

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

Andrei S. Batsanov* and
Joanna L. Hesselink†

Department of Chemistry, University of
Durham, South Road, Durham DH1 3LE,
England

† née Megson

Correspondence e-mail:
a.s.batsanov@durham.ac.uk

Key indicators

Single-crystal X-ray study

$T = 295\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.044

wR factor = 0.113

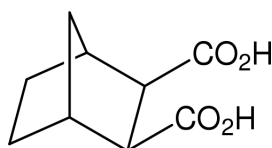
Data-to-parameter ratio = 14.1

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

Both carboxyl groups in the title molecule, $\text{C}_9\text{H}_{12}\text{O}_4$, have *gauche* orientations [relative to the $(\text{HOOC}-)\text{C}-\text{C}(-\text{COOH})$ bond] and participate in hydrogen bonds, linking the molecules into an infinite chain.

Comment

The title compound, (I), bicyclo[2.2.1]heptane-*exo-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 by catalytic hydrogenation of the $\text{C}=\text{C}$ bond in 2-norbornene-*exo-cis*-5,6-dicarboxylic acid, or bicyclo[2.2.1]hept-2-ene-*exo-cis*-5,6-dicarboxylic acid, (II), similar to the procedure described by Bartlett & Schneider (1946), but using palladium catalyst instead of PtO_2 .

The asymmetric unit of (I) comprises one molecule (Fig. 1), having neither crystallographic nor local symmetry. The latter is violated by the rotation of both carboxyl groups in the same direction, with the torsion angles $\text{O1}-\text{C8}-\text{C2}-\text{C3} -60.7(2)^\circ$ and $\text{C2}-\text{C3}-\text{C9}-\text{O3} 133.3(1)^\circ$. However, both carboxyls have their hydroxyl O atoms on the *endo*, and carbonyl O atoms on the *exo*-side of the $\text{C8}/\text{C2}/\text{C3}/\text{C9}$ plane. Such a conformation is also predominant in the crystal structure of (II) (Batsanov & Hesselink, 2002). Both carboxyl groups form the usual pair of hydrogen bonds; the $\text{H03}-\text{O3}-\text{C9}-\text{O4}$ group with its inversion equivalent, and the $\text{H01}-\text{O1}-\text{C8}-\text{O2}$ group with its equivalent related *via* a twofold axis. Thus, the molecules are linked into an infinite zigzag chain, parallel to the crystallographic c axis.

Experimental

Hydrogen was introduced to a stirred mixture of (II) (0.65 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,

Received 10 October 2002

Accepted 16 October 2002

Online 25 October 2002

Dicarboxylic Diels–Alder
products, Part 2. Part 1, see
Batsanov &, Hesselink (2002).

3 mmol). The melting point of 424–425 K agrees with 425–426 K reported by Alder & Stein (1933) and Bartlett & Schneider (1946), although Craig (1951) measured a melting point of 428–429 K for freshly prepared (I) and 431–432 K after several days. Single crystals of (I) suitable for X-ray study were grown from ethyl acetate.

Crystal data

C₉H₁₂O₄
M_r = 184.19
 Monoclinic, *C*2/*c*
a = 15.327 (2) Å
b = 11.503 (2) Å
c = 10.643 (2) Å
 β = 107.57 (1)°
V = 1788.9 (5) Å³
Z = 8

D_x = 1.368 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 443 reflections
 θ = 10.2–20.8°
 μ = 0.11 mm⁻¹
T = 295 (2) K
 Prism, colourless
 0.40 × 0.26 × 0.22 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 6844 measured reflections
 2358 independent reflections

1895 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.030
 θ_{\max} = 29.0°
h = -17 → 20
k = -15 → 15
l = -14 → 14

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.044
wR(*F*²) = 0.113
S = 1.10
 2358 reflections
 167 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.2379P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0175 (12)

Table 1

Selected geometric parameters (Å, °).

C1–C7	1.525 (3)	C4–C7	1.531 (3)
C1–C2	1.5373 (19)	C4–C5	1.534 (2)
C1–C6	1.540 (2)	C5–C6	1.546 (3)
C2–C8	1.512 (2)	C8–O2	1.2361 (17)
C2–C3	1.568 (2)	C8–O1	1.2942 (18)
C3–C9	1.5074 (18)	C9–O4	1.2261 (17)
C3–C4	1.549 (2)	C9–O3	1.2948 (17)
C7–C1–C2	101.78 (12)	C5–C4–C3	107.66 (14)
C7–C1–C6	101.84 (15)	C4–C5–C6	103.02 (14)
C2–C1–C6	107.56 (13)	C1–C6–C5	103.28 (14)
C8–C2–C1	115.04 (12)	C1–C7–C4	94.57 (12)
C8–C2–C3	113.95 (11)	O2–C8–O1	123.51 (14)
C1–C2–C3	103.23 (12)	O2–C8–C2	122.05 (13)
C9–C3–C4	110.68 (12)	O1–C8–C2	114.39 (12)
C9–C3–C2	115.98 (11)	O4–C9–O3	123.80 (13)
C4–C3–C2	102.14 (12)	O4–C9–C3	122.49 (12)
C7–C4–C5	101.64 (14)	O3–C9–C3	113.67 (12)
C7–C4–C3	102.37 (13)		

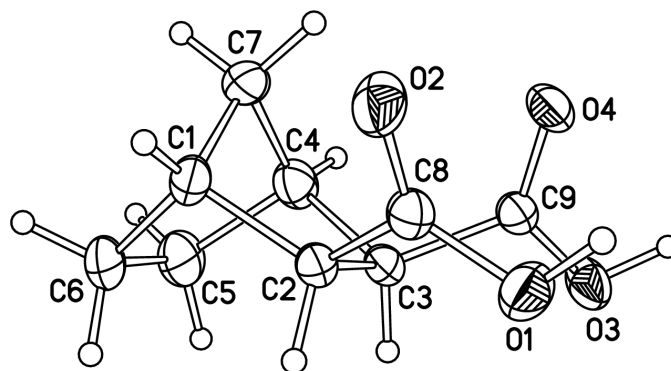


Figure 1

The molecular structure of (I), showing displacement ellipsoids at the 30% probability level.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1–H01...O2 ⁱ	0.99 (3)	1.68 (3)	2.6628 (16)	168 (3)
O3–H03...O4 ⁱⁱ	0.95 (3)	1.69 (3)	2.6378 (16)	175 (3)

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

All H atoms were refined in isotropic approximation; *Csp*³–H bond lengths were in the range 0.96 (2)–1.00 (2) Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

The authors thank Professor W. J. Feast for fruitful advice.

References

- Alder, K. & Stein, G. (1933). *Ann. Chem.* **504**, 216–257.
 Bartlett, P. D. & Schneider, A. (1946). *J. Am. Chem. Soc.* **68**, 6–8.
 Batsanov, A. S. & Hesselink, J. L. (2002). *Acta Cryst.* **E58**, o1272–o1274.
 Bruker (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Craig, D. (1951). *J. Am. Chem. Soc.* **73**, 4889–4892.
 Feast, W. J., Hesselink, J. L., Khosravi, E. & Rannard, S. P. (2002). *Polym. Bull.* In the press.
 Megson, J. L. (1997). PhD Thesis, Durham University, England.
 Siemens (1995). *SMART* and *SAINT*. Versions 4.050. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.