Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}
O(1)	0.4421 (2)	1/4	0.1122 (2)	5.63 (9)
O(2)	0.2731 (2)	1/4	0.0469 (2)	6.28 (9)
O(3)	0.3725 (1)	1/4	0.3227 (1)	3.33 (6)
N(1)	0.3408 (2)	1/4	0.1247 (2)	4.21 (9)
N(2)	0.4677 (2)	1/4	0.5401 (2)	3.59 (8)
N(3)	0.5048 (2)	1/4	0.6525 (2)	3.52 (7)
N(4)	0.4365 (2)	1/4	0.7451 (2)	4.72 (9)
N(5)	0.6190 (2)	1/4	0.7968 (2)	4.37 (9)
C(1)	0.2966 (2)	1/4	0.2374 (2)	3.41 (9)
C(2)	0.1908 (2)	1/4	0.2736 (2)	4.4 (1)
C(3)	0.1992 (2)	1/4	0.3934 (2)	4.8 (1)
C(4)	0.3090 (2)	1/4	0.4203 (2)	3.65 (9)
C(5)	0.3618 (2)	1/4	0.5299 (2)	3.80 (9)
C(6)	0.5100 (3)	1/4	0.8280 (2)	4.9 (1)
C(7)	0.6117 (2)	1/4	0.6850 (2)	3.87 (9)

Table 2. *Selected geometric parameters (Å, °)*

O(1)—N(1)	1.220 (3)	O(2)—N(1)	1.218 (3)
O(3)—C(1)	1.349 (3)	O(3)—C(4)	1.372 (3)
N(1)—C(1)	1.421 (3)	N(2)—N(3)	1.389 (3)
N(2)—C(5)	1.271 (3)	N(3)—N(4)	1.357 (3)
N(3)—C(7)	1.333 (3)	N(4)—C(6)	1.309 (4)
N(5)—C(6)	1.353 (4)	N(5)—C(7)	1.312 (3)
C(1)—C(2)	1.334 (4)	C(2)—C(3)	1.406 (4)
C(3)—C(4)	1.350 (4)	C(4)—C(5)	1.430 (3)
C(1)—O(3)—C(4)	104.2 (1)	O(3)—C(1)—C(2)	113.7 (2)
O(1)—N(1)—O(2)	124.7 (2)	N(1)—C(1)—C(2)	130.3 (2)
O(1)—N(1)—C(1)	118.7 (2)	C(1)—C(2)—C(3)	104.4 (2)
O(2)—N(1)—C(1)	116.6 (2)	C(2)—C(3)—C(4)	107.6 (2)
N(3)—N(2)—C(5)	114.0 (2)	O(3)—C(4)—C(3)	110.1 (2)
N(2)—N(3)—N(4)	124.4 (2)	O(3)—C(4)—C(5)	120.2 (2)
N(2)—N(3)—C(7)	125.2 (2)	C(3)—C(4)—C(5)	129.7 (2)
N(4)—N(3)—C(7)	110.4 (2)	N(2)—C(5)—C(4)	121.6 (2)
N(3)—N(4)—C(6)	100.9 (2)	N(4)—C(6)—N(5)	116.5 (2)
C(6)—N(5)—C(7)	101.8 (2)	N(3)—C(7)—N(5)	110.4 (2)
O(3)—C(1)—N(1)	115.9 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C(6)—H(C6)···O(1^{i})	0.938 (4)	2.492 (3)	3.425 (3)	173.1 (6)
C(7)—H(C7)···O(2^{ii})	0.965 (4)	2.410 (3)	3.331 (3)	159.5 (6)
C(5)—H(C5)···N(5^{iii})	0.965 (4)	2.597 (3)	3.541 (3)	166.9 (6)

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

Data were corrected for Lp effects. The structure was solved by direct methods. H atoms were included as fixed contributors at positions found in the difference synthesis and refined with an overall isotropic displacement parameter which converged to 0.064 (4) Å². The refinement was by blocked-matrix least-squares methods.

Programs used: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1142). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chiral α-Hydroxy Acids: Racemic 2-Hydroxy-2,3,3-trimethylbutanoic Acid and 2-Hydroxy-2-trimethylsilylpropanoic Acid

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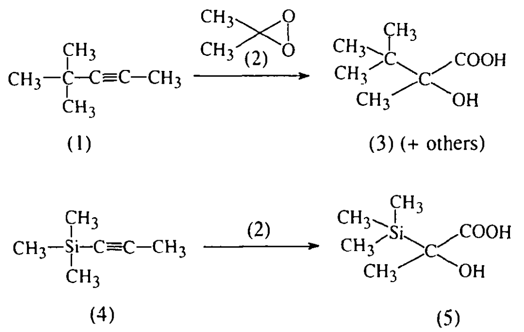
Abstract

Both $C_7H_{14}O_3$ and $C_6H_{14}O_3Si$ crystallize as racemates from acetone solution, the former incorporating water of crystallization ($C_7H_{14}O_3.0.5H_2O$). The crystal structures display extensive intermolecular hydrogen bonding involving the hydroxy and carboxylic acid groups to give polymeric networks.

Comment

α-Hydroxy acids are well known for their important roles in biochemistry and in synthetic organic chemistry. More recently they have achieved new prominence because of their importance to the cosmetic industry (Marcet, 1993; Hagan, Parrott & Taylor, 1993; Nowak, 1993; Armengol, 1993). We have recently described the reaction of dimethyldioxirane with some alkynes (Murray & Singh, 1993). In some cases these reactions give α-hydroxy acids as products. Thus, the reaction of 4,4-dimethyl-2-pentyne, (1), with dimethyldioxirane, (2), gave a number of products including a small amount (8%) of 2-hydroxy-2,3,3-trimethylbutanoic acid, (3). Similarly, the reaction of 1-(trimethylsilyl)propyne, (4), with (2) gave 2-hydroxy-2-trimethylsilylpropanoic acid, (5), in 93% yield. Acid (3) was recrystallized from methylene chloride/hexane to give colourless needles which exhibited the same melting-point behaviour as that reported in the literature (Evans & Landor, 1965). The trimethylsilyl-substituted acid (5) was recrystallized from petroleum ether to give colourless needles with melting point 375–377 K. Single-crystal X-ray diffraction analysis demonstrates that both acids crystallize from acetone as racemates.



The solid-state structure of (5) has two unique molecules in the asymmetric unit. The bond angles and distances are consistent with those of the published structures of α-hydroxy acids. Compound (3) crystallizes with half a molecule of water per molecule of acid, the water being derived from incompletely dried acetone solvent. The crystal packing for both α-hydroxy acids involves extensive linear intermolecular hydrogen bonding.

The solid-state structure of (3) forms eight-membered rings due to hydrogen bonding between two carboxy groups related by an inversion centre. The O···O distance for this type of hydrogen bond is 2.702 (3) Å. The O atom of the water molecule hydrogen bonds to two α-hydroxy H atoms. The O···O distances for the hydrogen bonds involving the O atom of the water molecule are 2.723 (3) and 2.775 (3) Å. Each H atom of the water molecule forms two hydrogen bonds to the α-hydroxy O and the carbonyl O atoms, forming five-membered rings. A packing diagram, with the ^{t}Bu group omitted, is presented in Fig. 3.

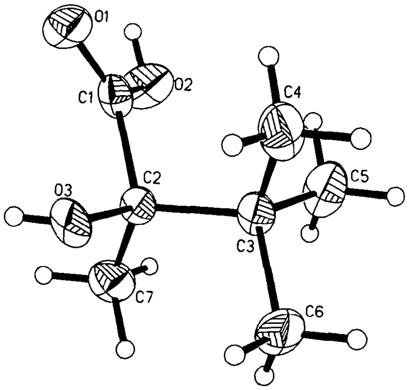


Fig. 1. A view of (3) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 75% probability level; H atoms are drawn as small circles of arbitrary radii. The solvent water molecule is not shown.

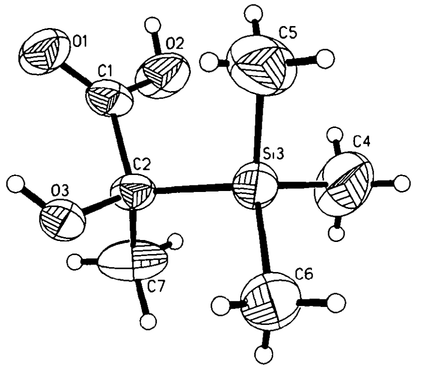


Fig. 2. A view of one of the two unique molecules of (5) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

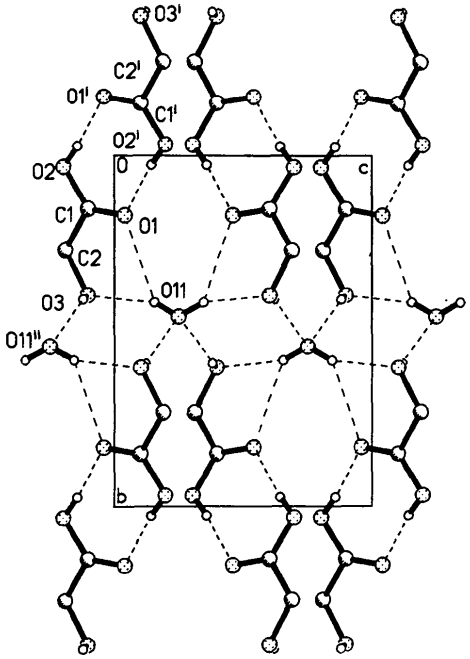


Fig. 3. Crystal packing of (3) showing the hydrogen bonding (a-axis projection).

Compound (5) also exhibits an extended hydrogen-bonding network, involving two sets of three intermolecular hydrogen bonds, and forms eight- and eleven-membered rings. The polymeric network involves both the unique molecules and their symmetry-related pair (related by glide plane). The intermolecular hydrogen-bonding distances are in the range 2.616 (4)–2.834 (4) Å. However, no carboxy pairing due to hydrogen bonding was observed for (5). The α-hydroxy H atoms are involved in intramolecular hydrogen bonding with the carbonyl O atom of the carboxy group, with O···O

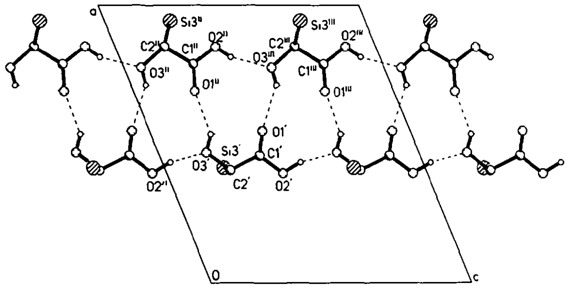


Fig. 4. Crystal packing of (5) showing the hydrogen bonding (*b*-axis projection).

distances of 2.640 (4) and 2.647 (4) Å, and forms five-membered rings. The H atom is bent towards the carbonyl O atom due to this hydrogen-bonding interaction. The hydrogen-bonded network is shown in Fig. 4.

Experimental

Crystals of (3) and (5) used for X-ray diffraction analysis were obtained by recrystallization from acetone.

Compound (3)

Crystal data

$C_7H_{14}O_3.0.5H_2O$
M_r = 155.19
Monoclinic
$C2/c$
a = 24.282 (5) Å
b = 9.544 (2) Å
c = 7.4120 (15) Å
β = 106.60 (3)°
V = 1646.1 (6) Å^3
Z = 8
D_x = 1.252 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 16 reflections
θ = 4.0–10.2°
μ = 0.099 mm^{-1}
T = 128 (2) K
Irregular
0.3 × 0.2 × 0.06 mm
Colourless

Data collection

Siemens $R3$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4820 measured reflections
2319 independent reflections
1019 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.1143

$\theta_{\rm max}$ = 30.09°
$h = -34 \rightarrow 32$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 100 reflections intensity decay: 3.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0726
$wR(F^2)$ = 0.1573
S = 1.086
2319 reflections
98 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.49 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.39 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3)*

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

	x	y	z	$U_{\rm eq}$
O1	0.48529 (10)	0.1687 (2)	0.0406 (3)	0.0212 (6)
O2	0.43719 (10)	0.0317 (2)	−0.1970 (4)	0.0258 (6)
O3	0.42644 (10)	0.3968 (2)	−0.1030 (3)	0.0190 (5)
C1	0.44580 (13)	0.1505 (3)	−0.1020 (5)	0.0151 (6)
C2	0.40260 (13)	0.2680 (3)	−0.1891 (5)	0.0144 (6)
C3	0.34511 (13)	0.2481 (3)	−0.1341 (5)	0.0171 (7)
C4	0.35714 (15)	0.2570 (4)	0.0794 (5)	0.0252 (8)
C5	0.31618 (14)	0.1069 (3)	−0.2019 (6)	0.0273 (9)
C6	0.30309 (14)	0.3661 (3)	−0.2260 (6)	0.0263 (8)
C7	0.39458 (15)	0.2750 (3)	−0.3994 (5)	0.0214 (7)
O11	1/2	0.4570 (3)	1/4	0.0210 (7)

Table 2. *Intermolecular hydrogen-bond geometry (Å, °) for (3)*

	O···O	O—H	H···O	O—H···O
O11—H11···O3	2.775 (3)	0.831	1.985	158.3
O2—H2···O1$^{\rm i}$	2.702 (3)	0.825	1.879	174.5
O3—H3···O11$^{\rm ii}$	2.723 (3)	0.724	2.106	144.2

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

Compound (5)

Crystal data

$C_6H_{14}O_3Si$
M_r = 162.26
Monoclinic
$P2_1/c$
a = 13.141 (3) Å
b = 13.741 (3) Å
c = 11.551 (2) Å
β = 112.36 (3)°
V = 1928.9 (7) Å^3
Z = 8
D_x = 1.118 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 15 reflections
θ = 5.0–16.6°
μ = 0.201 mm^{-1}
T = 298 (2) K
Rectangular plate
0.6 × 0.4 × 0.3 mm
Colourless

Data collection

Siemens $R3$ diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*SHELXTL*; Sheldrick, 1994)
$T_{\rm min}$ = 0.941, $T_{\rm max}$ = 1.000
5008 measured reflections
4748 independent reflections
2621 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.040
$\theta_{\rm max}$ = 30.07°
$h = -18 \rightarrow 17$
$k = -19 \rightarrow 0$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 100 reflections intensity decay: 24.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0799
$wR(F^2)$ = 0.2416
S = 1.239
4643 reflections
205 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1649P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ < 0.001
$\Delta\rho_{\rm max}$ = 0.583 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.320 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (5)*

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

	x	y	z	$U_{\rm eq}$
Si3	0.05596 (9)	0.61716 (9)	0.24884 (9)	0.0525 (3)
Si3′	0.41369 (11)	0.06744 (9)	0.22692 (13)	0.0660 (4)
O1	0.3110 (2)	0.7365 (2)	0.2643 (2)	0.0618 (8)
O2	0.1502 (2)	0.7739 (3)	0.1150 (3)	0.0669 (9)
O3	0.2256 (2)	0.7029 (2)	0.4337 (2)	0.0472 (6)
O1′	0.5460 (2)	0.2677 (3)	0.4319 (2)	0.0701 (9)
O2′	0.3938 (3)	0.2080 (2)	0.4454 (3)	0.0691 (9)
O3′	0.4678 (2)	0.2527 (2)	0.1849 (2)	0.0498 (6)
C1	0.2130 (3)	0.7471 (2)	0.2284 (3)	0.0418 (7)
C2	0.1497 (3)	0.7287 (2)	0.3107 (3)	0.0381 (7)
C4	−0.0691 (4)	0.6505 (6)	0.1109 (4)	0.104 (2)
C5	0.1371 (5)	0.5233 (4)	0.2050 (6)	0.094 (2)
C6	0.0160 (4)	0.5752 (4)	0.3779 (4)	0.0758 (14)
C7	0.0863 (4)	0.8198 (3)	0.3192 (4)	0.0698 (13)
C1′	0.4572 (3)	0.2323 (3)	0.3840 (3)	0.0453 (8)
C2′	0.4051 (3)	0.2055 (2)	0.2479 (3)	0.0391 (7)
C4′	0.3711 (10)	0.0454 (5)	0.0572 (6)	0.172 (5)
C5′	0.3218 (6)	0.0020 (4)	0.2895 (7)	0.121 (3)
C6′	0.5583 (6)	0.0315 (5)	0.3102 (8)	0.146 (4)
C7′	0.2886 (3)	0.2453 (4)	0.1883 (4)	0.0655 (11)

Table 4. *Intermolecular hydrogen-bond geometry (Å, °) for (5)*

	O···O	O—H	H···O	O—H···O
O3$^{\rm ii}$—H3$^{\rm ii}$···O1$^{\rm ii}$	2.640 (3)	0.810	2.213	113.3
O3$^{\rm iii}$—H3$^{\rm iii}$···O1′	2.834 (4)	0.810	2.117	147.6
O2$^{\rm ii}$—H2$^{\rm ii}$···O3$^{\rm iii}$	2.655 (4)	0.803	1.902	155.7
O3′—H3′···O1′	2.647 (4)	0.830	2.309	105.0
O3′—H3′···O1$^{\rm ii}$	2.747 (4)	0.830	2.009	147.9
O2′$^{\rm i}$—H2′$^{\rm i}$···O3′	2.616 (4)	0.939	1.699	164.4

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

Methyl group H atoms were refined using a riding model. Hydroxy H atoms were refined with a riding model for (3), allowing torsional freedom, and were freely refined along with the solvent water unique H atom for (5). For riding H atoms, $U({\rm H}) = 1.5U_{\rm eq}(X)$, where X is the parent bonded atom. The relatively high residuals are due to poor quality for both compounds and to probable unresolved disorder and crystal decomposition for (5).

For both compounds, data collection: *P3/PC Diffractometer Program* (Siemens, 1989); cell refinement: *P3/PC Diffractometer Program*; data reduction: *SHELXTL* (Sheldrick, 1994); program(s) used to solve structures: *SHELXTL*; program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1021). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Phenyl-4-morpholinecarbothioamide and *N*-(2-Tolyl)-4-morpholinecarbothioamide

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Abstract

The structures of two unsymmetrically substituted thiourea derivatives, $C_{11}H_{14}N_2OS$, (1), and $C_{12}H_{16}N_2OS$, (2), are reported. In (1), the two molecules present in the asymmetric unit show differences in the orientations of the phenyl and cyclohexyl rings. In both of the structures, N—H···S hydrogen bonds link the molecules into chains that run parallel to a crystallographic axis.

Comment

Unsymmetrically substituted thioureas are found to exhibit agrochemical properties (Sarkis & Faisal, 1985; Ramadas, Srinivasan & Janarthanan, 1993). As a part of our investigations on substituted thiourea derivatives, we have determined the crystal structures of two more unsymmetrically substituted thiourea derivatives, (1) and (2).

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