tion of the dimethoxypleiadone, and demethylation with hydrobromic and acetic acids gave *II*.

Coupling and Rearrangement Tests.—The 1,5-diethyl, 1,5-dibenzyl and 1,5-diallyl derivatives of 2,6-dihydroxynaphthalene, as well as 1,6-dihydroxydihydropleiadene, are all sensitive to oxidation in alkaline solution by air or by nitrous acid, and in carrying out coupling tests some precautions had to be taken to avoid some discoloration arising from these sources. The naphthols were dissolved in alkali in an inert atmosphere, and the diazotized sulfanilic acid used was precipitated as the inner salt, washed with water and suspended in water containing a trace of urea. *p*-Nitrobenzene diazonium chloride was prepared in glacial acetic acid solution, precipitated and washed with ether. There was in no case any appreciable color change on bringing the components together in alkaline solution under these conditions, and the naphthols could be recovered on acidification. The behavior of 1-ethyl-2-naphthol (which does not couple) was noted for comparison, and β-naphthol was always used for a control.

In three cases (see table) the diallyl ethers were prepared and the possibility of their rearrangement investigated. It was found that the substances decompose somewhat when heated for a prolonged period, even in the absence of air, but no alkali-soluble products were found. When heated for five minutes at 210°, that is, under conditions more than sufficient for the complete rearrangement of the diallyl ether of 2,6-dihydroxynaphthalene, the substances could be recovered essentially unchanged.

Etherification Experiments.—The methylations summarized in Table I were carried out in sealed tubes heated in a steam bomb, and care was taken to maintain identical conditions. After cooling, the contents of a tube was transferred to a flask, diluted with water and the product extracted with ether. The ethereal solution was extracted thoroughly with 5% alkali, and this was then acidified and extracted with ether. The ethereal solutions were dried, the solvent removed and both the naphthol fraction and the naphthol ether fraction were weighed. The identity and purity of the products were checked by melting point determinations. In Table I is given the total amount of material accounted for and the percentage of the total found as the ether. Duplicate runs agreed within 2% or better.

Summary

Methods which have served to locate the enol double bond of β-naphthol have been applied to a study of the bond structure of 2,6- and 2,7-dihydroxynaphthalene. The results indicate the presence in these compounds of enol groupings between the α- and β-positions in both rings and the absence of double bonds at the β,β-positions. It is clear that naphthalene contains two Kekulé rings, that these have the symmetrical arrangement of the Erlenmeyer formula, that the bond structure is immobile, and that the hydrocarbon cannot exist to any appreciable extent in the unsymmetrical form. The special structure very probably arises from the general tendency of unsaturated rings to assume and to preserve the aromatic type.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS
RECEIVED JUNE 5, 1935

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Quantitative Studies of the Infra-red Absorption of Organic Compounds Containing NH and OH Groups[1]

BY OLIVER R. WULF[2] AND URNER LIDDEL

This paper constitutes a second report[3] in a program of study of the quantitative infra-red absorption of organic compounds, being carried out in this Laboratory with the purpose of applying the data thus obtained to the chemistry and structure of these molecules. The absorption coefficients of a considerable number of compounds containing the NH group involving several different types have now been measured as well as those for a number of typical OH compounds, and this material has been applied to the analysis and structural study of a number of unknowns, working in conjunction with the organic section of this Laboratory. These first steps in the application of our results have given sufficient promise to justify their extension to other problems, which involve more interest to the organic chemist[4] and such studies are now in progress.

Experimental

The procedure used in carrying out these measurements has been described in the papers referred to above,[1,3] though some improvements in

---

[1] For the first paper of this series see THIS JOURNAL, **55**, 3574 (1933).

[2] Fellow of the John Simon Guggenheim Memorial Foundation during part of this work.

[3] Since our first paper, Liddel and Kasper, at the suggestion of the late Dr. E. W. Washburn, have also measured the absorption of a large number of pure hydrocarbons using the apparatus and technique described in our first paper; see *Bureau of Standards Journal of Research*, **11**, 599 (1933).

[4] Hilbert, Wulf, Hendricks and Liddel, *Nature*, **135**, 147 (1935), a method for detecting some forms of chelation.

technique have been made since then. Suffice it here to say that the absorption is measured in carbon tetrachloride solution (this solvent being itself free of absorption across the spectral region of interest) usually at a concentration of the order of 0.01 molal and in 10 cm. cell length, and that the data recorded in one measurement of any one substance consist of two plates, one containing the record of the spectral intensity of light passing through the solution and the other through the same cell containing only pure solvent. The cell is placed in parallel light between the source and the slit of the spectrograph. In each case the record is frequently interrupted by a timing mechanism to give segments showing the light intensity with the cell automatically removed from the path (thus giving a control on the behavior of the source lamp) and also to give segments showing the zero point of the galvanometer deflection by means of an opaque shutter in the path (thus giving a control on any zero drift that may occur).

Character of the Results

Anticipating a little the discussion of the significance of these measurements, it is helpful to mention here that the absorptions characteristic of the presence of the groups NH, OH or CH show variations principally in three observable respects, namely, in position in the spectrum, in the shape of the outline of absorption, and in the area under the absorption coefficient against frequency curve.

Position of such an absorption is a difficult thing to define. The position of the maximum may be given and is empirically a useful thing to know, but there seems to be no reason to believe that the maximum of the absorption for one molecule bears any direct relation to that of another. As illustration of position, the characteristic NH absorption of pyrrole and that of fluorenoneimide lie at obviously different frequencies; those for aniline and β,β-dinaphthylamine, on the contrary, extend over approximately the same part of the NH region. The shapes of the latter, however, are different and their maxima lie at different and distinguishable frequencies.

The shape of the absorption differs widely, varying from a single peak of surprisingly sharp and narrow absorption to broadly spread material sometimes possessing two or three prominent maxima. Indole and phenylhydrazine offer contrasting examples.

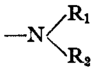
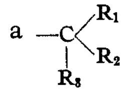
Probably the most fundamental of the three above-mentioned characteristics is the last. In most cases the transmission of a particular molecular species on either side of the central portion of the characteristic NH or OH absorption rises to nearly unity, *i. e.*, the substance is transparent, before absorption due to another part of the molecule sets in at higher or lower frequencies. This area under the absorption coefficient against frequency curve stands in close analogy to the area under a spectral line or better the area under a vibration-rotation band, which has been the subject of much interest.[5] There is considerable justification, furthermore, for considering the CH, NH and OH absorption in the region 1.7–1.4 μ to be, at least chiefly, the first overtone of these groups, whose fundamental is the well-known absorption in the region of 3 μ.[6] Strictly speaking it is not these groups, but rather it is the hydrogen atom linked to something more complicated than carbon, nitrogen or oxygen atom alone, namely, this atom to which other groups are already attached. The area under such an absorption curve is related to the mechanical and electrical characteristics of the absorbing oscillator,[5] here the CH, NH or OH group. Hence there is considerable hope that a correlation may be developed between the results of these measurements and the chemical behavior of these groups in various molecules.

The fundamental and first overtones of the isolated molecules CH, NH and OH lie in these same regions,[6] though of course not observable by absorption methods, since these molecules cannot normally be obtained in the free state. Adding a group to the oxygen atom as a benzene ring in phenol, or two groups to the nitrogen, as two benzene rings in diphenylamine, undoubtedly alters somewhat the characteristic vibrational absorption of the group, but leaves it still quite recognizable as to species. In other words, the organic molecules containing OH are somewhat analogous to the hydrogen halides in that H atom is linked to an —O—R group. Variation in R may cause a change in the magnitude and position of the absorption, but only a moderate change, much less than occurs in the hydrogen halides in passing from HF to HI, where the atom connected di-

---

(5) See for example Bartholomé, *Z. physik. Chem.*, **B23**, 131 (1933). This paper contains references to and discussions of other papers on this subject.

(6) See for example Weizel, "Bandenspektren," Akademische Verlagsgesellschaft m. b. h., Leipzig, Germany, 1931, p. 420.

rectly to the hydrogen is changed. In a similar way the NH containing compounds may comprise an H atom linked to an  $-N\begin{matrix}R_1\\R_2\end{matrix}$ group. In the case of CH, which presents a further analogy and which will be discussed somewhat below, the H atom may be linked to a  $-\underset{R_3}{C}\begin{matrix}R_1\\R_2\end{matrix}$ group such as in triphenylmethane. The case of sulfur is similar of course to that of oxygen.

It is to be noted furthermore that the groups added to the O, N and C atoms, respectively, are usually not widely different, not in the sense that are Na in HONa and NO_2 in $HONO_2$. They are generally of the form of one, two or three carbon atoms with various other groups attached to these.

Results

In view of the points brought out in the preceding discussion it seems that the best way to present the results of these measurements is to give the curve of the absorption coefficient plotted against frequency for each of the compounds studied, and to tabulate the area under the respective curves. Tables Ia, Ib and II give these areas, the curves of the absorption coefficients being given in Figs. 1a, 1b and 2. This permits a fair idea of all three factors, position, shape and area. These areas show variations which are well beyond experimental error and it is, of course, necessary to know these variations in using this absorption technique as an analytical method. At the same time, however, it is to be noted that, so far as the compounds contained in the tables go, the absolute value of the area per individual bond *does not vary by an order of magnitude*. Thus it seems possible that this characteristic absorption may be used as a criterion of the presence or absence of these groups. It is being used in this

TABLE Ia

Substance	Molal absorption area (liter/sq. cm. mole)
Aniline	150
β-Naphthylamine	170
o-Chloroaniline	160
2,4,6-Trichloroaniline	200
2,4,6-Tribromoaniline	165
o-Nitroaniline	105
m-Nitroaniline	140
p-Nitroaniline	200
Methyl anthranilate	65
o-Phenylenediamine (per NH_2 group)	135
m-Phenylenediamine (per NH_2 group)	155
p-Phenylenediamine (per NH_2 group)	160
Benzidine (per NH_2 group)	190
n-Butylamine	90
Cyclohexylamine	85
9-Fluorylamine	115
9-Amino-9-α-naphthylfluorene	100
Phenylhydrazine minus 120	165
α-Methyl-α-phenylhydrazine	140
Benzamide[a] (Table II)	145

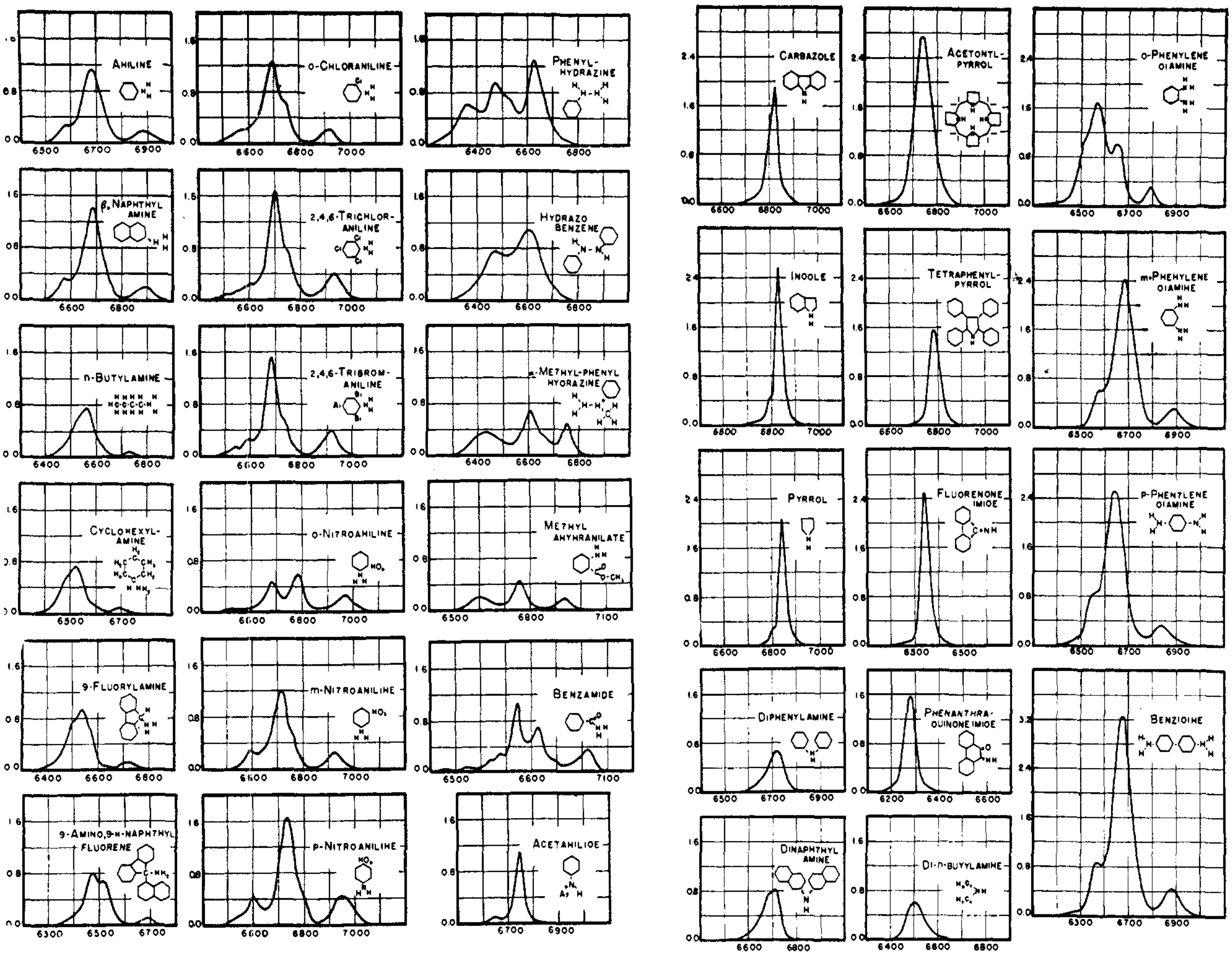
TABLE Ib

Substance	Molal absorption area (liter/sq. cm. mo
Pyrrole	85
Indole	105
Carbazole	105
Tetraphenylpyrrole	95
Acetonylpyrrole (per NH group)	70
Diphenylamine	65
β,β-Dinaphthylamine	80
Di-*n*-butylamine	55
9-Fluorenoneimide	125
Phenanthraquinoneimide	105
Acetanilide	55
Hydrazobenzene (per NH group)	120
Phenylhydrazine minus 140	145

TABLE II

Substance	Molal absorption area (liter/sq. cm. mole)
Phenol	155
m-Nitrophenol	165
o-Chlorophenol	135
2,4,6-Trichlorophenol	150
p-Hydroxyacetophenone	165
p-Hydroxybenzaldehyde	170
Catechol (per OH group)	170
Resorcinol (per OH group)	145
Hydroquinone (per OH group)[a]	160
8-Hydroxyquinoline	90
Methanol	105
Ethanol	120
Isopropanol	95
Methylisopropylcarbinol	110
Phenylmethylcarbinol	105
Triphenylcarbinol	95
o-Methoxybenzyl alcohol	70
Benzoin	90
Ethylene glycol monoacetate	75
Ethyl lactate	110

[a] Hydroquinone, included in the above because of the importance of its shape, position and approximate area, in the series catechol, resorcinol and hydroquinone, is only very slightly soluble in carbon tetrachloride at room temperature. It was run also at 60° where its solubility is much greater. Recent results indicate that the area given above is high and may be so by somewhat more than 15%. One other substance of those given above, benzamide, the single example of an amide, was, because of its low solubility, also run at 60°. Its area is similarly to be considered as somewhat more uncertain than the others.



(a) NH_2 compounds. (b) NH compounds.

Fig. 1.—Molal absorption coefficients (ordinates) plotted against frequency in wave numbers (abscissas); solutions in carbon tetrachloride.

way to study the phenomenon of chelation,[4] and will be further commented upon later in this paper.

In some cases the curves of the absorption coefficient are from two or more separate sets of data, in others from but one. In a few fundamental cases, such as carbazole, aniline and phenol, for instance, a number of measurements at different path lengths and different concentrations were made and in these the accuracy of the curves is correspondingly greater. The accuracy with which the area under the curve is determined also varies appreciably with the shape of the curve. Actually the computation of the area is made by the summing of ordinates at every 5 cm.$^{-1}$ interval, the ordinates being the absorption coefficient k, where $k = -(1/cd) \log (I/I_0)$ where c designates the concentration in moles per liter and d the cell length in centimeters, the I's being the final and initial intensities, respectively. Usually the only serious source of error enters in the determination of $\log (I/I_0)$. This error depends upon the absolute value of the ratio, but if care is taken to work with transmissions which are not too small nor too nearly unity, as those in the range 0.8 to 0.3, this source of difficulty may be greatly reduced.

From a study of the melting points, boiling points, or refractive indices, we have tried to ensure the inclusion only of pure substances. It seems probable that in none of the compounds reported are impurities present to more than a per cent. or two. However, we wish to emphasize that very minor effects which may evidence themselves in the absorption should not be given weight. An extended study of a compound is

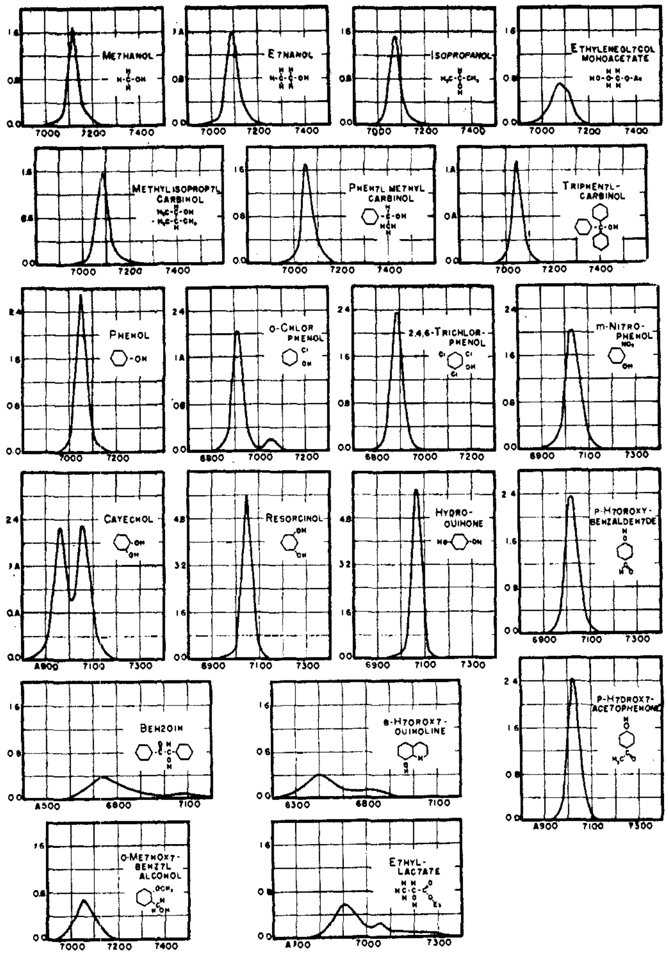


Fig. 2.—Molal absorption coefficients (ordinates) of OH containing compounds in dilute CCl_4 solution against frequency in wave numbers (abscissas).

necessary before very small differences between it and another can be regarded as established.

By choice of path length and concentration we have attempted to work in the range where the actual absorption would be favorable for the determination of the absorption coefficient. However, other factors not infrequently cause trouble, such as filtrable turbidity, the effect of which must be deducted. Also, because of the large variations in shapes of the absorption curves, as well as the frequent low solubility of compounds and the occasional occurrence of chemical or photochemical change in the solution during a measurement, the error in the areas varies considerably. It has seemed wisest, in view of the exploratory nature of this work, to study as many different compounds as practicable rather than to concentrate at this time upon a highly detailed and accurate study of some one or two. Allotting a reasonable time to the research, some compromise was, of course, necessary and we have chosen to sacrifice somewhat in the accuracy of determination of area and position in order to accomplish a reasonably broad survey of the major distinguishing characteristics. Thus, for instance, the measured areas under curves which are considerably narrower than that for carbazole may be in error in the direction of being too low. A test of the value of the proposed application of such results was needed before the extent to which more elaborate measurements were justified could be known. In the first application, namely, to the phenomena of chelation,[4] the principal requirement was a knowledge of the approximate area and position of absorption for as large a number of OH-containing compounds as was possible. We do not feel justified in claiming an accuracy greater than ±15% in the areas.

Application

The theoretical interpretation of these results is, we believe, worthy of considerable effort, this in spite of the common and, in a certain sense, justified antipathy against attempting to treat such measurements in solution. It is believed that there are elements present in such curves that can lend some help in the discussion of the structure and behavior of organic molecules, not alone in their identification. However, the practical value of such results at present lies in their utilization in the identification and quantitative determination of groups in unknown organic molecules which can be obtained in such solutions.

First, the tendency for the absorption due to the presence of a particular group to lie in a particular region offers a possible method of determining the presence of that group, thus, for example, whether OH or NH is present in the solute molecule. It must be clearly stated that our survey has shown that there is a decided tendency for these regions to overlap, and this, of course, acts to endanger the usefulness of this first application. In most cases, however, the method would be helpful. Secondly, the variation in shape of the absorptions due to the presence of the same group but bound differently in different molecules offers a means of distinguishing between types, for example, pyrrole-like and amine-like NH. Actually this second factor aids also the first, since in cases where overlapping occurs it may offer a means of recognizing this. It has limitations which will be mentioned later. Lastly, the absolute value for the absorption area, once the probable nature of the absorbing entity has been determined, as outlined above, permits an approximate quantitative analysis of the solution for these groups. Though not possessing what might be termed "analytical accuracy," it is, however, a method that may be applied in some cases where no other method exists.

In this more obvious use the method has already been tested on some fifty unknown solutions made up for this purpose. The degree of success encountered is perhaps best conveyed by citing a few of the actual cases. These unknowns were studied during the course of our regular measurements, experience being gained with each unknown run, and also added experimental data, since after making each report the composition of the solution was disclosed.

The technique is fairly obvious. The concentration c in the formula given above for the absorption coefficient is here, of course, unknown, and the purpose is to identify the group and determine its concentration. After deciding upon the type of the absorbing group from position and shape of the absorption, a mean value of the absorption coefficient for that type from past experience is used, and the concentration c is calculated, the other quantities being determined experimentally. Thus, what is called the absorbency $A = -(1/d) \log (I/I_0)$ is plotted, giving an area which when divided by the average molal area for this type (from the quantities given in Tables Ia, Ib and II) gives the molality. The unknowns were analyzed quantitatively for NH and OH only. Figure 3 shows the absorbency curves as they were determined for a number of these unknowns. The following is a brief historical account of these cases, in which the examples are given under their original numbers.

Unknown 11.—Strong absorption showed in the 5600–6000 cm.$^{-1}$ region also. There was reported phenolic-like OH in concentration 0.11 M and the presence of much more CH than corresponded to phenol. Solution was 0.092 M in C_6H_5OH and 0.167 M in $C_6H_5N(C_2H_5)_2$, and was diluted five-fold for measurement.

Unknown 18.—There was uncertainty as to whether NH and OH were present or OH alone. OH was reported in molality 0.032 M. Solution was catechol at 0.0155 M. We were unable to distinguish between the two groups in one molecule, or one such group in two molecules. The accuracy of the report is fortuitous.

Unknown 24.—There was some uncertainty as to whether OH or NH were present, but OH was reported at 0.028 M. Solution was 2,4,6-trichlorophenol at 0.026 M.

Unknown 25.—There was uncertainty as to whether OH alone was present, or both OH and NH. A double indecisive report was made, 0.022 M in OH if only OH were present, and 0.013 M if a molecule were present containing both OH and NH. Solution was 0.0424 M in methylanthranilate. This is a good example of an early bad report on a new type of absorption.

Unknown 26.—NH was reported and in amount 0.017 M, with a considerable possible error in the direction of this being low. An upper limit of 0.032 M was given, however. Solution was o-nitroacetanilide at 0.0323 M.

Unknown 30.—OH was reported at 0.031 M. The solution was ethyl lactate at 0.0382 M.

Unknown 32.—OH was reported at 0.030 M. The solution was ethyl tartrate at 0.0198 M. As in Unknown 18, we could not identify the presence of two OH groups in the molecule.

Unknown 37.—OH was reported at 0.0150 M. The solution was m-nitrophenol at 0.0141 M.

Unknown 45.—NH was reported at 0.030 M. The solution was o-nitroaniline at 0.031 M.

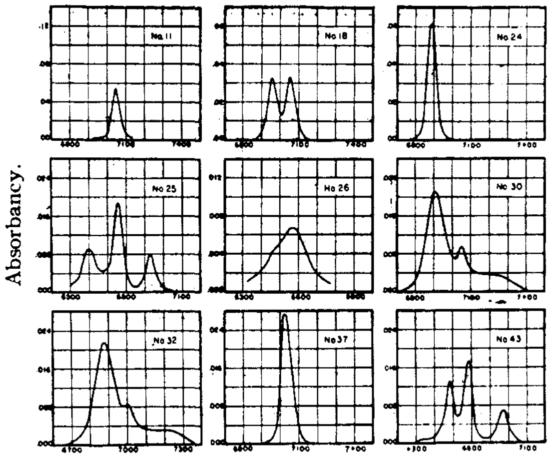
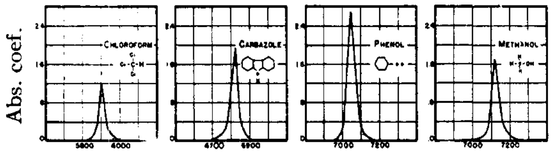


Fig. 3.—Absorbency of some experimental unknowns.

A considerable fraction of the remaining unknowns were of the chelated type upon which a report has already been made elsewhere.[4] In these cases, as for example, o-nitrophenol, the report was simply the absence of any absorption characteristic of OH or NH. We estimate that in the concentration usually used, an absorption one-fiftieth that of a normal OH could, without any reasonable doubt, be detected. Results upon a very dilute solution of a normal OH compound support this. Weak absorption can, of course, be detected long after it is too weak to measure with accuracy. Organic acids are interesting in this respect and will be the subject of a later report. Several of these occurred among the unknowns. If in these cases the solute were taken to be unassociated our results were always far too low. Where association occurs, runs must be made at a series of concentrations. Thus this is not an inadequacy of the method, but rather an illustration of its use in studying the phenomenon of association.

Discussion

There is a further possible application to which we wish especially to call attention, and to do this it is necessary to consider what the probable nature of the absorption act is in such solutions. In most of the compounds mentioned above, the rotational structure of the rotation–vibration absorption of the molecule, thought of as in the attenuated gas phase, would be very complicated indeed, because of large moments of inertia about all three axes. At pressures, however, where the gas density is still far from that in the liquid phase, rotational fine structure, even in the simplest molecules, has already been obliterated by broadening.[5]



Frequency in wave numbers.

Fig. 4.—Examples of typical simple absorptions.

The present work has been carried out in carbon tetrachloride solution, chiefly because this solvent possesses no absorption itself across the spectral region studied and because it can be obtained quite pure at a reasonable cost. We furthermore have tried to work at as high dilutions as possible, both in order to hold the influence of the environment constant (the surrounding carbon tetrachloride molecules far outnumbering the solute molecules themselves), and in order to minimize other effects, such as association in acids and alcohols, which increase with concentration. The actual disturbing factors influencing the absorption of light by molecules in solution are undoubtedly very complicated, but it is believed that in the present work these are both relatively constant, and also small for such a nonpolar solvent in comparison with the changes which occur in absorptive power from one kind of solute molecule to another. Several reasons will be given for this point of view, but here there may be mentioned, as an example, the consistent behavior of aniline, such that from dilute solution through very concentrated solution, even to pure liquid aniline, the absorption, though undergoing some change, still lies in about the same position and has roughly the same absorption. It appears very probable that the important influences affecting the observed differences in the position, shape and absolute absorption due to the presence of such groups as NH, OH and CH, are the ways in which these are linked to the molecules of which they are parts, and the extent to which motions within the particular group are coupled with the rest of the molecule. It is from this viewpoint that we wish to discuss the extension of these results.

In carbon tetrachloride solution the density is approximately 6×10^{21} molecules per cubic centimeter, or more pictorially about 0.2×10^{8} molecules in a row along the side of a centimeter cube, if the molecules were regularly spaced and at rest. This would give a distance between centers of adjacent molecules of about 5×10^{-8} cm. and since molecular diameters are of the order of 5×10^{-8} cm., it is clear how closely packed the molecules are in the liquid phase. At such densities it seems probable that rotational absorption in such complex molecules as dealt with in this paper is impossible, and that the absorption becomes essentially a vibration phenomenon. The molecules are to a considerable degree sterically interlocked with one another. Simple vibrational absorption can persist, however, after the possibility for undisturbed molecular rotation has been prohibited by such interlocking. While not uninfluenced by the neighboring molecules, the oscillation between the parts of a molecule, particularly between a little hydrogen atom and the heavy and bulky remainder which stays almost at rest in the oscillation, can occur with relatively little disturbance from neighboring molecules. It is of interest to note that the frequency of oscillation even in the simple molecules OH, NH and CH is of the order of one hundred times greater than the frequency of rotation of these molecules. Thus, in the gas phase at only moderate pressures, rotation–vibration bands show pronounced influence upon the rotational phenomenon[5] due to the frequent collisions of molecules, while the vibrational phenomenon remains essentially unaffected. A long uninterrupted train of oscillations can be made in the time interval between collisions, which is not true of rotation.

In order to give this point of view experimental support the behavior of a few typical compounds will be described. Their absorptions are illustrated in Fig. 4. The molecule of chloroform contains a single CH group with the remaining atoms all relatively heavy. At 5900 cm.$^{-1}$ this CH group shows a single symmetrical peak, the first overtone of the well-known CH fundamental at 3000 cm.$^{-1}$. It has a half breadth of roughly 35 cm.$^{-1}$ while for the simple CH molecule in the gas phase, if it could be examined in absorption, there would be two maxima of rotational absorption[7] the separation of which at room temperature would be approximately 160 cm.$^{-1}$. Again the molecule carbazole shows a single symmetrical peak at 6800 cm.$^{-1}$, the first overtone of the NH fundamental at 3400 cm.$^{-1}$. The half breadth is about 40 cm.$^{-1}$ while, again, in the gas phase the simple NH molecule would show a separation of rotational maxima about the same as that for CH. Finally, the molecules methanol and phenol show single symmetrical peaks at about 7100 cm.$^{-1}$, the first overtone of the OH fundamental at 3500 cm.$^{-1}$. The half breadth is again about 45 cm.$^{-1}$, while for the simple OH molecule in the gas phase the separation in the rotational maxima would be about the same as for the molecules CH and NH.

Curves such as these are very suggestive of simple vibrational absorption, and it is indeed difficult to see how such a molecule as carbazole could accomplish rotation at these densities. It is equally difficult to imagine the NH group rotating freely in such a molecule. In such molecules as phenol, while here the possibility might seem to present itself of persistent rotation of the OH group around the bond to carbon, it appears from these measurements that this does not occur in the spectral sense. For these and other similar reasons it will be assumed in an effort to devise a working hypothesis of the origin of such absorption spectra, that rotation absorption in such complex molecules at so high a density is impossible, and that the spectrum becomes one solely of the oscillations of the various parts of the molecules studied, in these investigations of the NH, OH and CH groups. If true, this introduces considerable simplification into the treatment and discloses a new and relatively simple type of spectra. Thus the carbazole curve is presumed to represent essentially the simple oscillation of the hydrogen with respect to the nitrogen. The breadth or decrement of the curve can then be explained as a combination of mechanical and electromagnetic damping of the oscillator.

Owing to the fact that the NH, OH and CH groups are attached to the rest of the molecule, there is, however, always the possibility that the oscillator in question is coupled appreciably to nearby oscillators on the main body of the molecule, this possibility being especially present for adjacent groups. Where coupling with another oscillator exists, displacements are to be expected in the positions of the two frequencies from the positions they would have if the two oscillators were independent of one another. In the present work if the second oscillator possesses a frequency widely different from the one of chief interest, the coupling will manifest itself in a shift in the position of the latter, the former not being seen at all since it lies in another spectral region. Such coupling to groups of widely different frequencies probably accounts for much of the observed shifting of position of the absorptions recorded in this work, in passing from molecule to molecule. If coupling exists with an oscillator of the same or nearly the same frequency, then the two resulting absorptions may overlap and either an unsymmetrical peak or two separate but adjacent peaks will result, indicating the presence of these two frequencies. The separation of two such peaks depends, of course, on the original frequencies, and also upon the strength of the coupling, two frequencies resulting, however, even in the case of two identical oscillators. The intensities of the two peaks may be quite different. They depend upon the effective charge or change in electric moment associated with the two new motions, and thus they also depend upon the coupling.

Since in such cases as carbazole, fluorenone-imide, phenol and ethanol, to give some examples, no such multiple absorption appears, it is concluded that these are cases where any coupling to nearby oscillators of nearly the same frequency is so small as to be negligible. On the other hand, when in the case of pyrrole there is definite evidence of a small subsidiary maximum to long wave length,

---

(7) See for example Ruark and Urey, "Atoms, Molecules and Quanta," McGraw-Hill Book Co., Inc., New York, 1930, p. 374.

it would seem that the coupling with the adjacent CH group is no longer negligible. This belief becomes much strengthened when we find that, while present also in indole, this subsidiary maximum is absent in carbazole, thus the adjacent CH groups having been completely removed.

The NH_2 group has the complication, as compared with the CH, NH and OH groups, of possessing two characteristic modes of vibration instead of one. Actually it possesses three, but the one associated with the bending of the bonds to nitrogen will undoubtedly have a much lower frequency, and will not lie in the region studied. The two above mentioned will differ from one another by an amount dependent upon the force constants of valence binding and distortion of angle, and upon the angle itself. They would be expected, however, to be not greatly different, the situation resembling that in the H_2O molecule.[8] The intensity of the two peaks would not be expected to be the same, since the two modes of vibration will not, in general, have the same effective charge connected with them.

Now one of the simplest regularities, which has been found in these measurements, is that the absorption due to the NH_2 group is comprised of two peaks, the lower frequency one being usually much the more intense. This holds throughout all the simple amines, both aliphatic and aromatic. In the aromatic amines, it is true, a third frequency makes its appearance, slightly displaced to lower frequencies from the principal peak, but, as described above, this would be interpreted as due to a coupling of this NH frequency with the adjacent CH groups, and this becomes a rather probable explanation when it is observed that it appears quite prominently in aniline and *p*-toluidine, for instance, but is almost absent in 2,6-xylidine.[1] In 2,4,6-trichloro and 2,4,6-tribromo aniline this is also weak and the two principal frequencies much accentuated, though indications of other weak frequencies appear, indicating still some coupling with oscillations in the ring, despite the absence now of adjacent CH groups. Oscillations characteristic of the complicated CH portion of the molecule are very numerous.[3] Though in most cases of molecules containing only CH these are extremely weak in the spectral region of NH and OH, they nevertheless are distributed over practically the entire region being studied. We wish to stress here only the persistence of the two frequencies of the NH_2 group, characterizing it throughout a series of marked changes in the rest of the molecule to which it is attached.

Where there is pronounced coupling to a heavy group such as C=O, damping of the oscillator is apt to be large, since the slow swinging of the latter is more readily disturbed by collisions. Through collisions with other molecules such a group transforms more efficiently the energy of oscillation into heat motion than can the light group alone. This damping would be expected to decrease the absorption of an OH, NH or NH_2 group which is so coupled to a heavier group and this seems to be generally the case. An illustration lies in the instance of the nitro anilines, the area under the curve decreasing markedly in passing from para through meta and finally to ortho nitroaniline. Similarly such damping through coupling with a group easily affected by collisions, should lead to broadening of the absorption and there is a decided tendency toward this. Examples are to be found in benzoin, and in ethyl lactate, the latter, for example, standing in interesting contrast to isopropanol. Because of this frequent tendency of the absorption due to an OH, NH or NH_2 group to decrease as well as to broaden when affected by a neighboring group such as C=O, we incline toward explaining the broadening as due to damping. It may, however, be that it is due to a periodically changing binding force, as the group oscillates in a waving motion about its equilibrium position with respect to the main body of the molecule. Furthermore, since there seems to be a tendency for the effect of another group to depend on characteristics other than its mass, it seems, as might be expected, that electrical forces play a more prominent part than do mechanical forces in this coupling or interaction between two groups.

A further interesting case which lends conviction of the reality of this coupling or interaction, is the instance of the dihydroxy alcohols, as seen in the curves of catechol, resorcinol and hydroquinone. While hydroquinone and resorcinol show the typical sharp single peak of an OH group not coupled appreciably to any adjacent groups, catechol shows in a striking way the splitting of the single frequency due to the coupling of the now adjacent two OH groups.

Such an interpretation of this type of spectra,

---

(8) See for example, Stuart, "Molekülstruktur," Verlag J. Springer, Berlin, 1934.

if substantiated in fact, affords a new means of the determination of the structure of unknown molecules. It should be possible, for example, not only to say whether or not an NH or OH group is present in the molecule and quantitatively how much there is, but also to gain some idea of the spatial orientation of the group, and of the character of neighboring groups, when the behavior of the NH and OH groups adjacent to other groups has been sufficiently studied. Of the cases with which we are working at present the most complicated is that of an adjacent C=O group. This affects strongly the absorption of the NH_2 and OH groups.

To add one further illustration of the splitting of a characteristic frequency of two independent like oscillators when these are coupled together, there are the phenylenediamines, which possess considerable interest. It is a more complicated case, because the absorption of an aromatic attached NH_2 group, as described above, is already fairly complicated. Nevertheless, the general character of the result is obvious from the curves given above. Benzidine and *p*- and *m*-phenylenediamine all show curves resembling remarkably that of aniline except that the area embraced is approximately two-fold greater than for aniline itself, as would be expected owing to the presence of two NH_2 groups. Passing to *o*-phenylenediamine, evidence is clearly afforded of the splitting of two frequencies, the area under the curve, however, still remaining approximately that of the former. It appears that the frequency of the principal peak in aniline is the one which in this case is coupled.

In conclusion, though the above is but a small beginning, it seems to warrant the extension of such measurements because of the possibilities which such spectrum analysis presents. It will be necessary to study as large and representative a group of molecules as the inherent restrictions of the method permit, and above all to increase the quantitative measurements of absorption areas in cases where the absorbing groups are linked in other than the simplest ways in the molecules. Already there is evidence from the results on some substituted aminodibiphenylene-ethane compounds that the absorption coefficient of the NH group can be reduced to values lower than we have hitherto found. Similar behavior is evidenced in the case of OH. It is obviously impossible to assert the presence or absence of an NH or OH group on the basis of the presence or absence of its "characteristic" absorption, when the possibility exists that its absorption coefficient has simply been reduced to a very low value. The usefulness of such procedure, as we have for instance applied it in certain cases of chelation, can only be determined by the empirical study of as many and different molecules as is possible, and we are continuing the research with this purpose.

The authors gratefully acknowledge their indebtedness to Drs. G. E. Hilbert and S. B. Hendricks for much help throughout this work.

Summary

Results are given for the quantitative absorption of light in the region 6000–7400 cm.$^{-1}$ (1.65–1.35 μ) by a large number of organic compounds, containing NH, NH_2 and OH groups, in carbon tetrachloride solution. These absorptions are characteristic of the presence of these groups.

The use of this material in the identification of the presence of particular groups and in the quantitative estimation of some types of organic molecules is outlined, and some illustrations of its application are given.

Discussion of the probable origin of such spectra is given, and evidence is advanced for the existence of measurable influence on these characteristic absorptions through coupling with other groups in the molecule which are adjacent or near the absorbing groups.

It is suggested that this provides a method for the investigation of the structure of some organic molecules through an analysis of such spectra.

WASHINGTON, D. C. RECEIVED JUNE 3, 1935