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## 2-Bromo-3-methyl-2-butenoic Acid (2-Bromosenecioic Acid)

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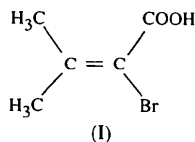
(Received 30 January 1997; accepted 11 April 1997)

### Abstract

The title compound, C<sub>5</sub>H<sub>7</sub>BrO<sub>2</sub>, crystallized in space group *P* $\bar{1}$ . Molecules are linked to form normal centrosymmetric hydrogen-bonded dimers with O $\cdots$ O 2.625 (4) Å. The carboxyl H and O atoms are ordered, but the H atoms of both methyl groups are disordered. The Br and C atoms lie very nearly in a plane which makes a dihedral angle of 30.0 (1)° with the carboxyl group plane.

### Comment

This study is one of a continuing series on hydrogen bonding in carboxylic acids. In 2-bromo-3-methyl-2-butenoic acid, (I), the hydrogen bonding is of the cyclic dimer type about a center of symmetry as shown in Fig. 1, which also shows our numbering scheme.



The five C atoms and the Br atom of the title acid lie very nearly in a plane, the maximum deviation of an atom from the best-fit plane through them being 0.018 (4) Å, the average deviation being 0.007 (4) Å. The dihedral angle between this plane and the carboxyl group plane is 30.0 (1)°.

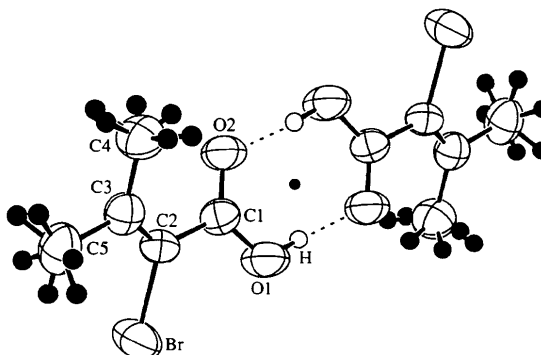


Fig. 1. *ORTEP* (Johnson, 1976) diagram of the hydrogen-bonded cyclic dimer of 2-bromo-3-methyl-2-butenoic acid showing the molecular numbering scheme and the center of symmetry about which the dimer is formed. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set arbitrarily small. The half-occupancy H atoms of the disordered methyl groups are shown as filled spheres. The center of symmetry is shown as a filled sphere and the hydrogen bonds as dashed lines.

The best available comparison of molecular geometry is perhaps afforded by trichloroacrylic acid, Cl<sub>2</sub>C=CClCOOH (Fleck, Göckel & Weiss, 1987), which was found to be slightly less planar: the maximum deviation of an atom from the best-fit plane through the three C atoms and the three Cl atoms (the analog of the plane described above for the title acid) is reported to be 0.05 Å. Using our numbering scheme, with values for trichloroacrylic acid in brackets, distances are: C1—O1 1.277 (4) [1.285 (3)], C1—O2 1.239 (4) [1.207 (3)], C1—C2 1.475 (5) [1.502 (3)] and C2—C3 1.315 (4) Å [1.319 (3) Å], and angles are: O1—C1—O2 122.3 (3) [124.9 (2)], C2—C1—O1 116.9 (3) [112.7 (2)] and C2—C1—O2 120.8 (3)° [122.4 (2)°]. In the cyclic dimer hydrogen bond of trichloroacrylic acid, O<sub>d</sub>—H is reported as 0.69 (3) Å, O<sub>d</sub>⋯O<sub>a</sub> as 2.677 (3) Å and O<sub>d</sub>—H⋯O<sub>a</sub> as 165°, the latter two values agreeing well with those for the title compound (Table 2).

It should be noted that in the Fourier difference map used to assign the coordinates of the carboxyl H atom near O1 there was no peak near O2 assignable as a (fractional occupancy) H atom. Thus, the H atom on O1 was assigned as ordered. The presence of the Br atom, however, makes this assessment less definitive than would be expected, for example, for the unsubstituted analog, (CH<sub>3</sub>)<sub>2</sub>C=CHCOOH.

All intramolecular distances and angles fell within normal ranges. The closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxyl groups, are between H4 and H11<sup>ii</sup> [symmetry code: (ii)  $x, y, 1+z$ ] and are 0.18 Å less than the corresponding Bondi (1964) radius sum. No other approach is deficient by more than 0.05 Å.

## Experimental

2-Bromo-3-methyl-2-butenic acid was obtained from the Dr M. S. Newman chemical collection as large almost colorless polycrystals. These were dissolved in water and recrystallized by slow evaporation at room temperature to produce colorless prisms suitable for study. The experimental sample was coated with clear nail polish to prevent sublimation.

### Crystal data

C<sub>5</sub>H<sub>7</sub>BrO<sub>2</sub>  
*M<sub>r</sub>* = 179.01  
 Triclinic  
*P* $\bar{1}$   
*a* = 7.4058 (9) Å  
*b* = 8.7129 (10) Å  
*c* = 6.0114 (6) Å  
 $\alpha$  = 94.915 (10)°  
 $\beta$  = 102.386 (10)°  
 $\gamma$  = 114.847 (8)°  
*V* = 336.96 (7) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.764 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 14.8–17.4°  
 $\mu$  = 6.028 mm<sup>-1</sup>  
*T* = 296 K  
 Prism  
 0.50 × 0.46 × 0.38 mm  
 Colorless

### Data collection

AFC-5S diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 $\psi$  scan (North, Phillips & Mathews, 1968)  
*T<sub>min</sub>* = 0.686, *T<sub>max</sub>* = 0.997  
 3112 measured reflections  
 1556 independent reflections  
 1082 reflections with  
 $I > \sigma_I$   
*R<sub>int</sub>* = 0.036

$\theta_{\max}$  = 27.56°  
 $h$  = -9 → 9  
 $k$  = -11 → 11  
 $l$  = -7 → 7  
 6 standard reflections every 150 reflections  
 intensity variation: ±3.1% (average maximum relative intensity)

### Refinement

Refinement on *F*  
*R* = 0.043  
*wR* = 0.209  
*S* = 1.81  
 1082 reflections  
 75 parameters  
 H atoms: see below  
 $w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\max} < 0.01$   
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.47 \text{ e } \text{Å}^{-3}$

Extinction correction: Zachariasen (1963, 1968)  
 Extinction coefficient: 83 (7) × 10<sup>-7</sup>  
 Scattering factors from Stewart, Davidson & Simpson (1965) (H), and Creagh & McAuley (1992) (C, O, Br)

Table 1. Selected geometric parameters (Å, °)

Br—C2	1.903 (3)	C3—C5	1.510 (6)
C3—C4	1.497 (5)		
Br—C2—C1	113.1 (2)	C2—C3—C4	123.9 (4)
Br—C2—C3	121.6 (3)	C2—C3—C5	122.4 (3)
C1—C2—C3	125.3 (3)	C4—C3—C5	113.7 (3)

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

D—H $\cdots$ A	<i>D</i> —H	H $\cdots$ A	<i>D</i> $\cdots$ A	<i>D</i> —H $\cdots$ A
O1—H $\cdots$ O2 <sup>i</sup>	0.98	1.66	2.625 (4)	166

† Note that no e.s.d.'s are given for quantities involving H since its coordinates were fixed.

Symmetry code: (i) 1 - *x*, 2 - *y*, 2 - *z*.

The Laue group assignment indicated space group *P*1 or *P* $\bar{1}$  (No. 1 or 2). *P* $\bar{1}$  was given initial preference and, since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. On the basis of peak heights in the Fourier difference maps, all the methyl H-atom occupancy factors were fixed at 0.5. Of the twelve half-occupancy H atoms assigned in the two disordered methyl groups, all but one was isotropically refined prior to making the methyl groups' geometry canonical with a C—H distance of 0.98 Å and *U<sub>iso</sub>* = 1.2*U<sub>eq</sub>* of the associated C atom. After all other atoms were assigned, the carboxylic H atom was fixed in position from a Fourier map but its *U<sub>iso</sub>* was refined.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1293). Services for accessing these data are described at the back of the journal.

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## Hydrogen Bonding and Ring Asymmetry in a Substituted Cyclopropane: (+)-*trans*-(1*S*,2*S*)-2-Phenylcyclopropanecarboxylic Acid at 208 K

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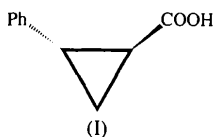
(Received 10 March 1997; accepted 11 April 1997)

### Abstract

The title compound, C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>, crystallized in space group *P*2<sub>1</sub> with two molecules in the asymmetric unit. In this structure, hydrogen bonding of the cyclic dimer type [with O··O 2.623(2)–2.637(2) Å] links the two molecules of the asymmetric unit. The two carboxylic H atoms are ordered, as are the O atoms. Each of the two non-equivalent molecules exhibits an asymmetric cyclopropane ring; the values found for the asymmetry parameters are  $\delta(\text{COOH}) = -0.034(4)$  and  $-0.025(4)$  Å, and  $\delta(\text{phenyl}) = -0.028(4)$  and  $-0.023(4)$  Å.

### Comment

This study is one of a continuing series on hydrogen bonding in carboxylic acids. In the title compound, (I), the hydrogen bonding is of the cyclic dimer type and links the two crystallographically non-equivalent molecules of the asymmetric unit, as shown in Fig. 1. The absolute configuration is known from previous chemical studies (see *Experimental* section). Geometric details of the hydrogen bonds are given in Table 2. The hydrogen bonds run very nearly along [10 $\bar{2}$ ].



Additional interest in (I) is associated with determination of substituent-induced bond-length asymmetry in the cyclopropane ring, as discussed in detail by Allen (1980), particularly since there are few characterized structures in which lightly substituted phenyl groups are substituents. Bond asymmetry in the cyclopropane ring is observed in both the *A* and *B* molecules of (I); in both molecules, the bond distal to the unsubstituted ring site is longer than the two proximal bonds, which have nearly equal lengths. Consistent with the principle of additivity of bond-length asymmetries (Allen, 1980), bond-asymmetry parameters for the carboxyl and phenyl groups are found to be  $\delta(\text{COOH}) = -0.034(4)$  and  $-0.025(4)$  Å, and  $\delta(\text{phenyl}) = -0.028(4)$  and  $-0.023(4)$  Å for the *A* and *B* molecules, respectively. For the *A* molecule, the rounded torsion angles X1A—C1A—C4A—O2A, X2A—C2A—C5A—C6A and X2A—C2A—C5A—C10A (in which X1A and X2A are the midpoints of the respective distal bonds) are 21,  $-167$  and  $11^\circ$ , indicating *cis* bisected and perpendicular conformations for the carbonyl and phenyl groups, respectively; for the *B* molecule, the analogous torsion angles are  $-161$ ,  $178$  and  $-2^\circ$ , indicating *trans* bisected and perpendicular configurations for the carbonyl and phenyl groups, respectively. How such similar values for the bond-shortening effects of carbonyl groups can arise, despite differences in their configurations with respect to the ring, has been studied by Allen (1980). The values for  $\delta(\text{COOH})$  reported here are in good agreement with Allen's (1980) mean value for carbonyl groups,  $-0.026(5)$  Å, and the values for  $\delta(\text{phenyl})$  are in reasonable agreement with his mean value for phenyl groups,  $-0.018(2)$  Å. The most direct individual comparisons for (I) are from *trans*-2-(*p*-tolyl)cyclopropanecarboxylic acid (Ramirez, Rivera, Rodulfo de Gil, Alonso & Pékerar, 1990) and from ethyl *trans*-2-phenylcyclopropanecarboxylate (Mora, Rivera, Rodulfo de Gil, Alonso & Pékerar, 1991). The first cited study gives asymmetry parameters  $\delta(\text{tolyl}) = -0.009$  and  $\delta(\text{COOH}) = -0.026$  Å, but based on the stated e.s.d.'s, the estimated uncertainty of these values is  $\sim 0.015$  Å; thus, they cannot be regarded as very firmly established. In the second cited study, no ring asymmetry was detected, most likely (as noted by the authors) due to the large uncertainties (0.02 Å) in ring bond lengths. It should be noted further that in the structure of *cis*-1,2-diphenylcyclopropane (Schmidbaur, Bublak, Schier, Reber & Müller, 1988), the two bonds proximal to the unsubstituted ring site are reported to differ from each other in length almost as much as the larger differs from the distal bond; thus, calculation of a (single) phenyl asymmetry parameter is precluded.

The geometric disposition of the two rings and the carboxyl group can be characterized by three dihedral angles between pairs of planes. The phenyl groups of the *A* and *B* molecules are closely planar, the maximum deviation of a phenyl C atom from the best-fit plane