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THE INFRARED SPECTRA OF PRIMARY AROMATIC AMIDES

by

Edward Leroy Farquhar

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DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1962

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INTRODUCTION

The infrared absorption spectrum of any organic molecule is as distinctive and unique as a fingerprint. Since the observed set of absorption bands are, in essence, a display of some of the resonant vibrational frequencies of the molecule, the infrared spectrum is directly related to molecular parameters such as bond lengths and angles, bond groups ("functional groups") and molecular symmetry. Thus, an infrared spectrum not only provides information on the identity of "unknown" compounds, but also yields definite data on its molecular structure.

The specific chemical properties of most organic compounds are best described in terms of the functional groups present. For the chemist, it is indeed fortunate that most chemically important functional groups also possess characteristic absorption frequencies. Therefore, certain characteristic absorption bands in an infrared spectrum provide valuable information concerning the chemical nature of the compound. As a first approximation, functional group frequencies persist relatively unchanged even if alterations are made in the rest of the molecule. Thus, the identification of functional groups is based on the occurrence of a band within the specified frequency range while specific information concerning the bonding is obtained from the exact frequency, intensity and shape of the band.

A common technique for studying group frequencies is to search for absorption bands which are common to all spectra containing a particular functional group. In many cases this approach is successful and is certainly valuable in finding the extremes of the region which must be examined in order to determine the presence or absence of a particular group. However, complications may arise when group frequencies overlap. For example, compounds containing a carbonyl and an NH_2 group often show two bands in the 1600 to 1650 cm^{-1} region, consequently it is frequently difficult to make an unequivocal assignment.

Another method of studying group frequencies involves isotopic substitution in the molecules. In this approach, one or more of the atoms in the normal molecule are replaced by an isotope of that atom. This leaves the electronic structure of the bond and its force constant essentially unchanged. However, since the frequency of a vibration is dependent on the mass of the vibrating atoms as well as the force constant of the bond, a frequency shift will be produced. Comparison of the spectra of the normal and isotopic molecules permits identification of the frequencies associated with vibrations involving the substituted atom or atoms. This approach is extremely valuable in distinguishing between vibrations of functional groups that lie in the same frequency region.

Until recently the use of isotopic substitution has been confined largely to the replacement of hydrogen with deuterium atoms. This can be used quite successfully in distinguishing between "hydrogen" vibrations and "heavy atom" vibrations. With the increased availability of isotopes, it is now possible to prepare organic molecules containing isotopes of heavier atoms such as nitrogen and oxygen, and hence permit the identification of vibrations associated with that atom.

Isotopic substitution is especially valuable in studying the infrared spectra of nitrogen containing compounds, as these compounds are often difficult to study in a systematic fashion. The introduction of a nitrogen atom into an organic compound usually involves extensive and often subtle changes in the electronic distribution of the parent molecule. As a consequence, the normal concepts of isolated functional group frequencies may not apply to these compounds. Further complications arise from the tendency of many nitrogen containing compounds to undergo inter- and intramolecular association and to interact with solvents. These molecular interactions often produce pronounced frequency shifts which cause difficulties in correlating the absorptions between spectra run under different conditions.

The tendency for changes in electronic structure and for inter- and intramolecular association is even more pronounced in compounds that have a highly polar group adjacent to the nitrogen atom. Such is the case in primary acid amides, which have a polar carbonyl group adjacent to the nitrogen atom. The picture is even more complex in primary aromatic amides, for in these compounds there is a phenyl group in conjugation with the carbonyl group. Conjugated and polar structures are especially pronounced in compounds of this type, further complicating their infrared spectra. The above considerations make it difficult to determine the nature and frequency of the characteristic amide vibrations.

Although the infrared spectra of primary acid amides have been extensively investigated, most of the studies have been concentrated on primary aliphatic amides. Only a limited amount of work has been done on aromatic amides, especially ring substituted benzamides. Even in the aliphatic amides, all of the amide vibrations have not been identified, and the group of atoms contributing to the vibrations is not known with certainty. The present investigation was undertaken to identify the nature and frequencies of the characteristic amide vibrations in benzamide and ring substituted benzamides. The identification of the amide group frequencies was accomplished by the use of ^{15}N substitution combined with selective deuteration.

THE ORIGIN OF GROUP FREQUENCY SHIFTS AND THEIR SIGNIFICANCE

The concept of group frequencies, generally recognized as an over-simplification, requires that the absorption arising from a specific vibration of a functional group lie within a narrow frequency range. However, its exact position within this range is dependent upon the specific environment of the functional group. For convenience, these environmental factors may be divided into two categories, inter- and intramolecular effects. The intermolecular effects include such things as changes of state, solvent effects and bonding while the intramolecular effects are associated with coupling between vibrations, steric effects and electrical influences of substituent groups.

Rather marked differences are often observed between gaseous, liquid and solid state spectra of a substance. These differences are produced to a large extent by the degree of intermolecular association prevailing in the gaseous, liquid and solid state. In the gaseous phase at low pressures, the vibrating system is relatively free from the influence of other molecules, whereas in the liquid and solid, adjacent molecules have a pronounced effect upon the vibration. Molecular association reduces the electron density and consequently the force constants of the bonds involved. Also, motion perpendicular to the bond is restricted. The result of the above effects is a lowering of stretching frequencies and a corresponding increase in deformation frequencies. Except in the cases where the molecular association occurs through strong hydrogen bonds, the frequency shifts are not large.

Hydrogen bonding, which is a specialized form of molecular association, has been studied in greater detail than any other type, largely because of its repeated occurrence. Hydrogen bonds will be formed only between quite electronegative atoms, for only these will enhance the effective positive charge on the hydrogen atom and account for the increased attraction for the nonmetallic atoms. Practically speaking, reasonably stable bonds are formed only with nitrogen, oxygen, fluorine and perhaps chlorine.

It is seen that the conditions for hydrogen bonding are readily satisfied in such organic molecules as the carboxylic acids and primary acid amides. These compounds can associate intermolecularly via O - H --- O and N - H --- O linkages respectively to form dimers. Because of the changes in vibrational spectra produced by linkages of this sort, hydrogen bonding is of considerable interest to the infrared spectroscopist.

Hydrogen bonding produces a similar but much more pronounced effect upon vibrational frequencies than other types of molecular association. For example, in primary acid amides the free NH stretching vibrations are observed near 3500 and 3400 cm^{-1} and the corresponding hydrogen bonded NH stretching frequencies are found near 3350 and 3180 cm^{-1} (4). A much more pronounced effect is observed in the free and bonded OH stretching frequencies of carboxylic acids. In these compounds, the free OH stretching vibration is observed between 3560 and 3500 cm^{-1} and the bonded frequency is in the 2700-2500 cm^{-1} region (4). The decrease in the C = O stretching frequencies is much less than that observed for the OH and NH stretching vibrations.

In addition to lowering the frequency of the XH stretching vibrations, hydrogen bonding produces a pronounced broadening of these absorptions (31, 36). In general, the effect of hydrogen bonding upon XH deformation modes is not as pronounced. While these absorptions are raised in frequency (usually less than 100 cm^{-1}), no pronounced broadening is observed (31).

The effect of solvents upon infrared spectra has not been thoroughly investigated, nor is the effect completely understood. However, the fact still remains that the transition from one solvent to another is frequently accompanied by frequency shifts. Except in the cases where hydrogen bonds or complex formations are involved, the shifts are usually small and are attributed to changes in the dielectric constant and polarity of the solvents.

Steric and electrical effects also play an important role in the spectra of complex molecules i.e., the exact frequency of a specific functional group is partially determined by its spatial arrangement and inductive, mesomesic and field effects. The above factors do not produce large frequency shifts but are indeed quite significant. For example, they account for the very important differences observed between the carbonyl frequencies in such compounds as ketones and esters.

In addition to the above factors the infrared spectra of complex molecules are further complicated by mixing (coupling) of vibrations. This phenomena results from repulsion of vibrational levels belonging to different group vibrations of nearly the same energy. This repulsion of energy levels increases the frequency of the high energy vibration and lowers the frequency of the low energy component. In addition to having similar energies, the vibrating groups must be physically situated close to each other, have strong forces between them and the vibrations must be in the same symmetry class. While the symmetry requirement is an important restriction in highly symmetrical molecules, for molecules of low symmetry this requirement is easily satisfied. The concept of coupling must always be borne in mind when abnormal group frequencies are encountered.

A well known example of coupling occurs in secondary amides. In these compounds, the amide II and III bands do not arise from simple vibrations but are produced by coupling of the NH deformation and amide skeletal vibrations (14, 15). Nevertheless, these bands are highly characteristic of secondary amides and are extremely valuable for their identification. A similar situation occurs in carboxylic acids in which the C = O stretching and OH deformation modes are coupled (19) but provide useful group frequencies in the constant environment of the RCOOH group. Thus, coupling complicates the nature of the vibrations producing group frequencies but does not limit the use of the latter as an analytical tool in the identification of functional groups.

As mentioned previously, isotopic substitution is quite useful in identifying group frequencies. By analogy, it is also useful in correlating absorptions observed in different environmental conditions, especially when hydrogen bonds are formed or broken, producing large frequency shifts. Whereas correlation of absorptions can be made merely by noting that similar frequency shifts occur, the magnitude of these shifts is useful in interpreting the nature of the vibration.

In order to better understand the information gained from isotopic frequency shifts, it is well to calculate the expected isotopic frequency shift. Assuming that the link, AB, in a molecule behaves as a simple harmonic oscillator (an over-simplification to be sure) the frequency of vibration will be given by the formula

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2}$$

where k is the force constant of the bond and μ the reduced mass of AB. If either A or B is replaced by an isotope, the frequency of vibration becomes

$$\nu_i = \frac{1}{2\pi}\left(\frac{k}{\mu_i}\right)^{1/2}$$

where μ_i is now the reduced mass of the isotopic atom pair. Since the force constant will be essentially unaltered by isotopic substitution, division of the equations gives the relation:

$$\frac{\nu}{\nu_i} = \left(\frac{\mu_i}{\mu}\right)^{1/2}$$

In the present investigation ^{15}N and deuterium substitution are employed to identify the position and nature of the vibrations of the $CONH_2$ group. The substitution of ^{15}N produces only small frequency shifts. For example, the calculated frequency ratio for a C-N vibration is 1.015. The expected ratio for an NH_2 vibration is even less and is usually between 1.002 and 1.004. Because of the smallness of these shifts, the deviations from calculated values are difficult to interpret, but in many cases are useful. Deuterium substitution, on the other hand, produces large frequency shifts i.e., if the hydrogen in a nitrogen-hydrogen group is replaced by deuterium, the ratio of the hydrogen to deuterium frequencies should approximate $(2)^{1/2}$ because $m_D = 2m_H$. In general, if $\frac{\nu}{\nu_i}$ has a value between 1.3 and 1.4, the vibration can be safely assigned to a hydrogen vibration. For values of $\frac{\nu}{\nu_i}$ of less than 1.3, the vibration must involve movement of other atoms and hence arise from coupling of modes.

EXPERIMENTAL

A list of the compounds studied in the present investigation, along with their melting points and methods of preparation, are listed in Table 1. All of the commercial products were recrystallized before use.

Except for the aminobenzamides, all of the ^{15}N derivatives were prepared from the corresponding benzoyl chlorides, following a procedure similar to that of Fones and White (13), the only difference being that the reaction flask was not cooled. Approximately one gram of the benzoyl chloride was reacted with a slight excess of ^{15}N ammonia. Yields between 60 and 70 percent of theoretical were obtained. The source of ^{15}N was ammonium sulfate having an isotopic purity of greater than 95 atom percent. In the cases where the benzoyl chlorides were not commercially available, they were prepared by refluxing the appropriate benzoic acid with an excess of thionyl chloride (5, 27, 28). The excess thionyl chloride was removed by distillation and the benzoyl chloride purified by fractional distillation under reduced pressure. The ^{15}N aminobenzamides were prepared by reducing the corresponding ^{15}N nitrobenzamides with ferrous sulfate in an ammoniacal solution, following the method of Jacobs and Heidelberger (20). Approximately 0.5 gram of the ^{15}N nitrobenzamides were reduced giving yields between 50 and 60 percent of theoretical.

The deuterated benzamides were prepared by direct exchange

Table 1. Methods of preparation and melting points of the compounds that were studied

Compound	m. p. °C	Derivatives prepared ^{15}N	D_2
benzamide[a]	126-127	yes	yes
o-chlorobenzamide[b]	140-142	no	yes
m-chlorobenzamide[b]	133-134	no	no
p-chlorobenzamide[a]	178-179	yes	yes
o-bromobenzamide[a]	155-156	no	yes
m-bromobenzamide[b]	155-156	yes	yes
p-bromobenzamide[c]	189-190	no	yes
o-iodobenzamide[b]	183-184	yes	yes
m-iodobenzamide[b]	186-187	no	yes
p-iodobenzamide[c]	217-218	no	no
o-methylbenzamide[a]	139-140	yes	yes
m-methylbenzamide[d]	96-97	no	yes

---

[a] Commercial product.

[b] These compounds were prepared following the modified method of Fones and White (13).

[c] These compounds were prepared following the method of Kao and Ma (23).

[d] These compounds were prepared from the appropriate benzoic acids by refluxing for a period of two hours with excess thionylchloride. After cooling, the reaction mixture was poured into three times its volume of ice-cold concentrated ammonium hydroxide. The amides were removed by filtration and recrystallized from appropriate solvents before use.

Table 1. (Continued)

Compound	m. p. °C	Derivatives prepared ^{15}N	D_2
p-methylbenzamide[a]	159-160	yes	no
o-nitrobenzamide[d]	174-176	yes	yes
m-nitrobenzamide[d]	142-143	yes	no
p-nitrobenzamide[a]	199-200	yes	yes
o-aminobenzamide[a]	110-112	yes	yes
m-aminobenzamide[e]	113-114	yes	no
p-aminobenzamide[e]	182-183	yes	no

[e] These compounds were prepared following the method of Jacobs and Heidelberger (20).

with D_2O. The samples were treated with a 200 percent excess of D_2O and allowed to equilibrate for a few hours, then dried by lypholization. Four such exchanges were usually sufficient to produce almost complete deuteration. Para-methylbenzamide, m-nitrobenzamide, m-aminobenzamide and p-aminobenzamide were notable exceptions. These compounds were only partially deuterated after eight exchanges with D_2O. The preparations of all deuterated samples were conducted in an atmosphere of dry nitrogen to avoid back exchange with water from the atmosphere.

The infrared spectra from 300 to 4000 cm^{-1} were obtained with a Beckman IR-7 prism-grating spectrometer using interchangeable sodium chloride and cesium iodide optics. The calibration for this instrument was "spot checked" against atmospheric water and carbon dioxide bands. The spectra of the normal benzamides and the ^{15}N-labeled benzamides were recorded as chloroform and dibromomethane solutions using 0.8 mm cells and as potassium bromide pellets. Because the deuterated benzamides "back exchanged" rather readily in chloroform solutions, spectra of these compounds were recorded only as dibromomethane solutions and as potassium bromide pellets.

Since ^{15}N substitution involves frequency shifts of only a few wavenumbers, special care was taken in measuring these frequency shifts. The following scheme was employed to determine the ^{15}N frequency shifts. Fiducial marks corresponding to known calibration points were placed on the spectra of the normal compounds and on the spectra of the ^{15}N-labeled compounds. The spectra of the normal and ^{15}N-labeled compounds were then superimposed and the distance between band centers measured. These distances were then converted to wavenumbers. To illustrate the precision of the frequency shift determinations, Table 2 shows a typical series of frequency shifts obtained from a sequential series of measurements on spectra of five different potassium bromide pellets of ^{14}N and ^{15}N o-methylbenzamide. These measurements were obtained by

Table 2. Variation in observed frequency shifts of several absorptions as determined from five different potassium bromide pellets of ^{14}N and ^{15}N o-methylbenzamide

$^{\nu}{}^{15}\mathrm{NH}_2 - {}^{\nu}{}^{14}\mathrm{NH}_2$ (cm^{-1})

3369 band	3184 band	1654 band	1620 band	1392 band
-9.5	-6.0	-4.9	-2.0	-8.1
-10.0	-5.5	-5.4	-2.6	-7.0
-9.0	-5.5	-5.4	-1.6	-7.4
-8.5	-5.0	-5.2	-2.5	-7.4
-10.5	-5.0	-4.9	-1.6	-7.5
-9.0	-6.5	-5.4	-2.6	-7.8
-10.5	-5.0	-5.3	-1.8	-7.6
-10.0	-5.0	-4.8	-2.1	-7.6
-9.5	-5.5	-5.1	-2.9	-7.2
-9.0	-6.0	-4.7	-1.7	-7.1
-9.5	-6.0	-4.8	-2.6	-7.0
-9.0	-5.5	-5.0	-1.9	-7.3
-9.5	-5.0	-5.2	-1.6	-7.3
-9.0	-5.5	-4.9	-1.8	-8.0
-10.0	-4.5	-5.6	-2.2	-7.4
-9.5	-6.0	-4.9	-2.4	-7.4
-10.0	-5.5	-4.6	-2.6	-7.2
-10.0	-5.5	-5.4	-1.5	-7.0
-9.0	-5.0	-5.0	-2.4	-7.9
-9.0	-5.0	-5.6	-2.2	-7.1
-10.0	-6.5	-5.1	-2.2	-8.4
-9.5	-6.0	-4.7	-2.3	-7.8
-9.0	-5.5	-4.9	-2.1	-7.9
-9.0	-5.5	-5.4	-1.6	-7.4
-8.5	-5.0	-4.7	-1.8	-7.2
σ=0.56	σ=0.57	σ=0.29	σ=0.40	σ=0.32

superimposing the five spectra of the ^{15}N compound on first one spectrum of the normal compound and then another until all possible combinations were obtained. The frequency shifts show a standard deviation, σ, of less than 0.4 below 2000 cm^{-1}

and a value less than 0.6 above 2000 cm^{-1}. No frequency shifts of less than one wavenumber are reported.

Potassium bromide pellet spectra of the normal benzamides and their deuterium derivatives as obtained from sodium chloride optics are shown in Figures 1-19. The observed solid state and solution absorption frequencies of these compounds are listed in Tables 13-44. These frequencies are given to the nearest wavenumber and are estimated to be accurate to ± 3 wavenumbers above 2000 cm^{-1} and to ± 2 wavenumbers below 2000 cm^{-1}. No frequencies are reported between 1700 and 2000 cm^{-1}. The frequency of the 1375 cm^{-1} solution band in all the normal compounds was taken from chloroform solution spectra because dibromomethane, when used in 0.8 mm cells, tended to absorb strongly in this region producing a broad ill-defined band. This "blanking" by the dibromomethane solvent also accounts for the fact that several strong absorptions which appear in the solid state spectra are absent in the solution spectra. No solution frequencies below 1100 cm^{-1} are given. All the intensities are estimates based on relative peak transmittance values.

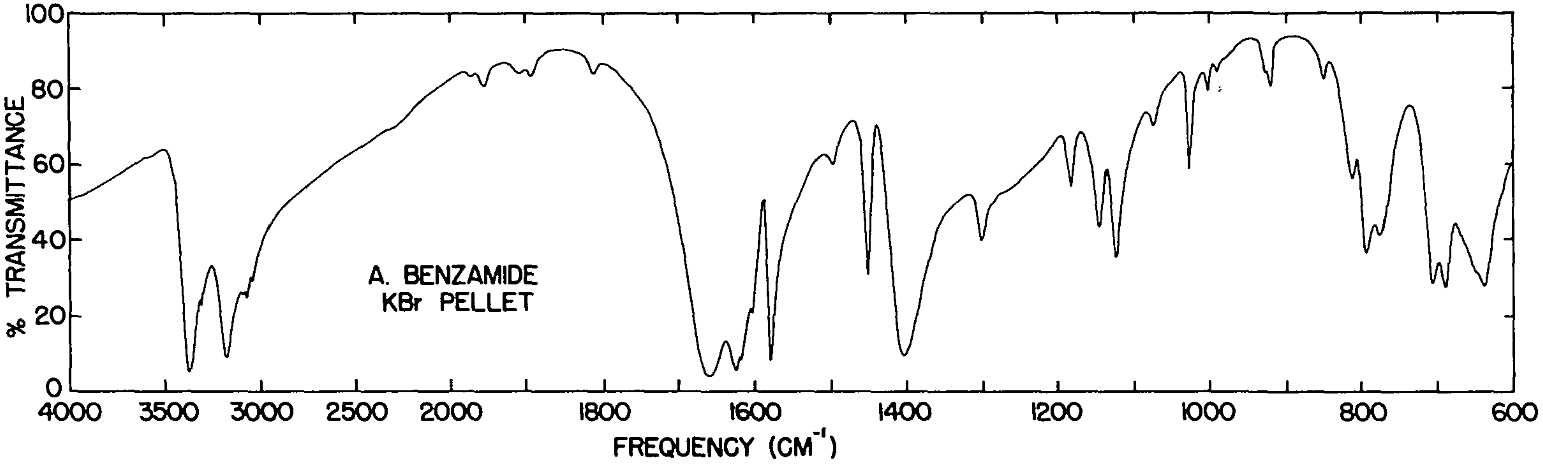
It is relevant to note that below 650 cm^{-1}, the spectra obtained using sodium chloride optics may not be realistic. The large spectral slit width required in this region causes poor resolution, distorting band contours and intensities.

For these reasons, all frequencies and intensities below 650 cm^{-1} were taken from spectra recorded on cesium iodide optics.

Figure 1. Potassium bromide pellet spectra of benzamide

A. Normal

B. Deuterated


A. BENZAMIDE
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

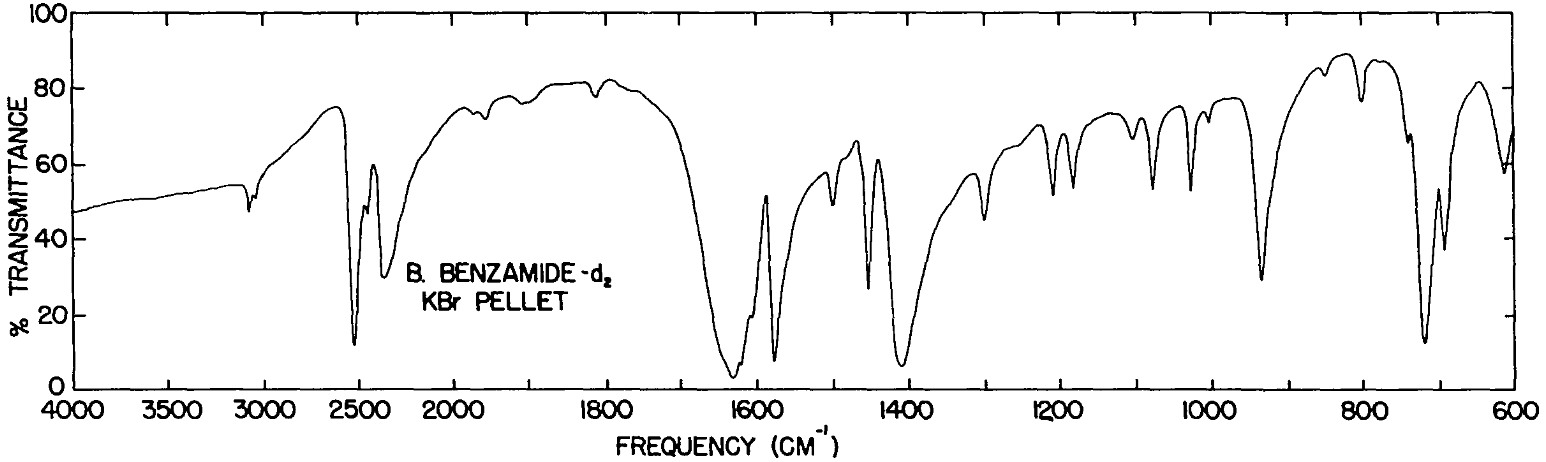
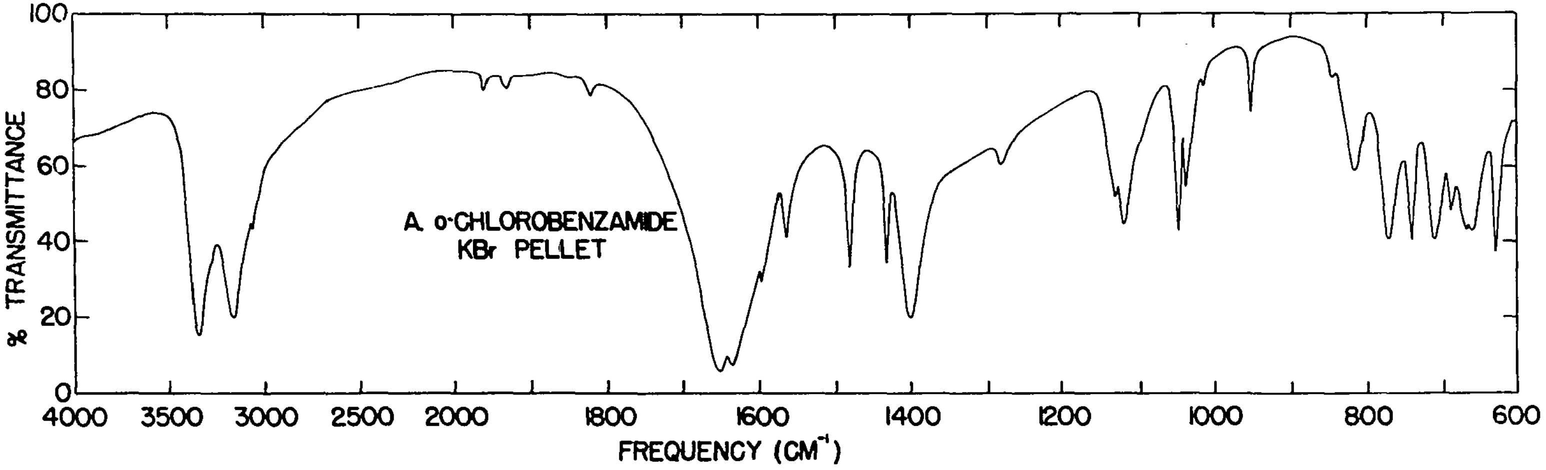

B. BENZAMIDE-d_2
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 2. Potassium bromide pellet spectra of o-chlorobenzamide

A. Normal

B. Deuterated


A. o-CHLOROBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

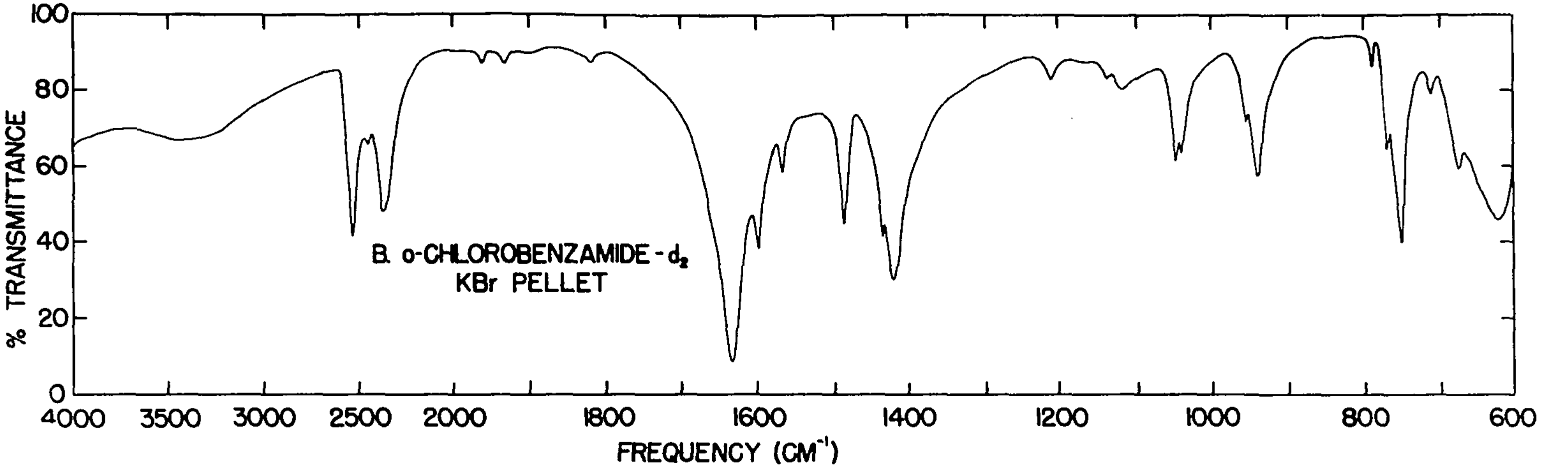

B. o-CHLOROBENZAMIDE-d₂
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 3. Potassium bromide pellet spectrum of m-chlorobenzamide

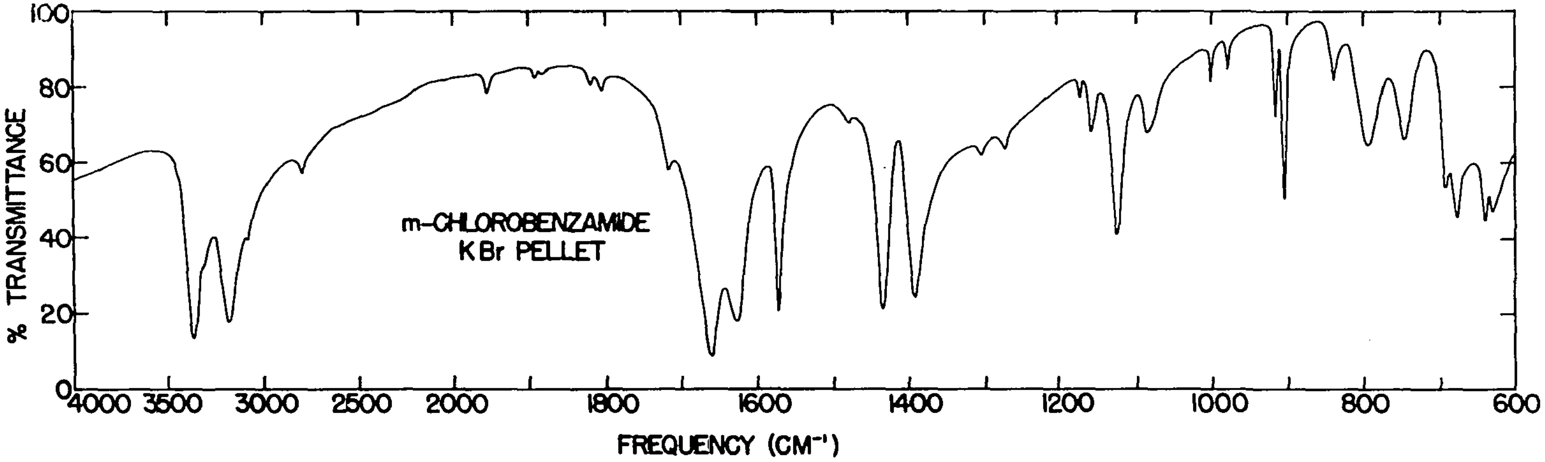
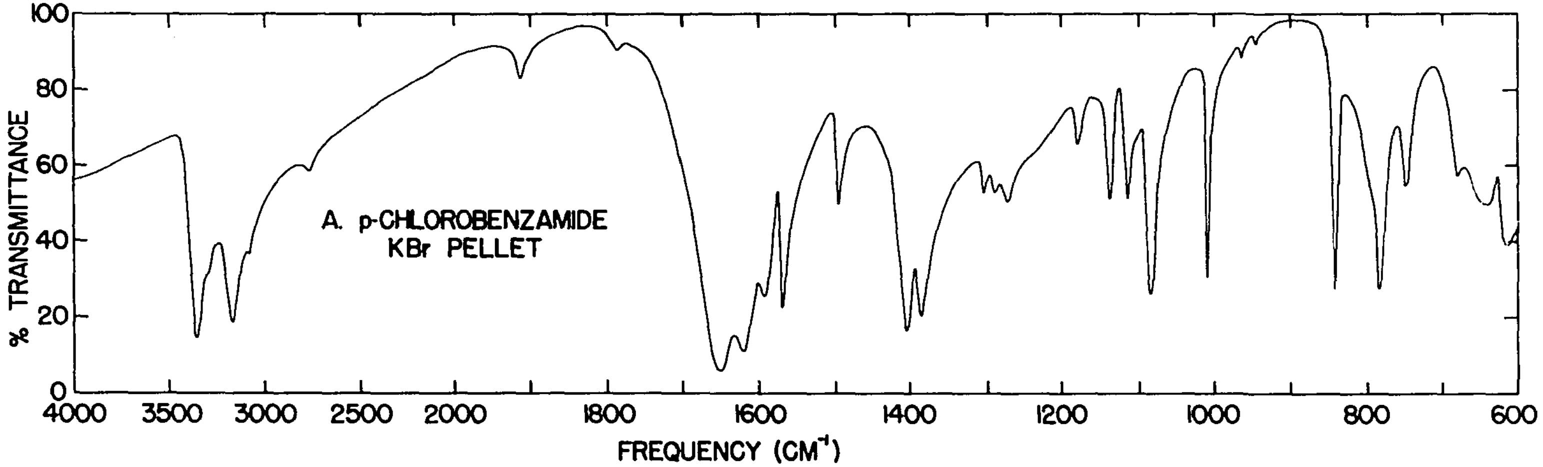

m-CHLOROBENZAMIDE
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 4. Potassium bromide pellet spectra of p-chlorobenzamide

A. Normal

B. Deuterated


A. p-CHLOROBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

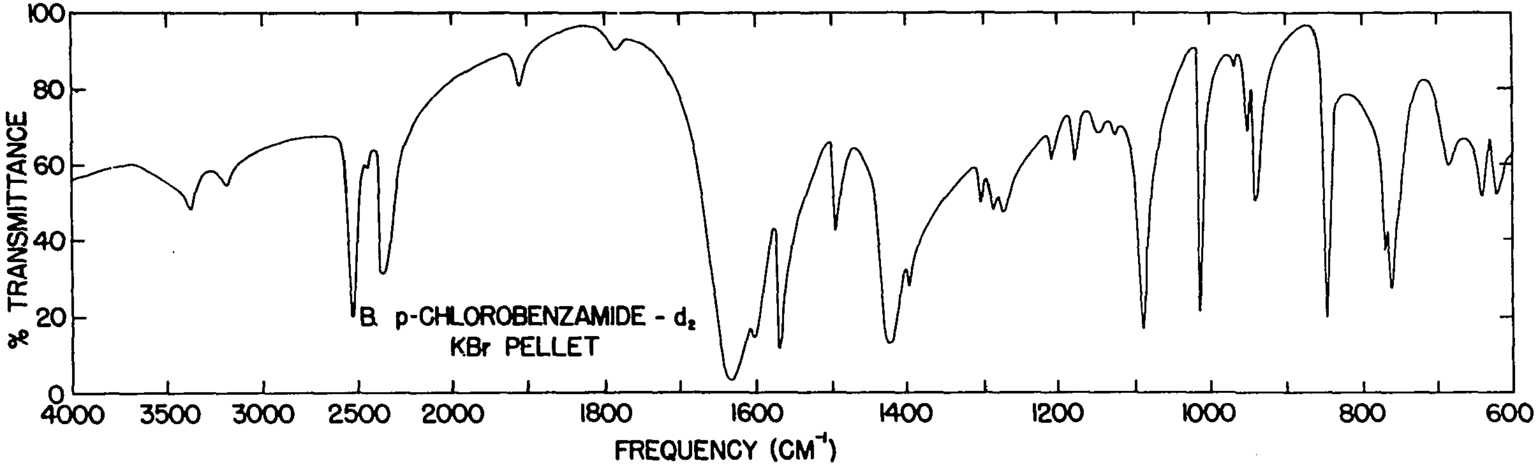
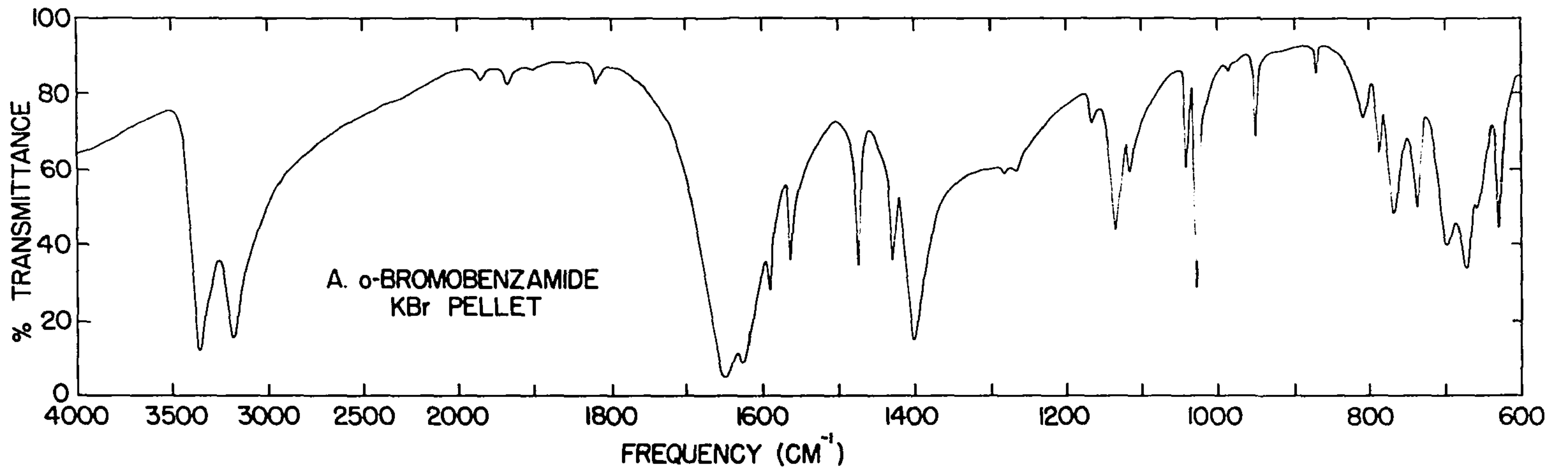

B. p-CHLOROBENZAMIDE - d₂
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

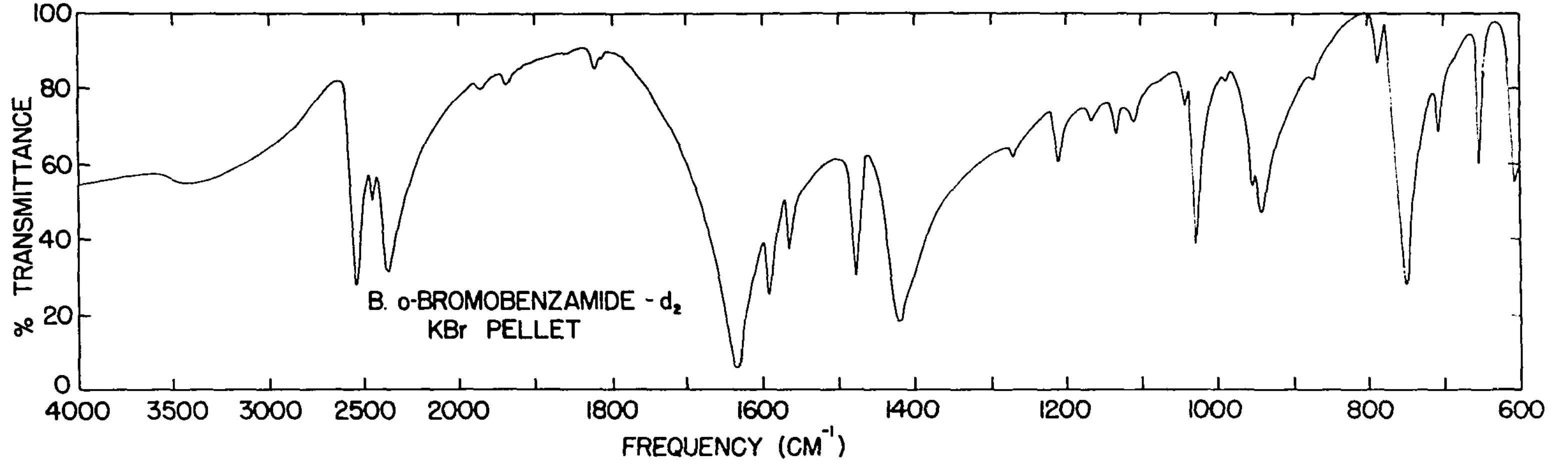
Figure 5. Potassium bromide pellet spectra of o-bromobenzamide

A. Normal

B. Deuterated



A. o-BROMOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

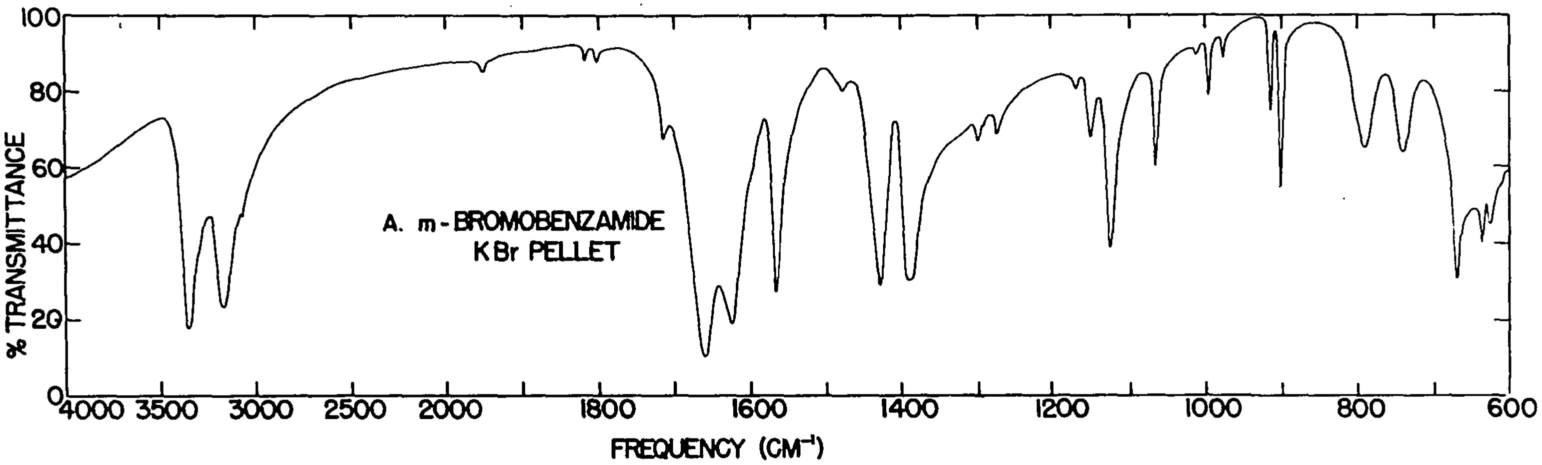


B. o-BROMOBENZAMIDE - d$_2$
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 6. Potassium bromide pellet spectra of m-bromobenzamide

A. Normal

B. Deuterated


A. m-BROMOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

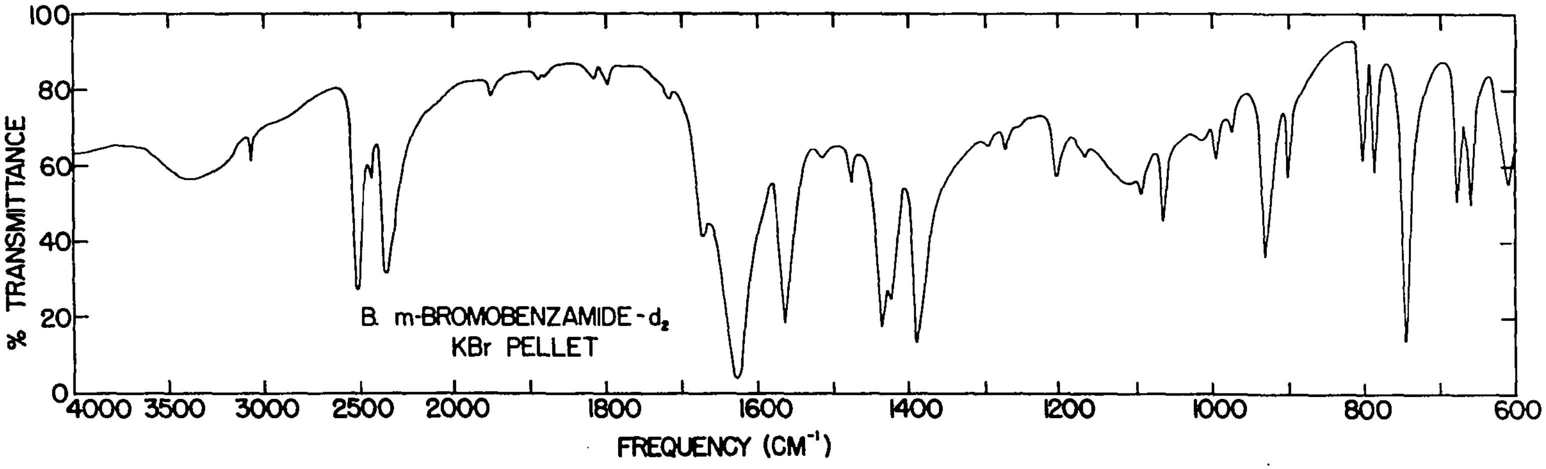
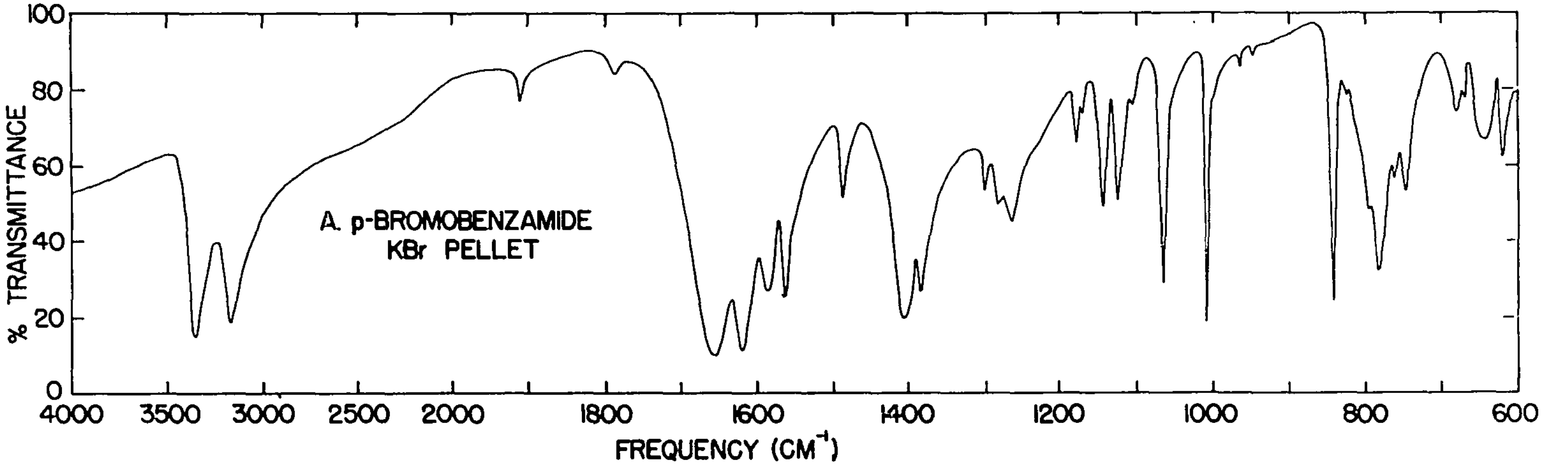

B. m-BROMOBENZAMIDE-d₂
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 7. Potassium bromide pellet spectra of p-bromobenzamide

A. Normal

B. Deuterated


A. p-BROMOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

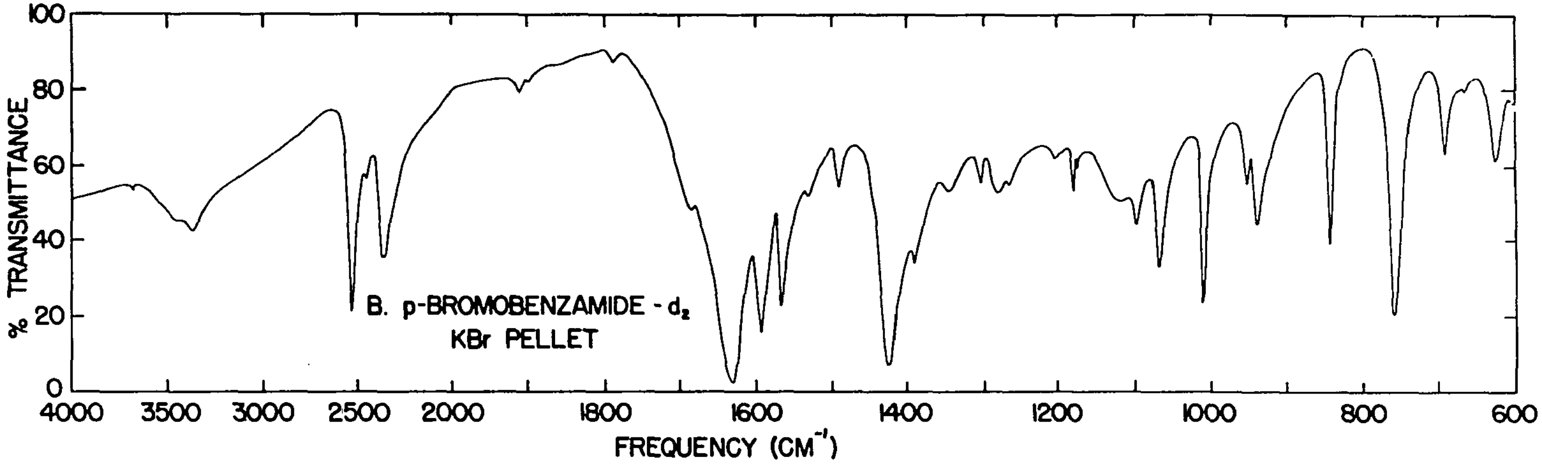
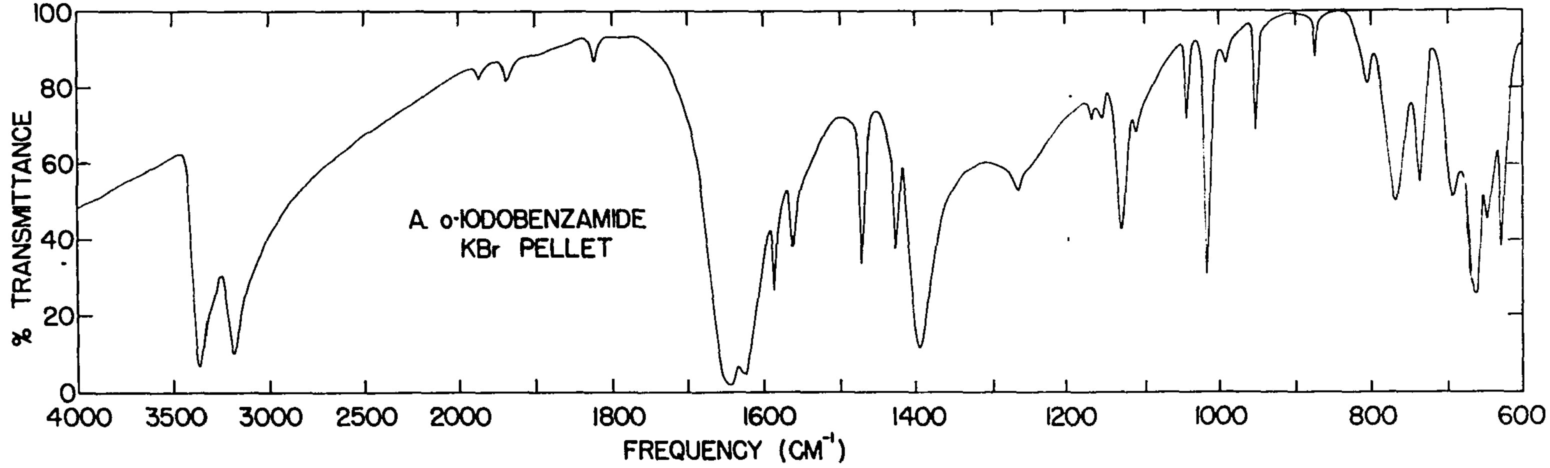

B. p-BROMOBENZAMIDE - d₂
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 8. Potassium bromide pellet spectra of o-iodobenzamide

A. Normal

B. Deuterated


A. o-IODOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

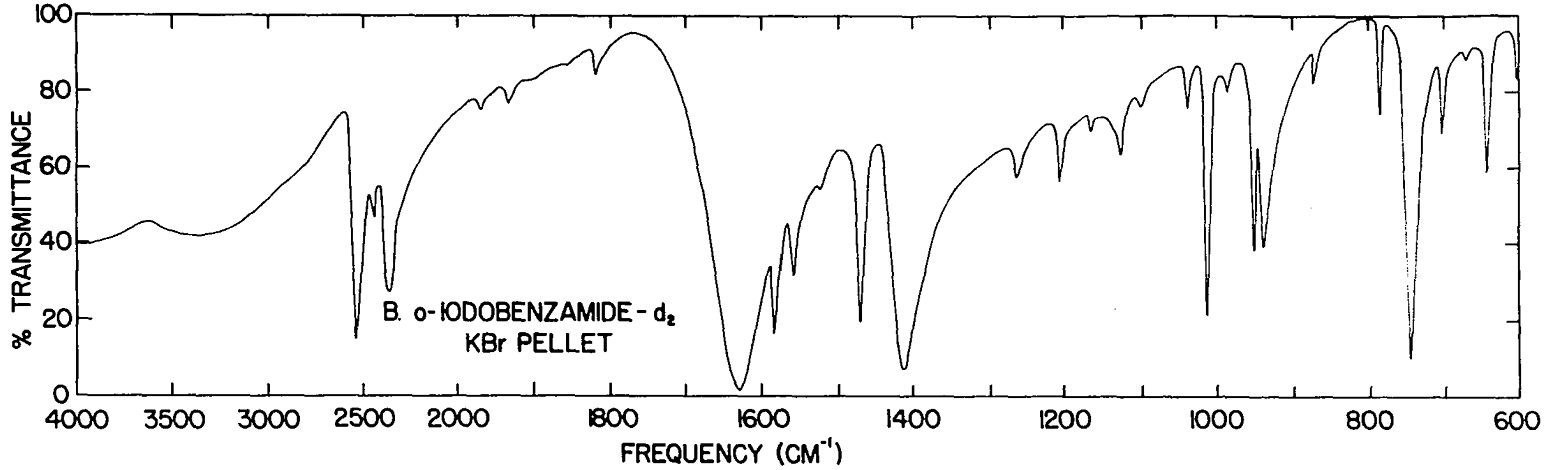
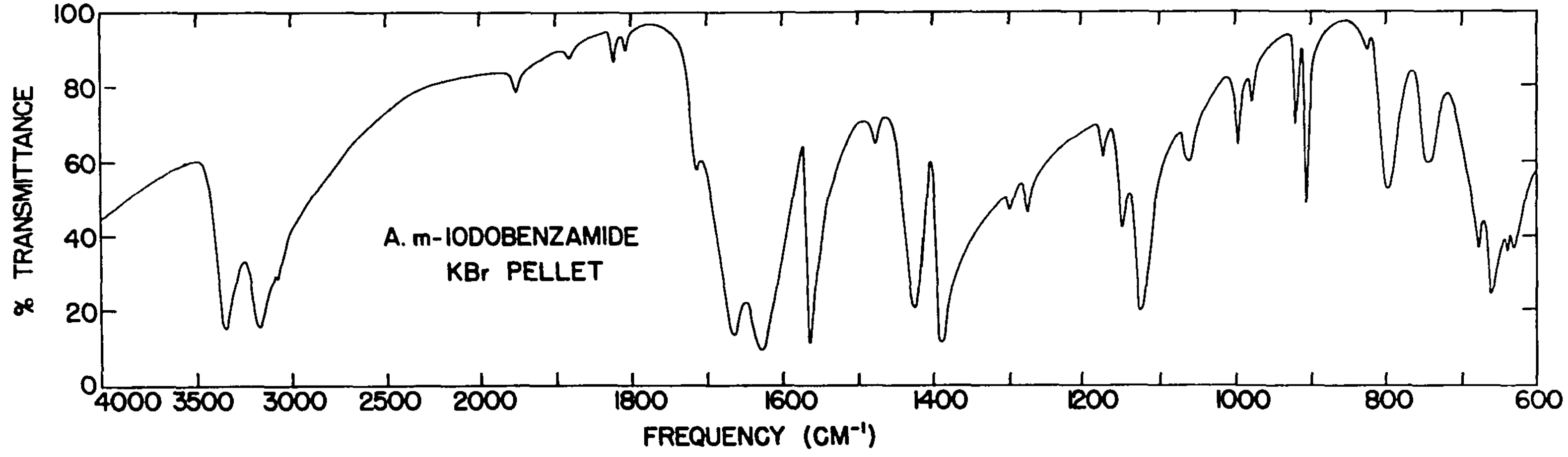

B. o-IODOBENZAMIDE-d_2
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 9. Potassium bromide pellet spectra of m-iodobenzamide

A. Normal

B. Deuterated


A. m-IODOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

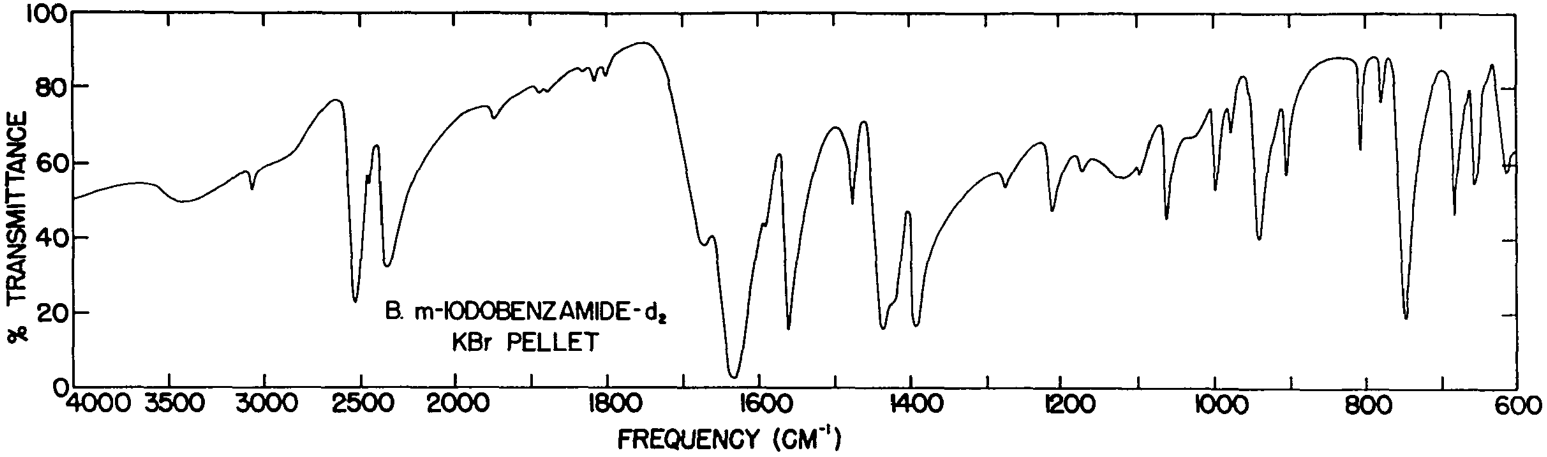

B. m-IODOBENZAMIDE-d₂
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 10. Potassium bromide pellet spectrum of p-iodobenzamide

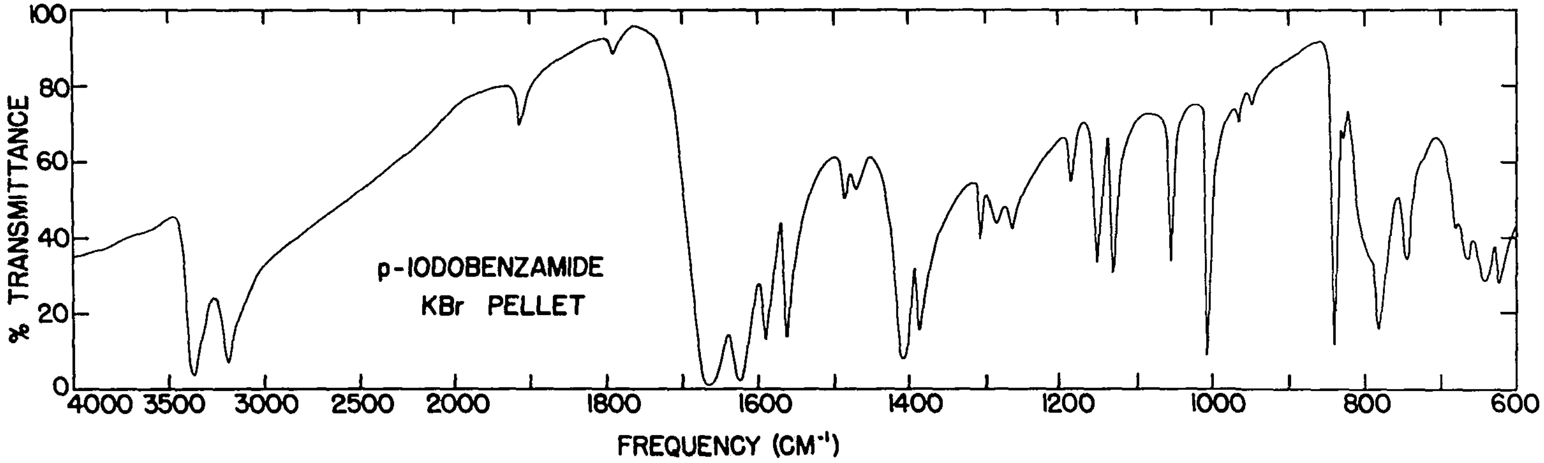
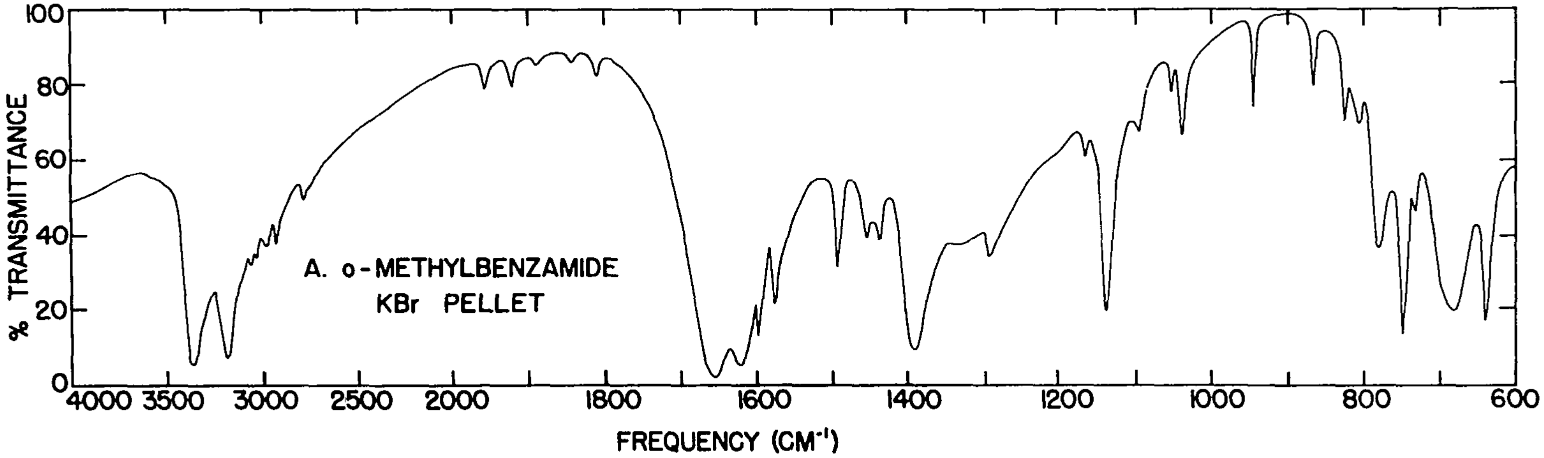

p-IODOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 11. Potassium bromide pellet spectra of o-methylbenzamide

A. Normal

B. Deuterated


A. o-METHYLBENZAMIDE
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

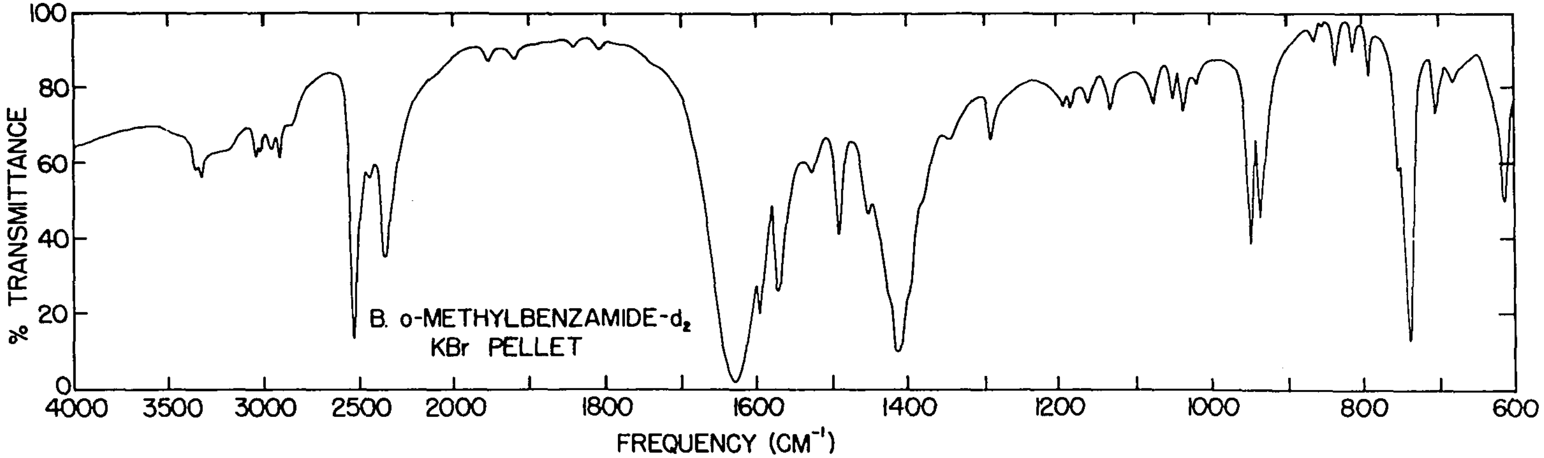
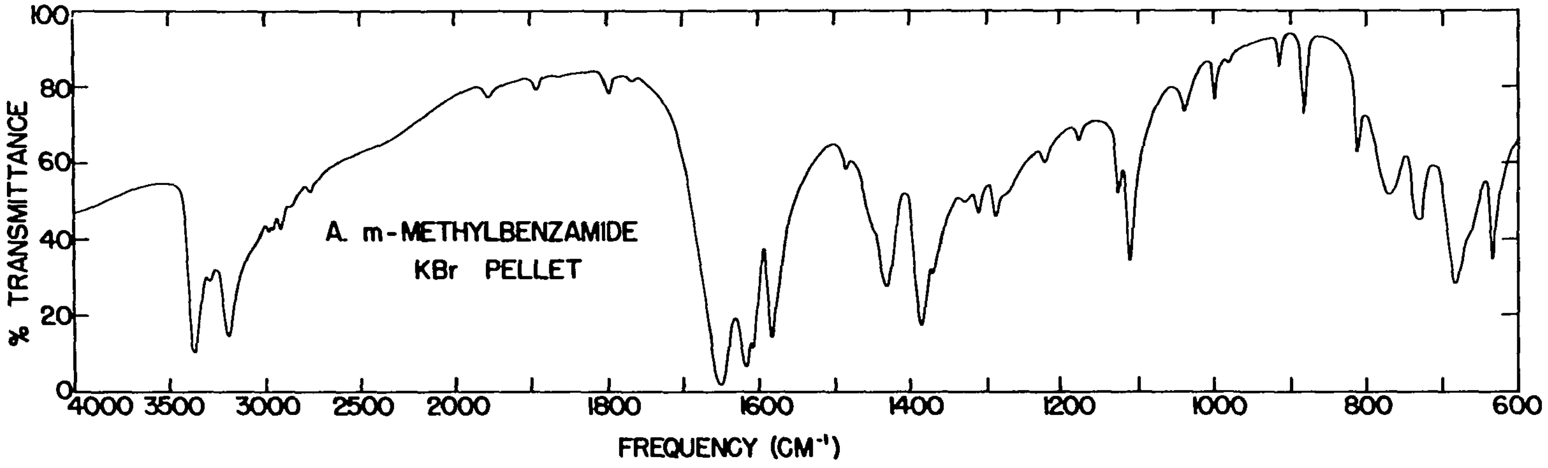

B. o-METHYLBENZAMIDE-d$_2$
KBr PELLET
% TRANSMITTANCE
0
20
40
60
80
100
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 12. Potassium bromide pellet spectra of m-methylbenzamide

A. Normal

B. Deuterated


A. m-METHYLBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

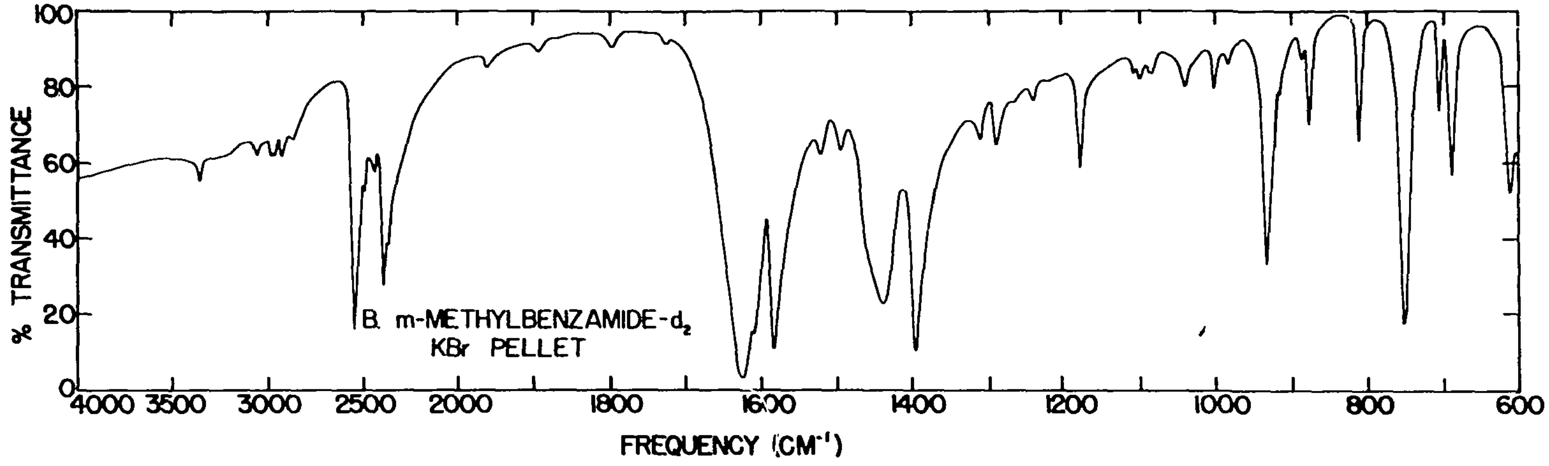

B. m-METHYLBENZAMIDE-d₂
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 13. Potassium bromide pellet spectrum of p-methylbenzamide

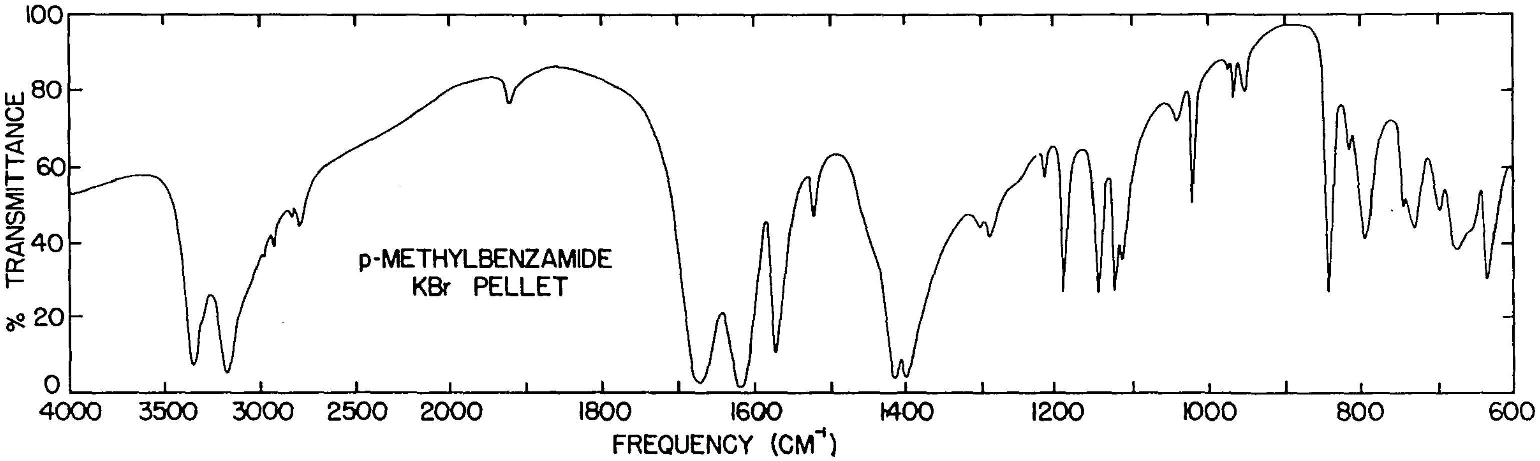
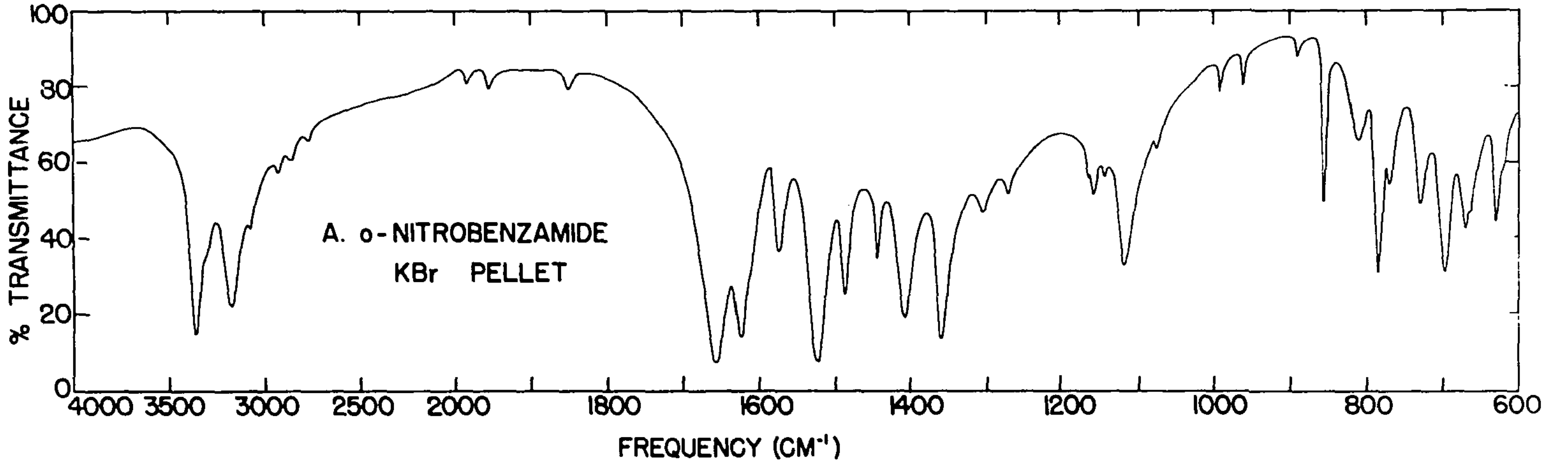

p-METHYLBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 14. Potassium bromide pellet spectra of o-nitrobenzamide

A. Normal

B. Deuterated


A. o-NITROBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

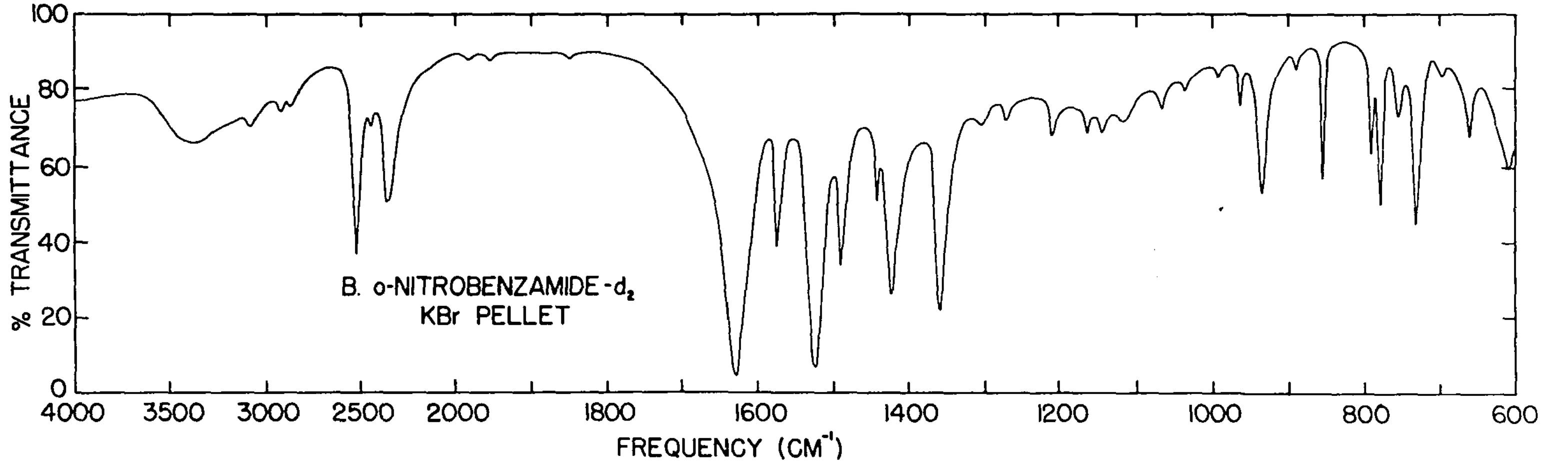

B. o-NITROBENZAMIDE-d₂
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 15. Potassium bromide pellet spectrum of m-nitrobenzamide

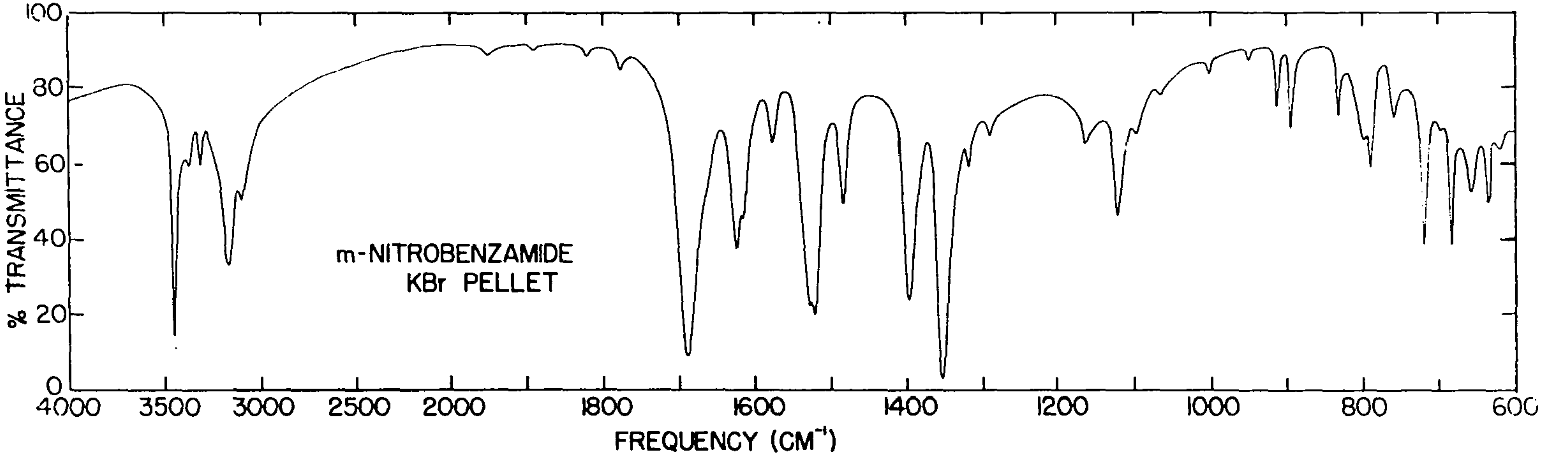
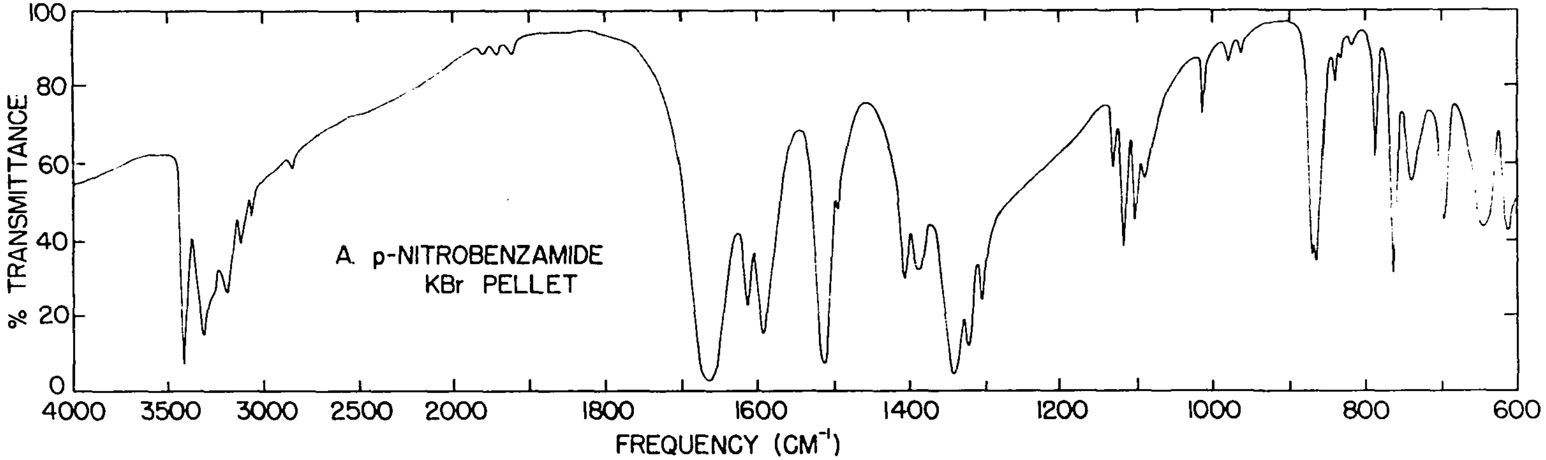

m-NITROBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

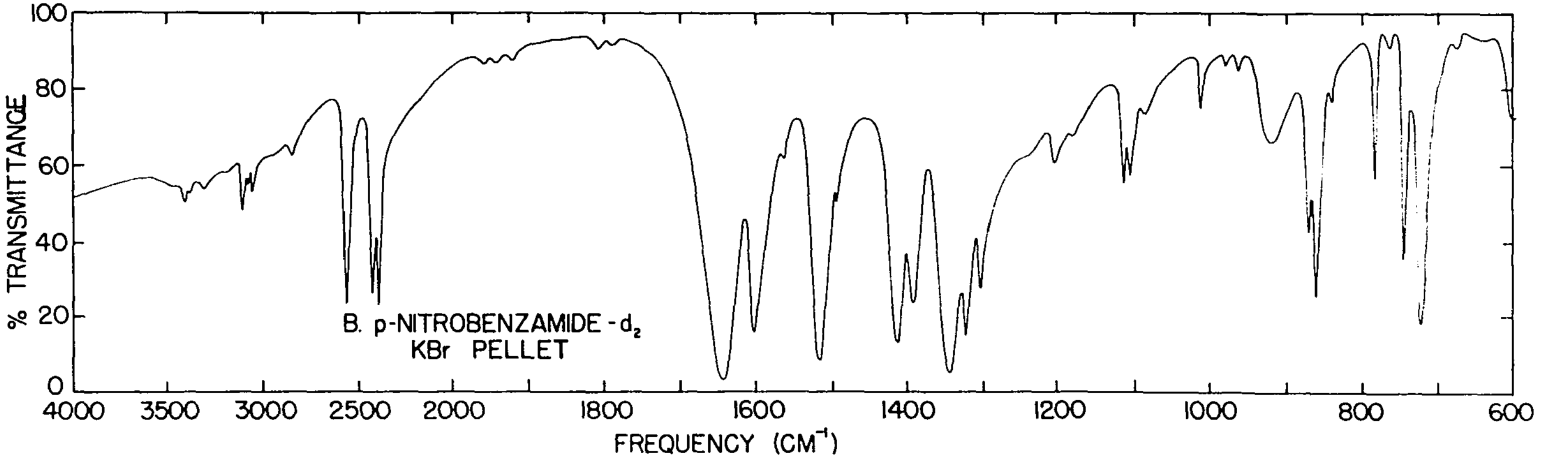
Figure 16. Potassium bromide pellet spectra of p-nitrobenzamide

A. Normal

B. Deuterated



A. p-NITROBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

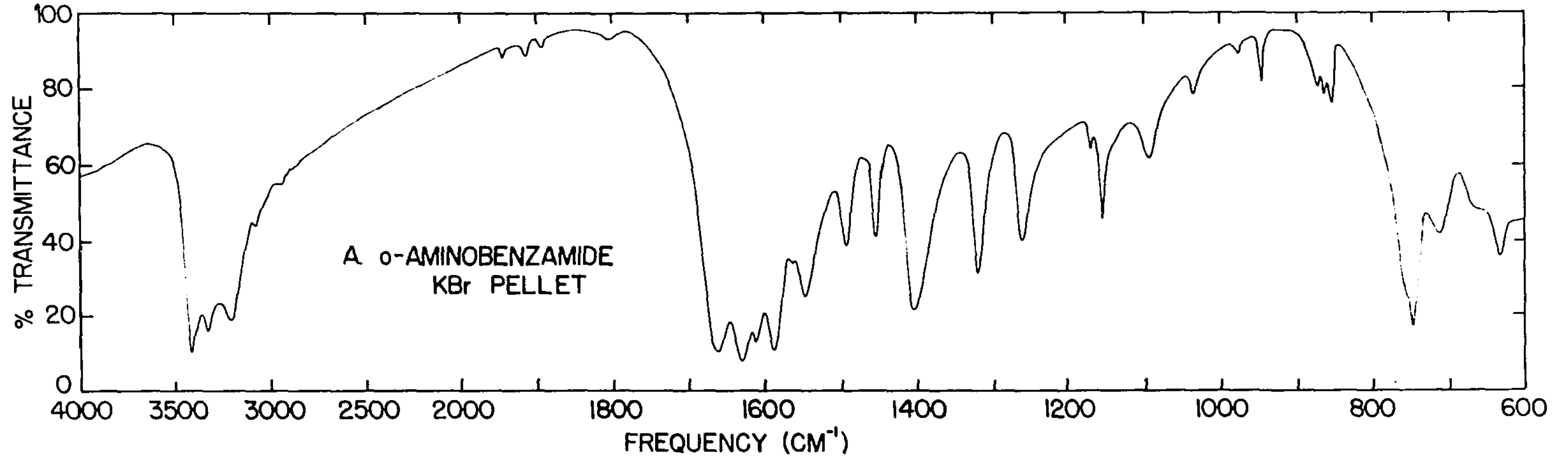


B. p-NITROBENZAMIDE - d₂
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 17. Potassium bromide pellet spectra of o-aminobenzamide

A. Normal

B. Deuterated


A. o-AMINOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

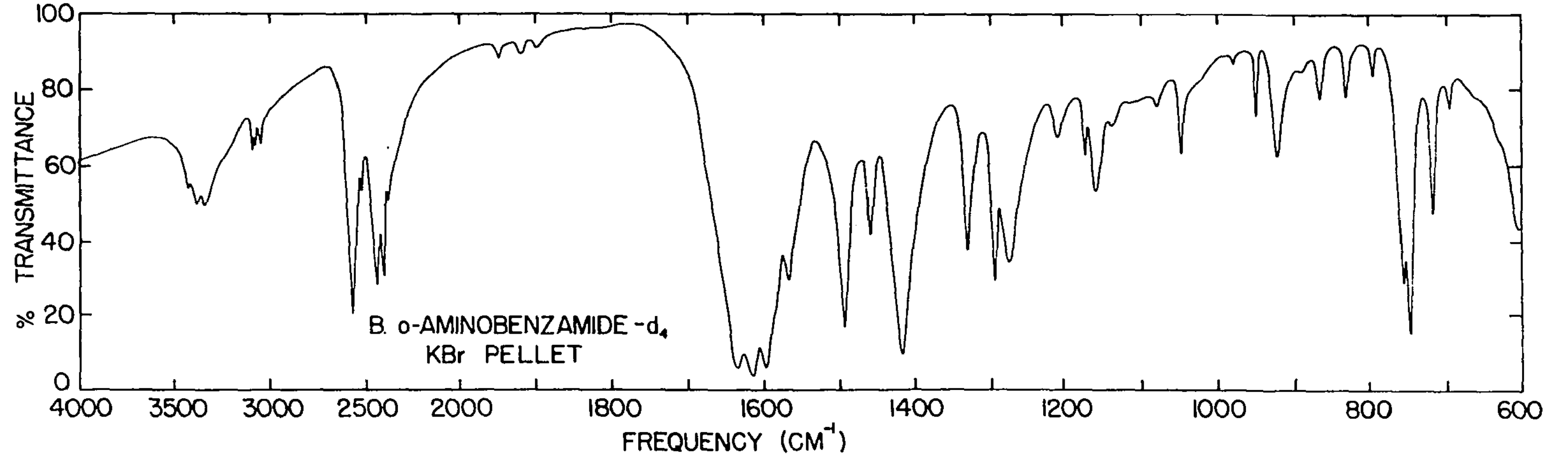

B. o-AMINOBENZAMIDE-d₄
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 18. Potassium bromide pellet spectrum of p-aminobenzamide

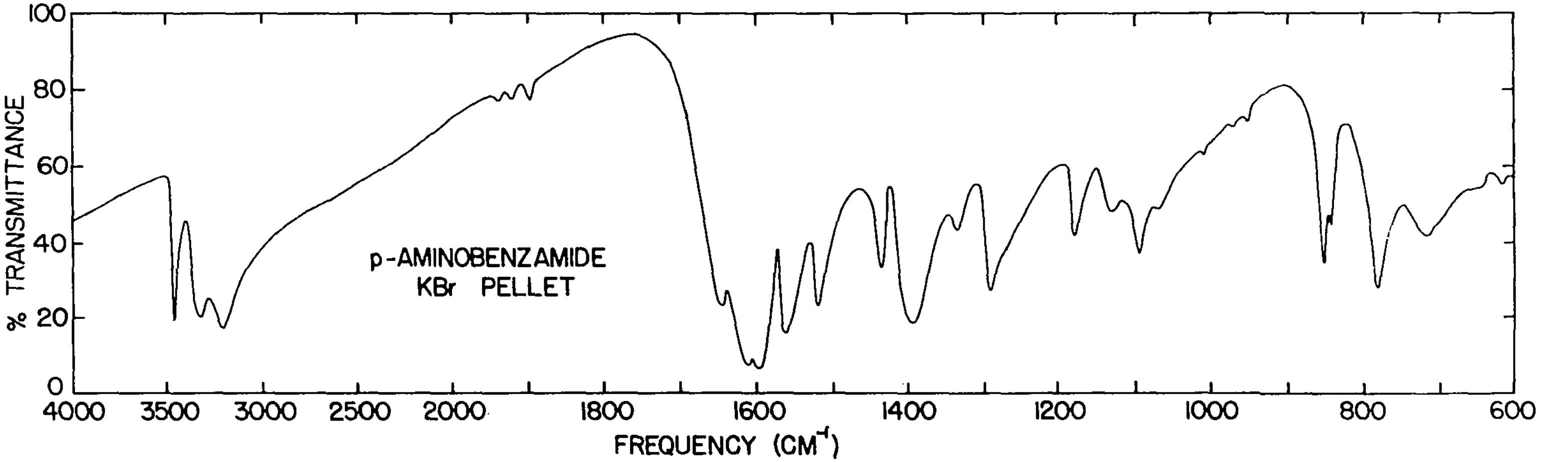
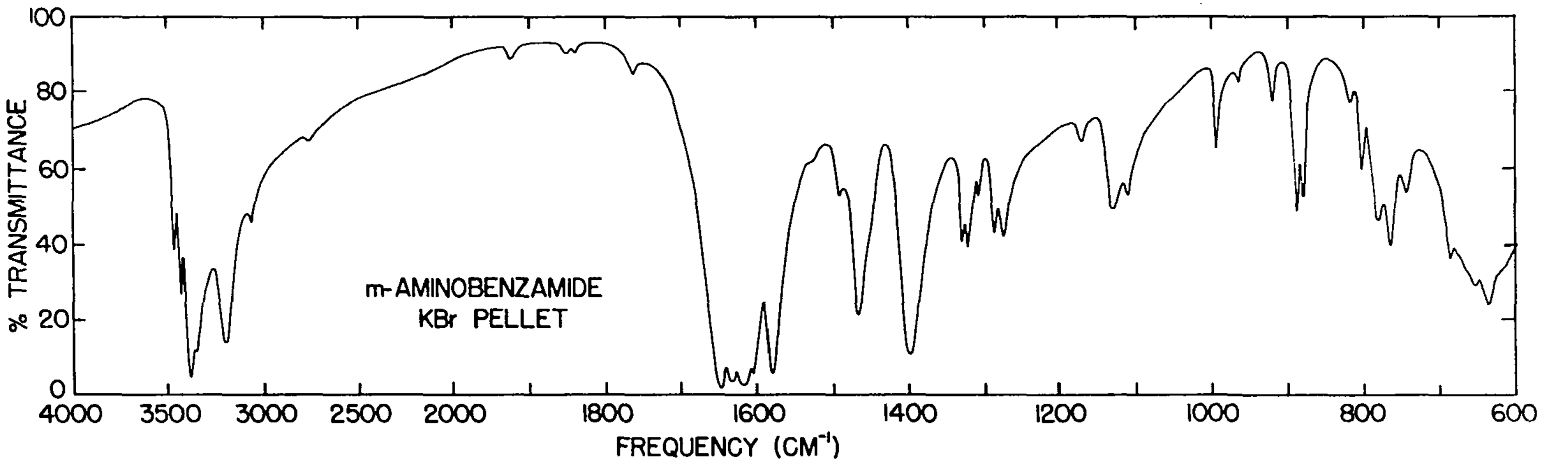

p-AMINOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 19. Potassium bromide pellet spectrum of m-aminobenzamide


m-AMINOBENZAMIDE
KBr PELLET
% TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

THE NH STRETCHING VIBRATIONS

The most widely studied of all the characteristic amide absorptions are those produced by the NH stretching vibrational modes. In dilute solutions, the NH asymmetric and symmetric stretching vibrations fall near 3500 and 3400 cm^{-1} respectively (4, 6, 7, 9, 35). The typical appearance of these bands is exhibited by the spectra of o-chlorobenzamide and p-nitrobenzamide shown in Figure 20. As shown in Table 3, the solution spectra of all of the compounds studied in the present investigation, except the aminobenzamides, exhibited the expected pattern of two characteristic frequencies in the 3500 to 3300 cm^{-1} range. The observed isotopic shifts correspond to values between 1.0015 and 1.004 for the ratio $\frac{\nu_{^{14}NH_2}}{\nu_{^{15}NH_2}}$ and to a value of near 1.33 for the ratio $\frac{\nu_{NH_2}}{\nu_{ND_2}}$. It is apparent that the isotopic frequency ratios are in harmony with the expected values. Consequently, these frequencies can be assigned with confidence to the asymmetric and symmetric NH stretching vibrations.

For the aminobenzamides, it is necessary to differentiate between the amine and amide hydrogen vibrations, since they fall in the same region. The spectrum of o-aminobenzamide shown in Figure 20 reflects this problem as two additional absorption bands are detected. Deuterium substitution offers no hope for differentiating between these frequencies because this reaction loses its selectivity when both amine and amide functional groups are present. It is possible to prepare

Figure 20. Infrared spectra of selected primary aromatic amides in the 2800 to 4000 cm^{-1} region

A. Solution and solid state spectra of o-chlorobenzamide

B. Solution and solid state spectra of o-aminobenzamide

C. Solution and solid state spectra of p-nitrobenzamide

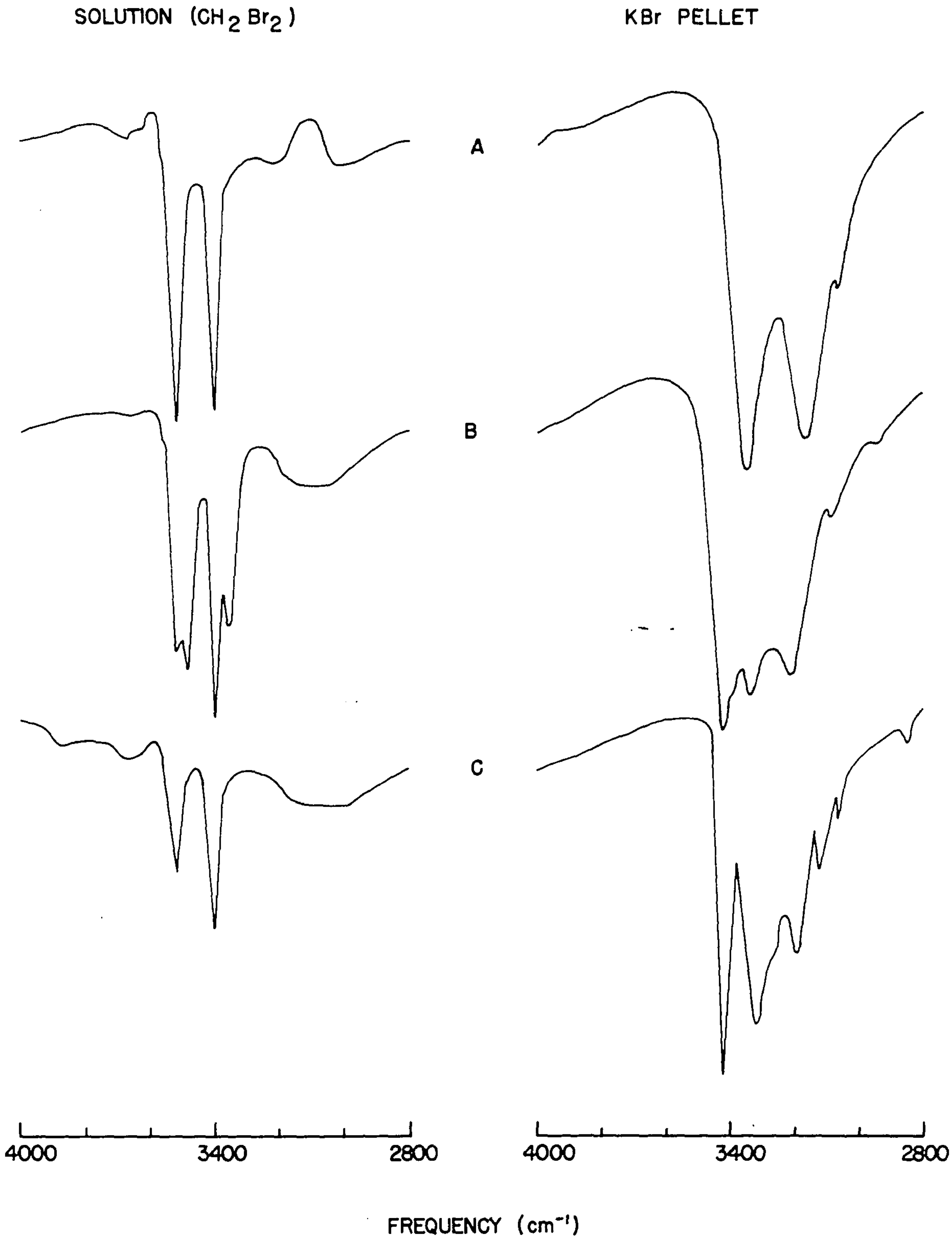

SOLUTION (CH_2Br_2)
KBr PELLET
A
B
C
4000
3400
2800
4000
3400
2800
FREQUENCY (cm^{-1})

Table 3. Observed NH and ND stretching frequencies in dilute dibromomethane solutions of primary aromatic amides

Compound	NH stretching frequencies[a] (cm^{-1})		ND stretching frequencies (cm^{-1})	
benzamide	3519 (-10.5)	3402 (-9.5)	2637	2486
o-chlorobenzamide	3513	3395	2638	2482
m-chlorobenzamide	3519	3402		
p-chlorobenzamide	3519 (-7.5)	3403 (-5.5)	2640	2483
o-bromobenzamide	3509	3392	2631	2476
m-bromobenzamide	3520 (-9.0)	3405 (-8.0)	2636	2486
p-bromobenzamide	3521	3404	2638	2484
o-iodobenzamide	3508 (-11.5)	3390 (-5.0)	2629	2471
m-iodobenzamide	3524	3408	2630	2487
p-iodobenzamide	3522	3406		
o-methylbenzamide	3515 (-12.0)	3397 (-7.5)	2634	2482
m-methylbenzamide	3528	3411	2641	2491
p-methylbenzamide	3524 (-14.5)	3406 (-7.5)		
o-nitrobenzamide	3509 (-12.0)	3394 (-9.5)	2630	2474
m-nitrobenzamide	3528 (-11.5)	3412 (-8.5)		
p-nitrobenzamide	3514 (-7.5)	3399 (-6.5)	2640	2483
o-aminobenzamide				
amide NH_2	3522 (-14.5)	3406 (-7.0)	2640	2484
amine NH_2	3488 (+1.0)	3357 (+1.5)	2616	2554

---

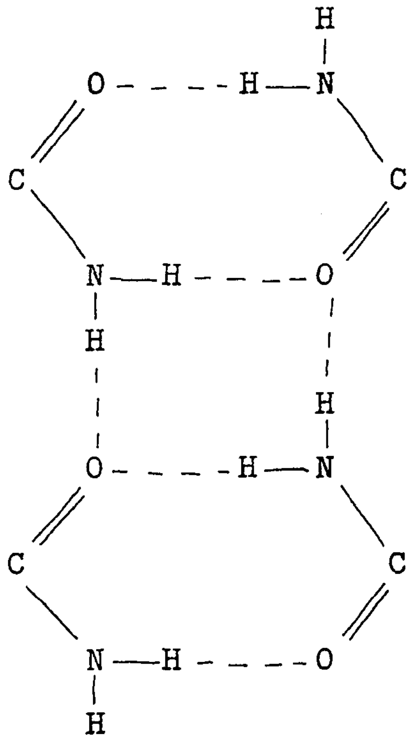
[a] Frequency shifts produced by ^{15}N substitution given in parenthesis.

Table 3. (Continued)

Compound	NH stretching frequencies[a] (cm^{-1})	ND stretching frequencies (cm^{-1})
m-aminobenzamide		
amide NH_2	3525 (-11.5)	3404 (-7.0)
amine NH_2	3488 (+1.5)	3359 (<1)
p-aminobenzamide		
amide NH_2	3517 (-14.0)	3407 (-14.5)
amine NH_2	3470 (-1.0)	3375 (<1)

compounds by the method of Jacobs and Heidelberger (20) in which only the nitrogen of the amide group is replaced by ^{15}N. Since in these compounds, only the amide NH vibrations are affected, the observed ^{15}N frequency shifts can be used to make this differentiation. The appropriate assignments are shown at the bottom of Table 3.

As compared with the solution spectra, the solid state spectra of primary acid amides show a pronounced decrease in the frequency of the NH stretching vibrations. These absorptions broaden and are found near 3350 and 3180 cm^{-1} (4, 21, 41). It is generally agreed that these changes are produced by intermolecular association through hydrogen bonds, although the nature of the species is in dispute (3, 6, 7, 9, 10, 11). However, according to the results of crystal structure research (30), benzamide is associated by means of hydrogen bonding both as dimers and as chain aggregates of the type shown below:



The N --- O distance in the dimer is 2.96 A and the N --- O distance between dimers is 2.91 A (30).

As shown in Table 4, with the exception of the aminobenzamides and the m- and p-nitrobenzamide, the solid state spectra of the primary aromatic amides show two medium strength bands in the 3370 - 3170 cm^{-1} region. This is illustrated for o-chlorobenzamide in Figure 20. The sensitivity of these absorptions to ^{15}N and deuterium substitution is very similar to that observed for the NH stretching absorptions in solution, verifying the assignment

Table 4. Observed NH and ND stretching frequencies in potassium bromide pellets of primary aromatic amides

Compound	NH stretching frequencies[a] (cm^{-1})		ND stretching frequencies (cm^{-1})	
benzamide	3367 (-11.5) 3306[b] (-12.5)	3173 (-11.0)	2528 2446[b]	2361
o-chlorobenzamide	3362	3180	2527 2446[b]	2368
m-chlorobenzamide	3364	3183		
p-chlorobenzamide	3370 (-12.5)	3173 (-3.5)	2529 2442[b]	2368
o-bromobenzamide	3365	3180	2531 2438[b]	2370
m-bromobenzamide	3357 (-13.0)	3174 (-8.0)	2522 2441[b]	2358
p-bromobenzamide	3363	3175	2527 2446[b]	2367
o-iodobenzamide	3364 (-7.5)	3182 (-8.5)	2528 2436[b]	2369
m-iodobenzamide	3343	3159	2518 2438[b]	2360
p-iodobenzamide	3360	3176		
o-methylbenzamide	3369 (-11.0)	3184 (-5.5)	2535 2442[b]	2363
m-methylbenzamide	3381 3291[b]	3198	2540 2522[b]	2384

---

[a] Frequency shifts produced by ^{15}N substitution given in parenthesis.

[b] Shoulders.

Table 4. (Continued)

Compound	NH stretching frequencies[a] (cm^{-1})		ND stretching frequencies (cm^{-1})	
p-methylbenzamide	3350 (-13.5)	3168 (-6.5)		
o-nitrobenzamide	3364 (-6.5)	3178 (-4.5)	2530 2453[b]	2376
m-nitrobenzamide	3448 (-10.5) 3371[b] (-13.0)	3160 (-11.5) 3308[c] (-9.5)		
p-nitrobenzamide	3419 (-9.0) 3262[b] (1)	3315 (-6.5) 3197 (-13.5)	2569 2396	2431
o-aminobenzamide				
amide NH_2	3400[b] (-14.0)	3201 (-8.5)	2494[b]	2385
amine NH_2	3417 ($<$ 1)	3328 (-1.5)	2554 2356[b]	2425
m-aminobenzamide				
amide NH_2	3385 (-9.0)	3199 (-6.5)		
amine NH_2	3468[b] (-1.0) 3353[b] ($<$ 1)	3434[b] (+1.0)		
p-aminobenzamide				
amide NH_2	3470 (-8.5)	3328 (-7.0)		
amine NH_2	3212 (+2.0)			

[c] Weak absorptions.

of the solid state bands to the asymmetric and symmetric NH stretching modes. The shoulders that appear at 3306 cm^{-1} in benzamide and at 3291 cm^{-1} in m-methylbenzamide are assigned to overtones of the amide II band, the fundamental of which falls at 1658 and 1649 cm^{-1} respectively for the two compounds. This is in agreement with the assignment of Badger and Pullin (2).

The NH stretching region of the solid aminobenzamides is again complicated by absorptions arising from both the amide and amine NH_2 groups. Although the solid state spectra are more difficult to interpret than the solution spectra, the ^{15}N frequency shift data make it possible to differentiate between the amide and amine NH stretching vibrations.

As can be seen from Figure 20, the solid state spectrum of o-aminobenzamide has only three absorptions in the NH stretching region, instead of four as would be expected. The absorption at 3417 cm^{-1} does have a definite shoulder at approximately 3400 cm^{-1} which could account for the fourth NH stretching absorption. The data in Table 4 show that only the shoulder at 3400 cm^{-1} and the absorption at 3201 cm^{-1} are appreciably sensitive to ^{15}N substitution and these frequencies can be assigned as the amide NH stretching frequencies. The absorptions at 3417 cm^{-1} and 3328 cm^{-1} thus arise from vibrations of the amine NH_2 group.

In the solid state, the NH stretching region of m-aminobenzamide is characterized by two medium strength absorptions at 3385 cm^{-1} and 3199 cm^{-1} and well defined shoulders at 3468 cm^{-1}, 3434 cm^{-1}, and 3353 cm^{-1}. Only the absorptions at 3385 cm^{-1} and 3199 cm^{-1} are sensitive to ^{15}N substitution and thus must arise from vibrations of the amide NH_2 group. The three shoulders must arise from the amine stretching vibrations. The fact that there are three NH stretching frequencies associated with the amine NH_2 group suggests that different types of association are occurring simultaneously.

Solid p-aminobenzamide shows three bands in the NH stretching region. Of these absorptions, only the ones at 3470 and 3328 cm^{-1} show appreciable ^{15}N frequency shifts and can be assigned to the stretching vibrations of the amide NH_2 group. The band at 3212 cm^{-1} can be associated with the symmetric amine NH stretching mode and it is possible that the corresponding asymmetric stretching vibration is accidentally degenerate with the symmetric stretching mode of the amide NH and falls at 3328 cm^{-1}.

Comparison of the solution and solid state NH stretching frequencies shows that in o- and m-aminobenzamide, the amide NH stretching frequencies decrease much more upon going from solution to solid than do the amine stretching frequencies. This behavior is in harmony with the formation of hydrogen bonds of the type shown on page 62. On the other hand, the amine stretching vibrations in p-aminobenzamide are much more dependent upon the state of aggregation than the amide NH stretching absorptions, indicating that in p-aminobenzamide, the primary bonding occurs through the amine NH_2 group.

As illustrated in Table 4 and Figure 20, the NH stretching region of solid p-nitrobenzamide is also complicated by the presence of multiple absorptions. These multiple bands must indicate that different types of association are occurring simultaneously. Bonding to both the nitro and carbonyl group is probably responsible for this behavior. The principal NH stretching absorptions in m-nitrobenzamide are separated by more than the amount expected for asymmetric and symmetric NH stretching vibrations. As will be seen in the next section, this large splitting could be produced by the formation of a cyclic dimer via hydrogen bonding to the nitro group. Also this compound has a shoulder at 3371 cm^{-1} and a weak band at 3308 cm^{-1}. These could arise from overtones or combination bands but the possibility of different types of hydrogen bonding cannot be overlooked as a source of these bands.

THE AMIDE I AND AMIDE II BANDS

The infrared spectra of primary acid amides are characterized by the presence of two absorptions in the 1550 - 1700 cm^{-1} region. These bands are commonly referred to as the amide I and amide II bands. The amide I band is usually reported near 1650 cm^{-1} in the solid state (4, 21, 35, 41) and between 1715 and 1675 cm^{-1} in solution (4, 21, 32, 35). The amide II band usually falls between 1650 and 1580 cm^{-1} (21, 24, 33, 35, 41). About the correct nature of these vibrations, some have said much, many have said little, but none enough.

Since the solution spectra are somewhat easier to interpret, it is well to discuss these first. The amide I and amide II band frequencies, along with the shifts produced by ^{15}N substitution, are summarized in Table 5. Figure 21 shows the amide I - amide II band region of selected aromatic amides and their deuterium derivatives as observed in dibromomethane solutions. The data in Table 5 show that for the most part, the higher frequency band which falls between 1665 and 1700 cm^{-1} is relatively insensitive to both ^{15}N and deuterium substitution. Although deuterium substitution gives rise to frequency shifts up to 15 cm^{-1}, this corresponds to an $\frac{NH_2}{ND_2}$ frequency ratio of only 1.009 which for deuterium substitution is not significant. These observations are in accord with prior assignments of this band to primarily a carbonyl stretching vibration (4, 21, 35). However, it is interesting to note

Table 5. Observed frequencies of the amide I and amide II bands in dilute dibromomethane solutions of primary aromatic amides

Compound	Frequency $(cm^{-1})^a$ Amide I band	Amide II band
benzamide	1679 (-1.8)	1587 (-7.7)
benzamide - d_2	1670	1194^b
o-chlorobenzamide	1683	1587
o-chlorobenzamide - d_2	1674	--
m-chlorobenzamide	1684	1585
p-chlorobenzamide	1682 (-1.0)	1596 (-10.5)
p-chlorobenzamide - d_2	1677	--
o-bromobenzamide	1684	1585
o-bromobenzamide - d_2	1677	1196^b
m-bromobenzamide	1685 (-1.8)	1586 (-6.3)
m-bromobenzamide - d_2	1678	--
p-bromobenzamide	1685	1599
p-bromobenzamide - d_2	1677	--
o-iodobenzamide	1684 ($<$ 1)	1586 (-8.5)
o-iodobenzamide - d_2	1679	--
m-iodobenzamide	1685	1585
m-iodobenzamide - d_2	1679	--

---

[a] Frequency shifts produced by ^{15}N substitution given in parenthesis.

[b] Frequencies taken from carbon tetrachloride solution spectra.

Table 5. (Continued)

Compound	Frequency (cm^{-1})^a	
	Amide I band	Amide II band
p-iodobenzamide	1682	1596
o-methylbenzamide	1681 (-1.8)	1585 (-7.8)
o-methylbenzamide - d_2	1670	--
m-methylbenzamide	1681	1591
m-methylbenzamide - d_2	1670	--
p-methylbenzamide	1679 (-2.2)	1589 (-8.8)
o-nitrobenzamide	1694 (-2.0)	1586 (-6.5)
o-nitrobenzamide - d_2	1691	--
m-nitrobenzamide	1694 (-3.5)	1594 (-10.8)
p-nitrobenzamide	1690 (-2.7)	1587 (-5.3)
p-nitrobenzamide - d_2	1682	--
o-aminobenzamide	1665 ($<$ 1)	1594 (-2.6)
o-aminobenzamide - d_2	1650	--
m-aminobenzamide	1678 ($<$ 1)	1588 (-10.4)
p-aminobenzamide	1670 ($<$ 1)	1589 (-7.0)

that small but definite ^{15}N frequency shifts are observed for the amide I band in several instances. The classification of amide skeletal modes by Lecomte and Freymann (25, 26) includes a vibration which is primarily a carbonyl stretching mode in association with a small amount of nitrogen motion. More

Figure 21. Solution spectra of selected primary aromatic amides in the 1500 to 1800 cm^{-1} region

I_A. Dibromomethane solution spectrum of benzamide

I_B. Dibromomethane solution spectrum of benzamide - d_2

II_A. Dibromomethane solution spectrum of o-chlorobenzamide

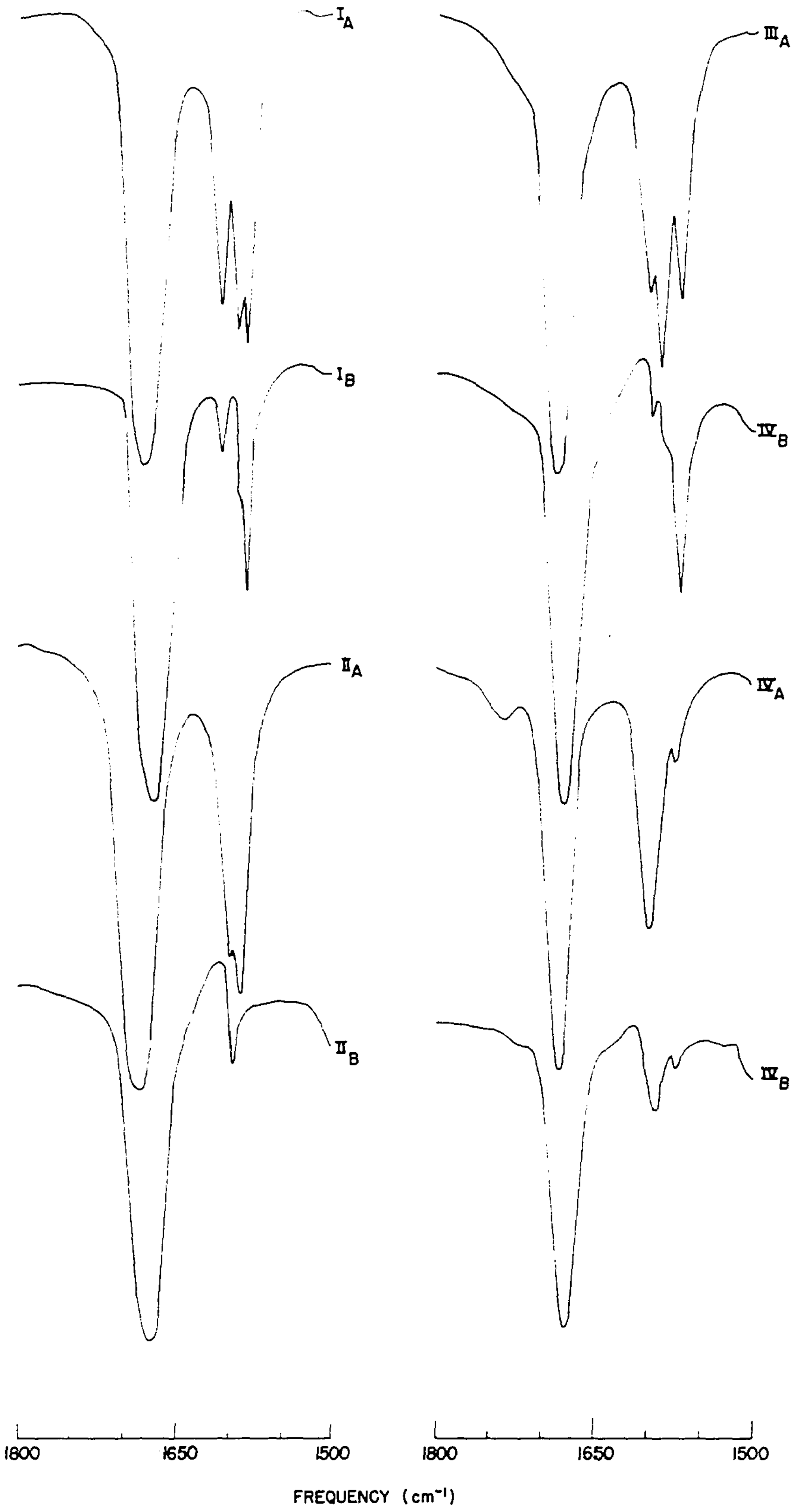
II_B. Dibromomethane solution spectrum of o-chlorobenzamide - d_2

III_A. Dibromomethane solution spectrum of m-bromobenzamide

III_B. Dibromomethane solution spectrum of m-bromobenzamide - d_2

IV_A. Dibromomethane solution spectrum of p-chlorobenzamide

IV_B. Dibromomethane solution spectrum of p-chlorobenzamide - d_2


I_A
I_B
II_A
II_B
III_A
IV_B
IV_A
IV_B
1800
1650
1500
1800
1650
1500
FREQUENCY (cm⁻¹)

recently Smith and Robinson (37) and Miyazawa (29), working with formamide and formamide - d_2 have associated the amide I band with an asymmetric stretching of the O - C - N system. The magnitude of the observed ^{15}N frequency shifts hardly seem sufficient for assignment of an O - C - N mode and appear more consistent with the assignment of Lecomte and Freymann.

As illustrated in Figure 21, the region of the amide II band (1570 - 1650 cm^{-1}) is complicated in the solution spectra of primary aromatic amides by the presence of absorptions arising from skeletal modes of the phenyl ring. The two phenyl bands that appear in this region arise from the A_1 νc-c and B_1 νc-c modes of the phenyl ring in the case of monosubstituted benzenes, o-substituted benzenes, and m-substituted benzenes and from the A_g νc-c and B_{1g} νd-d modes in p-substituted benzenes (34). It is not clear whether the A_1 νc-c or B_1 νd-d mode lies at a higher frequency, but the two absorptions near 1600 cm^{-1} arise from these two modes. In the case of p-substituted benzenes, the A_g νc-c mode probably lies at a higher frequency than the B_{1g} νc-c mode (34). Frequently in substituted benzenes only one band appears in the 1600 cm^{-1} region. This single band could correspond to either of the two modes or an accidental degenercy of the two. For example, Randle and Whiffen (34) observed only a single band in 23 out of 55 monosubstituted benzenes, 19 out of 35 o-substituted benzenes, 5 out of 22 m-substituted benzenes, and 14 out of 43 p-substituted benzenes.

Since the amide II vibration involves considerable nitrogen and hydrogen motion, ^{15}N and deuterium substitution provide a simple and direct means of identifying this absorption. The disappearance of the amide II band upon deuteration is illustrated for typical aromatic amides in Figure 21 and Table 5 summarizes the sensitivity of this band to ^{15}N substitution.

It is interesting to note that in the p-halogen benzamides and m-aminobenzamide the amide II band is accidentally degenerate with a vibration of the phenyl ring. For example, the 1596 cm^{-1} band in p-chlorobenzamide does not completely disappear upon deuteration and splits upon ^{15}N substitution forming two bands of nearly equal intensity at 1597 cm^{-1} and 1586 cm^{-1}. The band remaining in the deuterated compound and the 1597 cm^{-1} in the ^{15}N derivative evidently correspond to the Ag $\nu c\text{-}c$ mode of the phenyl ring which was originally covered by the amide II band. The amide II band in the other p-halogen benzamides and in m-aminobenzamide show similar behavior to isotopic substitution in those cases where isotopic derivatives were prepared.

The amide II band region in the aminobenzamides is complicated by the presence of the scissoring vibration of the amine NH_2 group. However, as observed for the NH stretching vibrations, utilization of the information obtained from ^{15}N substitution makes it possible to distinguish between the NH_2

scissoring vibration of the amine and that of the amide. As illustrated in Figure 22, the solution spectrum of o-aminobenzamide exhibits two bands in the amide II band region, one at 1616 cm^{-1} and a stronger absorption at 1594 cm^{-1}. Both of these bands apparently disappear upon deuteration, although weak absorptions remain at 1583 and 1611 cm^{-1} possibly arising from residual NH_2. Since the absorption at 1616 cm^{-1} is completely insensitive to ^{15}N substitution, it can be assigned to the amine scissoring vibration. The band at 1594 cm^{-1} shows some ^{15}N sensitivity and must arise from the scissoring vibration of the amide NH_2 group. The solution spectrum of m-aminobenzamide has absorptions at 1588 and 1620 cm^{-1}. As discussed previously, the band at 1588 cm^{-1} arises from the accidental degeneracy of the amide II band and a skeletal mode of the phenyl ring. Thus the absorption at 1620 cm^{-1} must correspond to the amine scissoring vibration. In dibromomethane solution, p-aminobenzamide shows bands at 1622, 1605 and 1589 cm^{-1}. The data obtained from ^{15}N substitution show that the amide II band is at 1589 cm^{-1}. The remaining bands must correspond to the scissoring mode of the amine and to a skeletal mode of the phenyl ring. Although it is impossible to differentiate between these vibrations, the assignment of the 1620 cm^{-1} band to the amine scissor is consistent with the assignments made for o- and m-aminobenzamide.

Assuming that the amide II band is primarily an NH_2

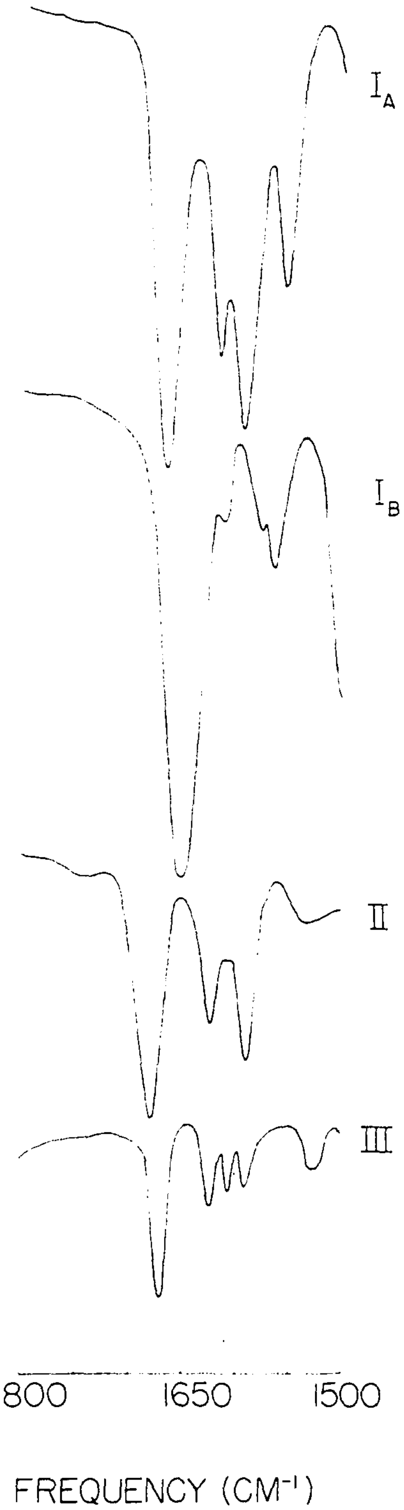
Figure 22. Solution spectra of the aminobenzamides in the 1500 to 1800 cm^{-1} region

I_A. Dibromomethane solution spectrum of o-aminobenzamide

I_B. Dibromomethane solution spectrum of o-aminobenzamide - d_4

II. Dibromomethane solution spectrum of m-aminobenzamide

III. Dibromomethane solution spectrum of p-aminobenzamide


I_A
I_B
II
III
1800
1650
1500
FREQUENCY (CM⁻¹)

scissoring vibration, the expected frequency in the ND_2 analog is in the 1200 cm^{-1} region. This region of the spectrum is "blanked" by the dibromomethane solvent, obscuring all absorptions. However, carbon tetrachloride has a narrow region near 1200 cm^{-1} that is not "blanked" and it was possible to obtain a carbon tetrachloride spectrum of benzamide and deuterated benzamide using 2.5 mm cells. Under these conditions, a new band of moderate intensity appears at 1194 cm^{-1}. This band is sensitive to ^{15}N substitution, falling at 1189 cm^{-1} in benzamide - $^{15}ND_2$. This sensitivity to ^{15}N substitution lends further support to the assignment of the 1194 cm^{-1} absorption to the amide II band (ND_2 scissoring mode) in deuterated benzamide. The deuterium derivative of o-bromobenzamide was the only substituted benzamide to show an ND_2 absorption in carbon tetrachloride solution similar to the 1194 cm^{-1} band in benzamide - d_2. In this compound, the frequency of the ND_2 scissoring mode was found to be 1196 cm^{-1}.

The fact that the ND_2 scissoring vibration is not observed in the carbon tetrachloride solution spectra of the deuterium derivatives of the other substituted benzamides is not surprising. The narrowness of the "window" in the carbon tetrachloride solvent requires that the absorption fall in a rather restricted frequency range if it is to be observed. Also, the insolubility of most of the substituted benzamides in carbon tetrachloride makes it impossible to obtain spectra of reasonable intensity even in 2.5 mm cells.

The observations discussed above are in reasonable accord with the assignment of the amide II band to an NH_2 scissoring mode. However, as will be seen in the next section, there exists considerable evidence for some degree of coupling between the amide II and the amide III absorptions.

As compared with the solution spectra, the solid state spectra of primary acid amides show a pronounced decrease in the frequency of the amide I band and a concurrent increase in the frequency of the amide II band (4, 21). These frequency shifts are normally attributed to the formation of strong intermolecular hydrogen bands of the type illustrated on page 62, although Cannon (8) has suggested that dipole interactions provide a more satisfactory explanation for the small shift in NH_2 stretching frequencies relative to the large change in the carbonyl stretching frequency. As a result of these frequency shifts, most primary acid amides examined in the solid state show two characteristic absorptions in the 1660 - 1620 cm^{-1} region (4, 33, 35, 38, 39, 41). The solid state spectra of most of the primary aromatic amides show two characteristic absorptions in this region, the exceptions being m- and p-nitrobenzamide and the aminobenzamides. Although the two bands in p-methylbenzamide do not fall within the specified range, this compound will not be considered an exception. Figure 23 shows the amide I - amide II band region of the

Figure 23. Solid state spectra of selected primary aromatic amides in the 1500 to 1800 cm^{-1} region

I_A. Potassium bromide pellet spectrum of benzamide

I_B. Potassium bromide pellet spectrum of benzamide - d_2

II_A. Potassium bromide pellet spectrum of m-bromobenzamide

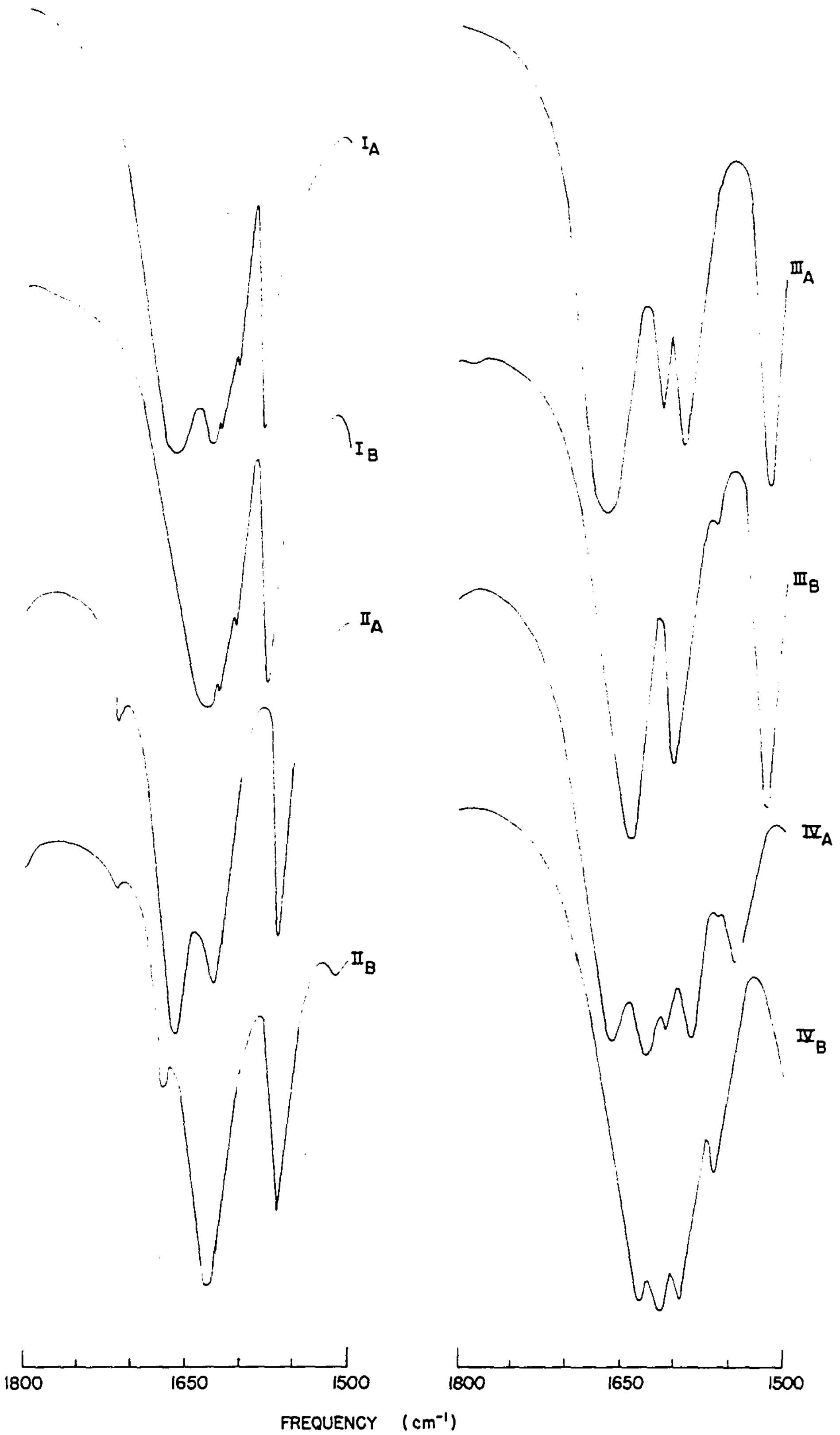
II_B. Potassium bromide pellet spectrum of m-bromobenzamide - d_2

III_A. Potassium bromide pellet spectrum of p-nitrobenzamide

III_B. Potassium bromide pellet spectrum of p-nitrobenzamide - d_2

IV_A. Potassium bromide pellet spectrum of o-aminobenzamide

IV_B. Potassium bromide pellet spectrum of o-aminobenzamide - d_4


I_A
I_B
II_A
II_B
III_A
III_B
IV_A
IV_B
1800
1650
1500
1800
1650
1500
FREQUENCY (cm⁻¹)

spectra of selected primary aromatic amides and their deuterium derivatives as observed in potassium bromide pellets. The solid state frequencies of the amide I and amide II bands along with the frequency shifts produced by ^{15}N substitution are summarized in Table 6.

As illustrated for benzamide and m-bromobenzamide in Figure 23, only one of the two strong bands remains in the solid state spectrum of the deuterium compounds in those cases where two characteristic absorptions appear in the 1660 - 1600 cm^{-1} region. This absorption usually falls at a frequency between the values observed for the two bands in the normal compound, the only exception being the deuterium derivative of o-chlorobenzamide, where the absorption is lower in frequency than either of the original absorptions. The absorption that remains in the spectra of the deuterated compounds could arise from the high frequency absorption (near 1650 cm^{-1}) shifting to a lower frequency by some 20 to 30 cm^{-1} or from the low frequency band shifting to a higher frequency by a few cm^{-1}. The former interpretation would lead to the identification of the absorption near 1650 cm^{-1} as the amide I band and the absorption near 1625 cm-1 as the amide II band and the latter interpretation would lead to inverted assignments.

Since in solution, the amide I band shifts to a lower frequency upon deuterium substitution, the absorption observed near 1650 cm^{-1} in the solid state could logically be assigned

Table 6. Observed frequencies of the amide I and amide II bands in potassium bromide pellet spectra of primary aromatic amides

Compound	Frequency $(cm^{-1})^a$ Amide I band	Amide II band
benzamide	1624 (-1.2)	1658 (-4.9)
benzamide - d_2	1630	1211
o-chlorobenzamide	1633	1650
o-chlorobenzamide - d_2	1632	1210
m-chlorobenzamide	1629	1660
p-chlorobenzamide	1620 (-1.8)	1658 (-8.6)
p-chlorobenzamide - d_2	1633	1208
o-bromobenzamide	1628	1651
o-bromobenzamide - d_2	1633	1209
m-bromobenzamide	1623 (-2.1)	1658 (-6.8)
m-bromobenzamide - d_2	1630	1211
p-bromobenzamide	1620	1660
p-bromobenzamide - d_2	1631	1203
o-iodobenzamide	1623 (-1.8)	1649 (-8.0)
o-iodobenzamide - d_2	1628	1206
m-iodobenzamide	1622	1659
m-iodobenzamide - d_2	1626	1208
p-iodobenzamide	1619	1658

[a] Frequency shifts produced by ^{15}N substitution given in parenthesis.

Table 6. (Continued)

Compound	Frequency (cm^{-1})^a	
	Amide I band	Amide II band
o-methylbenzamide	1620 (-1.8)	1654 (-5.4)
o-methylbenzamide - d_2	1630	1211
m-methylbenzamide	1615	1649
m-methylbenzamide - d_2	1623	1178
p-methylbenzamide	1616 (-2.1)	1669 (-7.1)
o-nitrobenzamide	1624 (-1.5)	1656 (-5.6)
o-nitrobenzamide - d_2	1631	1214
m-nitrobenzamide	1687 (-4.2)	1622 (-2.8)
p-nitrobenzamide	1663 (-3.7)	1614 (-2.7)
p-nitrobenzamide - d_2	1643	1206
o-aminobenzamide	1629 (-1.4)	1662 (-6.6)
o-aminobenzamide - d_4	1633	1207
m-aminobenzamide	1631 (-1.8)	1647 (-4.9)
p-aminobenzamide	1613 ($<$ 2)	1598 (-1.2)

to the amide I band and the absorption near 1625 cm^{-1} to the amide II band. However, the data obtained from ^{15}N substitution (summarized in Table 6) show that the absorption near 1650 cm^{-1} is significantly sensitive to ^{15}N substitution whereas the absorption near 1625 cm^{-1} is relatively insensitive to ^{15}N substitution. This indicates that if the absorption near 1650 cm^{-1} is in fact the amide I band, it must arise from a vibration involving considerable nitrogen motion. As discussed previously, various authors (25, 26, 29, 37) have proposed vibrational modes which would account for this ^{15}N sensitivity. However, as will be seen, a more consistent pattern of ^{15}N frequency shifts is obtained if the amide I and amide II frequencies are inverted in the solid state i.e., the amide II band lying at a higher frequency than the amide I band. This point is emphasized by the data summarized in Table 7 and Table 8. The data in Table 7 show that if the absorption near 1650 cm^{-1} in the solid state is correlated

Table 7. Comparison of ^{15}N frequency shifts between solution and solid state spectra assuming the high frequency absorption in the solid state corresponds to the amide I solution band

	^{15}N frequency shifts			
	Amide I band		Amide II band	
Compound	Solid	Solution	Solid	Solution
benzamide	-4.9	-1.8	-1.2	-7.7
p-chlorobenzamide	-8.6	-1.0	-1.8	-10.5
m-bromobenzamide	-6.8	-1.8	-2.1	-6.3
o-iodobenzamide	-8.0	<1	-1.8	-8.5
o-methylbenzamide	-5.4	-1.8	-1.8	-7.8
p-methylbenzamide	-7.1	-2.2	-2.1	-8.8
o-nitrobenzamide	-5.6	-2.0	-1.5	-6.5

Table 8. Comparison of ^{15}N frequency shifts between solution and solid state spectra, assuming that the amide II band lies at a higher frequency than the amide I band in the solid state

Compound	^{15}N frequency shifts Amide I band Solid	 Amide I band Solution	 Amide II band Solid	 Amide II band Solution
benzamide	-1.2	-1.8	-4.9	-7.7
p-chlorobenzamide	-1.8	-1.0	-8.6	-10.5
m-bromobenzamide	-2.1	-1.8	-6.8	-6.3
o-iodobenzamide	-1.8	<1	-8.0	-8.5
o-methylbenzamide	-1.8	-1.8	-5.4	-7.8
p-methylbenzamide	-2.1	-2.2	-7.1	-8.8
o-nitrobenzamide	-1.5	-2.0	-5.6	-6.5

with the amide I solution band, much larger ^{15}N frequency shifts are obtained in the solid state than in solution. On the other hand, as illustrated in Table 8, the inverted assignment in the solid state leads to a highly consistent pattern of ^{15}N frequency shifts. Although Randall _et al._ (33) suggested that this inversion of frequencies sometimes occurs, it was not illustrated in any of the spectra that they reproduced.

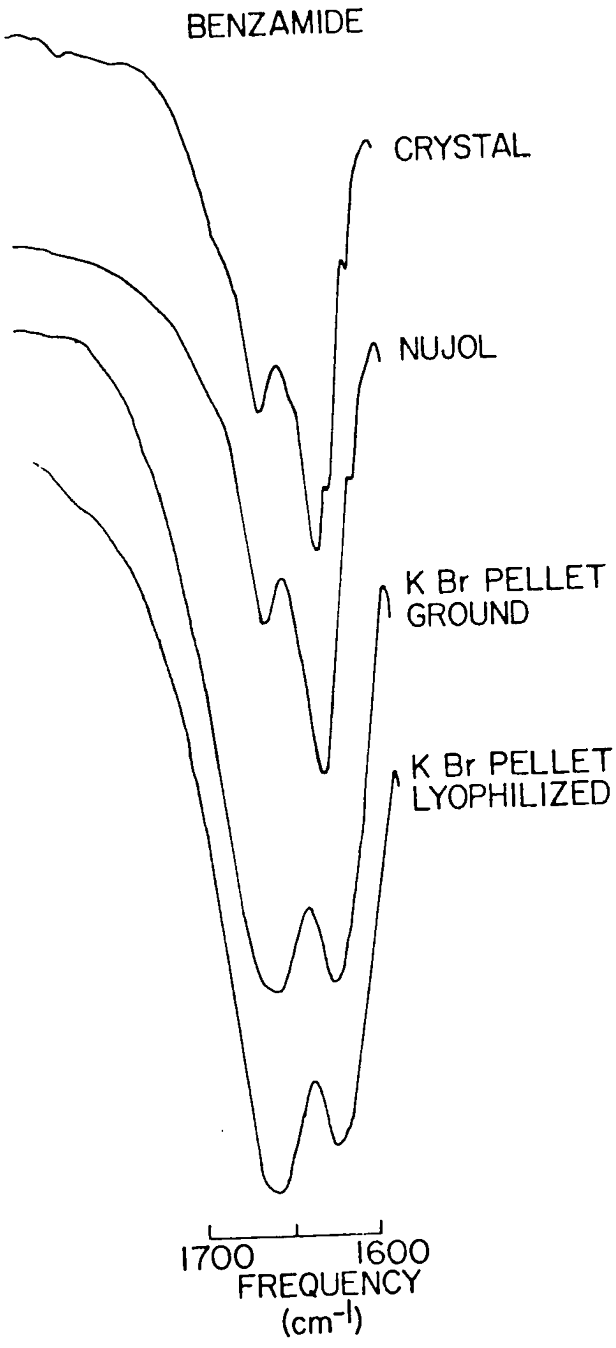
Other data can be cited which will lend credence to the inverted assignment. The single absorption remaining in the 1660 - 1620 cm^{-1} region of the spectra of the deuterated compounds was observed to be essentially insensitive to ^{15}N substitution in benzamide - d_2 and m-bromobenzamide - d_2 whose $-^{15}ND_2$ derivatives were prepared. Thus, the absorption remaining in the deuterated compounds evidently corresponds to the low frequency absorption (near 1625 cm^{-1}) in the normal compounds. This insensitivity to ^{15}N substitution was also observed for the amide I solution band in the deuterium derivatives of benzamide and m-bromobenzamide.

If the amide II band arises from the scissoring mode of the amide NH_2 group, the corresponding ND_2 absorption should appear in the 1200 cm^{-1} region. In the solid state spectra of the deuterated compounds a new absorption near 1200 cm^{-1} shows an ^{15}N frequency shift in benzamide - d_2 and m-bromobenzamide - d_2 similar to that observed for the absorption near 1650 cm^{-1} in these compounds. Thus this absorption can be identified as the amide II band in the deuterated compounds and evidently corresponds to the absorption near 1650 cm^{-1} in the normal compounds.

From the spectra on pages 19-56, it can be seen that the intensity of the 1200 cm^{-1} absorption in the deuterated compounds is much less than the intensity of the original amide II band. It is relevant to note that the intensity of the 1200 cm^{-1} band depends on the technique used for preparing the solid sample. For example, this absorption appears much stronger in the crystal spectrum of benzamide than in the corresponding potassium bromide pellet spectrum. The intensity of the 1658 cm^{-1} and 1624 cm^{-1} absorptions in the solid state spectrum of benzamide also show considerable variations in intensity. These intensity variations are illustrated in Figure 24 which shows these two bands as observed in different solid state samples. In the potassium bromide pellet prepared by grinding the sample and potassium bromide together, the two absorptions are about equal in intensity and both appear broader. In the pellet prepared by lypholizing a mixture of potassium bromide and benzamide, the intensity of the 1658 cm^{-1} band exceeds the intensity of the 1624 cm^{-1} band and again the bands are broader. It should be noted that no detailed study has been made on the intensity of these absorptions in the various substituted benzamides. The foregoing was pointed out merely to indicate that differences in intensity were observed and to suggest that perhaps the intensity of the 1200 cm^{-1} band in the deuterated compounds depends to some extent on the method used for sample preparation. Also worthy of note is the fact that the 1600 cm^{-1} phenyl bands in normal benzamide are not reproducible in potassium bromide pellet spectra. This is illustrated by their presence in Figure 23 and their absence in Figure 24.

Although the data discussed in the preceding pages lends support to the inverted assignment of the amide I and amide II bands in the solid state spectra, they also present a serious

Figure 24. Effect of the method of sample preparation on band intensities in the 1600 to 1700 region


BENZAMIDE
CRYSTAL
NUJOL
K Br PELLET
GROUND
K Br PELLET
LYOPHILIZED
1700
1600
FREQUENCY
(cm^{-1})

inconsistency, namely, the fact that the amide I band lies at a higher frequency in the deuterated derivatives than in the normal compounds. Although the cause of this reverse shift is not known, it is pertinent to mention that an expansion of intermolecular hydrogen bonds has been observed upon substituting deuterium for hydrogen in strongly hydrogen bonded crystals (16). An extensive study of N - H --- O bonds with respect to this expansion has not been made, nor is the author aware of any studies on the effect of this bond expansion on infrared frequencies.

In the aminobenzamides, the 1600 - 1660 cm^{-1} region of the spectrum is complicated by the presence of the absorption arising from the scissoring mode of the amine NH_2 group. Figure 23 shows this region of the spectrum of o-aminobenzamide and its deuterium derivative as observed in potassium bromide pellets.

Considering first o-aminobenzamide, it can be seen from Figure 23 that four absorptions (1662, 1629, 1610 and 1590 cm^{-1}) occur in the amide I - amide II band region. Absorptions corresponding to the amide I band, the amide II band, the scissoring mode of the amine NH_2 group and the A_1 ν_{c-c} mode of the phenyl ring are expected in this region. It is also conceivable that the B_1 ν_{c-c} mode of the phenyl ring could occur as high as 1590 cm^{-1}. At any rate, two absorptions should disappear upon deuteration, the absorption corresponding to the amide II band and the one arising from the scissoring mode of the amine NH_2 group. However, referring to Figure 23, it is seen that three absorptions (1633, 1612 and 1596 cm^{-1}) remain, the absorption at 1662 cm^{-1} definitely disappearing. The data obtained from ^{15}N substitution show that the 1662 cm^{-1} band is the only one that shifts significantly and can be assigned as the amide II band. A possible explanation for three bands remaining in the deuterated compound is that the absorption arising from the scissoring mode of the amine was originally under the envelope of the 1662, 1629, 1610 and 1590 cm^{-1} bands. Thus three bands would then remain in the deuterated compound. If this is the case, the 1633 cm^{-1} band in the normal compound can be correlated with the 1629 cm^{-1} absorption in the deuterated compound and assigned to the amide I band. The other two absorptions would correspond to the A_1 νc-c and B_1 νc-c modes of the phenyl ring.

The band at 1546 cm^{-1} in the unsubstituted o-aminobenzamide apparently disappears upon deuteration, which indicates that this absorption could arise from an NH_2 vibration, and thus could possibly be assigned to the scissoring mode of the amine NH_2 group. However, it is difficult to believe that an NH_2 deformation mode would lie at such a low frequency in the solid state. Another possibility is that this absorption could arise from the combination of the vibration at 1034 cm^{-1} and the one at 513 cm^{-1} ($1034 + 513 \neq 1547$). Upon deuteration the 1034 cm^{-1} band apparently shifts to 1044 cm^{-1} and becomes much sharper, whereas the 513 cm^{-1} absorption is not changed by deuteration. An absorption produced by the combination of these bands should lie at approximately 1557 cm^{-1} and a new band does appear at 1563 cm^{-1} in the spectrum of the deuterated compound which is much sharper than the 1546 cm^{-1} band in the normal compound. The difficulty in this assignment is that the intensity of the two bands (1034 and 513 cm^{-1}) is less than that of the 1546 cm^{-1} band and similarly for the bands in the deuterated compound.

The solid state spectrum of m-aminobenzamide has only three strong absorptions (1647, 1631 and 1618 cm^{-1}) in the amide I - amide II band region. Of these absorptions, only the one at 1647 cm^{-1} is appreciably sensitive to ^{15}N substitution and can be assigned to the amide II band. The band at 1631 cm^{-1} which is only slightly sensitive to ^{15}N substitution can be assigned to the amide I band and the absorption at 1618 cm^{-1} can be attributed to the scissoring mode of the amine NH_2 group.

Solid p-aminobenzamide also has three absorptions (1649, 1613 and 1598 cm^{-1}) in the 1600 - 1660 cm^{-1} region. None of these absorptions are significantly sensitive to ^{15}N substitution, hence little information can be gained from the ^{15}N frequency shifts. The appearance of these bands is also quite different from the three observed in m-aminobenzamide, in that the absorption at 1649 cm^{-1} is much weaker than the other two bands and appears as a shoulder on the 1613 cm^{-1} absorption. As discussed previously, the NH stretching absorptions indicate that the primary intermolecular bonding in this compound occurs through the amine NH_2 group, which would raise the frequency of the amine scissoring vibration to a higher than normal position. Based on this fact and on the intensity of the absorptions, the band at 1649 cm^{-1} is assigned to the scissoring mode of the amine NH_2 group, the absorption at 1613 cm^{-1} to the amide I band and the absorption at 1598 cm^{-1} to the amide II band. Thus, the amide I and II bands appear to be in the normal order in solid p-aminobenzamide. The small ^{15}N frequency shifts observed in the solid state compared to the relatively large ^{15}N frequency shifts in solution indicate that different vibrations may be involved in the two cases.

The solid state spectrum of m-nitrobenzamide (Figure 15) is characterized by the presence of a strong band at 1687 cm^{-1} and a medium strength absorption at 1622 cm^{-1}, similarly solid p-nitrobenzamide shows a strong band at 1663 cm^{-1} and a moderate band at 1614 cm^{-1}. As illustrated in Figure 23, the 1614 cm^{-1} absorption in solid p-nitrobenzamide apparently disappears upon deuteration and can be correlated with the 1587 cm^{-1} solution band which was assigned to the amide II band. The strong 1663 cm^{-1} band in solid p-nitrobenzamide shifts to 1643 cm^{-1} in the spectrum of its deuterium derivative and can be associated with the amide I solution band. Although it was not possible to completely deuterate m-nitrobenzamide, sufficient exchange was completed to indicate that the 1687 and 1622 cm^{-1} absorptions parallel the behavior of the corresponding bands in p-nitrobenzamide.

The solid state amide I band in both m- and p-nitrobenzamide is also sensitive to ^{15}N substitution, shifting by 4.2 and 3.7 cm^{-1} respectively. These values are in reasonable accord with the shifts observed for the amide I solution band and indicate that the amide I vibration involves nitrogen motion. However, the 1643 cm^{-1} band in p-nitrobenzamide - d_2 is only slightly sensitive to ^{15}N substitution, shifting by less than 2 cm^{-1}.

It should be pointed out that the above assignment of the amide I and II bands presents a serious difficulty in that the observed ^{15}N frequency shifts for the amide II band in the solid are much less than the corresponding shifts in solution. This change in ^{15}N sensitivity upon going from solid state to solution was observed for the other nitrogen vibrations, indicating that the nature of the vibration is dependent upon the state of aggregation.

It is interesting to note that the solid state amide I frequencies in m- and p-nitrobenzamide are extremely high compared to the other compounds that were studied. The high amide I frequency in these compounds is probably present because of the nature of the hydrogen bonding. It is quite conceivable that in m-nitrobenzamide, bonding to the nitro group could result in a cyclic dimer, leaving the C = O completely unbonded, one bonded NH and one "free" NH. This type of bonding is in harmony with the large splitting observed for the principal NH stretching absorptions. In p-nitrobenzamide, the bonding is probably more complex, involving both the nitro and carbonyl group. Mixed bonding of this type would lead to hydrogen bonds of varying strength in agreement with the observed multiple NH absorptions. Also, the nitro stretching absorptions in m- and p-nitrobenzamide fall at a lower frequency than in o-nitrobenzamide, indicating that bonding to the nitro group is present in the former compounds.

From the preceding discussion and the results summarized in Table 6, it is seen that in the solid state only three of the aromatic amides have the amide I and II bands in the normal order, these being m- and p-nitrobenzamide and p-aminobenzamide. The inverted assignments suggested for the other compounds do not imply that the origins of the amide I and II bands in the solution are necessarily the same as in the solid state. The data obtained simply indicate that the high frequency absorption (near 1650 cm^{-1}) in the solid state is more closely related to the amide II solution band than to the amide I solution band. Similarly, the low frequency band (near 1625 cm^{-1}) is more closely related to the amide I solution band.

THE AMIDE III AND AMIDE IV BANDS

Two absorptions which may be of value in the identification of primary aromatic amides occur in the region of the spectrum between 1420 and 1100 cm^{-1}. The first of these bands, commonly referred to as the amide III band, is a prominent absorption usually found near 1400 cm^{-1}. This band undoubtedly involves at least some C - N stretching motion and thus should show ^{15}N sensitivity. The second band of interest is a band of variable intensity in the 1100 - 1150 cm^{-1} region and is sometimes referred to as the amide IV band. Since this band is associated with the NH_2 rock (24, 41) it is easily identified by its deuterium sensitivity. The frequencies of the amide III and IV bands as observed in the normal aromatic amides and their deuterium derivatives are summarized in Table 9. The ^{15}N frequency shifts are given in parentheses.

The solution spectra of the primary aromatic amides examined in the present investigation show a prominent absorption between 1365 and 1385 cm^{-1} that can easily be identified as the amide III band. Likewise, with the exception of the p-substituted benzamides, the solid aromatic amides show a moderately intense amide III band at 1400 ± 14 cm^{-1}. The ^{15}N frequency shifts readily verify the above assignments.

Except for p-aminobenzamide which has a broad band at 1396 cm^{-1}, the solid p-substituted benzamides show two bands near 1400 cm^{-1}. The identification of the amide III band

Table 9. Observed amide III and amide IV band frequencies

	Frequency (cm^{-1})^{a}		
	Amide III band		Amide IV band
Compound	Solution (CHCl$_3$)	KBr pellet	KBr pellet
benzamide	1375 (-4.0)	1402 (-4.5)	1122 (-6.4)
benzamide - d$_2$		1416 (-8.0)	936 (-4.3)
o-chlorobenzamide	1377	1403	1121
o-chlorobenzamide - d$_2$		1418	937
m-chlorobenzamide	1368	1393	1127
p-chlorobenzamide	1374 (-5.5)	1409 (-4.8)	1124 (-6.2)
p-chlorobenzamide - d$_2$		1424	940
o-bromobenzamide	1378	1403	1134
o-bromobenzamide - d$_2$		1419	941
m-bromobenzamide	1369 (-7.2)	1388 (-7.0)	1125 (-8.7)
m-bromobenzamide - d$_2$		1397 (-9.2)	938 (-5.6)
p-bromobenzamide	1369	1404	1125
p-bromobenzamide - d$_2$		1425	940
o-iodobenzamide	1375 (-5.8)	1397 (4.8)	1134 (-6.2)
o-iodobenzamide - d$_2$		1411	937
m-iodobenzamide	1371	1386	1124
m-iodobenzamide - d$_2$		1391	937
p-iodobenzamide	1374	1404	1126

[a] Frequency shifts produced by ^{15}N substitution given in parenthesis.

Table 9. (Continued)

Compound	Frequency $(\mathrm{cm}^{-1})^a$		
	Amide III band		Amide IV band
	Solution $(CHCl_3)$	KBr pellet	KBr pellet
o-methylbenzamide	1369 (-7.2)	1392 (-7.4)	1139 (-4.3)
o-methylbenzamide - d_2		1416	939
m-methylbenzamide	1374	1388	1113
m-methylbenzamide - d_2		1395	932
p-methylbenzamide	1373 (-5.6)	1397 (-3.2) or 1413 (-2.2)	1124 (-2.4)
o-nitrobenzamide	1374 (-5.5)	1408 (-4.9)	1120 (-5.9)
o-nitrobenzamide - d_2		1424	936
m-nitrobenzamide	1378 (-4.8)	1396 (-3.2)	1122 (-2.6)
p-nitrobenzamide	1375 (-2.7)	1387 (-1.8)	1133 (-2.1)
p-nitrobenzamide - d_2		1393 (-6.4)	921 (-3.4)
o-aminobenzamide	1384 (-7.5)	1403 (-6.2)	1093 (-7.4)
o-aminobenzamide - d_2		1415	918
m-aminobenzamide	1374 (-6.1)	1399 (-5.2)	1133 (-3.9)
p-aminobenzamide	1376 (-8.0)	1396 (-2.6)	1136 (-3.6)

presents no serious difficulties in the p-substituted halogen benzamides and is found to be the higher frequency band. However in p-methylbenzamide and p-nitrobenzamide two bands of approximately equal intensity occur in the amide III band region and the observed isotopic frequency shifts are not sufficient to distinguish between the two bands.

In p-methylbenzamide, the two bands fall at 1388 and 1413 cm^{-1} and both shift by approximately the same amount upon ^{15}N substitution. By analogy to the p-halogenbenzamides, the high frequency (1413 cm^{-1}) absorption is assigned to the amide III band. As can be seen from Table 9, larger ^{15}N frequency shifts are observed for the amide III band in the deuterium derivatives than in the normal compounds. Hence by preparing p-methylbenzamide-^{15}Nd$_2$, it should be possible to make a more reliable assignment of the amide III band. Unfortunately, it was not possible to prepare the deuterium derivative of this compound by the technique used in this investigation.

Solid p-nitrobenzamide has moderate to weak absorptions at 1387 and 1406 cm^{-1}. Of these bands, only the one at 1387 cm^{-1} shows any sensitivity to ^{15}N substitution. However, the observed shift of 1.8 cm^{-1} is hardly sufficient to assign this absorption to the amide III band. In the deuterium derivative the two bands fall at 1393 and 1411 cm^{-1} respectively. The 1393 cm^{-1} band shows an ^{15}N frequency shift of 6.4 cm^{-1} while the 1411 cm^{-1} band shows a shift of only 3.1 cm^{-1}. Thus the 1393 cm^{-1} band in the deuterium derivative, corresponding to the 1387 cm^{-1} band in the normal compound can be assigned to the amide III band with a reasonable degree of confidence.

The nature of the vibration producing the amide III band is questionable. Various authors (11, 24, 33) have assigned this band to the C - N stretching vibration. Other authors (29, 37, 41) have assigned it to coupled vibrations of the O - C - N group. The data in Table 9 show that ^{15}N substitution produces a shift of less than 8 cm^{-1} in the amide III band and deuterium substitution produces a significant "backward" shift. The largest ^{15}N frequency shifts correspond to a value of only 1.006 for the ratio $\frac{\nu_{^{14}NH_2}}{\nu_{^{15}NH_2}}$, much less than the calculated value for a C - N stretching vibration. Thus these isotopic frequency shifts are not in agreement with the assignment of the amide III band to a C - N stretching vibration. In most cases, the amide I band did not show sufficient sensitivity to ^{15}N substitution to indicate that the O - C - N system vibrates as a unit, indicating that the amide III band is not produced by coupled vibrations of the O - C - N group.

The "backward" shift produced by deuterium substitution could only result from a coupling of the amide III band with a neighboring vibration. This coupling is most likely to involve the NH_2 scissoring vibration in the normal compounds and/or the ND_2 scissoring mode in the deuterium derivatives. That is, the frequency of the amide III band could be forced lower as a result of coupling with the amide II band and, upon deuteration, since the ND_2 scissor now lies below the amide III band, the coupling would be relieved and the amide III absorption would consequently shift "backward" toward its normal position. Likewise, if the amide III and ND_2 scissoring mode were coupled, the amide III band would be forced toward a higher frequency in the deuterated compound. The greater sensitivity of the amide III frequency to ^{15}N substitution in the deuterated compounds shows that the coupling is somewhat less and thus indicates that the coupling with the NH_2 scissor is greater than with the ND_2 scissor. Such an assumption leads to the assignment of the amide III band to a coupled vibration originating from C - N stretching and NH_2 deformation modes.

It should be mentioned at this point that the above band correlations and interpretations are perhaps over-simplified. The principal vibrational unit in the amide skeleton is apparently the C - C - N group which has two stretching modes. The higher frequency stretching vibration could couple with the NH_2 scissor and give rise to two absorptions, the amide II and amide III bands. Thus, these two bands would be assigned to the resulting coupled vibrations involving the C - C - N stretch and the NH_2 deformation. Upon deuteration, the coupling would change and the band near 1400 cm^{-1} would now assume a greater amount of C - C - N stretching character and the band near 1200 cm^{-1} would assume a greater ND_2 scissoring character. This assignment of modes would correspond to the assignments for acetanilides[1] whose behavior toward ^{15}N and

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[1] Day, E. W., Jr., Iowa State University of Science and Technology, Ames, Iowa. Data from isotopic substitution. Private communication (1962).

deuterium substitution parallels that of the benzamides very closely. This reasoning eliminates the problems associated with the "backward" shift of the amide III as well as the change in the ^{15}N sensitivity of amide III band upon deuteration.

As mentioned previously, the amide IV band is a band of variable intensity and occurs in the 1100 - 1150 cm^{-1} region. Because this is in the expected frequency range for an NH_2 rocking vibration (1, 12, 17, 24, 29, 37, 40), the amide IV band has been associated with such a vibration. Weckerlin and Luttke (41) found the amide IV band in benzamide to be sensitive to ^{15}N substitution lending further support to the assignment.

All of the aromatic amides that were investigated, except o-aminobenzamide, show a band between 1100 and 1150 cm^{-1} that can be assigned to the amide IV band. In o-aminobenzamide the amide IV band falls at 1093 cm^{-1}. As can be seen from the data summarized in Table 9, the amide IV band is sensitive to ^{15}N substitution and shifts to between 920 and 940 cm^{-1} upon deuteration. The frequency shift produced by deuterium substitution corresponds to a value of approximately 1.31 for the frequency ratio, $\frac{\nu_{NH_2}}{\nu_{ND_2}}$. While this is consistent with the assignment of the amide IV band to an NH_2 rocking vibration, it should be noted that in certain instances this band shows ^{15}N frequency shifts resulting in values greater than 1.006

for $\frac{\nu^{14}NH_2}{\nu^{15}NH_2}$ which is larger than the expected value for an NH_2 vibration, thus indicating that perhaps some coupling with the amide III band occurs.

Referring to the tables in the appendix, it is seen that quite frequently a second band in the 1100 - 1150 cm^{-1} region is somewhat sensitive to isotopic substitution. This band probably arises from a breathing mode of the phenyl ring which is sensitive to the masses of the substituent atoms (34). The isotopic shifts observed are larger than those expected for such a vibration and probably result because of coupling with a vibration involving motion of the amide group.

CHARACTERISTIC AMIDE ABSORPTIONS BELOW 800 cm^{-1}

The interpretation of the isotopic shifts in this region is quite difficult and necessarily involves considerable subjective judgement. Because of coupling with vibrations of the amide group, some absorptions arising from skeletal modes of the phenyl ring show significant isotopic frequency shifts. Nevertheless, isotopic substitution is of some value in the identification of the low frequency amide absorptions. The vibrations remaining to be assigned are the in-plane and out-of-plane rocking modes and the in-plane scissoring mode of the O - C - N system together with the NH_2 symmetric out-of-plane (wagging) vibration. The NH_2 asymmetric out-of-plane (twisting) mode could also fall in this region but other authors (11, 18, 41) have assigned it at higher frequencies.

Although the skeletal deformation frequencies are quite uncertain, it is expected that the in-plane scissoring mode should lie at the higher frequency and the in-plane rocking vibration at the lower frequency. Previous investigations of primary acid amides (11, 22, 26, 29, 37, 41) have led to the assignment of various bands in the 450 - 700 cm^{-1} region to the O - C - N scissoring vibration, but there is no indication that these limits are rigid. The position of the planar and nonplanar rocking vibrations is even more questionable. Weckerlin and Luttke (41) working with benzamide and ^{15}N-labeled benzamide assigned the nonplanar rocking vibration at 792 cm^{-1} while Gray (18) also working with benzamide and ^{15}N-labeled benzamide suggested that this mode was below 420 cm^{-1}. Gray (18) also suggested that the planar rocking vibration of the O - C - N system lies below 420 cm^{-1}.

The data obtained in the present investigation, although not conclusive, may be of some value in the identification of the deformation modes of the O - C - N group. As can be seen from Table 10, the solid aromatic amides show an absorption between 740 and 800 cm^{-1} that is usually sensitive to ^{15}N substitution and could arise from the O - C - N planar scissoring vibration. If the planar scissoring mode of the O - C - N group is in the 700 - 800 cm^{-1} region, it is anticipated that the out-of-plane rocking mode should lie in the 500 - 600 cm^{-1} region, but no bands in this region consistently show ^{15}N frequency shifts. However, all of the aromatic amides do consistently show a band between 530 and 560 cm^{-1} which, because of its persistence, appears to be characteristic of the $CONH_2$ group and thus is assigned the O - C - N out-of-plane rocking vibration. The lack of sensitivity to ^{15}N substitution could result from coupling with a nonplanar vibration of the phenyl ring. The assignments of the planar scissoring and non-planar rocking vibrations are summarized in Table 10.

The above assignments are by no means unequivocal and, of course, leave the planar rocking vibration of the O - C - N system unassigned. Some of the spectra show a band near 450

Table 10. Suggested assignments of the planar scissoring and nonplanar rocking vibrations

Compound	Frequency (cm^{-1})[a] Scissoring vibrations	Rocking vibrations
benzamide	791 (-2.2)	529 (-3.0)
o-chlorobenzamide	777	563
m-chlorobenzamide	798	566
p-chlorobenzamide	792 (-2.4)	537 (0)
o-bromobenzamide	770	559
m-bromobenzamide	794 (< 1)	559 (-1.1)
p-bromobenzamide	783	534
o-iodobenzamide	771 (-2.4)	557 (-1.3)
m-iodobenzamide	795 or 739	554
p-iodobenzamide	782	534
o-methylbenzamide	779 (< 1)	537 (< 1)
m-methylbenzamide	771	521
p-methylbenzamide	795 (-2.4)	535 (< 1)
o-nitrobenzamide	771 (0)	556 (-1.0)
m-nitrobenzamide	798 (< 1)	560 (+1.0)
p-nitrobenzamide	768 (-3.8)	539 (< 1)
o-aminobenzamide	754 (-2.1)	537 (0)
m-aminobenzamide	764 (-1.0)	538
p-aminobenzamide	781 (-1.4)	537 (-1.4)

[a] Frequency shifts produced by ^{15}N substitution given in parenthesis.

cm^{-1} that could arise from such a vibration but not enough evidence was obtained to substantiate such an assignment. Because of the complexity of the phenyl substitution bands in the low frequency region, a more satisfactory assignment of the skeletal modes of the amide group would require a detailed study of the phenyl vibrations in similar compounds. Also polarization studies would be of value in differentiating between the planar and nonplanar amide skeletal vibrations.

Various authors (18, 29, 41) have assigned the NH_2 wagging vibration in the 600 - 800 cm^{-1} region. The data listed in Table 11 show that all the aromatic amides included in the present investigation have a band in the region of the spectrum between 620 and 680 cm^{-1} that is sensitive to ^{15}N substitution and disappears upon deuteration, apparently shifting to near 500 cm^{-1}. The observed isotopic frequency shifts give values of approximately 1.3 and 1.004 for the ratios, $\frac{\nu_{NH_2}}{\nu_{ND_2}}$ and $\frac{\nu_{^{14}NH_2}}{\nu_{^{15}NH_2}}$, in harmony with the expected ratios for an NH_2 vibration, further verifying the assignment of this band to the NH_2 wagging mode.

The only NH_2 vibration remaining to be assigned is the asymmetric out-of-plane deformation. Since this vibration involves very little nitrogen motion, the use of ^{15}N substitution will be of no value in its identification. Deuterium substitution, however, should be of value, as shifts comparable to those observed for other NH_2 vibrations would be expected.

Table 11. Observed frequencies of the NH_2 and ND_2 wagging vibrations in potassium bromide pellets of primary aromatic amides

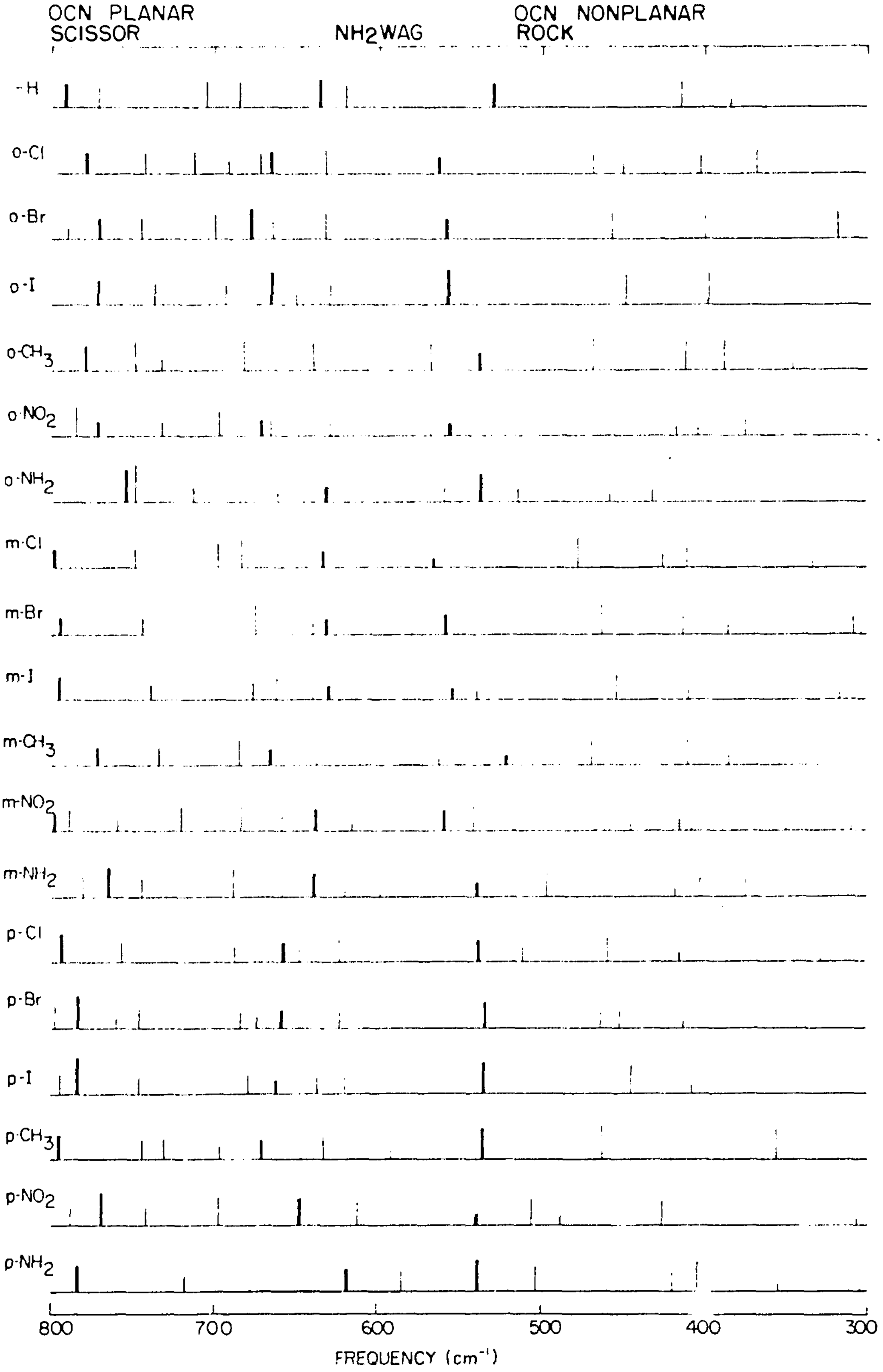
	Frequency (cm^{-1})[a]	
Compound	NH_2 wag	ND_2 wag
benzamide	636 (-3.0)	480
o-chlorobenzamide	666	504
m-chlorobenzamide	634	---
p-chlorobenzamide	657 (-2.0)	489
o-bromobenzamide	676	503
m-bromobenzamide	631 (-2.6)	480
p-bromobenzamide	657	485
o-iodobenzamide	665 (-2.3)	496
m-iodobenzamide	630	493
p-iodobenzamide	661	---
o-methylbenzamide	682 (-2.8)	510
m-methylbenzamide	666	505
p-methylbenzamide	671 (-2.6)	---
o-nitrobenzamide	671 (-3.0)	502
m-nitrobenzamide	638 (-2.8)	---
p-nitrobenzamide	648 (-2.3)	479
o-aminobenzamide	631 (-2.5)	489
m-aminobenzamide	639 (-2.6)	---
p-aminobenzamide	619 (-2.4)	---

[a] Frequency shifts produced by ^{15}N substitution given in parenthesis.

Davies and Hallam (11) assigned the 856 cm^{-1} band in acetamide to the NH_2 twisting vibration. Similarly Gray (18) assigned the 851 cm^{-1} band in benzamide to this vibration while Weckerlin and Luttke (41) assigned it to a band at 1261 cm^{-1} in benzamide. In the present work, no band was found at 1261 cm^{-1} in the potassium bromide pellet spectrum of benzamide but a weak band was observed at 1250 cm^{-1} in the crystal spectrum. Neither the band at 1250 cm^{-1} nor the one near 850 cm^{-1} show significant deuterium shifts, indicating that the above assignments are incorrect. However no bands were observed in the substituted benzamides that could be satisfactorily assigned to such a vibration. Because the absorption arising from the twisting mode of the NH_2 group could be quite weak, it might not be observed in the potassium bromide pellet spectra. This being the case, spectra of solidified melts of the normal and deuterium compounds would be valuable in the identification of this band.

Figure 24 summarizes by means of line charts, the absorptions below 800 cm^{-1} in the various aromatic amides. The amide vibrations are represented by heavy lines.

Figure 25. Infrared absorptions of primary aromatic amides in the 300 to 800 cm^{-1} region


OCN PLANAR SCISSOR
NH2 WAG
OCN NONPLANAR ROCK
-H
o-Cl
o-Br
o-I
o-CH3
o-NO2
o-NH2
m-Cl
m-Br
m-I
m-CH3
m-NO2
m-NH2
p-Cl
p-Br
p-I
p-CH3
p-NO2
p-NH2
800
700
600
500
400
300
FREQUENCY (cm-1)

SUGGESTIONS FOR FUTURE WORK

The greatest need for additional work occurs in the spectral region below 650 cm^{-1}. Satisfactory assignment of the amide vibrations in this region requires a more thorough knowledge of phenyl substitution bands than is presently available. A possible approach to this problem is to identify the vibrations of the phenyl ring by investigating simple disubstituted benzenes and then extend the study to substituted benzamides and similar compounds.

Valuable information concerning the infrared spectra of aromatic amides could be obtained from polarization studies. A study of this type would be especially valuable in differentiating between in-plane and out-of-plane vibrations. Also, comparison of the polarized spectra of the normal and deuterium compounds would be quite useful in correlating absorptions. Experimental difficulties limit the application of this technique to some extent, since it is difficult to grow well oriented crystals sufficiently thin for infrared work and secondly, commercially available polarizers do not transmit below 500 cm^{-1}.

Another possible source of information is the spectra of the molten amides and their isotopic derivatives. The correlation of bands between the solid and melt would then be possible and the frequency shifts upon going from the solid to the melt would give some idea of the nature of the hydrogen bonding in the melt, and hence the molecular species present. Extension to the gaseous phase would give information concerning the molecular structure of the vapor.

SUMMARY

Isotopic substitution was used to identify the characteristic amide absorptions in benzamide, the halogen substituted benzamides, the methylbenzamides and the nitrobenzamides. Table 12 lists the solid state frequencies of the amide vibrations which are valuable in identifying the above compounds.

The isotopic frequency shifts indicate that with the possible exception of m- and p-nitrobenzamide, the amide I band is primarily a carbonyl stretching vibration. The origin of the amide II and III bands is somewhat more complicated. However, these bands undoubtedly arise from coupled vibrations of the C - C - N stretching and NH_2 scissoring modes, the extent of coupling being difficult to assess. The amide IV absorption is primarily an NH_2 rocking vibration with possibly a small amount of C - N character.

The solid state frequencies of the amide I and II bands are determined largely by the strength of the intermolecular hydrogen bonds. As a result of this bonding, the amide I and II bands are inverted in the solid state spectra of all the primary aromatic amides except m- and p-nitrobenzamide and p-aminobenzamide.

Table 12. Characteristic amide frequencies as observed in potassium bromide pellets of primary aromatic amides

Compound	Principal amide NH stretching absorptions		Amide I band	Amide II band	Amide III band	Amide IV band	NH_2 wag
benzamide	3367	3173	1624	1658	1402	1122	636
o-chlorobenzamide	3362	3180	1633	1650	1403	1121	666
m-chlorobenzamide	3364	3183	1629	1660	1393	1127	634
p-chlorobenzamide	3370	3173	1620	1658	1409	1124	657
o-bromobenzamide	3365	3180	1628	1651	1403	1134	676
m-bromobenzamide	3357	3174	1623	1658	1388	1125	631
p-bromobenzamide	3363	3175	1620	1660	1404	1125	657
o-iodobenzamide	3364	3182	1623	1649	1397	1134	665
m-iodobenzamide	3343	3159	1622	1659	1386	1124	630
p-iodobenzamide	3360	3176	1619	1658	1404	1126	661
o-methylbenzamide	3369	3184	1620	1654	1392	1139	682
m-methylbenzamide	3381	3198	1615	1649	1388	1113	666
p-methylbenzamide	3350	3168	1616	1669	1397	1124	671
o-nitrobenzamide	3364	3178	1624	1656	1408	1120	671
m-nitrobenzamide	3448	3160	1687	1622	1396	1122	638
p-nitrobenzamide	3419	3315					
	3197		1663	1614	1387	1133	648
o-aminobenzamide	3400	3201	1629	1662	1403	1093	631
m-aminobenzamide	3385	3199	1631	1647	1399	1133	639
p-aminobenzamide	3470	3328	1613	1598	1396	1136	619

BIBLIOGRAPHY

1. Angell, C. L., Sheppard, N., Yamaguchi, A., Shimanouchi, T., Miyazawa, T. and Mizushima, S. *Trans. Faraday Soc.* *53*, 589 (1957).

2. Badger, R. M. and Pullin, A. D. E. *J. Chem. Phys.* *22*, 1142 (1954).

3. ________ and Rubalcava, H. *Proc. Nat. Acad. Sci. U. S.* *40*, 12 (1954).

4. Bellamy, L. J. "The infrared spectra of complex molecules." 2nd ed. New York, N. Y., John Wiley and Sons, Inc. 1958.

5. Blicke, F. F. and Lilenfeild, W. M. *J. Am. Chem. Soc.* *65*, 2282 (1943).

6. Buswell, A. M., Downing, J. R. and Rodebush, W. H. *J. Am. Chem. Soc.* *62*, 2759 (1940).

7. ________, Rodebush, W. H. and Roy, M. F. *J. Am. Chem. Soc.* *60*, 2444 (1938).

8. Cannon, C. G. *Mikrochim. Acta* 555 (1955).

9. Davies, M. and Evans, J. C. *J. Chem. Phys.* *20*, 342 (1952).

10. ________, ________ and Jones, R. L. *Trans. Faraday Soc.* *51*, 761 (1955).

11. ________ and Hallam, H. E. *Trans. Faraday Soc.* *47*, 1170 (1951).

12. Evans, J. C. *J. Chem. Phys.* *22*, 1228 (1954).

13. Fones, W. S. and White, J. *Arch. Biochem.* *20*, 118 (1952).

14. Fraser, D. B. and Price, W. C. *Nature* *170*, 490 (1952).

15. ________ and ________ *Proc. Roy. Soc. (London) B* *141*, 66

16. Gallagher, K. J. "The isotope effect in relation to bond length in hydrogen bonds in crystals." In Hadzi, D., ed. "Hydrogen bonding." pp. 45-54. New York, N. Y., Pergamon Press. 1959.

17. Gray, A. P. and Lord, R. C. *J. Chem. Phys. 26*, 690 (1957).

18. Gray, L. S. "Characteristic infrared absorption frequencies of nitrogen-containing bonds." Unpublished Ph. D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1958.

19. Hadzi, D. and Sheppard, N. *Proc. Roy. Soc. (London) A 216*, 247 (1953).

20. Jacobs, W. A. and Heidelberger, M. *J. Am. Chem. Soc. 39*, 1435 (1917).

21. Jones, R. N. and Sandorfy, C. "The application of infrared and raman spectrometry to the elucidation of molecular structure." In Weissberger, A., ed. "Technique of organic chemistry." Vol. 9 pp. 247-580. New York, N. Y., Interscience Publishers, Inc. 1956.

22. Kahovec, L. and Wusmuth, H. *Z. physik. chem. (Leipzig) B48*, 70 (1941).

23. Kao, C. H. and Ma, S. Y. *J. Chem. Soc.* 443 (1931).

24. Kuratani, K. *Bull. Chem. Soc. Japan 25*, 258 (1952).

25. Lecomte, J. and Freymann, R. *Bull. soc. chim. France 8*, 601 (1941).

26. ________ and ________ *Bull. soc. chim. France 8*, 612 (1941).

27. McElvain, S. M. and Carney, T. P. *J. Am. Chem. Soc. 68*, 2599 (1946).

28. Miller, W. H., Dessert, A. M. and Anderson, G. W. *J. Am. Chem. Soc. 70*, 502 (1948).

29. Miyazawa, T. *J. Chem. Soc. Japan, Pure Chem. Sect. 76*, 821 (1955).

30. Penfold, B. R. and White, J. C. B. *Acta Cryst. 12*, 130 (1959).

31. Pimentel, G. C. and McClellan, A. L. "The hydrogen bond." San Francisco, Calif., W. H. Freeman and Company. 1960.

32. Pinchas, S., Samuel, D. and Weiss-broady, M. *J. Chem. Soc.* 1688 (1961).

33. Randall, H. M., Fowler, R. G., Fuson, N. and Dangl, J. R. "Infrared determination of organic structures." New York, N. Y., D. Van Nostrand, Inc. 1949.

34. Randle, R. R. and Whiffen, D. H. "The characteristic vibration frequencies of substituted benzenes." In Sell, G., ed. "Molecular spectroscopy." pp. 111-128. London, England, The Institute of Petroleum. 1955.

35. Richards, R. E. and Thompson, H. W. J. Chem. Soc. 1248 (1947).

36. Sheppard, N. "Infrared spectroscopy of hydrogen bonding-band-widths and frequency shifts." In Hadzi, D., ed. "Hydrogen bonding." pp. 45-54. New York, N. Y., Pergamon Press. 1959.

37. Smith, C. H. and Robinson, J. D. J. Am. Chem. Soc. 79, 1349 (1957).

38. Thompson, H. W., Brattain, R. R., Randall, H. M. and Rasmussen, R. S. "Infrared spectroscopic studies of penicillin." In Clarke, H. T., Johnson, J. R. and Robinson, R., ed. "The chemistry of penicillin." pp. 382-414. Princeton, N. Y., Princeton University Press. 1949.

39. _______, Nicholson, D. L. and Short, L. N. Discuss. Faraday Soc. 9, 222 (1950).

40. Tsuboi, M. Spectrochim. Acta 16, 505 (1960).

41. Weckerlin, Von S. and Luttke, W. Z. Elektrochem. 64, 1228 (1960).

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APPENDIX

Notation Used in Tables 13-44

The following notation was used in describing the absorptions observed in the infrared spectra of the primary aromatic amides:

vs = very strong absorption
s = strong absorption
sh = shoulder
ms = medium to strong absorption
m = medium absorption
mw = medium to weak absorption
w = weak absorption
vw = very weak absorption

Table 13. Observed infrared absorptions in benzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{^{14}NH_2}-\nu_{^{15}NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{^{14}NH_2}-\nu_{^{15}NH_2}$ (cm^{-1})
3367 (ms)	-11.5	3519 (m)	-10.5
3306 (sh)	-12.5		
3173	-11.0	3402 (m)	-9.5
3079 (sh)	-1.0		
3064 (sh)	+1.0		
3028 (sh)	+2.5		
1658 (s)	-4.9	1587 (m)	-7.7
1624 (ms)	-1.2	1679 (vs)	-1.8
1616 (sh)	+1.0		
1603 (sh)	+1.0	1602 (mw)	<1
1577 (m)	<1	1579 (sh)	-1.6
1495 (vw)	--	1494 (vw)	--
1449 (m)	-1.0	1449 (w)	<1
1402 (ms)	-4.5	1375[a] (m)	-4.0
1298 (w)	+1.9	1301 (vw)	<1
1181 (w)	--		
1142 (w)	-1.8		
1122 (mw)	-6.4		
1073 (w)	<1		
1026 (w)	<1		
1001 (w)	--		
987 (vw)	--		
925 (sh)	--		
919 (w)	--		
849 (w)	1		
810 (mw)	-2.4		
791 (m)	-2.2		
771 (mw)	-1.3		
705 (m)	+1.2		
685 (m)	<1		
636 (m)	-3.0		
620 (mw)	<1		
529 (m)	-3.0		
414 (m)	--		
384 (vw)	-2.2		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 14. Observed infrared absorptions in deuterated benzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3063 (w)	
3033 (vw)	
2528 (ms)	2637 (mw)
2446 (sh)	2578 (sh)
2361 (ms)	2486 (mw)
1630 (s)	1670 (s)
1618 (sh)	
1602 (sh)	1604 (w)
1576 (mw)	1582 (m)
	1507 (w)
1497 (w)	1498 (w)
	1476 (w)
1451 (m)	1451 (m)
1416 (ms)	
1296 (w)	
1211 (w)	
1179 (w)	
1105 (vw)	
1075 (w)	
1025 (w)	
1001 (vw)	
936 (m)	
849 (vw)	
798 (w)	
738 (sh)	
715 (m)	
688 (m)	
606 (m)	
559 (m)	
480 (m)	
405 (m)	
375 (sh)	

Table 15. Observed infrared absorptions in o-chlorobenzamide

KBr pellet frequency (cm-1)	Solution (CH_2Br_2) frequency (cm^{-1})
3362 (ms)	3513 (m)
3180 (ms)	3395 (m)
3058 (sh)	
1650 (s)	1587 (m)
1633 (vs)	1683 (vs)
1596 (sh)	1596 (sh)
1565 (w)	
1481 (mw)	1477 (w)
1433 (w)	1439 (w)
1403 (m)	1377[a] (m)
1278 (w)	
1133 (sh)	
1121 (m)	
1048 (m)	
1039 (mw)	
1014 (vw)	
954 (w)	
844 (sh)	
822 (mw)	
777 (mw)	
742 (mw)	
712 (mw)	
691 (w)	
672 (sh)	
666 (mw)	
632 (m)	
563 (mw)	
469 (mw)	
450 (w)	
402 (mw)	
368 (m)	
301 (vw)	

[a] Frequency taken from a chloroform solution spectrum.

Table 16. Observed frequencies in deuterated o-chlorobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
2527 (m)	2638 (w)
2446 (sh)	
2368 (m)	2482 (w)
1632 (s)	1674 (vs)
1596 (sh)	1595 (sh)
1564 (w)	
1483 (mw)	1476 (w)
1433 (sh)	1439 (w)
1418 (m)	
1210 (vw)	
1136 (vw)	
1116 (vw)	
1046 (mw)	
1038 (sh)	
954 (sh)	
937 (mw)	
788 (vw)	
767 (sh)	
750 (m)	
711 (vw)	
672 (mw)	
609 (m)	
575 (mw)	
546 (m)	
504 (mw)	
467 (mw)	
442 (w)	
395 (w)	
366 (m)	
294 (vw)	

Table 17. Observed infrared absorptions in m-chlorobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3364 (m)	3519 (m)
3183 (m)	3402 (m)
3077 (sh)	
1660 (vs)	1585 (ms)
1629 (s)	1684 (s)
	1598 (sh)
1571 (m)	1571 (sh)
1478 (vw)	1479 (vw)
1435 (m)	1420 (w)
1393 (m)	1368[a] (m)
1301 (vw)	
1270 (vw)	
1171 (vw)	
1157 (w)	
1127 (mw)	
1084 (w)	
1001 (vw)	
979 (vw)	
917 (w)	
905 (mw)	
839 (w)	
798 (mw)	
749 (mw)	
697 (mw)	
683 (mw)	
645 (mw)	
634 (mw)	
566 (w)	
477 (m)	
425 (w)	
410 (mw)	
333 (m)	

[a] Frequency taken from a chloroform solution spectrum.

Table 18. Observed infrared absorptions in p-chlorobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})
3370 (m)	-12.5	3519 (m)	-7.5
3173 (m)	-3.5	3403 (m)	-5.5
3058 (sh)	-3.0		
2748 (vw)	--		
1658 (vs)	-8.6	1596 (s)	+1.0 -10.5
1620 (s)	-1.8	1682 (vs)	-1.0
1594 (sh)	-1.9		
1568 (m)	--	1572 (w)	--
1493 (mw)	--	1492 (w)	--
1409 (m)	-4.8	1374^a(ms)	-5.5
1389 (mw)	-3.0		
1302 (vw)	--		
1288 (vw)	--		
1268 (w)	--		
1181 (w)	<1		
1148 (w)	-3.2		
1124 (w)	-6.2		
1092 (m)	-1.5		
1015 (m)	--		
968 (vw)	+1.0		
948 (vw)	--		
848 (m)	<1		
792 (m)	-2.4		
756 (mw)	-2.3		
686 (w)	+1.5		
657 (mw)	-2.0		
648 (mw)	+1.5		
624 (m)	--		
537 (m)	--		
511 (mw)	-1.5		
459 (m)	--		
415 (w)	<1		
329 (m)	--		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 19. Observed infrared absorptions in deuterated p-chlorobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3376 (vw)	
3182 (vw)	
2529 (m)	2640 (w)
2442 (sh)	
2368 (m)	2483 (w)
1633 (vs)	1677 (vs)
1600 (sh)	1594 (w)
1568 (m)	1571 (w)
1494 (w)	1491 (w)
1424 (m)	
1391 (sh)	
1301 (vw)	
1285 (w)	
1282 (w)	
1208 (vw)	
1178 (w)	
1146 (vw)	
1123 (vw)	
1092 (ms)	
1015 (ms)	
966 (vw)	
950 (sh)	
940 (mw)	
847 (ms)	
769 (sh)	
763 (m)	
685 (w)	
643 (w)	
623 (w)	
570 (w)	
535 (m)	
512 (w)	
489 (mw)	
458 (m)	
414 (w)	
325 (m)	

Table 20. Observed infrared absorptions in o-bromobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm-1)
3365 (m)	3509 (m)
3180 (m)	3392 (m)
1651 (vs)	1585 (m)
1628 (s)	1684 (vs)
1593 (sh)	1593 (m)
1566 (w)	
1477 (wm)	1472 (w)
1431 (w)	1433 (w)
1403 (m)	1378[a] (m)
1281 (vw)	
1263 (vw)	
1166 (w)	
1134 (m)	
1117 (sh)	
1043 (w)	
1030 (m)	
985 (vw)	
953 (wm)	
873 (w)	
812 (w)	
790 (w)	
770 (wm)	
745 (wm)	
700 (m)	
676 (m)	
665 (sh)	
632 (m)	
559 (wm)	
457 (m)	
400 (m)	
319 (m)	

[a] Frequency taken from a chloroform solution spectrum.

Table 21. Observed infrared absorptions in deuterated o-bromobenzamide

KBr pellet frequency (cm-1)	Solution (CH_2Br_2) frequency (cm^{-1})
2531 (m)	2631 (w)
2438 (w)	
2370 (m)	2476 (w)
1633 (vs)	1677 (vs)
1591 (sh)	1593 (m)
1564 (w)	
1477 (mw)	1472 (w)
	1436 (w)
1419 (ms)	
1267 (vw)	
1209 (w)	
1165 (vw)	
1132 (vw)	
1109 (vw)	
1041 (sh)	
1028 (m)	
989 (vw)	
954 (mw)	
941 (m)	
876 (vw)	
788 (w)	
750 (s)	
707 (w)	
655 (mw)	
610 (m)	
562 (mw)	
537 (mw)	
503 (m)	
456 (m)	
398 (m)	
315 (m)	

Table 22. Observed infrared absorptions in m-bromobenzamide

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{15NH_2}-\nu_{14NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{15NH_2}-\nu_{14NH_2}$ (cm^{-1})
3357 (ms)	-13.0	3520 (m)	-9.0
3174 (ms)	-8.0	3405 (m)	-8.0
3070 (sh)	--		
1658 (vs)	-6.8	1586 (m)	-6.3
1623 (s)	-2.1	1685 (vs)	-1.8
		1599.0 (sh)	-1.3
1565 (ms)	--	1568.0	<1
1477 (vw)	--	1478.0 (vw)	--
1428 (ms)	-2.9	1421 (w)	--
1388 (ms)	-7.0	1369[a] (m)	-7.2
1299 (vw)	--		
1292 (sh)	--		
1275 (vw)	--		
1175 (vw)	--		
1151 (w)	-2.8		
1125 (m)	-8.7		
1068 (mw)	--		
1012 (vw)	--		
997 (w)	< 1		
977 (vw)	< 1		
918 (w)	--		
903 (mw)	--		
794 (mw)	< 1		
744 (mw)	-1.4		
675 (m)	<1		
640 (w)	--		
631 (w)	-2.6		
559 (mw)	-1.1		
461 (m)	--		
412 (mw)	<1		
385 (vw)	-1.5		
309 (mw)	<1		
304 (sh)	-1.1		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 23. Observed infrared absorptions in deuterated m-bromobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3070 (vw)	
2522 (m)	2636 (mw)
2441 (sh)	
2358 (m)	2486 (mw)
1670 (sh)	
1630 (s)	1678 (s)
	1597 (sh)
1565 (m)	1572 (m)
1515 (w)	
1476 (w)	1469 (w)
1443 (m)	1432 (w)
1426 (sh)	
1397 (m)	
1296 (vw)	
1274 (vw)	
1211 (w)	
1170 (vw)	
1112 (w)	
1095 (vw)	
1067 (w)	
1015 (vw)	
997 (w)	
977 (vw)	
938 (m)	
903 (w)	
805 (mw)	
791 (mw)	
748 (s)	
680 (mw)	
664 (mw)	
614 (mw)	
562 (w)	
480 (mw)	
463 (mw)	
413 (w)	
385 (vw)	
308 (m)	
302 (sh)	

Table 24. Observed infrared absorptions in p-bromobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3363 (m)	3521 (m)
3175 (m)	3404 (m)
1660 (s)	1599 (s)
1620 (s)	1685 (vs)
1585 (mw)	
1564 (mw)	1572 (sh)
1486 (w)	1490 (m)
1404 (m)	1369[a] (m)
1383 (mw)	
1301 (w)	
1283 (mw)	
1265 (w)	
1181 (w)	
1171 (sh)	
1145 (mw)	
1125 (mw)	
1105 (sh)	
1067 (m)	
1010 (m)	
962 (vw)	
945 (vw)	
843 (m)	
823 (sh)	
796 (sh)	
783 (m)	
759 (w)	
745 (mw)	
683 (mw)	
673 (sh)	
657 (mw)	
624 (mw)	
534 (m)	
463 (sh)	
451 (mw)	
412 (vw)	
300 (w)	

[a] Frequency taken from a chloroform solution spectrum.

Table 25. Observed infrared absorptions in deuterated p-bromobenzamide

KBr pellet frequency (cm-1)	Solution (CH_2Br_2) frequency (cm-1)
3675 (vw)	
3356 (w)	
3440 (w)	
2527 (m)	2638 (w)
2446 (sh)	
2367 (mw)	2484 (w)
1685 (sh)	
1631 (s)	1677 (s)
1591 (m)	1593 (mw)
1564 (m)	1571 (sh)
1530 (sh)	
1486 (w)	1488 (w)
1425 (m)	
1390 (sh)	
1345 (w)	
1301 (w)	
1280 (w)	
1265 (sh)	
1203 (vw)	
1180 (w)	
1173 (sh)	
1119 (w)	
1097 (w)	
1068 (mw)	
1012 (m)	
952 (sh)	
940 (mw)	
843 (m)	
757 (ms)	
694 (m)	
666 (vw)	
626 (m)	
573 (m)	
521 (mw)	
485 (m)	
455 (mw)	
437 (mw)	
412 (vw)	
297 (w)	

Table 26. Observed infrared absorptions in o-iodobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})
3364 (m)	-7.5	3508 (m)	-11.5
3182 (m)	-8.5	3390 (m)	-5.0
1649 (vs)	-8.0	1586 (sh)	-8.5
1623 (s)	-1.8	1684 (vs)	<1
1584 (w)	--	1588 (m)	-1.2
1556 (w)	<1		
1468 (mw)	--	1465 (w)	--
1425 (w)	<1	1432 (w)	--
1397 (m)	-4.8	1375[a] (m)	-5.8
1262 (vw)	--		
1166 (vw)	--		
1152 (vw)	--		
1134 (mw)	-6.2		
1109 (vw)	--		
1040 (w)	+1.2		
1015 (mw)	--		
985 (vw)	--		
951 (w)	--		
873 (vw)	--		
807 (w)	-2.4		
771 (mw)	-2.4		
736 (mw)	<1		
693 (mw)	<1		
665 (m)	-2.3		
650 (w)	-1.0		
630 (mw)	<1		
557 (m)	-1.3		
447 (m)	-1.2		
397 (m)	--		
296 (mw)	<1		

[a] Frequency and ^{15}N frequency shifts taken from chloroform solution spectra.

Table 27. Observed infrared absorptions in deuterated o-iodobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm-1)
2528 (m)	2629 (w)
2436 (sh)	
2369 (m)	2471 (w)
1628 (vw)	1679 (vs)
1582 (mw)	1586 (w)
1557 (w)	
1521 (w)	
1469 (m)	1464 (w)
	1430 (w)
1411 (s)	
1262 (vw)	
1206 (w)	
1166 (vw)	
1126 (w)	
1100 (vw)	
1040 (w)	
1012 (m)	
986 (vw)	
951 (mw)	
937 (mw)	
870 (w)	
786 (w)	
745 (s)	
703 (w)	
660 (w)	
646 (mw)	
605 (m)	
558 (w)	
533 (w)	
496 (m)	
445 (m)	
390 (m)	
290 (mw)	

Table 28. Observed infrared absorptions in m-iodobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3343 (m)	3524 (m)
3159 (m)	3408 (m)
3070 (sh)	
1659 (s)	1585 (mw)
1622 (s)	1685 (s)
	1595 (mw)
1559 (m)	1564 (mw)
1471 (vw)	1477 (vw)
1420 (m)	1422 (w)
1386 (m)	1371[a] (m)
1297 (vw)	
1271 (vw)	
1172 (vw)	
1147 (w)	
1124 (m)	
1057 (w)	
993 (w)	
975 (vw)	
917 (w)	
903 (mw)	
813 (vw)	
795 (m)	
739 (mw)	
676 (mw)	
661 (mw)	
639 (w)	
630 (w)	
554 (w)	
538 (sh)	
454 (m)	
409 (w)	
317 (w)	

[a] Frequency taken from a chloroform solution spectrum.

Table 29. Observed infrared absorptions in deuterated m-iodobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3060 (vw)	
2518 (m)	2630 (w)
2438 (sh)	
2360 (m)	2487 (w)
1670 (sh)	
1626 (vs)	1679 (s)
1588 (sh)	1694 (w)
1560 (m)	1564 (m)
1471 (w)	1471 (w)
1429 (m)	1426 (w)
1419 (sh)	
1391 (m)	
1270 (vw)	
1208 (w)	
1174 (vw)	
1122 (w)	
1095 (vw)	
1060 (w)	
993 (w)	
975 (w)	
937 (mw)	
903 (w)	
804 (w)	
776 (w)	
746 (ms)	
679 (mw)	
653 (mw)	
613 (mw)	
593 (mw)	
557 (w)	
539 (w)	
454 (m)	
409 (w)	
317 (w)	

Table 30. Observed infrared absorptions in p-iodobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3360 (m)	3522 (m)
3176 (m)	3406 (m)
1658 (s)	1596 (m)
1619 (s)	1682 (s)
1586 (m)	
1558 (m)	1572 (w)
1482 (w)	1492 (vw)
1467 (w)	
1404 (m)	1374[a] (m)
1370 (mw)	
1303 (w)	
1281 (w)	
1260 (w)	
1182 (w)	
1147 (mw)	
1126 (mw)	
1054 (mw)	
1007 (m)	
962 (vw)	
946 (vw)	
837 (m)	
826 (sh)	
794 (sh)	
782 (m)	
745 (mw)	
679 (sh)	
661 (w)	
636 (mw)	
620 (mw)	
534 (m)	
444 (m)	
407 (vw)	

[a] Frequency taken from a chloroform solution spectrum.

Table 31. Observed infrared absorptions in o-methylbenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})
3369 (m)	-11.0	3515 (m)	-12.0
3184 (m)	-5.5	3397 (m)	-7.5
3051 (sh)	<1		
3029 (sh)	<1		
2971 (vw)	+1.5		
2921 (vw)	-1.0		
2880 (vw)	--		
1654 (vw)	-5.4	1585 (m)	-7.8
1620 (s)	-1.8	1681 (s)	-1.8
1596 (w)	<1	1603 (sh)	-1.1
1574 (mw)	--		
1491 (mw)	--	1490 (w)	+1.0
1454 (w)	+1.2	1458 (w)	--
1437 (w)	<1		
1392 (m)	-7.4	1369^a(m)	-7.2
1292 (w)	<1		
1167 (w)	<1		
1139 (m)	-4.3		
1095 (w)	-1.2		
1053 (w)	--		
1038 (w)	--		
944 (w)	<1		
866 (w)	-1.2		
825 (w)	-1.3		
806 (w)	--		
779 (m)	<1		
748 (m)	<1		
732 (vw)	<1		
682 (m)	-2.8		
640 (m)	--		
567 (m)	--		
537 (mw)	<1		
468 (m)	--		
412 (m)	--		
389 (m)	<1		
346 (vw)	-1.4		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 32. Observed infrared absorptions in deuterated o-methylbenzamide

KBr pellet frequency (cm-1)	Solution (CH_2Br_2) frequency (cm-1)
3358 (w)	
3330 (w)	
3038 (vw)	
3016 (sh)	
2960 (vw)	
2920 (vw)	
2535 (m)	2634 (mw)
2442 (sh)	
2363 (m)	2482 (mw)
1630 (vs)	1670 (s)
1597 (w)	1603 (sh)
1574 (m)	
1528 (w)	
1494 (mw)	1490 (w)
1455 (sh)	1458 (vw)
1416 (ms)	
1347 (vw)	
1293 (w)	
1198 (vw)	
1183 (vw)	
1165 (w)	
1136 (w)	
1092 (w)	
1052 (w)	
1034 (w)	
1019 (vw)	
951 (mw)	
939 (mw)	
966 (vw)	
839 (w)	
816 (w)	
795 (w)	
781 (sh)	
743 (ms)	
707 (w)	
683 (w)	
618 (mw)	
569 (mw)	
557 (m)	
510 (m)	
464 (m)	
405 (m)	
389 (m)	
336 (vw)	

Table 33. Observed infrared absorptions in m-methylbenzamide

KBr pellet frequency (cm-1)	Solution (CH_2Br_2) frequency (cm^{-1})
3381 (m)	3528 (m)
3291 (sh)	
3198 (m)	3411 (m)
2981 (vw)	
2963 (vw)	
2924 (vw)	
2865 (vw)	
2760 (vw)	
1649 (s)	1591 (m)
1615 (ms)	1681 (s)
1606 (sh)	1606 (sh)
1581 (m)	
1487 (vw)	1488 (w)
1433 (m)	
1388 (m)	1374[a] (m)
1373 (sh)	
1330 (vw)	
1312 (w)	
1290 (w)	
1225 (vw)	
1181 (vw)	
1128 (sh)	
1113 (m)	
1042 (w)	
1002 (w)	
980 (vw)	
916 (w)	
885 (w)	
814 (w)	
771 (mw)	
734 (mw)	
685 (m)	
666 (sh)	
638 (m)	
563 (mw)	
521 (w)	
469 (m)	
410 (m)	
384 (w)	
354 (mw)	

[a] Frequency taken from a chloroform solution spectrum.

Table 34. Observed infrared absorptions in deuterated m-methylbenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3358 (vw)	
3056 (vw)	
2978 (vw)	
2960 (vw)	
2920 (vw)	
2868 (vw)	
2540 (m)	2641 (w)
2522 (sh)	
2434 (vw)	
2384 (m)	2491 (w)
2359 (sh)	
1623 (vs)	1670 (s)
1607 (sh)	1608 (sh)
1581 (ms)	
1520 (w)	
1492 (w)	1488 (vw)
1437 (m)	
1395 (m)	
1309 (w)	
1288 (w)	
1240 (vw)	
1178 (w)	
1108 (vw)	
1099 (vw)	
1084 (vw)	
1040 (w)	
1002 (w)	
982 (vw)	
932 (m)	
915 (sh)	
886 (sh)	
876 (w)	
811 (mw)	
751 (s)	
704 (w)	
688 (mw)	
613 (m)	
559 (mw)	
540 (m)	
505 (m)	
464 (m)	
406 (m)	
382 (w)	
340 (mw)	

Table 35. Observed infrared absorptions in p-methylbenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{15NH_2}-\nu_{14NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{15NH_2}-\nu_{14NH_2}$ (cm-1)
3350 (m)	-13.5	3524 (m)	-14.5
3168 (m)	-6.5	3406 (m)	-7.5
2984 (vw)	--		
2923 (w)	--		
2830 (vw)	--		
2790 (w)	+1.5		
1669 (s)	-7.1	1589 (m)	-8.8
1616 (s)	-2.1	1679 (s)	-2.2
		1614 (mw)	-1.0
1570 (m)	<1	1573 (sh)	--
1520 (w)	-1.3	1514 (w)	<1
		1456 (vw)	<1
1413 (m)	-2.2	1373[a] (m)	-5.6
1397 (m)	-3.2	1407 (w)	--
1301 (vw)	--		
1287 (w)	-3.0		
1215 (w)	--		
1190 (mw)	-1.8		
1145 (mw)	-2.2		
1124 (mw)	-2.4		
1114 (sh)	-1.1		
1043 (w)	<1		
1020 (mw)	--		
973 (vw)	+1.3		
967 (w)			
952 (w)	<1		
841 (m)	--		
814 (sh)	--		
795 (mw)	-2.4		
744 (sh)	--		
730 (mw)	-3.2		
696 (w)	-2.4		
671 (mw)	-2.5		
633 (mw)	-1.2		
592 (m)	<1		
535 (m)	<1		
462 (m)	--		
355 (m)	+1.3		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectrum.

Table 36. Observed infrared absorptions in o-nitrobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm-1)	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm-1)	Frequency (cm-1)	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm-1)
3364 (m)	-6.5	3509 (mw)	-12.0
3178 (m)	-4.5	3394 (mw)	-9.5
3085 (sh)	-2.0		
2925 (vw)	+2.5		
2875 (vw)	--		
2770 (vw)	--		
1656 (s)	-5.6	1586 (m)	-6.5
1624 (ms)	-1.5	1694 (s)	-2.0
1575 (mw)	+1.8		
1523 (ms)	+1.0	1534 (m)	--
1487 (mw)	<1	1482 (vw)	+1.0
1444 (w)	--		
1408 (m)	-4.9	1374[a](m)	-5.5
1359 (m)	--		
1305 (w)	--		
1372 (w)	+1.3		
1168 (sh)	<1		
1160 (w)	-2.0		
1148 (vw)	--		
1120 (m)	-5.9		
1076 (sh)	--		
995 (w)	--		
964 (w)	<1		
894 (vw)	--		
858 (mw)	--		
811 (w)	<1		
785 (mw)	<1		
771 (sh)	--		
732 (w)	<1		
698 (mw)	-2.0		
671 (w)	-3.0		
666 (sh)	<1		
629 (mw)	<1		
568 (vw)	--		
556 (w)	-1.0		
417 (w)	+1.0		
404 (vw)	+1.0		
375 (mw)	<1		
341 (w)	-1.0		

[a] Frequency and ^{15}N frequency shift taken from a chloroform solution spectrum.

Table 37. Observed infrared absorptions in deuterated o-nitrobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3081 (vw)	
2926 (vw)	
2876 (vw)	
2530 (mw)	2630 (w)
2453 (vw)	
2376 (mw)	2474 (w)
1631 (s)	1691 (s)
1577 (mw)	
1526 (s)	1536 (m)
1490 (mw)	1484 (vw)
1444 (w)	
1424 (m)	
1359 (ms)	
1306 (vw)	
1274 (vw)	
1214 (w)	
1167 (vw)	
1148 (vw)	
1119 (vw)	
1069 (vw)	
1038 (vw)	
995 (vw)	
966 (w)	
936 (mw)	
893 (vw)	
857 (mw)	
793 (w)	
780 (mw)	
757 (w)	
734 (m)	
699 (vw)	
663 (mw)	
609 (m)	
576 (mw)	
562 (sh)	
543 (w)	
502 (m)	
411 (mw)	
401 (sh)	
366 (mw)	
338 (w)	

Table 38. Observed infrared absorptions in m-nitrobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm-1)	Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})
3448 (ms)	-10.5	3528 (mw)	-11.5
3371 (sh)	-13.0		
3308 (w)	-9.5		
3160 (m)	-11.5	3412 (mw)	-8.5
3093 (sh)	-1.5		
1687 (vs)	-4.2	1694 (s)	-3.5
1622 (m)	-2.8	1594 (m)	-10.8
1613 (sh)	<1	1619 (mw)	+1.0
1574 (w)	+1.0		
1526 (sh)	--		
1521 (m)	<1	1536 (m)	--
1483 (mw)	--	1482 (w)	--
		1441 (vw)	--
1396 (m)	-3.2	1378[a] (mw)	-4.8
1352 (s)	<1		
1317 (w)	--		
1291 (w)	--		
1164 (w)	<1		
1122 (m)	-2.6		
1093 (sh)	+1.2		
1065 (vw)	--		
1000 (vw)	--		
949 (vw)	--		
912 (w)	--		
893 (mw)	--		
831 (w)	<1		
798 (sh)	<1		
788 (mw)	--		
758 (w)	--		
720 (m)	<1		
683 (m)	-1.2		
658 (w)	--		
638 (m)	-2.8		
616 (sh)	-1.0		
560 (sh)	+1.0		
541 (m)	+1.5		
445 (w)	--		
415 (w)	+1.5		
407 (w)	-1.5		
350 (w)	--		
310 (mw)	--		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 39. Observed infrared absorptions in p-nitrobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})
3419 (m)	-9.0	3514 (m)	-7.5
3315 (m)	-6.5	3399 (m)	-6.5
3262 (sh)	<1		
3197 (m)	-13.5		
3116 (w)	--		
3058 (vw)	-1.0		
2840 (vw)	--		
1663 (vs)	-3.7	1690 (s)	-2.7
1614 (mw)	-2.7	1587 (m)	-5.3
1592 (m)	-1.1	1605 (m)	-1.0
1513 (s)	--	1530 (s)	--
1493 (sh)	-1		
1406 (mw)	--		
1387 (mw)	-1.8	1375[a] (sh)	-2.7
1342 (s)	<1	1347 (s)	<1
1322 (mw)	+1.0	1318 (w)	+2.0
1304 (w)	+1.2	1298 (vw)	<1
1133 (w)	-2.1		
1119 (mw)	--		
1103 (mw)	--		
1090 (w)	-4.8		
1014 (w)	--		
980 (vw)	--		
967 (vw)	<1		
870 (sh)	<1		
865 (m)	<1		
840 (w)	+2.2		
833 (vw)	+1.0		
818 (vw)	<1		
787 (mw)	<1		
768 (m)	-3.8		
741 (mw)	+1.0		
696 (m)	<1		
538 (m)	-2.3		
612 (mw)	-1.0		
539 (w)	<1		
505 (m)	+1.5		
487 (w)	--		
425 (m)	--		
306 (w)	+1.5		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 40. Observed infrared absorptions in deuterated p-nitrobenzamide

KBr pellet frequency (cm-1)	Solution (CH_2Br_2) frequency (cm-1)
3408 (vw)	
3380 (sh)	
3304 (vw)	
3115 (w)	
3076 (sh)	
3061 (w)	
2844 (vw)	
2569 (m)	2640 (w)
2431 (m)	
2396 (m)	2483 (w)
1643 (vs)	1682 (s)
1602 (s)	1606 (m)
1560 (sh)	
1515 (s)	1530 (s)
1493 (sh)	
1411 (s)	
1393 (m)	
1344 (s)	1347 (s)
1322 (mw)	1319 (vw)
1303 (mw)	1299 (vw)
1206 (w)	
1181 (vw)	
1116 (mw)	
1106 (mw)	
1087 (sh)	
1015 (w)	
980 (vw)	
964 (vw)	
921 (mw)	
871 (mw)	
862 (m)	
842 (sh)	
783 (mw)	
764 (vw)	
745 (m)	
722 (ms)	
675 (vw)	
605 (m)	
539 (mw)	
500 (sh)	
479 (m)	
454 (m)	
413 (w)	
306 (w)	

Table 41. Observed infrared absorption in o-aminobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})	Frequency (cm^{-1})	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm^{-1})
3417 (m)	<1	3488 (mw)	+1.0
3400 (sh)	-14.0	3522 (mw)	-14.5
3328 (m)	-1.5	3357 (mw)	+1.5
3201 (m)	-8.5	3406 (m)	-7.0
3073 (sh)	-2.5		
2936 (vw)	--		
1662 (s)	-6.6	1594 (ms)	-2.6
1629 (s)	-1.4	1665 (s)	<1
1610 (sh)	<1	1616 (mw)	--
1590 (s)	-1.5		
1562 (vw)	--		
1546 (m)	-2.2	1553 (m)	+1.0
1492 (mw)	--	1492 (w)	--
1453 (mw)	-1.3	1452 (w)	--
1403 (m)	-6.2	1384[a] (m)	-7.5
		1330 (mw)	<1
1318 (m)	<1	1322 (sh)	<1
1261 (m)	-1.5	1268 (mw)	<1
1169 (sh)	-1.1		
1154 (mw)	<1		
1093 (w)	-7.4		
1034 (w)	<1		
974 (vw)	-1.1		
944 (w)	-1.4		
871 (w)	<1		
863 (w)	-1.2		
853 (w)	-1.9		
754 (sh)	-2.1		
747 (ms)	-2.2		
713 (w)	-2.3		
661 (sh)	--		
631 (w)	-2.5		
559 (w)	<1		
537 (m)	--		
513 (w)	<1		
457 (vw)	+1.5		
431 (w)	<1		
400 (w)	-1.0		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 42. Observed infrared absorptions in deuterated o-aminobenzamide

KBr pellet frequency (cm^{-1})	Solution (CH_2Br_2) frequency (cm^{-1})
3409 (sh)	
3366 (w)	3406 (w)
3322 (w)	
3068 (w)	
3053 (w)	
3022 (w)	
	2736 (w)
2554 (m)	2616 (sh)
2494 (sh)	2640 (w)
2425 (m)	2554 (w)
2385 (mw)	2484 (mw)
2356 (sh)	
1633 (s)	1650 (s)
1612 (s)	1611 (sh)
1596 (s)	1583 (sh)
1563 (sh)	1563 (mw)
1489 (m)	1494 (m)
1454 (mw)	1454 (w)
1415 (ms)	
1327 (m)	
1292 (m)	1297 (m)
1271 (m)	1273 (mw)
1207 (w)	
1172 (w)	
1157 (mw)	
1133 (sh)	
1074 (w)	
1044 (mw)	
973 (vw)	
944 (w)	
918 (mw)	
892 (vw)	
859 (w)	
827 (w)	
789 (w)	
753 (sh)	
744 (ms)	
712 (mw)	
689 (w)	
603 (mw)	
559 (w)	
513 (sh)	
489 (mw)	
446 (mw)	
410 (mw)	
390 (w)	

Table 43. Observed infrared absorptions in m-aminobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm-1)	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm-1)	Frequency (cm-1)	$\nu_{^{15}NH_2}-\nu_{^{14}NH_2}$ (cm-1)
3468 (sh)	-1.0		
3434 (sh)	+1.0	3488 (sh)	+1.5
3385 (ms)	-9.0	3525 (w)	-11.5
3353 (sh)	<1	3359 (sh)	--
3199 (m)	-6.5	3404 (w)	-7.0
3058 (sh)	--		
2668 (vw)	--		
1647 (s)	-4.9	1588 (m)	<1 -10.4
1631 (s)	-1.8	1678 (s)	<1
1618 (s)	-1.4	1620 (mw)	-2.4
1604 (sh)	<1		
1580 (m)	--		
1492 (sh)	--	1494 (w)	-1.6
1466 (m)	<1	1462 (w)	<1
1399 (m)	-5.2	1374[a] (m)	-6.1
1329 (w)	<1		
1322 (w)	<1		
1308 (sh)	--		
1287 (w)	-1.9		
1275 (w)	-1.0		
1174 (vw)	-1.5		
1133 (mw)	-3.9		
1114 (w)	-7.6		
994 (w)	--		
965 (vw)	--		
920 (w)	-1.5		
887 (mw)	--		
879 (mw)	+1.0		
815 (sh)	--		
803 (sh)	--		
780 (mw)	-1.0		
764 (m)	-1.0		
744 (w)	-2.8		
688 (sh)	--		
659 (sh)	<1		
639 (mw)	-2.6		
620 (sh)	--		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.

Table 43. (Continued)

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu^{15}NH_2-\nu^{14}NH_2$ (cm^{-1})	Frequency (cm^{-1})	$\nu^{15}NH_2-\nu^{14}NH_2$ (cm^{-1})
598 (sh)	<1		
538 (w)	--		
496 (m)	--		
417 (w)	-1.0		
401 (mw)	<1		
374 (mw)	--		

Table 44. Observed infrared absorptions in p-aminobenzamide with frequency shifts produced by ^{15}N substitution

KBr pellet		Solution (CH_2Br_2)	
Frequency (cm^{-1})	$\nu^{15}NH_2-\nu^{14}NH_2$ (cm^{-1})	Frequency (cm^{-1})	$\nu^{15}NH_2-\nu^{14}NH_2$ (cm^{-1})
3470 (mw)	-8.5	3517 (w)	-14.0
3328 (mw)	-7.0	3407 (w)	-14.5
		3470 (sh)	-1.0
3212 (mw)	+2.0	3375 (sh)	<1
1649 (sh)	-1.5	1622 (mw)	--
1613 (s)	<2	1670 (s)	<1
		1605 (mw)	--
1598 (s)	-1.2	1589 (mw)	-7.0
1561 (m)	<1		
1519 (mw)	--	1519 (mw)	--
1436 (mw)	-1.7		
1396 (m)	-2.6	1376[a] (m)	-8.0
1334 (w)	<1		
1292 (mw)	<1		
1181 (w)	+1.2		
1136 (w)	-3.6		
1096 (mw)	-2.1		
1069 (sh)	<1		
1009 (vw)	<1		
970 (vw)	--		
952 (vw)	<1		
851 (m)	--		
843 (sh)	-1.6		
781 (m)	-1.4		
716 (w)	-2.4		
619 (mw)	-2.4		
585 (mw)	-2.6		
537 (m)	-1.4		
502 (sh)	--		
418 (sh)	--		
403 (m)	<1		
353 (w)	<1		

[a] Frequency and ^{15}N frequency shift taken from chloroform solution spectra.