

Ammonium hydrogen tartronate at
240 and 20 KYoshimitsu Moritani,^{a†} Takeo Fukunaga,^b Hiroyuki
Ishida^b and Setsuo Kashino^{b*}^aGraduate School of Natural Science and Technology, Okayama University,
Tsushima, Okayama 700-8530, Japan, and ^bDepartment of Chemistry, Faculty
of Science, Okayama University, Tsushima, Okayama 700-8530, Japan
Correspondence e-mail: kashinos@cc.okayama-u.ac.jp

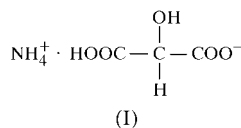
Received 15 August 2001

Accepted 28 August 2001

The low-temperature structure determination of the title compound, alternatively called ammonium hydrogen hydroxypropanedioate, $\text{NH}_4^+ \cdot \text{C}_3\text{H}_3\text{O}_5^-$, has revealed that the H atom involved in a very short asymmetric $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond [$\text{O} \cdots \text{O} = 2.448(2) \text{ \AA}$ at 240 K and $2.4393(10) \text{ \AA}$ at 20 K] is disordered.

Comment

A previous study of the title compound, (I), at 295 K showed that a very short asymmetric $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond [$\text{O} \cdots \text{O} = 2.443(2) \text{ \AA}$] is formed between the carboxylate and carboxyl groups of neighboring moieties related by a twofold screw axis (Taka *et al.*, 1998). A least-squares refinement of (I) resulted in a long $\text{O}-\text{H}$ bond length of $1.18(3) \text{ \AA}$ in the short hydrogen bond; a similar observation was made earlier for several short hydrogen bonds (Olovsson & Jönsson, 1976; Misaki *et al.*, 1986). The structure was not refined by assuming a disorder of the H atom involved in the short hydrogen bond, because no peak was observed in a difference Fourier map around the region expected for a disordered H atom and the residual electron density in the region was as low as 0.12 e \AA^{-3} (Taka *et al.*, 1998). Valuable temperature experiments have been undertaken recently for several compounds by neutron or X-ray diffraction in order to obtain information on the bonding behavior of the H atom involved in short hydrogen bonds (Olovsson *et al.*, 2001; Wilson, 2001; Kashino *et al.*, 1998, 2001).



The present work is part of a study on the behavior of H atoms in very short hydrogen bonds. In (I), the short bond is formed between O5 and O3^i [symmetry code: (i) $-x, y - \frac{1}{2}$,

[†] On leave from Mitsui Chemical Analysis & Consulting Service Inc., Waki 6-1-2, Waki-cho, Kuga-gun, Yamaguchi 740-0061, Japan.

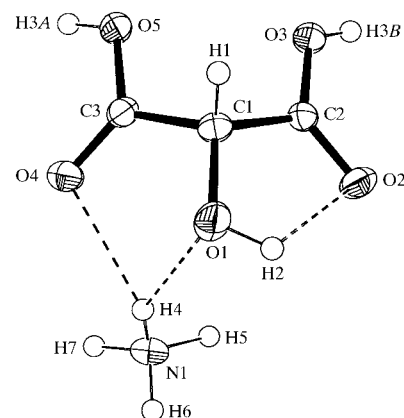


Figure 1

ORTEP-3 (Farrugia, 1997) drawing of the formula unit of (I) at 240 K with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The occupancy factors for H3A and H3B are 0.6 and 0.4, respectively. Hydrogen bonds are indicated by dashed lines.

$\frac{3}{2} - z$] (Figs. 1–3, and Tables 2 and 4). It has been confirmed that at 240 and 20 K, the H atom involved in the short hydrogen bond is disordered between two positions with non-equivalent occupancies. This indicates that the potential function is of an asymmetric double-minimum type for this short hydrogen bond. The apparent $\text{H3A} \cdots \text{H3B}$ distance is $0.89(7) \text{ \AA}$ at 240 K and $0.78(5) \text{ \AA}$ at 20 K. It is noted that the $\text{O5}-\text{C3}$ bond is significantly longer than the $\text{O3}-\text{C2}$ bond (Tables 1 and 3), in accordance with the fact that the occupancy factor of H3A (0.60 at 240 K and 0.55 at 20 K) is larger than that of H3B (0.40 at 240 K and 0.45 at 20 K). The $\text{O5} \cdots \text{O3}^i$ distances at 240 and 20 K [$2.448(2)$ and $2.4393(10) \text{ \AA}$, respectively] are essentially the same as that observed at 295 K [$2.443(2) \text{ \AA}$]. The longest two $\text{N} \cdots \text{O}$ distances of the $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds are shortened compared with the values at 295 K of $3.129(3)$ and $3.044(3) \text{ \AA}$.

A recent study of a short asymmetric $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond [$\text{O} \cdots \text{O} = 2.400(5) \text{ \AA}$ at 150 K, $2.405(6) \text{ \AA}$ at 250 K, $2.420(7) \text{ \AA}$ at 295 K and $2.430(9) \text{ \AA}$ at 335 K] in urea-phosphoric acid (1/1) by neutron diffraction showed that the

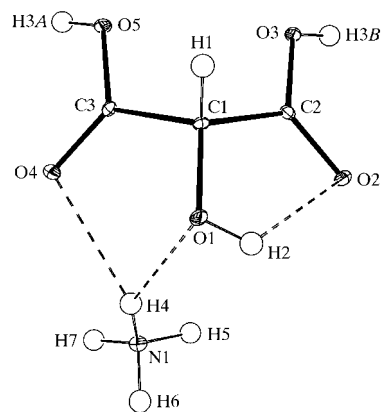


Figure 2

ORTEP-3 (Farrugia, 1997) drawing of the formula unit of (I) at 20 K with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The occupancy factors for H3A and H3B are 0.55 and 0.45, respectively. Hydrogen bonds are indicated by dashed lines.

position of the H atom involved in the hydrogen bond becomes effectively centered at the highest temperatures studied (Wilson, 2001). The disorder and occupancy of the H atom were examined (Wilson, 2001). The short hydrogen bond in (I) should be studied further in order to clarify the temperature dependence of the occupancy of the H atom and the nature of the disorder by combining neutron and X-ray diffraction methods at low temperatures.

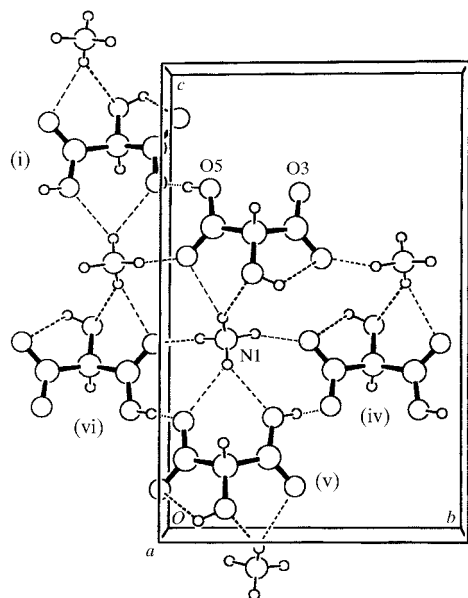


Figure 3
The molecular arrangement based on the atomic parameters of (I) at 240 K. Hydrogen bonds are indicated by dashed lines. The H3B atom with an occupancy factor of 0.4 and the formula units (ii) and (iii) have been omitted for clarity. The symmetry codes are as given in Table 2.

Experimental

Crystals of (I) were grown by slow evaporation from an aqueous solution containing equimolar amounts of tarttronic acid and ammonia. A crystal was mounted on a sapphire rod and a thermocouple was fixed to the rod adjacent to the crystal. The temperature was regulated to within ± 0.2 K of the setting temperature using a closed-cycle He refrigerator (Cryogenics HC-2) equipped with a temperature control (Chino KP1000). Cell constants were checked over the temperature range 20–298 K. Intensity data for structure analysis were collected at 20 and 240 K. The range of χ angles was limited within 173 and 373 K for low-temperature measurements. Reflections which suffered from scattering by the sapphire rod were removed from the diffraction data.

Compound (I) at 240 K

Crystal data

$\text{NH}_4^+ \cdot \text{C}_3\text{H}_3\text{O}_5^-$
 $M_r = 137.10$
 Monoclinic, $P2_1/c$
 $a = 4.299$ (3) Å
 $b = 9.0650$ (16) Å
 $c = 14.262$ (6) Å
 $\beta = 92.67$ (5) $^\circ$
 $V = 555.2$ (5) Å 3
 $Z = 4$

$D_x = 1.640$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.5$ – 11.0°
 $\mu = 0.16$ mm $^{-1}$
 $T = 240$ K
 Prismatic, colorless
 $0.40 \times 0.30 \times 0.30$ mm

Data collection

Huber off-center four-circle diffractometer
 ω – 2θ scans
 1811 measured reflections
 1584 independent reflections
 1059 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 30.0^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 12$
 $l = -20 \rightarrow 20$
 3 standard reflections every 97 reflections
 intensity decay: 2.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.125$
 $S = 0.98$
 1584 reflections
 114 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.1104P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.25$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.25$ e Å $^{-3}$

Table 1
Selected geometric parameters (Å, $^\circ$) for (I) at 240 K.

O1–C1	1.406 (2)	O5–C3	1.2914 (19)
O2–C2	1.2318 (19)	C1–C3	1.528 (2)
O3–C2	1.2724 (19)	C1–C2	1.539 (2)
O4–C3	1.2243 (19)		
O1–C1–C3	109.85 (13)	O3–C2–C1	114.75 (13)
O1–C1–C2	111.51 (13)	O4–C3–O5	125.63 (16)
C3–C1–C2	111.15 (13)	O4–C3–C1	121.28 (14)
O2–C2–O3	126.47 (16)	O5–C3–C1	113.09 (14)
O2–C2–C1	118.76 (13)		

Table 2
Hydrogen-bonding geometry (Å, $^\circ$) for (I) at 240 K.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5–H3A \cdots O3 ⁱ	0.78 (4)	1.67 (4)	2.448 (2)	177 (4)
O3–H3B \cdots O5 ⁱⁱ	0.78 (5)	1.67 (5)	2.448 (2)	177 (6)
O1–H2 \cdots O2	0.79 (3)	2.26 (3)	2.657 (2)	112 (2)
O1–H2 \cdots O2 ⁱⁱⁱ	0.79 (3)	2.11 (3)	2.7781 (19)	143 (3)
N1–H4 \cdots O4	0.86 (3)	2.23 (3)	2.902 (2)	134 (3)
N1–H4 \cdots O1	0.86 (3)	2.32 (3)	3.112 (3)	153 (3)
N1–H5 \cdots O2 ^{iv}	1.00 (3)	2.04 (3)	3.020 (2)	164 (3)
N1–H6 \cdots O5 ^v	0.93 (3)	2.13 (3)	2.898 (2)	139 (2)
N1–H6 \cdots O3 ^v	0.93 (3)	2.25 (3)	2.893 (2)	125 (2)
N1–H7 \cdots O4 ^{vi}	0.88 (3)	2.02 (3)	2.884 (2)	166 (3)

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $-x, -y, 1 - z$.

Compound (I) at 20 K

Crystal data

$\text{NH}_4^+ \cdot \text{C}_3\text{H}_3\text{O}_5^-$
 $M_r = 137.10$
 Monoclinic, $P2_1/c$
 $a = 4.2418$ (7) Å
 $b = 9.0258$ (12) Å
 $c = 14.217$ (3) Å
 $\beta = 94.335$ (15) $^\circ$
 $V = 542.76$ (16) Å 3
 $Z = 4$

$D_x = 1.678$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.5$ – 11°
 $\mu = 0.16$ mm $^{-1}$
 $T = 20$ K
 Prismatic, colorless
 $0.40 \times 0.30 \times 0.30$ mm

Data collection

Huber off-center four-circle diffractometer
 ω – 2θ scans
 2464 measured reflections
 2216 independent reflections
 1738 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 34.8^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 14$
 $l = -22 \rightarrow 22$
 3 standard reflections every 97 reflections
 intensity decay: 7.0%

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\max} = 0.003$
2216 reflections	$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
114 parameters	$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters (\AA , $^\circ$) for (I) at 20 K.

O1—C1	1.4072 (11)	O5—C3	1.2971 (11)
O2—C2	1.2410 (10)	C1—C3	1.5329 (12)
O3—C2	1.2788 (11)	C1—C2	1.5399 (12)
O4—C3	1.2291 (10)		
O1—C1—C3	109.73 (7)	O3—C2—C1	114.53 (7)
O1—C1—C2	111.95 (7)	O4—C3—O5	125.89 (8)
C3—C1—C2	111.09 (7)	O4—C3—C1	121.14 (8)
O2—C2—O3	126.70 (8)	O5—C3—C1	112.97 (7)
O2—C2—C1	118.75 (7)		

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (I) at 20 K.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H3A \cdots O3 ⁱ	0.86 (3)	1.58 (3)	2.4393 (10)	178 (3)
O3—H3B \cdots O5 ⁱⁱ	0.82 (4)	1.63 (4)	2.4393 (10)	169 (4)
O1—H2 \cdots O2	0.790 (19)	2.234 (19)	2.6715 (10)	115.6 (16)
O1—H2 \cdots O2 ⁱⁱⁱ	0.790 (19)	2.114 (18)	2.7686 (10)	140.4 (18)
N1—H4 \cdots O4	0.870 (16)	2.202 (16)	2.8871 (11)	135.4 (15)
N1—H4 \cdots O1	0.870 (16)	2.301 (16)	3.0756 (11)	148.2 (14)
N1—H5 \cdots O2 ^{iv}	0.906 (17)	2.090 (17)	2.9882 (11)	170.9 (14)
N1—H6 \cdots O5 ^v	0.872 (19)	2.182 (18)	2.8849 (11)	137.5 (15)
N1—H6 \cdots O3 ^v	0.872 (19)	2.224 (18)	2.8940 (11)	133.5 (14)
N1—H7 \cdots O4 ^{vi}	0.874 (17)	1.990 (17)	2.8592 (11)	173.0 (16)

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $-x, -y, 1 - z$.

All H atoms for both determinations were located from difference Fourier maps and refined isotropically. The sum of the occupancy factors of the H3A and H3B atoms was constrained to 1.0. At the final stage of the least-squares refinement, the occupancy factor of H3A was fixed at 0.6 for the 240 K determination and at 0.55 for the 20 K determination. The O5—H3A and O3—H3B distances became essentially the same [0.78 (4) and 0.78 (5) \AA , respectively, at 240 K, and 0.86 (3) and 0.82 (4) \AA , respectively, at 20 K]. The U_{iso} values of H3A were close to those of H3B, and the U_{eq} values of O5 [0.0284 (3) \AA^2 at 240 K and 0.00650 (13) \AA^2 at 20 K] were close to

those of O3 [0.0277 (3) \AA^2 at 240 K and 0.00608 (13) \AA^2 at 20 K]. Thus, the refinements were terminated. U_{iso} values at 240 K: 0.029 (5) \AA^2 for H1, 0.026 (9) \AA^2 for H3A and 0.030 (15) \AA^2 for H3B; the range of U_{iso} values for the H atoms of the ammonium ion was 0.061 (8)–0.082 (10) \AA^2 . U_{iso} values at 20 K: 0.009 (3) \AA^2 for H1, 0.018 (7) \AA^2 for H3A and 0.020 (9) \AA^2 for H3B; the range of U_{iso} values for the H atoms of the ammonium ion was 0.022 (4)–0.027 (4) \AA^2 . Refined distances: C—H = 0.99 (2) \AA , N—H = 0.86 (3)–1.00 (3) \AA and O—H = 0.78 (5)–0.79 (3) \AA at 240 K; C—H = 1.008 (14) \AA , N—H = 0.870 (16)–0.906 (17) \AA and O—H = 0.790 (19)–0.86 (3) \AA at 20 K.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows*.

This work was supported by a Grant-in-Aid for Scientific Research (No. 09640609) from the Ministry of Education, Science, Sports and Culture, Japan.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1043). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Kashino, S., Taka, J., Fukunaga, T. & Ishida, H. (2001). *Acta Cryst.* **C57**, 549–552.
- Kashino, S., Taka, J., Yoshida, T., Kubozono, Y., Ishida, H. & Maeda, H. (1998). *Acta Cryst.* **B54**, 889–894.
- Misaki, S., Kashino, S. & Haisa, M. (1986). *Bull. Chem. Soc. Jpn.*, **59**, 1059–1065.
- Molecular Structure Corporation (1990). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1999). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
- Olovsson, J. & Jönsson, P.-G. (1976). *The Hydrogen Bond – Recent Developments in Theory and Experiments*, edited by P. Schuster, G. Zundel & C. Sandorfy, pp. 426–433. Amsterdam: North-Holland.
- Olovsson, J., Ptasiwicz-Bak, H., Gustafsson, T. & Majerz, I. (2001). *Acta Cryst.* **B57**, 311–316.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Taka, J., Ogino, S. & Kashino, S. (1998). *Acta Cryst.* **C54**, 384–386.
- Wilson, C. C. (2001). *Acta Cryst.* **B57**, 435–439.