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Structure of Tetramethyl Reductic Acid (TMRA, 4,4,5,5-Tetramethyl-2,3-dihydroxy-2-cyclopenten-1-one), a Reductate Ligand Involved in Dioxygen Activation by Multinuclear Iron Complexes

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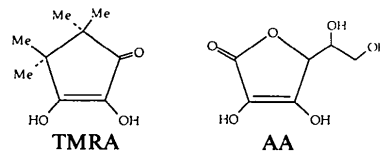
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Abstract. $C_9H_{14}O_3$, $M_r = 170.21$, orthorhombic, $Pbca$, $a = 11.651$ (2), $b = 12.279$ (2), $c = 26.257$ (4) Å, $V = 3756$ Å³, $Z = 16$, $D_x = 1.204$, $D_m = 1.19$ (1) g cm⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 7.01$ cm⁻¹, $F(000) = 1472$, $T = 297$ (1) K, $R = 0.051$ for 2152 observed reflections with $F > 6\sigma(F)$. The title compound adopts a well-defined conjugated structure corresponding to one of its expected resonance forms. There are two independent molecules in the asymmetric unit owing to two different intermolecular hydrogen-bonding modes.

Introduction. Tetramethyl reductic acid (TMRA) was synthesized several years ago (Hesse & Wehling, 1964) and later used in a photographic developer (Bloom & Cramer, 1971). As an analog of ascorbic acid (AA), its functions as both reductant and ligand in many transition-metal-ion-mediated chemical and biological redox processes have been of much current interest (Bryan, Pell, Kumar, Clarke, Rodriguez, Sherban & Charkoudian, 1988). Work in our laboratory has indicated that complexes of TMRA with several diiron(III) salts can catalyze oxidation of saturated hydrocarbons by molecular oxygen (Roth, 1988). Although spectroscopic and electrochemical properties of TMRA have been studied (Hesse & Wehling, 1964; Inbar, Ehret & Norland, 1987), a definitive structural characterization has not been

reported to date. Here, we present the crystal and molecular structure.



Experimental. Tetramethyl reductic acid was obtained from Polaroid Corporation. Crystals were grown from acetonitrile at 253 K. One colorless, transparent needle of approximate dimensions 0.3 × 0.35 × 0.5 mm was mounted in a capillary tube. X-ray data were collected on an Enraf–Nonius CAD-4 diffractometer with Ni-filtered $Cu K\alpha$ radiation. The cell parameters were measured from a least-squares fit of 24 high-angle reflections ($2\theta > 55^\circ$). Intensity data were collected by $\omega/2\theta$ scans using a peak scan width of $(0.80 + 0.15 \tan\theta)^\circ$ with an additional 25% before and after each reflection for background determination. The scan time was 10–150 s. A total of 4655 reflections in the 2θ range 2–130° (h 0–13, k 0–14, l –30–30) were measured. Three standard reflections monitored every 3600 s of exposure time showed no significant variation. No correction was made for extinction or absorption. 2152 unique reflections observed with $F > 6\sigma(F)$, R_{int}

= 0.015, were used in the analysis. Structure was solved by direct methods and difference Fourier syntheses. All non-H atoms were refined with anisotropic thermal parameters. Sufficient H atoms were located on a difference map to enable the remainder to be generated by geometry. All hydrogens were allowed to ride on the appropriate carbon [$B(\text{H}) = 1.2B_{\text{eq}}(\text{C})$] except for those on hydroxyl groups, the coordinates and isotropic thermal parameters of which were refined.

The methyl groups in one of two crystallographically independent molecules were disordered over two positions and refined with relative occupancies of 1:1. The final refinement on F employed 278 parameters and converged at $R = 0.051$, $wR = 0.069$, where $w = 1/\sigma^2(F)$. In the final difference Fourier synthesis, $\Delta\rho_{\text{max}}$ was 0.202 and $\Delta\rho_{\text{min}} - 0.246 \text{ e } \text{\AA}^{-3}$; $(\Delta/\sigma)_{\text{max}} < 0.004$. Scattering factors for non-H atoms were taken from *International Tables for X-ray Crystallography* (1974) and those for the H atoms were obtained from Stewart, Davidson & Simpson (1965). All calculations were carried out with the *TEXSAN* programs (Molecular Structure Corporation, 1988).

Atomic coordinates and isotropic thermal parameters are listed in Table 1.*

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

	x	y	z	B_{eq}
O(1)	0.1719 (2)	0.1148 (2)	0.21466 (6)	5.07 (9)
O(2)	0.0491 (2)	0.2269 (1)	0.29393 (8)	5.2 (1)
O(3)	0.1220 (2)	0.1182 (2)	0.39220 (7)	5.3 (1)
O(11)	0.4771 (2)	0.2304 (2)	0.58035 (8)	5.9 (1)
O(12)	0.3480 (2)	0.3195 (2)	0.66174 (7)	4.53 (8)
O(13)	0.1020 (2)	0.2340 (2)	0.64761 (9)	5.8 (1)
C(1)	0.1776 (2)	0.0885 (2)	0.26063 (9)	3.9 (1)
C(2)	0.1196 (2)	0.1397 (2)	0.3014 (1)	3.8 (1)
C(3)	0.1539 (2)	0.0942 (2)	0.34540 (9)	3.7 (1)
C(4)	0.2458 (2)	0.0089 (2)	0.3388 (1)	4.4 (1)
C(5)	0.2469 (2)	-0.0073 (2)	0.2798 (1)	4.1 (1)
C(6)	0.2234 (4)	-0.0914 (3)	0.3705 (1)	7.9 (2)
C(7)	0.3596 (3)	0.0640 (4)	0.3569 (2)	8.1 (2)
C(8)	0.1796 (3)	-0.1091 (2)	0.2638 (1)	6.8 (2)
C(9)	0.3659 (3)	-0.0115 (3)	0.2550 (1)	6.2 (2)
C(11)	0.3727 (2)	0.2125 (2)	0.5857 (1)	4.4 (1)
C(12)	0.3023 (2)	0.2539 (2)	0.62500 (9)	3.7 (1)
C(13)	0.1945 (2)	0.2166 (2)	0.61889 (9)	3.8 (1)
C(14)	0.1813 (2)	0.1466 (2)	0.5723 (1)	4.4 (1)
C(15A)	0.2971 (9)	0.1595 (6)	0.5442 (3)	4.2 (3)
C(15)	0.3090 (8)	0.1208 (6)	0.5587 (3)	4.2 (4)
C(16)	0.127 (1)	0.2270 (8)	0.5321 (3)	8.3 (5)
C(16A)	0.0748 (7)	0.169 (1)	0.5417 (3)	7.4 (5)
C(17A)	0.160 (1)	0.0296 (6)	0.5947 (3)	7.0 (4)
C(17)	0.1013 (7)	0.0539 (8)	0.5782 (4)	6.9 (5)
C(18A)	0.2854 (6)	0.2379 (6)	0.4982 (2)	6.2 (3)
C(18)	0.3453 (6)	0.0112 (5)	0.5812 (3)	6.1 (3)
C(19)	0.3394 (8)	0.124 (1)	0.5022 (3)	7.7 (5)
C(19A)	0.3578 (8)	0.0565 (7)	0.5263 (4)	7.8 (5)
H(1)	-0.019 (4)	0.216 (3)	0.308 (1)	8 (1)
H(2)	0.063 (3)	0.172 (4)	0.396 (1)	9 (1)
H(15)	0.297 (3)	0.347 (2)	0.679 (1)	5.4 (8)
H(16)	0.122 (3)	0.275 (3)	0.672 (1)	6.4 (9)

Atoms of molecule 2 correspond to those of molecule 1 through the addition of 10 to the atom label. The symbol 'A' refers to disordered atoms (see Fig. 4).

Discussion. The structure of one of the unique molecules (molecule 1) is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. There are two unique molecules in the asymmetric unit of the crystal lattice which differ primarily through their hydrogen-bonding interaction. Molecule 1 utilizes its hydroxyl protons to interact with the carbonyl and one hydroxyl oxygen of molecule 2 while both hydroxyl protons of molecule 2 are hydrogen bonded to the carbonyl oxygen of a different molecule 1, as shown in Fig. 2. This particular hydrogen-bonding scheme results in the formation of sheets, two molecules thick, which lie virtually parallel to the ac plane, as illustrated in the packing diagram (Fig. 3). The disordered methyl groups lie in the grooves separating these sheets. The methyl groups and one of the ring C atoms in molecule 2 are disordered as shown in Fig. 4. The disordered ring carbons [C(15) and C(15A)], refined at 0.5 occupancy, are separated by 0.625 (7) \AA .

Deviations from best least-squares planes through portions of molecules 1 and 2 are listed in Table 3. The five-membered ring in molecule 1 is nearly planar while only four of the C atoms of the ring in

molecule 2 are coplanar. The fifth C atom lies $\sim 0.25 \text{ \AA}$ out of the plane and is disordered. In both molecules, these deviations are larger than found in the parent compound, reductic acid (RA, 2,3-dihydroxy-2-cyclopenten-1-one), in which all non-H atom displacements from the ring plane are less than 0.031 \AA (Semmingen, 1977). Nevertheless, the conjugated portions of the TMRA molecule, O(1)—C(1)—C(2)—C(3)—O(3) in molecule 1 and O(11)—C(11)—C(12)—C(13)—O(13) in molecule 2, are planar, reflecting electron delocalization. As a consequence, the C—O bonds of terminal hydroxyl groups, C(3)—O(3) in molecule 1 or C(13)—O(13) in molecule 2, are shorter than those of the central hydroxyl groups, C(2)—O(2) in molecule 1 and C(12)—O(12) in molecule 2. A similar phenomenon was observed in the structure of RA (Semmingen, 1977). The difference between the C—O bond lengths was believed to be responsible for the higher acidity of the terminal, compared to that of the central, hydroxyl group (Semmingen, 1977). Another consequence of electron delocalization is that C(1)—C(2) in molecule 1 and C(11)—C(12) in molecule 2 of TMRA are shorter than other C—C single bonds in the molecule (Table 2).

It is interesting to note that hydrogen-bonding schemes for RA and TMRA are very different. In the structure of RA, the carbonyl group accepts

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, bond lengths and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52744 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and angles (°) for TMRA with *e.s.d.*'s in parentheses

Molecule 1		Molecule 2	
O(1)—C(1)	1.251 (3)	O(11)—C(11)	1.243 (3)
O(2)—C(2)	1.363 (3)	O(12)—C(12)	1.365 (3)
O(3)—C(3)	1.318 (3)	O(13)—C(13)	1.333 (3)
C(1)—C(2)	1.413 (3)	C(11)—C(12)	1.414 (4)
C(1)—C(5)	1.514 (3)	C(11)—C(15)	1.525 (9)
		C(11)—C(15A)	1.55 (1)
C(2)—C(3)	1.345 (3)	C(12)—C(13)	1.346 (3)
C(3)—C(4)	1.507 (3)	C(13)—C(14)	1.503 (3)
C(4)—C(5)	1.563 (4)	C(14)—C(15)	1.56 (1)
		C(14)—C(15A)	1.55 (1)
C(4)—C(6)	1.509 (4)	C(14)—C(16)	1.577 (9)
		C(14)—C(16A)	1.502 (9)
C(4)—C(7)	1.563 (5)	C(14)—C(17)	1.479 (9)
		C(14)—C(17A)	1.573 (8)
C(5)—C(8)	1.534 (4)	C(15)—C(18)	1.53 (1)
		C(15A)—C(18A)	1.55 (1)
C(5)—C(9)	1.532 (4)	C(15A)—C(19A)	1.52 (1)
		C(15)—C(19)	1.53 (1)
O(2)—H(1)	0.89 (4)	O(12)—H(15)	0.83 (3)
O(3)—H(2)	0.96 (4)	O(13)—H(16)	0.84 (4)
O(1)⋯O(12)	2.606 (3)	O(11)⋯O(3)	2.612 (3)
O(1)⋯O(13)	2.685 (3)	O(12)⋯O(2)	2.677 (3)
		O(11)—C(11)—C(12)	125.9 (2)
O(1)—C(1)—C(2)	126.2 (2)	O(11)—C(11)—C(15)	123.7 (4)
O(1)—C(1)—C(5)	123.4 (2)	O(11)—C(11)—C(15A)	123.5 (4)
		C(12)—C(11)—C(15)	108.8 (4)
C(2)—C(1)—C(5)	110.4 (2)	C(12)—C(11)—C(15A)	109.6 (4)
		O(12)—C(12)—C(11)	120.1 (2)
O(2)—C(2)—C(1)	121.9 (2)	O(12)—C(12)—C(13)	130.5 (2)
O(2)—C(2)—C(3)	129.0 (2)	O(11)—C(12)—C(13)	109.4 (2)
C(1)—C(2)—C(3)	108.9 (2)	O(13)—C(13)—C(12)	129.2 (2)
O(3)—C(3)—C(2)	128.6 (2)	O(13)—C(13)—C(14)	118.0 (2)
O(3)—C(3)—C(4)	117.6 (2)	C(12)—C(13)—C(14)	112.8 (2)
C(2)—C(3)—C(4)	113.7 (2)	C(13)—C(14)—C(15)	101.8 (4)
C(3)—C(4)—C(5)	102.0 (2)	C(13)—C(14)—C(15A)	103.9 (4)
		C(13)—C(14)—C(16)	103.2 (4)
C(3)—C(4)—C(6)	112.4 (2)	C(13)—C(14)—C(16A)	114.7 (4)
		C(13)—C(14)—C(17)	114.8 (4)
C(3)—C(4)—C(7)	105.6 (2)	C(13)—C(14)—C(17A)	103.5 (3)
		C(15)—C(14)—C(16)	110.8 (5)
C(5)—C(4)—C(6)	116.3 (2)	C(15A)—C(14)—C(16A)	116.6 (5)
C(5)—C(4)—C(7)	110.4 (2)	C(15)—C(14)—C(17)	117.8 (5)
		C(15A)—C(14)—C(17A)	114.1 (5)
C(6)—C(4)—C(7)	109.4 (3)	C(16)—C(14)—C(17)	107.5 (6)
		C(16A)—C(14)—C(17A)	103.7 (6)
C(1)—C(5)—C(4)	103.1 (2)	C(11)—C(15)—C(14)	102.0 (5)
C(1)—C(5)—C(8)	105.6 (2)	C(11)—C(15)—C(14)	101.8 (6)
		C(11)—C(15)—C(18)	109.6 (6)
C(1)—C(5)—C(9)	111.5 (2)	C(11)—C(15A)—C(18A)	109.7 (6)
		C(11)—C(15)—C(19)	108.6 (6)
C(4)—C(5)—C(8)	111.8 (2)	C(11)—C(15A)—C(19A)	107.5 (7)
C(4)—C(5)—C(9)	115.7 (2)	C(14)—C(15)—C(18)	110.7 (6)
		C(14)—C(15A)—C(18A)	111.0 (6)
C(8)—C(5)—C(9)	108.6 (2)	C(14)—C(15)—C(19)	115.9 (7)
		C(14)—C(15A)—C(19A)	117.9 (7)
		C(18)—C(15)—C(19)	109.6 (8)
		C(18A)—C(15A)—C(19A)	108.5 (8)

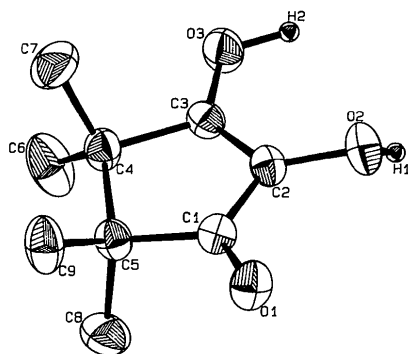


Fig. 1. Structure of one of the independent molecules (molecule 1) in the unit cell showing the atomic numbering scheme.

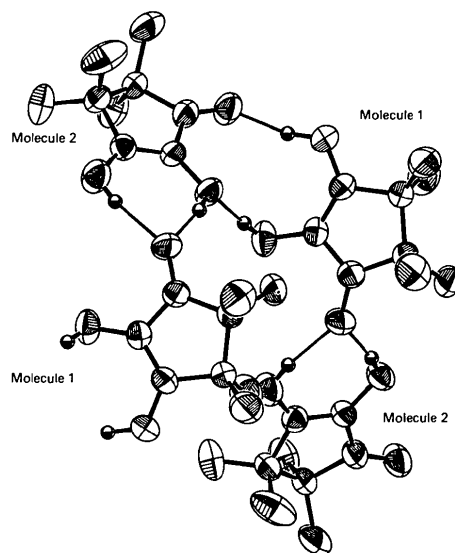


Fig. 2. Two asymmetric units of TMRA, showing the various modes of hydrogen bonding. Only one of two disordered sets of C atoms is depicted for molecule 2 (see text).

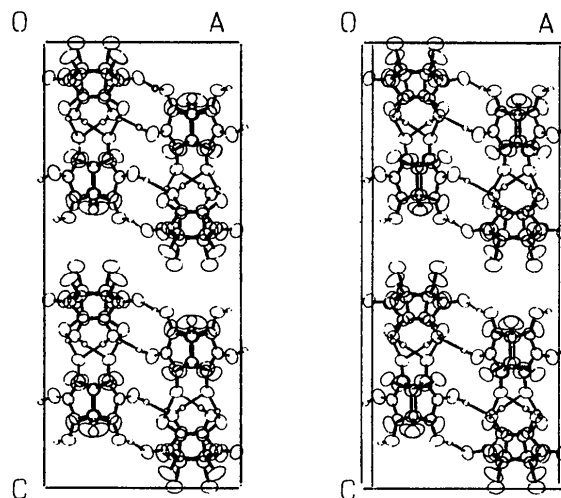


Fig. 3. Stereoview of the unit-cell packing.

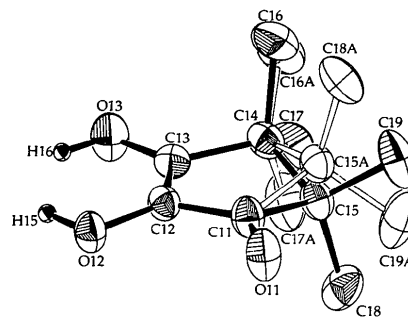


Fig. 4. Structure of molecule 2 showing the atomic numbering scheme and the model used to define the disordered C atoms (see text).

Table 3. Deviations (Å) of non-H atoms from the least-squares planes through different parts of the molecules

Deviations of atoms which do not define the plane are listed in parentheses.

Molecule 1			Molecule 2		
C(1)	0.0543	-0.0315	C(11)	-0.0324	0.0352 (-0.0033)
C(2)	-0.0119	-0.0270	C(12)	0.0030	-0.0159 (-0.0078)
C(3)	-0.0342	-0.0023	C(13)	0.0210	-0.0015 (-0.0064)
C(4)	0.0897	(0.0864)	C(14)	-0.0434	0.0211 (-0.0427)
C(5)	-0.0834	(-0.1679)	C(15)	0.2974	(0.3360)
			C(15A)	-0.2018	(-0.2889)
O(1)	(0.1730)	0.0304	O(11)	(-0.0444)	(0.0490) 0.0085
O(2)	(0.0556)	(0.0539)	O(12)	(0.0355)	(-0.0493) (-0.0073)
O(3)	(-0.0823)	0.0206	O(13)	(0.0747)	(-0.0160) 0.0105

hydrogen bonds from two hydroxyl groups of two different neighboring molecules. In the TMRA structure, the carbonyl group from molecule 1 accepts hydrogen bonds from two hydroxyl groups of one of its neighbors while the carbonyl group of molecule 2 only accepts one hydrogen bond from the hydroxyl group of its neighboring molecule (Fig. 2). In addition, the hydroxyl groups in RA only act as hydrogen-bond donors while one of the hydroxyl groups in molecule 2 in TMRA acts as both a hydrogen-bond donor and acceptor.

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Structure of a 5,6-Lactone*

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Abstract. 6,6-Dimethyl-7-vinyl-8-oxatricyclo[5.2.2.0^{1,5}]undec-4-ene-9-one, C₁₄H₁₈O₂, $M_r = 216.30$, orthorhombic, $Pna2_1$, $a = 13.114$ (6), $b = 8.244$ (7), $c = 11.148$ (6) Å, $V = 1205$ (2) Å³, $Z = 4$, $D_m = 1.19$ (2) (floatation), $D_x = 1.189$ g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 5.889$ cm⁻¹, $F(000) = 472$, $T = 298$ K, final $R = 0.051$, $wR = 0.063$ for 943 reflections with $I > 3\sigma(I)$. The lactone ring exists in the boat conformation and the molecules in the crystal are stabilized by van der Waals interactions. Bond lengths and angles are similar to those observed in other lactones.

Introduction. Lactones like coumarins, xanthenes and flavones are found to occur in several plants and

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fungi and they are found to possess antitumour activity (Bowman & Rand, 1980). The present paper reports the crystal structure of a lactone synthesized at the department of Organic Chemistry, University of Madras (Ganesh Raj, Janardhanam & Rajagopalan, 1988).

Experimental. D_m by floatation, white needles from benzene, $0.40 \times 0.30 \times 0.20$ mm, Nonius CAD-4 graphite-monochromated single-crystal diffractometer, $\omega/2\theta$ scan, Cu $K\alpha$ radiation, cell parameters refined from 25 accurately centered reflections, $30 \leq 2\theta \leq 60^\circ$, Lp correction, θ -dependent absorption correction using *DIFABS* from the *SDP* package (Frenz, 1978) (max., min. transmission 0.98, 0.90), 1080 unique reflections with $2\theta \leq 120^\circ$ and $0 \leq h \leq 14$, $0 \leq k \leq 9$, $0 \leq l \leq 12$, 943 reflections with $I > 3\sigma(I)$; three standard reflections monitored

* DCB contribution No. 755.

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