180–182° (24 mm.) was obtained. Analysis showed this oil to be the ester; yield, 55.9%, after deducting the unchanged chloride recovered. This ester is a heavy, colorless oil with slight aromatic odor. It is insoluble in water but soluble in the common solvents.

Anal. Calcd. for $C_{10}H_9O_2N$: N, 8.0. Found: (Kjeldahl) 7.8.

(b) *o*-**Cyanobenzyl Benzoate.**—Sixty g. of benzoic acid was dissolved in the calculated amount of 10% sodium hydroxide solution and the whole made up to 300 cc. Fifty g. of *o*-cyanobenzyl chloride was added and the mixture stirred for seven hours at 100–110°. A reddish-brown, crystalline mass settled as the liquid cooled; this was extracted with ether. The ether extract was washed with water, dried and the ether distilled. The unchanged *o*-cyanobenzyl chloride was distilled under diminished pressure and 17 g. was recovered. The residue in the flask was fractionally crystallized from alcohol. This ester is a white, odorless, crystalline solid. It is insoluble in water but soluble in the common solvents; m. p., 54–55°; yield, 18 g., or 34.8%, calculated on the amount of unchanged chloride recovered.

Anal. Calcd. for $C_{15}H_{11}O_2N$: N, 5.9. Found: (Kjeldahl) 5.8.

p-**Carboxybenzyl Acetate.**—Ten g. of *p*-carboxybenzyl alcohol and 15 g. of acetyl chloride were heated together for five hours on a boiling water-bath. The resulting clear oil was poured into 200 cc. of water, and 12 g. of a crude, white solid was obtained. This was crystallized from a mixture of ether and petroleum ether; yield, 7.5 g., or 58.6%; m. p., 123–124°. This ester is soluble in the common solvents and in alkaline solutions but insoluble in water.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.83; H, 5.19. Found: C, 61.59; H, 5.12.

Summary

An improvement in the preparation of *o*- and *p*-cyanobenzyl chloride has been described and some new esters of *o*-cyanobenzyl alcohol and *p*-carboxybenzyl alcohol have been made. The reaction that the sodium salt of *p*-carboxybenzyl chloride undergoes in a neutral water solution has been investigated and the new ester, *p*-carboxybenzyl-*p*-chloromethyl benzoate has been isolated.

LEXINGTON, KENTUCKY

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC DERIVATIVES OF AMMONIA. I. ANILINE AND SOME MONO- AND DIALKYL ANILINES

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RECEIVED APRIL 27, 1925 PUBLISHED AUGUST 5, 1925

Introduction

The relation between light absorption and chemical constitution is a subject that has received considerable attention. Aside from the theoretical significance of such a relation, its practical aspect which presents the possibility of both qualitative and quantitative analysis of unknown substances is of especial interest to the chemist.

A survey of the literature reveals clearly that, in the case of organic compounds, at least, attention has been directed particularly to the study of the visible and ultraviolet regions of the spectrum with the result that information concerning the infra-red absorption is of a very general nature.

The infra-red region, by virtue of its greater extent, offers a fertile field for investigation, and the fact that the measurement of infra-red absorption is especially adapted to the study of small quantities of substances is of great importance in certain lines of investigation.

On the other hand, the preparation of layers of solid substances for study in this region presents certain unfortunate difficulties, and both of our universal solvents, water and alcohol, are too opaque to the longer infra-red rays to permit the use of these liquids.

Of the more recent literature concerning the measurement of infra-red absorption spectra, first attention must be directed to a monograph by W. W. Coblentz[1] in which the absorption spectra, as far as 15.0μ, of more than 130 compounds are described together with the method of measurement.

The work of Henri and his collaborators, covering a period of some years, has appeared in the form of a convenient monograph[2] which is devoted largely to a consideration of the relation between the infra-red and ultraviolet absorption spectra.

Weniger[3] has employed a graphic method of recording the infra-red absorption of 37 organic compounds, including alcohols, acids and esters, which were selected so as to show the influence of homology and isomerism on the absorption spectra as far as 14.0μ.

Spence[4] has measured the absorption spectra, between 0.5 and 15.0μ, of 25 alkaloids. Johnson and Spence[5] studied the reflection and transmission of 24 aniline dyes as far as 12.0μ. Stang[6] determined the absorption of solutions of naphthalene and some of its mono-derivatives, using both carbon disulfide and carbon tetrachloride as solvents. In the near infra-red as far as 2.5μ, Ellis[7] studied the absorption of 31 organic liquids. Recent papers by Lecomte[8] embrace the study of more than 100 organic liquids between 1.0 and 14.0μ, particular attention being directed to the influence of homology and isomerism.

Purpose of the Investigation

In the study of compounds elaborated in the animal organism or by bacteria, the investigator is often confronted with complex mixtures of unknown substances whose isolation and identification would be greatly facilitated by any data, even if only qualitative, as to their chemical nature. Since organic derivatives of ammonia play such an important role in all phases of biology and medicine, a number of simple representatives of various types of nitrogen bases have been selected for systematic study.

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[1] Coblentz, "Investigations of Infra-Red Spectra," Carnegie Inst. Pub., **35** (1905).

[2] Henri, "Études de Photochimie," Gauthier-Villars et Cie., Paris, **1919**.

[3] Weniger, *Phys. Rev.*, **31**, 388 (1910).

[4] Spence, *Astrophys. J.*, **39**, 243 (1914).

[5] Johnson and Spence, *Phys. Rev.*, **5**, 349 (1915).

[6] Stang, *ibid.*, **9**, 542 (1917).

[7] Ellis, *ibid.*, **23**, 48 (1924).

[8] Lecomte, *Compt. rend.*, **178**, 1530, 1698, 2073 (1924).

In this first paper are described the absorption spectra of aniline and a number of its mono- and dialkyl derivatives in the region from 1.0 to 12.0μ.

Description of Apparatus

General.—In the selection of the experimental method and apparatus, the existing literature and the usual standard texts[9] have furnished many suggestions.

The description of the optical system employed may be conveniently divided into two sections: the external system by means of which an image of the light source is projected upon the entrance slit of the spectroscope, and the spectroscope itself.

This optical system is shown diagrammatically in Fig. 1.

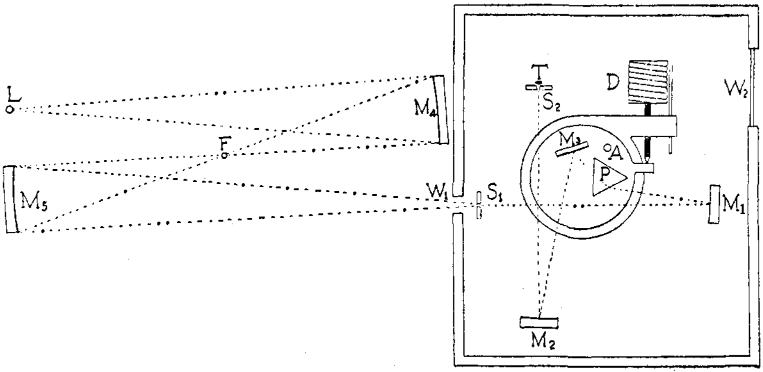

Fig. 1.

The light from a Nernst filament at L falls upon the concave mirror M_4, which projects a reduced image of L at F. The light then falls on the concave mirror M_5, which throws an image of L on S_1, the entrance slit of the spectroscope. The dotted line proceeding from S_1 indicates the path of a single light ray in the spectroscope system.

An image of the illuminated slit S_1 is projected upon the concave mirror M_1. The light reflected by this mirror is dispersed by the prism P and, after falling on the plane mirror M_3, is reflected upon the concave mirror M_2, and thence to the slit S_2, back of which is situated a thermopile T, which was connected with a mirror galvanometer.

The External System.—The Nernst filament in series with the usual resistance was operated directly from the lighting circuit. The similar concave mirrors M_4 and M_5 had an aperture of 8 cm., a radius of curvature of 40 cm. and were silvered on the first surface. Both mirrors were mounted in brass fixtures, and screw caps were provided. The position of Mirror M_4 was permanently fixed while the mounting of Mirror M_5 included three set screws by means of which the position of the image thrown on S_1 could be accurately and readily adjusted. The mountings of the Nernst filament and the two mirrors were tightly clamped on separate heavy iron stands whose bases were screwed to the top of the work table. A system of heavy iron braces minimized the possibility of any individual movement of either mirror or of the light source.

The light source L and the mirror M_5 were placed as close together as possible in order to minimize distortion of the image at S_1.

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[9] Particularly, Kayser's "Handbuch der Spectroscopie," S. Hirzel, Leipzig, 1902.

A hood was placed around the Nernst filament and was of sufficient length to prevent any light falling directly on the entrance slit of the spectroscope.

The Spectroscope.—The infra-red spectroscope was a stock instrument as listed and supplied by the Gaertner Scientific Corporation. It is a constant deviation spectroscope of the Wadsworth type.

Four arms of the spectroscope served as mountings, respectively, for the slit S_1, mirrors M_1 and M_2, and slit S_2 together with the thermopile T. The central pedestal served as a mounting for the rock salt prism P, and the mirror M_3. The relative position of this mirror and the prism was permanently fixed on a table which could be rotated eccentrically about the axis A by rotating the calibrated drum D. The drum was calibrated in tenths of a micron and the limit of the instrument was 12.0μ. It is thus seen that any desired wave-length region could be made to fall on Slit S_2 by proper setting of Drum D.

The mirrors M_1, M_2 and M_3 were gold-plated on glass and were carefully covered when not in use. Similarly and more importantly, the rock-salt prism was covered at all times when not in use. For this purpose a screw cap with fine thread was supplied with the instrument.

The spectroscope was enclosed in a heavy wooden box as indicated in Fig. 1. The inner walls were blackened. The glass window at W_2 was provided with a shutter which was opened when drum settings were made. An opening at W_1 was also supplied with a shutter by means of which light could be admitted to or excluded from the entrance slit of the spectroscope.

An extension arm from the micrometer of each slit (S_1 and S_2) made adjustment of the slit width possible without opening the box. Similarly, the drum D was equipped with an extension arm.

The thermopile at T was of the Coblentz type, and as an additional precaution a small wooden box was built around that arm of the spectroscope and packed with cotton.

Galvanometer.—The two leads from the thermopile were connected with a Leeds and Northrup mirror galvanometer of high sensitivity. The usual lamp and scale were used for measuring galvanometer deflections.

Mountings.—Unfortunately, a basement room was not available for the present work and particular attention was directed to minimizing the influence of vibration. To this end, a heavy shelf was built directly from one wall of the room which was an outside wall of the building. All apparatus indicated in Fig. 1 was mounted on this shelf together with the lamp and scale of the galvanometer system.

The galvanometer was mounted on the opposite wall of the room at a distance of approximately 5 meters from the lamp and scale. An oil suspension according to the method of White[10] was found to be highly satisfactory.

The Absorption Cell.—In the preparation of the absorption cells some slight changes have been made in the methods already described in the literature. Rock-salt plates were used for making the cells. The plates were cleaved from a selected crystal and no attempt was made to polish the surfaces. The size of the plates was approximately 20 × 30 × 5 mm. Such a plate was cleaved to yield two plates of 2.5 mm. thickness.

[10] White, *Phys. Rev.*, **19**, 305 (1904).

On the newly cleaved surface of one of the plates, a U-shaped piece of lead foil of proper thickness was placed so that the open end of the U projected somewhat beyond one of the edges of the plate. A narrow, shallow channel was then cut in the plate along the inside edge of the lead foil. One end of the channel was enlarged to approximately the size of the tip of a fine capillary pipet used to introduce the liquid into the finished cell. After covering that portion of the surface of the plate outside of the lead foil U with Le Page's liquid glue, the second plate was placed upon it in such a way that the two plates occupied the same position relative to each other that they did before cleavage except that they were separated from each other by a distance equivalent to the thickness of the lead foil. They were then clamped together by means of two wooden spring-clips which were left in position for several days until the glue had thoroughly set. Without the aid of the channel described above, it would be extremely difficult, if not impossible, to fill cells of the thicknesses used, 0.025 and 0.05 mm. Inasmuch as little confidence could be placed in attempts to clean such cells after use, they were discarded after being used once.

The cell containing the substance whose absorption is to be measured is to be placed at the point F (in Fig. 1) which represents a reduced image of the Nernst filament, the size of which was approximately 1.5 × 10 mm. These dimensions, then, give the minimum size of the U-shaped chamber of the cell. Actually, the chambers were made much larger than this minimum.

It is of course necessary to correct for the absorption of the cell material, rock salt. In other words, the absorption of the cell containing the liquid under investigation must be compared with the absorption of the empty cell or, more practically, with the absorption of a rock-salt plate having the same thickness as that of the cell.

To this end, a device very similar to that used by Coblentz has been employed. A brass plate having the necessary attachments such that it could be displaced vertically along two guide rods was placed at F so that its face was normal to the light reflected from the mirror M_4.

Two openings, each 1 cm. wide and 2 cm. long, were cut in the brass plate and were located in a vertical line separated by a distance of 2 cm. By raising or lowering the plate, either one of the two openings could be made to include the image of the Nernst filament at F. Stops were placed above and below at the proper positions on the guide rods, so that when the plate rested on the lower stop the upper opening of the plate was in the path of the light and when the plate was raised as far as the upper stop permitted, the lower opening of the plate was in the path of the light. The raising and lowering of the brass plate was accomplished by means of a string and pulley system.

The absorption cell was clamped securely over one of the openings of the plate and over the other opening a rock-salt plate of proper thickness was clamped. In this way, all light reaching the entrance slit of the spectroscope could be made to pass, at will, either through clear rock salt or through the absorption cell.

Procedure

After the cell, containing the substance to be studied, and the rock-salt plate had been clamped in their proper positions on the vertical slide, the set screws of Mirror M_5 were adjusted until the image of the slit S_1 on the mirror M_1 was sharp, properly centered and of uniform brilliance.

The lid of the box enclosing the spectroscope was closed and the galvanometer was connected with the thermopile. After a lapse of approximately 30 minutes, temperature equilibrium was established and the zero of the galvanometer became constant.

The wave-length drum was then set at 12.0μ. With the cell in the path of the light, the shutter at W_1, which had been previously closed, was raised and the deflection of the galvanometer as shown on the scale was recorded. Then without closing the shutter, the vertical slide was adjusted so as to bring the rock-salt plate in the path of the light, and the deflection of the galvanometer was again noted. The shutter was then closed.

Since these galvanometer deflections are directly proportional to the amount of light falling on the thermopile, their ratio gives the percentage transmission of the given substance for the wave length indicated by the drum setting.

The wave-length drum was then set for 11.9μ and a similar pair of readings was obtained. This procedure was continued at intervals of 0.1μ. No readings were made for wave lengths shorter than 1.0μ.

Each pair of readings was made in approximately 30 seconds and an interval of one minute between each pair of readings was usually sufficient time for the galvanometer to return to its zero position. A complete series of readings from 1.0 to 12.0μ required approximately four hours.

It will thus be seen that by taking readings in pairs the influence of variation in the intensity of the light source and other variable factors could be at least partially eliminated.

The two spectroscope slits were always used at their maximum height of 15 mm. The widths of the slits were reduced from time to time as the shorter wave lengths were approached. The widths of both slits were kept the same at all times.

In the present work, the initial slit width (at 12.0μ) was 0.5 mm. Since the distribution of energy in the radiation from the Nernst filament is not uniform, but reaches a maximum in the region of 2.5μ, reduction in slit width becomes necessary in order to keep the galvanometer deflection on the scale. More important, the dispersion of rock salt is greatly reduced in the region of 3.0μ and the higher resolving power due to reduced slit width becomes especially desirable. The exact control of the slit widths is indicated in Table I.

Materials

In the present investigation 11 compounds were studied: aniline, mono- and dimethylaniline, methylethylaniline, mono- and diethylaniline, mono- and di-*n*-propylaniline, mono- and di-*n*-butylaniline and *iso*-amylaniline. All of these substances were obtained from the Eastman Kodak Company and were designated as of "highest purity."

TABLE I

DIMETHYLANILINE

Thickness of cell, 0.05 mm.

λ	I	I_0	I/I_0	λ	I	I_0	I/I_0	λ	I	I_0	I/I_0
12.0[a]	20	25	80.0	8.3	14	61	23.0	4.6	27	29	93.1
11.9	22	26	84.6	8.2	17	67	25.4	4.5	29	31	93.5
11.8	21	26	80.7	8.1	12	67	17.9	4.4	30	33	90.9
11.7	18	25	72.0	8.0	17	73	23.3	4.3	29	32	90.6
11.6	14	28	50.0	7.9[c]	13	31	42.0	4.2	17	20	85.0
11.5	12	28	42.9	7.8	15	31	48.4	4.1	20	23	87.0
11.4	20	30	66.7	7.7	18	35	51.5	4.0	38	43	88.4
11.3	25	31	80.6	7.6	16	36	44.5	3.9	40	47	85.1
11.2	26	33	78.8	7.5	10	37	27.0	3.8	43	51	84.3
11.1	28	35	80.0	7.4	6	38	15.8	3.7	45	57	79.0
11.0	28	34	82.4	7.3	6	40	15.0	3.6	47	61	77.0
10.9	29	36	80.5	7.2	13	40	32.5	3.5[f]	11	21	52.4
10.8	29	39	74.3	7.1	21	42	50.0	3.4	4	24	16.7
10.7	23	39	59.0	7.0	21	44	47.7	3.3	4	27	14.8
10.6	15	41	36.6	6.9	14	43	32.6	3.2	7	21	33.3
10.5	14	41	34.2	6.8	8	43	18.6	3.1	18	35	51.5
10.4	25	45	55.5	6.7	10	44	22.8	3.0	30	36	83.3
10.3	31	47	66.0	6.6	8	44	18.2	2.9	37	42	88.0
10.2	30	47	63.9	6.5	9	38	23.7	2.8	39	45	86.6
10.1	24	51	47.1	6.4	13	40	32.5	2.7	40	45	88.9
10.0	22	53	41.5	6.3	14	50	28.0	2.6	36	39	92.2
9.9[b]	20	30	66.7	6.2	10	66	15.2	2.5	38	41	92.7
9.8	23	32	71.9	6.1	14	66	21.2	2.4	50	54	92.6
9.7	16	32	50.0	6.0	31	58	53.5	2.3	59	67	88.0
9.6	12	33	36.4	5.9[d]	20	31	64.3	2.2	65	73	89.0
9.5	18	35	51.5	5.8	24	32	75.0	2.1	76	82	92.7
9.4	11	38	29.0	5.7	27	37	73.0	2.0	84	86	97.7
9.3	15	39	38.5	5.6	31	39	79.5	1.9	86	88	97.8
9.2	22	41	53.7	5.5	39	46	84.8	1.8	83	85	97.6
9.1	24	43	55.9	5.4	40	50	80.0	1.7	85	88	96.6
9.0	25	45	55.5	5.3	45	54	83.3	1.6	81	84	96.4
8.9	20	46	43.5	5.2	47	59	79.7	1.5	77	79	97.5
8.8	15	48	31.3	5.1[e]	15	20	75.0	1.4	66	68	97.1
8.7	15	52	28.9	5.0	19	23	82.6	1.3	55	57	96.5
8.6	13	53	24.6	4.9	23	25	92.0	1.2	43	44	97.7
8.5	11	56	19.6	4.8	24	27	88.9	1.1	30	32	93.7
8.4	14	58	24.1	4.7	22	26	84.6	1.0	20	21	95.2

[a] Initial slit width 0.5 mm.

[b] Slit width reduced to 0.375 mm.

[c] Slit width reduced to 0.25 mm.

[d] Slit width reduced to 0.19 mm.

[e] Slit width reduced to 0.125 mm.

[f] Slit width reduced to 0.08 mm.

Tabulation of Results

In Table I the complete data for the absorption of dimethylaniline are given. This data sheet has been selected at random and is typical of the entire series. In the first column under λ are indicated the wave-length settings in microns. The second and third columns represent the galvanometer deflections in millimeters, corresponding to the transmission of the filled cell, I, and rock-salt plate, I_0, respectively. In the fourth column under I/I_0 the ratios of the deflections indicated in the second and third columns are given and represent, therefore, the percentage transmission.

It will be seen that the values for I_0 also give an idea of the distribution of energy in the light source. It is not surprising that pronounced minima occur in the regions of 6.0μ, 4.2μ and 2.6μ, which are undoubtedly due to the absorption of atmospheric carbon dioxide and water vapor.

The usual method of graphic representation has been employed as shown in Figs. 2 to 12. Wave lengths in microns (values of λ in Table I) are plotted as abscissas against the percentage transmission (values of I/I_0 in Table I) as ordinates. The minima of such a curve therefore represent regions of absorption. The thickness of the cell used in each case is indicated on the corresponding curve.

Sources of Error

Perhaps the most significant source of error in the experimental method used was due to variations in the intensity of the light source which resulted from fluctuations in the source of electric current.

Galvanometer deflections were recorded within a millimeter and, on referring to Table I, it will be seen that the percentage error involved in reading the deflections is subject to considerable variation depending upon the magnitude of the total deflection.

A slow drift in the zero of the galvanometer was usually observed, but it is believed that this drift took place so slowly that error from this source was insignificant, especially since all readings for a definite wave length were made within a period of 30 seconds.

Since the wave-length drum was calibrated in tenths of a micron and intermediate settings would therefore be purely approximate, it is apparent that it would be inconsistent to attempt to determine the exact location of absorption maxima, even in the absence of any other sources of error. The transmission curves represent, rather, the most probable course of the curves as determined by points obtained at intervals of 0.1μ.

In the past it has been desirable to repeat measurements on numerous substances and, in this way, definite information has been obtained concerning the reproducibility of the results. It is believed that the accuracy of the absorption curves is within 0.05μ.

It should be noted that the calibration of the wave-length drum was frequently checked against the D lines of sodium and the green line of mercury. At the same time, the angle of deviation of the prism was checked by means of an auxiliary prism supplied with the spectroscope.

Discussion

Of the compounds used in this investigation, only three appear to have been previously studied in the infra-red. Coblentz[11] has measured aniline and mono- and dimethylaniline. Considering the higher degree of accuracy of his measurements, the agreement between his curves and those given in Figs. 2, 3 and 4 is satisfactory. It is to be noted, however, that the shallow band at 3.2μ of aniline (Fig. 2) was not resolved by the smaller spectroscope of Coblentz; but was obtained by his larger instrument. Furthermore, in the case of methylaniline, Coblentz found a single band at 3.4μ, while the present study revealed a band at 2.8μ and another at 3.3μ. It seems certain that his larger spectroscope would have resolved these two bands.

The curves given in Figs. 2 to 12 all show a region of transparency from 3.4 to 6.0μ. The substituted anilines have in common with aniline the following bands: a deep band at 6.1μ, a shallow band at 2.3μ, a shallow band at 5.1μ, at 10.0μ (apparently present, but not resolved for diethylaniline), at 6.6μ and at 8.6μ.

The 11.3μ band of aniline has been shifted to 11.5 or 11.6μ in the substituted anilines with the exception of di-*n*-propylaniline where two bands appear, 11.3 and 11.7μ. The 3.2μ band of aniline appears consistently at 3.3μ in all of the derivatives.

Between the limits 3.5 and 12.0μ no striking change in the absorption of aniline is produced by alkylation of the amino group, and it will be noted that several pairs of isomers are included in these alkyl derivatives; ethylaniline and dimethylaniline, methylethylaniline and *n*-propylaniline, and diethylaniline and *n*-butylaniline.

The region of most striking interest is between 2.7 and 3.4μ; this region will be discussed in connection with the absorption of ammonia which has been measured by Coblentz[12] and more recently by Schierkolk.[13] Coblentz's curve for ammonia shows the absorption bands at 6.1 and 6.6μ which are found in aniline and the alkyl anilines.

In the light of the present discussion, it is indeed fortunate that Coblentz showed that the 2.98μ band of ammonia is not due to the presence of water which has a band at 3.0μ, since the absorption curves of aniline, methylaniline, ethylaniline, *n*-propylaniline, *n*-butylaniline and *iso*-amylaniline all show a pronounced band in the region from 2.7 to 2.9μ. This band is quite deep in the case of aniline and markedly shallower in the case of the

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[11] Coblentz, Ref. 1, p. 84.

[12] Coblentz, Ref. 1, p. 53.

[13] Schierkolk, *Z. Physik,* **29,** 277 (1924).

substituted anilines mentioned above. Most importantly, it appears in aniline and the mono-alkyl anilines while it is practically absent in the dialkyl anilines.

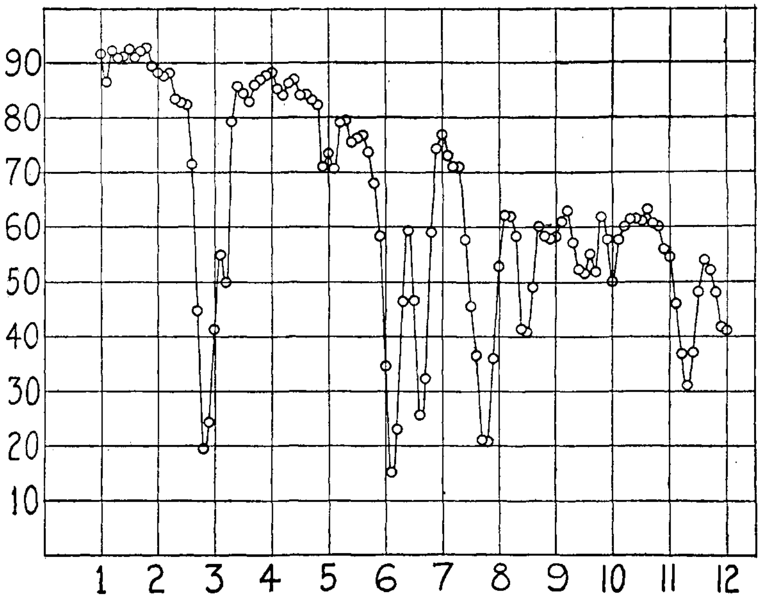

Fig. 2.—Aniline. $T = 0.025$ mm.

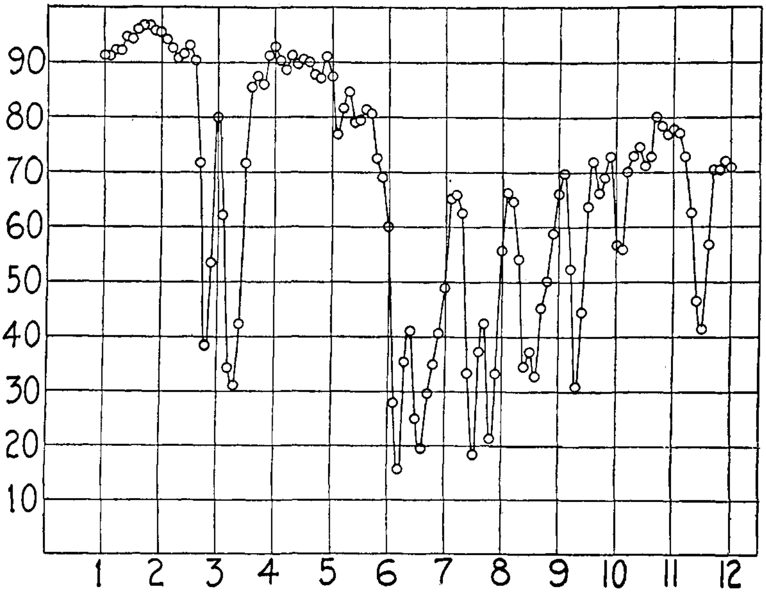

Fig. 3.—Methylaniline. $T = 0.025$ mm.

As noted by Coblentz, the introduction of the amino group seriously disturbs the spectrum of the benzene nucleus except at 3.25μ and the band shown at 3.2μ in Fig. 2 may be regarded as due to the benzene nucleus.

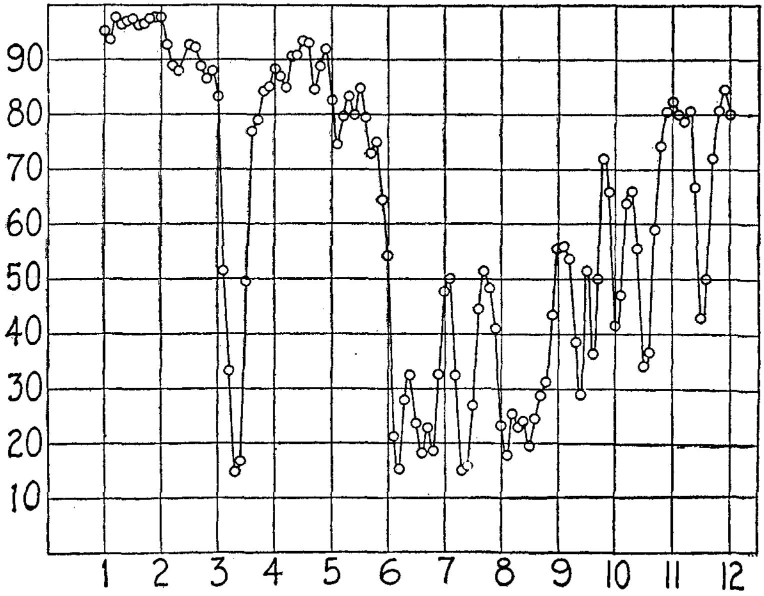

Fig. 4.—Dimethylaniline. $T = 0.05$ mm.

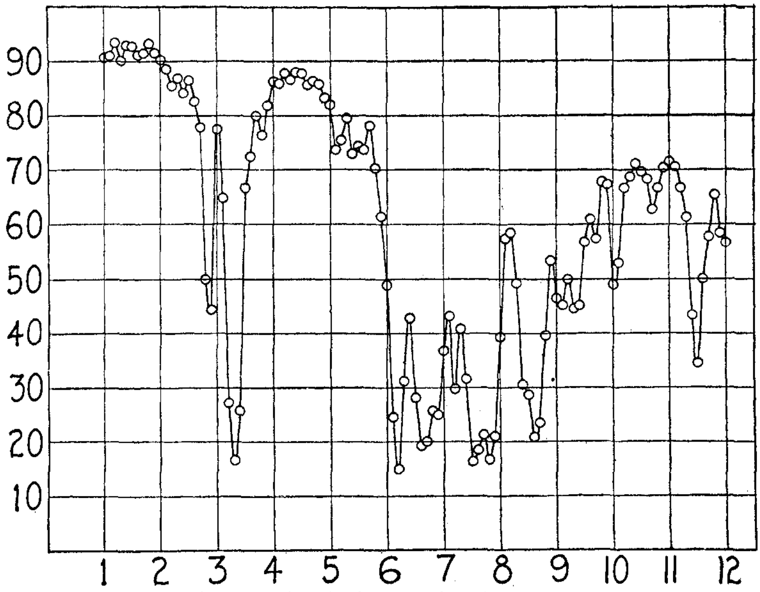

Fig. 5.—Ethylaniline. $T = 0.05$ mm.

Furthermore, the band occurring in the region of 2.8μ may be regarded as due to the amino group.

Starting with ammonia we have a single deep band at 2.98μ. By intro-

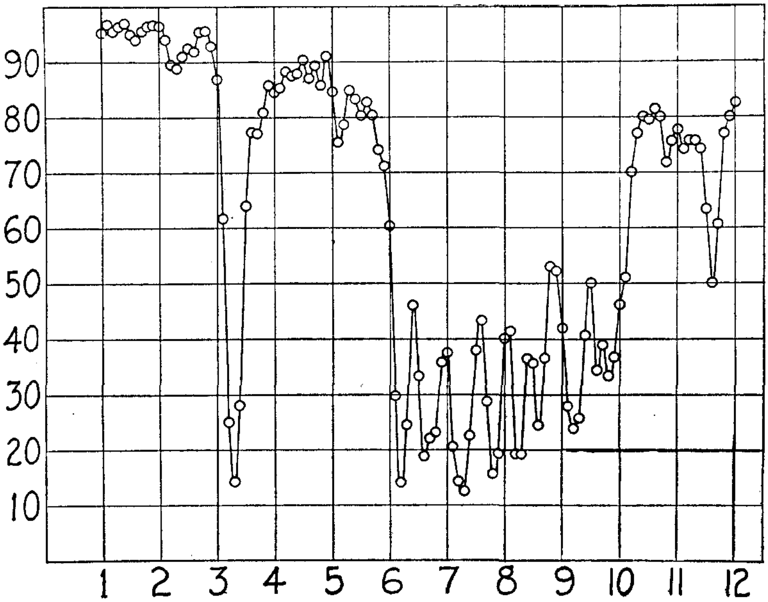

Fig. 6.—Diethylaniline. $T = 0.05$ mm.

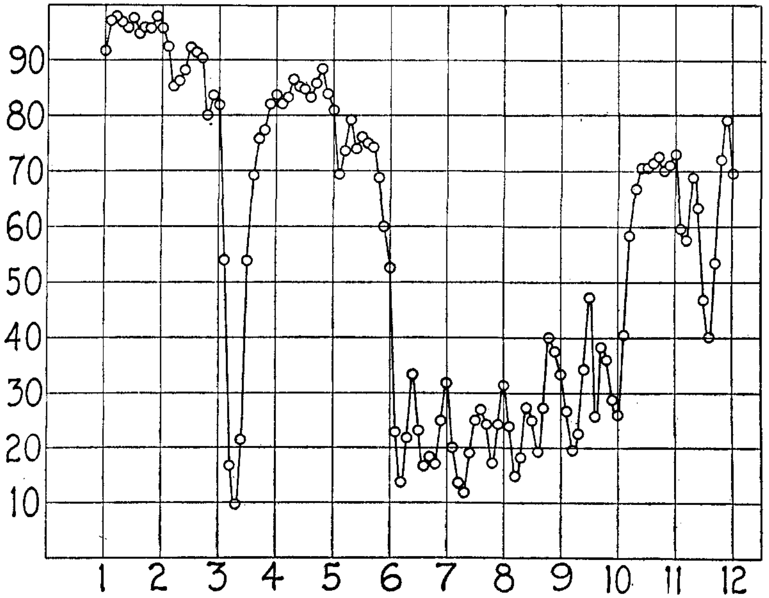

Fig. 7.—Methylethylaniline. $T = 0.05$ mm.

ducing a phenyl group, this band shifts to 2.8μ and becomes shallower and the 3.25μ band of benzene appears. By introducing an alkyl group into the

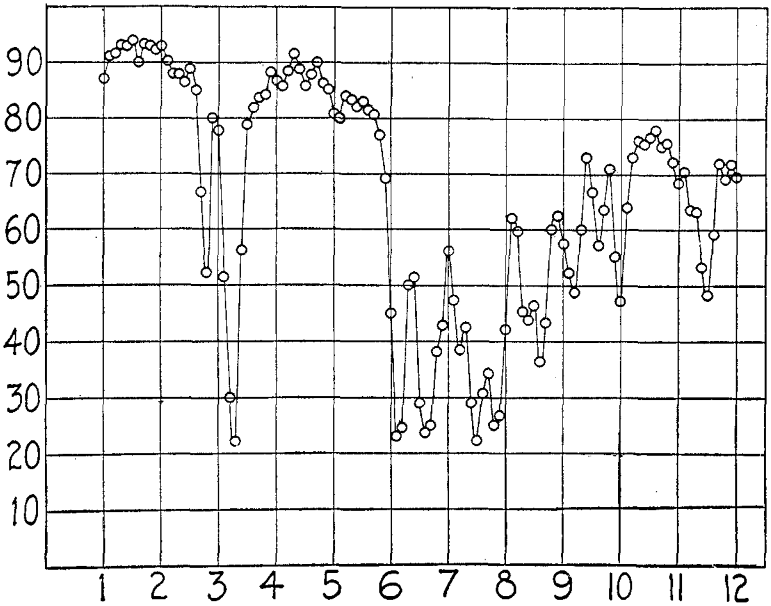

Fig. 8.—*n*-Propylaniline. T = 0.025 mm.

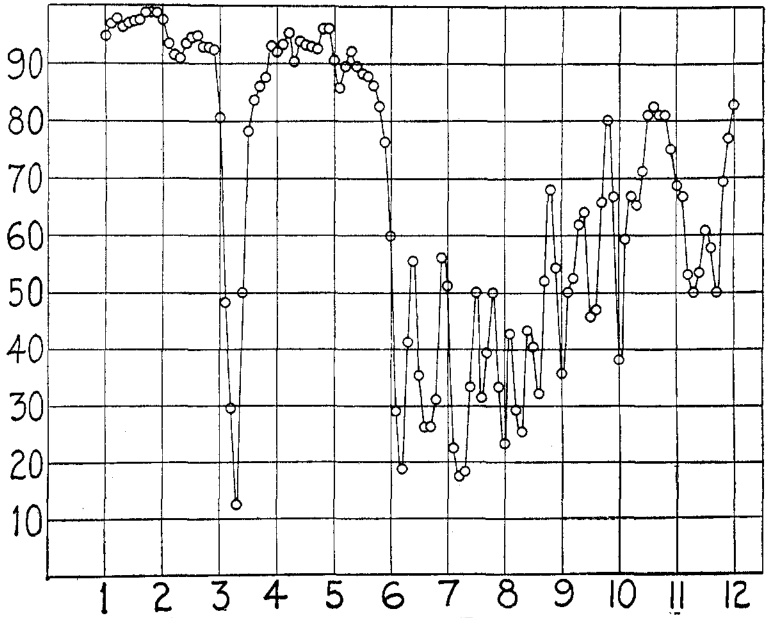

Fig. 9.—Di-*n*-propylaniline. T = 0.025 mm.

amino group of aniline, the 2.8μ band again becomes shallower and the 3.25μ band shifts to 3.3μ and is consistently deeper than the 2.8μ band

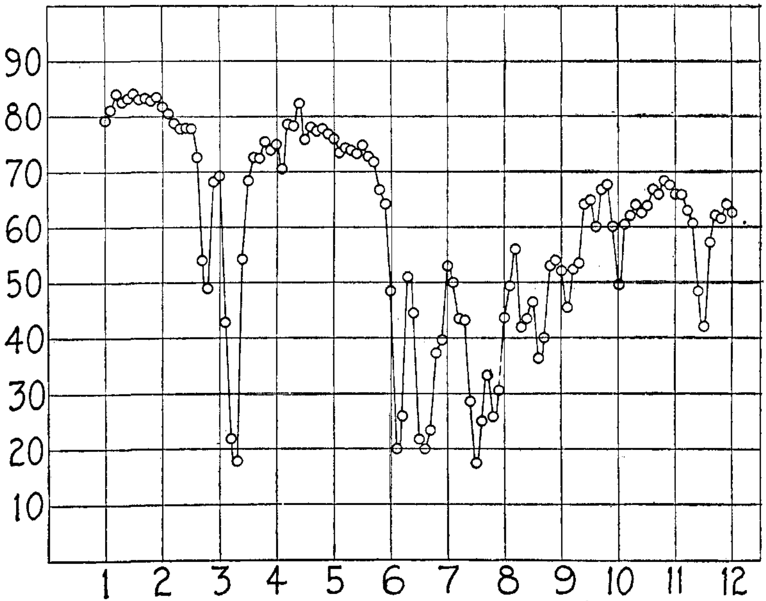

Fig. 10—*n*-Butylaniline. T = 0.025 mm.

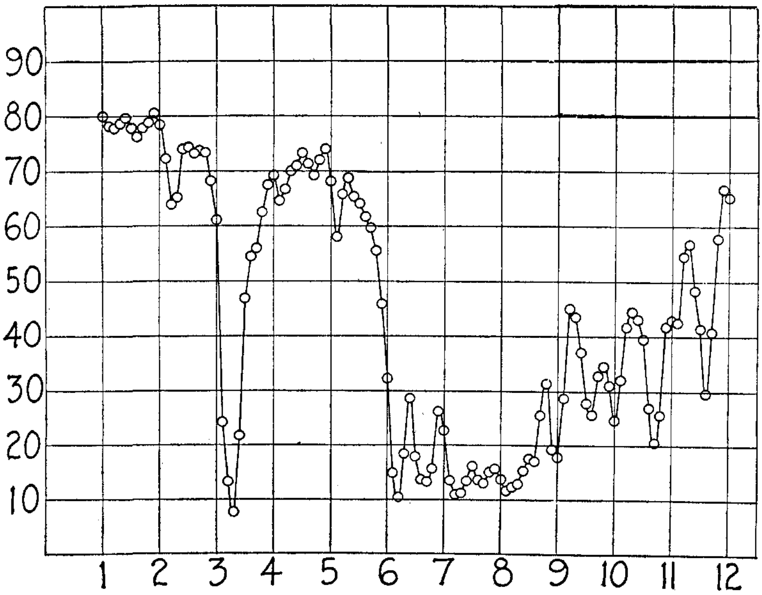

Fig. 11.—Di-*n*-butylaniline. T = 0.025 mm.

On introducing another alkyl group (yielding a tertiary amine), the 2.8μ band practically disappears and the 3.3μ band becomes deeper.

The band occurring at 3.3μ in the mono- and dialkyl anilines is the mean of the 3.25μ band of benzene and the 3.43μ band characteristic of the methyl group and may be regarded as a combination of these two bands.

It appears, therefore, that with progressive substitution oft he three hydrogen atoms of ammonia with first the phenyl group and then alkyl groups, the specific influence of the trivalent nitrogen on the absorption in the region of 2.8μ is progressively diminished until it is practically absent from the tertiary amino group.

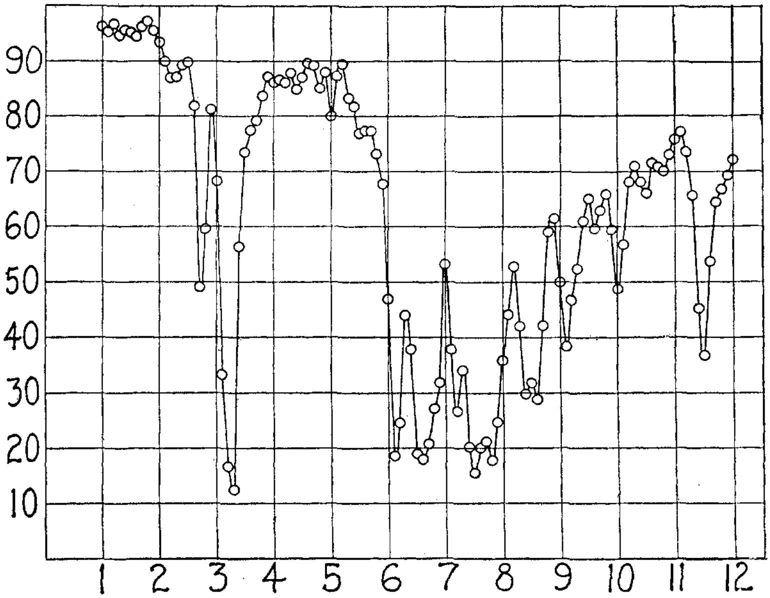

Fig. 12.—*Iso*-amylaniline. $T = 0.025$ mm.

The data obtained are believed to offer conclusive evidence that aniline and secondary and tertiary alkyl anilines may be readily differentiated qualitatively by their absorption in this region.

It is anticipated that work now in progress on the alkyl amines, toluidines and naphthylamines will throw further light on the possibility of a general differentiation of the primary, secondary and tertiary amino groups.

The author welcomes the opportunity of expressing his deepest sense of gratitude to Professor Pfund of the Department of Physics for his many timely suggestions.

Summary

1. The absorption spectra of aniline and ten alkyl anilines have been explored between 1.0 and 12.0μ.

2. The influence of progressive substitution of the hydrogen atoms of ammonia by certain organic radicals on the absorption spectrum has been noted.

3. Between 2.7 and 3.4μ, the absorption reveals a pronounced qualitative differentiation between aniline and mono-alkyl anilines and dialkyl anilines.

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[CONTRIBUTION FROM THE DIVISION OF PHARMACOLOGY, HYGIENIC LABORATORY, UNITED STATES PUBLIC HEALTH SERVICE]

SYNTHESIS OF N,N'-DIMETHYLENESULFONATES OF ORTHO-, META- AND PARA-DIAMINO-ARSENOBENZENE

BY KOZO KASHIMA[1]

RECEIVED APRIL 27, 1925 PUBLISHED AUGUST 5, 1925

Disodium 3,3'-diamino-4,4'-dihydroxyarsenobenzene, N,N'-dimethylenesulfonate, known under the official name sulfarsphenamine, has proved to be of practical value in the treatment of syphilis. A satisfactory method of preparation of this drug has been described by Voegtlin and Johnson.[2] These workers obtained the product by subjecting an aqueous solution of arsphenamine (dihydrochloride of 3,3'-diamino-4,4'-dihydroxyarsenobenzene) to the action of formaldehyde and sodium bisulfite. The work to be reported deals with the preparation of similar dimethylenesulfonates, derived from *o*-, *m*- and *p*-diamino-arsenobenzene. The synthesis of these products involved the preparation of a number of intermediates. One of the latter, 3,3'-diamino-arsenobenzene, had not been described previously. These methylenesulfonates are now being tested in this Laboratory as to their chemotherapeutic potency in experimental syphilis.

Experimental Part

2-Nitrophenylarsonic Acid, (2)$O_2NC_6H_4AsO_3H_2$.—This acid was prepared from *o*-nitro-aniline according to the method of Schmidt.[3] It was found advantageous to use sulfuric acid for the final precipitation of the nitrophenylarsonic acid. When recrystallized, the product was obtained in the form of almost colorless needles; m. p., 231°; yield, 85%.

Anal. Calcd. for $C_6H_6O_5NAs$: As, 30.35. Found: 30.14, 30.25.

2-Aminophenylarsonic Acid, 2-$H_2N.C_6H_4AsO_3H_2$.—Benda[4] obtained the acid from 2-amino-5-nitrophenylarsonic acid by a complicated procedure. A simpler method is the following.

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[1] Lecturer in Chemistry, Tokyo Imperial University.

[2] Voegtlin and Johnson, THIS JOURNAL, **44**, 2573 (1922).

[3] Schmidt, *Ann.*, **421**, 172 (1920). Bart, Ger. pat. 250,264.

[4] Benda, *Ber.*, **44**, 3304 (1911).