Norbornane-*endo-cis*-2,3-dicarboxylic acid

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Key indicators

Single-crystal X-ray study
$T = 150$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.049
wR factor = 0.123
Data-to-parameter ratio = 13.9

For details of how these key indicators were
automatically derived from the article, see
http://journals.iucr.org/e.

The structure of the title compound, $C_9H_{12}O_4$, contains two independent molecules in the asymmetric unit, with an unusually strong twist around the norbornane C2—C3 bond.

Comment

The title compound, (I), alternatively called bicyclo[2.2.1]-heptane-*endo-cis*-2,3-dicarboxylic acid, was studied as part of a series of small-molecule models of organic polymers influencing the crystallization of inorganic salts, particularly $CaCO_3$ (Megson, 1997; Feast *et al.*, 2002).

(I)
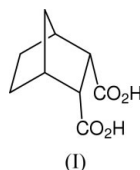
Compound (I) was prepared following the usual route through 'kinetic' (at moderate temperature) Diels–Alder addition of cyclopentadiene to maleic anhydride, hydrolysis of the anhydride to form 2-norbornene-*endo-cis*-5,6-dicarboxylic acid, (II), and hydrogenation of the C=C bond of the latter (Diels & Alder, 1928; Alder & Stein, 1933*a,b*). The only previous structural characterization of (I) was in the form of a copper complex of its monoanion (Geraghty *et al.*, 1999). However, the precision of that structure is too low ($R = 0.18$) to permit any meaningful comparison with the present one.

The asymmetric unit of (I) comprises two molecules, *A* and *B* (Fig. 1). Both show rather large torsion angles (HO_2)C—C2—C3—C(O_2H) of −18.4 (2) and −19.7 (2)°. Obviously, this can be attributed to the steric repulsion between *cis*-carboxylic acid groups. However, the corresponding torsion angles are much smaller in some closely related molecules, where the steric overcrowding must be comparable, *viz.* 6.2° in (II) (Bolte *et al.*, 2000), 5.2° in its potassium salt (Cser & Sasvari, 1976), 3.6 (2)° in the *exo–cis* isomer of (I) (Batsanov & Hesselink, 2002*b*), 4.7 (2), 0.6 (2) and 6.3 (2)° in the three independent molecules of the *endo–cis* isomer of (II) (Batsanov & Hesselink, 2002*a*), 12.2 and 11.5° in the isostructural Mn and Co complexes, containing anions of (II) as monodentate ligands (Hartung *et al.*, 1993), and 4.5° in the Mn complex with a bidentate dianion of (II), coordinated *via* both carboxylate groups (Devereux *et al.*, 1995). A possible explanation is a peculiar orientation of the carboxylic acid groups in (I). In both independent molecules, one of the carboxyl C=O bonds is almost eclipsed with the norbornane C2—C3 bond. Thus, a carbonyl O atom of one carboxylic acid group forms a short intramolecular contact with the C atom of
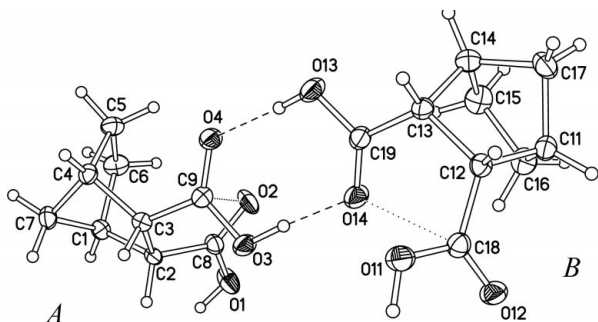
Figure 1
The independent molecules, *A* and *B*, in the structure of (I), showing displacement ellipsoids at the 50% probability level, hydrogen bonds (dashed lines) and short intramolecular O···C contacts (dotted lines).
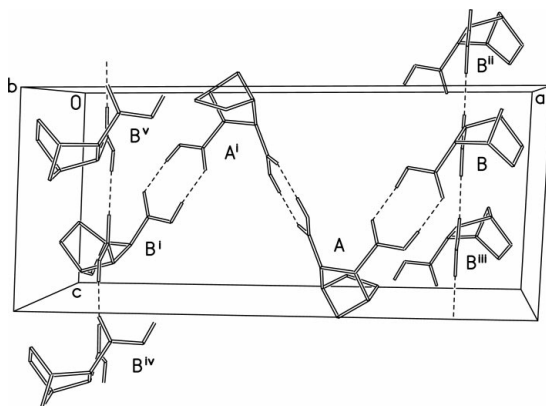

Figure 2
Hydrogen bonding in the structure of (I). [Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x, \frac{1}{2} - y, z + \frac{1}{2}$; (iv) $1 - x, y + \frac{1}{2}, \frac{3}{2} - z$; (v) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$.]

the other carboxylic acid group, *viz.* O2···C9 = 2.694 (2) Å and O14···C18 = 2.762 (2) Å, much shorter than the normal van der Waals O···C contact distance of 3.24 Å (Rowland & Taylor, 1996). The conformation of (II) is somewhat similar, but the corresponding O···C contact is much longer, 2.92 Å. In other analogues (see above), carboxylic acid groups are inclined with respect to the C1/C2/C3/C4 plane in the same direction, in a 'propeller' conformation.

Molecules *A* and *B* are linked by a pair of hydrogen bonds, as shown in Fig. 1. The other carboxylic acid group of molecule *B* forms a similar pair of hydrogen bonds with its inversion equivalent, thus forming an $A \cdots B \cdots B^{i} \cdots A^{i}$ tetramer (symmetry code as in Fig. 2). The remaining carboxylic acid group of molecule *A* adopts a less common *anti* conformation [the O2═C8—O1—H01 torsion angle is 178 (3)°], and forms, with its equivalents (related by the *c*-glide plane), an infinite chain of hydrogen bonds —H01···O2═C8—O1—H01···O2═C8—, running parallel to the *c* axis. The hydrogen bonds of the latter type link the tetramers into a layer, parallel to the crystallographic (100) plane and roughly perpendicular to the longest dimension of the tetramer itself.

Experimental

Hydrogen was introduced, with stirring, to a mixture of (II) (0.66 g, 4 mmol), palladium on carbon (5% Pd, 100 mg) and acetic acid (10 ml). The catalyst was filtered off and the solvent removed using a

rotary evaporator. The product was recrystallized from doubly distilled water, giving colourless crystalline (I) in 88% yield (0.58 g, 3 mmol). Single crystals of (I), suitable for X-ray study, were grown from ethyl acetate. The melting point of (I) agreed with that (433–434 K) quoted in the literature (Alder & Stein, 1933*b*).

Crystal data

$C_9H_{12}O_4$	$D_x = 1.409$ Mg m^{-3}
$M_r = 184.19$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 489
$a = 20.737$ (5) Å	reflections
$b = 9.310$ (2) Å	$\theta = 7.5$–20.7°
$c = 9.003$ (2) Å	$\mu = 0.11$ mm^{-1}
$\beta = 92.59$ (1)°	$T = 150$ (2) K
$V = 1736.4$ (7) Å^3	Prism, colourless
$Z = 8$	$0.45 \times 0.35 \times 0.15$ mm

Data collection

SMART 1K CCD area-detector diffractometer	3553 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.049$
Absorption correction: none	$\theta_{max} = 29.0°$
12920 measured reflections	$h = -27 \rightarrow 28$
4594 independent reflections	$k = -9 \rightarrow 12$
	$l = -12 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 0.9532P]$
$wR(F^2) = 0.123$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} = 0.001$
4594 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
331 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

C1—C7	1.536 (2)	C11—C12	1.534 (2)
C1—C6	1.537 (2)	C11—C17	1.539 (2)
C1—C2	1.563 (2)	C11—C16	1.545 (2)
C2—C8	1.503 (2)	C12—C18	1.506 (2)
C2—C3	1.566 (2)	C12—C13	1.563 (2)
C3—C9	1.505 (2)	C13—C19	1.505 (2)
C3—C4	1.537 (2)	C13—C14	1.565 (2)
C4—C7	1.539 (2)	C14—C17	1.537 (3)
C4—C5	1.543 (2)	C14—C15	1.538 (3)
C5—C6	1.559 (2)	C15—C16	1.552 (3)
C8—O2	1.215 (2)	C18—O12	1.222 (2)
C8—O1	1.329 (2)	C18—O11	1.318 (2)
C9—O4	1.2251 (19)	C19—O14	1.219 (2)
C9—O3	1.3222 (19)	C19—O13	1.3196 (19)
C7—C1—C6	100.61 (13)	C12—C11—C17	99.09 (13)
C7—C1—C2	101.16 (12)	C12—C11—C16	110.36 (14)
C6—C1—C2	110.15 (13)	C17—C11—C16	102.59 (14)
C8—C2—C1	110.42 (13)	C18—C12—C11	116.81 (14)
C8—C2—C3	115.75 (13)	C18—C12—C13	119.03 (13)
C1—C2—C3	102.41 (12)	C11—C12—C13	103.21 (12)
C9—C3—C4	118.51 (13)	C19—C13—C12	116.71 (13)
C9—C3—C2	116.95 (13)	C19—C13—C14	110.69 (14)
C4—C3—C2	103.27 (12)	C12—C13—C14	102.03 (13)
C3—C4—C7	99.07 (12)	C17—C14—C15	100.43 (14)
C3—C4—C5	111.10 (13)	C17—C14—C13	102.20 (14)
C7—C4—C5	102.05 (13)	C15—C14—C13	109.31 (14)
C4—C5—C6	103.35 (13)	C14—C15—C16	102.57 (14)
C1—C6—C5	102.86 (13)	C11—C16—C15	103.38 (14)
C1—C7—C4	94.67 (12)	C14—C17—C11	94.23 (13)
O2—C8—C2—C3	−18.6 (2)	O12—C18—C12—C13	129.44 (17)
C8—C2—C3—C9	−18.4 (2)	C18—C12—C13—C19	−19.7 (2)
C2—C3—C9—O4	124.25 (17)	C12—C13—C19—O14	−12.6 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H01$\cdots$O2^{ii}	0.88 (3)	1.85 (3)	2.7371 (19)	177 (3)
O3—H03$\cdots$O14	0.96 (3)	1.74 (3)	2.6996 (17)	174 (3)
O11—H011$\cdots$O12^{i}	0.94 (3)	1.69 (3)	2.6222 (18)	175 (3)
O13—H013$\cdots$O4	0.92 (3)	1.72 (3)	2.6294 (18)	170 (3)

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

All H atoms were refined isotropically; Csp^3-H bond lengths were in the range 0.96 (2)–1.02 (2) Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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