522. *The Infrared Absorption of Normal and* ^{18}O*-Labelled* N*-Methylbenzamide.*

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The infrared absorptions of normal and 89 atom % *N*-methylbenz[^{18}O]-amide were measured in solution in carbon tetrachloride, chloroform, and bromoform, and as Nujol mulls, in the 3700—670 cm.$^{-1}$ region. The bands are assigned to molecular vibrations, and the origin of the characteristic secondary amide bands is discussed in the light of their location in the labelled spectra. The C=^{18}O stretching band was about 20% stronger than that due to the C=^{16}O group (in CCl_4).

The infrared absorption of a number of various X=^{18}O compounds (X = C, P, N) was recently investigated, especially in connection with the intensities of the X=^{18}O stretching bands compared with those of the corresponding X=^{16}O bands.[1] It was observed [1d] that benz[^{18}O]amide behaves differently in showing a higher intensity for its C=^{18}O band (in CCl_4) instead of the lower intensity observed with such X=O bands [1] in the other cases studied. We have therefore investigated *N*-methylbenzamide. The infrared spectrum of normal ^{18}O-labelled methylbenzamide is also of interest from the point of view of the interpretation of the " II and III amide bands " of secondary amides, which is a matter of much controversy.[2] The spectra obtained for solutions in carbon tetrachloride, chloroform, and bromoform and for Nujol mulls, in the 3700—670 cm.$^{-1}$ region, are reported in Table 1, where the optical densities are added in parentheses.

That 0·007 g. of *N*-methylbenzamide in 1 ml. of carbon tetrachloride shows a considerable band (which disappears on further dilution) at 3350 cm.$^{-1}$ and only a weak band at about 3460 cm.$^{-1}$ is proof that in these solutions the amide exists mainly in the dimeric form; the (*trans*) secondary amides N–H stretching frequency of the dimer is known to appear at about 3350 cm.$^{-1}$, while their monomeric N–H vibration is in the 3450 cm.$^{-1}$ region.[3] With 0·7 g./l., however, the amide is practically fully in the monomeric modification,

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[1] Halmann and Pinchas, *J.*, 1958, (*a*) 1703, (*b*) 3264; (*c*) 1960, 1246; Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, (*d*) 1688, (*e*) 2382.

[2] See, *e.g.*, Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., 2nd edn., London 1959, pp. 217, 218.

[3] Klemperer, Cronyn, Maki, and Pimentel, *J. Amer. Chem. Soc.*, 1954, **76**, 5846.

as judged from the presence of only the 3470—3480 cm.$^{-1}$ band in this range of its spectrum. This value for this band seems to show that the *N*-methylbenzamide exists in its *trans*-configuration, in analogy with *N*-methylacetamide,[4] since the range for *trans*-N–H groups is usually 3440—3460 cm.$^{-1}$ while it is 3420—3440 cm.$^{-1}$ for *cis*-groups.[4] Steric interaction between the bulky methyl group and the aromatic hydrogen atoms probably contributes to stabilise further the less hindered *trans*-form of this amide.

TABLE 1. *Infrared absorption bands of normal and* ^{18}O-*labelled* N-*methylbenzamide.*

					Bands (cm.$^{-1}$)	
No.	Material	Solvent	Concn.	Thickness (mm.)	νN–H	νN–H
1	Normal	CCl_4	0·007 g. + 1 ml.	0·5	3460(0·07)	3350(0·12)
2	89% ^{18}O	CCl_4	0·0076 g. + 1 ml.	0·5	3470(0·05)	3350(0·10)
3	Normal	CCl_4	0·3 g./l.	20	3480(0·10)	
4	89% ^{18}O	CCl_4	0·7 g./l.	20	3470(0·24)	
5	Normal	$CHCl_3$	0·0064 g./ml.	0·5	3470(0·06)	
6	89% ^{18}O	$CHCl_3$	0·0073 g./ml.	0·5	3460(0·11)	
7	Normal	$CHBr_3$	0·0077 g. + 1 ml.	0·5	[c]	
8	89% ^{18}O	$CHBr_3$	0·0093 g. + 1 ml.	0·5	[c]	

			Bands (cm.$^{-1}$)				
No.	νC_{ar}–H [e,f]	νCH_3 [g]	νC=O	$\nu(C=C)_{ar}$	II amide	antisym. δCH_3	sym. δCH_3
1	3080(0·05)	2940(0·07)	1673(0·73)	1579(0·20)	1524(0·36)	1484(0·31)	1415(0·16)
2	3070(0·05)	2950(0·05)	1649(0·50)	1579(0·14)	1524(0·6)	1483(0·31)	1413(0·17)
3	3050(0·04)	2940(0·07)	1675(1·0) [b]				1413(0·15)
4	3050(0·22)	2940(0·28)	1651vs [b]				1413(0·39)
5	[a]		1657(1·06)	1578(0·19)	[a]	1484(0·26)	1421(0·15)
6	[a]		1633(1·07)	1575(0·36)	[a]	1484(0·45)	1420
7			1653(0·94)	1575(0·20)	1524(0·58)	1484(0·33)	1415(0·19)
8			1633(0·93)	1573(0·38)	1523(0·91)	1484(0·46)	1416(0·34)

			Bands (cm.$^{-1}$)				
				δC_{ar}–H			
No.	III amide	?	CH_3–N rock			νC_{ar}–CO	
1	1276(0·32)	1163(0·12)	1150(0·08)	1071(0·05)	1030(0·04)	921(0·04)	
2	1275(0·35)	1215(0·22)	1150(0·10)	1071(0·05)	1033(0·05)	926(0·05)	
3							
4							
5	1282(0·37)	[a]	[1156(0·07)]	1072(0·07)	1036(0·07)	[a]	
6	1278(0·37)	[a]	[1154(0·07)]	1072(0·06)	1033(0·05)	[a]	
7							797(0·06)
8							797(0·07)

No.	Material				νC_{ar}–CO	γC_{ar}–H
9	Normal	Nujol	(mull)	Capillary [d]	935(0·78)	830(0·64)
10	89% ^{18}O	Nujol	(mull)	Capillary [d]	935(1·04)	826(0·68)

No.	γC_{ar}–H		γN–H		γC_{ar}–H [f]	γC_{ar}–H [f]
9	802(0·72)		716—706vs, br		696vs	685vs
10	800(0·79)	719vs	709vs	705vs	698vs	690(0·90)

[a] Absorption in this region is obliterated by the solvent band. [b] The high cell-thickness masks the absorption in the 1630—1460 cm.$^{-1}$ zone and below 1300 cm.$^{-1}$. [c] Measured only in the 1680—1410 and 880—710 cm.$^{-1}$ regions. [d] Measured only in the 940—670 cm.$^{-1}$ range. [e] This heading refers to the bands at 3050 cm.$^{-1}$ only, since the 3070—3080 bands contain a bonded N–H absorption (ref. 2, p. 205). [f] Ref. 2, p. 65. [g] *Ibid.*, p. 16.

Values in square brackets were observed with higher concentrations; their optical densities are, however, reduced in accord with the given concentration.

Methylbenzamide shows a higher tendency to form dimers than does ethylacetamide,[3] a 0·04M-solution of which in carbon tetrachloride is mainly monomeric while a 0·05M-solution of methylbenzamide shows the monomeric frequency almost solely as a shoulder. This is noteworthy and might be connected with the higher conjugation of the C=O group in the former.

The 0·007 g./ml. chloroform solutions, which show only a 3460—3470 cm.$^{-1}$ band in

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[4] Ref. 2, p. 207.

the N–H range, are however clearly monomeric. A phenomenon similar to the effect of chloroform on the dissociation of amide dimers has been observed for benzamide[1d] and other (secondary) amides[3] and is the result of strong (CH · · · OC) interaction between the chloroform and the amide dissolved in it. This interaction also exists between bromoform and dissolved amide, as is shown by the comparable values for the amide C=O stretching frequencies in chloroform and bromoform (in normal methylbenzamide, *e.g.*, 1657 and 1653 cm.$^{-1}$, respectively, as compared with 1673 cm.$^{-1}$ for a CCl_4 solution), hence the amide in solutions of 0·0077—0·0093 g. in 1 ml. of bromoform is also mostly monomeric. Thus, all the solution results reported in Table 1, except those for 0·007 g./ml. carbon tetrachloride solutions, refer to monomeric methylbenzamides.

When the normal dimeric spectrum (in CCl_4) is compared with the monomeric absorption (in CCl_4 and, where no such data exist, in $CHCl_3$) it is seen that outside the N–H region the differences are usually very small and the bands appear in almost the same place in both spectra. Hence the *trans*-dimerization affects the N–H bond strength much more than it affects the binding force of even the C=O group.

The big changes observed in the frequency of the 1675—1633 cm.$^{-1}$ band on exchange of ^{16}O for ^{18}O in the amide, and/or on change of the solvent from carbon tetrachloride to bromoform, show unequivocally that this band is mainly due to the stretching of the C=O group. Thus, the isotopic decrease of this band in carbon tetrachloride (and chloroform) amounts to 24 cm.$^{-1}$ (from 1675 to 1651) as compared with 31 cm.$^{-1}$ for di-isopropyl ketone,[5] 29 cm.$^{-1}$ for benzophenone,[1a] and 24 cm.$^{-1}$ for benzamide.[1d] This is in harmony with the calculations of Miyazawa, Shimanouchi and Mizushima[6] for the 1653 cm.$^{-1}$ band of *N*-methylacetamide, according to which this band is 80% CO stretching, and seems to show that Price and Fraser's view,[7] that the secondary amide I frequency has in fact an asymmetrical OCN stretching nature, is somewhat exaggerated.

The value of 1675 cm.$^{-1}$ for C=O stretching of the monomeric normal methylbenzamide (in CCl_4) compares favourably with that (1690 cm.$^{-1}$) reported[1d] for the corresponding benzamide frequency, since it is known that monoalkyl substitution decreases such a frequency by some 10 cm.$^{-1}$ because of electronic effects.[8] The lower frequency (about 1667 cm.$^{-1}$) observed for an analogous band of *solid* *N*-ethylbenzamide[9] is no doubt the result of strong hydrogen-bonding in the solid state which as a rule lowers the amidic C=O frequency.[10]

The decrease in the C=O frequencies of monomeric methylbenzamide on changing the solvent from carbon tetrachloride to chloroform is 18 cm.$^{-1}$ for both of the isotopic modifications although it was smaller and somewhat different for the isotopic species of benzamide[1d] (15 for the normal and 11 for the labelled). This seems to suggest a somewhat stronger chloroform–amide interaction with the more polar secondary amides.

The band observed in all the spectra at about 1575 cm.$^{-1}$ is probably due to an aromatic C=C stretching[11] while the other aromatic C=C absorption expected,[11] at about 1500 cm.$^{-1}$, is probably masked by the strong 1524 cm.$^{-1}$ band. The latter seems to be the strong[1d] II amide band which is shown by hydrogen-bonded *N*-methylacetamide[6] at 1567 cm.$^{-1}$ and by solid *N*-ethylbenzamide[9] at about 1570 cm.$^{-1}$, as it is well known that hydrogen-bonding increases the frequency of such bands.[2] According to Miyazawa *et al.*,[6] ~60% of this absorption, with methylacetamide, is due to N–H bending and 40% to C–N stretching. That *N*-methylbenz[^{18}O]amide shows this band almost at the same place (1523) supports such an assignment. The even higher intensity of this band for the dimers also favours this interpretation since in the dimers the free charges on the nitrogen atoms

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[5] Karabatsos, *J. Org. Chem.*, 1960, **25**, 315.

[6] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1958, **29**, 611.

[7] Price and Fraser, *Proc. Roy. Soc.*, 1953, *B*, **141**, 66.

[8] Richards and Thompson, *J.*, 1947, 1248.

[9] Lenormant, *Ann. Chim. (France)*, 1950, **5**, 476.

[10] Ref. 2, p. 209.

[11] Ref. 2, p. 69.

can be expected to rise as a result of the hydrogen-bonding; such a rise should increase the absorption intensity of those frequencies which concern these atoms.

The bands at about 1480 and 1420 cm.$^{-1}$ seem to be due to antisymmetric and symmetric bending of the *N*-methyl groups, respectively, which in C–CH_3 groups cause absorption at about [12] 1460 and 1380 cm.$^{-1}$. In the case of $CH_3 \cdot ND_2$ (gas) these bands probably appear [13] at about 1470 and 1430 cm.$^{-1}$, respectively, while the symmetric N–CH_3 band of (hydrogen-bonded) *N*-methylacetamide [6] is at 1413 cm.$^{-1}$.

The 1282—1278 cm.$^{-1}$ band of monomeric *N*-methylbenzamide corresponds to the 1299 cm.$^{-1}$ III amide band of (bonded) methylacetamide [6] which was calculated [6] to be due 40% to C–N stretching and 30% to N–H bending. The exchange of ^{16}O for ^{18}O shifts it, in this case, by 4 cm.$^{-1}$ only, and this agrees with such an interpretation as also does the fact that it is affected moderately by dissociation and/or change of solvent from carbon tetrachloride to chloroform (normal dimer in CCl_4 1276; normal monomer in $CHCl_3$ 1282). This is so since it is known that such variations of conditions affect [14] the N–H bending and C–N stretching [1d] of amides.

The 1150 cm.$^{-1}$ bands are analogous to the 1159 cm.$^{-1}$ band of *N*-methylacetamide which was assigned to the CH_3–N rocking.[6] The 1072 and 1036 cm.$^{-1}$ bands seem to be due to the monosubstituted benzene moiety.[15] The absorptions observed with a Nujol mull of the isotopic amides are more difficult to assign to specific modes of vibration since the materials are then in a strongly hydrogen-bonded structure where the lattice forces affect seriously and split the original vibrations. It appears, however, that the 935 cm.$^{-1}$ absorption can be correlated with the stretching of the C_{ar}–CO bond since it is shown at the same place by solid *N*-ethylbenzamide,[9] at about 925 cm.$^{-1}$ by acetophenone,[16] at 932 cm.$^{-1}$ by benzoyl chloride,[1e] at 934 cm.$^{-1}$ by methyl benzoate [1e] (unaffected by ^{18}O), at 940 cm.$^{-1}$ in benzophenone,[1a] at 923 cm.$^{-1}$ in benzaldehyde,[17] and near 900 cm.$^{-1}$ in many substituted benzaldehydes.[18] This band seems to shift to 921—926 cm.$^{-1}$ for dimer solutions.

The 830 and 802 cm.$^{-1}$ (normal) bands (in $CHBr_3$ only one band at 797) correspond to the out-of-plane aromatic C–H bending frequencies of solid benzamides [1d] observed at 790 and 771 cm.$^{-1}$. The bands observed at 719—705 cm.$^{-1}$ are probably due to associated secondary amides NH out-of-plane bending, which is shown by *N*-methylacetamide [6] and other secondary amides [19] at about 720 cm.$^{-1}$.

The Intensity of the Isotopic C=O *Bands.*—The optical-density measurements for the C=O bands of the isotopic *N*-methylbenzamides in solution are given in Table 2, together with the molecular extinction coefficients and relative integrated absorption intensities (obtained by multiplying these coefficients by the corresponding apparent half-widths; the last, in cm.$^{-1}$, are added in parentheses after the intensities).

Table 2 seems to show that, as could be suspected, the intensity of the monomeric *N*-methylbenzamide C=O absorption in carbon tetrachloride is (as in benzamide) appreciably higher for the ^{18}O-modification than for the normal one, the respective mean relative integrated absorption values being 10,900 ± 300 and 8900 ± 300 units. These values can be compared with those of 12,800 and 10,400 for benzamide.[1d] The small increase in half-width of the C=^{18}O band in CCl_4 observed here (from 33 to 35·5) is also analogous to the change observed there [1d] (from 20 to 22). This increase was also found for other C=^{18}O bands.[1b,e] The mean integrated absorption results for the chloroform solutions of the two *N*-methylbenzamides, 12,400 ± 400 and 11,900 ± 400 units, are practically

[12] Ref. 2, p. 21.

[13] Gray and Lord, *J. Chem. Phys.*, 1957, **26**, 690.

[14] Ref. 2, p. 219.

[15] Ref. 2, p. 82.

[16] National Research Council, National Bureau of Standards Infrared Spectral Catalogue, card no. 289.

[17] Documentation of Molecular Spectra Catalogue, curve no. 2410, Butterworths, London.

[18] Pinchas, *Analyt. Chem.*, 1957, **29**, 335.

[19] Ref. 2, p. 205.

TABLE 2. *Absorption intensity of the isotopic* N-*methylbenzamides:* C=O *bands.*

Material	Frequency (cm.$^{-1}$)	Solvent	Concn. (g./l.)	Thickness (mm.)	Optical density	Mol. extinction coeff. (l. mole^{-1} cm.$^{-1}$)	Rel. integrated absorption (l. mole^{-1} cm.$^{-2}$)
Normal monomer ...	1675	CCl_4	0·122	20	0·478	264 ± 12	8700 ± 400 (33)
Normal monomer ...	1675	CCl_4	0·194	20	0·787	274 ± 7	9000 ± 300
89% ^{18}O monomer...	1651	CCl_4	0·126	20	0·504 [a]	308 ± 7 [b]	10,900 ± 300 (35·5)
89% ^{18}O monomer...	1651	CCl_4	0·144	20	0·581 [a]	310 ± 14 [b]	11,000 ± 500
Normal dimer	1673	CCl_4	5·94	0·5	0·588	267 ± 7	11,200 ± 300 (42)
89% ^{18}O dimer	1649	CCl_4	6·9	0·5	0·498 [a]	222 ± 9 [b]	11,100 ± 300 (50)
Normal monomer ...	1657	$CHCl_3$	5·62	0·5	0·784	377 ± 10	12,400 ± 400 (33)
89% ^{18}O monomer...	1633	$CHCl_3$	5·3	0·5	0·576 [a]	334 ± 16 [b]	11,700 ± 500 (35)
89% ^{18}O monomer...	1633	$CHCl_3$	6·28	0·5	0·709 [a]	347 ± 9 [b]	12,100 ± 400

[a] Uncorrected for the absorption of the normal amide content. [b] Corrected for the lower effective concentration.

identical, in analogy with the situation in the case of benzamide [1d] (14,500 in both modifications).

It is noteworthy that the C=O absorption intensity of the dimers is also the same in both of the isotopic methylbenzamides although their band half-widths are in this case appreciably different.

Experimental.—N-*Methylbenz*[^{18}O]*amide.* [^{18}O]Benzoyl chloride [1e] (90 atom % of ^{18}O) was dissolved in dry dioxan with cooling (ice-bath). Methylamine, dried over potassium hydroxide, was bubbled through it in excess. After ½ hr. the methylamine hydrochloride was filtered off and washed with benzene. The benzene–dioxan solution was dried (Na_2SO_4), decolorised with charcoal, and evaporated until crystals began to appear. The crystals were redissolved by adding dioxan and reprecipitated by dry light petroleum. The solid, m. p. 77—79°, contained 88·5 atom % of oxygen-18.

N-*Methylbenz*[^{16}O]*amide.* This was prepared in an identical manner from normal benzoyl chloride.

The infrared spectra were measured with a Perkin–Elmer model 12 C spectrophotometer equipped with a sodium chloride prism as already described.[1e].

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