

# DL- $\alpha$ , $\gamma$ -Dimethyltetronic Acid. A Redetermination of the Crystal Structure Based on New Experimental Data

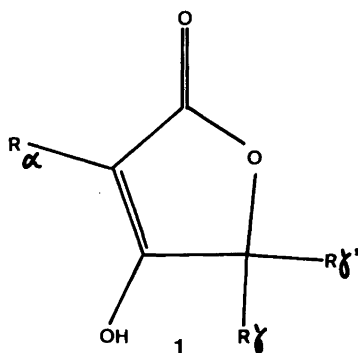
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Andersen, E. K., Andersen, I. G. K. and Ploug-Sørensen, G., 1987. DL- $\alpha$ ,  $\gamma$ -Dimethyltetronic Acid. A Redetermination of the Crystal Structure Based on New Experimental Data. – Acta Chem. Scand., Ser. A 41: 213–217.

The structure of  $\alpha$ ,  $\gamma$ -dimethyltetronic acid was redetermined from single crystal diffractometer data. It crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 6.796(2)$ ,  $b = 14.540(6)$ ,  $c = 6.557(2)$  Å,  $\beta = 100.93(3)^\circ$  and  $Z = 4$ . Full matrix least-squares refinement of 106 parameters gave  $R = 0.04$  for 1384 observed reflections [ $I > 2.5\sigma(I)$ ]. The molecular structure is similar to that of  $\alpha$ -methyltetronic acid.

The structure of  $\alpha$ ,  $\gamma$ -dimethyltetronic acid ( $R_\alpha = R_\gamma = \text{CH}_3$ ,  $R_\beta = \text{H}$  in formula 1, in the following abbreviated as DMTA) was determined by Lawrence and MacDonald<sup>1</sup> (hereafter L and M). The structures of  $\alpha$ -methyltetronic acid ( $R_\alpha = \text{CH}_3$ ,



$R_\beta = \text{H}$ , in the following abbreviated as  $\alpha$ MTA) and of ascorbic acid ( $R_\alpha = \text{OH}$ ,  $R_\beta = \text{CHOHCH}_2\text{OH}$ ,  $R_\gamma = \text{H}$ ) were refined by Krogh Andersen and Krogh Andersen<sup>2</sup> and determined by Hvorslev<sup>3</sup>, respectively. The reinvestigation of the DMTA structures was made because Lawrence and MacDonald's determination is of limited accuracy and because tetronic acids are interesting in connection with considerations of the relationship between structure and acidity.

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## Experimental

Substituted tetronic acids may be prepared by cyclisation of brominated  $\beta$ -keto esters.<sup>5</sup> The material used in the present study of the structure of DMTA was supplied by Svendsen and Boll. L and M mention in their publication that DMTA very often forms twins. This phenomenon was also experienced by us. Several attempts to grow DMTA from chloroform and tetrachloromethane solutions resulted in crystal twins. One attempt using glacial acetic acid did, however, produce crystals with no detectable twinning.

Density measurements by flotation and lattice constant determinations (from quartz-calibrated Guinier-Hägg diagrams) provided the data recorded in Table 1. Our crystal data are significantly different in two respects from the results obtained by L and M. The length of the  $b$ -axis differs by 0.36 Å and the observed density differs by 0.444 g cm<sup>-3</sup>. Crystal and experimental data are given in Table 1. Intensities were measured with an Enraf-Nonius CAD-4 diffractometer.

## Structure determination and refinement

The structure was determined independently of a previous determination by direct methods (SINGEN, PHASE).<sup>4</sup> Full matrix least-squares refinement (CRYLSQ<sup>4</sup>) of oxygen and carbon atom positions and anisotropic temperature parame-

Table 1. Crystal and experimental data for DL- $\alpha$ ,  $\gamma$ -dimethyltetronic acid.

Formula	C <sub>6</sub> H <sub>8</sub> O <sub>3</sub>
$M_r$	128.1
Unit cell dimensions/Å or °	$a = 6.796(2)$ , $b = 14.540(6)$ $c = 6.557(2)$ , $\beta = 100.93(3)$
Radiation/Å	Monochromated Cu $K\alpha_1$ radiation, $\lambda = 1.54051$
Space group	$P2_1/c$
$Z$	4
$D_m/g\text{ cm}^{-3}$	1.336(2)
$D_c/g\text{ cm}^{-3}$	1.338
Colour and habit	Colourless needles
m.p./°C	124–125
Crystal size/mm	0.5×0.3×0.3
Temperature/°C	Room temperature ca. 22
$\theta_{\max}/^\circ$	30
Scan technique	$\omega/2\theta$
Scan angle/°	1–1.58
Max scan time/sec.	600
Radiation/Å	graphite-monochromated, discriminated Mo $K\alpha$ , $\lambda = 0.71069$
Standard reflection	$\bar{1}71$ , max. correction for decrease 10 %
Number of reflections measured	1990
Number of reflections used in calculation	1384 [ $I > 2.5\sigma(I)$ ]
$\mu/\text{mm}^{-1}$	13.2, no correction
Correction for	Lorentz and polarization effects
Structure determination	By direct methods (X-RAY 76 programmes <sup>4</sup> )
Structure refinement	By least squares calculation (programme CRYLSQ <sup>4</sup> )
No. of parameters refined	106
Weights calculated from	$w = 1/(2.08 +  F_o  + 0.008 F_o ^2)$
$R$	0.039
$R_w$	0.056
$(\Delta/\sigma)_{\max}$	0.0004
Max. and min. residual electron density/e Å <sup>-3</sup>	0.31 and -0.24

ters gave  $R = 0.076$ . Inclusion of hydrogen atoms (positions from a difference Fourier map) and further refinement (fixed temperature parameters for hydrogen) gave a final  $R$  value of 0.039. Further details concerning the refinement

are given in Table 1. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.<sup>6</sup> Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. A list of structure factors, hydrogen atom positions, anisotropic thermal parameters and deviations of atoms from the least-squares plane may be obtained from the authors on request.

## Discussion

The planes of the DMTA molecules are nearly parallel to the (010) plane, and the molecules are linked by hydrogen bonds to form infinite ribbons running along the  $c$ -axis direction. Four ribbons traverse the unit cell. The fractional  $y$  coordinates of the ribbons are approximately 0.125, 0.375, 0.625 and 0.875. Two glide-plane-related ribbons with  $y$  coordinates ca. 0.625 and ca. 0.875 are shown in Fig. 1b, where the numbering of the atoms is also given. In Fig. 1a, the other two bands traversing a unit cell ( $y$  coordinates ca. 0.125 and 0.375) are shown. They are related to the planes of Fig. 1b by the screw axes of the space group. The bands are separated by ca. 3.6 Å in the  $b$ -axis direction and there is no contact shorter than 3.4 Å between molecules belonging to different ribbons.

The hydrogen bonds are between O(3)–H(3) groups and the O(1) atoms. They are rather short and almost linear. The O(3)–O(1) distance is 2.630 Å, the H(3)⋯O(1) distance is 1.806(7) Å and the angle O(3)–H(3)⋯O(1) is 175.2(6)°. Besides the hydrogen bonds there are short contacts within the ribbons between the O(1) atoms and the C(44), C(4) and C(3) atoms (contact distances 3.272(2), 3.286(2) and 3.327(2) Å, respectively). All other intermolecular contacts involving carbon and oxygen atoms are longer than 3.4 Å. There are short hydrogen-hydrogen and heavy atom-hydrogen contacts between atoms belonging to different molecules. The shortest of these is 2.49(1) Å between H(441) and H(443). All other contacts between hydrogen atoms are longer than 2.5 Å.

Bond lengths and angles in DMTA are shown in Figs. 2 and 3. In Table 3, the molecular structures of  $\alpha$ -methyltetronic acid ( $\alpha$ MTA) and DMTA are compared. The two structures do not deviate significantly in respects in which they can be compared. The carbon atoms in these tetronic

Table 2. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ). Standard deviations in parentheses.

Atom	x	y	z	$B_{\text{eq}}^a$
C(1)	6630(2)	5927(1)	6676(2)	3.14(10)
C(2)	4975(2)	6182(1)	7655(2)	2.72(9)
C(3)	5653(2)	6122(1)	9712(2)	2.51(8)
C(4)	7825(2)	5849(1)	10176(2)	2.80(9)
C(22)	2948(2)	6438(1)	6481(3)	3.89(12)
C(44)	9218(2)	6573(1)	11315(3)	4.26(13)
O(1)	6736(2)	5880(1)	4848(2)	4.84(11)
O(3)	4596(2)	6283(1)	11181(2)	3.73(9)
O(4)	8277(1)	5716(1)	8125(2)	3.60(8)

$$^a B_{\text{eq}} = 4/3 \sum_i \sum_j b_{ij} (a_i a_j).$$

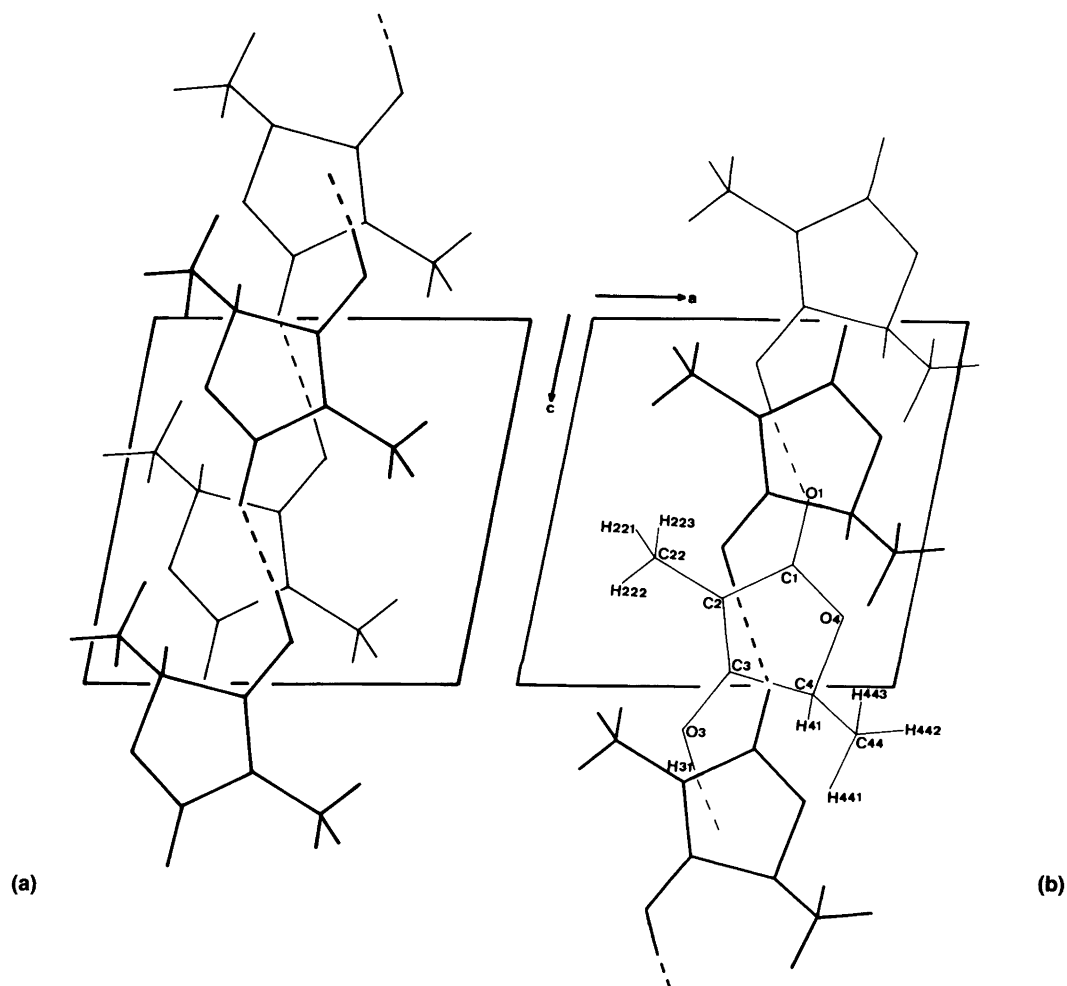


Fig. 1. The structure viewed down the  $b$ -axis.

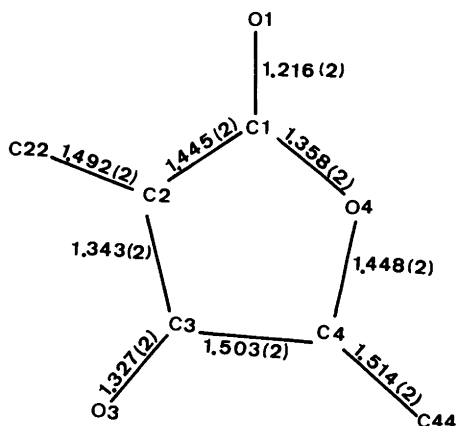


Fig. 2. The molecular structure of  $\alpha$ ,  $\gamma$ -dimethyltetronic acid. Bond lengths in Å (e.s.d.'s in parentheses).

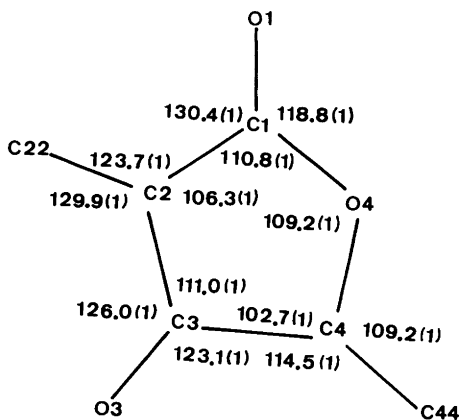


Fig. 3. The molecular structure of  $\alpha$ ,  $\gamma$ -dimethyltetronic acid. Angles in degrees (e.s.d.'s in parentheses).

acids form carbon-carbon bonds of four kinds. They form single bonds between two carbon atoms with tetragonal surroundings (tetr.-tetr. in Table 4), single bonds between two carbon atoms of which one has trigonal and the other has tetragonal surroundings (tr.-tetr.), single bonds where both carbon atoms have trigonal surroundings (tr.-tr.), and finally double bonds between carbon atoms with trigonal surroundings atoms (tr.=tr. in Table 4). The carbon atoms form three types of bonds to oxygen, namely double bonds (tr.=O in Table 4) and two types of single bonds (tetr.-O and tr.-O).

In both compounds, the

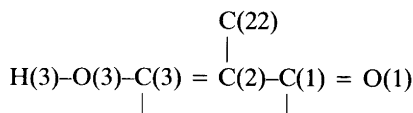


Table 3. Bond lengths (Å) and angles (°) in  $\alpha$ -methyl- and  $\alpha$ ,  $\gamma$ -dimethyltetronic acid. Standard deviations in parentheses.

Bond lengths	$\alpha$ -methyl-	$\alpha$ , $\gamma$ -dimethyltetronic acid	
	tetronic acid	L and M	This work
C(1)–O(1)	1.222(4)	1.22 <sup>a</sup>	1.216(2)
C(2)–C(22)	1.502(5)	1.52	1.492(2)
C(3)–O(3)	1.329(4)	1.30	1.327(2)
C(4)–C(44)		1.52	1.514(2)
C(1)–C(2)	1.437(4)	1.45	1.445(2)
C(2)–C(3)	1.337(4)	1.34	1.343(2)
C(3)–C(4)	1.493(5)	1.53	1.503(2)
C(4)–O(4)	1.439(4)	1.43	1.448(2)
O(4)–C(1)	1.358(4)	1.34	1.358(2)
O(3)–H(31)	0.9 <sup>b</sup>		0.83(1)
C(4)–H(41)	1.0 <sup>b</sup>		1.05(1)
C(22)–H(221)	0.9 <sup>b</sup>		0.97(1)
C(22)–H(222)	0.9 <sup>b</sup>		0.95(1)
C(22)–H(223)	0.9 <sup>b</sup>		0.98(1)
C(44)–H(441)			0.94(1)
C(44)–H(442)			0.97(1)
C(44)–H(443)			1.05(1)
Angles			
O(1)–C(1)–O(4)	118.3(3)	121	118.8(1)
O(1)–C(1)–C(2)	130.5(3)	128	130.4(1)
O(4)–C(1)–C(2)	111.1(3)	111	110.8(1)
C(1)–C(2)–C(3)	106.3(3)	105	106.3(1)
C(1)–C(2)–C(22)	123.7(3)	124	123.7(1)
C(3)–C(2)–C(22)	130.0(3)	131	129.9(1)
O(3)–C(3)–C(2)	126.5(3)	126	126.0(1)
O(3)–C(3)–C(4)	122.7(3)	122	123.1(1)
C(2)–C(3)–C(4)	110.7(3)	111	111.0(1)
O(4)–C(4)–C(3)	103.4(3)	102	102.7(1)
O(4)–C(4)–C(44)		110	109.2(1)
C(3)–C(4)–C(44)		115	114.5(1)
C(1)–O(4)–C(4)	108.4(3)	111	109.2(1)

<sup>a</sup>Standard deviations are not given by Lawrence and MacDonald; for bond lengths they are probably about 0.02 Å. <sup>b</sup>Standard deviations unknown. Position parameters not refined.

Table 4. Bond lengths (Å) in tetrionic acid molecules compared with bond lengths in acrolein, butadiene, propene, ethanol and methyl vinyl ether. Standard deviations in parentheses.

Bond	Type	DMTA	$\alpha$ MTA	Acrolein <sup>a</sup>	Butadiene <sup>a</sup>	Propene <sup>a</sup>	Ethanol <sup>a</sup>	Methyl vinyl ether <sup>a</sup>
C(1)–C(2)	tr.–tr.	1.445(2)	1.437(4)	1.470(3)	1.465(3)			
C(2)=C(3)	tr.=tr.	1.343(2)	1.337(4)	1.345(3)	1.345(2)	1.336(4)		
C(3)–C(4)	tr.–tetr.	1.503(2)	1.493(5)			1.501(4)		
C(2)–C(22)	tr.–tetr.	1.492(2)	1.502(5)			1.501(4)		
C(4)–C(44)	tetr.–tetr.	1.514(2)					1.5115(50)	
C(1)=O(1)	tr.=O	1.216(2)	1.222(4)	1.219(5)				
C(3)–O(3)	tr.–O	1.327(2)	1.329(4)					1.360(5)
C(1)–O(4)	tr.–O	1.358(2)	1.358(4)					1.360(5)
C(4)–O(4)	tetr.–O	1.448(2)	1.439(4)				1.4310(50)	1.428(4)

<sup>a</sup>Ref. 7.

moiety is nearly planar [maximum deviation from least-squares plane is 0.008 Å for O(3)], but the O(4) and C(4) atoms are displaced from the plane by 0.01 Å and 0.04 Å, respectively. In table 4, the data for bonds in tetrionic acids are also compared with accurate data (obtained from spectroscopic measurements on gases) for bonds in small molecules. There are only small – but significant – deviations in two bonds. The C(1)–C(2) bond is definitely shorter than corresponding bonds in acrolein and butadiene. The length of C–(OH) bonds at carbon atoms with trigonal coordination is usually found to be in the range 1.3–1.4 Å. It has been found<sup>8</sup> that there is an inverse proportionality between C–(OH) bond lengths and acid strength (acid dissociation constants). It is therefore not surprising that tetrionic acids (with dissociation constants around 10<sup>-4</sup> M) have C–(OH) bond lengths at the lower end of the above-mentioned range. The C–O bonds in the lactone ring have, as usual, different lengths. Their lengths are in agreement with those of the two types of carbon-oxygen bonds in methyl vinyl ether.

*Acknowledgement.* It is a pleasure to thank A. Svendsen and P. M. Boll for providing the DMTA sample used in this investigation.

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Received December 12, 1986.