Proton Magnetic Resonance Studies of Fluoride and Acetate Solutions in Glacial Acetic Acid. The Shielding and Thermodynamics of Strong Hydrogen Bonds

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Investigations have been made of the proton shifts of the very strong hydrogen bonds in the anions $F^- \cdots HOAc$ and $AcO^- \cdots HOAc$. An attempt has been made to use glacial acetic acid as the solvent and some of the problems involved in its use are discussed. Studies of $Bu^n_4NF,AcOH$ and $Bu^n_4NOAc,AcOH$ solutions in $CDCl_3$ gave δ values of 14·45 and 15·73 p.p.m. (Me_4Si) respectively for the hydrogen-bonding proton, and values of K_{298}, $\Delta G°_{298}$, and $\Delta S°_{298}$. The entropy changes are very large (+357 and +313 J K^{-1} mol^{-1} respectively) and are another indication of the strong H-bonding in these systems.

THE importance of ^1H n.m.r. spectroscopy being considered, it is remarkable that its use in studying the very strong H-bonds of certain anions has only recently been undertaken. Practical difficulties are the reason. Tuck, in his comprehensive review[1] of XHX^- and XHY^- anions, attributes it to the lack of suitable systems free from solvent interference.[2] Where preliminary studies have been made they showed that the δ of the proton of XHX^- was at considerably lower fields than the parent acid HX in the same solvent.[3]

Recently ^1H n.m.r. studies have been performed on the XHX^- anions (X = F, Cl, Br, and I) as their tetra-n-butylammonium salts in dipolar aprotic solvents such as MeCN and $MeNO_2$.[4] In all these cases the proton shift is over 14 p.p.m. (Me_4Si) downfield of the parent acid, and splitting of the ^1H n.m.r. signal was observed for the bifluoride anion.

We now report on the anions formed between acetate and acetic acid, $AcO^- \cdots HOAc$, and between fluoride and acetic acid, $F^- \cdots HOAc$. Both are known to be very strong H-bonds, the strength of the former being shown by the short O–O internuclear distance in crystals, and for both of them by the related effect of large $\Delta v(O-H)$ i.r. shifts.[5-7] For the $F^- \cdots HOAc$ system[6] the bond enthalpy has been estimated thermochemically to be ca. 120 kJ mol^{-1}.

An attempt has been made to study fluoride and acetate solutions in glacial acetic acid by ^1H n.m.r. spectroscopy. As a consequence it has been necessary to discuss the anomalous behaviour of this solvent as displayed by the proton shift of the hydroxyl group, $\delta(OH)$, which increases with increasing dilution and then at very high dilutions decreases rapidly.[8,9]

Early attempts to calculate $\delta(OH)$ of the cyclic dimer, $\delta(OH)_d$, and of the monomer, $\delta(OH)_m$, gave a wide spread of values[9,10] and doubt was cast on these by the

discovery that traces of water had a disproportionate effect.[11] The problem was finally solved by Jentschura and Lippert.[12,13] They arrived at values of 12·32 (CCl_4 as diluent) and 12·48 (cyclohexane) p.p.m. (Me_4Si) for $\delta(OH)_d$, and 5·88 (CCl_4) and 5·56 (C_6H_{12}) p.p.m. (Me_4Si) for $\delta(OH)_m$.

On glacial acetic acid itself there has been relatively little work done. Because of its low relative permittivity, ε_r, of 6·2 it has commonly been assumed to consist exclusively of cyclic dimers. However this is inconsistent with the ^1H n.m.r. data. Ultrasonic absorption measurements[14] of glacial acetic acid–acetone mixtures could best be interpreted in terms of a cyclic dimer $\rightleftharpoons$ linear dimer equilibrium (1). It was concluded that the

$$(AcOH)_2 \rightleftharpoons AcOH,AcOH \qquad (1)$$

stability of the linear dimer was greater than expected and that it did not readily extend its chain length. These observations seem incompatible with the ε_r and $\delta(OH)_{obs}$ data. The presence of linear dimer in the amounts necessary to explain the ultrasonic experiments should increase ε_r and decrease $\delta(OH)_{obs}$. For the linear dimer $\delta(OH)_{obs}$ would be the mean of the H-bonding and free hydroxyl protons, which would almost certainly be less than $\delta(OH)_d$. These results are complicated by the use of acetone as diluent. This solute can participate via H-bonding with the 'free' OH and is therefore not a neutral solute.

Arguments for and against linear H-bonding polymers boil down to the value of the linear H-bond's shift, $\delta(OH)_n$. Can this, when weighted with the $\delta(OH)$ of the end-of-chain hydroxyl, explain why $\delta(OH)_{obs}$ increases on dilution? To a first approximation $\delta(OH)$ of this free OH will be about that of $\delta(OH)_m$. Davis and Pitzer

[1] D. G. Tuck, 'Progress in Inorganic Chemistry,' ed. F. A. Cotton, Interscience, New York, 1968, vol. 9, p. 161.

[2] R. Haque and L. W. Reeves, *J. Amer. Chem. Soc.*, 1967, **89**, 250.

[3] D. G. Tuck, unpublished work on Et_4NHCl_2 in Me_2SO and MeCN mentioned in ref. 1.

[4] J. S. Martin and F. Y. Fujiwara, *Canad. J. Chem.*, 1971, **49**, 3071.

[5] J. J. Bellamy, *Spectrochim. Acta*, 1969, **25**, A, 319 (with R. J. Pace) and 329 (with A. J. Owen).

[6] John Emsley, *J. Chem. Soc. (A)*, 1971, 2702.

[7] R. Blinc, D. Hadži, and A. Novak, *Z. Elektrochem.*, 1960, **64**, 567.

[8] L. W. Reeves and W. G. Schneider, *Trans. Faraday Soc.*, 1958, **54**, 314.

[9] L. W. Reeves, *Trans. Faraday Soc.*, 1959, **55**, 1684.

[10] J. C. Davis, jun., and K. S. Pitzer, *J. Phys. Chem.*, 1960, **64**, 886.

[11] N. I. Muller and P. I. Rose, *J. Amer. Chem. Soc.*, 1963, **85**, 2173.

[12] U. Jentschura and E. Lippert, *Chem. Ber.*, 1971, **75**, 556.

[13] E. Lippert, *Chem. Ber.*, 1963, **67**, 267.

[14] R. D. Corsaro and G. Atkinson, *J. Chem. Phys.*, 1971, **54**, 4090.

argued [10] that $\delta(OH)_n > \delta(OH)_d$ but even so that value of $\delta(OH)_{obs}$ of an n-mer, $(AcOH)_{n-1}AcOH$, would require n or $\delta(OH)_n$ to be large for $[(n - 1)\delta(OH)_n + \delta(OH)_m]/n$ to behave as observed. The low value of ε_r mitigates against there being long-chain polymers in glacial acetic acid.

Carbon-13 [15] and oxygen-17 [16,17] n.m.r. spectroscopic studies however are in favour of the open dimer or higher linear polymers, although in most of this work [15,16] diluents were of the type which would interfere with the H-bonding (e.g., H_2O, Me_2CO, MeCN, etc.). No one has yet postulated the presence of higher cyclic polymers in glacial AcOH. These could well have hydroxyl proton shifts, $\delta(OH)_{cp}$, different from the dimer and at the same time have low ε_r. At the end of the paper we attempt to fit the data obtained from AcOH–cyclohexane studies with this model.

EXPERIMENTAL

Instruments.—Measurements were made on a Perkin-Elmer R12B spectrometer operating at 60 MHz at 25 °C and referenced internally to tetramethylsilane. Under these conditions there is no evidence of splitting due to coupling with [19]F. Such splitting has been observed for $Bu^n_4NHF_2$ in MeCN below 50 °C and in $MeNO_2$ below -25 °C.[4] A concentrated solution of $Bu^n_4NF,AcOH$ in $CDCl_3$ studied on a Bruker HFX90 spectrometer (90 MHz) at temperatures down to -50 °C showed considerable peak broadening but no definite splitting.

Materials.—Aristar grade glacial AcOH when dried over molecular sieves for a long period will give a constant $\delta(OH)_{obs}$ of 11·55 p.p.p. (Me_4Si). Generally the value falls between this and the undried acid value of 11·66 p.p.m. (Me_4Si). Metal fluorides and acetates were commercial samples where available and these were dried by heating at 100 °C *in vacuo*. Rubidium and caesium acetates were prepared from the corresponding carbonates and AcOH, recrystallized from acetone, and dried at 150 °C. These compounds are very hygroscopic.

Preparation of Tetra-n-butylammonium Acetate and its Acetic Acid Monosolvate.—An attempt was made to prepare a solution of Bu^n_4NOAc in glacial AcOH by the metathesis (2). However, when an equimolar mixture of reactants in

$$Bu^n_4NI + KOAc \xrightarrow{AcOH} Bu^n_4NOAc + KI(\downarrow) \quad (2)$$

AcOH was warmed no precipitation occurred. Removal of the surplus solvent gave crystals, m.p. 117—120 °C, which analysed approximately as the mixed solvated salt $Bu^n_4NI,KOAc,AcOH$ (Found: C, 43·5; H, 7·64; N, 2·40. Calc. for $C_{20}H_{43}IKNO_4$: C, 45·2; H, 8·14; N, 2·65%). Titration with standard base showed there to be one mol. equiv. of AcOH, and the [1]H n.m.r. spectrum in $CDCl_3$ and CCl_4 solutions was consistent with a mixed salt and had the correct integral ratios. The mixed salt is soluble in a large

variety of organic solvents and appears to be recrystallized unchanged from water as fine white needles.

Tetra-n-butylammonium acetate was prepared from 40% aqueous Bu^n_4NOH solution by neutralization with AcOH followed by removal of the water under reduced pressure. This gave an oil from which crystals [m.p. 117 °C (lit.,[18] 116·5—117·5 °C)] were finally obtained by pumping alternating with treatments with acetone. The acetic acid monosolvate, $Bu^n_4NOAc,AcOH$, m.p. 106 °C, was obtained by dissolving the acetate in AcOH and removing the excess of acid at 100 °C under reduced pressure.

Preparation of Tetra-n-butylammonium Fluoride and its Acetic Acid Monosolvate.—Previous workers have been unable to get crystals of the fluoride.[19,20] However by a method analogous to that used for the acetate, *i.e.*, $Bu^n_4NOH + HF$, followed by exhaustive pumping and treatments with dry solvent, crystals of the fluoride were eventually obtained, m.p. *ca.* 40 °C. These were very hygroscopic. The solvate, $Bu^n_4NF,AcOH$, m.p. *ca.* 55 °C,

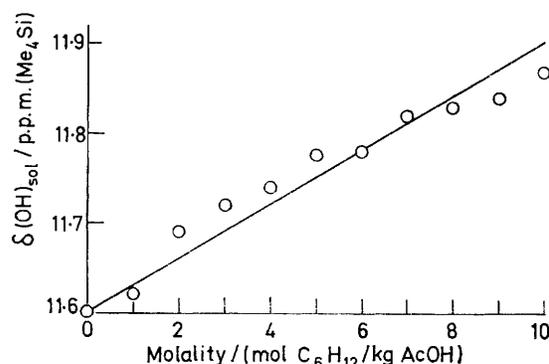FIGURE 1   Hydroxyl [1]H n.m.r. shift, $\delta(OH)_{obs}$, against the molality of cyclohexane in glacial acetic acid

was obtained by treating the fluoride with AcOH and removal of surplus acid (Found: C, 66·2; H, 12·6; N, 4·39. Calc. for $C_{18}H_{40}FNO_2$: C, 67·4; H, 12·5; N, 4·36%).

DISCUSSION

Of the carboxylic acids, glacial AcOH is the best non-aqueous solvent and is widely used as such being second only to liquid NH_3 in this respect. As a solvent for [1]H n.m.r. studies it finds little use.[21]

As a solvent for acetates and fluorides[22] glacial acetic acid is especially good because of the strong H-bonding between these anions and the solvent. A study of this aspect of these solutions is desirable but is complicated by the variation in $\delta(OH)_{obs}$ of the hydroxyl proton of the solvent caused by the addition of solutes. This affects the equilibria existing between the various polymers. Addition of a neutral (*i.e.* non-H-bonding) solute such as cyclohexane to AcOH causes a change in $\delta(OH)_{obs}$ which varies almost linearly over the range 0—10 molal (Figure 1). This plot can be used to ' correct ' the values

[15] G. E. Maciel and D. D. Traficante, *J. Amer. Chem. Soc.*, 1966, **88**, 220.
[16] J. Reuben, *J. Amer. Chem. Soc.*, 1969, **91**, 5725.
[17] D. Ziessow, U. Jentschura, and E. Lippert, *Chem. Ber.*, 1971, **75**, 901.
[18] J. Steyman and P. M. Lorenz, *J. Amer. Chem. Soc.*, 1966, **88**, 2093.

[19] F. Allerhand and P. V. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 1233.
[20] W. Y. Wen, S. Saito, and C. M. Lee, *J. Phys. Chem.*, 1966, 1244.
[21] A. I. Popov, ' The Chemistry of Non-aqueous Solvents,' vol. III, ed. J. J. Lagowski, Academic Press, New York, 1970.
[22] J. Emsley, *J. Chem. Soc. (A)*, 1971, 2511.

observed in the studies of acetate and fluoride solutions by using the relationship (3). It has been shown that KF in AcOH at concentrations above 0·1 molal is

$$\delta(OH)_{sol} = 11·60 + 0·031M \qquad (3)$$

extensively ion-paired [6] and the same applies to metal acetates.[23] It is therefore reasonable to use the formula weight as the basis for the calculation of M in (3) without making allowance for the number of moles of ionic species.

Fluoride Solutions in Glacial Acetic Acid.—The effect of heavy alkali-metal fluorides and tetramethylammonium fluoride on the $\delta(OH)_{obs}$ of AcOH is shown in Figure 2. To a good approximation the results for the metal
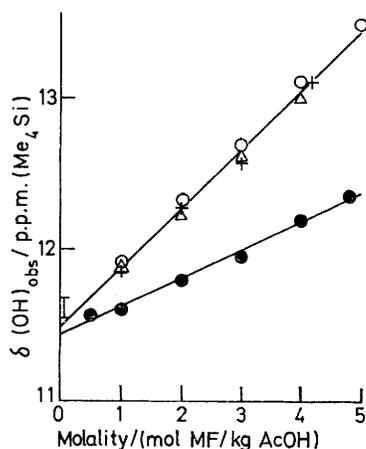
FIGURE 2 Hydroxyl ¹H n.m.r. shift, $\delta(OH)_{obs}$, against the molality of fluorides in glacial acetic acid: +, KF; △, RbF; ○, CsF, and ●, Me₄NF. Glacial acetic acid range shown by bar

fluorides fall on the same straight line which rises more steeply than that for Me₄NF. The signal observed is the time-averaged resonance of AcOH in all environments: as the bulk solvent, as the cation solvation sphere, and as the anion solvation molecule. The first of these is dealt with by use of equation (3). The second is probably of minor importance since the cations K⁺, Rb⁺, and Cs⁺ show negligible variation although they do differ from Me₄N⁺ and this may partly reflect ion size, or ion-pairing. The third aspect, the AcOH forming a strong H-bond to the fluoride ion, has the largest effect on $\delta(OH)_{obs}$.

If the H-bond in the solvated anion is strong then the proton should be greatly deshielded. Assuming that all dissolved F⁻ is solvated, and that the proton in this environment has shift $\delta(OH)_{FHO}$, we can write the Gutowsky and Saika [24] type of weighted equation (4) for $\delta(OH)_{obs}$;

$$\delta(OH)_{obs} = [(x - y)\delta(OH)_{sol} + y\delta(OH)_{FHO}]/x \qquad (4)$$

x and y are the numbers of moles of AcOH and F⁻

* This is justified on the grounds that the charge is the same on both sides of equilibrium (6). Although K_c should vary with concentration this variation will be small and has been neglected.

respectively. Combination of (3) and (4) unfortunately leads to a quadratic relationship in y. But since the variation of $\delta(OH)_{sol}$ with respect to molality is comparatively small it is more convenient to assume $\delta(OH)_{sol}$ to be constant so that (4) rearranges to (5) which predicts

$$\delta(OH)_{obs} = \delta(OH)_{sol} + y/x[\delta(OH)_{FHO} - \delta(OH)_{sol}] \qquad (5)$$

the linear plot observed in Figure 2. The slope in Figure 2 is thus equivalent to the term $[\delta(OH)_{FHO} - \delta(OH)_{sol}]/x$ where $\delta(OH)_{sol}$ is obtained from the intercept. It can be seen that this is 11·50 for the metal fluorides and 11·45 p.p.m. (Me₄Si) for Me₄NF. These values represent truer values for pure AcOH that those which are obtained experimentally and which tend to vary somewhat.

For the metal fluorides the slope term of (5) becomes $[\delta(OH)_{FHO} - 11·50]/16·67$; 1 kg AcOH = 16·67 mol. By use of this simple approach a value of 17·91 p.p.m. (Me₄Si) is obtained for $\delta(OH)_{FHO}$ of the metal fluoride anion and 14·87 p.p.m. (Me₄Si) for Me₄NF. Adjustment of these values by use of (3) for $M = 16·67$ gives the 'corrected' values of 17·39 and 14·34 p.p.m. (Me₄Si) respectively. The former value is thought to be large owing to ion-pairing effects, whereas the latter comes very close to the value determined for the F⁻ · · · HOAc ion by another method which is described next.

In order to study the H-bond of the F⁻ · · · HOAc anion in isolation it is necessary to dissolve a salt of this in an inert solvent. It was found that the salt solvate Buⁿ₄NF,AcOH was soluble in CDCl₃ up to ca. 0·5 molal. In such solutions the equilibrium (6) will be set up and

$$F^- \cdots HOAc \overset{K}{\rightleftharpoons} F^- + AcOH \qquad (6)$$
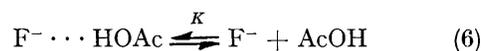
$\delta(OH)_{obs}$ for this system will be a time-averaged value for both the H-bonding and the free AcOH forms. From (6) and using $K_c = [AcOH][F^-]/[F^- \cdots HOAc]$ instead of K based on activities,* and a modified form of equation (5), we obtain (7) in which M is the total concentration

$$\delta(OH)_{obs} = \delta(OH)_{FHO} + K_c^{\frac{1}{2}}M^{-\frac{1}{2}}[\delta(OH)_m - \delta(OH)_{FHO}] \qquad (7)$$

of Buⁿ₄NF,AcOH and $\delta(OH)_m$ is the shift of the hydroxyl proton of AcOH monomer in CDCl₃. From a study of solutions of AcOH in this solvent we found $\delta(OH)_{obs}$ projected to infinite dilution to be 5·65 p.p.m. (Me₄Si), which is very much in keeping with Lippert's values, and shows the solvent to be effectively neutral in terms of H-bonding interference. According to (7) a plot of $\delta(OH)_{obs}$ against $M^{-\frac{1}{2}}$ should give a straight line of which the intercept is the desired $\delta(OH)_{FHO}$. Moreover the slope of such a graph will yield a value of K_c. The plot is shown in Figure 3, and $\delta(OH)_{FHO}$ is 14·45 p.p.m. (Me₄Si). This result fits very well with that from

²³ O. W. Kolling and H. E. Gracey, *Inorg. Chem.*, 1972, 11, 2566.
²⁴ H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, 1953, 21, 1688.

Me₄NF in AcOH and is the same order as that of other strong H-bonding systems such as FHF⁻ [16·3 p.p.m. (Me₄Si)] and the enol form of acetylacetone in which the hydroxyl proton has a shift of 15·5 p.p.m. (Me₄Si).[25]
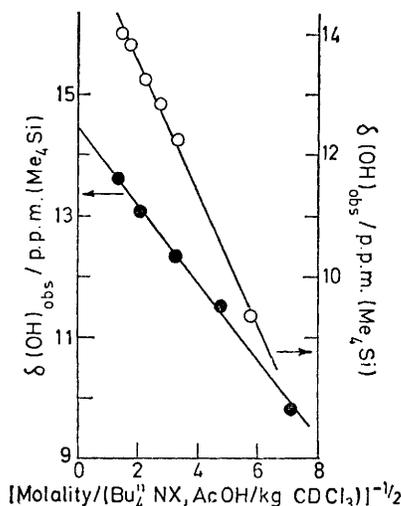
FIGURE 3 Hydroxyl ¹H n.m.r. shift, $\delta(OH)_{obs}$, against (molality)⁻½ of solutions of ●, of Buⁿ₄NF,AcOH (left-hand scale), and ○, Buⁿ₄NOAc,AcOH (right-hand scale)

The slope of the F⁻ · · · HOAc plot gives a value of $K_c = 5·39 \times 10^{-3}$ molal; in other words F⁻ · · · HOAc is ca. 7% dissociated in CDCl₃ solution. Use of this value of K_c in (8) leads to a value for $\Delta G°$ of +13·0 kJ mol⁻¹.

$$\Delta G° = -RT \ln K_c \qquad (8)$$

The enthalpy of formation of this bond was found [6] to be −120 kJ mol⁻¹; $\Delta S°$ is thus +357 J K⁻¹ mol⁻¹. A value of this magnitude is exceptionally high and fits with the complex having a very strong H-bond. Typical H-bonds have $\Delta S° = 50$—70 J K⁻¹ mol⁻¹.[26] In general one would expect $\Delta S°$ to increase with $\Delta H°$ [27,28] since the tighter the bonding the more ' organized ' the complex.

Acetate Solutions in Glacial Acetic Acid.—The above method was adapted to the alkali-metal acetates and Buⁿ₄NOAc in glacial AcOH and the results are in Figure 4. In this study all the alkali-metal acetates were used and all are found to lie approximately on the same straight line, whereas the Buⁿ₄NOAc results are significantly lower for the same concentrations. From the intercepts and slopes were obtained the shifts for the H-bonding protons in AcOHOAc⁻, $\delta(OH)_{OHO}$; this was 17·37 p.p.m. (Me₄Si) for the metal acetates and 15·78 for Buⁿ₄NOAc. Corrected for solvent effects these values become 16·85 and 15·26 p.p.m. (Me₄Si) respectively. Again like the fluoride solutions there is a difference between the values for metal salts and the substituted ammonium salts. Also surprisingly the latter value is higher than that of $\delta(OH)_{FHO}$. That this is really so was

²⁵ L. W. Reeves, *Canad. J. Chem.*, 1957, **35**, 1351.
²⁶ J. E. Crooks and B. H. Robinson, *Trans. Faraday Soc.*, 1971, **61**, 1707.

confirmed by studies of Buⁿ₄NOAc,AcOH in CDCl₃ solution. The plot of $\delta(OH)_{obs}$ against $M^{-\frac{1}{2}}$ for this system is shown in Figure 3 (right-hand co-ordinates). From this is obtained $\delta(OH)_{OHO} = 15·73$ p.p.m. (Me₄Si). Thus as shown by its shift the proton of the OHO bond is more deshielded than that of the FHO bond, and therefore one would suppose it to be the stronger. Thermodynamic parameters are contrary to this assumption; Figure 3 yields $K_c = 1·17 \times 10^{-7}$ molal (*i.e.*, ca. 10% dissociated) and $\Delta G° = +11·1$ kJ mol⁻¹. Before the latter term can be converted to $\Delta S°$ it is necessary to have $\Delta H°$ for the dissociation step.

In the determination of $\Delta H°$ for the formation of the H-bond in F⁻ · · · HOAc it was shown that the calorimetric method and that based on $\Delta v(O-H)$ were in agreement at −120 kJ mol⁻¹. This being so, it seems possible to obtain the same information for AcOHOAc⁻ from the published $\Delta v(O-H)$ of this species,[7] which is 3620 − 1700 cm⁻¹, i.e. 1920 cm⁻¹. On a *pro rata* basis of comparison with F⁻ · · · HOAc this corresponds to a value for $\Delta H°$ of −105 kJ mol⁻¹; in other words the bond enthalpy of the OHO H-bond is slightly less than that of FHO. Too much weight cannot be placed on this value for $\Delta H°$ for this anion since the assumptions on which it is based have not been proved, but it now permits the calculation of $\Delta S°$ as +313 J K⁻¹ mol⁻¹. Again this is large but not unacceptable.

The data for the F⁻ · · · HOAc and AcOHOAc⁻ anions, summarized in the Table, pose two questions: (i) why does the former anion have $\delta(OH)_{FHO}$ less than
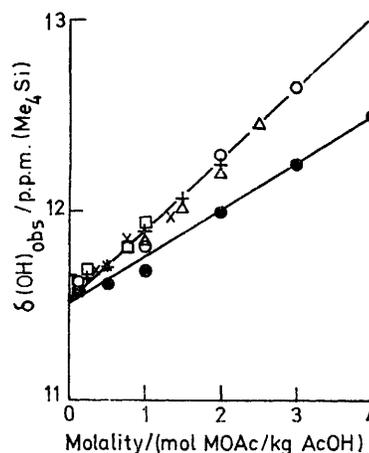

FIGURE 4 Hydroxyl ¹H n.m.r. shift, $\delta(OH)_{obs}$, against molality of acetates in glacial acetic acid: ×, LiOAc; □, NaOAc; +, KOAc; △, RbOAc; ○, CsOAc; and ●, Buⁿ₄NOAc. * Signifies all metal acetates coincident at 0·5 molal. Glacial acetic acid range shown by bar

$\delta(OH)_{OHO}$ of the latter despite its being the stronger of the two H-bonds as measured by $\Delta H°$ and $\Delta S°$? and (ii), why is the shielding of $\delta(OH)_{FHO}$ in metal fluorides greater

²⁷ J. E. Crooks, P. J. Sheridan, and D. O'Donnell, *J. Chem. Soc. (B)*, 1970, 1285.
²⁸ J. W. Bayles and A. F. Taylor, *J. Chem. Soc.*, 1961, 417.

than that calculated for Me_4NF and Bu^n_4NF, and moreover is greater than that of $\delta(OH)_{OHO}$ in metal acetates?

The second question is easier to deal with than the first. Extensive ion-pairing may bring the cation sufficiently near to the anion to affect the H-bond. An

Parameters of the strong hydrogen bonds

	$F^- \cdots HOAc$	$AcOHOAc^-$
$\Delta H^\circ/kJ\ mol^{-1}$	120 [6]	105
$\Delta G^\circ/kJ\ mol^{-1}$	13·0	11·1
$\Delta S^\circ/J\ K^{-1}\ mol^{-1}$	357	313
$K_c[X^- \cdots HOAc = X^- + HOAc]/$ molal	$5·39 \times 10^{-3}$	$1·17 \times 10^{-2}$
$\delta(OH \cdots X)/(p.p.m.\ (Me_4Si)$ $Bu^n_4NX, HOAc\ in\ CDCl_3$	14·45	15·73
$\delta(OH \cdots X)/(p.p.m.\ (Me_4Si)$ $R_4NX\ in\ AcOH$	14·34	15·26
$\delta(OH \cdots X)/(p.p.m.\ (Me_4Si)$ $MX\ in\ AcOH$	17·39	16·85

[ΔH°, ΔG°, ΔS°, error $\pm 20\%$; δ values, error $\pm 0·05$ p.p.m. (Me_4Si).

alternative explanation is that the AcOH solvating the metal cation is less shielded than the solvent dimers, but if this were so then cation solvation numbers would be important and one would expect changes down the alkali-metal group. This is not the case as the metal acetate studies show (Figure 4).

Both systems are extensively ion-paired [6,23] but beyond this one can only speculate as to how ion-pairing could decrease the shielding. Kolling and Gracey's work [23] shows that lithium to caesium acetates are all ion-pairing to about the same extent ($pK\ ca.$ 6, ranging from 6·79 for LiOAc to 5·84 for CsOAc) which may explain why these in solution produce essentially the same effect.

The first question is more a paradox. It has always been assumed that the stronger the H-bond the less shielded the proton. For $F^- \cdots HOAc$ and $AcOHOAc^-$ the reverse is true. ΔH°, $\Delta v(O-H)$, K_c, and ΔS° values all point to the fluoride forming the stronger H-bond to acetic acid yet the H-bonding proton is more shielded. One explanation could be that the proton has been pulled sufficiently near to the fluoride anion to have entered the region shielded by its electron cloud, or that an equilibrium of type (9) exists. This would increase the bond strength without deshielding the proton. In symmetrical H-bonds such as FHF^- and $AcOHOAc^-$ the

$$F^- \cdots H-OAc \rightleftharpoons F-H \cdots {}^-OAc \qquad (9)$$
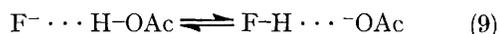
proton is attracted equally to two identical centres and consequently takes up a position equidistant from either, and is *ipso facto* the least shielded. As suggested by a Referee, the magnetic anisotropy of AcO^- as compared with that of the spherically symmetrical F^- might also be an explanation of the larger $\delta(OH)_{OHO}$ of the $AcOHOAc^-$ anion.

Another anomalous situation regarding symmetric as opposed to asymmetric H-bonds is found with the cyclic dimers $(AcOH)_2$ and $(CF_3 \cdot CO_2H)_2$ which have lower dissociation constants than the mixed dimer $(AcOH, CF_3 \cdot CO_2H)$.[29]

Glacial Acetic Acid.—Most work on this has concentrated on the high dilution range where the only equilibrium is between the cyclic dimer and the monomer. Over the middle range of concentrations the cyclic dimer predominates but at high concentrations of AcOH other equilibria are set up. It is possible to treat these by a modified Lippert approach [12,13] assuming only one type of equilibrium, in this instance between the cyclic dimer and higher polymers which may or may not be cyclic. Assuming them to be linear we get the more general equation (10). For this we can set up equations (11), (12), and (13) where C_n is the concentration of the n-mer

$$\frac{n}{2}(AcOH)_2 \xrightleftharpoons{K} (AcOH)_{n-1}AcOH \qquad (10)$$

cyclic dimer n-mer

$$K = C_n/C_d^{n/2} \qquad (11)$$

$$C = C_d + \frac{n}{2}C_n \qquad (12)$$

$$\delta_{obs} = (2\delta_d C_d + (n-1)\delta_n C_n + \delta_e C_n)/2C \qquad (13)$$

and C_d the cyclic dimer, C is the initial concentration of acetic acid (dimer/mol dm^3), δ_d is the ${}^1H$ n.m.r. shift of the H-bonding proton of the cyclic dimer, δ_n of the n-mer, and δ_e of the end-of-chain free hydroxyl proton.

Solving for C_d and C_n and substituting in (11) we obtain (14) in which where δ_p is the weighted ${}^1H$ n.m.r. shift of

$$\frac{C}{C^{n/2}} = \frac{Kn}{2}\left(\frac{\delta_{obs} - \delta_p}{\delta_d - \delta_p}\right)^{n/2}\left(\frac{\delta_d - \delta_{obs}}{\delta_d - \delta_p}\right)^{-1} \qquad (14)$$

the polymer, i.e., (15). Equation (14) rearranges to (16)

$$\delta_p = \left(\frac{n-1}{n}\right)\delta_n + \frac{1}{n}\delta_e \qquad (15)$$

in which $\delta' = (\delta_{obs} - \delta_p)/(\delta_d - \delta_p)$. In (16) δ_p is δ';

$$C^{(2/n-1)} = \left(\frac{Kn}{2(1-\delta')}\right)^{2/n}\delta' \qquad (16)$$

n and K are unknowns but to a first approximation it is reasonable to assume that $\delta_n \rightarrow \delta_d$, i.e., 12·5 p.p.m. (Me_4Si), and $\delta_e \rightarrow \delta_m$, i.e., 5·5 p.p.m. (Me_4Si). From (16) we get (17). A plot of $\log C$ against the term

$$\log C = \frac{2}{2-n}[\log K + \log n - \log 2] +$$

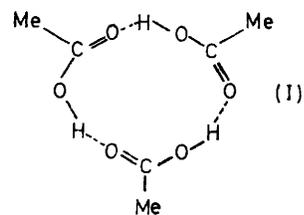$$\frac{1}{2-n}[n\log \delta' - 2\log(1-\delta')] \qquad (17)$$

$[n\log\delta' - 2\log(1-\delta')]$ based on the cyclohexane-acetic acid system and various n values (2,3,4 . . .) gave straight lines from which an average n value was obtained. This was then used to tighten the relationship and a further plot made which produced an improved n value of 3·60 and thence a K value of 0·466. These in turn led to a value for δ_p of 11·27 p.p.m. (Me_4Si) when substituted in equation (14). It is possible to refine the

[29] S. D. Christian, H. E. Affsprung, and Chii Ling, *J. Chem. Soc.*, 1965, 2378.

calculations still further by using this as a basis, which eventually gives $n = 3\cdot08$ and $K = 0\cdot298$. In terms of the composition of glacial acetic acid this means that it is composed of 79% cyclic dimer and 21% trimer.

Is the trimer, which these calculations suggest is the predominant species of polymer, cyclic or linear? Relative permittivity favours the former as does the δ_p value calculated above. For a linear trimer species the end-of-chain proton's shift should be about that of the free monomer, in which case the shift of the linear H-bonding protons would need to be ca. $14\cdot3$ p.p.m. (Me_4Si), which is the order of a very strong H-bond. Thus the Lippert approach, when applied to the ^{1}H n.m.r. results of concentrated glacial acetic acid solutions of cyclohexane, shows these to be consistent with the presence of cyclic trimers (I) as well as the expected dimers. In the cyclic

trimers $\delta(OH)_t$ is $11\cdot27$ p.p.m. (Me_4Si), less than in the cyclic dimers (as observed) and evidence for a weaker H-bond, as Reeves originally suggested.[8,9]

(I)