230. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part VI.* Sodium Hydrogen Diacetate.*

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Sodium hydrogen diacetate is one of the simplest acid salts of type *A* (see Part V), and it displays the corresponding spectral anomaly in a pronounced form. It crystallises in the cubic system, with 24 $NaH(C_2H_3O_2)_2$ molecules in a unit cell, of edge $15{\cdot}9_2$ Å, belonging to the space group *Ia*3. Its crystal structure has now been determined, and refined by three-dimensional methods. The sodium ions are crystallographically of two kinds, Na(1) and Na(2), and they are present—3·3 Å apart—as linear triads, Na(2) ··· Na(1) ··· Na(2), lying along a three-fold axis. The two acetate residues in the formula are crystallographically equivalent, being related by a two-fold axis, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. This bond is of the symmetrical type, with $O \cdots O = 2{\cdot}44_4 \pm 0{\cdot}010$ Å. These hydrogen-bonded units are linked together by the interposition of sodium ions to give infinite three-dimensional sequences. Therefore any vibration of the proton in one unit might interact with the motions of protons in other units extending over a wide region of the crystal. The significance of the " very short," and quasi-symmetrical, hydrogen bond is discussed.

ACID salts of acetic acid have been known since the time of Thomas Thomson, but sodium hydrogen diacetate (" sodium binacetate "), $NaH(C_2H_3O_2)_2$, was not discovered until 1877, when it was independently described by Villiers [1] and Lescoeur.[2] The compound crystallises in the cubic system, and its morphology was examined by Haushofer.[3] In 1922 Wyckoff [4] made it the subject of the earliest explicit determination, by *X*-rays, of a complex space group. The historian may appreciate the contrast between Lescoeur's surprise that a compound of relatively complex composition (" $C^4H^3NaO^4,C^4H^4O^4$ ") should crystallise in the simplest system and Wyckoff's comment that " such a relatively simple (organic) substance as this sodium acid acetate has . . . a very complicated (crystal) structure."

As explained in Part V, the crystalline acid salts examined in this laboratory fall into two classes, *A* and *B*, between which differences of structural type are paralleled by differences of infrared spectra. Sodium hydrogen diacetate shows the anomalous infrared spectrum, characteristic of type *A* salts, to a pronounced degree (see Fig. 1). For this reason, as well as because it is the simplest acid salt of almost the simplest carboxylic acid, its structural analysis was of unusual interest. A preliminary account of this work has appeared.[5]

EXPERIMENTAL

Preparation, Infrared Spectrum, and Crystal Data.—Sodium hydrogen diacetate separates as well-formed, and evidently cubic, crystals when a solution of acetic acid and half an equivalent of sodium hydroxide in water, or aqueous alcohol, is allowed to cool or evaporate. The crystals quickly become opaque owing to a superficial loss of acetic acid; but the bulk of the crystal remains unchanged for days or weeks (depending on the atmospheric conditions), and there is no difficulty in obtaining adequate *X*-ray patterns.

The infrared spectrum of the solid material was recorded both for a Nujol mull and for a KCl disc. There is some difficulty in obtaining a spectrum that is definitive in the high-frequency region; for, if a large, freshly prepared, single crystal is used for preparing the sample,

* Part V, preceding paper.

[1] Villiers, *Compt. rend.*, 1877, **84**, 774; 1877, **85**, 755.
[2] Lescoeur, *Compt. rend.*, 1877, **84**, 1029; *Ann. Chim. Phys.*, 1893, **28**, 237.
[3] Haushofer, *Z. Krist.*, 1880, **4**, 572.
[4] Wyckoff, *Amer. J. Sci.*, 1922, **4**, 175.
[5] Speakman, *Proc. Chem. Soc.*, 1959, 316.

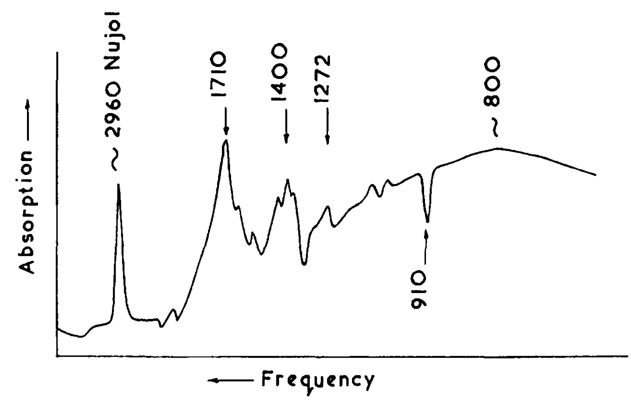
it may contain mother-liquor, absorbed or occluded; whilst, if small and properly dried crystals are used, the superficial decomposition may affect the spectrum. However the main features of the spectrum shown in Fig. 1 (Nujol mull) are reproducible. (Dr. Hadži has provided a spectrum from Ljubljana, and it is essentially identical with that recorded in Glasgow.)

The unit-cell parameter was determined by single-crystal rotation photographs, against calcite as reference substance, and by powder photographs against metallic copper. Systematic absences were determined from moving-film photographs. Copper $K\alpha$-radiation was used throughout.

$NaH(C_2H_3O_2)_2$, $M = 142{\cdot}09$, cubic diakisdodecahedral, class $m3$, $a = 15{\cdot}92 \pm 0{\cdot}01$ Å, $U = 4035$ Å^3, $D_m = 1{\cdot}40_0$ (by flotation in chlorobenzene–chloroform), $Z = 24$, $D_c = 1{\cdot}403$, $F(000) = 1776$, absorption coefficient for X-rays $17{\cdot}6$ cm.$^{-1}$.

Absent reflexions. These are $hk0$ when h or k is odd (and correspondingly for $h0l$ and $0kl$) and hkl when $(h + k + l)$ is odd; they uniquely indicate the space group, $Ia3$ (T_h^7, No. 206), as found by Wyckoff. The implication is that the sodium and acidic hydrogen atoms are in special positions, and the others in 48-fold, general positions.

FIG. 1. *Infrared spectrum of sodium hydrogen diacetate, solid in Nujol mull.*



Determination of the Structure.—The space group $Ia3$ is centro-symmetric, and the phase problem reduces to one of sign-determination. To find the gross structure of this crystal, it suffices to fix the positions of only five atoms, these positions being defined by only thirteen parameters. Nevertheless the problem proved difficult, for the following reasons: (1) the high symmetry causes there to be a large number of atoms in the cell, and results in an absence of reflexions of relatively high intensity; the highest unitary structure amplitude appears to be 0·41 for 7,8,13, a reflexion which had not been recorded until the later stages of the refinement, and only one or two others exceed 0·3. (2) The sodium atoms are not heavy enough to dominate the X-ray scattering; and it is impossible to replace them isomorphously. (3) Until a late stage, only two-dimensional methods of analysis were readily available. Through the courtesy of Professor Ray Pepinsky, a three-dimensional Patterson synthesis was computed on XRAC during 1958. That this synthesis did not lead to a ready elucidation of the structure must be attributed to the high symmetry, which causes superpositions of many vector-peaks in some positions, so that the recognition of individually significant peaks is difficult. [For instance, the most heavily weighted vector-peak is that between Na(1) and Na(2), and no less than 8 of these vectors coincide to yield a Patterson peak at $u = v = w \approx 0{\cdot}120$. *A posteriori* this peak can be recognised, but it makes only an insignificant appearance in the appropriate Patterson section.] The phase problem was in fact finally solved by simple trial, though it became possible to advance from an approximately correct trial-structure only when facilities were to hand for the rapid calculation of three-dimensional electron-density syntheses. These facilities were provided on the Glasgow University DEUCE computer by way of the crystallographic programmes developed by Dr. J. S. Rollett.

Besides 48-fold, general positions—(e) of the *International Tables*—the space group $Ia3$ affords 24-fold positions (d) on two-fold axes, 16-fold positions (c) on three-fold axes, and 8-fold positions (a) and (b) at centres of inversion ($\bar{3}$) on the three-fold axes. The 24 acidic hydrogen atoms can hardly be located elsewhere than on the two-fold axes—unless they be disordered in some way—which implies that they are probably involved in a crystallographically symmetrical hydrogen bond. The 24 sodium atoms (or ions) might also occupy positions (*d*), but there is the alternative possibility that they might be of two crystallographically distinct kinds—8 Na(1) in positions (*a*) or (*b*), and 16 Na(2) in positions (*c*). The former arrangement, thought to be more likely *a priori*, was assumed in many trial structures; the latter proved to be correct.

With positions (*a*) chosen for Na(1), two such ions are about 14 Å apart at the corner (0,0,0) and centre ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) of the unit cell. A three-fold axis along a body-diagonal joins them, with an unoccupied centre of symmetry between them at ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$); and on this axis twice as many Na(2) ions are to be sited. Packing considerations suggested that the Na(2) ions might lie about 3 Å on either side of Na(1), thus constituting a " triad " of sodium ions, Na(2) ··· Na(1) ··· Na(2); and that the acetate group must be placed so that a triangle of oxygen atoms, generated by operation of the three-fold axis on O(1), can cushion the tightly packed cations, and so that its other oxygen atom, O(2), is close enough to a two-fold axis to enter into hydrogen bonding across that axis *via* the acidic hydrogen. On this basis it was possible to construct trial structures, one (at least) of which was sufficiently close to the truth to enable the (three-dimensional) Fourier-series method to be applied successfully. This starting structure had the sodium atoms and one oxygen atom nearly in their correct positions; refinement proceeded satisfactorily despite errors in the placings of the other atoms.

Refinements.—Intensities were derived visually from multiple-film exposures in the usual way. Altogether some 760 independent reflexions should be accessible to copper radiation. In the earlier stages, refinement was based on some, or all, of 195 reflexions recorded on photographs covering the reciprocal-lattice nets, *hk*0 ··· *hk*5. In the later stages, when the nets *hk*6 ··· *hk*8 and the diagonal net *h*,*k*,(2–*h*–*k*) were also included, 323 reflexions were observed—43% of those accessible. If the region of reciprocal space is curtailed at $2 \sin \theta = 1{\cdot}58$, which corresponds to half the volume theoretically accessible, 65% coverage is attained. Though far from complete, the coverage is fairly satisfactory for a structure composed only of light atoms; it represents a nine-fold excess of observations over all parameters. During the scrutiny of these photographs, many equivalent reflexions were measured several times. This made it

TABLE 1. *Progress of refinement and atomic co-ordinates.*

Phase	1	2	3	4	5
Procedure	Electron-density syntheses	6 Cycles of L-S (O & C only)	3 Cycles of L-S [With Na(2)]	4 Cycles of L-S	2 Cycles of L-S
No. of terms	130	195	195	319	323 +29 unobsd.
Co-ordinates					
Na(2)	0·1196	(0·1195)	0·1196	0·1195	0·11956 *
O(1) *x*	0·0325	0·0326	0·0320	0·0324	0·03213
y	0·3788	0·3903	0·3904	0·3913	0·39144
z	0·0963	0·0999	0·1006	0·0999	0·09994
O(2) *x*	0·0769	0·0736	0·0742	0·0749	0·07525
y	0·2629	0·2651	0·2659	0·2652	0·26521
z	0·1362	0·1386	0·1389	0·1396	0·13970
C(1) *x*	0·091	0·0910	0·0903	0·0899	0·08964
y	0·336	0·3365	0·3371	0·3394	0·33971
z	0·115	0·1117	0·1115	0·1103	0·11036
C(2) *x*	0·174	0·1772	0·1778	0·1785	0·17885
y	0·363	0·3593	0·3583	0·3587	0·35908
z	0·090	0·0906	0·0897	0·0889	0·08904
O(2) ··· O(2′) (Å)	2·48	2·39 ± 0·03	2·42 ± 0·02	2·433 ± 0·013	2·444 ± 0·010
R (%) (all currently obsd. terms)	20·0	15·9	12·2	9·7	9·2

* The co-ordinates in this column represent the final values from the analysis. The origin chosen is at the centre of inversion occupied by Na(1).

possible to assess the accuracy of the mean structure amplitudes on the basis of internal consistency. The estimate was $\sigma(|F_o|) \approx 0{\cdot}09_4|F_o|$. Absorption corrections were not applied. This omission is not serious with the crystals used (having cross-section areas $\sim 0{\cdot}5 \times 0{\cdot}5$ mm.^{2}), but it will tend slightly to depress the values derived for the temperature factors.

The progress of refinement is summarised in Table 1, which should be self-explanatory with the aid of the following comments.

(1) In calculations of structure factors, F_c, standard atomic-scattering functions [6] were used for carbon and hydrogen. For Na^+, Freeman's [7] function was used; for oxygen, since these atoms were regarded as partially ionic, a scattering curve appropriate to $O^{\frac{1}{2}-}$ was derived by taking, at each value of sin θ, the means of his values for O and O^-. In the first phase, the isotropic Debye temperature factor, B, was taken as 2·6 Å^2 initially, and subsequently as 2·0. In later phases the least-squares (L-S) programme led to anisotropic temperature factors which were treated as variable parameters. In phase 1, $|F_o|$ values were placed on an absolute scale by correlation of $\sum|F_o|$ and $\sum|F_c|$. Subsequently the scaling factor was treated as a variable parameter in the L-S refinement.

(2) To ensure correct symmetry in electron-density syntheses, such terms as $F(hkl)$ had necessarily to be included in the triple Fourier series in all three forms, *hkl*, *klh*, and *lhk*. The structure factors for three such reflexions are equivalent however, and in the L-S refinement only one of them was needed.

(3) The L-S programme is not designed directly to handle atoms in special positions. In phase 2 therefore, refinement was restricted to oxygen and carbon atoms; the position of Na(1) is precisely fixed by the space group, whilst the single parameter needed to locate Na(2) had been well determined by the early electron-density calculations. In phase 3, however, Na(2) was introduced into the refinement. For an atom in the special position x, x, x, three identical normal equations will be developed for the co-ordinate shifts, Δx, Δy, and Δz; and, by using the Gauss–Seidel iteration for their solution, the L-S programme arrives at the erroneous result that $\Delta y = \Delta z = 0$, whilst Δx is three times its true value. The refinement could then be simply rectified by putting the new co-ordinates all equal to the mean of those produced by the programme: *i.e.*, $(x + \Delta x), x, x$ is rectified to $(x + \frac{1}{3}\Delta x), (x + \frac{1}{3}\Delta x), (x + \frac{1}{3}\Delta x)$. An analogous procedure was followed for the thermal parameters of Na(2). No direct refinement of the thermal parameter of Na(1) was attempted; but in the last phase it was adjusted to be smaller than those for Na(2) in a ratio suggested by its higher electron-density peak—23·9 electrons Å^{-3} against 21·7.

(4) The L-S weighting system was $\sqrt{w} = (|F_o|/F^*)$ when $|F_o| < F^*$, and $\sqrt{w} = (F^*/|F_o|)$ when $|F_o| > F^*$, where F^* was put equal to 57 (the mean value of the observed structure amplitudes). Half-shifts were generally applied.

(5) Hydrogen atoms were disregarded until phase 4, when an $(F_o - F_c)$ synthesis revealed peaks (see Fig. 5) at positions appropriate to methyl-hydrogen atoms. The appearance of these peaks suggested the presence of large thermal vibrations, as was expected, and these atoms

TABLE 2. *Atomic co-ordinates from Fourier syntheses.*

(Methyl-hydrogen atoms from difference synthesis; other atoms from final electron-density synthesis.)

	x	y	z		x	y	z
H(1)	0·204	0·402	0·136	Na(2)	0·1193	0·1193	0·1193
H(2)	0·181	0·388	0·027	O(1)	0·0321	0·3906	0·0994
H(3)	0·215	0·301	0·089	O(2)	0·0766	0·2630	0·1399
				C(1)	0·0895	0·3405	0·1103
				C(2)	0·1775	0·3601	0·0899

were included in subsequent F_c-calculations, though not in L-S refinement, with an isotropic B-value of 7·0 Å^2. As to the acidic hydrogen atom, a peak of height 1·9 electrons Å^{-3} appeared in the ordinary electron-density section at $z = 33/240$, and at the expected position $x = 0$, $y = \frac{1}{4}$ (see Fig. 2). This height is surprising, and it may have been enhanced by the tendency for residual errors to produce small false peaks at special positions. However, the peak is undoubtedly due principally to the hydrogen atom, and for it a lower B-value of 4·0 Å^2 was adopted. This atom was included in subsequent F_c-calculations, and its region became satisfactorily flattened in an $(F_o - F_c)$ synthesis. The co-ordinates for the methyl-hydrogen atoms, listed in Table 2, were chosen to be consistent with Fig. 5 whilst maintaining trigonal symmetry for the methyl group. No great accuracy is claimed for them.

(6) At phase 5 account was taken of the unobserved reflexions. Structure amplitudes were

[6] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[7] Freeman, *Acta Cryst.*, 1959, **12**, 261.

calculated for all such terms out to $2 \sin \theta = 1{\cdot}58$, and in 29 cases $|F_c|$ implied that the reflexion should have been observable. These terms were then included in later L-S refinement, each with a value of $|F_o|$ equal to half the minimum locally observable. When these reflexions are

TABLE 3. *Standard deviations of the final atomic co-ordinates* (Å).

	(*x*)	(*y*)	(*z*)		(*x*)	(*y*)	(*z*)
Na(2)	0·0094	0·0094	0·0094	C(1)	0·0073	0·0082	00081
O(1)	0·0055	0·0058	0·0063	C(2)	0·0086	0·0108	0·0093
O(2)	0·0053	0·0053	0·0063				

TABLE 4. *Thermal parameters* ($b_{ij} \times 10^5$).

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Na(1)	228	228	228	—	—	—
Na(2)	268	268	268	—	—	—
O(1)	306	330	507	245	23	48
O(2)	279	248	675	−48	−184	65
C(1)	226	305	250	−157	−134	65
C(2)	273	632	571	89	445	−105

TABLE 5. *Observed structure amplitudes and calculated structure factors.*

k	*l*	$\lvert F_o \rvert$	F_c
		0*kl*	
0	2	144	+158
	4	291	−508
	6	163	−167
	8	223	+253
	10	115	+121
	12	30	+36
	14	59	−59
	18	24	+28
2	2	39	+28
	4	166	+192
	6	20	−7
	8	57	+57
	10	94	+90
	12	53	+57
	14	52	−45
	18	39	+43
4	2	96	−96
	4	199	+206
	6	220	+238
	8	58	+50
	10	47	−43
	12	26	+13
	14	70	+79
	16	29	+33
	18	18	+22
6	2	162	+166
	6	34	−24
	8	28	+20
	10	105	+97
	14	63	+65
	16	46	+48
	18	21	+22
8	2	173	+193
	4	137	−133
	6	43	−34
	8	70	+66
	10	101	+111
	16	20	+22
	18	13	−4
10	2	52	+50
	4	55	+53
	6	74	+84
	8	33	+32
	10	30	+29
	12	21	+19
	14	20	−19
12	2	39	−39
	4	108	+108
	6	109	+108
	10	52	−49
	12	48	+46
	14	20	+18
14	2	27	−17
	4	127	+130
	6	24	+16
	8	26	−22
	12	52	+56
	14	33	+40
16	2	29	+12
	8	45	+41
18	2	30	+43
	10	29	+36
20	2	24	+35
		1*kl*	
1	2	110	−121
	4	70	−72
	6	168	+200
	8	76	+72
	10	52	−51
	12	30	−29
	14	37	+45
2	3	82	−90
	5	15	+18
	7	43	+43
	9	38	+34
	11	30	−29
	13	39	+45
	15	35	−37
	19	30	+36
3	2	100	+104
	4	113	−106
	6	117	+118
	8	115	+113
	12	44	−42
	14	57	+57
4	3	26	+21
	7	59	−54
	9	28	+20
	13	44	+47
5	2	109	+116
	4	57	+60
	6	43	−44
	8	114	−111
	10	35	+39
	12	69	+67
	16	57	−64
6	3	64	−68
	5	108	−108
	9	54	+58
	13	19	−22
	19	12	−23
7	2	172	+186
	4	20	+17
	6	203	−202
	8	65	−64
	10	65	+66
	14	40	−41
8	5	56	−50
	7	21	+11
	9	45	+46
	11	30	+37
	13	66	−71
	2	109	−105
	4	49	+51
	8	42	−50
	10	31	−22
	12	31	+28
10	3	33	+34
	5	34	+30
	9	32	−37
	11	32	+30
13	2	36	+45
	8	29	+29
14	3	44	−49
	5	43	−52
	7	19	+22
15	2	43	+42
		1*kl*	
19	2	25	−39
		2*kl*	
2	2	136	+148
	4	94	+92
	8	24	+21
	10	73	+81
	12	41	+45
	18	29	+24
3	3	130	−138
	5	118	−116
	7	64	+63
	9	78	+75
	11	23	−16
	13	63	−65
4	4	24	+32
	6	21	+21
	10	29	+23
	12	69	+70
	14	69	+72
	16	29	+30
5	3	131	−126
	5	87	−96
	7	101	−96
	9	81	+79
	11	30	−21
	13	59	−59
6	4	91	+99
	6	75	+74
	8	71	+64
	10	44	+42
	12	29	+17
	16	32	+27
	18	23	+24
7	3	59	−64
	5	98	+99
	7	49	−41
	9	38	−36
	11	56	−58
	13	33	+29
	15	32	+34
8	4	48	+47
	6	77	+69
	8	85	+76
	10	29	+28
	18	27	+24
9	5	71	+66
	7	48	+48
	11	36	−35
	13	31	+28
	15	47	+46
10	4	36	+35
	10	36	+36
	12	30	+41
11	3	36	+36
	5	33	+30
	9	29	−22
	11	65	+76
12	6	44	+35
	8	19	+27
	14	24	+29
13	3	100	+99
		2*kl*	
	5	97	−99
	7	38	−47
	11	33	+59
14	4	59	+62
	6	38	+51
		3*kl*	
3	6	107	−105
	8	50	+47
	10	39	+37
	14	77	−80
4	7	51	−51
	9	37	+34
5	4	38	+32
	6	47	+40
	8	30	+21
	10	55	−49
	16	36	+35
6	5	49	−47
	7	105	+109
	9	85	+87
	11	68	−63
	13	74	−78
	4	32	+23
	6	61	+55
	10	52	−52
	14	59	+55
8	5	77	−71
	7	19	−21
	9	49	+42
	13	70	−66
9	4	36	−29
10	7	36	−34
	9	38	−30
	11	43	+42
11	4	55	−58
	8	40	+28
	10	45	+45
	12	39	−38
14	5	60	−55
	7	51	+50
	9	52	+41
		4*kl*	
4	4	59	+51
	6	135	+133
	8	127	+120
	10	30	+24
	12	41	−29
	14	22	−30
	16	22	+29
5	5	48	−47
	9	32	−29
	11	30	−27
6	6	84	+76
	10	32	−26
	12	64	+62
7	5	21	−26
	7	42	+39
8	12	102	+95
	14	45	+41

TABLE 5. (*Continued.*)

k	e	$\|F_o\|$	F_c
		4*kl*	
9	5	32	−30
	7	26	+18
	9	40	+34
10	8	72	+64
	10	67	+59
11	5	69	+67
	7	37	−33
	9	38	−35
	11	33	+24
12	8	70	+66
	10	66	+63
	12	32	−31
13	5	40	−29
	7	44	−40
14	6	35	+28
	8	31	+26
	10	29	+33
16	6	27	+33
		5*kl*	
5	6	52	+50
	8	73	+67

k	e	$\|F_o\|$	F_c
		5*kl*	
	10	34	−31
	12	43	−45
	16	38	+46
6	9	85	−79
	13	42	+46
	15	32	+30
7	6	146	+140
	8	60	+48
	10	44	−40
	14	39	+43
8	7	21	+21
	11	46	−50
9	8	68	+61
10	9	49	+57
	11	40	−33
11	12	21	−27
12	7	45	−53
	9	39	+30
	11	34	+29
		6*kl*	
6	6	133	+122
	8	28	+26

k	e	$\|F_o\|$	F_c
		6*kl*	
	14	49	+42
7	9	32	−32
	11	36	+38
8	8	21	+22
	10	48	+61
	12	43	+38
9	7	84	−81
10	8	34	+36
	10	60	+64
	12	32	+29
11	11	44	−32
12	10	38	+29
13	7	52	+49
	11	47	−54
14	8	56	+57
	10	21	−7
16	8	23	+27
	10	21	+22
		7*kl*	
7	8	34	−30
	10	19	+21

k	e	$\|F_o\|$	F_c
		7*kl*	
	12	19	+18
	14	19	−21
	16	19	−14
8	9	75	−75
	13	82	+84
9	8	26	+34
11	10	52	−52
12	11	19	−18
	13	34	−43
14	9	26	−30
15	10	29	+24
		8*kl*	
8	8	56	+55
	10	52	+49
	12	19	−23
9	9	48	−53
	13	38	+36
11	11	21	−32
13	11	21	−25
16	8	42	+43

Unobserved terms used in phase 5.

h	k	l	$\|F_o\|$	F_c		k	l	$\|F_o\|$	F_c	h	k	l	$\|F_o\|$	F_c	h	k		$\|F_o\|$	F_c
0	8	14	<19	+17	1	11	8	<20	+22	3	4	13	<20	+24	5	9	10	<20	+19
0	16	4	<19	+19	1	11	10	<20	−16	3	4	15	<19	−31	5	9	12	<19	−32
0	18	8	<14	+37	1	12	9	<20	−29	3	7	12	<20	+18	5	13	8	<19	−29
0	20	4	<12	+29	1	15	6	<19	−16	3	9	10	<20	+20	6	9	11	<20	+33
1	4	11	<18	−20	2	5	15	<19	−30	3	13	6	<20	+17	6	12	8	<19	+18
1	6	11	<19	−15	2	13	9	<19	+25	3	15	4	<19	+38	7	10	9	<20	+18
1	11	4	<18	+17	2	16	2	<19	+19	4	9	13	<19	−16	9	9	10	<19	−34
1	11	6	<18	+16															

taken into account, the final R-value rises from 9·2 to 10·9%. Since only the more unfavourable of the unobserved terms have thus been included, the value of R is a conservative one. Either of these values approximates to the estimated standard deviation of $|F_o|$, which suggests that the analysis has been refined as far as the accuracy of the observational data warrants.

The final co-ordinates are those listed in the right-hand column of Table 1. The atoms—particularly the acetate group—corresponding to these co-ordinates are taken as the "representative molecule," which is the one whose atoms are denoted by unprimed numerals in Fig. 4. Relevant standard deviations, worked out from the L–S residuals in the usual way, are listed in Table 3. Thermal parameters are in Table 4; they are values of b_{ij} in the equation,

$$\exp\,(-B\sin^2\theta/\lambda^2) = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{31}lh)}$$

The final values of $|F_o|$ and F_c are shown in Table 5. For the intense, low-order reflexion 400, $|F_c|$ always greatly exceeded $|F_o|$; as the difference could reasonably be attributed to extinction, the latter was given a value substantially equal to the former in all L–S cycles after phase 3. This higher value was used in calculating R.

DESCRIPTION OF THE STRUCTURE

The operations of the space group produce from the representative molecule an intricate, but elegant, structure, suggested by Fig. 2 which shows part of the atomic arrangement near one corner of the unit cell. The Figure is a rough perspective of the structure, viewed nearly in the line of the cube-diagonal. Along this diagonal, which embodies a three-fold axis, is a triad of sodium ions, Na(2) · · · Na(1) · · · Na(2), with Na(1) at the corner of the cube, which is a centre of inversion and has been chosen as origin. Parallel to the cube-edges, and a quarter of the way along each face, are three two-fold axes, as shown. Two equivalent acetate groups lie on either side of each such axis; joined by the hydrogen bond (shown as a broken line) involving the acidic hydrogen atom, they constitute a complex anion of the form XHX^-, which has axial symmetry (2). Three such complexes are grouped round each end of the sodium triad, only the nearer three being shown in Fig. 2. Altogether twelve acetate groups make ionic contact with a given sodium triad. Of each acetate group, one oxygen atom, O(1), makes contact with a sodium ion of either type; the other, O(2), makes contact with Na(2) of a different triad and also takes part in a hydrogen bond. In accordance with the symmetry of its point-position, Na(1) has as nearest neighbours six equidistant O(1)-atoms, arranged at the corners of a regular trigonal antiprism. (Only the nearer half of this environment appears in Fig. 2.) Na(2) also makes contact with six oxygen atoms—three O(1), three O(2); these atoms are at the corners of a less regular antiprism, though one still necessarily of trigonal symmetry. The three types of Na ••• O distances are listed in Table 6, which also gives the dimensions of the acetate group.

FIG. 2. *Partial view of the structure near to one corner of the unit cell. (The largest circles correspond to sodium atoms, the smallest to carbons. The " representative " acetate group is that drawn with heavy lines and with oxygen atoms bearing unprimed numerals. Hydrogen bonds are marked by broken lines. A three-fold axis and three two-fold axes are shown.)*

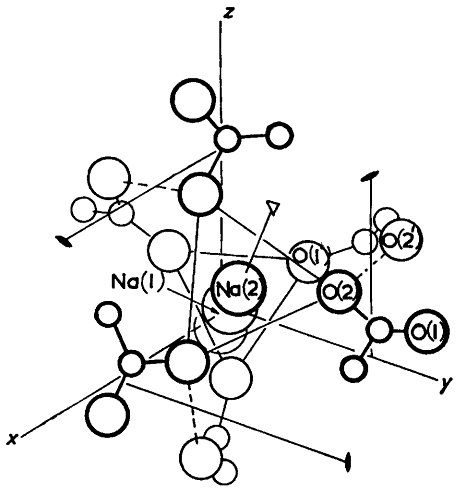


FIG. 3. *Electron-density sections near the centres of the sodium, oxygen, and carbon atoms. (For an interpretation see* Fig. 4. *The first contour-line is at* 1 *electron per cubic* Å, *with subsequent lines at unit intervals, but only alternate lines are shown for sodium.)*

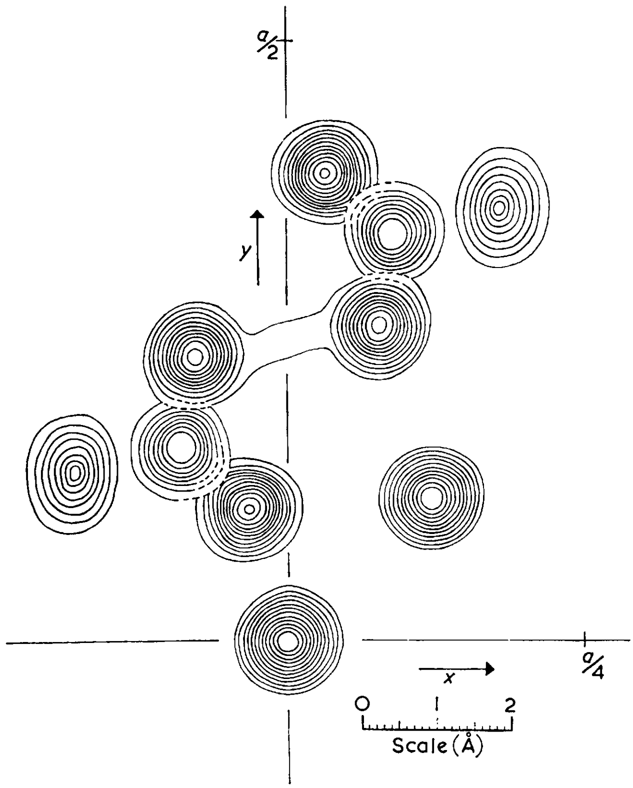


TABLE 6. *Interatomic distances* (Å) *and bond-angles, with their estimated standard deviations.*

Na(1) ••• Na(2)	3·297 ± 0·016	O(2) ••• O(2′)	2·444 ± 0·010	O(1)–C(1)–O(2)	121·65 ± 0·71°
Na(1) ••• O(1)	2·404 ± 0·011	C(1)–O(1)	1·243 ± 0·010	O(1)–C(1)–C(2)	122·27 ± 0·70°
Na(2) ••• O(1)	2·441 ± 0·011	C(1)–O(2)	1·295 ± 0·010	O(2)–C(1)–C(2)	116·08 ± 0·70°
Na(2) ••• O(2)	2·445 ± 0·011	C(1)–C(2)	1·492 ± 0·012	C(1)–O(2) ••• O(2′)	110·79 ± 0·48°

The only non-bonded contacts requiring special mention are those between methyl groups, which cluster in the general region of the centre of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, and at a distance of about 3·3 Å from it. Two pairs of methyl groups have C ••• C separations much less than the conventional van der Waals contact of 4·0 Å; identified by dotted lines in Fig. 4, the distances are 3·629 and 3·834 Å. The positions of the methyl-hydrogen

FIG. 4. *Projection of part of the structure, showing the "representative molecule" (drawn with heavier lines, atoms at* x, y, *and* z *with unprimed numerals), and the following symmetry-related acetate groups*: *I* ($\bar{x}$, $\frac{1}{2} - y$, z); *II* (z, x, y); *III* (y, z, x); *IV* ($\frac{1}{2} - y$, z, $\bar{x}$); *V* ($\frac{1}{2} - z$, $\frac{1}{2} - x$, $\frac{1}{2} - y$); *VI* ($\frac{1}{2} - x$, y, $\bar{z}$); *VII* (z, $\bar{x}$, $\frac{1}{2} - y$).

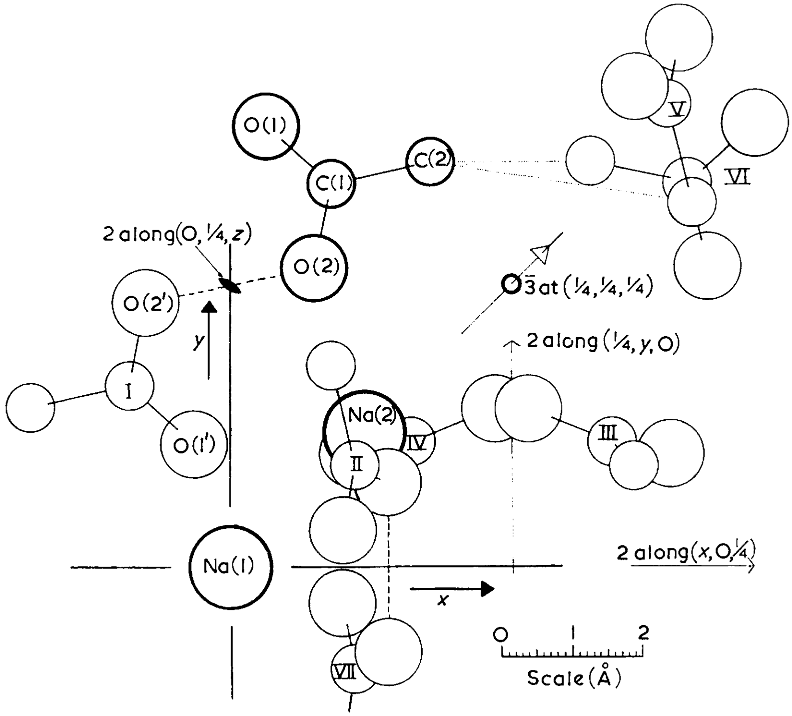
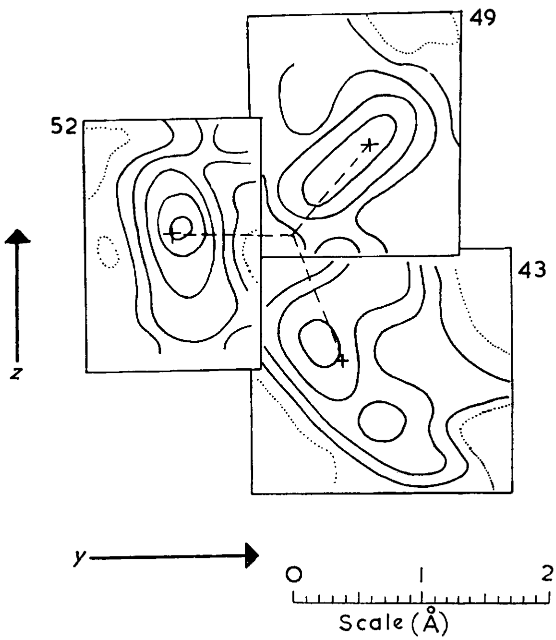


FIG. 5. *Electron-density difference map compiled from sections at* x = 49/240, 43/240, *and* 52/240, *covering the region of the methyl-hydrogen atoms.* (C–H *bonds are indicated by broken lines. Contour-line interval*: 0·1 *electron per cubic* Å, *with the zero line dotted.*)



atoms show that their conformation about the C–C axis is such as to pack a hydrogen atom of one group into the space between two hydrogens of the other. Some such interdigitation is probably necessary whenever methyl groups make unusually close contact. Where a separation of 4·0 Å has to be maintained, free rotation of the groups may be effective. The methyl-hydrogen atoms make a relatively large contribution to the 112-reflexion, and hence must lie nearly in the corresponding planes; this may have some connexion with the fact that, besides faces of the cubic form {100}, crystals sometimes occur with the tristetrahedral {112} faces.

The signs of F_c given in Table 5 were used with $|F_o|$ to compute a final electron-density synthesis, part of which is represented in Fig. 3 by sections near the centres of certain atoms. This Figure takes in the representative molecule, together with a second acetate group generated by operation of the two-fold axis along $0,\frac{1}{4},z$. The two acetate groups comprise an entire anionic complex. This electron-density map is interpreted and extended in Fig. 4. Atomic co-ordinates derived from the synthesis will be less accurate than those in the last column of Table 1, since they involve termination-of-series errors, but they are listed in Table 2. Fig. 5, composed of three sections from a three-dimensional "difference" synthesis, reveals the methyl-hydrogen atoms of the representative molecule, seen in the direction of the x-axis, and hence in a line of sight somewhat inclined to the C–C bond. Since only the sodium ions and one oxygen atom were correctly placed in the initial trial structure, and since all the other atoms of the acetate group were located by Fourier-series methods, without chemical assumptions beyond the molecular formula, the structure analysis was absolute so far as this group is concerned. It may perhaps be seen as a formal, physical confirmation of the structure of acetic acid, first explicitly drawn by Loschmidt in 1861.[8]

Discussion

This analysis has been taken to a higher level of accuracy than had been possible with any of the acid salts of type *A* studied hitherto. Certain structural features, which may be common to all these compounds, are now more firmly defined.

There are well-marked differences between the dimensions of ionised and un-ionised carboxyl groups:[9] in the former, the two C–O bond-lengths and the two C–C–O angles are substantially equal at about 1·25 Å and 118° respectively; in the latter they differ, the lengths being about 1·30 (C–OH) and 1·20 Å, and the angles about 110° (C–C–OH) and 125°. In type *A* acid salts, the carboxylic groups are equivalent and they must be of an intermediate character, which should be reflected in their dimensions. Table 6 shows that this is so. The carbon and oxygen atoms of the acetate group are coplanar: C(1) is only 0·005 Å from the plane defined by the co-ordinates of its other three atoms, *viz.*:

$$0{\cdot}62418x + 1{\cdot}47818y + 4{\cdot}01570z = 1$$

A specific study of the thermal motions in sodium hydrogen diacetate has not yet been attempted,* though a superficial inspection of the parameters in Table 4, as well as of the elongations of certain electron-density peaks in Fig. 3, shows that some of the atoms are undergoing highly anisotropic vibrations, and that their directions of greatest amplitude are those to be expected. Any movement of O(2), for instance, along x will affect the length of the hydrogen bond, and any movement along y will affect the electrovalent bonding to Na(2); hence freedom of movement should be greatest in the z-direction, and this accords with the fact that b_{33} is much larger than either b_{11} or b_{22}. Again, C(2) has higher thermal parameters than C(1), and its greatest amplitude of vibration is in a direction corresponding to libration of the anionic complex about its centre of mass.

* It is hoped that such a study will be undertaken in due course at Leeds.

[8] Loschmidt, "Konstitutions-Formeln der organischen Chemie in graphischer Darstellung," 1861 (Reprinted in Ostwald's Klassiker, No. 190).

[9] Hahn, *Z. Krist.*, 1957, **109**, 438.

The C(1)–C(2) distance in Table 6 should be increased to offset the apparent shortening effects of this torsional oscillation.[10] The magnitude of the correction has not been calculated, but it may be roughly assessed at about 0·01 Å, so as to increase the bond-length to 1·50 Å. This value differs, though not significantly, from the 1·54 ± 0·04 Å found in a careful study of solid acetic acid; [11] it is in good agreement with values found for the corresponding bonds in a series of acetyl compounds by micro-wave spectroscopy.[12]

The apparent symmetry of the hydrogen bond occurring in acid salts of type *A* was briefly discussed in Parts I, III, and V.[13] A fuller consideration may now be attempted. When a hydrogen bond is long (O ··· O > 2·7 Å), the proton is much nearer to one oxygen atom than to the other: O–H is less than H ··· O, and indeed it approximates to the normal covalent distance of about 1·0 Å. As, in a series of bonds, O ··· O diminishes overall, O–H will tend to increase and H ··· O to decrease, until, if the shortening is sufficient, they become equal.[14] What the critical O ··· O distance might be, and whether it is attained in any actual bond, is still uncertain. Coulson [15] has tentatively suggested that the upper limit for true symmetry might be about 2·45 Å. A promising field in which to search for examples is surely amongst these acid salts.

A truly symmetrical hydrogen bond would have very different properties from the normal bond, which owes its bonding energy mainly to simple coulombic forces. A major contribution would need to be added on account of delocalisation (or resonance) energy, since the canonical forms, O:H–O and O–H:O would now be equivalent, or as nearly so as the environment of the oxygen atoms allows. In most hydrogen bonds the environment is not itself symmetrical; but in type *A* acid salts (and in a few other cases such as potassium hydrogen maleate [16]—the acid salt of a *dibasic* acid) the setting is wholly symmetrical by crystallographic requirement. This circumstance might favour the establishment of symmetry within the bond itself.

In nearly all type *A* acid salts the absent *X*-ray reflexions do not indicate a space group unambiguously: for example, the space group of potassium hydrogen bisphenylacetate is either *I*2/*a* or the non-centrosymmetrical *Ia*. The former was chosen on indirect evidence, and the choice was assumed to have been vindicated by the success of the analysis. But there is the possible objection that the latter is the true space group, with the atomic positions of the heavier atoms merely approximating closely to the requirements of *I*2/*a*, and that of the hydrogen atom perhaps not at all, so that the crystallographic evidence for symmetry in the hydrogen bond would fail. In this context formal significance attaches to cases in which the space group is uniquely determined by the absences: sodium hydrogen diacetate is such a case, as also is potassium hydrogen di-*p*-anisate.[17]

The crystallographic symmetry element affecting the hydrogen bond in all the acid salts of type *A* studied hitherto is a centre of inversion which, taken at its face value, requires the proton to be exactly at the mid-point between the oxygen atoms. In the diacetate the element is a diad axis, wherefore the symmetry requirement could be met without the proton's being necessarily at the mid-point. It must lie on the axis, but it might be at a different *z*-level from that of the atoms O(2) and O(2′) in Fig. 4. The evidence on this point is not definitive: a three-dimensional line-synthesis along the two-fold axis shows an appropriate electron-density maximum at $z = 0{\cdot}140$, which does not differ appreciably from the co-ordinate of O(2). But this is not a sensitive method for locating a hydrogen atom linked to electronegative neighbours. The angle C(1)–O(2) ··· O(2′) is very close to tetrahedral; this angular relationship, favourable for

[10] Cruickshank, *Acta Cryst.*, 1956, **9**, 757.
[11] Jones and Templeton, *Acta Cryst.*, 1958, **11**, 484.
[12] Krisher and Wilson, *J. Chem. Phys.*, 1959, **31**, 882; see also Tabor, *ibid.*, 1957, **27**, 974.
[13] *J.*, 1949, **3357**; 1954, 180; preceding paper.
[14] Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.
[15] Coulson, *Research*, 1957, **10**, 149; see also Hadži, "Hydrogen Bonding," Pergamon Press, London, 1959, p. **339**.
[16] Darlow; see Hadži, ref. 15, p. 37.
[17] Skinner, Thesis, Glasgow, 1950.

the formation of a strong hydrogen bond,[18] would not be utilised if the proton were far displaced from the O(2) • • • O(2′) line.

Neutron diffraction provides a more powerful method for locating hydrogen atoms, and reference should be made to the work of Peterson and Levy [19] on potassium hydrogen maleate and particularly to that of Bacon and Curry [20] on potassium hydrogen bisphenylacetate. In the latter the mean position is at the centre of the hydrogen bond; and, in the *b*-axial projection studied, the peak does not show signs of elongation in the O • • • O direction, as it would if the proton were executing anisotropic vibration along the bond, or if it were randomly disordered between two potential wells an appreciable distance on either side of the mid-point. (However, the proton, in a short and symmetrical hydrogen bond, might well have its greatest amplitude of vibration in a lateral direction. The vibrational ellipsoid would then be flattened along the bond-axis.) The work on the bisphenylacetate has been repeated at liquid-nitrogen temperature; [21] generally all the protonic peaks are sharpened, but that for the acidic proton still shows circular contours. The neutron-diffraction analysis, whilst not excluding the possibility of a subtly disordered situation, is most simply explained in terms of a genuinely central proton.

During refinement the O • • • O distance over the hydrogen bond in the diacetate has increased from the very low value suggested in the preliminary note (see Table 1). However, the probable limits of error have contracted, and the final results make it unlikely that the bond is longer than 2·46 Å. Certainly it is in the small group of " very short " hydrogen bonds that have been accurately measured. It appears to be longer than the bond, briefly reported to have O • • • O = 2·40 Å, in acetamide hemihydrochloride; [22] and it is longer than the bond in the hydrogen maleate anion (2·42—2·43 Å).[16] This latter is symmetrical by virtue of a crystallographic mirror-plane, so that again the proton does not necessarily lie exactly on the line between the two oxygen atoms. That this *intramolecular* hydrogen bond closes a quasi-conjugated ring of six carbon or oxygen atoms may result in its experiencing a compressional stress; were the six atoms coplanar, the natural distance separating the oxygens would be only about 1·5 Å.

Those features of the infrared spectrum associated with the hydroxyl group, as it occurs in the normal hydrogen bond, would be greatly changed if the bond were to become symmetrical. Any vibration of the proton along the O • • • O direction would cause a large oscillation of electrostatic charge in the environment ($\bar{\mathrm{O}}$:H–O $\rightleftharpoons$ O–H:$\bar{\mathrm{O}}$), and this would intensify the absorption; whilst the stretching frequency—which diminishes with strength of bonding [14]—would be very low. When a number of such hydrogen-bonded units are linked together, the charge-swing in any one will affect those in neighbouring units, and they will probably enhance one another.[22] An example would be pairs of carboxylate groups (Y) joined by hydrogen bonds to give $\bar{\mathrm{Y}}$:H–Y units, and these linked into infinite sequences *via* metallic ions:

$$\cdots\bar{\mathrm{Y}}{:}\mathrm{H{-}Y}\,\overset{+}{\mathrm{M}}\,\bar{\mathrm{Y}}{:}\mathrm{H}{-}\overset{+}{\mathrm{Y}}\,\bar{\mathrm{M}}\,\mathrm{Y}{:}\mathrm{H{-}Y}\cdot\cdot \rightleftharpoons \cdot\cdot\bar{\mathrm{Y}}{-}\overset{+}{\mathrm{H}}{:}\mathrm{Y}\,\mathrm{M}\,\bar{\mathrm{Y}}{-}\overset{+}{\mathrm{H}}{:}\mathrm{Y}\,\mathrm{M}\,\bar{\mathrm{Y}}{-}\mathrm{H}{:}\mathrm{Y}\cdots$$

This is the kind of system which obtains in the type *A* acid salts. (In the hydrogen maleate ion, by contrast, the system is intramolecularly short-circuited; and the infrared spectrum is less remarkable than those typical of class *A* salts.[23]) In most cases the $\overset{\frac{1}{2}-}{\mathrm{Y}}{-}\mathrm{H}{-}\overset{\frac{1}{2}-}{\mathrm{Y}}$ units are linked so as to produce an infinite two-dimensional net; the bisphenylacetate, for example, has sheets of acidic hydrogen atoms and potassium ions sandwiched

[18] Donohue, *J. Phys. Chem.*, 1952, **56**, 502.
[19] Peterson and Levy, *J. Chem. Phys.*, 1958, **29**, 948.
[20] Bacon and Curry, *Acta Cryst.*, 1957, **10**, 524.
[21] Bacon and Curry, *Acta Cryst.*, 1960, **13**, 717.
[22] Albert and Badger, *J. Chem. Phys.*, 1958, **29**, 1193.
[23] Cardwell, Dunitz, and Orgel, *J.*, 1953, 3740.

between layers of carboxyl groups. In sodium hydrogen diacetate the cubic symmetry promotes the array of interlinked units to a three-dimensional lattice. Moreover, the chemical simplicity of the acid causes the crystal to contain a high density of such units: there are about 6 hydrogen bonds per $m\mu^3$, compared with 2·6 in the bisphenylacetate. These facts must surely constitute a basis for an explanation of the remarkable spectrum shown in Fig. 1.

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