Compound (II)

Crystal data

$C_{15}H_{16}O_3$
$M_r = 244.28$
Monoclinic
$P2_1/c$
$a = 7.646\ (2)$ Å
$b = 10.799\ (4)$ Å
$c = 15.446\ (5)$ Å
$\beta = 93.02\ (2)°$
$V = 1273.5\ (7)$ Å^3
$Z = 4$
$D_x = 1.274$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 6.07–15.01°$
$\mu = 0.088$ mm^{-1}
$T = 293\ (2)$ K
Hexagonal column
$0.65 \times 0.50 \times 0.30$ mm
Colorless

Data collection

Siemens $P4$ diffractometer
$2\theta/\theta$ scans
Absorption correction: none
3106 measured reflections
2245 independent reflections
1659 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$

$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.101$
$S = 1.02$
2244 reflections
169 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.399P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1—C9	1.224 (2)	O3—C8	1.301 (2)
O2—C8	1.238 (2)		
O2—C8—C2	121.56 (16)	O3—C8—C2	115.55 (17)

Table 4. *Hydrogen-bonding and close contact geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2$^{\rm i}$	0.98 (3)	1.69 (3)	2.675 (2)	178 (2)
C5—H5B···O1$^{\rm ii}$	0.97	2.49	3.423 (3)	161

Symmetry codes: (i) $1 - x, 2 - y, 2 - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

For both (I) and (II), all H(—C) atoms were found in electron-density difference maps but were replaced in calculated positions and allowed to refine in riding models. Displacement parameters for the methylene, methine and aromatic protons were refined as individual groups. Carboxyl protons were found in electron density difference maps and their positional parameters were allowed to refine with their displacement parameters fixed at 0.08 Å^2.

For both compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1565). Services for accessing these data are described at the back of the journal.

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(+)-*cis*-Pinonic acid: catemeric hydrogen bonding in a non-racemic ε-keto acid

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Abstract

The title compound, (1S,3S)-(+)-*cis*-3-acetyl-2,2-dimethylcyclobutaneacetic acid, $C_{10}H_{16}O_3$, forms carboxyl-to-ketone hydrogen-bonding catemers, with a chain of screw-related molecules passing through the cell in the b direction [O···O = 2.713 (3) Å]. Two intermolecu-

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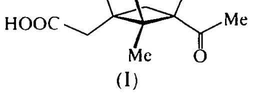
lar C—H···O═C close contacts were found to the acid carbonyl. Comparisons are made with the crystal structure of the racemate.

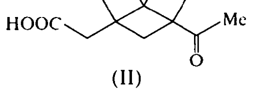
Comment

Functionally unelaborated carboxylic acids most commonly aggregate in the solid as mutually hydrogen-bonded dimers, but the presence of additional functions expands the repertoire of available hydrogen-bonding modes. For keto acids, five solid-state hydrogen-bonding motifs are known. In order of diminishing prevalence, these involve formation of acid dimers (Thompson *et al.*, 1998), carboxyl-to-ketone chains (catemers) (Zewge *et al.*, 1998), intramolecular hydrogen bonds (Thompson *et al.*, 1996), carboxyl-to-ketone dimers (Kosela *et al.*, 1995) and acid-to-acid catemers (Lalancette *et al.*, 1998). Several cases also exist of hydrates with more complex hydrogen-bonding patterns (Lalancette *et al.*, 1997, 1998).

In our continuing study of the solid-state hydrogen-bonding patterns in keto acids, *cis*-pinonic acid, commercially available as the racemate, (II), attracted our early interest because of the dramatic carbonyl-absorption shifts in its IR spectrum, signaling its unusual hydrogen-bonding pattern (Vanderhoff *et al.*, 1986). One issue of interest was whether the catemeric hydrogen-bonding mode in the non-racemic material would be altered by the packing changes forced by the absence of the enantiomer (Eliel & Kofron, 1953; Walborsky *et al.*, 1961; Simpson & Marsh, 1966; Lalancette *et al.*, 1991). However, a crystal structure of a single enantiomer eluded us because of our inability to obtain usable crystals. We now report the structure of the title compound, (+)-*cis*-pinonic acid, (I).



(I)



(II)

The asymmetric unit with the atom-numbering, identical to that used previously for the racemate, (II), is shown in Fig. 1. The conformation of (I) corresponds closely to that seen in (II), except for modest rotations about C3—C7, C1—C9 and C9—C10. The angle of fold for the cyclobutane ring in (I) is 29.8 (2)° (*cf.* 29.4° in the racemate), the C4—C3—C7—O1 torsion angle is −6.8 (4)° [(II): 1.2°], the C2—C1—C9—C10 torsion angle is 165.6 (2)° [(II): 170.8°] and the C1—C9—C10—O2 torsion angle is −17.6 (4)° [(II): 0.7°]. These angular differences are sufficiently cumulative that their net result is that, within (I), the dihedral angle for the carboxyl (C9—C10—O2—O3) *versus* acetyl (C3—C7—C8—O1) groups is 54.8 (1)°, while in (II), it is 81.9°. As in (II), both methyl groups at C2 adopt staggered arrangements and show no disorder. However, unlike the case for (II), rotational disorder was observed in the acetyl methyl for (I), with an apparent ratio of 62:38 for the two contributors.

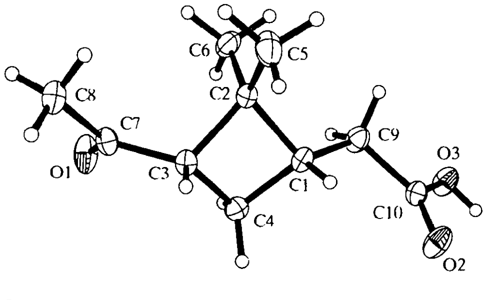


Fig. 1. Compound (I) with the atom-numbering scheme. Ellipsoids are set at the 20% probability level and H atoms are drawn as spheres of arbitrary radii. Only the major rotamer for methyl C8 is shown.

Complete or partial averaging of acid bond lengths and angles by disorder is frequent in carboxyl groups (Leiserowitz, 1976). However, this behavior is characteristic only of dimerized carboxyls and is not seen in other hydrogen-bonding arrangements, whose geometries preclude the mechanisms responsible for the usual disordering processes. Carboxyl groups in such species, including catemers, are typically highly ordered. Our own survey of 56 keto acid structures which are not acid dimers gives average values of 1.20 (1) and 1.32 (2) Å (C═O and C—O, respectively), and 124 (1) and 113 (2)° (C—C═O and C—C—O, respectively) for these lengths and angles. Values cited as typical for highly ordered dimeric carboxyls are 1.21 and 1.31 Å, and 123 and 112° (Borthwick, 1980). In (I), these values are 1.192 (3) and 1.331 (3) Å, with angles of 126.2 (2) and 111.3 (2)° [(II): 1.201 (2) and 1.329 (2) Å, and 126.1 (1) and 110.7 (1)°].

The packing of (I) in the cell, with extracellular molecules included to show two of the helical hydrogen-bonding chains of screw-related molecules, is illustrated in Fig. 2. The intermolecular O···O distance and O—H···O angle are 2.713 (3) Å and 158 (4)° [(II): 2.701 Å and 159°]. The dihedral angle between the plane of the ketone and carboxyl groups involved in any hydrogen bond is 32.9 (1)° [(II): 45.9°]. The approach of the acid proton to the ketone acceptor can be characterized using the H···O═C angle and H···O═C—C torsion angle, which describe the approach of the acid H atom to the ketone O atom in terms of its deviation, respectively, from C═O axiality (ideal = 120°) and from planarity with the ketone (ideal = 0°). In (I), these angles are

151 (1) and −6 (2)°, respectively [(II): 147 and −33.5°]. These relatively poor hydrogen-bond geometries are in accord with the slightly longer hydrogen bonds found in catemeric systems *versus* acid-to-acid dimeric systems. For 53 catemers the average O···O distance is 2.710 Å, whereas for 69 acid-to-acid dimers the average O···O distance is 2.641 Å.

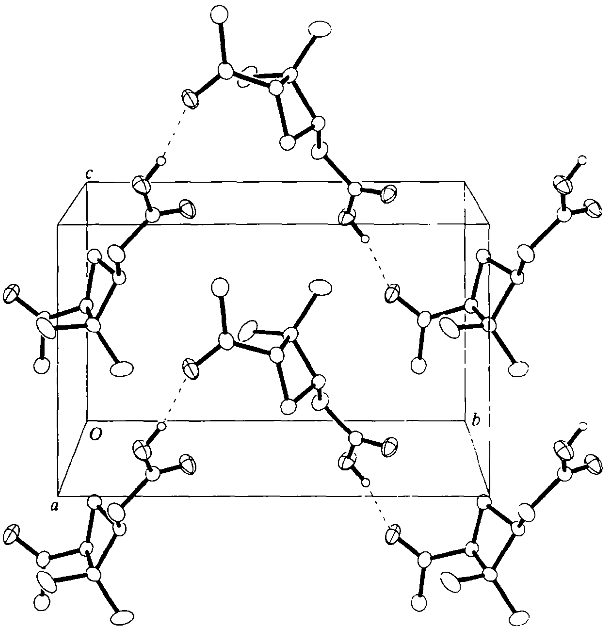


Fig. 2. A packing diagram for (I), with extracellular molecules to illustrate the acid-to-ketone catemers passing through the cell. All non-carboxyl H atoms have been removed for clarity. Ellipsoids are set at the 20% probability level.

The pitch of the hydrogen-bonding helix in (I), as previously defined by Coté *et al.* (1997), is found to be very similar to that for (II) [50.0° for (I) *versus* 51.2° for (II)] and the length of the *b* cell axis is nearly identical [11.476 (1) Å for (I) *versus* 11.484 Å for (II)].

The volume per molecule for (I) is 261.66 Å^3 *versus* 251.86 Å^3 for the racemate, reflecting a corresponding 3.9% greater density for (II). It is frequently observed that racemates pack more efficiently than single antipodes (Wallach, 1895); the density difference between (I) and (II) is larger than average, but is still well within the normal range (Brock *et al.*, 1991). Two intermolecular C—H···O═C close contacts were found to the acid carbonyl (O2), involving H4*A* (2.70 Å) and H8*F* (in the minor methyl-disorder contributor; 2.56 Å) in different screw-related neighbors. Somewhat surprisingly, considering its denser packing, the racemate has no such intermolecular contacts within 2.7 Å.

The KBr IR spectrum of (I) displays absorptions at 1735 and 1682 cm^{-1}, conforming to known shifts due, respectively, to removal of hydrogen bonding from an acid C═O and addition of hydrogen bonding to a saturated ketone. In (II), these peaks are at 1733 and 1683 cm^{-1} (Vanderhoff *et al.*, 1986). In $CHCl_3$ solution, where dimers predominate, the peaks for both (I) and (II) coalesce to a single absorption at 1709 cm^{-1}.

Experimental

Compound (I), of known absolute configuration and rotation, was synthesized by $KMnO_4$ oxidation (Delépine, 1936; Muscio & Poulter, 1974) of (+)-pinene of known absolute configuration, purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, USA. Crystals of (I) (m.p. 341 K) were obtained from *tert*-butyl methyl ether/hexane after failure with numerous other solvent systems, which gave crystals showing IR evidence of dimers but yielding unsolvable data sets.

Crystal data

$C_{10}H_{16}O_3$
$M_r = 184.23$
Monoclinic
$P2_1$
$a = 6.625\,(1)$ Å
$b = 11.476\,(1)$ Å
$c = 7.127\,(1)$ Å
$\beta = 105.03\,(1)°$
$V = 523.32\,(12)$ Å^3
$Z = 2$
$D_x = 1.169$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 3.48$–$15.57°$
$\mu = 0.085$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
0.58 × 0.46 × 0.38 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: analytical (face-indexed numerical; Sheldrick, 1997)
$T_{\min} = 0.96$, $T_{\max} = 0.97$
2350 measured reflections
1090 independent reflections
966 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.022$
$\theta_{\max} = 26°$
$h = -8 \rightarrow 8$
$k = -14 \rightarrow 14$
$l = -8 \rightarrow 8$
3 standard reflections every 97 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.089$
$S = 1.06$
1090 reflections
135 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.0367P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.11$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C7	1.206 (3)	O3—C10	1.331 (3)
O2—C10	1.192 (3)		
O2—C10—C9	126.2 (2)	O3—C10—C9	111.3 (2)

Table 2. *Hydrogen-bonding and C—H···O contact geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.75 (4)	2.00 (4)	2.713 (3)	158 (4)
C4—H4A···O2^{ii}	0.97	2.70	3.661 (3)	173
C8—H8F···O2^{iii}	0.96	2.56	3.451 (3)	154

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

All H atoms were found in electron-density difference maps but were replaced in calculated positions and allowed to refine as riding models, except for the hydroxyl H3 atom whose coordinates and isotropic temperature factor were allowed to refine individually. The occupancy for the disordered methyl group (C8) was refined. Isotropic displacement parameters for methylene and carboxyl H atoms were allowed to refine individually, whilst isotropic displacement parameters for the methyl protons on C5, C6 and C8 were refined as individual groups.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1455). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1911–1913

N,*N*′-Bis(3-methoxyphenyl)-1,8:4,5-naphthalenetetracarboximide–trifluoroacetic acid–phenol (1/2.5/0.5)

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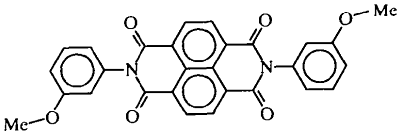
Abstract

In the title compound, $C_{28}H_{18}N_2O_6 \cdot 2.5C_2HF_3O_2 \cdot 0.5C_6H_6O$, the naphthalenetetracarboxylic diimide moiety lies about an inversion centre and is planar, but conjugation between the phenyl substituent and the tetracyclic fragment is disrupted due to rotation around C—N bonds.

Comment

Derivatives of 1,8:4,5-naphthalenetetracarboxylic diimide (NTCDI) have been known for a long time (Patai, 1970). Their electronic and spectral properties and the ability to co-polymerize with different amines to give rigid-chain heterocyclic polyimides have been widely studied and used (Khiefets *et al.*, 1977; Zhong *et al.*, 1992; Cammarata *et al.*, 1992; Orzeszko & Sikorski, 1993; Gajiwala & Zand, 1993, 1995; Zhou & Lu, 1995; Adachi *et al.*, 1995; Lokey *et al.*, 1997; Borsenberger *et al.*, 1996). Knowledge of the molecular structure of NTCDI derivatives is essential for explaining and understanding their unusual properties. However, only a few structures of intercalative complexes of NTCDI have been studied (Jazwinski *et al.*, 1987; Shimizu *et al.*, 1994; Houghton *et al.*, 1997; Staab *et al.*, 1997). Here we report the results of an investigation of the *N*,*N*′-bis[(3-methoxyphenyl)imide] of 1,8:4,5-naphthalenetetracarboxylic acid, (I).



$\cdot 2.5C_2HF_3O_2 \cdot 0.5C_6H_6O$

(I)

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