| | | | |
|---|---|---|---|
| C2—O1—C3—C3$^i$ | 174.2 (3) | C6—C7—O3—C8 | −168.8 (3) |
| C10—N1—C4—C5 | −167.6 (3) | C7—O3—C8—C9 | 151.6 (3) |
| N1—C4—C5—O2 | −62.7 (4) | O3—C8—C9—N1$^i$ | 172.2 (3) |

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

Synthesis: 0.00797 mol (3 g) cryptand[2.2.2] were allowed to react with 0.017 mol (1.06 ml) methyl iodide in 30 ml methanol for 6 h. The solvent was evaporated *in vacuo* and the white product recrystallized from methanol and washed with dry diethyl ether, yielding 4.37 g (83%) of the title compound as colourless crystals.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55958 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1028]

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*Acta Cryst.* (1993). C**49**, 1222–1224

# (*R*)-2-Bromo-1,4-butanedioic Acid

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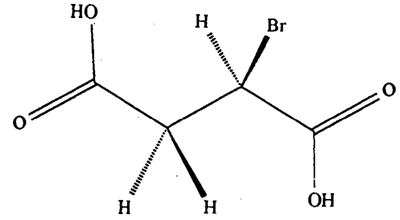
## Abstract

The absolute configuration of (+)-bromosuccinic acid has been determined to be (*R*). Bond lengths and angles are normal.

## Comment

Thiol and phosphine thiol complexes of gold(I) are used in the treatment of rheumatoid arthritis (Skosey, 1985). D-Penicillamine has similar efficacy and toxicity (Howard-Lock, Lock, Mewa & Kean, 1986). We have shown that this drug and other thiols inhibit activation of the protein kinase *C* pathway, the pathway of action in all inflammatory cells, in a similar fashion to the gold drug, disodium aurothiomalate (McKague, Lock, McCrae, Smith, Buchanan, Kean & Reglinski, 1993). These facts raise the question as to whether gold is a necessary constituent of the gold drugs or whether it is acting as an expensive carrier for the thiol ligand. Thus, we have been examining the biochemistry and structure of various thiol ligands, particularly the separate enantiomers of chiral molecules, since these can have dramatically different biological effects (Kean, Lock & Howard-Lock, 1991).



We attempted to synthesize the (*S*) enantiomer of thiomalic acid, from (−)-(*R*)-aspartic acid, by diazotization and bromination to give (*R*)-bromosuccinic acid, followed by reaction with *O*-ethyl dithiocarbonic acid in cold aqueous $Na_2CO_3$, to give (*S*)-2-(*O*-ethyl dithiocarbonato)succinic acid. Hydrolysis of the protected thiol group should give the desired compound. Structural studies showed that the protected compound was a racemate (Duarte, Frampton, Howard-Lock, Lock & Wu, 1989).

Diazotization reactions can proceed both by mechanisms where configuration is retained or where configuration is inverted; the configuration of the brominated product is very dependent on the reaction conditions (Brewster, Hughes, Ingold & Rao, 1950; Ingold, 1953). The reaction undertaken here had the important requirement for retention of configuration, namely an $\alpha$-carboxyl group, and we conducted the preparation under conditions which should retain the configuration. We also wished to confirm that racemization had not taken place in this step of the reaction and to this end we determined the absolute configuration of the bromosuccinic acid.

All the crystals examined were twinned and a number were studied by X-ray diffraction before a suitable one was obtained. Even then, refinement showed that many of the reflections in the $k = 6$ layer had $F_o$ much smaller than $F_c$, and the peak profiles showed a large and skewed background, suggesting overlap with the twinned reflections. Thus, all reflections from the $k = 6$ layer were omitted from the refinement.

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The structure was originally solved with the molecule having the (*S*) configuration, but a refinement using the method of Rogers (1981) showed that $\eta = -0.55$ (7), which suggested that the enantiomer was incorrect. This was confirmed by a comparison of the final residuals for the (*S*) ($R = 0.0521$, $wR = 0.0524$, $S = 2.47$) and (*R*) ($R = 0.0424$, $wR = 0.0419$, $S = 1.97$) configurations.

Thus, the molecule had an (*R*) configuration, which is what would be found if the reaction had proceeded with retention of configuration. The molecule is shown in Fig. 1. Bond lengths and angles, shown in Table 2, are normal. The orientation of the carboxylate groups appears to be determined primarily by the Br atom. Thus, although the C(3)···O(1) distance (2.81 Å) is considerably shorter than the van der Waals distance (3.15–3.20 Å; Bondi, 1964), it is still longer than the C(2)···O(4) distance, but the Br(1)—C(2)—C(1)—O torsion angles are nearly 90° [O(1) 90.5°, O(2) −90.4°]. The Br(1)···O distances are then nearly equal [O(1) 3.41, O(2) 3.36 Å] and close to the van der Waals distance (3.30–3.50 Å; Bondi, 1964). Similarly, if the O(3)—C(4)—C(3)—C(2) angle were 180° it would make little difference to the O(4)···C(2) distance [2.75 *vs.* 2.79 Å (observed)] and the O(3)···H(3*A*),H(3*B*) distances would be equal, even though shorter than the van der Waals distance (2.70–3.15 Å; Bondi, 1964). The O(3)—C(4)—C(3)—C(2) angle of −156.3° means that the O(3)···H(3*A*) and O(3)···H(3*B*) distances (2.72 and 2.45 Å, respectively) are energetically less favourable than the symmetric arrangement, but the O(4)···Br(1) distance is now 3.39 Å, close to the van der Waals distance. It should be noted that it appears to be more difficult to bring very electronegative atoms closer than the van der Waals distance compared to atoms where the electronegativity difference is much greater. The packing is shown in Fig. 2. Molecules form chains in the **a** direction and are held together by quite strong hydrogen bonds between the C(1) carboxylate group on one molecule and the C(4) carboxylate group on the next [O(1)···O(3)′ 2.67 (1), O(2)···O(4)′ 2.66 (1) Å]. In the **b** and **c** directions, the interactions between the molecules are of van der Waals type.

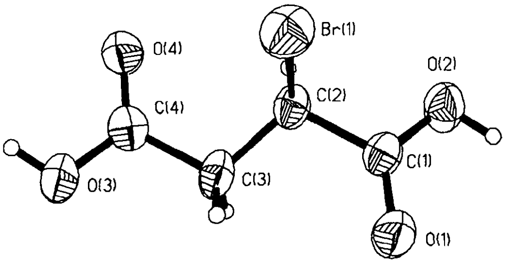

Fig. 1. View of the title molecule, showing the atom-numbering scheme.

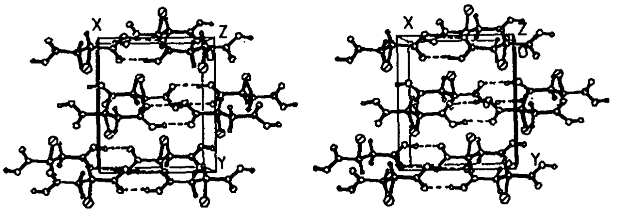

Fig. 2. The packing within the unit cell. **a*** and **b** are parallel to the bottom and sides of the page and the view is down **c**. Hydrogen bonds are indicated by broken lines.

## Experimental

### *Crystal data*

$C_4H_5BrO_4$
$M_r = 197.0$
Orthorhombic
$P2_12_12_1$
$a = 7.578$ (2) Å
$b = 8.735$ (2) Å
$c = 9.371$ (2) Å
$V = 620.3$ (3) Å$^3$
$Z = 4$
$D_x = 2.109$ Mg m$^{-3}$
$D_m = 1.99$ (3) Mg m$^{-3}$
Density measured by suspension in $CCl_4/CHBr_3$

Cu *Kα* radiation
$\lambda = 1.54178$ Å
Cell parameters from 24 reflections
$\theta = 38-40°$
$\mu = 6.564$ mm$^{-1}$
$T = 296$ (1) K
Plate
0.25 × 0.20 × 0.10 mm
Colourless
Crystal source: (*R*)-aspartic acid, diazotization and then bromination

### *Data collection*

Rigaku AFC-6 diffractometer
$\theta$-$2\theta$ scans
Absorption correction: refined from $\Delta F$ (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.568$, $T_{max} = 1.396$
1882 measured reflections
793 independent reflections

779 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.082$
$\theta_{max} = 55°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity variation: −13.8%

### *Refinement*

Refinement on $F$
Final $R = 0.0424$
$wR = 0.0419$
$S = 1.97$
705 reflections
82 parameters
H-atom parameters not refined

$w = 1/\sigma^2$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.79$ e Å$^{-3}$
$\Delta\rho_{min} = -0.58$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Br(1) | 0.9032 (1) | 0.7224 (1) | 0.5547 (1) | 0.055 (1) |
| O(4) | 0.5741 (8) | 0.5075 (8) | 0.6968 (7) | 0.050 (2) |
| C(2) | 0.9377 (10) | 0.5577 (11) | 0.6965 (9) | 0.037 (3) |
| C(3) | 0.8274 (9) | 0.5916 (12) | 0.8277 (10) | 0.045 (3) |

| | | | | |
|---|---|---|---|---|
| O(3) | 0.5368 (7) | 0.6593 (8) | 0.8832 (7) | 0.057 (3) |
| C(4) | 0.6318 (10) | 0.5817 (11) | 0.7968 (10) | 0.039 (3) |
| O(1) | 1.1920 (7) | 0.6483 (9) | 0.8257 (8) | 0.062 (3) |
| C(1) | 1.1344 (10) | 0.5666 (11) | 0.7283 (10) | 0.039 (3) |
| O(2) | 1.2303 (8) | 0.4818 (9) | 0.6476 (7) | 0.053 (3) |

Table 2. *Bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Br(1)—C(2) | 1.975 (9) | O(4)—C(4) | 1.22 (1) |
| C(2)—C(3) | 1.52 (1) | C(2)—C(1) | 1.52 (1) |
| C(3)—C(4) | 1.51 (1) | O(3)—C(4) | 1.28 (1) |
| O(1)—C(1) | 1.25 (1) | C(1)—O(2) | 1.28 (1) |
| Br(1)—C(2)—C(3) | 109.3 (6) | Br(1)—C(2)—C(1) | 102.9 (6) |
| C(3)—C(2)—C(1) | 111.8 (7) | C(2)—C(3)—C(4) | 112.0 (7) |
| O(4)—C(4)—C(3) | 121.9 (8) | O(4)—C(4)—O(3) | 124.5 (7) |
| C(3)—C(4)—O(3) | 113.6 (8) | C(2)—C(1)—O(1) | 121.3 (8) |
| C(2)—C(1)—O(2) | 114.2 (8) | O(1)—C(1)—O(2) | 124.5 (7) |

Reflections were corrected for crystal decay. The structure was solved by direct methods. Reflections in the range $-3\sigma_I \leq I \leq 3\sigma_I$ [$\sigma_I = (N_p + N_b)^{1/2}$, where $N_p$ is the number of counts in the peak and $N_b$ is the number of counts in the background] were treated by the method of French & Wilson (1978). Reflections with $k = 6$ were not used in refinement because the crystal was twinned and the twin interfered with this layer. H atoms were placed in calculated positions, with fixed temperature factors, and were constrained to ride on the atoms to which they were attached. Anomalous-dispersion corrections were applied to N, O and Br atoms. Calculations were made using *SHELXTL PC* (Sheldrick, 1990) and Laser386 or IBM486 computers.

We acknowledge, with thanks, financial support from the Natural Sciences and Engineering Council of Canada.

Lists of structure factors, anisotropic thermal parameters, H-atom positional parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55932 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1027]

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# (+)-(*R*)- and Racemic Forms of 2,2′-Dihydroxy-1,1′-binaphthyl

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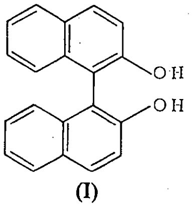
## Abstract

The molecules of 1,1′-binaphthyl-2,2′-diol, related by a $3_1$ axis in the (+)-(*R*) form and by a $2_1$ axis in the racemic form, are linked through hydrogen bonds between the hydroxyl groups. The dihedral angles between the planes of the naphthyl groups are close to 90° for the molecules in both crystals: 101.65 (5)° in the (+)-(*R*) form and 90.58 (4)° in the racemic form.

## Comment

Optical isomers exist for the title compound (I) because of steric hindrance around the C($sp^2$)—C($sp^2$) bond between the naphthyl groups (Akimoto, Shioiri, Iitaka & Yamada, 1968). The present work has been carried out in order to determine the molecular conformation, the mode of hydrogen bonding and the relationship between the molecular arrangements in the crystals of the (+)-(*R*) and racemic forms which were formed from toluene and ethanol solutions, respectively, by slow evaporation. For the latter form, the atomic parameters of the non-H atoms have been reported (Gridunova, Furmanova, Shklover, Struchkov, Ezhkova & Chayanov, 1982), but the H-atom positions to specify the hydrogen bonding have not been determined.



(I)

Corresponding bond lengths and angles in both forms of the crystals are in agreement within their e.s.d.'s. Corresponding bond lengths and angles of the two naphthyl groups in each molecule are substantially the same. In both crystals, C(1)—C(2)