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Key indicators

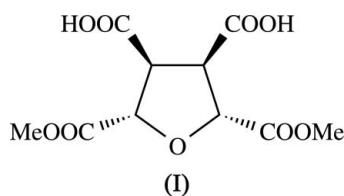
Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.039
 wR factor = 0.100
Data-to-parameter ratio = 12.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Dimethyl 3*t*,4*t*-dicarboxytetrahydrofuran-
2*r*,5*c*-dicarboxylate

Esterification of tetrahydrofuran-2*r*,3*t*,4*t*,5*c*-tetracarboxylic acid gave selectively the title compound, $\text{C}_{10}\text{H}_{12}\text{O}_9$, in which the two more acidic carboxylic acid groups, in positions 2 and 5, have been esterified. The five-membered ring is in a twist conformation. Hydrogen bonding results in double chains, or ribbons, running along the c axis.

Received 29 March 2006
Accepted 31 March 2006

Comment

Tetrahydrofuran-2*r*,3*t*,4*t*,5*c*-tetracarboxylic acid (THFTCA) has been shown to be a potential extractant for selective partitioning of uranyl from transuranic and lanthanide ions (Nash *et al.*, 1996; Morss *et al.*, 2000). The uranyl complexes formed by THFTCA in the presence of *N*-ethylpiperidine or triethylamine are trinuclear and tetranuclear metallacycles, respectively (Thuéry *et al.*, 2004). THFTCA is also a model for humic acids (Leenheer *et al.*, 1995). The acid groups in the 2- and 5-positions were anticipated to be the more acidic (Barnes & Paton, 1984) but the 2, 4, 5, 3 deprotonation sequence was later proposed (Feil-Jenkins *et al.*, 1995). Esterification of THFTCA, as a model for fulvic acid, by methanol was investigated by electrospray ionization mass spectrometry, but the two esterified acid groups were not identified (McIntyre *et al.*, 2002). We synthesized the dimethyl ester of THFTCA, (I), by heating in methanol for three days. The two ester groups were identified in the ^1H NMR spectrum as two singlets.



The crystal structure of (I) (Fig. 1) shows that the two acid groups that have been esterified are those in positions 2 and 5. The five-membered ring in (I) is twisted about the C1–C4 bond, with atoms C1 and C4 lying -0.280 (5) and 0.350 (5) Å, respectively, from the plane defined by atoms O1, C2 and C3 (torsion angles are given in Table 1). Apart from two examples in which THFTCA is in an envelope conformation with the ether O atom in the ‘flap’ position (Barnes, 2002; Thuéry *et al.*, 2004, the latter with THFTCA in ideal mirror symmetry), conformations twisted on $\text{C}\alpha-\text{C}$ bonds are commonly encountered in the structures of THFTCA and its complexes reported in the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002). The stability of this conformation is probably due to the minimization of the steric hindrance between the acid groups in the 3- and 4-positions (Barnes & Paton, 1984).

The two remaining acid groups in (I) are involved in hydrogen bonds (Table 2). Dimers are formed through a double hydrogen bond involving the acid group containing O6 and O7 and its image by the inversion centre [graph-set assignment $R_2^2(8)$; Etter, 1990]. These dimers are further linked to one another by hydrogen bonds connecting the acid atom O8 and the ester atom O2 from neighbouring molecules along the c axis [graph-set assignment $C(8)$], thus forming double chains, or ribbons, running along this axis (Fig. 2).

Experimental

THFTCA and MeOH were purchased from Aldrich Chemical Co. and used as supplied. The deuterated solvent was purchased from Eurisotop. A solution of THFTCA (1.24 g, 5 mmol) in MeOH (100 ml) was refluxed for 3 d. After evaporation of the solvent, (I) was recovered in crystalline form (1.35 g, 98% yield). ^1H NMR (200 MHz, THF- d_8): δ 3.57 (*dd*, 2H, 3 and 4H), 3.61 and 3.62 (2*s*, 6H, 2 COOMe), 4.70 (*dd*, 2H, 2 and 5H).

Crystal data

$\text{C}_{10}\text{H}_{12}\text{O}_9$	$Z = 4$
$M_r = 276.20$	$D_x = 1.608 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.5117(4) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$b = 25.419(3) \text{ \AA}$	$T = 100(2) \text{ K}$
$c = 8.1970(7) \text{ \AA}$	Block, colourless
$\beta = 96.634(6)^\circ$	$0.26 \times 0.22 \times 0.17 \text{ mm}$
$V = 1140.73(19) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	2112 independent reflections
φ scans	1700 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.033$
7691 measured reflections	$\theta_{\text{max}} = 25.7^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0165P)^2 + 0.7399P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
2112 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
175 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.015 (3)

Table 1

Selected torsion angles ($^\circ$).

O1—C1—C4—C3	−39.85 (17)	C2—O1—C1—C4	33.32 (18)
O1—C2—C3—C4	−13.31 (19)	C2—C3—C4—C1	31.15 (18)
C1—O1—C2—C3	−12.0 (2)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O6—H6 \cdots O7 ⁱ	0.95	1.72	2.6649 (19)	173
O8—H8 \cdots O2 ⁱⁱ	0.91	1.77	2.681 (2)	174

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $x, y, z + 1$.

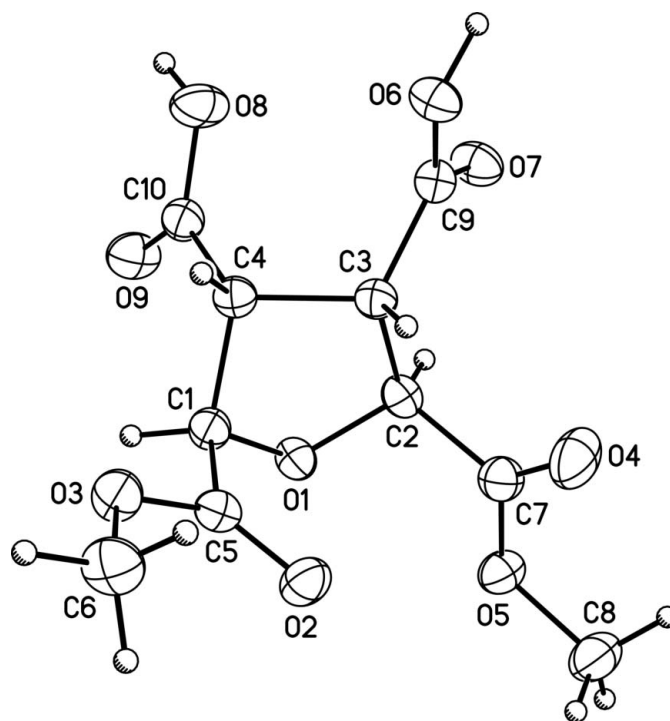


Figure 1

A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

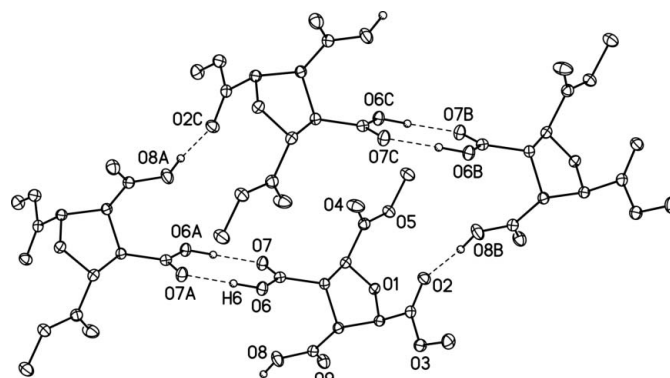


Figure 2

Partial view of a ribbon running along the c axis. The hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (A) $-x, 1 - y, 2 - z$; (B) $x, y, z - 1$; (C) $-x, 1 - y, 1 - z$.]

The two carboxylic H atoms were found in a difference Fourier map and treated as riding atoms with an isotropic displacement parameter equal to $1.2U_{\text{eq}}(\text{O})$. All other H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.98 (CH) or 0.96 \AA (CH₃), and isotropic displacement parameters equal to $1.2U_{\text{eq}}$ (CH) or $1.5U_{\text{eq}}$ (CH₃) of the parent atom.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *HKL2000* (Otwinowski & Minor, 1997); data reduction: *HKL2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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