Hydrogen Bond Studies. CIV. Dimethylammonium Hydrogen Oxalate: an X-ray Structure Determination

By John O. Thomas and Supanich Pramatus*

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

Abstract. Monoclinic, $P2_1/c$, $a = 5\cdot630$ (1), $b = 9\cdot767$ (1), $c = 12\cdot425$ (1) Å, $\beta = 111\cdot29$ (1)°, $V = 636\cdot60$ Å³ at 25°C, $(CH_3)_2NH_2HC_2O_4$, $Z = 4$, $D_x = 1\cdot410$ g cm⁻³. Single-crystal four-circle diffractometer data. The $HC_2O_4^-$ anions link *via* $2\cdot533$ (1) Å O–H···O hydrogen bonds to form infinite chains along [100]. These chains are linked transversely *via* N–H···O hydrogen bonds from the $(CH_3)_2NH_2^+$ cations to form interlocking puckered layers. Interactions between adjacent layers are *via* van der Waals contacts and possibly weak C–H···O hydrogen bonds. Dihedral twist between the COO planes within the oxalate group is $3\cdot6$ (1)°.

Introduction. Flat prism-shaped crystals of $(CH_3)_2NH_2HC_2O_4$ were prepared in a manner analogous to that described for $CH_3NH_3HC_2O_4$ by Thomas (1975). They showed signs of a phase transition or partial decomposition in the range 50–85°C and finally melted at 148–150°C. The crystal chosen for data collection measured roughly $0\cdot33 \times 0\cdot26 \times 0\cdot24$ mm. A set of Weissenberg films indicated absences $h0l$ for l odd and $0k0$ for k odd. Cell parameters were refined from 43 θ values measured on a Guinier–Hägg XDC-700 powder camera calibrated with silicon. Intensity data were collected on a Stoe–Philips four-circle X-ray diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å) [see also Thomas (1972)]. 2876 reflexions were collected out to $\sin\theta/\lambda = 0\cdot594$ Å⁻¹. Removal of systematic absences and averaging of hkl and $h\bar{k}l$ reflexions resulted in 1108 reflexions, of which 987 were in excess of 2σ and used in the refinements. An absorption correction ($\mu =$

* Permanent address: Department of Physics, Faculty of Sciences, Chulalongkorn University, Bangkok, Thailand.

$1\cdot36$ cm⁻¹) was made employing a crystal description made in terms of eight rational boundary planes.

The structure was solved without difficulty by direct methods following the iterative procedure programmed by Long (1965). All hydrogen atoms were located unambiguously in a subsequent difference synthesis. The reflexions were weighted (based on F^2) according to the expression: $w = 1/\sigma^2(F^2)$; where $\sigma^2(F^2) = \sigma_{\text{count}}(F^2) + (0\cdot03F^2)^2$. An isotropic extinction parameter g (Coppens & Hamilton, 1970) was also refined in the final cycles of full-matrix least-squares refinement: final value of g was 6480 (1010). Final $R(F^2)$ and $R_w(F^2)$ values for 119 varied parameters were 0·049 and 0·075; equivalent to $R(F) = 0\cdot030$. Atomic scat-

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

The refined isotropic temperature factors (B, Å²) for the hydrogen atoms are also included.

	x	y	z	B
O(1)	−16452 (17)	10644 (11)	38794 (7)	
O(2)	−19796 (18)	21805 (10)	53792 (8)	
O(3)	30829 (19)	26402 (11)	61802 (9)	
O(4)	33199 (18)	15895 (9)	46318 (8)	
C(1)	−7681 (24)	17074 (12)	47855 (10)	
C(2)	21200 (24)	20171 (11)	52806 (10)	
N	3182 (22)	5658 (11)	21738 (10)	
C(3)	−21289 (30)	−491 (18)	14554 (15)	
C(4)	24958 (31)	−3759 (17)	23974 (15)	
H(1)	514 (4)	185 (2)	493 (2)	5·2 (4)
H(2)	62 (3)	132 (2)	182 (1)	3·0 (3)
H(3)	11 (3)	81 (1)	284 (1)	3·4 (3)
H(4)	−201 (4)	−28 (2)	72 (2)	4·8 (4)
H(5)	−235 (4)	−88 (2)	182 (2)	4·9 (4)
H(6)	−347 (4)	64 (2)	138 (2)	5·1 (4)
H(7)	410 (4)	11 (2)	278 (2)	5·3 (4)
H(8)	260 (3)	−64 (2)	167 (2)	4·4 (4)
H(9)	217 (4)	−116 (2)	277 (2)	5·1 (4)

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

The expression used 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 included.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
O(1)	203 (4)	138 (1)	51 (1)	−28 (2)	44 (1)	−23 (1)	162 (2)	172 (1)	268 (1)
O(2)	205 (4)	134 (1)	75 (1)	−22 (2)	76 (1)	−36 (1)	140 (2)	194 (1)	282 (1)
O(3)	216 (4)	132 (1)	72 (1)	−25 (2)	50 (1)	−44 (1)	170 (2)	172 (2)	288 (1)
O(4)	173 (4)	119 (1)	60 (1)	−15 (2)	56 (1)	−23 (1)	138 (2)	185 (1)	255 (1)
C(1)	176 (5)	69 (1)	46 (1)	0 (2)	46 (2)	1 (1)	143 (2)	178 (2)	183 (2)
C(2)	173 (5)	61 (1)	49 (1)	1 (2)	43 (2)	−3 (1)	147 (2)	171 (2)	184 (2)
N	279 (5)	74 (1)	45 (1)	−11 (2)	59 (2)	−2 (1)	158 (2)	186 (2)	204 (2)
C(3)	273 (6)	104 (2)	75 (1)	−10 (3)	40 (2)	−10 (1)	193 (2)	218 (2)	240 (2)
C(4)	265 (6)	109 (2)	74 (1)	12 (3)	56 (2)	2 (1)	188 (2)	224 (2)	231 (2)

tering factors were as used in Thomas (1975). Final positional and thermal parameters are given in Tables 1 and 2.*

Discussion. This is the second of a series of three papers in which the structures of $(CH_3)_nNH_{4-n}HC_2O_4$ for $n = 1$, 2 and 3 are described. This simple series has been selected for study to observe the effect on the geometry of $HC_2O_4^-$ chains as their hydrogen-bond environment is changed.

The structure of $(CH_3)_2NH_2HC_2O_4$ is shown in Fig. 1 and the significant bond distances and angles in Fig. 2.

In contrast to the complicated three-dimensional hydrogen-bond network found in $CH_3NH_3HC_2O_4$, the situation here is relatively simple. The $HC_2O_4^-$ ions link via O–H···O hydrogen bonds of length 2·533 (1) Å to form infinite chains running along [100]. These

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31016 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
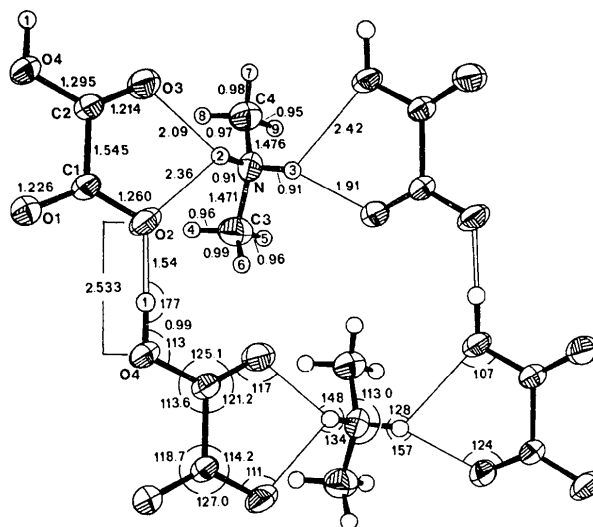

Fig. 2. Bond distances and angles. Thermal ellipsoids for non-hydrogen atoms are drawn to include 50 % probability. The average standard deviations are X–X: 0·002 Å, X–H: 0·02 Å, $\angle$X–X–X: 0·11° and $\angle$X–X–H (or $\angle$X–H–X): 1·0°.

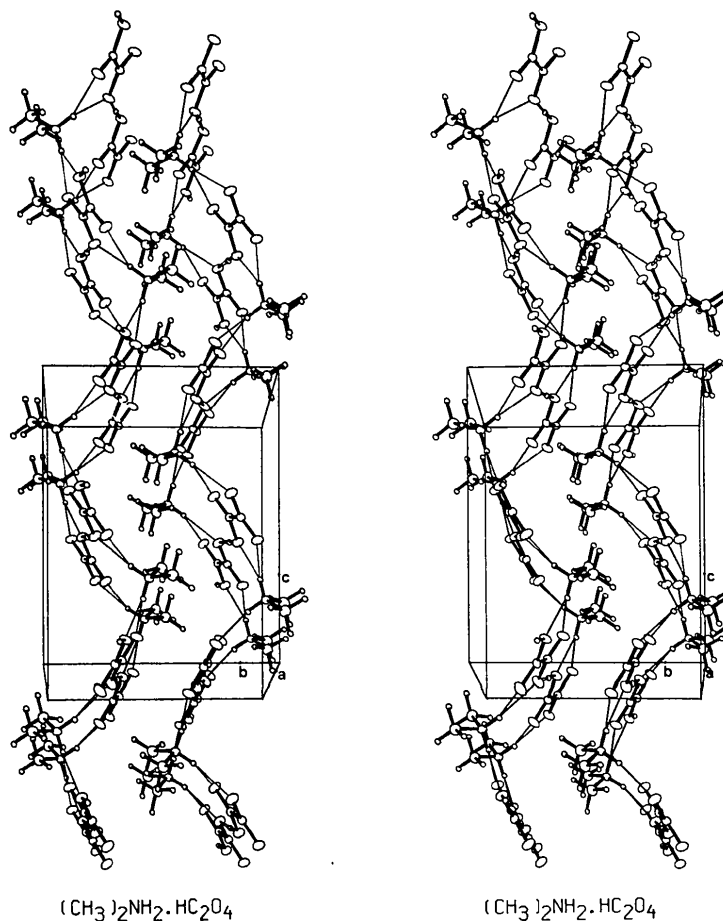$(CH_3)_2NH_2.HC_2O_4$ $(CH_3)_2NH_2.HC_2O_4$

Fig. 1. A general stereoscopic view showing the puckered-layer nature of the structure. Covalent bonds: thick lines; short H···O interaction in $HC_2O_4^-$ ion chains: thick unfilled lines; longer H···O interactions: thin unbroken lines. Thermal ellipsoids for non-hydrogen atoms are drawn to include 20 % probability.

chains are themselves linked together transversely by means of N–H$\cdots$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$\cdots$O hydrogen bonds; the H$\cdots$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$\cdots$O(1)=2·766 (1) Å, N$\cdots$O(4)=3·072 (1) Å and N$\cdots$O(3)=2·900 (1) Å, N$\cdots$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$\cdots$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$\cdots$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 $CH_3NH_3HC_2O_4$.

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

BY JOHN O. THOMAS AND NICOLAS RENNE

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

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$\cdots$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$\cdots$O interaction; N$\cdots$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