CCXI.—*The Relation between Absorption Spectra and Chemical Constitution. Part XII. Some Amino-aldehydes and -ketones of the Aromatic Series.*

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IN a previous paper (Bally and Collie, Trans., 1905, **87**, 1332), the absorption spectra of benzaldehyde and acetophenone were described, and it was shown that both these compounds exhibit only a very small absorption band, the view being put forward that the motions of the benzene ring were to a very great extent restrained by the presence of the ketonic oxygen in the β -position in the side-chain. We have now investigated some of the amino-aldehydes and -ketones of the benzene series with the view of determining the influence of the amino-group. From a comparison of the absorption of aniline with that of benzene, it is evident that the influence of the amino-group is directly opposite to that of the ketonic oxygen in the β -position, for the very large absorption band of aniline would suggest that the dynamic activity of this compound is even greater than that of

benzene itself. This fact is, of course, in agreement with the results obtained by magnetic rotation (Perkin, Trans., 1896, **79**, 1025). In the amino-aldehydes and -ketones we have therefore two well-defined influences brought simultaneously to bear on the phenyl group, namely, first the ketonic oxygen in the β -position tending to restrain and lock up the motions of the phenyl group, and secondly, the amino-group with an influence of exactly the opposite nature.

Inasmuch as the absorption curves of these compounds all show large absorption bands, it is evident that the restraining influence of the ketonic or aldehydic group is more than counteracted by the amino-group.

It is interesting, moreover, to note that in these compounds generally the ortho-isomeride exhibits the greatest absorption band and the para the least; the meaning of this is not at present clear. It may be pointed out that these substances are coloured yellow, owing to their absorption bands being situated in the visible region of the spectrum. If to the solution of one of the aminoaldehydes or aminoketones in alcohol a small quantity of alcoholic hydrogen chloride is added, the yellow colour of the solution is very much intensified, and the absorption spectrum now shows a new absorption band nearer to the red and at greater concentration than the original band. In the presence therefore of very small quantities of hydrogen chloride, the alcoholic solution of amino-aldehydes and -ketones shows two absorption bands, the principal band being unaltered by the small amount of free mineral acid.

The effect of the mineral acid is most pronounced in the para-isomeride and least in the case of the meta-compound. In Fig. 1 the full curve shows the absorption spectrum of *o*-aminobenzaldehyde, and the dot and dash curve that of the para-isomeride; the upper and lower dotted curves show the absorption of the two compounds in presence of 1/2 equiv. and 1/10 equiv. of hydrogen chloride respectively. The greater effect produced in the case of the para-compound by 1/10 equiv. of hydrogen chloride than by as much as 1/2 equiv. in the case of the ortho-isomeride is very evident. The lower portions of both curves are not altered in any way by such small quantities of acid. Fig. 2 (full and dotted curves) and Fig. 3 (dot and dash, dash and two dots curves) represent the absorption of *p*- and *o*-aminoacetophenone in neutral and slightly acid alcoholic solutions respectively. We give only the results obtained with the ortho- and para-compounds; the results were quite similar with the meta-isomerides, but in a less degree than in the case of the ortho-derivative.

The amount of acid necessary depends very much on the nature of the compound, and it appears that less acid is required with the aldehydes than with the ketones, and, moreover, as has already

been pointed out, less is required with the para-compound than with the two other isomerides. The most sensitive compound is *p*-aminobenzaldehyde, which develops a large and very persistent absorption band with only 1/10 equiv. of hydrogen chloride, and, since the band

FIG. 1.
Oscillation frequencies.

Full curve : *o*-Aminobenzaldehyde.

Upper dotted curve : *o*-Aminobenzaldehyde + 1/2 eq. HCl.

Dot and dash curve : *p*-Aminobenzaldehyde.

Lower dotted curve : „ „ + 1/10 eq. HCl.

Dash and two dots curve : „ „ + excess of aqueous HCl.

is obtained with *N*/1000 solution, so the concentration of the acid is only *N*/10,000. The extreme sensitiveness of the reaction is thus manifest. If too much hydrogen chloride is added, the effect is destroyed, owing to the conversion of the compounds into the hydrochlorides, which in every case are perfectly white compounds. The

maximum amount allowable is of the order of $1/2$ equiv. ; more than this quantity causes the whole spectrum to tend towards that of the hydrochloride. Indeed, in the curve of *o*-aminobenzaldehyde with $1/2$ equiv. of hydrogen chloride (Fig. 1, upper dotted curve), it will be noticed

Full curve : *p*-Aminoacetophenone.

Upper dotted curve : *p*-Aminoacetophenone + $1/25$ eq. HCl.

Dash and three dots curve : " in excess of aqueous HCl.

Dash and dot curve : *p*-Dimethylaminobenzaldehyde.

Middle dotted " : " + $2/5$ eq. HCl.

Dash and two dots curve : 4 : 4'-Tetramethyldiaminobenzophenone.

Lower dotted curve : " " + $1/2$ eq. HCl.

that it does not quite coincide with the curve of the compound in neutral solution; this is owing to the partial conversion into the hydrochloride.

If the aminic hydrogen atoms be replaced by alkyl groups, the same

results are obtained, although in a less degree. This can be seen from the curves of *p*-dimethylaminobenzaldehyde (Fig. 2, dot and dash and middle dotted curves) and of 4:4'-tetramethyldiaminobenzophenone (Fig. 2, dash and two dots and lower dotted curves).

If the substances are dissolved in water or dilute alcohol, the above

FIG. 3.

Oscillation frequencies.

effect is no longer produced on the addition of hydrochloric acid; the spectrum merely tends towards that of the hydrochloride, although this latter spectrum is only finally reached in presence of considerable excess of acid. The absorption of *p*-aminobenzaldehyde hydrochloride and of *p*-aminoacetophenone hydrochloride is shown in Fig. 1

(dash and two dots curve) and Fig. 2 (dash and three dots curve) respectively.

The effect of the addition of hydrogen chloride to these compounds seems to be due undoubtedly to the amino-group. Some experiments at present in progress on certain complex amino-compounds would support this view, for it appears that the nature of the substituent group in the aniline residue is immaterial. For example, the amino-benzaldoximes exhibit the same phenomenon as can be seen from the full and dotted curves on Fig. 3, which show the absorption of *o*-aminobenzaldoxime. It would appear that the addition of the acid produces an increase in the amount of the residual affinity of the amino-group; in neutral solution the nitrogen atom is undoubtedly trivalent, and possibly the addition of the acid makes it functionate as a quinquevalent atom, so that its residual affinity is increased in the ratio of 5 to 3. This increase in the residual affinity, being as it were superadded to that of the neutral molecule, would no doubt account for the new absorption bands. The increase in the residual affinity produced by the addition of acid would account also for the catalytic action of mineral acid on the acetylation of amino-compounds.

Conclusions.

1. The amino-aldehydes and -ketones of the aromatic series in neutral alcoholic solution exhibit one broad absorption band.

2. The addition of small quantities of alcoholic hydrogen chloride to the solution causes the development of a second absorption band, the first remaining unaltered, provided that insufficient acid has been added to produce the hydrochloride.

3. This effect is most marked in the amino-aldehydes and further in the para-isomeride. It is not produced at all in aqueous solution.

4. The phenomenon appears to be due to the amino-group; it is possible that the nitrogen atom is caused to functionate as a quinquevalent atom, so that the residual affinity is increased in the ratio of 5 to 3.

5. The results throw considerable light on the catalytic action of mineral acid in the acetylation of amines.

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