Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond distances and angles involving H atoms, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71832 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1055]

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threo-3-Fluoro-2-hydroxy-1,3-diphenyl-1-propanone and (1*RS*,2*RS*,3*RS*)-3-Fluoro-1,3-diphenyl-1,2-propanediol

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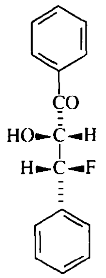
Abstract

The steric assignment of *threo*-3-fluoro-2-hydroxy-1,3-diphenyl-1-propanone, $C_{15}H_{13}FO_2$, has been confirmed. Reduction of this compound with sodium tetrahydridoborate gave a crystalline product identified as (1*RS*,2*RS*,3*RS*)-3-fluoro-1,3-diphenyl-1,2-propanediol, $C_{15}H_{15}FO_2$.

Comment

1,2-Diaryl-1,3-propanediols can be synthesized starting from 1,3-diaryl-2,3-epoxy-1-propanones. Treatment of such epoxides with boron trifluoride causes a rearrangement leading to 3-oxopropanals (or their difluoroboron complexes) (House & Ryerson, 1961; Li, Lundquist & Stomberg, 1993) and subsequent reduction yields the desired 1,2-diaryl-1,3-propanediols (Kristersson & Lundquist, 1980; Ahvonen, Brunow, Kristersson & Lundquist, 1983; Ralph, Ede, Robinson & Main, 1987; Tanaka, Hiroo, Ichino & Ito, 1989; Li, Lundquist & Stomberg, 1993). In some instances the boron trifluoride treatment leads to formation of fluorohydrins as by-products. Thus 2,3-epoxy-1,3-diphenyl-1-propanone gives substantial amounts of *threo*-3-fluoro-2-hydroxy-1,3-diphenyl-1-propanone (1) on treatment with about equimolar amounts of boron trifluoride in ether (House, 1956*a*; House & Ryerson, 1961).



(1)

The steric assignment of fluorohydrin (1) was derived from comparisons with the analogous *threo*-chlorohydrin (House, 1956*b*). The crystal structure determination described in this paper confirms that (1) has the *threo* configuration.

In two recent investigations (Ralph, Ede, Robinson & Main, 1987; Tanaka, Hiroo, Ichino & Ito, 1989) fluorohydrin formation on treatment of 1,3-diaryl-2,3-epoxy-1-propanones with boron trifluoride is reflected in the presence of 1,3-diaryl-3-fluoro-1,2-propanediols (together with 1,2-diaryl-1,3-propanediols) in the reaction mixtures resulting from reduction of the rearrangement products with tetrahydridoborate. Reduction of (1) with sodium tetrahydridoborate gave such a fluoro-substituted reduction product, namely (1*RS*,2*RS*,3*RS*)-3-fluoro-1,3-diphenyl-1,2-propanediol (2) (Li, Lundquist & Stomberg, 1993). The product was crystallized from benzene (m.p. 374–375 K). Its stereochemistry was elucidated by the crystal structure analysis presented in this paper. ^{1}H NMR examination of the mother liquor revealed the presence of small amounts of a stereoisomer of (2), the structure of which is proposed to be (1*RS*,2*SR*,3*SR*)-3-

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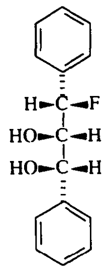
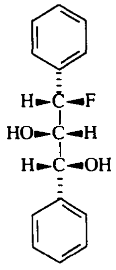
fluoro-1,3-diphenyl-1,2-propanediol (3). Our reduction experiments with (1), together with the structural study of (2), suggest that the stereochemistry of the 1,3-diaryl-3-fluoro-1,2-propanediols, described earlier in the literature (Ralph, Ede, Robinson & Main, 1987; Tanaka, Hiroo, Ichino & Ito, 1989) is analogous to that of (2).



(2)



(3)

Perspective views of the molecules (1) and (2) are shown in Figs. 1 and 2, respectively. The crystals are stabilized by hydrogen bonds between O(1) and O(2) in both (1) and (2) (Table 2), and in (1) there is a short intermolecular contact C(9)···O(1)(1 − *x*, 1 − *y*, 1 − *z*) of 2.957 (2) Å.

In (1) the benzylic atom C(7) is twisted 0.113 (2) Å out from the benzene ring plane C(1)–C(6) and the benzylic atom C(9) is twisted 0.024 (2) Å out from the benzene ring plane C(10)–C(15). In (2) the corresponding twists of C(7) and C(9) are 0.028 (3) and 0.101 (3) Å, respectively. The angle between the benzene ring planes is 44.8 (2)° in (1) and 78.0 (3)° in (2).

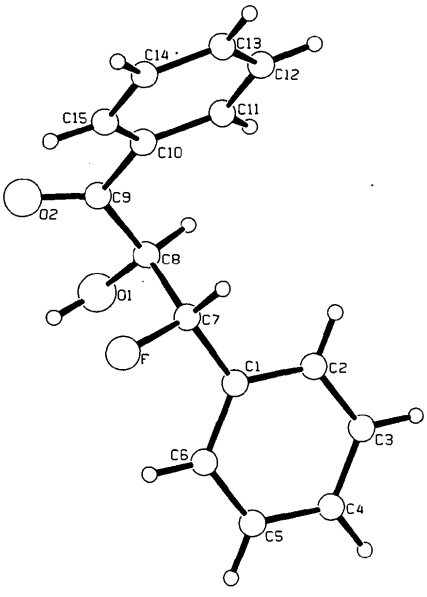


Fig. 1. A perspective drawing (*ORTEP*; Johnson, 1976) of (1).

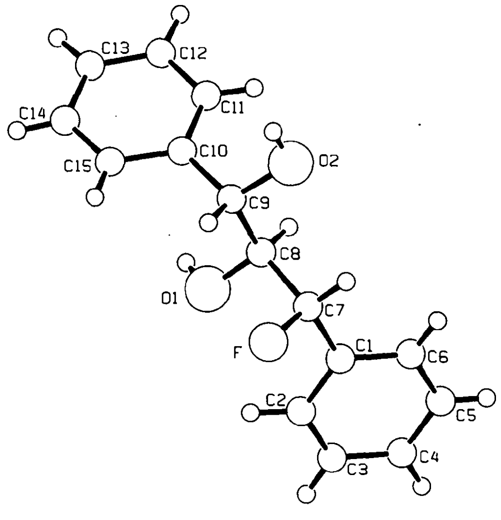


Fig. 2. A perspective drawing (*ORTEP*; Johnson, 1976) of (2).

Experimental

Compound (1)

Crystal data

$C_{15}H_{13}FO_2$
M_r = 244.26
Triclinic
$P\bar{1}$
a = 5.7500 (6) Å
b = 9.651 (1) Å
c = 11.194 (2) Å
α = 91.43 (1)°
β = 104.83 (1)°
γ = 92.54 (1)°
V = 599.5 (1) Å^3
Z = 2

D_x = 1.353 Mg m^{-3}
Cu *K*α radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 37.4–39.9°
μ = 0.79 mm^{-1}
T = 296 K
Plate
0.87 × 0.41 × 0.04 mm
Colourless

Data collection

Syntex *P*2$_1$ diffractometer
ω-2θ scans
Absorption correction: none
2000 measured reflections
1794 independent reflections
1407 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.029
$\theta_{\rm max}$ = 60.1°

$h = 0 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 150 reflections
intensity variation: 0.1% average (range −0.2 to 0.5%)

Refinement

Refinement on *F*
R = 0.035
wR = 0.050
S = 1.59
1407 reflections
215 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o) + 0.05(F_o)^2]$
$(\Delta/\sigma)_{\rm max}$ = 0.00
$\Delta\rho_{\rm max}$ = 0.15 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.13 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$C_{15}H_{15}FO_2$
$M_r = 246.28$
Monoclinic
$P2_1/n$
$a = 5.325$ (2) Å
$b = 9.900$ (3) Å
$c = 23.778$ (2) Å
$\beta = 95.47$ (1)°
$V = 1247.9$ (7) Å^3
$Z = 4$

$D_x = 1.311$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 24 reflections
$\theta = 29.0$-37.3°
$\mu = 0.76$ mm^{-1}
$T = 296$ K
Prism
0.53 × 0.35 × 0.17 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
ω-2θ scans
Absorption correction: none
2378 measured reflections
2125 independent reflections
1333 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.022$
$\theta_{\rm max} = 62.6$°

$h = 0 \rightarrow 6$
$k = 0 \rightarrow 11$
$l = -27 \rightarrow 27$
3 standard reflections monitored every 150 reflections intensity variation: −2.3% average (range −1.7 to −2.8%)

Refinement

Refinement on F
$R = 0.038$
$wR = 0.047$
$S = 1.94$
1333 reflections
223 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o) + 0.03(F_o)^2]$
$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.14$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
(1)				
C(1)	0.9066 (3)	0.5969 (2)	0.8521 (2)	3.84 (7)
C(2)	0.7359 (4)	0.6096 (2)	0.9183 (2)	4.49 (8)
C(3)	0.7519 (5)	0.7207 (2)	1.0010 (2)	5.2 (1)
C(4)	0.9396 (5)	0.8178 (2)	1.0187 (2)	5.6 (1)
C(5)	1.1060 (5)	0.8073 (2)	0.9516 (2)	5.7 (1)
C(6)	1.0905 (4)	0.6979 (2)	0.8679 (2)	4.95 (9)
C(7)	0.8943 (3)	0.4703 (2)	0.7698 (2)	3.96 (7)
C(8)	0.7122 (3)	0.4729 (2)	0.6441 (2)	3.74 (7)
C(9)	0.7325 (3)	0.3392 (2)	0.5719 (2)	3.94 (7)
C(10)	0.6695 (3)	0.2035 (2)	0.6189 (2)	3.60 (6)
C(11)	0.4937 (4)	0.1870 (2)	0.6834 (2)	4.28 (8)
C(12)	0.4453 (4)	0.0585 (2)	0.7251 (2)	5.1 (1)
C(13)	0.5738 (4)	−0.0533 (2)	0.7059 (2)	5.4 (1)
C(14)	0.7469 (5)	−0.0379 (2)	0.6425 (2)	5.2 (1)
C(15)	0.7946 (4)	0.0891 (2)	0.5990 (2)	4.41 (8)
F	1.1215 (2)	0.4539 (1)	0.7461 (1)	5.43 (5)
O(1)	0.7462 (3)	0.5924 (1)	0.5806 (1)	4.42 (6)
O(2)	0.8197 (3)	0.3446 (2)	0.4841 (1)	5.30 (6)
(2)				
C(1)	−0.2370 (4)	0.2621 (3)	0.6613 (1)	3.9 (1)
C(2)	−0.0203 (5)	0.1945 (3)	0.6827 (1)	4.6 (1)
C(3)	0.1057 (6)	0.2335 (4)	0.7335 (1)	5.8 (2)
C(4)	0.0211 (7)	0.3399 (4)	0.7632 (1)	6.2 (2)
C(5)	−0.1908 (7)	0.4078 (4)	0.7423 (1)	6.2 (2)
C(6)	−0.3214 (6)	0.3690 (3)	0.6917 (1)	5.0 (1)
C(7)	−0.3770 (5)	0.2239 (3)	0.6058 (1)	3.9 (1)
C(8)	−0.2451 (4)	0.2611 (3)	0.5544 (1)	3.5 (1)
C(9)	−0.3964 (4)	0.2259 (3)	0.4985 (1)	3.8 (1)
C(10)	−0.2490 (4)	0.2570 (2)	0.4491 (1)	3.4 (1)
C(11)	−0.2310 (5)	0.3881 (3)	0.4293 (1)	4.0 (1)
C(12)	−0.0834 (5)	0.4175 (3)	0.3861 (1)	4.4 (1)
C(13)	0.0518 (5)	0.3175 (3)	0.3626 (1)	4.8 (1)
C(14)	0.0359 (6)	0.1878 (3)	0.3818 (1)	5.0 (1)
C(15)	−0.1147 (5)	0.1565 (3)	0.4241 (1)	4.3 (1)
F	−0.4176 (3)	0.0835 (2)	0.60468 (7)	5.86 (8)
O(1)	−0.0093 (3)	0.1964 (2)	0.55913 (8)	5.2 (1)
O(2)	−0.6249 (3)	0.3031 (2)	0.49705 (8)	4.9 (1)

Table 2. *Selected geometric parameters* (Å, °) *for compounds* (1) *and* (2)

	(1)	(2)
C(1)—C(2)	1.380 (3)	1.388 (4)
C(1)—C(6)	1.380 (3)	1.380 (4)
C(1)—C(7)	1.500 (3)	1.502 (3)
C(2)—C(3)	1.384 (3)	1.380 (4)
C(3)—C(4)	1.369 (3)	1.369 (5)
C(4)—C(5)	1.365 (4)	1.365 (5)
C(5)—C(6)	1.378 (3)	1.387 (4)
C(7)—C(8)	1.525 (3)	1.512 (3)
C(7)—F	1.413 (2)	1.407 (3)
C(8)—C(9)	1.530 (3)	1.528 (3)
C(8)—O(1)	1.403 (2)	1.405 (3)
C(9)—C(10)	1.487 (3)	1.505 (3)
C(9)—O(2)	1.213 (2)	1.435 (3)
C(10)—C(11)	1.391 (3)	1.387 (3)
C(10)—C(15)	1.388 (3)	1.392 (4)
C(11)—C(12)	1.378 (3)	1.382 (4)
C(12)—C(13)	1.377 (3)	1.374 (4)
C(13)—C(14)	1.368 (4)	1.369 (4)
C(14)—C(15)	1.372 (3)	1.380 (4)
C(2)—C(1)—C(7)	119.1 (2)	121.7 (2)
C(1)—C(7)—C(8)	115.0 (1)	114.8 (2)
C(1)—C(7)—F	109.5 (1)	109.1 (2)
C(8)—C(7)—F	106.5 (2)	107.9 (2)
C(7)—C(8)—C(9)	107.5 (2)	113.6 (2)
C(7)—C(8)—O(1)	111.9 (1)	107.7 (2)
C(9)—C(8)—O(1)	112.6 (1)	111.0 (2)
C(8)—C(9)—C(10)	119.1 (1)	111.1 (2)
C(8)—C(9)—O(2)	119.6 (2)	105.9 (2)
C(10)—C(9)—O(2)	121.0 (2)	112.1 (2)
C(9)—C(10)—C(11)	122.9 (2)	121.0 (2)
C(1)—C(7)—C(8)—C(9)	177.7 (1)	−177.8 (2)
C(1)—C(7)—C(8)—O(1)	53.6 (2)	58.7 (3)
C(2)—C(1)—C(7)—C(8)	80.4 (2)	−71.7 (3)
C(2)—C(1)—C(7)—F	−159.7 (2)	49.6 (3)
C(7)—C(8)—C(9)—C(10)	64.2 (2)	−176.4 (2)
C(7)—C(8)—C(9)—O(2)	−109.3 (2)	61.6 (3)
C(8)—C(9)—C(10)—C(11)	31.9 (3)	−79.1 (3)
C(9)—C(8)—C(7)—F	56.3 (2)	60.2 (3)
C(10)—C(9)—C(8)—O(1)	−172.1 (2)	−54.8 (3)
C(11)—C(10)—C(9)—O(2)	−154.8 (2)	39.3 (3)
F—C(7)—C(8)—O(1)	−67.9 (2)	−63.2 (2)
O(1)—C(8)—C(9)—O(2)	14.5 (2)	−176.8 (2)

D—H···A	D···A	D—H···A
(1)		
O(1)—H(O1)···O(2$^{\rm i}$)	2.817 (2)	159 (2)
(2)		
O(1)—H(O1)···O(2$^{\rm ii}$)	2.839 (3)	169 (3)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 + x, y, z$.

Symmetry and approximate cell dimensions were derived from rotation and Weissenberg photographs. The structures were solved and refined using the *TEXSAN* crystallographic software package of the Molecular Structure Corporation (1985), which included *SHELXS*86 (Sheldrick, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71817 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1075]

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Ammonium Salt of Nitroacetamide

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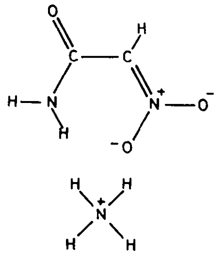
Abstract

The title compound, $NH_4^+.C_2H_3N_2O_3^-$ (1), has a nearly planar anion with an intramolecular hydrogen bond and delocalization of the negative charge. All the H atoms in the ammonium ion are involved in hydrogen bonds.

Comment

The present structure determination is part of a study of aliphatic nitro compounds and their salts, and has been undertaken to study structural changes connected with nitroacetamide salt formation. Compound (1) was prepared as described by Steinkopf (1904) and suitable single crystals were obtained from an ammonia–water solution (25% NH_3) by evaporation at room temperature.



(1)

A least-squares plane defined by all non-H atoms in the anion reveals a nearly planar system with a maximum deviation of 0.071 (7) Å (N1) from the least-squares plane. The angle C1—C2—N2 is 108.6 (2)° in nitroacetamide (Thorup, Dreier & Simonsen, 1981) and changes to 126.9 (4)° by the release of a proton from C2; hence the atom C2 becomes sp^2 hybridized by salt formation.

Apart from C1—N1, all bond lengths involving non-H atoms are changed significantly by the release of a proton from C2 (Table 3). The bond lengths in (1) are very much like the lengths of the corresponding bonds in the anion of nitromalonamide (Table 3) and indicate delocalization of the negative charge over the system O1—C1—C2—N2—(O21,O22).

All H atoms except H2 participate in hydrogen bonds. The stacking of the anions and NH_4^+ ions is stabilized by an infinite network of hydrogen bonds (Fig. 2). The four strongest N3···O hydrogen bonds are in the range 2.798 (5)–2.921 (6) Å. The only intramolecular hydrogen bond, N1—H11···O21, has the dimensions N1—H11 0.98 (3), H11···O21 2.08 (3), N1···O21 2.736 (7) Å.

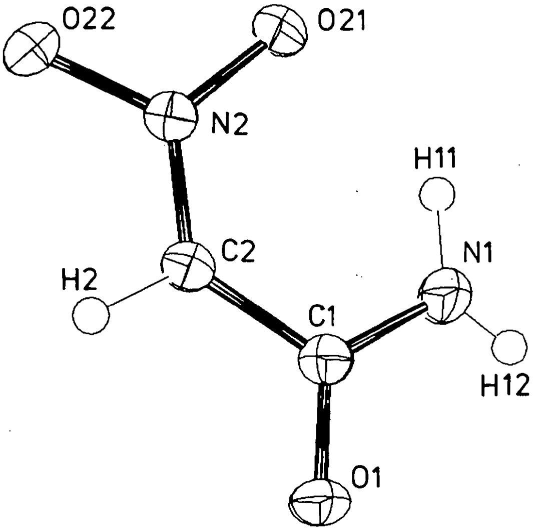


Fig. 1. View of (1) showing atomic numbering.

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