A Structural Model for Lewis Acids and Bases. An Analysis of the Structural Chemistry of the Acetate and Trifluoroacetate Ions

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In the solid state acetate and trifluoroacetate ions show a variety of internal and external bonding geometries that can be directly related to the differences between the two anions and to differences in the Lewis-acid strengths of the counter ions. The structures and crystalline environments of 38 such anions have been examined. The results are interpreted in terms of a model of acid and base strength based on bond valences (bond strengths) determined from the observed bond lengths. In this model each atom is assigned *a priori* an acid or base strength equal to the valence of the bonds it normally forms. Acid–base bonds will only occur when the acid and base have similar strengths but some degree of mismatch can be accommodated by small but predictable deviations from the idealised structure. Thus when acetate and trifluoroacetate ions crystallise with weak Lewis acids (acid strength <0.5) the anions are symmetric and show little variation in their internal geometry but when they crystallise with strong Lewis acids the anions are often asymmetric and the methyl H atoms show enhanced acidity. The scales of acid and base strength proposed here account quantitatively for the observed variations in both the structure and chemical activity of the two anions examined.

OVER the years many scales of Lewis acidity and Lewis basicity have been proposed but few if any have made use of the large number of accurate measurements of molecular structure that are now available from *X*-ray and neutron-diffraction investigations. Most scales are based on solution measurements, for example the pK_a measured in aqueous solution and Gutmann's [1] Donicities and Acceptor Numbers which were measured for non-polar solvents. While these scales are useful in ranking acids and bases in order of strength and in predicting thermodynamic properties, they give little direct information about the structure of the acid, base, and solvent complexes that are formed. Theoretical calculations of residual charges on atoms in discrete ions and molecules can also be correlated with known acid and base character [2] but these calculations usually consider the molecule in isolation and therefore explicitly ignore the interactions with neighbouring groups.

The solid state provides an ideal opportunity for studying intermolecular interactions and their influence on the internal structure of the molecule. With a doubling of the number of known crystal structures during the past seven years it is now possible to compare the structures of many similar molecules in different solid-state environments and to examine the influence of neighbouring ions and molecules. For example, Dunitz and his co-workers [3] have used this technique to plot the reaction pathway followed during the S_N1 addition of a ligand to a planar AX_3 molecule. This paper shows that a similar analysis of solid-state structure can be used to examine the changes that occur in acid–base bonding as the strengths of the acid and base are varied.

The particular systems chosen for examination are the acetate and trifluoroacetate ions since both contain two strong base groups (O) and additional weakly acidic (H) or weakly basic (F) groups and since both crystallize with cations of a wide range of Lewis-acid strengths. Although this study focuses on only two molecular ions the principles elucidated here should apply to a wide range of acid–base complexes.

In order to analyse the influence of acid and base strength on structure, it is necessary to have structure-related scales of acid and base strength. These are provided by the empirical bond valence model [4] which has proved to be very successful in analysing inorganic structures and which is here applied for the first time to a problem in physical organic chemistry.

RESULTS AND DISCUSSION

The Bond Valence Model.—The principles underlying the empirical bond valence model and its applications have recently been reviewed.[4] It treats acid–base complexes as networks of bonds in which atoms occur at the nodes. The valence (formal charge or oxidation state), V_i, of each atom is assumed to be shared between the bonds it forms so that for all atoms equation (1) holds,

$$V_i = \sum_j s_{ij} \quad (1)$$

where s_{ij} is the valence of the bond between atoms i and j. For many types of bond s_{ij} has been found to correlate inversely with the bond length, r_{ij}, according to some empirical relation such as equation (2) where r_0

$$s_{ij} = (r_{ij}/r_0)^{-n} \quad (2)$$

and n are fitted parameters that have been tabulated by Brown and Wu.[5] Experimentally measured bond lengths can be used with equations (1) and (2) to calculate experimental atomic valences that are usually found to lie within 0.05 valence units (v.u.) of the theoretical integer values. Bond valences thus provide an experimental bond-strength scale which is independent of atomic size and which is related in a very simple way to formal oxidation number (valence).

Since the valence of bonds formed by most cations vary little from one compound to another they will fit

$$s_a = V_a/N_a \quad (3)$$

closely [see equation (1)] to equation (3) where V_a is the valence (formal positive charge) and N_a is the average

TABLE 1

Cation acid strengths calculated from equation (3) for oxygen co-ordination

Cation	Typical co-ordination number	Cation acid strength
H	to donor base	0.80 *
	to acceptor base	0.20
NH_4	4	0.25
Li	4—6	0.22
Na	6	0.17
Ag^{I}	2—6	0.17—0.50
Be	4	0.50
Mg	6	0.33
Ca	8	0.28
Cr^{II}, Mn^{II}, Co^{II}, Ni^{II}, Mo^{II}, Rh^{II}	6	0.33
Cu^{II}	4—6	0.40
Cd^{II}	4—8	0.38
Hg^{II}	2—6	0.70
B	3—4	0.88
Al	4—6	0.63
Tl^{III}	6—7	0.46
C	4	1.00
Si	4	1.00
Sn^{IV}	6	0.67
Te^{IV}	4—6	0.73
S^{VI}	4	1.50

* A full discussion of the bonding of H and the assignment of valences to O–H bonds as given by I. D. Brown, *Acta Cryst.*, 1976, **A32**, 24.

co-ordination number of the cation. Since the values of s_a (Table 1) increase with the Lewis-acid strength of the cation they can be used as a scale of acidity. The advantage of this scale is that the numerical value of the acid strength can be taken as a first approximation to the valence of the bonds that will be formed by that cation in any particular compound.

A similar scale of base strengths (s_b) can be constructed although the strengths of bonds formed by bases is more variable. In SiO_2 oxygen forms bonds of valence $2/2 = 1.0$ but in MgO it forms bonds of valence $2/6 = 0.33$. In $Li_2[SO_4]$ it simultaneously forms a bond of valence 1.5 to S and two bonds of valence 0.25 to Li. Nevertheless, when the particular chemical context is taken into account it is usually possible to assign an appropriate base strength to O.

Since the valence of an acid–base bond will normally be close to both s_a (strength of the acid) and s_b (strength of the base), it follows that ' bonds will normally form only when the Lewis-acid strength of the electron acceptor is close to the Lewis-base strength of the electron donor '. This valence-matching principle is not as restrictive as may at first appear since it is frequently possible for the base to adapt its bonding [within the limits dictated by equation (1)] to match a wide range of acid strengths. The sections that follow explore the ways in which the acetate and trifluoroacetate ions are found to adapt themselves to acids ranging in strength from 0.17 to 1.00 v.u. For weak acids ($s_a < 0.5$ v.u.) this is achieved chiefly through changes in the external bonding of the ion but for stronger acids internal changes also play an important role.

Acetates and Trifluoroacetates.—Internal geometry. For

TABLE 2

(a) Bonding of acetates

Compound	Acid strength of cation		Σs_b bonds at O	Σs_a bonds at H	C–O(1)	C–O(2)	C–C	O(1)–C–O(2)	C–C–O(1)	C–C–O(2)	Methyl Σs_a average	Asym. $\frac{s[C-O(1)]}{s[C-O(2)]}$	R [a]	Footnote
	Ideal	Obs.				v.u.			°					
(*i*) Cations with acid strengths <0.55														
$[Na(OH_2)_3][O_2CMe]$ (1)	0.17	0.18	0.96	0.05	1.48	1.45	1.12	124	119	118	0.04	1.02	0.034	*b*
$[NH_4][O_2CMe]$ (2)	0.25	0.18	0.85 [c]	0.07	1.48	1.48	1.13	123	118	118	0.10	1.00	0.09	*d*
$[NH_4][O_2CMe]\cdot MeCO_2H$ (3)	0.25	0.32	0.92 [c]	0.03	1.48	1.36	1.12	123	120	117	0.08	1.09	0.085	*e*
$[NH_4][O_2CMe]\cdot NH_3$ (4)	0.25	0.20	0.85 [c]	0.02	1.52	1.51	1.07	124	118	118	0.04	1.01	0.069	*f*
$[NH_4][O_2CMe]\cdot 2NH_3$ (5)	0.25	0.18	0.88 [c]	0.00	1.46	1.46	1.01	124	118	118	0.01	1.00	0.11	*g*
$[Li(OH_2)_2][O_2CMe]\cdot H_2O$ (6)	0.22	0.27	0.98	0.18	1.51	1.51	1.06	126	117	117	0.07	1.00	0.052	*h*
$[Cd(OH_2)_2(O_2CMe)_2]$ (7)	0.38	0.35	1.10	0.13	1.46	1.36	1.10	120	122	118	0.11	1.07	0.028	*i*
		0.34	1.02	0.05	1.45	1.41	1.13	121	120	119	0.13	1.03		
$[Mn_3(OH_2)_4(O_2CMe)_2]\cdot 8H_2O$ (8)	0.33	0.31	1.25	0.12	1.54	1.33	1.10	121	120	120	0.16	1.16	0.05	*j*
		0.36	1.04	0.09	1.48	1.46	1.14	125	118	118	0.09	1.01		
		0.36	1.10	0.07	1.46	1.45	1.07	123	119	118	0.08	1.01		
$[Ni(OH_2)_4(O_2CMe)_2]$ (9)	0.33	0.32	1.03	0.14	1.50	1.37	1.14	123	119	118	0.10	1.09	0.028	*k*
$[Rh_2(OH_2)_2(O_2CMe)_4]$ (10)	0.33	0.46	1.13	0.13	1.42	1.38	1.14	125	118	117	0.13	1.03	0.031	*l*
		0.48	1.08	0.12	1.40	1.40	1.13	125	118	117	0.11	1.00		
$[Cr_2(OH_2)_2(O_2CMe)_4]$ (11)	0.33	0.44	1.20	0.08	1.42	1.40	1.18	123	119	118	0.10	1.01	0.034	*l*
		0.46	1.08	0.14	1.43	1.41	1.16	124	118	118	0.13	1.01		
$[Cu_2(OH_2)_2(O_2CMe)_4]$ (12)	0.40	0.40	1.16	0.08	1.46	1.43	1.13	124	118	118	0.12	1.02	0.061	*m*
		0.46	1.05	0.14	1.44	1.43	1.13	125	117	118	0.11	1.01		
$[Tl(O_2CMe)_3]$ (13)	0.46	0.47	1.04	0.06	1.49	1.49	0.91	121	120	120	0.00	1.00	0.057	*n*
		0.42	1.14	0.13	1.52	1.44	1.14	117	121	121	0.14	1.06		
$[Be_4O(O_2CMe)_6]$ (14)	0.50	0.51	1.36	0.17	1.51	1.51	1.13	123	119	119	0.22	1.00	0.056	*o*
(*ii*) Cations with acid strengths >0.55														
$Na[H(O_2CMe)_2]$ (15)	0.80	0.47	1.16	0.08	1.55	1.28	1.12	123	121	116	0.12	1.21	0.038	*p*
$[NH_4][O_2CMe]\cdot MeCO_2H$ (16)	0.80	0.46	0.94 [c]	0.02	1.63	1.36	1.10	124	120	116	0.06	1.20	0.085	*c*
		0.67	0.98 [c]	0.05	1.70	1.18	1.18	122	125	112	0.12	1.44		
$MeCO_2H$ (17)	0.80	0.75	1.12	0.12	1.72	1.19	1.13	122	125	113	0.12	1.45	0.092	*q*
$C_5H_7(CO_2H)_2NH_3\cdot MeCO_2H$ (18)	0.80	0.71	0.98	0.09	1.78	1.21	1.18	123	125	112	0.08	1.47	0.068	*r*
$H_3PO_4\cdot MeCO_2H$ (19)	0.80	0.76	1.28	0.08	1.56	1.25	1.19	122	123	115	0.18	1.25	0.051	*s*
		0.74	1.23	0.10	1.59	1.26	1.24	121	123	115	0.19	1.26		
$Na[MeC(O)PO_3H]\cdot MeCO_2H$ (20)	0.80	0.79	1.29	0.06	1.67	1.25	1.15	123	123	114	0.17	1.34	0.038	*t*
$[Ni(MeCO_2H)_6][BF_4]_2$ (21)	0.80	0.87	1.35	0.24	1.66	1.24	1.19	121	126	113	0.26	1.34	0.058	*k*
		0.81	1.28	0.27	1.65	1.21	1.24	120	126	124	0.26	1.36		
		0.86	1.32	0.18	1.66	1.19	1.19	121	126	114	0.23	1.39		
$[MeCO_2H_2][SFO_3]$ (22)	0.80	0.71	1.44	0.31	1.43	1.38	1.24	119	124	118	0.33	1.04	0.09	*u*
$[MeCO_2H_2][HSO_4]$ (23)	0.80	0.68	1.38	0.19	1.42	1.38	1.21	118	124	118	0.26	1.03	0.076	*v*
O-Methyl sparvenone-acetate⁻(24)	1.00	0.74	0.98	0.06	1.78	1.10	1.06	123	126	111	0.03	1.62	0.047	*w*
Levoglucosantriacetate (25)	1.00	0.83	1.20	0.21	1.80	1.05	1.13	122	128	110	0.18	1.71	0.048	*x*
		0.80	1.32	0.22	1.69	1.08	1.17	112	126	111	0.23	1.56		
		0.83	1.34	0.24	2.00	1.19	1.21	122	127	112	0.26	1.68		
$Si(O_2CMe)_4$ (26)	1.00	1.00	1.18	0.10	1.78	1.01	1.17	119	128	113	0.15	1.77	0.08	*y*

TABLE 2 (*Continued*)

(*b*) Bonding of trifluoroacetates (tfa)

Compound	Acid strength of cation: Ideal	Acid strength of cation: Obs.	Σs_b bonds at O	Σs_a bonds at F	C–O(1)	C–O(2)	C–C	⟨C–F⟩	O(1)–C–O(2)	C–C–O(1)	C–C–O(2)	Methyl Σs_b average	Asym. $\frac{s[C\text{–}O(1)]}{s[C\text{–}O(2)]}$	*R*	Footnote
					v.u.				°						
(*i*) Cations with acid strength <0.45															
$Me_2C_8H_4N_2(OH)_2\cdot CF_3CO_2\cdot CF_3CO_2H$ (27)	0.20	0.37	0.77	0.08	1.60	1.54	1.01	1.04	130	116	114	0.15	1.04	0.046	*z*
$[Fe(CO)_3(C_5H_7N_2)][tfa]$ (28)	0.20	0.25	0.51	0.09	1.63	1.51	1.02	1.01	129	117	114	0.27	1.08	0.04	*i*
$[NH_4][tfa]$ (29)	0.25	0.16	0.62[c]	0.18	1.48	1.43	1.02	0.86	128	115	117	0.18	1.03	0.11	*ii*
$[Cu_2(OH)(tfa)_3(C_9H_7N)_2]$ (30)	0.40	0.44	1.00	0.18	1.58	1.47	1.03	0.95	129	117	114	0.09	1.07	0.073	*iii*
		0.49	0.84	0.07	1.64	1.48	1.13	1.11	129	115	114	0.12	1.11		
		0.41	0.79	0.17	1.66	1.46	1.08	0.96	129	117	114	0.19	1.14		
$[Mo_2(tfa)_4(C_5H_5N)_2]$ (31)	0.33	0.48	0.98	0.09	1.49	1.48	1.03	0.97	127	117	116	0.06	1.01	0.06	*iv*
		0.45	0.96	0.05	1.44	1.40	1.20	1.04	125	118	117	0.04	1.03		
(*ii*) Cations with acid strength >0.45															
$\{Ag(tfa)\}_2$ (32)	0.50	0.36	0.98	0.09	1.67	1.56	0.98	0.93	130	115	114	0.06	1.11	0.044	*v*
$[Sn_4Me_8O_2(tfa)_4]$ (33)	0 67	0.48	0.81	0.08	1.69	1.68	0.98	1.03	130	115	115	0.14	1.01	0.026	*vi*
		0.44	0.75	0.08	1.82	1.43	1.00	1.04	128	118	115	0.16	1.27		
$[\{SnMe_2(tfa)\}_2]$ (34)	0.67	0.38	0.76	0.14	1.68	1.49	1.02	1.01	130	116	114	0.19	1.13	0.042	*vii*
$[SnMe_3(tfa)]$ (35)	0.67	0.52	0.99	0.18	1.70	1.35	0.99	1.10	129	118	113	0.10	1.26	0.055	*viii*
$C\{Hg(tfa)\}_4$ (36)	0.70	0.76	0.96	0.04	1.87	1.50	1.05	0.99	128	120	112	0.04	1.25	0.028	*ix*
$TePh_2O(tfa)_2$ (37)	0.73	0.63	0.83	0.12	1.80	1.35	1.06	1.10	127	119	114	0.14	1.33	0.062	*x*
		0.57	0.84	0.09	1.82	1.35	1.06	1.13	127	119	114	0.12	1.35		
$Cs[H(tfa)_2]$ (38)	0.80	0.51	0.91	0.08	1.75	1.19	1.07	0.90	127	119	114	0.08	1.47	0.10	*xi*
$K[H(tfa)_2]$ (39)	0.80	0.48	0.88	0.12	1.67	1.41	1.00	0.88	129	120	111	0.12	1.18	0.052	*xii*
$Me_2C_8H_4N_2(OH)_2\cdot CF_3CO_2\cdot CF_3CO_2H$ (40)	0.80	0.74	0.85	0.05	1.79	1.28	1.04	1.04	128	121	111	0.10	1.40	0.046	*z*
(*iii*) Structures not used															
$[Mo_2(tfa)_4]$ (41)	0.33	0.50	1.10	0	1.55	1.38	1.30	0.98	123	118	119	0.05	1.12	0.08	*xiii*
		0.71	1.34	0	1.43	1.42	1.80	0.82	129	116	115	0.17	1.01		
$[Mo(CO)_2(tfa)(MeCHCH_2)(MeOEtOMe)]$ (42)	0.33	0.46			1.44	1.19	1.07	1.00	129	129	110		1.21	0.12	*xiv*
$\{Cu(tfa)\}_4(C_6H_6)_2$ (43)	0.40													0.11	*xv*
$[AsPh_4]_2[Co(tfa)_4]$ (44)	0.33	0.40			1.70	1.59	0.74	1.15	127	130	103		1.07	0.11	*xvi*
$[Sn(H_2C{=}CH)_2(tfa)_2(C_{10}H_8N_2)]$ (45)	0.67	0.53			1.93	1.19	1.27	1.44	126	123	111		1.62	0.07	*xvii*
		0.44			1.93	1.66	1.22	1.46	128	116	117		1.16		
$[Hg_2(tfa)_2]$ (46)	0.70	0.61	0.96	0	1.44	1.02	1.81	0.82				0.02	1.41	0.10	*xviii*

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each of a series of selected acetate and trifluoroacetate structures the bond valences both within the ion and between the ion and its neighbours were calculated (see Appendix and Table 2). In most cases it is not easy to obtain a clear picture of the bonding within the methyl and trifluoromethyl groups because the H atoms are poorly resolved by *X*-ray diffraction and the CF_3 groups are frequently disordered or rotating, making the measured C–H and C–F distances unreliable. However the geometry of the CO_2^- group can be studied and Figure 1 shows the O–C–O and C–C–O angles (θ) plotted against the average bond valence (⟨*s*⟩) of the C–O and C–C bonds that define them. Both sets of angles in both the acetate and trifluoroacetate ions are well described by the single equation (4).*

$$\theta = 71 + 36.7\langle s\rangle\ ^\circ \qquad (4)$$

Figure 1 also shows that the C–O bonds are stronger and the O–C–O angles larger in the trifluoroacetate ion than they are in the acetate ion. These differences can be attributed to the acid character of the methyl H atoms and the base character of the trifluoromethyl F atoms. Both the acetate and the trifluoroacetate ions carry a formal charge of −1 which will, to a first approximation, be divided between the two O atoms giving each a base strength of 0.5 v.u. This will be modified by the basicity or acidity of the atoms on the methyl group

$$\Sigma s_b - \Sigma s_a = 1 \qquad (5)$$

since the total base strength (minus any acid strength) of the ion must be equal to 1.0, *i.e.* equation (5).

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* Following the suggestion of P. Murry-Rust *et al.* [3] this equation should describe the acetate ion as it decomposes into a CO_2^- and a CH_3 fragment. The equation predicts that the CO_2^- fragment should be bent with an O–C–O angle of 144°, much smaller than the value of 180° found in the CO_2 molecule but close to the values of 130—150° predicted for CO_2^- by A. D. Walsh (*J. Chem. Soc.*, 1953, 2266) and 134° found by e.s.r. in $NaHCO_3$ by D. W. Ovenall and D. H. Whiffen (*Mol. Phys.*, 1961, **4**, 135).

Thus in the acetates with weakly acidic methyl H atoms the base strength of the two O atoms will be enhanced, but in the trifluoroacetates with weakly basic F atoms it will be diminished in agreement with the observation that the trifluoroacetate ion is a weaker Lewis base than the acetate ion. An examination of the observed bond valences for these ions when they are bonded to weakly acidic cations (Table 2, columns 4 and 5) shows that normally the total base strength of the two O atoms is *ca.* 1.1 v.u. for the acetates but only 0.9 v.u. for the trifluoroacetates. Correspondingly the 3 H atoms together contribute an acid strength of *ca.* 0.1 v.u. and the 3 F atoms a base strength of *ca.* 0.1 v.u. These latter effects occur mostly through C–H · · · O, C–H · · · F, and C–F · · · H interactions that are weak but quantifiable.

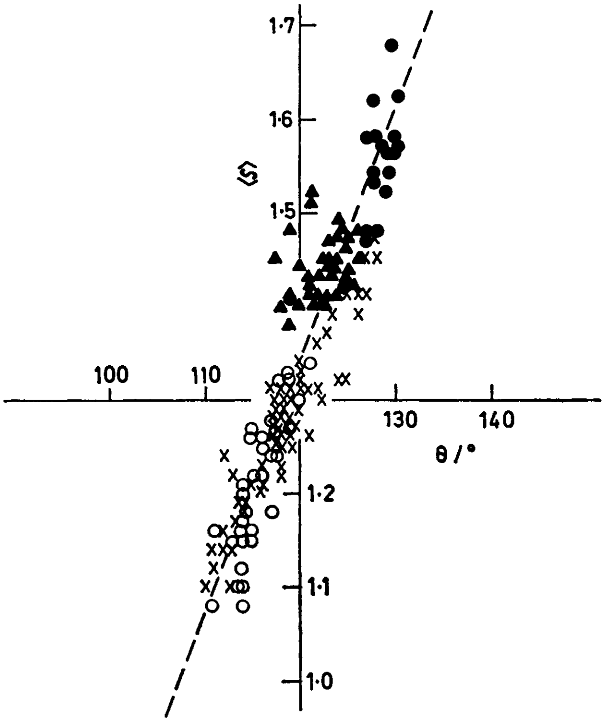
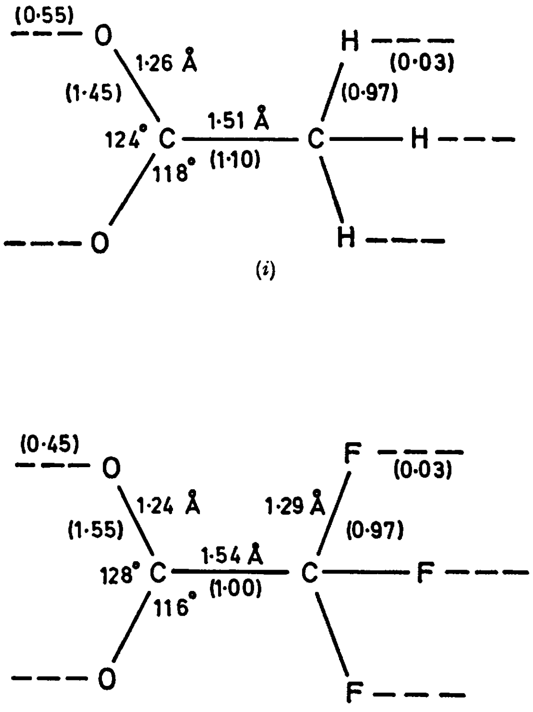


FIGURE 1 C–C–O and O–C–O angles in acetates (×,▲) and trifluoroacetates (○,●) respectively, plotted against the average valence of the bonds defining the angle. The dashed line corresponds to equation (4)

Once the acid and base strengths shown by the O, H, and F atoms have been determined, equation (1) can be invoked to predict the internal structure of the anions. If one assumes that the anion will be symmetric, only one assignment of bond valences is possible for the acetate ion and this can be used with equations (2) and (4) to predict the bond lengths and angles shown in Figure 2(*i*). In the trifluoroacetate ion [Figure 2(*ii*)] since both carbon atoms are formally treated as Lewis acids no assignment of bond valences can give correct atomic valences at both carbon atoms, but a C–C bond of 1.0 v.u. gives the correct average valence for carbon as discussed in the Appendix. Otherwise, bond lengths and angles are calculated in the same way as for the acetate ion. From Figure 1 it can be seen that the structures proposed in Figure 2 are typical of those observed.

Influence of the environment. The symmetric structures shown in Figure 2 are the ones expected when the counter ions have acid strengths less than 0.5 v.u. In these cases the base strength of O accommodates cations of varying strength by forming one, two, or more cation–oxygen bonds. When the counter ions have a larger acid strength some adjustment is needed if the base strength of the O atoms is to match the acid strength. Figure 3 shows extreme examples of the three possible adjustments, *viz*: (*a*) the cation adjusts its bonding to match the base strength of O; (*b*) the acetate ion becomes asymmetric so as to provide a greater base strength for one O at the expense of the base strength of the other O; or (*c*) the methyl H atoms become more acidic so as to increase the O base strength according to equation (5).

In practice some mixture of these three effects is expected, the extent of mixing varying according to the circumstances. For example (*c*) has limited value for trifluoroacetates since the F atoms will always act as bases. This is what makes it difficult for trifluoroacetate to bond to very strong Lewis acids. In silicon tetra-acetate (26),* (*a*) will not be possible because the four acetate ions around Si are chemically equivalent and the



(*i*)

(*ii*)

FIGURE 2 Idealised structures of symmetric acetate (*i*) and trifluoroacetate (*ii*) ions. The numbers in parentheses are the assigned bond valences from which the bond lengths and angles have been calculated

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* The numbers following compound names refer to the listings given in Table 2.

valence of one Si–O bond can only be decreased by increasing the valence of the others. But in most cases the cation is able to form bonds somewhat weaker than its acid strength (See Table 2, columns 2 and 3). For example, ester linkages have an acid strength of 1.0 v.u. but bond valences of *ca.* 0.8 v.u. Hydrogen with an acid strength of 0.80 v.u. normally forms bonds in these compounds with valences between 0.70 and 0.75 v.u. In the hydrogen diacetates and hydrogen bistrifluoroacetates the valence of the O–H bond is even reduced to 0.5 v.u., the presence of the two identical acetates providing an opportunity for a symmetrical hydrogen bond.

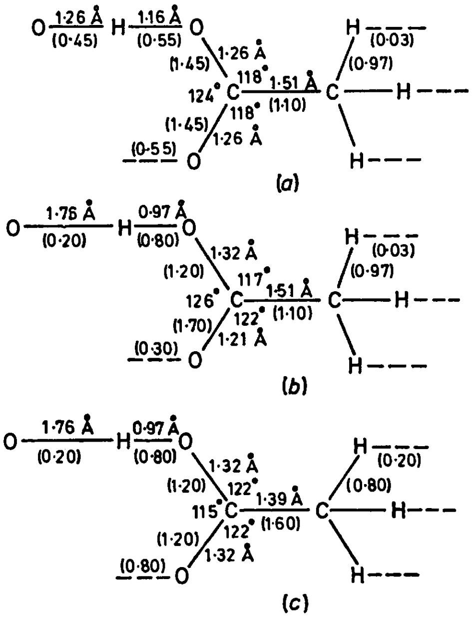

FIGURE 3 Three extreme idealised structures for an acetate ion bonded to a strong Lewis acid (H): (*a*) environment of the Lewis acid adapts to the base strength of O; (*b*) the acetate ion becomes asymmetric; (*c*) the acidity of methyl H increases. The conventions are the same as in Figure 2

The extent to which the methyl acidity is increased (or trifluoromethyl basicity is decreased) and the extent to which the anions become asymmetric is displayed graphically in Figure 4. Anions bonded to weak acids (indicated by ×) show little asymmetry and show methyl-acid or trifluoromethyl-base strengths of *ca.* 0.10 v.u. Anions bonded to strong acids (indicated by numbers) cover a wide range of both parameters. Acetic acid (17) shows little increase in methyl acidity but considerable asymmetry. The presence of additional strong acids competing for O base strength or weak bases competing for the methyl-acid strength will tend to enhance the methyl acidity as observed in the $CH_3C(OH)_2^+$ ion [(22) and (23)] and in $[Ni(HOOCCH_3)_6][BF_4]_2$ (21) respectively. In the ester levoglucosantriacetate (25) the relatively large number of weakly basic organic O atoms (0.53) competing for each methyl H ensures high methyl acidity while the much smaller number (0.28) in *O*-methyl asparvenoneacetate (24) results in the methyl groups showing very little acidity.

Conclusions. It has been shown that chemical structure can provide the basis for a measurement of acid and base strength and that these in turn can be used to predict and understand the changes in the internal structure of ions such as acetate. The proposed measures of acid and base strength can also be related to more traditional measures. The base strength, s_b, is related * to the acid pK value by equation (6). This relation with

$$s_b = 0.42 + 0.032\ \mathrm{p}K \qquad (6)$$

$s_b = 0.55$ for the acetate O atoms and $s_b = 0.45$ for the trifluoroacetate O atoms predicts pK values respectively of 4.1 and 0.9, compared to the observed values of 4.8 and 0.3.

Gutmann's Acceptor Number [1] refers to the acid strength of the proton co-ordinated to the O atoms of the acetate or trifluoroacetate ion. As indicated above, this is sensitive to the environment and the internal structure of the ion and consequently is difficult to predict *a priori*; but if one assumes that the acid strengths (s_a) are related to Acceptor Numbers (AN) by equation (7), the Acceptor

$$s_a = 0.003\ \mathrm{AN} \qquad (7)$$

Numbers of 52.9 for acetic acid and 105.3 for trifluoroacetic acid would correspond to H acid strengths of 0.16 v.u. and 0.32 v.u. and hence O–H strengths of 0.84 and 0.68 v.u. respectively, values that are not unreasonable.

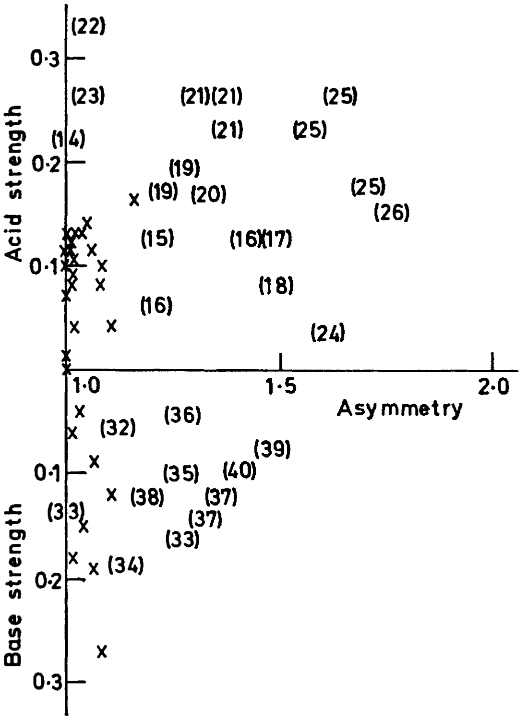

FIGURE 4 Methyl acid strength and trifluoromethyl base strength plotted against anion asymmetry. The numbers refer to compounds in Table 2. (×), Compounds with cation acid strengths less than 0.5 v.u.

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* See ref. 6, p. 30, where the base strength of an oxy-anion is expressed as the number of hydrogen bonds, N_a, of strength 0.2 v.u. that each O atom can accept. Hence $s_b = 0.2\ N_a$.

APPENDIX

All 19 known crystal structures containing trifluoroacetate ions and 25 of the more accurately determined acetate-ion structures were examined. Of the compounds containing trifluoroacetate ions, six were not used because they either lacked published co-ordinates or were not accurately enough determined. In three other cases unpublished co-ordinates were supplied by the authors. All interatomic distances and angles were recalculated from the original co-ordinates except for H atoms determined by *X*-ray where the O–H and C–H bonds were set at the length expected from neutron diffraction (0.97 Å and 1.07 Å respectively). Valences (*s*) for bonds not involving H were calculated from the bond lengths (*r*) using equation (2) where the values for r_0 and n are given in the Table or are taken from ref. 5. Bonds involving H were treated differently. Firstly, valences were assigned to the weak H · · · O and H · · · F bonds using Figure 3 of ref. 4;[6] H · · · F bonds were assumed to have the same valence as H · · · O bonds that were 0.1 Å longer. The strong C–H and O–H bonds were then determined by differences to ensure that the valences at H added up to 1.00. This procedure was necessary since the valences of these poorly determined bonds are extremely sensitive to even small uncertainties in the distance.* The C–F bonds are susceptible to large errors and were not used in the analysis although they are summarised together with other valences and angles in Table 2.

Parameters for calculating bond valences

Bond	r_0/Å	n
Sn^{IV}–O	1.94	5.5 *
C–O	1.37	4.4 *
C–C	1.543	4.45
C–F	1.288	4.4
Sn^{IV}–C	2.17	3.5
Tl^{III}–O	2.00	6.0
S^{VI}–F	1.550	3.8
B–F	1.288	3.9

* Values better than those given in ref. 5.

The contribution of the methyl H acidity to the properties of the ion can be measured by three independent numbers that should be equal: the strength of the bonds formed between the methyl group and neighbouring bases in other molecules [Table 2(*a*), column 5], the amount by which the valence of the external bonds formed by the two O atoms [Table 2(*a*), column 4] exceeds 1.0, and the amount by which the valence of the C–C bond [Table 2(*a*), column 8] exceeds 1.0. The average of these three values [listed in Table 2(*a*), column 12] is plotted in Figure 4. For trifluoroacetate ions the C–C bond does not vary with the base strength of the O and F ions since there is no valence that can be assigned to this bond that will simultaneously give the correct valence sums at both C atoms. The reason for this is that in this model both C atoms are formally regarded as Lewis acids and the C–C bond is therefore not an acid–base bond. The observed valence of close to 1.0 for this bond in all trifluoroacetate ions can be rationalized in one of two ways: either the observed valence can be recognized as the one that ensures that the *average* of the valence sums at C is 4.00 but with the carboxyl C exceeding this value and the trifluoromethyl C being below; or one can visualize the electron pair in the bond acting as a pseudo base of valence 2, forming a stronger bond to the CF_3 group and a weaker bond to the CO_2^- group. For simplicity in computation the former viewpoint has been adopted here except where otherwise noted. In computing the average CF_3 base strength [Table 2(*b*), column 13] for use in Figure 4, the sum of the valences of external bonds formed by the F atoms [Table 2(*b*), column 5] was averaged with the amount by which the valence of the external bonds formed by the O atoms [Table 2(*b*), column 4] fell short of 1.0.

The asymmetry [Table 2(*a*), column 13; Table 2(*b*), column 14] used in plotting Figure 4 is the ratio of the valences of the two C–O bonds. To obtain the average valence of the two defining bonds for plotting Figure 1 the following procedure was adopted. For acetate ions the valences of the two bonds were averaged and decreased by one third of the amount by which the valence sum at the central C atoms exceeds 4.0. This eliminates systematic errors in the calculation of the valence and ensures that the points are normalized on the vertical scale. A normalising correction of more than 0.1 v.u. was taken to indicate an error in the bond lengths and the points for that anion were not plotted. For the trifluoroacetate ions the valence at C is expected to exceed 4.0 by an average of 0.1 v.u. as discussed above. For these ions the valence of the C–C bond was assumed to be the valence necessary to ensure a sum of 4.0 at the carboxyl C atom. This is equivalent to adopting the second description of the C–C bond discussed above.

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* For the weak hydrogen bonds formed by the methyl and trifluoromethyl groups, however, an error of 0.1 Å in the bond length results in an error of only 0.01 in the bond valence.