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Hydrogen Bonding and Ring Asymmetry in a Substituted Cyclopropane: (+)-*trans*-(1*S*,2*S*)-2-Phenylcyclopropanecarboxylic Acid at 208 K

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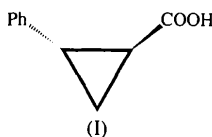
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Abstract

The title compound, C₁₀H₁₀O₂, crystallized in space group *P*2₁ with two molecules in the asymmetric unit. In this structure, hydrogen bonding of the cyclic dimer type [with O··O 2.623(2)–2.637(2) Å] links the two molecules of the asymmetric unit. The two carboxylic H atoms are ordered, as are the O atoms. Each of the two non-equivalent molecules exhibits an asymmetric cyclopropane ring; the values found for the asymmetry parameters are $\delta(\text{COOH}) = -0.034(4)$ and $-0.025(4)$ Å, and $\delta(\text{phenyl}) = -0.028(4)$ and $-0.023(4)$ Å.

Comment

This study is one of a continuing series on hydrogen bonding in carboxylic acids. In the title compound, (I), the hydrogen bonding is of the cyclic dimer type and links the two crystallographically non-equivalent molecules of the asymmetric unit, as shown in Fig. 1. The absolute configuration is known from previous chemical studies (see *Experimental* section). Geometric details of the hydrogen bonds are given in Table 2. The hydrogen bonds run very nearly along [10 $\bar{2}$].



Additional interest in (I) is associated with 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 lightly substituted phenyl groups are substituents. Bond asymmetry in the cyclopropane ring is observed in both the *A* and *B* molecules of (I); in both molecules, the bond distal to the unsubstituted ring site is longer than the two proximal bonds, which have nearly equal lengths. Consistent with the principle of additivity of bond-length asymmetries (Allen, 1980), bond-asymmetry parameters for the carboxyl and phenyl groups are found to be $\delta(\text{COOH}) = -0.034(4)$ and $-0.025(4)$ Å, and $\delta(\text{phenyl}) = -0.028(4)$ and $-0.023(4)$ Å for the *A* and *B* molecules, respectively. For the *A* molecule, the rounded torsion angles X1A—C1A—C4A—O2A, X2A—C2A—C5A—C6A and X2A—C2A—C5A—C10A (in which X1A and X2A are the midpoints of the respective distal bonds) are 21, -167 and 11° , indicating *cis* bisected and perpendicular conformations for the carbonyl and phenyl groups, respectively; for the *B* molecule, the analogous torsion angles are -161 , 178 and -2° , indicating *trans* bisected and perpendicular configurations for the carbonyl and phenyl groups, respectively. How such similar values for the bond-shortening effects of carbonyl groups can arise, despite differences in their configurations with respect to the ring, has been studied by Allen (1980). The values for $\delta(\text{COOH})$ reported here are in good agreement with Allen's (1980) mean value for carbonyl groups, $-0.026(5)$ Å, and the values for $\delta(\text{phenyl})$ are in reasonable agreement with his mean value for phenyl groups, $-0.018(2)$ Å. The most direct individual comparisons for (I) are from *trans*-2-(*p*-tolyl)cyclopropanecarboxylic acid (Ramirez, Rivera, Rodulfo de Gil, Alonso & Pékerar, 1990) and from ethyl *trans*-2-phenylcyclopropanecarboxylate (Mora, Rivera, Rodulfo de Gil, Alonso & Pékerar, 1991). The first cited study gives asymmetry parameters $\delta(\text{tolyl}) = -0.009$ and $\delta(\text{COOH}) = -0.026$ Å, but based on the stated e.s.d.'s, the estimated uncertainty of these values is ~ 0.015 Å; thus, they cannot be regarded as very firmly established. In the second cited study, no ring asymmetry was detected, most likely (as noted by the authors) due to the large uncertainties (0.02 Å) in ring bond lengths. It should be noted further that in the structure of *cis*-1,2-diphenylcyclopropane (Schmidbaur, Bublak, Schier, Reber & Müller, 1988), the two bonds proximal to the unsubstituted ring site are reported to differ from each other in length almost as much as the larger differs from the distal bond; thus, calculation of a (single) phenyl asymmetry parameter is precluded.

The geometric disposition of the two rings and the carboxyl group can be characterized by three dihedral angles between pairs of planes. The phenyl groups of the *A* and *B* molecules are closely planar, the maximum deviation of a phenyl C atom from the best-fit plane

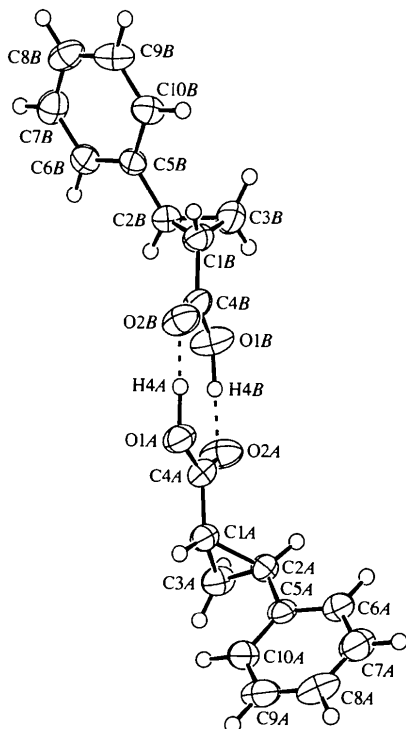


Fig. 1. An ORTEP (Johnson, 1976) diagram of the cyclic hydrogen-bonded dimer of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all non-H atoms; H atoms have been drawn artificially small. The hydrogen bonds are shown as dashed lines.

being 0.008 Å for the A molecule and 0.006 Å for the B molecule. The dihedral angles for the A and B molecules are, respectively, phenyl–cyclopropyl 88.3 (2) and 86.9 (2)°, carboxyl–cyclopropyl 82.5 (4) and 81.9 (4)°, and carboxyl–phenyl 89.0 (2) and 72.0 (3)°.

Bond distances and angles of special interest are given in Table 1. The remaining intramolecular distances and angles fell within normal ranges. Refined H atoms gave C—H distances ranging from 0.94 (3) to 1.00 (2) Å; the two refined O—H distances appear in Table 2. The closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxyl groups, are between O2A and H3B²¹ [symmetry code: (i) 1 - x, 1/2 + y, 2 - z], and are 0.16 Å less than the corresponding Bondi (1964) radius sum. No other approach is deficient by more than 0.08 Å. Thus, there should be no substantial steric influence on the asymmetry parameter values given above for (I).

Experimental

The title compound was obtained for X-ray study as a colorless clear plate from a small sample so labeled in the chemical collection of Dr M. S. Newman. This crystal was mounted

with Apiezon grease on a quartz pin for low-temperature study. A 15.8 (5) mg portion from the same sample, consisting largely of clear plates but containing some adherent small clusters of pale ecru needles, was dissolved in absolute ethanol to form a 2.00 (6) ml solution for optical polarimetry. The optical data show that the sample is dextrorotatory, as labeled, with $[\alpha]_D^{20} = +283^\circ$; the estimated uncertainty in c (the dominant uncertainty in these measurements), due approximately equally to mass and volume measurements, is ~6%, consistent with an upper limit for $[\alpha]_D^{20}$ of $+302^\circ$. Inouye, Sugita & Walborsky (1964) reported $[\alpha]_D^{22}$ ($c = 1.776$, EtOH) = $+311.7^\circ$ for a sample of this acid of high optical purity; the same report established the absolute configuration as 1*S*,2*S*. Since the conditions of the two polarimetry determinations are very similar, the degree of optical purity of the premium single-crystal X-ray sample can be properly expected to be very high. The X-ray results are thoroughly consistent with this expectation.

Crystal data

$C_{10}H_{10}O_2$
 $M_r = 162.19$
 Monoclinic
 $P2_1$
 $a = 12.038$ (2) Å
 $b = 5.506$ (1) Å
 $c = 13.087$ (1) Å
 $\beta = 94.576$ (9)°
 $V = 864.6$ (2) Å³
 $Z = 4$
 $D_x = 1.246$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 15.0$ – 17.2°
 $\mu = 0.080$ mm⁻¹
 $T = 208$ K
 Plate
 $0.50 \times 0.42 \times 0.11$ mm
 Colorless

Data collection

Rigaku AFC-5S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2892 measured reflections
 2777 independent reflections
 2773 reflections with $I > 0$
 $R_{int} = 0.024$

$\theta_{max} = 30.06^\circ$
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 7$
 $l = -18 \rightarrow 18$
 6 standard reflections
 every 150 reflections
 intensity variation: $\pm 2.1\%$
 (average maximum relative intensity)

Refinement

Refinement on F^2
 $R = 0.058$
 $wR = 0.068$
 $S = 1.60$
 2773 reflections
 256 parameters
 H atoms: see below
 $w = 1/\sigma^2(F^2)$
 $(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max} = 0.31$ e Å⁻³
 $\Delta\rho_{min} = -0.27$ e Å⁻³
 Extinction correction: none
 Scattering factors from Stewart, Davidson & Simpson (1965) (H), and Creagh & McAuley (1992) (C, O)

Table 1. Selected geometric parameters (Å, °)

O1A—C4A	1.291 (3)	O1B—C4B	1.277 (4)
O2A—C4A	1.238 (3)	C1B—C2B	1.523 (4)
C1A—C2A	1.539 (3)	C1B—C3B	1.488 (4)
C1A—C3A	1.497 (4)	O2B—C4B	1.250 (3)
C2A—C3A	1.488 (4)	C2B—C3B	1.485 (3)

C2A—C1A—C3A	58.7 (2)	C2B—C1B—C3B	59.1 (2)
C1A—C2A—C3A	59.2 (2)	C1B—C2B—C3B	59.3 (2)
C1A—C3A—C2A	62.1 (2)	C1B—C3B—C2B	61.6 (2)
O1A—C4A—O2A	123.7 (2)	O1B—C4B—C1B	116.9 (3)
O1A—C4A—C1A	115.6 (2)	O1B—C4B—O2B	124.0 (2)
O2A—C4A—C1A	120.6 (2)	C1B—C4B—O2B	119.2 (3)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H4A...O2B	1.15 (4)	1.49 (4)	2.637 (2)	177 (5)
O1B—H4B...O2A	1.10 (4)	1.53 (4)	2.623 (2)	176 (6)

Fourier difference methods were used to locate the initial H-atom positions. In later stages of the refinement, the benzene ring H atoms were made canonical with a C—H distance 0.98 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the associated C atom. All other H atoms were refined isotropically.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1312). Services for accessing these data are described at the back of the journal.

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Intermediates in the Synthesis of Cembrane Diterpenes. I

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Abstract

The molecular structure of *rac*-(1*R*,2*R*,3*S*,7*S*)-3-hydroxy-5-isopropyl-2-methyltricyclo[8.4.0.0^{2,7}]tetradeca-4,9-dien-6-one, C₁₈H₂₆O₂, has an all-*cis* ring-fusion tricyclic structure, with an overall distorted hemispherical conformation (the hydroxyl group is opposite the other substituents). The cyclohexenone ring is in a half-chair conformation, the cyclohexene ring is in a distorted half-chair conformation and the cyclohexane ring adopts an almost ideal chair conformation. The molecules are linked through a hydrogen bond.

Comment

In our synthetic endeavors towards the cembrane diterpenes [carbon skeleton (1)], we have envisaged the construction of tricyclic intermediates by way of recently developed Diels–Alder reactions and further functional modifications preceding key fragmentation reactions (Brocksom *et al.*, 1994). The success of this reaction sequence depends mainly on the generation of key intermediates with the correct functionality and relative stereochemistry for C—C bond fragmentation, which is basically an antiperiplanar process. Therefore, unambiguous stereostructure determination of the intermediates is required.

