[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA, SOUTHERN BRANCH]

INFRA-RED ABSORPTION BY THE N—H BOND. I. IN ANILINE AND ALKYL ANILINES

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RECEIVED NOVEMBER 1, 1926 PUBLISHED FEBRUARY 5, 1927

Recently F. K. Bell[1] graphically presented the results of a careful examination of the infra-red absorption of aniline and of ten mono- and dialkyl anilines in the spectral region between 1μ and 12μ. An infra-red spectrometer of the Hilger type, equipped with a single rock-salt prism and a linear thermopile, was used in the investigation. The appearance of a deep band of absorption at 2.8μ in the spectrum of aniline and a band of somewhat lesser intensity at the same wave-length position in the spectra of the mono-alkyl anilines is of especial interest in connection with the present investigation. The complete disappearance of this band in the spectra of three of the dialkyl anilines and its near disappearance in the spectra of the remaining two suggest that the band originates in the N—H bond.

Subsequent reports by Bell[2] on the absorption in the same spectral region by α-naphthylamine, mono- and dialkyl-α-naphthylamine, di- and triphenylamine, and mono-, di- and tribenzylamine further support this theory. The band varies in position between 2.8μ and 3.0μ in the spectra of these substances, but in every instance it is clearly resolved from the 3.25μ band characteristic of benzene and the 3.4μ band characteristic of alkyl groups.

In the region between 3.5μ and 12μ, Bell points out that no essential spectral changes are produced by alkylation of the amino group in aniline. If there were changes below 2.8μ they would scarcely be detectable because of the poor resolving power resulting from the low dispersion of rock salt.

The purpose of the present study is to investigate the absorption of these compounds below 2.8μ, using a dispersing system much superior to that of rock salt in this particular portion of the spectrum. The apparatus, shown again in plan and in elevation in Fig. 1, has already been described.[3] The source of radiation S is the spiral filament of a 100-candle power, series-burning street lamp, which is operated on direct voltage since the fluctuations of the available alternating voltage are of the order of several per cent. The radiation is brought to a focus upon the symmetrical slit B by means of a quartz lens L of 10 cm. focal length. The rays are reflected by means of the plane front-surface mirror M upon a parabolic mirror R of 3.4 cm. aperture and 30.4 cm. focal length.

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

[2] Bell, *ibid.*, (a) **47**, 3039 (1925); (b) **48**, 813; (c) 818 (1926).

[3] Ellis, *J. Optical Soc. Am.*, **11**, 647 (1925).

They are then dispersed as they pass through a 30° and a 60° quartz prism. The former prism is set so that the rays strike one face practically normally, while the second prism is fixed for minimum deviation for an approximate median wave-length value. Reflection at the plane mirror N causes the rays to retrace their paths through the prisms, causing a narrow spectral region to become focused upon the thermo-elements of a Hilger linear thermopile T. The thermopile actuates a Leeds and Northrup galvanometer G, which gives a deflection of 9.3 mm. per microvolt at a distance of one meter. Rotation of N causes the various parts of the spectrum to pass over the thermo-elements. This is accomplished by having the mirror mounted upon a table capable of rotation about a vertical axis and held taut by a spring K. Uniform motion of the mirror table is secured by means of a threaded collar C on the shaft Q, which in turn is driven by a motor through two worm reduction gears D. At the other end of the shaft is a pair of small bevel gears which lower a photographic plate-holder by means of a rack and pinion. Uniform motion of the plate-holder, however, was not secured until it was counterbalanced by a weight over a pulley P.

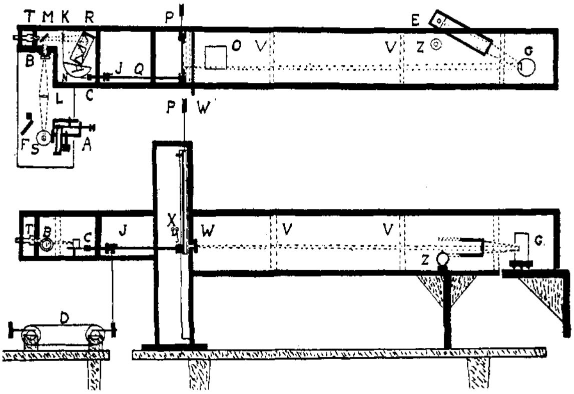

Fig. 1.—The self-registering spectrograph.

The energy-distribution curves are recorded upon regular photographic plates, 11.7 × 43.2 cm., securely held in the plate-holder. The tracing system consists of a straight-filament automobile lamp E, a small portion of whose image is allowed to fall upon the plate through a 1-mm. aperture running the whole width of the plate, when the shutter W is removed. It was found necessary to introduce Diaphragms V to prevent a fogging of the plate due to stray light originating from E. O represents a window for the observation of the position of the tracing image at the beginning of the exposure.

The following steps will reveal the procedure followed in taking a record. The yellow sodium line is used as the reference line in the spectrum. The light is secured without the removal of the source S by swinging the mirror F around to throw the light from a carbon arc A upon the slit. The line observed through the eyepiece on the thermopile mount is brought into approximate coincidence with the thermo-elements through a rotation of the shaft by hand. The plate holder is then engaged and its cover removed. The pin J is inserted and the motor caused to bring the sodium line into exact coincidence with the thermo-elements. At this time the shutter W is removed and the lamp Z turned on for a moment to give a reference line exposure. About ten minutes is required to trace the spectrum to 3μ. At the completion of the run the motor is automatically shut off by a trip X which is released by a stop on the plate-holder.

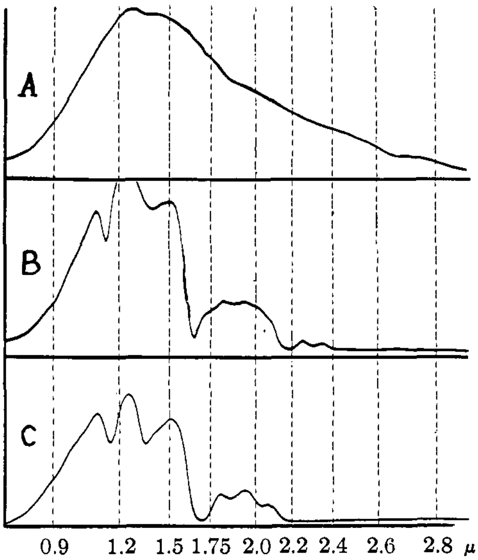

Fig. 2.—*A*, intensity-distribution curve, 8 mm.; *B*, benzene, 8 mm.; *C*, *m*-xylene, 8 mm.

It is found possible to prevent fluctuations of the tracing beam due to jarring by mounting the galvanometer on an isolated support fastened to the outside wall, and by mounting the driving mechanism and the spectrograph on separate tables.

Fig. 2A is a record of the energy-distribution curve as produced by the quartz prism pair and modified by reflection and absorption losses in the optical system and by atmospheric absorption bands due to carbon dioxide and water vapor. The wave-length calibration given is based upon the accepted values for the bands at 2.66μ and 2.73μ for water vapor and carbon dioxide, respectively, and upon early observations of the positions of emission lines caused by introducing certain salts into the carbon arc. The reference line given in Figs. 2–8 is 0.70μ.

The writer[4] has used this recording instrument and also a similar one equipped with flint glass prisms to study the near infra-red absorption spectra of compounds of the aromatic and paraffin series, including compounds with halogen substitutions. A series of outstanding bands has been found to be characteristic of the C—H bond, and although variations in the positions of these bands occur among the compounds, due to the type of molecule and to superpositions of other bands, a parabolic series

[4] Ellis, (a) *Phys. Rev.*, **23,** 48 (1924); (b) **27,** 298 (1926); (c) **28,** 25 (1926); (d) *J. Optical Soc. Am.*, **8,** 1 (1924).

has been found to fit the average frequency values of all the compounds examined. Expressing the frequency ν as the wave number per millimeter, this formula may be written

$$\nu_n = 148n - 2.61n^2 \tag{1}$$

where n takes on integral values, 1,2,3, etc., thus defining the position of the member in the series. The first two members of the series lie outside the region transmitted by quartz or glass, but may be identified in spectra obtained by other investigators using rock-salt or fluorite prisms. The first member occurs between 6μ and 7μ while the second member is the band referred to above as occurring at 3.25μ and 3.4μ in phenyl and alkyl groups, respectively. As high as the tenth member has been found in a number of instances, this band lying in the visible red near 0.76μ.

Bands of lesser intensity have been identified with other bonds. Thus, it appears that C—Cl, C—Br, C—I and C—C bonds give rise to *linear* series of bands with initial members at 16.8μ, 17.2μ, 17.5μ and 28μ, respectively.

The present investigation was undertaken to learn if there are bands below 2.8μ characteristic of the N—H bond which bear a series relationship to the 2.8μ band observed by Bell. Small quantities of aniline and of the ten alkyl anilines studied by Bell were purchased from the Eastman Kodak Company, from whom this investigator also secured his compounds. The alkyl anilines used were methylaniline, dimethylaniline, ethylaniline, diethylaniline, methylethylaniline, n-propylaniline, di-n-propylaniline, n-butylaniline, di-n-butylaniline and *iso*-amylaniline.

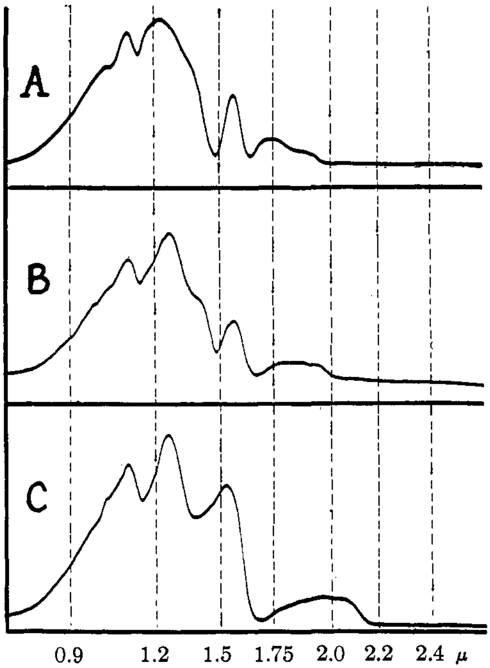

Fig. 3.—*A*, aniline, 8 mm.; *B*, methylaniline, 8 mm.; *C*, dimethylaniline, 8 mm.

Reproductions of the original records are shown in Figs. 3–8. The cell thickness was 8 mm. in Figs. 3–6, but to bring out certain details records were taken for 50mm. cells of aniline and methylaniline, Fig. 7, and for 0.5mm. cells of aniline, methylaniline and ethylaniline, Fig. 8. For comparative purposes records of 50mm. and 0.5mm. cells of benzene are included in these figures. The variation in the ordinates among these curves is not due to varying general absorption for the various compounds, but is due to unequal intensities in the source, unequal reflection losses, etc.

In Fig. 2, in addition to the energy-distribution curve, the absorption curves for 8mm. cells of benzene and *m*-xylene are shown, the latter being typical of the modifications introduced into the benzene spectrum by the replacement of hydrogen atoms by alkyl groups. The benzene bands at 2.18μ, 1.66μ, 1.39μ, 1.145μ, 1.03μ and 0.885μ, appearing in Figs. 2, 7 and 8, are the third to the eighth members of the C—H series of the benzene type. The positions of some of the bands, however, are affected by the partial superposition of other bands. The first and second members of this series appear in the work of Coblentz[5] at 6.75μ and 3.25μ, respectively. Bands corresponding to these have been recorded near 6.86μ and 3.45μ in the spectra of saturated hydrocarbons, while compounds containing both phenyl and alkyl groups show bands at intermediate positions. In the work of Bell[2c] upon di- and tribenzylamine, these two types of band have been separated through the increased resolving power of the instrument used. The writer's curves appearing in the articles referred to above show the C—H bands shifted toward longer wave lengths in the paraffin compounds, while they show an actual duplicity in some instances in the spectra of compounds containing both phenyl and alkyl groups and a broadening indicative of duplicity in other instances. Thus, in the spectrum of *m*-xylene, Fig. 2, is seen the broadening of the bands at 2.2μ, 1.7μ, 1.18μ and 0.9μ.

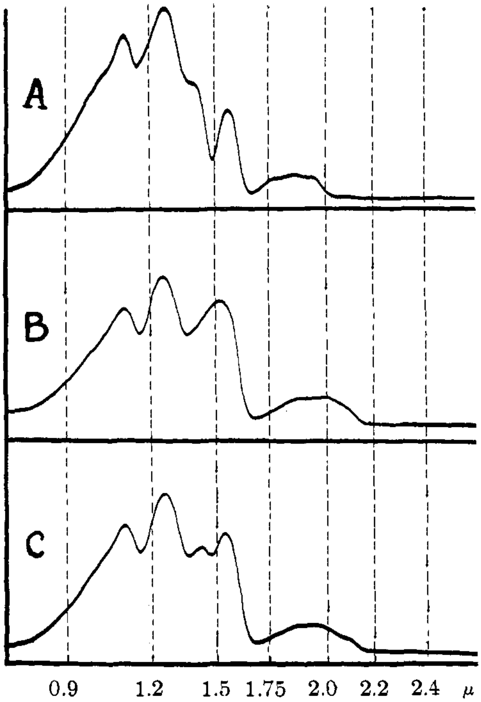

Fig. 4.—*A*, ethylaniline, 8 mm.; *B*, diethylaniline, 8 mm.; *C*, methylethylaniline, 8 mm.

The replacement of a hydrogen atom in benzene by an amino group introduces two new bands as shown in the spectrum of aniline in Fig. 3.

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[5] Coblentz, "Investigations of Infra-red Spectra," *Carnegie Inst. Publ.*, 1905.

These bands lie at 1.47μ and 1.04μ. Upon the replacement of one hydrogen atom of the amino group by a methyl group (Fig. 3) these bands still occur, but with diminished intensity while, when both N—H bonds are destroyed as in dimethylaniline (Fig. 3C) at the most only a trace of these bands appear. Likewise, in the spectra of ethylaniline, *n*-propylaniline, *n*-butylaniline and *iso*-amylaniline these bands occur with intensities comparable to those of methylaniline, although the slope of the intensity-distribution curve tends to obscure the 1.04μ band. Again, in the spectra of diethylaniline and di-*n*-propylaniline these bands have disappeared, but in the case of di-*n*-butylaniline there is a very distinct trace of the 1.47μ band and in the spectrum of methylethylaniline there is a very pronounced band at this position. This band in the latter two substances was suspected to be due to impurities in the compounds, and to test this, steps were taken to purify the substance in which the suspected impurity seemed to appear in the greatest amount. This process of purification was carried out by Dr. G. R. Robertson of the Department of Chemistry, whose description of the method used is given in the following paragraph.

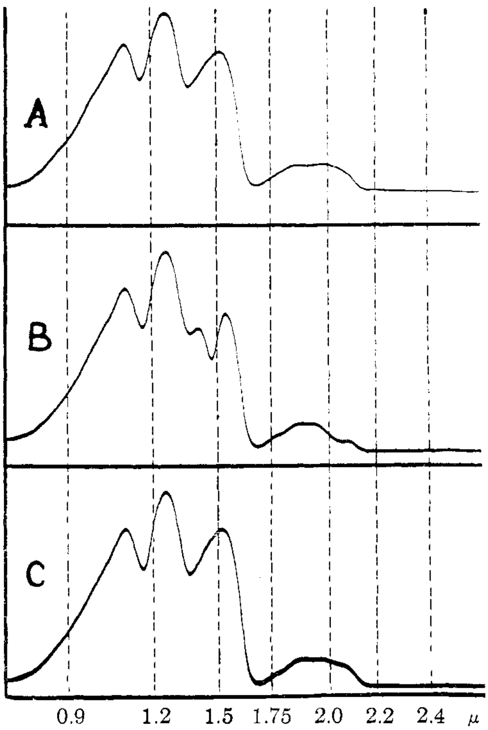

Fig. 5.—*A*, methylethylaniline (purified), 8 mm.; *B*, *n*-propylaniline, 8 mm.; *C*, di-*n*-propylaniline, 8 mm.

"The methylethylaniline was mixed with an excess of freshly distilled acetic anhydride, whereupon a decided rise in temperature was noted, suggesting the possible presence of a primary or secondary amine. The mixture was heated to 100° and allowed to stand for several hours with the aim of converting these lower amines into their water-soluble and involatile acetyl derivatives. The liquid was now washed with water and dilute alkali to eliminate the excess of anhydride as well as the supposed acetyl derivatives. It was then extracted with ether, the extract dried with anhydrous sodium sulfate, freed from ether on the steam-bath and distilled through an air condenser. The wide boiling range (200–215°) indicated the possible presence of impurities such as diethylaniline or other high-boiling tertiary amines not affected by acetic anhydride."

When a record of the purified sample was taken, the band in question had completely disappeared (Fig. 5).

It is of interest to note that in Bell's records it is the methylethylaniline which shows the presence of the 2.8μ band, traces of which are also found in his record of dimethylaniline.

To make certain that the presence of the 1.47μ band of methylethylaniline was not due to moisture in the liquid, a portion of the original sample was distilled and observations were made on a middle portion of the distilled product. The band in question, however, remained.

The 1.04μ and 1.47μ bands, taken with the one at 2.8μ, form a parabolic series similar to the C—H series represented by Equation 1. The exact form of this equation is

$$\nu_n = 376n - 18.3n^2 \qquad (2)$$

where ν again is expressed in waves per millimeter. The degree of accuracy with which this equation fits the experimental data is shown by Table I. It is believed that the two wave-length values determined by the author are accurate within ±1% and the wave-number values are expressed within these limits. Although Bell does not give a third significant figure for his 2.8μ value, the instrument which he used should yield such a figure. In Table I, therefore, this value is assumed to be $2.80 \pm 0.03\mu$.

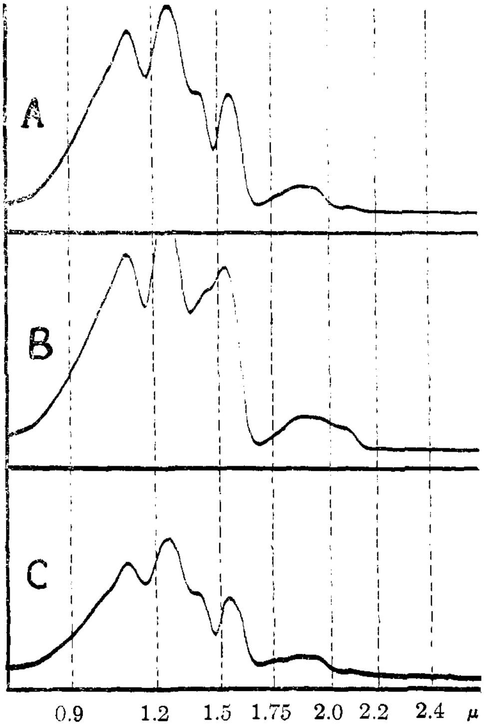

Fig. 6.—*A*, *n*-butylaniline, 8 mm.; *B*, di-*n*-butylaniline, 8 mm.; *C*, *iso*-amylaniline, 8 mm.

TABLE I

BANDS CHARACTERISTIC OF N—H

n	λ, obs., μ	ν, obs.	ν, calcd.
1	2.80 ± 0.03	357 ± 4	358
2	$1.47 \pm .015$	680 ± 7	679
3	$1.04 \pm .01$	961 ± 10	963

The absorption bands whose frequencies are expressed by Equations

1 and 2 may arise from oscillations of the C—H and N—H pairs of atoms, respectively. On the basis of the classical radiation theory they may be looked upon as determined by a fundamental rate of vibration of the atomic pair and approximate harmonics of this rate, that is, as true resonance frequencies. On the basis of the quantum theory they may be regarded as determined by energy changes occasioned by changes in the rates of vibration of the atomic pair. In either case the departure from Hooke's law in the bonding force would cause a deviation from linearity in the resulting series of absorption bands. The writer[4b] has already pointed out that the degree of departure from linearity in the case of the C—H series probably arises from the finite amplitude of vibration of the hydrogen atom, which thus causes a marked failure of Hooke's law. There is a much greater deviation in the case of the N—H series, suggesting an even greater amplitude of the hydrogen atom in this instance. Since energy is proportional to the square of the amplitude, it follows that the N—H pair should absorb more strongly than the C—H pair. Such is actually seen to be the case in Bell's curves, the two N—H groups in aniline producing a deeper band than the five C—H groups.

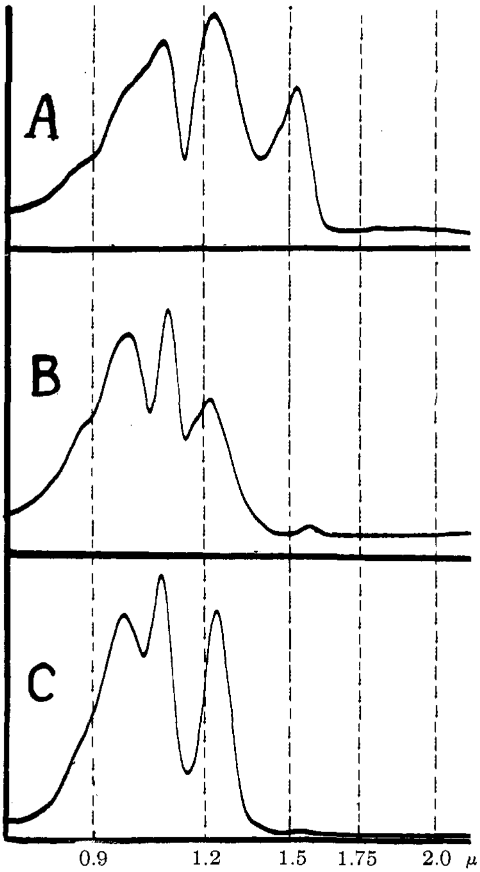

Fig. 7.—*A*, benzene, 50 mm.; *B*, aniline, 50 mm.; *C*, methylaniline, 50 mm.

To bring out more clearly the 1.04μ band and to seek a possible fourth member of the N—H series near 0.8μ, curves were obtained for 50mm. cells of aniline and methylaniline. No band corresponding to the latter could be detected, but the 1.04μ band was clearly brought out.

The spectra of the mono- and the dialkyl anilines show the presence of both the phenyl and the alkyl type of C—H band. This is especially noticeable in the neighborhood of 1.7μ and 1.2μ.

The curves of Figs. 3–6 show that absorption near 2.0μ is modified by the presence of N—H groups within the molecule. To study this region more advantageously, curves for three of the compounds, namely, aniline, methylaniline and ethylaniline, were recorded for cells of 0.5 mm. thickness (Fig. 8). A similar curve for benzene is also to be found in this figure. The segment of a curve in Fig. 8 is likewise due to ethylaniline, greater intensity in the source of energy having been used in this instance. These curves show a strong band at 2.00μ for aniline which is shifted to 2.05μ for methylaniline and ethylaniline. In previous papers the writer has shown considerable evidence indicating the existence of bands whose frequencies are determined by the addition of frequencies characteristic of different groups within the molecule. This has led him to attempt to identify the 2μ band above in a similar manner. The initial C—H band of aniline occurs at 6.6μ in Bell's spectra. Representing the frequency of this band by ν_1' and that of the 2.8μ band by ν_1, a wave-length value of 1.965μ is obtained for a $\nu_1+\nu_1'$ band, which is in fair agreement with the 2.00μ band observed. Taking 6.85μ as the initial C—H wave-length value of an alkyl group and calculating a corresponding $\nu_1 + \nu_1'$ band, an increased value of 1.985μ as compared with the 2.05μ band observed in methylaniline and ethylaniline is obtained.

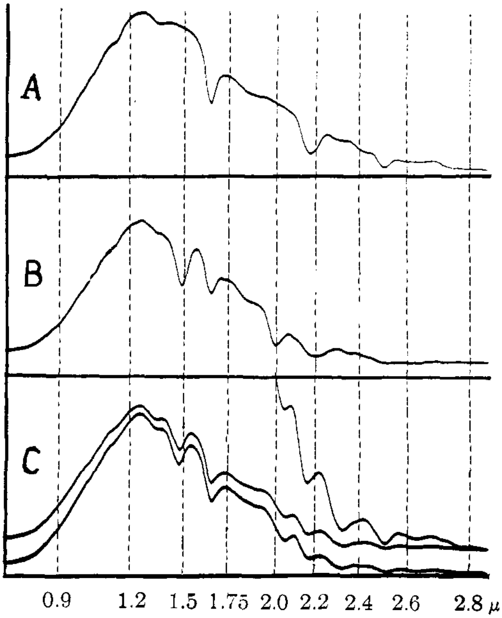

Fig. 8.—*A*, benzene, 0.5 mm.; *B*, aniline, 0.5 mm.; *C*, ethylaniline (upper), 0.5 mm. *C*, methylaniline (lower), 0.5 mm.

Designating the frequency of the 1.47μ N—H band by ν_2, a value of 1.20μ is obtained for $\nu_2 + \nu_1'$. The aniline curve in Fig. 7B shows a band at this position which does not occur in the spectrum of benzene. Such a band could not be detected in the spectra of methylaniline and ethylaniline because of the occurrence at that position of an alkyl C—H band.

Salant[6] has made a special examination of the absorption of some di- and trialkyl amines, di- and triphenylamine and di- and tribenzylamine in the region 2.7μ to 3.5μ and has found that a band varying from 2.89μ to 3.08μ which characterizes each of the secondary amines, completely

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

vanishes in the tertiary amines. From this he deduces the conclusion that this band represents the first overtone frequency characteristic of the N—H bond, the fundamental band occurring near 6.1μ. He is led to this conclusion through the fact that ammonia has bands of absorption at 6.1μ and 2.96μ. Although the measurements by Bell on alkyl, benzyl- and phenylamines show a variation in absorption near 6μ as well as distinct bands near 3μ, thus supporting Salant's hypothesis, the hypothesis receives no support in the case of the anilines, for no detectable change in absorption occurs at 6μ.

The author plans to extend the investigation to a study of a number of alkyl amines, benzylamines, phenylamines and alkyl naphthylamines.

Summary

1. The infra-red absorption spectra below 2.8μ have been recorded for aniline and ten mono- and dialkyl anilines by means of a self-registering spectrograph.

2. Absorption bands occurring at 1.47μ and 1.04μ are associated with the presence of N—H bonds within the molecule, and these taken with a band found by Bell at 2.8μ are shown to form a three-membered, parabolic frequency series.

3. A possible identification of bands near 2.0μ and 1.2μ as combinations of N—H frequencies and a fundamental C—H frequency is suggested.

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DIPHENYLBENZIDINE AS AN INTERNAL INDICATOR FOR THE TITRATION OF ZINC WITH POTASSIUM FERROCYANIDE

By W. H. Cone and L. C. Cady

Received November 1, 1926 Published February 5, 1927

At present there is no suitable internal indicator for the titration of zinc with potassium ferrocyanide. The authors have been able to find only one inside indicator suggested for this titration, namely, the use of ferrous sulfate by Scott.[1] This indicator had been suggested for use only in the titration of zinc ores prepared for analysis by the hydrogen sulfide method, in which case there are no oxidizing agents present.

Uranium nitrate, the indicator largely used at present, has the disadvantage of being an external indicator. Much time is required to determine the exact end-point and an error is introduced in removing portions of the solution for testing. At best, the titration must proceed slowly and a blank correction be applied to the volume of titrating solution required.

The use of diphenylamine or diphenylbenzidine as indicators depends

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[1] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1920, p. 484.