Five of the samples were analyzed by Miss Margery Walker and Mr. Ronald Benson. Particular attention is called to the last sample in the table, as it represents the sea water taken near the mouth of a pipe discharging bleach waste from a paper pulp mill into Puget Sound. In this case by determining the grams of chlorine per liter and per kilo of sea water and converting the former with the aid of the conversion table to grams per kilo, an indication of the extent of pollution may be ascertained from the difference between the calculated and determined values for Cl_w.

The excellent agreement of the calculated results and those obtained by analyses demonstrates not only the accuracy of the tables but also of the method of analysis. The relatively high degree of precision of the analytical method is also cited by Helland-Hansen[10] and others. The suggestion of Giral[5] for increasing the permissible error recommended by the International Council for the Exploration of the sea is unwarranted.

Conclusion

1. Sodium chloride may be substituted for standard water for standardizing silver nitrate solutions to be used for oceanographic studies. Both standards give practically identical results.
2. An empirical formula has been derived and corrections have been calculated therefrom permitting the conversion of grams of chlorine per liter at 20° of sea water to grams of chlorine *per mille* or *vice versa*.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

INFRA-RED ABSORPTION BY THE N-H BOND
II. IN ARYL, ALKYL AND ARYL-ALKYL AMINES

BY JOSEPH W. ELLIS

RECEIVED NOVEMBER 23, 1927 PUBLISHED MARCH 7, 1928

This paper represents a continuation of a study of the near infra-red absorption in primary, secondary and tertiary amines, Part I[1] of which was limited to an examination of aniline, five mono- and five dialkyl anilines. The present paper presents the absorption curves to about 2.5μ of the following compounds, all of which were bought from the Eastman Kodak Company: mono-, di- and tri-*n*-propyl-, *n*-butyl- and *iso*-amylamine; mono- (aniline), di- and triphenylamine; mono-, di- and tribenzylamine; α-, methyl-α-, dimethyl-α-, ethyl-α- and diethyl-α-naphthylamine; and *p*-, methyl-*p*- and dimethyl-*p*-toluidine. The primary purpose of the investigation is to test further the hypothesis advanced in

[10] "Internat. Rev. Hydrobiol. und Hydrograph.," Hydrograph. suppl., Series I. part 2, **1912**, p. 39.

[1] Ellis, THIS JOURNAL, **49**, 347 (1927).

Part I that certain definite absorption bands below 3μ are associated with the N-H bond.

Two cell thicknesses, 2 mm. and 40 mm., were used with each of the liquid members of this group of compounds. The 2mm. cells were microscope depression slides with thin cover glasses. It was found that these slides, even in a vertical position, retained the liquid indefinitely without any sealing. The 40mm. cell was of glass with quartz ends of 2 mm. thickness held on by pressure exerted by threaded brass collars.

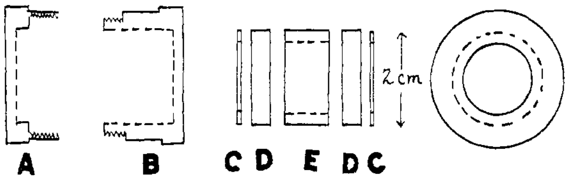

Fig. 1.—A demountable absorption cell.

The four members which are solids at room temperature, namely, di- and triphenylamine, α-naphthylamine and *p*-toluidine, were maintained in a molten state at temperatures just above their respective melting points. A demountable cell, 10 mm. in length, sketched in Fig. 1, was constructed for this purpose. A and B are two parts of a brass housing, threaded to screw together. D, D are 4mm. quartz end-plates which fit snugly against the ground faces of the Pyrex glass cell E. C, C are steel spring washers designed to allow for the unequal expansions of brass, quartz and glass. The cell was packed with the compound which was to be examined and fitted into a well in an asbestos block, 10 × 10 × 3.5 cm., which could be raised to the desired temperature. Heat was produced in the block by maintaining a controlled current in a high resistance wire which threaded it. If the cell was not sufficiently filled after melting took place, it was cooled and more of the substance added.

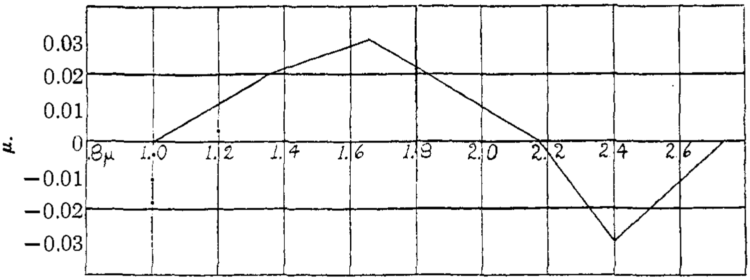

Fig. 2.—Wave length corrections to previous values.

In Figs. 3–18 are given the absorption records of the above-mentioned amines as traced by the recording spectrograph which has been used throughout this and other investigations. During another study[2] it was discovered that, because of inaccurate calibration, slight corrections must be made to many of the wave length values previously published by the author in several papers. These corrections apply to some of the values given for absorption bands in aniline and the alkyl anilines of Part I of this paper. In Fig. 2 a correction curve is given which should be used with all values previously published. Throughout this article only corrected values will be stated when quoting previous work.

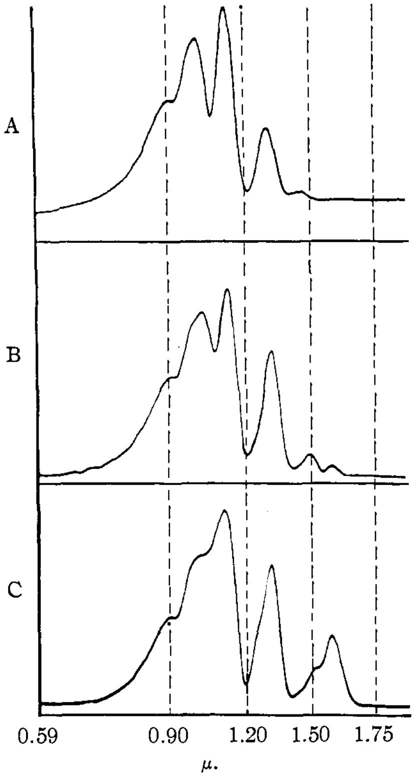

Fig. 3.—A, *n*-propylamine, 40 mm.; B, di-*n*-propylamine, 40 mm.: C, tri-*n*-propylamine, 40 mm.

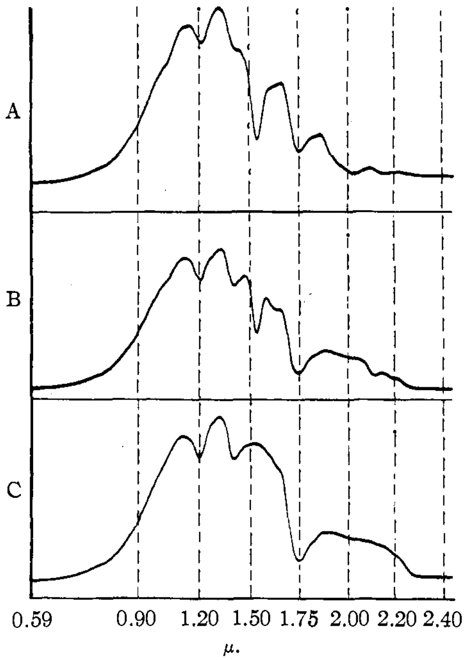

Fig. 4.—A, *n*-propylamine, 2 mm.; B, di-*n*-propylamine, 2 mm.; C, tri-*n*-propylamine (purified), 2 mm.

Absorption maxima at 1.49μ and 1.03μ[3] have been discovered in the spectra of aniline and five mono-alkyl anilines which, when taken with a strong isolated maximum discovered by Bell[4] at 2.8μ, form a parabolic series when expressed in wave numbers. The disappearance of these three bands

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[2] Ellis, *Proc. Nat. Acad. Sci.*, **13**, 202 (1927).

[3] A careful recheck of this value gives 1.03μ instead of the 1.04μ value previously given.

[4] Bell, THIS JOURNAL, **47**, 2192 (1925).

in the spectra of the corresponding dialkyl anilines lent support to the hypothesis advanced by the writer that these maxima represent characteristic frequencies associated with natural oscillations of the N-H pair of atoms.

Bell[5] has continued his study with four additional papers in which he has found absorption bands for numerous primary and secondary alkyl, aryl and aryl-alkyl amines analogous to the 2.8μ band in aniline and mono-alkyl anilines, varying in position from 2.9μ to 3.05μ. These are considerably diminished in the secondary amines and disappear, or practically disappear, in the tertiary amines.

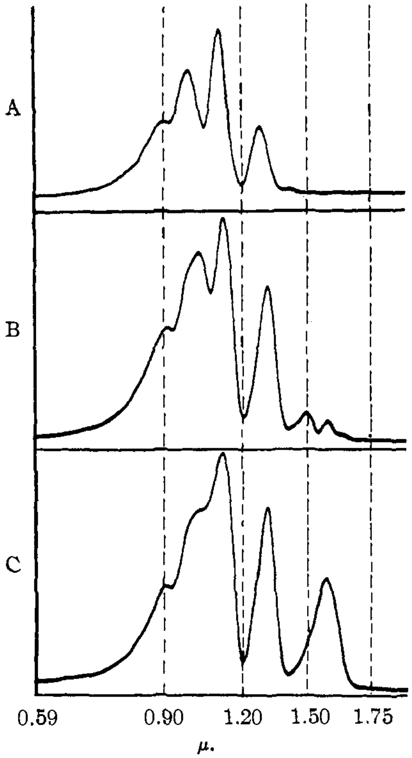

Fig. 5.—A, *n*-butylamine, 40 mm.; B, di-*n*-butylamine, 40 mm.; C, tri-*n*-butylamine, 40 mm.

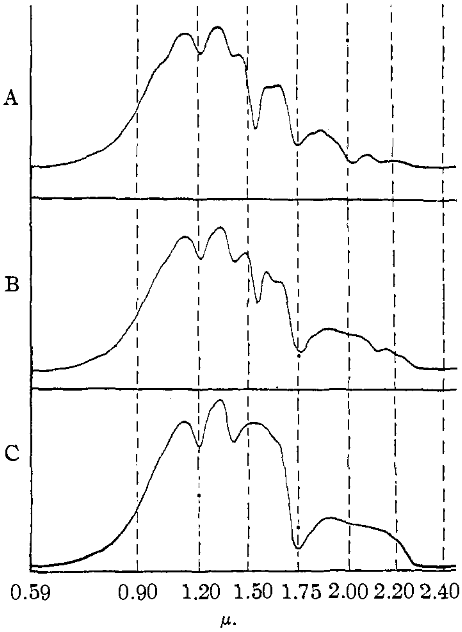

Fig. 6.—A, *n*-butylamine, 2 mm.; B, di-*n*-butylamine, 2 mm.; C, tri-*n*-butylamine, 2 mm.

In the records of the primary and secondary amines, Figs. 3–18, it is seen that there are two bands varying respectively from 1.49μ to 1.55μ and 1.03μ to 1.06μ. These are analogous to the 1.49μ and 1.03μ bands of the anilines. In general it is noticed that a shift toward longer wave lengths of the band near 3μ is accompanied by a corresponding shift in the two

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[5] (a) Bell, This Journal, **47,** 3039 (1925); (b) **48,** 813 (1926); (c) **48,** 818 (1926); (d) **49,** 1837 (1927).

shorter wave length bands. Furthermore, these latter absorption maxima disappear in most of the tertiary amines. In the cases where they remain as traces in the original samples of the tertiary compounds they have been proved to be due to impurities, as will be pointed out later.

The records for the alkyl amines are shown in Figs. 3–8. The bands ascribed to the N-H linkage are found at 1.54–1.55μ and 1.06μ. These may well be interpreted as the second and third members of series analogous to that found for the anilines or, in terms of the older phraseology, as the first and second harmonics (or overtones) of the value found by Bell at 3.00–3.05μ. A trace of the 1.55μ absorption remains in the record of tri-*n*-propylamine, Fig. 3C. A portion of the original sample of this material was treated by Dr. G. R. Robertson of the Chemistry Department with the aim of removing any possible primary or secondary amines. The process adopted was similar to that used in the purification of methylethylaniline (Part I).[6] That the trace of a band present in Fig. 3C is

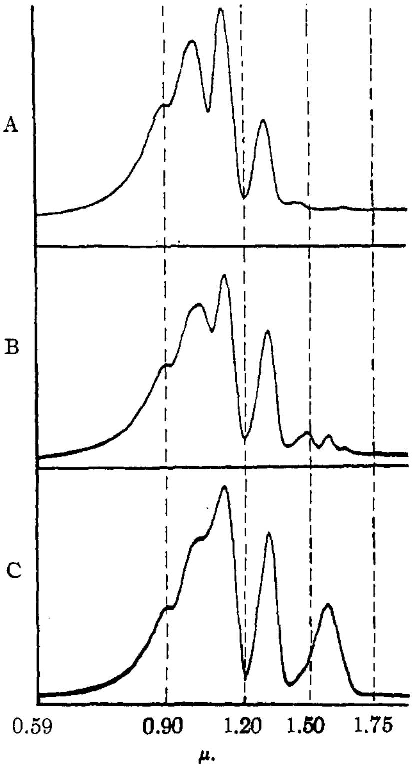

Fig. 7.—A, *iso*-amylamine, 40 mm.; B, di-*iso*-amylamine, 40 mm.; C, tri-*iso*-amylamine, 40 mm.

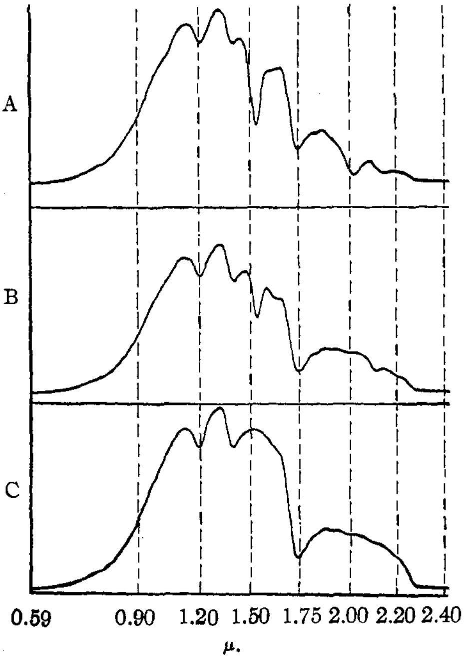

Fig. 8.—A, *iso*-amylamine, 2 mm.; B, di-*iso*-amylamine, 2 mm.; C, tri-*iso*-amylamine, 2 mm.

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[6] Ref. 1, p. 352.

not due to tri-*n*-propylamine is proved by its absence in the records of the treated substance, Figs. 18A and 4C.

The maxima at 1.75, 1.40, 1.20, 1.02 and 0.92μ are the established C-H bands characteristic of alkyl groups.

The 1.49μ and 1.03μ bands of aniline are found diminished in the record of diphenylamine, Fig. 9, while they are essentially lacking in the record of triphenylamine. The 1.68, 1.41 and 1.15μ maxima are C-H bands characteristic of the phenyl group.

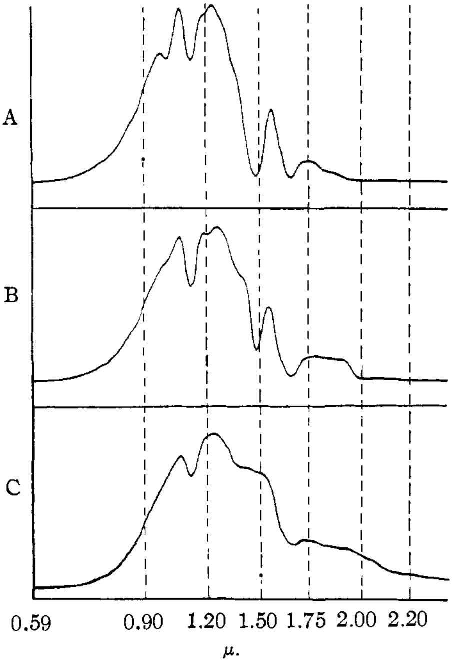

Fig. 9.—A, aniline, 10 mm.; B, diphenylamine, 10 mm.; C, triphenylamine, 10 mm.

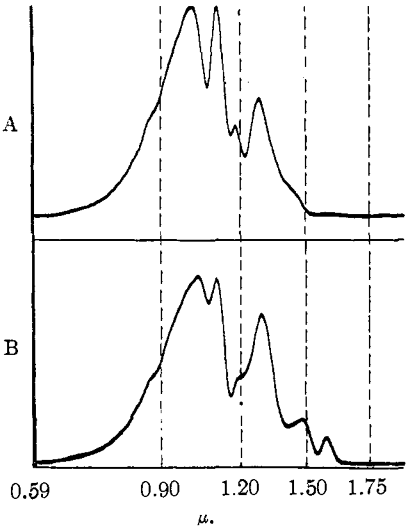

Fig. 10.—A, benzylamine, 40 mm.; B, dibenzylamine, 40 mm.

The shift toward shorter wave lengths of the absorption maxima associated with carbon-hydrogen linkages in the case of aryl compounds is doubtless to be associated with the lack of saturation in the molecules. It appears that this unsaturation also affects an amino group attached to an aryl group. Thus we have low wave length values for the N-H bands in aniline as compared with the corresponding values in the alkyl amines. In mono- and dibenzylamine, Figs. 10 and 11, where the amino group is attached to an alkyl rather than to the phenyl group, the N-H bands have the high wave length values 1.55μ and 1.06μ. The contributions of both the phenyl and alkyl C-H pairs are seen in the [1.68, 1.75μ], and possibly the [1.15, 1.20μ] regions.

In the spectra of α-, methyl-α- and ethyl-α-naphthylamine, *p*-, methyl-

p- and ethyl-*p*-toluidine, Figs. 12–17, the N-H bands have the anticipated low values of 1.49–1.51 μ and 1.03 μ. There are traces of the 1.49 μ band in the records of dimethyl-α- and diethyl-α-naphthylamine and dimethyl-*p*-toluidine. That these disappear when treated for the removal of probable primary or secondary amines is shown in the case of the last two substances in the records of Fig. 18. No attempt was made to purify dimethyl-α-naphthylamine. It is of interest to note that the tertiary amines which retain traces of the 3 μ band in Bell's records are included among the compounds which have here been shown to contain impurities.

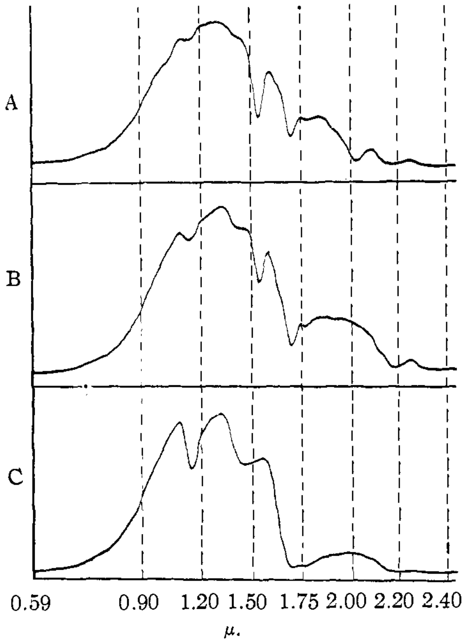

Fig. 11.—A, benzylamine, 2 mm.; B, dibenzylamine, 2 mm.; C, tri-benzylamine, 10 mm.

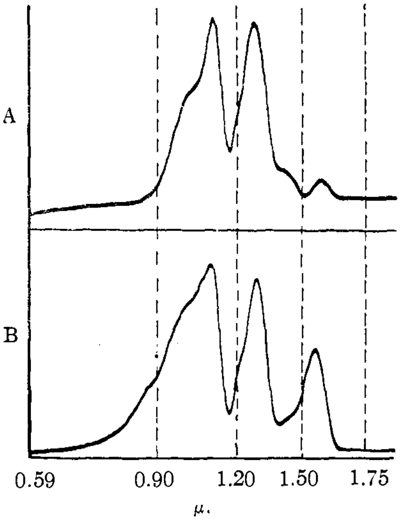

Fig. 12.—A, methyl-α-naphthylamine, 40 mm.; B, di-methyl-α-naphthylamine, 40 mm.

Bell[5d] has found a very pronounced absorption band at 6.25 μ in monoalkyl amines, which practically disappears in the di- and trialkyl amines. He points out that his spectra of primary aryl and aryl-alkyl amines show evidence of absorption by the amino group in this region, although a band characteristic of benzene, naphthalene and their derivatives tends to make interpretation difficult.

Salant[7] has examined the spectra of certain secondary and tertiary amines in the 6.2 μ region with the definite purpose of testing his previous assumption[8] that a fundamental band characteristic of the N-H bond

[7] Salant, *Nature*, **119**, 926 (1927).

[8] Salant, *Proc. Nat. Acad. Sci.*, **12**, 74 (1926).

occurs there. He concludes that such a fundamental does not exist. The strength of the 6.25μ band, however, found by Bell in the monoalkyl amines suggests this as a fundamental.

This band is of interest in connection with a maximum at 2.01–2.03μ observed in the spectra of primary amines in the present paper. It might be regarded as the second harmonic of the 6.25μ band, while those at 1.49–1.51μ and 1.03–1.06μ might be regarded as the third and fifth harmonics respectively. There are two arguments, however, against this interpretation: (1) the deviation from integral multiple relationship among these bands is of the wrong sense; that is, a harmonic should have a slightly longer rather than a shorter wave length than one-half, one-third, etc., of the value of its fundamental; (2) whereas the 1.49–1.55μ and 1.03–1.06μ maxima retain their positions with diminished intensities in passing to the secondary amines, the 2.01–2.03μ maximum either shifts to a longer wave length value or disappears.

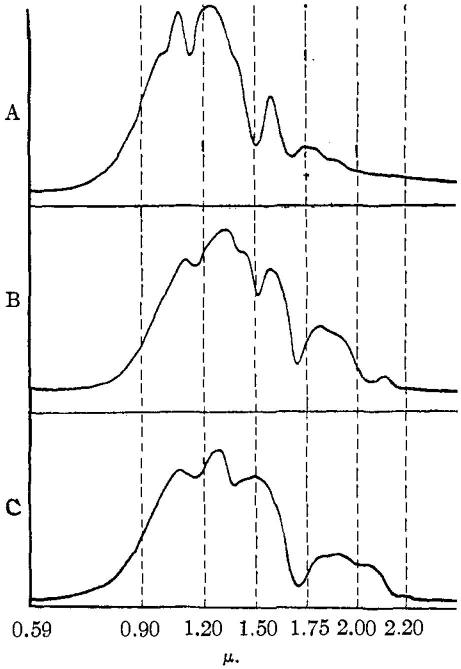

Fig. 13.—A, α-naphthylamine, 10 mm.; B, methyl-α-naphthylamine, 2 mm.; C, dimethyl-α-naphthylamine, 2 mm.

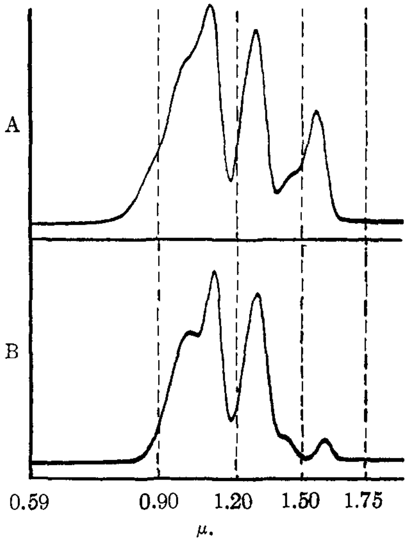

Fig. 14.—A, ethyl-α-naphthylamine, 40 mm.; B, diethyl-α-naphthylamine, 40 mm.

The writer is inclined to interpret the N-H bands in a manner analogous to his modified interpretation of the C-H bands.[2] The 6.9μ and 3.45μ bands, and the 6.75μ and 3.25μ bands, characteristic of alkyl and aryl groups, respectively, are assumed to be associated with two fundamental modes of vibration of the C-H pair. The longer wave length fundamental seems to have no harmonics, while the [1.75 (alkyl), 1.68μ (aryl)], [1.20μ, 1.15μ] and [0.92μ, 0.88μ] bands are regarded as the first three harmonics of the 3.45μ (3.25μ) fundamental. The maxima in the regions of 2.30μ (2.18μ), 1.40μ, 1.02μ and 0.83μ are interpreted as "combinations" of the 6.9μ (6.75μ) band with the 3.45μ (3.25μ) fundamental and its overtones, respectively. A combination band is one whose frequency is determined by the addition of two other frequencies.

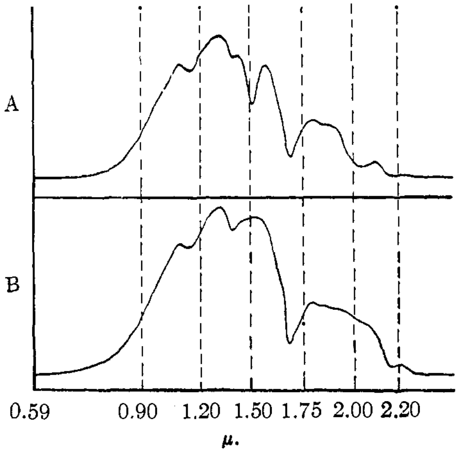

Fig. 15.—A, ethyl-α-naphthylamine, 2 mm.; B, diethyl-α-naphthylamine (purified), 2 mm.

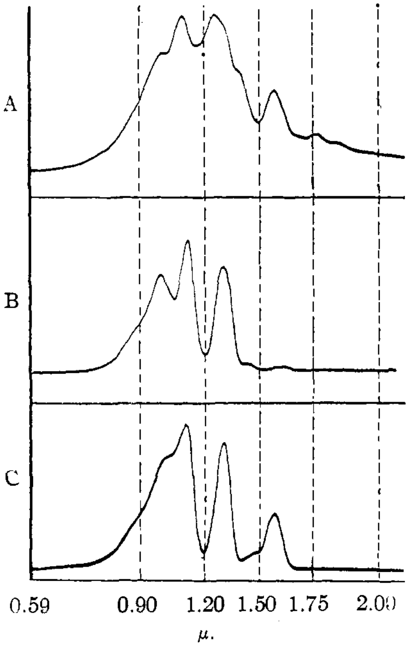

Fig. 16.—A, *p*-toluidine, 10 mm.; B, methyl-*p*-toluidine, 40 mm.; C, dimethyl-*p*-toluidine, 40 mm.

The 6.25μ N-H band may be regarded as analogous to the one at 6.9μ (6.75μ) due to C-H, while the 3.05–2.80μ, 1.55–1.49μ, 1.06–1.03μ series may parallel the 3.45μ (3.25μ) fundamental and its overtones. A combination of the 6.25μ and 3.00–3.05μ frequencies yields a wave length value of 2.03–2.05μ in good agreement with the 2.02μ value observed for the primary alkyl amines and benzylamine. This is illustrated by the following addition of the frequencies of the 6.25μ and 3.00μ values expressed in mm.$^{-1}$: 160 + 333 = 493 mm.$^{-1}$. The wave number of the observed 2.02μ band is 495 mm.$^{-1}$. The agreement is less satisfactory in the case of aniline, however, with a calculated value of 1.93μ as compared to an observed value of 2.01μ. (It will be observed that the interpretation of this band in aniline differs from that given in Part I of this paper.)

In the spectra of methyl-α- and ethyl-α-naphthylamine and methyl-*p*-toluidine this band occurs at 2.03μ, while in the dialkyl amines and dibenzylamine it has apparently shifted to 2.10μ.

In the region 1.21–1.23μ there seems to be evidence of a contribution to absorption by the amino group. This is shown by the records for aniline and diphenylamine in Fig. 9 and for benzyl- and dibenzylamine in Fig. 10. These values are in good agreement with the 1.20–1.24μ combination band calculated from the 6.25μ and 1.49–1.55μ maxima. There is also evidence of the existence of this band in the records for the primary and secondary alkyl amines, but the occurrence of C-H absorption at 1.20μ practically obscures it.

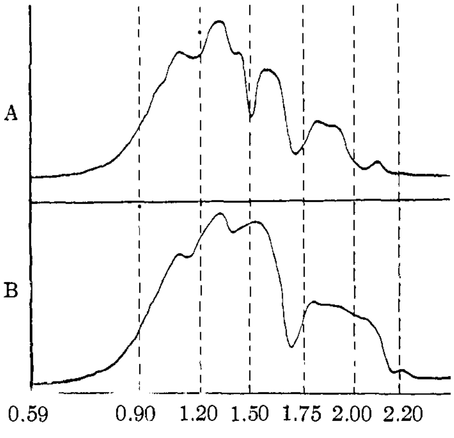

Fig. 17.—A, methyl-*p*-toluidine, 2 mm.; B, dimethyl-*p*-toluidine (purified), 2 mm.

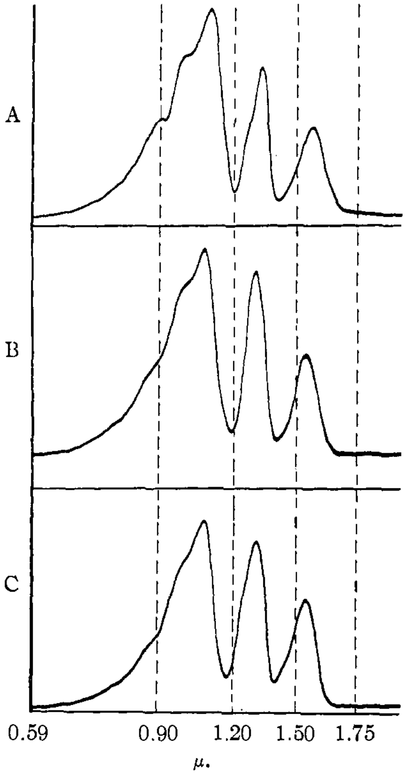

Fig. 18.—A, tri-*n*-propylamine (purified), 40 mm.; B, dimethyl-*p*-toluidine (purified), 40 mm.; C, diethyl-α-naphthylamine (purified), 40 mm.

In Table I is given a summary of the values attributed to the nitrogen-hydrogen linkage, including the measurements on mono-alkyl anilines recorded in the first portion of this paper. The values found by Bell and by Salant for the band near 3μ are included.

TABLE I

BANDS CHARACTERISTIC OF THE N-H BOND

n-Propylamine	3.05μ	1.55μ	1.06μ	2.02μ
Di-*n*-propylamine	3.05; 3.04 S[a]	1.55	1.06	2.10
n-Butylamine	3.00	1.55	1.06	2.02
Di-*n*-butylamine	3.05; 3.01 S	1.55	1.06	2.10
iso-Amylamine	3.00	1.55	1.06	2.02
Di-*iso*-amylamine	3.05; 3.07 S	1.54	1.06	2.10
Aniline	2.80	1.49	1.03	2.01
Diphenylamine	2.90; 2.89 S	1.49	1.03	[b]
Methylaniline	2.80	1.49	1.03	2.06
Ethylaniline	2.90	1.49	1.03	2.06
n-Propylaniline	2.80	1.49	1.03	[b]
n-Butylaniline	2.80	1.49	1.03	[b]
iso-Amylaniline	2.70	1.49	1.03	[b]
Benzylamine	3.00	1.55	1.06	2.02
Dibenzylamine	3.00; 3.00 S	1.55	1.06	2.10
α-Naphthylamine	2.90	1.51	1.03	[b].
Methyl-α-naphthylamine	2.90	1.51	1.03	2.03
Ethyl-α-naphthylamine	2.90	1.51	1.03	2.03
p-Toluidine	...	1.49	1.03	[b]
Methyl-*p*-toluidine	...	1.51	1.03	2.03

[a] All of the 3μ values are from Bell's papers, with the exception of those marked S, which are due to Salant.

[b] Records do not permit of measurement in this region.

The writer is grateful to Dr. G. R. Robertson, who purified certain of the compounds used and to Mr. W. A. Munson for assistance in obtaining the spectra recorded.

Summary

1. Using a registering spectrograph, the infra-red absorption spectra below 2.5μ have been obtained for mono-, di- and tri-*n*-propyl, *n*-butyl and *iso*-amylamine; mono- (aniline), di- and triphenylamine; mono-, di- and tribenzylamine; α-, methyl-α-, dimethyl-α-, ethyl-α- and diethyl-α-naphthylamine; and *p*-, methyl-*p*- and dimethyl-*p*-toluidine.

2. Bands which occur at 1.49–1.55μ and 1.03–1.06μ for the primary amines and with diminished intensities for the secondary amines but which disappear for the tertiary amines, thus apparently originating in the nitrogen-hydrogen linkages, form an "harmonic" series with a band found by Bell at 2.80–3.05μ.

3. Absorption maxima at 2.01–2.03μ and 1.21–1.23μ, apparently also characteristic of the amino group, are suggested as "combination" bands arising from the 2.80–3.05μ and 1.49–1.55μ values taken with a band found by Bell at 6.25μ.

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