Crystal Structures of Some Acid Salts of Monobasic Acids. Part XVII.[1] Structure of Sodium Hydrogen Diacetate, redetermined by Neutron Diffraction

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The crystal structure of the title compound has now been studied by neutron diffraction, based on some 300 independent reflexions, and refined by anisotropic least-squares to *R* 8·3%. The main features determined previously by *X*-ray diffraction of this highly symmetrical (cubic) structure are confirmed; the positions and vibrational motions of the hydrogen atoms have been elucidated.

The short hydrogen bond, lying across a two-fold axis between two crystallographically equivalent acetate groups, has O · · · O 2·475(14) Å, and O · · · H · · · O 176(2)°, implying that the bond is not significantly bent. There is a large amplitude of internal libration of the methyl group, estimated at *ca.* 26° (root-mean-square). This is discussed in relation to the packing of the methyl groups, which is evidently loose, in spite of there being two C · · · C contacts much closer than twice the conventional van der Waals radius of methyl carbon (2·0 Å).

SODIUM HYDROGEN DIACETATE, $NaH(C_2H_3O_2)_2$, crystallises in the cubic system (a = 15·92 Å, space group $Ia3$, Z = 24). The structure, determined by *X*-ray diffraction,[2] possesses symmetry that is impressively high for the salt of an organic acid. It contains anions $H(C_2H_3O_2)_2^-$, the two acetate residues of which are linked by a 'very short' hydrogen bond lying across a two-fold axis (see Figure). From the *X*-ray determination O · · · H · · · O was 2·444(10) Å, though the standard deviation[2] may have been underestimated.

The structure has now been studied by neutron diffraction. Though crystals of a size suitable for neutron diffraction are easily grown, they are of poor quality, and our intensity measurements are not therefore of high accuracy. Nevertheless the positions of the hydrogen atoms, and their vibrational motions, have

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[1] Part XVI, A. L. Macdonald and J. C. Speakman, *J.C.S. Perkin II*, 1972, 1564.

[2] Part VI, J. C. Speakman and H. H. Mills, *J. Chem. Soc.*, 1961, 1164.

been determined with better precision than had been possible by X-ray diffraction. The other features of this remarkable crystal structure have been independently confirmed.

EXPERIMENTAL

This acid salt has been known for a century,[3] and is easily prepared by mixing glacial acetic acid, in a 2 : 1 molar proportion, with sodium hydroxide in a little water, and then allowing the solution to cool or evaporate. However, it is difficult by this method to obtain crystals suitable for neutron-diffraction study. Large crystals are often obtained, but they are soft and seem to contain mother-liquor; they cannot easily be dried because they tend to lose acetic acid, and thus become contaminated with neutral salt. Besides being of poor quality, the crystals give high background intensity with neutron diffraction because 7 of the 16 atoms are hydrogen, which scatters incoherently. For these reasons we were unable to record significant intensities for as many reflexions as was desired.

Data were collected at the DIDO reactor of the Atomic Energy Research Establishment at Harwell, by use of a Grubb–Parsons Mark VI four-circle diffractometer, controlled by a PDP 8 computer *via* the Andromache system. The neutron beam was monochromated to λ 1·181 Å (118·1 pm). Crystals were sealed in thin-walled glass capsules and two sets of data were obtained. Set (I) consisted of over 400 independent reflexions greater than background, most of them weak, from a crystal of dimensions 3 × 4 × 6 mm. Refinement based on this set was abandoned when R did not fall below 21·8%, though the results did not differ significantly from those subsequently derived from set (II). For set (II) we used a larger crystal (4 × 4 × 8 mm) and longer counting times. The ω—2θ scan consisted of 2 × 10 steps on the backgrounds, and 40 steps of 0·04° over the peak; for each step counting lasted until a monitor-count of 60,000 had accumulated. Of the 941 reflexions measured, 511 were unique, and of these 341 were greater than three times their standard deviations based on counting statistics; 70 weak terms, with poor profiles, were subsequently removed. The resulting set was supplemented by 28 reflexions from set (I) which had not been covered in set (II). This reconstituted set of 299 reflexions was used in the final stages of refinement. No absorption corrections were made.

TABLE 1

Fractional co-ordinates, with standard deviations in parentheses (for hydrogen ×10^4, for other atoms ×10^5). The numbering of atoms is shown in the Figure

	x	y	z
O(1)	3136(41)	39114(44)	9930(51)
O(2)	7626(45)	26509(44)	14015(51)
C(1)	8818(40)	33930(39)	11120(38)
C(2)	17921(49)	35992(66)	9105(72)
Na(1)	0	0	0
Na(2)	11988(68)	11988(68)	11988(68)
H(1)	1802(12)	4081(17)	432(15)
H(2)	2053(14)	3862(26)	1367(17)
H(3)	2074(14)	3111(19)	656(22)
H(4)	0	2500	1429(12)

Full-matrix least-squares refinement started from the X-ray parameters (Part VI [2]), using the program CRYLSQ;[4] other necessary programs were also taken from ref. 4. The values of the neutron-scattering factors were: hydrogen −3·78, carbon 6·61, oxygen 5·77, and sodium 3·51 fermi (1 fermi = 10^{-15}m). At convergence R was 8·3%, and R' 6·3% [$R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] for the 299 reflexions, and the standard deviation of an observation of unit weight was 1·59. Weighting factors were based on counting statistics in the usual way. Final co-ordinates are listed in Table 1, anisotropic vibrational parameters in Table 2, and a weighting analysis in Table 3. Structure factors are listed in Supplementary Publication No. SUP 21150 (2 pp.). A final difference synthesis showed no peaks outside the range, 0·9 to −0·7 fermi Å^{-3}.

TABLE 2

Vibrational parameters (Å^2) (for hydrogen ×10^3, for all other atoms ×10^4), with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	267(36)	348(36)	562(50)	33(32)	−28(37)	120(43)
O(2)	274(38)	285(45)	605(47)	35(36)	−8(41)	26(43)
C(1)	278(32)	295(33)	317(32)	0(33)	33(31)	−29(30)
C(2)	246(42)	520(50)	624(60)	−12(43)	99(43)	31(51)
Na(1)	266(51)	266(51)	266(51)	−85(77)	−85(77)	−85(77)
Na(2)	243(47)	243(47)	247(47)	37(50)	37(50)	37(50)
H(1)	67(12)	158(21)	161(22)	9(15)	47(13)	103(20)
H(2)	71(12)	299(55)	97(18)	−44(21)	11(13)	−39(29)
H(3)	66(13)	134(21)	209(34)	3(14)	65(18)	−5(24)
H(4)	56(11)	45(9)	59(10)	2(11)		

TABLE 3

Analysis of structure-factor agreement and weighting

$\lvert F_o\rvert$ range	N	R(%)	Mean $w\Delta^2$
0—20	0		
20—40	5	15·2	0·4
40—60	45	20·1	1·02
60—80	60	12·1	0·82
80—100	76	12·0	2·62
100—140	58	6·2	1·73
140—300	52	3·0	1·94
300—	1	(11·0)	
sinθ range			
0·00—0·20	21	7·8	10·4
0·20—0·30	38	4·2	1·37
0·30—0·40	68	6·1	1·05
0·40—0·45	45	9·3	1·33
0·45—0·50	50	8·3	1·22
0·50—0·55	55	13·1	1·33
0·55—0·60	20	14·5	0·98

RESULTS AND DISCUSSION

The Figure gives the atom-numbering scheme, and shows the more important features of the structure. (For fuller diagrams see Part VI.[2]) Table 4 compares the principal geometric details obtained here with those from the X-ray analysis. Only in two cases are the differences of more than ' possible significance,' and they are not serious. The positions for the hydrogen atoms given in Part VI were approximate and had not been refined. Discussion will be confined to points where neutron diffraction has disclosed features not accessible to X-ray analysis.

Though the O · · · H · · · O bond has digonal symmetry, the proton is not constrained to be collinear with

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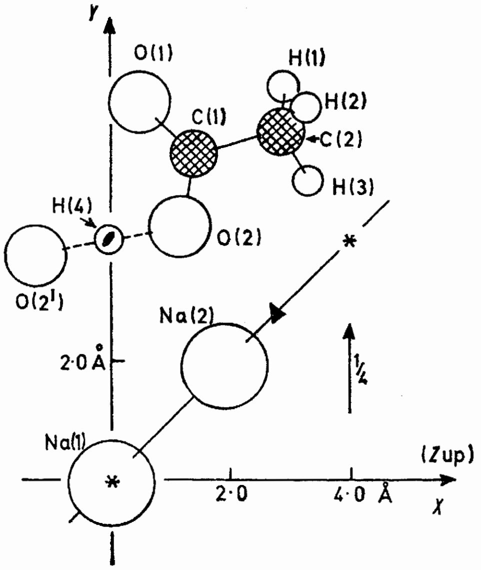
* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

[3] A. Villiers, *Compt. rend.*, 1877, **84**, 774; H. Lescoeur, *ibid.*, p. 1029.

[4] ' X-Ray ' Program system, eds. J.M.Stewart, F. A. Kundell, and J. C. Baldwin, version of June, 1972, University of Maryland Report TR 192.

O(2) and O(2^I); its z co-ordinate need not be the same as that of O(2). In fact z for H(4) differs only by 0·044 Å, twice its standard deviation, and the O(2) · · · H(4) · · · O(2^I) angle is 176(2)°. Thus there is no significant divergence of this bond from ' internal ' centrosymmetry.



The essence of the crystal structure of sodium hydrogen diacetate. Carbon atoms are represented by cross-hatched circles. Asterisks denote points of $\bar{3}$ symmetry

TABLE 4

Comparison of some interatomic distances (Å) and angles (deg.), with standard deviations in parentheses, obtained by neutron and by X-ray diffraction

	X-Ray	Neutron
C(1)–C(2)	1·492(12)	1·520(10)
C(1)–O(1)	1·243(10)	1·239(9)
C(1)–O(2)	1·295(10)	1·282(9)
O(2) · · · O(2^I)	2·444(10) *	2·475(14)
O(1)–C(1)–O(2)	121·7(7)	124·1(7)
C(2)–C(1)–O(1)	122·3(7)	121·3(7)
C(2)–C(1)–O(2)	116·1(7)	114·6(7)
C(1)–O(2) · · · O(2^I)	110·8(5)	108·9(5)
Na(1) · · · Na(2)	3·297(16)	3·306(10)
Na(1) · · · O(1)	2·404(11)	2·398(8)
Na(2) · · · O(1)	2·441(11)	2·436(7)
Na(2) · · · O(2)	2·445(11)	2·435(8)
C(2)–H(1)		1·08(3) †
C(2)–H(2)		0·94(3) †
C(2)–H(3)		0·98(3) †
H(1)–C(2)–H(2)		103(3)
H(1)–C(2)–H(3)		105(3)
H(2)–C(2)–H(3)		118(3)

* This σ may have been underestimated in Part VI. † The large libration found for the methyl group implies that these distances need correction. An increase of *ca.* 0·10 Å is estimated. Roman numeral superscript I denotes molecule at $-x$, $\frac{1}{2}-y$, z

To our knowledge there is only one other case where the O · · · H · · · O bond in an A type [5] crystal lies across a two-fold axis and has been studied by neutron diffraction: potassium hydrogen succinate.[6,*] Here, in contrast, the proton is a little off the bond centre, by 0·17(4) Å.

In many cases when A type hydrogen bonds have been examined by neutron diffraction the proton has been found to vibrate, relatively to the oxygen (or fluorine) atoms, with its greatest mean-square amplitude along the bond, or nearly so.[7–9] The vibrational parameters of Table 2 are of low precision, but they show this anisotropy in sodium hydrogen diacetate. If, adopting the riding model, we subtract the tensor components of O(2) from those of H(4), we find U_{11} 0·029, U_{22} 0·017, U_{33} −0·002, and U_{12} 0·002 Å^2. (The negative value of U_{33} reflects the imprecision; it is not significantly negative.) The O · · · H · · · O bond is perpendicular to z; in the z direction the relative vibration of H(4) is evidently small. In the xy plane, the mean-square amplitude is 0·028(12) Å^2 along and 0·017(9) across the bond. The sense of the anisotropy, at any rate, is as would be expected. The neutron results for potassium hydrogen succinate show the same trend.

Inspection of the vibrational parameters of the methyl hydrogen atoms indicates that there is a large torsional motion of the group. Large librations have also been found in the methyl groups of copper acetate dimer, where they have been investigated in some depth,[10] and the mean of the root-mean-square angular amplitudes of the two independent methyl groups is 24°. We have again adopted the riding model, and assumed that residual motion of the hydrogen nuclei, tangential to their circle of rotation, could be attributed exclusively to libration. This will probably lead to an overestimate. For atoms H(1), H(2), and H(3) we find mean-square amplitudes of 0·201, 0·246, and 0·146 Å^2, which correspond to root-mean-square angular amplitudes of 29, 31, and 24°. The internal libration of the methyl group in alanine has been studied with some precision.[11] Its librational amplitude was estimated at 9·3°, and the height of the energy-barrier opposing rotation at 5·6 kcal mol^{-1}. Libration is much wider in copper acetate and in sodium hydrogen diacetate. Assessment of barriers is very uncertain, but they cannot be much higher than in the free, gaseous molecule (*ca.* 0·5 kcal mol^{-1}).

The packing of the methyl groups in sodium hydrogen diacetate is therefore of some interest. In the X-ray study two short C · · · C contacts were recorded: 3·63 to C(2^{VI}) and 3·83 Å to C(2^{V}). [V and VI denote units at $\frac{1}{2}-z$, $\frac{1}{2}-x$, $\frac{1}{2}-y$ and $\frac{1}{2}-x$, y, $-z$, respectively.] The neutron study now finds 3·67(1) and 3·79(1) Å for these

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* *Added in proof:* Another example of a short O · · · H · · · O bond across a two-fold axis occurs in rubidium hydrogen oxydiacetate. A neutron-diffraction study (J. Albertsson and I. Grenthe, *Acta Cryst.*, 1973, **B29**, 2751) shows the proton to be 0·053(3) Å along the axis from the mid-point between the oxygen atoms, which are 2·449(3) Å apart.

[5] H. N. Shrivastsava and J. C. Speakman, *J. Chem. Soc.*, 1961, 1151; M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923; see also J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141.

[6] A. McAdam, M. Currie, and J. C. Speakman, *J. Chem. Soc.* (*A*), 1971, 1194.

[7] B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.

[8] A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Structure*, 1967, **1**, 283.

[9] A. L. Macdonald and J. C. Speakman, *J.C.S. Perkin II*, 1972, 825.

[10] G. M. Brown and R. Chidambaram, *Acta Cryst.*, 1973, **B29**, 2388, 2393.

[11] M. S. Lehmann, T. F. Koetzle, and W. C. Hamilton, *J. Amer. Chem. Soc.*, 1972, **94**, 2657.

same contacts, well below the 4·0 Å required by the conventional van der Waals radius of methyl carbon. This was attributed to the interdigitation of the hydrogen atoms, and the suggestion is confirmed by the results of the neutron analysis. There are only three H ··· H contacts <2·9 Å: *viz.* H(3) ··· H(3^{VI}) 2·49(6), H(3) ··· H(2^{V}) 2·61(4), and H(1) ··· H(1^{VI}) 2·61(5) Å. Despite a seemingly close C ··· C approach, the hydrogen atoms maintain (equilibrium) separations well in excess of twice the van der Waals radius of 1Å now often adopted for hydrogen. The lively libration of this methyl group is therefore not surprising. Strongly hydrogen-bonded crystals are usually hard. The softness of sodium hydrogen diacetate must be connected with the soft packing of the methyl groups.

The i.r. spectrum of sodium hydrogen diacetate is remarkable.[2,12a,b] Extensive spectroscopic studies of this, and other Type *A*, acid salts have now been made, and are discussed in a recent review by Novak.[13] He includes a detailed interpretation of the i.r. and Raman spectra of sodium hydrogen diacetate, and concludes that its hydrogen bond has a symmetric single-minimum potential.

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[12] (*a*) D. Hadži and A. Novak, ' I.r. Spectra of, and Hydrogen Bonding in, Some Acid Salts of Carboxylic Acids,' University of Ljubljana, 1960; (*b*) M. F. Claydon and N. Sheppard, *Chem. Comm.*, 1969, 1431.

[13] A. Novak, *Structure and Bonding*, 1974, **18**, 177.