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1-Acetyl-3-hydroxyadamantane and 1-Carboxy-3-hydroxyadamantane

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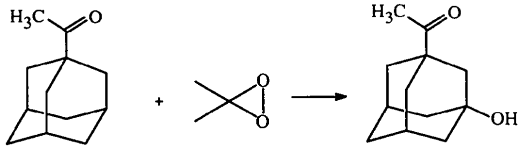
Abstract

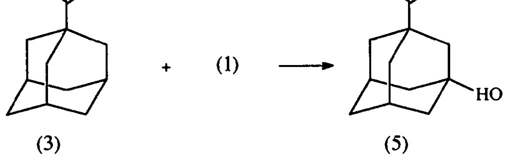
The crystal structures of the adamantane derivatives, 1-acetyl-3-adamantanol, $C_{12}H_{18}O_2$, (4), and 3-hydroxyadamantane-1-carboxylic acid, $C_{11}H_{16}O_3$, (5), have been determined by X-ray diffraction. Both structures show extensive intermolecular hydrogen bonding involving the hydroxyl and acetyl groups in compound (4), and the hydroxyl and carboxyl groups in compound (5).

Comment

We have recently described (Murray & Gu, 1995) linear free-energy relationship (LFER) studies of the C—H insertion reaction of dimethyldioxirane, (1), in two series of substrates. In one of these series, 1-substituted adamantanes are reacted with (1) to give the 3-hydroxy insertion product derivatives. Thus, 1-acetyladamantane, (2), and 1-carboxyadamantane, (3), give 1-acetyl-3-hydroxyadamantane, (4), and 1-carboxy-3-hydroxyadamantane, (5), respectively.



(2) (1) (4)



(3) (5)

Single-crystal X-ray diffraction analyses of (4) and (5) (Figs. 1 and 3) demonstrate that both adamantane derivatives have extensive intermolecular hydrogen bonding in the solid state. In the acetyl compound, (4), chains of linear hydrogen bonds are formed between the OH group of one molecule and the carbonyl group of a neighboring molecule (Fig. 2). The O···O distance [O2—O1′(*x*, *y* , *z* − 1)] is 2.819 (2) Å and the geometry around the H2 atom is H2—O2 0.88 (4), H2—O1′ 1.94 (4) Å and O2—H2—O1′ 172 (3)°. In compound (5), hydrogen bonding produces an extensive polymeric network since the hydroxyl group substituents are simultaneously hydrogen bonded to the OH group of the carboxyl group on an adjacent molecule and the carbonyl group of a different neighbor forming a 12-membered ring as shown in Fig. 4. A 14-membered ring is formed by intermolecular hydrogen bonding between the carbonyl O and hydroxyl H atoms of two molecules. The alternating 12- and 14-membered rings which form the hydrogen-bonding network are cen-

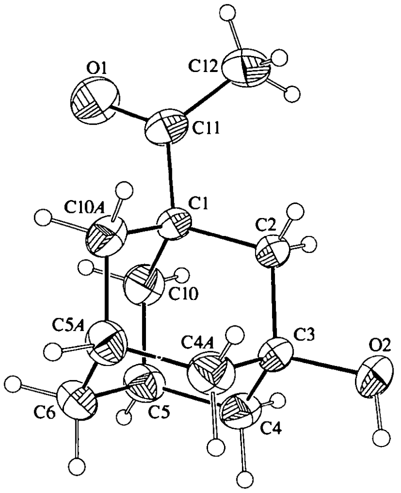


Fig. 1. View of (4) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

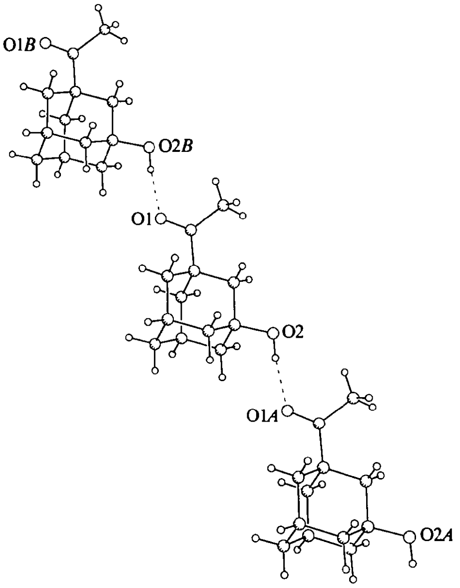


Fig. 2. The hydrogen bonding in compound (4).

tered around inversion centers. The geometric parameters for the hydrogen bonds formed for (5) are as follows: $O1^{i}\cdots O2$ 2.777 (4), $O1^{i}\cdots H2$ 1.98 (5) Å and $O1^{i}\cdots H2—O2$ 178 (5)°; $O3\cdots O2^{ii}$ 2.615 (4), $O2^{ii}\cdots H3$ 1.69 (5) Å and $O3—H3\cdots O2^{ii}$ 169 (4)° [symmetry codes: (i) $1-x$, $-y$, $2-z$; (ii) $1+x$, y, $1+z$].

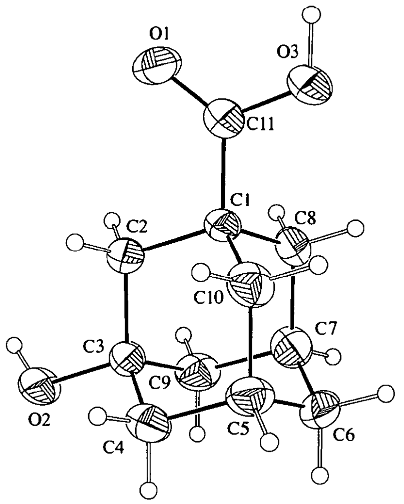


Fig. 3. View of (5) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

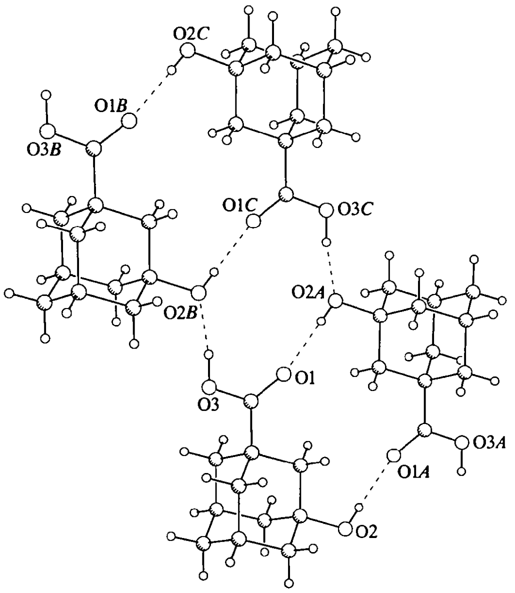


Fig. 4. The hydrogen bonding in compound (5).

Experimental

The acetyl derivative (4) was recrystallized from methylene chloride/hexane to give colorless orthorhombic crystals of melting point 432–433 K. The carboxyl derivative (5) was recrystallized from ether/hexane to give colorless rectangular plates of melting point 475.5–477.0 K. The melting point reported in the literature for (5) (Anderson, Burks & Harruna, 1988) is 476–478 K.

Compound (4)

Crystal data

$C_{12}H_{18}O_2$
$M_r = 194.26$
Orthorhombic
Pnma
$a = 17.762\ (2)$ Å
$b = 6.7914\ (8)$ Å
$c = 8.5267\ (11)$ Å
$V = 1028.6\ (2)$ Å^3
$Z = 4$
$D_x = 1.254$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 3.30–13.91°$
$\mu = 0.083$ mm^{-1}
$T = 293\ (2)$ K
Rectangular
0.4 × 0.3 × 0.2 mm
Colorless

Data collection

Siemens *P*4-*RA* diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2618 measured reflections
1517 independent reflections
1021 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.0397$
$\theta_{\max} = 30°$
$h = -1 \rightarrow 23$
$k = -8 \rightarrow 4$
$l = -1 \rightarrow 11$
3 standard reflections every 97 reflections intensity decay: 2.34%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.158$
$S = 1.040$
1509 reflections
116 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 0.1873P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.002$
$\Delta\rho_{\max} = 0.267$ e Å^{-3}
$\Delta\rho_{\min} = -0.168$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (4)*

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

	x	y	z	U_{eq}
O1	0.39684 (12)	1/4	1.5151 (2)	0.0851 (9)
O2	0.45783 (9)	1/4	0.8203 (2)	0.0515 (5)
C1	0.39420 (11)	1/4	1.2375 (2)	0.0303 (5)
C2	0.44802 (11)	1/4	1.0967 (2)	0.0315 (5)
C3	0.40314 (11)	1/4	0.9440 (2)	0.0325 (5)
C4	0.35348 (9)	0.4331 (3)	0.9365 (2)	0.0389 (4)
C5	0.29877 (8)	0.4332 (3)	1.0757 (2)	0.0375 (4)
C6	0.24951 (12)	1/4	1.0703 (3)	0.0427 (6)
C10	0.34401 (9)	0.4349 (3)	1.2288 (2)	0.0389 (4)
C11	0.43403 (13)	1/4	1.3958 (2)	0.0422 (6)
C12	0.5173 (2)	1/4	1.4051 (3)	0.0563 (8)

Table 2. *Selected geometric parameters (Å, °) for (4)*

O1—C11	1.213 (3)	C1—C11	1.524 (3)
O2—C3	1.434 (2)	C11—C12	1.481 (4)
O1—C11—C12	119.9 (2)	C12—C11—C1	120.7 (2)
O1—C11—C1	119.3 (2)		

Compound (5)

Crystal data

$C_{11}H_{16}O_3$
$M_r = 196.24$
Monoclinic
$P2_1/n$
$a = 6.675$ (6) Å
$b = 20.767$ (19) Å
$c = 7.109$ (7) Å
$\beta = 106.08$ (6)°
$V = 946.9$ (15) Å^3
$Z = 4$
$D_x = 1.377$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 7.55–17.97°$
$\mu = 0.099$ mm^{-1}
$T = 293$ (2) K
Irregular plate
0.50 × 0.30 × 0.05 mm
Colorless

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
3130 measured reflections
1856 independent reflections
969 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0664$

$\theta_{\rm max} = 26.01°$
$h = -8 \rightarrow 6$
$k = -19 \rightarrow 25$
$l = -8 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: 3.82%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0650$
$wR(F^2) = 0.1473$
$S = 1.051$
1818 reflections
135 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.1598P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.163$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.185$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.6823 (4)	0.02272 (12)	1.3418 (3)	0.0558 (7)
O2	0.0439 (4)	0.05938 (12)	0.7716 (3)	0.0479 (7)
O3	0.7011 (4)	0.10522 (13)	1.5351 (4)	0.0641 (9)
C1	0.4258 (4)	0.10552 (14)	1.2473 (4)	0.0292 (7)
C2	0.3296 (4)	0.06444 (15)	1.0677 (4)	0.0347 (8)
C3	0.1420 (4)	0.09863 (15)	0.9379 (4)	0.0323 (8)
C4	−0.0178 (5)	0.1101 (2)	1.0465 (5)	0.0398 (9)
C5	0.0766 (5)	0.1517 (2)	1.2245 (5)	0.0395 (8)
C6	0.1425 (5)	0.2148 (2)	1.1602 (5)	0.0444 (9)
C7	0.3020 (5)	0.2037 (2)	1.0503 (5)	0.0406 (9)
C8	0.4902 (5)	0.17021 (14)	1.1812 (5)	0.0360 (8)
C9	0.2087 (5)	0.1617 (2)	0.8726 (4)	0.0401 (8)
C10	0.2647 (5)	0.1171 (2)	1.3577 (4)	0.0393 (8)
C11	0.6143 (5)	0.0728 (2)	1.3773 (4)	0.0368 (8)

Table 4. *Selected geometric parameters* (Å, °) *for* (5)

O1—C11	1.190 (4)	O3—C11	1.299 (4)
O2—C3	1.436 (4)	C1—C11	1.501 (4)
O1—C11—O3	122.1 (3)	O3—C11—C1	113.3 (3)
O1—C11—C1	124.7 (3)		

The title structures were solved by direct methods and refined successfully in space groups *Pnma* and $P2_1/n$ for (4) and (5), respectively. Full-matrix least-squares refinement was carried out by minimizing $w(F_o^2-F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. H atoms were refined freely for (4) and only the H atoms connected to O were refined for (5). The other H atoms were treated using appropriate riding models.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1307). Services for accessing these data are described at the back of the journal.

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Three *trans*-Diphenylperfluorotrienes

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Abstract

The structures of (*E*)-1,1,1,6,6,6-hexafluoro-2,5-bis(pentafluorophenyl)-2,3,4-hexatriene, (1), $C_{18}F_{16}$, (*E*)-1,1,1,2,2,7,7,8,8,8-decafluoro-3,6-diphenyl-3,4,5-octatriene, (2), $C_{20}H_{10}F_{10}$, and (*E*)-1,1,1,2,2,3,3,8,8,9,9,10,10,10-