Ultraviolet and Nuclear Magnetic Resonance Spectra of Protonated Benzamide and [^{15}N]Benzamide in Concentrated Sulphuric Acid and Pure Fluorosulphuric Acid

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U.v. spectra of benzamide in concentrated sulphuric acid, which show a tautomeric change from *N*-protonated in 60% sulphuric acid to *O*-protonated in 100% sulphuric acid, are discussed and the estimated tautomeric ratios are shown to lead to reasonable activity coefficient ratios of the two types of cation. N.m.r. spectra of benzamide and [^{15}N]benzamide in 100% sulphuric acid and in pure fluorosulphuric acid are reported. The effect of diluting sulphuric acid with water on the spectra is consistent with a conversion of the *O*-protonated cation into the *N*-protonated cation, although under conditions of rapid proton exchange n.m.r. spectra do not provide information on the position of the tautomeric equilibrium.

THE structure of protonated amides, believed for about a decade to have been proved by n.m.r. spectroscopy to be predominantly carbonyl protonated under all conditions, has more recently been postulated to be tautomeric,[1] with a changeover from *N*-protonated in aqueous acid to *O*-protonated in concentrated and anhydrous acids. Benzamide is the first amide for which this tautomerism has been demonstrated by u.v. spectra in concentrated sulphuric acid solutions.[2] This paper discusses some deductions from these results and reports n.m.r. spectra of benzamide and [^{15}N]benzamide in concentrated sulphuric acid and pure fluorosulphuric acid.

Using [^{15}N]benzamide, difficulties due to the quadrupole broadening of the NH resonances by the ^{14}N nucleus and to their overlap with the aromatic region of the spectrum are obviated, and all the n.m.r. parameters of the *O*-protonated cation under anhydrous acid conditions could be determined. The temperature effect and the effect of diluting sulphuric acid with water on the spectra are also reported and discussed in comparison with earlier similar studies of [^{15}N]acetamide.[3] In view of a complete lack of information in the literature on the n.m.r. spectra of unprotonated benzamide, the spectrum of [^{15}N]benzamide in dimethyl sulphoxide is also reported and compared with the spectrum of [^{15}N]acetamide in the same solvent.[4]

Objections raised recently by several authors [5-7] to the possibility of dominant *N*-protonation of amides in aqueous acid are at variance with the present findings and will be discussed in detail elsewhere.

EXPERIMENTAL

Materials.—Benzamide (B.D.H. laboratory reagent) was recrystallised from alcohol. It had m.p. 129·5°, in agreement with the literature.

[^{15}N]Benzamide was obtained from Prochem. It was 95% enriched in ^{15}N and was not purified before use. A comparison of its n.m.r. spectrum for the aromatic region with that of purified benzamide indicated that no impurities were present.

Sulphuric acid (98%, B.D.H. AnalaR) was made up to 100% with oleum (maximum m.p. 10·4°) and was then used as a standard for the preparation of other solutions by weight.

Fluorosulphuric acid was a pure product of the Ozark Mahoning Co. and was used as obtained.

U.v. Measurements.—Benzamide is hydrolysed slowly in moderately concentrated mineral acids. Therefore, in order to obtain stable stock solutions, it was necessary to use either solutions in water or in 100% sulphuric acid. The consequent changes in the composition of solvent mixtures were minimised by accepting high dilution ratios (4×10^{-3} to 5×10^{-5}M; *i.e.* 80-fold). To achieve high accuracy of dilution, high grade micropipettes or a Hamilton syringe with a Teflon tip, were used. The agreement between measurements in 60% acid carried out using one stock solution or the other was within 2·5%. The stock solution in 100% acid was used for mixtures in $>60\%$ sulphuric acid and that in water for mixtures in $<60\%$ sulphuric acid. Overall reproducibility of the curves was within 3% from one independent series of measurement to another, but better than this in series covering the whole acid concentration range, measured in close succession. The temperature of the measurements was $23 \pm 2°$.

Two spectrophotometers were used: a Zeiss PMQ II and a Cecil 202. The agreement between the two instruments was tested using 5×10^{-5}M-acetophenone solutions in water and it was found to be within 3% in the region of maximum absorptions, but a discrepancy of almost 15% was found near 260 nm, tapering off to 3% elsewhere (higher readings were found on the Cecil instrument). The results obtained on the Cecil 202 were used in the calculations.

N.m.r. Spectra.—The solutions for n.m.r. recordings were made mostly 1M in the amide, using acid cooled in ice–water, although dissolution of samples in sulphuric acid was rather slow and cooling was hardly necessary.†

The recordings of n.m.r. spectra were carried out using two instruments: a Brüker HFX spectrometer with a variable temperature probe, operating at 90 MHz, and a

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† In attempting to prepare *ca.* 1M solutions of benzamide in 60—75% sulphuric acid crystals separate, which have been shown by analysis to be a 1 : 1 compound of benzamide and sulphuric acid. They have also been prepared by mixing directly 100% sulphuric acid and benzamide in an equimolar ratio and have been found to have m.p. 120°. A >1M solution of benzamide may be prepared in 60% sulphuric acid, for example, and may remain clear until it is seeded with the crystals of this compound. The structure of the sulphate is under investigation. Its crystallisation from solution with increasing dilution of sulphuric acid, may be explained by the conversion of the *O*-protonated cation into the *N*-protonated cation, and this suggests that in this salt the proton is on the nitrogen.

[1] M. Liler, *Chem. Comm.*, 1971, 115.

[2] Preliminary communication, M. Liler, *J.C.S. Chem. Comm.*, 1972, 527.

[3] M. Liler, *J.C.S. Perkin II*, 1972, 816.

[4] M. Liler, *J. Magnetic Resonance*, 1971, **5**, 333.

[5] H. Benderly and K. Rosenheck, *J.C.S. Chem. Comm.*, 1972, 179.

[6] R. B. Martin, *J.C.S. Chem. Comm.*, 1972, 793.

[7] C. R. Smith and K. Yates, *Canad. J. Chem.*, 1972, **50**, 771.

Perkin-Elmer R10 spectrometer, operating at 60 MHz, with a probe temperature of 33·5°. As sodium 4,4-dimethyl-4-silapentanesulphonate (DSS) is unstable in strongly acid solutions, tetramethylammonium ion was used as internal reference. Its chemical shift was determined relative to pure water as external reference (peak at −4·76 p.p.m.) and found to be −3·00 p.p.m. in pure fluorosulphuric acid and −3·25 p.p.m. in 100% sulphuric acid. Chemical shifts relative to NMe_4^+ (a) and recalculated to the δ scale using water as external reference (b) are both reported in Table 2.

RESULTS AND DISCUSSION

U.v. Spectra.—New repeated recordings of the u.v. spectra gave results closely similar to those reported,[2] except that with the purified sample of benzamide the extinction coefficients were found to be somewhat higher (Figure 1). The values of the absorption maxima were: in water, at 226 nm, $\varepsilon_{\text{max.}}$ 9500; in 60% sulphuric acid, at 245·5 nm, $\varepsilon_{\text{max.}}$ 12,600; and in 98—100% sulphuric acid, at 252·5 nm, $\varepsilon_{\text{max.}}$ 13,800. The isosbestic point was at 247 nm. The maximum absorption of acetophenone in water at 245·5 nm has $\varepsilon_{\text{max.}}$ 13,000 which is in very good agreement with the value reported by Braude and Sondheimer[8] for the solution in ethanol, although the maximum in ethanol is at 243 nm. There is a second flat maximum in the u.v. spectrum of acetophenone in water at 280 nm ($\varepsilon_{\text{max.}}$ 1380). The acetophenone spectrum in water and the benzamide spectrum in 60% sulphuric acid are almost superimposable, except that the maximum absorption of acetophenone is somewhat higher (*ca.* 3%) and its absorption at 260 nm a little lower. The lower maximum absorption and the higher absorption at 260 nm of benzamide in 60% sulphuric acid are consistent with a small percentage of the *O*-protonated form being present at this acid concentration. The second flat maximum in the spectrum of acetophenone in water appears only as an extended shoulder in the spectrum of benzamide in 60% sulphuric acid, but these differences are minor.

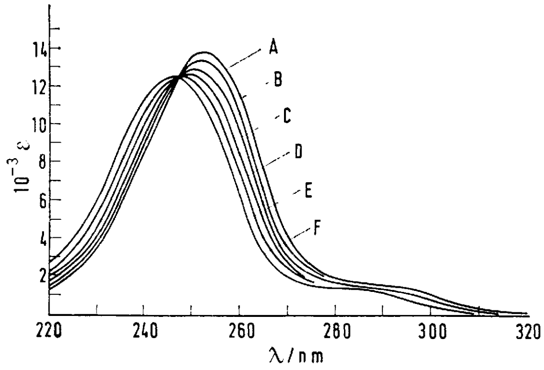
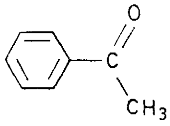
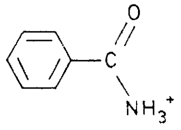


FIGURE 1 U.v. spectra of benzamide in concentrated sulphuric acid at 23 ± 2°. Acid (%): A, 98; B, 95; C, 90; D, 80; E, 70; F, 60

The close similarity of these spectra is consistent with the suggestion [1,2] that benzamide is present in 60% sulphuric acid virtually wholly in the *N*-protonated form (see later). The system of conjugated bonds giving rise to these absorptions is identical in acetophenone (I) and in the *N*-protonated cation of benzamide (II), and both



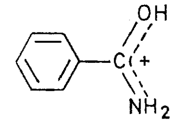
(I)



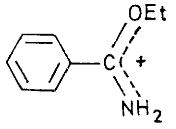
(II)

spectra are obtained in highly polar media of high dielectric constant. The spectroscopic effect of the NH_3^+ group is known to be closely comparable to that of the CH_3 group.[9,10]

At higher acid concentrations the spectra of benzamide undergo change and therefore the close similarity of the acetophenone spectrum in water and the benzamide spectrum in 60% sulphuric acid is the only evidence that benzamide is virtually fully *N*-protonated in this solution. The changes at higher acid concentrations can be traced to a tautomerisation of the *N*-protonated cation to the *O*-protonated cation (III), since the spectrum of benzamide in 100% sulphuric acid is virtually identical with that of ethyl benzimidate (IV) in the same solvent as was demonstrated by Hantzsch.[11] The maximum absorption of the *O*-protonated cation is shifted towards longer wavelengths and the absorption coefficient is enhanced by *ca.* 10% compared with the *N*-protonated cation. This absorption is a *K* band[12] [or a $p(^1L_a)$ band[13]] and is due to the transfer of charge in the excited state to the benzene ring. In acetophenone and the *N*-protonated cation of benzamide a benzoyl chromophore is present,[12] which is known to exhibit intense bands near 240 nm. In the *O*-protonated benzamide cation and protonated ethyl benzimidate a new chromophore is present which is responsible for the absorption maximum at 252·5 nm. A smaller amount of energy is thus required for this excitation, which may be due to the fact that the positive charge on the carbon is enhanced in these cations as compared with the carbonyl carbon and hence more readily transferable to the ring. Quantum mechanical calculations on these spectra are in progress.



(III)



(IV)

In the region of the secondary or benzenoid absorption

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[8] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 1955, 3754.

[9] R. N. Jones, *Chem. Rev.*, 1943, **32**, 14.

[10] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714.

[11] A. Hantzsch, *Ber.*, 1931, **64**, 667.

[12] E. A. Braude, in 'Determination of Organic Structures by Physical Methods,' eds. E. A. Braude and F. C. Nachod, Academic Press, New York, 1955, pp. 131—193.

[13] E. S. Stern and C. J. Timmons, 'Gillam and Stern's Introduction to Electronic Absorption Spectroscopy in Organic Chemistry,' Edward Arnold, London, 1970, 3rd edn., pp. 114 and 127.

maximum of benzamide in water ($\varepsilon_{max.}$ 800 at 273 nm), there is a steady shift of the maximum with increasing acid concentration towards longer wavelengths, but as the primary intense band shifts rather more in the same direction, the maximum gradually disappears (in *ca.* 35% sulphuric acid) and an extended shoulder is observed in 60% acid, as already mentioned. This shoulder shifts to longer wavelength and its height increases further in concentrated sulphuric acid, so that in 100% sulphuric acid it appears at 284 nm with ε 1700.

The absorption curves at lower acid concentrations, that we have recorded, are similar to those already published by Edward and Meacock,[14] who used the difference in the absorption coefficients at 225 (free amide) and at 240 nm to estimate the pK_{BH^+} value of benzamide. Their results show that this difference reaches a steady value in 55—60% sulphuric acid (virtually complete *N*-protonation), but the values change erratically at higher acid concentrations. Our results show that in >60% sulphuric acid absorptions at both 225 and 240 nm decrease and the changes are not relevant to the protonation, but are consequences of the tautomerisation of the *N*-protonated cation to the *O*-protonated cation.

The tautomeric equilibrium has been written in the form (1) [1] with an equilibrium constant given by equation

$$RCONH_3^+,pH_2O \rightleftharpoons RC(OH)NH_2^+,qH_2O + rH_2O \quad (1)$$

(2) where f_{OH} and f_{NH} are the activity coefficients of the

$$K_T = \frac{[RC^+(OH)NH_2,aq.]f_{OH}a_w^{\,r}}{[RCONH_3^+,aq.]f_{NH}} = Q_T\,\frac{f_{OH}}{f_{NH}}\,a_w^{\,r} \quad (2)$$

O- and the *N*-protonated forms, respectively, a_w is the activity of water, and Q_T is the tautomeric quotient. It has been suggested that r may have a minimum value of unity, if the *N*-protonated cation binds four water molecules by hydrogen bonding solvation and the *O*-protonated cation only three.[1]

The value of the equilibrium constant for the tautomerisation has been estimated [1] to be *ca.* 10^{-4} from the deviation of the pK_{BH^+} value of benzamide, as determined by Yates and Stevens [15] from u.v. spectra at moderate acid concentrations (and therefore referring to *N*-protonation), and the pK_{BH^+} value for carbonyl protonation predicted from a correlation of pK_{BH^+} values for a number of carbonyl bases with carbonyl frequencies.[16] Doubts have been expressed [17] about the assignment of the frequency used for the carbonyl group in benzamide in plotting this correlation and hence about the conclusion that amides are not carbonyl protonated under the conditions in which their pK_{BH^+} values have been determined (*i.e.* in the largely aqueous acid). The assignment of the i.r. absorption at 1675 cm^{-1} of benzamide in chloroform to its carbonyl frequency is due to Bellamy,[18] and as this frequency also fits very well a correlation of the carbonyl frequencies of a range of compounds of formula PhCOX with σ_m constants of the groups X,[16] there is little scope to doubt the assignment. The deviation of the pK_{BH^+} of benzamide from the correlation of pK_{BH^+} values *vs.* ν_{CO}, obeyed by a number of other carbonyl compounds, thus remains a fact, and we shall use it to estimate K_T as $1{\cdot}6 \times 10^{-4}$ (log $K_T = -3{\cdot}8$).

The tautomeric quotient, Q_T, is obtainable from u.v. spectra, and we choose the wavelength at which the absorptions of the *N*- and *O*-protonated forms differ most, which is 260 nm. At any single wavelength equation (3) applies, where ε_{OH} is the absorption in 100% sulphuric

$$Q_T = \frac{[RC(OH)NH_2^+]}{[RCONH_3^+]} = \frac{\varepsilon - \varepsilon_{NH}}{\varepsilon_{OH} - \varepsilon} \quad (3)$$

acid due to the *O*-protonated form, ε_{NH} is the absorption of the *N*-protonated form, and ε is the absorption of the tautomeric mixture. The value of ε_{NH} was first taken as the absorption in 60% acid, assuming that no appreciable amounts of the *O*-protonated form exist at that acid concentration. Also assuming $r = 1$, a set of values of activity coefficient ratios was obtained from equation (2). The logarithm of the ratios was plotted against acid concentration and, as at infinite dilution in water both activity coefficients become unity, the curve was extrapolated to zero at zero acid concentration. In this way an estimate of the activity coefficient ratio in 60% acid was obtained, and when this was inserted into equation (2), Q_T was found to be *ca.* 0·05—0·06 in 60% acid. Using this, a second approximation to the activity coefficient ratios was calculated. The same results were obtained if the absorption of acetophenone in water, which was mentioned to be a little lower at that wavelength than the absorption of benzamide in 60% sulphuric acid (ε_{260} 5800), was used. The tautomeric ratios and the activity coefficient ratios obtained in this way are shown in Table 1.

TABLE 1

Tautomeric quotient for protonated benzamide from u.v. spectra and the estimated activity coefficient ratios at 23 ± 2°

H_2SO_4 (%)	$-\log a_w$ *	$10^{-4}\varepsilon$ at 260 nm	Q_T	$\log (f_{NH}/f_{OH})$ ($r = 1$)
59·85	0·788	0·61	0·058	1·8
69·84	1·352	0·73	0·375	2·0
79·97	2·276	0·86	1·04	1·6
90·00	3·638	0·98	2·76	0·6
94·98	4·469	1·07	8·15	0·24
98—100	5·3—5·8	1·13	(40—100) [a]	(<0·1)

* W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, 1960, **82**, 62.

[a] Estimated from equation (2) assuming that the trend of the logarithms of the activity coefficient ratios continues up to 100% acid, in which the value becomes virtually zero.

The activity coefficients of cations are not measurable quantities, but Boyd [19] devised a method of obtaining activity coefficients of indicator cations in sulphuric

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[14] J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 1957, 2000.

[15] K. Yates and J. B. Stevens, *Canad. J. Chem.*, 1965, **43**, 529.

[16] M. Liler, *Spectrochim. Acta*, 1967, **23A**, 139.

[17] R. B. Homer and C. D. Johnson, in ' The Chemistry of Amides,' ed. J. Zabicky, Interscience, New York, 1970, p. 196.

[18] L. J. Bellamy, *J. Chem. Soc.*, 1955, 4221.

[19] R. H. Boyd, *J. Amer. Chem. Soc.*, 1963, **85**, 1555.

acid solutions referred to a common standard ion, tetraethylammonium (TEA^+), by measuring solubilities of their salts with a strong carbon acid (pentacyanopropane, anion PCP^-). An attempt was made by Sweeting and Yates [20] to apply this method to the benzamide salt, but since benzamide is very weakly basic and the cation ionises appreciably in dilute acid, relative activity coefficients at low acidities were obtainable only on certain assumptions. The estimate of relative activity coefficients for benzamide cations so obtained is plotted in Figure 2 (full line), and it has been pointed out [20] that the rise of the curve is steeper than for anilinium ions, as would be expected for the more strongly hydrated *N*-protonated cations of benzamide. Since the u.v. spectra show that the *O*-protonated form emerges in $>55\%$ acid, only up to that concentration do the values indicate the trend for the *N*-protonated cation. We have sketched a continuation of this trend up to 100% acid, and have then plotted the lower dotted curve for the *O*-protonated cation from the calculated activity coefficient ratios (Table 1). The relationship between the two relative activity coefficient curves does not seem unreasonable.

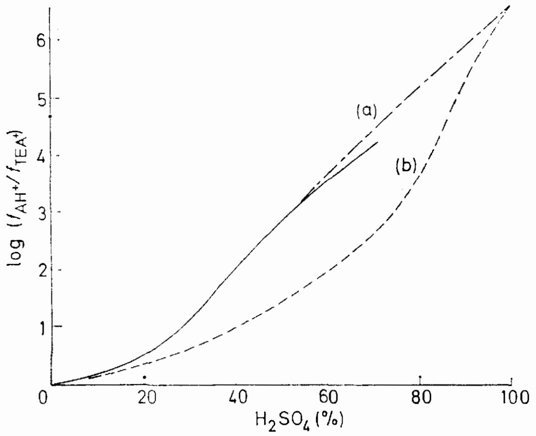

FIGURE 2 The estimated dependence upon acid strength of the relative activity coefficients (f_{AH^+}/f_{TEA^+}) for the *N*- and *O*-protonated cations of benzamide: (*a*) *N*-protonated cation; (b) *O*-protonated cation

We have explored the effect of choosing $r > 1$ and found that this leads to a reversal of the values of the activity coefficients of the two forms at high acid concentrations, which is unreasonable. In terms of the idea about chemical hydration of cations by hydrogen bonding, $r = 1$ is the most reasonable assumption and gives an acceptable relationship between the activity coefficients of the two forms, as shown in Figure 2.

Finally, the trend towards an activity coefficient ratio of unity in 100% sulphuric acid may seem surprising, but on the other hand the largest differences between the two activity coefficients are to be expected at those acid concentrations, at which water becomes progressively less available for cation hydration. Assuming the logarithm of the activity coefficient ratio as 0·1 in 98% acid and zero in 100% acid (as read off the diagram in Figure 2), estimates of $Q_T = 40$ and 100 are obtained, respectively. These estimates seem reasonable, since n.m.r. spectra show the *O*-protonated cation to be quite stable in 100% acid, whereas considerable exchange is apparent in 98% acid (see next section).

N.m.r. Spectra.—Information on the spectra of benzamide appears to be non-existent (*e.g.* there is no reference to it in a recent comprehensive review [21]), while its *N*-methyl and *NN*-dimethyl derivatives have been extensively studied.[22-24] This is due to the overlap of the resonances of the NH protons with those of the aromatic ring protons. With [^{15}N]benzamide the NH resonances are split by the ^{15}N nucleus with coupling constants of *ca.* 90 Hz, so that NH resonances are observed flanking the aromatic region. The only available information on protonated benzamide is that obtained by Gillespie and Birchall [25] in fluorosulphuric acid at 60 MHz. As the resonances of the two NH protons are shifted downfield in the *O*-protonated cation, owing to the enhanced positive charge on the nitrogen, a resonance was observed due to NH protons to low field

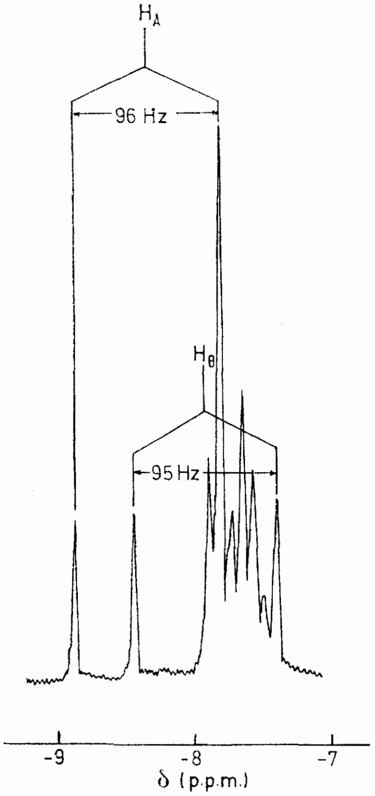

FIGURE 3 The n.m.r. spectrum of [^{15}N]benzamide in fluorosulphuric acid at 26° and 90 MHz

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[20] L. M. Sweeting and K. Yates, *Canad. J. Chem.*, 1966, **44**, 2395.

[21] W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 1970, **70**, 517.

[22] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, 1962, **66**, 540.

[23] C. W. Fryer, F. Conti, and C. Franconi, *Ricerca Sci.*, 1965, *A*, **35**, 788.

[24] L. M. Jackman, T. E. Kavanagh, and R. C. Haddon, *Org. Magnetic Resonance*, 1969, **1**, 109.

[25] R. J. Gillespie and T. Birchall, *Canad. J. Chem.*, 1963, **41**, 2642.

of the aromatic region and it was thought that the resonances of both NH protons possibly coincide.[25] Our results with [^{15}N]benzamide at 90 MHz reveal another resonance, due to NH protons, which overlaps with the aromatic region at 60 MHz (Figure 3). It can be seen that one of the peaks of the two doublets still overlaps with the aromatic region, but as these resonances are sharp, the overlapping peak can readily be picked out. The parameters reported in Table 2 were obtained from an expanded spectrum. In the benzamide spectrum in fluorosulphuric acid the high field peak overlaps with the aromatic region even at 90 MHz. The agreement in the chemical shift of the low field peak with the figure reported by Gillespie and Birchall ($-8\cdot59$ p.p.m.)[25] is only moderately good, but it is better for the OH resonance, which appears from the solvent peak at low temperature.

TABLE 2

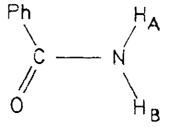
N.m.r. spectra of the *O*-protonated cations of benzamide and [^{15}N]benzamide in pure fluorosulphuric acid and in 100% sulphuric acid (ν_0 = 90 MHz)

	Fluoro-sulphuric acid *		100% Sulphuric acid *		Dimethyl sulphoxide *
	(a)	(b)	(a)	(b)	
δ_A (p.p.m.)	$-5\cdot36$	$-8\cdot36$	$-5\cdot56$	$-8\cdot83$	$-8\cdot01$
δ_B (p.p.m.)	$-4\cdot94$	$-7\cdot94$	$-4\cdot98$	$-8\cdot25$	$-7\cdot39$
$\Delta\delta_{AB}$ (p.p.m.)	$0\cdot42$		$0\cdot58$		$0\cdot62$
$\nu_0\cdot\Delta\delta_{AB}$/Hz	$37\cdot8$		$52\cdot2$		
$^1J(^{15}N-H_A)$/Hz	$95\cdot5$		98		89
$^1J(^{15}N-H_B)$/Hz	$94\cdot3$		95		89
$^2J(H_A-H_B)$/Hz	0		0		$\sim$0
$W_{\frac{1}{2}}$/Hz at 298 K	$3\cdot0$		$7\cdot0$		$7\cdot0$
$W_{\frac{1}{2}}$/Hz at 320 K	$4\cdot0$				
$W_{\frac{1}{2}}$/Hz at 340 K	$10\cdot5$		Coalescence at $\Delta\delta_{AB}$ at 338 K		
$W_{\frac{1}{2}}$/Hz at 360 K	$20\cdot0$				
δ_{OH} (p.p.m.) (at 183 K)	$-7\cdot14$	$-10\cdot14$			

* The parameters have been obtained mainly on the Brüker HFX 90 MHz spectrometer at 26°, except in cases of overlapping lines, where the spectra obtained on the Perkin-Elmer R10 60 MHz spectrometer at 33·5° have often proved more informative. Column (a) are shifts relative to NMe_4^+ and column (b) are shifts recalculated to the δ scale.

The assignment of the two NH peaks was carried out by analogy with the acetamide spectra.[3,4] For [^{15}N]acetamide in acetone and dimethyl sulphoxide the low field peak (H_A) was assigned to the NH proton *cis* to the methyl group, since the *cis*-position is generally less shielded than the *trans*-position in the spectra of amides in inert solvents.[21] The chemical shifts of both NH protons of [^{15}N]benzamide in dimethyl sulphoxide reported in Table 2 are larger than those of [^{15}N]acetamide[4] by exactly the same amount of 0·75 p.p.m., as one would expect for deshielding arising from the general electron-withdrawing effect of the benzene ring, and the same assignment (V) therefore appears reasonable.

In the *O*-protonated cations of the amide both NH resonances are shifted downfield, but in [^{15}N]benzamide the low-field peak is shifted much more than the high-field peak, as compared with [^{15}N]acetamide,[3] so that the relative shifts ($\Delta\delta_{AB}$) are much greater in both fluorosulphuric acid and 100% sulphuric acid. This may be due to the fact that in the cation the planar *O*-protonated amide group is forced much more into coplanarity with the benzene ring, owing to resonance interaction of the positively charged carbon atom with the ring (VII) than is the case in the unprotonated amide. This would bring the H_A proton within the zone of deshielding by the ring and hence produce a larger downfield shift. Thus the above assignment (VI) for the cation seems to be confirmed. The relative shift, $\Delta\delta_{AB}$, is again medium dependent (Table 2), but the difference between fluorosulphuric acid and 100% sulphuric acid is smaller for benzamide than for acetamide.[3] The relative chemical shift of the NH protons and the aromatic region is sufficiently enhanced at 90 MHz for both NH resonances to be observable in the benzamide spectrum in 100% sulphuric acid (Figure 4).



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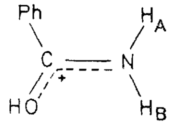

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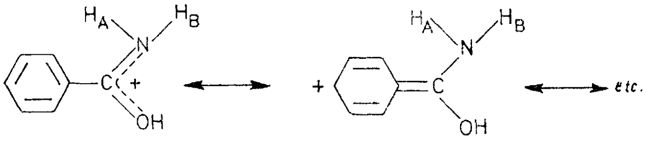

(VII)

In the temperature variation studies of the spectra of [^{15}N]benzamide in fluorosulphuric acid and in 100% sulphuric acid, there is evidence of both faster rotation and faster exchange, as compared with the spectra of [^{15}N]acetamide.[3] Line broadening of the NH resonances in fluorosulphuric acid, coupled with an *upfield* shift, is observed at higher temperatures ($W_{\frac{1}{2}}$ values in Table 2), under conditions where acetamide spectra still show quite sharp lines. This may be due to the importance of resonance (VII), owing to which the barrier to rotation around the C–N bond is reduced. At low temperatures the shift of the NH peaks is downfield, as already reported by Gillespie and Birchall.[25] These shifts afford no evidence of exchange of the NH protons with the solvent. In 100% sulphuric acid evidence for this is apparent in the benzamide spectra at much lower temperatures than in the acetamide spectra: coalescence of the two NH resonances is complete at 338 K, as compared with 353 K for acetamide. This is accompanied by a downfield shift and the NH resonances are hardly observable at 360 K, the exchange with the solvent being rapid at this temperature.

Faster exchange with the solvent of the *O*-protonated cations of benzamide as compared with those of acetamide is especially striking in sulphuric acid containing small amounts of water. Figure 5 shows the spectra of benzamide in 100, 95, and 90% sulphuric acid at 60 MHz 33·5°. It can be seen that the high-field peak overlaps with the aromatic region under these conditions in 100% sulphuric acid, but that the two peaks coalesce into a broad singlet in 95% acid This corresponds to a lifetime of the two NH protons of 7×10^{-4} s, *i.e.* exchange is much faster than with acetamide (*cf.* Figure 2 of ref. 3). In 85% acid the average resonance is further shifted downfield towards the solvent peak, and in 80% acid it is no longer discernible. This is consistent with the conjugate acid of benzamide being more acidic than that of acetamide, and being therefore more susceptible to exchange as the basicity of the solvent increases. Evidence of exchange is clearly apparent even in 98% acid, in which according to u.v. spectral evidence there cannot be more than 3% of the *N*-protonated form present.

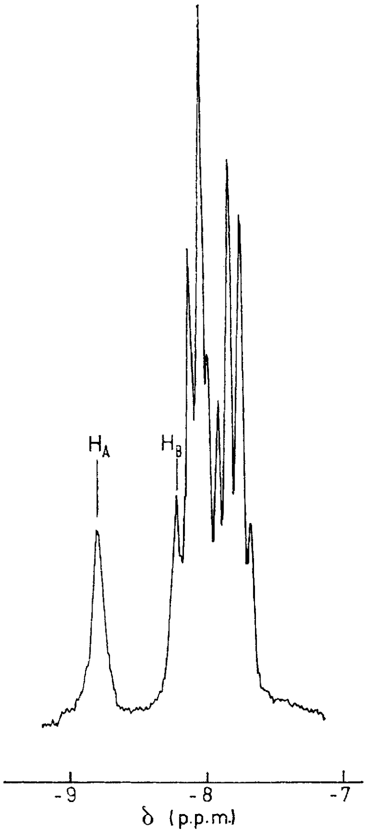

FIGURE 4 The n.m.r. spectrum of benzamide in 100% sulphuric acid at 26° and 90 MHz

Finally, the N–H coupling constants shown in Table 2 are closely similar to those reported for acetamide,[3,4] except for a smaller difference between the two coupling constants for benzamide in fluorosulphuric acid. The geminal coupling of the two NH protons is again not resolvable.

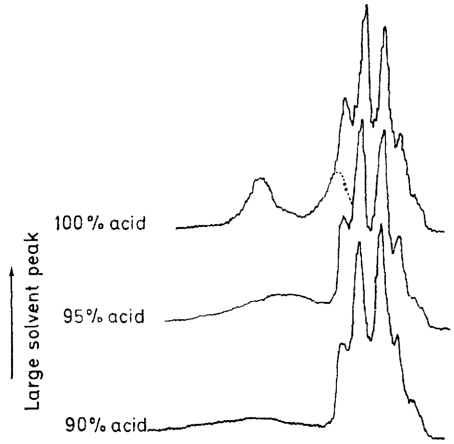

FIGURE 5 The n.m.r. spectra of benzamide in concentrated sulphuric acid of variable concentration at 33·5° and 60 MHz

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