586. *The Infrared Absorption of Normal and* ^{18}O-*Labelled* NN-*Dimethylbenzamide.*

By S. PINCHAS, DAVID SAMUEL, and MARTA WEISS-BRODAY.

The infrared absorption spectra of normal and 69 atom % ^{18}O-labelled *NN*-dimethylbenzamide in the 3700—670 cm.$^{-1}$ region were measured for carbon tetrachloride solutions and, where not possible, for Nujol mulls. The origins of the bands are discussed in relation to the shifts brought about by the isotopic substitution. Since the measured shift of 24 cm.$^{-1}$ in the tertiary amide C=O stretching frequency is equal to the corresponding shift of benzamide and its *N*-methyl derivative the " amide I " band of even the primary amides is a real C=O band.

The molecular extinction coefficient and relative integrated absorption intensity of the C=^{18}O band were found to be about 25% higher than the corresponding values for the C=^{16}O frequency, both for CCl_4 and for $CHCl_3$ solutions.

IT was shown recently that ^{18}O-labelled benzamide [1] and *N*-methylbenzamide [2] behave differently from the other substances studied which contain an X=^{18}O group [3] (X = C or P) by absorbing considerably more strongly (in CCl_4 solutions) than the corresponding normal compounds, at the X=O stretching frequency. It was thus of interest to investigate also the infrared absorption of the tertiary amides of this series *i.e.*, normal and labelled *NN*-dimethylbenzamide. The spectra of these compounds are also significant in interpretation of the characteristic amide bands. However, the infrared spectrum of even the unlabelled *NN*-dimethylbenzamide does not seem to have been reported. Samples of the normal and 68·7 atom % [^{18}O]-labelled *NN*-dimethylbenzamide were therefore synthesised and their infrared absorption bands were investigated (see Table 1 where the optical densities are in parentheses after the frequency).

The 3060 cm.$^{-1}$ band is due to the aromatic C–H stretching vibration; 2940 cm.$^{-1}$ is the asymmetrical methyl C–H stretching frequency: [4] normal *N*-methylbenzamide shows the methyl band at the same place.[2] The band that appears in the carbon tetrachloride solution spectrum of the normal amide at 1640 cm.$^{-1}$ and is shifted to 1616 cm.$^{-1}$ in the case of the ^{18}O-labelled compound is no doubt the C=O stretching band. The fact that this isotopic shift is the same as that for the analogous primary benzamide [1] and secondary *N*-methylbenzamide [2] (24 cm.$^{-1}$) shows again [2] that this " amide I " band is in practice a real C=O stretching absorption even though extensive coupling with an N–H bending or a

---

[1] Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 1688.

[2] Pinchas, Samuel, and Weiss-Broday, *J.*, in the press.

[3] Halmann and Pinchas, *J.*, 1958, (*a*) 1703, (*b*) 3264; (*c*) Pinchas, Samuel, and Weiss-Broday, *J.*, 1961, 2382.

[4] Jones and Sandorfy in " Technique of Organic Chemistry," Interscience Publ., Inc., New York, N.Y., 1956, Vol. IX, pp. 337, 392.

C–N stretching mode of vibration is often suggested for it.[5,6] Since the tertiary *NN*-dimethylbenzamide does not contain an N–H group and its normal C=O and C–N bands (amide I and III bands, respectively) are at considerably different frequencies from, for instance, their positions in benzamide (in CCl_4: 1640 and about 1390 cm.$^{-1}$, compared with[1] 1690 and 1358), one would expect that an appreciable coupling of N–H bending or C–N stretching with the C=O stretching in any (or all) of these amides to change the isotopic shift of the amide I band considerably from 24 cm.$^{-1}$.

TABLE 1. *Absorption bands of normal and* ^{18}O-*labelled* NN-*dimethylbenzamide.*

Material	State	Concentration	Cell-thickness (mm.)	Bands (cm.$^{-1}$)
Normal	Solution	0·040 g. ± CCl_4 1 ml.	0·2	3060 (0·04), 2940 (0·18), ~1638 (>1), 1578 (0·22), 1504 (0·35), 1445 (0·36), 1388 (0·84), 1267 (0·34), 1214 (0·22), 1075 (0·47), 1027 (0·14), 927 (0·06)
69% ^{18}O	Solution	0·026 g. ± CCl_4 1 ml.	0·2	3060 (0·08), 2940 (0·18), ~1615 (>1), 1576 (0·20), 1504 (0·20), 1443 (0·22), 1389 (0·61), 1261 (0·18), 1215 (0·12), 1072 (0·33), 1027 (0·11), 927 (0·05)
Normal	Solution	9 g./l. in CCl_4	0·2	1640 (0·48) [a]
69% ^{18}O	Solution	10 g./l. in CCl_4	0·2	1616 (0·49) [a]
Normal	Solution	8 g./l. in $CHCl_3$	0·2	1622 (0·45) [a]
69% ^{18}O	Solution	8 g./l. in $CHCl_3$	0·2	1602 (0·44) [a]
Normal	Mull in Nujol [b]	—	Capillary	791, 733, 696, 673
69% ^{18}O	Mull in Nujol [b]	—	Capillary	789, 734, 696, 674

[a] Measured precisely and only in this region. [b] Measured only in the 830—670 cm.$^{-1}$ region (where CCl_4 is not transparent).

The 1576/8 and 1504 cm.$^{-1}$ bands are probably due to the phenyl ring vibrations[7] of this region; the 1575/8 cm.$^{-1}$ band of *N*-methylbenzamide was assigned similarly.[2] The 1443/5 and 1388/9 cm.$^{-1}$ absorptions must be assigned to the asymmetrical and symmetrical methyl C–H bending vibrations, respectively. In *N*-methylbenzamide these vibrations bring about bands at 1484 and 1415 cm.$^{-1}$. The effect of the nitrogen atom, to which these methyl groups are bound, on their bending frequencies (causing them to shift from about[8] 1460 and 1380 cm.$^{-1}$) is, however, expected to be different in the *NN*-dimethylbenzamide case both because it is here split over two such groups and because the steric structure of this amide is different from that of *N*-methylbenzamide.[9] It is reasonable to assume that the very strong absorption at about 1390 cm.$^{-1}$ also includes the =C–N stretching band which appears in benzamide[1] at about 1360 cm.$^{-1}$ and should rise in frequency with methyl substitution on the nitrogen.[5]

The band which appears in the normal spectrum at 1267 cm.$^{-1}$ and is shifted by ^{18}O-labelling to 1261 cm.$^{-1}$ seems to be due to the asymmetrical C–CO–R stretching vibration, in analogy to the 1203 cm.$^{-1}$ band of benzoyl chloride,[3c] the 1250 cm.$^{-1}$ band of propionyl chloride,[10] and the 1200 cm.$^{-1}$ bands of ketones.[11] The material shift of 6 cm.$^{-1}$ because of ^{18}O-labelling strongly supports this assignment. A similar band also appears in the spectra of (melted) *NN*-diethylbenzamide[12] (at about 1280 cm.$^{-1}$), (liquid) *NN*-dimethylformamide[13] (at 1255 cm.$^{-1}$), *NN*-dimethylacetamide[12] (at about 1260 cm.$^{-1}$), and *NN*-diethylacetamide[12] (1270).

---

[5] Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1956, **24**, 408.

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

[7] Ref. 4, pp. 394—396.

[8] Ref. 4, p. 348.

[9] Edward and Meacock, *Chem. and Ind.*, 1955, 536.

[10] Nat. Acad. Sci., Nat. Bur. Standards, " Infrared Spectral Catalog," Compound Card No. 1687.

[11] Ref. 4, pp. 507—508.

[12] Lenormant, *Bull. Soc. chim. France*, 1948, **15**, 33.

[13] Cannon, British Nylon Spinners Collection, Documentation of Molecular Spectra Catalogue Compound Card No. 1001.

The absorption at about 1214 cm.$^{-1}$ seems to be connected with the relatively high intensity of the 1072/5 cm.$^{-1}$ band which amounts here to about 30% of the C=O band intensity while it is less than 10% in the case of *N*-methylbenzamide.[2] It appears reasonable to assume that these bands are due, to a large extent, to an asymmetrical and a symmetrical stretching vibration of the CH_3–N–CH_3 group, respectively. Colthup [14] also assigns two bands at about 1180 and 1080 cm.$^{-1}$ to tertiary amines; these bands are the result of the C–N stretching motions.[15] Dimethylformamide shows [13] similar bands at 1181 and 1094 cm.$^{-1}$. The band observed at about 1155 cm.$^{-1}$ in the spectra of *N*-methylacetamide [16] and *N*-methylbenzamide [2] can also be a C–N stretching [15] rather than an N–CH_3 rocking [16] band.

Part of the 1072/5 cm.$^{-1}$ absorption, as well as the 1027 cm.$^{-1}$ band, seems however to come from in-plane C–H bending frequencies of a monosubstituted benzene,[17] since *N*-methylbenzamide also shows such bands at [2] 1071 and 1030 cm.$^{-1}$.

The 927 cm.$^{-1}$ band is probably the result of the C_{ar}–CO stretching vibration, in analogy to the 935 cm.$^{-1}$ band of *N*-methylbenzamide.[2]

The bands observed with Nujol mulls of the isotopic *NN*-dimethylbenzamides at about 790, 696, and 673 cm.$^{-1}$ correspond to similar bands at about 802, 696, and 685 cm.$^{-1}$ in the spectrum of *N*-methylbenzamide which were assigned to aromatic C–H out-of-plane bending frequencies.[2] The additional absorption of the tertiary amides at 733/4 cm.$^{-1}$ may be the $(CH_3)_2N$-analogue of the $(CH_3)_2CH$-deformation band [18] at about 800 cm.$^{-1}$. Dimethylamine [19] also shows a (very intense) band at about 735 cm.$^{-1}$.

The value of 1640 cm.$^{-1}$ given in Table 1 for the C=O stretching band of normal *NN*-dimethylbenzamide, although somewhat lower than recently reported [20] (1644 cm.$^{-1}$) is in excellent agreement with the same value for this band in the case of *NN*-diethylbenzamide.[21] The published curve of the latter,[12] shows in the 5—8 μ region bands near 1650, 1530, 1470, 1440, 1380, 1315, and 1280 cm.$^{-1}$, similar to those of Table 1.

The Intensity of the Isotopic C=O *Bands.*—Optical-density measurements results for the C=O stretching bands of the normal and ^{18}O-labelled *NN*-dimethylbenzamide are collected in Table 2, with related results. It is evident that for *NN*-dimethylbenzamide, as for benzamide [1] and *N*-methylbenzamide,[2] there is a considerable increase in the relative integrated absorption intensity of the C=^{18}O band. Thus the mean value for this intensity is 9100 ± 400 units for the normal amide in carbon tetrachloride solution but

TABLE 2. *Absorption intensity of the* C=O NN-*dimethylbenzamide bands.*

Materia	Solvent	Concn. (g./l.)	Cell-thickness (mm.)	Frequency (cm.$^{-1}$)	Optical density	Mol. extinction coeff. (l. mole^{-1} cm.$^{-1}$)	Apparent half-width (cm.$^{-1}$)	Integrated absorption (l. mole^{-1} cm.$^{-2}$)
Normal	CCl_4	8·95	0·2	1640	0·480	400 ± 6	22	8800 ± 400
Normal	CCl_4	8·35	0·2	1640	0·461	411 ± 19	23	9500 ± 500
69 atom % ^{18}O	CCl_4	10·0	0·2	1616	0·464 [a]	510 [b] ± 10	21 [c]	10,700 ± 300
69 atom % ^{18}O	CCl_4	11·3	0·2	1616	0·563 [a]	547 [b] ± 30	22 [c]	12,000 ± 1000
Normal	$CHCl_3$	7·55	0·2	1622	0·431	425 ± 16	28	11,900 ± 800
69 atom % ^{18}O	$CHCl_3$	7·7	0·2	1602	0·394 [a]	562 [b] ± 11	25·2 [c]	14,200 ± 300
69 atom % ^{18}O	$CHCl_3$	12·9	0·2	1602	0·664 [a]	565 [b] ± 20	24 [c]	13,600 ± 500

[a] Corr. for the absorption of the normal amide at this point. [b] Corr. for the lower effective concentration of the labelled amide. [c] Calc. after absorption of the normal amide had been subtracted.

---

[14] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

[15] Ref. 4, p. 531.

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

[17] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1958, pp. 81—82.

[18] Ref. 17, p. 27.

[19] Barr and Haszeldine, ref. 13, Compound Card No. 558.

[20] Schmulbach and Drago, *J. Phys. Chem.*, 1960, **64**, 1957.

[21] Ref. 4, p. 525.

11,300 ± 700 units for the labelled amide (in CCl_4), an increase, due to the ^{18}O-labelling, of about 24%. It is remarkable that the corresponding values of the *N*-methylbenzamides are [2] 8900 ± 300 and 10,900 ± 300 units, and 22%. The values for the benzamides [1] are also in line, being 10,400 and 12,800 units, an increase of 23%.

The results for the chloroform solutions of the *NN*-dimethylbenzamides similarly show a marked increase in the absorption intensity of the ^{18}O-labelled modification (11,900 ± 800 to 13,900 ± 300). This behaviour of the tertiary amide is, however, different from that of benzamide [1] and *N*-methylbenzamide [2] the chloroform spectra of which do not show a significant change of intensity between the isotopic modifications (about 14,500 units with benzamides and about 12,000 with the *N*-methylbenzamides). It is also noteworthy that the width of the labelled tertiary amide CO band is as a rule lower than for the normal tertiary amide, while the opposite is true for the secondary benzamides.[2] The reason for these anomalies is unclear.

Ultraviolet Absorption.—*NN*-Dimethylbenzamide, when dissolved in propan-2-ol, showed (above 2200 Å) a single maximum of absorption at 2260 Å with a log ε of 3·83 (in ethanol, 3·87). The ^{18}O-labelled compound under identical conditions, however, showed a doublet at 2210 and 2280 Å with log ε 3·81 and 3·71 respectively. The reported absorption band of the normal compound [22] in methanol appears at 2250 Å (log ε 3·78). Lower ultraviolet absorption intensities (and a small change of the spectrum) as a result of exchanging an X=^{16}O group for X=^{18}O have been observed for [^{18}O]nitromethane and [^{18}O]benzophenone.[23] Methyl benzoate [3c] also shows differences in the intensity of its ultraviolet absorption as a result of ^{18}O-labelling.

EXPERIMENTAL

NN-*Dimethyl*[^{18}O]*benzamide*.—Dry dimethylamine was bubbled through [^{18}O]benzoyl chloride [3c] (2·5 g.) in dry ether, with cooling, to saturation. The precipitate was filtered off and washed repeatedly with dry ether. The combined filtrates were dried (Na_2SO_4) and evaporated to dryness. The *NN*-dimethylbenzamide (both portions), recrystallised from light petroleum, had m. p. 39—41° (Lieberman [24] gives m. p. 38—40° for the normal amide) (yield 90%). Care should be taken not to heat the amide at any stage above 30° to avoid difficulties in crystallisation. The product was analysed for its ^{18}O content as described by Samuel [25] and was found to contain 68·7 atom %. The normal amide was prepared in an analogous manner, and had the same m. p.

Infrared and ultraviolet absorption measurements were carried out as already described.[3c]

THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL.

[*Received, February 7th*, 1961.]

---

[22] Ley and Specker, *Ber.*, 1939, **72**, 199.

[23] Halmann and Pinchas, *J.*, 1960, 1246.

[24] Lieberman, *J. Amer. Chem. Soc.*, 1955, **77**, 1114.

[25] Samuel, *J.*, 1960, 1318.