

Hydrogen Bond Studies

35*. The Crystal Structure of the 1:1 Addition Compound of Ammonium Acetate and Acetic Acid

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The crystal structure of the 1:1 addition compound of ammonium acetate and acetic acid, $\text{CH}_3\text{COONH}_4 \cdot \text{CH}_3\text{COOH}$, has been determined from three-dimensional single-crystal X-ray data obtained at -56°C . The crystals are triclinic, space group $P\bar{1}$, with three formula units in a unit cell of dimensions: $a=10.532$, $b=8.293$, $c=7.177$ Å, $\alpha=102.1$, $\beta=113.0$, and $\gamma=99.3^\circ$. According to crystallographic and chemical evidence the structure contains CH_3COOH , CH_3COO^- , $\text{H}(\text{CH}_3\text{COO})_2^-$, and NH_4^+ groups. The acetic acid molecule and the acetate ion are joined to a dimer by a short, though unsymmetrical, hydrogen bond $\text{O}-\text{H}\cdots\text{O}=2.517$ Å. The hydrogen diacetate ion consists of two equivalent acid residues connected across a centre of symmetry by a virtually symmetrical hydrogen bond $\text{O}\cdots\text{H}\cdots\text{O}=2.474$ Å. The ammonium ions are of two kinds, one with ordered orientation and the other with probably twofold disorder. The acetate dimers and ammonium ions are connected by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds into a three-dimensional hydrogen-bond system.

The present investigation of the acid salt $\text{CH}_3\text{COONH}_4 \cdot \text{CH}_3\text{COOH}$, commonly called ammonium hydrogen diacetate, belongs to a series of crystal structure determinations of compounds formed in the system ammonia-acetic acid.¹ Earlier works in this series involve the crystal structures of $\text{CH}_3\text{COONH}_4 \cdot n\text{NH}_3$ ($n=0, 1, 2$).²⁻⁴ In these studies the main interest is focussed to the hydrogen bonding and the geometry of the acetate group.

The present compound is particularly interesting as several of the related crystalline acid salts formed by mono- and dicarboxylic acids have "very short" hydrogen bonds (2.4–2.5 Å). In the monocarboxylic salts the acid residues are joined to dimers⁵⁻⁹ by the short hydrogen bond, whereas in the dicarboxylic salts they are linked into infinite chains.¹⁰⁻¹² The hydrogen bond is mostly crystallographically symmetrical (exception, *e.g.*, potassium hydrogen diformate⁵) and the bridging proton may be at the midpoint of the bond or be randomly distributed between two equivalent sites close to this.

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EXPERIMENTAL

The present compound was prepared by mixing equimolar quantities of water-free acetic acid and ammonium acetate obtained as described earlier.² The substance was subsequently recrystallized from ethanol (99.5 %) and dried over calcium sulfate (Drierite). The melting point was found to be 67°C in agreement with the previously reported value.¹ Suitable crystals were chosen under a microscope and mounted in glass capillaries which were finally sealed. As the crystals were very hygroscopic their preparation and mounting were done in a dry-box filled with dried nitrogen.

A crystal mounted along the *c* axis and with the approximate dimensions 0.1 × 0.1 × 0.2 mm was used for the X-ray analysis. Multiple-film (five), equi-inclination Weissenberg photographs for the eight layers 0 ≤ *l* ≤ 7 were taken at +22 and -56°C using unfiltered CuK radiation. The total number of reflexions recorded at both temperatures was 2064 corresponding to 77 % of the reflexions within the CuK sphere. At -56°C only 1487 had measurable intensities and at +22°C the data set was further reduced due to a very large intensity decrease of the high-angle reflexions. As the comparison of the two data sets revealed no phase change, only the data recorded at -56°C were used in the further analysis. The relative intensities of the reflexions were obtained by visual comparison with an intensity scale. The intensity range was 1 to 16 000. The data were corrected for the Lorentz and polarization effects. No correction for absorption ($\mu = 9.8 \text{ cm}^{-1}$) or extinction effects was made.

The diffraction symmetry indicated a triclinic unit cell and space group $P\bar{1}$ or *P1* (No. 2 and 1, respectively, *International Tables for X-ray Crystallography*, 1952¹³). The subsequent refinement (see below) showed that $P\bar{1}$ is the most appropriate choice. The unit cell dimensions were determined from quartz-calibrated rotation and zero-layer oscillation photographs around the *a* and the *c* axes (program: CELSIUS). The following constants were used: *a* = 4.913 and *c* = 5.405 Å for α quartz (25°C), $\lambda(\text{CuK}\alpha_1) = 1.54051$ Å, $\lambda(\text{CuK}\alpha_2) = 1.54433$ Å, $\lambda(\text{CuK}\beta) = 1.39217$ Å. The cell dimensions obtained were not significantly different at the two temperatures. The crystallographic data are given in Table 1.

Table 1. Crystal data.

$\text{CH}_3\text{COONH}_4 \cdot \text{CH}_3\text{COOH}$	F.W.: 137.14 g mole ⁻¹
Triclinic; space group $P\bar{1}$	
<i>a</i> = 10.532(5) Å	α = 102.1(5)°
<i>b</i> = 8.293(4)	β = 113.0(5)
<i>c</i> = 7.177(4)	γ = 99.3(5)
<i>V</i> = 543.3 Å ³	D_x = 1.257 g cm ⁻³
<i>Z</i> = 3	

DETERMINATION OF THE CRYSTAL STRUCTURE

Location of the C, O, and N atoms. There are three $\text{CH}_3\text{COONH}_4 \cdot \text{CH}_3\text{COOH}$ formula units in the unit cell. Assuming a centric structure, one nitrogen atom has to be in a centre of inversion, which is not compatible with the geometry of the ammonium ion unless it is disordered. Thus, initially the space group was assumed to be *P1*. The positions of twelve atoms could be derived from the three-dimensional Patterson synthesis using the minimum-function method. The image location was performed graphically (see Buerger¹⁴). The coordinates of the other heavy atoms could be deduced by means of successive three-dimensional electron density calculations. From geometrical and chemical considerations the atoms could be assigned correct scattering factors.

Refinement and determination of the space group. The trial structure obtained was refined by least-squares using the full-matrix program LALS with minimization of the function $\sum w(|F_o| - |F_c|)^2$. The weights were calculated according to the expression $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$. Inter-layer scale factors, isotropic temperature factors and atomic coordinates were allowed to vary. After several cycles the shifts were one fifth of the standard deviations and the $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.141. The thermal parameters of all atoms were then subjected to anisotropic refinement. The inter-layer scale factors were fixed to the values obtained from the final isotropic refinement. The total number of parameters varied was 241 but due to the limitations of the computer only the overall scale factor and half of the atomic parameters could be refined simultaneously. When the shifts were negligible ($< 0.1\sigma$) the R value was 0.114. The standard deviations were still very large, 0.01–0.02 Å for the positional parameters, and the dimensions of nearly all of the acid residues were anomalous. In the last cycle two reflexions, probably affected by extinction, were excluded from the refinement.

After a translation of the origin to the position of one of the nitrogen atoms it became evident that the refined structure was approximately centrosymmetric. An isotropic and a subsequent anisotropic refinement were carried out in the space group $P\bar{1}$ refining the same parameters as described above. The number of parameters varied was 60 and 124, respectively. Both series of refinement were ended when the shifts were about 0.1σ . The standard deviations after the last cycle of anisotropic refinement were reasonable, 0.003–0.005 Å, for the positional parameters and the dimensions of the acid residues were no longer anomalous. The final R values for the isotropic and anisotropic refinements were 0.135 and 0.097, respectively. In particular the last value is appreciably lower than the corresponding R value obtained assuming an acentric structure which indicates that the minimum attained in the acentric case is false. Some series of refinements, starting with the symmetric structure but with the atomic positions slightly shifted and assuming the symmetry of $P1$, resulted in not significantly lower R values as compared with the centric case. In the light of this evidence the structure was interpreted as centrosymmetric, with six C, six O, and one N atoms in general positions and one N atom at a centre of symmetry.

All positions of the hydrogen atoms except those belonging to the centric NH_4^+ ion could now be derived from a three-dimensional difference synthesis based on reflexions with $\sin\theta/\lambda$ less than 0.5 \AA^{-1} . The hydrogen positions of the centric NH_4^+ ion were calculated from chemical and crystallographic considerations assuming a twofold-disordered orientation (see below). The anisotropic least-squares refinements were subsequently completed with another few cycles varying the same parameters as before but in addition including the hydrogen atoms with fixed parameters. The eight disordered H atoms were included as half atoms. The Debye-Waller factor, B , used for the hydrogen atoms was 6 \AA^2 . The final R value obtained was 0.085.

The Fourier calculations were made using the program DRF. At the least-squares refinement the final values used for the weight coefficients a , c , and d were 1.5, 0.1, and 0.0035, respectively. An analysis indicated suitable weighting factors. Reflexions too weak to be measured were given zero weight in

all calculations, and were also omitted in all calculations of R values. The atomic scattering factors were those for neutral O, N, C, and H given in *International Tables for X-ray Crystallography*.¹⁵

Table 2. Atomic coordinates, with standard deviations within parentheses. The positions of H(1)–H(11) and H(16)–H(19) were derived from the difference synthesis whereas those of H(12)–H(15) were calculated as described in the text.

	x	y	z		x	y	z
O(1)	0.2977(3)	0.2497(3)	0.2348(4)	H(1)	0.500	0.500	0.500
O(2)	0.5261(3)	0.3597(4)	0.4627(4)	H(2)	0.432	0.044	0.099
C(1)	0.4201(3)	0.2378(4)	0.3185(5)	H(3)	0.557	0.081	0.345
C(2)	0.4543(5)	0.0711(5)	0.2526(7)	H(4)	0.387	−0.021	0.271
O(3)	0.0391(3)	0.2273(5)	0.7365(4)	H(5)	−0.044	0.260	0.420
O(4)	0.0483(3)	0.2178(4)	0.4305(5)	H(6)	0.305	0.205	0.655
C(3)	0.0983(4)	0.2003(4)	0.6233(5)	H(7)	0.270	0.142	0.830
C(4)	0.2310(4)	0.1417(6)	0.6790(7)	H(8)	0.233	0.050	0.595
O(5)	−0.1469(2)	0.3083(3)	0.0304(4)	H(9)	−0.330	0.506	0.024
O(6)	−0.1789(3)	0.3115(4)	0.3195(4)	H(10)	−0.394	0.399	0.152
C(5)	−0.2154(3)	0.3345(4)	0.1372(5)	H(11)	−0.422	0.303	−0.086
C(6)	−0.3500(4)	0.3910(5)	0.0502(6)				
N(1)	0	0	0	H(12)	0.387	−0.021	0.271
				H(13)	0.330	0.494	−0.024
				H(14)	−0.394	0.399	0.152
				H(15)	−0.422	0.303	−0.086
N(2)	0.1558(3)	0.5114(4)	0.2705(4)	H(16)	0.212	0.425	0.281
				H(17)	0.050	0.464	0.187
				H(18)	0.190	0.593	0.210
				H(19)	0.180	0.587	0.420

Table 3. Thermal vibration tensor components ($\text{Å}^2 \times 10^4$) with standard deviations within parentheses. U_{ij} are coefficients in the expression $\exp[-2\pi^2(h^2a^{-2}U_{11} + \dots + 2hka^{-1}b^{-1}U_{13} + \dots)]$. For hydrogen the Debye-Waller factor $B=6.0 \text{ Å}^2$ was used.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	449(17)	522(16)	717(20)	166(13)	128(14)	38(13)
O(2)	422(17)	671(19)	802(22)	148(15)	78(15)	−121(15)
C(1)	437(21)	523(19)	441(21)	157(16)	229(16)	107(15)
C(2)	757(32)	609(26)	779(32)	313(24)	281(25)	150(22)
O(3)	806(24)	1236(29)	559(21)	586(22)	384(18)	381(19)
O(4)	817(22)	927(22)	719(22)	561(19)	480(18)	484(17)
C(3)	536(23)	454(19)	506(25)	163(17)	202(18)	149(16)
C(4)	571(27)	737(27)	736(30)	310(22)	230(22)	245(22)
O(5)	447(15)	641(16)	471(17)	193(12)	203(12)	231(12)
O(6)	681(19)	801(19)	456(18)	410(16)	309(14)	291(14)
C(5)	441(20)	368(16)	471(23)	83(14)	186(16)	102(14)
C(6)	523(24)	605(23)	670(28)	235(19)	212(20)	233(19)
N(1)	464(27)	685(29)	560(30)	174(23)	211(22)	220(23)
N(2)	374(17)	554(17)	460(19)	158(14)	153(14)	181(14)

Table 4. Root-mean-square components R_i (Å) of thermal displacement along principal axes of the ellipsoids of vibration. The standard deviations are ≤ 0.01 Å.

	R_1	R_2	R_3		R_1	R_2	R_3
O(1)	0.182	0.202	0.279	O(5)	0.178	0.188	0.239
O(2)	0.177	0.208	0.330	O(6)	0.171	0.191	0.280
C(1)	0.167	0.190	0.221	C(5)	0.178	0.192	0.195
C(2)	0.203	0.240	0.278	C(6)	0.186	0.235	0.237
O(3)	0.189	0.206	0.342	N(1)	0.187	0.212	0.245
O(4)	0.185	0.198	0.311	N(2)	0.165	0.194	0.222
C(3)	0.192	0.200	0.214				
C(4)	0.189	0.246	0.264				

The final positional parameters are listed in Table 2. The anisotropic thermal parameters β_{ij} were transformed into the vibration tensor components U_{ij} as described by Scheringer¹⁶ and these latter are shown in Table 3. The root-mean-square components of thermal displacement along the principal axes of the ellipsoids are given in Table 4. The observed and final calculated structure factors are compared in Table 5.

A description of the programs mentioned in the text has been given elsewhere.²

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

General. An illustration of the rather complicated molecular arrangement is given in Fig. 1. The asymmetric unit consists of three acetic acid residues, denoted *A*, *B*, and *C* in the subsequent discussion, and two NH_4^+ ions. The acid residues are coupled in pairs to dimers by short hydrogen bonds, *A* to

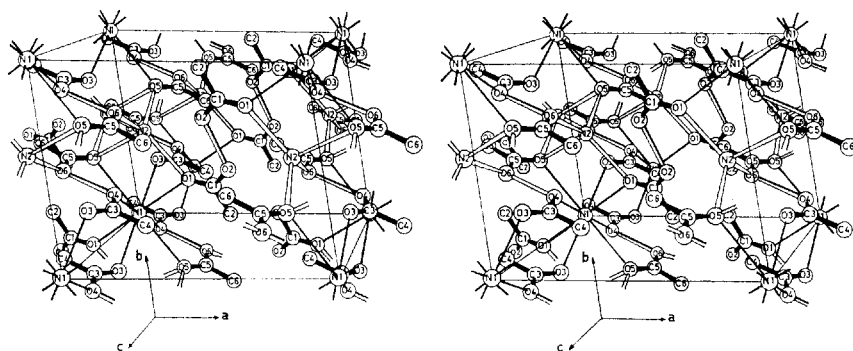


Fig. 1. A stereoscopic pair of drawings showing the structure of $\text{CH}_3\text{COONH}_4 \cdot \text{CH}_3\text{COOH}$. The hydrogen atoms are omitted. Covalent bonds are filled and hydrogen bonds are open. The very short $\text{O} \cdots \text{O}$ hydrogen bonds are half filled. The hydrogen-bond interaction with the disordered NH_4^+ ions is represented by single lines. All figures were drawn with the program ORTEP.

Table 5. Observed and calculated structure factors. Reflexions which were too weak to be measured are indicated with one asterisk and were assigned the intensity I_{\min} . Two asterisks indicate reflexions which were excluded from the final refinements. The three columns are in order: $h, k, |F_o|, |F_c|$.

h	k	$ F_o $	$ F_c $
2	1	1.0	1.0
3	1	1.5	1.5
4	1	2.0	2.0
5	1	2.5	2.5
6	1	3.0	3.0
7	1	3.5	3.5
8	1	4.0	4.0
9	1	4.5	4.5
10	1	5.0	5.0
11	1	5.5	5.5
12	1	6.0	6.0
13	1	6.5	6.5
14	1	7.0	7.0
15	1	7.5	7.5
16	1	8.0	8.0
17	1	8.5	8.5
18	1	9.0	9.0
19	1	9.5	9.5
20	1	10.0	10.0
21	1	10.5	10.5
22	1	11.0	11.0
23	1	11.5	11.5
24	1	12.0	12.0
25	1	12.5	12.5
26	1	13.0	13.0
27	1	13.5	13.5
28	1	14.0	14.0
29	1	14.5	14.5
30	1	15.0	15.0
31	1	15.5	15.5
32	1	16.0	16.0
33	1	16.5	16.5
34	1	17.0	17.0
35	1	17.5	17.5
36	1	18.0	18.0
37	1	18.5	18.5
38	1	19.0	19.0
39	1	19.5	19.5
40	1	20.0	20.0
41	1	20.5	20.5
42	1	21.0	21.0
43	1	21.5	21.5
44	1	22.0	22.0
45	1	22.5	22.5
46	1	23.0	23.0
47	1	23.5	23.5
48	1	24.0	24.0
49	1	24.5	24.5
50	1	25.0	25.0
51	1	25.5	25.5
52	1	26.0	26.0
53	1	26.5	26.5
54	1	27.0	27.0
55	1	27.5	27.5
56	1	28.0	28.0
57	1	28.5	28.5
58	1	29.0	29.0
59	1	29.5	29.5
60	1	30.0	30.0
61	1	30.5	30.5
62	1	31.0	31.0
63	1	31.5	31.5
64	1	32.0	32.0
65	1	32.5	32.5
66	1	33.0	33.0
67	1	33.5	33.5
68	1	34.0	34.0
69	1	34.5	34.5
70	1	35.0	35.0
71	1	35.5	35.5
72	1	36.0	36.0
73	1	36.5	36.5
74	1	37.0	37.0
75	1	37.5	37.5
76	1	38.0	38.0
77	1	38.5	38.5
78	1	39.0	39.0
79	1	39.5	39.5
80	1	40.0	40.0
81	1	40.5	40.5
82	1	41.0	41.0
83	1	41.5	41.5
84	1	42.0	42.0
85	1	42.5	42.5
86	1	43.0	43.0
87	1	43.5	43.5
88	1	44.0	44.0
89	1	44.5	44.5
90	1	45.0	45.0
91	1	45.5	45.5
92	1	46.0	46.0
93	1	46.5	46.5
94	1	47.0	47.0
95	1	47.5	47.5
96	1	48.0	48.0
97	1	48.5	48.5
98	1	49.0	49.0
99	1	49.5	49.5
100	1	50.0	50.0
101	1	50.5	50.5
102	1	51.0	51.0
103	1	51.5	51.5
104	1	52.0	52.0
105	1	52.5	52.5
106	1	53.0	53.0
107	1	53.5	53.5
108	1	54.0	54.0
109	1	54.5	54.5
110	1	55.0	55.0
111	1	55.5	55.5
112	1	56.0	56.0
113	1	56.5	56.5
114	1	57.0	57.0
115	1	57.5	57.5
116	1	58.0	58.0
117	1	58.5	58.5
118	1	59.0	59.0
119	1	59.5	59.5
120	1	60.0	60.0
121	1	60.5	60.5
122	1	61.0	61.0
123	1	61.5	61.5
124	1	62.0	62.0
125	1	62.5	62.5
126	1	63.0	63.0
127	1	63.5	63.5
128	1	64.0	64.0
129	1	64.5	64.5
130	1	65.0	65.0
131	1	65.5	65.5
132	1	66.0	66.0
133	1	66.5	66.5
134	1	67.0	67.0
135	1	67.5	67.5
136	1	68.0	68.0
137	1	68.5	68.5
138	1	69.0	69.0
139	1	69.5	69.5
140	1	70.0	70.0
141	1	70.5	70.5
142	1	71.0	71.0
143	1	71.5	71.5
144	1	72.0	72.0
145	1	72.5	72.5
146	1	73.0	73.0
147	1	73.5	73.5
148	1	74.0	74.0
149	1	74.5	74.5
150	1	75.0	75.0
151	1	75.5	75.5
152	1	76.0	76.0
153	1	76.5	76.5
154	1	77.0	77.0
155	1	77.5	77.5
156	1	78.0	78.0
157	1	78.5	78.5
158	1	79.0	79.0
159	1	79.5	79.5
160	1	80.0	80.0
161	1	80.5	80.5
162	1	81.0	81.0
163	1	81.5	81.5
164	1	82.0	82.0
165	1	82.5	82.5
166	1	83.0	83.0
167	1	83.5	83.5
168	1	84.0	84.0
169	1	84.5	84.5
170	1	85.0	85.0
171	1	85.5	85.5
172	1	86.0	86.0
173	1	86.5	86.5
174	1	87.0	87.0
175	1	87.5	87.5
176	1	88.0	88.0
177	1	88.5	88.5
178	1	89.0	89.0
179	1	89.5	89.5
180	1	90.0	90.0
181	1	90.5	90.5
182	1	91.0	91.0
183	1	91.5	91.5
184	1	92.0	92.0
185	1	92.5	92.5
186	1	93.0	93.0
187	1	93.5	93.5
188	1	94.0	94.0
189	1	94.5	94.5
190	1	95.0	95.0
191	1	95.5	95.5
192	1	96.0	96.0
193	1	96.5	96.5
194	1	97.0	97.0
195	1	97.5	97.5
196	1	98.0	98.0
197	1	98.5	98.5
198	1	99.0	99.0
199	1	99.5	99.5
200	1	100.0	100.0

A and B to C. All non-hydrogen atoms are in general positions except N(1) which occupies the centres of inversion at the corners of the unit cell. The compound forms a three-dimensionally hydrogen-bonded structure. The dimers and the NH_4^+ ions, with central atom N(2), are crosslinked by

Table 6. Bond distances and angles involving the nitrogen atoms.

(a) Environment around N(1).

Bonds		Angles	
N(1)...O(1)	3.045(2) Å	O(1)...N(1)...O(3)	109.7(1)°
N(1)...O(3)	3.025(3)	O(1)...N(1)...O(4)	111.3(1)
N(1)...O(4)	3.034(3)	O(1)...N(1)...O(5)	91.3(1)
N(1)...O(5)	3.207(2)	O(3)...N(1)...O(4)	109.9(1)
N(1)...other atoms >	3.6	O(3)...N(1)...O(5)	113.2(1)
		O(4)...N(1)...O(5)	119.8(1)

(b) Environment around N(2).

N(2)—H(16)...O(1)	2.851(4)	O(1)...N(2)...O(5)	100.7(1)
N(2)—H(17)...O(5)	2.954(3)	O(1)...N(2)...O(5')	110.7(1)
N(2)—H(18)...O(5')	2.854(4)	O(1)...N(2)...O(6)	119.9(1)
N(2)—H(19)...O(6)	2.896(4)	O(5)...N(2)...O(5')	94.9(1)
N(2)...O(2)	3.002(4)	O(5)...N(2)...O(6)	104.2(1)
N(2)...O(3)	3.212(4)	O(5')...N(2)...O(6)	120.2(1)
N(2)...O(4)	3.134(4)		
N(2)...other atoms >	3.6		

An ordered orientation of the NH_4^+ ion is not compatible with the space-group symmetry whereas a twofold disorder seems very likely. The $\text{N}\cdots\text{O}$ distances are 0.1–0.3 Å longer than the hydrogen bonds formed with the other NH_4^+ ion (without orientational disorder, see below) which is reasonable considering that the number of oxygen atoms hydrogen-bonded to nitrogen is increased from 4 to 8.¹⁷ As mentioned previously the positions of the hydrogen atoms connected to N(1) could not be derived from the difference synthesis. No resolved hydrogen peaks were found around the nitrogen atom. (A dif-

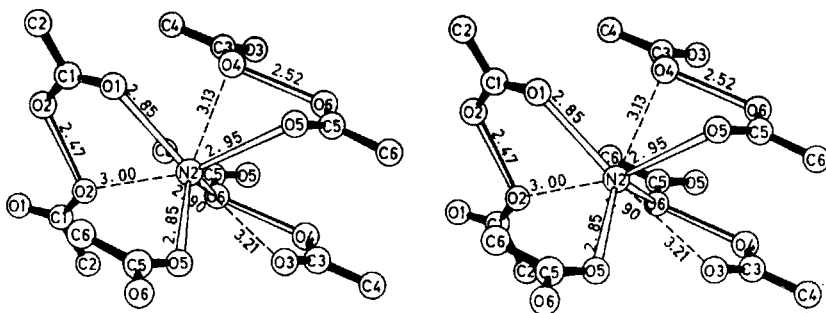


Fig. 3. A stereoscopic pair of drawings showing the environment of N(2). Broken lines represent distances less than 3.6 Å, which are not hydrogen bonds. The remaining bonds are denoted as in Fig. 1.

ference synthesis, based on the parameters from the last cycle of anisotropic refinement assuming an acentric structure, gave the same result). In the final cycles of refinement and in the interpretation of the structure the hydrogen atoms were assumed to lie 1.0 Å from N(1) on the straight lines connecting N(1) with its eight oxygen neighbours.

The nitrogen atom N(2) has seven oxygen neighbours at distances of 2.85–3.21 Å (*cf.* Fig. 3). From the positions of the hydrogen atoms, H(16)–H(19),

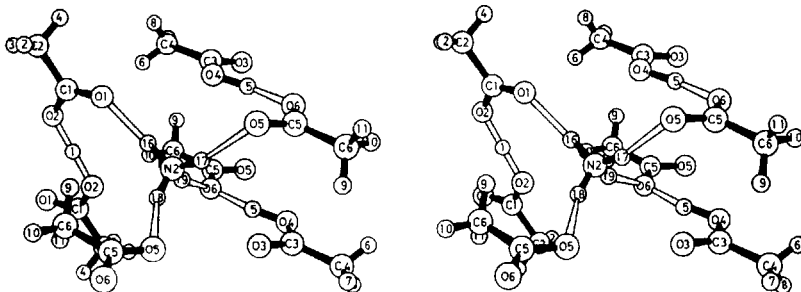


Fig. 4. A stereoscopic pair of drawings showing the locations of most of the hydrogen atoms; H(12)–H(15), assigned to N(1), are not illustrated. The hydrogen atoms are numbered 1–11 and 16–19. Covalent bonds are filled and open bonds represent O...H interaction in a hydrogen bond.

derived from the difference synthesis, the four shortest N...O distances, 2.85–2.95 Å, appear to represent hydrogen bonds (*cf.* Fig. 4). The bond lengths are comparable to those found by the author in ammonium formate and some ammonium acetate compounds (N–H...O = 2.80–2.88 Å^{18,2-4}). The

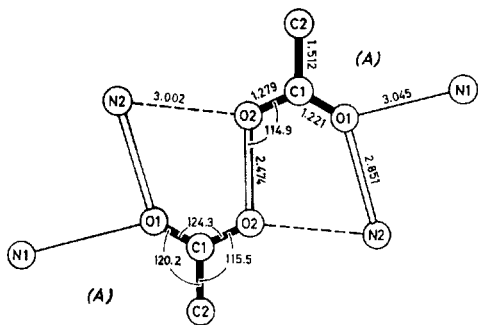


Fig. 5. Bond distances and angles involving the heavy atoms of the acetic acid residue A. Notation as in Figs. 1 and 3.

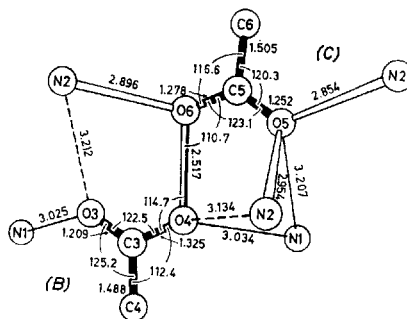


Fig. 6. Bond distances and angles involving the heavy atoms of the acetic acid residues B (numbered 3 and 4) and C (atoms 5 and 6). Notation as in Figs. 1 and 3.

hydrogen-bonded oxygen atoms are approximately tetrahedrally arranged; the $O\cdots N\cdots O$ angles range from 95 to 120° (cf. Table 6b).

The dimers and their hydrogen bonding. The geometry and the surroundings of the dimers $A-A$ and $B-C$ are shown in Figs. 5 and 6, respectively. The bond distances are not corrected for thermal motion.

$A-A$ consists of two equivalent acetic acid residues joined by a short hydrogen bond, 2.474 Å. The bridging hydrogen atom lies in the centre of inversion ($1/2, 1/2, 1/2$) or is randomly distributed between two equivalent sites close to this. The non-hydrogen atoms of A deviate by less than 0.003 Å from the least-squares plane of the molecule. The distance between the two co-parallel parts of the dimer is only 0.29 Å and accordingly the whole dimer may be regarded as nearly planar. The maximum deviation from the least-squares plane of $A-A$ is 0.08 Å. The equations of all least-squares planes mentioned in the text are listed in Table 7. All calculations are based on non-hydrogen atoms.

Table 7. Details of the planes of best fit. Each plane is represented by $lX + mY + nZ - p = 0$ where X , Y , and Z (in Å) refer to a right-handed orthogonal coordinate system in which X coincides with the crystallographic x axis and Y lies in the xy plane. The calculations (according to Blow²²) are based on non-hydrogen atoms belonging to the groups listed in the first column.

	l	m	n	p
A	0.4708	0.5356	-0.7011	0.8125
$A-A$	0.4696	0.4893	-0.7349	0.7014
B	-0.2845	-0.8796	-0.3814	-1.5706
C	-0.2633	-0.8651	-0.4269	-1.6770
$B-C$	-0.2720	-0.8749	-0.4006	-1.6532

The distances $C(1)-O(1)=1.221$ Å and $C(1)-O(2)=1.279$ Å differ significantly but the difference is only half as great as expected for an unionized carboxyl group. Speakman and co-workers have made the same observation in several acid salts containing two equivalent acid residues connected by a short hydrogen bond across a centre of inversion or a twofold axis.⁶ The character of A as a compromise between an ionized and an unionized molecule is also reflected in the magnitude of the $C-C-O$ and $O-C-O$ angles. Previously published dimensions of related carboxylic acid residues determined with comparable precision are: $C-O'=1.21-1.24$ Å, $C-O''=1.27-1.29$ Å, $C-C-O'=120-125^\circ$, $C-C-O''=112-116^\circ$, and $O'-C-O''=123-128^\circ$ ($\sigma \leq 0.006$ Å and 0.4° , Refs. 6-10). As seen from Table 8 the dimensions of A agree very well with these values.

The dimer $B-C$ consists of two nonequivalent acetic acid residues joined by a hydrogen bond, 2.517 Å. Each molecule B and C is closely planar as is the whole dimer $B-C$. The maximum deviations from the corresponding least-squares planes (cf. Table 7) are 0.005 , 0.006 , and 0.04 Å, respectively.

Table 8. Dimensions of the acetic acid residues. The values within square brackets are distances corrected for thermal "riding" motion.

	Bonds		Angles	
<i>A</i>	C(1)—O(1)	1.221(4) [1.238] Å	C(2)—C(1)—O(1)	120.2(3)°
	C(1)—O(2)	1.279(4) [1.308]	C(2)—C(1)—O(2)	115.5(3)
	C(1)—C(2)	1.512(5) [1.532]	O(1)—C(1)—O(2)	124.3(3)
<i>B</i>	C(3)—O(3)	1.209(4) [1.241]	C(4)—C(3)—O(3)	125.2(3)
	C(3)—O(4)	1.325(5) [1.342]	C(4)—C(3)—O(4)	112.4(3)
	C(3)—C(4)	1.488(5) [1.504]	O(3)—C(3)—O(4)	122.5(3)
<i>C</i>	C(5)—O(5)	1.252(4) [1.259]	C(6)—C(5)—O(5)	120.3(3)
	C(5)—O(6)	1.278(4) [1.296]	C(6)—C(5)—O(6)	116.6(3)
	C(5)—C(6)	1.505(5) [1.519]	O(5)—C(5)—O(6)	123.1(3)

The dimensions of *B* are almost exactly those expected for an unionized carboxyl group. The values given in Table 8 may be compared with corresponding bond distances and angles found in acids determined with similar precision: C=O = 1.20–1.22 Å, C—OH = 1.29–1.32 Å, C—C=O = 121–124°, C—C—OH = 112–113°, and O=C—OH = 124–127°, ($\sigma \leq 0.007$ Å and 0.6°; the references are given in an earlier work¹⁹).

If *B* is assumed to be an acetic acid molecule, *C* evidently has to be an acetate ion and the two C—O distances should be approximately equal (≈ 1.25 Å) as should the C—C—O angles ($\approx 118^\circ$).²⁻⁴ As seen in Table 8 the dimensions of *C* do not correspond exactly to an acetate ion; however, it is evident that *C* is appreciably more ionized than *B*.

According to earlier observations^{20,21} the C—C bond is expected to be shortest for the least ionized molecule. This is true for *B* whereas *A* and *C* have about the same C—C bond length. Although the orientation of the methyl groups is not very accurately determined it is evident that each of *A*, *B*, and *C* have one of their methyl hydrogen atoms situated approximately in the plane of the molecule (*cf.* Fig. 4). These hydrogen atoms, H(3), H(7), and H(10), deviate 0.09, 0.09, and 0.05 Å, respectively, from the least-squares planes of their corresponding molecules.

The hydrogen bonds within the dimers are of particular interest as they belong to the group of short hydrogen bonds, 2.4–2.6 Å, extensively studied by crystallographers and spectroscopists. The hydrogen bond joining the two equivalent *A* molecules (2.474 Å, $\sigma = 0.006$ Å) may, in principle, be truly symmetric as the chemical environment is the same about both molecules. Naturally, it is impossible to settle this question in this work, but in the analysis the hydrogen atom, H(1), was assumed to be at the centre of symmetry.

The molecules *B* and *C* are evidently different and as they are joined by a hydrogen bond which is not extremely short (2.517 Å, $\sigma = 0.004$ Å) it is reasonable to assume that the proton is associated more closely with one of the molecules. Furthermore, in the difference synthesis H(5) was located significantly closer to *B* in accordance with the observed molecular geometries.

According to the preceding discussion the dimer $B-C$ is thus best described as consisting of an acetic acid molecule and an acetate ion.

As seen from Figs. 5 and 6 the environment of A , B , and C is similar. However, a closer inspection of the chemically similar oxygen atoms reveals some important differences. If hydrogen bonds formed with $N(1)$ are counted as $\frac{1}{2}$ bonds the oxygen atoms of C take part in a total of $4\frac{1}{2}$ hydrogen bonds whereas those of B are involved only in 2. Thus, C is certainly more ionized than B in accordance with the preceding discussion. The oxygen atoms of A are involved in $2\frac{1}{2}$ hydrogen bonds. The bond angles subtended at the oxygen atoms are listed in Table 9.

Table 9. Bond angles subtended at the oxygen atoms (*cf.* Figs. 5 and 6).

A	C(1)—O(1)...N(1)	135.7(2) ^o	C(1)—O(2)...O(2')	114.9(3) ^o
	C(1)—O(1)...N(2)	136.1(2)		
	N(1)...O(1)...N(2)	86.2(1)		
B	C(3)—O(3)...N(1)	123.5(3)	C(3)—O(4)...O(6)	114.7(2)
			C(3)—O(4)...N(1)	134.2(2)
			O(6)...O(4)...N(1)	99.1(1)
C	C(5)—O(5)...N(2)	120.4(2)	C(5)—O(6)...O(4)	110.7(2)
	C(5)—O(5)...N(2')	111.4(2)	C(5)—O(6)...N(2)	137.5(2)
	C(5)—O(5)...N(1)	124.8(2)	O(4)...O(6)...N(2)	100.6(1)
	N(2)...O(5)...N(2')	85.1(1)		
	N(2)...O(5)...N(1)	113.9(1)		
	N(2')...O(5)...N(1)	81.7(1)		

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