329. *The Infrared Absorption of* ^{18}O*-Labelled Benzamide.*

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Dilute carbon tetrachloride, chloroform, and bromoform solutions of isotopically normal benzamide and benzamide containing 79 atom % of ^{18}O have been used in measurements of their spectra in the 3800—670 cm.$^{-1}$ region. The observed bands are discussed and assigned to their original vibrations. The C=^{18}O band is shifted by 24 cm.$^{-1}$ (in CCl_4), and the N–H bending (in $CHCl_3$) by 10 cm.$^{-1}$, but the C–N frequency is unaffected. The relative integrated band intensity of the C=^{18}O stretching (in CCl_4) is about 20% bigger than that of the corresponding C=^{16}O band.

THE assignment of the characteristic infrared absorption bands of amides, especially those at about 1550 and 1300 cm.$^{-1}$, has been discussed very extensively,[1] being the subject of many controversies. Since the infrared absorption spectra of ^{18}O-labelled amides might, in conjunction with the normal spectra, unravel the amount of participation of the amide-oxygen atom in the vibrations associated with the various bands, we now report

TABLE 1. *Infrared absorption bands of benzamide, isotopically normal and containing 79 atom % of* ^{18}O *(optical densities in parentheses).*

No.	Species	Solvent	Concentration	Cell-thickness (mm.)	Bands (cm.$^{-1}$)		
1	Normal	CCl_4	Satd. ($<$0·4 g./l.)	20	3540(0·12), 3420(0·14), 3160(0·10), 3080(0·09),		
2	^{18}O	CCl_4	,,	20	3535(0·11), 3430(0·13), 3160(0·09), 3080(0·085),		
3	Normal	$CHCl_3$	7·6 g./l.	1	3525(0·27), 3410(0·30), —		*c*
4	^{18}O	$CHCl_3$	4·3 g./l.	1	3530(0·12), 3425(0·16), —		*c*
1	Normal (contd.)	CCl_4	Satd. ($<$0·4 g./l.)		1689(1·1),	*a*	1357(0·88)*b*
2	^{18}O (contd.)	CCl_4	,,		1666(1·2),	*a*	1356(0·95)*b*
3	Normal (contd.)	$CHCl_3$	7·6 g./l.		1672($\gg$1·5)	1584(1·2),	1368(1·2)*d*
4	^{18}O (contd.)	$CHCl_3$	4·3 g./l.		1656(1·2)	1576(0·68),	1367(0·75)*d*
	Normal *e*	$CHBr_3$	0·02 g. + 1 ml.	1·4			800(0·48), 724(0·42)
	^{18}O *e*	$CHBr_3$	0·017 g. + 1 ml.	1·4			799(0·35), 723(0·30)
	Normal *f*	CCl_4	0·138 g./l.	20	1690(0·98)		1358(0·66)
	^{18}O *f*	CCl_4	0·065 g./l.	20	1666(0·48)		1358(0·30)
	Normal *f*	$CHCl_3$	1·39 g./l.	1	1675(0·66),	1606s,	1584(0·26)
	^{18}O	$CHCl_3$	1·39 g./l.	1	1655(0·61)	1605s,	1574(0·18)

a The 1640—1440 cm.$^{-1}$ region is masked by the solvent. No more bands observable down to 1280 cm.$^{-1}$. *c* The 3150—3050 cm.$^{-1}$ region is masked by the solvent. *d* In the 1270—1170 cm.$^{-1}$ region and from 830 cm.$^{-1}$ downwards the chloroform absorption practically obliterates that of the solute. *e* Measured only in the 830—670 cm.$^{-1}$ region. *f* Measured precisely and only at the vicinity of the main bands.

the spectra in the 3800—670 cm.$^{-1}$ region for dilute solutions of isotopically normal benzamide and benzamide containing 78·9 $\pm$ 0·4 atom % of ^{18}O in carbon tetrachloride, chloroform, and bromoform.

[1] Jones and Sandorfy in "Technique of Organic Chemistry," Interscience Publ. Inc., New York, N.Y., 1956, Vol. IX, pp. 521—530; Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1958, pp. 203—221; Fraser and Price, *Nature*, 1952, **170**, 490; Price and Fraser, *Proc. Roy. Soc.*, 1953, B, **141**, 66; Gierer, *Z. Naturforsch.*, 1953, 8b, 644, 654; Myazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **24**, 408; Becher and Griffel, *Naturwiss.*, 1956, **43**, 467; Becher, *Chem. Ber.*, 1956, **89**, 1593.

The infrared absorption of normal benzamide has already been reported several times; [2-6] a full solution spectrum, however, has not yet been published, the reported spectra being either for a solid sample [3,5,6] or of a fragmentary nature. [2,4] Table 1 summarises our results.

The medium bands at about 3530 and 3420 cm.⁻¹, which belong respectively to the asymmetrical and symmetrical stretching vibrations of a free NH_2 group, [7] show that even in ~1% solution in chloroform benzamide is largely monomeric. The barely visible band at 3160 cm.⁻¹, although observed with a <0·003M-carbon tetrachloride solution, must however be attributed to a hydrogen-bonded NH_2 stretching vibration existing in a dimer, since its relative intensity increases with concentration. [2] A small amount of dimer thus persists even in very dilute solutions of benzamide in carbon tetrachloride.

The values found for these bands with normal benzamide solutions agree well with those (3535, 3420, and 3170 cm.⁻¹) reported by Buswell, Rodebush, and Roy [2] for carbon tetrachloride solutions of benzamide, with the 3520 and 3410 cm.⁻¹ values reported by Richards and Thompson [4] for a chloroform solution, and with a value of about 3160 cm.⁻¹ for the hydrogen-bonded NH_2 group in the solid state. [6]

The 3080 cm.⁻¹ band is clearly due to the aromatic C–H stretching vibration; Buswell and his co-workers [2] observed it at the same frequency.

The 1690 cm.⁻¹ band of normal benzamide in carbon tetrachloride solution must be due to the carbonyl stretching vibration of the monomeric molecule, as is shown by its much lower frequency for the ¹⁸O-labelled modification. Richards and Thompson [4] observed it in this vicinity with a dioxan solution and assigned it in the same way. The value 1675 cm.⁻¹ given in Table 1 for a chloroform solution agrees with a reported value [8] of 1678 cm.⁻¹. For hydrogen-bonded solid benzamide this band appears [6] at about 1665 cm.⁻¹.

The strong 1584 and 1368 cm.⁻¹ bands of normal benzamide in chloroform solution (in solid benzamide: [6] 1630, 1410) are the well-known II amide band and the primary amide analogue of the III amide band, respectively (Myazawa *et al.*[1]). Their discussion is best deferred until after that of labelled benzamide.

The bands for bromoform solutions at 800 and 724 cm.⁻¹ are analogous to those for the hydrogen-bonded solid spectrum at 790, 771 (doublet), and 705 cm.⁻¹, respectively. [6,9] The higher bands seem to be due to the aromatic C–H out-of-plane bending vibrations of benzenes monosubstituted by an electron-accepting group [10] while the lower band is probably mainly due to the out-of-plane N–H bending (we are obliged to a Referee for this assignment).

The spectrum of the ¹⁸O-labelled benzamide, as can be expected, shows no appreciable difference for the NH and C–H stretching frequencies in carbon tetrachloride or chloroform solution.

The C=O stretching frequency of [¹⁸O]benzamide in carbon tetrachloride solution is decreased by 24 cm.⁻¹ from the normal (1690 to 1666 cm.⁻¹). This shift can be compared with the shift of 29 cm.⁻¹ for [¹⁸O]benzophenone in carbon tetrachloride [11] and shows that the vibration which is responsible for the 1690 cm.⁻¹ band in normal benzamide is mainly concentrated in the carbonyl group. This result is somewhat at variance with the

[2] Buswell, Rodebush, and Roy, *J. Amer. Chem. Soc.*, 1938, **60**, 2444.
[3] Barnes, Liddel, and Williams, *Ind. Eng. Chem., Analyt.*, 1943, **15**, 659.
[4] Richards and Thompson, *J.*, 1947, 1248.
[5] Mann and Thompson, *Proc. Roy. Soc.*, 1948, *A*, **192**, 489.
[6] Wyandotte Chemicals Co., National Research Council Infrared Spectral Catalog, Keysort compound card no. 670.
[7] Jones *et al.*, ref. 1, p. 513.
[8] Brown, Regan, Schuetz, and Steinberg, *J. Phys. Chem.*, 1959, **63**, 1324.
[9] Margoshes and Fassel, *Spectrochim. Acta*, 1955, **7**, 14.
[10] Kross, Fassel, and Margoshes, *J. Amer. Chem. Soc.*, 1956, **78**, 1332; Jones *et al.*, ref. 1, pp. 390—391.
[11] Halmann and Pinchas, *J.*, 1958, 1703.

calculations by Myazawa and his co-workers [1] for formamide, according to which there is a big contribution from the C–N stretching vibration to its 1688 cm.$^{-1}$ (I amide) frequency.

The II amide band is shifted in [^{18}O]benzamide from 1584 to 1574 cm.$^{-1}$ (in CHCl$_3$). The " III amide " band remains, however, almost unaffected by the isotopic substitution, at 1358 cm.$^{-1}$ (in CCl$_4$). The II amide band is usually,[4] at least for primary amides (Jones *et al.*, Bellamy [1]), assigned to the N–H bending mode of vibration although other modes have also been suggested as its origin (Bellamy,[1] Lenormant [12]). The decrease of 10 cm.$^{-1}$ in its frequency because of the isotopic replacement is therefore rather unexpected. It seems, then, that during the N–H bending vibration the amide-oxygen atom is also forced to move considerably because this bending affects the distribution of the bonding electrons of the whole amide group. Such a situation will explain why CH$_3$·CO·ND$_2$ does not show this band at about 1250 cm.$^{-1}$, as was expected on the assumption that the origin of this band is an N–H bending vibration,[13] since this vibration is now seen to be shared also by other parts of the molecule and cannot be expected to decrease so much on deuteration.

The " III amide " band was observed by Randall and his co-workers [14] in the spectra of solid primary amides in the 1418—1399 cm.$^{-1}$ region and was assigned to the =C–N stretching vibration, its frequency being higher in this case because of the partial double bond of this group in amides. The big difference between the solid-state value (1410 cm.$^{-1}$) and that of a carbon tetrachloride solution (1358 cm.$^{-1}$) must be attributed to the strong hydrogen bonding in the centrosymmetric dimeric solid state,[15] which opposes such a stretching vibration since the latter directly stretches this bond. The correctness of this assignment is shown by (*a*) the fact that all the tetraphenylporphins investigated show such a strong, =C–N stretching band [16] at about 1360 cm.$^{-1}$ (here also, resonance with forms having a –C=N– structure contributes to the structure of the molecule) and (*b*) the observation [17] that deuteration does not change the frequency of this band by more than 1—3 cm.$^{-1}$. Its high intensity (over 50% of that of the C=O stretching band), taken with the insensitivity to labelling with ^{18}O, also indicates its connexion with the movement of the polar nitrogen atom.

According to Myazawa *et al.*[1] the band due to that vibration in which the C–N group of formamide is stretched should appear at about 1310 cm.$^{-1}$. These authors assume that during this vibration the oxygen atom also moves considerably (the vibration being, in fact, a symmetrical stretching of the N–C=O group); hence an appreciable decrease in the frequency of the " III amide " band would have been expected in the spectrum of [^{18}O]benzamide. That this is by no means the case seems to show that because of the similarity between C–N and C–C$_{ar}$ bonds (both of partial double-bond character and between similar participants) in benzamide the vibration in which the C–N group is stretched (responsible for the 1358 cm.$^{-1}$ band) is shared by the C–C$_{ar}$ bond but only very little by the C=O linkage, the characteristic frequency of which is much higher than 1358 cm.$^{-1}$.

The higher frequency of the C–N band in chloroform solution than in carbon tetrachloride (1368 and 1367; 1358 cm.$^{-1}$) must be attributed to the increase in the polar character of the amide group due to interaction of this group with chloroform; this means a stronger partial double bond between the carbon and nitrogen.

The shoulder appearing in both spectra at about 1605 cm.$^{-1}$ is probably due to a phenyl band (at about 1595 cm.$^{-1}$ in the solid [6]) which is masked in part by the much stronger II amide band at about 1580 cm.$^{-1}$, while the phenyl band at about 1500 cm.$^{-1}$ seems to be too weak to be observed in the concentrations used for the measurements.

[12] Lenormant, *Bull. Soc. chim. France*, 1948, **15**, 33.
[13] Lenormant, *Ann. Chim. (France)*, 1950, **5**, 459.
[14] Randall, Fowler, Fuson, and Dangl, " Infrared Determination of Organic Structures," Van Nostrand, New York, 1949, Table opposite p. 21.
[15] Penfold and White, *Acta Cryst.*, 1959, **12**, 130.
[16] Thomas and Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 5111.
[17] Kniseley, Fassel, Gray, and Farquhar, personal communication.

The Intensity of the Amide Bands in [^{18}O]*Benzamide.*—It was shown recently [11] that the molar extinction coefficient of the C=O band of [^{18}O]benzophenone is about 15% lower than that of the normal benzamide. It was also found that for triphenylphosphine oxide both the molar extinction coefficient and the apparent relative integrated intensity of the P=^{18}O band are much lower than of the P=^{16}O band.[18] We therefore measured the

TABLE 2. *Absorption intensity of the amide bands of* $C_6H_5 \cdot C^{16}O \cdot NH_2$ *and* $C_6H_5 \cdot C^{18}O \cdot NH_2$
(apparent half-widths, in cm.$^{-1}$, in parentheses).

Material	Frequency (cm.$^{-1}$)	Cell-thickness (mm.)	Concn. (g./l.)	Solvent	Optical density	Mol. extinction coeff. (l. mole^{-1} cm.$^{-1}$)	Rel. integrated intensity (l. mole^{-1} cm.$^{-2}$)
Normal ...	1690	20	0·052	CCl$_4$	0·448	520	10,400(20)
Labelled ...	1666	20	0·065	CCl$_4$	0·479 [a]	580 [b]	12,800(22)
Normal ...	1358	20	0·052	CCl$_4$	0·234	272	3530(13)
Labelled ...	1358	20	0·065	CCl$_4$	0·296	280	3500(12·5)
Normal ...	1358	20	0·138	CCl$_4$	0·66	289	
Normal ...	1675	1	1·40	CHCl$_3$	0·664	578	14,500(25)
Labelled ...	1655	1	1·39	CHCl$_3$	0·61 [a]	690 [b]	14,500(21)
Normal ...	1584	1	1·40	CHCl$_3$	0·26	224	
Labelled ...	1574	1	1·39	CHCl$_3$	0·19	213 [b]	[c]

[a] Uncorrected for the absorption of the remaining normal benzamide at this point. [b] Corrected for the lower effective concentration due to the presence of normal amide. [c] No estimation of the integrated band intensity can be made here owing to the near-by shoulder at ~1605 cm.$^{-1}$.

intensity of the amide bands of $C_6H_5 \cdot C^{16}O \cdot NH_2$ and $C_6H_5 \cdot C^{18}O \cdot NH_2$. The relative integrated band intensities were estimated by multiplying the apparent maximum molecular extinction coefficients of the bands by their half-widths (on the assumption that the form of the bands is not changed much by the isotopic exchange); these intensities are given in Table 2.

This Table shows that the intensity of the band due to the C–N stretching is practically unaffected by the isotopic exchange. The C=O stretching band, however, appears to be stronger by ~20% for [^{18}O]benzamide in carbon tetrachloride. It is true that in chloroform solution the integrated intensity is equal in both isotopic modifications but it is quite possible that in this case the interaction of the chloroform with benzamide, which is shown by, *e.g.*, the general increase in the C=O band intensity in chloroform and might be somewhat weaker for the labelled compound,* obliterates the inherent difference between the ^{18}O- and ^{16}O-amides, as shown in the carbon tetrachloride results. Anyhow, the absorption intensity of the [^{18}O]benzamide-carbonyl group in carbon tetrachloride seems again to be appreciably different from that of a similar C=^{16}O group, although this time in the opposite direction to that for benzophenone [11] and triphenylphosphine oxide:[18] the reason for this is under investigation.

EXPERIMENTAL

Normal Benzamide.—A pure sample of this compound (m. p. 126°) was prepared from benzoic acid [see method (*b*) for the labelled amide].

[^{18}O]*Benzamide.*—This compound was prepared by two methods: (*a*) Partial acid-hydrolysis of benzonitrile (8 g., freshly distilled) was effected in a solution of ^{18}O-enriched water (40 ml.) saturated with dry hydrogen chloride. The mixture was heated in a sealed tube for about 2 hr. at 100° and, after cooling, the excess of water was distilled off, and the [^{18}O]benzamide extracted with dioxan and recrystallised repeatedly from light petroleum; it had m. p. 126°. No N–D bands could be discerned in its spectrum.

(*b*) Complete hydrolysis of benzonitrile (4 g.) was achieved in ^{18}O-enriched water (30 ml.) saturated with dry hydrogen chloride in a sealed tube for 24 hr. at 100°. The [^{18}O]benzoic acid was separated, recrystallised from ether, and treated with a slight excess of thionyl chloride. Fractional distillation gave [^{18}O]benzoyl chloride, b. p. 198°/760 mm., that was aminated in

* As suggested by the difference between the half-width of the C=^{16}O band (25 cm.$^{-1}$) and that of the C=^{18}O band (21 cm.$^{-1}$), in chloroform.

[18] Halmann and Pinchas, *J.*, 1958, 3264.

dioxan by passing in dry ammonia (ice-cooling) until saturated. The ammonium chloride formed was filtered off, the dioxan removed, and the [^{18}O]benzamide recrystallised from dioxan–light petroleum and washed with hexane; the amide then had m. p. 126°.

Isotopic-oxygen analyses were done by the method of Anbar and Gutmann [19] as described by Samuel.[20]

Infrared Measurements.—The instrument was a Perkin–Elmer, model 12C, spectrophotometer with a sodium chloride prism. Its calibration was checked daily by using atmospheric water vapour as standard. In each case the spectrum of the solvent was run in the same cell immediately before the spectrum of the measured solution. The intensity measurements were carried out in duplicate and in this case the spectra contained only the vicinity of the measured bands; the mean difference between the optical density of the solution and that of the solvent at each point was taken as the true optical density of the solution there. The slit used in the 1700—1550 cm.$^{-1}$ region was about 0·12 mm. The normal and the corresponding labelled spectrum were generally run one after the other in the same cell.

[19] Anbar and Gutmann, *Internat. J. Appl. Radn. Isotopes,* 1959, **4**, 234.
[20] Samuel, *J.,* 1960, 1318.