References

Albrecht, A. S., Wynn, C. M., Landee, C. P. & Turnbull, M. M. (1998). *Phys. Rev. B.* Submitted.

Anagnostis, J. & Turnbull, M. M. (1998). *Acta Cryst.* C54, 681–683.

Kerr, M. C., Preston, H. S., Ammon, H. L., Huheey, J. E. & Stewart, J. M. (1981). *J. Coord. Chem.* 11, 111–115.

Luque, A., Sertucha, J., Lezama, L., Rojo, T. & Román, P. (1997). *J. Chem. Soc. Dalton Trans.* pp. 847–854.

Mohedano, J. M., Florencio, F. & Garcia-Blanco, S. (1985). *Z. Kristallogr.* 171, 229–234.

Place, H. & Willett, R. D. (1987a). *Acta Cryst.* C43, 1050–1053.

Place, H. & Willett, R. D. (1987b). *Acta Cryst.* C43, 1497–1500.

Prince, B. J. & Turnbull, M. M. (1996). *Acta Cryst.* C52, 1843–1844.

Schmidbauer, H., Mair, A., Muller, G., Lachmann, J. & Gamper, S. (1991). *Z. Naturforsch. Teil B,* 46, 912–918.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–73.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1990). *SHELXTL/PC.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1992). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Comment

Keto carboxylic acids offer options for varying the pattern of dimeric hydrogen bonding that dominates functionally unadorned acids. Most often, the ketone fails to participate, resulting in typical carboxyl dimers, but less commonly, intermolecular carboxyl–ketone hydrogen bonds occur, yielding a catemer. A third, rare, arrangement has an internal hydrogen bond, while two instances are known of acid–ketone dimerization, and several cases are known of hydrates with more complex hydrogen-bonding patterns. In addition, we have recently reported an instance of carboxyl catemerization, not previously observed in keto acids (Lalancette *et al.*, 1998), and we have cited and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992; Coté *et al.*, 1996).

We report here the structure and hydrogen-bonding behavior of the title δ-keto acid, (I). This category of keto acids embraces examples of dimeric and internal hydrogen bonds, as well as both anhydrous and hydrated catemers. Compound (I) was of particular interest to us as the next-highest homolog of (±)-2,3-dihydro-3-oxo-1*H*-indenecarboxylic acid. The crystal structures for both the anhydrous and hydrated forms of this lower homolog, the former of which displays a homochiral (screw-related) catemeric hydrogen-bonding pattern, have been reported recently (Lalancette *et al.*, 1997).

(I)

(±)-4-Oxo-1,2,3,4-tetrahydronaphthalene-1-carboxylic Acid: Hydrogen Bonding and Carboxyl Disordering in a δ-Keto Acid

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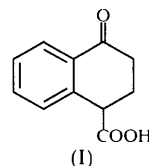
Abstract

The crystal structure of the title compound ($C_{11}H_{10}O_3$) contains hydrogen-bonded centrosymmetric carboxyl dimers. Significant carboxyl disorder was found, and was modeled by two rotational conformers, yielding two $O \cdots O$ distances of 2.649 (14) and 2.666 (17) Å.

Our analysis of (I) reveals that the carboxyl group is disordered, both rotationally and with respect to bond lengths and angles, and is turned approximately orthogonal to the plane of the aromatic ring, with the mean carboxyl plane producing a dihedral angle of 77.6 (4)° with the aromatic ring. Fig. 1 shows a centrosymmetric dimer pair and depicts the modeled rotational disorder of the acid group. The two $O \cdots O$ distances, one for each rotational conformer, are: $O3 \cdots O2^i = 2.649\,(14)$ and $O3' \cdots O2'^i = 2.666\,(17)$ Å [symmetry code: (i) $-x$, $1 - y$, $-z$]. A single molecule of this pair constitutes the asymmetric unit, and its numbering is shown. The flexible ketone ring adopts a conformation resembling a folded envelope, which allows the ketone to lie in the plane of the aromatic ring [torsion angle O1—C4—C4a—C5 = 0.8 (3)°], and which positions the carboxyl group pseudo-equatorially [torsion angle C9—C1—C2—C3 = −176.4 (2)°].

For highly ordered dimeric carboxyls, typical values cited for the C—O bond lengths and C—C—O angles are 1.21, 1.31 Å and 123, 112° (Borthwick, 1980).
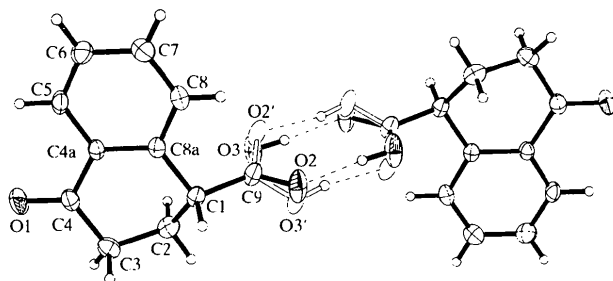
Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I), showing a disordered centrosymmetric dimer pair. The major carboxyl conformer [54 (2)%] is shown with filled bonds and segmented ellipsoids; the minor conformer is shown with open bonds and open ellipsoids. The numbering scheme is also shown. Ellipsoids are set at the 20% probability level.

The type of disorder most commonly encountered in carboxyl dimers, detected as an averaging of these values (Leiserowitz, 1976), is most plausibly attributed either to static positional disorder (180° rotation) in the crystal or to rapid tautomeric hydrogen exchange (Meier *et al.*, 1982; Nagaoka *et al.*, 1983; Wilson *et al.*, 1996) within the dimer. For (I), without modeling the rotational disorder, these bond lengths and angles are not only substantially averaged [1.240 (3), 1.238 (3) Å, and 119.5 (2), 118.3 (2)°], but the carboxyl O atoms are markedly prolated, suggesting that the averaging may be accompanied or caused by rotation of the dimer subunit. As a general measure of such prolation, we use the ratio of the length of the longest ellipsoidal axis to the sum of the remaining two. Significant electron density was also found within the O—H bond distance from both carboxyl O atoms. We have modeled this disorder most successfully as a carboxyl rotation of 156 (1)°, as shown in Fig. 1 (see refinement details). The major conformer in this treatment refined to a site occupancy of 54 (2)%, while the minor component was 46 (2)%. This refinement led to a partial ordering of the carboxyl bond lengths and angles [C9—O2 = 1.234 (8), C9—O3 = 1.263 (8), C9—O2' = 1.237 (9), C9—O3' = 1.259 (9) Å; O2—C9—C1 = 120.5 (6), O3—C9—C1 = 116.7 (5), O2'—C9—C1 = 122.5 (6), O3'—C9—C1 = 115.1 (7)°]. With this treatment, the atomic displacement parameters for the carboxyl O atoms are substantially reduced.

A close contact of 2.59 Å is found between the ketone oxygen, O1, and H7*A* of a translationally related neighbor. A further close contact of 2.69 Å to a translationally related neighbor is found between H2*B* and O2'; details are in Table 2. These may represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

The solid-state (KBr) infrared spectrum of (I) has a double peak (1688, 1691 cm^{-1}) amid several lesser peaks, for both C=O groups. In CHCl$_3$ solution, the

ketone absorption at 1687 cm^{-1} is accompanied by a less intense one at 1712 cm^{-1}, having a major shoulder at *ca* 1725 cm^{-1}.

Experimental

Compound (I) was synthesized by polyphosphoric acid cyclization (Lloyd & Horning, 1954) of 2-phenylglutaric anhydride, purchased from Acros Organics, Pittsburgh, PA, USA. Crystals of (I) (m.p. 368 K) were obtained by evaporation from a solution in a 3:1 cyclohexane/ethyl acetate mixture.

Crystal data

C$_{11}$H$_{10}$O$_3$	Mo $K\alpha$ radiation
M_r = 190.19	λ = 0.71073 Å
Monoclinic	Cell parameters from 23
$P2_1/n$	reflections
a = 6.4046 (9) Å	θ = 10.2–14.0°
b = 5.2550 (8) Å	μ = 0.099 mm^{-1}
c = 27.634 (3) Å	T = 293 (2) K
β = 92.111 (8)°	Parallelepiped
V = 929.4 (2) Å^3	0.56 × 0.20 × 0.10 mm
Z = 4	Colorless
D_x = 1.359 Mg m^{-3}	
D_m = 1.36 (1) Mg m^{-3}	
D_m measured by flotation in hexane/CCl$_4$	

Data collection

Siemens *P*4 diffractometer	R_{int} = 0.035
$2\theta/\theta$ scans	θ_{max} = 25°
Absorption correction:	$h = -1 \rightarrow 7$
face-indexed numerical	$k = -1 \rightarrow 6$
(Sheldrick, 1994)	$l = -32 \rightarrow 32$
T_{min} = 0.960, T_{max} = 0.982	3 standard reflections
2600 measured reflections	every 97 reflections
1642 independent reflections	intensity decay: 0.10%
1101 reflections with	
$F > 4\sigma(F)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = −0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.041	$\Delta\rho_{max}$ = 0.115 e Å^{-3}
$wR(F^2)$ = 0.108	$\Delta\rho_{min}$ = −0.128 e Å^{-3}
S = 1.03	Extinction correction:
1639 reflections	*SHELXTL/PC*
156 parameters	Extinction coefficient:
H atoms: see below	0.124 (10)
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.058P]$	Scattering factors from *International Tables for Crystallography* (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

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

O1—C4	1.219 (2)	O2'—C9	1.237 (9)
O2—C9	1.234 (8)	O3'—C9	1.259 (9)
O3—C9	1.263 (8)		
O2—C9—C1	120.5 (6)	O3'—C9—C1	115.1 (7)
O2'—C9—C1	122.5 (6)	O3—C9—C1	116.7 (5)

Table 2. *Hydrogen-bonding and close-contact geometry* ($\mathring{A}$, °)

D—H$\cdots$A	D—H	H$\cdots$A	D$\cdots$A	D—H$\cdots$A
O3—H33$\cdots$O2^i	0.82	1.842	2.649 (14)	168
O3′—H33′$\cdots$O2^{ii}	0.82	1.858	2.666 (17)	168
C2—H2B$\cdots$O2^{iii}	0.97	2.69	3.393 (9)	130
C7—H7A$\cdots$O1^{iii}	0.93	2.59	3.388 (3)	144

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

All non-carboxyl H atoms were found in electron-density difference maps but replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms, with their displacement parameters free to refine. Residual electron density near both the carboxyl O atoms, and averaging of carboxyl bond lengths and angles, was indicative of carboxyl disorder. The disordered carboxyl group was modeled as two rotational conformers, with carboxyl O-atom occupancies initially set to 50%. Each carboxyl group was restrained to be planar during the early cycles of refinement, but this restraint was removed once the refinement had converged. Carboxyl H atoms (with occupancies of 50% each) were added in calculated positions to the carboxyl O atom of each conformer having the longest C—O bond; their displacement parameters were fixed at 0.08$\mathring{A}^2$. The site occupancies of the two carboxyl O atoms and the H atom for both conformers were then allowed to refine with total occupancy constrained to be unity. The disordered C=O and C=O′ bond lengths were restrained to be equal to each other within 0.005 $\mathring{A}$; the same restraint was imposed on the disordered C—O and C—O′ bond lengths. The major carboxyl conformer refined to a site occupancy of 54 (2)%, and the minor component was 46 (2)%.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

References

Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). *J. Am. Chem. Soc.* **104**, 4052–4064.
Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.
Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1996). *Acta Cryst.* C**52**, 684–687.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Jönsson, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.
Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1997). *Acta Cryst.* C**53**, 1838–1842.
Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. (1998). *Acta Cryst.* C**54**, 421–424.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Lloyd, H. A. & Horning, E. C. (1954). *J. Am. Chem. Soc.* **76**, 3651–3653.
Meier, B. H., Graf, F. & Ernst, R. R. (1982). *J. Chem. Phys.* **76**, 767–779.
Nagaoka, S., Terao, T., Imashiro, F., Hirota, N. & Hayashi, S. (1983). *J. Chem. Phys.* **79**, 4694–4703.
Sheldrick, G. M. (1994). *SHELXTL/PC Users Manual.* Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *XSCANS Users Manual.* Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* C**48**, 66–70.
Wilson, C. C., Shankland, N. & Florence, A. J. (1996). *J. Chem. Soc. Faraday Trans.* **92**, 5051–5057.

β-Dihydroentandrophragmin–Ethyl Acetate (1/0.355)

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Abstract

Although the title compound, $C_{43}H_{58}O_{17}.0.355C_4H_8O_2$, from *Entandrophragma cylindricum*, exhibits significant disorder in its ester side chains, it was possible to determine the absolute configurations of the (2S)-2-methyl-butanoate and (2S)-2-hydroxy-2-methylbutanoate side-chain groups by comparison with the stereochemistry of the core secotetranortriterpenoid skeleton.

Comment

The commercially important mahogany timber trees of the genus *Entandrophragma* produce a small number of highly functionalized structurally complex secotetra-nortriterpenes, such as utilin, (I), and entandrophrag-min, (II), which are characterized by the presence of an orthoester function (Arene *et al.*, 1966; Taylor & Wragg, 1967; Harrison *et al.*, 1970; Taylor, 1974; Halsall *et al.*, 1977). Interest in natural products containing this relatively rare structural unit is stimulated by the toxic and antileukaemic activities of other orthoester-containing natural products, such as the daphnetoxin-type Thymelaeceae diterpenoids (Evans & Taylor, 1983; Baxter & Ziegler, 1994). β-Dihydroentandrophragmin, (III), was isolated previously by Halsall *et al.* (1977) and its structure deduced by comparison of its ^{13}C and ^1H NMR spectra with those of entandrophragmin, the structure and stereochemistry of which were in turn based on the crystal structure of utilin (Harrison *et al.*, 1970). However, the absolute stereochemistry of the 2-methyl-butanoate and 2-hydroxy-2-methylbutanoate side chains