chains are themselves linked together transversely by means of N–H···O hydrogen bonds from the $(CH_3)_2NH_2^+$ cations to form interlocking puckered layers perpendicular to **b**. The interaction between the layers involves van der Waals forces and possibly very weak C–H···O hydrogen bonds; the H···O contacts are 2·47 (2), 2·51 (2) and 2·54 (2) Å. It can be argued (see Fig. 2) that both unsubstituted hydrogen atoms of the cation participate in *bifurcated* hydrogen bonds [N···O(1) = 2·766 (1) Å, N···O(4) = 3·072 (1) Å and N···O(3) = 2·900 (1) Å, N···O(2) = 3·065 (1) Å]. The terms of reference for such a bonding situation are somewhat diffuse; see, for example, Donohue (1968). It is clear from this that any suggestion of bifurcation, if based on X-ray data, must be viewed with the utmost suspicion [*cf.* the case of α-glycine, Jönsson & Kvick (1972)] and can here await the more definitive findings of a current neutron diffraction study for verification.

The absence of spurious peaks in the final difference synthesis would suggest that both methyl groups are ordered in the structure at 25°C; here again neutron diffraction data is necessary to provide confirmation of the existence of C–H···O bonds.

The internal geometry of the $HC_2O_4^-$ ion is similar to geometries arising in other compounds [see Table 3 in Thomas & Renne (1975)]. The C(1)–O(2) and

C(2)–O(4) distances are here both marginally longer than the corresponding distances in $CH_3NH_3HC_2O_4$ (1·252 (3) and 1·291 (3) Å), the O···O hydrogen bond linking the $HC_2O_4^-$ ions is also slightly longer here (2·533 (1) compared with 2·515 (2) Å). The ion again shows a small distortion from planarity; the dihedral angle between the COO planes at the two ends of the ion is 3·6 (1)° compared with 1·1 (1)° in $CH_3NH_3HC_2O_4$.

References

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
DONOHUE, J. (1968). In *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 443–465. San Francisco, London: W. H. Freeman.
JÖNSSON, P.-G. & KVICK, Å. (1972). *Acta Cryst.* B28, 1827–1833.
LONG, R. E. (1965). Dissertation, Univ. of California, Los Angeles.
THOMAS, J. O. (1972). *Acta Cryst.* B28, 2037–2045.
THOMAS, J. O. (1975). *Acta Cryst.* B31, 2156–2158.
THOMAS, J. O. & RENNE, N. (1975). *Acta Cryst.* B31, 2161–2163.

Hydrogen Bond Studies. CV. Trimethylammonium Hydrogen Oxalate: an X-ray Structure Determination

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Abstract. Monoclinic, $P2_1/m$, $a = 5·608$ (1), $b = 8·402$ (1), $c = 8·513$ (1) Å, $\beta = 105·88$ (1), $V = 385·81$ Å^3 at 25°C, $(CH_3)_3NH.HC_2O_4$, $Z = 2$, $D_x = 1·284$ g cm^{-3}. Single-crystal four-circle diffractometer data. The $HC_2O_4^-$ ions link by means of asymmetric 2·489 (2) Å O–H···O hydrogen bonds to form infinite chains lying in the $y = \frac{1}{4}$ and $\frac{3}{4}$ planes and running along [100]. A $(CH_3)_3NH^+$ cation, also lying across the mirror plane, is hydrogen-bonded to an anion *via* a strong and a weak N–H···O interaction; N···O distances 2·759 (3) and 2·936 (2) Å. Large thermal vibration amplitudes along [010] suggest the possibility of statistical disordering across the mirror plane; refinements have been unable to provide satisfactory confirmation of this, however.

Introduction. Crystals of $(CH_3)_3NHHC_2O_4$ were prepared in a manner analogous to that described for

$CH_3NH_3HC_2O_4$ by Thomas (1975). They were observed to melt while decomposing at 160–170°C. Weissenberg films suggested a monoclinic space group, with only 0k0 for $k = 2n + 1$ absent. Cell dimensions were determined with a Guinier–Hägg XDC-700 powder camera calibrated with silicon. 30 observed θ values were used in the least-squares refinement. An automatic Stoe–Philips four-circle diffractometer fitted with a graphite monochromator was used for the data collection (radiation: Mo $K\alpha$, $\lambda = 0·71069$ Å). The specimen selected measured $0·40 \times 0·19 \times 0·11$ mm. General details relating to the data collection procedure appear in Thomas (1972). The 1779 reflexions (not including standards and systematic absences) measured out to sin $\theta/\lambda = 0·65$ Å^{-1} were reduced to 849 by averaging hkl and $h\bar{k}l$ reflexions. Of these, 726 were in excess of 2σ and used in the refinements. An absorption correction ($\mu = 1·19$ cm^{-1}) was made in

which the crystal was described in terms of its six rational boundary planes.

The oxalate group was located in a Patterson synthesis; the remaining atoms were found in Fourier difference syntheses following successive refinements. In the full-matrix least-squares refinements (based on F) the reflexions were weighted according to the expression: $w = 1/\sigma^2(F)$, where $\sigma^2(F) = \sigma^2(F^2)/4F^2$ and $\sigma^2(F^2) = \sigma^2_{count}(F^2) + (0.015F^2)^2$. An attempted refinement of an isotropic extinction parameter (Coppens & Hamilton, 1970) indicated that only two reflexions (012 and 020) were affected by extinction. These were removed from the final refinement and no extinction correction was applied. Final $R(F)$ and $R_w(F)$ values (for 83 varied parameters) were 0.045 and 0.057, respectively. Atomic scattering factors were used as in Thomas (1975).

Final positional and thermal parameters are given in Tables 1 and 2.*

Discussion. This is the third of three papers describing the structures of $(CH_3)_nNH_{4-n}HC_2O_4$. All three structures contain the familiar $HC_2O_4^-$ ion chains, and it is the prime purpose of these studies to examine the detailed geometry of these ions in the different hydrogen-bond environments provided in these three

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31017 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates* ($\times 10^5$) *for non-hydrogen atoms and* ($\times 10^3$) *hydrogen atoms*

The refined isotropic temperature factors (B, $Å^2$) for the hydrogen atoms are also included.

	x	y	z	B
O(1)	56202 (29)	25000	5479 (19)	
O(2)	62029 (27)	25000	−19121 (18)	
O(3)	12129 (31)	25000	−32057 (20)	
O(4)	7767 (27)	25000	−7009 (18)	
C(1)	48892 (37)	25000	−9372 (25)	
C(2)	20593 (37)	25000	−17539 (25)	
N	29827 (35)	25000	28494 (22)	
C(3)	53869 (60)	25000	40981 (37)	
C(4)	15004 (54)	10670 (29)	29431 (32)	
H(1)	−107 (6)	250	−125 (3)	5.7 (8)
H(2)	340 (5)	250	189 (3)	4.6 (6)
H(3)	506 (7)	250	516 (5)	7.4 (9)
H(4)	627 (5)	154 (3)	388 (3)	7.1 (7)
H(5)	123 (4)	104 (3)	405 (3)	5.6 (5)
H(6)	2 (5)	114 (3)	203 (3)	6.3 (6)
H(7)	250 (5)	19 (3)	279 (3)	7.6 (7)

compounds. The work also constitutes the structural basis for current n.m.r. measurements at this Institute.

The main features of the structure and all relevant distances and angles in $(CH_3)_3NH.HC_2O_4$ are summarized in Figs. 1 and 2.

As expected, the structure is the simplest of the three: $HC_2O_4^-$ ions link via asymmetric 2.489 (2) Å O–H···O hydrogen bonds to form infinite chains lying in the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$, and running along [100]. The cations also lie across the mirror planes, each forming a stronger and a weaker N–H···O bond

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Table 2. *Anisotropic thermal parameters* ($\beta_{ij} \times 10^4$) *for the non-hydrogen atoms*

The expression for the temperature factor is: $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$. The r.m.s. components of thermal displacement along the principal axes of the thermal vibration ellipsoids ($R_i \times 10^3$ Å) are also given.

|	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
O(1)	191 (6)	456 (6)	87 (3)	0	30 (3)	0	167 (3)	175 (3)	404 (3)
O(2)	182 (5)	294 (4)	107 (3)	0	64 (3)	0	148 (3)	194 (2)	324 (2)
O(3)	224 (6)	446 (6)	84 (3)	0	29 (3)	0	168 (3)	186 (3)	399 (3)
O(4)	155 (5)	291 (4)	95 (2)	0	48 (3)	0	144 (3)	181 (2)	323 (2)
C(1)	157 (7)	189 (5)	89 (3)	0	42 (4)	0	148 (3)	175 (3)	260 (3)
C(2)	177 (7)	188 (5)	89 (3)	0	45 (4)	0	155 (3)	175 (3)	259 (3)
N	257 (7)	197 (4)	85 (3)	0	52 (4)	0	165 (3)	195 (3)	265 (3)
C(3)	304 (11)	494 (13)	103 (5)	0	26 (6)	0	184 (4)	222 (4)	420 (6)
C(4)	552 (11)	169 (4)	185 (4)	−7 (5)	105 (6)	12 (3)	236 (3)	255 (3)	285 (3)
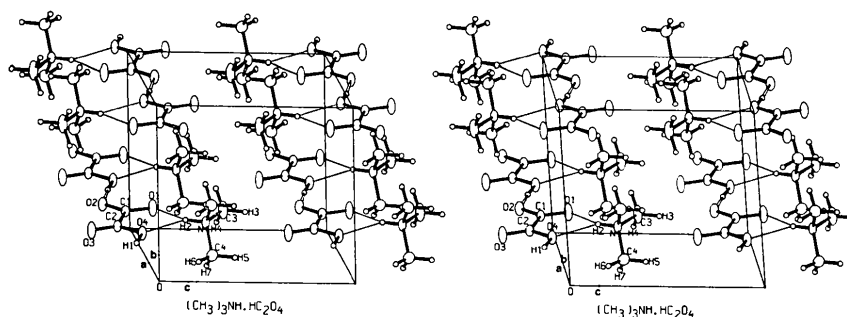
Fig. 1. A general stereoscopic view of the structure. The labelled atoms correspond to the chosen asymmetric unit. Covalent bonds: thick solid lines; short H···O contact in $HC_2O_4^-$ ion chain: thick unfilled line; longer H···O contacts: thin unbroken lines. The thermal ellipsoids for the non-hydrogen atoms are drawn to include 20% probability.

Table 3. *Summary of the observed geometries of* $HC_2O_4^-$ *ions when they occur in infinite chains*

The atom notation used in other studies has been converted to correspond to that used in this series. φ is the dihedral angle between the COO planes at either end of the oxalate group.

Compound	Reference	φ	O(2)$\cdots$O(4)	C(1)–C(2)	C(1)–O(1)	C(1)–O(2)	C(2)–O(3)	C(2)–O(4)
NaHC$_2$O$_4$.H$_2$O	Tellgren &	12·9 (1)°	2·571 (2) Å	1·552 (2) Å	1·242 (2) Å	1·251 (2) Å	1·207 (2) Å	1·313 (2) Å
NaDC$_2$O$_4$.D$_2$O	Olovsson (1971)	12·6 (1)	2·593 (2)	1·553 (3)	1·244 (2)	1·247 (2)	1·209 (2)	1·310 (2)
LiHC$_2$O$_4$.H$_2$O	Thomas (1972)	2·1 (1)	2·490 (1)	1·547 (1)	1·240 (1)	1·259 (1)	1·210 (1)	1·309 (1)
LiDC$_2$O$_4$.D$_2$O		2·2 (1)	2·506 (1)	1·547 (1)	1·239 (1)	1·259 (1)	1·209 (1)	1·312 (1)
N$_2$H$_5$HC$_2$O$_4$	Thomas (1973)	0	2·457 (1)	1·550 (2)	1·224 (1)	1·279 (1)	1·224 (1)	1·279 (1)
N$_2$D$_5$DC$_2$O$_4$		1·5 (1)	2·466 (2)	1·552 (2)	1·232 (3)	1·268 (3)	1·219 (3)	1·284 (3)
KHC$_2$O$_4$*	Einspahr, Marsh & Donohue (1972)	13·9 (1)	2·523 (2)	1·552 (2)	1·234 (2)	1·256 (2)	1·211 (2)	1·308 (2)
(CH$_3$)NH$_3$HC$_2$O$_4$	Thomas (1975)	1·1 (1)	2·515 (2)	1·544 (3)	1·225 (3)	1·252 (3)	1·194 (3)	1·291 (3)
(CH$_3$)$_2$NH$_2$HC$_2$O$_4$	Thomas & Pramatus (1975)	3·6 (1)	2·533 (1)	1·545 (2)	1·226 (2)	1·260 (2)	1·214 (2)	1·295 (2)
(CH$_3$)$_3$NHHC$_2$O$_4$	This work	0	2·489 (2)	1·549 (3)	1·218 (3)	1·251 (3)	1·196 (3)	1·294 (3)

* Note the somewhat different chain linkage in this case.
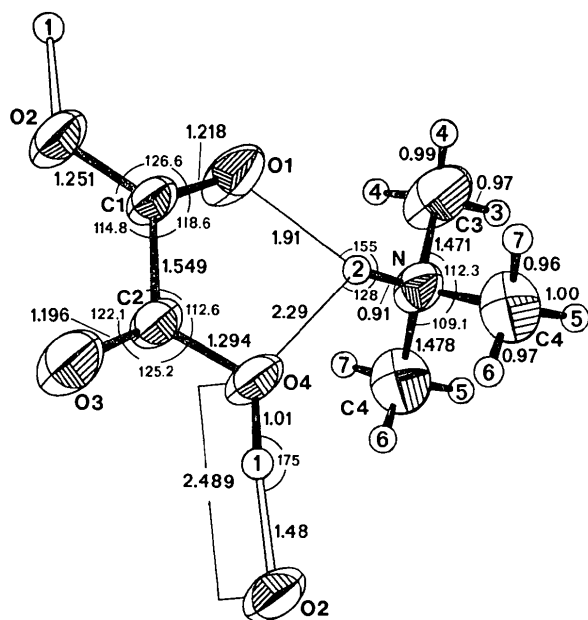

Fig. 2. Distances and angles in the structure. The thermal ellipsoids for the non-hydrogen atoms are drawn to include 50% probability. The average standard deviations are X–X: 0·003 Å, X–H: 0·03 Å, $\angle$X–X–X: 0·2° and $\angle$X–X–H (or $\angle$X–H–X): 1·5°.

$(N\cdots O(1) = 2\cdot759$ (3) Å and $N\cdots O(4) = 2\cdot936$ (2) Å) with one of the anions. Refinement in the non-centro-symmetric space group $P2_1$, though giving slightly better R values [$R(F) = 0\cdot040$, $R_w(F) = 0\cdot049$ for 134 varied parameters], resulted in an unrealistic geometry especially for the cation. Moreover, the statistical distribution of normalized structure factors E corresponded well with theoretical prediction for a centrosymmetric space group.

The elongation of the thermal ellipsoids (especially those associated with the oxygen atoms) along [010] suggested statistical disordering across the mirror planes. The suspicion is reinforced by the general observation that completely flat oxalate groups are rare; twists of up to 12·9° have been observed [in NaHC$_2$O$_4$.H$_2$O: Tellgren & Olovsson (1971)]. It has been impossible to resolve the disorder by refinement methods, however. The refinement of a statistically disordered model did not diverge but was unstable and resulted in inferior agreement indices.

A summary of the geometry of the C$_2$O$_4$ part of $HC_2O_4^-$ ion chains, as determined by X-ray diffraction, is given in Table 3.

References

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.

EINSPAHR, H., MARSH, R. E. & DONOHUE, J. (1972). *Acta Cryst.* B28, 2194–2198.

TELLGREN, R. & OLOVSSON, I. (1971). *J. Chem. Phys.* 54, 127–134.

THOMAS, J. O. (1972). *Acta Cryst.* B28, 2037–2045.

THOMAS, J. O. (1973). *Acta Cryst.* B29, 1767–1776.

THOMAS, J. O. (1975). *Acta Cryst.* B31, 2156–2158.

THOMAS, J. O. & PRAMATUS, S. (1975). *Acta Cryst.* B31, 2159–2161.