159. *Infrared Absorption Bands Associated with the* NH *Group. Part II.** *Some Secondary Thioamides and* N-*Methyltoluene*-p-*sulphonamide.*

By D. HADŽI.

Infrared spectra of thiobenzanilide, thiofuranilide, and *N*-methyl(thiofuramide) have characteristic bands near 1520—1535 and 1335—1375 cm.$^{-1}$, which are replaced on deuteration by two new ones near 1100 and 1380—1410 cm.$^{-1}$. These bands are analogous to the amide bands II and III, and II′ and III′, respectively, due to combined NH deformation and CN stretching vibrations. The C=S stretching band is near 1000 cm.$^{-1}$, and the NH out-of-plane bending band near 710 cm.$^{-1}$. With *N*-methyltoluene-*p*-sulphonamide, the S–N stretching band has been located at 839 cm.$^{-1}$, the NH bending at 1410 cm.$^{-1}$, and the CN stretching at 1060 cm.$^{-1}$. In the deuterated·compound the ND bending and the CN stretching vibrations couple strongly, yielding two bands at 918 and 1218 cm.$^{-1}$.

ALTHOUGH much work has been done on the spectra of secondary amides, the interpretation of the bands near 1550 (amide II) and 1250 cm.$^{-1}$ (amide III) seems to be still controversial.[1, 2] Calculations of the vibrational frequencies have given results which differ considerably from the experimental.[3] It was believed that investigations of compounds related to amides might be interesting, and therefore the spectra of secondary thioamides and of a secondary sulphonamide were studied.

N-*Substituted Thioamides.*—Previous work on this type of compound concerns only the high-frequency region.[4] After the present investigation a paper by Mecke *et al.* appeared [5] dealing with the spectra of thiolactams. The present work includes the spectra of thiofuranilide, thiobenzanilide, and thiofuramide as well as of their deuterated analogues. *N*-Methyl(thiofuranilide) and benzanilide were added for reference, but will not be dealt with in detail.

The high-frequency region of the spectra of the solid thioamides is characterised by a broad band of medium intensity between 3140 and 3190 cm.$^{-1}$. For solutions in carbon tetrachloride, this band is replaced by a narrow one near 3390 cm.$^{-1}$. It is certainly due to the NH stretching vibration, the different wave numbers for the solid and the solution

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* Part I, preceding paper.

[1] Fraser and Price, *Nature*, 1952, **170**, 490.

[2] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **25**, 408.

[3] Miyazawa, *J. Chem. Soc. Japan*, 1955, **76**, 341.

[4] Flett, *J.*, 1953, 347.

[5] Mecke, Rolf, Mecke, and Reinhard, *Chem. Ber.*, 1956, **89**, 343.

indicating hydrogen bonding in the solid state. The νNH band of the solids shows a slight splitting, more pronounced with the deuterated compounds. With thiofur[^{2}H]amide, for instance, peaks occur at 2447 and 2419 cm.$^{-1}$.

In the region between 1600 and 700 cm.$^{-1}$, the prominent features of the spectra investigated may be summarized as follows: (i) A strong band between 1523 and 1536 cm.$^{-1}$, absent from the spectra of deuterated thioamides, and also from that of *N*-methyl(thiofuranilide); the band at 1523 cm.$^{-1}$ of *N*-methyl(thiofuramide) has a shoulder, which remains after deuteration as an isolated band. (ii) A strong or a very strong band between 1330 and 1375 cm.$^{-1}$, removed on deuteration. (iii) A band of similar intensity to the last, which appears, after deuteration, between 1380 and 1410 cm.$^{-1}$; new bands of medium intensity appear also near 1100 cm.$^{-1}$, accompanied by a shift of one or more strong bands in the region 800—1000 cm.$^{-1}$ to smaller wave numbers. (iv) A band of medium intensity between 1220 and 1280 cm.$^{-1}$, which shifts slightly to higher wave numbers after deuteration. (v) A broad band of medium intensity near 715 cm.$^{-1}$, sensitive to deuteration.

FIG. 1. *Infrared spectra of thioanilides.*

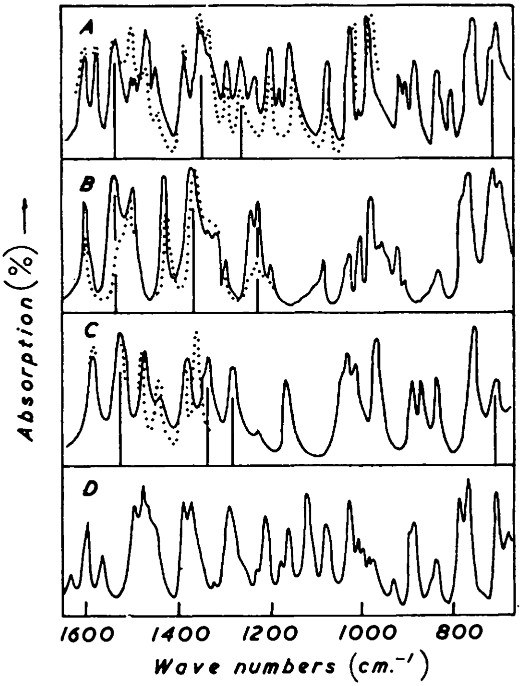
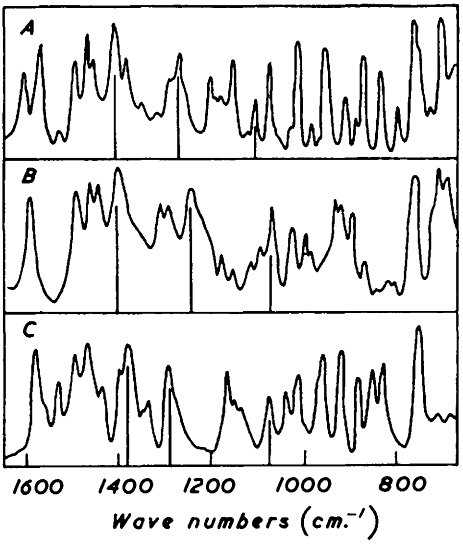


FIG. 2. *Infrared spectra of deuterated thioanilides.*



Key to Figs. 1 *and* 2.
A, thiofuranilide; B, thiobenzanilide; C, N-*methyl(thiofuramide); D,* N-*methyl(thiofuranilide). Broken lines: solutions in* CCl_4.

In interpretation of the spectra of the thioamides, difficulties are similar to those with amides. Regarding the number of bands which shift considerably after deuteration, it is clear that the vibrations of the hydrogen atom interact strongly with other vibrations of the thioamide group, and probably also with those of the rest of the molecule. Hence, if a band is attributed to a specific motion of some group of atoms, this should be understood to imply only a major contribution from that motion.

The characteristics (i)—(iii) of the thioamide spectra, *i.e.*, removal of the bands near 1530 and 1360 cm.$^{-1}$ on deuteration, and appearance of new bands near 1400 and 1100 cm.$^{-1}$, are very similar to characteristic features of the simple secondary amides, and there is no doubt that these bands belong to the vibrations of the C·NH and C·ND group, respectively. Some bands of the thioamide spectra might be easier to interpret with the deuterated compounds, if it were assumed that there is less interaction between the ND bending and the CN stretching vibrations, as in simple amides.[1, 2] Thus, the strong band which appears on deuteration between 1380 and 1410 cm.$^{-1}$ may be ascribed to the CN stretching vibration : it has somewhat smaller wave numbers than are observed with the analogous vibration in secondary amides, but very similar to those for aromatic amines.[6] Since the νCN band is among the strongest in the spectra of secondary thioamides, it seems necessary to correlate it with the similarly strong band (ii) of the undeuterated thioamides. The wave-number ratio of both bands being near 0·98, as with aromatic amines,[6] it seems legitimate to consider both bands as due essentially to the CN stretching vibration. Mecke *et al.*[5] assigned a strong band near 1300 cm.$^{-1}$ in the spectra of thiolactams and thioureas to the analogous vibration, the band being only slightly sensitive to deuteration.

After these assignments there appears to be only one possibility for the band (i) near 1530 cm.$^{-1}$, *viz.*, an essentially NH bending character. The wave number of this band closely resembles that of the amide II band. As an example, benzanilide and thiobenzanilide have bands at 1527 and 1533 cm.$^{-1}$. The similar position of the δNH band in secondary aromatic amines [6] should be stressed, also the coupling between δNH and νCN in both cases. If this analogy with the amides is extended, the ND bending band should be near 1100 cm.$^{-1}$. In fact, a new band at 1105 cm.$^{-1}$ appears on deuteration in the spectrum of thiofuranilide, and bands at 1148, 1138, and 1078 cm.$^{-1}$ in that of *N*-methyl(thiofuranilide). No definitely new band is observed with deuterated thiobenzanilide, but the band at 1078 cm.$^{-1}$ seems to be considerably stronger than that at 1075 cm.$^{-1}$ in the spectrum of simple thiobenzanilide, indicating possibly the superposition of a new band. The shifts mentioned above under (iii) are probably caused by coupling of the νC=S, and possibly some skeletal vibration modes, with the nearby δND. Definite assignment of any of the strong bands in this region to the νC=S, and detailed explanation of the shifts on deuteration, appear to be very difficult.

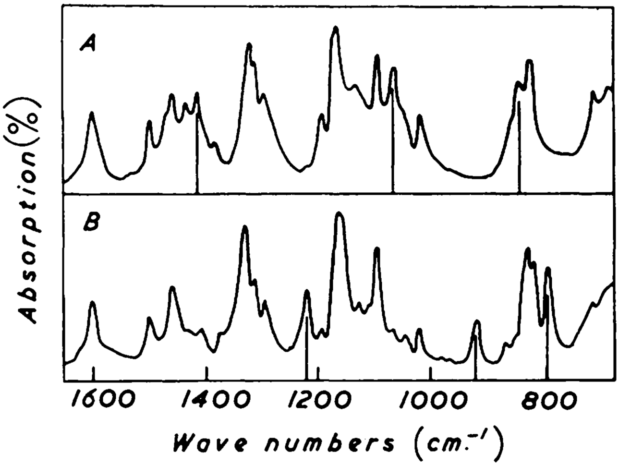


FIG. 3. *Infrared spectra of* N-*methyltoluene*-p-*sulphonamide* (*A*) *and its deuterated analogue* (*B*).

In secondary thioamides, two C–N bonds exist, and thus another CN stretching vibration should appear in their spectra, being possibly in-phase with respect to the νCN vibration discussed above. It is probably associated with the bands mentioned under (iv). In simple and deuterated thiobenzanilides, they are at 1220 and 1250 cm.$^{-1}$, respectively, in the thiofuranilidies at 1264 and 1274 cm.$^{-1}$, and in the *N*-methylfuramides at 1280 and 1292 cm.$^{-1}$. The position of these bands is similar to that for secondary amides,[2] and the shift on deuteration is also consistent with the assignment, showing some coupling, probably with the ND bending vibration.

There is little doubt about the assignment of the band (v), its broadness and position

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[6] Hadži and Škrbljak, preceding paper.

(similar to that in simple amides[2]) suggesting that it is due to the NH out-of-plane deformation. It does not appear clearly with thiobenzanilide, coinciding perhaps with some of the strong CH out-of-plane deformation bands.

It is necessary to comment briefly on a band which seems to appear with deuteration at 1497 cm.$^{-1}$ with thiofuranilide and thiofuramide, and at 1468 cm.$^{-1}$ with thiobenzanilide. It is very sharp and therefore probably not directly connected with the hydrogen-bonded thioamide group, but rather with a skeletal mode, interacting with the NH bending vibration or the νCN mode in the deuterated compounds.

The changes of positions of the bands involved in hydrogen bonding on going from the solid state to dilute solution (0·05M) were expected to confirm the above assignments. Unfortunately, the compounds examined do not behave consistently. With *N*-methyl(thiofuramide), the band at 1523 cm.$^{-1}$ has the same position in the solid and in solution, within the experimental error, whereas the νCN is at 1335 cm.$^{-1}$ in the solid and at 1350 cm.$^{-1}$ in solution, being relatively much stronger in the latter. This shift is to be expected for a stretching vibration on association. With thiobenzanilide, the δNH, strong at 1533 cm.$^{-1}$ in the solid, seems to form a weaker band just under the 1500 cm.$^{-1}$ aromatic band. The shift to lower wave numbers on breaking of the hydrogen bonds is in agreement with the assignment to a bending mode. However, the νCN band also shows a slight shift in the same direction (to 1350 cm.$^{-1}$). With thiofuranilide, the analogous band has the same position in both states, but in solution a new band at 1500 cm.$^{-1}$ is observed, formed apparently from the band at 1470 cm.$^{-1}$ in the solid, whereas the δNH shows a very slight shift of a few wave numbers towards lower ones.

N-*Methyltoluene*-p-*sulphonamide*.—At first sight, sulphonamides seem to bear little relation to the amides, except for the presence of the NH group. However, some spectral analogies are apparent on considering the spectrum of *N*-methyltoluene-*p*-sulphonamide together with its deuteration product. Amongst the prominent bands, those at 1317 and 1170 cm.$^{-1}$ may be immediately identified with the symmetric and asymmetric stretching of the O=S=O group,[8] the band at 1092 cm.$^{-1}$ being recently shown to belong also to this group.[9] It is interesting that the $\nu_{as}SO_2$ band shifts slightly to higher wave numbers on deuteration. The band at 1600 cm.$^{-1}$ may certainly be attributed to a ring vibration, that at 823 cm.$^{-1}$ to γCH (*para*-substitution), and the complex absorption at 1455 cm.$^{-1}$ to the aromatic ring and the methyl-CH deformation. The bands at 1410, 1062, and 839 cm.$^{-1}$ are displaced on deuteration, bands at 1281, 918, and 791 cm.$^{-1}$ appearing instead. These bands must be attributed in turn to the NH and ND bending, and to the CN and SN stretching vibrations. The latter has been assigned by Baxter, Cymerman-Craig, and Willis [10] to a band near 1090 cm.$^{-1}$, but this band is found regularly with all sulphonic compounds.[9] The νSN band is to be expected at lower wave numbers, νS–O being found also at lower wave numbers than the corresponding νC–O bands: thus Maschka and Aust [11] find νS–N lines at 800—900 cm.$^{-1}$ in the Raman spectra of various sulphonamides. We have found bands at 904, 918, and 909 cm.$^{-1}$ in the spectra of benzenesulphonamide and toluene-*o*- and -*p*-sulphonamide, respectively, which are not present with, for instance, the halides. It is to be expected that the corresponding band in a methylsulphonamide will have a smaller wave number, the light atom being replaced by a methyl group. Hence the assignment of the band at 839 cm.$^{-1}$ in the spectrum of methyltoluenesulphonamide to the SN stretching seems justified. The shift to 791 cm.$^{-1}$ on deuteration is in agreement with this. The band at 1060 cm.$^{-1}$, not present with other sulphonyl derivatives, may be associated with the CN stretching vibration, in agreement with the generally assumed position of νC–N bands in simple amines.[12] The only remaining assignment for the band

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[7] Mecke, Mecke, and Lüttringhaus, *Z. Naturforsch.*, 1955, **10b**, 367.

[8] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1954, p. 295.

[9] Detoni and Hadži, *Spectrochim. Acta*, in the press.

[10] Baxter, Cymerman-Craig, and Willis, *J.*, 1955, 669.

[11] Maschka and Aust, *Monatsh.*, 1954, **84**, 89.

[12] Ref. 8, p. 220.

at 1410 cm.$^{-1}$ is that of the NH bending. On deuteration, the corresponding vibration frequency is expected to be reduced in a ratio near $\sqrt{2} : 1$, which would bring it nearly to coincidence with the C–N vibration. These accidentally degenerate vibrations give rise to two new bands at 918 and 1218 cm.$^{-1}$, respectively.

Discussion.—The spectra of secondary amides and thioamides show close analogies, except for the differences caused by the replacement of the carbonyl by the C=S group. The present interpretation of the secondary thioamide spectra strongly favours assignment of the band near 1530 cm.$^{-1}$ to the vibration which has predominantly the character of the NH bending; nevertheless arguments could be certainly adduced in favour of the alternative assignment to the (mainly) CN stretching vibration whilst the band near 1360 cm.$^{-1}$ would then be connected with the NH bending vibration, as in the case of secondary amides.[13] More experimental material will be presented in forthcoming papers, with a discussion on a broader basis.

The separation of the δNH and the νCN bands in the spectrum of methyltoluenesulphonamide is so large that little interaction between the respective vibrations need be assumed. However, strong coupling results when hydrogen is replaced by deuterium. This has a counterpart among the simple secondary amides, where the νCN and the δNH are accidentally degenerate, the degeneracy being removed by deuteration.[1, 13]

Experimental.—The substances used in this investigation were presented by Professor V. Hahn (thioamides) and by Imperial Chemical Industries Limited, Dyestuffs Division (*N*-methyltoluenesulphonamide) (both of whom we thank), and were used without further purification. Deuteration was performed by recrystallisation of the substance from heavy water or by its dissolution in dioxan and addition of heavy water until precititation occurred, with subsequent drying in a stream of dry air. The spectra were recorded with a Perkin-Elmer spectrometer, equipped with a rock-salt prism. The solid substances were made into mulls with mineral oil or hexachlorobutadiene. The solutions were about 0·05M in CCl_4 in 0·1 mm. cells.

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[13] *Op. cit.*, p. 186.