place at room temperature or in the cold and the amount of alkali required to produce the dye. Classification in each part has been made in accordance with the position of the maximum absorption in acetone solution.

Summary

Azo dye derivatives of 45 phenolic compounds were examined spectrophotometrically. Absorption spectra maxima are reported for solutions of these dyes in water, alcohol and acetone.

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THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC DERIVATIVES OF AMMONIA

III. DI- AND TRIPHENYLAMINE

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RECEIVED DECEMBER 28, 1925 PUBLISHED MARCH 5, 1926

Introduction

In the previous papers of this series[1] of studies, mixed amines of the aryl-alkyl type were selected for investigation. The results obtained revealed the importance of the region of 3.3 μ of the infra-red absorption in the case of these ammonia derivatives.

It will be recalled that the aryl group (the phenyl and naphthyl groups, at least) displays a characteristic absorption at 3.25 μ and that the alkyl group has a characteristic band at 3.43 μ. It is unfortunate that these two bands occur so closely in a region in which the dispersion of rock salt is greatly reduced. The absorption curves previously obtained offer no promise of the possibility of resolving additional bands in this region, if they are present, by means of the experimental method employed.

As a possible alternative, indirect methods might aid in determining whether the alkyl and the aryl groups display their characteristic absorption in this region independently when both of these groups are present in the same compound or, more specifically, when these groups occur independently in the same molecule, the linkage of each group taking place by means of a common nitrogen atom. It appears that information concerning the absorption of pure aryl amines would be of importance in this connection and, therefore, aid in the interpretation of the results previously obtained in the examination of the aryl-alkyl amines.

To this end the phenylamines have been selected for examination. The infra-red absorption of the mono derivative (aniline) having been examined and reported in an earlier communication[2] need not be repeated. The infra-

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[1] THIS JOURNAL, (a) **47**, 2192, (b) 3039 (1925).

[2] Ref. 1 a, p. 2201.

red absorption spectra of di- and triphenylamine are recorded in this paper.

Experimental Part

No changes have been made in the experimental method and procedure as previously described.[3]

It will be recalled that di- and triphenylamine are solids at ordinary temperatures. The former melts at 54° and the latter, at 127°. Both of these substances were maintained in the molten state during the examination of their absorption spectra.[4]

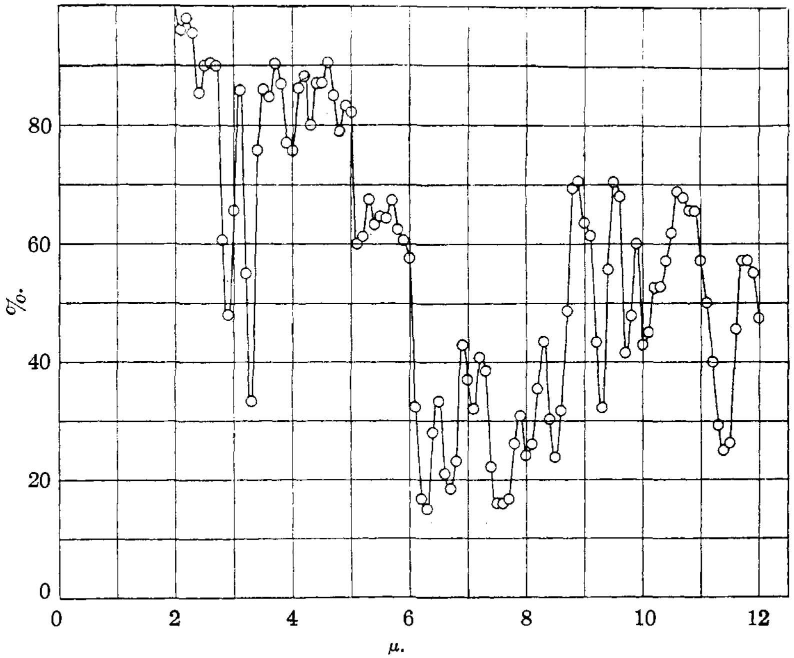

Fig. 1.—Diphenylamine. T = 0.05 mm. Temp. = 65°.

The absorption spectra obtained are shown graphically in Figs. 1 and 2 by means of the customary percentage-transmission—wave-length curves. The thickness of the absorbing layer, 0.05 mm. in each case, is indicated on these curves, and the temperature at which the determinations were made is likewise indicated: diphenylamine at 65° and triphenylamine at 145°.

The specimens of di- and triphenylamine which were examined were obtained from the Eastman Kodak Company and were designated as of "highest purity."

Discussion

A consideration of the curves shown in Figs. 1 and 2 in connection with the curve for aniline, referred to above, at once reveals the fact that the

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[3] Ref. 1 a, p. 2194.

[4] Bell, This Journal, **47**, 2812 (1925).

phenylamines are quite analogous to the aryl-alkyl amines in their behavior in the region between 2.7 μ and 3.4 μ. The deep ammonia band appears at 2.8 μ in aniline. In diphenylamine its intensity is markedly decreased and it appears at 2.9 μ. In the triphenyl derivative it is practically absent. The benzene band occurs in aniline at 3.2 μ and is decidedly shallower than the ammonia band. On passing to the diphenylamine, the benzene band at 3.3 μ is somewhat more intense than the ammonia band at 2.9 μ and in the triphenylamine the benzene band persists at 3.3 μ.

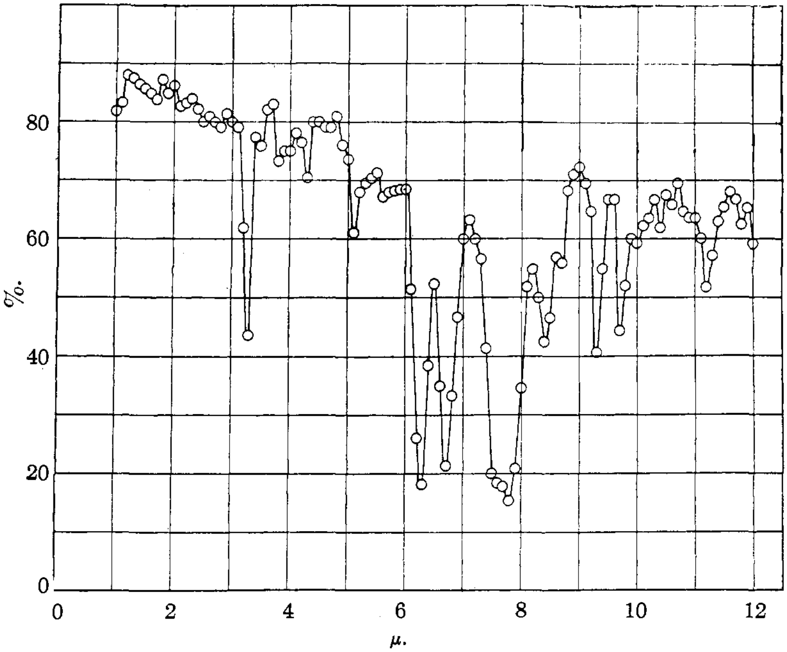

Fig. 2.—Triphenylamine. T = 0.05 mm. Temp. = 145°.

The absorption curves for the three phenylamines show that these substances have the same degree of general transparency; but when it is remembered that the thickness of the absorbing layer of aniline was 0.025 mm. while the diphenyl and triphenyl derivatives had the same layer thickness of 0.05 mm. it will be noticed that a definite increase in the transparency of aniline has been produced by further phenylation. On the other hand, the transition from the di- to the triphenylamine has been accompanied by no appreciable change in transparency.

The curves for the alkyl anilines show no consistent change in the general transparency as compared with that of aniline. The lower alkyl derivatives examined were found to be more transparent, while in the case of some of the higher alkyl derivatives an increase in opacity was noted.

Between the limits of 3.0 μ and 10.0 μ the di- and triphenylamine curves are decidedly similar. The 6.75 μ band characteristic of the benzene nucleus which appears at 6.65 μ in the aniline curve is shown at 6.7 μ in both of the present curves. Attention is also directed to the region of 6.2 μ. The deep and sharply resolved band at 6.1 μ in aniline appears somewhat broadened at 6.25 μ in diphenylamine. In triphenylamine it is again sharply resolved and is located at 6.3 μ. The probable significance of the character and apparent shifting of this band has been discussed in a previous communication.[5]

Concerning the intensity of the benzene band at 3.3 μ, after making due allowance for the smaller thickness of the aniline layer, it is apparent that no increase in the intensity of this band is to be observed with subsequent phenylation of aniline. This is in accord with the observation of Lecomte[6] that the repetition, in a given molecule, of a group having a characteristic absorption does not intensify that characteristic absorption. It follows, therefore, from this point of view, that the nitrogen linkage exerts no appreciable influence on the intensity of the benzene band or, more correctly, that whatever influence the nitrogen has in this respect, that influence remains constant regardless of the number of hydrogen atoms of ammonia which are substituted by the phenyl group.

It was first thought that the intensification of the 3.2 μ band of aniline with the introduction of an alkyl group indicated a dampening effect by the trivalent nitrogen structure on the vibration corresponding to the absorption in this region, which was weakened or nullified on passing to the secondary amino structure. In the light of the present discussion, it appears more probable that this apparent intensification denotes that the characteristic methyl band is relatively much stronger than the benzene band in these compounds.

Coblentz' extensive study of infra-red absorption spectra includes the examination of a number of compounds in which both the methyl and phenyl groups are present. Remembering that the phenyl band appears at 3.25 μ and the methyl band at 3.43 μ, his absorption curves reveal minima as follows: at 3.3 μ in toluene, at 3.38 μ in the xylenes, and at 3.4 μ in mesitylene.[7] He inclines to the view that there is not a real shifting of the absorption band in this region, but that the band is complex and not resolved by ordinary dispersion and that the observed minimum represents rather the center of gravity of several bands.

More recent investigations, employing a highly dispersive optical system, definitely indicate the high degree of complexity of absorption bands obtained by means of ordinary dispersion. Thus, Sleator and Phelps[8]

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[5] Ref. 1 b, p. 3043.

[6] Lecomte, *Compt. rend.*, **178**, 2074 (1924).

[7] Coblentz, *Carnegie Inst. Publ.*, **35**, 103 (1905).

[8] Sleator and Phelps, *Astrophys. J.*, **62**, 28 (1925).

have examined the fine structure of the near infra-red absorption bands of water. Using a grating they measured, for example, 56 lines in the 3.11 μ band.

The present curves for the phenylamines do not offer any conclusive evidence concerning the structure of the 3.3 μ band of the alkyl anilines, but they are regarded as supporting the view that the increased intensity of the 3.3 μ band of the alkyl anilines as compared with that of mono-, di- and triphenylamine is due to the fact that a new band (the methyl band) of relatively greater intensity appears with the alkylation of aniline. This view, therefore, requires the important assumption that the characteristic absorptions of the methyl and the phenyl groups are both present in the region of 3.3 μ in the alkyl anilines.

Applying this assumption directly to the case of aryl-alkyl compounds of other types, several possible explanations may be offered to account for the shifting of the minimum observed by Coblentz in toluene, the xylenes and mesitylene, as mentioned above. The relative intensities of these two vibrations may vary, depending upon the structure of the compound in question and thus cause a variation in the location of the observed minimum. Secondly, there may be true shifting of the position of one or both of these characteristic vibrations. Finally, a combination of these two factors as just stated may account for the observed variations.

The possible applications of these suggestions to the case of other organic derivatives of ammonia will be indicated in future studies of this series.

Summary

1. The infra-red absorption spectra, between 1.0 μ and 12.0 μ of molten diphenylamine (at 65°) and triphenylamine (at 145°) have been examined and described.

2. The absorption spectra obtained show, in the region between 2.8 μ and 3.4 μ, the same qualitative differentiation between aniline and di- and triphenylamine as in the case of aniline and the alkyl anilines.

3. The significance of the absorption spectra of these phenylamines in connection with the study of the 3.3 μ band of the alkyl anilines has been indicated.

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