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trans-(1*R*,2*R*)-1-Benzyl-2-phenylcyclopropanecarboxylic acid

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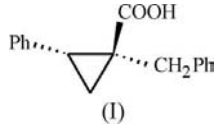
The cyclopropane ring of the title compound, $C_{17}H_{16}O_2$, shows a high level of substituent-induced bond-length asymmetry. The carboxyl group adopts a conformation that prompts electron-density transfer from the ring towards the carbonyl π system.

Comment

Cyclopropanes are interesting building blocks often used in modern organic synthesis (de Meijere *et al.*, 2006). In particular, cyclopropanecarboxylate groups are found in a number of biologically active species (Tombo & Bellus, 1991). Their synthesis is mostly based on a classical homologues Wittig reaction (Donaldson, 2001). Recently, we proposed a novel method based on transformation of the substituted α-phosphono-γ-lactones into the corresponding ethyl cyclopropanecarboxylates by treatment with sodium ethoxide in boiling tetrahydrofuran (Krawczyk *et al.*, 2005, 2008). The title compound, (I), is a key product of this synthesis. Moreover, cyclopropane is an obvious example of a simple chemical system characterized by a substantial ring strain energy. Its molecular orbitals are prone to interactions with the exocyclic π electrons (Cameron *et al.*, 1990). Spectroscopic and chemical studies have shown that the cyclopropyl group is similar to a double bond in many respects (Lauher & Ibers, 1975; Jason & Ibers, 1977).



(I)

A view of (I) with the atom-numbering scheme is shown in Fig. 1. The endocyclic C—C bonds show a distinctive bond-length asymmetry. The shortest bond (C1—C2; Table 1) is located opposite the carboxyl and benzyl substituents, while the longest (C2—C3) is positioned in front of the unsubstituted endocyclic C1 atom. C1—C3 is a distal bond for the phenyl substituent. Substituent-induced bond-length asymmetry in cyclopropanes was studied in a very systematic way by Allen (1980). He demonstrated that interactions of the Walsh (1947, 1949) orbitals with a π system of the substituent are responsible for the bond-length differences. In particular, for the carboxyl and carboxylate group, the maximum overlap occurs if the torsion angle τ ($X_{n,m}$—C—C═O) is 0 or 180° ($X_{n,m}$ is the mid-point of the distal C_n—C_m bond). For the title compound, the value is −164.6 (2)° (the *trans–gauche* conformation) and indicates a high level of orbital interactions. For the phenyl substituent, Allen suggests to calculate τ as an average of the two torsion angles $X_{C1,C3}$—C2—C12—C13 and $X_{C1,C3}$—C2—C12—C17; these angles should be normalized to the range (−90, 90°). The value calculated for (I) [τ = 63.4 (4)°] indicates that the phenyl ring adopts a conformation intermediate between *gauche* and *perpendicular*. The vicinal C3—C4 and C2—C12 bond lengths are very close to the model values (1.476 and 1.502 Å) as specified by Allen for the carboxylate and phenyl substituents, respectively.

The *trans–gauche* conformation of the carboxylic acid substituent prompts electronic interactions involving the bonding σ,π and antibonding σ*,π* orbitals. The most important interactions (Table 3 and Fig. 2) were computed by the Weinhold natural bond orbitals deletion procedure (Glendening *et al.*, 1992) for the wavefunctions calculated with *GAUSSIAN03* (Frisch *et al.*, 2004) at the B3LYP/6–311++G(*d*,*p*) level of theory for the X-ray-determined coordinates.

In particular, the endocyclic C1—C3 and C2—C3 bonds participate in electron-density transfer towards the carbonyl group in a σ–π* fashion (Graczyk & Mikołajczyk, 1994) (28.5 and 11.6 kJ mol^{-1}, respectively), while the reverse back-donation is much weaker (1.8 and 6.6 kJ mol^{-1}, respectively). In comparison with the above effect, interaction of the phenyl ring with the cyclopropane ring has a more complex character and involves significant mutual σ–π* and σ*–π interactions (19.7 and 13.1 kJ mol^{-1}, respectively).

In the crystal, molecules form centrosymmetric dimers connected by strong hydrogen bonds (Table 2) linking

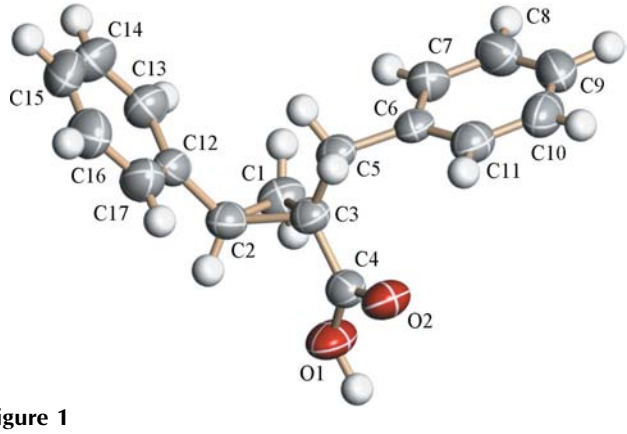


Figure 1
The molecule of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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carboxyl groups of both monomers. In terms of graph-set terminology (Etter *et al.*, 1990; Bernstein *et al.*, 1995), this system can be described as $R_2^2(8)$.

Experimental

To a suspension of sodium hydride (6.0 mmol) and α-diethoxyphosphoryl-α-benzyl-γ-phenyl-γ-butyrolactone (6.0 mmol) in tetrahydrofuran (15 ml) was added dropwise under an argon atmosphere at room temperature a solution of ethanol (0.40 ml) in tetrahydrofuran (15 ml). The reaction mixture was stirred for 0.5 h and then heated under reflux for 8 h. After cooling to room temperature, saturated NaCl solution (5 ml) was added, and the tetrahydrofuran was evaporated under reduced pressure. The residue was extracted with dichloromethane (3 × 15 ml) and dried (Na_2SO_4). After evaporation, the crude product was purified by column chromatography and subsequently hydrolyzed to give (I). Good quality single crystals were selected from the reaction mixture (Krawczyk *et al.*, 2007).

Crystal data

$C_{17}H_{16}O_2$
M_r = 252.30
Triclinic, $P\overline{1}$
a = 5.9983 (2) Å
b = 9.5439 (4) Å
c = 12.7293 (5) Å
α = 111.330 (1)°
β = 92.188 (1)°
γ = 97.965 (1)°
V = 669.15 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 (2) K
0.50 × 0.20 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2003)
T_{min} = 0.872, T_{max} = 0.988
9804 measured reflections
2348 independent reflections
2270 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.112
S = 1.07
2348 reflections
176 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.481 (2)	C3—C4	1.4779 (19)
C1—C3	1.508 (2)	O2—C4	1.2362 (17)
C2—C3	1.540 (2)	C3—C5	1.5152 (19)
C2—C12	1.491 (2)		
C2—C1—C3	62.02 (10)	C1—C3—C2	58.10 (10)
C1—C2—C3	59.88 (10)		
C1—C3—C4—O2	161.92 (14)	C1—C2—C12—C13	27.5 (2)
C2—C3—C4—O2	−132.99 (14)	C1—C2—C12—C17	−155.23 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	1.02 (3)	1.61 (3)	2.629 (2)	175 (2)

Symmetry code: (i) $-x+2, -y+2, -z$.

Table 3
Energy of the selected electronic interactions calculated with the natural bond orbital (NBO) theory.

Type of interaction	Stabilization energy (kJ mol^{-1})
σ(C1—C3)–π*(C4═O2)	28.5
π(C4═O2)–σ*(C1—C3)	1.8
σ(C2—C3)–π*(C4═O2)	11.6
π(C4═O2)–σ*(C2—C3)	6.6
σ(C1—C2)–π*(C12—C17)	19.7
π(C12—C17)–σ*(C1—C2)	13.1

H atoms were located in a difference Fourier map. Those bonded to C atoms were refined as riding. The hydroxyl atom H1 was refined without restraints.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used

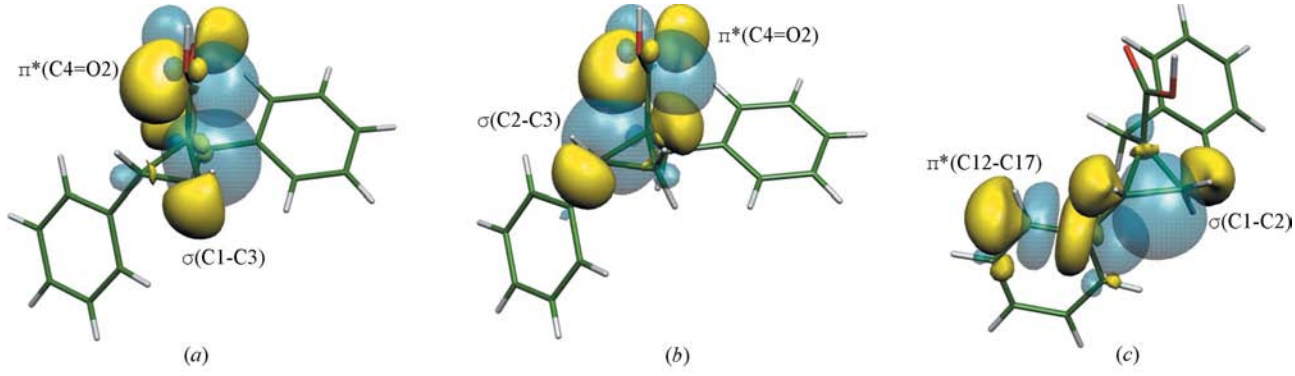

Figure 2
Natural bond orbitals, as in (I), involved in the electron-density transfer from the vicinal (*a*) C1—C3 and (*b*) C2—C3 bonds to the carbonyl group C4═O2, accompanied by (*c*) the orbitals describing the major cyclopropyl–phenyl interactions.

to prepare material for publication: *SHELXTL* and *publCIF* (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3113). Services for accessing these data are described at the back of the journal.

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