

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

The Character of the Absorption of Some Amines in the Near Infra-red¹

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Observations in the infra-red on the spectra associated with the CH, NH, OH and SH groups in aliphatic and aromatic organic molecules² have shown that such investigations constitute a fruitful approach to a study of differentiating characteristics of these molecules. At the suggestion of Dr. F. G. Cottrell, the authors have undertaken an investigation of a considerable number of aromatic and aliphatic amines for the purpose of correlating characteristic differences in their spectra, in so far as possible, with the known chemical properties of these molecules.³ In view of the importance attached by organic chemists to the electrical characteristics of portions of molecules in connection with their chemical properties, we were early convinced that the usefulness of such a study would be greatly increased by a quantitative determination of some physical property characteristic of the radical or group being studied and it was decided to measure the absorption coefficient in the region of characteristic N-H absorption.⁴ A beginning has now been made on this, and we are communicating in this paper the first results of a study of a number of amines in carbon tetrachloride solution working with the absorption lying in the vicinity of 1.50μ which is due to the N-H portion of the molecule.⁵

Experimental

The infra-red glass spectrograph used throughout this present work has been described by Brackett and Liddel.⁶ The excellent operating characteristics of this instrument have contributed greatly to the present work. Illustrative records for solutions of aniline and phenol in carbon tetrachloride under the conditions of slit width used in the present work are shown in Fig. 1, these being records of galvanometer deflections with wave length, and except in the positions of characteristic absorption of the compounds and the water vapor in the light path, they are records in arbitrary units, of the radiation from the tungsten lamp source modified by the transmission of the optical parts of the instrument. Certain characteristic absorptions are indicated. Determination of the absorption coefficients was carried out by recording at appropriate intervals on the experimental plate segments of both the base line of no galvanometer deflection (shutter introduced corresponding to complete opacity), and of the intensity of the lamp source by way of a second optical system carrying the light to the slit around the absorption cell rather than through it. Before and after each experimental plate a complete record was taken under the same conditions except that the cell contained pure

(1) This paper was presented before the Organic Division of the American Chemical Society at Washington, March 28, 1933.

(2) See for example Schaefer and Matossi, "Das ultra-rot Spectrum," Julius Springer, Berlin, 1930.

(3) Lack of a particular sort of chemical evidence plus the lack of adequate interpretation of the absorption differences as yet constitute a barrier to a definite correlation in the present paper.

(4) For previous work on the study of absorption coefficients in regions of absorption due to H linked with other elements, see Bonino, *Trans. Faraday Soc.*, **25**, 876 (1929), and reference (2).

(5) Ellis, *This Journal*, **49**, 347 (1927); **50**, 685 (1928).

(6) Brackett and Liddel, *Smithsonian Misc. Coll.*, **85**, No. 5 (1931).

carbon tetrachloride instead of the solution of the amine being studied. From the average of these two records it was possible to determine the curve of the galvanometer trace on the solution plate as it would have been had not the solute been present in the solution and to the same scale as this solution plate, even in the event of appreciable zero drift in the galvanometer reading and of changes in the lamp intensity with time, by using these traces of the base line and of the lamp intensity by way of the constant auxiliary light path, which are contained on all records. Thus one has a measure of the intensity of the radiation after passing through the solution and after passing through the same cell containing carbon tetrachloride but without the solute, hence the transmission of the solute. Since the concentration of the solution is known, the transmission for a definite number of molecules in the light path is known, and hence the absorption coefficient over the region of the spectrum covered may be calculated.

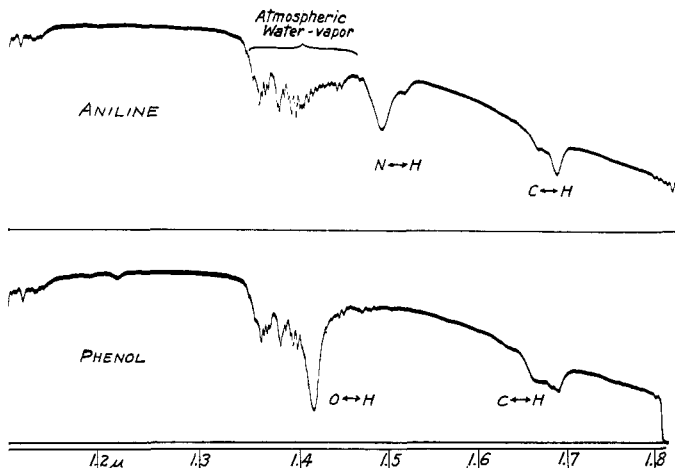


Fig. 1.—Illustrative records of aniline and phenol with characteristic absorptions indicated.

A small correction to the observed deflections was necessary owing to the presence of a certain amount of scattered light in the spectrograph. The determination of this correction was accomplished in the following manner. A measurement was made of the transmission of a certain concentration of aniline which reduced the intensity at the peak of the N-H absorption to roughly 70%. This value, which is a little in error owing to stray light, was used to compute a path length at the same concentration which would reduce the intensity at this same wave length to a fraction of 1% and the apparent intensity was then noted using this absorption. It showed a value of nearly 5%. This difference was taken as the fraction of the total deflection at this wave length that was due to scattered light, after applying a small additional correction. In the observation using the highly absorbing path of aniline, the stray light itself was somewhat reduced owing to the reduction of the total radiation entering the spectrograph. This latter was estimated as roughly 7% from the records themselves. In the case of the weakly absorbing paths ordinarily worked with, then, the stray light would be greater than the above by roughly 7% of itself. Therefore 5% of the deflection at this wave length in the absence of the solute or in the presence of weak N-H absorption seems a satisfactory estimate of stray light. To illustrate that this correction is small, the results for aniline solution containing 10^{20} molecules per square centimeter cross section of the light path may be cited. At the peak of absorption, the observed ratio of I/I_0 was found to be

0.67. If now both of the intensities making up the ratio are high by about 5%, the corrected ratio becomes 0.64. Thus, at the present stage of this research, while the correction is of sufficient importance to be taken into account, a small error in the estimation of the correction is not serious.

The estimate of stray light was also carried out in a constant path length at two different concentrations, reducing in this way the intensity in the same ratio as was mentioned above in the case where constant concentration and two different path lengths were used. The procedure at two different concentrations involves Beer's law, and a test of this law was made with aniline over a concentration range from 0.033 to 0.41 molal. Beer's law was followed within the limits of error of our measurements. At these dilutions this is not surprising, though in very concentrated solutions this law would undoubtedly fail.⁴

We have worked chiefly in a cell length of 5 cm. and a concentration of solute such that 10^{20} molecules are contained in one sq. cm. of light path, thus a concentration of 0.033 molal. Variations from this are noted in the table of results. All the amines have been studied in carbon tetrachloride solution. Many were originally Eastman Kodak Co. products, and, where we had reason to expect impurities, from age, discoloration, etc., redistillation or recrystallization was performed. β, β, β -Triphenylethylamine and γ, γ, γ -triphenylpropylamine were very kindly supplied by Professor L. Hellerman of the Johns Hopkins University, having been prepared by Dr. R. L. Garner. β -Phenylethylamine and γ -phenylpropylamine were supplied through the courtesy of Dr. W. H. Carothers of the du Pont Co. From a study of the boiling and melting points of the products finally used we believe that in no case, unless mentioned explicitly below, were impurities present to an extent of more than a few per cent. and usually much less. Since experience would not lead one to expect the presence of any substance having a much greater absorption power than the amine being studied and at the same position in wave length, we feel that the purity of the compounds has been ample to justify the conclusions which have been arrived at in this preliminary study. The principal conclusions are based upon the consistency of the data rather than the results of any one substance. The presence of any impurity not an amine, in any given percentage, could only affect the results by making our calculations of absorption coefficients too low by that amount.

Regarding the improbability of the presence of any highly absorbing impurity in this same region it should be pointed out that this region is apt to be rather free from possible trouble. Strong absorption depending upon electronic transitions rarely if ever comes so deep in the infra-red, so far as is known, while the absorption due to the oscillation of heavy masses, such as C-C, lie far enough in the infra-red that even their first overtones (higher overtones would be of such low intensity as to render them unimportant) are well beyond 1.5μ . Only the absorption associated in part at least with the oscillation in a H linkage can very well enter here. For these reasons, the question of small amounts of impurities in the materials studied is probably not a serious one in any case. Furthermore, fortunately, moderate absorption occurs in the first overtones of many H linkages in moderate path lengths of dilute solutions, thus, as in the present work, some hundredths molal in paths of a few centimeters. Solvents whose molecules possess only heavy atoms, such as carbon tetrachloride or tetrachloroethylene, are of course free of absorption in this region unless impurities, such as chloroform in carbon tetrachloride, are present. This region of wave length seems thus rather well adapted to the purpose of the present paper.

Results

The absorption curves to follow are plots of the absorption coefficient ϵ against frequency of absorption in cm.^{-1} ; $\epsilon = \log_{10} I/I_0/cd$, the units being

those commonly employed, c in moles per liter and d in centimeters. We do not feel justified in claiming a greater absolute accuracy than ± 0.05 in the values of ϵ and ± 8 cm.^{-1} in frequency. Some differences in the curves within these limits are probably real, since the magnitude of some effects is undoubtedly small, even beyond detection in the present experiments.

The points on the curves represent the calculated values for the absorption coefficient determined from the records themselves and the lines are interpolations of these points.

Measurements for calculation of absorption coefficients were made from the records at arbitrary wave lengths, hence points were not always read at the exact peaks of absorption; however, close visual comparisons of the original records with the drawn curves of absorption, given in the results to follow, showed their exact similarity.

A series of aromatic amines was chosen to observe the effects, if any, of the substitution of a methyl group for one or two of the hydrogen atoms in various positions of the aromatic nucleus on the absorption of the NH portion. All the primary amines (Fig. 2) are very similar, both in the form of the curve and intensity of absorption. However, small differences occur, reproduced on two independent sets of data of which the average is recorded.

Aniline has a fairly symmetrical absorption with a maximum at 6693 cm.^{-1} , and another much weaker band around 6600 cm.^{-1} unresolved from the main peak. Methyl substitution ortho to the amine group reduces the absorption in the region of 6600 cm.^{-1} and apparently shifts the median of the main absorption to very slightly higher frequency. Substitution in the meta position has no obvious effect, and in the para position shifts the peak to lower frequencies and increases the absorption coefficient of the peak. In the xylidines, substitution of the second methyl group seems to have only the added effect of

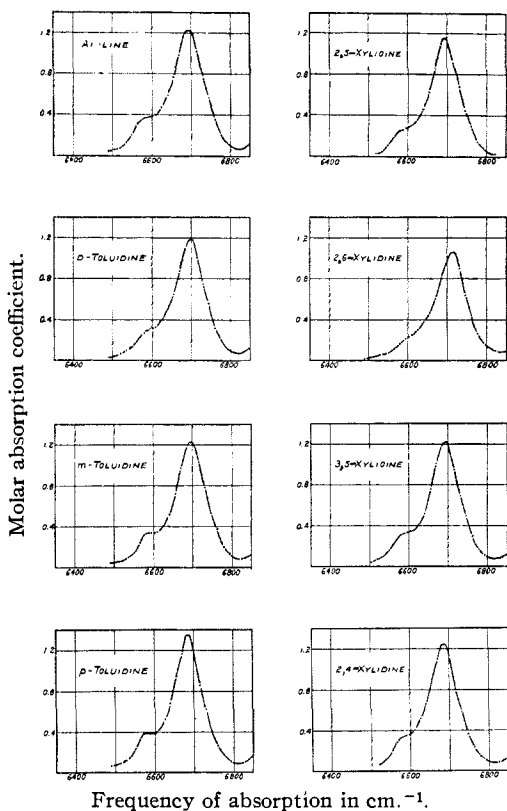


Fig. 2.

the methyl group in the second position; *i. e.*, 3,5-xylidine is exactly like *m*-toluidine; 2,4-xylidine a rough composite of ortho and para toluidines. It must be mentioned that there is real absorption in the vicinity of 6950 cm.^{-1} which apparently varies in intensity with the long wave length dissymmetry of the bands, *i. e.*, in *p*-toluidine and aniline, it is appreciable, and in 2,6-xylidine it is negligible; however, its apparent variation with the dissymmetry of the peak would suggest a definite relation which should be investigated. No measurements can be given on this absorption at the present time, since it lies in the midst of strong absorption, due to water vapor, which, although removable with this spectrograph, we are using as a check on the dispersion of the instrument.

A methyl group attached to the N atom of aniline and *p*-toluidine decreases the intensity of absorption to about two-thirds that of the corresponding primary amine and very appreciably increases the frequency of

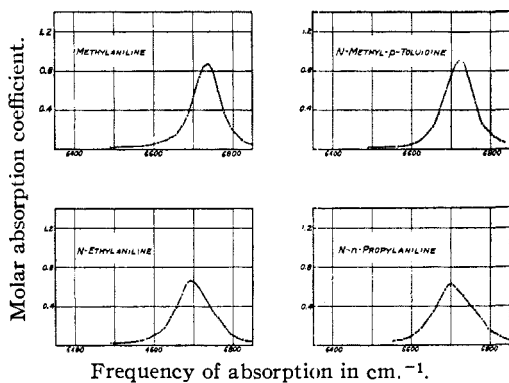


Fig. 3.

absorption of the remaining N-H bond, whereas an ethyl group in aniline decreases the absorption to one-half and has no effect on the main frequency. In propylaniline the intensity is the same as ethylaniline, though absorption occurs at a slightly higher frequency. Thus the absorption per N-H bond is about the same in ethyl- and propylaniline as in aniline, but greater in methylaniline by some 35%. In all these compounds the absorptions at 6600 cm.^{-1} and around 6950 cm.^{-1} have so diminished as to be no longer observable (Fig. 3).

The normal aliphatic primary amines are characterized by an appreciable decrease in the absorption coefficient compared with the aromatic amines, as well as the known⁵ shift in the frequency of absorption. A very interesting result is the exact similarity within experimental error of the curves for *n*-propyl, butyl, amyl and heptyl amines, so that only the curve for *n*-butylamine is given in Fig. 4. The same is true for the secondary amines di-*n*-propyl, di-*n*-butyl and di-*n*-amyl. These differ from the primary amines in having a lower absorption coefficient, which, however, is greater per N-H bond by about 50% in the secondary than in the primary amines. The peak of absorption is at a longer wave length, 6504 cm.^{-1} compared to 6556 cm.^{-1} for the primary.

Methylamine (Fig. 5) differs from the foregoing aliphatic amines by absorbing at a higher frequency and with greater intensity, while ethyl-

amine differs oppositely. Benzylamine, β -phenylethylamine and γ -phenylpropylamine are to all appearances normal aliphatic amines, as to shape of the curve and frequency of absorption, except that benzylamine absorbs with slightly greater intensity and β -phenylethylamine possibly slightly less. The intensity measurements of these latter two, however, are not reliable, and no measurements at all can be given for the phenylpropylamine, due to a peculiar reaction between these compounds and the solvent, carbon tetrachloride, increasing in speed with the length of the carbon chain, so that in γ -phenylpropylamine a record suitable only for wave length determinations could be obtained. It was observed that reaction occurred between the solvent and many other of the amines after several days, causing, however, no experimental difficulties over the short time required for experimental work. These reactions will be the subject of a note soon to be published by Dr. L. B. Howard.

The secondary amines shown in Fig. 6 differ markedly among themselves and from their corresponding primary compounds. The only secondary aromatic amine we have been able to obtain is diphenylamine, which absorbs at a higher frequency than aniline,

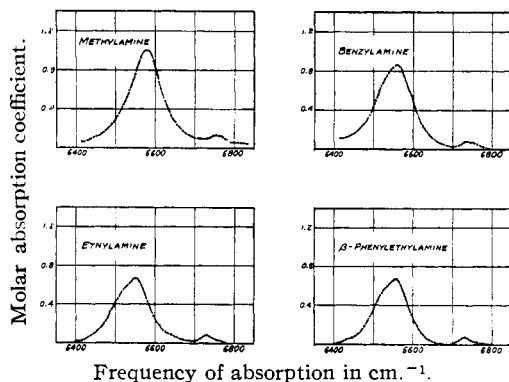


Fig. 5.

The absorption curve of dibenzylamine is perhaps the oddest of all, and leads to suspicion of impurities; however, careful redistillation of the amine *in vacuo* failed to have any effect on the absorption, and also the carbylamine reaction for the presence of primary amines was entirely negative.

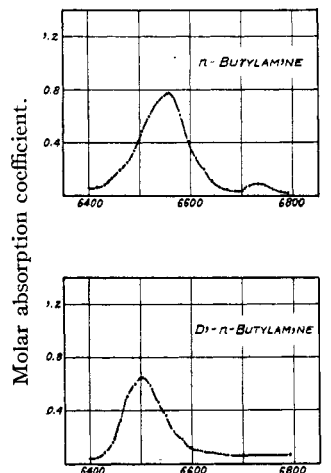
Frequency of absorption in cm.^{-1} .

Fig. 4.

has only one apparent absorption maximum, but here again with an intensity value greater than one-half that of aniline, and by about 35%. Dimethylamine has a quite symmetrically peaked absorption but an intensity greater than one-half methylamine by about 180%. The absorption of diethylamine has only one apparent maximum, which is greater in intensity than ethylamine.

Triphenylpropylamine (Fig. 7) is very similar in shape and position to

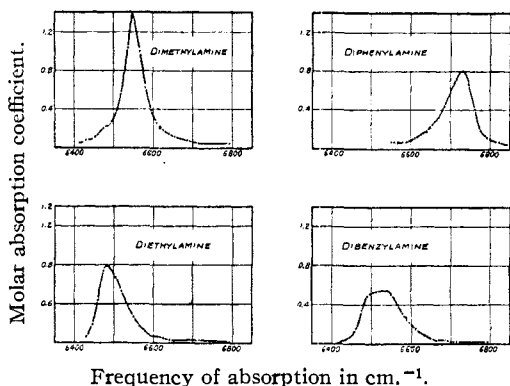


Fig. 6.

As examples of other types of amines, the absorption of pyrrole and fluorylamine is shown (Fig. 8). Fluorylamine has a distinctly aliphatic type of absorption, very similar to benzylamine, absorbing with possibly slightly greater intensity, and at somewhat longer wave lengths. The absorption of pyrrole apparently consists of a single intense band, greater in intensity at the peak than any other amine studied, and lying at the highest frequency observed, which might not be unexpected, on account of the linking of the N atom to two ethylenic carbon atoms.

Since a composite of the curves of diphenylamine and *n*-propylamine in certain concentrations might result in a curve similar to that of *p*-toluidine, records of a mixed solution of these in concentrations purposely chosen to resemble as nearly as possible *p*-toluidine were clearly differentiable from the latter by the separation of the maxima, there being no close resemblance.

Discussion

While the present results are preliminary in a study to be continued and extended to a much greater number of types of amines, they seem to indicate a few important facts.

benzylamine; the median of the absorption of triphenylmethylamine lies at a slightly longer wave length, of triphenylethylamine at slightly shorter wave length. Although these compounds were probably quite pure no certain measurement of the purity could be obtained, hence no emphasis can be placed on the alternation in intensity of absorption at the maximum in this series.

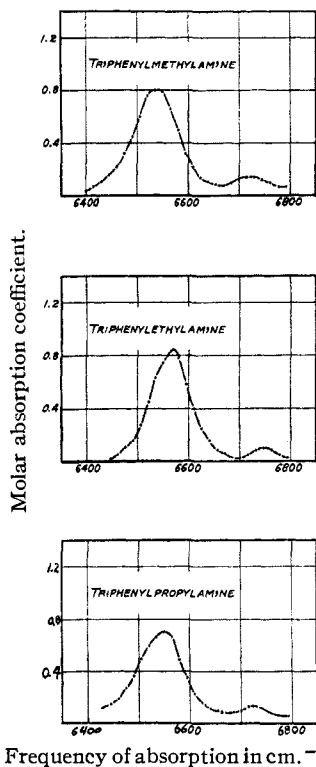


Fig. 7.

First, the absorption coeffi-

cient for the N-H bond in its absorption at 1.5μ throughout a very considerable range in character of the compounds, comprising aliphatic and aromatic primary and secondary amines, remains of the same order of magnitude. Second, there are measurable differences in this absorption coefficient from class to class, *i. e.*, primary aliphatic, secondary aliphatic, primary aromatic, and secondary aromatic, as well as differences in the position of the maximum of the absorption. Third, when a normal paraffin radical greater than two carbon atoms long is attached to the amine group, the absorption coefficient and position of the maximum of absorption vary very little, less than our present ability to detect. A similar remark holds for the corresponding secondary aliphatic amines, the absorption per N-H bond being somewhat greater in this group than in the former. A measurable variation is found within the primary aromatic amines studied, a dissymmetry in the absorption appearing in varying amounts in these compounds and perhaps accounting for the variation in the total absorption and in the position of the maximum within this group. Only one secondary purely aromatic amine has been

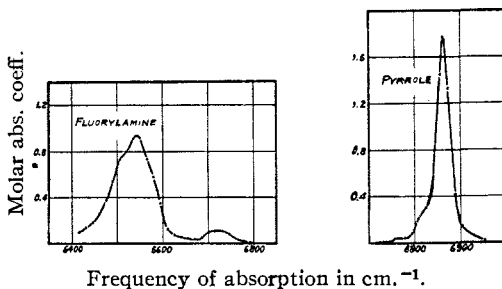


Fig. 8.

studied, diphenylamine. It has a greater absorption coefficient per N-H bond and a different position of the maximum than has aniline, its closest analog in the primary group, thus exhibiting a behavior somewhat similar to that observed in the aliphatic amines. However, it should be pointed out that in the case of the aliphatic amines the secondary amine maximum was shifted to lower frequency, while in the aromatic amines diphenylamine had its maximum at a higher frequency than aniline.

The first point mentioned above suggests the use of this quantitative data as a method of determining the total number of N-H bonds present in a given amount of unknown substance. Thus, for example, it is possible that it may be applied in this way to a study of such molecules as the alkaloids and chlorophyll. The second point suggests that a differentiation between classes may be possible from the differentiation in the position of the maximum of absorption, the quantitative measure of the absorption coefficient of the N-H bond for the respective classes making possible a determination of the number of N-H bonds of any one kind present by a method which seemingly may be brought to considerable accuracy. The third point, interesting but less useful, may permit a certain amount of differentiation within the primary aromatic amines. It is proposed to utilize the first two points in the extension of this work and to continue the

work to the other commonly occurring forms of the N-H group as well, for example pyrroles, imines, etc. Also, it should be possible to carry these measurements to other solvents, in some cases more suitable than carbon tetrachloride, such as tetrachlorethylene, and in a similar way to the above, to the O-H and S-H bonds. In principle also it could be carried to the C-H bond, though in organic molecules the practical application of the latter might be limited to compounds containing only a few C-H groups. Spectra are now being recorded in this Laboratory of some aliphatic and aromatic hydrocarbons enabling a study of this last point.

VALUES OF THE ABSORPTIONS AT THEIR MAXIMA

	ν , cm.^{-1}	λ (μ)	ϵ	$\epsilon/\text{N-H bond}$	Remarks
Ammonia	6571	1.522	0.54	0.18	0.0458 <i>M</i> soln.
Methylamine	6576	1.521	1.00	.50	0.066 <i>M</i> soln.
Ethylamine	6549	1.527	0.67	.34	0.1086 <i>M</i> soln. I_0^a reduced 3%
<i>n</i> -Propylamine	6556	1.525	.78	.39	
<i>n</i> -Butylamine	6556	1.525	.78	.39	
<i>n</i> -Amylamine	6556	1.525	.78	.39	
<i>n</i> -Heptylamine	6556	1.525	.82	.41	
Dimethylamine	6546	1.528	1.40	1.40	0.0288 <i>M</i> soln.
Diethylamine	6482	1.543	0.77	0.77	
Di- <i>n</i> -propylamine	6504	1.537	.61	.61	
Di- <i>n</i> -propylamine	6504	1.537	.64	.64	
Di- <i>n</i> -amylamine	6504	1.537	.60	.60	
Aniline	6693	1.494	1.22	.61	
<i>o</i> -Toluidine	6703	1.492	1.19	.60	
<i>m</i> -Toluidine	6693	1.494	1.22	.61	
<i>p</i> -Toluidine	6685	1.496	1.35	.68	
2,5-Xylidine	6699	1.493	1.16	.58	
2,6-Xylidine	6716	1.489	1.06	.53	
3,5-Xylidine	6693	1.494	1.22	.61	
2,4-Xylidine	6685	1.496	1.24	.62	
Methylaniline	6730	1.486	0.86	.86	
Ethylaniline	6693	1.494	.64	.64	
Propylaniline	6700	1.492	.63	.63	
<i>N</i> -Methyl- <i>p</i> -toluidine	6725	1.487	.89	.89	
Diphenylamine	6730	1.486	.80	.80	
Dibenzylamine	6500-6530	1.53-1.54	.55	.55	
Benzylamine	6556	1.525	.86	.43	I_0^a reduced 7%
β -Phenylethylamine	6556	1.525	.68	.34	
γ -Phenylpropylamine	6556	1.525	0.0446 <i>M</i> soln. I_0^a reduced 8%
Triphenylmethylamine	6534	1.530	.80	.40	
Triphenylethylamine	6564	1.523	.83	.42	I_0^a reduced 16%
Triphenylpropylamine	6549	1.527	.71	.36	
Fluorylamine	6541	1.529	.93	.47	
Pyrrole	6859	1.458	1.77	1.77	

^a In calculation of the transmission coefficients of this solution, which was slightly turbid, this value was used as the correction factor, and was determined on the basis of 100% transmission at 6300 cm.^{-1} .

The authors gratefully acknowledge the interest of Dr. F. G. Cottrell,

and the assistance of Drs. G. E. Hilbert and L. B. Howard, as well as valuable discussions with other members of the Staff of the Fixed Nitrogen Research Laboratory.

Summary

Absorption coefficients have been measured in the absorption lying at about 1.5μ due to the N-H group in a number of primary and secondary aliphatic and aromatic amines, and the positions of the maxima of absorption have been determined.

A method is suggested for the utilization of such data, as yet in a somewhat restricted field, for the detection of the presence of N-H groups, and for the approximate determination of the number of N-H groups present per cubic centimeter of a solution as well as the way in which this group is linked in the molecule.

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Complex Compounds in Eder's Solution

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Several attempts have been made to explain the mechanism of Eder's reaction, $2\text{HgCl}_2 + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{CO}_2 + 2\text{Cl}^-$. Most of the students of this reaction have assumed, as will be pointed out later in the discussion of their work, that the photochemical properties of this solution of oxalate and mercuric chloride are dependent on a mercuri-oxalate complex.

The present work was undertaken in order to determine the nature of the complexes which exist in Eder's solution and the extent to which they form. This information was sought by: (1) experiments on the partition of mercuric chloride between benzene and aqueous oxalate solutions, and (2) determinations of the freezing point depressions in Eder mixtures. Preliminary freezing point experiments made in this Laboratory by Mr. F. B. Slagle showed that the formation of the complex or complexes is attended by a small diminution in the number of molecules.

Since chloride ion is known to have a marked effect on the reaction and is also known to form complexes with mercuric chloride, a careful study of the literature on mercuri-chloro complexes as well as that on mercuri-oxalate complexes was made.

Throughout this work, the ionization of mercuric chloride is neglected,

(1) This paper is abstracted from the dissertation presented by S. L. Goldheim to the Faculty of Philosophy of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.