C1—O1—C4	111.1 (1)	O1—C4—C10	106.8 (2)
O1—C1—O2	121.4 (2)	C3—C4—C9	114.0 (2)
O1—C1—C2	109.8 (2)	C3—C4—C10	113.9 (2)
O2—C1—C2	128.8 (2)	C9—C4—C10	111.8 (2)
C1—C2—C3	102.7 (1)	C3—C5—C6	113.5 (1)
C2—C3—C4	102.5 (1)	C5—C6—C7	115.6 (2)
C2—C3—C5	115.6 (1)	O3—C7—C6	122.1 (2)
C4—C3—C5	115.1 (1)	O3—C7—C8	121.8 (2)
O1—C4—C3	102.8 (1)	C6—C7—C8	116.1 (2)
O1—C4—C9	106.6 (2)		
O1—C1—C2—C3	−19.5 (2)	C1—C2—C3—C5	157.0 (1)
O1—C4—C3—C2	−31.8 (2)	C2—C1—O1—C4	−1.2 (2)
O1—C4—C3—C5	−158.1 (1)	C2—C3—C4—C9	83.1 (2)
O2—C1—O1—C4	179.2 (2)	C2—C3—C4—C10	−147.0 (2)
O2—C1—C2—C3	160.0 (2)	C2—C3—C5—C6	65.7 (2)
O3—C7—C6—C5	0.5 (3)	C3—C5—C6—C7	71.4 (2)
C1—O1—C4—C3	21.3 (2)	C4—C3—C5—C6	−175.1 (2)
C1—O1—C4—C9	−99.0 (2)	C5—C3—C4—C9	−43.2 (2)
C1—O1—C4—C10	141.4 (2)	C5—C3—C4—C10	86.8 (2)
C1—C2—C3—C4	31.0 (2)	C5—C6—C7—C8	179.8 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H21···$O2^{i}$	1.01 (2)	2.51 (2)	3.449 (3)	154 (1)
C3—H31···O3	0.97 (1)	2.64 (2)	3.164 (3)	114 (1)
C5—H51···$O2^{ii}$	1.02 (2)	2.49 (2)	3.493 (3)	167 (2)
C5—H52···O3	0.99 (2)	2.60 (2)	2.815 (3)	92 (1)
C6—H61···$O2^{i}$	1.00 (2)	2.80 (2)	3.640 (3)	142 (1)
C6—H62···$O1^{iii}$	1.06 (2)	2.76 (2)	3.729 (2)	152 (2)
C9—H92···$O2^{ii}$	1.04 (2)	2.73 (2)	3.583 (4)	139 (2)

Symmetry codes: (i) $2-x, y-\frac{1}{2}, -z$; (ii) $1-x, y-\frac{1}{2}, -z$; (iii) $x, y-1, z$.

Anisotropic displacement parameters were applied for all non-H atoms. H atoms were found in a difference Fourier map and refined isotropically, except H atoms attached to C8, which were set as riding and refined isotropically. The absolute structure was determined by the Rogers η-test (Rogers, 1981) (using *SHELXTL/PC*; Sheldrick, 1991). Results: η = 1.1 (3), η_{inv} = −1.1 (3).

Data collection and cell refinement: *CAD*-4 (Schagen, Straver, van Meurs & Williams, 1989; Frenz, 1986). Intensity data correction: *DECAY* (*SDP*; Frenz, 1986); correction factors: 1.00007 (min) and 1.09991 (max). Structure solution and refinement: *SHELXTL/PC* (Sheldrick, 1991). Molecular graphics: *SHELXTL/PC*; *CSU* (Vicković, 1988).

Financial support by the Foundation for the Polish Science (for JB) is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1217). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diethyl 2,5-Dihydroxyterephthalate at 200 K

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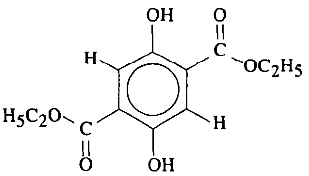
Abstract

The crystal structure of the title compound, $C_{12}H_{14}O_6$, has been determined by X-ray diffraction at 200 K. The ester molecules, which are connected by intermolecular O—H···O hydrogen bonds, form infinite strings along the *b* axis. Within the molecules, both ester groups as well as the hydroxy H atoms are almost in the plane of the six-membered ring, thus allowing the formation of intramolecular O—H···O hydrogen bonds. Each hydroxy H atom is therefore involved in a bifurcated inter/intramolecular hydrogen bond.

Comment

Halogenated terephthalic acid esters are well known for their conformational polymorphism (Byrn, Curtin & Paul, 1972; Yang, Richardson & Dunitz, 1985, 1989) due to the formation of different intra- and intermolecular hydrogen-bond patterns as well as the formation of halogen–oxygen contacts. Our investigations on diethyl 3,6-dibromo-2,5-dihydroxyterephthalate have established that this compound crystallizes in two different crystal forms which differ in their molecular conformation as well as in their hydrogen bonding and halogen–oxygen interactions (Näther, Nagel, Bock, Seitz & Havlas, 1996). In the high-temperature stable modification, both ester groups are twisted out of the ring plane into nearly perpendicular arrangements and form predominantly intermolecular hydrogen bonds. In contrast, in the room-temperature stable form only one ester group is twisted while the second one remains almost within the plane of the six-membered ring and forms an intramolecular O—H···O hydrogen bond. In this form, additional intermolecular Br···O interactions are observed. We were therefore interested in the crystal structure and molecular conformation of the halogen-free compound diethyl 2,5-dihydroxyterephthalate, (I).



(I)

In the crystal structure of (I) (Fig. 1), the hydroxy H atom is involved in a bifurcated inter/intramolecular hydrogen bond. The molecules are connected by intermolecular O—H···O hydrogen bonds involving the hydroxy groups and carbonyl O atoms of adjacent molecules, and form an infinite string along the *b* axis (Fig. 2). The intermolecular distances O···O^i of 2.978 (1) and H···O^i of 2.33 (2) Å provide evidence for a relatively

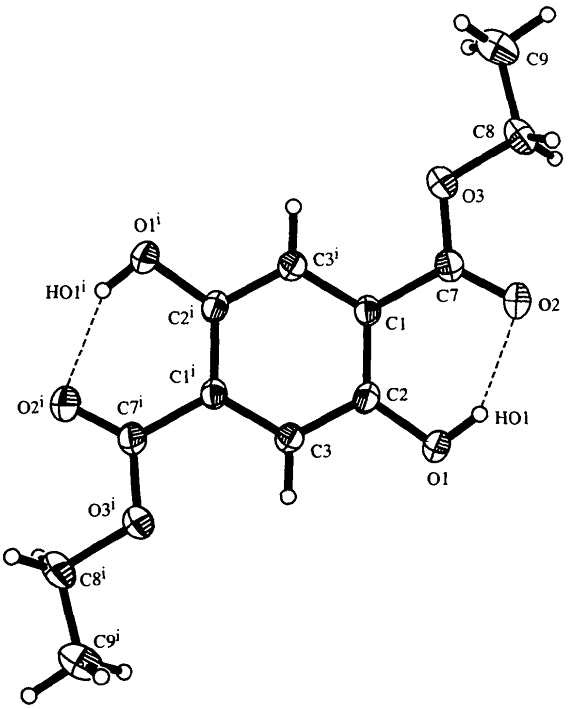


Fig. 1. A labelled view of diethyl 2,5-dihydroxyterephthalate with displacement ellipsoids at the 50% probability level.

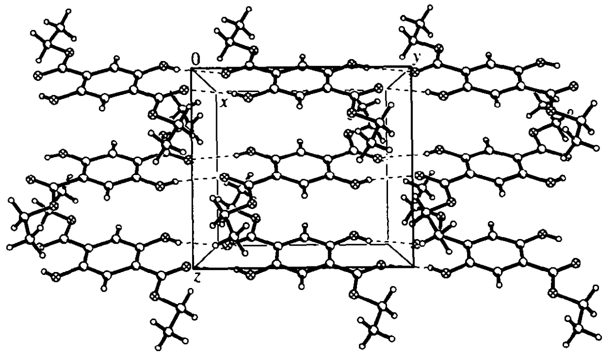


Fig. 2. The crystal structure of diethyl 2,5-dihydroxyterephthalate viewed along ($\bar{1}00$).

weak hydrogen bond (Ichikawa, 1978), with a rather small O—H···O^i angle of 132 (2)° [symmetry code: (i) $1-x$, $-y$, $-z$]. The molecules are stacked perpendicular to (101), with an interplanar distance of about 3.40 Å and an interplanar angle of 3.3° between the six-membered rings of adjacent molecules.

In the molecular structure of (I), the ester groups are twisted by only 5.5 (1)° and the hydroxy H atom by only 7 (2)° out of the plane of the six-membered ring, and two intramolecular O—H···O hydrogen bonds result between the hydroxy H and carbonyl O atoms. The O1···O2 distance is 2.672 (1) Å and the O1···HO1 distance is 1.92 (2) Å and, for geometric reasons, the O1—HO1···O2 angle is only 144 (2)°. Steric interactions widen the C1—C2—O1 angle to 124.3 (1)°. The ester group is in the antiperiplanar conformation [ω (C1—C7—O3—C8) −179.2 (1)°] normally found for analogous esters (Schweitzer & Dunitz, 1982). The torsion angle C7—O3—C8—C9 of 179.9 (1)° represents the energetically most favourable conformation derived from a microwave study of ethyl formate (Wilson, 1972).

Experimental

Diethyl 2,5-dihydroxyterephthalate is commercially available from the Aldrich Chemical Co. Crystals for the structure determination were obtained by recrystallization from dioxane.

Crystal data

$C_{12}H_{14}O_6$	Mo $K\alpha$ radiation
$M_r = 254.23$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 112 reflections
Pbcn	$\theta = 16–23.5°$
$a = 16.680$ (1) Å	$\mu = 0.115$ mm^{-1}
$b = 8.886$ (1) Å	$T = 200$ (2) K
$c = 8.054$ (1) Å	Plate
$V = 1193.8$ (2) Å^3	0.6 × 0.4 × 0.25 mm
$Z = 4$	Yellow–green fluorescent
$D_x = 1.415$ Mg m^{-3}	
D_m not measured	

Data collection

Stoe AED-4 four-circle diffractometer	R_{int} = 0.0123
ω–θ scans	θ_{max} = 30.03°
Absorption correction: none	$h = -23 \rightarrow 23$
3174 measured reflections	$k = -12 \rightarrow 12$
1747 independent reflections	$l = 0 \rightarrow 11$
1292 observed reflections [$I > 2\sigma(I)$]	4 standard reflections frequency: 120 min intensity decay: <1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F)$ = 0.0377	$\Delta\rho_{max}$ = 0.425 e Å^{-3}
$wR(F^2)$ = 0.1185	$\Delta\rho_{min}$ = −0.186 e Å^{-3}
S = 1.040	Extinction correction: none
1747 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
89 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.2061P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.43274 (5)	0.22979 (9)	0.10006 (13)	0.0319 (2)
O2	0.55785 (6)	0.10204 (10)	−0.0518 (2)	0.0475 (3)
O3	0.64056 (5)	0.24775 (8)	−0.19972 (11)	0.0302 (2)
C1	0.53848 (6)	0.36706 (10)	−0.04674 (13)	0.0221 (2)
C2	0.46767 (6)	0.35979 (10)	0.04885 (14)	0.0232 (2)
C3	0.43051 (6)	0.49337 (11)	0.09363 (14)	0.0236 (2)
C7	0.57882 (6)	0.22629 (12)	−0.0982 (2)	0.0266 (2)
C8	0.68173 (7)	0.11251 (13)	−0.2561 (2)	0.0351 (3)
C9	0.74834 (8)	0.1629 (2)	−0.3680 (2)	0.0433 (3)

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.3580 (12)	C1—C2	1.4114 (14)
O2—C7	1.2169 (14)	C1—C7	1.4795 (14)
O3—C7	1.3290 (14)	C2—C3	1.3867 (14)
O3—C8	1.4566 (13)	C3—C1^i	1.3958 (14)
C1—C3^i	1.3958 (14)	C8—C9	1.499 (2)
C7—O3—C8	116.03 (9)	C3—C2—C1	118.47 (9)
C3^i—C1—C2	119.89 (9)	C2—C3—C1^i	121.64 (9)
C3^i—C1—C7	120.46 (9)	O2—C7—O3	122.80 (10)
C2—C1—C7	119.64 (9)	O2—C7—C1	123.40 (11)
O1—C2—C3	117.22 (9)	O3—C7—C1	113.79 (9)
O1—C2—C1	124.31 (9)	O3—C8—C9	106.87 (10)
C8—O3—C7—O2	1.1 (2)	C3^i—C1—C7—O3	−5.0 (2)
C8—O3—C7—C1	−179.14 (10)	C2—C1—C7—O3	174.30 (9)
C3^i—C1—C7—O2	174.79 (12)	C7—O3—C8—C9	179.93 (11)
C2—C1—C7—O2	−5.9 (2)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

The C and O atoms were refined with anisotropic displacement parameters. The H atoms were located from a difference map and refined with free isotropic displacement parameters (groupwise for methyl and methylene) using a riding model, with aromatic C—H distances of 0.95, methylene C—H distances of 0.99 and methyl C—H distances of 0.98 Å. The atom HO1 was refined with free coordinates and free isotropic displacement parameters.

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *CIFTAB* in *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: SK1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Maltol Hydrochloride

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Abstract

The unit cell of the title compound, 3-hydroxy-2-methyl-4*H*-pyran-4-onium chloride, $C_6H_7O_3^+.Cl^-$, contains Cl^- anions and carbonyl-protonated maltolium cations connected into perfectly planar ribbons *via* hydrogen bonding. The C=O bond length is increased by *ca* 0.06 Å upon protonation whereas greater delocalization in the