases. In carbon disulfide the two bands either come closer together or merge completely. The same shift to lower frequency with increasing mass of the substituent atom as was observed by Plyler[11] for the halobenzenes is evident in these compounds. Plyler has assigned this absorption band in the halobenzenes to the vibration designated as 6A by Pitzer and Scott.[10] This vibration involves compression of the ends of the ring, with the atoms on the side of the ring moving outward in the plane of the ring. Table 5 lists the frequency of this vibration in a few monosubstituted benzenes. Plyler's data is for the liquid, the rest is for carbon disulfide solutions unless otherwise stated. The difference in frequency for the same compound in the solid state or carbon disulfide solution is only a few wave numbers. The variation of frequency with mass of the substituent atom can be seen clearly from this data.

Table 5. Frequency of the 6A Vibration in Monosubstituted Benzenes

Compound	Frequency
Nitrobenzene	532 (liquid)
Toluene	521[a]
Triphenylcarbinol	583
Triphenylmethane	493
Triphenylmethylchloride	506
Benzoic Acid	552 (mineral oil slurry)
Fluorobenzene	519[a]
Tetraphenylsilane	512
Triphenylsilanol	508
Chlorobenzene	467[a]
Tetraphenylgermane	475, 465
Hexaphenyldigermane	461
Bromobenzene	458[a]
Tetraphenylstannane	446
Hexaphenyldistannane	445
Iodobenzene	448[a]
Tetraphenylplumbane	440
Hexaphenyldiplumbane	439

[a] Data of E. K. Plyler, Disc. Faraday Soc. 9, 100 (1950).

Considerably less information is available on the spectra of para-disubstituted benzenes in this region, but the little that is available indicates that structure-spectra correlations should not be too difficult to establish. Tetra-p-tolylsilane has a strong band at 509 cm^{-1} and a moderately strong doublet at 630 and 636 cm^{-1}; tetra-p-tolylstannane has a similar spectrum with a strong band at 484 cm^{-1} and a moderately strong band at 580 cm^{-1}. The similarity between the spectra of the two compounds is striking and the change in band frequency with the mass of the substituent atom is the same as for the monosubstituted benzenes. The spectra of hexa-p-tolyldisilane and hexa-p-tolyldisiloxane are similar to the spectrum of tetra-p-tolylsilane, and in a series of tetra-arylsilanes and hexa-arldisilanes containing both phenyl and p-tolyl groups the bands characteristic of both aromatic groups are present and readily recognised.

The nature of the vibrations responsible for the absorption bands in para-disubstituted benzenes cannot be stated with any degree of certainty. In p-xylene the bands are at 483 and 645 cm^{-1} and have been assigned [10, 11] to the 6A and 6B vibrations, respectively. The form of the 6A vibration is described above, and the 6B vibration also involves compression of the ends of the ring but with a slightly different motion of the carbon atoms on the side of the ring than in the 6A vibration. If the assignment of the bands is correct, the 6A vibration must act differently as the mass of the substituents changes in the para-disubstituted benzenes than in the monosubstituted benzenes. In the monosubstituted benzenes this vibration shifts regularly to lower frequency with increasing mass of the substituent atom, with the methyl group acting normally for its mass. However, in the para-disubstituted benzenes it would appear that the normal shift to lower frequency with increasing mass is observed for the p-tolylsilanes and stannanes, but that in p-xylene the methyl group acts as a heavy atom.

Interpretation of the spectra of the disubstituted benzenes is, of course, more difficult than for the monosubstituted benzenes because the effect of both substituents must be taken into account. Not enough data have been collected to enable making the necessary correlations, but the data discussed here for the para-disubstituted benzenes are sufficient to indicate that a search for such correlations would be productive.

The similarity between the spectra of tetra-p-tolylsilane and tetra-p-tolylstannane is not repeated in the ortho-tolyl compounds. While all the ortho-tolylsilanes studied (tri-o-tolylchlorosilane, tri-o-tolylphenylsilane, and tetra-o-tolylsilane) have a number of strong, sharp bands between 465 and 570 cm^{-1}, the tin compounds (tri-o-tolylchlorostannane and hexa-o-tolyldistannane) have one and two (respectively) rather weak bands in this region and a moderately strong band at about 435 cm^{-1}. In compounds of this type the steric interaction between the several aromatic groups is considerable and depends somewhat upon the size of the central atom. This steric effect, which is much less important in the monosubstituted and para-disubstituted benzenes, may be sufficient to account for the lack of similarity between the spectra of the o-tolylsilanes and stannanes. All of the o-tolylsilanes studied have nearly the same band structure in this region, so it would be possible to recognize the presence of this group.

However, the considerably steric effects make it likely that no simple structure-spectra correlations will be found in this region for the ortho-disubstituted benzenes.

Not enough data have been collected on meta-disubstituted benzenes or trisubstituted benzenes to make a discussion of their spectra worthwhile.

LOW TEMPERATURE STUDIES: ROTATIONAL ISOMERISM

Study of the vibrational spectra of molecules can give evidence concerning rotational isomerism.[44] The various possible rotational forms of a molecule have differing symmetries, so that the selection rules determining which bands will appear in the infrared and the Raman spectra are different. The force constants may also be changed slightly by rotation of one part of the molecule with respect to the rest, so that a particular vibration may occur at slightly different frequencies in the different forms. Since there is a difference in energy of the two forms, the amount of each form present in an equilibrium mixture will be temperature dependent and the absorption intensity of the bands in the spectrum will vary with temperature. When there is a phase change, as in melting, the concentrations of the different forms may change radically; there may even be complete disappearance of one of the isomers and, correspondingly, disappearance of some of the absorption bands.

Two molecules with possible rotational isomerism were chosen for study because in each case one of the forms would have an electronegative atom close to a ring hydrogen atom and the other would not. These compounds were phenyl acetate and benzyl chloride. The compounds were studied as capillary films in the liquid and solid states, using a low temperature cell designed by the late M. Parasol of the x-ray group at Iowa State College. The cell consisted of a brass jacket, designed to replace the cell holder of the Baird Associates spectrophotometer, with salt windows for the radiation to enter and leave, and a cell holder that fit tightly to the top of the jacket so that the jacket could be evacuated for insulation. The cell holder was constructed of brass tubing through which nitrogen vapor was passed for cooling, the sample being contained between silver chloride plates that fit snugly in the cell holder. The nitrogen vapor was obtained by boiling liquid nitrogen in a Dewar flask and was passed into the cell through the inner tube of a double-walled tubing, the space between the walls being evacuated for insulation. The temperature of the sample was measured by a thermocouple in contact with one of the silver chloride plates of the cell and could be controlled within 2 or 3 degrees Centigrade by varying the rate of boiling of the liquid nitrogen by means of a heating coil controlled by an auto-transformer (Variac). This low temperature cell made possible the production and maintenance of any temperature from room temperature to approximately 100° K, though some difficulty was encountered at the lowest temperature range from formation of frost on the windows.

Phenyl Acetate

The melting point of phenyl acetate has apparently never been reported in the literature. The compound was found to supercool readily if cooled quickly, eventually forming a glass. By slow cooling, it could be frozen into crystals that melted at -9.5° C. Aside from a general sharpening of the bands and some rather small band shifts, there was no change in the spectrum on passing from the liquid to the solid state. Either phenyl acetate exists in only one of the possible rotational forms, or else the concentration of the two forms is not affected by the phase change. This is in agreement with the observed dipole moment of phenyl acetate, which is somewhat smaller than that of ethyl acetate. Edgerley and Sutton[45] have interpreted this to mean that the carbonyl group is not in the plane of the ring, so there is no interaction between the carbonyl group and the benzene ring. Apparently, phenyl acetate exists only in the non-planar form.

Benzyl Chloride

Unlike phenyl acetate, benzyl chloride showed marked differences between the spectra of the liquid and solid forms. The same general sharpening and slight shifts of absorption bands were observed and, in addition, several bands decreased considerably in intensity in the solid as compared to the liquid. The most likely reason for the weakening of some absorption bands in a phase change is the decrease in concentration of one form of the compound. Particular attention was paid to changes in the region from 12 to 14 microns, since it was felt that it might be possible to determine from a study of this region which form of the compound persisted in the solid state.

Liquid benzyl chloride, at room temperature, has a moderately strong absorption band at 768 cm^{-1}, a weak band at 802 cm^{-1}, and another moderately strong band at 815 cm^{-1}. In the solid, at -56° C. (melting point is -48° C.) the first band remains moderately strong and is shifted slightly to 773 cm^{-1}, the second remains weak and is at 807 cm^{-1}, while the third band becomes very weak and is at 817 cm^{-1}. It appears reasonable to interpret the data as indicating that the form of the compound in which the halogen atom is out of the plane of the ring is responsible for the band at 768 cm^{-1} in the liquid, and the band at 815 cm^{-1} in the liquid is from the form in which the halogen atom is in the plane of the ring and is perturbing the C-H bending vibrations. The form in which the halogen atom is out of the plane of the ring is then the more stable, since it is the one that persists at low temperature. Because of the difficulty with formation of frost on the windows, it was not possible to study the effect of cooling the sample further in order to determine whether the band at 817 cm^{-1} would finally disappear completely.

SUGGESTIONS FOR FURTHER STUDY

Throughout the body of this dissertation some suggestions have been made for further work. In this section, some of these will be repeated in order to collect them in one place, and some further suggestions will be made.

In the 11.5 to 14.5 micron region, it should be possible to improve on the correlation between the nature of the substituent groups and the frequency of various vibrations presented in Table 1 and Figures 2, 3, 4, 5, and 6. In particular, it should be possible to correct for the effect of neighboring molecules on the frequencies of the various absorption bands. If all of the spectra could be obtained for the vapor state at a reasonably low pressure, the effect of neighboring molecules would be eliminated, but many of the compounds have too low a vapor pressure to permit the observation of vapor phase spectra. The most fruitful line of attack would probably be to find some correction for the effect of the solvent, as previously suggested.

A further study of the band near 13 microns in para-disubstituted and 1,2,4-trisubstituted benzenes with a nitro or carboxyl group as one of the substituents might show the nature of the vibration responsible for this band. A normal coordinate treatment would be invaluable, but would probably be quite difficult because of the complexity of the spectra. Study of the spectra of single crystals with polarized light would at least show the direction of change of dipole moment in the vibration and would provide information that might make a normal coordinate treatment possible. The only data available on this point[27] indicate that the change of dipole moment in this vibration is in the same direction as in the out-of-plane hydrogen bending vibration.

Study of the spectra of such compounds as triphenylsilyltriphenylstannane indicates that as the mass of the substituent atom increases, the intensity of the band between 725 and 775 cm^{-1} in monosubstituted benzenes increases. Further study of this phenomenon may yield useful information.

Little is known of the effect of substituent groups on the frequency and intensity of the C-H stretching vibrations near 3070 cm^{-1}. A rather rough preliminary study of benzene, nitrobenzene, and aniline has indicated that the peak intensity in this region is proportional to the number of hydrogen atoms attached to the benzene ring, but further study is necessary to establish this. If it is true, it would be possible to perform functional group analyses using this band with greater confidence. It should also be possible to relate the frequency changes that occur in these compounds to the nature of the substituent groups, though the work that has been done so far does not point to any simple relationship. Possible solvent effects must be taken into account.

In the region between 15 and 26 microns, further study of the relation between mass of the substituents and frequency of the absorption bands would be worth while. The data presented here on the monosubstituted and para-disubstituted benzenes suggest that it should be possible to establish such relationships empirically. This data would be valuable in the determination of molecular structure by infrared spectroscopy because of the relatively few groups that absorb in this region.

Similarly, it may be possible to establish relations between substituent atoms and absorption frequency in the 9.5 to 10.5 micron region for disubstituted benzenes, as has been done for the monosubstituted benzenes. A complicating factor in studying these bands is interference from absorption bands of some substituent groups.

An extension of the functional group analysis of tetra-arylsilanes and hexa-aryldisilanes containing phenyl and p-tolyl groups to other compounds should be possible. The corresponding carbon compounds are not stable because of dissociation into free radicals and the corresponding compounds of germanium, tin, and lead have not yet been prepared. When these latter compounds are available, however, the method should be tested. It is possible that the same analytical curve could be used for the germanium, tin, and lead compounds as for the silanes.

LITERATURE CITED

1. Kent, J. W. and J. Y. Beach, Ind. Eng. Chem., Anal. Ed. 19, 290 (1947).

2. Badger, R. M., J. Chem. Phys. 2, 128 (1934), 3, 710 (1935).

3. Thompson, H. W., J. Chem. Soc. (London) 328 (1948).

4. Barnes, R. B., R. C. Gore, R. W. Stafford, and V. Z. Williams, Anal. Chem. 20, 402 (1948).

5. Randall, H. M., R. G. Fowler, N. Fuson, and J. R. Dangl, Infrared Determination of Organic Structures, D. Van Nostrand Co., New York, 1949.

6. Colthup, N. B., J. Opt. Soc. Am. 40, 397 (1950).

7. Ingold, C. K. and others, J. Chem. Soc. (London) 912-1210 (1936), 222-333 (1946).

8. Miller, F. A. and B. Crawford, J. Chem. Phys. 14, 282, 292 (1946).

9. Crawford, B. and R. G. Parr, J. Chem. Phys. 17, 726 (1949).

10. Pitzer, K. S. and D. W. Scott, J. Am. Chem. Soc. 65, 803 (1943).

11. Plyler, E. K., Disc. Faraday Soc. 9, 100 (1950).

12. Depaigne-Delay, A. and J. Lecomte, J. physique rad., Series 8, 7, 38 (1946).

13. Bell, R. P., H. W. Thompson, and E. E. Vago, Proc. Royal Soc. London, A192, 498 (1948).

14. Cole, A. R. H. and H. W. Thompson, Trans. Faraday Soc. 46, 103 (1950).

15. McMurry, H. L. and V. Thornton, Anal. Chem. 24, 318 (1952).

16. Cannon, C. G. and G. B. B. M. Sutherland, Spec. Acta 4, 373 (1951).

17. Barnes, R. B., U. Liddell, and V. Z. Williams, Ind. Eng. Chem., Anal. Ed. 15, 659 (1943).

18. Baird, W. S., H. M. O'Bryan, G. Ogden, and D. Lee, J. Opt. Soc. Am. 37, 754 (1947).

19. Plyler, E. K. and C. W. Peters, J. Res. Nat'l. Bur. Stds. 45, 462 (1950).

20. Whiffen, D. H. and H. W. Thompson, J. Chem. Soc. (London) 268 (1945).

21. Thompson, H. W. and P. Torkington, Trans. Faraday Soc. 41, 246 (1945).

22. Crawford, B., Sci. Am. 189, No. 4, 42 (Oct., 1953).

23. Flett, M. St. C., J. Chem. Soc. (London) 962 (1951).

24. Tiers, G. V. D. and J. H. Tiers, J. Chem. Phys. 20, 761 (1952).

25. Bomstein, J., Anal. Chem. 25, 513 (1953).

26. Kirkwood, J. G., quoted by L. H. Jones and R. M. Badger, J. Am. Chem. Soc. 73, 3132 (1951).

27. Mann, J. and H. W. Thompson, Proc. Royal Soc. London A211, 168 (1952).

28. American Petroleum Institute Research Project 44, Carnegie Institute of Technology. Catalog of Infrared Spectral Data. Serial No. 1208.

29. Bailey, M. Acta Cryst. 2, 120 (1949).

30. Coggeshall, N. D., J. Chem. Phys. 18, 978 (1950).

31. Abrahams, S. C. Acta Cryst. 3, 194 (1950).

32. Mathieson, A. McL. and J. M. Robertson, J. Chem. Soc. (London) 724 (1949).

33. Francel, R. J., J. Am. Chem. Soc. 74, 1265 (1952).

34. Cochran, W., Acta Cryst. 6, 260 (1953).

35. American Petroleum Institute Research Project 44. Carnegie Institute of Technology. Catalog of Infrared Spectral Data. Serial No. 1026.

36. Bonino, G. B., Trans. Faraday Soc. 25, 876 (1929).

37. Fox, J. J. and A. E. Martin, Proc. Royal Soc. London A162, 419 (1937).

38. Barchewitz, P. and R. Chabbal, J. physique rad. 12, 637 (1951).

39. Ingold, C. K., C. G. Raisin, and C. L. Wilson, J. Chem. Soc. (London) 915 (1936).

40. Fieser, L. F., Experiments in Organic Chemistry, 2nd. Edition, D. C. Heath and Co., Boston, 1941. Pg. 144.

41. Lauer, W. M. and W. E. Noland, J. Am. Chem. Soc. 75, 3689 (1953).

42. Gilman, H. and T. C. Wu, J. Am. Chem. Soc. 75, 3762 (1953).

43. Jones, R. N., D. A. Ramsey, D. S. Kier, and K. Dobriner, J. Am. Chem. Soc. 74, 80 (1952).

44. Brown, J. K. and N. Sheppard, Disc. Faraday Soc. 9, 144 (1950).

45. Edgerley, P. G. and L. E. Sutton, J. Chem. Soc. (London) 1069 (1951).

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