[Contribution from the Department of Pharmacology of Johns Hopkins University]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC DERIVATIVES OF AMMONIA

IV. MONO-, DI-, AND TRIBENZYLAMINE

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Introduction

Of the various general types of aryl-alkyl compounds containing the trivalent nitrogen atom, three are at once recognized: (1) the aryl and alkyl groups are independent, having separate bonds to the common nitrogen atom, and the aryl and alkyl groups are directly connected, linkage to the nitrogen atom taking place through (2) the aryl group or (3) the alkyl group.

As representatives of the first group, the alkyl anilines and the alkyl naphthylamines have been previously examined. The toluidines are, of course, representatives of the second group. The present study is concerned with compounds of the third type and to this end the three benzylamines have been selected for investigation.

In the preceding article[1] the infra-red absorption spectra of the three phenylamines were described and this was the first treatment of pure or unmixed amines in this series of studies. It will be noted that the benzylamines are likewise pure amines in that each hydrogen atom of ammonia is substituted by the same residue (benzyl) corresponding to the primary, secondary and tertiary amines. The benzyl radical, of course, is not homogeneous, but represents the phenyl-methyl structure with the free bond on the methyl group.

Experimental Part

In view of the results obtained in the present study, it is of particular importance to note that no alterations have been made in the experimental method as employed in the previous studies.

Mono- and dibenzylamine are liquids at ordinary temperatures and, therefore, were examined in the usual manner. Tribenzylamine, with a melting point of 91°, was examined in the molten state at a temperature of 105°.

Figs. 1, 2 and 3 show graphically the absorption spectra which have been obtained. In these curves wave lengths in microns have been plotted against the percentage transmissions. Values of T indicate the thickness of the absorbing layer used in each case, and in Fig. 2 it is to be noted that

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[1] Bell, This Journal, **48**, 813 (1926). Earlier papers of this series will be found in *ibid.*, **47**, 2192, 3039 (1925).

between 3.1 μ and 3.7 μ examinations were made for two different thicknesses of the absorbing layer.

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

Discussion

The curves for monobenzylamine (Fig. 1) and dibenzylamine (Fig. 2) show the same degree of general transparency when due correction is made for the difference in thickness of the absorbing layer employed in each case. On the other hand, the absorption curve for the tribenzyl derivative (Fig. 3) reveals a higher degree of transparency, and it should be noted that in this case the spectrum was determined at a temperature of 105°.

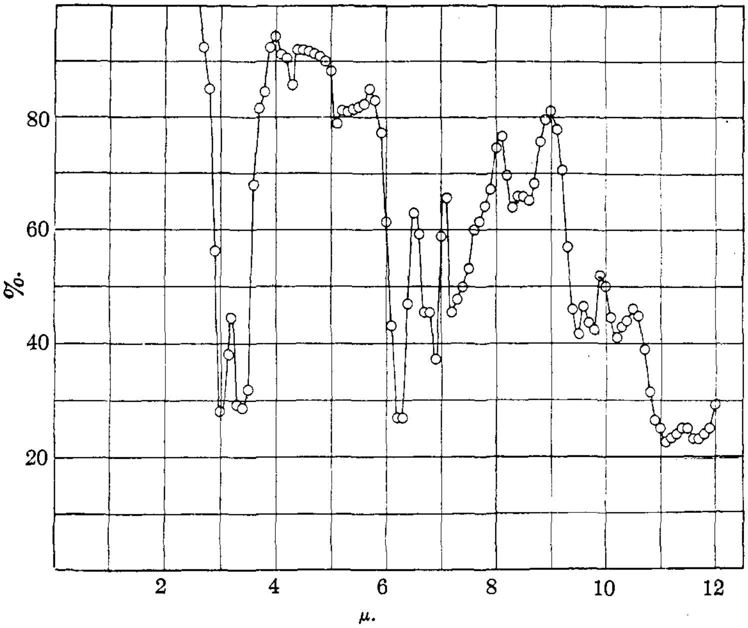

Fig. 1.—Monobenzylamine. $T = 0.025$ mm.

The monobenzylamine curve is characterized by relatively few sharp and deep bands and appears in marked contrast, in this respect, to the curve for aniline and to that for its isomer, monomethylaniline. Several regions may be noticed in which bands are indicated but have not been resolved. The region of maximum opacity, lying between 11.0 μ and 12.0 μ, is poorly defined. At least two bands are present in this region. The general character of the curve suggests that of a simple alkyl rather than an aryl compound, which is in accord with the structure of monobenzylamine.

On passing to the dibenzylamine, the number of bands which have been resolved is considerably increased, giving a general impression of improved definition. The region from 9.0 μ to 12.0 μ has undergone a marked change.

Further improvement is noticed in the resolution in the curve for tribenzylamine, which stands in marked contrast to that of the mono derivative. The general behavior of the tribenzyl derivative in the infra-red suggests a compound in which the influence of the aryl group predominates.

It is thus seen that with the three successive stages of the benzylation of ammonia, the general appearance of the absorption spectrum of the mono substituted compound suggests the predominance of the alkyl structure while that of the tri-derivative indicates the aryl structure, and the dibenzylamine absorption spectrum represents a transition between these two.

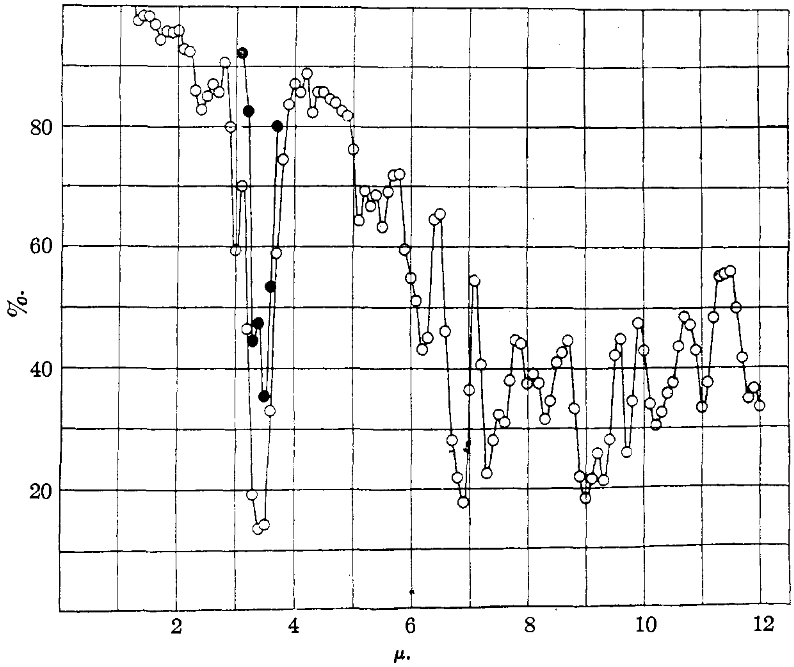

Fig. 2.—Dibenzylamine. ○ = T, 0.05 mm. ● = T, 0.025 mm.

These striking differences in the three absorption curves have not been observed in any series of primary, secondary and tertiary amines of the same type previously examined.

Several bands are to be noticed which are common to all three benzylamines. The 6.86 μ methyl band, which is probably an harmonic of the 3.43 μ band, appears at 6.9 μ in each case. The presence of the 6.75 μ benzene band is indicated but has not been resolved in the case of the mono- and dibenzylamines. In tribenzylamine, however, it has been sharply resolved at 6.7 μ. The weakening of the 6.25 μ band of monobenzylamine with the two subsequent stages of benzylation is in accord with the observation recorded in the study of the alkyl naphthylamines.

A shallow but definite band appears at 5.1 μ in each of the three benzylamines. This same band has been observed in all of the amino derivatives thus far examined. In the author's curve for benzene[2] a deep band appears at 5.1 μ. Its definite occurrence in aniline and α- and β-naphthylamine eliminates any specific influence of the alkyl group in this region and its presence in benzene and naphthalene likewise eliminates the trivalent nitrogen structure as a causative factor. It follows, therefore, that this band at 5.1 μ is dependent upon and characteristic of the benzene nucleus.

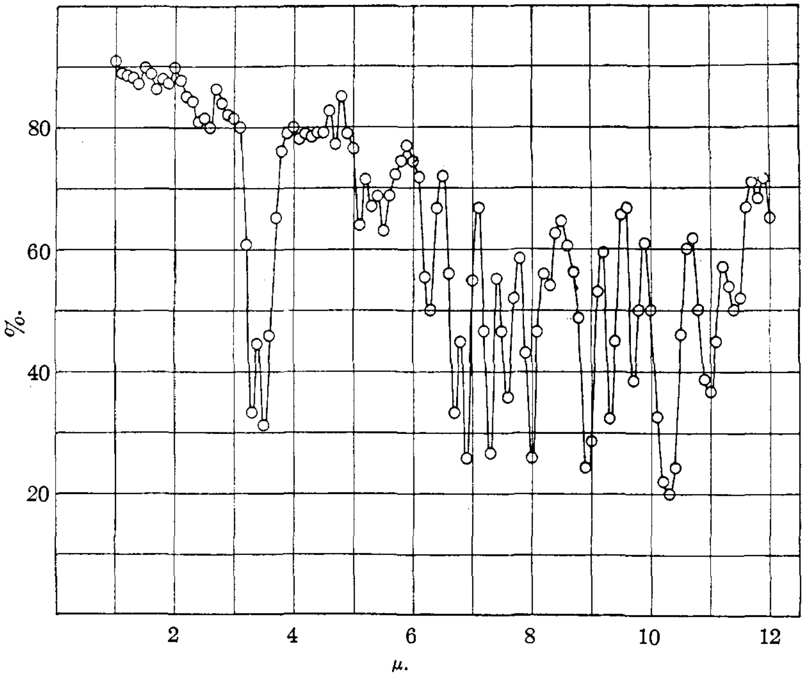

Fig. 3.—Tribenzylamine. $T = 0.05$ mm. Temp. = 105°.

In the region of particular interest between 2.8 μ and 3.7 μ, the 2.98 μ band of ammonia will be considered first. It appears in monobenzylamine at 3.0 μ as a deep and sharply defined band. In dibenzylamine its location remains at 3.0 μ but its intensity is greatly decreased, notwithstanding a doubling of the thickness of the absorbing layer. The band is absent from the tribenzylamine curve. With the exception of the weakness of this band in dibenzylamine, its behavior is quite analogous to that observed previously in the case of other primary, secondary and tertiary amines.

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[2] Bell, This Journal, **47**, 2814 (1925).

At 3.4 μ a broad band appears in monobenzylamine and its intensity is approximately equal to that of the ammonia band, while in aniline and the α- and β-naphthylamines this band was found to be considerably less intense than the ammonia band and sharply defined.

On doubling the thickness of the absorbing layer in the case of dibenzylamine, the 3.4 μ band is intensified and remains broad. For purposes of direct comparison this region was also examined using a layer thickness of 0.025 mm. In this portion of the complete curve as shown in Fig. 2, two bands have been resolved: at 3.3 μ, which is undoubtedly the benzene band, and at 3.5 μ, the characteristic methyl band, indicating conclusively that in this compound the characteristic vibrations of the benzene and methane groups are both present in this region.

Even with a layer thickness of 0.05 mm. these two bands have been sharply resolved in the absorption curve of tribenzylamine. Improvement in the definition of the 3.3 μ band is apparent.

Failure to resolve the 3.4 μ band in the mono derivative is not readily explained unless it is assumed that one, or both, of the two component bands shows a shift in position and that the difference in position increases progressively on passing from the mono- to the dibenzylamine and, finally, to the tribenzylamine. Unfortunately, the accuracy of the experimental method employed does not permit the detection of the small degree of shifting which this assumption presupposes.

The relative intensities of the 3.3 μ and 3.5 μ bands as shown in Figs. 2 and 3 are of the same degree. The intensity of the 3.3 μ band is approximately that which would be predicted from a consideration of the absorption of aniline and di- and triphenylamine in this region. On the other hand, the absorption curves of the alkyl anilines indicate a much greater intensity of the 3.5 μ band than that shown in the present spectra, and this is especially pronounced in the case of the tertiary amino structure. This condition may be due to a dampening influence of the phenyl group on the characteristic vibration of the methyl group, since in the benzylamines the phenyl group is substituted in the methyl group.

The two instances of the presence of the 3.3 μ and 3.5 μ bands in the same compound as given in the present study, do not justify the generalization that in all compounds containing both the alkyl and aryl residues these two bands are always present, but they may be regarded as a strong indication of the probability of such a generalization, which would then necessarily presuppose the reality of the phenomenon of band shifting.

Summary

1. The infra-red absorption spectra of mono-, di- and tribenzylamine have been explored between 1.0 μ and 12.0 μ. The last-named compound was examined in the molten state at 105°.

2. These compounds follow, with certain qualifications, the same qualitative differentiation previously found to exist between primary, secondary and tertiary amines of the aryl and aryl-alkyl types.
3. In di- and tribenzylamine both the 3.3 μ band and the 3.5 μ band have been resolved. The significance of this observation has been indicated.
4. A new band characteristic of the benzene nucleus has been located at 5.1 μ.

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[CONTRIBUTION NO. 110 FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE PREPARATION AND PROPERTIES OF METHYL-ISOPROPYL-QUINOLINE YELLOW

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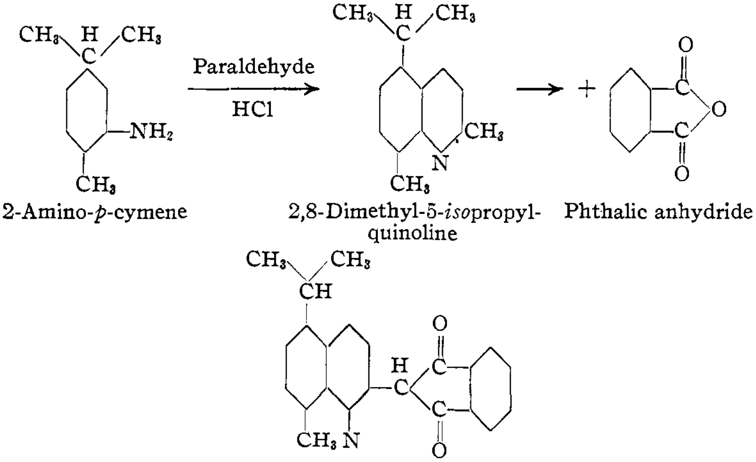
An investigation was undertaken for the purpose of ascertaining the effect of the methyl-*iso*propyl substitution on the absorption and fastness of quinoline yellow. The starting material for the preparation of the new dye was 2-amino-*p*-cymene. This amino compound was converted into 2,8-dimethyl-5-*iso*propyl-quinoline by the Doebner and Miller[1] modification of the Skraup synthesis. When condensed with phthalic anhydride this quinoline derivative yielded methyl-*iso*propyl-quinoline yellow. The reactions involved may be represented as follows:



2-Amino-*p*-cymene

2,8-Dimethyl-5-*iso*propyl-quinoline

Phthalic anhydride

Methyl-*iso*propyl-quinoline yellow (Quinophthalone)

Experimental Part

Methyl-*iso*propyl-quinaldine (2,8-Dimethyl-5-*iso*propyl-quinoline).—Sixty-four g. of cymidine was added to 80 g. of concd. hydrochloric acid, and to this a solution of 60 g.

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[1] Doebner and Miller, *Ber.*, **14**, 2814 (1881).