Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2-Norbornene-*exo*-*cis*-5,6-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

Received 8 October 2002
Accepted 15 October 2002
Online 25 October 2002

Dicarboxylic Diels–Alder products, Part 1.

Key indicators

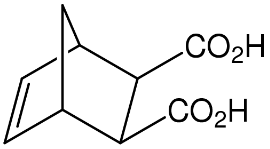
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.049
wR factor = 0.102
Data-to-parameter ratio = 12.1

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

The crystal structure of the title compound, $C_9H_{10}O_4$, contains three independent molecules in the asymmetric unit, with different orientations of carboxyl groups, all linked into an infinite chain through hydrogen bonds.

Comment

Various stereoisomers of 5,6-dicarboxylic acids with a 2-norbornene or 7-oxanorbornene core, and their norbornane analogues, are easily accessible through the Diels–Alder reaction (Diels & Alder, 1928; Alder & Stein, 1933). The crystal structure of 2-norbornene-(or bicyclo[2.2.1]hept-2-ene-)-*endo*-*cis*-5,6-dicarboxylic acid has been determined repeatedly by Avitabile *et al.* (1973), Pfluger *et al.* (1973) and, at low temperature, by Bolte *et al.* (2000). This isomer has also been structurally characterized as a mono-anion, in its potassium salt sesquihydrate (Cser & Sasvari, 1976), and as a ligand in Mn and Co complexes (Hartung *et al.*, 1993; Devereux *et al.*, 1995). However, to our knowledge, no other acid of this class (without additional substituents on the bicyclic core) has been structurally studied in the neutral form, and there is only one structure of a complex, with the norbornane-*endo*-*cis*-2,3-dicarboxylic acid ligand (Geraghty *et al.*, 1999). Since these acids are of interest as model compounds for organic additives to influence the crystal growth of $CaCO_3$ (Megson, 1997; Feast *et al.*, 2002), we undertook a systematic study of their structures.



(I)

2-Norbornene-*exo*-*cis*-5,6-dicarboxylic acid, or bicyclo[2.2.1]hept-2-ene-*exo*-*cis*-5,6-dicarboxylic acid, (I), was prepared by the usual route of hydrolysing the corresponding *exo*-anhydride, obtained in turn by 'thermodynamic' Diels–Alder addition of cyclopentadiene to maleic anhydride at high (451 K) temperature (Diels & Alder, 1928; Alder & Stein, 1933).

The asymmetric unit of (I) comprises three molecules (Fig. 1) of similar geometry. In molecule (i), each carboxyl group is rotationally disordered between two orientations, *A* and *B*. Assigning occupancies 92% to position *A* and 8% to position *B* gave the best agreement with the experiment. For the 5-carboxyl group the two orientations differ by a 30 (1)°

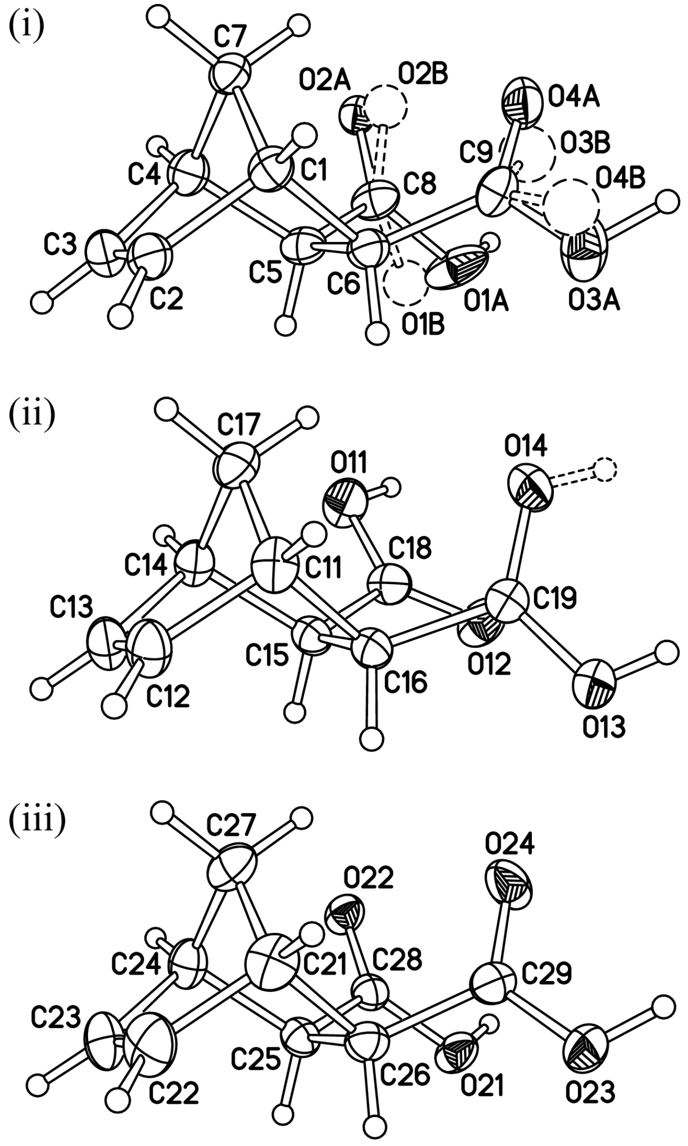


Figure 1
The three independent molecules of (I), showing the disorder in molecule (i). Displacement ellipsoids are drawn at the 50% probability level.

rotation around C5—C8, while for the 6-carboxyl group the rotation around the C6—C9 bond amounts to 150 (2)°, *i.e.* the carbonyl and hydroxyl O atoms almost exchange places. In molecule (ii) there is no disorder of non-H atoms, but one carboxyl group has the C19—O3 and C19—O4 bonds almost equal in length, and the acidic H atom disordered between O13 and O14. As this carboxyl group forms a hydrogen-bonded dimer with its own inversion equivalent, this disorder means that both hydrogen bonds in the dimer are disordered. Molecule (iii) shows no disorder.

All acidic H atoms in the structure are involved in intermolecular hydrogen bonds, which link molecules into infinite zigzag chains, running in the direction [01$\overline{1}$]. The chain includes all independent molecules, in the sequence ···(iii)···(iii)···(i)···(ii)···(ii)···(i)··· (Fig. 2). Each pair of adjacent molecules in the chain is linked by two hydrogen bonds, typical for carboxylic acid dimers [*e.g.* see recent review by Steiner (2002)]; the (ii)···(ii) and (iii)···(iii) pairs involve crystallographic inversion centres.

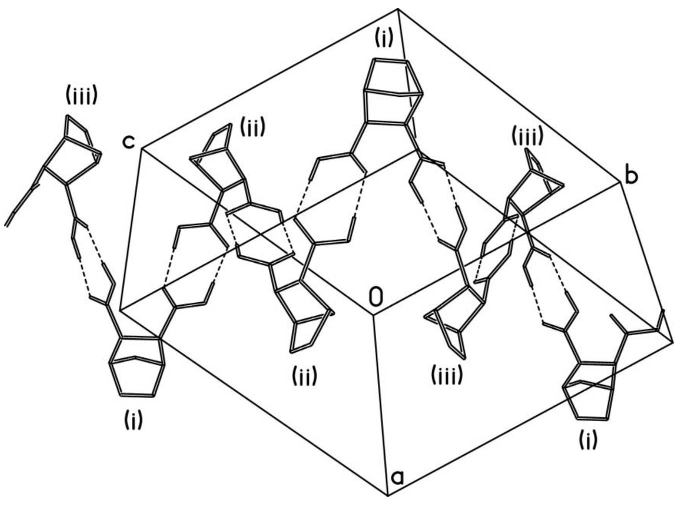


Figure 2
Hydrogen bonding in the structure of (I). Crystallographically independent molecules are labelled (i), (ii) and (iii); see Fig. 1.

It is noteworthy that the melting point of our crystals (from ethyl acetate) is close to those found by Alder & Stein (1933) and Bartlett & Schneider (1946) for the samples crystallized from water (421–422 K). However, Craig (1951) reported that, under such conditions, only a monohydrate of (I) (m.p. 426–427 K) could be crystallized, which loses water on heating *in vacuo* to give pure (I), with m.p. 434–435 K. Could it be another polymorph?

Experimental

2-Norbornene-*exo*-5,6-dicarboxy anhydride (3.17 g, 19 mmol) in 40 ml of doubly distilled water was refluxed for 2 h. The solution was allowed to cool overnight. The precipitate of (I) was filtered off, identified by elemental analysis, ^{1}H and ^{13}NMR, IR and MS, and recrystallized for X-ray study from ethyl acetate (m.p. 423–424 K).

Crystal data

$C_9H_{10}O_4$
M_r = 182.17
Triclinic, $P\overline{1}$
a = 11.282 (2) Å
b = 11.482 (2) Å
c = 11.702 (2) Å
α = 114.22 (1)°
β = 97.44 (1)°
γ = 101.93 (1)°
V = 1313.0 (4) Å^3
Z = 6
D_x = 1.382 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 429 reflections
θ = 12.1–20.6°
μ = 0.11 mm^{-1}
T = 150 (2) K
Block, colourless
0.4 × 0.3 × 0.2 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
ω scans
9582 measured reflections
5970 independent reflections
4833 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024
$\theta_{\rm max}$ = 27.6°
$h = -14 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -10 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.102$
$S = 1.12$
5970 reflections
493 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + 1.1369P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0205 (9)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.520 (3)	C14—C17	1.533 (3)
C1—C7	1.535 (2)	C14—C15	1.560 (2)
C1—C6	1.578 (2)	C15—C18	1.513 (2)
C2—C3	1.328 (3)	C15—C16	1.571 (2)
C3—C4	1.518 (3)	C16—C19	1.505 (2)
C4—C7	1.535 (3)	C18—O12	1.222 (2)
C4—C5	1.560 (3)	C18—O11	1.314 (2)
C5—C8	1.509 (3)	C19—O14	1.252 (2)
C5—C6	1.574 (3)	C19—O13	1.273 (2)
C6—C9	1.504 (3)	C21—C22	1.514 (3)
C6—H6	0.943 (19)	C21—C27	1.529 (3)
C8—O2*A*	1.225 (3)	C21—C26	1.578 (3)
C8—O2*B*	1.25 (4)	C22—C23	1.322 (3)
C8—O1*B*	1.31 (2)	C23—C24	1.518 (3)
C8—O1*A*	1.323 (2)	C24—C27	1.533 (3)
C9—O4*B*	1.16 (4)	C24—C25	1.556 (3)
C9—O4*A*	1.224 (2)	C25—C28	1.510 (2)
C9—O3*B*	1.29 (2)	C25—C26	1.571 (2)
C9—O3*A*	1.327 (3)	C26—C29	1.502 (3)
C11—C12	1.518 (3)	C28—O22	1.222 (2)
C11—C17	1.536 (3)	C28—O21	1.320 (2)
C11—C16	1.577 (3)	C29—O24	1.223 (2)
C12—C13	1.324 (3)	C29—O23	1.305 (2)
C13—C14	1.521 (3)		
C2—C1—C7	101.20 (15)	C18—C15—C14	114.74 (15)
C2—C1—C6	104.02 (14)	C18—C15—C16	114.46 (15)
C7—C1—C6	101.12 (14)	C14—C15—C16	102.90 (14)
C3—C2—C1	107.20 (16)	C19—C16—C15	116.31 (15)
C2—C3—C4	107.91 (17)	C19—C16—C11	111.07 (15)
C3—C4—C7	100.88 (15)	C15—C16—C11	101.72 (14)
C3—C4—C5	103.92 (15)	C14—C17—C11	93.87 (15)
C7—C4—C5	101.10 (14)	C22—C21—C27	100.83 (17)
C8—C5—C4	114.25 (15)	C22—C21—C26	105.46 (16)
C8—C5—C6	114.49 (15)	C27—C21—C26	101.00 (15)
C4—C5—C6	103.03 (14)	C23—C22—C21	107.35 (18)
C9—C6—C5	115.61 (15)	C22—C23—C24	107.84 (19)
C9—C6—C1	110.82 (15)	C23—C24—C27	100.37 (16)
C5—C6—C1	101.64 (14)	C23—C24—C25	104.78 (16)
C1—C7—C4	93.93 (14)	C27—C24—C25	100.66 (15)
C12—C11—C17	100.29 (15)	C28—C25—C24	113.64 (15)
C12—C11—C16	104.30 (15)	C28—C25—C26	114.78 (14)
C17—C11—C16	101.84 (14)	C24—C25—C26	103.48 (14)
C13—C12—C11	107.40 (17)	C29—C26—C25	115.17 (15)
C12—C13—C14	107.77 (17)	C29—C26—C21	109.94 (15)
C13—C14—C17	100.35 (15)	C25—C26—C21	101.15 (14)
C13—C14—C15	106.04 (15)	C21—C27—C24	93.94 (16)
C17—C14—C15	100.35 (14)		
O2*A*—C8—C5—C6	−111.7 (2)	C15—C16—C19—O14	61.7 (2)
C8—C5—C6—C9	4.7 (2)	O22—C28—C25—C26	−120.13 (19)
C5—C6—C9—O4*A*	36.4 (3)	C28—C25—C26—C29	6.3 (2)
O12—C18—C15—C16	54.3 (2)	C25—C26—C29—O24	47.2 (3)
C18—C15—C16—C19	0.6 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H01*A*···O24	0.94 (4)	1.66 (4)	2.599 (2)	175 (3)
O3*A*—H03*A*···O12	0.98 (3)	1.71 (3)	2.688 (3)	174 (3)
O11—H011···O4*A*	0.92 (3)	1.76 (3)	2.680 (2)	179 (3)
O13—H013···O14$^{\rm i}$	0.81 (5)	1.81 (5)	2.600 (2)	167 (5)
O14—H014···O13$^{\rm i}$	0.80 (7)	1.80 (7)	2.600 (2)	173 (6)
O21—H021···O22$^{\rm ii}$	0.93 (3)	1.71 (3)	2.6374 (19)	175 (3)
O23—H023···O2*A*	0.93 (3)	1.72 (3)	2.640 (3)	176 (3)
O23—H023···O2*B*	0.93 (3)	1.56 (4)	2.48 (3)	169 (3)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, 1 - y, -z$.

All H atoms were refined in isotropic approximation; bond lengths Csp^3—H 0.94 (2)–1.01 (2) Å and Csp^2—H 0.95 (2)–0.99 (2) Å. The H atoms on O1*B* and O3*B* (occupancies 8%) were not included.

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*.

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

References

Alder, K. & Stein, G. (1933). *Ann. Chem.* **504**, 216–257.

Avitabile, G., Ganis, P. & Nemiroff, M. (1973). *Cryst. Struct. Commun.* **2**, 455–457.

Bartlett, P. D. & Schneider, A. (1946). *J. Am. Chem. Soc.* **68**, 6–8.

Bolte, M., Degen, A. & Egert, E. (2000). *Acta Cryst.* C**56**, 1338–1342.

Bruker (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Cser, F. & Sasvari, K. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 478–480.

Craig, D. (1951). *J. Am. Chem. Soc.* **73**, 4889–4892.

Devereux, M., Curran, M., McCann, M. & McKee, V. (1995). *Polyhedron*, **14**, 2247–2253.

Diels, O. & Alder, K. (1928). *Ann. Chem.* **460**, 98–122.

Feast, W. J., Hesselink, J. L., Khosravi, E. & Rannard, S. P. (2002). *Polym. Bull.* In the press.

Geraghty, M., Sheridan, V., McCann, M., Devereux, M. & McKee, V. (1999). *Polyhedron*, **18**, 2931–2939.

Hartung, H., Baumeister, U., Kaplonek, R. & Fechtel, G. (1993). *Z. Anorg. Allg. Chem.* **619**, 1196–1202.

Megson, J. L. (1997). PhD Thesis, Durham University, England.

Pfluger, C. E., Harlow, R. L. & Simonsen, S. H. (1973). *J. Cryst. Mol. Struct.* **3**, 277–283.

Siemens (1995). *SMART* and *SAINT*. Versions 4.050. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Steiner, T. (2002). *Angew. Chem. Int. Ed. Engl.* **41**, 48–76.