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CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES OF NITROGEN-CONTAINING BONDS

by

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OBJECTIVES

The infrared spectra of nitrogen containing organic compounds have been extensively studied. In many cases it has not been possible to assign with certainty those absorption frequencies which arise from vibrations involving motion of the nitrogen atom. The frequency shift upon isotopic substitution is useful in relating observed frequencies and modes of vibration involving the substituted atom. Studies using isotopic nitrogen have been almost entirely limited to very simple molecules. The objective of this thesis is the preparation of organic compounds labeled with nitrogen-15, the identification of frequencies associated with nitrogen motion, and the assignment of those frequencies to specific modes of vibration. The choice of general types of compounds was governed mainly by the existence of either controversy about assignments or slight knowledge about their spectra. The specific types of compounds studied are: unsubstituted amide, monosubstituted amide, primary amine hydrochloride, alkyl nitrite, diazonium salt, and azo.

INTRODUCTION

In a simple diatomic molecule, XY, the atoms are able to move back and forth along the bond joining the atoms. In this manner the bond is alternately stretched and compressed by the vibration of the atoms. The frequency of the vibration is determined by the force constant of the bond and by the masses of the atoms to the extent that the molecule behaves as a simple harmonic oscillator. This frequency may be expressed by the equation

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

where k is the force constant of the bond and μ is the reduced mass of the molecule XY. The expression for the reduced mass is

$$\mu = \frac{Mm}{M + m}$$

where M and m are the masses of the two atoms.

Although all diatomic molecules possess a characteristic stretching frequency, some of them do not absorb infrared radiation. In order to absorb energy from an incoming beam of infrared radiation, a change in the dipole moment must take place during the vibration of the molecule. With diatomic molecules this means that only those molecules possessing a permanent dipole moment can exhibit infrared absorption.

When more complex molecules are considered, the same principles apply. Absorption in the infrared occurs only for those vibrations which involve a change in the dipole moment. It is no longer necessary, however, that the molecule possess a permanent dipole moment. The frequencies of the vibrations are determined by the force constants of the bonds and the masses of the atoms comprising the molecule. It might be thought that all of the absorption frequencies of the molecule would be determined by the totality of its structure; thus, qualitative examination of the spectrum would tell little about the structure of the molecule. Actually, a particular group of atoms often absorbs within a small frequency range in a large number of molecules. For example, molecules containing a C=O group absorb in one range and those containing an N-H group absorb in another range. If the molecules contain both the C=O and N-H groups, absorption is found in both regions.

Groups of atoms in a molecule can often be characterized by more than one absorption frequency. These absorptions arise because motions perpendicular to the bond involved are no longer necessarily simple translation or rotation as in the diatomic case. As a result, vibrations of this type may absorb in the infrared region. For a particular bond the stretching vibration lies at a higher frequency than a bending vibration. Stretching of the bond involves a displacement of the atoms from their equilibrium separation with severe distortion of the electron distribution, which results in a strong restoring force within the bond. A bending vibration, however, leaves the atoms at their normal separation and has a smaller effect on the structure of the bond. As a result, bending of the bond requires less energy than stretching. Further consideration shows that, depending on the molecular configuration, different bending modes are possible. For example, if the molecule has a planar form it is possible for the vibration to be in the plane or perpendicular to the plane. Of the two vibrations the motion perpendicular to the plane appears at the lower frequency because there is less interaction with other atoms which, though not directly attached to the group, approach it closely in space.

Since group frequencies show whether the group is in the molecule the conditions under which they occur must be considered. The electronic structure of the bond is almost the same in similar molecules so the force constant, and thus the vibrational frequency, change very little. This does not explain why there is essentially no interaction between the vibrations of adjacent bonds. If one of the atoms in a pair is very light compared to the other atom and is bonded only to that atom, lack of interaction can arise. In this case almost all of the vibration appears in the amplitude of the light atom. The heavier atom moves with such small amplitude that there is no interaction with the remainder of the molecule.

A group frequency can occur even though the masses of the atoms in the group and of the adjacent atoms are nearly the same if the force constants of adjacent bonds are very different. Although this group may have one of the atoms bonded only to the other, as in the case of the very light atom, such a condition is not necessary. For example, the grouping $-\overset{|}{\underset{|}{C}}-\overset{|}{C}=C\langle$ would exhibit an absorption resulting from the stretching of the C=C group. In many cases it is not possible to localize the vibration to a pair of atoms, but it is often possible to consider a larger set of atoms as a group. An example of this is the phenyl ring. No absorption resulting from the stretching of individual carbon-carbon bonds is observed but many vibrations characteristic of the entire ring skeleton are found. These arise from simultaneous motion of most or all of the atoms of the ring.

The major limitation of the concept of group frequencies arises from interaction of vibrations. The phenyl group is one case of this, but fortunately with characteristic results. Interaction can be expected when the masses and force constants in the system are similar. The system $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-N\langle$, for example, does not possess vibrations characteristic purely of C-N or C-C bonds but does have vibrations involving simultaneous motion of all the atoms. Even small changes in structure will cause considerable alteration in the nature of the vibrations.

It was noted earlier that group frequencies occur not at characteristic points but in limited ranges. Of considerable interest are the factors which cause the force constant to vary from molecule to molecule. The first of these factors is the inductive effect of the groups connected to the system under consideration. Generally the absorption frequency is decreased by substitution of a more electronegative atom upon one of the atoms involved in the group absorption. Since the substituent pulls more on the electrons in the bond and reduces its electron density, the force constant of the bond decreases and, as a result, the absorption frequency is lowered. Another factor which affects the frequency is conjugation of multiple bonds, i.e., the alternation of single and multiple bonds in the system. Resonance decreases the electron density in the multiple bonds causing their absorptions to shift to lower frequencies. A third intramolecular consideration which causes shifts within the characteristic ranges is strain, i.e., factors which force the bond angles to deform from the normal. This subject has not been studied sufficiently to make broad generalizations. The C=O stretching vibration of cyclic compounds moves to higher frequencies as the ring is made smaller. In the case of cycloölefins the C=C stretching vibration shifts to lower frequencies as the ring angle increases. Beyond this not much can be said. Another major cause of frequency shifts is association. The effect of this phenomenon depends upon the type of vibration involved. Stretching vibrations shift to lower frequencies because the electron density of the bond is decreased by association. Bending vibrations are displaced to higher frequencies by association since more work is required to move the atom from the position stabilized by the two bonding systems.

There are, in general, two methods of studying group frequencies in assigning the vibrations involved. The procedures are complementary, neither one being sufficient in itself. The first and most common attack on the problem is the compilation of the absorption frequencies of many similar compounds. These lists are compared in an attempt to locate a frequency range which contains a band common to all of the compounds. This range is assigned to a vibration of whatever group is in all of the molecules. In many cases this method has proved successful. Such an approach is necessary in order to find the extremes of the region which must be examined in the spectrum of an unknown compound to determine the presence or absence of a particular group. The major drawback of this approach is that the assigned band may arise from an entirely different system which is also common to all of the molecules. This would lead to erroneous conclusions about a molecule which contained the group to which the frequency was assigned but did not possess the group actually characterized by the absorption. It is also possible to assign a band to a particular two-atom group when the absorption actually arises from a complex vibration involving these atoms and several others. Uncertainties arise with molecules which do contain the two atoms thought to give rise to the absorption but which do not possess the entire group actually involved in the vibration.

Another attack on the problem involves isotopic substitution in the molecule. In this approach, to be considered more fully shortly, one or more of the atoms in the normal molecule is replaced by an isotope of that atom. This leaves the electronic structure of the bond, and thus its force constant, essentially unchanged. However, as indicated earlier in the equation for the absorption frequency of a diatomic molecule, the mass of the atom also affects the position of the band. Isotopic substitution causes a shift in the frequencies of vibrations involving the substituted atom without affecting the molecule in any other way. 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 makes certain that the band under consideration is more nearly characteristic of the species being studied. It does not, however, provide any information about the frequency range to be considered in the examination of other molecules. Compilation methods must be used to provide this information. If the band falls in a complex region of the spectrum it may be necessary to use more than one isotopic molecule to trace the actual frequency range to be considered.

Information can be obtained from the size of the shift resulting from isotopic substitution as well as from the qualitative fact that a shift occurs. The simplest case arises when the group of atoms approximates a diatomic molecule, i.e., a two-atom vibrating system with negligible interaction with other bonds. The frequency shift then may be fairly closely calculated from

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

where the subscript i refers to the isotopically substituted molecule. For systems with considerable interaction, the deviations from the ratios calculated with this equation can become very large.

Substituting the relation previously given for the reduced mass into the above equation the term in parentheses is

$$\frac{M_i}{M} \times \frac{M + m}{M_i + m}$$

The ratio of the isotopic masses determines the extreme value of the frequency ratio for those isotopes and the other term determines the value between zero and the extreme which will be observed. When m is much less than M the frequency ratio is very small, whereas m much larger than M approaches the largest ratio possible. The range of values can be related to the amplitude of motion of the substituted atom during the vibration under consideration. When m is small the much heavier M atom is only slightly displaced to compensate for the motion of m. A large m on the other hand causes a large amplitude to appear in the motion of the lighter M atom. The frequency ratio varies in the same manner as the amplitude.

When larger groups of atoms are involved, the simple ratio calculation is no longer so useful. The angles between the bonds in the group must be considered in the potential function. Interaction terms which express the effect of distortion of other bonds on the force constant of a particular bond must also be included. One result of increased complexity is inability to cancel the force constants by division. Another difficulty arises when the frequencies usually appear as sums or products of several different frequencies.

The application of group theory to molecular vibrations (54, 133) can be of assistance in connection with either of the approaches to the assignment of group frequencies. By means of this technique the number of vibrations which will absorb in the infrared and something of their nature can be predicted. Comparison of this knowledge with spectral data on bands that shift position upon isotopic substitution often permits assignment of certain frequencies to particular vibrations.

OXIDATION OF AMMONIA

The nitrogen-15 used in this study was obtained as ammonium sulfate. This was the best form for the preparation of some of the compounds to be studied. However, in order to prepare three of the compounds, n-hexyl nitrite, benzenediazonium chloride, and p-N,N-dimethylaminoazobenzene, it was necessary to convert part of the ammonium sulfate to a nitrite.

The conversion of ammonia to nitrates and nitrites has been attempted in many ways. Several methods of oxidation, such as biological (88), photochemical (42), electrolytic (91), exposure to X-ray irradiation (103), and passage through silent electrical discharges (32) have given good yields based upon unrecovered ammonia but low actual conversions. Chemical oxidations have given low yields until recently (100, 79). Since the catalytic oxidation of ammonia has been shown to give high conversions, greater than 90 per cent in industrial practice, it was decided to utilize this approach in the conversion of ammonia into useful intermediates.

The first consideration is the selection of the catalyst. A gauze woven of platinum-rhodium alloy wires is the most commonly used material (106) with the rhodium added because it reduces the loss of platinum during the oxidation reaction (2). Catalysts which have been studied are shown in

Tables 1 and 2. In addition, Scott (111) listed 52 substances which he studied, and noted that platinum gauze gave the highest conversion, with cobalt metal, cobalt oxide, and iron oxide following fairly closely. These oxides can give yields roughly comparable to platinum if mixed in the proper proportions with other oxides. Cobalt oxide was found to be activated by three per cent bismuth oxide or cerium oxide (111) or with nine per cent aluminum oxide (112) while ferric oxide was activated by three to five per cent bismuth oxide (89, 123). Since platinum gauze requires no special preparation and gives yields as good as, or better than, any other catalyst it was chosen as the catalyst to be used.

There are many variables in the catalytic oxidation of ammonia. Several investigators have studied the effect of catalyst temperature and gas flow rate on the conversion obtained (10, 13, 14, 65, 96, 101, 123, 137). It was found that high conversions could be obtained at catalyst temperatures starting at 700° C. and extending beyond 1200° C. At any temperature the conversion is determined by the time the gases are in contact with the catalyst. The maximum yield for a given temperature occurs at a particular gas flow rate, with the yield decreasing at both higher and lower rates. The optimum flow rate increases as the catalyst temperature is raised. Several studies have shown that the yield can be increased by using more than one thickness of platinum gauze

Table 1. Metallic catalysts reported for the oxidation of ammonia

Catalyst	Yield (%)	Reference
Mn-27.40%Cu-8.55% Ag-3.25%Fe-1.25%SiO_2	92	95
Pd	<Pt	40
Pt	80-90	101
Pt	88	129
Pt	91-92	80
Pt	94.1	135
Pt	95.5	92
Pt	94-97	17
Pt	96	89
Pt	96-97	19
Pt	97.3	123
Pt	97.7	130
Pt	100	136
Pt-0.5%Pd	90-97	41
Pt-5.0%Pd	90-97	41
Pt-Rh	94.1	135
Pt-10%Rh-10%Ag	95.7	4
Pt-7%Rh	96.5-97.5	21
Pt-5%Rh-3%W	97-98	5
Pt-10%Ag	87.9	4
Pt-3%W	>Pt	3
Rh	69.7	130

Table 2. Oxide catalysts reported for the oxidation of ammonia

Catalyst	Yield (%)	Reference
Co	76.6	111
Co	93	109
Co	92-94	110
Co	equal to Pt	51
Co	79.3	112
Co-1%Al	78.6	112
Co-3%Al	89.1	112
Co-9%Al	94.8	112
Co-1%Be	83.5	112
Co-2.9%Be	84	111
Co-3%Be	84.4	112
Co-9%Be	88.2	112
Co-9%Be	92	111
Co-50%Bi	17	111
Co-25%Bi	76	111
Co-0.1%Bi	81-90	111
Co-1%Bi	89.0	112
Co-9%Bi	89.1	112
Co-3%Bi	91.8	112
Co-3%Bi	95-97	111
Co-3%Bi-3%Ni	87-94	111
Co-1%B	62	112
Co-1%Cd	63	112
Co-1%Ce	75.1	112
Co-9%Ce	90.5	111
Co-3%Ce	94.6	111
Co-1%Cr	71.5	112
Co-5%Cr	93% of Pt	51
Co-1%Cu	79.3	112
Co-9%Cu	82.6	112
Co-3%Cu	87.4	112
Co-1%Au	73.7	112
Co-1%Fe	74.9	112

Table 2. (Continued)

Catalyst	Yield (%)	Reference
Co-9%Fe	78.7	112
Co-3%Fe	86.5	112
Co-1%Pb	81.5	112
Co-3%Pb	83.4	112
Co-9%Pb	85.6	112
Co-1%Mg	68.0	112
Co-1%Hg	77.5	112
Co-9%Ni	73.5	112
Co-1%Ni	74.0	112
Co-3%Ni	76.7	112
Co-3%Ni	91	111
Co-5%Ni	91% of Pt	51
Co-1%Ag	70.0	112
Co-9.9%Th-0.1%Ce	91	111
Co-9%Sn	84.0	112
Co-1%W	60.0	112
Co-1%U	65.0	112
Co-1%V	57.3	112
Co-3%Zn	68.7	112
Co-1%Zn	78.3	112
Fe	Poor	137
Fe	80-90	101
Fe	90	89
Fe-Bi-Th-Si	72	56
Fe-33%Bi	85	55
Fe-Bi	95	89
Fe-3.8%Bi	99.2	123
Mn-21.43%Cu-7.14%Ag	51.6	95
Mn-40%Cu	93.3	95
Mn-37.5%Ag	82.8	95
Sn-Cu-Si	81.5	6

(20, 80, 92, 126, 129). The gauze layers may be in contact although this is not necessary. A small increase in the yield may be obtained by increasing the oxygen-ammonia ratio above the minimum value of 1.25 (17, 19, 21). Andrussow, in a series of articles (8, 9, 11, 12), has collected the earlier work into relations which can be used to calculate conditions giving high conversions. The oxidations described in the present study are based upon his work.

The features required in the oxidation equipment result mainly from two factors: (1) the oxidation reaction is highly exothermic, and (2) ammonia-oxygen mixtures containing 15.5-27 per cent ammonia are explosive (11). The first factor is important from a control standpoint because the amount of ammonia in the gas stream can be roughly monitored by observing the rise of the catalyst temperature above that provided by external heating. The ammonia concentration must be kept low enough so the heat resulting from the reaction, plus the heat added to the catalyst externally, does not exceed the melting point of the platinum. Keeping the ammonia concentration low also prevents exceeding the lower explosive limit.

The apparatus devised for the oxidation of ammonia liberated from ammonium sulfate is shown in Figure 1. Cylinder oxygen passes through rotameter A and the gas stream is divided into two portions at B. One part continues toward

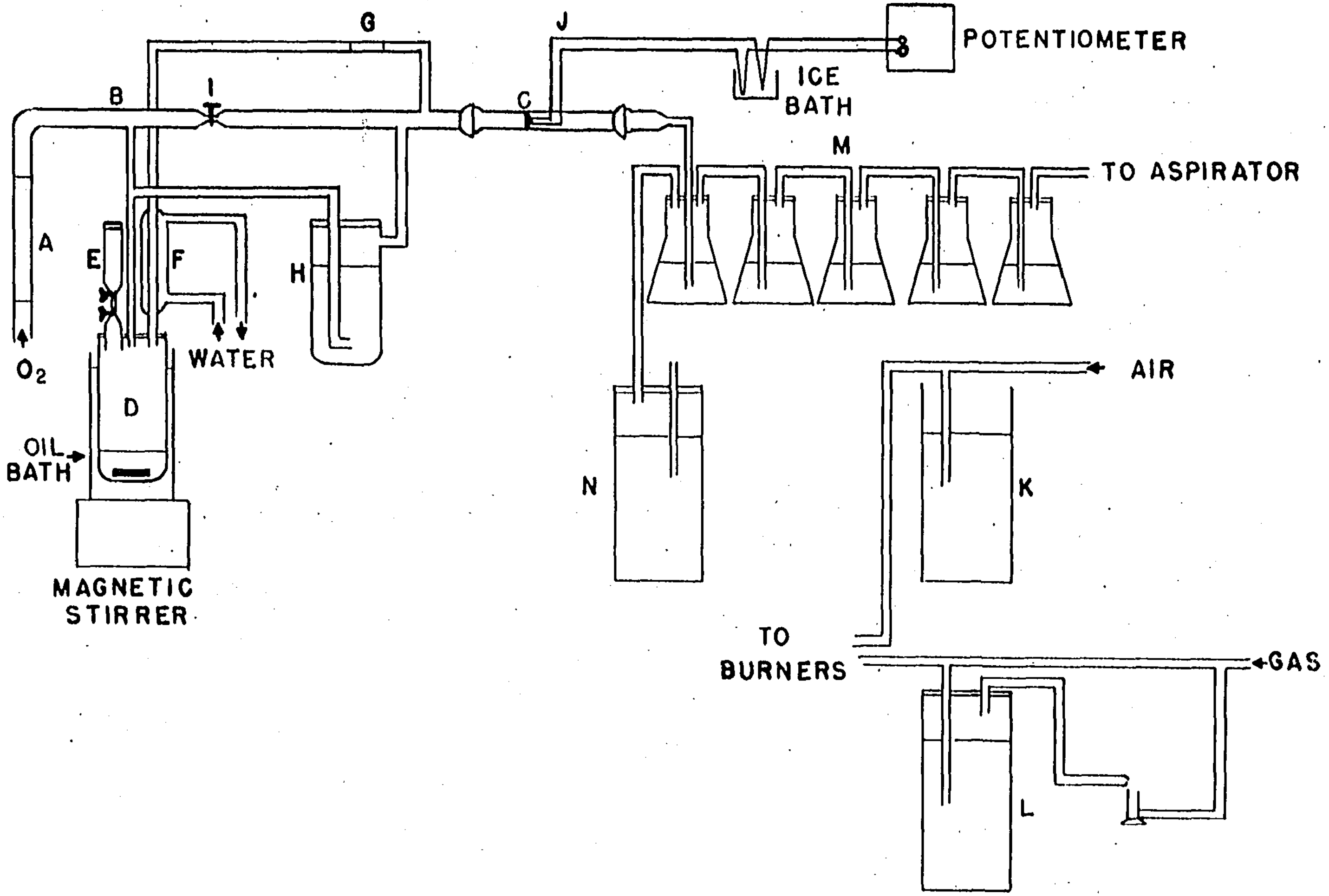

Figure 1. Apparatus for the oxidation of ammonia (not to scale)

the catalyst at C. The other part passes into the chamber D. In this chamber ammonia is liberated by dropping sodium hydroxide pellets from the stoppered tube E into an ammonium sulfate solution which is stirred with a magnetic stirrer. The lower end of tube E is connected to the ammonia chamber by a piece of flexible plastic tubing which is closed by two pinchclamps placed one above the other. When the upper clamp is opened a few pellets fall into the tubing between the two clamps. The upper clamp is then closed and the lower clamp opened. The pellets from the tube drop into the 30 per cent ammonium sulfate solution. This procedure permits fairly close control over the base addition. The ammonium sulfate solution is heated by the oil bath after excess sodium hydroxide has been added. The oxygen-ammonia mixture from D passes through condenser F which is present to remove water from the gas stream since excess water vapor reduces the catalyst temperature. The gas traverses capillary G and mixes with the oxygen which continues toward the catalyst from B. The amount of oxygen diverted through the ammonia chamber is determined by the capillary G, the pressure regulator H, and the screw clamp I. The screw clamp controls the size of the opening in a piece of flexible plastic tubing. The capillary throttles the system so that a relatively small flow occurs through D under the starting conditions. The pressure regulator maintains a differential pressure between chamber D and the catalyst chamber. Pressure adjustments are made by setting the depth of the inlet tube to regulator H and then changing the screw clamp until oxygen bubbles slowly through the regulator. None of the dimensions in this portion of the equipment are critical except that of the capillary. This was found to be satisfactory if the bore was not more than one mm. With larger bore capillary tubing the equipment was damaged twice by explosions, and the catalyst was melted on one of these occasions. Both incidents resulted from the accidental addition of too large an amount of sodium hydroxide early in a run.

The catalyst at C consists of three layers of platinum gauze contained in a Vycor tube of 13 mm. outside diameter. Thermocouple J, for measuring the catalyst temperature, is inserted through the wall of the tubing about two and one-half inches behind the catalyst and contacts the center portion of the last piece of platinum gauze. The thermocouple opening is sealed with "Sauereisen" cement. (This cement was not entirely satisfactory for this use because it developed leaks, but nothing better was found.) The temperature measured by the thermocouple provides an indication of the amount of ammonia in the gas stream. In order to monitor the ammonia concentration in this manner the external heating must be closely controlled. The flames of three hand burners, arranged at 120° intervals around the tube, are directed toward C so that heat is directly supplied only at the catalyst. Pressures of the air and gas supplied to the burners are regulated by means of water columns K and L. Excess air is merely vented into the room, while the gas bubbling through its column is led through a nozzle and burned. With these regulators the temperature of the catalyst can be controlled within ± 1.5° C.

After passing through the heated catalyst the product gases enter the absorption train M, which consists of five 250 ml. Erlenmeyer flasks containing potassium hydroxide solution. Rather than use large pressures to overcome both catalyst resistance and the depth of the absorbing medium, the outlet of the final absorption flask is connected to a water aspirator. The vacuum pulled on the system is reproduced by bleeding air into the first flask through column N. A vacuum of one and one-half inches of water was chosen since it essentially reduces the flow resistance of the absorption train to zero. The proportion of nitrite to nitrate obtained on alkaline absorption depends upon the amount of nitric oxide oxidized to nitrogen dioxide (18, 46), which in turn depends upon the temperature and time of reaction (25, 57, 108). The distance from the catalyst to the first absorption flask is empirically adjusted to yield mainly nitrite.

Thirty oxidation runs were made on the equipment essentially in the form described. The flow rates studied ranged from 0.49 to 0.71 liters per minute. Initial temperatures studied varied between 808° and 896° C. and the largest temperature rise used was 34° C. Runs were long enough to bring the catalyst temperature at the finish down to the initial value. The absorption products were analyzed by their ultraviolet absorption spectra as done by Addingson *et al.*(7). The highest conversion to nitrite was only 68 per cent. Several attempts were made to improve the yield. Most of the work was done using an air-natural gas mixture in the burners and working with the highest temperature obtainable from these gases. The higher temperatures were investigated using an oxygen-natural gas flame but the yield was not improved. Passage of the gas through a one liter flask before absorption showed that insufficient oxidation of nitric oxide to nitrogen dioxide was not the problem because the increase in the proportion of nitrate in the product was not accompanied by an increase in the total yield. The absorption solutions were all prepared by addition of potassium hydroxide to 150 ml. of distilled water. The amount of base was varied so that the solutions were from 3.8 to 21.7 per cent potassium hydroxide. A solution 14.3 per cent in potassium hydroxide was selected for regular use because it performed as well as the more concentrated solutions and better than the weaker ones. The conditions used for the two oxidation runs on nitrogen-15 ammonia were those from which the best nitrite conversion was obtained. These conditions were a flow rate of 0.59 liters per minute, initial temperature of 834° C., and maximum temperature rise of 18° C. With the nitrogen-15 enriched ammonia (95.55 per cent N^{15}) the first run gave 66 per cent conversion to nitrite but the second run yielded only 26 per cent nitrite. Evidently the catalyst was poisoned by something in the nitrogen-15 ammonia, but the nature of the poison is not known since many materials affect the platinum catalyst adversely (106). Since sufficient nitrite was obtained during the two runs on nitrogen-15 additional study on the ammonia oxidation did not appear warranted.

SPECTROSCOPIC APPARATUS AND TECHNIQUES

All infrared spectra in this study were obtained with a Perkin-Elmer Model 112 double-pass prism spectrometer using LiF, CaF_2, NaCl, and KBr prisms. The frequency range studied was 4000-420 $cm.^{-1}$. The sample space of the instrument was enclosed by polyethylene film and the entire instrument was flushed with helium to eliminate atmospheric absorption. The prisms were calibrated with NH_3, water vapor, CO_2, HCl, HBr, and CO, and the important gaps in these data were filled in by means of the Friedel-McKinney extrapolation (44, 58). All frequencies reported are the average of three separate instrument scans, as were all calibration points. The frequency ratios resulting have an average deviation of ± 0.001 when large shifts assigned to particular vibrations are excluded. Since the ratio to be expected from an N-H vibration is 1.002, there is uncertainty about assignments of N-H modes except where deuteration data are available.

When possible the spectra were obtained from solutions of the sample in appropriate solvents. The solvents were selected primarily in accordance with the solubility of the sample and with consideration of solvent absorption. The solution cell in this work was approximately 1 mm. thick and had KBr windows. In several cases it was not possible to dissolve a sample in any solvent which was transparent over an extended region. In this case the sample was run as a KBr disk. In this technique a small portion of the sample was placed in a plastic vial with a larger amount of dry KBr and a plastic covered metal rod. The closed vial was then agitated violently in a mechanical shaker for several seconds. The resulting powder was placed in an evacuable die and formed into a disk by application of several thousand pounds pressure. The disk was used in the spectrometer sample beam in the same manner as a solution cell.

BENZAMIDE

Experimental

Benzamide labeled with nitrogen-15 was prepared by the reaction

$$2NH_3 + C_6H_5COCl \rightarrow C_6H_5CONH_2 + NH_4Cl$$

following the method of Fones and White (47).

A solution of 8.9 g. of benzoyl chloride in 200 ml. of anhydrous ether was placed in a 500 ml. two-necked flask with one neck connected to a trap containing boric acid solution. The other neck was connected to a 250 ml. flask containing 7.94 g. of ammonium sulfate (97.00 per cent N^{15}) dissolved in 50 ml. of distilled water. The flask containing the benzoyl chloride was cooled by a dry ice-acetone bath throughout the reaction, and the solution was stirred with a magnetic stirrer. A solution of 16 g. of sodium hydroxide in 50 ml. of distilled water was added to the ammonium sulfate and the resultant solution refluxed for 4 hours. After this period the dry ice-acetone bath was removed and stirring discontinued. The system was left closed overnight.

The ether phase was separated by filtration from the solid formed during the reaction. The solid ammonium chloride was washed with five 50 ml. portions of absolute ethanol and the washings were added to the ether. The mixture of ether solution and ethanol washings was concentrated until slight deposition of ammonium chloride was noted, at which time 200 ml. of benzene was added. The solution was heated to boiling, filtered, and the residue washed with three 100 ml. portions of hot benzene. This residue plus the solid filtered from the reaction mixture was 2.52 g. of ammonium chloride. The solution was concentrated to 100 ml., cooled, and the resulting crystals removed by filtration. Further concentration to 10 ml. gave additional crystals. The total weight of the benzamide was 6.21 g.

The liquid remaining after liberation of the nitrogen-15 enriched ammonia was steam distilled and the distillate was passed into dilute hydrochloric acid. Evaporation of the hydrochloric acid yielded 0.14 g. of ammonium chloride. After correcting the initial weight of the ammonium sulfate, the yield of benzamide nitrogen-15 was 87.8 per cent and that of ammonium chloride nitrogen-15 was 79.0 per cent.

The benzamide containing normal nitrogen was a commercial product and was recrystallized before use.

The samples of benzamide were examined as KBr disks except in the region covered by the LiF prism where chloroform solutions were used. The chloroform permitted the free N-H stretching vibrations to be observed readily, but a solvent absorption obscured the C-H stretching bands. Since these bands are not in dispute and do not affect the nitrogen vibrations, no attempt was made to study them. The results are shown in Table 3. The prominent bands which show a significant shift are marked with an asterisk. The spectrum in the region 5000-625 cm.$^{-1}$ of the normal nitrogen compound, run as a KBr disk, is shown in Figure 2.

Discussion

According to Kuratani (67) the benzamide molecule probably exists in a planar configuration. The phenyl ring vibrations are little affected by the nature of the substituent (99), so it is assumed that the vibrations of the group C-CO-NH_2 can be considered separately. On this basis the molecule would have C_s symmetry and the amide group would have nine in-plane vibrations, species A', and three out-of-plane vibrations, species A". Six of these 12 modes would arise almost solely from NH_2 vibrations, four in-plane and two out-of-plane. Reasonable modes of vibration for the amide group are shown in Figure 3*. The six N-H vibrations are those generally applicable to such conformations, while the development of the six skeletal vibrations will be discussed subsequently.

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*In all modes shown in this study the directions of the arrows attached to the atoms indicate the approximate direction and relative phasing of the atomic motions. In the case of out-of-plane vibrations motion away from the plane of the paper is shown by plus and minus signs, with the plus sign indicating a direction above the plane and the minus sign showing a direction below the plane.

Table 3. Observed frequencies of benzamide and its nitrogen-15 analog with the ratio of corresponding frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
*3549.9	3540.5	1.003
*3435.2	3430.2	1.002
*1658.1	1649.7	1.005
*1627.2	1624.1	1.002
*1582.3	1579.9	1.002
1547.1	1543.4	1.002
1518.2	1520.2	0.999
1510.0	1507.0	1.002
1496.9	1494.5	1.002
1473.0	1471.2	1.001
*1450.9	1448.6	1.002
*1403.1	1398.4	1.003
1304.5	1303.4	1.001
1256.0	1253.0	1.002
1191.4	1189.8	1.001
1187.2	1185.9	1.001
*1149.9	1146.7	1.003
*1128.7	1121.3	1.007
1077.3	1076.2	1.001
1030.6	1030.1	1.001
1006.0	1005.5	1.001
928.2	928.0	1.000
921.6	921.2	1.000
851.1	851.2	1.000
*811.4	810.2	1.002
*792.8	791.5	1.002
*772.7	771.2	1.002
709.1	709.7	0.999
688.0	688.0	1.000
649.1	650.1	0.998
*639.8	637.2	1.004
619.7	620.0	0.999
*534.6	531.5	1.006

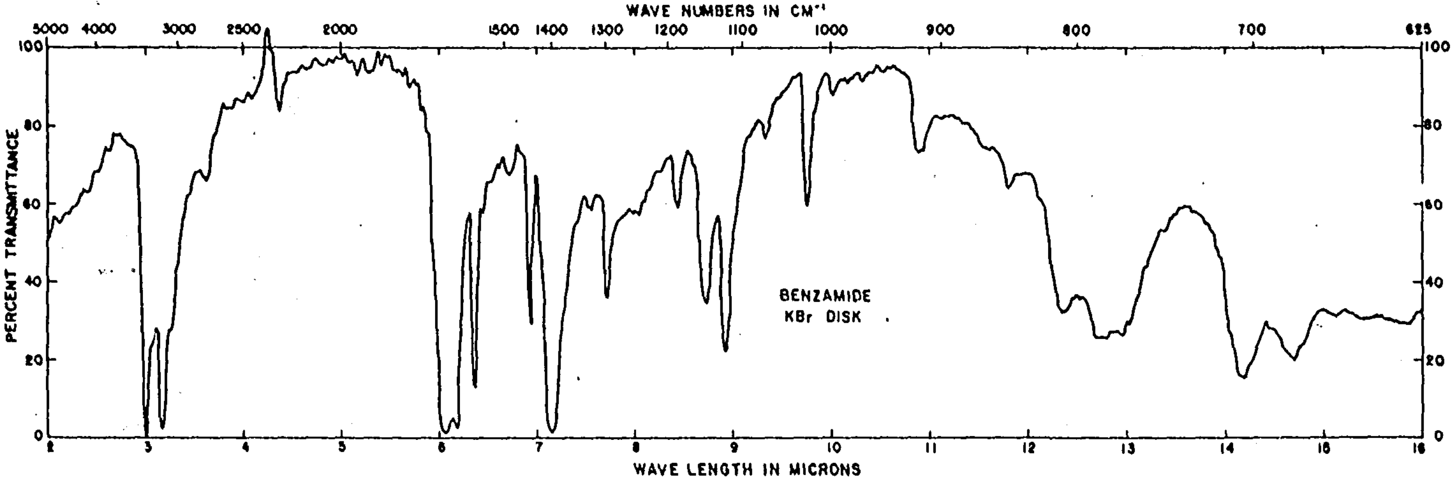


Figure 2. Spectrum of benzamide

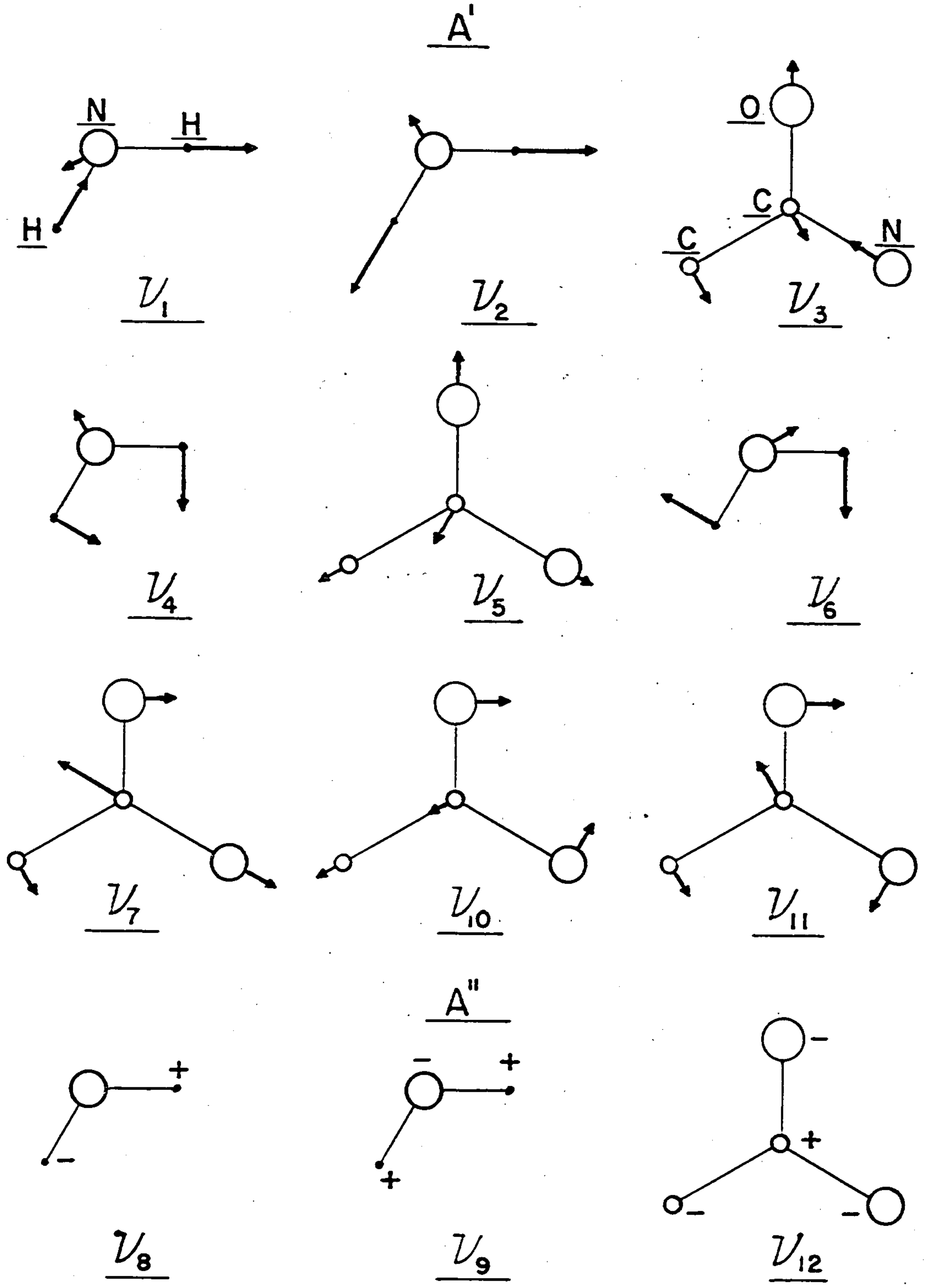


Figure 3. Suggested modes of vibration of the amide group

The highest frequency bands which shift upon nitrogen-15 substitution are those at 3549.9 cm.$^{-1}$ and 3435.2 cm.$^{-1}$. In dilute solutions the asymmetric and symmetric N-H stretching vibrations, ν_1 and ν_2 in Figure 3, have been assigned near 3530 cm.$^{-1}$ and 3415 cm.$^{-1}$, respectively (28, 29, 37, 39, 102). The observed bands are in agreement with these previous assignments and are assigned in like manner. The N-H stretching modes display an unusual concentration dependence; at higher concentrations the normal bands disappear and are replaced by other absorptions at lower frequencies. In solid benzamide these bands have been noted near 3400 cm.$^{-1}$ and 3200 cm.$^{-1}$ (67). This phenomenon is shown in Figure 2, which is a solid phase spectrum. It is generally agreed that molecular association through hydrogen bonding is involved, although the nature of the species is in dispute (22, 28, 29, 37, 38, 39). It was felt that little could be added on the latter subject by nitrogen-15 substitution since such small shifts would be involved.

The prominent absorption at 1658.1 cm.$^{-1}$ is commonly referred to as the Amide I band. Its frequency falls near 1650 cm.$^{-1}$ in solid amides and at higher frequencies in solutions (102). This frequency has been assigned to stretching of the C=O bond (102). Such a vibration should show no shift upon nitrogen-15 substitution. Since the observed frequency ratio is 1.005, this assignment is probably incorrect. Lecomte and Freymann's (70, 71) classification of the skeletal modes for amides included a mode involving primarily a C=O stretching in association with a small amount of nitrogen motion. The shift observed in the present study is too large to serve as supporting evidence for such a mode. Since it was necessary for Lecomte and Freymann (70, 71) to include this mode in order to depict the C-C-N interaction as they considered it, the major interacting system is probably not the C-C-N system. More recently Smith and Robinson (114) and Miyazawa (82), working with formamide and formamide-N-d_2, have associated this band with an asymmetric stretching of the O-C-N system. Such an assignment is consistent with the shift observed, and it also explains the fact that no shift comparable to that expected from a pure C-N vibration appears in Table 3. For this reason the 1658.1 cm.$^{-1}$ absorption is assigned as ν_3, which is primarily an asymmetric O-C-N stretching vibration.

The band at 1627.2 cm.$^{-1}$ falls in the region commonly assigned to the Amide I band of unsubstituted amides (67, 98, p. 29, 102). Richards and Thompson (102) assigned this vibration to the N-H deformation mode, ν_4. Observations on the isotopic shift of deuterated samples have verified this assignment (67, 82, 114). Since the isotopic shift observed in this study is in agreement with the N-H deformation assignment, the 1627.2 cm.$^{-1}$ band is assigned to ν_4.

Bands are observed at 1582.3 cm.$^{-1}$ and 1450.9 cm.$^{-1}$ which are also prominent and shift by a factor of 1.002, which would be expected from a N-H vibration. Deuteration data have not indicated that any bands at these positions are associated with hydrogenic vibrations. The data obtained in this study do not suggest an assignment for these bands, but it is possible that they are combination bands.

The band at 1403.1 cm.$^{-1}$ is strong and shows significant shift. Randall et al.(98, p. 13) assigned a band in the 1399-1418 cm.$^{-1}$ range in the unsubstituted amides to the C-N stretching vibration, and Davies and Hallam (39) and Kuratani (67) concurred. The data in Table 3 show that the band at 1403.1 cm.$^{-1}$ shifts much less than would be expected for a pure C-N vibration. Kahovec and Wasmuth (59) suggested that the C-N stretching vibration was associated with a displacement of 1312 cm.$^{-1}$ in the Raman spectrum of formamide. Miyazawa (82) and Smith and Robinson (114) found the same frequency in the infrared spectrum of formamide, but in both cases the band was assigned to the symmetric O-C-N stretching mode. It is reasonable to expect that the observed frequency in formamide would differ somewhat from other amides. Because the 1658.1 cm.$^{-1}$ band has been assigned as ν_3 and the 1403.1 cm.$^{-1}$ band does not shift enough to be a pure C-N stretching vibration the latter band is assigned as ν_5. This is primarily an O-C-N symmetric stretching but also includes significant motion of the other carbon atom.

Bands at 1149.9 cm.$^{-1}$ and 1128.7 cm.$^{-1}$ also exhibit significant shifts. Deuteration studies have placed the N-H rocking vibration, ν_6, in the region 1100-1150 cm.$^{-1}$ (67, 82, 114). The band at 1149.9 cm.$^{-1}$ shifts a reasonable amount for an N-H vibration and on this basis is assigned as ν_6. The 1128.7 cm.$^{-1}$ absorption exhibits the largest shift in the region studied. Davies and Hallam (39) suggested that a band at 1121 cm.$^{-1}$ in acetamide might involve a C-N deformation, but they said nothing further about the nature of the mode. Lecomte and Freymann (70, 71) felt that the band was associated with a symmetric stretching of the C-C and C-N bonds in acetamide. Their system has, however, been rejected on the basis of the 1658.1 cm.$^{-1}$ band which exhibited too large a shift for the mode they proposed. The vibration designated as ν_7 in Figure 3 is suggested as a reasonable possibility.

The next bands which shift are at 772.7 cm.$^{-1}$, 792.8 cm.$^{-1}$, and 811.4 cm.$^{-1}$. The absorption at 772.7 cm.$^{-1}$ is probably an out-of-plane vibration of the phenyl group (66, 81) which might shift as the result of coupling with a vibration of the amide group. No other bands shift between 640 cm.$^{-1}$ and 1120 cm.$^{-1}$. In the latter region a few suggestions have been made previously. Miyazawa (82) felt that the N-H wagging vibration, ν_9, might fall at 700 cm.$^{-1}$ in formamide, which agreed with the suggestion of Kahovec and Wasmuth (59) that the analogous Raman frequency was 691 cm.$^{-1}$. Davies and Hallam (39), however, considered the 700 cm.$^{-1}$ absorption in acetamide as the amide group scissoring mode, ν_{10}. The latter authors suggested that the N-H torsional mode, ν_8, might be associated with the 856 cm.$^{-1}$ band in acetamide. It is evident from Table 3 that none of the bands mentioned shift on nitrogen-15 substitution. Since the torsional vibration, ν_8, should not show an isotopic shift it is tentatively assigned to the band at 851.1 cm.$^{-1}$, in agreement with the proposal of Davies and Hallam (39). The bands at 811.4 cm.$^{-1}$ and 792.8 cm.$^{-1}$ shift enough to be associated with N-H vibrations, so one of them might be associated with the N-H wagging mode, ν_9, but it is impossible to choose between them on the basis of the evidence available. Neither band shifts sufficiently to be assigned as ν_{10}.

In the region from 640 cm.$^{-1}$ to 420 cm.$^{-1}$, the lower limit of this study, only the bands at 639.8 cm.$^{-1}$ and 534.6 cm.$^{-1}$ shift significantly. The only previous assignment in this region is the amide scissoring vibration, ν_{10}. Lecomte and Freymann (71) suggested that this vibration was at 448 cm.$^{-1}$ in the Raman spectrum of acetamide. This assignment cannot be correct in benzamide since no band exists there. Others have assigned ν_{10} at 600-605 cm.$^{-1}$ (59, 82, 114). The absorption observed at 639.8 cm.$^{-1}$ in this study lies near this range and shifts enough to be assigned as ν_{10}.

Only the amide rocking vibration, ν_{11}, and the out-of-plane bending mode, ν_{12}, remain to be assigned. Out-of-plane vibrations are normally of lower frequency than in-plane vibrations, therefore the 534.6 cm.$^{-1}$ absorption is assigned as ν_{11}, and ν_{12} must lie below 420 cm.$^{-1}$.

ANILINE HYDROCHLORIDE

Experimental

The nitrogen-15 labeled benzamide was converted to aniline by the reaction

$$C_6H_5CONH_2 + NaOCl + 2NaOH \rightarrow C_6H_5NH_2 + Na_2CO_3 + NaCl + H_2O$$

following the procedure of Fones and White (47).

Chlorine was bubbled into a solution of 13.9 g. of sodium hydroxide in 50 ml. of water to which was added 71 g. of ice. The chlorine gas was passed through the solution until the weight of the solution had increased 3.9 g. After addition of 5.74 g. of benzamide the cold, stirred solution was heated quickly to reflux and was maintained at that temperature for one hour. The reaction mixture was cooled in an ice bath, and the labeled aniline was extracted with four 100 ml. portions of ether. The extract was dried by filtering through anhydrous sodium sulfate, and the aniline was separated by bubbling anhydrous hydrogen chloride into the solution. The aniline hydrochloride was filtered and dried. The weight of the crude material was 5.05 g., giving a yield of 82.3 per cent.

For spectroscopic use a portion of the aniline hydrochloride was dissolved in water and reprecipitated by the addition of concentrated hydrochloric acid. The unlabeled aniline hydrochloride was prepared by addition of concentrated hydrochloric acid to a sample of commercial aniline. All samples were run as potassium bromide disks. The results are shown in Table 4. The prominent bands which show a significant shift are marked with an asterisk. The spectrum in the region 5000-625 cm.$^{-1}$ of the normal nitrogen compound, run as a KBr disk, is shown in Figure 4.

Discussion

The aniline hydrochloride molecule cannot readily be assigned to any particular symmetry class. However, several types of vibrations are certain to take place. The $-NH_3^+$ group has symmetric and asymmetric stretching and deformation modes and rocking and torsional vibrations. Stretching and bending modes might be assignable for the C-N bond. However, the bond between the nitrogen atom and the phenyl ring is exceptionally short (26), so interaction with the ring vibrations is possible.

The highest frequency fundamental mode associated with the $-NH_3^+$ group is the asymmetric stretching mode, shown as ν_1 in Figure 5. No absorptions were observed at higher frequencies than the band at 2932.3 cm.$^{-1}$, which exhibits an isotopic shift in the right range. Assignment of this absorption to the asymmetric N-H stretching vibration is substantially in agreement with the results of Bellanato and Barceló (24), Edsall and Scheinberg (45), Larsson (68), Lord

Table 4. Observed frequencies of aniline hydrochloride and its nitrogen-15 analog with the ratios of corresponding frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
*2932.3	2922.5	1.003
2885.0	2900.0	0.995
*2596.9	2587.3	1.004
2574.0	2561.1	1.005
1599.9	1599.4	1.000
1558.6	1558.2	1.000
*1516.3	1511.8	1.003
*1494.3	1491.9	1.002
1371.3	1388.9	0.987
1332.3	1332.3	1.000
1296.9	1297.2	1.000
*1200.3	1196.5	1.003
*1118.9	1113.3	1.005
*1095.4	1092.3	1.003
1055.4	1053.2	1.002
1035.2	1035.3	1.000
983.8	983.9	1.000
745.3	745.8	0.999
686.0	686.0	1.000
671.2	671.2	1.000
619.9	619.9	1.000
*528.8	521.7	1.014
478.7	478.0	1.001
469.4	469.3	1.000

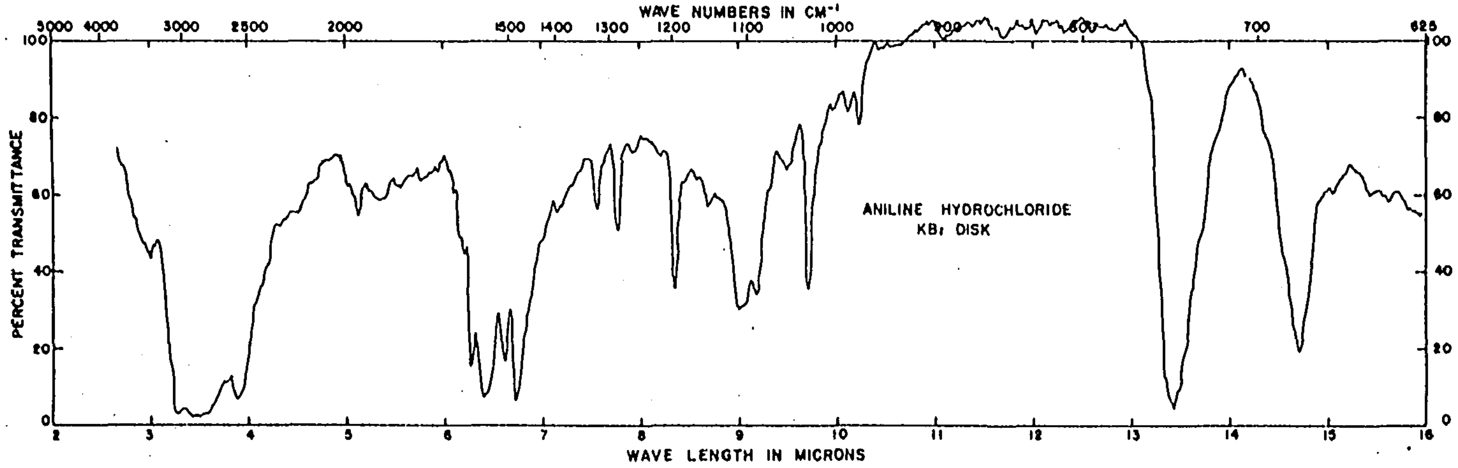


Figure 4. Spectrum of aniline hydrochloride

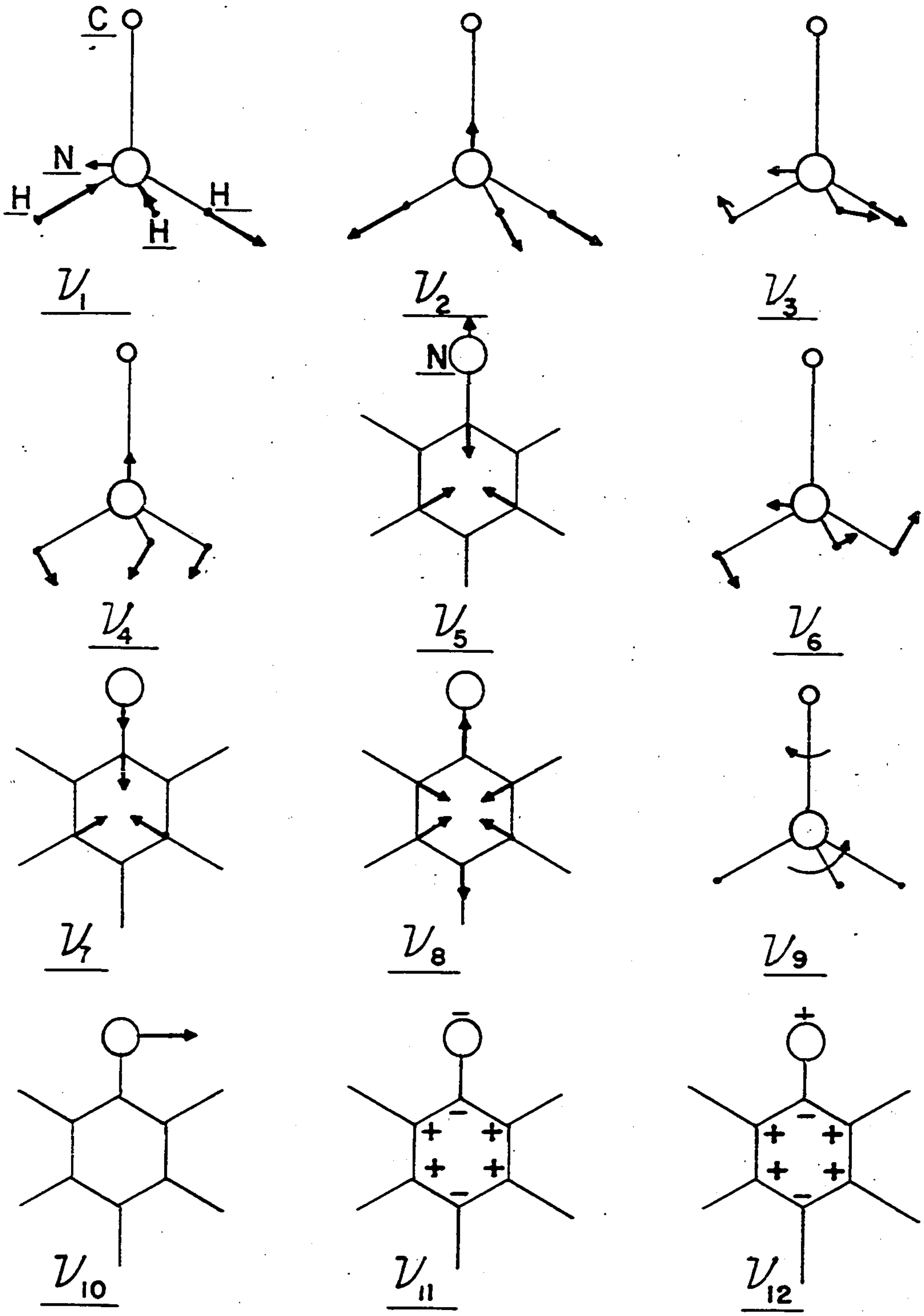


Figure 5. Suggested modes of vibration of aromatic primary amine hydrochlorides

and Merrifield (78), and Waldron (128).

The symmetric N-H stretching mode, ν_2, should occur at a lower frequency than the asymmetric vibration, ν_1. Only the band at 2596.9 cm.$^{-1}$ falls at a high enough frequency to be considered and also exhibits an isotopic shift in the proper range. The band listed in Table 4 at 2574.0 cm.$^{-1}$ is not resolved in the spectrum in Figure 4. It appears as a weak shoulder on the higher frequency band only under high resolution and may be a combination band. The absorption at 2596.9 cm.$^{-1}$ is assigned as ν_2, the symmetric N-H stretching vibration. This assignment agrees with a suggestion by Larsson (68) in the case of n-butylamine hydrochloride, but the frequency is much lower than that assigned by Bellanato and Barceló (24) and Waldron (128) in methylamine hydrochloride. This discrepancy cannot be readily explained; studies on the spectrum of deuterated aniline hydrochloride would be necessary to resolve the disagreement.

Between the bands discussed above and the absorption at 1200.3 cm.$^{-1}$, only the bands at 1516.3 cm.$^{-1}$ and 1494.3 cm.$^{-1}$ shift significantly. Edsall and Scheinberg (45) associated a Raman band at 1620 cm.$^{-1}$ in methylamine hydrochloride with a N-H deformation, and Klotz and Gruen (62) made a similar assignment at 1590 cm.$^{-1}$ in isohexylamine hydrochloride. Larsson (68) assigned the asymmetric deformation, ν_3, and the symmetric deformation, ν_4, to 1603 cm.$^{-1}$ and 1511 cm.$^{-1}$

in n-butylamine hydrochloride. Waldron (128) made similar assignments to 1580 cm.$^{-1}$ and 1538 cm.$^{-1}$ in methylamine hydrochloride, while for the same compound Bellanato and Barceló (24) determined the frequencies as 1570 cm.$^{-1}$ and 1502 cm.$^{-1}$. Bellamy (23, p. 202) noted that in amino acids and amino acid hydrochlorides the asymmetric and symmetric N-H deformation vibrations are assigned to the regions 1590-1660 cm.$^{-1}$ and 1485-1550 cm.$^{-1}$, respectively. The band observed at 1516.3 cm.$^{-1}$ in this study is tentatively assigned as ν_3, the asymmetric deformation vibration, although this frequency is below the normal range of 1570-1660 cm.$^{-1}$. It is possible that the lower frequency results from the presence of the phenyl ring in the compound. Further information could be obtained from the study of deuterated aniline hydrochloride. The band observed at 1494.3 cm.$^{-1}$ falls in the range associated with the symmetric deformation, ν_4, and is assigned as such. Table 4 shows that the shift of the 1494.3 cm.$^{-1}$ band upon substitution of nitrogen-15 is not sufficient for its association with the C-N stretching vibration as suggested by Layton et al. (69).

In the region 800-1250 cm.$^{-1}$, Table 4 shows that three prominent bands shift significantly upon nitrogen substitution: 1200.3, 1118.9, and 1095.4 cm.$^{-1}$. In methylamine hydrochloride the C-N stretching vibration has been assigned at 995-1010 cm.$^{-1}$ (24, 45, 128). This frequency might be raised by the presence of the phenyl ring, so it is not surprising that no band shifts in this region. The difficulty that arises, however, is that the biggest shift observed is only one-third of the value to be expected of a C-N stretching vibration. A possible explanation lies in the suggestions of Randle and Whiffen (99), who concluded that the vibrations of the bond between the substituent and the ring carbon in monosubstituted benzenes involved motions of other ring carbons. They proposed that the modes designated as ν_5, ν_7, and ν_8 involved stretching of the ring-substituent bond. The ranges assigned by Whiffen (132) in monohalogenated benzenes are 1060-1220 cm.$^{-1}$, 654-806 cm.$^{-1}$, and 266-520 cm.$^{-1}$, respectively, for ν_5, ν_7, and ν_8. Since the 1118.9 cm.$^{-1}$ band exhibits the greatest isotopic shift it is assigned as ν_5. In this same region the N-H rocking mode in methylamine hydrochloride was assigned by Waldron (128) as either 1265 cm.$^{-1}$ or 958 cm.$^{-1}$ and by Bellanato and Barceló (24) as 926 cm.$^{-1}$. This vibration could reasonably be assigned to either of the bands, 1200.3 or 1095.4 cm.$^{-1}$. The 1095.4 cm.$^{-1}$ absorption is tentatively assigned as ν_6 because it involves the least deviation from the expected region. The latter assignment could be checked with deuterated aniline hydrochloride.

If the suggestions of Randle and Whiffen (99) are correctly applied in this case, a shift associated with ν_7

should be observed in the region 654-806 cm.$^{-1}$. Table 4 shows no shift in this range, but it is possible that the band is hidden by the very strong phenyl absorption at 745.3 cm.$^{-1}$. No definite assignment can be made for this mode.

The band at 528.8 cm.$^{-1}$ is the only absorption of aniline hydrochloride which exhibits a large shift. According to the proposals of Randle and Whiffen (99), the in-plane bending vibration of aniline hydrochloride, ν_{10}, should exhibit a shift near that of a pure C-N vibration. The shift of the 528.8 cm.$^{-1}$ band is only slightly less than predicted. Therefore, the 528.8 cm.$^{-1}$ band is assigned as ν_{10}.

Four modes in Figure 5 have not been discussed. The out-of-plane vibrations suggested by Randle and Whiffen (99), ν_{11} and ν_{12}, both involve nitrogen motion, but they would probably fall below 420 cm.$^{-1}$ and would not be observed in this study. Whiffen (132) assigned ν_8 to the region 266-520 cm.$^{-1}$, and Waldron (128) associated the torsional N-H vibration, ν_9, with a band at 487 cm.$^{-1}$ in methylamine hydrochloride. Neither mode involves any nitrogen motion so no shift should be observed. It is possible that the bands at 478.7 cm.$^{-1}$ and 469.4 cm.$^{-1}$, which are in the right range and do not shift on nitrogen-15 substitution, are associated with these two modes. Nothing certain can be said, but deuterated aniline hydrochloride would permit ν_9 to be assigned.

n-HEXYL NITRITE

Experimental

The nitrogen-15 labeled n-hexyl nitrite was prepared by the reaction

$$KNO_2 + C_6H_{13}OH + HCl \longrightarrow C_6H_{13}ONO + KCl + H_2O$$

The solution from the ammonia oxidation, containing potassium nitrite and potassium hydroxide, was evaporated to a volume of 100 ml. The hydroxide and nitrite ions reacted simultaneously with all reagents used for forming an alkyl nitrite with a resultant low yield. It was therefore necessary to remove the hydroxide prior to the formation of the hexyl nitrite. A solution of 146.69 g. of zinc chloride in 100 ml. of water was added slowly with stirring. After cooling, the precipitate of zinc hydroxide was filtered off and washed until the washings gave a negative test for nitrite. This test was performed by adding a crystal of ferrous sulfate to one drop of wash water followed by one drop of concentrated sulfuric acid. Formation of a brown coloration around the crystal occurred when nitrite was present. The combined filtrate and washings were placed in a 2 liter three-necked round-bottom flask with 21.33 g. of n-hexanol. A stirring attachment was placed through the center neck, an addition funnel was placed in a second neck, while the third neck was closed with a stopper. Hydrochloric acid (5.65 ml. of concentrated acid diluted to 25 ml.) was added dropwise in 1 hour and 15 minutes. After the addition was completed, the organic layer, which contained the n-hexyl nitrite, was separated and filtered through anhydrous sodium sulfate. The product was weighed and, on the assumption that the nitrite formed in the oxidation was completely converted to hexyl nitrite, the amount of alcohol present was calculated. This information was used in determining the amount required in subsequent preparative work. Because of the instability of the hexyl nitrite the compound could not readily be purified for spectroscopic purposes. The greater part of the alcohol was removed by a single vacuum distillation, as indicated by the decrease in intensity of the O-H absorption in the infrared spectrum.

The unlabeled n-hexyl nitrite was prepared by the method of Chrétien and Longi (30) according to the reaction

$$6KNO_2 + 6C_6H_{13}OH + Al_2(SO_4)_3 \longrightarrow 6C_6H_{13}ONO + 3K_2SO_4 + 2Al(OH)_3$$

A solution of 35.20 g. of potassium nitrite in 200 ml. of water was placed in a 2 liter three-necked round-bottom flask, arranged as described previously, and 29.85 g. of n-hexanol was added. A solution of 46.31 g. of $Al_2(SO_4)_3 \cdot 18H_2O$ was added dropwise in 2 hours and 40 minutes with constant stirring. After completion of the addition the organic layer was separated and dried with anhydrous sodium sulfate. The infrared spectrum showed only a trace of alcohol to be present so no purification was made.

The infrared spectra of these compounds were obtained from solutions in carbon disulfide and carbon tetrachloride. In the brief wavelength span where both of these solvents absorb, solutions in hexanol were used. The results are shown in Table 5. The prominent bands which show a significant shift are marked with an asterisk. The spectrum in the region 5000-625 cm.$^{-1}$ of the normal nitrogen compound, run as a capillary film, is shown in Figure 6.

Discussion

The first information about the geometrical structure of alkyl nitrites was provided by Rogowski (104), who made an electron diffraction study of methyl nitrite. He suggested that the molecule existed in a cis form, $\mathrm{R - O}^{\nearrow \overset{\mathrm{O}\searrow}{\;\;\mathrm{N}}}$, stabilized by a C-H•••O hydrogen bond. More recently Tarte (116) found doubling in some of the infrared absorption bands in methyl nitrite. From this he concluded that alkyl nitrites existed in a trans form, $\mathrm{R - O}^{\nearrow \mathrm{N} = \mathrm{O}}$, as well as in the cis form proposed earlier. The temperature dependence of the relative intensities of the members of the band pairs was used as evidence for the isomerism. Haszeldine and Jander (52), Haszeldine and Mattinson (53), and Wagner (127) agreed that the two isomers must exist.

Support for the isomerism of alkyl nitrites was provided

Table 5. Observed frequencies of n-hexyl nitrite and its nitrogen-15 analog with ratios of the frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
2975.2	2973.8	1.001
2947.0	2945.1	1.001
2886.6	2885.6	1.000
2875.8	2875.7	1.000
2736.3	2742.3	0.998
*1651.5	1622.1	1.018
*1606.7	1583.0	1.015
1469.8	1469.4	1.000
1460.7	1460.4	1.000
1439.1	1438.9	1.000
1419.7	1417.7	1.001
1381.6	1380.0	1.001
1301.0	1300.4	1.001
1272.6	1271.8	1.001
*1235.6	1220.8	1.012
1171.0	1174.9	0.997
1119.1	1119.2	1.000
1055.8	1056.3	0.999
1032.2	1031.8	1.000
*931.2	918.1	1.014
*784.2	773.8	1.013
*732.2	729.2	1.004
*686.4	677.8	1.013
*674.6	670.9	1.005
*658.1	656.3	1.003
*599.2	594.7	1.008

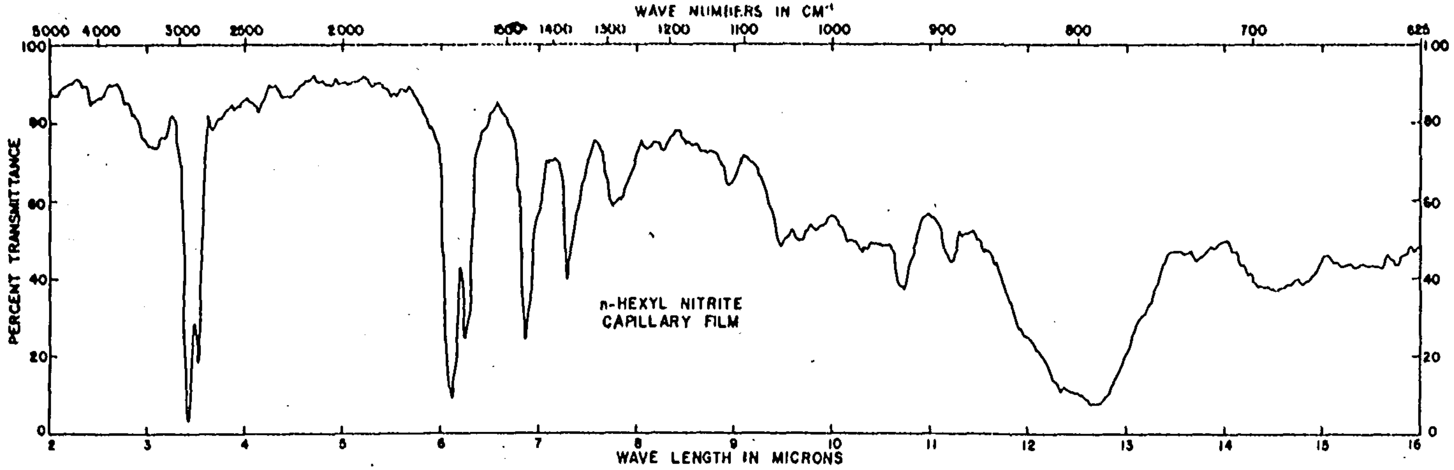


Figure 6. Spectrum of n-hexyl nitrite

by nuclear magnetic resonance studies (93, 94) which showed the definite existence of two forms of alkyl nitrites. Phillips et al. (93) disputed the hypothesis that hydrogen bonding in the cis form was the cause of the isomerism. They concluded that the two forms existed because of restricted rotation about the O-N bond as a result of its partial double bond character. This conclusion was based on the determination that the barrier to rotation was too small to result from hydrogen bonding.

The cis and the trans forms of n-hexyl nitrite probably have C_s symmetry considering only the C-O-N=O group. There are five in-plane vibrations and one out-of-plane vibration for each form. The probable nature of these modes can only be developed by a consideration of the experimental results.

The highest frequency bands showing a significant shift are those at 1651.5 cm.$^{-1}$ and 1606.7 cm.$^{-1}$. Strong bands have been observed in this region in alkyl nitrites by Dadieu et al. (34), Lenormant and Clément (76) and Kopper et al. (64). The latter authors suggested that the Raman displacement they observed might be associated with the N=O stretching vibration. Tarte (116, 117, 118) and D'Or and Tarte (43) reported two strong bands at 1653-1681 cm.$^{-1}$ and 1613-1625 cm.$^{-1}$ in 15 alkyl nitrites and assigned the bands to the N=O stretching vibrations of the trans and cis forms, respectively. The presence of these two bands was also noted by Haszeldine and

Jander (52), Haszeldine and Mattinson (53), and by Wagner (127). These authors all agreed with the above assignment. The data in Table 5 show that the band at 1651.5 cm.$^{-1}$ shifts by a factor of 1.018, which is the value expected from a pure N=O stretching. The 1606.7 cm.$^{-1}$ absorption shifts somewhat less but must still be primarily an N=O stretching vibration. These bands are assigned as N=O stretching vibrations of the trans and cis forms, in agreement with previous assignments. The modes are approximately represented as ν_1 in Figure 7, where similar modes in the two forms are numbered identically. No motion is indicated for some atoms in most of the modes since their contribution is probably small and could be determined exactly only by extensive calculations.

The next lower frequency band which is observed to shift is the one at 1235.6 cm.$^{-1}$. Tarte (118) assigned the first overtone of the O-N=O deformation vibration in this region. This assignment is unlikely because the only band, 658.1 cm.$^{-1}$, of which it could reasonably be a harmonic has a much smaller frequency ratio. In order to explain this discrepancy it is necessary to consider the remainder of the spectrum and previous assignments. Tarte (116, 117, 118) assigned the C-O stretching vibrations of the two forms in methyl nitrite to bands at 993 cm.$^{-1}$ and 1045 cm.$^{-1}$. Such a vibration should show no shift upon nitrogen-15 substitution.

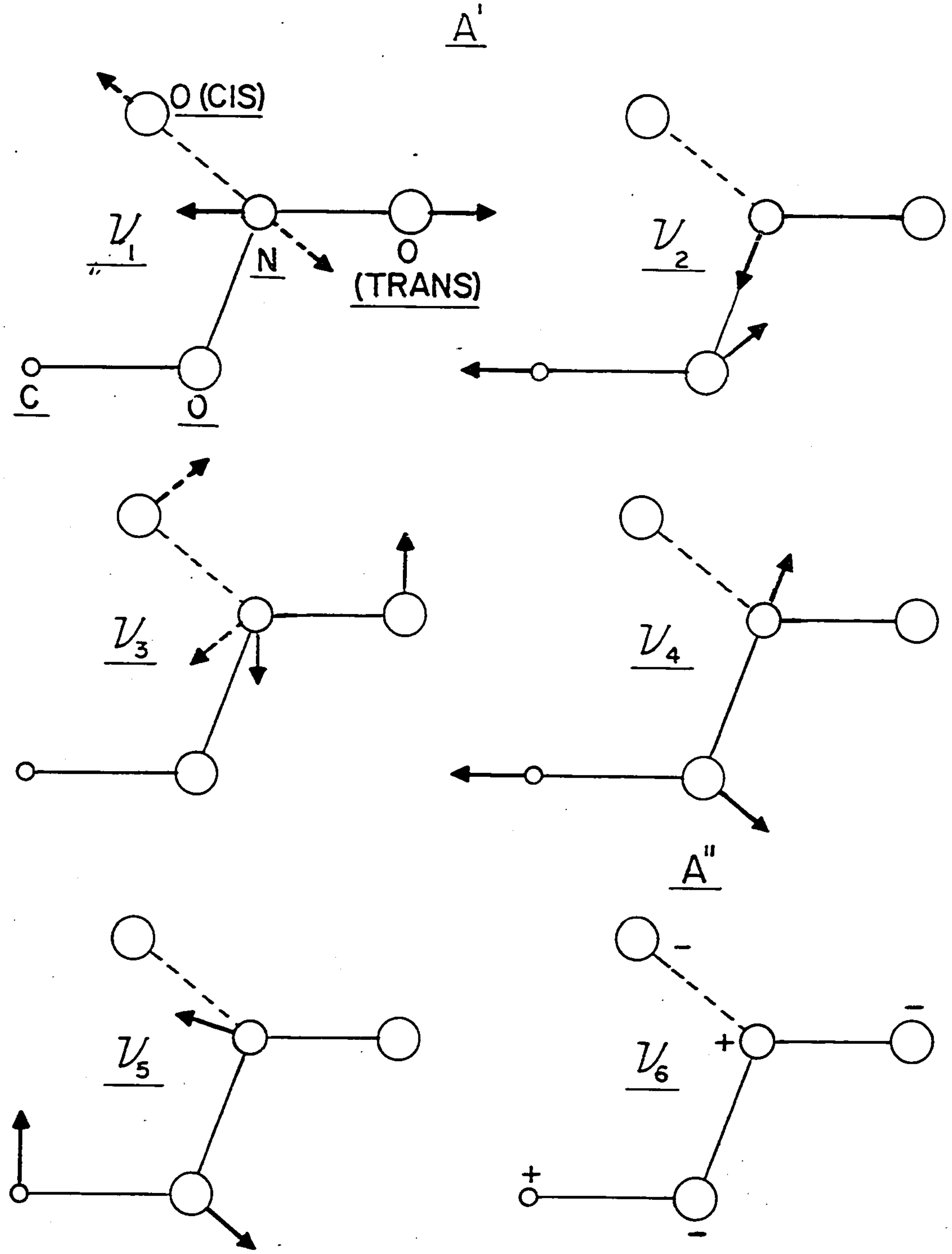


Figure 7. Suggested modes of vibration of the cis and trans forms of alkyl nitrites

The N-O stretching vibration was assigned to a band between 750 cm.$^{-1}$ and 840 cm.$^{-1}$. He noted that in low molecular weight nitrites, bands for both forms could be resolved in this region. In addition, bands at 678-691 cm.$^{-1}$ and 580-625 cm.$^{-1}$ were assigned to the O-N=O deformation vibration of the cis and trans forms, respectively. Wagner (127) agreed with the latter assignments in methyl nitrite and also suggested that the C-O-N deformation mode fell at 350 cm.$^{-1}$. If these assignments are correct, there should be no more than six bands in the region studied which shift upon nitrogen-15 substitution. However, ten bands in this region are observed to shift. The assignments of previous investigators therefore do not appear to be correct.

As noted previously, the results of the present study are in agreement with earlier assignments of the N=O stretching vibrations and show that there is little interaction between this bond and the remainder of the molecule. Thus the N=O bending vibration (ν_3 in Figure 7) should also be relatively independent and exhibit a large isotope shift. Since the stretching mode shows intense absorption, the bending mode should likewise exhibit high intensity. The intense band at 784.2 cm.$^{-1}$ exhibits the expected isotope shift and can therefore be reasonably assigned to the N=O bending mode, ν_3. The analogous band for the cis form is assigned at 686.4 cm.$^{-1}$ since it exhibits a similar shift. By analogy with the relative intensities of the bands associated with the N=0 stretching vibration of the cis and trans forms the bending vibration in the trans form is assigned to the band at 784.2 cm.$^{-1}$ and the cis form to the 686.4 cm.$^{-1}$ absorption. The fact that both bands shift somewhat less than would be expected for a pure N=0 vibration indicates that there is some 0-N=0 deformation character in this vibration.

The masses of the carbon and nitrogen atoms and the force constants of the C-0 and N-0 bonds are probably sufficiently similar to expect some interaction to occur. These interactions should give rise to essentially asymmetric and symmetric stretching modes of the C-0-N system (ν_2 and ν_4 in Figure 7) and to a C-0-N in-plane deformation, ν_5. The nature of the out-of-plane vibration, ν_6, cannot be readily predicted. Of these the asymmetric stretching mode, ν_2, should possess the highest frequency so the bands at 1235.6 cm.$^{-1}$ and 931.2 cm.$^{-1}$ are assigned in this manner. The higher frequency band is associated with the cis form solely because of its lower intensity.

The symmetric stretching vibration, ν_4, should be of higher frequency than the in-plane bending mode, ν_5,and should show a relatively small isotopic shift. The two bands at 732.3 cm.$^{-1}$ and 674.6 cm.$^{-1}$ are assigned to ν_4. The band at 674.6 cm.$^{-1}$ is assigned to the cis form because it is of lower intensity although this information cannot be obtained from the spectrum in Figure 6. The remaining two bands in Table 5, 658.1 cm.$^{-1}$ and 599.2 cm.$^{-1}$, are assigned as the in-plane bending mode, ν_5. The band at 658.1 cm.$^{-1}$ is associated with the cis form on the basis of the temperature dependence studies of Tarte (116, 117, 118) and Wagner (127).

The out-of-plane bending mode, ν_6, probably has a frequency below 420 cm.$^{-1}$ and would not be observed in this study. The band reported at 350 cm.$^{-1}$ in methyl nitrite by Wagner (127) might be associated with this vibration.

BENZENEDIAZONIUM CHLORIDE

Experimental

Benzenediazonium chloride with both nitrogens substituted by nitrogen-15 was prepared by the reaction

$$C_6H_5NH_2 + C_6H_{13}ONO + HCl \longrightarrow C_6H_5N_2Cl + C_6H_{13}OH + H_2O$$

A solution of 0.57 g. of aniline hydrochloride and 0.07 g. of concentrated hydrochloric acid in 25 ml. of absolute ethanol was placed in a 38 x 200 mm. test tube. The test tube was suspended in an ice-salt mixture, and the solution was stirred until it reached a temperature of 0° C. At this time 1.75 g. of n-hexyl nitrite was added slowly enough that the temperature did not rise above 1° C.; this required 12 minutes. The solution was then maintained in the ice-salt mixture with constant stirring for 3-1/2 hours. Then approximately 0.8 ml. of the solution was removed and the benzenediazonium chloride was precipitated by the addition of anhydrous ether. When not needed for spectroscopic studies the salt was stored under ether in a refrigerator. The remainder of the solution was used in the preparation of p-N,N-dimethylaminoazobenzene. The sample of diazonium salt containing normal nitrogen was prepared in the same manner.

The sample of the nitrogen-15 substituted benzenediazonium chloride and the sample containing the normal nitrogen were run as KBr disks. As a result of sample decomposition it was necessary to prepare fresh KBr disks for use with each prism. The results are shown in Table 6. The prominent bands which show a significant shift are marked with an asterisk. The spectrum in the region 5000-625 cm.$^{-1}$ of the normal nitrogen compound, run as a KBr disk, is shown in Figure 8.

Discussion

Aromatic diazonium salts are usually pictured as a linear grouping of two nitrogen atoms in the plane of the ring. On this basis the benzenediazonium cation is of C_{2v} symmetry. The vibrations of the diazonium group and the vibrations of the phenyl ring can be considered separately since their interaction is probably small (99). When the group is considered to be made up of the two nitrogen atoms and the ring carbon atom to which the nitrogens are attached, there are four modes of vibration, all infrared active. Two of these vibrations are of species A_1; they must be stretching modes since they retain all symmetry properties. One of the remaining vibrations is species B_1, while the other is species B_2. These are, respectively, in-plane and out-of-plane deformation vibrations of the diazonium group.

Only one band has been assigned in the infrared spectra of aromatic diazonium compounds. Aroney et al.(15) examined the spectra of 21 diazonium salts and attributed a very strong

Table 6. Observed frequencies of benzenediazonium chloride and its nitrogen-15 analog with the ratio of corresponding frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
3087.8	3089.2	0.999
3041.2	3040.9	1.000
3010.8	3010.8	1.000
*2302.1	2227.5	1.033
1576.6	1576.6	1.000
1548.4	1549.0	1.000
1527.5	1527.5	1.000
1513.8	1513.5	1.000
*1499.9	1477.8	1.015
1496.5	1494.4	1.001
1463.0	1462.9	1.000
1440.7	1440.7	1.000
1423.6	1424.1	1.000
1313.2	1313.0	1.000
1180.7	1181.9	0.999
1156.4	1156.4	1.000
1085.1	1084.0	1.001
1022.3	1021.5	1.001
769.9	770.8	0.999
758.9	758.6	1.000
669.9	668.4	1.002
622.5	620.8	1.003
*518.4	510.6	1.015

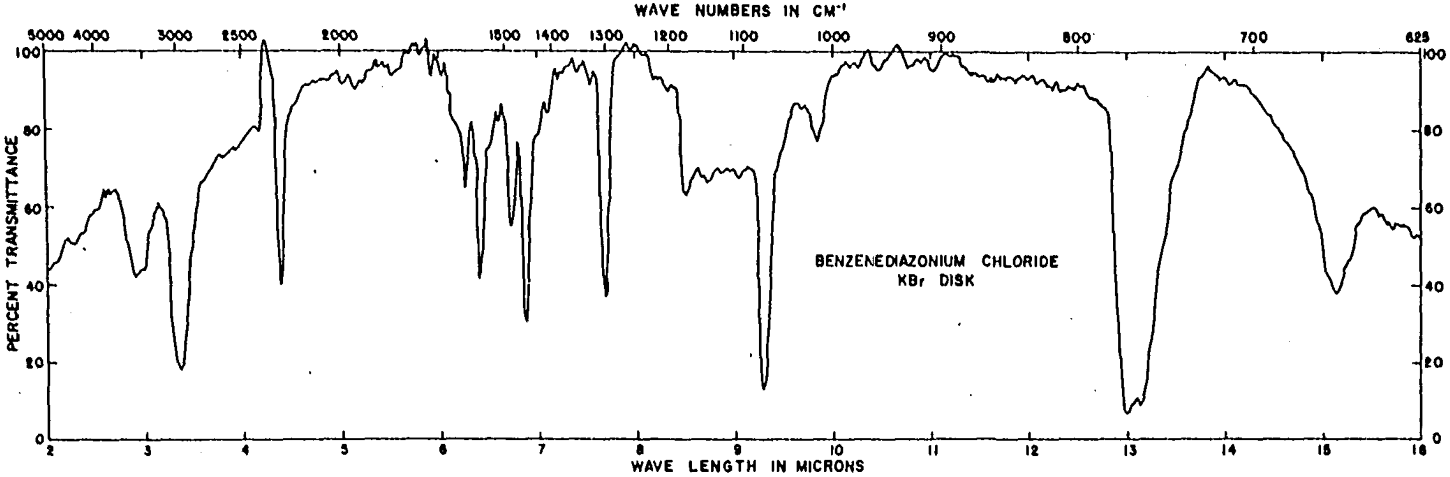


Figure 8. Spectrum of benzenediazonium chloride

absorption in the region 2230-2310 cm.$^{-1}$ to stretching of the bond between the nitrogen atoms. The same strong band was noted in the region 2137-2294 cm.$^{-1}$ by Whetsel _et_ _al_.(131), who studied the spectra of 30 diazonium salts and related compounds. These authors also assigned the absorption to stretching of the nitrogen-nitrogen bond. Both groups suggested that the region of this absorption band was confirmation of the usual assignment of a triple bond between the nitrogens.

The data in Table 6 confirm the assignment made in the earlier studies. The band at 2302.1 cm.$^{-1}$ exhibits a shift of 1.033, which compares well with the value 1.035 calculated for a pure nitrogen-nitrogen vibration. It is assigned as ν_1 in Figure 9.

The bands at 1499.9 cm.$^{-1}$ and 518.4 cm.$^{-1}$ were found to shift considerably upon isotopic substitution. The 1499.9 cm.$^{-1}$ absorption is observed to shift 1.015, which compares well with the value 1.016 expected for a pure carbon-nitrogen vibration. It is assigned as ν_2. This frequency suggests considerable double bond character in the carbon-nitrogen bond.

The band at 518.4 cm.$^{-1}$ exhibits a significant shift and must be associated with a vibration of the diazonium group. The in-plane bending mode and the out-of-plane bending mode, ν_3 and ν_4, have not been assigned. Since the out-of-plane

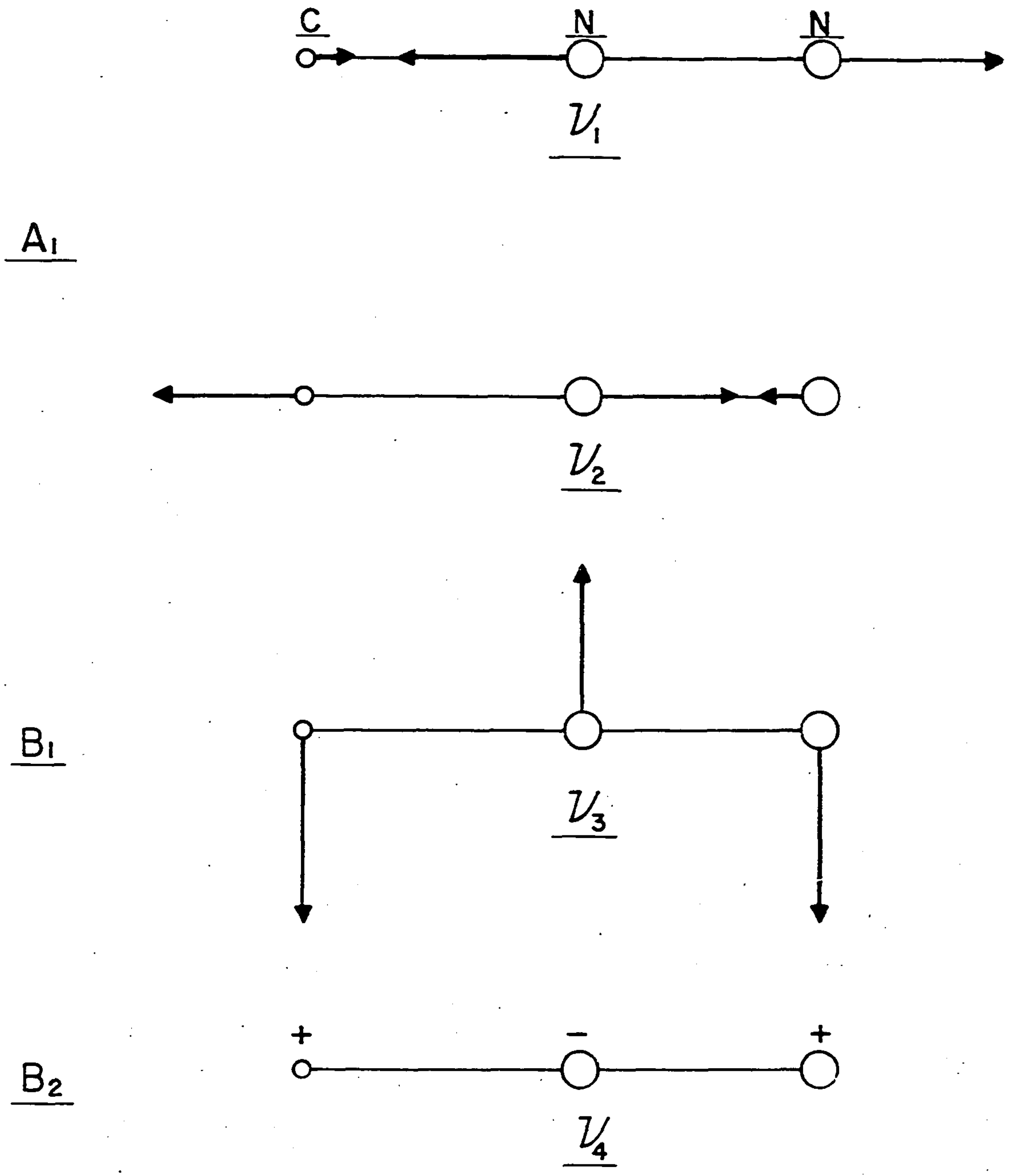


Figure 9. Suggested modes of vibration of the aromatic diazonium group

mode would be expected to have a lower vibrational frequency than the in-plane mode, this band is assigned to the in-plane bending vibration, ν_3. This assignment indicates that the out-of-plane vibration must absorb below 420 cm.$^{-1}$, the lower limit of this investigation.

p-N,N-DIMETHYLAMINOAZOBENZENE

Experimental

The azo compound p-N,N-dimethylaminoazobenzene, with both azo nitrogens substituted by nitrogen-15, was prepared by the reaction

$$C_6H_5N_2Cl + C_6H_5N(CH_3)_2 \longrightarrow C_6H_5N{=}NC_6H_4N(CH_3)_2 + HCl$$

The procedure was patterned after that of Fones and White (47).

The alcoholic solution of labeled benzenediazonium chloride was kept in the ice-salt mixture and, after removal of the spectroscopic sample, 1.19 g. of N,N-dimethyaniline was added. After stirring for an hour, one-half of a solution of 1.11 g. of anhydrous sodium acetate in 10 ml. of distilled water was added. The remainder of the sodium acetate solution was added 1 hour later and the ice-salt bath removed. Stirring was continued an additional hour and then the solution was allowed to stand overnight.

The solid azo compound which settled out of the reaction mixture was separated from the liquid by filtration. After drying, this product weighed 0.18 g. and melted at 112-114° C. This material was recrystallized three times from 95 per cent ethanol, giving a sample melting at 117.5-118° C. The recrystallized product was used for the spectroscopic work performed later. The liquid from the reaction mixture was taken up in ether and extracted with 0.0001 N hydrochloric acid. When no further color was extracted with the hydrochloric acid, the ether solution was evaporated and yielded an additional 0.52 g. of the azo compound. The ethanol from the recrystallizations was evaporated and the material recovered was added to that obtained from the liquid of the reaction mixture. The yield based on aniline hydrochloride was 70 per cent.

The azo compound containing normal nitrogen was prepared by the method of Fones and White (47) with the same time intervals used in the preparation of the nitrogen-15 compound. The product had a melting point of 117-118° C.

All samples were run as solutions of approximately 10 mg./ml. concentration using carbon disulfide and carbon tetrachloride as solvents in their respective transparent spectral regions. The results are shown in Table 7. The prominent bands which show a significant shift are marked with an asterisk. The spectra in the region 5000-625 $cm.^{-1}$ of the normal nitrogen compound, run as a carbon tetrachloride solution and as a KBr disk, are shown in Figure 10.

Discussion

The molecule p-N,N-dimethylaminoazobenzene possesses no element of symmetry on an exact basis. Assuming that there is little interaction between the vibrations of the azo

Table 7. Observed frequencies of p-N,N-dimethylaminoazobenzene and its nitrogen-15 analog with the ratio of corresponding frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
3088.8	3087.5	1.000
3057.1	3052.9	1.001
3002.8	2996.8	1.002
2912.2	2924.7	0.996
2869.0	2871.2	0.999
2821.4	2821.4	1.000
2650.7	2650.6	1.000
2556.1	2553.3	1.001
1601.1	1599.5	1.001
1522.9	1522.5	1.000
*1463.3	1445.4	1.012
1443.9		0.999
1439.0	1437.6	1.001
*1423.3	1390.0	1.023
1362.0	1362.0	1.000
1315.2	1314.9	1.000
1236.7	1237.6	0.999
1196.2	1195.0	1.001
1172.0	1174.0	0.998
1158.1	1158.4	1.000
1144.1	1140.7	1.003
1068.4	1069.9	0.999
1022.9	1023.7	0.999
949.6	950.1	0.999
822.2	822.8	0.999
766.3	766.3	1.000
726.9	727.4	0.999
690.7	691.4	0.999
670.0	671.4	0.998
656.3	657.3	0.998
548.6	547.1	1.003
*538.7	529.3	1.018
516.2	512.2	1.008

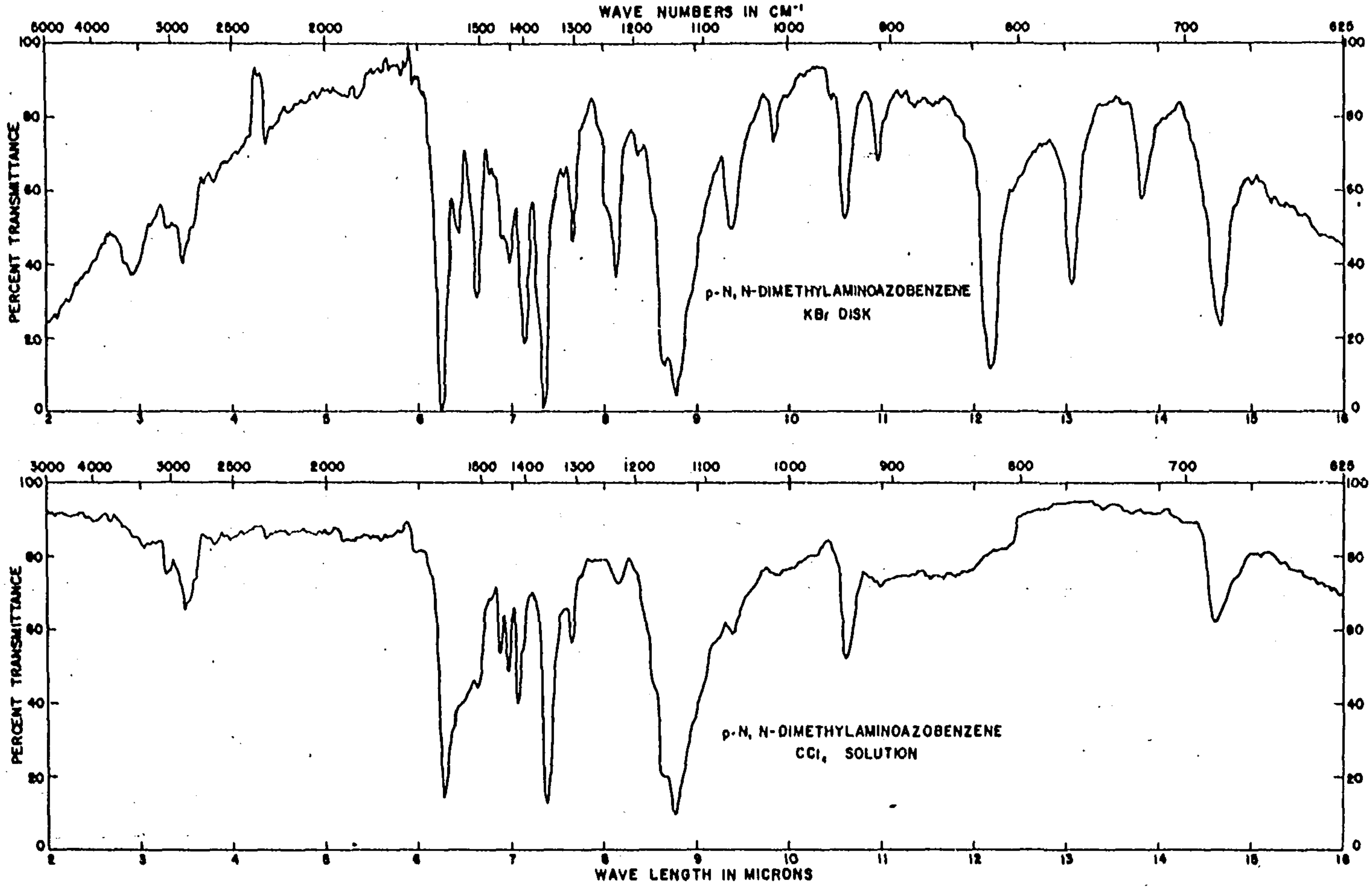


Figure 10. Spectra of p-N,N-dimethylaminoazobenzene

grouping and those of the aromatic rings, the modes of the C-N=N-C system may be treated separately. This is reasonable because the majority of the vibrations of aromatic rings are not greatly affected by the nature of the substituent (99). The C-N=N-C group would have six normal modes of vibration. Replacement of the dimethylamino group with an equivalent point mass gives the molecule a plane of symmetry which places it in the group C_s. Then five of the modes would be in-plane vibrations, species A', and the other mode would be an out-of-plane vibration, species A". All six modes would be infrared active. Another possibility remains to be considered. The dimethylamino group is located relatively far from the azo bond so the neighborhood of the azo group possesses a high degree of local symmetry. It is possible that the effect of local symmetry is so great that the C-N=N-C group falls essentially in the C_{2h} group. If this is the case, three of the group vibrations will be totally symmetric, species A_g, and will be active only in the Raman spectrum. Of the remaining three vibrations, two will be in-plane vibrations which are antisymmetric with respect to both the center of symmetry and the axis of rotation, species B_u. The third vibration will be an out-of-plane mode antisymmetric with respect to the center of symmetry, species A_u. The A_u and B_u modes will be active only in the infrared.

The data in Table 7 show that only the absorptions at

1463.3, 1423.3, and 538.7 cm.$^{-1}$ shift significantly upon isotopic substitution indicating that the assumption of local symmetry applies in this case. Modes of vibration similar to those shown by Kohlrausch (63, p. 69) are given in Figure 11. Since out-of-plane vibrations occur at lower frequencies than other vibrations of a group, the absorption at 538.7 cm.$^{-1}$ must be ν_3. The bands at 1463.3 cm.$^{-1}$ and 1423.3 cm.$^{-1}$ must then be assigned to ν_1 and ν_2. One of the higher frequency vibrations involves bond stretching while the other is an in-plane bending. The stretching mode ν_1 is assigned to 1463.3 cm.$^{-1}$ because stretching vibrations usually have higher frequencies than the corresponding bending vibrations. The band at 1423.3 cm.$^{-1}$ is then ν_2. However, the proximity of these two absorptions makes absolute differentiation very difficult.

These assignments must be compared with the associations other investigators have made for the spectra of aromatic azo compounds. All reports have assigned a N=N stretching vibration to the region 1400-1600 cm.$^{-1}$. In the Raman spectrum of azobenzene Kanda and Imanishi (60) made the assignment to a displacement of 1433 cm.$^{-1}$. Stammreich (115) agreed, placing the shift at 1442 cm.$^{-1}$, and specified that this arose from the trans form of the molecule. This is inconsistent with the assignments made in the present study since trans-azobenzene is strictly C_{2h} symmetry and has selection rules

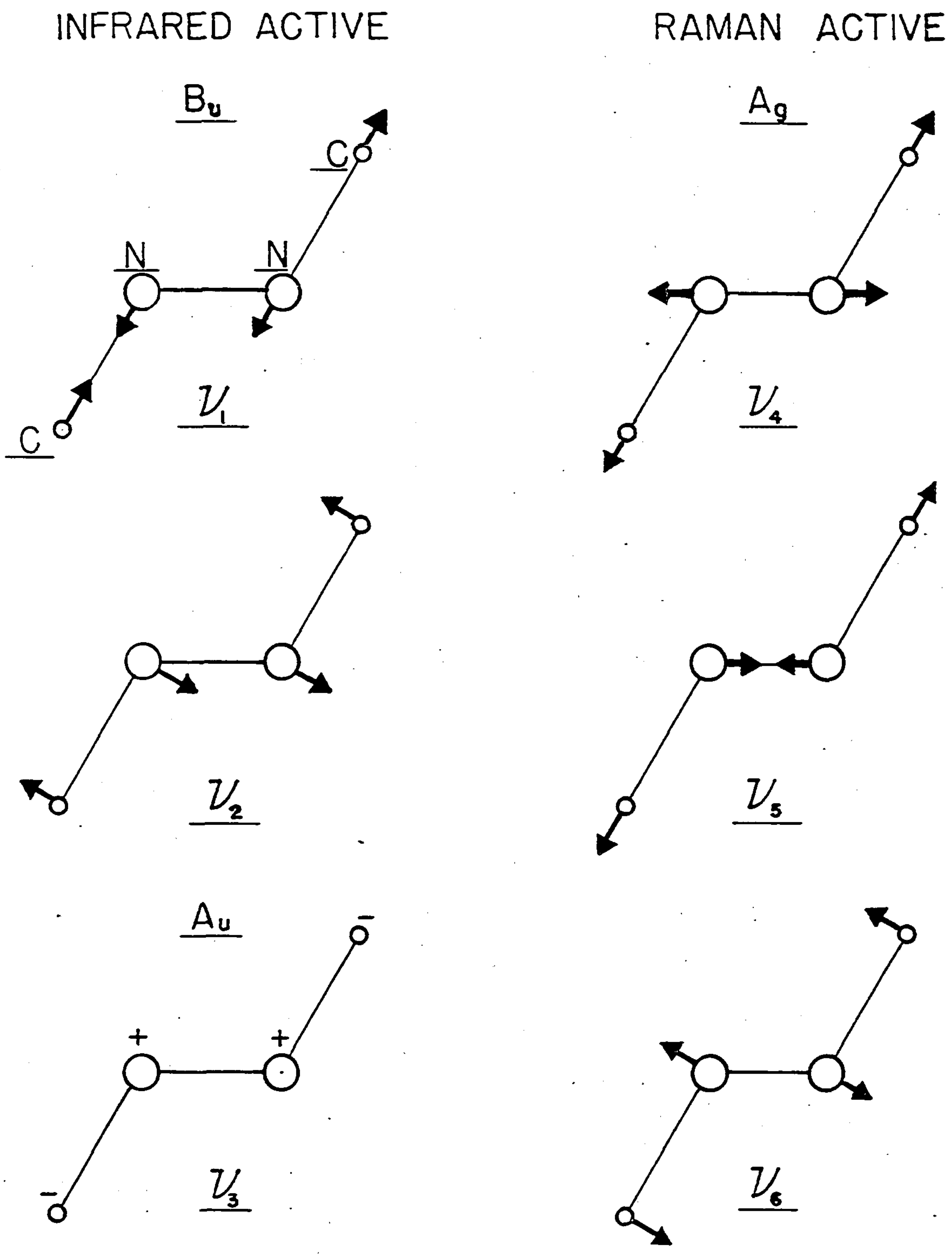
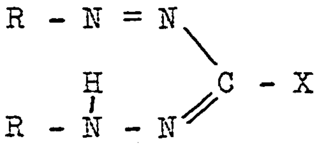


Figure 11. Suggested modes of vibration of the azo group

identical to those used here. The observation of an unshifting band at 1443.9 cm.$^{-1}$ in this study makes an assignment to a phenyl absorption more reasonable. Randle and Whiffen (99) note that phenyl rings have infrared and Raman active absorptions in this region, which also supports such an assignment.

All other assignments of a N=N stretching frequency have been made from infrared spectra. Le Fèvre *et al.*(72) studied the mineral oil suspensions of 43 compounds and said that a N=N stretching vibration might be associated with either of two bands, 1406 ± 14 cm.$^{-1}$ or 1579 ± 9 cm.$^{-1}$. In their study the 1455 cm.$^{-1}$ region was blanked out by the suspending medium. After examining several formazans, of which the general structure is



Le Fèvre *et al.*(73) found a common feature at 1450 cm.$^{-1}$ and inferred that the band in simpler azo compounds must be that near 1579 cm.$^{-1}$. Study of 25 additional azo compounds led Le Fèvre and Werner (74) to reconsider this assignment and to report that the N=N stretching vibration must absorb in the region 1400-1450 cm.$^{-1}$. Ueno (125) felt that such a vibration must give rise either to a band near 1400 cm.$^{-1}$ or to one near 1455 cm.$^{-1}$. He concluded (124) that the 1400 cm.$^{-1}$ band was the more probable. Costa (33) said that the band associated with the N=N stretching vibration should be in the region 1400-1600 cm.$^{-1}$.

The results of the present study are not in complete agreement with previous investigations. While there are two bands in the region 1400-1470 cm.$^{-1}$ which are characteristic of the C-N=N-C group, neither of them can be a pure N=N stretching vibration. The largest frequency ratio observed was 1.023, whereas a ratio of 1.035 would be expected of a N=N vibration. This indicates that the vibrations must involve the entire C-N=N-C group. The absorption reported at 1579 cm.$^{-1}$, even in molecules with C_{2h} symmetry (72), cannot be a vibration of the azo group since no shift was found near this region.

Several authors have associated bands with C-N vibrations without specifying the nature of the modes. Kanda and Imanishi (60) suggested that a Raman shift at 1138 cm.$^{-1}$ in azobenzene was a C-N vibration. Stammreich (115), however, felt that this arose from an aromatic ring vibration.
Le Fèvre _et al_.(72) suggested that infrared absorption frequencies near 900, 1150, and 1300 cm.$^{-1}$ could be associated with some form of C-N vibration. Ueno (125) agreed, giving the frequencies as 920, 1145, and 1300 cm.$^{-1}$. Costa (33) also gave the 920 and 1300 cm.$^{-1}$ assignments but assigned the other band at 1220 cm.$^{-1}$. Le Fèvre and Werner (74) suggested the ranges 903-957, 1142-1164, and 1264-1314 cm.$^{-1}$. Tetlow

(119) assigned a band at 927 $cm.^{-1}$ in both cis- and trans-azobenzene as characteristic of the C-N=N-C group.

Table 7 shows that in the entire region covered by the above suggestions no bands shift enough to be assigned to one of the infrared inactive modes shown in Figure 11. The band at 1144.1 $cm.^{-1}$ does shift somewhat, but it is probably assignable to a phenyl ring vibration which involves some substituent motion. Six such modes have been noted (99), and one of them has been assigned in this region (132). Although some of the inactive modes may absorb in this region in less symmetrical compounds, it is unlikely that the true absorptions have been assigned.

In concluding this section it may be noted that the bands assigned in this study should be characteristic of all aromatic azo compounds. The two higher frequency bands have been reported in all previous studies where the solvent or suspending medium did not interfere. The vicinity of the lower frequency absorption has not been studied previously.

MONOSUBSTITUTED AMIDES

Experimental

Acetanilide labeled with nitrogen-15 was prepared according to the following equation:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

Approximately 0.1 g. of aniline hydrochloride labeled with nitrogen-15 was dissolved in 10 ml. of water. One ml. of acetic anhydride was added and the resulting mixture was stirred. A solution of 1 g. of sodium acetate in 10 ml. of water was added and the material which crystallized after chilling was filtered out. The impure acetanilide was recrystallized twice from cyclohexane prior to spectroscopic examination. The unlabeled acetanilide was a commercial product and was similarly recrystallized.

Benzanilide and n-hexananilide labeled with nitrogen-15 were prepared by the reaction

$$2C_6H_5NH_2 + RCOCl \longrightarrow C_6H_5NHCOR + C_6H_5NH_2HCl$$

Approximately 0.1 g. of aniline hydrochloride labeled with nitrogen-15 was added to 15 ml. of 10 per cent sodium hydroxide solution. The resulting solution was extracted three times with ether. The ether extract was dried by filtering it through anhydrous sodium sulfate. An excess of the appropriate acid chloride was added and the mixture was warmed for approximately ten minutes. The ether solution was filtered to remove aniline hydrochloride and then extracted successively with 5 per cent sodium hydroxide solution and 5 per cent hydrochloric acid. The ether solution was dried by filtering through anhydrous sodium sulfate and then was evaporated. The benzanilide was recrystallized from cyclohexane prior to use. It was deemed unnecessary to recrystallize the n-hexananilide because its melting point was 94-95° C. The unlabeled benzanilide and n-hexananilide were prepared in an identical manner. The n-hexanoyl chloride required was prepared by refluxing n-hexanoic acid with excess thionyl chloride for one-half hour and then distilling the product until the infrared spectrum indicated that the excess thionyl chloride had been removed.

The spectra of these compounds were all obtained in potassium bromide disks except in the region above 2000 cm.$^{-1}$. In this region acetanilide and benzanilide were run as solutions in chloroform, and n-hexananilide was dissolved in carbon tetrachloride. The frequencies found are listed in Tables 8, 9, and 10. The spectra in the region 5000-625 cm.$^{-1}$ of the normal nitrogen compounds, run as KBr disks, are shown in Figure 12.

Discussion and Literature Survey

The spectra of the monosubstituted amides have been studied thoroughly because of the role played by this group

Table 8. Observed frequencies of acetanilide and its nitrogen-15 analog with the ratio of corresponding frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
3459.9	3450.9	1.003
3417.0	3409.3	1.002
3346.4	3336.8	1.003
1659.0	1658.1	1.001
1602.0	1601.6	1.000
1557.2	1549.2	1.005
1543.5	1535.2	1.005
1501.5	1501.1	1.000
1491.0	1489.8	1.001
1433.8	1433.6	1.000
1393.2	1395.0	0.999
1370.3	1372.4	0.999
1325.1	1322.3	1.002
1269.9	1267.6	1.002
1236.5	1231.0	1.005
1185.1	1185.0	1.000
1164.9	1163.3	1.001
1084.7	1083.6	1.001
1044.0	1043.2	1.001
1017.5	1016.9	1.001
1002.6	1002.5	1.000
965.5	953.4	1.013
909.9	909.3	1.001
851.9	851.9	1.000
758.2	757.6	1.001
699.0	698.9	1.000
611.0	609.0	1.003
538.7	536.1	1.005
513.8	513.4	1.001
509.1	508.8	1.001

Table 9. Observed frequencies of benzanilide and its nitrogen-15 analog with the ratio of corresponding frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
3458.4	3451.0	1.002
3354.9	3345.6	1.003
1658.0	1654.8	1.002
1604.0	1601.2	1.001
1582.7	1582.0	1.000
1561.5	1562.6	0.999
1532.3	1521.8	1.007
1496.0	1493.1	1.002
1440.2	1436.5	1.003
1388.0	1388.0	1.000
1326.3	1323.6	1.002
1305.2	1307.0	0.999
1267.1	1266.1	1.001
1184.1	1183.9	1.000
1170.2	1170.4	1.000
1118.7	1116.1	1.002
1079.9	1077.6	1.002
1032.4	1033.2	0.999
1005.3	1006.9	0.998
930.6	931.2	0.999
912.9	910.6	1.003
887.6	880.0	1.009
793.4	793.1	1.000
753.2	752.9	1.000
718.7	718.7	1.000
694.9	695.0	1.000
654.9	652.3	1.004
620.6	620.1	1.001
589.5	584.5	1.009
511.9	511.0	1.002

Table 10. Observed frequencies of n-hexananilide and its nitrogen-15 analog with the ratio of corresponding frequencies

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
3464.8	3455.9	1.003
3346.9	3344.9	1.001
3077.4	3076.8	1.000
3044.7	3043.0	1.001
2973.5	2973.2	1.000
2943.2	2944.0	1.000
2885.0	2884.7	1.000
2874.8	2874.8	1.000
1668.0	1667.8	1.000
1617.1	1616.2	1.001
1603.5	1602.3	1.001
1553.8	1548.4	1.004
1500.3	1500.8	1.000
1483.2	1484.0	0.999
1465.9	1466.7	0.999
1444.4	1442.9	1.001
1413.8	1415.0	0.999
1380.0	1378.9	1.001
1329.2	1326.1	1.002
1309.2	1305.0	1.003
1265.6	1262.3	1.003
1246.0	1242.8	1.003
1195.0	1192.7	1.002
1184.9	1185.1	1.000
1119.0	1117.8	1.001
1111.9	1113.5	0.999
1083.5	1083.3	1.000
1064.2	1064.8	0.999
1056.1	1054.1	1.002
1036.8	1037.2	1.000
1017.5	1014.8	1.003
1002.3	1002.4	1.000
969.8	960.7	1.010

Table 10. (Continued)

Frequency N^{14} compound (cm.$^{-1}$)	Frequency N^{15} compound (cm.$^{-1}$)	Ratio (N^{14}/N^{15})
900.8	900.9	1.000
837.4	836.1	1.002
758.2	756.9	1.002
728.8	728.2	1.001
694.1	694.0	1.000
671.5	671.4	1.000
620.7	621.4	0.999
509.0	508.7	1.001

in protein molecules. Despite this extensive work there is much disagreement concerning the nature of the vibrations responsible for many of the absorptions found.

The amide group in monosubstituted amides is probably a trans-planar structure. Worsham and Hobbs (134) found such a configuration necessary to explain dipole moment data for several N-monosubstituted benzamides. The trans-planar form was found in an X-ray study of acetanilide (27). Brown and Corbridge (27) also found that the phenyl ring in acetanilide is coplanar with the amide group. Other anilides probably have the same form. Interaction between the phenyl group vibrations and those of the amide group should be small (99), so the group C-CO-NH-C can be considered separately, subject to limitations to be considered subsequently. On the basis

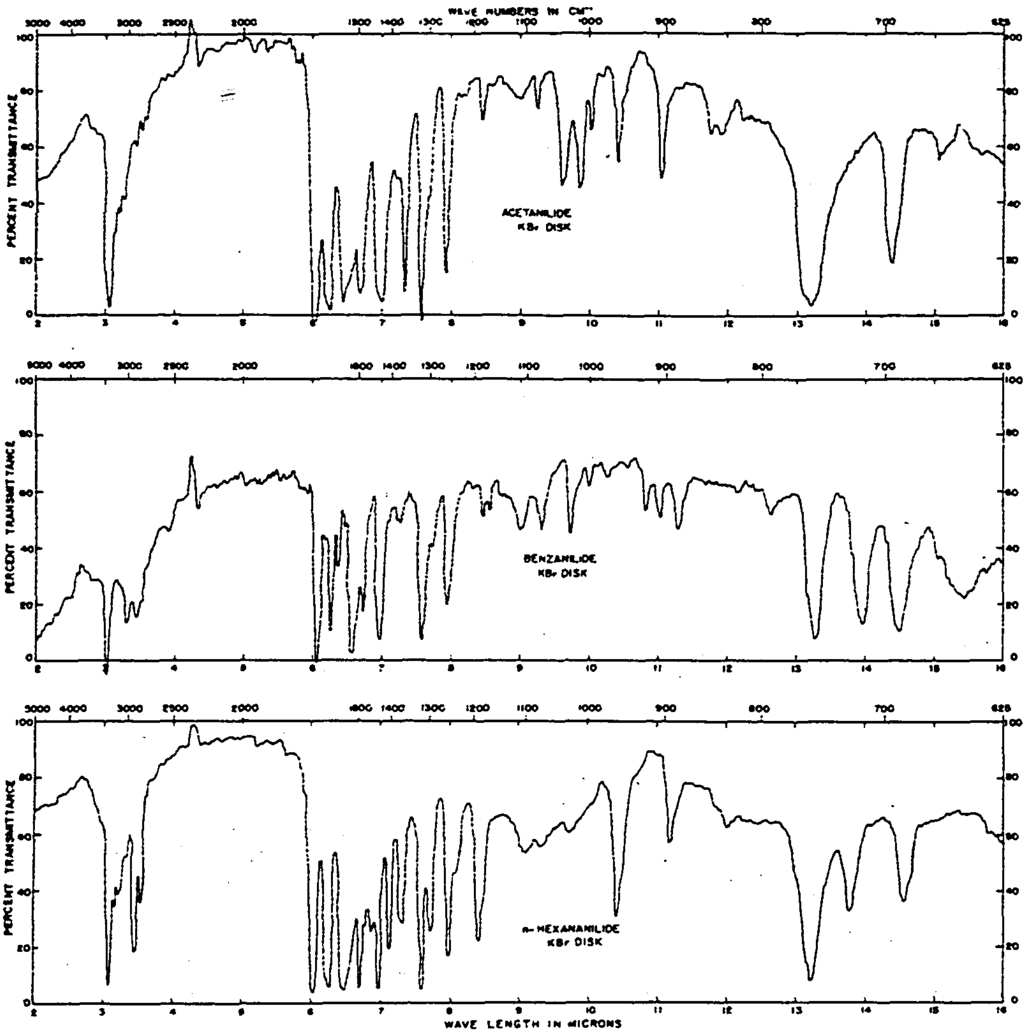


Figure 12. Spectra of acetanilide, benzanilide and n-hexananilide

of the above considerations, the compounds studied can be considered to belong to the C_s group, and they will then have nine in-plane vibrations, species A', and three out-of-plane vibrations, species A". Of these twelve modes the only three that can arise from N-H vibrations are an in-plane stretching, an in-plane bending, and an out-of-plane bending. These are shown in Figure 13 as ν_1, ν_4, and ν_8.

The three molecules studied were chosen to provide as much information as possible about the nature of the vibrations involved in any bands observed to shift. Acetanilide and n-hexananilide have essentially the same electronic effect while benzanilide and n-hexananilide have nearly the same mass. In addition both acetanilide and benzanilide act as point masses with respect to the amide group vibrations while n-hexananilide provides opportunity for interaction with the vibrations of the aliphatic chain.

All three compounds have bands that shift in the region 3458-3464 cm.$^{-1}$, and acetanilide has an additional band at 3417.0 cm.$^{-1}$. In dilute solutions the monosubstituted amides show the free N-H stretching vibration near or somewhat above 3400 cm.$^{-1}$ (16, 22, 28, 29, 35, 38, 49, 50, 85, 87, 102, 105, 113). The shift to the expected frequency on deuteration has been reported by Gierer (49, 50). Russell and Thompson (105) reported that some monosubstituted amides show two bands in this region and ascribed the behavior to cis-trans isomerism

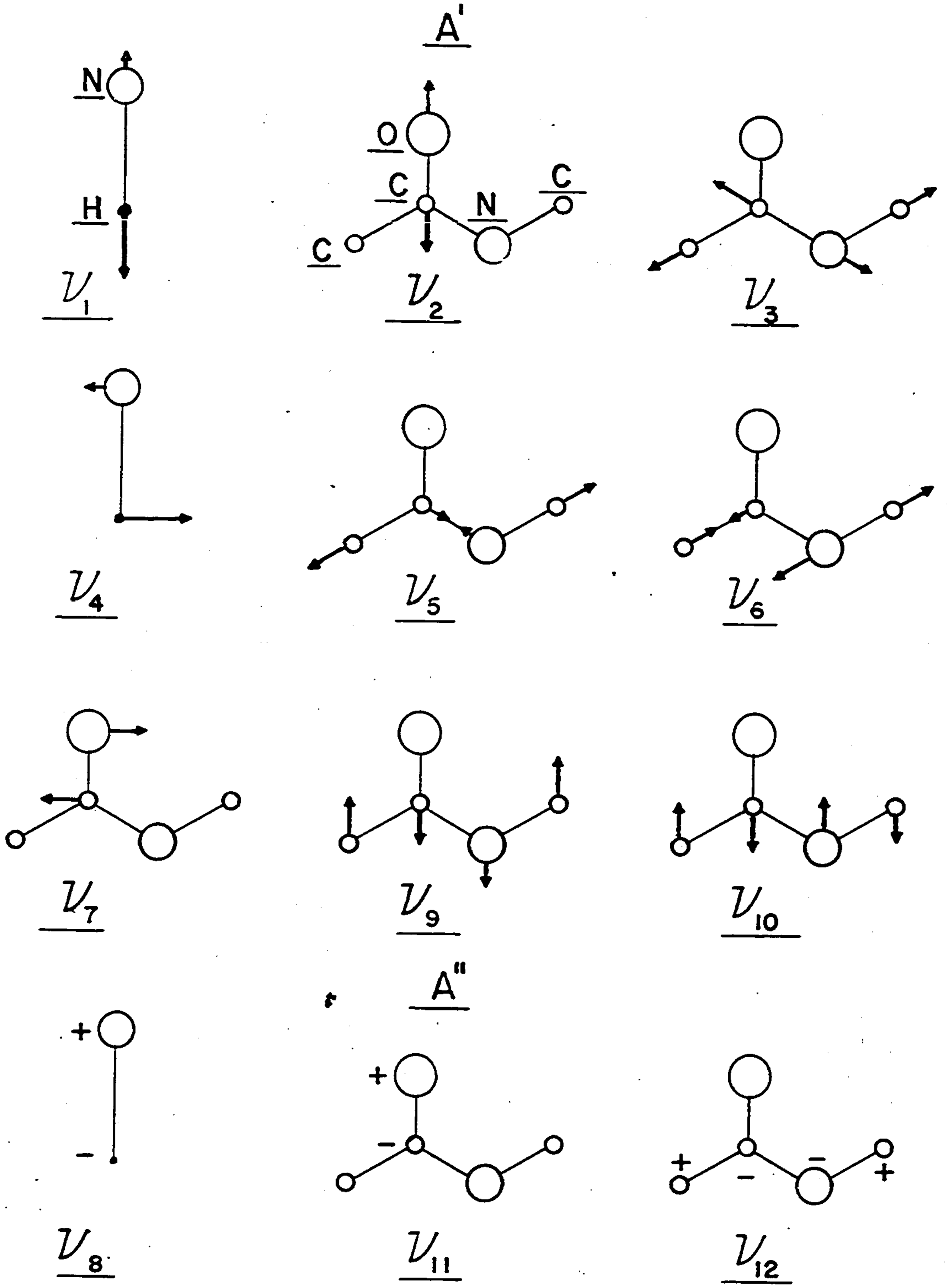


Figure 13. Suggested modes of vibration of the amide group in monosubstituted amides

about the amide C-N bond. The cis form absorbed at a somewhat lower frequency than the trans form. The isotope shifts of the bands at 3458-3464 cm.$^{-1}$ conform to a hydrogenic vibration, hence they are assigned to the N-H stretching vibration, ν_1. The 3417.0 cm.$^{-1}$ absorption in acetanilide may arise from the N-H stretching vibration of the cis form.

In more concentrated solutions the absorption resulting from the unbonded N-H stretching vibration decreases in intensity while new bands appear at lower frequencies. Although there is general agreement that this phenomenon results from association through hydrogen bonding there is much less unanimity about the nature of the species involved (1, 16, 22, 28, 29, 35, 38, 49, 50, 75, 77, 86, 87, 107, 121, 122). The bands observed at 3346-3355 cm.$^{-1}$ probably result from such association. All of the spectra in Figure 12 show the lower frequency bands obtained in concentrated solutions and solid samples. The fact that the band at 3346.9 cm.$^{-1}$ in n-hexananilide only shifts 1.001 illustrates the difficulty of working with N-H vibrations unless deuteration data are also available.

The next band of importance is the strong band at 1658-1668 cm.$^{-1}$. In acetanilide and n-hexananilide this absorption does not shift significantly. The shift in benzanilide suggests that a very small amount of nitrogen motion may be introduced into the mode by the changed electronic character of the molecule. It has been generally recognized that monosubstituted amides have a strong characteristic band in the region 1600-1730 cm.$^{-1}$, called the Amide I band (31, 98, p. 10). Richards and Thompson (102) assigned the Amide I band to a C=O stretching vibration, an assignment which has been generally followed until recently. Fraser and Price (48, 97) suggested, however, that the Amide I band should actually be considered as the asymmetric stretching vibration of the amide O=C-N system and more recent authors have generally accepted the assignment. The data in Tables 8, 9, and 10 agree with the assignment of the Amide I band to the C=O stretching vibration, ν_2. The assignment of Fraser and Price (48, 97) does not agree with the results of this study since a larger shift on nitrogen-15 substitution would be required.

A band that shows significant isotope shifts in all three compounds is found in the region 1532-1557 cm.$^{-1}$. In the case of acetanilide a pair of bands at 1543.5 cm.$^{-1}$ and 1557.2 cm.$^{-1}$ shift, but the lower frequency band is much weaker than the other; it may be associated with the cis form of the molecule. A band characteristic of monosubstituted amides has been noted by others in this region; it has commonly been referred to as the Amide II band (31, 98, p. 10). Richards and Thompson (102) assigned the absorption to an N-H deformation vibration since the disubstituted amides have no absorption in this region. Thompson *et al.*(120) also found that a partial replacement of the amide hydrogen by deuterium reduced the intensity of the Amide II band and caused a new band to appear near 1130 cm.$^{-1}$. These results support the N-H deformation assignment. Darmon and Sutherland (36) reported that substitution of 32 per cent nitrogen-15 into acetylglycine shifted the Amide II band only about 2 cm.$^{-1}$, which would not be inconsistent with a N-H vibration. The shifts observed in the present study are too great to be readily associated with a vibration of a single N-H bond. Other authors, too, have disagreed with the assignment of the Amide II band to a N-H in-plane deformation mode. The arguments against the assignment have been reviewed by Lenormant (75) including the observation that the band observed near 1130 cm.$^{-1}$ by Thompson *et al.*(120) was too weak to account for the reduction in Amide II intensity on deuteration.

Letaw and Gropp (77) assigned this band to the stretching vibration of the amide C-N bond. These authors explained the absence of the Amide II band in disubstituted amides to an accidental degeneracy of the C=O and C-N stretching frequencies. If this were the case either the Amide I band should be affected by nitrogen-15 substitution or the Amide II band should exhibit the shift of a pure C-N vibration.

Neither circumstance is observed in the present study. A further assignment involving the amide C-N bond was made by Lenormant (75). He noted that the change in intensity of the Amide II band on deuteration could be accounted for by a strong new band at 1470 cm.$^{-1}$ and that the frequency shift would then correspond to that noted by Edsall and Scheinberg (45) in the C-N stretching vibrations of CH_3NH_2 and CH_3ND_2. Lenormant (75) assigned the Amide II band to the C-N stretching of an ionic species while the Amide I band was assigned to the C=O stretching vibration of the normal ketonic species. Failure of the Amide II band to appear in the spectra of disubstituted amides was explained as resulting from an inability to form the necessary ionic species. The dipole moment data of Worsham and Hobbs (134) have, however, shown that no ionic form exists so the assignment of Lenormant (75) cannot be considered correct.

Fraser and Price (48, 97) suggested that the Amide II band was associated with a symmetric stretching of the O=C-N system with subsequent interaction with the N-H in-plane bending mode. This would explain the effect of deuteration upon the band. As has already been discussed, however, the Amide I band arises from a vibration involving little nitrogen motion so the assignment of Fraser and Price (48, 97) disagrees with the results of this study.

None of the previous assignments appear to be correct although the results of the present study indicate that the vibration must involve considerable nitrogen motion. An examination of the remainder of the shifts listed in Tables 8, 9, and 10 shows that no bands shift enough to be a C-N vibration, which indicates that the bond between the nitrogen and the phenyl ring probably is also involved. Skeletal modes consistent with these data can be developed from the vibrations shown by Kohlrausch (63, p. 69) for the trans X_2Y_2 species although the exact character is not certain. Of these modes the ones with the highest frequency will be those which involve some stretching of the amide C-N bond. These two vibrations are shown as ν_3 and ν_5 in Figure 13. The Amide II band is assigned to ν_3 because this vibration would involve the greater nitrogen amplitude.

The next band observed to shift is in benzanilide at 1440.2 cm.$^{-1}$. No assignment is made of this absorption since similar bands in the other two compounds do not shift. Previous investigators have not attached any significance to this region.

All three compounds have bands in the 1195-1329 cm.$^{-1}$ region which show significant shifts in frequency on isotope substitution. In this range acetanilide has bands which shift at 1325.1, 1269.9, and 1236.5 cm.$^{-1}$, but the latter band is quite weak and need not be considered further. There are five strong bands in n-hexananilide at 1195.0, 1246.0

1267.6, 1309.2, and 1329.2 cm.$^{-1}$ which all shift. In benzanilide only the band at 1326.3 cm.$^{-1}$ can really be said to shift, although a strong band is observed at 1267.1 cm.$^{-1}$ which exhibits a ratio of 1.001. Since both of the other compounds exhibit shifting bands in this region this low ratio may be due to experimental error or to a change in the character of the vibration. Miyazawa et al. (83) noted that monosubstituted amides have a characteristic band in the region 1200-1300 cm.$^{-1}$ which they assigned to the N-H in-plane deformation vibration, ν_4, perturbed by interaction with the symmetric O=C-N stretching vibration as proposed by Fraser and Price (48, 97). The deuteration data presented by these authors (83) did show some abnormally small shifts, but only in unusual compounds where the amide nitrogen was connected either to another amide nitrogen or to a formyl group so that O=C-N interaction is almost forced. In N-methyl- and N-ethylacetamide the deuteration shifts deviated very little from normal values. Newman and Badger (90) inferred from deuteration studies and the use of polarized infrared radiation that the N-H in-plane deformation vibration of N-acetylglycine was at 1340 cm.$^{-1}$. Abbott and Elliott (1), also using deuteration and polarized radiation, assigned this mode at 1325 cm.$^{-1}$ in acetanilide. Because the results of the present study agree with the previous investigators (1, 90) the N-H in-plane bending mode, ν_4, is assigned at

1325-1329 cm.$^{-1}$ in the three compounds examined here. A band which shifts is found in acetanilide and n-hexananilide between 1267-1270 cm.$^{-1}$. In benzanilide a band also occurs in this region; failure to observe a significant shift of this band has been discussed previously. Assignment of this region to a skeletal mode of vibration is complicated, however, by the fact that n-hexananilide has three other bands near this region which also shift upon isotope substitution. A possible reason for this multiplicity of bands can be found in the work of Mizushima (84, p. 103) who has noted that n-paraffins have several bands in this region with each band resulting from a distinct rotational isomer of the carbon chain. Probably the amide C-C-N-C acts merely as a continuation of the aliphatic chain and thus would exhibit an isotope shift in bands at several frequencies which arise from different chain rotational isomers. The vibration shown as ν_5 could exhibit these properties and would be consistent with the rest of the modes evolved from the vibrations shown by Kohlrausch (63, p. 69).

In the range 888-970 cm.$^{-1}$ all three compounds show a very pronounced shift but not enough to be a pure C-N vibration. The mode which would probably involve the greatest nitrogen motion is ν_6 in Figure 13. Other authors have assigned the stretching vibration of the bond between the amide nitrogen and the substituent upon it to the region 880-1120 cm.$^{-1}$ (36, 77, 83, 86, 113). Darmon and Sutherland (36) found that substitution of 32 per cent N^{15} into N-acetylglycine caused a band at 996 cm.$^{-1}$ to diminish in intensity and develop a shoulder at 986 cm.$^{-1}$. Miyazawa et al.(83) do not really state that the mode was a C-N stretching but that the skeletal vibration involved the C-N stretching. The latter indication agrees with the present study.

The C=O in-plane bending vibration, ν_7, is very difficult to assign. Miyazawa et al.(83) gave the range for this vibration as 627-771 cm.$^{-1}$, and Mizushima et al.(86) assigned this mode to a Raman shift of 440 cm.$^{-1}$ in N-methylacetamide. No bands were observed below 500 cm.$^{-1}$ in this study so the latter assignment is unlikely. All three compounds show bands in the regions 694-699 cm.$^{-1}$ and 753-758 cm.$^{-1}$, but both of these absorptions are undoubtedly associated with phenyl vibrations (99). Benzanilide and n-hexananilide have a strong absorption at 718.7 cm.$^{-1}$ and 728.8 cm.$^{-1}$, respectively. Acetanilide has no such strong absorption. Although it is possible that the band is hidden by either the 699.0 cm.$^{-1}$ or the 758.2 cm.$^{-1}$ absorptions, it is unlikely because acetanilide and n-hexananilide would be expected to behave similarly, with benzanilide deviating. A deviation in benzanilide would be expected because the C=O bending does not involve motion of the amide group skeleton so any differences would be electronically induced. Another possibility is the region 901-931 cm.$^{-1}$. Phenyl rings have a medium intensity band near 910 cm.$^{-1}$ (99). Acetanilide and n-hexananilide have strong bands at 909.9 cm.$^{-1}$ and 900.8 cm.$^{-1}$, respectively, while benzanilide has two medium intensity bands at 912.9 cm.$^{-1}$ and 930.6 cm.$^{-1}$. It is possible that ν_7 in acetanilide and n-hexananilide coincides with the phenyl absorption and that in benzanilide ν_7 shifts because of the electronic effect of the additional phenyl ring, placing the phenyl absorption at 912.9 cm.$^{-1}$ and ν_7 at 930.6 cm.$^{-1}$. Two regions then are possible assignments for the C=0 in-plane bending vibration, ν_7, and of these the 901-931 cm.$^{-1}$ region is preferred.

In n-hexananilide a weak band at 837.4 cm.$^{-1}$ shifts slightly, but since acetanilide and benzanilide show weak bands at 851.9 cm.$^{-1}$ and 793.4 cm.$^{-1}$, respectively, which do not shift, no significance is attached to the band in n-hexananilide.

The N-H out-of-plane bending mode, ν_8, is another vibration which cannot be confidently assigned in this study. There is general agreement that this vibration must lie in the region 640-800 cm.$^{-1}$ (38, 49, 50, 61, 83), but the data obtained in the present study show no bands which can be assigned to N-H vibrations. The 654.9 cm.$^{-1}$ in benzanilide exhibits too large a shift for such an assignment. Gierer (50) suggested that ν_8 in acetanilide was hidden by the strong absorption at 758 cm.$^{-1}$, but Abbott and Elliott (1) noted no diminution in the intensity of that absorption after replacement of the amide hydrogen by deuterium. No information on this point is provided by this study, but if ν_8 in acetanilide is hidden by the strong phenyl absorption then it would certainly also be hidden in benzanilide and n-hexananilide.

The C=0 out-of-plane deformation, ν_{11}, should not shift upon nitrogen-15 substitution. This mode was assigned in the range 537-606 cm.$^{-1}$ by Miyazawa et al.(83), but Davies et al. (38) suggested that the absorption was at 440 cm.$^{-1}$ in N-methylacetamide. Although nothing conclusive can be said from the data of the present study, only the bands at 508-512 cm.$^{-1}$ can be assigned as ν_{11} and be in reasonable agreement with the earlier assignments. The observation of Davies et al.(38) is ruled out by failure of any bands to appear below 500 cm.$^{-1}$. In acetanilide there are bands at 508.0 cm.$^{-1}$ and 512.3 cm.$^{-1}$, but the higher frequency band is assigned as ν_{11} since the lower frequency band appears only as a weak shoulder.

The remaining three modes, ν_9, ν_{10}, and ν_{12}, are all skeletal vibrations. The frequency of the out-of-plane mode, ν_{12}, should be low and probably lies below 420 cm.$^{-1}$. At frequencies below the strong phenyl absorption near 695 cm.$^{-1}$ n-hexananilide has only two relatively strong bands, since the 671.5 cm.$^{-1}$ absorption is very weak, while benzanilide has four and acetanilide has three. In acetanilide and benzanilide two of these bands shift while in n-hexananilide no shifts are observed. Both ν_9 and ν_{10} are deformation modes. The aliphatic hydrocarbons have their deformation vibrations below 400 cm.$^{-1}$ (84, p. 115), so in n-hexananilide interaction with the aliphatic chain may have shifted ν_9 and ν_{10} below the range of this study. It is felt that ν_9 will have a higher frequency than ν_{10}, placing ν_9 at 604.9 and 653.3 cm.$^{-1}$ and ν_{10} at 534.1 and 581.5 cm.$^{-1}$ in acetanilide and benzanilide, respectively.

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