Table 5. *The least-squares plane through the carbon atoms in the benzene ring*

The equation is expressed in terms of the crystal axes:

$$-0{\cdot}6662X+0{\cdot}6378Y+0{\cdot}3866Z-0{\cdot}1559=0.$$

Deviations from the plane

C(1)	0·012 Å	C(6)	−0·009 Å
C(2)	−0·009	C(7)	−0·026
C(3)	−0·004	Se(1)	−0·018
C(4)	0·015	O(1)	−0·003
C(5)	−0·004	O(2)	−0·074

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The Crystal Structure and Phase Transition of Ammonium Hydrogen Bis-chloroacetate. II.* The Crystal Structure of the Ferroelectric Phase

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The crystal structure of the ferroelectric phase, below 128° K, of ammonium hydrogen bis-chloroacetate, $NH_4H(ClCH_2COO)_2$, has been determined by a three-dimensional X-ray analysis at 80 °K. The symmetry of the crystal changes from $C2/c$ to Cc, and unit-cell parameters are $a=10{\cdot}47$, $b=11{\cdot}40$, $c=8{\cdot}22$ Å, $\beta=119{\cdot}3°$; $Z=4$. The structure was refined by the block-diagonal least-squares method using data collected on Weissenberg photographs. The final R is 0·106. The chloroacetate dimer retains almost the same conformation as that in the paraelectric phase including a very short hydrogen bond, 2·457 (16) Å. The nitrogen atom of the ammonium ion shifts by 0·240 Å from the twofold axis existing in the paraelectric phase. The mechanism of the ferroelectric phase transition is discussed.

Introduction

Ammonium hydrogen bis-chloroacetate (abbreviated to AHCA), $NH_4H(ClCH_2COO)_2$, exhibits ferroelectricity below 128 °K (Ichikawa & Mitsui, 1966). The crystal structure of the paraelectric phase was determined at room temperature (Ichikawa, 1972). In the paraelectric phase the two acidic radicals are crystallographically equivalent and are linked by a very short OHO hydrogen bond across the centre of symmetry. The present paper deals with a three-dimensional X-ray crystal structure analysis of the ferroelectric phase, carried out at 80 °K by the photographic method.

Experimental

All data were collected at 80 °K. A Weissenberg camera was put in a box, which was filled with dry nitrogen gas to prevent icing of the sample, and the temperature was controlled by blowing cold nitrogen gas over the sample (Itoh, Shiozaki, Hashiguchi & Mitsui, 1968). The temperature was measured by an Au:2·1 % Co–Cu thermocouple placed at about 1 mm from the crystal, and was maintained manually within ±2°. Weissenberg photographs were taken with Cu $K\alpha$ radiation to determine the space group and unit-cell parameters. The systematic absences of reflexions are the same as those observed at room temperature and, because the crystal is now polar the space group changes from $C2/c$ to Cc. Unit-cell parameters were determined from

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* Part I: *Acta Cryst.* (1972). B**28**, 755–760.

a least-squares treatment, using θ values for 50 reflexions measured on zero-layer Weissenberg photographs taken around each crystallographic axis. The crystal data are given in Table 1.

Table 1. *Crystal data at* 80°K

a	$10{\cdot}47 \pm 0{\cdot}02$ Å
b	$11{\cdot}40 \pm 0{\cdot}01$
c	$8{\cdot}22 \pm 0{\cdot}01$
β	$119{\cdot}3 \pm 0{\cdot}1°$
U	857 ± 2 Å^3
Formula: $NH_4H(ClCH_2COO)_2$	
Systematic absences hkl for $h+k=2n$	
$h0l$ for $l=2n$	
Space group	Cc
F.W.	206·0
D_x	1·60 g cm^{-3}
$F(000)$	424
Z	4
λ(Cu $K\alpha_1$)	1·5405 Å
λ(Cu $K\alpha_2$)	1·5443

Three-dimensional intensity data were obtained from equi-inclination Weissenberg photographs taken about the a, b and c axes (layers: $h=0\sim5$; $k=0\sim6$; and $l=0\sim4$) with Cu $K\alpha$ radiation and the multiple-film technique. Cylindrical crystals 0·38 ~ 0·42 mm in diameter coated with nail varnish were used. The intensities were measured by a Rigaku Denki Recording Microphotometer MP-3 and were corrected for Lorentz, polarization, and absorption effects (μCu $K\alpha=63$ cm^{-1}). The absorption correction factors used were taken from *International Tables for X-ray Crystallography* (1959). Corrections for the elongation of spots on the high layers were made according to Phillips (1956). The data from each layer were correlated by the method of Rollett & Sparks (1960) and then placed on an absolute scale by Wilson's (1942) method. 647[illegible] independent reflexions including those with non-zero intensity were obtained.

Refinement of the structure

The positional parameters obtained at room temperature (Ichikawa, 1972) and the overall temperature factor of the low-temperature modification derived from Wilson's (1942) method were used as the initial parameters in successive refinements. Positional parameters and individual isotropic temperature factors were refined by a block-diagonal least-squares method, except for hydrogen atoms, although the contribution of hydrogen was taken into consideration in the calculation of the structure factors. The quantity minimized was $\sum(|F_o| - 1/k|F_c|)^2$. Refinement was continued until all parameter shifts were less than one third their standard deviations. In the final cycle, those reflexions that were too weak to be detected, but which had calculated structure factors less than the minimum observable values, were included in the computation. Six strong reflexions were excluded, because they were probably affected by extinction. The damping factor of 0·8 was applied to the shifts of all parameters. The final R was 0·106 (0·097 if undetectably weak reflexions were excluded). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

All the calculations were made on a FACOM 230-60 computer with UNICS (1967). The final positional parameters and temperature factors are given in Table 2 together with their standard deviations.*

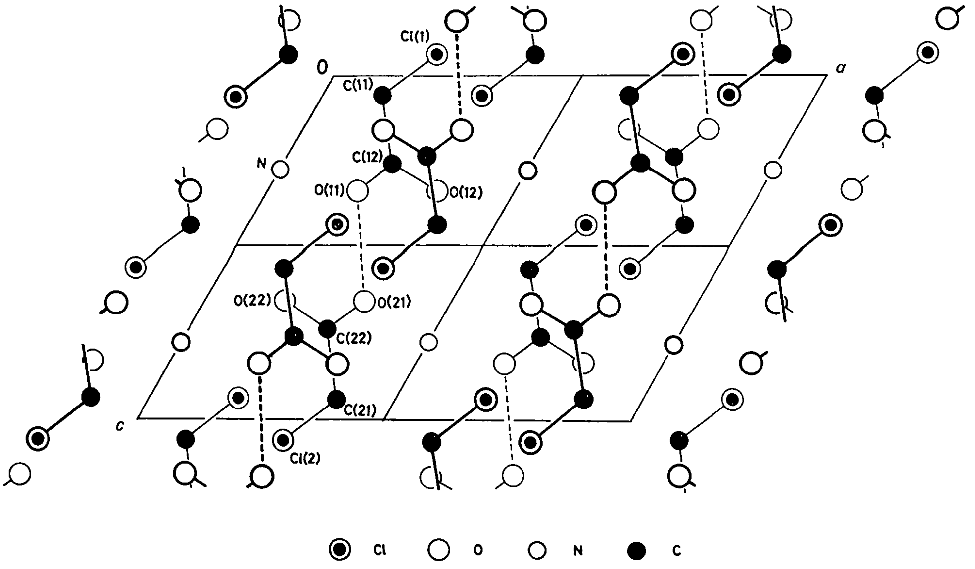

Fig. 1. The structure viewed along the b axis. The OHO hydrogen bonds are shown by broken lines.

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* The table of $|F_o|$ and $|F_c|$ has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30267 (4 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *The atomic positional parameters* ($\times 10^4$) *and the temperature factors at* 80°K *with their standard deviations*

	x	y	z	B (Å^2)
Cl(1)	1864 (4)	4276 (3)	− 687 (6)	1·57 (5)
Cl(2)	3150 (4)	797 (3)	10733 (6)	1·76 (6)
O(11)	1663 (11)	2527 (9)	3162 (15)	1·70 (18)
O(12)	3412 (12)	3679 (10)	3312 (16)	2·01 (19)
O(21)	3179 (12)	2446 (10)	6572 (16)	2·16 (20)
O(22)	1600 (10)	1175 (8)	6693 (14)	1·03 (15)
N	0 (17)	440 (9)	2791 (18)	1·44 (20)
C(11)	1174 (17)	3416 (14)	458 (23)	1·84 (26)
C(12)	2164 (13)	3240 (11)	2421 (18)	0·68 (19)
C(21)	3915 (16)	1622 (12)	9495 (21)	1·48 (24)
C(22)	2723 (15)	1713 (13)	7350 (20)	1·25 (22)

For numbering of atoms, see Table 4.

Results and discussion

The structure viewed along the *b* axis is shown in Fig. 1. Structural changes, due to symmetry change accompanying the ferroelectric phase transition, are as follows. The nitrogen atom which occupies the special position on a twofold axis in the paraelectric phase is now located at the general position. The two chloroacetate radicals [abbreviated CA(1), CA(2)] become non-equivalent and the acidic hydrogen atom which connects the two radicals is not necessarily exactly at the mid-point between the two oxygen atoms. The correspondence between the atomic numbering for the para- and the ferroelectric phases is listed in Table 3. The interatomic distances and angles are shown in Table 4 and Fig. 2. Those obtained at room temperature are also given for comparison in Table 4.

Table 3. *Correspondence of numbering of atoms in the para- and ferroelectric phases*

Paraelectric phase ↔	Ferroelectric phase
Cl	Cl(1), Cl(2)
O(1)	O(11), O(21)
O(2)	O(12), O(22)
N	N
C(1)	C(11), C(21)
C(2)	C(12), C(22)

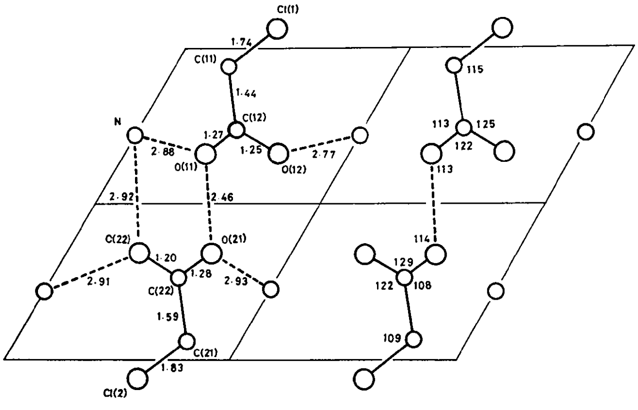

Fig. 2. The interatomic distances (Å) and angles (°) for structure at 80°K.

Chloroacetate dimer

The carboxyl group and the α-carbon atom in each chloroacetate radical are approximately coplanar. The least-squares plane of the two carbon and two oxygen atoms of CA(1) is represented by the equation

$$-0{\cdot}5892\,X+0{\cdot}7746\,Y+0{\cdot}2298\,Z=2{\cdot}4820\,,$$

where the direction cosines are referred to the orthogonal axes *a*, *b* and *c**, and *X*, *Y* and *Z* are expressed in Å. The deviations of atoms from the plane are: O(11) −0·006, O(12) −0·006, C(11) −0·005, C(12) 0·017 Å. The Cl(1) atom lies −0·131 Å out of the plane. The equation of the best plane of the two carbon and two oxygen atoms of CA(2) is given by

$$-0{\cdot}6274\,X+0{\cdot}7487\,Y+0{\cdot}2142\,Z=2{\cdot}6646\,,$$

and the deviations of atoms from the plane are: O(21) 0·003, O(22) 0·003, C(21) 0·002, C(22) −0·008 Å. The Cl(2) atom lies 0·301 Å out of the plane.

The conformation of the chloroacetate dimer in the ferroelectric phase shows no definite change as compared with that in the paraelectric phase, including a very short hydrogen-bond distance of 2·457 (16) Å. If in the ferroelectric phase one of the two chloroacetate radicals were in the form of carboxylate (–COO$^-$, fully ionized) and the other in the form of carboxyl (–COOH, neutral), the following tendency would be expected: in a carboxylate group the two C–O bond-lengths and two C–C–O angles are equal, whereas they differ in a carboxyl (Hahn, 1957). Moreover, the length of the OHO hydrogen bond linking the two radicals should show a definite increase as compared with that of the room-temperature structure, in which the hydrogen bond was thought to be most probably of the true symmetrical single-minimum type (Ichikawa, 1972). The bond lengths and angles of CA(1) and CA(2), however, do not show such a systematic tendency (Fig. 2). The length of the OHO hydrogen bond, 2·457 (16) Å, is still close to the 2·432 (5) Å of the room-temperature value and to 2·446 (3) Å, which is the weighted mean for seven type-*A* acid salts (Speakman, 1967). Judging from the results of the present analysis, the chloroacetate dimer at 80°K seems to retain still the same character as that found at room temperature, *i.e.*, a character intermediate between fully ionized and neutral.

Ammonium ion

The nitrogen atom of the ammonium ion is displaced 0·240 Å along the *c* axis from its position on the twofold axis in the paraelectric phase. This shift results in a considerable change in interatomic distances between the nitrogen atom and the oxygen atoms of CA(1) and CA(2) surrounding the nitrogen atom, as compared with the room-temperature structure. In particular, the following variations in the interatomic distances are noted: an increase of 0·221 Å in $N^{iv}\cdots O(12)$, a decrease of 0·225 Å in $N\cdots O(22)$ and a decrease of 0·109 Å in $N^{iii}\cdots O(12)$ (see Table 4).

On the ferroelectric phase transition

The acidic hydrogen atom or the ammonium ion is commonly said to play an important role in the phase transition of hydrogen-bonded ferroelectrics such as KH_2PO_4 and $(NH_4)_2SO_4$. One of the features which AHCA has as a ferroelectric is that the asymmetric unit contains only one acid hydrogen atom and one ammonium ion so that the mechanism of the phase transition should be simpler than for ferroelectrics whose asymmetric units contain more than one of these ions, *e.g.* $(NH_4)_2SO_4$.

The ^{35}Cl nuclear-quadrupole relaxation time T_1 of AHCA, which shows a large dip in the vicinity of the transition temperature, was measured and accounted for by an analysis based on the Ising model assuming order–disorder of the hydrogen atom in a double-minimum potential well (Okuma & Chihara, 1970; Chihara, Inaba, Nakamura, Okuma, Soda & Yamamoto, 1972). The value of the transition entropy is 2·90 (22) JK^{-1} mol^{-1} which is nearly equal to $\frac{1}{2}R \ln 2$, but this measured value cannot be explained by the Ising model (Chihara & Inaba, 1972; Chihara, Inaba, Nakamura, Okuma, Soda & Yamamoto, 1972). Very recently Hadži & Orel (1973) carried out an infrared absorption study of this compound at 293°K and 93°K, and found that no significant change of bands associated with the OHO and carboxyl group vibration occurs. The present results seem to indicate that the hydrogen bonding does not play the role of a trigger for the phase transition, because a hydrogen bond having a symmetrical single-minimum potential cannot be a trigger. This interpretation is compatible with the value of the transition entropy and also with the result of the infrared absorption study.

With reference to the ammonium ion, it seems necessary to begin by investigating whether the electron density of the nitrogen atom at room temperature can be explained by a superposition of two stable sites. For this purpose, two electron-density maps of the nitrogen atom are compared in Fig. 3. Fig. 3(*a*) is the contour map obtained from the photographic data at room temperature (Ichikawa, 1972), where the final R value is 0·070 (0·063 without zero reflexions).† Fig. 3(*b*) is the calculated map, $\varrho'(x,y,z) = \frac{1}{2}\{\varrho(x,y,z) + \varrho(-x,y,\frac{1}{2}-z)\}$, from the electron density $\varrho(x,y,z)$ of the nitrogen atom at 80°K, assuming a disorder distribution satisfying the presence of the twofold axis. This implies that the displacement of the nitrogen atom from the twofold axis is independent of temperature, *i.e.*, a pure order–disorder. The shape of the contours in the two maps should be the same if the above assumption

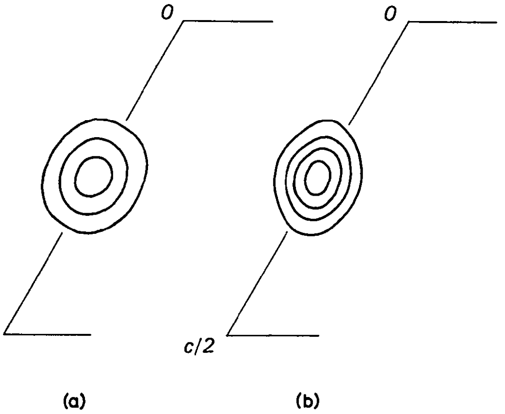

Fig. 3. The electron-density maps of the nitrogen atom viewed along the *b* axis at room temperature (*a*) and the calculated average one at 80°K (*b*). See text for details.

Table 4. *Interatomic distances and bond angles at* 80°K *and at room temperature with their standard deviations*

	80°K	R.T.		80°K	R.T.
C(11)–Cl(1)	1·742 (21)	1·768 (4) Å	Cl(1) –C(11)–C(12)	114·9 (1·1)	113·4 (2)°
C(11)–C(12)	1·444 (19)	1·506 (4)	C(11)–C(12)–O(11)	112·7 (1·2)	111·4 (2)
C(12)–O(11)	1·272 (20)	1·278 (4)	C(11)–C(12)–O(12)	125·0 (1·5)	123·2 (3)
C(12)–O(12)	1·249 (16)	1·225 (3)	O(11)–C(12)–O(12)	122·2 (1·2)	125·4 (3)
C(21)–Cl(2)	1·833 (20)		Cl(2) –C(21)–C(22)	109·3 (1·1)	
C(21)–C(22)	1·589 (19)		C(21)–C(22)–O(21)	108·4 (1·2)	
C(22)–O(21)	1·279 (23)		C(21)–C(22)–O(22)	122·2 (1·5)	
C(22)–O(22)	1·196 (17)		O(21)–C(22)–O(22)	129·4 (1·3)	
O(11)···O(21)	2·457 (16)	2·432 (5)	C(12)–O(11)···O(21)	112·5 (8)	114·8 (3)
			C(22)–O(21)···O(11)	113·9 (8)	
N······O(11)	2·876 (17)	2·926 (4)			
N^{iii} ····O(12)	2·771 (20)	2·880 (3)			
N^{iv}·····O(12)	3·369 (19)	3·148 (3)			
N^{iv}·····O(21)	2·929 (17)				
N^{ii}·····O(22)	2·915 (21)				
N······O(22)	2·923 (17)				

Superscripts refer to atoms at:

(i)	x	y	z	(iii)	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
(ii)	x	$-y$	$\frac{1}{2}+z$	(iv)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$

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† For this comparison, further refinement with photographic data was carried out after the publication of the preceding paper.

holds. The shape of the superposed contours, however, is slightly elongated along the c^* axis in comparison with that at room temperature.

We now consider the temperature factors. The component of the displacement of the nitrogen atom along the c and c^* axes from the twofold axis is denoted by ΔR_c and ΔR_{c*}, respectively, where ΔR_{c*} is expressed by $\Delta R_{c*}=\Delta R_c \cos(\beta-90°)$. Assuming a pure order–disorder, the r.m.s. amplitude of the thermal vibration obtained from the results at room temperature, U^d_{c*}, is expressed by $U^d_{c*}=\Delta R_{c*}+U^o_{c*}$, where U^o_{c*} is the r.m.s. amplitude which would be expected if the nitrogen atom were ordered. This equation can be applied at 80°K as well, and U^o_{c*} can be obtained directly from the present analysis. If the above model is correct, U^d_{c*} is expected to be greater at room temperature than at 80°K. However, at room temperature, U^d_{c*} obtained from B_{33} was 0·296 (8) Å and 0·280 (4) Å from the photographic and the counter data respectively, whereas at 80°K, U^d_{c*} obtained through B was 0·344 (22) Å. Judging from the shape of the contours in Fourier maps (Fig. 3) and the r.m.s. amplitude of thermal vibrations, a pure order–disorder mechanism of the nitrogen atom of the ammonium ion may also be excluded from consideration.

Spontaneous polarization is switched by a change of CA(1) ↔ CA(2). The displacements of each atom during switching are listed in Table 5. It is seen that the displacement of the nitrogen atom is fairly large as compared with those of the other atoms. The value of the spontaneous polarization at 77°K is 0·18 μC cm^{-2} along [102] (Ichikawa & Mitsui, 1966). This is smaller by one or two orders of magnitude compared with well-known ferroelectrics such as $BaTiO_3$, SbSI, $NaNO_2$, KH_2PO_4 and $(NH_2CH_2COOH)_3 . H_2SO_4$ (Landolt–Börnstein, 1969).

Table 5. *Displacements of atoms during switching* (Å)

	Δa	Δb	Δc	Total Δ
Cl(1) ↔ Cl(2)	0·015	0·082	0·038	0·089 (5)
O(11) ↔ O(21)	0·166	0·030	0·219	0·202 (14)
O(12) ↔ O(22)	0·012	0·143	0·004	0·167 (14)
N ↔ N	0·001	—	0·479	0·479 (24)
C(11) ↔ C(21)	0·093	0·044	0·039	0·125 (29)
C(12) ↔ C(22)	0·119	0·054	0·189	0·175 (18)

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