binning. The unit-cell parameters were determined by a least-squares fit of the angular settings of 27 strong reflections; 97% of the whole sphere of data was collected. Processing was carried out using the program *SAINT* (Siemens, 1996*a*), which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. Except for four hydroxyl H atoms on the sugars, which were found from a difference map, all H atoms were positioned geometrically. During the refinement H atoms were 'riding' on their parent atoms. Two reflections (001 and $00\bar{1}$) were rejected due to severe extinction phenomena. The relatively high *wR* values are due to crystal quality. In the outermost 5° in θ there are approximately 1000 reflections of which about 150 are observed. Omitting these data from the refinement led to improved *R*1 (0.07) and *wR*2 (0.23), but made no significant difference to the molecular geometry (maximum difference in bond length was 0.005 Å).

Data collection: *SMART*. Cell refinement: *SMART*. Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995) and *ORTEP*III (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1303). Services for accessing these data are described at the back of the journal.

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4-[Hydroxy(phenyl)methylene]-5-oxo-3-phenyl-2-cyclohexenecarboxylic Acid

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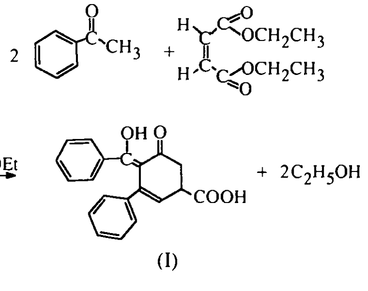
Abstract

In the title compound, $C_{20}H_{16}O_4$, the cyclohexene ring adopts a twisted-boat conformation. The molecule contains an enol sub-unit and the hydroxyl group forms an intramolecular hydrogen bond to the cyclic carbonyl group, with an O···O distance of 2.485 (3) Å and an O—H···O angle of 148 (3)°. Enantiomeric pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxyl groups, with O···O distances of 2.649 (3) Å.

Comment

Many studies have been concerned with the synthesis and chemistry of cyclic ketones among which cyclic ketoacids have received special attention due to their biological activity as sexual hormones (Lazarević, Vorkapić-Furač & Mühl, 1992; Bu'Lock, Austin, Snatzke & Hruban, 1970; Bacigaluppo *et al.*, 1994; Hervouet & Guingant, 1996). In this paper, we report the structure of a new cyclohexene ketoacid, (I), prepared by base-catalysed condensation of acetophenone with diethyl maleate.



(I)

The molecule contains a chiral centre (C1), but both enantiomers are present in the crystal. The cyclohexene ring adopts a twisted-boat conformation. The dihedral angles between the least-squares best plane through

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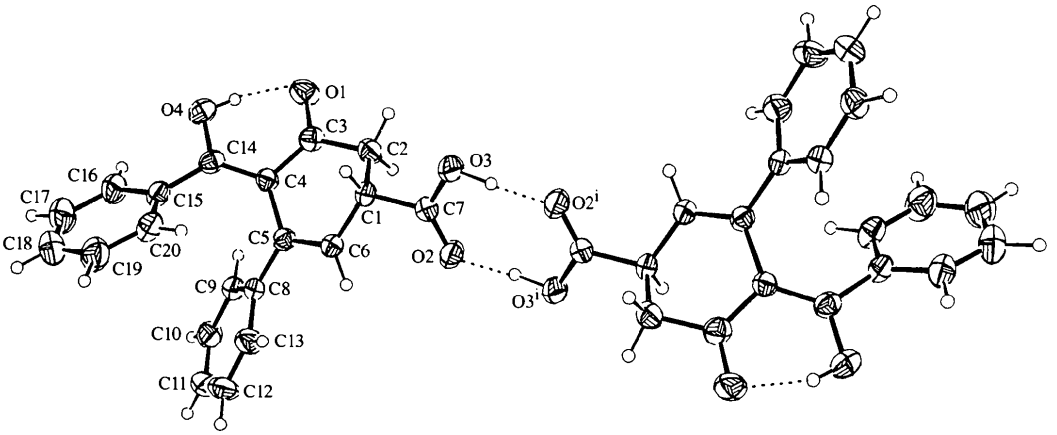

Fig. 1. *ORTEP* (Johnson, 1965) view of the enantiomeric pairs of the title molecule with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen bonds are denoted by dashed lines.

atoms C2–C6, and the planes through C6, C1, C2 and C3–C5 are 43.8 (2) and 18.5 (2)°, respectively. The enol C4—C14 and C14—O4 bond distances are 1.387 (3) and 1.331 (2) Å, respectively, which are consistent with those found previously (Semmingsen, 1972; Jones, 1976; Prince, Fronczek & Gandour, 1989). The enolic H atom, H4O, and the ketonic O atom, O1, are connected by a very short intramolecular hydrogen bond [O1···O4 2.485 (3) Å] which is clearly asymmetric and within the expected range [O4—H4O 0.86 (3) and O1···H4O 1.72 (3) Å] (Jeffrey, 1995). The enol ring (O1—C3—C4—C14—O4—H4O) is nearly planar, with a maximum deviation of atom H4O from the mean molecular plane of 0.20 (3) Å. The dihedral angle between the phenyl- (C15–C20) and enol-ring planes is 38.3 (1)°. There is twisting about the axis through atoms C5 and C8 as well as about the axis through C1 and C7 [C6—C5—C8—C13 37.6 (3), C4—C5—C8—C9 33.8 (3), C6—C1—C7—O2 22.8 (3) and C2—C1—C7—O3 79.5 (2)°]. Enantiomeric pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxyl groups (Fig. 1). The hydrogen bond is asymmetric [O3—H3O 1.04 (4), O2^i···H3O 1.61 (3) and O3···O2^i 2.649 (3) Å; symmetry code: (i) $-x$, $1-y$, $1-z$] with values similar to those found in many of the carboxylic acid dimers (Stiles & Selegue, 1991; Coté, Lalancette & Thompson, 1995).

Experimental

To a freshly prepared etheral suspension of sodium ethoxide (25 mmol) cooled to 268 K, diethyl maleate (10 mmol) and acetophenone (20 mmol) were slowly added. The reaction mixture was stirred for a few hours and the precipitated sodium salt was filtered off and hydrolyzed with cold acetic acid (ω = 0.20). Recrystallization from acetone afforded the pure compound (m.p. 422–423 K) in 35% yield. ^{1}H NMR (δ p.p.m., acetone-d_6): 2.70 (*d*, J = 6.9 Hz, 2H), 3.80 (*m*, $J_{4,5}$ = 6.9, $J_{5,5}$ = 5.4 Hz, 1H), 6.02 (*d*, J = 5.4 Hz, 1H), 6.85–7.70 (*m*, 10H) (Varian EM-390). UV/vis (methanol): $\lambda_{\max}$ 250, 360 nm (Hitachi Perkin-Elmer 124 spectrophotometer). IR (KBr disk): $\nu_{C=O}$ 1705 and 1560, ν_{OH} 3250–2300 cm^{-1} (Perkin-Elmer Model 783 spectrophotometer). Diffraction-quality crystals were grown by slow evaporation from an acetone solution of the compound.

Crystal data

$C_{20}H_{16}O_4$
M_r = 320.33
Triclinic
$P\bar{1}$
a = 6.474 (1) Å
b = 11.393 (1) Å
c = 11.862 (3) Å
α = 66.16 (2)°
β = 89.20 (4)°
γ = 84.92 (2)°
V = 796.9 (2) Å^3
Z = 2
D_x = 1.335 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 21 reflections
θ = 8.8–12.2°
μ = 0.093 mm^{-1}
T = 295 (1) K
Prism
0.60 × 0.35 × 0.15 mm
Yellow

Data collection

Philips PW1100 diffractometer updated by Stoe
$\theta/2\theta$ scans
Absorption correction: none
4522 measured reflections
4522 independent reflections
1700 reflections with $I > 2\sigma(I)$

$\theta_{\max}$ = 30.06°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 16$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 3.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.143
S = 0.925
4521 reflections
281 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.055
$\Delta\rho_{\max}$ = 0.161 e Å^{-3}
$\Delta\rho_{\min}$ = −0.154 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C3	1.256 (2)	C2—C3	1.513 (3)
O2—C7	1.222 (2)	C3—C4	1.438 (3)
O3—C7	1.299 (2)	C4—C14	1.387 (3)
O4—C14	1.331 (2)	C4—C5	1.493 (3)
C1—C6	1.490 (3)	C5—C6	1.345 (3)
C1—C7	1.508 (3)	C5—C8	1.477 (3)
C1—C2	1.542 (3)	C14—C15	1.480 (3)
C6—C1—C7	113.4 (2)	C6—C5—C8	120.9 (2)
C6—C1—C2	108.5 (2)	C6—C5—C4	117.6 (2)
C7—C1—C2	109.9 (2)	C8—C5—C4	121.2 (2)
C3—C2—C1	110.0 (2)	C5—C6—C1	121.5 (2)
O1—C3—C4	123.0 (2)	O2—C7—O3	123.4 (2)
O1—C3—C2	117.7 (2)	O2—C7—C1	122.6 (2)
C4—C3—C2	119.2 (2)	O3—C7—C1	114.1 (2)
C14—C4—C3	117.7 (2)	O4—C14—C4	121.3 (2)
C14—C4—C5	125.5 (2)	O4—C14—C15	112.4 (2)
C3—C4—C5	116.8 (2)	C4—C14—C15	126.3 (2)

All non-H atoms in the structure were found by direct methods, whereas all H atoms were located in subsequent $\Delta\rho$ maps.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1478). Services for accessing these data are described at the back of the journal.

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L-Phenylalanine L-Phenylalaninium Perchlorate

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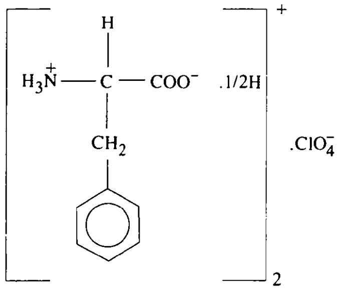
Abstract

The crystal of the title compound, $C_9H_{11}NO_2.C_9H_{12}NO_2^+.ClO_4^-$, is made up of a twofold symmetric hydrogen-bonded dimer carrying a net positive charge and a negatively charged perchlorate ion. The crystal structure involving alternating polar and non-polar zones is stabilized by hydrogen bonds and van der Waals interactions.

Comment

The crystal structures of amino acids and their complexes have provided a wealth of interesting information pertaining to the patterns of their aggregation and the effect of other molecules and ions on their interactions and molecular properties (Vijayan, 1988; Prasad & Vijayan, 1993). The structure analysis of the title compound, (I), has been carried out as a contribution to this body of information.



(I)

The structure of L-phenylalanine L-phenylalaninium perchlorate, (I), contains two formula units of phenylalanine and one unit of perchlorate in the asymmetric unit (Fig. 1). The amino group in both molecules is protonated and positively charged. The phenylalanine molecules are related by a non-crystallographic pseudo-twofold symmetry. The carboxyl groups share a proton in what appears to be a symmetric O···O hydrogen bond. The symmetric hydrogen-bonded dimer thus formed has a net positive charge which is neutralized by the negatively charged perchlorate ion.

Both phenylalanine molecules have a similar conformation. They have the sterically least favourable *g*+ con-

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