Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

2-Bromomaleic acid

Andreas Fischer

Inorganic Chemistry, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), 100 44 Stockholm, Sweden
Correspondence e-mail: afischer@kth.se

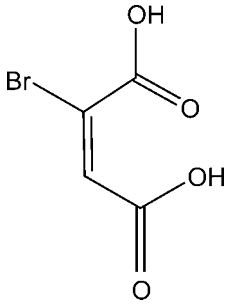
Received 15 May 2009; accepted 24 July 2009

Key indicators: single-crystal X-ray study; T = 299 K; mean σ(C–C) = 0.005 Å; R factor = 0.042; wR factor = 0.075; data-to-parameter ratio = 16.9.

The title compound, $C_4H_3BrO_4$, was obtained from a solution of *meso*-2,3-dibromosuccinic acid and vanadium(IV) oxide. The crystals are isostructural with chloromaleic acid and the molecule has two geometrically different carboxyl groups, one of which has delocalized C—O bonds and is essentially coplanar with the olefinic bond plane [give dihedral angle 15.08 (16)°], whereas the other has a localized C═O bond and forms a dihedral angle of 99.6 (3)° with the C═C bond plane. Two symmetry-independent O—H···O hydrogen bonds link the molecules into layers parallel to the *bc* plane.

Related literature

For the structure of chloromaleic acid, see: Wong *et al.* (2006). For the synthesis and structure of 2-bromofumaric acid, see: Fischer (2006). For the structure and polymorphism of maleic acid, see: Day *et al.* (2006). For the structure of 2-methylmaleic acid, see: Batchelor & Jones (1998).



Experimental

Crystal data

$C_4H_3BrO_4$
M_r = 194.97
Monoclinic, $P2_1/c$
a = 7.5074 (12) Å
b = 4.9272 (6) Å
c = 16.966 (4) Å
β = 94.213 (12)°
V = 625.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.50 mm^{-1}
T = 299 K
0.15 × 0.13 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: numerical *HABITUS* (Herrendorf & Bärnighausen, 1997)
T_{min} = 0.325, T_{max} = 0.455
8638 measured reflections
1420 independent reflections
1046 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.075
S = 1.16
1420 reflections
84 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O4^{i}	0.82	1.80	2.617 (4)	171
O2—H2···O1^{ii}	0.82	1.86	2.681 (4)	176

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

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2009).

The Swedish Research Council (VR) is acknowleged for providing funding for the single-crystal diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YA2098).

References

Batchelor, E. & Jones, W. (1998). *Acta Cryst.* C**54**, 238–240.
Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Day, G. M., Trask, A. V., Motherwell, W. D. S. & Jones, W. (2006). *Chem. Commun.* pp. 54-56.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Fischer, A. (2006). *Acta Cryst.* E**62**, o4190–o4191.
Herrendorf, W. & Bärnighausen, H. (1997). *HABITUS*. University of Karlsruhe, Germany.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2009). *publCIF.* In preparation.
Wong, A., Pike, K. J., Jenkins, R., Clarkson, G. J., Anupõld, T., Howes, A. P., Crout, D. H. G., Samoson, A., Dupree, R. & Smith, M. E. (2006). *J. Phys. Chem. A*, **110**, 1824–1835.

supplementary materials

Acta Cryst. (2009). E**65**, o2240 [**doi:10.1107/S1600536809029602**]

2-Bromomaleic acid

A. Fischer

Comment

During the ongoing investigation of the bromo-substituted dicarboxylic acids with four carbon atoms, our group tried to prepare and characterize pure acids as well as their metal salts. One of these syntheses involved the reaction of vanadium(IV) oxide with *meso*-dibromosuccinic acid. It had been shown earlier (Fischer, 2006), that hydrogen bromide can easily be eliminated from racemic 2,3-dibromosuccinic acid, yielding 2-bromofumaric acid. Elimination of hydrogen bromide from *meso*-2,3-dibromosuccinic acid does not occur as easily. However in the presence of strong bases and at elevated temperature, elimination is observed; it yields 2-bromomaleic acid, whose structure is described here.

While most of bond lengths and angles in the molecule of 2-bromomaleic acid (Fig. 1) are close to those found in 2-bromofumaric acid (Fischer, 2006) and unsubstituted maleic acid (Day *et al.*, 2006), the title compound, in contrast to the aforementioned molecules, is essentially non-planar. In fact, two carboxylic groups in 2-bromomaleic acid form dihedral angle of 77.6 (3)° with each other and only one of them (O3–C4–O4) is almost coplanar with the C2=C3 double bond plane, whereas the second one (O1–C1–O2) forms with the latter plane dihedral angle of 99.6 (3)° The carboxylic group, which is almost coplanar with the olefinic bond, shows much higher degree of delocalization (C4–O3 1.269 (4) and C4–O4 1.254 (5) Å), than the second carboxylic group, bonded to the bromo-substituted carbon atom (C1–O1 1.197 (4) and C1–O2 1.299 (5) °). It is noteworthy that similar geometrical peculiarities were observed in other known structures of monosubstituted maleic acid derivatives, namely in 2-chloromaleic acid (Wong *et al.*, 2006), isostructural with the title compound, and 2-methylmaleic acid (Batchelor & Jones, 1998).

There are two symmetry independent O—H..O bonds (Table 1), one of which involves delocalized carboxyl group and is responsible for formation of dimeric centrosymmetric motives traditional to carboxylic acid crystal structures. Another H-bond involves non-symmetric carboxylic group and further links dimeric aggregates into layers parallel to the *bc*-plane (Fig. 2).

Experimental

89 mg of VO_2 (AlfaAesar, 99%), was added to a solution of 270 mg of *meso*-dibromosuccinic acid (Sigma Aldrich, 98%) in 4.2 ml of demineralized water. Upon heating to 90°C, vanadium oxide got dissolved, yielding a dark-blue solution, which was put aside for evaporation. Within a week, colourless crystals of the title compound were obtained.

Refinement

H atoms could be located in the Fourier map, however, their isotropic refinement did not yield satisfactory *X*–H distances. Therefore, H atoms were placed at calculated positions with d(C–H)=0.93 Å, d(O–H)=0.82 Å and included in the subsequent refinement in riding motion approximation with U_{iso}=1.2U_{eq} of the carrier atom (1.5 U_{eq} for hydroxyl H atoms).

Figures

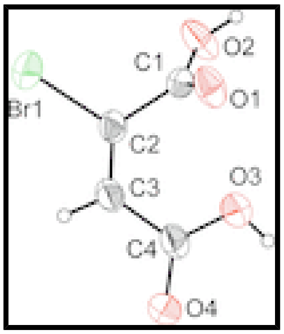


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level; H atoms are drawn as small circles of arbitrary radius.

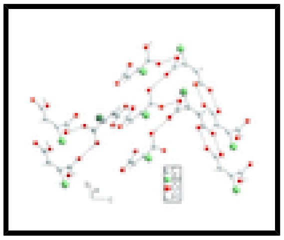


Fig. 2. Crystal packing of the title compound viewed down the *a* axis. Hydrogen bonds are drawn as dashed lines.

2-Bromomaleic acid

Crystal data

$C_4H_3BrO_4$

M_r = 194.97

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

a = 7.5074 (12) Å

b = 4.9272 (6) Å

c = 16.966 (4) Å

β = 94.213 (12)°

V = 625.9 (2) Å^3

Z = 4

F_{000} = 376

D_x = 2.069 Mg m^{-3}

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 28 reflections

θ = 5.6–19.2°

μ = 6.50 mm^{-1}

T = 299 K

Block, colourless

0.15 × 0.13 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer

Radiation source: fine-focus sealed tube

φ and ω scans

Absorption correction: numerical
HABITUS (Herrendorf & Bärnighausen, 1997)

T_{min} = 0.325, T_{max} = 0.455

8638 measured reflections

1420 independent reflections

1046 reflections with $I > 2\sigma(I)$

R_{int} = 0.064

θ_{max} = 27.5°

θ_{min} = 4.7°

$h = -9 \rightarrow 9$

$k = -6 \rightarrow 6$

$l = -17 \rightarrow 22$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0113P)^2 + 1.1107P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.075$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.16$	$\Delta\rho_{max} = 0.63$ e Å^{-3}
1420 reflections	$\Delta\rho_{min} = -0.43$ e Å^{-3}
84 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.7961 (5)	0.0222 (7)	0.6839 (2)	0.0317 (8)
C2	0.6344 (4)	−0.0621 (8)	0.6312 (2)	0.0330 (8)
C3	0.6332 (5)	−0.2221 (8)	0.5700 (2)	0.0369 (9)
C4	0.7955 (5)	−0.3400 (8)	0.5399 (2)	0.0369 (9)
Br1	0.42183 (5)	0.08537 (10)	0.66527 (3)	0.05260 (18)
O1	0.8584 (3)	−0.1231 (6)	0.73530 (16)	0.0440 (7)
O2	0.8501 (4)	0.2664 (6)	0.66922 (17)	0.0493 (8)
O3	0.9456 (3)	−0.2426 (6)	0.56482 (17)	0.0466 (7)
O4	0.7746 (4)	−0.5294 (6)	0.49066 (17)	0.0482 (8)
H3A	0.5236	−0.2646	0.5439	0.044*
H2	0.9357	0.3049	0.7000	0.074*
H3	1.0256	−0.3258	0.5449	0.070*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0278 (18)	0.031 (2)	0.036 (2)	0.0046 (15)	−0.0024 (15)	−0.0024 (17)
C2	0.0275 (17)	0.031 (2)	0.039 (2)	0.0043 (15)	−0.0055 (14)	0.0019 (19)

C3	0.0288 (19)	0.035 (2)	0.045 (2)	−0.0016 (16)	−0.0066 (16)	−0.003 (2)
C4	0.0306 (19)	0.040 (2)	0.039 (2)	−0.0025 (16)	−0.0063 (16)	0.0006 (19)
Br1	0.0335 (2)	0.0616 (3)	0.0615 (3)	0.0137 (2)	−0.00437 (17)	−0.0122 (3)
O1	0.0380 (14)	0.0415 (17)	0.0498 (17)	−0.0045 (12)	−0.0160 (12)	0.0119 (14)
O2	0.0504 (17)	0.0353 (17)	0.0578 (19)	−0.0113 (13)	−0.0256 (14)	0.0076 (15)
O3	0.0332 (14)	0.0487 (18)	0.0578 (19)	−0.0067 (13)	0.0038 (13)	−0.0141 (16)
O4	0.0408 (15)	0.055 (2)	0.0476 (17)	0.0022 (13)	−0.0058 (12)	−0.0205 (15)

Geometric parameters (Å, °)

C1—O1	1.197 (4)	C4—O4	1.254 (5)
C1—O2	1.299 (5)	C4—O3	1.269 (4)
C1—C2	1.512 (5)	C3—H3A	0.9300
C2—C3	1.302 (5)	O2—H2	0.8200
C2—Br1	1.883 (4)	O3—H3	0.8200
C3—C4	1.475 (5)		
O1—C1—O2	125.6 (3)	O4—C4—O3	124.6 (4)
O1—C1—C2	121.3 (3)	O4—C4—C3	117.3 (3)
O2—C1—C2	112.9 (3)	O3—C4—C3	118.1 (4)
C3—C2—C1	126.5 (3)	C2—C3—H3A	118.1
C3—C2—Br1	121.5 (3)	C4—C3—H3A	118.1
C1—C2—Br1	112.0 (3)	C1—O2—H2	109.5
C2—C3—C4	123.9 (3)	C4—O3—H3	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4$^{\mathrm{i}}$	0.82	1.80	2.617 (4)	171
O2—H2···O1$^{\mathrm{ii}}$	0.82	1.86	2.681 (4)	176

Symmetry codes: (i) −*x*+2, −*y*−1, −*z*+1; (ii) −*x*+2, *y*+1/2, −*z*+3/2.

Fig. 1

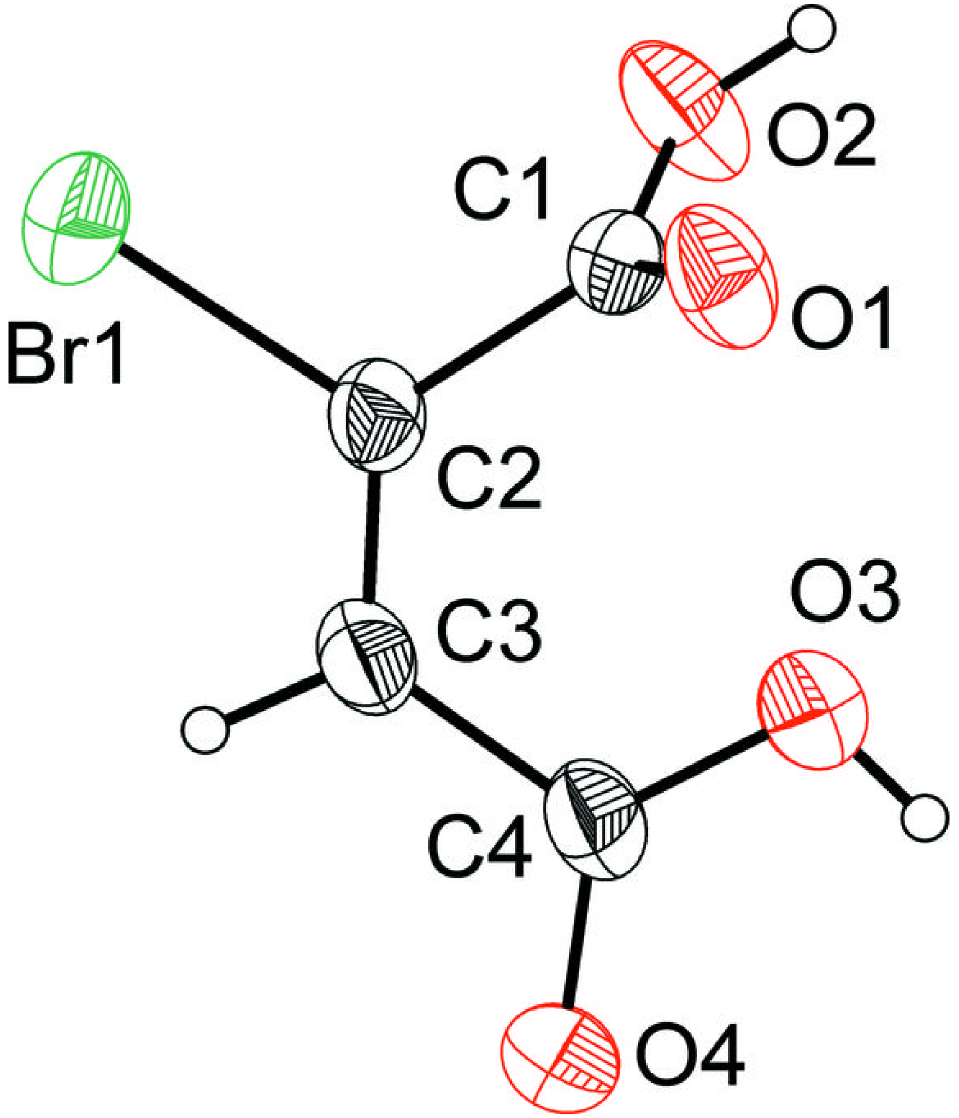


Fig. 2