158. *Infrared Absorption Bands Associated with the* NH *Group. Part I. Some Secondary Aromatic Amines.*

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Infrared spectra of seven secondary aromatic amines derived from aniline contain bands characteristic of the C·NH group near 1510 and 1260 cm.$^{-1}$, the first due mainly to an NH deformation vibration, and the other to the stretching of the C–N bond. The corresponding bands in the spectra of the deuterated compounds are near 1120 cm.$^{-1}$, and between 1320 and 1370 cm.$^{-1}$, respectively.

Infrared spectra can be used to differentiate with certainty between the OH and the NH group by means of stretching vibrations, only if the band positions for the free groups can be measured. If hydrogen bonding cannot be disrupted, owing either to its being of intramolecular type or to the low solubility of the compound in the appropriate solvents, the distinction becomes unreliable. Bands due to deformation vibrations may be helpful in such cases, but there are difficulties in such cases. First, it is difficult to detect these bands without the use of deuterium substitution. Secondly, the deformation vibrations of the light atoms are seldom independent of those of the molecular skeleton, this coupling being the cause of multiple shifts of bands on deuteration; hence, these vibrations do not give rise to bands characteristic of OH or NH groups alone, although the situation seems to be better with analogous OD and ND vibrations.[1, 2] Finally, the positions of the bands associated with deformation motions are known only for few compounds containing OH groups. The first of these difficulties is not serious: by appropriate techniques, most compounds may be deuterated satisfactorily with a few drops of deuterium oxide in quantities sufficient for spectroscopic examination, the time required for the whole operation being less than an hour. The second difficulty may be turned to an advantage: if there are in fact no bands characteristic of OH or NH bending vibrations as such, groups of several bands depending on hydrogen motions and their shift on deuterium substitution may be found to be characteristic of larger groups of atoms; for instance, the bands associated mainly with the in-plane bending of OH groups in alcohols,[3] phenols,[4] carboxylic acid dimers,[5] and unsaturated hydroxy-carbonyl compounds[1] appear within rather a wide range of wave numbers, but the positions of the corresponding OD bands together with the shifts of other bands, particularly those associated mainly with the stretching of the oxygen bonds, offer suitable means of recognising the functional groups. The bands of the secondary amide group and their behaviour[6] on deuteration also exemplify this. A systematic study of various types of compounds containing OH and NH groups, severally, will doubtless disclose further characteristic groups of bands and widen the scope of the infrared analysis, particularly for the determination of structures of complicated natural products. Moreover, it is possible that some empirical relation will be established between the frequencies of the hydrogen bending vibrations and the associated skeletal vibrations on one hand, and between the electronic structure and bond interactions in the functional group on the other. There appears to be very little known of the bending frequency of various types of NH groups, although the situation is better with the NH_2 group.[7] It is proposed in this series of papers to present and discuss the infrared spectra of several types of compounds containing the secondary amino-group,

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[1] Bratož, Hadži, and Rossmy, *Trans. Faraday Soc.*, 1955, **52**, 464.
[2] Frazer and Price, *Nature*, 1952, **170**, 490.
[3] Stuart and Sutherland, *J. Chem. Phys.*, 1956, **24**, 559.
[4] Mecke and Rossmy, *Z. Elektrochem.*, 1955, **59**, 866.
[5] Hadži and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247.
[6] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1954, p. 175.
[7] *Idem, op. cit.*, p. 212.

including aromatic amines, thioamides, aliphatic amines, hydroxamic acids, hydrazones, and the hydrohalides of pyridine.

This paper is concerned with the spectra of some nitrogen- and ring-substituted anilines, attention being centred on the bands due to the NH bending and CN stretching vibrations. The NH stretching bands will not be dealt with, since they presented no new features during this study. Comparison of the spectra of simple compounds with their ND analogues has been adopted as the main method for the detection of the bands associated with the $^{\mathrm{C}}_{\mathrm{C}}\!\!>\!\mathrm{NH}$ group. The spectral differences between the compounds in the free and the hydrogen-bonded state, which are often used for the detection of bands due to the vibrations of the bonded groups, were too small to be of use, except for the νNH bands. This is also the reason why only the spectra of the liquid substances are discussed.

Results.—Most of the spectra investigated show one, more or less distinct band near 1510 cm.$^{-1}$ in addition to the aromatic band near 1500 cm.$^{-1}$ (Fig. 1 and Table). The former appears well resolved with diphenylamine and *N*-ethyl-*m*-toluidine, but less well so with *N*-ethylaniline and *p*-chloro-*N*-methylaniline. With *N*-methylaniline, *N*-ethyl-*o*-toluidine and *N*-methyl-*p*-toluidine, there is one band only near 1500 cm.$^{-1}$. The extra band disappears on deuteration, whereas the single band in the rest of compounds becomes somewhat narrower and slightly displaced. There appears a single, narrow band in this part of the spectra of the three tertiary amines examined (dimethylaniline, diethylaniline, and triphenylamine). A strong feature of the secondary amine spectra near 1260 cm.$^{-1}$ belongs obviously to the C·NH group vibrations because it disappears regularly on deuteration and is replaced by new bands: one of these is near 1350 cm.$^{-1}$, but the situation appears to be complicated by the simultaneous changes in intensity and slight displacements of a band near 1320 cm.$^{-1}$, which is possibly an aromatic band; the other new band is between 1080 and 1120 cm.$^{-1}$, is rather strong with *p*-chloro-*N*-methylaniline and *N*-methylaniline, but weak with diphenylamine, and does not appear distinctly with *N*-ethyl-*m*-toluidine for which only a change of the relative intensities of the bands near 1120 cm.$^{-1}$ takes place.

Wave numbers of the bands due to the C·NH·C *group of secondary aromatic amines (liquid, except diphenylamine).*

			Deuterated	
Compound	δNH	νC$_{ar}$–N	δND	νC$_{ar}$–N
N-Methylaniline	(1511) *	1262	1122	1351
N-Ethylaniline	1513	1256	1127	1346 1366
Diphenylamine	1514	1241	1083	1370
N-Ethyl-*o*-toluidine	(1515)	1261	1148	1326
N-Ethyl-*m*-toluidine	1508	1259	1149	1342
N-Methyl-*p*-toluidine	(1527)	1261	1126	1335
p-Chloro-*N*-methylaniline	1511	1261	1129	1348

* Wave numbers in parentheses refer to bands due to ring vibrations, and probably embrace also the NH bands.

The vibrations of the C·NH·C group are expected to give rise to three bands in the region between 1600 and 1100 cm.$^{-1}$. Two of the corresponding vibrations are to be associated with the stretching of the C–N bonds, the third being an angle-bending mode in which the hydrogen atom presumably moves asymmetrically to the plane bisecting the CNC angle. There is little experimental evidence available as to the probable position of the last band. In aliphatic secondary amines, the NH bending band is assumed [8] to be near 1450 cm.$^{-1}$, and the amide II band near 1550 cm.$^{-1}$ is associated [2] with a mainly NH bending motion. Therefore we may take the band or the shoulder near 1510 cm.$^{-1}$ as a possibility for this vibration. We can support this with the fact that the band is absent

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[8] Barr and Haszeldine, *J.*, 1955, 4169.

from the spectra of the two tertiary amines examined as well as from those of the deuterated compounds. In the three cases in which no second band appears near 1510 cm.$^{-1}$, the δNH band may be covered by the strong aromatic band at 1500 cm.$^{-1}$. The ND bending band is to be expected at lower wave numbers. We find actually a new band in the spectra of the deuterated compounds near 1120 cm.$^{-1}$ (Fig. 2), the ratio of the frequencies approximating to the theoretical one of 1·38. Smaller shifts observed with other bands demonstrate, however, that the bending vibrations of the NH (or ND) group couple

FIG. 1.

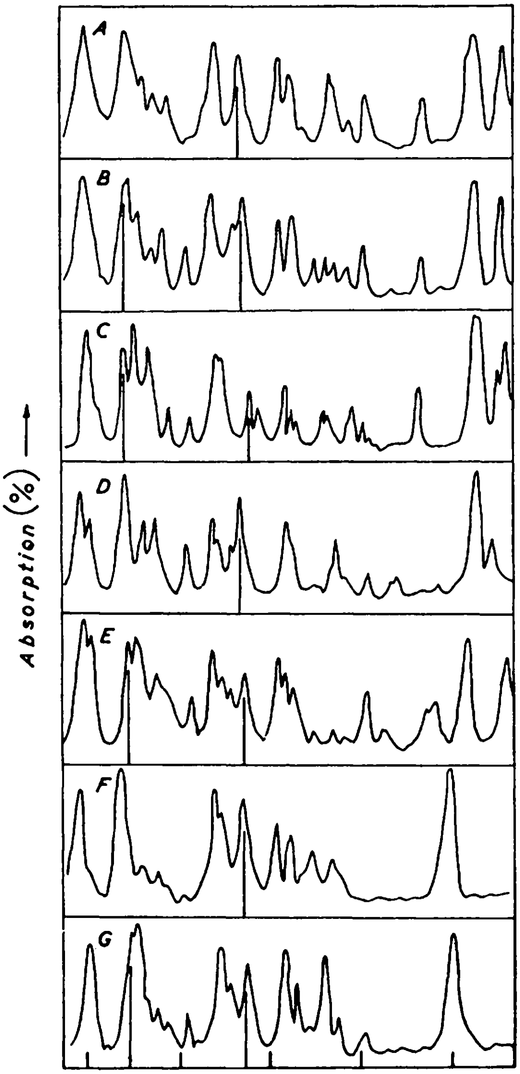

FIG. 2.

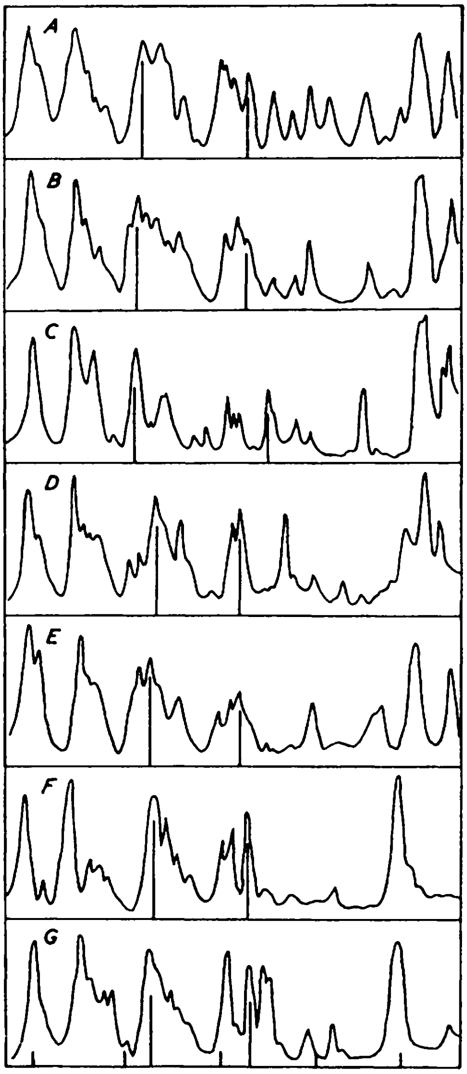

FIG. 1. *Infrared spectra of secondary aromatic amines* : *A,* N-*methylaniline*; *B,* N-*ethylaniline*; *C, diphenylamine*; *D,* N-*ethyl*-o-*toluidine*; *E,* N-*ethyl*-m-*toluidine*; F, N-*methyl*-p-*toluidine*; G, p-*chloro*-N-*methylaniline. Liquid films, except C (solid, mulled with Nujol and hexachlorobutadiene).*

FIG. 2. *Infrared spectra of deuterated aromatic amines. Key as in Fig.* 1.

considerably with the vibrations of the other atoms, and therefore the assignment of the bands near 1510 and 1120 cm.$^{-1}$ to the δNH and δND modes, respectively, are rough approximations only.

The CN stretching vibration in methylamine has been established[9] at 1044 cm.$^{-1}$, and the spectra of simple secondary aliphatic amines show a strong band between 1130 and 1170 cm.$^{-1}$, which is to be associated with skeletal vibrations in which the CN bonds participate strongly.[10] The C–N bond, the carbon atom of which is part of an aromatic ring, is appreciably shorter[11] than the CN bond in aliphatic amines;[12] hence, the aromatic νCN vibration should absorb at higher wave numbers corresponding to the increase in the double-bond character. Therefore the strong band near 1260 cm.$^{-1}$ in the spectra of the ordinary amines and the similarly strong band near 1350 cm.$^{-1}$ in the spectra of their deuterated analogues appear suitable for assignment to the stretching vibration of the C_{ar}–N bond. This assignment, together with that of the band near 1510 cm.$^{-1}$ due mainly to the NH deformation vibration, forms a parallel to one of the current interpretations[2] of the secondary amide spectra. The explanation of the shift on deuteration of the band attributed at present to the νCN vibration from about 1260 cm.$^{-1}$ to near 1350 cm.$^{-1}$ may be explained accordingly[2] by assuming a strong coupling between this vibration and the δNH. The interpretation of the amine spectra may alternatively be made along the lines adopted recently by Miyazawa *et al.*[13] for the interpretation of the amide spectra. This would lead to the assumption that the band near 1510 cm.$^{-1}$ has mainly the character of the CN stretching whereas that near 1260 cm.$^{-1}$ would be preponderantly δNH in character, both being strongly coupled. Deuteration would lift the accidental degeneracy so that the resulting bands near 1120 and 1350 cm.$^{-1}$ would be almost " pure " δNH and νCN. However, our present standpoint is favoured by the comparison with the spectra of the tertiary and primary aromatic amines. Colthup's table[14] shows that the tertiary amines have medium bands in the region 1180—1250 cm.$^{-1}$, and secondary amines at 1230—1280 cm.$^{-1}$. It has been observed also in this laboratory that the spectra of tertiary amines do not show any reduction in the number of bands in this region compared with the secondary amines, as would be expected if the δNH vibration absorbed here. Thus dimethylaniline, diethylaniline, and triphenylamine have bands at 1226, 1260, and 1275 cm.$^{-1}$, respectively, resembling the corresponding secondary amines. Primary amines also have strong bands[14] between 1250 and 1350 cm.$^{-1}$. This points to the conclusion that the C_{ar}–N stretching vibration absorbs in the region near 1300 cm.$^{-1}$. It has been already mentioned that none of the tertiary amines investigated shows the second band near 1510 cm.$^{-1}$, which also fits the present assignments.

Not much can be said about the $C_{aliphatic}$–N bond stretching. In the spectra of deuterated *N*-methylaniline, *N*-methyl-*p*-toluidine, and *p*-chloro-*N*-methylaniline, a new band of medium intensity appears near 950 cm.$^{-1}$. This seems to be formed in place of a similarly intense band near 1060 cm.$^{-1}$ in the spectra of the corresponding undeuterated amines. This couple of bands resembles that described by Edsall[15] in the Raman spectra of dimethylamine and deuterated dimethylamine, respectively, and attributed to the CN stretching vibration. This might be the case also with the three amines mentioned above, but the fact that these amines contain only the N–CH_3 group suggests the possibility that the shifted band may be due to a vibration (probably rocking) of the methyl group, interacting with the ND bending mode.

A second deformation of the NH bond angle, in which the hydrogen atom vibrates perpendicularly to the plane defined by the CNC atoms, might be expected to absorb

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[9] Barceló and Bellanato, *Spectrochim. Acta*, 1956, **8**, 27.
[10] Hadži and Škrbljak, unpublished work.
[11] Brown, *Acta Cryst.*, 1949, **2**, 228; 1951, **4**, 100.
[12] Allen and Sutton, *ibid.*, 1950, **3**, 46.
[13] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **25**, 408.
[14] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[15] Edsall, *J. Chem. Phys.*, 1937, **5**, 225.

below 800 cm.$^{-1}$. However, no band suitable for assignment to this vibration could be detected in the spectra investigated.

Experimental.—Most of the compounds used in this investigation were given to us by the Imperial Chemical Industries Limited, Dyestuffs Division, and were used without further purification. *N*-Methylaniline and diphenylamine were of commercial origin and were distilled and recrystallised, respectively. Exchange with deuterium was performed by shaking the liquids with heavy water for 12 hr., but diphenylamine was deuterated in dioxan solution. The spectra were recorded with a Perkin Elmer Model 21 spectrometer, the liquids spread between two rock-salt plates and the solid mulled with mineral oil and hexachlorobutadiene.

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