Scan widths were $(1.50 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group *Pbca* (No. 61). Since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The maximum effect of extinction was 9.3% of F_o for 002. The maximum positive residual peak was located ~1.5 Å from O2 and the maximum negative peak was located ~1.7 Å from C13.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MITHRIL*84 (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

I thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1083). Services for accessing these data are described at the back of the journal. Least-squares planes data and a list of C—H···O interactions have also been deposited.

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Hydrogen Bonding and Ring Asymmetry in (±)-*cis*-2-Phenylcyclopropanecarboxylic Acid

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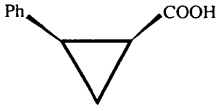
Abstract

The title compound, (±)-*cis*-2-phenylcyclopropanecarboxylic acid, $C_{10}H_{10}O_2$, crystallized in the centrosymmetric space group $P2_1/n$. The hydrogen bonding is of the cyclic dimer type about a center of symmetry; the $O_{donor}\cdots O_{acceptor}$ distance is 2.645 (2) Å. The carboxylic H atom is ordered, as are the O atoms. The cyclopropane ring is asymmetric; the values found for the asymmetry parameters are δ(COOH) = −0.045 (4) Å and δ(phenyl) = −0.027 (4) Å.

Comment

This study of (±)-*cis*-2-phenylcyclopropanecarboxylic acid, (I), is one of a continuing series on hydrogen bonding in carboxylic acids and follows a study of (+)-*trans*-(1*S*,2*S*)-2-phenylcyclopropanecarboxylic acid (Gerkin, 1997). In the title acid, hydrogen bonding is of the cyclic dimer type about a center of symmetry, as shown in Fig. 1, which also presents the adopted numbering scheme. The first-level graph set (Bernstein *et al.*, 1995) is thus $R_2^2(8)$ and there are no higher level sets. Geometric details of the hydrogen bond are given in Table 1. Data presented in Table 1 establish that the carboxylic H atom and the carboxylic O atoms are ordered.



(I)

Additional interest in the title molecule is, as for the *trans* isomer, associated with the determination of substituent-induced bond-length asymmetry in the cyclopropane ring, as discussed in detail by Allen (1980), particularly since there are few characterized structures in which sparsely substituted phenyl groups are substituents. In the present molecule, pronounced bond asymmetry in the cyclopropane ring is again observed: the bond distal to the unsubstituted ring site is longer than each of the two vicinal bonds, which

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have rather different lengths from each other. Consistent with the principle of additivity of bond-length asymmetries (Allen, 1980), bond asymmetry parameters for the carboxy and phenyl groups are found to be δ(COOH) = −0.045 (4) Å and δ(phenyl) = −0.027 (4) Å. The rounded values of the torsion angles $X1$—C1—C4—O2, $X2$—C2—C5—C6 and $X2$—C2—C5—C10 (in which $X1$ and $X2$ are the midpoints of the respective distal bonds) are 17, 130 and −53°, respectively, indicating *cis* bisected and *gauche*(2) configurations for the carboxy and phenyl groups, respectively. The value for δ(COOH) reported here is in only moderate agreement with Allen's mean value for carbonyl groups, −0.026 (5) Å, but in better agreement with the value found for δ(COOH) for the *trans* isomer, −0.034 (4) Å. The value for δ(phenyl) is in reasonable agreement with Allen's mean value for phenyl groups, −0.018 (2) Å, but in excellent agreement with the value for the *trans* isomer, −0.028 (4) Å.

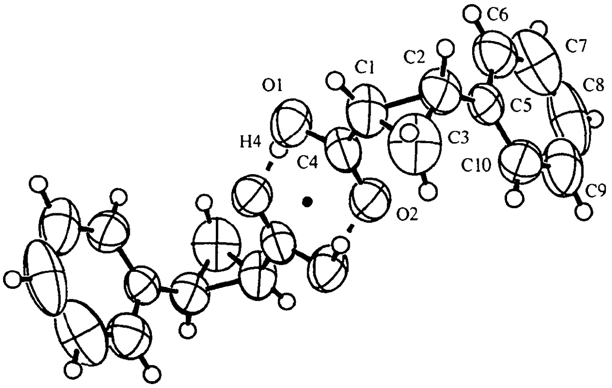

Fig. 1. *ORTEP*II (Johnson, 1976) diagram of the (±)-*cis*-2-phenylcyclopropanecarboxylic acid cyclic hydrogen-bonded dimer showing the molecular numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H for which they have been set artificially small. The hydrogen bonds are shown as dashes, the center of symmetry as a filled sphere.

The geometric disposition of the two rings and the carboxy group can be characterized by three dihedral angles between pairs of planes. The phenyl group of the molecule is very closely planar, the maximum deviation of a phenyl C atom from the best-fit plane being 0.002 (2) Å. The dihedral angles are: phenyl–cyclopropyl 60.6 (2)°, carboxy–cyclopropyl 81.2 (3)° and carboxy–phenyl 74.2 (3)°.

Bond distances and angles of special interest are given in Table 1. As noted above, bonds C1—C3 and C2—C3 have rather different lengths, in contrast to the case for the *trans* isomer in which they are virtually equal. In addition to the *trans* isomer, a suitable molecule for geometric comparisons of the cyclopropyl ring is (*E*)-2-*p*-nitrophenylcyclopropyl methyl ketone (Bordner, Jones & Johnson, 1972), in which the bond distances are as follows: C1—C3 1.49 (1), C2—C3 1.48 (1) and C1—C2 1.51 (1) Å. In view of the variable geometry of the cyclopropyl ring depending upon the identity and orientation of the substituent groups, this represents quite satisfactory agreement. The remaining intramolecular distances and angles fall within normal ranges. Refined H atoms give C—H distances ranging from 0.89 (2) to 0.99 (2) Å, with a mean value of 0.95 Å, and $U_{\rm iso}$ values ranging from 0.75 to 1.34 times the $U_{\rm eq}$ value of the respective attached C atom, the mean being $1.10U_{\rm eq}$(C). The refined O—H distance is given in Table 1. The closest intermolecular approach, excluding pairs of atoms in hydrogen-bonded carboxy groups, is between O2 and H7$^{\rm ii}$ [symmetry code: (ii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$] and differs by less than its e.s.d. (0.02 Å) from the corresponding sum of the Bondi (1964) van der Waals radii. Thus, there should be no influence of crowding on the values of the asymmetry parameters given above for the title molecule.

Experimental

(±)-*cis*-2-Phenylcyclopropanecarboxylic acid was obtained as colorless small plates and granules from a sample in the chemical collection of Dr M. S. Newman. This material was dissolved in ether. Evaporation of the solution at room temperature produced slabs, one of which was cut to provide the experimental sample.

Crystal data

$C_{10}H_{10}O_2$
M_r = 162.19
Monoclinic
$P2_1/n$
a = 8.480 (1) Å
b = 9.336 (1) Å
c = 11.187 (1) Å
β = 98.351 (2)°
V = 876.3 (2) Å^3
Z = 4
D_x = 1.229 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.0–17.3°
μ = 0.085 mm^{-1}
T = 296 K
Cut chunk
0.50 × 0.35 × 0.31 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2249 measured reflections
2147 independent reflections
2018 reflections with $I > 0$
$R_{\rm int}$ = 0.010

$\theta_{\rm max}$ = 27.56°
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
6 standard reflections every 150 reflections intensity decay: 11.2%

Refinement

Refinement on F^2
R = 0.060
wR = 0.080

$\Delta\rho_{\rm max}$ = 0.26 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.29 e Å^{-3}
Extinction correction: none

$S = 1.39$
2018 reflections
149 parameters
All H atoms refined
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{\max} < 0.01$

Scattering factors from Stewart, Davidson & Simpson (1965) (H) and Creagh & McAuley (1992) (C, O)

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

O1—C4	1.308 (2)	C1—C4	1.463 (3)
O2—C4	1.217 (2)	C2—C3	1.462 (3)
C1—C2	1.529 (3)	C2—C5	1.487 (3)
C1—C3	1.488 (3)		
C2—C1—C3	58.0 (2)	O1—C4—O2	123.1 (2)
C1—C2—C3	59.6 (2)	O1—C4—C1	113.2 (2)
C1—C3—C2	62.4 (2)	O2—C4—C1	123.7 (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H4···O2^{i}	0.93 (2)	1.71 (3)	2.645 (2)	176 (2)

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

One quadrant of data was collected in the $P2_1/c$ setting. Scan widths were $(1.50 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences following a cell transformation and centrosymmetric intensity statistics then indicated space group $P2_1/n$. Since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions. The extinction parameter was predicted to be negative and was not included in the refinement. The maximum positive residual peak was located ~1.0 Å from C7; the maximum negative peak was located ~1.0 Å from O1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

I thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1081). Services for accessing these data are described at the back of the journal.

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1,4,5,8-Naphthalenetetracarboxylic Acid Cyclic 1,8-Anhydride Bis(dimethyl sulfoxide) Solvate and 1,4,5,8-Naphthalenetetracarboxylic 1,8:4,5-Dianhydride

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Abstract

1,4,5,8-Naphthalenetetracarboxylic acid cyclic 1,8-anhydride crystallized from dimethyl sulfoxide (DMSO) as the solvate, $C_{14}H_6O_7.2C_2H_6OS$, in the centrosymmetric space group $P\bar{1}$. Two O—H···O hydrogen bonds with O···O distances of 2.592 (3) and 2.598 (3) Å are formed, with the two carboxylic acid OH groups as donors and the O atoms of the two inequivalent DMSO molecules as acceptors. The carboxylic H atoms are ordered, as are the carboxylic O atoms. In addition to the conventional hydrogen bonds, there are numerous C—H···O interactions consistent with the large number of potential CH donors and O-atom acceptors. 1,4,5,8-Naphthalenetetracarboxylic 1,8:4,5-dianhydride, $C_{14}H_4O_6$, crystallized in the centrosymmetric space group $P2_1/c$ with half the molecule as the asymmetric unit. Each molecule is involved in four significant C—H···O interactions as a donor and in an additional four as an acceptor. These eight interactions link each molecule to six neighboring molecules, forming a three-dimensional network. Geometric parameters of both substances are in general agreement with analogous parameters for naphthalic anhydride, monosodium 1,4,5,8-naphthalenetetracarboxylic acid cyclic 1,8-anhydride monohydrate and 1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-dianhydride, as reported previously.

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