Structure of Ammonium Hydrogen Succinate at 80 and 20 K

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Abstract

The crystal structure of ammonium hydrogen succinate has been determined at 80 and 20 K in order to clarify the structural change at the second-order phase transition at 170 K. The geometries of all the hydrogen bonds in the structure were analyzed by combining new geometric data with data obtained previously at 297, 190 and 150 K. The O$\cdots$O distances of two O—H$\cdots$O hydrogen bonds involving the hydrogen succinate ions increase as the temperature decreases below T_c and the N$\cdots$O distance of a weak bifurcated hydrogen bond involving the ammonium ion decreases below T_c. It is noted that the phase transition occurs so that the bifurcated hydrogen bond is retained below T_c. There was no evidence of a descent in space group from $P\bar{1}$ to $P1$ below T_c and the formation of a superstructure below T_c was not detected.

1. Introduction

A second-order phase transition in ammonium hydrogen succinate, (I), at around 170 K was reported by Haussühl & Schreuer (1993). They found two O—H$\cdots$O hydrogen bonds between hydrogen succinate ions which were disordered around inversion centers at room temperature. They predicted that the hydrogen bonds might be ordered below the phase transition temperature T_c and that the space group might descend from $P\bar{1}$ above T_c to $P1$ below T_c.

Many studies of short O—H$\cdots$O hydrogen bonds in acidic salts of carboxylic acids have been carried out (Kalsbeek, 1992). However, second-order phase transitions have not often been found for these compounds because the diffraction studies have been performed at most at only two temperatures: room temperature and 110–120 K (Kalsbeek, 1991, 1992; Kalsbeek & Larsen, 1991).

We recently determined the X-ray structure of (I) assuming the space group to be either $P\bar{1}$ or $P1$. The results showed that the H-atom positions in the O—H$\cdots$O hydrogen bonds disordered at 190 and 150 K, and both structures above and below T_c can be described in $P\bar{1}$ (Hirano *et al.*, 1996). A significant change in the structures at 190 and 150 K was found only in the geometry of one of the N—H$\cdots$O hydrogen bonds between an ammonium ion and a hydrogen succinate ion. However, the difference in the structures was too small to elucidate clearly the structural change at the phase transition. Furthermore, the study did not show whether the structure determined below T_c is the average of a superstructure. In the present work, the temperature dependence of the geometries of the hydrogen bonds was determined and an additional experiment to detect any reflections from a superlattice was carried out.

2. Experimental

Crystals of (I) were grown by slow evaporation of an aqueous solution of ammonium succinate and succinic acid in a molar ratio of 1:1. The crystal was mounted on a sapphire stick and a thermocouple was fixed to the stick adjacent to the crystal. The temperature was regulated to within ± 0.5 K of the setting temperature using a closed-cycle He refrigerator (Cryogenics, HC-2) equipped with a temperature controller (Cino, KP1000). The diffractometer was equipped with a rotating anode (50 kV, 200 mA).

Cell constants based on the unit cell determined by Hirano *et al.* (1996) ('original cell') were determined over the temperature range 297–20 K. Intensity data for structure analysis were collected at 80 and 20 K as described in Table 1 and were corrected for Lorentz and polarization effects. Three reflections which suffered from scattering by the sapphire stick were removed from the data at 80 and 20 K. Non-H atoms were refined anisotropically by a full-matrix least-squares method using the structure in $P\bar{1}$ at 150 K (Hirano *et al.*, 1996) as a starting model. All H atoms were found from difference Fourier maps and were refined isotropically. Refinements were also tried in $P1$. Difference Fourier maps showed two peaks of similar height between the O atoms for each O—H$\cdots$O hydrogen bond involving the hydrogen succinate ions, as reported previously (Hirano *et al.*, 1996). Further least-squares refinements including the H atoms were unsuccessful because of parameter correlations. Although the average bond lengths of corresponding bonds in the two independent moieties

Table 1. *Experimental details*

	80 K	20 K
Crystal data		
Chemical formula	$NH_4^+.C_4H_5O_4^-$	$NH_4^+.C_4H_5O_4^-$
Chemical formula weight	135.12	135.12
Cell setting	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.456 (1)	7.460 (1)
b (Å)	8.813 (2)	8.805 (2)
c (Å)	4.6806 (5)	4.6768 (5)
α (°)	91.74 (1)	91.84 (1)
β (°)	92.85 (1)	92.73 (1)
γ (°)	101.11 (1)	101.20 (1)
V (Å³)	301.10 (5)	300.73 (8)
Z	2	2
D_x (Mg m⁻³)	1.490	1.492
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	25	25
θ range (°)	10–11.5	10–11.5
μ (mm⁻¹)	0.134	0.134
Temperature (K)	80	20
Crystal form	Prism	Prism
Crystal size (mm)	$0.43 \times 0.33 \times 0.30$	$0.43 \times 0.33 \times 0.30$
Crystal color	Colorless	Colorless
Data collection		
Diffractometer	Huber off-center	Huber off-center
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None
No. of measured reflections	3815	3814
No. of independent reflections	3497	3497
No. of observed reflections	2720	2819
Criterion for observed reflections	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$
R_{int}	0.017	0.020
θ_{max} (°)	39.1	39.1
Range of h, k, l	$-12 \rightarrow h \rightarrow 12$	$-12 \rightarrow h \rightarrow 12$
	$-13 \rightarrow k \rightarrow 13$	$-13 \rightarrow k \rightarrow 13$
	$0 \rightarrow l \rightarrow 8$	$0 \rightarrow l \rightarrow 8$
No. of standard reflections	3	3
Frequency of standard reflections	Every 97 reflections	Every 97 reflections
Intensity decay (%)	0	0
Refinement		
Refinement on	F	F
R	0.035	0.034
wR	0.033	0.034
S	1.77	1.79
No. of reflections used in refinement	2720	2819
No. of parameters used	123	123
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$	0.001	0.032
$\Delta\rho_{max}$ (e Å⁻³)	0.42	0.42
$\Delta\rho_{min}$ (e Å⁻³)	-0.29	-0.28
Extinction method	$I_{corr} = I_o(1 + gI_c)$	$I_{corr} = I_o(1 + gI_c)$
Extinction coefficient	0.489×10^{-4}	0.488×10^{-4}
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)

were in agreement with those of the $P\bar{1}$ structure, the lengths of the C=O carbonyl bonds were too long in one of the two independent succinate moieties and too short in the other.

The measurement of superstructure reflections was carried out at 40 K based on a unit cell ('large cell') obtained by doubling a, b and c of the original cell. Reflections $hk0$ and $0kl$ with $\theta_{max} \leq 24°$ were measured

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
80 K				
O1	0.30301 (9)	0.03070 (8)	0.2496 (1)	0.0158 (3)
O2	0.03265 (9)	0.10142 (7)	0.1983 (1)	0.0118 (3)
O3	0.41353 (9)	0.41598 (8)	0.1716 (1)	0.0122 (3)
O4	0.27370 (9)	0.61393 (7)	0.2567 (1)	0.0124 (3)
N1	0.3287 (1)	0.8093 (1)	−0.2234 (2)	0.0157 (4)
C1	0.1940 (1)	0.1124 (1)	0.3221 (2)	0.0119 (4)
C2	0.2396 (1)	0.2294 (1)	0.5699 (2)	0.0100 (3)
C3	0.1857 (1)	0.3844 (1)	0.5141 (2)	0.0096 (3)
C4	0.2979 (1)	0.4805 (1)	0.3004 (2)	0.0100 (3)
20 K				
O1	0.30253 (8)	0.03031 (7)	0.2505 (1)	0.0129 (3)
O2	0.03270 (8)	0.10164 (7)	0.1992 (1)	0.0093 (3)
O3	0.41362 (8)	0.41599 (7)	0.1723 (1)	0.0093 (3)
O4	0.27367 (8)	0.61416 (7)	0.2572 (1)	0.0096 (3)
N1	0.3292 (1)	0.8097 (1)	−0.2224 (2)	0.0134 (3)
C1	0.1940 (1)	0.1123 (1)	0.3232 (2)	0.0099 (3)
C2	0.2397 (1)	0.2296 (1)	0.5716 (2)	0.0074 (3)
C3	0.1861 (1)	0.38464 (9)	0.5162 (2)	0.0070 (3)
C4	0.2981 (1)	0.4808 (1)	0.3014 (2)	0.0079 (3)

Table 3. *Selected geometric parameters (Å, °)*

	80 K	20 K
C1—C2	1.509 (1)	1.511 (1)
C2—C3	1.523 (1)	1.522 (1)
C3—C4	1.509 (1)	1.511 (1)
C1—O1	1.238 (1)	1.237 (1)
C1—O2	1.294 (1)	1.295 (1)
C4—O3	1.284 (1)	1.285 (1)
C4—O4	1.245 (1)	1.245 (1)
O1—C1—O2	123.03 (8)	123.09 (8)
O1—C1—C2	121.60 (9)	121.63 (8)
O2—C1—C2	115.35 (8)	115.26 (7)
O3—C4—O4	124.04 (8)	124.09 (8)
O3—C4—C3	116.30 (8)	116.20 (7)
O4—C4—C3	119.66 (8)	119.70 (7)
C1—C2—C3	114.33 (8)	114.29 (7)
C2—C3—C4	114.87 (7)	114.91 (7)

for the large cell following the same procedure as that given in Table 1.

X-ray diffraction data were measured at the X-ray Laboratory of Okayama University. Calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). Atomic scattering factors were taken from Cromer & Waber (1974) for non-H atoms and from Stewart *et al.* (1992) for H atoms.

3. Results and discussion

The structure is described based on the results of refinements in the space group $P\bar{1}$. The temperature dependence of the lattice constants of the original cell is shown in Fig. 1 in the range 297–20 K. The dependence is consistent with that reported previously for 297–100 K (Hirano *et al.*, 1996).

Atomic parameters are listed in Table 2† and geometric parameters are listed in Table 3. A displacement-ellipsoid plot of the asymmetric unit with the atomic numbering is shown in Fig. 2. The bond lengths between non-H atoms at 80 and 20 K are longer than those at 150 K (Hirano *et al.*, 1996) by 0.004 (1) Å on average, and the difference in bond angles is within the standard uncertainty.

The crystal structure is shown in Fig. 3 and the geometries of the hydrogen bonds are listed in Table 4. The O—H···O hydrogen bonds O2—H1···O2^i and O3—H6···O3^{ii} are located around inversion centers at (0,0,0) and ($\frac{1}{2},\frac{1}{2}$,0), respectively. Hydrogen succinate ions related by these inversion centers form a chain along [110]. The first hydrogen bond is longer than the second in the temperature range 20–150 K; this is also the case
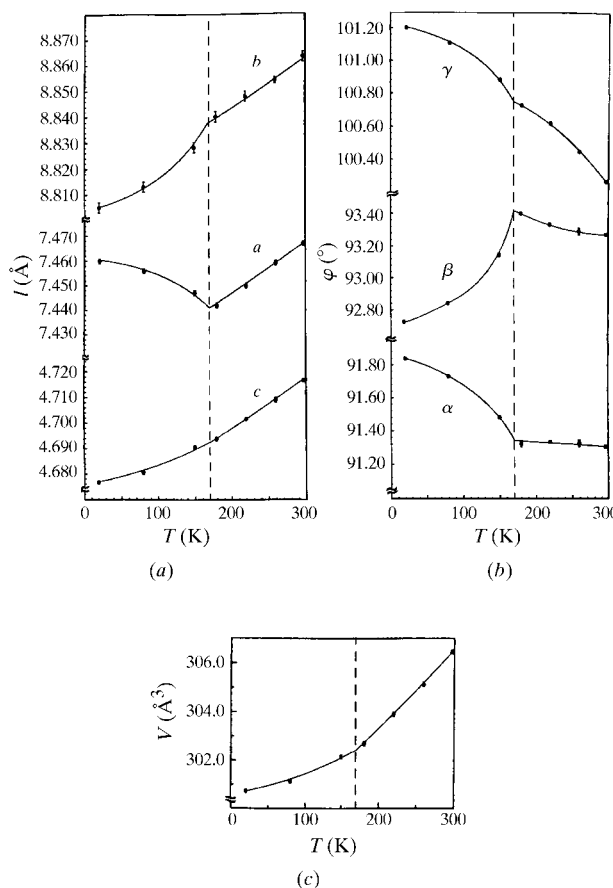

Fig. 1. The temperature dependence of the lattice constants. (*a*) *a, b* and *c versus T*. (*b*) α, β and γ *versus T*. (*c*) V *versus T*. Solid lines are drawn as a guide to the eye.

in the temperature range 150–297 K (Hirano *et al.*, 1996). Difference Fourier maps at 20, 80 and 150 K calculated by eliminating the H atoms involved in these hydrogen bonds are shown in Fig. 4. These maps each show two peaks, one either side of the midpoint between the O atoms involved in each hydrogen bond. Similar splitting of the peaks also occurs for the structure in $P1$ reported previously (Hirano *et al.*, 1996). Therefore, this splitting may reflect some kind of disorder. The resolution of the peaks in the maps of the O3—H6···O3^{ii} hydrogen bond at 20 and 80 K is not better than at 150 K, even though the O3···O3^{ii} distances at 20 and 80 K are longer than at 150 K [2.456 (2) Å]. This feature of the difference Fourier maps below T_c cannot be explained by thermal disorder alone and suggests that there is a contribution from static disorder below T_c.

The temperature dependence of the hydrogen-bond distances is shown in Fig. 5. The data for 150, 190 and 297 K are taken from the previous study (Hirano *et al.*, 1996). As can be seen from Fig. 5, the O···O distances of the hydrogen bonds O2—H1···O2^i and O3—H6···O3^{ii} decrease as the temperature decreases above T_c, with minimum values at T_c. In chloranil, a second-order phase transition occurs to avoid the stress induced by a too-short O···C contact [O···C = 2.776 (6) Å at $T_c =$
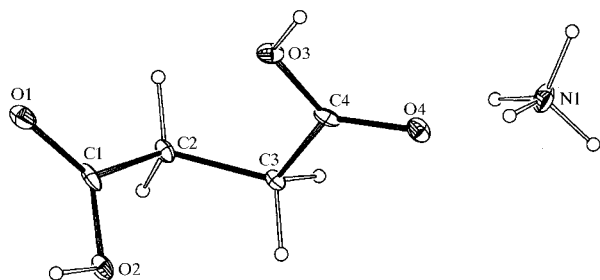

Fig. 2. A displacement-ellipsoid plot (50% probability) of the structure of (I) at 20 K showing the atomic numbering. H atoms are represented as spheres with $B = 0.3$ Å^2.

Table 4. *Geometries (Å, °) of hydrogen bonds below T_c*

Data at 150 K are taken from Hirano *et al.* (1996).

	D···A	D—H	H···A	D—H···A
O2—H1···O2^i				
150 K	2.485 (2)	0.86 (4)	1.62 (4)	178 (4)
80 K	2.500 (1)	0.85 (2)	1.66 (2)	174 (3)
20 K	2.505 (1)	0.86 (2)	1.65 (2)	170 (3)
O3—H6···O3^{ii}				
150 K	2.456 (2)	0.86 (5)	1.60 (5)	172 (5)
80 K	2.460 (1)	0.84 (3)	1.62 (3)	178 (4)
20 K	2.461 (1)	0.85 (3)	1.61 (3)	175 (3)
N1—H9···O1^{ii}				
150 K	2.849 (1)	0.87 (2)	1.98 (2)	174 (2)
80 K	2.846 (1)	0.97 (1)	1.88 (1)	173 (1)
20 K	2.845 (1)	0.96 (2)	1.90 (2)	171 (1)
N1—H10···O4				
150 K	2.873 (1)	0.94 (2)	1.95 (2)	167 (2)
80 K	2.870 (1)	0.98 (1)	1.91 (1)	165 (1)
20 K	2.868 (1)	0.97 (1)	1.91 (1)	166 (1)
N1—H7···O4^{iii}				
150 K	2.909 (1)	0.93 (3)	1.99 (3)	169 (3)
80 K	2.903 (1)	0.90 (2)	2.02 (2)	169 (1)
20 K	2.902 (1)	0.89 (2)	2.02 (2)	169 (1)
N1—H8···O2^{iv}				
150 K	2.945 (2)	0.88 (3)	2.14 (3)	152 (3)
80 K	2.955 (1)	0.90 (2)	2.15 (2)	149 (1)
20 K	2.958 (1)	0.92 (2)	2.14 (2)	149 (1)
N1—H8···O1^v				
150 K	2.967 (1)	0.88 (3)	2.50 (3)	114 (2)
80 K	2.944 (1)	0.90 (2)	2.42 (2)	117 (1)
20 K	2.936 (1)	0.92 (2)	2.40 (2)	117 (1)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, -z$; (iii) $x, y, z-1$; (iv) $-x, 1-y, -z$; (v) $x, 1+y, z$.

90 K] between neighboring molecules (Kubozono *et al.*, 1997). However, in the present case, the minimum O···O distances of both O—H···O hydrogen bonds are significantly longer than the shortest distance of around 2.44 Å found so far in hydrogen biscarboxylates (Kalsbeek & Larsen, 1991). Therefore, it seems that these hydrogen bonds do not play a similar role in the phase transition of (I) to that of the O···C contact in chloranil.
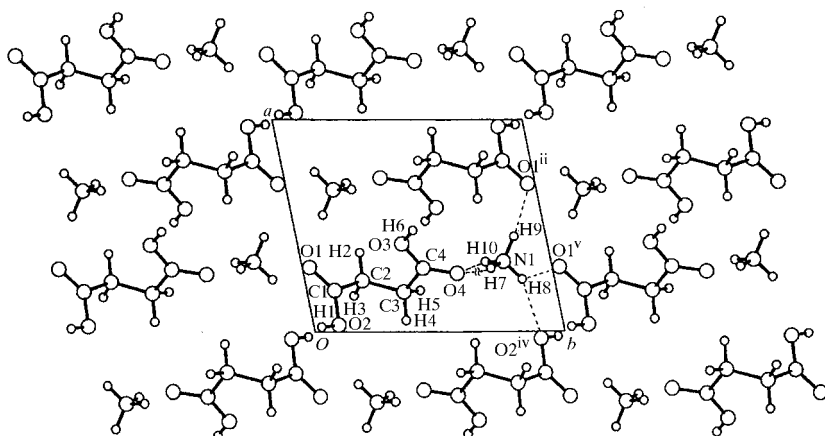

Fig. 3. A projection of the crystal structure along the c axis at 20 K. Hydrogen bonds involving the ammonium ion are shown as dashed lines.

In addition to the O—H$\cdots$O hydrogen bonds, there are N—H$\cdots$O hydrogen bonds between the ammonium and hydrogen succinate ions. The H8 atom of the ammonium ion is involved in a bifurcated hydrogen bond (Hirano *et al.*, 1996). The N1$\cdots$O1^v distance in the bifurcated hydrogen bond at 297 K [2.981 (2) Å] is the longest of all the hydrogen bonds in (I). It has been pointed out previously that the N1—H8$\cdots$O1^v hydrogen bond is weakened as the temperature is decreased from 297 to 190 K (Hirano *et al.*, 1996). In fact, the angle N1—H8$\cdots$O1^v [110 (2)°] and the contact H8$\cdots$O1^v [2.59 (2) Å] at 190 K are close to the critical values at which the hydrogen bond can no longer be held. As can be seen from Fig. 5 and Table 4, the N1$\cdots$O1^v and H8$\cdots$O1^v distances decrease as the temperature decreases below T_c, and thus the N1—H8$\cdots$O1^v hydrogen bond is strengthened below T_c. In the N1—H8$\cdots$O2^{iv} hydrogen bond, which is a counterpart of the bifurcated hydrogen bond, the N1$\cdots$O2^{iv} distance

increases slightly below T_c. However, stabilization of the bifurcated hydrogen-bond system below T_c is attainable by strong stabilization of its counterpart. Therefore, the phase transition occurs such that the bifurcated hydrogen bond is kept below T_c. As can be seen from Fig. 5, the N$\cdots$O distances for the other three N—H$\cdots$O hydrogen bonds decrease as the temperature decreases and the temperature dependency is smaller below T_c than above T_c.

Disorder of the H-atom positions of the O—H$\cdots$O hydrogen bonds is observed even below T_c, as described above. However, it should be noted that this does not necessarily mean that the H atoms within a chain of anions extending along [110] are disordered. In a second-order structural phase transition, the space group of the high-temperature phase usually descends to its maximal isomorphic subgroup, which results in a superstructure in the low-temperature phase. Therefore, the possibility of the formation of a superstructure which gives an average structure in $P\bar{1}$ as observed was examined. The simplest model of such a superstructure was constructed by the alternate arrangement of chains related by inversion centers along **a** and/or **b** and/or **c** of the original unit cell, where the H atoms were assumed to be ordered in each chain. The superstructure reflections were checked based on the large cell obtained by doubling the dimensions of a, b and c of the original cell as described in §2. Among 154 reciprocal points surveyed at 40 K, only seven reflections had values of $F_o/\sigma(F)$ larger than 3 and the maximum value of
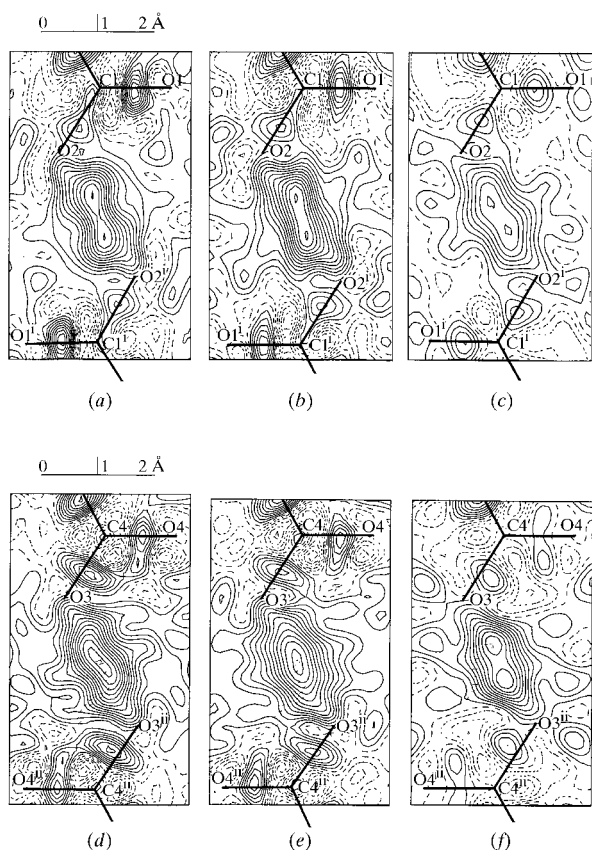

Fig. 4. Difference Fourier maps around the inversion centers: (a)–(c) at $(0,0,0)$; (d)–(e) at $(\frac{1}{2},\frac{1}{2},0)$. Contours are drawn as solid lines above 0.05 e Å^{-3} and as dashed lines below −0.05 e Å^{-3} with an interval of 0.05 e Å^{-3}. Sections through the planes of the hydrogen carboxylate groups are shown. (a) and (d) are at 20 K, (b) and (e) are at 80 K, and (c) and (f) are at 150 K. The maps at 150 K were calculated based on previous results (Hirano *et al.*, 1996).
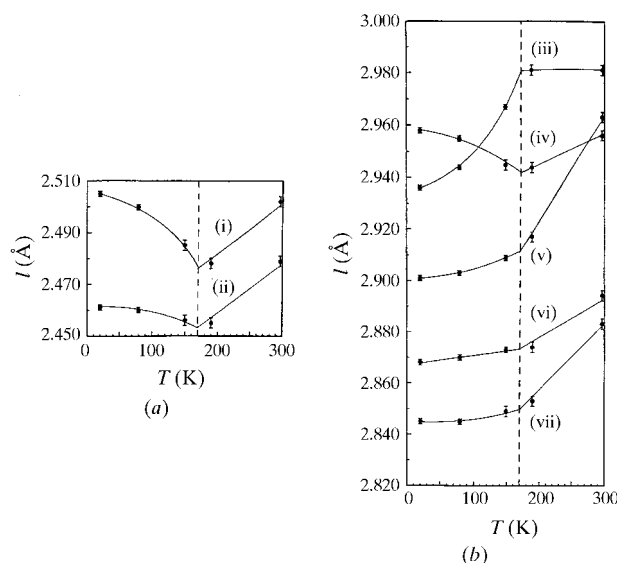

Fig. 5. The temperature dependence of hydrogen-bond distances in the range 297–20 K. The solid lines are drawn as a guide to the eye. (a) O—H$\cdots$O hydrogen bonds: (i) O2$\cdots$O2^i, (ii) O3$\cdots$O3^{ii}; (b) N—H$\cdots$O hydrogen bonds: (iii) N1$\cdots$O1^v, (iv) N1$\cdots$O2^{iv}, (v) N1$\cdots$O4^{iii}, (vi) N1$\cdots$O4, (vii) N1$\cdots$O1^{ii}. See Table 4 for symmetry codes. Hydrogen-bond distances at 297, 190 and 150 K were taken from Hirano *et al.* (1996).

$F_o/\sigma(F)$ was 5.7. Moreover, there was no indication of an abnormal background on either side of each reflection. These facts show that there is no prominent contribution from this type of superstructure to the structure below T_c.

4. Conclusions

The geometries of the hydrogen bonds in (I) have been analyzed based on results obtained over the wide temperature range 20–296 K. The geometries of all the hydrogen bonds change at the phase transition. It was confirmed that the weak bifurcated hydrogen bond involving the ammonium ion is maintained below T_c. The formation of a superstructure below T_c was not detected. However, the disordered structure in $P\bar{1}$ may be produced by a statistically disordered arrangement of chains or domains in which the H atoms are ordered. This possibility would need to be confirmed by further studies. A comparative study (especially below T_c) using deuterated crystals would provide more insight into the mechanism of the phase transition.

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