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THE CRYSTAL STRUCTURES OF FERROELECTRIC $NH_4H(ClCH_2COO)_2$ AND ITS RELATIONSHIP ON THE ISOTOPE EFFECT OF THE HYDROGEN BOND

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BY
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Synopsis

The Crystal Structures of Ferroelectric $NH_4H(ClCH_2COO)_2$ and Its Relationship on the Isotope Effect of the Hydrogen Bond

A brief historical description of ferroelectrics and ferroelectric phenomena is given. In this context, a particular significance of the structural studies in ferroelectric $NH_4H(ClCH_2COO)_2$ with a possibility of a single-minimum potential well of the acidic H atom is emphasized. Furthermore, the significance of studying the characteristic of the hydrogen bond and the isotope effect from the viewpoint of the bonding parameters is described.

In chapter II the results of the structure analysis in the paraelectric phase at room temperature are described, in which the final R value was 0.068. It is found that $NH_4H(ClCH_2COO)_2$ has the shortest symmetric hydrogen bond, 2.432(5) Å , connecting two chloroacetate residues among hydrogen-bonded ferroelectrics. It is concluded that the shape of the hydrogen-atom potential is effectively of a single-minimum type and $NH_4H(ClCH_2COO)_2$ is the first example with a single-minimum potential well, from the O...O length and the anomalous characteristic of the infrared spectrum together with the conclusion drawn from the neutron diffraction and spectroscopic data in other Type A acid salts.

In chapter III the results of the structure analysis in the ferroelectric phase at 80 K is given, in which the final R value was 0.106. No appreciable change was found in the conformation of the chloroacetate dimers including the very short hydrogen bond (2.457 Å), whereas a considerable shift in the ammonium ion was observed. The mechanism of ferroelectric phase transition is discussed. The order-disorder model of the acidic hydrogen atom is excluded since the hydrogen atom in a single-minimum potential cannot play the crucial role in the phase transition, in contrast to the order-disorder model adopted usually in hydrogen-bonded ferroelectrics with assumption of a double-minimum potential well such as in KH_2PO_4. The conclusion is compatible with that from other experimental technique mainly by Chihara and coworkers, i.e. the ^{35}Cl nuclear quadrupole resonance frequency and relaxation time, the heat capacity measurement, and infrared and Raman spectra. A possibility of a pure order-disorder mechanism of the nitrogen atom in the ammonium ion was examined, but was ruled out from the consideration of the shape of Fourier map and the r.m.s amplitude of thermal vibrations. This conclusion is also compatible with other experiments.

Chapter IV is related to the correlation between O-H vs O...O distances and the geometric isotope effect ΔR in OHO bonds. Symmetric bonds are continuously distributed at least up to about 2.6 Å, in which the shape of the H atom

potential curve seems to vary continuously from single to double-minimum type with increasing O...O distance, retaining the symmetry requirement. The average correlation curve of asymmetric bonds appears to coincide with 'symmetric' straight line at the shortest limit around 2.4 Å. On deuteration an expansion was seen in the O...O distance range 2.44-2.64 Å.

The equilibrium position of the H atom in symmetric bonds is considered with two correlation curves (O-H vs O...O and ΔR vs O...O) used as empirical basis, under assumption that the potential curve can be expressed as the superposition of two asymmetric bonds. The correspondence is pointed out between two kinds of the isotope effect, i.e. the isotope effect of the distance between two equilibrium positions (or ΔR) and the isotope effect of the transition temperature in hydrogen-bonded crystals which undergo ferro-, antiferroelectric, and other structural phase transitions.

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Chapter IV. The O-H vs O...O Distance Correlation and the Geometric Isotope Effect in OHO Hydrogen Bonds

Chapter I. Introduction

I.1. Ferroelectricity and hydrogen bond

The first ferroelectric, Rochelle salt, was discovered in 1920 and the second, KH_2PO_4(KDP), in 1935. These two crystals were the only two known ferroelectrics before the discovery of $BaTiO_3$ after World War II. Thus, the hydrogen bond was in intimate relations with ferroelectricity from the times that ferroelectricity appeared to be a rare and isolated phenomenon and was considered to be 'one of Nature's great accidents' (B. T. Matthias). It was plausible that not only OHO but NHO hydrogen bond may be important for the occurrence of ferroelectricity and was a clue to searching new ferroelectrics, in the course of the subsequent discoveries of $(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ (GASH), $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS), a number of alums, and $(NH_4)_2SO_4$ and so on. (See, for example, Jona and Shirance,[1)] and Landolt-Bernstein[2)])

Recently the number of known ferroelectrics amounts to a few hundreds, a considerable part of which are yet the hydrogen-bonded ferroelectrics, with various types of the hydrogen bond such as OHO, NHO, ClHCl. Today ferroelectricity is no more isolated phenomenon, but occupies a definite position as a field in the solid state physics and chemistry.

It should be borne in mind here that among many hydrogen-bonded ferroelectrics,

(i) there are a great variety of the hydrogen-bond strength, i.e. the hydrogen-bond length (the distance between a donor and an acceptor atom), and several types of the hydrogen-bond such as OHO, NHO, ClHCl.

I.2. Developement of studies of displacive-type ferroelectrics by the soft-mode concept

The discovery of the third ferroelectric $BaTiO_3$ in 1945-46 was a great step in advance toward a better understanding of ferroelectric phenomeon; its structure is far simpler than that of any other ferroelectric known and is common to large family of compounds called perovskite-type structure. It was shown by Devonshire³⁾ that three successive phase transitions in $BaTiO_3$ can be described phenomenologically by taking the cubic perovskite structure as prototype. In 1960 it was proposed by Cochran4) and also by Anderson5) that the phase transition for the $BaTiO_3$-type ferroelectrics results from an instability of one of the normal vibrational modes of lattice (soft-mode theory). In this theory, the phonon frequency of a particular transverse optic mode ω_{TO} decreases and tends to zero on approaching the transition temperature T_c with

$$\omega_{TO}^2 = A(T - T_o) \quad ,$$

where A is a constant, T_o the paraelectric Curie temperature. At T_c the restoring force for the mode displacement become zero and this soft phonon motion freezes into the static displacement of the low-temperature phase.

The neutron scattering occupies a unique position as a very powerful tool among many experimental technique; it has important advantages in contrast to light and X-ray scattering because the neutron scattering can cover a wide range of Q and the neutron energy $\hbar\omega$ is of the same order of magnitude with phonon in measuring the scattering function $S(Q,\omega)$ by which the dynamical properties of solids can be characterized.6) Experimental development of the neutron inelastic scattering revealed the soft mode condensation of Γ (q = 0) mode at Brillouin zone center in the displacive-type ferroelectrics with perovskite structure such as $BaTiO_3$, $PbTiO_3$, $KNbO_3$, and $KTaO_3$. Furthermore the inelastic neutron scattering made possible the mode determination from intensity analysis, i.e. to obtain the atomic motion involved in the soft mode, in $KTaO_3$ and several other cases.7)

Apart from the perovskite-type displacive ferroelectrics, the soft mode concepts was extended to order-disorder type8) and to zone boundary phonon9); The soft mode condensations at Γ point in order-disorder ferroelectric KD_2PO_4, at M point of Brillouin zone boundary in ND_4Br, at M point in ferroelectric $Tb_2(MoO_4)_3$, at M and R points in perovskite $SrTiO_3$, $KMnF_3$, $NaNbO_3$, $LaAlO_3$ are examples.7) The soft phonons are also observed in other various structural phase transitions; their examples are the Γ mode condensation in quartz, in semiconductor GeTe, SnTe etc., and the transverse acoustic (TA) mode softening in superconductor Nb_3Sn, V_3Si.7) Recently the structural phase transitions in some MX_2-type 2-dimensional metals and in 1-dimensional conductors KCP and TTF-TCNQ are discussed in terms of enhanced Kohn anomaly (acoustic phonon softening at $q = 2\ k_F$) through electron-phonon interaction. Studies along these lines are now in progress and present interesting topics such as 'central modes problem'.10,28)

Thus, the generalization of the soft mode concept brought the unified understanding of the fundamental mechanism of structural phase transitions. It can be said again that ferroelectricity is no more isolated phenomenon, but has many related phenomena and common mechanisms with other field of solid state physics and chemistry, in addition to the well known similarity and dissimilarity to ferromagnetism.

I.3. Anomalously large isotope effects on physical quantities in some hydrogen-bonded ferroelectrics.

In order to understand better the nature of ferroelectricity on the basis of knowledge obtained from the lattice dynamical approach such as the soft-mode concept, knowledge of structural details and chemical-bonding characteristic in individual ferroelectric crystal is necessary; Both approaches may be said to be the complement of each other. Importance of static 'structural' approaches should be emphasized because ferroelectrics have generally complex structure with relatively low symmetry and with many atoms in an asymmetric unit. One of the clues to the unified understanding from the structural point of view may be the hydrogen bonding, as can be seen from (i).

The most striking and dramatic phenomenon in hydrogen=bonded ferroelectrics is anomalous isotope effects on some physical properties such as transition temperature T_c which are seen in some acid salt crystals such as KH_2PO_4 (KDP) type crystals. Transition temperature rises about 100 K by substituting deuterium for hydrogen atom (H→D)11); This isotope effect is very remarkable and not so much precendented over the fields in solid state physics. It seems to be owing to these circumstances that the hydrogen-bonded ferroelectrics mean KDP-type ferroelectrics in a narrow sense.

The first molecular theory of the phase transition in KH_2PO_4 was proposed by Slater in 1941,12) where he assumed prior to experimental evidence that each proton, which is contained in the OHO bond linking neighbouring PO_4 groups, takes one of two positions in a double-minimum potential well (order-disorder model). After about a decade, Bacon and Pease[13)] showed by neutron-diffraction structure analysis that an average density distribution of proton changes remarkably through the transition temperature; this result was compatible with Slater's assumption. Furthermore, in order to explain the large isotope effect, Blinc[11)] and subsequently Tokunaga and Matsubara[14, 15)] proposed a proton tunneling model in which proton is assumed to make a tunneling motion between two minima of the double-minimum potential well. Subsequently Kobayashi[15)] took into consideration the coupling between transverse optic mode in K-PO_4 ion and the tunneling motion of proton (spin-phonon coupling).[17)] Thereafter very extensive experimental and theoretical work has been reported. However, the problem of the origin of anomalously large isotope effect is still one of the main problems in the fields of ferroelectricity today, but does not attain to the complete understanding.[18, 19)]

Assumptions used in the theories of phase transition of KH_2PO_4, i.e. that the proton is distributed in a double-minimum potential and that proton play a crucial role (trigger) in phase transition, seem to exert farreaching influence on the phase-transition mechanism of the other general hydrogen-bonded ferroelectrics explicitly or implicitly. For example, the same phase transition mechanism as KDP was proposed in TGS by Hoshino, Okaya and Pepinsky.[20)] However, recently Fletcher, Keve and Skapski state that it is difficult to accept any major role attributed to proton in the short hydrogen bond connecting two glycine molecules as the motive force for the phase transition.[21)] It should be stressed here again that next points are assumed in the KH_2PO_4 theories;

(ii) the potential shape is of a double-minimum type,

(iii) the hydrogen-bond length O...O or the potential shape of the proton does not change by H→D.

B. T. Matthias states in the paper[22)] with the title of "Ferroelectricity: Why did it take so long?" that "Very often in science a mistaken notion expressed by one or a few investigators has had a very decisive influence for an inordiately long time afterwards both on the correct and incorrect work of a great many hundred believers. Again and again this has happended".

I.4. A peculiar significance of ferroelectrics with the potential curve of single-minimum type

The shape of the potential curve may probably be of single-minimum type in the very short hydrogen bond, where the hydrogen atom cannot be a trigger of the phase transition. Thus, it may be possible that the role of the phase transition differs in each compound; some may play the crucial role (a trigger), but some play only the secondary role, since the hydrogen bond, involved in many hydrogen-bonded ferroelectrics, are full of variety.

The potential of hydrogen atom of a single-minimum type is supposed to be realized in the FHF hydrogen bond (See, for example, Hamilton and Ibers$^{23)}$). With reference to the OHO system, a group of acid salts of carboxyl acids, classified as Type A and A_2, attracts particluar attention.$^{24)}$ Firstly, Type A and A_2 acid salts involve most of the shortest OHO bonds so far measured, whose O...O length are concentrated with a mean of 2.445(2)Å and 2.450(2)Å respectively. Secondly, the conclusion with respect to the potential shape, obtained from neutron diffraction and spectroscopic techniques, is converged into the opinion that

(iv) in all type A acid salts, the hydrogen bond has the potential curve of effectively single-minimum type.

Furthermore, it has been found by us$^{25)}$ that

(v) ammonium hydrogen bis-chloroacetate, $NH_4H(ClCH_2COO)_2$, is a member of Type A acid salts and exhibits ferroelectricity.

These results strongly suggest the possibility that $NH_4H(ClCH_2COO)_2$ has also a very short hydrogen bond as in all other members of Type A acid salts, and this compound offers the first example of ferroelectrics with a single-minimum potential, where the hydrogen bond is too short to play the role as trigger of the phase transition. Thus, the experimental verification of the hydrogen-bond structure by the crystal structure analysis of $NH_4H(ClCH_2COO)_2$ seems indispensable for further and more general understanding of the phase-transition mechanism in hydrogen-bonded ferroelectrics.

I.5. Correlations between hydrogen-bond parameters and geometric isotope effect in OHO hydrogen bonds

From now discussion is restricted within the OHO bond because much data are available, there are full of variety in the OHO bond, and present interest is concentrated on the short and very short bond. It is commonly said that, as illustrated in Fig.1 the potential function for a hydrogen atom in a hydrogen bond may be characterized qualitatively by one of the curves, which may perhaps be determined by the factors as the O...O distance, symmetry and surroundings of the hydrogen bond. Hydrogen-bond parameter, such as O-H, H...O, O...O length and OHO angle, can be obtained by X-ray and neutron-diffraction structure analyses. But X-ray data are inadequate because of inaccuracy of the hydrogen-atom position. The existence of correlation between O-H and O...O length was first pointed out by Nakamoto, Margoshes and Rundle$^{26)}$ in 1955; the O-H decreases with increasing the O...O distance. Since then correlations between hydrogen-bond parameters has been refined according to the accumulation of data at that time, and seems well established in an intermediate and long region of O...O distance. However,

(vi) for the short and very short region, about

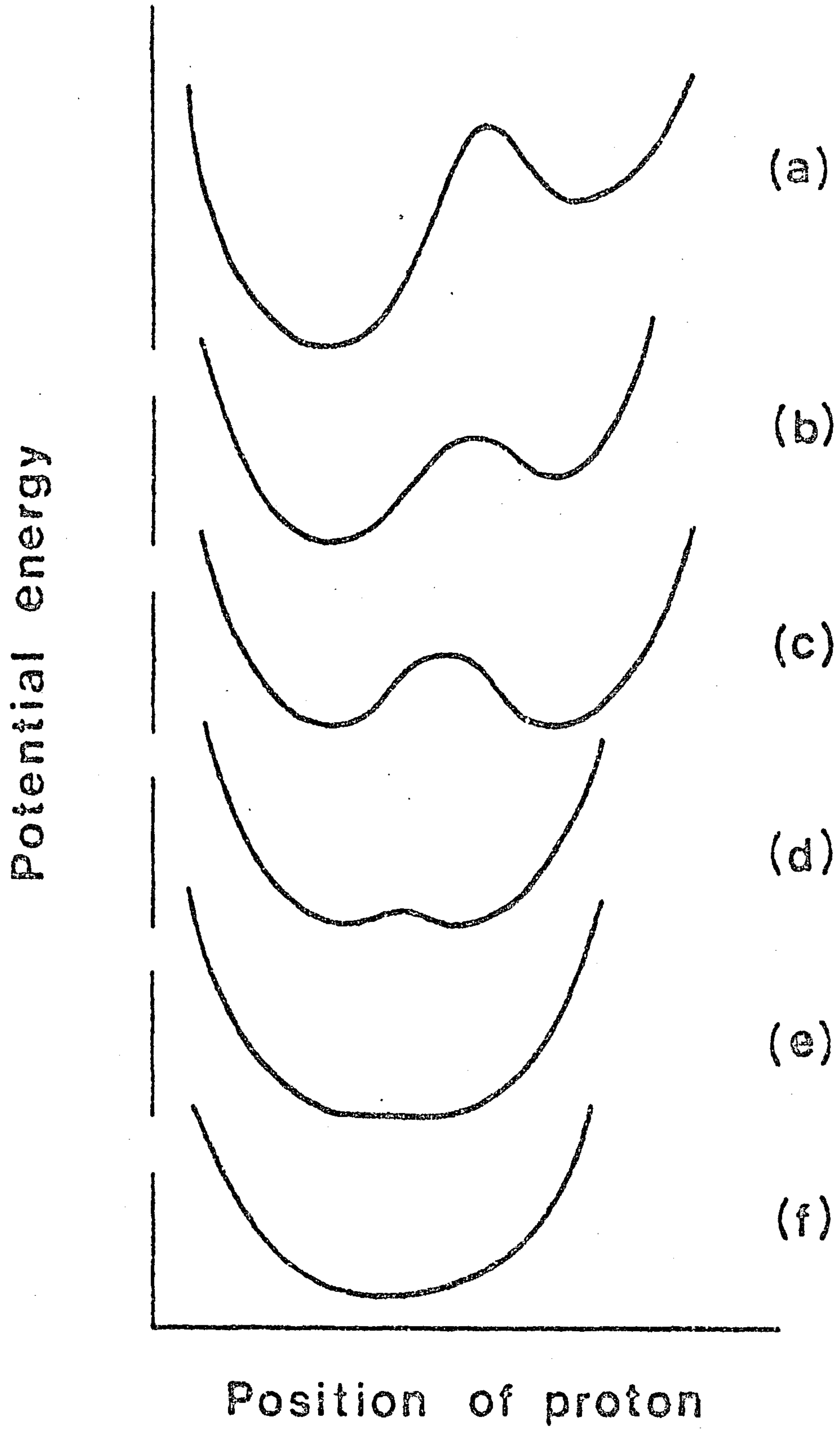

Fig. 1. Schematic illustration of possible potential energy curves for OHO bonds, assumed to be characteristic of different O...O length.

O...O $<$ 2.6 Å, the correlation remain unsettled with respect to the dependence on the O...O distance and symmetry of the hydrogen bond.

This may probably be partly because the compounds having the short and very short hydrogen bond are rare, partly because both of the facilities and precision of neutron diffraction structure analyses were insufficient yet for present purpose.

The other key problem from structural aspects is a geometrical isotope effect, i.e. the variation of the O...O distance when deuterium is substituted for hydrogen. From about four decades before, it has been pointed out by Ubbelohde and co-workers[27)] that an expansion of the O...O distance is observed. However,

(vii) there is uncertainty about whether the size of the geometric isotope effect exhibits the O...O dependence and how large is it.

This circumstances seem to arise from that magnitude of the effect is usualy as small as $\sim 10^{-2}$ Å and thus an accuracy of $\sim 10^{-3}$ Å are required in both of the hydrogen and the deuterium compounds.

I.6. Scope of this paper

Generally speaking, what role the hydrogen bond plays in the phase transition of hydrogen-bonded ferroelectrics and other related materials? Where anomalously large isotope effects results from?

In order to elucidate these problems, as emerge from (i) ~ (vii) described above, first of all the next points may be indispensable:

(1) to verify experimentally an example of ferroelectrics with the hydrogen-atom potential of a single-minimum type, i.e. the crystal structure analysis of ferroelectric $NH_4H(ClCH_2COO)_2$ at present.

(2) to establish the characteristic of the potential shape of the hydrogen atom under the condition of a definite O...O distance, symmetry of the hydrogen bond, together with the information from spectroscopic measurements.

(3) to build up the details of the geometric isotope effect on the O...O distance and other factors dependence.

(4) to consider the phase-transition mechanism for the explanation of observed physical quantities on the basis of the latest information of the hydrogen-bond structure, such as, from (2) and (3).

(5) to find out the condition and origin of the anomalous isotope effect.

Studies of this paper have been performed under the strategy described above.

References

1) F. Jona and G. Shirance: Ferroelctric Crystals (The Macmillan Company, New York, 1962).

2) T. Mitsui: Landolt-Börnstein. Numerical Data and Functional Relationships in Science and Technology ed. K. -H. Hellwege and A. M. Hellwege (Springer, Berlin, 1969) New Series III/3. Ferro- and Antiferroelectric Substances.

3) A. F. Devonshire: Phil. Mag. 40 (1949) 1040; Advances in Phys. 3 (1954) 85.

4) W. Cochran: Advances in Phys. 9 (1960) 387.

5) P. W. Anderson: Fizika dielekrikov, ed. G. I. Skanavi (Acad. Nauk SSSR, Moscow, 1960) 290.

6) W. Cochran: The Structures and Properties of Solids 3 The Dynamics of Atoms in Crystals (Edward Arnold, London, 1973) Chap.5.

7) G. Shirane: Rev. mod. Phys. 46 (1974) 437.

8) W. Cochran: Advances in Phys. 10 (1961) 401.

9) W. Cochran and A. Zia: Phys. Status Solidi 25 (1968) 273.

10) Anharmonic Lattices, Structural Transitions and Melting, ed. T. Riste (Noordhoff, Leiden, 1974).

11) R. Blinc: J. Phys. Chem. Solids 13 (1960) 204.

12) J. C. Slater: J. Chem. Phys. 9 (1941) 16.

13) G. E. Bacon and R. S. Pease: Proc. Roy. Soc. A220 (1953) 397; A230 (1955) 359.

14) M. Tokunaga and T. Matsubara: Progr. Theor. Phys. **35** (1966) 581.

15) M. Tokunaga: Progr. Theor. Phys. **36** (1966) 857.

16) K.K. Kobayashi: J. Phys. Soc. Japan **24** (1968) 497.

17) W. Cochran: Advances in Phys. **18** (1969) 157.

18) M. Tokunaga: Ferroelectrics **1** (1970) 195.

19) G. A. Samara: Ferroelectrics **5** (1973) 25.

20) S. Hoshino, Y. Okaya and R. Pepinsky: Phys. Rev. **115** (1959) 323.

21) S. R. Fletcher, E. T. Keve and A. C. Skapski: Ferroelectrics **14** (1976) 775; **14** (1976) 789.

22) B. T. Matthias: Ferroelectrics **16** (1977) 21.

23) W. C. Hamilton and J. A. Ibers: *Hydrogen Bonding in Solids* (Benjamin, New York, 1968) Chap.3.

24) J. C. Speakman: Structure and Bonding **12** (1972) 141.

25) M. Ichikawa and T. Mitsui: Phys. Rev. **152** (1966) 495.

26) K. Nakamoto, M.Margoshes and R. E. Rundle: J. Amer. Chem. Soc. **77** (1955) 6480.

27) J. M. Robertson and A. R. Ubbelohde: Proc. Roy. Soc. London. **A170** (1939) 222; A. R. Ubbelohde: Proc. Roy. Soc. London. **A173** (1939) 417; A. R. Ubbelohde and I. Woodward: Proc. Roy. Soc. London. **A179** (1942) 399.

28) R. Blinc and B. Zeks: *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974)

Chapter II. The X-ray Crystal Structure Analysis of Ferroelectric $NH_4H(ClCH_2COO)_2$ of the Paraelectric Phase at Room Temperature

II.1. Introduction

It has been discovered that ammonium hydrogen bis (chloroacetate) $NH_4H(ClCH_2COO)_2$, is ferroelectric below 128 K.[1) This compound belongs to acid salts MHX_2 of monocarboxylic acid HX. It is known that a group of MHX_2 compounds called Type A involve the very short hydrogen bond connecting two X with the hydrogen-atom potential of single-minimum type.[2) Ferroelectric $NH_4H(ClCH_2COO)_2$ is of a particular interest in connection with the phase-transition mechanism and the hydrogen-atom potential function in OHO bond, since ordinarily the phase-transition mechanism of hydrogen-bonded ferroelectrics with short hydrogen bonds are interpreted in terms of order-disorder model, where the hydrogen positions are assumed to be distributed between double minima in the potential functions.

With a special attention to the hydrogen-bond structure, a three dimensional X-ray crystal structure analysis of the paraelectric phase has been carried out at room temperature.[3)

II.2. Experimental

Crystal data

The crystal data of ammonium hydrogen bis (chloroacetate) are given in Table 1, of which preliminary results were previously reported.1) Unit-cell parameters at room temperature were obtained from a least-squares treatment, using values of θ for 74 high angle reflections measured on zero-layer Weissenberg photographs taken around each crystallographic axis with CuKα radiation. In this procedure, the systematic errors due to inaccurate value of Weissenberg camera radius and due to shrinkage of X-ray films are corrected using Al as standard material. Systematic errors from deviation of specimen from the center of the camera and due to other causes were taken into consideration by adding a term proportional to $\sin 2\theta$ in the observation equations.

Data collection

Two sets of three-dimensional intensity data were used in this work; one is phtographic data and other is diffractometer data. The first set was obtained from equi-inclination Weissenberg photographs taken with CuKα radiation using the multiple film technique about a, b, and c axes. Following efforts were directed to obtain accurate data. Integrated Weissenberg photographs with seven films were taken with exposure of 60 KV, 100 mA, and

Table 1. Crystal data

a = 10.521 (4) Å
b = 11.576 (4)
c = 8.387 (3)
β = 119.48 (3) °
V = 889.2 (5) Å^3

Formula : $NH_4H(ClCH_2COO)_2$
Space group $C2/c$
F. W. 206.0
ρ_m = 1.528 $g.cm^{-3}$
ρ_c = 1.538 $g.cm^{-3}$
F(000) = 424
Z = 4
$\lambda(Cu\ K\alpha_1)$ = 1.5405 Å

about half a day. As many photographs as possible were taken to get the reliable scaling factors and many number of reflections, as far as the camera setting is permitted, i.e. layer: $h = 0 \sim 6$; $k = 0 \sim 7$; $l = 0 \sim 5$. Cylindrical crystals with dimension of 0.22~0.24 mm in diameter were used. The intensities were measure by visual comparison with a calibrated scale. They were corrected for Lorentz and polarization factors, absorption correction being applied (μCuKα = 63 cm^{-1}). Absorption correction factors used for calculation were taken from International Tables for X-ray Crystallography. 4) Corrections for the elongation of spots on the high layers were made according to Phillips.5) The data from each layer were correlated by the method of Rollett and Sparks6) and then placed on an absolute scale by Wilson's method.7) A total of 738 independent reflections were obtained, of which 227 were too weak to be measured.

The second set of data were obtained on a Rigaku Denki automatic four-circle diffractometer, AFC, controlled by a FACOM 270-20 computer. A spherical crystal with dimension of 0.35 mm in diameter was used. Integrated intensities were collected for $2\theta \leq 70°$ by the $\omega - 2\theta$ scanning technique with Mo Kα radiation monochromatized with a LiF crystal. A scanning speed of 2° per minute was employed and the scanning range varied by $\Delta 2\theta = 2° + 0.8° \tan\theta$. Background was measured for twenty seconds at the beginning and at the end of each scan.

As a check on the stability of the crystal and the instruments, three standard reflections were measured every fifty reflections: no singificant variation in their intensities was noted. No correction was made for absorption (μMoKα = 7.0 cm^{-1}). A total of 1967 reflections were measured, of which 706 had the $|F_o|$ values less than three times its standard deviation derived from counting statistics, and were given the value of zero. The calculation of the unit-cell parameters and the whole processing of intensity data were carried out on a HITAC 5020E computer with UNICS.[8)]

II.3. Determination and refinement of the structure

Phase determination

As is well known, electron-density distribution $\rho(x,y,z)$ is expressed by

$$\rho(x,y,z) = \frac{1}{V}\sum_h\sum_k\sum_l F(hkl)\exp[-2\pi i(hx + ky + lz)]$$

, where V is unit-cell volume, (hkl) indicates Miller indices. However, we can not obtain directly the structure factor F(hkl), since F(hkl) is usualy complex and only the magnitude $|F(hkl)|$ is known from intensity measurements;

$$F(hkl) = \left|F(hkl)\right| \exp\left[i\alpha(hkl)\right] \quad .$$

Thus it becomes nesessary to know the phases $\alpha(hkl)$; This is called 'phase problem' and is essentially one of the key problems for structure determination. This problem is now developing.

One of the important situations in which the phases can be determined is that the compound involves a heavy atom, whose scattering power dominates, and controls some or all phases. Then the structure factor is written by

$$F(khl) = \sum_{H=1}^{Z} f_H \exp[2\pi i(hx_H+ky_H+lz_H)] + \sum_{j=1}^{N-Z} f_j \exp[2\pi i(hx_j+ky_j+lz_j)] \quad ,$$

where Z and N denote the number of heavy atoms and total atoms in unit cell respectively, f_H and f_j are atomic scattering factors of heavy atom and other light atoms respectively, (x_H, y_H, z_H) and (x_j, y_j, z_j) are the position of heavy atoms and other light atoms respectively. The first term on the right hand side expresses the contribution of heavy atoms and the second is that of other light atoms. On the other hand the phase $\alpha(hkl)$ is given by

$$\alpha(hkl) = \tan^{-1} \frac{\sum f_H \sin 2\pi(hx_H+ky_H+lz_H) + \sum f_j \sin 2\pi(hx_j+ky_j+lz_j)}{\sum f_H \cos 2\pi(hx_H+ky_H+lz_H) + \sum f_j \cos 2\pi(hx_j+ky_j+lz_j)} \quad .$$

If the light atoms are distributed in relatively uniform fashion, it will be expected that the second terms in a numerator and a denominator cancel each other. Then the phase $\alpha(hkl)$ will be approximately equal to the phase $\alpha_H(hkl)$ from heavy atoms only:

$$\alpha(hkl) \simeq \alpha_H(hkl) \quad .$$

Thus the phases can be obtained if we know the heavy-atom position. Fourier synthesis with the heavy-atom phases reveals the positions of other atoms and ordinarily several Fourier syntheses with the phases refined successively lead to satisfactory results. This method for the phase determination is called 'heavy atom method'.[9)] It is roughly said that the heavy atom method is good approximation when

$$\sum f_H^2 \sim \sum f_j{}^2$$

holds.

One way of locating of the heavy atom is with the aid of Patterson synthesis. The Patterson function is defined as

$$P(u,v,w) = \int_0^1 \int_0^1 \int_0^1 \rho(x,y,z)\rho(x+u,y+v,z+w)V dx dy dz$$

and can be represented by Fourier series

$$P(u,v,w) = \frac{1}{V}\sum_h \sum_k \sum_l |F(hkl)|^2 \exp[-2\pi i(hu+kv+lw)] \quad .$$

Patterson function is an auto-correlation function of electron density, which is obtainable directly from experiment, and gives the vector distance between every pair of atoms in a unit cell. Thus, the peaks showing the distance between heavy atoms is far and away high among the peaks of other various pair of atoms, from which the heavy-atom position is obtained.

Refinement procedure

The phase determination and successive Fourier syntheses for structure determination were performed along the line described above; for $NH_4H(ClCH_2COO)_2$ has the heavy atom Cl, which satisfies the suitable condition for heavy atom method. The structure determination was initiated using the photographic data. The coordinates of the chlorine atoms were determined from a three-dimensional sharpened Patterson function. Four cycles of Fourier iterations led to an R value ($\sum \left| k|F_o| - |F_c| \right| / \sum k|F_o|$) of 0.26. Refinement was carried out using a block-diagonal least-squares method for positional parameters, and individual isotropic and anisotropic temperature factors. The quantity minimized was $\sum w(|F_o| - 1/k|F_c|)^2$. A difference Fourier syntheses revealed all the hydrogen atoms at the expected positions.

At this stage the diffractometer data became available and subsequent least-squares calculations were performed with these data. The starting parameters were those obtained in the final cycle of the isotropic refinement using photographic data. Refinement was carried out on the coordinates of heavy atoms with anisotropic temperature factors and on the coordinates of hydrogen atoms with isotropic temperature factors. The temperature factor of H(3) atom, however, was given a fixed value of the overall temperature factor, because its value was found to be unusually large. All parameter shifts were less than one tenth of their standard deviations in the final cycle. The standard deviations of the parameters were calculated from the sum of the weighted residuals and the diagonal terms of the inverse matrix of the normal equations. Unit weight was assigned for all the reflections, except those with zero intensity and five strong refletions which are likely affected by extinction; these five reflections were given zero weight in the refinement. The damping factor of 0.8 was applied to the scale factor, the overall temperature factor and also to the parameters of the heavy atoms, and 0.1 to those of the hydrogen atoms. The final R value for the counter data was 0.068 (0.070 for photographic data). Atomic scattering factors were taken from International Tables for X-ray Crystallography.4)

Fourier, least-squares, bond-length and bond-angle, and best-plane calculations were done on a HITAC 5020E and a FACOM 230-60 computer with UNICS.5) The final positional parameters and temperature factors are given in Tables 2 and 3 respectively, together with their standard deviations

Table 2. The atomic positional parameters and their standard deviations (e.s.d.'s in Å)

	x	y	z	σ(x)	σ(y)	σ(z)
Cl	0.1842	0.4237	-0.0607	0.0011	0.0011	0.0010
O(1)	0.1770	0.2548	0.3340	0.0025	0.0023	0.0025
O(2)	0.3401	0.3781	0.3363	0.0021	0.0019	0.0021
N	0.0000	0.0453	0.2500	—	0.0032	—
C(1)	0.1161	0.3404	0.0575	0.0034	0.0034	0.0037
C(2)	0.2242	0.3255	0.2580	0.0028	0.0025	0.0032
H(1)	0.2500	0.2500	0.5000	—	—	—
H(2)	0.0727	-0.0045	0.2366	0.0386	0.0362	0.0392
H(3)	0.0351	0.0820	0.3521	0.0418	0.0349	0.0361
H(4)	0.0906	0.2678	-0.0055	0.0391	0.0353	0.0376
H(5)	0.0283	0.3785	0.0479	0.0447	0.0366	0.0417

Table 3. The temperature factors and their standard deviations ($\times 10^4$).

The anisotropic temperature factors are of the form : $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$. The temperature factors for hydrogen atoms are isotropic B (Å^2).

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Cl	144	1	127	1	207	2	-69	2	76	2	98	2
O(1)	140	3	96	2	243	5	-107	4	182	6	8	5
O(2)	92	2	69	2	193	4	-48	3	121	5	-4	4
N	80	3	55	2	291	9	0	-	126	9	0	-
C(1)	106	3	92	3	232	7	-61	5	84	8	30	7
C(2)	89	3	54	2	208	5	-21	4	133	7	-16	5
H(1)	8.1	(1.9)										
H(2)	3.7	(0.8)										
H(3)	4.1	(-)										
H(4)	3.6	(0.8)										
H(5)	4.7	(0.9)										

and list of $|F_o|$ and F_c values for the counter data is given in Table 4 (for photographic data in Table 5). In Fig.1 a composite drawing of a three-dimensional electron-density map is shown, while in Fig.2 that of a difference map is shown, for which the contributions of the hydrogen atoms were excluded from the calculated structure factors.

II.4. Description of the structure

Type-A acid salts

The structure viewed along a and b axes is shown in Figs.3 and 4, respectively. A layer of ammonium ions, lying in the $(40\bar{4})$-planes, has a layer of chloroacetate residues on either side, or vice versa, and the packing between the ammonium ion and the chloroacetate residue is dominated by a three-dimensional network of hydrogen bond. Moreover, two chloroacetate residues are related to one another by a symmetry center, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. According to Shrivastava and Speakman, these structural features of ammonium hydrogen bis (chloroacetate) are the characteristic of acid salts, MHX_2, of monocarboxylic acid, HX, belonging to Type A. In Type B two acidic radicals are crystallographically distinct. Type-A acid salts found so far are summarized in Table 6.

Table 4. Observed and calculated structure factors (× 10) for the counter data.

```
  K  FO  FC
H,L=  0   0
  2  75 -59
  4 462-464
  6 506-500
  8  64 -53
 10 145-141
 12 113 107
 14  40 -44
 16  35  31
 18  24  14
H,L=  1   0
  1 145-127
  3 285 307
  5  52 -34
  7 158 153
  9  94  93
 11  73 -73
 13  97 -97
 15  22  11
H,L=  2   0
  2 320 320
  4 227 229
  6 331 325
  8  39  33
 10  40 -40
 12 133-133
 14  22  26
 16  35 -26
H,L=  3   0
  1 756 749
  3 211 194
  5  40  28
  7 454-452
  9 272-278
 11  65  65
 13  89  98
 15  33 -32
H,L=  4   0
  2 131 131
  4 162 155
  6  18  20
  8 149-143
 10  44  46
 12  23  17
 14  46 -49
 16  30  -6
H,L=  5   0
  1 233-233
  3  20 -31
  5 170 174
  7 220 208
  9  44  45
 11 124-123
 13  50 -54
 15  23  -9
H,L=  6   0
  0 681 669
  2 161 161
  4  43 -36
  6 359-367
  8  23  21
 10  57 -58
 12  30 -26
 16  32  24
H,L=  7   0
  1 203 219
  3 105 -99
  5 130-133
  7  39  43
  9  30 -21
 11  29  24
 13  32 -37
H,L=  8   0
  0 202-203
  2  72 -70
  6 270 275
  8  29 -20
 10  29 -31
 12  55 -49
 14  30  -9
H,L=  9   0
  1  23  13
  3 204 206
  7 161-155
  9  24 -19
 11  51 -49
H,L= 10   0
  0  67  61
  2  43  43
  6  49 -49
  8  43 -38
 10  31 -17
 12  43  37
H,L= 11   0
  1  36 -33
  3  36 -38
  5  61  76
  7  35  36
  9  31 -15
H,L= 12   0
  0  52  50
  2  37  38
  6  54 -51
 12  43 -30
H,L= 13   0
  1  61  59
  5  55 -51
  7  28   8
H,L= 14   0
  6  39  31
H,L=-15   1
  3  58 -45
H,L=-13   1
  3  33  18
  5  28  -6

  K  FO  FC
  7  31 -23
  9  25  74
H,L=-12   1
  2  51 -55
  4  50 -51
  6  37 -51
  8  37 -78
 10  56  62
H,L=-11   1
  1  95  93
  3  67  76
  5 102-104
  7  25  -5
  9  66 -63
 13  37  77
H,L=-10   1
  4  95  95
  8  26 -15
 10  59 -56
H,L= -9   1
  1 170-172
  3 337-340
  5  36  34
  7  33 -35
  9  61  66
 11  31   0
H,L= -8   1
  4 109-115
  8  52 -48
 10  49 -47
 12  45  -9
 14  53  52
H,L= -7   1
  1  74  57
  3 270 264
  5  23  14
  7  23  24
  9 123-126
 11  34 -39
H,L= -6   1
  2 118-125
  4 379-370
  6 228-228
  8  97  88
 10 174 167
H,L= -5   1
  1 149-138
  3 139 130
  5 260-253
  7 277-276
 11 120 130
 13  29 -27
 15  27  25
H,L= -4   1
  2 357 360
  4 397 374
  6  69  71
  8 137-140
 10 248-251
 12  39  35
 14  22  15
H,L= -3   1
  1 232 227
  5  94 -96
  7 133 126
  9 166 154
 11 108-120
 13  87  86
H,L= -2   1
  4 163-150
  8 153-134
 10  96  97
 14  31  23
 16  39  41
H,L= -1   1
  1  36  38
  5  28 -22
  9 309-305
 11  67 -67
 15  58  57
H,L=  0   1
  2 435 425
  4 757-762
  6 310-302
  8 102  90
 10  64  70
 12  45  43
 16  28 -31
 18  30  33
H,L=  1   1
  1 405-406
  3 548-560
  5 416-406
  7 274-267
  9 168 169
 11 167 172
 15  29 -29
H,L=  2   1
  2 643 647
  4 507 499
  6 115-114
  8 161-161
 10 108-107
 12  67 -75
 16  55  56
H,L=  3   1
  1  81 -73
  3 577-558
  5 146 148
  7  35 -40
  9  41 -42
 11  55 -63
 13  65  64
H,L=  4   1
  2 652-655

  K  FO  FC
  4 544-545
  6  25  21
  8 149 153
 12  59  54
 14  24  24
H,L=  5   1
  1  97 -96
  3 470 403
  5  32  22
  7  33  29
  9 173-175
 11  24 -30
 13  29 -22
 15  45  45
H,L=  6   1
  2  57  54
  4 112 122
  6 109-114
  8 196-201
 10  75  78
H,L=  7   1
  1 101 102
  3 245-241
  5 301-291
  7  21 -14
  9 129 131
 11  29  21
 13  34  28
H,L=  8   1
  2 103  98
  4  50  39
  8  23 -10
 10  44 -48
H,L=  9   1
  1  41 -41
  3  26  15
  5  81  84
  7  90 -94
  9  29 -30
 15  31  31
H,L= 10   1
  2 122-123
  4 131-131
  6  31 -21
  8  57  53
H,L= 11   1
  1  26 -29
  7  37  39
  9  62 -51
H,L= 12   1
  2  34  46
  4  33  23
  6  24 -22
  8  47 -46
H,L= 13   1
  5  30 -28
  7  31 -37
H,L=-14   2
  0  35 -32
  6  29 -35
  8  52  52
H,L=-13   2
  1  49  48
  3  53 -49
  7  41 -39
 11  37  31
H,L=-12   2
  0 117-118
  6  65  64
  8  34 -35
H,L=-11   2
  1 175-176
  3  69  63
  7  31  31
  9  32  33
 11  29  30
H,L=-10   2
  0 183 181
  2  30 -29
  4  43 -37
  6  86 -85
  8  26 -10
 12  49  59
 14  29  27
H,L= -9   2
  3  77 -75
  5  45  42
  7  64  49
H,L= -8   2
  0 117-122
  2 191-190
  4 108-114
  6 137 129
  8 196 199
 10  44  47
 14  33 -32
H,L= -7   2
  1 199 197
  5 261-259
  7 152-145
  9 129 128
 13  74  66
H,L= -6   2
  0 448-454
  2 211 197
  4  75  69
  6  94  92
  8 210-218
 10  71  65
 16  32   7
H,L= -5   2
  1 740-729
  3 204-204
  5 503 495
  7 332 319

  K  FO  FC
  9 109-107
 11  94  94
 15  37 -40
H,L= -4   2
  0 196 206
  2 131-102
  4 226 220
  6 542-526
  8 105 114
 10  32  27
 12  98  88
 14  54  51
H,L= -3   2
  1 255 227
  3  36  30
  5 268-265
  7  91 -96
  9  61  48
 11  28 -26
 13  27  24
 15  42  48
H,L= -2   2
  0 371-369
  2 767-778
  4 540-526
  6 750 735
  8 279 287
 12  63 -60
 14  52 -59
 18  29  19
H,L= -1   2
  1  53  56
  3 116-118
  5 324-307
  7 149-134
  9 167 171
 11  67  62
H,L=  0   2
  0  53  47
  2 453 431
  4 217-225
  6 254-251
  8 179-187
 10  22  19
 12  48  56
 14  86  93
 16  32 -19
 18  34 -13
H,L=  1   2
  3  94  81
  5 530 524
  7 229 222
 11  23  19
 15  26 -18
H,L=  2   2
  0  84  84
  2 524-512
  4 344 325
  6 116-113
  8  19  -4
 12 119 115
 14  32 -35
H,L=  3   2
  1 524 515
  3 111-114
  5 378-366
  7 132-129
  9  44 -36
 11  74  73
 13  49  49
 15  29  24
H,L=  4   2
  0 635-623
  2  31 -15
  4 147-135
  6 136 125
  8 229 229
 10  98 105
 12 120-120
H,L=  5   2
  3 234-229
  5  65  65
  7 125 127
  9  38  34
 11  24 -21
H,L=  6   2
  0 310 309
  2  91  92
  4 109-114
  6  92 -91
  8 129-131
 12  78  82
H,L=  7   2
  1 278-267
  3 105 109
  5  56  56
  9  78  73
H,L=  8   2
  0 116-126
  2 118-123
  4  90  94
  6  60  63
  8  40  36
 10  32 -34
 12  33  29
H,L=  9   2
  1 100 103
  5  60 -66
  7  68 -63
 11  60  63
H,L= 10   2
  0  33 -24
  4  63 -69
  6  23  12
  8  38  36

  K  FO  FC
 10  44  43
H,L= 11   2
  1  42 -44
  3  29 -27
  7  48  43
  9  36  32
 11  35 -26
H,L= 12   2
  8  25  -5
H,L=-14   3
  2  27  37
  4  76  71
H,L=-13   3
  1  66  67
  7  40  27
  9  38  37
H,L=-12   3
  2  50 -41
  6  23  22
H,L=-11   3
  1  28 -30
  3  92  88
  5 116 117
  7  24  19
  9  52 -53
 11  41 -43
H,L=-10   3
  2  68 -67
  6 114 117
  8  61  64
 12  51 -58
H,L= -9   3
  1  28 -37
  3  64 -59
  5 152-163
  7  96  93
  9  28  21
 11  73  74
 15  29 -23
H,L= -8   3
  2 409 406
  4 214 207
  6 132-123
 10  60 -49
 14  29 -13
H,L= -7   3
  1 126 119
  3  78  78
  5 338 337
  7 151-151
  9 130 126
 13  67 -66
 15  45 -36
H,L= -6   3
  2 236-223
  4 342-335
  6  77  75
  8  99  96
 10  77  85
 12  52  54
 14  25   3
 16  45 -51
H,L= -5   3
  1  36  34
  3 378 363
  7 202 208
  9 204-196
 11  96 -88
 13  49  57
 15  32  29
H,L= -4   3
  2 264-250
  4 549 532
  6 381 380
  8  60 -56
 10  33 -48
 12  79 -89
H,L= -3   3
  1 268-266
  3 460-454
  5 305-294
  7 163 152
  9 232 230
 11  86  89
 13  42 -41
 15  24 -12
H,L= -2   3
  2 741 730
  4 218 206
  6 198-169
  8  24 -16
 10  44 -26
 12  54  63
H,L= -1   3
  1 886 877
  3 477 472
  5 475 467
  7 167-163
 11  66 -72
 15  52 -46
 17  25  12
H,L=  0   3
  2 444-449
  4 329-325
  6  77 -72
  8 207 202
 10 203 192
 14  31 -32
 18  28 -23
H,L=  1   3
  1 602-578
  3 100  90
  5  82  84
  7 160 161
  9 121-111

  K  FO  FC
 11  34  34
 15  30  15
H,L=  2   3
  2 465 448
  4 249 238
  6 329 323
  8  32 -15
 10 208-215
 12  43 -43
 14  45  48
H,L=  3   3
  1 183-185
  3 307-309
  5  49 -36
  7  57  64
  9 118 114
 11  38  42
 15  26 -22
H,L=  4   3
  2  92 -96
  4  88  85
  6  80 -80
 10 113 126
 14  38 -45
H,L=  5   3
  1 418 419
  3 343 340
  5  82  80
 11  72 -67
H,L=  6   3
  2  52 -56
  4  74 -71
  8  47  50
 10  26  23
 12  31  29
 14  35 -24
H,L=  7   3
  1 161-168
  3  67 -73
  5  26 -24
  7  58  67
  9  35  37
 11  26  24
 13  36 -35
H,L=  8   3
  2  82  83
  4 116 113
  6  93  91
  8  28 -23
 10  49 -47
 12  36 -32
H,L=  9   3
  3  32 -30
  5  28  29
H,L= 10   3
  2  24  -7
  4  42 -43
  8  40  35
H,L= 11   3
  1  27  19
  3  53  59
  5  42  42
  7  30 -22
H,L= 12   3
  2  27  19
H,L=-16   4
  2  37  35
H,L=-15   4
  5  27  15
H,L=-14   4
  0  26  24
H,L=-13   4
  3  63  73
  7  34 -47
  9  35 -46
H,L=-12   4
  0  43 -46
  4  43  47
  6  46  41
  8  39  44
 10  52 -53
 12  30 -29
H,L=-11   4
  1  81  85
  3  75 -78
  7  22 -13
  9  43  47
 13  23 -13
H,L=-10   4
  0 228 248
  2 131 147
  4 153-156
  8  77 -91
 14  26  15
H,L= -9   4
  1 113-116
  3 151 156
  7  74  54
 11  64 -71
 13  62 -63
H,L= -8   4
  2 115-123
  4 147 160
  6  84 -80
 10  28  28
 12  43  42
 14  35 -49
H,L= -7   4
  1 270 289
  7 180-201
  9 197-214
 11  42  56
 13  64  72
H,L= -6   4
  0 406-424

  K  FO  FC
  2  77  76
  4 239 233
  6  79  79
 10  83 -88
 12  87 -90
H,L= -5   4
  1  52 -58
  3 126-136
  7 108 130
  9 137 155
 11  66 -79
H,L= -4   4
  0 811 869
  2 460 484
  4 541-551
  6 138-146
  8 151-162
 10  29  37
 12  22  -5
H,L= -3   4
  1  38  25
  3 102  90
  5  95  98
  7  73  56
  9  73 -86
 11  46 -43
 13  77 -80
H,L= -2   4
  0 198-217
  2 433-446
  4 373 361
  6  70  80
  8 199 219
 10  69 -79
 16  31 -25
H,L= -1   4
  1 249 259
  3 401 433
  5 184-177
  7 330-353
  9  74 -82
 11  51  53
 13  52  54
 17  32 -23
H,L=  0   4
  0  81  50
  2 122 121
  4  82  85
  6 175 175
  8 198-219
 10  55 -59
 12  21  16
 14  29 -19
H,L=  1   4
  1 223-239
  3 135-141
  5 208 225
  7 219 241
  9  57  63
 11  63 -69
 13  44 -54
 15  33 -23
H,L=  2   4
  0 275 286
  2 354 372
  4 166-178
  6 280-295
 10  52  51
 12  53 -61
 14  35  25
H,L=  3   4
  1 287 296
  3  79 -90
  5  66 -66
  9  56 -60
 11  36 -26
H,L=  4   4
  0 175-185
  2 242-256
  4 176 193
  6 156 171
  8  63  68
 10  33 -45
 14  41 -44
H,L=  5   4
  1  40  31
  3 137 142
  5  44 -42
  7  90 -94
  9  33 -39
H,L=  6   4
  0  67  71
  2 126 131
  4  32 -30
  6  46 -48
  8  81 -87
 10  23  -8
H,L=  7   4
  1 104-109
  5  78  86
  7  28  43
  9  30  22
 11  23 -12
 13  34 -25
H,L=  8   4
  0  96 100
  2  26  11
  4  38 -38
H,L=  9   4
  1  77  83
  3  21  13
  5  56 -61
  7  37 -30
H,L= 10   4
  0  46 -47

  K  FO  FC
  4  29  27
H,L= 11   4
  5  30  29
H,L=-16   5
  6  30 -25
H,L=-15   5
  5  27 -24
  7  26 -27
H,L=-14   5
  6  33  36
 10  36 -27
H,L=-13   5
  1  78 -81
  3  60 -59
  5  37 -31
  7  31  35
H,L=-12   5
  2  71 -74
  6  45 -53
  8  38 -24
H,L=-11   5
  1 133 134
  5  23  30
  9  26 -17
 11  57 -59
H,L=-10   5
  2  26  30
  4 136-139
  6  69 -65
  8  57  55
 10  77  73
H,L= -9   5
  1 114-117
  3  53  41
  5  63 -71
  7 176-177
  9  30  -9
 11  88  98
H,L= -8   5
  2 155 148
  4  87  93
  6  51  60
  8  89 -86
 10  99-102
 16  28   4
H,L= -7   5
  1 186-189
  3 227-214
  5  90 -86
  7 212 209
  9  22 -10
 13  23  -1
H,L= -6   5
  2 379-361
  4 112-131
  6  82 -92
 12  56  67
 16  26  19
H,L= -5   5
  1 345 331
  3 160 155
  5 204 212
  7 216-209
  9  48 -33
 11 106-109
 15  35  38
H,L= -4   5
  2  40  46
  4 105-104
  6  27 -32
  8  44  30
 10  77  73
 14  36 -42
H,L= -3   5
  1  66 -55
  3 119-110
  5 478-491
  9  38  42
 11  98 114
 13  30  38
H,L= -2   5
  2 259 265
  4 296 301
  6  57 -54
  8 200-189
 10  57 -58
 12  37 -34
 14  25  30
 16  39  35
H,L= -1   5
  1 270-265
  3 125-126
  5 190 197
  7  62  58
  9  29 -42
 13  33 -26
H,L=  0   5
  2 318-306
  4 463-466
  6  25 -33
  8 161 162
 10  29 -22
 12  45  49
 14  35  35
H,L=  1   5
  1 163 167
  3  90  89
  5 169 174
  7 141-144
  9  95 -69
 11  47 -36
 13  31  29
H,L=  2   5
  2 103  98
  4 162 163

  K  FO  FC
  6  49 -48
  8  62 -65
 10  32  26
 12  25 -24
 14  36 -20
H,L=  3   5
  1 103 -98
  3 133-131
  5 299-307
  7  41  36
  9  78 -81
 11  57  64
 15  25  -6
H,L=  4   5
  2  78  87
  8  65 -63
 10  24 -23
H,L=  5   5
  1  43  44
  3  55  61
  5  68  71
 11  43 -44
 15  25  17
H,L=  6   5
  2 197-194
  4  93 -97
  8  36  24
H,L=  7   5
  3  30 -21
H,L=  8   5
  2  94  96
  4  29  28
H,L=  9   5
  1  46 -46
  3  34 -24
  9  26  12
H,L=-16   6
  6  26   8
H,L=-15   6
  1  36 -37
H,L=-14   6
  0  24 -34
  8  28  -1
H,L=-13   6
  3  27 -24
  5  23   2
H,L=-12   6
  0  54  49
  2  88 -92
  4  46 -45
  6  43  46
  8  69  73
H,L=-11   6
  3  35  38
  5 110-106
  7  56 -53
  9  66  67
H,L=-10   6
  0  70 -52
  4  79  84
  8  57 -60
 10  27 -28
H,L= -9   6
  1 156-168
  3  66 -72
  5 187 180
  7  65  67
 11  23   2
 15  31 -33
H,L= -8   6
  0  76 -86
  2  82  78
  4 107-105
  6  45 -29
  8  48 -45
 10  92  97
 12  29  24
 14  31  29
H,L= -7   6
  1 110 121
  3  34  37
  5 122-125
  9  41 -48
 11  29 -28
 15  49  48
H,L= -6   6
  0  30 -31
  2 235-240
  4  60  48
  6  84  80
  8 203 213
 12  50 -54
 14  39 -38
H,L= -5   6
  1  95  91
  3 185-187
  5  85 -70
  9  57  69
 11 103 103
 15  29 -26
H,L= -4   6
  0  86  90
  2 174 187
  4  28 -19
  6 124-124
  8 117-130
 10  25 -26
 12  34  48
 14  56  52
H,L= -3   6
  1 450-451
  3 194 182
  5 235 223
  7  45  43
  9  30  47

  K  FO  FC
 11  53 -55
H,L= -2   6
  0 104 -94
  2  90 -85
  4 113-123
  6 121 138
  8  41 -31
 10  65  71
 12  73  61
H,L= -1   6
  1 285 287
  3  31 -21
  5 191-187
  7 122-123
  9  41 -47
 11  42  44
 13  31  27
H,L=  0   6
  0 111-119
  2 141-158
  4 105 106
  6  52  -8
  8 165 173
 10  32 -27
 12  69 -66
 16  33  19
H,L=  1   6
  1  73 -66
  3 134-145
  7 121 132
  9  51  57
 13  23  -5
H,L=  2   6
  0 155 159
  2 125 132
  4  73 -77
  6 105-105
  8 120-124
 10  30  33
 12  43  45
 14  24  13
H,L=  3   6
  1 113-126
  3  24  24
  5 103 101
  9  26 -20
H,L=  4   6
  0 205-208
  2  63 -62
  4  42  44
  6  53  56
  8  33  45
H,L=  5   6
  1  90 102
  5  77 -79
  7  72 -69
 11  33  26
H,L=  6   6
  0  83  76
  2  48 -45
  4  32 -27
  6  33  22
H,L=  7   6
  1  67 -72
  5  22  11
  7  41  44
  9  38  32
H,L=  8   6
  2  45  33
  6  28 -24
H,L=  9   6
  5  24  14
H,L=-15   7
  5  37  34
H,L=-14   7
  2  37 -40
  6  50  37
 10  30  14
H,L=-13   7
  1  28  25
  5  50 -47
  7  31  25
H,L=-12   7
  2 117 109
  4  25  15
H,L=-11   7
  1  49 -40
  3  69  78
  5  44  50
 13  43 -43
H,L=-10   7
  2  76 -76
  4  24 -33
  8  67  60
 12  33  31
H,L= -9   7
  1  83  70
  3  27 -39
  5  77  84
  9  40 -43
 11  43 -42
 13  63  54
H,L= -8   7
  4  33  58
  6 142 151
 10  49 -55
 12  45 -52
H,L= -7   7
  1 156-146
  3  77 -64
  5  62 -65
  7  45  36
  9 116 110
 11  54  53
 13  31 -44
```

Table 4. (continued)

K	FO	FC
H,L=	-6	7
2	146	131
4	43	34
6	67	-69
8	91	-83
10	36	35
12	48	36
H,L=	-5	7
1	212	196
3	245	244
5	37	16
7	66	78
9	54	-56
11	37	-50
H,L=	-4	7
2	221	-205
4	52	-50
8	102	94
10	89	79
14	36	-38
H,L=	-3	7
1	41	-25
3	146	-147
5	101	97
7	88	-91
13	36	34
H,L=	-2	7
2	194	182
4	122	123
6	119	133
10	120	-124
12	43	-39
H,L=	-1	7
1	148	-150
3	88	-85
5	37	-39
7	116	111
9	44	37
11	35	33
15	31	-21
H,L=	0	7
4	59	-54
6	90	-96
8	26	-13
10	64	76
14	28	-5
H,L=	1	7
1	132	135
3	231	226
5	76	81
7	63	-57
9	36	-35
13	32	-12
H,L=	2	7
4	38	-39
6	32	34
8	51	52
10	24	4
14	26	-15
H,L=	3	7
1	28	-19
3	125	-121
5	45	-43
7	29	18
9	29	35
H,L=	4	7
4	130	125
6	38	40
8	47	-45
10	27	-27
12	28	-11
H,L=	5	7
7	39	36
9	34	-5
H,L=	6	7
4	71	-65
6	35	-12
8	27	21
10	28	16
H,L=	7	7
3	47	48
5	27	33
7	29	-28
H,L=	-16	8
2	24	6
H,L=	-14	8
0	77	78
H,L=	-13	8
3	40	31
H,L=	-12	8
0	56	-62
2	24	24
4	21	-3
10	38	30
H,L=	-11	8
1	35	31
3	31	30
7	34	-37
9	64	-65
11	29	32
H,L=	-10	8
2	43	-37
4	84	80
6	43	31
H,L=	-12	8
8	26	-13
H,L=	-10	8
10	58	-54
H,L=	-9	8
3	26	-30
5	33	-27
7	56	67
9	57	62
11	34	-30
H,L=	-8	8
0	144	140
2	79	78
4	41	-72
6	113	-111
10	29	19
H,L=	-7	8
1	48	55
3	43	-36
5	86	87
9	55	-59
11	27	-28
H,L=	-6	8
0	191	-200
4	21	3
6	95	95
8	26	29
10	29	30
12	26	-30
H,L=	-5	8
1	25	25
3	114	117
5	100	-93
7	103	-110
11	36	42
13	29	24
H,L=	-4	8
0	114	120
2	25	-31
4	95	95
6	59	-63
10	85	-89
H,L=	-3	8
1	103	-102
3	48	-53
5	84	80
7	99	101
9	33	39
11	33	-21
13	39	-41
H,L=	-2	8
0	135	128
2	77	83
4	122	-118
6	92	-92
10	37	41
14	26	6
H,L=	-1	8
1	112	112
3	29	28
5	51	-40
7	32	-39
9	29	-30
11	32	-37
H,L=	0	8
0	170	-166
2	58	-61
4	67	59
6	113	112
10	28	-1
H,L=	1	8
3	24	-13
11	31	31
H,L=	2	8
0	63	61
2	57	58
4	34	46
6	85	-88
8	29	-33
H,L=	3	8
1	74	-68
5	45	45
7	42	45
H,L=	4	8
0	49	49
2	26	-6
4	45	-50
H,L=	5	8
1	48	57
5	42	-40
7	45	-35
H,L=	6	8
0	39	-37
6	30	21
H,L=	-13	9
1	31	12
7	54	-48
H,L=	-12	9
4	33	31
6	33	-33
H,L=	-11	9
1	42	-35
3	48	-43
7	55	51
H,L=	-10	9
2	32	-25
4	71	-72
H,L=	-9	9
3	64	76
7	54	-39
9	35	-31
11	28	-1
H,L=	-8	9
6	30	-10
8	37	31
H,L=	-7	9
1	81	78
3	74	-60
5	87	-90
7	29	-31
9	53	49
13	28	32
H,L=	-6	9
2	57	44
4	73	63
6	27	-6
8	92	-83
10	30	-22
H,L=	-5	9
1	86	-83
5	49	56
7	56	57
13	25	-24
H,L=	-4	9
2	111	-105
4	114	-119
8	40	42
H,L=	-3	9
1	47	36
3	57	50
7	39	-33
9	58	-58
13	30	21
H,L=	-2	9
2	67	61
4	56	58
H,L=	-1	9
1	30	-28
3	100	-96
5	42	-41
7	27	-34
9	61	65
11	37	33
H,L=	0	9
2	52	46
8	32	-27
12	27	15
H,L=	1	9
3	59	54
7	35	33
9	29	-32
H,L=	2	9
2	105	-104
6	26	16
8	28	10
H,L=	3	9
5	30	-16
H,L=	4	9
2	49	50
4	28	26
H,L=	5	9
1	29	-9
H,L=	-14	10
4	29	22
H,L=	-13	10
1	38	-29
5	27	26
H,L=	-12	10
4	27	-12
H,L=	-11	10
11	28	-26
H,L=	-10	10
0	50	-46
H,L=	-9	10
1	32	15
3	48	-49
H,L=	-8	10
0	40	36
4	32	32
6	55	-50
8	29	-30
H,L=	-7	10
1	88	-78
3	49	46
5	58	53
H,L=	-6	10
0	34	-26
2	26	-27
H,L=	-5	10
1	77	71
3	24	-13
5	42	-32
7	49	-47
H,L=	-4	10
6	54	48
12	38	-30
H,L=	-3	10
1	33	-39
7	45	42
9	35	47
H,L=	-2	10
0	80	76
6	60	-56
10	31	4
H,L=	-1	10
1	26	-21
5	57	49
9	43	-35
H,L=	0	10
0	94	-94
2	25	-18
4	34	16
6	32	17
H,L=	1	10
1	44	41
5	34	-37
H,L=	2	10
0	33	24
H,L=	3	10
1	29	-31
3	26	-8
H,L=	-15	11
3	30	9
H,L=	-13	11
5	26	0
H,L=	-10	11
2	28	21
8	29	-20
H,L=	-9	11
1	34	29
3	49	43
H,L=	-8	11
2	35	-26
H,L=	-7	11
1	29	-28
H,L=	-6	11
4	36	43
10	32	-31
H,L=	-5	11
3	45	-33
7	38	30
H,L=	-4	11
4	37	-26
6	39	-35
10	31	25
H,L=	-3	11
3	61	64
7	32	-25
9	30	-19
H,L=	-2	11
8	36	24
H,L=	-1	11
3	37	-35
H,L=	0	11
4	35	14
H,L=	-12	12
0	29	17
6	25	-22
H,L=	-6	12
0	47	41
4	29	-22
H,L=	-5	12
1	23	15
5	24	-13
7	47	-16
H,L=	-4	12
0	39	-29
H,L=	-2	12
4	27	6
H,L=	-10	13
4	25	3
H,L=	-9	13
5	24	18

Table 5. Observed and calculated structure factors (× 10) for the photographic data

```
  K  FO  FC  DF
H,L=  0   0
  4 396-424  28
  6 461-487  26
  8  53 -46  -7
 10 120-123   3
 12  89  91  -2
H,L=  1   0
  1 136-122 -14
  3 263 305 -42
  5   0  -6   6
  7 133 140  -7
  9  73  76  -3
 11  63 -49 -14
 13  66 -65  -1
H,L=  2   0
  2 312 322 -10
  4 223 231  -8
  6 328 316  12
H,L=  3   0
  1 757 783 -26
  3 213 214  -1
  7 384-401  17
  9 218-230  12
H,L=  4   0
  0 266-235 -31
  2 111 128 -17
  4 151 149   2
  6   0  15 -15
  8 126-109 -17
H,L=  5   0
  1 209-197 -12
  5 155 166 -11
  7 188 175  13
H,L=  6   0
  0 617 605  12
  2 159 168  -9
v 4   0 -20  20
  6 328-319  -9
H,L=  7   0
  1 166 183 -17
  3  93 -85  -8
  5 115-130  15
H,L=  8   0
  0 177-160 -17
  2  60 -63   3
  6 212 229 -17
H,L=  9   0
  1   0   6  -6
  3 172 161  11
  5   0   6  -6

  K  FO  FC  DF
  7 113-121   8
H,L= 10   0
  0  56  50   6
  6  30 -36   6
H,L= 11   0
  5  52  52   0
H,L=-12   1
  2  29 -34   5
H,L=-11   1
  1  48  68 -20
  3  43  57 -14
  5  66 -74   8
H,L=-10   1
  4  91  87   4
H,L= -9   1
  3 281-274  -7
H,L= -8   1
  4 106-111   5
H,L= -7   1
  1  57  44  13
  3 233 231   2
  5  96 -90  -6
H,L= -6   1
  2  89-106  17
  6 188-190   2
 10 136 128   8
H,L= -5   1
  1 124-113 -11
  3 118 115   3
  5 232-234   2
  7 231-242  11
  9   0  -3   3
H,L= -4   1
  2 304 337 -33
  4 374 357  17
  6  58  72 -14
    116-120   4
    222-207 -15
H,L= -3   1
    201 224 -23
  312021256  54
  5  85 -84  -1
  7 114  95  19
  9 137 150 -13
H,L= -2   1
  4 162-176  14
  8 138-124 -14
H,L= -1   1
  1  44  42   2
  311521141  11

  K  FO  FC  DF
  5  35 -28  -7
  7   0   1  -1
  9 309-268 -41
H,L=  0   1
  2 424 419   5
  4 684-747  63
  6 288-290   2
  8  82  76   6
 10  60  62  -2
 14   0   1  -1
H,L=  1   1
  1 382-386   4
  3 525-559  34
  5 383-393  10
  7 232-232   0
  9 143 143   0
 11 127 132  -5
H,L=  2   1
  2 616 636 -20
  4 481 473   8
  6 112-103  -9
 10 102 -92 -10
 12  49 -56   7
H,L=  3   1
  1  78 -82   4
  3 571-538 -33
  5 124 133  -9
 13  37  42  -5
H,L=  4   1
  2 640-614 -26
  4 489-491   2
  6   0   8  -8
  8 126 139 -13
 10   0  -9   9
 12  50  38  12
H,L=  5   1
  1  90 -90   0
  3 377 365  12
  7  76  46  30
H,L=  6   1
  4 103 106  -3
H,L=  7   1
  1  80  83  -3
  3 216-191 -25
  5 251-238 -13
  9 103 110  -7
H,L=  8   1
  2  79  81  -2
  6   0  13 -13
H,L=  9   1

  K  FO  FC  DF
  5  57  59  -2
  7  69 -65  -4
H,L= 10   1
  2  83 -90   7
  4  91 -92   1
  6   0 -15  15
H,L=-12   2
  0  76 -82   6
H,L=-11   2
  3  46  50  -4
H,L=-10   2
  0 145 148  -3
  6  62 -51 -11
H,L= -9   2
  1   0   5  -5
  3  57 -51  -6
H,L= -8   2
  0 100-102   2
  2 149-151   2
  4 100 -97  -3
  6 113 102  11
  8 154 153   1
H,L= -7   2
  1 152 168 -16
  3   0  -6   6
  5 228-219  -9
  7 123-121  -2
  9 101 100   1
H,L= -6   2
  0 414-407  -7
  2 175 182  -7
  4  71  66   5
  6  88  76  12
  8 170-193  23
H,L= -5   2
  1 640-686  46
  3 175-190  15
  5 430 420  10
  9  77 -84   7
 11  68  61   7
H,L= -4   2
  0 161 170  -9
  2 114-123   9
  4 191 188   3
  6 466-475   9
  8  89 104 -15
 12  63  65  -2
H,L= -3   2
  1 223 216   7
  3   0  11 -11

  K  FO  FC  DF
  5 227-235   8
  7  73-102  29
H,L= -2   2
  2 715-758  43
  4 493-513  20
  6 643 661 -18
  8 235 254 -19
H,L= -1   2
  3 113-133  20
  5 291-282  -9
  7 139-124 -15
H,L=  0   2
  0  67  55  12
  2 444 414  30
  4 189-217  28
  6 238-234  -4
  8 156-167  11
 10   0  11 -11
 14  51  58  -7
H,L=  1   2
  112971256 -41
  3  87  79   8
  5 497 485  12
  7 210 202   8
  9   0   1  -1
 11   0   4  -4
H,L=  2   2
  0  71  76  -5
  2 496-492  -4
  4 324 310  14
  6 111-106  -5
  8   0   3  -3
 10   0  -7   7
H,L=  3   2
  1 508 482  26
  3  97-107  10
  5 341-328 -13
  7 121-119  -2
 11  49  60 -11
H,L=  4   2
  0 588-574 -14
  2  35 -23 -12
  4 136-117 -19
  6 119 109  10
  8 197 181  16
 10  87  83   4
 12  83 -84   1
H,L=  5   2
  1   0 -10  10
  3 202-196  -6

  K  FO  FC  DF
  7 116 109   7
H,L=  6   2
  0 269 258  11
  2  70  81 -11
  4  97 -96  -1
  6  82 -69 -13
H,L=  7   2
  1 218-221   3
  3  85  79   6
  9  57  52   5
H,L=  8   2
  0  97 -93 [illegible]
  2  86 -96 [illegible]
  4  76  79  -3
  6  43  46  -3
H,L=  9   2
  1  66  71  -5
  5  40 -53  13
H,L= 10   2
  0   0 -14  14
H,L=-12   3
  6   0  14 -14
H,L=-11   3
  3  73  55  18
  5  84  76   8
H,L=-10   3
  2  43 -47   4
  6  88  85   3
H,L= -9   3
  3  61 -48 -13
  5 125-131   6
  7  74  66   8
H,L= -8   3
  2 329 330  -1
  4 194 165  29
  6 110-112   2
H,L= -7   3
  1  99 101  -2
  3  77  71   6
  5 304 293  11
  7 115-120   5
  9  99  89  10
H,L= -6   3
  4 305-298  -7
  6  71  70   1
  8  84  67  15
H,L= -5   3
  3 333 315  18
  7 156 156   0
  9 165-155 -10

  K  FO  FC  DF
H,L= -4   3
  4 512 484  28
  6 336 338  -2
H,L= -3   3
  1 242-239  -3
  3 440-428 -12
  5 265-263  -2
  7 130 129   1
  9 192 191   1
H,L= -2   3
  2 722 683  39
  4 193 184   9
  6 184-177   7
H,L= -1   3
  1 890 845  45
  3 456 451   5
  5 418 429 -11
  7 152-135 -17
  9   0  -2   2
H,L=  0   3
  2 408-410   2
  4 294-299   5
  6  73 -67  -6
  8 167 165   2
 10 161 153   8
 12   0  -9   9
 14  27 -21  -6
H,L=  1   3
  1 582-545 -37
  3  86  77   9
  5  73  72   1
  7 139 132   7
  9  97 -88  -9
H,L=  2   3
  2 404 417 -13
  4 219 225  -6
  6 288 268  20
 10 167-161  -6
H,L=  3   3
  1 156-171  15
  3 271-276   5
  9  83  78   5
H,L=  4   3
  0   0   0   0
  2  80 -79  -1
  4  78  71   7
  6  69 -65  -4
  8   0 -12  12
 10  86  86   0
H,L=  5   3
```

Table 5. (continued)

K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF	K	FO	FC	DF
1	329	361	-32	2	421	425	-4	2	209	-220	11	4	85	-82	-3	2	45	-53	8	H,L=	0	6		3	221	182	39
3	286	288	-2	4	498	-478	-20	4	157	166	-9	6	0	-9	9	6	27	26	1	0	89	-80	-9	H,L=	-4	7	
5	77	71	6	6	128	-129	1	6	134	129	5	H,L=	-3	5		H,L=	-11	6		2	108	-132	24	2	144	-149	5
9	0	-15	15	8	128	-128	0	8	60	60	0	1	48	-34	-14	5	71	-69	-2	4	83	83	0	6	0	-2	2
11	43	-49	6	H,L=	-3	4		10	27	-32	5	3	104	-101	-3	7	47	-36	-11	6	0	-4	4	H,L=	-3	7	
H,L=	6	3		1	47	46	1	H,L=	5	4		5	372	-406	34	H,L=	-10	6		8	119	120	-1	3	132	-117	-15
4	62	-57	-5	3	96	89	7	3	121	109	12	7	0	2	-2	0	44	-34	-10	H,L=	1	6		5	64	67	-3
6	0	-15	15	5	81	83	-2	7	74	-65	-9	11	66	81	-15	2	0	10	-10	1	68	-57	-11	H,L=	-2	7	
H,L=	7	3		7	62	48	14	9	28	-34	6	H,L=	-2	5		4	59	60	-1	3	115	-114	-1	2	125	134	-9
1	107	-128	21	13	52	-50	-2	H,L=	6	4		2	216	219	-3	H,L=	-9	6		5	0	-10	10	4	88	93	-5
3	51	-53	2	H,L=	-2	4		0	57	53	4	4	242	256	-14	1	86	-113	27	7	97	98	-1	6	90	96	-6
H,L=	8	3		0	204	-203	-1	2	97	103	-6	6	51	-44	-7	3	57	-48	-9	9	35	44	-9	H,L=	-1	7	
2	55	60	-5	2	452	-398	-54	H,L=	7	4		8	184	-148	-36	5	136	129	7	H,L=	2	6		1	92	-111	19
6	54	70	-16	4	357	331	26	1	76	-86	10	H,L=	-1	5		H,L=	-8	6		2	87	104	-17	3	81	-60	-21
H,L=	-13	4		6	76	71	5	5	54	56	-2	1	226	-232	6	0	61	-65	4	4	58	-58	0	7	76	81	-5
3	45	45	0	8	182	190	-8	H,L=	-13	5		5	156	167	-11	2	52	51	1	8	80	-85	5	H,L=	0	7	
H,L=	-12	4		H,L=	-1	4		1	37	-49	12	H,L=	0	5		4	79	-71	-8	H,L=	3	6		6	60	-69	9
0	31	-24	-7	1	246	230	16	3	36	-34	-2	2	261	-270	9	6	0	-15	15	1	87	-93	6	8	0	-7	7
6	29	31	-2	3	420	387	33	H,L=	-12	5		4	381	-387	6	H,L=	-7	6		3	0	12	-12	H,L=	1	7	
H,L=	-10	4		5	167	-152	-15	2	39	-50	11	8	129	125	4	1	61	94	-33	5	71	75	-4	3	168	165	3
0	193	184	9	7	318	-298	-20	6	34	-33	-1	10	0	-4	4	5	94	-93	-1	H,L=	4	6		5	55	60	-5
2	100	105	-5	H,L=	0	4		H,L=	-11	5		H,L=	1	5		7	0	2	-2	0	169	-159	-10	7	40	-37	-3
4	141	-120	-21	0	77	60	17	1	68	95	-27	1	139	142	-3	H,L=	-6	6		2	43	-48	5	9	17	-24	7
6	0	-2	2	2	120	111	9	3	0	1	-1	3	76	60	16	0	0	-15	15	4	34	35	-1	H,L=	3	7	
8	55	-62	7	4	75	77	-2	H,L=	-10	5		5	139	149	-10	2	179	-173	-6	6	34	41	-7	1	0	-11	11
H,L=	-9	4		6	161	140	21	4	96	-91	-5	7	121	-110	-11	6	72	62	10	H,L=	5	6		3	78	-86	8
3	134	129	5	8	171	-169	-2	6	48	-44	-4	9	77	-67	-10	H,L=	-5	6		1	65	70	-5	H,L=	4	7	
7	64	57	7	10	0	12	-12	H,L=	-9	5		11	27	-27	0	1	56	69	-13	5	49	-56	7	4	71	81	-10
11	43	-41	-2	H,L=	1	4		7	119	-126	7	H,L=	2	5		3	161	-158	-3	H,L=	6	6		H,L=	-12	8	
H,L=	-8	4		1	227	-215	-12	H,L=	-8	5		2	78	92	-14	5	70	-49	-21	0	54	54	0	0	29	-35	6
0	0	-13	13	3	128	-126	-2	2	111	113	-2	4	130	131	-1	7	0	-2	2	H,L=	-12	7		2	0	11	-11
4	147	125	22	5	198	194	4	4	71	70	1	6	59	-35	-24	H,L=	-4	6		2	66	65	1	H,L=	-10	8	
6	68	-59	-9	7	202	196	6	10	63	-73	10	8	47	-45	-2	0	80	65	15	H,L=	-11	7		0	0	10	-10
H,L=	-7	4		9	44	56	-12	H,L=	-7	5		H,L=	3	5		2	133	151	-18	3	50	48	2	4	50	44	6
3	0	0	0	11	46	-44	-2	3	185	-167	-18	1	92	-89	-3	4	0	-10	10	H,L=	-10	7		H,L=	-8	8	
7	148	-156	8	13	28	-35	7	5	70	-53	-17	3	113	-100	-13	6	104	-103	-1	2	47	-48	1	0	91	89	2
9	163	-153	-10	H,L=	2	4		7	152	160	-8	5	237	-240	3	H,L=	-3	6		H,L=	-9	7		2	45	46	-1
H,L=	-6	4		0	245	258	-13	H,L=	-6	5		9	46	58	-12	1	309	-367	58	1	40	41	-1	4	51	-49	-2
0	363	-366	-17	2	310	327	-17	2	302	-304	2	H,L=	4	5		3	174	151	23	5	48	47	1	6	75	-69	-6
4	232	195	37	4	151	-158	7	4	92	-108	16	6	0	-1	1	5	180	178	2	H,L=	-8	7		H,L=	-7	8	
6	72	68	4	6	254	-238	-16	6	69	-76	7	8	50	-43	-7	H,L=	-2	6		2	0	10	-10	5	51	50	1
8	0	-2	2	8	0	7	-7	8	0	0	0	H,L=	5	5		0	92	-93	1	6	96	101	-5	H,L=	-6	8	
10	70	-68	-2	12	35	-32	-3	10	0	2	-2	3	54	45	9	2	71	-74	3	H,L=	-7	7		0	126	-137	11
12	56	-62	6	H,L=	3	4		H,L=	-5	5		H,L=	6	5		4	94	-100	6	1	84	-105	21	6	71	59	12
H,L=	-5	4		1	284	263	21	1	251	264	-13	2	122	-145	23	6	107	109	-2	3	61	-44	-17	H,L=	-5	8	
3	115	-122	7	3	72	-78	6	3	138	127	11	4	64	-72	8	H,L=	-1	6		H,L=	-6	7		3	87	81	6
7	90	114	-24	5	60	-65	5	5	161	170	-9	H,L=	-13	6		1	217	230	-13	2	94	98	-4	5	65	-61	-4
9	107	124	-17	7	0	1	-1	7	159	-160	1	3	0	-16	16	3	0	-15	15	6	70	-69	-1	7	66	-67	1
H,L=	-4	4		H,L=	4	4		11	70	-77	7	H,L=	-12	6		5	144	-147	3	H,L=	-5	7		H,L=	-4	8	
0	821	795	26		165	-155	-10	H,L=	-4	5		0	37	38	-1	7	115	-96	-19	1	121	151	-30	0	77	84	-7

Table 5. (continued)

```
   K   FO   FC   DF      K   FO   FC   DF      K   FO   FC   DF      K   FO   FC   DF      K   FO   FC   DF      K   FO   FC   DF      K   FO   FC   DF

   4   64   66   -2      4   83  -82   -1      5    0   -4    4      3   55   40   15      4   67  -72    5   H,L=  -10   10           0    0  -12   12
   6    0    2   -2      6   65  -57   -8   H,L=    2    8         H,L=   -7    9         H,L=   -3    9            0   23  -19   -4   H,L=   -2   10
H,L=   -3    8         H,L=   -1    8            0   36   42   -6      1   38   49  -11      3   42   26   16   H,L=   -7   10           0   39   41   -2
   1   46  -65   19      1   59   82  -23      4   29   32   -3      3   52  -45   -7      5    0   -6    6      1   30  -43   13
   5   61   56    5   H,L=    0    8         H,L=  -11    9            5   51  -55    4   H,L=   -2    9            3   34   28    6
   7   59   65   -6      0 107-111    4      3   28  -24   -4   H,L=   -5    9            2   36   40   -4      5   30   29    1
H,L=   -2    8            4   43   39    4   H,L=  -10    9            1   38  -54   16   H,L=    0    9         H,L=   -5   10
   0   90   91   -1   H,L=    1    8            4   33  -41    8   H,L=   -4    9            2   22   27   -5      1   28   39  -11
   2   42   55  -13      3    0   -8    8   H,L=   -9    9            2   62  -69    7      4    0   -8    8   H,L=   -4   10
```

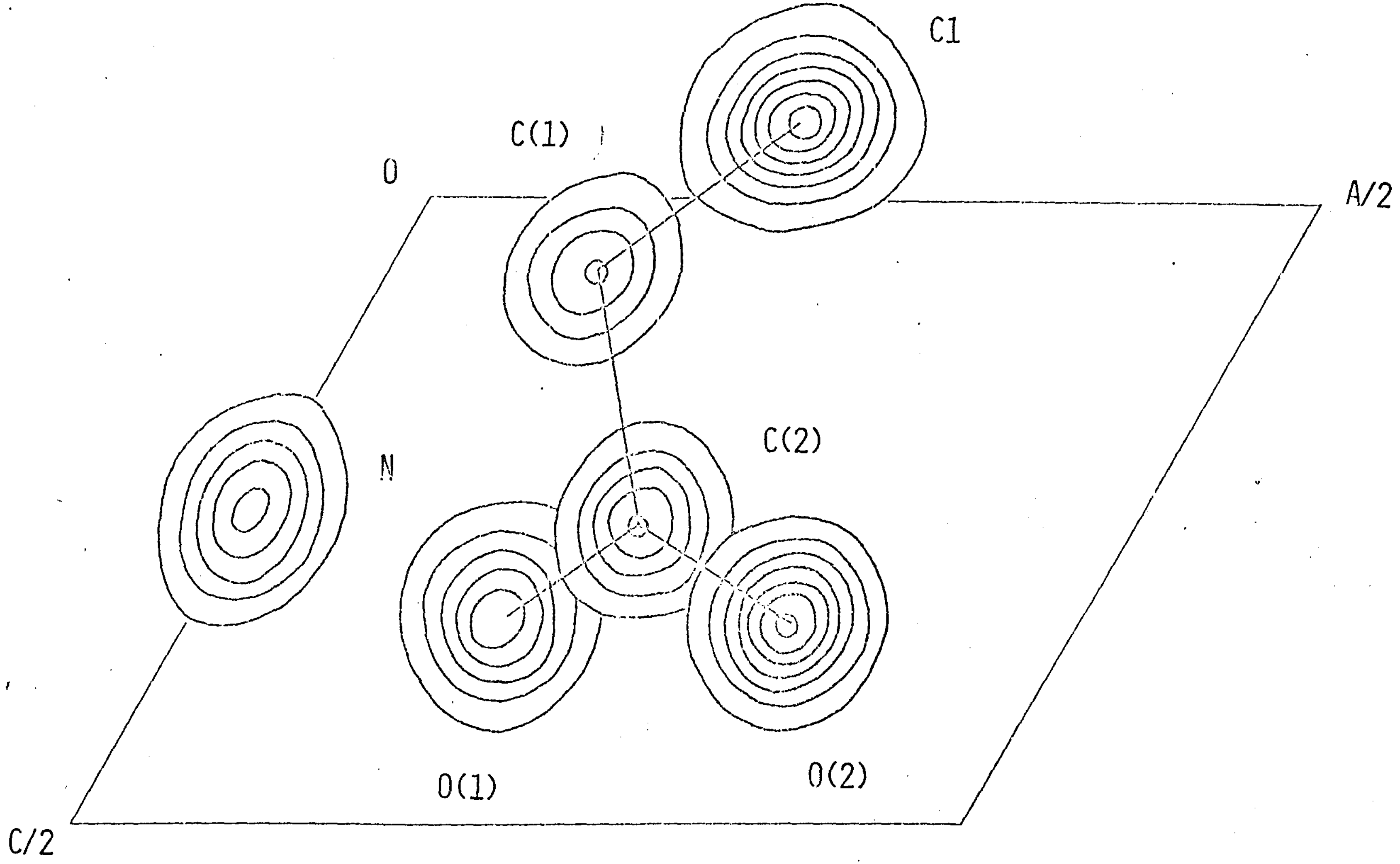

Fig. 1. A composite drawing of the final electron-density map, viewed along b-axis. Contours are drawn at intervals of 4 e.$\mathring{A}^{-3}$ for the chlorine atom and 2 e.$\mathring{A}^{-3}$ for the other atoms, beggining with 2 e.$\mathring{A}^{-3}$.

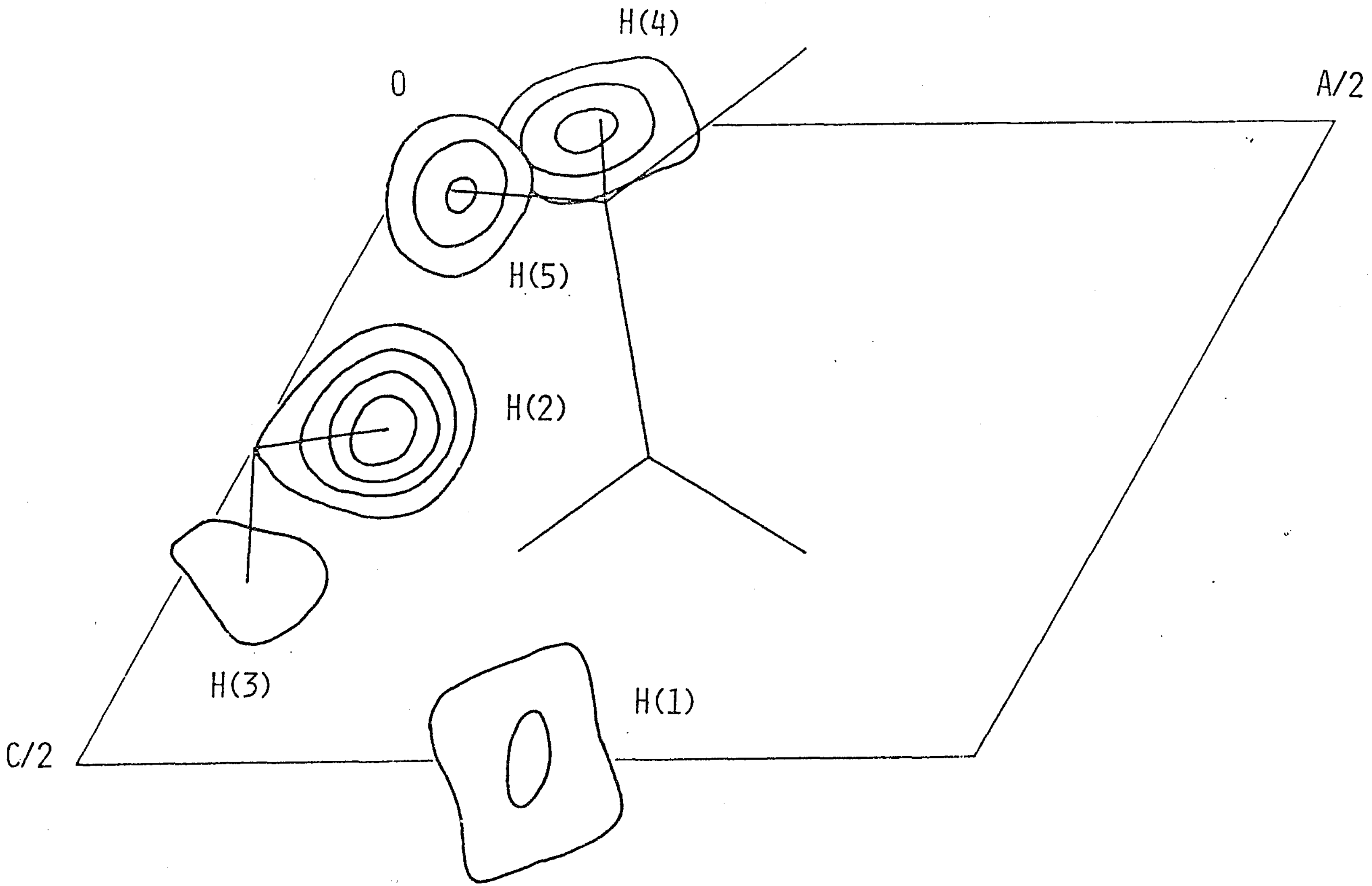

Fig. 2. A composite drawing of the final difference electron-density map, viewed along b axis. The contribution of the hydrogen atoms were excluded from the calculated structure factors. Contours are drawn at intervals of 0.1 e.$\mathring{A}^{-3}$, beginning with 0.2 e.$\mathring{A}^{-3}$.

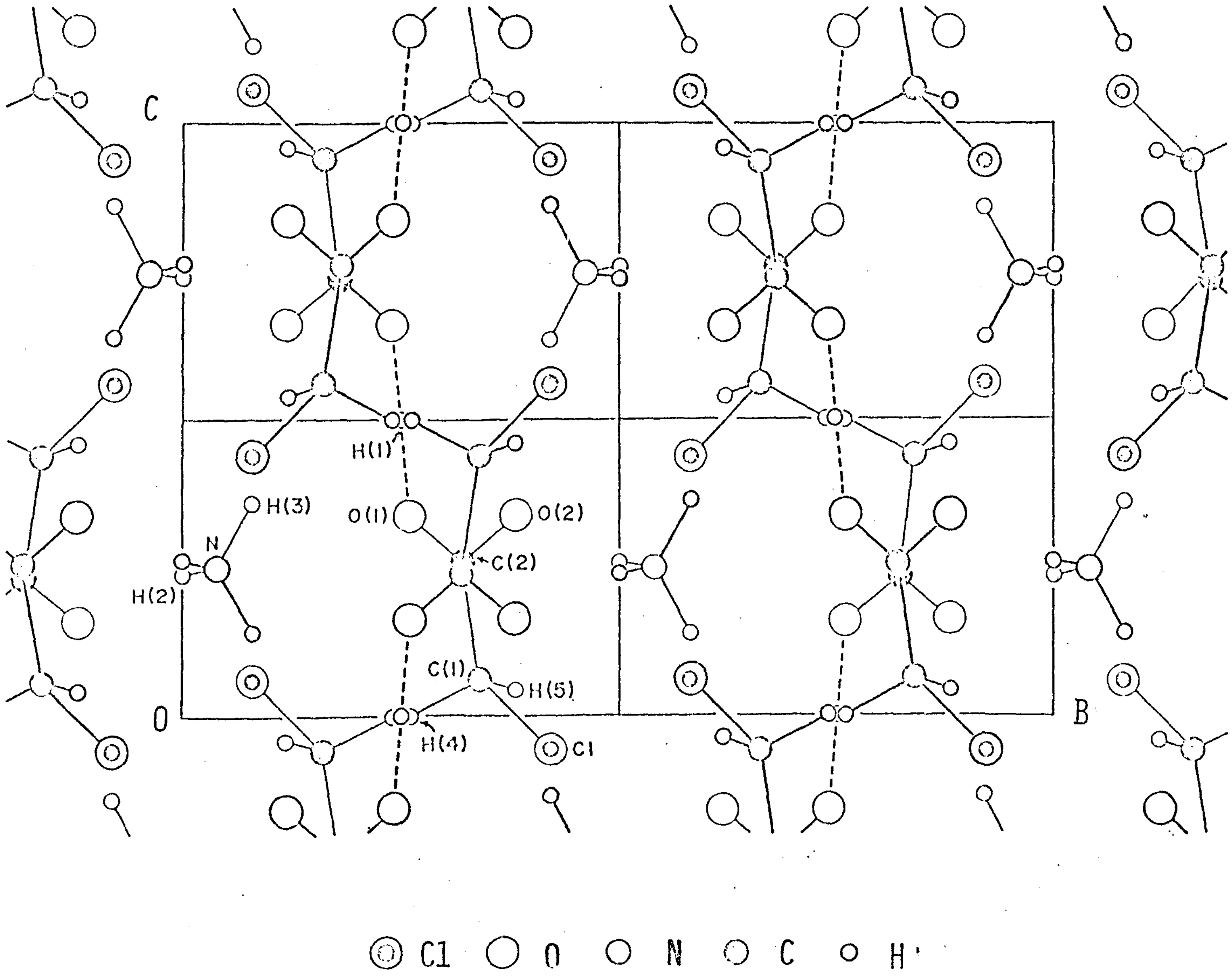

Fig. 3. The structure viewed along a axis. The crystallographically symmetrical hydrogen bonds are shown by broken lines.

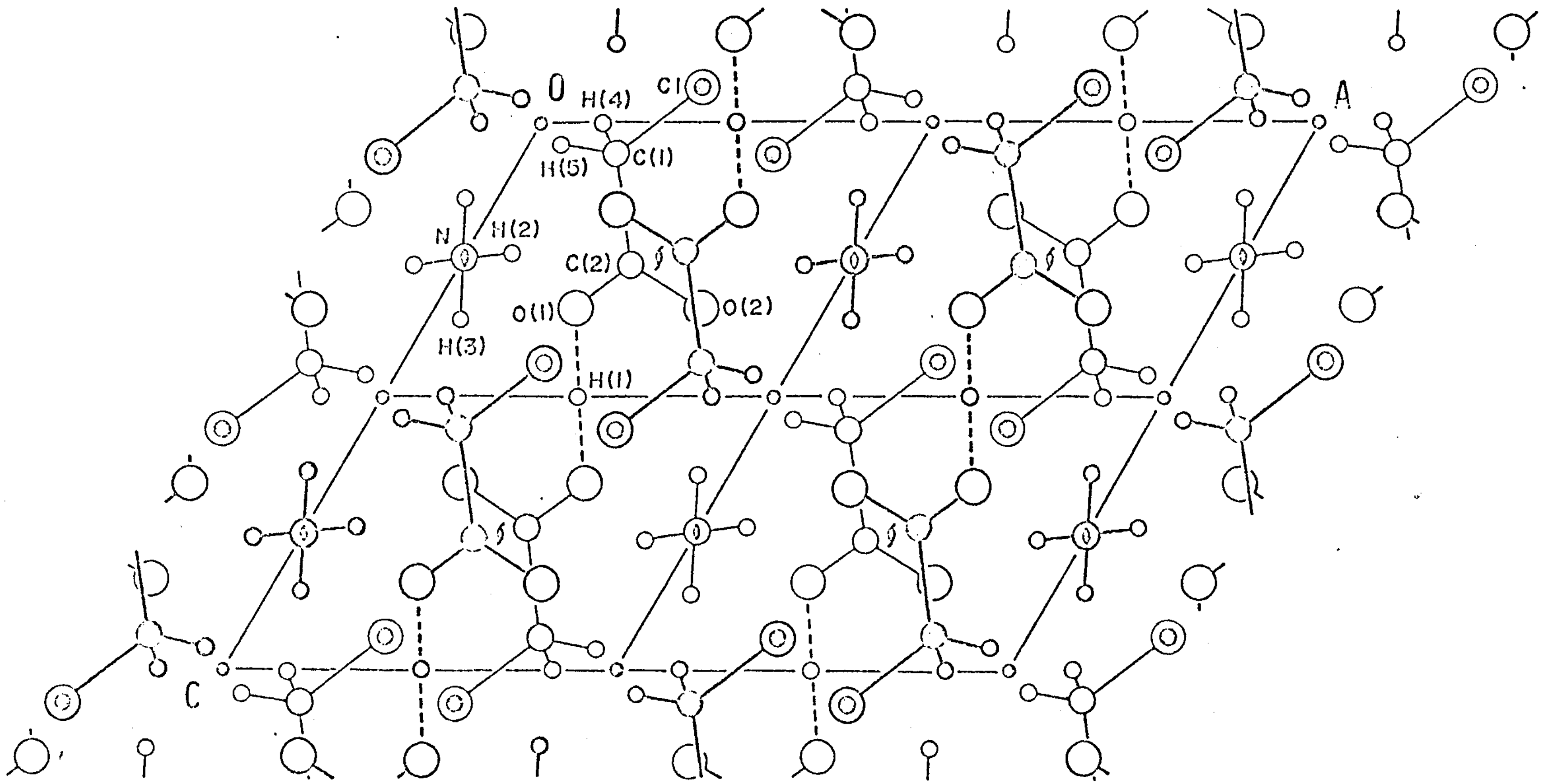

Fig. 4. The structure viewed along b axis.

Table 6. Summary of the inter-carboxyl hydrogen bonds in some Type A acid salts of monocarboxylic acids, MHX_2.

HX	M	space group	Molecules per cell	Symmetry of bond	O...H...O	Ref.
phenylacetic	K	I2/a	4	$\bar{1}$	2.443(4)	11
benzoic	K	C2/c	4	$\bar{1}$	2.51(4)	12
p-HO-benzoic	K	P/2c	2	$\bar{1}$	2.458(6)	13
acetic	Na	Ia3	24	2	(X) 2.444(10) (N) 2.475(14)	14 15
cinnamic	NH_4	C2/c	4	$\bar{1}$	2.51(3)	16
p-Cl-benzoic	K	C2/c	4	$\bar{1}$	2.457(13)	17
m-Cl-benzoic	K	C2/c	4	$\bar{1}$	2.437(6)	18
trifluoroacetic	Cs	A2/a	4	$\bar{1}$	2.38(3)	19
	K	C2/c	4	$\bar{1}$	(X) 2.435(7) (N) 2.437(4)	19 20
aspirin	K	C2/c	4	$\bar{1}$	(X) 2.455(5) (N) 2.448(4)	21 22
	Rb				2.48(2)	23
$O-NO_2$-benzoic	Rb	$P\bar{1}$	1	$\bar{1}$	2.43(6)	10
anisic	K	Rbcn	4	2	2.476(18)	24

The ammonium ion

The ammonium ion lies on a twofold axis surrounded by oxygen atoms from six different carboxyl groups, making hydrogen bonds with them. The interatomic distances and angles of the ammonium ion and the hydrogen bond are listed in Table 7. The atom H(2) is adjacent to the atom $O(2^{iv})$, while H(3) is adjacent to $O(2^{i})$ and O(1).

The chloroacetate residue

The best plane of the carboxyl group and C(1) is represented by the equation

$$-0.6279\ X + 0.7488\ Y + 0.2121\ Z = 2.4190\ ,$$

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 the atoms from the plane are:

O(1) 0.003, O(2) 0.004, C(1) 0.003, C(2) -0.010 Å

The Cl atom lies 0.21 Å out of the plane.

The bond lengths and angles in the chloroacetate residue are presented in Table 7 and Fig.5. The Cl-C(1) bond length of 1.768 Å is in good agreement with the value of 1.767 Å given by Sutton.25) The bond length of C(1)-C(2), 1.506 Å, agrees with that found in other Type A acid salts and also with that given by Sutton.25) The C-O bond lengths are 1.278 Å for C(2)-O(1) and 1.225 Å for C(2)-O(2), and the C-C-O angles are 111.4° for C(1)-C(2)-O(1) and 123.2° for C(1)-C(2)-O(2).

Table 7. Interatomic distances and bond angles with their standard deviations

The e.s.d.'s given in parentheses refer to the last figure.

	ammonium ion		
N - H(2)	1.01(4) Å	H(2) - N - $H(2^{ii})$	110(4)°
N - H(3)	0.86(3)	H(2) - N - H(3)	115(3)
		H(2) - N - $H(3^{ii})$	99(4)
		H(3) - N - $H(3^{ii})$	121(5)
	chloroacetate residue		
C(1) - Cl	1.768(4)	Cl - C(1) - C(2)	113.4(2)
C(1) - C(2)	1.506(4)	C(1) - C(2) - O(1)	111.4(2)
C(2) - O(1)	1.278(4)	C(1) - C(2) - O(2)	123.2(3)
C(2) - O(2)	1.225(3)	O(1) - C(2) - O(2)	125.4(3)
C(1) - H(4)	0.96(3)	Cl - C(1) - H(4)	104(3)
C(1) - H(5)	0.99(5)	H(4) - C(1) - H(5)	111(3)
		H(5) - C(1) - Cl	109(2)
		H(4) - C(1) - C(2)	112(2)
		H(5) - C(1) - C(2)	108(2)
	hydrogen bond		
N ...$O(2^{iv})$	2.880(3)	N - H(2)...$O(2^{iv})$	163(3)
H(2)...$O(2^{iv})$	1.90(4)	N - H(3)...$O(2^{i})$	161(3)
N ...$O(2^{i})$	3.148(3)	N - H(3)...O(1)	108(3)
H(3)...$O(2^{i})$	2.32(3)		
N ...O(1)	2.926(4)	C(2) - O(1)...$O(1^{i})$	114.8(3)
H(3)...O(1)	2.55(4)		
O(1)...$O(1^{i})$	2.432(5)		

Superscripts refer to atoms at :

i	1/2-x, 1/2-y, 1-z	iii	-x, y, -1/2-z
ii	-x, y, 1/2-z	iv	1/2-x, -1/2+y, 1/2-z

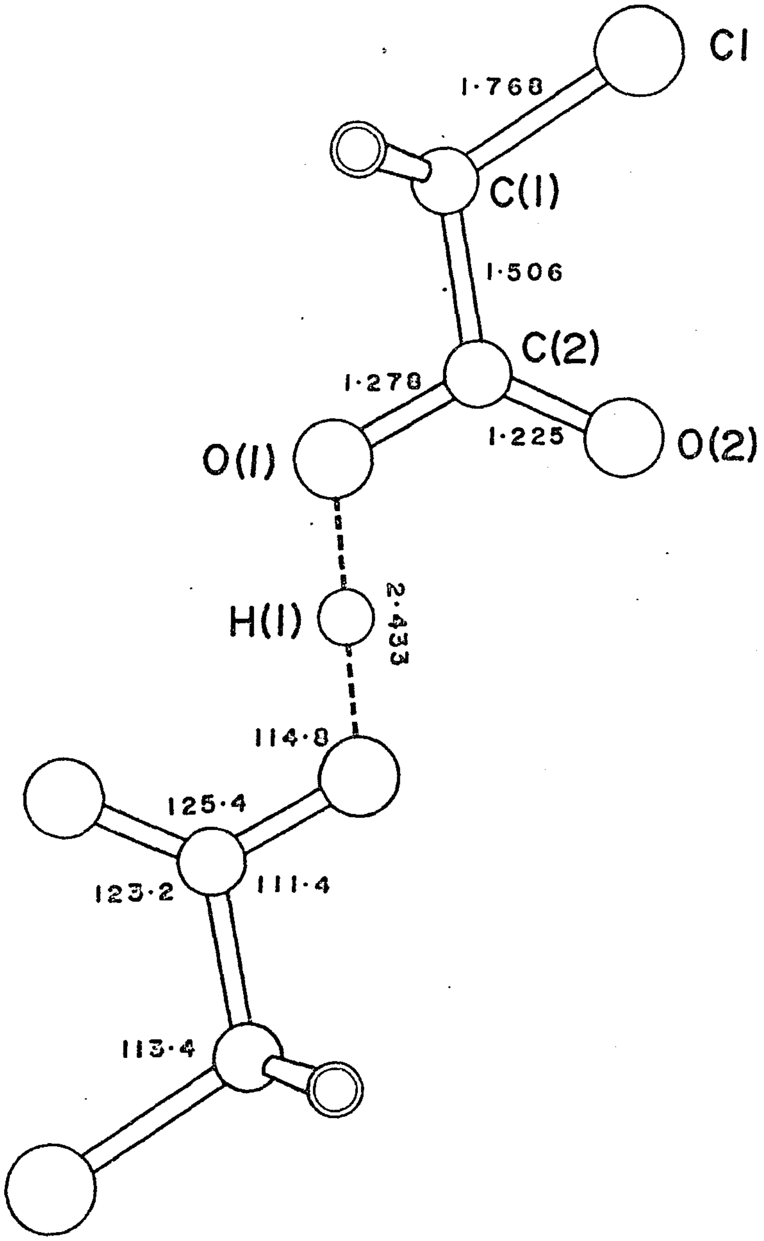

Fig. 5. Bond distances and angles in the chloroacetate residue.

It is pointed out that in the fully ionized carboxyl group the two C-O bond-lengths and the two C-C-O angles are equal, while in un-ionized carboxyl group they differ.26) The difference of the bond-lengths, 0.053 Å, and the deviation of the angles from 118° seem to indicate that the carboxyl group in ammonium hydrogen bis (chloroacetate) is intermediate in character between fully ionized and neutral, as is pointed out in the study of other Type-A acid salts.11,13) It should be noted here that this character is caused by the very short hydrogen bond27) described below. The distance of $Cl-Cl^{iii}$, 3.604 Å, is nearly equal to the sum of van der Waals radii. There is no abnormal intermolecular contact.

II.5. The very short hydrogen bond

The chief interest in $NH_4H(ClCH_2COO)_2$ lies in the crystallographically symmetric hydrogen bonds $O(1)...O(1^i)$, which are shown by broken lines in Figs.3 and 4. As in most Type A acid salts (Table 6), symmetry element affecting the hydrogen bond is a center of symmetry which requires the proton to be exactly at the mid-point between the oxygen atoms.

However, X-ray analysis cannot distinguish between the two cases: (a) the case in which the proton vibrates in a symmetric single-minimum potential well at the mid-point, and (b) the case in which it is distributed at random in a set of symmetric double-minimum well, situated close to either side of the mid-point. Even with the neutron diffraction analysis which is more powerful method than X-ray for studying the location of hydrogen atoms, it is difficult to distinguish definitely the two cases. It is shown in the case of $NaHF_2$ by McGaw and Ibers[28)] that it is equally possible to interprete the observed scattering density by the case (a) or by the case (b). Meanwhile it is known that crystals having a very short and possibly symmetric hydrogen bond show anomalous infrared spectra, although the assignment of each band does not seem to have been established enough. There is a remarkably intense background absorption over several hundred cm^{-1} of which the maximum lies between 700 and 900 cm^{-1}, with various peaks and often with a transmission 'window' in it.[2)]

It has been pointed out by McGaw and Ibers[28)] that a combination of diffraction and spectroscopic data, i.e. comparison of r.m.s. amplitude of thermal motion derived from both data, provides the most powerful evidence that FHF hydrogen bond in $NaHF_2$ has the potential of single-minimum type. In Type A acid salts, the precise neutron diffraction results in potassium hydrogen bis (trifluoroacetate)[20)] and potassium hydrogen bis (aspirinate)[22)] were analysed along this line.

Thermal vibration ellipsoids of OHO group contain some overall motion which are causing oxygen and hydrogen atoms to move in the same direction. A more useful information may be obtained by subtracting the oxygen atom motion from the hydrogen atom motion: $U_\Delta = U_H - U_O$. The difference ellipsoid is strikingly elongated along the OHO bond, and indicates that the major motion of the hydrogen atom is along the bond. The difference ellipsoid should closely approximate the motion of the hydrogen atom in a static field of two motionless oxygen atoms; in particular the amplitude along the bond should be closely related to the asymmetric stretching frequency of the idealized OHO system. The U_Δ values of 0.19 (0.17) Å for KH (aspirinate)$_2$ (KH(CF$_3$COO)$_2$) were obtained along the bond from the difference ellipsoid. On the other hand, the asymmetric stretching frequency in both compounds are assigned to 800 cm^{-1}.[20,29)] If a simple harmonic motion of a particle with mass 1 is assumed, the r.m.s. amplitude of 0.14 Å is derived. The difference $U_\Delta - U_{IR}$ 0.05 (0.03) Å for KH (aspirinate)$_2$ (KH(CF$_3$COO)$_2$) are not large and are plausibly accounted for some departure of the hydrogen atom potential functions from a simple harmonic one., i.e. anharmonicity. If a double-minimum potential well is assumed, and the difference $U_\Delta^2 - U_{IR}^2$ is ascribed to the displacement of an equilibrium point from the center, the values of 0.13 (0.09) Å are obtained for KH (aspirinate)$_2$ (KH(CF$_3$COO)$_2$), which are less than 0.14 Å of U_{IR}. Thus the double-minimum model leads to that a half-hydrogen atom undergoes a simple harmonic motion with a r.m.s. amplitude of 0.14 Å around the equilibrium position displaced 0.13 (0.09) Å from the mid-point of the OHO bond in KH (aspirinate)$_2$ (KH(CF$_3$COO)$_2$); the r.m.s. magnitude of 0.14 Å from one of the assumed equilibrium points would bring the hydrogen atom from one well to the other. Therefore it is concluded that the hydrogen motion can be described in terms of a broad, flat anharmonic potential, possibly with a hump below zero-point vibrational level, i.e. that the hydrogen atom potential is effectively of single-minimum type.

The very short hydrogen-bond lengths in $NH_4H(ClCH_2COO)_2$ is 2.432 Å, which is one of the shortest among those of Type A acid salts determined precisely with the estimated standard deviations equal to or less than 0.010 Å (Table 6). The infrared spectrum of $NH_4H(ClCH_2COO)_2$ was measured at room temperature, which is shown in Fig.6. The expected anomalies common to other Type A acid salts were found: the very broad and strong absorption lies in the region of 400-1600 cm^{-1} with its maximum at about 900 cm^{-1}.

Therefore it can be concluded that the hydrogen atom potential of the very short hydrogen bond of $NH_4H(ClCH_2COO)_2$ is effectively of a single-minimum type, at least to same extent as other Type A acid salts from the following points: (i) the hydrogen-bond length 2.432 (5) is one of the shortest among Type A acid salts, (ii) the infrared

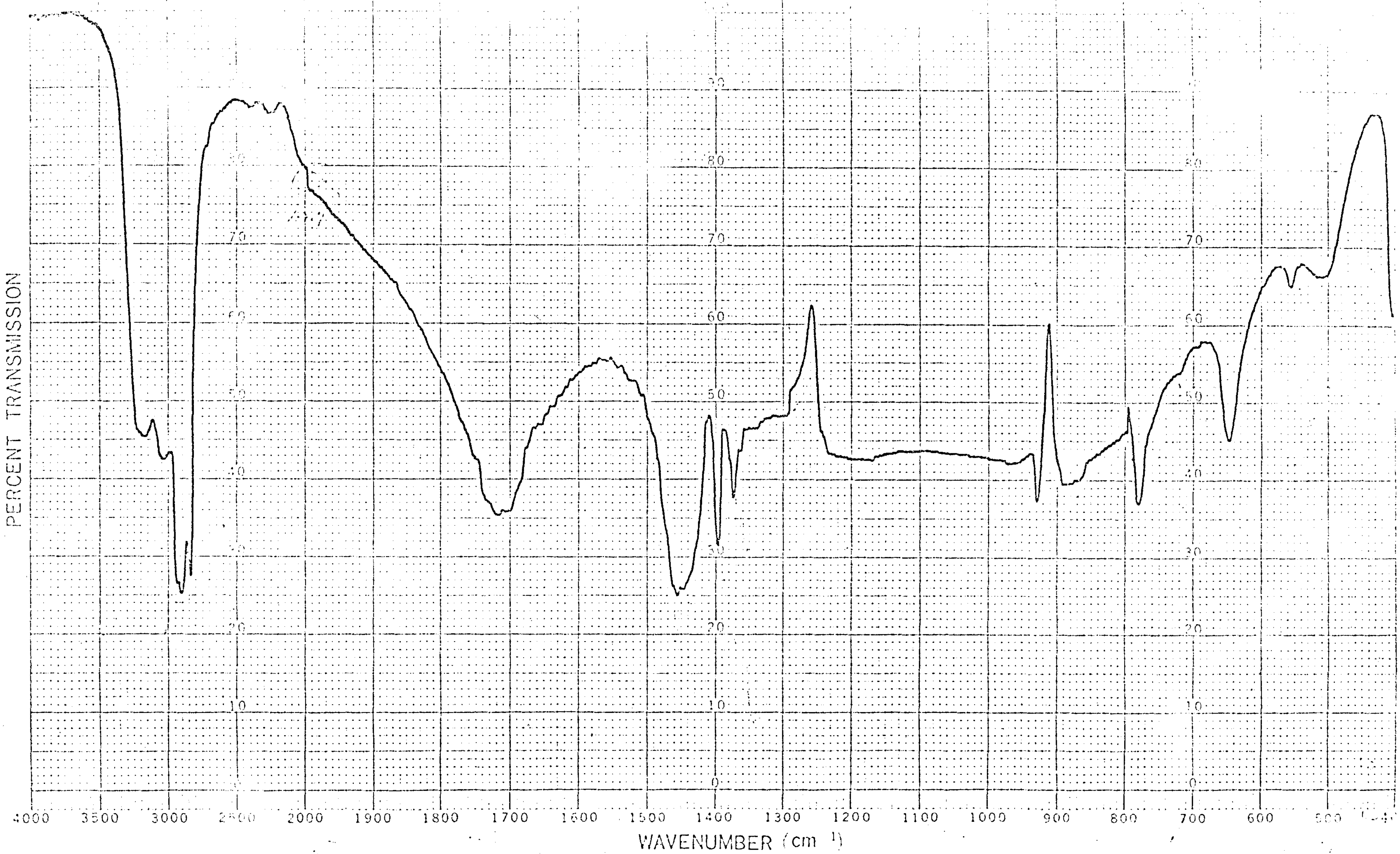

Fig. 6. The infrared spectrum of $NH_4H(ClCH_2COO)_2$ at room temperature (Nujol).

spectrum at room temperature has anomalous characteristic common to Type A acid salts, (iii) the hydrogen-bond lengths in Type A acid salts are concentrated around mean of six most precise values 2.445 Å, in spite of much varieties of chemical surroundings (Table 6), (iv) in Type A acid salts, the conclusions concerning the shape of the potential from diffraction and spectroscopic data are in agreement with the opinion of being effectively of a single-minimum type.$^{2)}$

Ferroelectric $NH_4H(ClCH_2COO)_2$ has the shortest hydrogen-bond among hydrogen-bonded ferroelectrics precisely measured until now, as far as the author is aware, and offers the first example of hydrogen-bonded ferroelectrics with a single-minimum potential well. Occurence of a ferroelectric with a single-minimum potential well is of a particular significance, because the phase transition mechanism in hydrogen-bonded ferroelectrics with short hydrogen bonds is ordinarily considered on the basis of the order-disorder model such as KH_2PO_4, where the shape of the potential is assumed to be of double-minimum type, and the hydrogen atom in the OHO bond cannot play a crucial role as trigger of phase transition in a single-minimum potential well. Ferroelectric $NH_4H(ClCH_2COO)_2$ seems to give a new clue to unified understanding of hydrogen-bonded ferroelectrics, which are full of variety, from structural characteristics of hydrogen bonding.

References

1) M. Ichikawa and T. Mitsui: Phys. Rev. **152** (1966) 495.

2) J. C. Speakman: chem. Commun. (1967) 32;
Structure and Bonding **12** (1972) 141.

3) M. Ichikawa: Acta Cryst. B**28** (1972) 755.

4) *International Tables for X-ray Crystallography*
(Kynoch Press, Birmingham, 1959 and 1962)
Vol.II and Vol.III.

5) D. C. Phillips: Acta Cryst. **9** (1956) 819.

6) J. S. Rollett and R. A. Sparks; Acta Cryst.
13 (1960) 273.

7) A. J. C. Wilson: Acta Cryst. **2** (1949) 378.

8) UNICS *Universal Crystallographic Computing System*,
ed. T. Sakurai (Crystallographic Society of Japan,
1967).

9) M. J. Buerger: *Crystal-structure analysis*
(John Wiely & Sons, New York, 1960); H. Lipson and
W. Cochran: *The Crystalline State. Vol.III.*
The Determination of Crystal Structures,
ed. Sir L. Bragg (G. Bell and Sons, London, 1966).

10) H. N. Shrivastava and J. C. Speakman: J. chem. Soc.
(1961) 1151.

11) L. Manojlović and J. C. Speakman: Acta Cryst.
B**24** (1968) 323.

12) J. M. Skinner, G. M. D. Stewart and J. C. Speakman:
J. chem. Soc. (1954) 180.

13) L. Manojlović: Acta Cryst. B24 (1968) 326.

14) J. C. Speakman and H. H. Mills: J. chem. Soc. (1961) 1164.

15) M. J. Barrow, M. Currie, K. W. Muir, J. C. Speakman and D. N. J. White: J. chem. Soc. Perkin II. (1975) 15.

16) R. F. Bryan, H. H. Mills and J. C. Speakman: J. chem. Soc. (1963) 4350.

17) H. H. Mills and J. C. Speakman: J. chem. Soc. (1965) 4355.

18) A. L. Macdonald and J. C. Speakman: J. chem. Soc. Perkin II. (1973) 1564.

19) L. Golić and J. C. Speakman: J. chem. Soc. (1965) 2530.

20) A. L. Macdonald, J. C. Speakman and D. Hadži: J. chem. Soc. Perkin II. (1972) 825.

21) L. Manojlović and J. C. Speakman: J. chem. Soc. A. (1967) 971.

22) A. Sequeira, C. A. Berkebile and W. C. Hamilton: J. molecular Struct. 1 (1967) 283.

23) S. Grimvall, R. F. Wengelin: J. chem. Soc. A. (1967) 968.

24) D. R. McGregor and J. C. Speakman: J. chem. Soc A. (1968) 2106.

25) L. E. Sutton: *Tables of Interatomic Distances and Configuration in Molecules and Ions* (The Chemical Society, London, 1965) Supplement.

26) T. Hahn: Z. Krist. **109** (1957) 438.

27) M. Ichikawa: Submitted to Acta Cryst. B (1978).

28) B. L. McGaw and J. A. Ibers: J. chem.Phys. **39** (1963) 2677; W. C. Hamilton and J. A. Ibers: *Hydrogen Bonding in Solids* (Benjamin, New York, 1968) Chap.3.

29) A. Novak: Structure and Bonding **18** (1974) 177.

Chapter III. The X-ray Crystal Structure Analysis of Ferroelectric $NH_4H(ClCH_2COO)_2$ of the Ferroelectric Phase at 80 K

III.1. Introduction

In chapter II the results of the X-ray crystal structure analysis of ferroelectric $NH_4H(ClCH_2COO)_2$ in the paraelectric phase at room temperature have been described.$^{1)}$ It has been shown that $NH_4H(ClCH_2COO)_2$ has the shortest hydrogen bond among the hydrogen-bonded ferroelectrics precisely measured so far and it offers the first example with the hydrogen-atom potential of a single-minimum type. In this chapter the results of the crystal structure analysis of the ferroelectric phase at 80 K is described,$^{2)}$ which has been carried out with an interest in the structural change accompanying the ferroelectric phase transition, in particular the structural changes in the OHO bond and the NH_4^+ ion. On the basis of the structures of the paraelectric and the ferroelectric phase, the mechanism of the ferroelectric phase transition is discussed together with the results of other experimental technique mainly by chihara and coworkers; the ^{35}Cl nuclear quadrupole resonance frequencies$^{3)}$; Raman and infrared spectra$^{4)}$ in $NH_4H(ClCH_2COO)_2$ and $ND_4D(ClCH_2COO)_2$, the ^{35}Cl nuclear quadrupole resonance frequencies and relaxation times in $NH_4H(ClCH_2COO)_2$,5) heat capacity of $NH_4H(ClCH_2COO)_2$ and $ND_4D(ClCH_2COO)_2$.6)

III.2. Experimental

Low-temperature apparatus

The apparatus of cold-gas blowing type (Fig. 1) was used to take low temperature Weissenberg photographs by equi-inclination method, which was intended firstly for helium gas,*) but nitrogen gas was used in this study. A Weissenberg camera is put in a box. Air in the box was replaced with dry nitrogen gas to prevent icing of the sample. Then liquid nitrogen was transferred to a small cylindrical box with heaters for evapolation, by pressure added from nitrogen bomb in addition to pressure due to natural evaporation in a metal Dewar vessel. Cold nitrogen gas was blowed over the sample. All data were collected at 80 K. Stability of temperature was attained by controlling the nitrogen gas gas flow of the bomb and the leak valve and was maintained within ± 2°. The temperature was measured by an Au: 2.1 % Co-Cu thermocouple placed at about 1 mm from the crystal.

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*) K. Itoh, Y. Shiozaki, A. Hashiguchi and T. Mitsui: private communication.

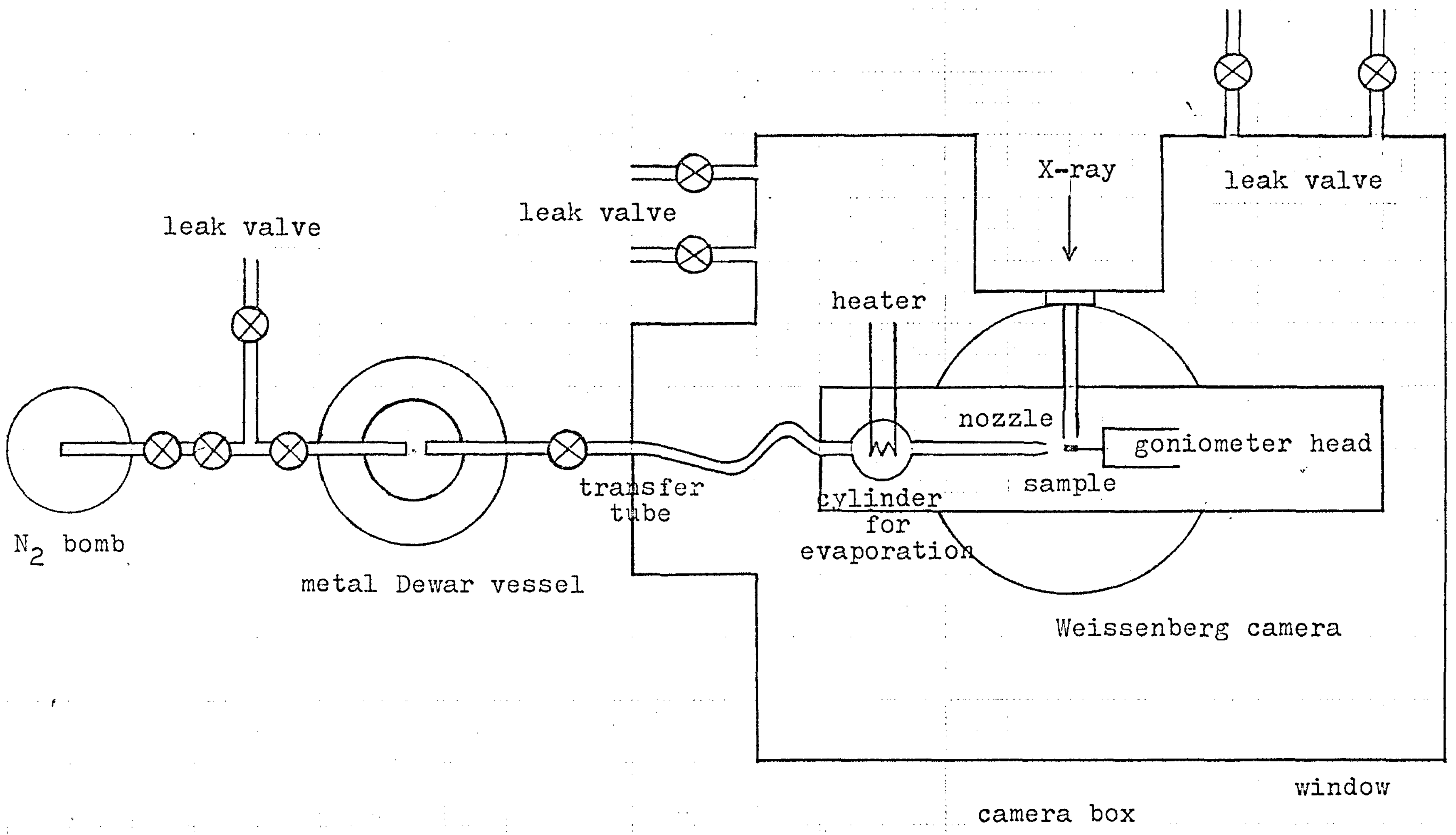


Fig. 1. A schematic diagram of the low-temperature Weissenberg camera apparatus of cold gas blowing type

Data collection and processing

Weissenberg photographs were taken with Cu $K\alpha$ radiation to determine the space group and unit-cell parameters. The systematic absences of reflections 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 a least-squares treatment, using θ values for 50 reflections measured on zero-layer Weissenberg photographs taken around each crystallographic axis. The systematic errors described in II.2 were considered partly by adding a $\sin 2\theta$ term in the observation equations. The crystal data are given in Table 1.

Three-dimensional intensity data were obtained from Weissenberg photographs of four multiple film taken about the a, b and c axes with Cu $K\alpha$ radiation of 50 KV, 24 mA and about two and half hours exposure. Cylindrical crystals 0.38 ~ 0.42 mm in diameter with nail varnish were used. Possible efforts for obtaining accurate data were exerted in the following respects; as many photographs as possible were taken to get the reliable scaling factors and many numbers of reflections (layers: $h = 0 \sim 5$; $k = 0 \sim 6$; $l = 0 \sim 4$) and the integrated intensities were measured by tracing manually the spots with a Rigaku Denki Recording Microphotometer MP-3. Intensities were corrected for Lorentz, polarization, and absorption effects (μ CuKα = 63 cm^{-1}). Absorption correction factors used

Table 1. Crystal data at 80°K

$a = 10.47 \pm 0.02$ Å
$b = 11.40 \pm 0.01$
$c = 8.22 \pm 0.01$
$\beta = 119.3 \pm 0.1$ °
$U = 857 \pm 2$ 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
$D_x = 1.60$ gcm^{-3}
F(000) = 424
Z = 4
$\lambda(Cu\ K\alpha_1) = 1.5405$ Å
$\lambda(Cu\ K\alpha_2) = 1.5443$

were taken from International Tables for X-ray Crystallography.7) Corrections for the elongation of spots on the high layers were made according to Phillips.8) The data from each layer were correlated by the method of Rollett and Sparks9) and then placed on an absolute scale by Wilson's method.10) 647 independent reflections including those with non-zero intensity was obtained.

III.3. Refinement of the structure

The positional parameters obtained at room temperature1) and the overall temperature factor of the low-temperature modification derived from Wilson's method10) 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 structure factors. The quantity minimized was $\sum(|Fo| - 1/k|Fc|)^2$. Refinement was continued until all parameter shifts were less than one third their standard deviations. In the final cycle, those reflections that were unable to be detected, but which had calculated structure factor less than the minimum observable values, were included in the computation. Six strong reflections were excluded, because they are 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 reflections were excluded). The atomic scattering factors were taken from International Tables for X-ray Crystallography.7)

All the calculations were made on a FACOM 230-60 computer with UNICS.11) The final positional parameters and temperature factors are given in Table 2 together with their standard deviations and the table of $|Fo|$ and $|Fc|$ is in Table 3.

III.4. Description of the structure

General view

The structure viewed along the b axis is shown in Fig.2. Structural changes, due to symmetry change accompanying the ferroelectric phase transition, are as follows. The nitrogen atom which occupies the special position on a two fold 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 two oxygen atoms. The correspondence between atomic

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

	x	y	z	B ($\mathring{A}^2$)
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)

As for numbering of atoms, see Table 4.

Table 3. Observed and calculated structure factors

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L=	0	0	6	8	8	10	12	13	H,L=	-3	2	4	13	16	H,L=	1	3	4	30	26	2	15	19	H,L=	-8	6	4*	0	[illegible]
4	46	49	10	21	21	12	16	17	1	15	18	6	18	18	1	58	59	6	21	23	4*	0	4	2	26	36	6	16	19
6	62	66	H,L=	-7	1	H,L=	5	1	3	15	14	8	11	15	3	21	19	8	21	23	8	17	18	4	26	19	8	10	13
8	16	17	1	11	9	1	15	15	5	41	40	H,L=	9	2	5	28	31	12	38	29	H,L=	7	4	H,L=	-6	6	H,L=	1	7
10	27	25	3	45	45	3	54	57	7	10	6	1	22	25	7	23	24	H,L=	-5	4	1	28	23	0	16	23	1	22	20
12	38	40	7*	0	4	5	10	6	9	14	12	3	8	4	9	29	26	1	13	10	5	24	22	2	42	44	3	46	41
14*	4	6	9	37	36	9	30	36	13	7	7	5	23	18	11	7	6	3	18	13	H,L=	-12	5	H,L=	-5	6	5	19	17
H,L=	1	0	11	9	9	11	20	20	H,L=	-2	2	H,L=	-13	3	13	5	7	5	9	9	6*	0	4	1	35	35	7	9	8
3	30	32	H,L=	-6	1	H,L=	6	1	0	37	44	1	16	10	H,L=	2	3	7	17	16	H,L=	-11	5	H,L=	-4	6	H,L=	2	7
5	7	10	2	26	23	2	7	6	2	93	88	H,L=	-12	3	2	52	52	9	21	17	1	27	31	0*	0	3	2	15	15
7	23	22	4	60	61	4	15	20	6	112	103	2	14	15	4	29	29	11	20	22	H,L=	-10	5	2	17	20	4	25	25
9	19	22	6	37	38	6	9	12	8	48	46	4	8	6	6	38	38	H,L=	-4	4	4	34	42	H,L=	-3	6	6	7	3
11	20	19	8	22	19	8	20	23	10*	0	3	H,L=	-11	3	10	47	48	0	100	107	H,L=	-8	5	1	67	75	H,L=	3	7
13	25	24	10	44	43	10	8	6	12	27	24	3	32	34	12	15	14	2	62	62	2	27	32	5	43	38	1	6	3
H,L=	2	0	12	6	8	H,L=	7	1	14	26	26	5	28	30	H,L=	3	3	4	73	67	H,L=	-7	5	H,L=	-2	6	3	22	20
2	23	27	H,L=	-5	1	1	12	11	H,L=	-1	2	7	7	2	1	32	32	6	32	29	1	32	36	0	14	18	5*	0	0
4	26	25	1	14	13	3	39	41	1	18	17	H,L=	-10	3	3	44	42	8	43	39	3	50	52	4	24	23	H,L=	4	7
6	50	46	3	16	15	5	45	53	3*	0	4	2	16	19	5	16	16	12	9	12	5	33	32	H,L=	-1	6	2	11	3
8	13	14	5	20	19	7*	0	5	5	44	38	4	8	10	7	9	11	H,L=	-3	4	H,L=	-6	5	1	41	37	H,L=	-10	8
10*	0	2	7	29	23	9	26	31	7	29	31	6	9	6	9	31	32	1	23	23	2	34	36	5	30	32	0	15	13
12	36	32	9*	0	4	H,L=	8	1	9	15	12	8	13	8	11	21	23	5	26	24	6*	0	1	H,L=	0	6	2	19	24
14	5	8	11	16	12	2	15	17	11	10	9	H,L=	-9	3	H,L=	4	3	7	25	25	H,L=	-5	5	0	30	29	H,L=	-8	8
H,L=	3	0	13	9	11	4	14	16	13	10	11	1	9	10	2*	0	5	11	14	10	1	45	53	2	34	33	0	39	40
3	22	23	H,L=	-4	1	6*	0	5	H,L=	0	2	3	19	13	4	11	12	13	25	23	3	42	37	4	19	18	2	18	22
5	6	9	2	45	45	H,L=	9	1	0	8	8	5	24	25	6	15	16	H,L=	-2	4	H,L=	-4	5	6	17	16	H,L=	-7	8
7	72	67	4	56	46	1*	0	1	2	48	42	7	19	20	8	9	10	0	14	20	4	37	34	8	55	49	5	30	23
9	42	42	6	16	14	H,L=	10	1	4	29	29	9	11	14	10	19	21	2	50	47	H,L=	-3	5	10	10	10	H,L=	-6	8
11	22	21	8	30	31	2	30	28	6	37	31	H,L=	-8	3	H,L=	5	3	4	56	53	1*	0	3	H,L=	1	6	0	42	44
13	32	34	12	13	12	6*	0	3	8	34	32	2	72	71	1	54	61	6	11	10	5	66	59	1	8	5	2*	0	4
H,L=	4	0	H,L=	-3	1	H,L=	-12	2	10	15	15	4	43	42	3	46	48	8	34	30	H,L=	-2	5	3	14	15	H,L=	-5	8
0	32	27	1	22	21	0	39	33	12	20	19	8	13	10	5	19	18	10	21	22	2	32	34	5*	0	1	1	21	22
2	22	22	5	24	22	2	13	11	14	35	29	10	24	22	7	6	5	12	5	9	4	63	57	7	13	11	3	24	25
4	18	20	7	19	16	4	12	8	H,L=	1	2	H,L=	-7	3	9	14	14	H,L=	-1	4	H,L=	-1	5	9*	0	1	H,L=	-4	8
8	23	25	9	36	33	H,L=	-11	2	3	13	11	1	14	12	H,L=	6	3	1	40	39	1	41	42	H,L=	2	6	2	20	25
10	7	5	11	9	8	1	35	29	5	67	64	5	33	31	2	18	16	3	65	59	3	35	31	0	24	23	H,L=	-2	8
12*	0	4	13	25	24	3	15	14	7	39	39	7	34	31	4	15	16	5	33	29	H,L=	0	5	2	19	21	0	40	63
H,L=	5	0	H,L=	-2	1	7	6	2	9	9	9	9	25	21	6*	0	4	7	64	67	2	37	34	4	7	8	2	21	24
1	34	36	4	9	8	H,L=	-10	2	11	9	6	11	7	10	8	11	11	9	22	21	6*	0	3	6	25	29	4	22	22
3	29	28	6	9	8	0	51	49	13	21	20	H,L=	-6	3	H,L=	7	3	11	17	18	8	37	33	8	35	32	H,L=	-1	8
7	47	49	8	21	16	2	13	8	H,L=	2	2	2	36	40	1	28	28	13	22	22	10*	0	3	H,L=	3	6	3*	0	2
9	17	14	10	16	17	4	13	10	0	29	33	6	11	6	3	16	12	H,L=	0	4	12	18	15	1	34	31	5*	0	2
11	25	25	12	14	13	6	28	33	2	52	52	8	32	33	5	10	10	0*	4	4	H,L=	1	5	5	23	22	H,L=	0	8
13	17	24	14*	4	6	8	13	13	4	39	33	10	23	23	7	12	11	2*	0	4	1	26	27	7	17	16	0	42	34
H,L=	6	0	H,L=	-1	1	H,L=	-9	2	6	25	23	12	14	14	H,L=	8	3	4	6	6	3	26	24	H,L=	4	6	2	12	14
2	18	21	5	10	6	1	13	11	8	7	7	H,L=	-5	3	2	19	18	6	39	35	5	41	44	0	31	32	4	13	13
4	7	8	7*	0	2	3	16	18	10	10	10	1	9	8	4	29	29	8	19	17	7	28	27	2	10	8	6	37	30
6	60	60	9	63	59	5	8	6	12	26	25	3	60	60	6	20	18	10	5	4	9	23	22	4	7	8	H,L=	1	8
10	6	7	11	26	25	7	17	19	H,L=	3	2	5	24	26	H,L=	-13	4	12*	0	1	11	21	22	6	8	10	1	21	23
H,L=	7	0	13	7	8	9	10	9	1	57	57	7	41	38	1	5	3	H,L=	1	4	H,L=	2	5	H,L=	5	6	3	6	6
1	30	35	H,L=	0	1	H,L=	-8	2	3	15	18	9	39	45	3	21	12	1	23	25	2	9	10	1	26	26	5	11	7
3	10	12	2	35	37	0	21	23	5	51	46	11	30	30	H,L=	-12	4	3	15	15	4	10	15	3*	0	1	H,L=	2	8
5	10	12	4	92	93	2	27	24	7	24	26	13	8	6	0	32	27	5	31	29	6	14	17	H,L=	-12	7	0	6	3
9	10	15	6	40	41	4	13	10	9	11	10	H,L=	-4	3	2	15	14	7	38	41	8	7	9	4	16	21	2	8	7
H,L=	8	0	8	17	18	6	32	31	11	14	13	2	40	34	4	10	12	9	20	18	10	10	10	H,L=	-11	7	H,L=	-9	9
0	39	41	10	18	18	8	33	32	13	28	28	4	58	53	6	25	22	11	24	23	H,L=	3	5	3*	0	5	1*	0	4
2	15	15	12	10	12	10	7	4	H,L=	4	2	8	18	22	H,L=	-11	4	H,L=	2	4	1	16	13	5*	0	2	H,L=	-7	9
8	12	13	14	6	7	H,L=	-7	2	0	73	76	10*	0	2	1	25	26	0	46	46	3	28	25	H,L=	-10	7	1	19	21
H,L=	9	0	H,L=	1	1	1	38	38	4	11	11	12	11	9	3	7	3	2	50	56	5	50	50	2	18	24	5	21	14
1	6	4	3	53	56	3	10	8	6	25	26	H,L=	-3	3	5	16	13	4	26	28	7	13	12	4	24	26	H,L=	-6	9
3	31	31	5	50	49	5	43	40	8	40	43	1	20	28	7	15	12	6	48	49	9	23	21	H,L=	-9	7	4	44	37
5	11	11	7	30	28	7	38	36	10	15	15	3	62	56	H,L=	-10	4	8	12	13	H,L=	4	5	5	35	37	H,L=	-5	9
7	36	29	9	33	32	9	9	4	12	33	37	5	44	49	0	46	43	10	12	12	2	18	19	H,L=	-8	7	1	19	23
H,L=	10	0	11	38	36	11	6	8	H,L=	5	2	7	18	22	2	25	24	12*	4	5	4	18	19	2*	0	0	H,L=	-4	9
0	27	23	13	5	8	H,L=	-6	2	1*	0	2	9	42	48	8	20	18	H,L=	3	4	6	6	6	4*	0	4	2	19	21
2	15	13	H,L=	2	1	0	69	65	3	30	33	13	9	5	H,L=	-9	4	1	29	29	8	16	17	H,L=	-7	7	4	26	25
6	15	10	2	66	71	2	17	15	5	8	8	H,L=	-2	3	1	38	41	3	16	17	H,L=	5	5	1	21	29	6*	0	3
H,L=	11	0	4	63	63	4	11	11	7	18	19	2	87	91	3	20	12	5	8	6	1*	0	2	3	27	26	H,L=	-3	9
1	20	18	6	9	8	6	18	14	9*	0	4	6	16	14	5	22	19	7	7	6	3	9	7	5	26	28	3	35	32
3	8	7	8	28	30	8	21	18	11*	0	3	8	13	12	7	31	27	9	14	15	5	10	13	H,L=	-6	7	H,L=	-1	9
H,L=	-11	1	10	33	37	10	22	22	H,L=	6	2	10	18	16	9	15	20	11	6	4	7	5	5	2	29	35	3	29	[illegible]
1	27	20	12	17	21	12*	0	3	0	37	38	12	8	9	H,L=	-8	4	H,L=	4	4	H,L=	6	5	4	33	28	H,L=	-7	10
3	24	23	14	12	12	H,L=	-5	2	2	20	22	H,L=	-1	3	0	15	15	0	31	32	2	39	41	H,L=	-5	7	1	24	37
H,L=	-10	1	H,L=	3	1	1	74	82	4	17	20	3	51	46	2	12	9	2	36	38	4	23	24	1	23	28	H,L=	-6	10
2*	0	3	1	10	13	3	27	27	6	31	27	5	54	47	4	30	28	4	27	33	6*	0	2	3	32	33	0	16	19
4	13	10	3	65	66	5	70	72	8	30	32	7	27	29	6	22	19	6	26	27	H,L=	7	5	H,L=	-3	7	H,L=	-4	10
6	9	8	5	24	25	9	11	8	10	8	7	9*	0	2	8	7	8	8	19	22	3*	0	1	1*	0	4	0	19	20
8	9	12	7	11	12	11	8	3	H,L=	7	2	11	20	21	10	10	11	10	13	8	H,L=	-12	6	5	33	35			
H,L=	-9	1	9	9	9	13	11	10	1	40	42	13	5	4	H,L=	-7	4	H,L=	5	4	2	22	23	H,L=	-2	7			
1	29	30	11	13	14	H,L=	-4	2	3	18	20	H,L=	0	3	1	41	45	1	16	14	4*	0	2	2	27	28			
3	63	63	13	17	16	0	48	43	5	12	13	2	63	62	5	8	7	3	21	22	H,L=	-11	6	4	26	17			
7	10	11	H,L=	4	1	2	14	8	7	9	8	4	57	48	7	40	37	5	12	12	5	27	30	H,L=	-1	7			
9	26	27	2	65	72	4	33	30	9	16	14	6	16	14	9	40	40	7	26	27	H,L=	-10	6	1	30	29			
H,L=	-8	1	4	66	75	6	94	85	H,L=	8	2	8	37	35	11	17	23	9	12	12	0	15	19	3	33	28			
2	9	7	6*	0	1	10	12	11	0	21	19	10	46	45	H,L=	-6	4	H,L=	6	4	H,L=	-9	6	H,L=	0	7			
4*	0	2	8	21	24	12	24	25	2	22	26	12	9	11	0	72	77	0	14	13	5	36	37	2	13	13			

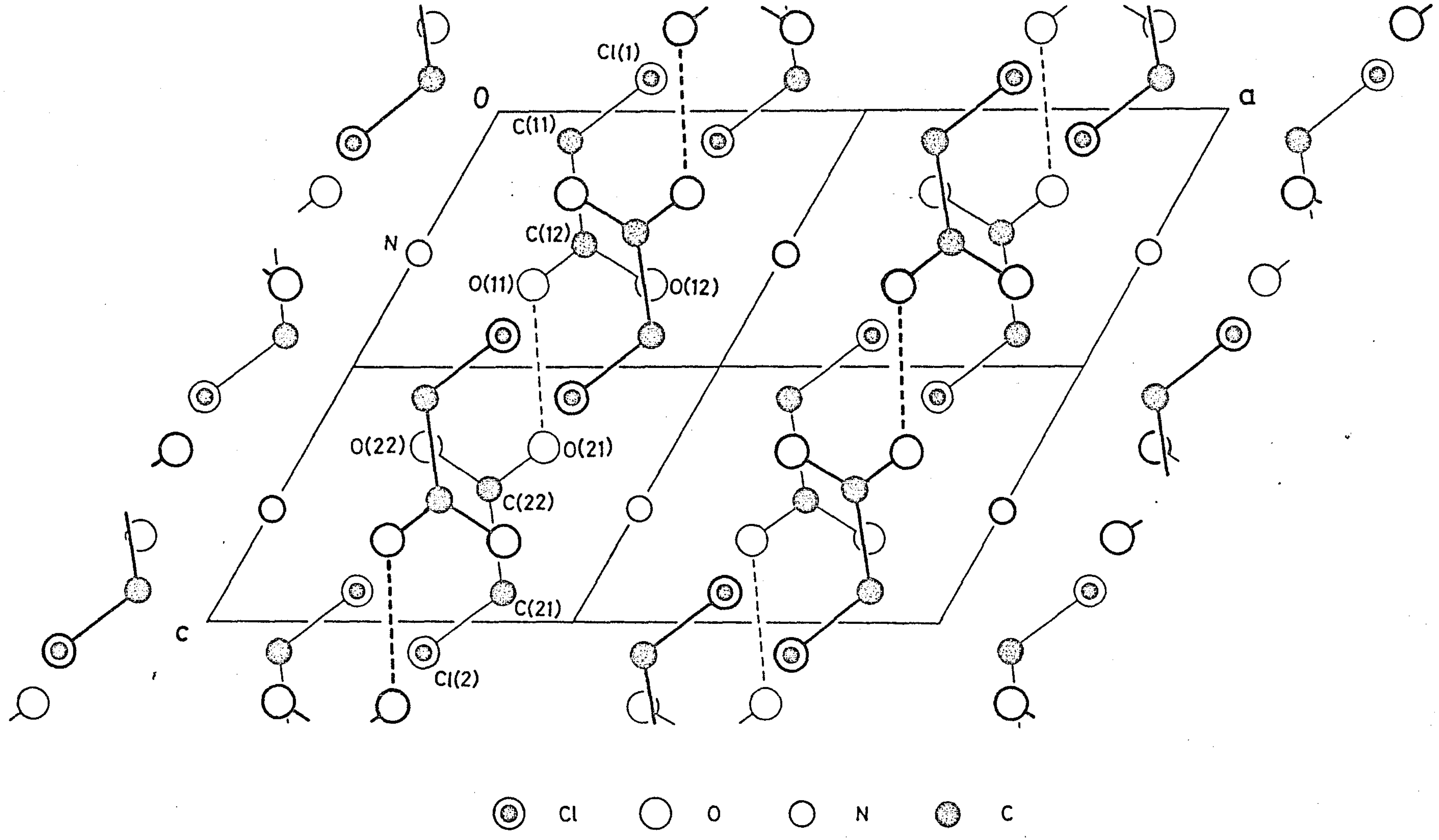


Fig. 2. The structure viewed along the b axis. The OHO hydrogen bonds are shown by broken lines.

numbering for the para- and the ferroelectric phase is listed in Table 4. The interatomic distances and angles are shown in Table 5 and Fig.3. Those obtained at room temperature are also given for comparison in Table 5.

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

$$-0.5892\ X + 0.7746\ Y + 0.2298\ Z = 2.4820,$$

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

$$-0.6274\ X + 0.7487\ Y + 0.2142\ Z = 2.6646,$$

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)

Table 4. Correspondence of numbering of atoms in the para- and ferroelectric phase.

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)

Table 5. 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) 1/2+x, 1/2+y, z

ii) x, -y, 1/2+z iv) 1/2+x, 1/2-y, 1/2+z

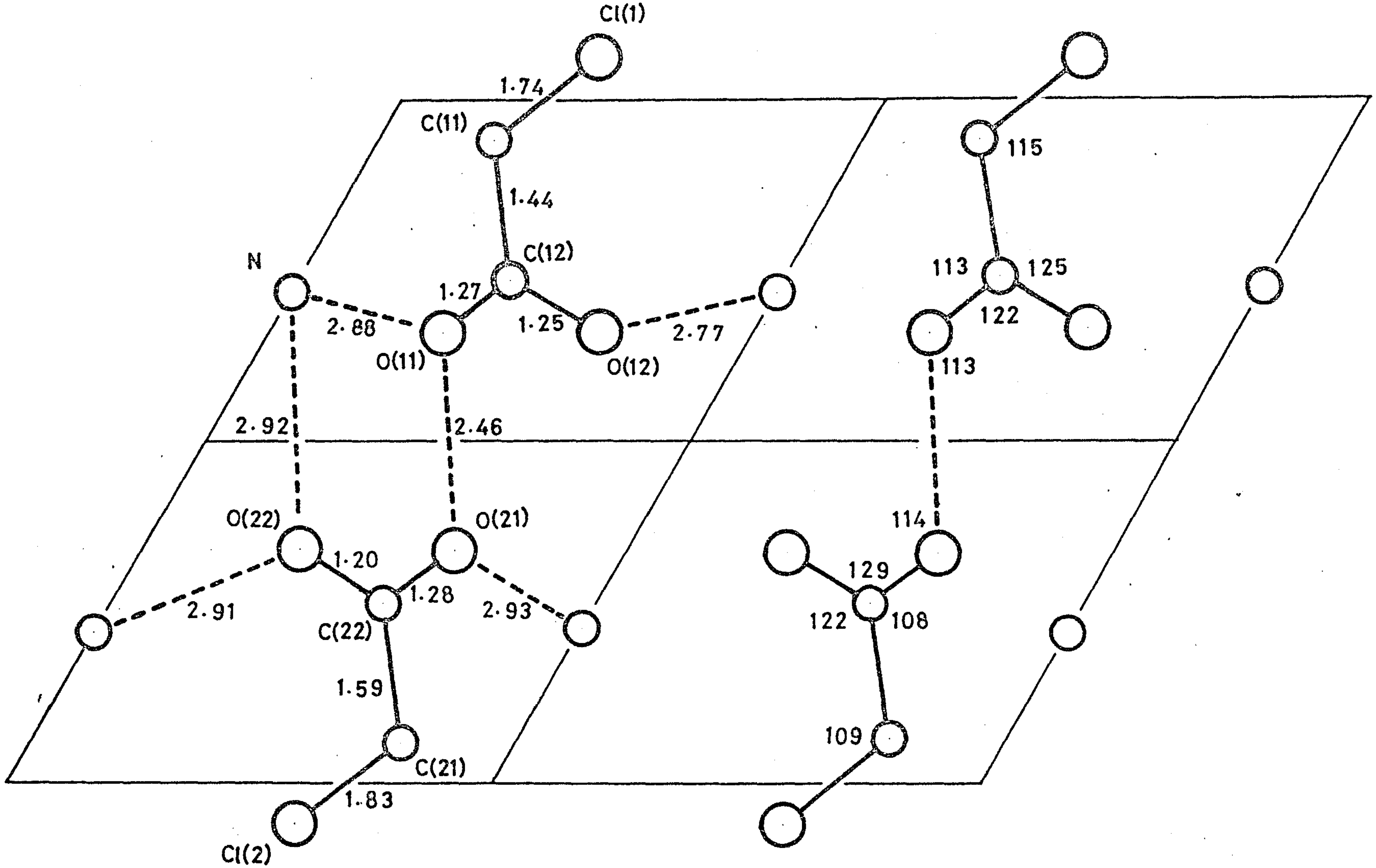


Fig. 3. The interatomic distances (Å) and angles (°) for structure at 80 K.

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.[12)] Moreover, the length of the OHO hydrogen bond linking the two radicals should show a definite increase[13)] as compared with that of the room-temperature structure, in which the potential of the hydrogen atom was thought to be of the single-minimum type.[1)] The bond lengths and angles of CA(1) and CA(2), however, do not show such a systematic tendency (Fig.3). The length of the OHO hydrogen bond, 2.457(16) Å is still close to 2.432(5) Å of the room-temperature value and to 2.445 Å which is the mean of six most precise values for Type-A acid salts (Table 6 in Chap.II). 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 ammonium ion is displaced 0.240 Å along the c axis from its position on the two-fold axis which exists 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 particluar, the following variations in the interatomic distances are noted: an increase of 0.221 Å in N^{iv}...O(12), and a decrease of 0.225 Å in N...O(22) and a decrease of 0.109 Å in N^{iii}...O(12)(see Table 5).

III.5. On the ferroelectric phase transition

The acidic hydrogen atom or the ammonium ion is one of the most commonly found constituents of hydrogen-bonded ferroelectrics and is said to play an important role in the phase transition such as KH_2PO_4 and $(NH_4)_2SO_4$. One of the structural features of ferroelectric $NH_4H(ClCH_2COO)_2$ is that the asymmetric unit contains only one acid hydrogen atom and one ammonium ion. Thus the mechanism of the phase transition of $NH_4H(ClCH_2COO)_2$ should be simpler than the cases which asymmetric unit contains more than one of these ions, e.g. $(NH_4)_2SO_4$ and NH_4HSO_4, if these constituents solely play the crucial role. The special attention is paid to the OHO bond and the ammonium ion below.

The OHO bond

It has been concluded from the structure analysis at room temperature that the shape of the hydrogen atom in the OHO bond connecting two chloroacetate residues is effectively of a single-minimum type in the paraelectric phase. This result necessarily leads to the conclusion that the acidic hydrogen atom does not drive the phase transition, i.e. cannot be the trigger, in contrast to the hydrogen atom in a double-minimum potential well. This is also supported from the result that the hydrogen-bond length remains still short at 80 K (2.457(16) Å) and falls in the range of other Type A acid salts within the accuracy of the present analysis.

Chihara and coworkers[3-6] have extensively studied the ferroelectric phase transtion in $NH_4H(ClCH_2COO)_2$ and $ND_4D(ClCH_2COO)_2$ by various experimental technique. Chihara, Inaba, Nakamura and Yamamoto measured temperature dependence of the ^{35}Cl nuclear quadrupole resonance frequencies in $NH_4H(ClCH_2COO)_2$ and $ND_4D(ClCH_2COO)_2$ and determined principal values of the electric field gradient tensors at Cl sites for two phases of H salts.[3] It was found that a single resonance line in the high temperature paraelectric phase splits into a pair of lines, whose separation is proportional to the spontaneous polarization. Next isotope effects were found; The transition temperature rises by 11 K, the ratio of the splitting ν_D/ν_H was 2.17, and the ratio of the splitting in the C-Cl stretching frequency in infrared spectra Δ_D/Δ_H was 2.16.[4] Two possible mechanisms of the ferroelectric phase transition, continuous displacive type and order-disorder type, are examined, but definite conclusion could not be drawn because both mechanisms account equally for the experimental results. Successively the ^{35}Cl nuclear quadrupole frequencies in the ferroelectric phase and the relaxation times T_1 were measured in two phases by Chihara, Nakamura and Okuma.$^{5)}$ T_1 decreases steeply in the vicinity of the transition temperature, the anomalous part of which was attributed to the critical fluctuations of the polarization. A large dip of T_1 in the critical region was analyzed by two models as well, i.e. order-disorder model and displacive model. The order-disorder type of mechanism can explain the T_1 data of the paraelectric phase, but cannot explain the different temperature dependence of T_1 of two lines, while displacive type mechanism gives a reasonable description of the T_1 anomaly both in the ferro- and paraelectric phase. The difficulty in order-disorder model also emerged from the heat capacity measurement in $NH_4H(ClCH_2COO)_2$ and $ND_4D(ClCH_2COO)_2$ by Chihara and Inaba$^{6)}$ in which the observed entropy 2.90 $JK^{-1}mol^{-1}$ is only half the magnitude predicted by a simple order-disorder model, Rln 2 or 5.76 $JK^{-1}mol^{-1}$. It was also pointed out from the heat capacity as well as differential analysis$^{3)}$ that the transitions are of second or higher order in contrast to our suggestion.$^{14)}$

Temperature dependencies of infrared and Raman spectra in $NH_4H(ClCH_2COO)_2$ and $ND_4D(ClCH_2COO)_2$ were reported by Chihara, Nakamura and Inaba.[4)] No well defined soft mode was found in Raman spectrum, but they report weak peaks aroun 200 cm^{-1} which depend on temperature. The broad and intense O-H (900 cm^{-1}) and O-D (850 cm^{-1}) stretching bands was also observed in the infrared spectrum, which is consistent with our observation (II.5., Fig.6). The significant temperature dependence of the band width and intensity was observed in the OCO in-plane bending mode. Hadži and Orel[15)] carried out an infrared absorption study of $NH_4H(ClCH_2COO)_2$ at 293 K and 93 K, and found that no significant change of bands associated with the OHO and carboxyl group vibration occurs. They concluded that the short hydrogen bond is not directly involved in the constituents which play the major role in the ferroelectric phase transition. As a whole, as for the mechanism of the ferroelectric phase transition in $NH_4H(ClCH_2COO)_2$ there are no serious contradictions between the conclusion drawn from our present structure analyses and those from other experimental techniques, i.e. the ^{35}Cl nuclear quadrupole resonance frequency and relaxation time, heat capacity measurement, and infrared and Raman spectrum, in the point that order-disorder mechanism of the acidic hydrogen atom is ruled out.

The ammonium ion

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.4. Fig.4(a) is the contour map obtained from the photographic data at room temperature.$^{1)}$ Fig.4(b) is the calculated map, $\rho'(x,y,z) = \frac{1}{2}\left\{\rho(x,y,z) + \rho(-x,y,\frac{1}{2}-z)\right\}$, from the electron density $\rho(x,y,z)$ 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 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

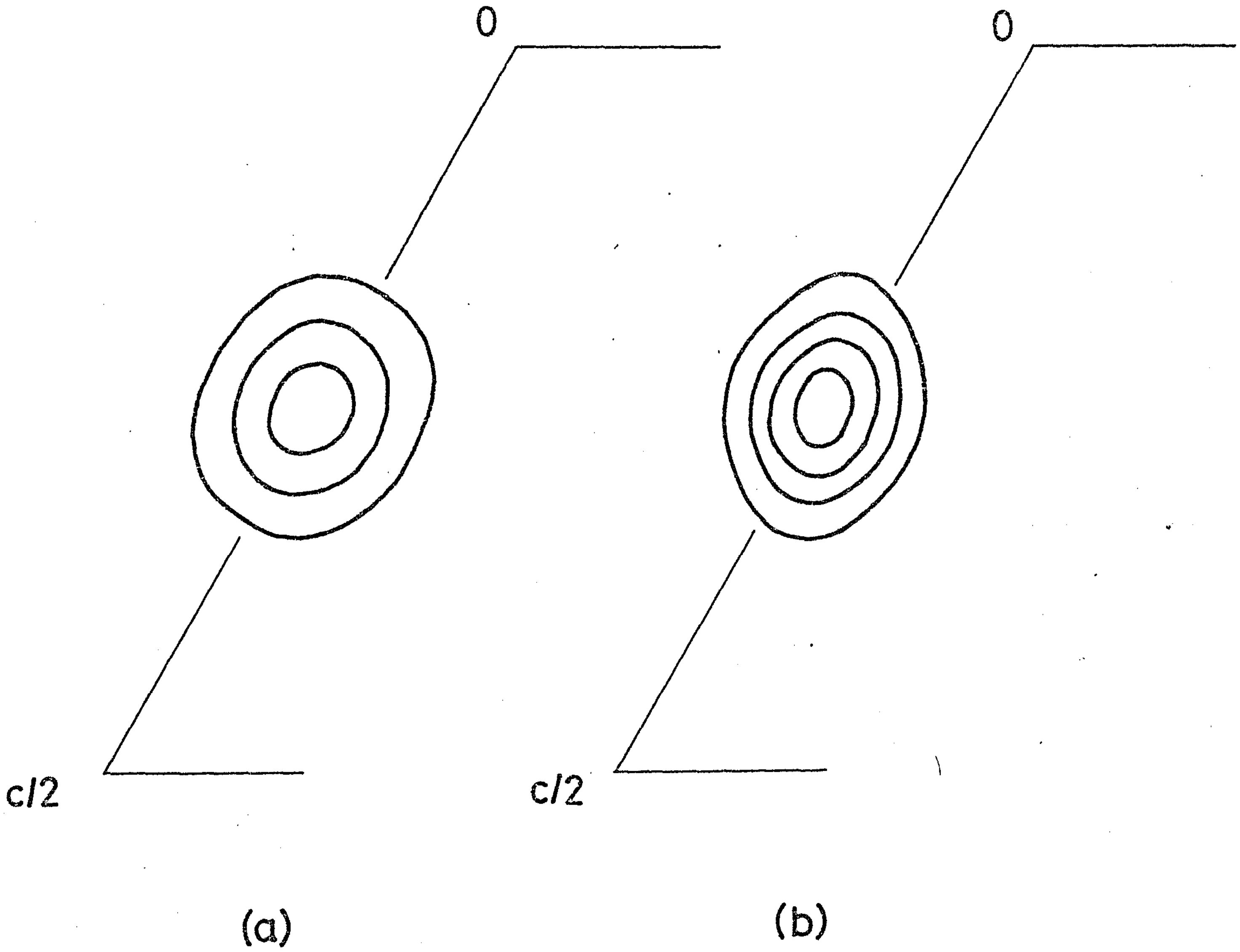


Fig. 4. The electron-density maps of the nitrogen atom viewed along the b axis at room temperature (a) and the calculated average one at 80 K (b). See text for details.

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.4) 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 taking into consideration.

Chihara, Inaba, Nakamura and Yamamoto$^{3)}$ examined a possibility that some motion of the ammonium ion play a role in the phase transition by proton magnetic resonance. However, it was ruled out since no discontinuous change was found at the transition temperature in the line width as well as in the spin-lattice relaxation time. This is also supported by the result that the spin-spin relaxation time T_2 shows only a shallow dip in the neighbourhood of the transition temperature, which is closely associated with the motion of the ammonium ion. Thus there is also no discrepancy between the conclusion from our structural aspect and those from the proton magnetic resonance and the ^{35}Cl nuclear quadrupole resonance studies.

Polarization reversal

Spontaneous polarization is switched by a change of CA(1)⟷CA(2). The displacements of each atom during switching are listed in Table 6. 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].[14] This is smaller by one or two order of magnitude compared with well-known ferroelectrics such as $BaTiO_3$, SbSI, $NaNO_2$, KH_2PO_4 and $(NH_2CH_2COOH)_3 \cdot H_2SO_4$.[16]

One of the future problems in $NH_4H(ClCH_2COO)_2$ will be the study of origin of the ferroelectric phase transition based upon more detailed knowledge of temperature variation of the atomic configuration and the atomic motion. Chihara, Inaba and Okuma[5] suggest that the ferroelectric transition in $NH_4H(ClCH_2COO)_2$ is one of the displacive type where one of the transverse optic modes associated with the proton motion couples anharmonically with other normal mode including ammonium ions, and this strong anharmonicity comes from the dipolar coupling between the ammonium ions and protons via the chloroacetate anions. Recently Chihara and Inaba[6] pointed out a possibility of an improper ferroelectric, which is compatible with a small value of Curie-Weiss constant (44).[14]

The other problem is what position the characteristic of the hydrogen bond (symmetric, 2.432 Å) and the deuteration effect in transition temperature (11 K) occupy

Table 6. 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)

in general hydrogen bonds and general hydrogen-bonded ferroelectrics and whether this problem can be explained reasonably, which are discussed in next chapter.

References

1) M. Ichikawa: Acta Cryst. **B28** (1972) 755.
2) M. Ichikawa: Acta Cryst. **B30** (1974) 651.
3) H. Chihara, A. Inaba, N. Nakamura and T. Yamamoto: J. Phys. Soc. Japan **35** (1973) 1480.
4) H. Chihara, N. Nakamura and A. Inaba: J. Phys. Soc. Japan **36** (1974) 1710.
5) H. Chihara, N. Nakamura and H. Okuma: J. Phys. Soc. Japan **37** (1974) 1385.
6) H. Chihara and A. Inaba: J. Phys. Soc. Japan **40** (1976) 1383.
7) *International Tables for X-ray Crystallography* (Kynoch Press, Birmingham, 1959 and 1962) Vol.II and Vol.III.
8) D. C. Phillips: Acta Cryst. **9** (1956) 819.
9) J. S. Rollett and R. A. Sparks: Acta Cryst. **13** (1960) 273.
10) A. J. C. Wilson: Acta Cryst. **2** (1949) 378.
11) UNICS *Universal Crystallographic Computing System*, ed. T. Sakurai (Crystallographic Society of Japan, 1967).
12) T. Hahn: Z. Krist. **109** (1957) 438.
13) M. Ichikawa: Submitted to Acta Cryst. B (1978).
14) M. Ichikawa and T. Mitsui: Phys. Rev. **152** (1966) 495.
15) D. Hadži and B. Orel: J. mol. Struct. **18** (1973) 227.
16) T. Mitsui: Landolt-Börnstein. *Numerical Data and*

Functional Relationships in Science and Technology
ed. K.-H. Hellwege and A. M. Hellwege
(Springer, Berlin, 1969) New Series III/3.
Ferro- and Antiferroelectric Substances.

Chapter IV. The O-H vs O...O Distance Correlation and the Geometric Isotope Effect in OHO Hydrogen Bonds

IV. 1. Introduction

It is well known that there exist some correlations between H-bond parameters, since in 1955 Nakamoto, Margoshes and Rundle1) have pointed out that the O-H bond length decreases with increasing the O...O distance.2-4) However, it seems that the details of the correlation remain unsettled in the short and very short regions of O...O length, especially with respect to the dependence on the O...O distance, surroundings and symmetry of the hydrogen bond system.

The other important phenomenon for the understanding of the nature of hydrogen bonding is a geometric isotope effect. Since the works by Ubbelohde and coworkers5) it seems to have been established that an expansion of the hydrogen bond length is observed when deuterium is substituted for hydrogen in crystals. However, there is still uncertainty about the following respects: whether the size of the geometric isotope effect is a function of the hydrogen bond length, and how large is its maximum, and what are the factors influencing the isotope effect. This mainly seems to result from that the magnitude of the effect is as small as $\sim 10^{-2}$ Å. Thus, the results obtained from indirect information of lattice-spacing measurement, which assumes that any changes from isotopic substitution are confined to the hydrogen-bond system, may not be regarded as the real effect with sufficient reliability. Even with recent direct structure analysis the accuracy of $\sim 10^{-3}$ Å in hydrogen-bond length, which is desirable in discussing the geometric isotope effect, is not always attained. However, since the accuracy of crystal structure determinations has greatly increased, particularly in the past ten years, many hundred accurate structures have been published, thus giving us the opportunity to reinvestigate the correlation between structural data in detail.

On the other hand, it is well known that some of hydrogen-bonded crystals, which undergo ferro-, antiferroelectrics, or other type of phase transition, exhibit an anomalous isotope effect. For example, in a series of KH_2PO_4-type crystals, the transition temperature Tc rises by a maximum of about 100 K on deuteration. The role of the hydrogen bond in the phase transition and the origin of the isotope effect in these crystals seems to be not yet fully understood. The phase-transition mechanism and the isotope effect in hydrogen-bonded ferro-, antiferroelectrics, and other materials are expected to be closely associated with the characteristic of the hydrogen bond. To obtain further knowledge on the nature of the hydrogen bond seems indispensable for deeper understanding of these problems in hydrogen-bonded crystals.

The purpose of this chapter is to establish the correlation between the hydrogen-bond parameters and the geometric isotope effect, and to discuss the relation of the structural isotope effect of the symmetric hydrogen bond with the anomalous increase in Tc by using these correlation curves as an empirical basis.6) Brown7) discussed the geometry of OHO bonds, mainly in the medium and long regions, in connection with the bond valence. Olovsson and Jönsson8) has recently surveyed X-ray and neutron crystal structural data and referred to the correlation between hydrogen-bond parameters and the geometric isotope effect independently. Hence, the results on the O-H vs O...O correlation and the geometric isotope effect are described briefly and these application and discussion are stressed.

IV.2. Data collection

Crystal structure data obtained by X-ray and neutron diffraction have been taken from the literature. A part of the literature used was retrieved with TOOL-IR system.9) Hydrogen-bond parameters were recaluculated with UNICS[10)] if they and their estimated standard deviations were not specified in the literature. The data were used for a discussion of correlations between hydrogen-bond parameters only if the e.s.d's of all the relevant length were equal to or less than 0.010 Å, the O...O distance was less than 3 Å, and O-H...O angle larger than 150°. The data used consisted of 227 bonds and 79 compounds, including the data of Brown[7)] and Olovsson and Jönsson.[8)] A list of the data were given in Appendix. The values not corrected for thermal motion were used. If two or more studies are made on the same compound, the data with the smaller e.s.d's were adopted.

For discussion of the geometric isotope effect, the threshold value of a combined standard deviation of 0.005 Å was taken; the combined standard deviation is defined as $\sigma = (\sigma_H^2 + \sigma_D^2)^{\frac{1}{2}}$, where σ_H and σ_D are e.s.d's of O...O distance in the hydrogen and corresponding deuterium compound. The remaining data include those from X-ray as well as neutron diffraction. If both were available, they are both listed (Table 1), but the data with the smallest e.s.d's are plotted (Fig.2), as any systematic difference could not be found within experimental error.

IV.3. The symmetric hydrogen-bond

For the following discussion, first the term 'symmetric hydrogen bond' should be referred to because its implication seems equivocal among literature, as pointed out by olovsson and Jönsson.8) As far as the author is aware one is used with respect to the type of the hydrogen-atom potential curve: (i) a hydrogen bond is said to be symmetric when the potential is of single-minimum type, or when the potential is of single-minimum type with a minimum at the mid-point of two oxygen atoms, whether there is crystallographic equivalence between a donor and an acceptor atom or not. The second refers to crystallographic symmetry: (ii) a hydrogen bond is said to be symmetric if the donor and acceptor atom are crystallographically equivalent, regardless of the type of potential curve.

Speakman and coworkers4,11) classified acid salt of carboxylic acids using criterion (ii). Catti and Ferraris12,13) took the position of (i) and , furthermore, introduced the word 'symmetry restricted' (SR) for (ii). In this paper the description 'symmetric' is confined to (ii), the term 'single' of 'double minimum' being added if necessary to describe the bonding situation. It is possible to express all probable types of hydrogen bond by using these terms. The terms 'symmetric' and 'centered' proposed by Olovsson and Jönsson8) are mostly consistent with our standpoint if 'symmetric' is restricted within (ii), and 'centered' is replaced by 'single-minimum'.

IV.4. The Correlation between O-H vs O...O distance

A correlation diagram of O-H vs O...O distance is shown in Fig.1.

Symmetric bond

In a region of R(O...O) $<$ 2.5 Å, i.e. very short hydrogen bonds in Speakman's classification,[4,11] symmetric bonds are continuously distributed 2.419 to 2.468 Å. In this region the conclusion drawn from an thermal ellipsoid analysis agrees with the theory that the potential curve is effectively of single-minimum type; it is of single-minimum, or broad and anharmonic or if a barrier exists it is small compared with the ground state vibrational level.[12,30] It should be stressed that symmetric hydrogen bonds are not restricted to the very short region, but can be found also at least up to 2.6 Å, though the bonding situation may be different from those in the very short region. Examples are a series of KH_2PO_4-type crystals[3] (around 2.5 Å), $KH_3(SeO_3)_2$ (2.566 Å),[13] $NaH_3(SeO_3)_2$ (2.602 Å)[14], and the number will increase further taking into consideration much amount of X-ray data. Lehmann and Larsen[13] performed a least-squares refinement of symmetric hydrogen bond (2.566 Å) of $KH_3(SeO_3)_2$ with two models, i.e. one that distributes the H atom statistically on two side of a special position (disordered model) and one that locates

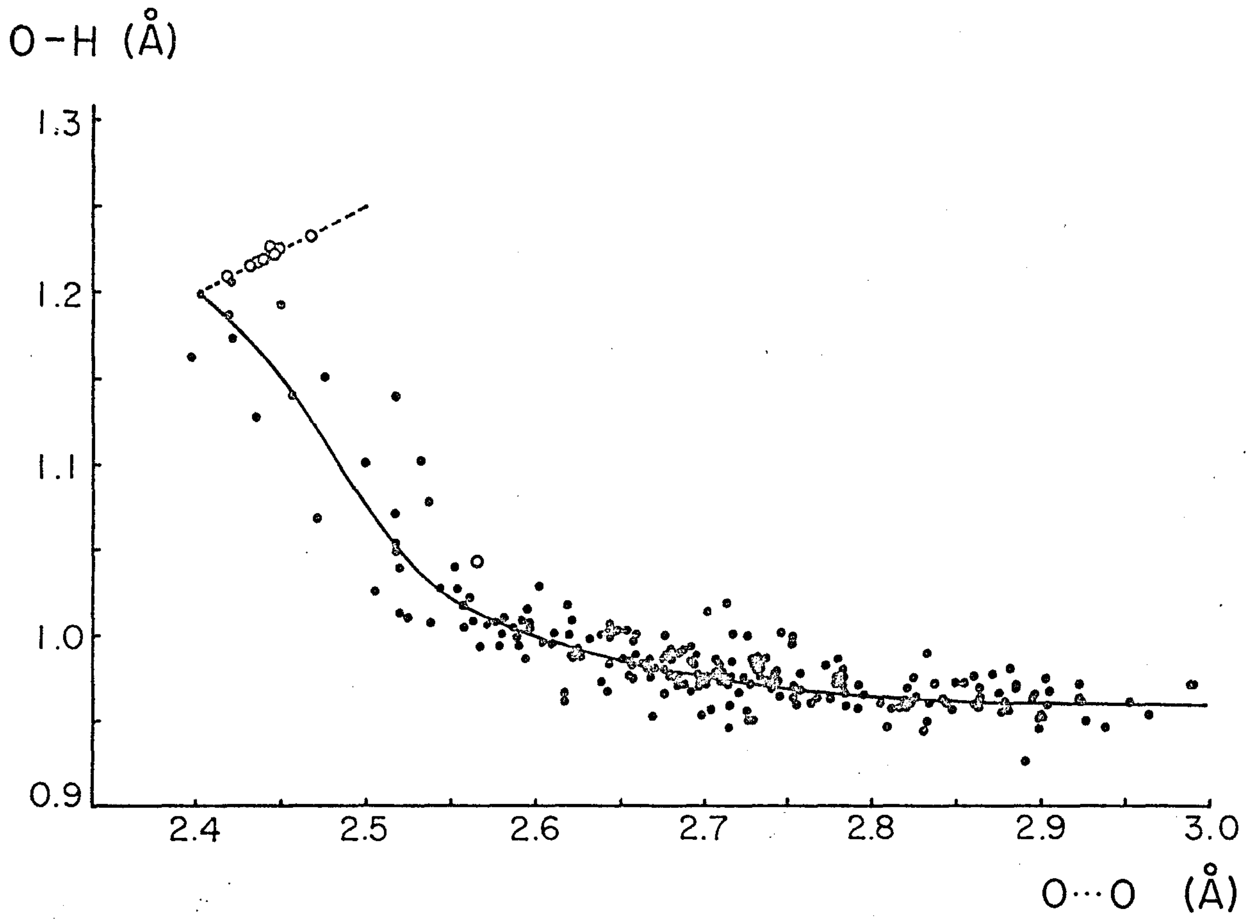


Fig. 1. A diagram of correlation between O-H and O...O distance in OHO hydrogen bonds. Open circle : symmetric bond ; filled circle : asymmetric bond.

it in a special position (ordered model). On the basis of the Hamilton test on the weighted R factor ratio they reached the conclusion that the disordered description is significantly better than the ordered one. It is worth mentioning that the O-H length refined with a disordered model falls on the correlation line of the asymmetric bonds. It will be worthwhile to note here that the analysis of the thermal motion is done within the framework of a harmonic approximation and therefore the better fit of the disordered model indicates the potential curve to be anharmonic, but not necessarily mean it to be of real double-minimum type with the meaning that the barrier is higher than the ground state vibraional level, as discussed in II.5. Kaplan, Kay and Morosin14) reported for the symmetric bond of 2.602 Å in $NaH_3(SeO_3)_2$ that the difference synthesis indicates disorder.

It can be concluded that symmetric hydrogen bonds are distributed continuously at least up to about 2.6 Å, and that the shape of the H atom potential curve seems to vary continuously from single- to double-minimum type with increasing O...O distance, retaining the symmetry requirement (schematically as (e)→(d)→(c) in Fig.1 of Chap. I). Because of this situation regarding symmetric bonds it appears extremely difficult to distinguish between single and double-minimum for symmetric hydrogen bonds around 2.5 Å.

Asymmetric bond

Asymmetric hydrogen bonds are distributed over all region. As an average the O-H length increases gradually in a medium and a long region with decreasing the O...O, and increases more rapidly in the region less than about 2.55 Å (schematically as (a)→ (b)→ (f) in Fig.1 of Chap.I). The average correlation curve does not jump discontinuously or approach very rapidly the 'symmetric' straight line at a particular O...O length, but appears to coincide with it at the shortest limit near 2.4 Å.

The deviation of each point from the average correlation curve becomes large as the O...O distance is less than about 2.55 Å; In the longer-bond region more than 90 % of the points are within 0.02 Å of the smoothed curve, whereas in the shorter-bond region this figure is only 40 %. This seems to reflect that the potential curve become flat when the O...O distance is shorter than 2.55 Å and the equilibrium position of the H atom shifts from the average according to the characteristic of the differing environment of the hydrogen bond.

IV.5. Geometric isotope effect

The difference in the O...O distance caused by substituting deuterium for hydrogen, ΔR, is called the geometric isotope effect in this paper;

$\Delta R = R(O...O)_D - R(O...O)_H$ where $R(O...O)_D$ and $R(O...O)_H$ denote the hydrogen and corresponding deuterium bond length. The $(O...O)_H$ and $(O...O)_D$ notation are used only if it is necessary to distinguish between them, otherwise O...O is used. The relevant data are listed in Table 1 and ΔR is plotted against O...O distance in Fig.2.

Fig.2 shows that there exists a correlation between ΔR and $R(O...O)_H$: the positive isotope effect, i.e. expansion can be seen in the O...O region of about 2.44-2.64 Å, with a maximum value of 0.027 Å. This corresponds to the correlation between the isotope ratio of antisymmetric OH stretching frequency νOH/ νOD and $R(O...O)_H$ by Novak.$^{15)}$ ΔR appears to increase and decrease rapidly near 2.44 and 2.64 Å respectively. For the region shorter than 2.44 Å and longer than 2.64 Å, no isotope effect can be recognized except for the case of α-$(COOH)_2 \cdot 2H_2O^{16)}$ discussed below. These results are compatible with theoretical prediction by Rundle$^{17)}$ and Singh and Wood.$^{18)}$ Further definite conclusion cannot be drawn at present for lack of number of data.

It may be worth while to consider here what factors smear the correlation, since there seems to be room for argument as to whether a correlation between ΔR and $R(O...O)_H$ is present or not. Finholt and Williams$^{19)}$ state that no correlation seems to exist. Thomas$^{20)}$ and Olovsson and Jönsson$^{8)}$ considered that in a crystal with more than one species of hydrogen bond only short bonds

Table 1. Geometric isotope effect

The O...O distance is the value at room temperature. X and N denote X-ray and neutron diffraction method respectively.

Compound & references		O...O (Å)	ΔR (Å)	D content	Method
Squaric acid	23	2.548(1)	0.027(1)		X
		2.549(1)	0.024(1)		
$YH(C_2O_4)_2 \cdot 3H_2O$	24	2.440(3)	0.013(5)	0.884	N
		2.643(2)	-0.003(3)	0.918	
		2.680(2)	0.000(3)	0.913	
KH_2PO_4	25	2.496(1)	0.023(1)		X
$KHCO_3$	26	2.585(2)	0.022(3)		X
		2.587(1)	0.020(2)		N
α-$(COOH)_2 \cdot 2H_2O$	16	2.512(1)	0.019(1)		X
		2.864(2)	0.016(3)		
		2.883(1)	0.024(1)		
		2.506(4)	0.018(4)		N
		2.864(5)	0.015(5)		
		2.881(4)	0.025(4)		
$KH_3(SeO_3)_2$	13	2.566(1)	0.014(2)	0.846	N
		2.602(2)	0.021(3)	0.871	
$LiHC_2O_4 \cdot H_2O$	20	2.490(1)	0.016(1)		X
		2.702(1)	-0.002(1)		
		2.777(1)	0.001(1)		
$N_2H_5HC_2O_4$	27	2.457(1)	0.009(2)		X

Table 1. (continued)

Compound & references		O...O (Å)	ΔR (Å)	D content	Method
$(H_5O_2^+)_2SO_4^{2-}$	28	2.431(3)	-0.005(4)		X
		2.664(2)	0.002(3)		
		2.655(2)	0.000(3)		
$NaHC_2O_4\ H_2O$	29	2.571(2)	0.022(3)		X
		2.826(2)	0.000(3)		
		2.808(2)	0.001(3)		
$KH(CF_3COO)_2$	30	2.437(4)	0.000(5)	0.905	N

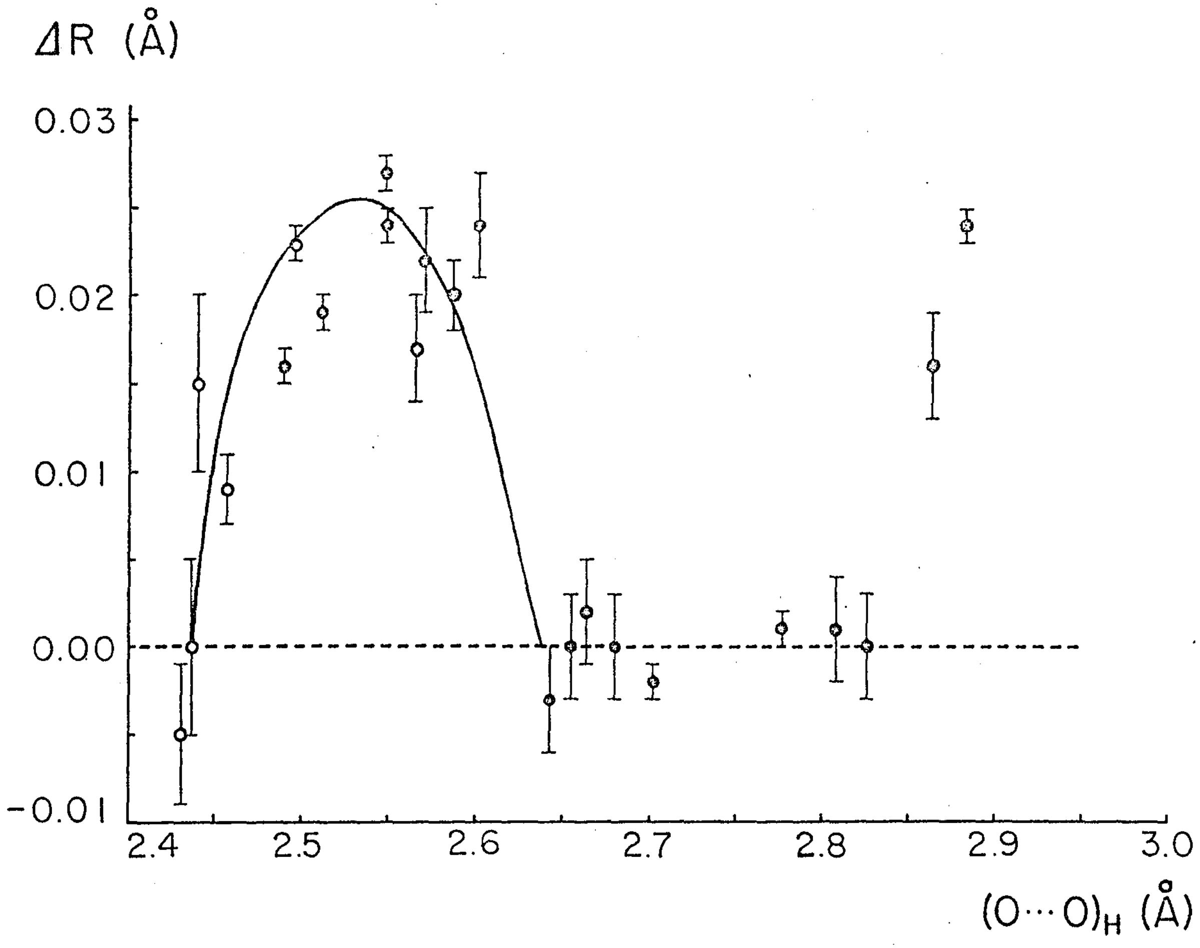


Fig. 2. The geometric isotope effect, ΔR , as a function of $(O\ldots O)_H$ length.

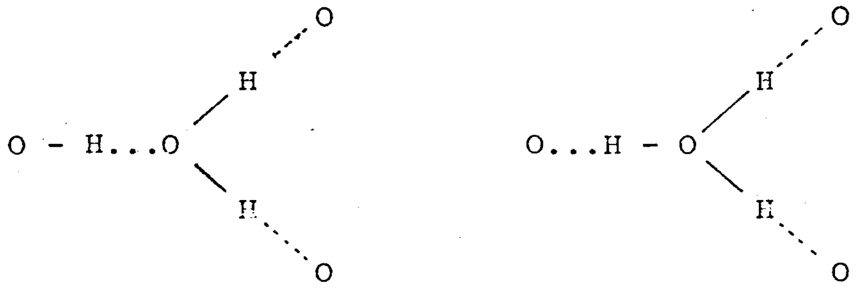
(up to 2.6 Å) exhibit the genuine isotope effect and long bonds do not, since changes in the latter are exerted by the influence of the structural rearrangement induced by the genuine isotope effect of the short bonds.

The following may be pointed out as possible factors smearing the correlation. (i) Insufficient accuracy. (ii) Incomplete deuteration. (iii) Direct coupling of the geometric isotope effect of an individual bond in a crystal involving with two or more species of hydrogen bond.

As the geometric isotope effect is of the order of $\sim 10^{-2}$ Å at most (Fig.2), high accuracy of structure determination is required. First it should be emphasized that collection only of accurate data revealed the correlation. Secondly, perfect deuteration can not be achieved in spite of many times of recrystallization in D_2O and precaution taken to prevent H_2O contamination.19) From the average of the real deuterium contents (0.899) in the crystals quoted in Table 1 intended as perfectly deuterated, which were obtained from least-squares refinement of the deuterium scattering amplitude for neutrons, deuterated crystals are considered to involve usually about 10 % incompleteness.

The third respect is associated with the hydrogen-bond arrangement in a crystal. Deviation from the above general trend of the isotope effect can be recognized in α-$(COOH)_2 \cdot 2H_2O$16) and in crystalline $H_3O^+CH_3C_6H_4SO_3^-$

crystal; in the former the two longer bonds also show the large positive effect as well as the short one, whereas in the latter three short bonds in the region expected to show the large isotope effect exhibit only much smaller effect. However, the common feature of hydrogen bond arrangement can be pointed out in two cases. It may be denoted schematically as follows for a) α-$(COOH)_2 \cdot 2H_2O$ and b) $H_3O^+CH_3C_6H_4SO_3^-$;



(a) (b)

in two cases three H-bonds directly couple each other through the central oxygen and each of them is crystallographically independent. This situation seems to make it difficult to obtain the genuine isotope effect of the individual bond separately.

Strictly speaking, the geometric isotope effect cannot be confined to hydrogen-bond system and necessarily leads to the structural change of its neighbours. The degree of coupling between hydrogen bonds may be different from crystal to crystal. However, it may still be possible that substitution of D for H does not result in the rearrangement distributed throughout the structure, if the hydrogen-bond systems are not directly coupled each other. We believe that for long bonds the geometric isotope effect is equally genuine as well as for short bonds except some special cases as mentioned above.

IV.6. Symmetric bond and phase transition

Let's consider the structure of a linear symmetric hydrogen bond on the basis of the assumption that the potential curve of the symmetric bond can be expressed as a superposition of the curves of two asymmetric bonds, and the correlation curve between O-H and O...O distance can be used as an empirical basis for the equilibrium position of the H atom. This seems plausible since the symmetric bonds exist continuously at least up to about 2.6 Å and the values of O-H length refined with a disordered model agree with those of the asymmetric bond. Catti and Ferraris[21)] discussed the disordered nature of symmetric bonds in the very short region, which is compatible with the present assumption. Then the distance between two equilibrium positions of H atom, δ , is written as

$$\delta = R(O...O) - 2R(O\text{-}H)$$

As shown in Fig.3, δ increases, with a maximum slope

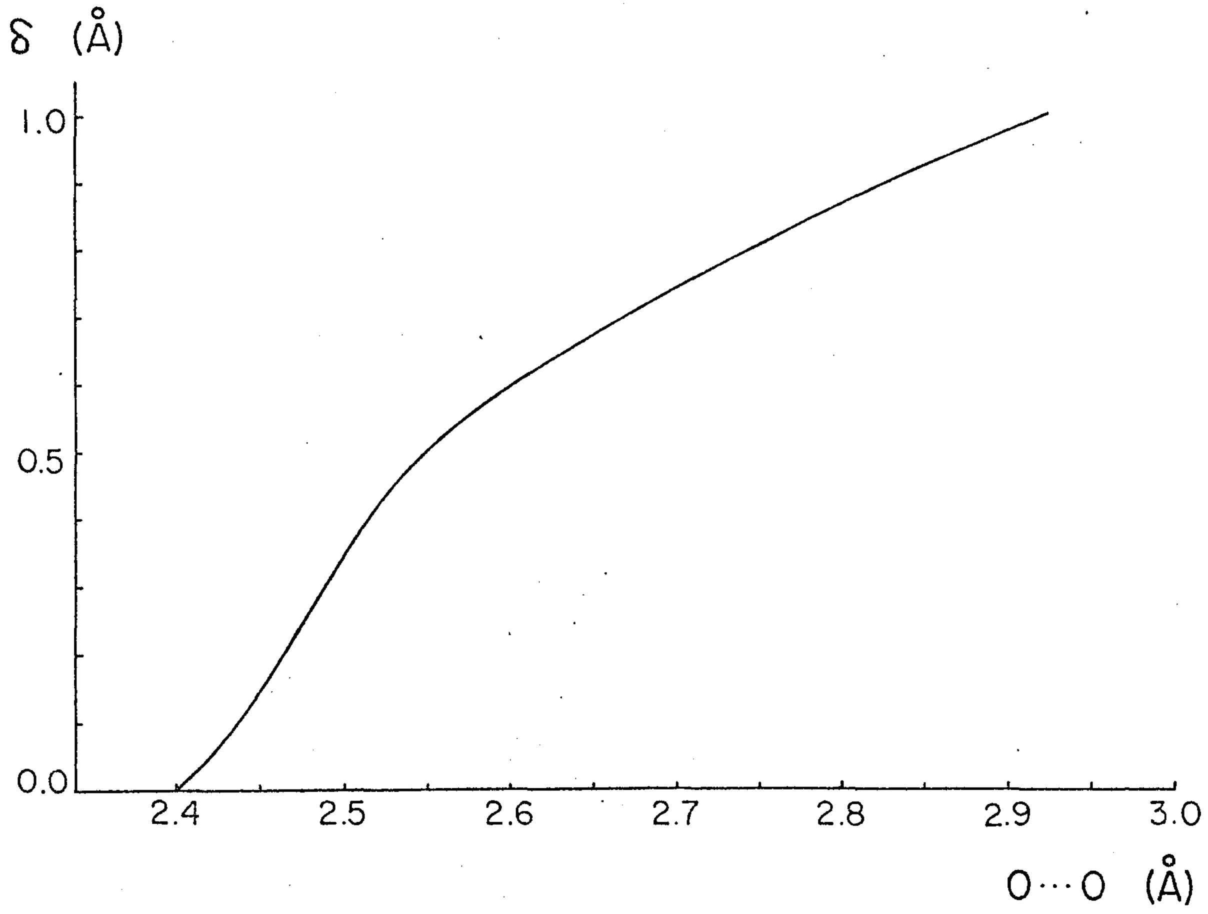


Fig. 3. The distance between two equilibrium positions in a symmetric hydrogen bond, δ , as a function of O...O length.

around 2.48 Å as the O...O distance increases, and gradually approaches a straight line. It is noted here that δ does not mean immediately the distance between two minima in a double-minimum potential well since the shape of the basic potential-energy surface and the vibrational level are not known from diffraction data alone.

If the O...O distance expands by an amount of ΔR according to the ΔR vs R(O...O) correlation curve when a D atom is substituted for H, the O-D distance will be equal to the O-H value corresponding to the length $R(O...O)_H + \Delta R$ from the O-H vs $R(O...O)_H$ curve; $R(O\text{-}D) = R(O\text{-}H) - \Delta R(O\text{-}H)$, where $\Delta R(O\text{-}H)$ denotes a contraction of the O-H distance due to an expansion of R(O...O) by ΔR. Then the distance between the two equilibrium positions of the corresponding D bond is expressed as

$$\begin{aligned}\delta_D &= R(O...O)_D - 2R(O\text{-}D)\\ &= \delta_H + 2\Delta R(O\text{-}H) + \Delta R,\end{aligned}$$

where the subscript H and D are used only if it is necessary to distinguish between the H and D bond. This situation is illustrated in Fig.4. The isotope effect of the distance between two equilibrium positions $\delta_D - \delta_H$ consists of two terms: in the short-bond region where the O-H length varies rapidly with O...O distance,

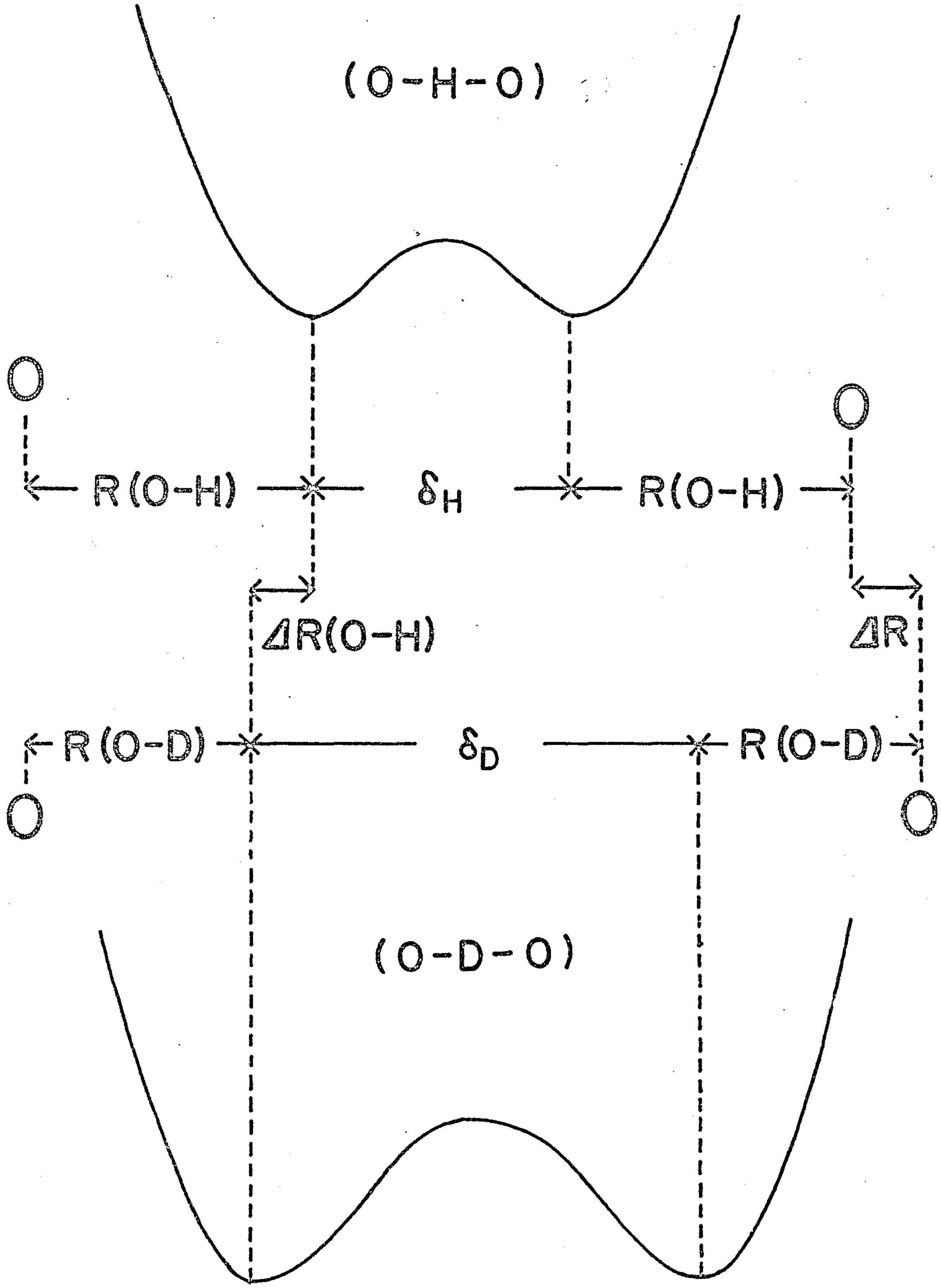


Fig. 4. Schematic illustration of the geometric isotope effect in a symmetric bond.

$2\Delta R(O\text{-}H)$ contributes mainly to the total $\delta_D - \delta_H$ and amounts to about three times ΔR at maximum, whereas in the long-bond region where O-H varies more slowly with O...O, ΔR is the more dominant. With increasing O...O $\delta_D - \delta_H$ increases rapidly and reaches its maximum value around 2.49 Å and then decreases more slowly, as shown in Fig.5. The functional behavior of δ_H and $\delta_D - \delta_H$ should not be regarded as being fully established at the present stage because it largely depends on the accuracy of the correlation curve of R(O-H) vs R(O...O) and ΔR vs R(O...O). However, it should be emphasized that if ΔR itself is small, $\delta_D - \delta_H$ induced by ΔR becomes four times as large as ΔR. The effect of ΔR seems to have been overlooked or underestimated so far.22)

The role of the hydrogen bond in hydrogen-bonded crystals which exhibit ferroelectric, antiferroelectric and other structural phase trnasition seems closely associated with the characteristic of the hydrogen bond, i.e. that of the potential curve. Therefore, an anomalous isotope effect in physical quantities, such as the transition temperature T_c is likely to be closely related with difference between the features of the potential curve of the hydrogen bond and its corresponding deuterium bond; it may be reflected in the magnitude of ΔR and $\delta_D - \delta_H$. A large shift of T_c may be expected when the crystal has a symmetric hydrogen bond in a paraelectric or high temperature phase, and its O...O

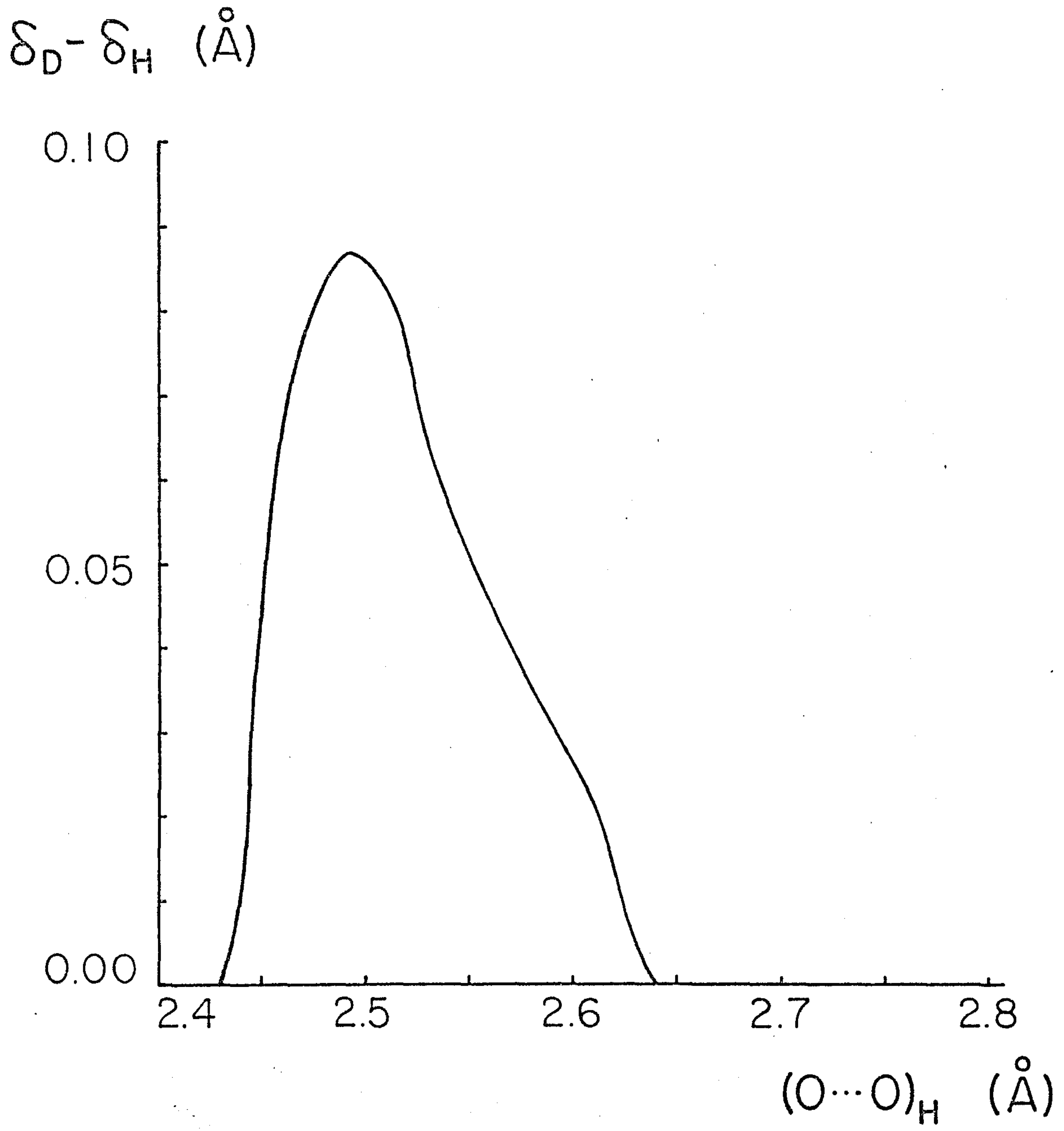


Fig. 5. The isotope effect of the distance between two equilibrium position in a symmetric bond, $\delta_D - \delta_H$, as a function of $(O\ldots O)_H$ length.

length is in a region of $\Delta R > 0$ and is longer than that expected for a single-minimum type bond. The relevant values of some ferro-, antiferroelectric, and other materials are listed in Table 2. The data are compatible with the above statement. ΔT_c is large when the hydrogen bond is symmetric and O...O is in the range of about 2.5-2.6 Å. ΔT_c is only about 10° or negative when O...O length is around 2.44 Å even if symmetric, or when the hydrogen bond is asymmetric even if O...O is in a range of 2.5-2.6 Å. However, in order to confirm this relation further examination may be necessary both by the structural and by the dielectric studies.

Table 2. O...O distance in the paraelectric phase, Curie temperature T_c and its shift on deuteration ΔT_c in some ferro- and antiferroelectrics

The O...O distance is the room temperature value if not specified. F and AF denote ferro-and antiferroelectric respectively. The references to structural data are marked with an asterisk and dielectric data were quoted from Landolt-Börnstein39) if not mentioned expressly.

Compound	references	O...O (Å)	Type of bond	T_c (°K)	ΔT_c (°K)	
$NH_4H(ClCH_2COO)_2$	31*,32	2.432(5)	symmetric	120	11	F
TGS at 330°K	33*	2.443(7)	symmetric	322	11	F
KH_2PO_4	25*	2.496(1)	symmetric	123	90	F
$NH_4H_2PO_4$	34*	2.490(1)	symmetric	148	94	AF
$NH_4H_2AsO_4$	34*	2.512(2)	symmetric	216	88	AF
$NaH_3(SeO_3)_2$	14*	2.556(6)	asymmetric	194	75	F
		2.602(9)	symmetric			
$RbHSO_4$	35*,36	2.53 (1)	asymmetric	264	-11	F
		2.62 (1)	asymmetric			
NH_4HSO_4	37*,38	2.514(6)	asymmetric	270	- 8	F
		2.598(5)	asymmetric			
$KH_3(SeO_3)_2$	13*,38	2.566(1)	symmetric	201	70	

References

1) K. Nakamoto, M. Margoshes and R. E. Rundle: J. Amer. Chem. Soc. 77 (1955) 6480.

2) F. F. Iwasaki, H. Iwasaki and Y. Saito: Acta Cryst. 23 (1967) 64.; G. C. Pimentel and A. L. McClellan: Ann. Rev. phys. Chem. 22 (1971) 347.

3) W. C. Hamilton and J. A. Ibers: Hydrogen Bonding in Solids (Benjamin, New York, 1968).

4) J. C. Speakman: Structure and Bonding 12 (1972) 141.

5) J. M. Robertson and A. R. Ubbelohde: Proc. Roy. Soc. London. A170 (1939) 222; A. R. Ubbelohde: Proc. Roy. Soc. London. A173 (1939) 417; A. R. Ubbelohde and I. Woodward: Proc. Roy. Soc. London. A179 (1942) 399.

6) M. Ichikawa: Acta Cryst. B34 (1978) 2074.

7) I. D. Brown: Acta Cryst. A32 (1976) 24.

8) I. Olovsson and P. -G. Jönsson: The Hydrogen Bond, ed. P. Schuster, G. Zundel and C. Sandorfy (North-Holland, Amsterdam,1976) Vol.II, chap.8.

9) T. Yamamoto, M. Negishi, M. Ushimaru, Y. Tozawa, K. Okabe and S. Fujiwara: Proc. 2nd USA-Japan Computer Conf. (1975) 159.

10) UNICS Universal Crystallographic Computing System, ed. T. Sakurai (Crystallographic Society of Japan, 1967).

11) H. N. Shrivastava and J. C. Speakman: J. chem Soc. (1961) 1151.

12) A. Sequeira, C. A. Berkebile and W. C. Hamilton: J. mol. Struct. **1** (1967) 283; Å. Nilsson, R. Liminga and I. Olovsson: Acta Chem. Scand. **22** (1968) 719; M. Currie and J. C. Speakman: J. Chem. Soc. A. (1970) 1923; B. Dickens, E. Prince, L. W. Schroeder and W. E. Brown: Acta Cryst. B**29** (1973) 2057.

13) M. S. Lehmann and F. K. Larsen: Acta Chem. Scand. **25** (1971) 3859.

14) S. F. Kaplan, M. I. Kay and B. Morosin: Ferroelectrics **1** (1970) 31.

15) A. Novak: Structure and Bonding **18** (1974) 177.

16) R. G. Delaplane and J. A. Ibers: Acta Cryst. B**25** (1969) 2423 ; T. M. Sabine, G. W. Cox, B. M. Craven: Acta Cryst. B**25** (1969) 2437; P. Coppens and T. M. Sabine: Acta Cryst. B**25** (1969) 2442.

17) R. E. Rundle: J. Phys. Radium **25** (1964) 487.

18) T. R. Singh and J. L. Wood: J. chem. Phys. **50** (1969) 3572.

19) J. E. Finholt and J. M. Williams: J. chem. Phys. **59** (1973) 5114.

20) J. O. Thomas: Acta Cryst. B**28** (1972) 2037.

21) M. Catti and G. Ferraris: Acta Cryst. B**32** (1976) 2754.

22) M. Tokunaga: Ferroelectrics **1** (1970) 195; G. A. Samara: Ferroelectrics **5** (1973) 25.

23) D. Semmingsen: Acta Chem. Scand. **27** (1973) 3961; ibid A**29** (1975) 470.

24) G. D. Brunton and C. K. Johnson: J. chem Phys. **62** (1975) 3797.

25) J. Nakano, Y. Shiozaki and E. Nakamura: J. Phys. Soc. Japan **34** (1973) 1423.

26) J. O. Thomas, R. Tellgren and I. Olovsson: Acta Cryst. B**30** (1974) 1155; ibid B**30** (1974) 2540.

27) J. O. Thomas: Acta Cryst. B**29** (1973) 1767.

28) T. Kjällman and I. Olovsson: Acta Cryst. B**28** (1972) 1692.

29) R. Tellgren and I. Olovsson: J. chem. Phys. **54** (1971) 127.

30) A. L. Macdonald, J. C. Speakman and D. Hadži: J. Chem Soc. Perkin II. (1972) 825.

31) M. Ichikawa: Acta Cryst. B**28** (1972) 755.

32) H. Chihara, A. Inaba, N. Nakamura and T. Yamamoto: J. Phys. Soc. Japan **35** (1973) 1480.

33) K. Itoh and T. Mitsui: Ferroelectrics **5** (1973) 235.

34) A. A. Khan and W. H. Baur: Acta Cryst. B**29** (1973) 2721.

35) J. P. Ashmore and H. E. Petch: Can. J. Phys. **53** (1975) 2694.

36) M. Kasahara and I. Tatsuzaki: J. Phys. Soc. Japan **38** (1975) 1389.; M. Kasahara: private communication.

37) R. J. Nelmes; Acta Cryst. B**27** (1971) 272.

38) E. C. Subbarao; Ferroelectrics **5** (1973) 267.

39) T. Mitsui: Landolt-Börnstein. *Numerical Data and Functional Relationships in Science and Technology*

ed. K. -H. Hellwege and A. M. Hellwege
(Springer, Berlin, 1969) New Series III/3.
Ferro- and Antiferroelectrice Substances

Chapter V. Summary

The X-ray crystal structure analyses of ferroelectric $NH_4H(ClCH_2COO)_2$ have been carried out both in the paraelectric phase at room temperature and in the ferroelectric phase at 80K. The refinements of a block-diagonal least-squares method resulted in the final R value of 0.068 for the counter data (0.070 for the photographic data) with anisotropic temperature factors at room temperature and in the final R value of 0.106 for the photographic data with isotropic temperature factors at 80K.

It has been found that $NH_4H(ClCH_2COO)_2$ has the shortest symmetric hydrogen bond connecting two chloroacetate residues, 2.432 Å at room temperature among hydrogen-bonded ferroelectrics precisely measured so far. It has been concluded that the shape of the H-atom potential is effectively of a single-minimum type and $NH_4H(ClCH_2COO)_2$ offers the first example with a single-minimum potential well, judging from the O...O length and the anomalies in the infrared spectrum together with a complete agreement of the combined consideration of neutron diffraction and spectroscopic data, and so on in other Type A acid salts.

This result necessarily led to the conclusion that the acidic hydrogen atom does not play the crucial role in the phase transition, (not the trigger) in contrast to the hydrogen atom in a double-minimum potential well, on the basis of which ordinarily the phase transitions in hydrogen-bonded ferroelectrics such as KH_2PO_4 are considered. The above conclusion was supported by the results of the structure analysis at 80K, which showed no definite change in the conformation of the chloroacetate dimer including a very short hydrogen bond of 2.457(16)Å as compared with the room-temperature structure, whereas a considerable shift was observed in the ammonium ion. It has been shown that there is no contradiction between the conclusion drawn from our present structure analyses and those from other experimental technique mainly by Chihara and coworkers, i.e. the ^{35}Cl nuclear quadrupole resonance frequency and relaxation time, the heat capacity measurement, and infrared and Raman spectra.

A possibility of a pure order-disorder mechanism of the nitrogen atom of the ammonium ion was examined, but ruled out by the comparison of the observed and calculated shape of contours in Fourier maps and the r.m.s amplitude of thermal vibrations. This conclusion is also compatible with the ^{35}Cl spin-spin relaxation time and the proton magnetic resonance measurements.

The correlation between O-H vs O...O distances and the geometric isotope effect in OHO bonds have been investigated on the basis of recent accurate X-ray and neutron crystal-structure data. Symmetric bonds are continuously distributed at least to about 2.6 Å, in which the shape of the H atom potential curve seems to vary continuously from single to double-minimum type with increasing O...O diatance, retaining the symmetry requirement. The average correlation curve of asymmetric bonds appears to coincide with 'symmetric' straight line at the shortest limit around 2.4 Å. On deuteration an expansion was seen in the O...O distance range 2.44-2.64 Å, with a maximum value of 0.027 Å.

The equilibrium position of the H atom in symmetric bonds was considered with the correlation curve of O-H vs O...O distance and the geometric isotope effect used as empirical basis, under the assumption that the potential curve can be expressed as the superposition of two asymmetric bonds. The correspondence was pointed out between two kinds of isotope effect, i.e. the isotope effect of the distance between two equilibrium positions or the geometric isotope effect and the isotope effect of the transition temperature of hydrogen-bonded crysrals which undergo ferro-, antiferroelectric, and other structural phase transitions; The shift of the transition temperature is large when the hydrogen bond is symmetric and O...O is in a range of 2.5-2.6 Å.

Appendix

Table. Hydrogen-bond parameters as determined by neutron diffraction

Only OHO bonds are included, and these only if the bond lengths have standard deviations equal to or less than 0.010 Å, the O...O distance is less than 3 Å, and the O-H...O angle is larger than 150°. Numbers in parentheses are the standard deviations in the least significant digit. All distances are uncorrected for thermal motion.

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
$MnCl_2.4H_2O$	2.923(2)	0.963(2)	1.969(3)	170.4(2)	
El Saffar AC B27, 66 (1971)*	2.964(2)	0.953(3)	2.014(3)	174.4(3)	
$Th(NO_3)_4.5H_2O$	2.697(4)	0.971(5)	1.726(5)	177.5(6)	
Taylor AC 20, 842 (1966)	2.698(4)	0.953(6)	1.749(6)	173.2(5)	
	2.901(4)	0.954(6)	1.962(6)	167.9(6)	
	2.953(4)	0.961(6)	1.996(5)	173.6(6)	
$UO_2(NO_3)_2.2H_2O$	2.834(3)	0.961(5)	1.892(5)	166.1(5)	
Dalley IC 10, 323 (1971)	2.924(4)	0.961(5)	1.964(5)	179.8(6)	
	2.899(4)	0.951(4)	1.982(5)	161.2(4)	
$Ba(ClO_3)_2.H_2O$	2.891(5)	0.926(10)	1.991(10)	163.6(9)	
Sikka JCP 48, 1883 (1968)					
$BeSO_4.4H_2O$	2.617(5)	0.967(6)	1.656(8)	171.7(8)	
Sikka AC B25, 310 (1969)	2.684(5)	0.971(8)	1.719(6)	172.3(6)	
$MgSO_4.7H_2O$	2.692(6)	0.967(7)	1.726(7)	176.4(7)	
Ferraris JCSDT 816 (1973)	2.703(7)	0.976(9)	1.732(9)	172.8(7)	
	2.728(5)	0.961(7)	1.772(7)	173.1(6)	
	2.734(5)	0.985(8)	1.758(9)	170.9(7)	
	2.704(7)	0.956(9)	1.758(9)	169.7(7)	
	2.756(6)	0.959(10)	1.804(10)	172.1(7)	
	2.768(7)	0.963(9)	1.810(9)	172.9(8)	
	2.792(6)	0.957(9)	1.842(9)	172.0(8)	
	2.825(6)	0.975(8)	1.854(8)	173.9(6)	
	2.820(7)	0.962(10)	1.891(9)	161.7(8)	
	2.901(6)	0.952(9)	1.961(8)	169.6(8)	
	2.923(6)	0.972(8)	1.965(8)	168.0(6)	
	2.903(6)	0.959(10)	1.980(10)	161.0(9)	

Compoud and reference	O...O (Å)	O – H (Å)	H...O (Å)	O-H...O (degrees)	Comments
$Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$	2.683(2)	0.976(3)	1.715(3)	171.3(2)	
Brown AC B25, 676 (1969)	2.707(2)	0.978(3)	1.730(3)	178.1(3)	
	2.732(2)	0.981(3)	1.760(3)	170.4(3)	
	2.743(2)	0.978(3)	1.765(3)	177.5(3)	
	2.826(2)	0.964(3)	1.871(3)	170.1(3)	
	2.821(2)	0.963(3)	1.871(3)	168.7(3)	
$CaHPO_4 \cdot 2H_2O$	2.781(6)	0.971(9)	1.811(8)	175.7(11)	
Curry JCSA 3725 (1971)	2.831(7)	0.944(10)	1.902(10)	167.3(14)	
$KH_5(PO_4)_2$	2.422(3)	1.174(4)	1.252(4)	173.0(3)	
Phillippot RCM 9, 825 (1972)	2.567(3)	0.994(5)	1.574(5)	176.6(4)	
	2.592(3)	1.009(5)	1.583(4)	177.5(3)	
	2.579(3)	0.994(5)	1.586(4)	176.6(3)	
	2.624(3)	0.991(5)	1.638(5)	173.4(3)	
$Ca(H_2AsO_4)_2$	2.436(3)	1.218(1)	1.218(1)	180.0(0)	symmetric $(\bar{1})$
Ferraris AC B28, 2430 (1972)	2.444(3)	1.222(1)	1.222(1)	180.0(0)	symmetric $(\bar{1})$
	2.659(2)	1.001(3)	1.663(3)	173.9(3)	
	2.692(2)	0.994(3)	1.725(3)	163.4(3)	
	2.875(2)	0.966(3)	1.997(3)	150.2(3)	
$CaHAsO_4 \cdot H_2O$	2.632(6)	0.998(10)	1.657(10)	164.6(8)	
Ferraris AC B28, 209 (1972)					
InOOH	2.537(3)	1.079(7)	1.458(7)	179.1(6)	
Lehmann ACS 24, 1662 (1970)					
$Te(OH)_6$	2.685(2)	0.990(3)	1.698(3)	174.5(2)	
Lindqvist ACS 27, 85 (1973)	2.676(2)	0.987(3)	1.704(3)	167.2(3)	
	2.695(2)	0.989(3)	1.711(3)	173.4(3)	
	2.696(2)	0.977(3)	1.720(3)	175.8(3)	
	2.709(2)	0.983(3)	1.727(3)	175.3(3)	
	2.730(2)	0.983(3)	1.750(3)	175.1(3)	

Compound and reference	O...O (Å)	O – H (Å)	H...O (Å)	O-H...O (degrees)	Comments
H_2SeO_3	2.621(2)	1.009(3)	1.621(3)	170.6(3)	
Larsen ACS 25, 1233 (1971)	2.667(2)	0.986(3)	1.749(3)	153.4(3)	
$LiH_3(SeO_3)_2$	2.518(3)	1.141(7)	1.378(7)	176.6(5)	
Tellgren JSSC 4, 255 (1972)	2.552(3)	1.040(6)	1.517(6)	173.3(4)	
	2.646(4)	1.003(4)	1.649(5)	172.3(4)	
$KH_3(SeO_3)_2$	2.566(1)	1.044(7)	1.529(6)	171.1(4)	symmetric (2)
Lehmann ACS 25, 3859 (1971)	2.602(2)	1.029(3)	1.575(3)	175.2(2)	
$LiHCOO.H_2O$	2.714(2)	0.976(3)	1.742(3)	173.6(3)	
Tellgren F 6, 191 (1974)	2.896(2)	0.965(4)	1.949(4)	166.6(3)	
KHC_2O_4	2.518(3)	1.054(5)	1.467(5)	174.6(4)	
Moore INCL 7, 873 (1971)					
$K_2C_2O_4.H_2O$	2.754(2)	0.963(3)	1.801(3)	169.7(2)	
Sequeira AC B26, 77 (1970)					
$(COOH)_2.2H_2O$ α-form	2.506(4)	1.026(7)	1.480(7)	179.3(6)	
Sabine AC B25,2437 (1969)	2.864(5)	0.964(7)	1.917(8)	166.9(6)	
	2.881(4)	0.956(9)	1.979(9)	156.6(7)	
$CH_3COOH.H_3PO_4$	2.558(4)	1.005(6)	1.558(5)	172.9(4)	
Jönsson ACS 26, 1599 (1972)	2.574(3)	1.009(6)	1.570(5)	172.3(4)	
	2.590(3)	0.995(5)	1.596(5)	176.7(4)	
	2.594(3)	0.987(5)	1.609(5)	175.5(5)	
	2.617(4)	0.962(6)	1.662(5)	171.1(5)	
	2.667(4)	0.985(6)	1.685(5)	174.2(4)	
	2.681(4)	0.986(7)	1.697(6)	175.4(4)	
	2.688(4)	0.992(8)	1.699(6)	175.2(5)	

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
$HOCH_2COOH$	2.638(2)	1.001(2)	1.640(2)	175.2(2)	
Ellison AC B27, 333 (1971)	2.647(2)	1.003(2)	1.646(2)	175.5(3)	
	2.714(2)	0.971(3)	1.753(3)	169.7(2)	
	2.696(2)	0.970(3)	1.774(3)	157.6(2)	
KH oxydiacetate Albertsson AC B29, 2751 (1973)	2.476(2)	1.152(3)	1.328(3)	174.2(3)	
RbH oxydiacetate Albertsson AC B29, 2751 (1973)	2.449(3)	1.226(2)	1.226(2)	175.0(4)	symmetric (2)
KH bis(trifluoroacetate) Macdonald JCSPTII 825 (1972)	2.437(4)	1.218(2)	1.218(2)	180.0(0)	symmetric ($\bar{1}$)
KH diaspirinate Sequeira JMS 1, 283 (1968)	2.448(4)	1.224(2)	1.224(2)	180.0(0)	symmetric ($\bar{1}$)
KH malonate Currie JCSA 1923 (1970)	2.468(6)	1.234(3)	1.234(3)	180.0(0)	symmetric ($\bar{1}$)
KH chloromaleate Ellison AC 19, 260 (1965)	2.403(3)	1.199(5)	1.206(5)	175.4(4)	intramolecular
KH succinate McAdam JCSA 1994 (1971)	2.444(9)	1.227(6)	1.227(6)	169.3(9)	symmetric (2)
$H_3O^+CH_3C_6H_4SO_3^-$	2.520(5)	1.013(8)	1.508(7)	178.0(5)	
Lundgren JCP 58, 788 (1973)	2.525(5)	1.011(8)	1.516(7)	174.3(5)	
	2.538(5)	1.008(8)	1.535(7)	172.3(5)	
$H_5O_2^+C_6H_2(NO_2)_3SO_3^-.2H_2O$	2.436(2)	1.128(4)	1.310(4)	175.0(3)	
Lundgren AC B30, 1937 (1974)	2.604(3)	0.996(4)	1.609(4)	177.2(3)	
	2.621(2)	0.988(3)	1.634(3)	176.4(3)	
	2.685(2)	0.977(4)	1.720(4)	168.7(3)	
	2.734(2)	0.976(4)	1.776(3)	166.4(3)	

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
Dialuric acid.H_2O	2.571(7)	1.007(8)	1.574(9)	169.8(7)	
Craven AC B25, 1970 (1969)					
D-Glucitol A-form	2.652(5)	0.986(7)	1.695(7)	162.5(7)	
Park AC B27, 2393 (1971)	2.676(5)	0.966(8)	1.724(8)	168.2(6)	
	2.669(5)	0.953(8)	1.730(8)	168.0(8)	
	2.882(6)	0.980(9)	1.915(9)	168.3(8)	
	2.991(6)	0.972(9)	2.019(9)	177.9(7)	
$(NH_4)_2C_2O_4 \cdot H_2O$	2.773(3)	0.982(5)	1.807(5)	166.8(5)	
Taylor AC B28, 3340 (1972)					
Sucrose	2.716(2)	0.976(3)	1.760(3)	165.4(3)	
Brown AC B29, 790 (1973)	2.781(2)	0.974(3)	1.851(3)	158.6(3)	intramolecular
	2.855(2)	0.972(3)	1.892(3)	170.2(3)	
	2.850(2)	0.972(3)	1.895(3)	167.1(3)	intramolecular
	2.862(2)	0.959(3)	1.907(3)	172.8(3)	
	2.864(2)	0.969(3)	1.908(3)	168.5(2)	
	2.848(2)	0.956(4)	1.921(4)	162.9(3)	
$NH_4HC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$	2.500(4)	1.102(7)	1.399(7)	177.1(7)	
	2.472(4)	1.069(7)	1.403(9)	178.2(6)	
Currie JCSA 1862 (1967)	2.520(5)	1.040(7)	1.483(10)	173.3(7)	
	2.721(4)	0.966(7)	1.765(7)	169.5(6)	
	2.745(4)	0.973(6)	1.787(6)	167.4(6)	
	2.833(5)	0.949(8)	1.906(7)	164.8(7)	
	2.899(5)	0.945(8)	2.000(8)	158.2(7)	
$N_2H_5H_2PO_4$	2.517(7)	1.072(10)	1.446(10)	176.9(9)	
Jönsson ACS 25, 1729 (1971)	2.561(7)	1.023(10)	1.542(10)	173.9(10)	

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
$N_2H_6(H_2PO_4)_2$	2.609(2)	0.995(4)	1.616(4)	175.3(4)	
Kvick ACS 26, 1087 (1972)	2.643(2)	1.003(3)	1.643(3)	174.7(3)	
$N_2H_5HC_2O_4$	2.448(7)	1.224(4)	1.224(4)	180.0(0)	symmetric ($\bar{1}$)
Nilsson ACS 22, 719 (1968)					
$(NH_2)_2CO.H_3PO_4$	2.421(3)	1.207(6)	1.223(6)	169.9(4)	
Kostansek AC B28, 2454 (1972)	2.589(3)	0.999(4)	1.591(4)	176.4(4)	
	2.658(3)	0.997(5)	1.664(5)	173.7(4)	
$(NH_2)_2COH^+NO_3^-$	2.596(2)	1.006(3)	1.591(3)	178.2(3)	
Worsham AC B25, 572 (1969)					
$[Ni(C_5H_{11}N_2O)_2H^+]Cl^-.H_2O$	2.420(5)	1.187(5)	1.242(5)	169.9(4)	intramolecular
Schlemper JCP 54, 3990 (1971)					
L-Asparagine.H_2O	2.812(2)	0.957(3)	1.879(3)	164.3(3)	
Verbist AC B28, 3006 (1972)	2.843(2)	0.962(3)	1.888(3)	171.5(3)	
L-Glutamic acid β-form	2.519(2)	1.050(4)	1.475(5)	172.3(3)	
Lehmann JCMS 2, 225 (1972)					
L-Lysine.HCl.$2H_2O$	2.805(5)	0.960(9)	1.857(7)	169.2(7)	
Koetzle AC B28, 3207 (1972)					
Glycylglycine.HCl.H_2O	2.644(5)	1.003(7)	1.658(6)	166.8(5)	
Koetzle AC B28, 2083 (1972)	2.728(4)	0.972(6)	1.764(6)	170.7(6)	
DL-Serine	2.671(1)	0.981(1)	1.692(2)	175.1(1)	
Frey AC B29, 876 (1973)					

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
L-Serine.H_2O	2.785(4)	0.958(7)	1.843(6)	166.8(4)	
Frey AC B29, 876 (1973)	2.809(5)	0.946(7)	1.868(6)	173.2(5)	
	2.877(5)	0.955(8)	1.922(7)	177.4(5)	
L-Arginine.$2H_2O$	2.738(4)	0.974(6)	1.770(6)	172.1(5)	
Lehmann JCSPTII 133 (1973)	2.715(5)	0.946(7)	1.789(7)	164.9(7)	
L-Tyrosine	2.666(3)	0.981(4)	1.689(4)	173.8(3)	
Frey JCP 58, 2547 (1973)					
L-Tyrosine.HCl	2.619(4)	1.018(6)	1.609(5)	170.7(4)	
Frey JCP 58, 2547 (1973)					
4-Hydroxy-L-proline	2.792(2)	0.971(3)	1.843(3)	164.9(3)	
Koetzle AC B29, 231 (1973)					
$Cu_2(CH_3COO)_4.2H_2O$	2.823(2)	0.961(3)	1.863(3)	179.2(3)	
Brown AC B29, 2393 (1973)	2.927(2)	0.949(3)	1.994(3)	167.1(3)	
$LiClO_4.3H_2O$	2.989(2)	0.972(7)	2.044(7)	163.6(8)	
Sequeira AC B31, 1735 (1975)					
$HgSO_4.4H_2O$	2.884(5)	0.969(10)	1.919(10)	173.6(8)	
Baur AC 17, 863 (1964)	2.833(6)	0.989(10)	1.847(10)	173.8(9)	
	2.734(5)	0.981(10)	1.753(10)	177.7(9)	
$NaCO_3.H_2O$	2.677(7)	0.988(9)	1.699(8)	169.9(8)	
Wu AC B31, 890 (1975)	2.905(6)	0.967(10)	1.987(9)	157.9(8)	

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
$K_2[Cu(H_2O)_6](SO_4)_2$	2.742(4)	0.977(6)	1.775(6)	170.4(5)	
Robinson CSC 1, 185 (1972)	2.781(5)	0.974(6)	1.813(7)	171.9(5)	
	2.711(4)	0.978(5)	1.733(6)	178.0(5)	
	2.764(5)	0.960(6)	1.805(6)	176.1(5)	
	2.668(4)	0.976(6)	1.697(6)	173.3(5)	
	2.657(5)	0.983(6)	1.680(6)	171.7(4)	
$Rb_2[Cu(H_2O)_6](SO_4)_2$	2.741(8)	0.971(5)	1.772(7)	175.0(5)	
vanderZee CSC 1, 367 (1972)	2.754(9)	0.970(7)	1.791(8)	171.8(5)	
	2.688(7)	0.971(6)	1.724(7)	171.7(5)	
$Cs_2[Cu(H_2O)_6](SO_4)_2$	2.714(7)	1.019(10)	1.704(9)	170.9(7)	
Shields CSC 1, 189 (1972)	2.780(7)	0.986(10)	1.798(9)	173.2(8)	
	2.702(7)	1.014(10)	1.697(9)	170.5(6)	
$Tl_2[Cu(H_2O)_6](SO_4)_2$	2.730(7)	0.985(8)	1.751(8)	172.1(6)	
Shields CSC 1, 371 (1972)	2.758(7)	0.978(8)	1.787(9)	171.6(6)	
	2.753(7)	0.999(7)	1.756(7)	175.1(7)	
	2.707(7)	0.986(7)	1.728(8)	171.6(6)	
K D-Gluconate.H_2O A-form	2.726(5)	0.956(7)	1.783(6)	168.1(5)	
Panagiotopoulos AC B30, 1421 (1974)	2.776(4)	0.963(6)	1.834(6)	165.3(5)	
	2.938(4)	0.946(6)	2.001(6)	171.0(5)	
	2.639(4)	0.973(5)	1.666(5)	177.3(5)	
	2.872(4)	0.977(6)	1.982(6)	150.4(5)	
B-form	2.745(5)	0.965(7)	1.805(7)	164.2(6)	
	2.784(5)	0.966(7)	1.817(7)	178.0(6)	
	2.844(5)	0.961(7)	1.887(7)	173.2(6)	
	2.894(5)	0.963(7)	1.974(7)	159.1(6)	
	2.783(5)	0.975(7)	1.809(7)	178.0(6)	
	2.885(5)	0.972(7)	1.915(7)	176.2(6)	
α-Resorcinol	2.717(4)	0.985(6)	1.734(5)	175.9(5)	
Bacon ZK 138, S.19 (1973)	2.732(5)	0.987(7)	1.765(7)	165.7(5)	

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
$(H_3PO_4)_2 \cdot H_2O$	2.563(1)	1.008(2)	1.556(2)	176.2(2)	
Dickens AC B30, 1470 (1974)	2.581(1)	1.011(2)	1.571(2)	176.6(2)	
	2.580(1)	1.002(2)	1.583(2)	171.8(2)	
	2.611(1)	1.001(2)	1.618(2)	170.3(2)	
	2.659(1)	0.989(2)	1.675(2)	172.2(2)	
	2.692(2)	0.985(3)	1.714(2)	171.5(2)	
LiH_2PO_3	2.558(4)	1.018(4)	1.547(4)	171.6(3)	
Johansson AC B32, 412 (1976)					
$Ca(H_2PO_4)_2$	2.620(4)	1.000(8)	1.625(7)	173.6(6)	
Dickens AC B29, 2057 (1973)	2.677(5)	1.000(8)	1.710(6)	162.8(6)	
	2.817(4)	0.957(8)	1.922(8)	154.5(6)	
	2.434(5)	1.218(3)	1.218(3)	180.0(0)	symmetric $(\bar{1})$
	2.419(6)	1.210(3)	1.210(3)	180.0(0)	symmetric $(\bar{1})$
$Ca(H_2PO_4)_2 \cdot H_2O$	2.595(3)	1.016(4)	1.584(4)	172.5(3)	
Schroeder AC B31, 9 (1975)	2.622(3)	0.987(5)	1.679(4)	172.3(4)	
	2.694(3)	0.983(5)	1.728(5)	166.4(5)	
	2.626(3)	0.987(5)	1.653(5)	167.5(4)	
$NH_4H_3(SeO_3)_2$	2.644(4)	1.007(5)	1.643(5)	172.3(5)	
Tellgren AC B30, 2497 (1974)	2.596(4)	1.004(7)	1.595(6)	174.3(5)	
	2.554(4)	1.027(5)	1.532(6)	172.4(5)	
$YH(C_2O_4)_2 \cdot 3H_2O$	2.440(3)	1.221(1)	1.221(1)	175.3(3)	symmetric (2)
Brunton JCP 62, 3797 (1975)	2.643(2)	0.983(3)	1.674(3)	167.9(3)	
	2.680(2)	0.992(3)	1.688(3)	178.2(3)	
$KHCO_3$	2.587(1)	1.005(2)	1.587(2)	173.0(2)	
Thomas AC B30, 2540 (1974)					
$CCl_3CH(OH)_2$	2.903(2)	0.975(2)	1.929(2)	176.7(2)	
	2.838(2)	0.972(2)	1.915(2)	157.5(2)	
Brown CSC 2, 107 (1973)					

Compound and reference	O...O (Å)	O - H (Å)	H...O (Å)	O-H...O (degrees)	Comments
$K_2[Cu(H_2O)_6](SeO_4)_2$	2.868(3)	0.958(4)	1.924(4)	167.8(4)	
Whitnall CSC 4, 709 (1975)	2.821(3)	0.969(5)	1.867(5)	167.7(4)	
	2.655(3)	0.976(3)	1.679(3)	178.8(4)	
	2.718(3)	1.001(4)	1.719(3)	175.4(4)	
	2.677(4)	0.980(5)	1.700(4)	174.5(3)	
	2.654(3)	1.003(4)	1.657(4)	171.6(3)	
$K_2[Cu(H_2O)_6](SO_4)_2$	2.784(3)	0.980(3)	1.813(3)	170.5(4)	
Hodgeson CSC 4, 713 (1975)	2.795(3)	0.965(5)	1.838(4)	170.8(3)	
	2.658(2)	0.975(3)	1.684(4)	178.2(4)	
	2.737(3)	0.987(4)	1.755(4)	173.1(4)	
	2.715(3)	0.959(4)	1.766(4)	169.3(3)	
	2.656(3)	0.985(4)	1.681(4)	170.1(3)	
$K_2[Zn(H_2O)_6](SO_4)_2$	2.679(6)	0.976(9)	1.703(8)	179.3(7)	
Whitnall CSC 4, 717 (1975)	2.746(6)	1.002(10)	1.746(9)	175.1(8)	
	2.726(6)	1.000(10)	1.734(10)	170.7(7)	
	2.642(7)	0.967(10)	1.684(9)	170.6(6)	
$[Zn(H_2O)_4[Hg(CN)_2]_2][NO_3]_2 \cdot 3H_2O$	2.728(3)	0.952(6)	1.777(5)	176.3(4)	
Power JCSDT 2072 (1975)	2.724(4)	0.976(5)	1.750(5)	175.7(4)	
	2.753(4)	0.995(4)	1.769(5)	169.4(4)	
	2.756(5)	0.968(5)	1.792(6)	173.6(4)	
	2.861(4)	0.976(5)	1.887(6)	175.7(5)	
Quinolinic acid	2.398(3)	1.163(5)	1.238(5)	174.4(4)	intramolecular
Kvick JCP 60, 3866 (1974)					
Squaric acid	2.544(4)	1.028(7)	1.516(7)	178.8(9)	
Wang JCSPTII 35 (1974)	2.532(4)	1.104(9)	1.435(9)	171.8(9)	
Methyl α-D-Altropyranoside	2.879(4)	0.961(6)	1.922(6)	173.0(6)	
Poppleton AC B31, 2400 (1975)	2.702(4)	0.971(5)	1.737(5)	172.8(5)	
Tetraacetylethane	2.450(4)	1.194(9)	1.319(9)	154.3(4)	intramolecular
Power JCMS 5, 59 (1975)					
3,3'-Trithiobis-(2,4-pentanedione)	2.457(4)	1.141(7)	1.388(8)	152.6(5)	intramolecular
Power JCMS 5, 125 (1975)					

* only first author's name is quoted and journal names are abbreviated as follows :

AC	Acta Cryst.
ACS	Acta Chem. Scand.
CSC	Cryst. Struct. Commun.
F	Ferroelectrics
IC	Inorg. Chem.
INCL	Inorg. Nucl. Chem. Letters
JCMS	J. Cryst. Mol. Struct.
JCP	J. Chem. Phys.
JCSA	J. Chem. Soc. (A)
JCSDT	J. Chem. Soc. Dalton Trans.
JCSPTII	J. Chem. Soc. Perkin Trans. II
JMS	J. Mol. Struct.
JSSC	J. Solid State Chem.
RCM	Rev. Chim. Mineral.
ZK	Z. Kristallogr.

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