

Fig. 3. Stereoscopic view of an arrangement of (+)-(-)-3 molecules in the unit cell showing N—H(Cl) hydrogen bonds along [100].

The cyclohexanone ring is in the chair conformation. C(2), C(3), C(5) and C(6) are almost coplanar within 0.07 Å and C(1) and C(4) deviate by 0.65 and 0.40 Å, respectively, from this plane. The benzyl group is in the axial and the α -phenylethylamino group in the equatorial position. The benzyl group and the carbonyl group are on opposite sides of the C(2), C(3), C(5), C(6) plane. The dihedral angle

between this least-squares plane 1 and the least-squares plane 2 [C(1'), C(2'), C(3'), C(4'), C(5'), C(6')] is 62.96° and that between plane 1 and the least-squares plane 3 [C(1''), C(2''), C(3''), C(4''), C(5''), C(6'')] is 118.71°. Planes 2 and 3 form a dihedral angle of 63.27°.

The packing of the molecules is presented in Fig. 3, showing clearly the sandwich structure of adjoining benzyl groups and the N—H(Cl) hydrogen bonds along [100].

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Structure of 1,1,1,7,7,7-Hexafluoro-2,6-dihydroxy-2,6-bis(trifluoromethyl)-4-heptanone

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Abstract. C₉H₆F₁₂O₃, *M_r* = 390.13, monoclinic, *P*2₁/*c*, *a* = 11.724 (1), *b* = 10.265 (1), *c* = 11.350 (2) Å, β = 99.39 (1)°, *V* = 1347.6 (3) Å³, *Z* = 4, *D_m* = 1.923 (2), *D_x* = 1.923 Mg m⁻³, λ (Cu *K* α) = 1.54184 Å, μ = 2.28 mm⁻¹, *F*(000) = 768, *T* = 295 K, final *R_f* = 0.073, *wR* = 0.063 for 1510 observations with *I* \geq 2.5 σ (*I*). The structure consists of discrete molecules arranged in pairs with weak dipolar interactions between the functional groups. Within each molecule there are hydrogen bonds

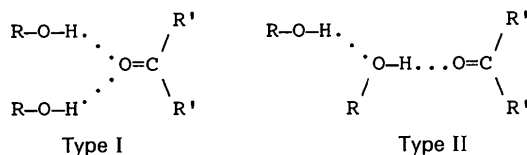
between the ketonic carbonyl O atom and both of the alcohol functions, forming two six-membered rings.

Introduction. It is well established that highly fluorinated alcohols form strong hydrogen bonds (Willis, 1988, and references therein). We have recently shown that in the anionic alkoxy copper(II) complex [HOC(CF₃)₂O]₄Cu]²⁻, four hydrogen bonds link the alcohol residues into a 16-membered ring (Hynes, Payne & Willis, 1990). In general, hydrogen bonding is stronger between a fluorinated alcohol and another

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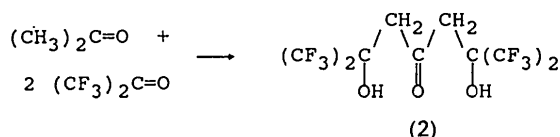
donor than between two fluorinated alcohol molecules because the presence of the highly electronegative trifluoromethyl groups makes the O atom a relatively poor donor and the H atom a good acceptor. For example, interactions between fluorinated alcohols and ethers can be sufficiently strong that stable 1:1 adducts may be distilled (Chang, Price, Tomlinson & Willis, 1972). Hydrogen bonding to ketones is weaker because of the reduced basicity of the carbonyl O atom; the interaction may be studied by infrared spectroscopy. Symons & Eaton (1985) report a decrease in the C=O frequency of acetone when dissolved in $(\text{CF}_3)_2\text{CH}(\text{OH})$, which they attribute to hydrogen-bond formation.

The general problem of hydrogen bonding between alcohols and ketones has been studied by many workers (Mizuno, Saito, Uchida & Shindo, 1985, and references therein). The spectroscopic evidence shows that either 1:1 or 2:1 alcohol-ketone adducts may be formed, but the nature of the latter is not always clear. It is possible that two hydroxyl groups are simultaneously bonded to the carbonyl group (type I), or that one alcohol is bonded to a second, which is in turn bonded to the ketone (type II).



On the basis of spectroscopic studies, one or other of these structures has been assigned in different systems. However, there is a lack of precise structural data on simple molecules where a carbonyl group is hydrogen bonded to an alcohol because such systems rarely form well defined crystals.

In a previous publication (Martin & Willis, 1977), we reported synthetic studies using the fluorinated keto-alcohol $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}$ (1), made by the thermal addition of acetone to hexafluoroacetone (Simonyan, Gambaryan & Knunyants, 1966). Compound (1) is a liquid, b.p. 423 K, but the addition reaction also produces the solid 1:2 adduct 1,1,1,7,7,7-hexafluoro-2,6-dihydroxy-2,6-bis(trifluoromethyl)-4-heptanone (2), m.p. 347–385 K.



We have reported a study of the complexes formed by coordination of the singly ionized diol (2) to Ni^{2+} and Cu^{2+} (Loeb, Martin & Willis, 1978). Apart from

a few studies of its physiological properties, no other work on (2) has been reported since its initial synthesis in 1966 (Simonyan, Gambaryan & Knunyants, 1966). From consideration of the functional groups present, together with the relatively high melting point, it is clear that either inter- or intramolecular hydrogen bonding between the ketone and alcohol functions is likely to be present and we have therefore undertaken a structural determination.

Experimental. Compound (2) was prepared by the reaction of hexafluoroacetone with acetone in a sealed tube at 408 K as described previously (Martin & Willis, 1977). The solid remaining after excess acetone and compound (1) had been distilled off was recrystallized from ethanol; m.p. 347–348 K. Single crystals of (2) were obtained on the lid of the sample container during a very slow sublimation process over a period of several years at room temperature.

A suitable single crystal of approximate dimensions $0.38 \times 0.39 \times 0.42$ mm was mounted in a thin-walled capillary tube since the crystal sublimed completely in 120 min of X-ray exposure time when mounted in air. The density of the crystal was measured by the neutral buoyancy method using CCl_4 and $\text{C}_2\text{H}_4\text{Br}_2$ mixtures. The cell parameters were determined from a least-squares fit of 21 high-angle reflections ($30.3 < \theta < 38.2^\circ$). X-ray intensity data were collected on an Enraf-Nonius CAD-4F diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation at 295 K with ω - 2θ scan mode, variable scan speed (1.50 – $2.75^\circ \text{ min}^{-1}$), scan width $(0.9 + 0.14 \tan \theta)^\circ$, with an additional 25% before and after each reflection for background determination (Enraf-Nonius, 1982). 2856 reflections in the 2θ range 0 – 130° ($-13 < h < 13$, $-12 < k < 2$, $-13 < l < 0$) were measured. Three standard reflections ($400, 0\bar{2}0, 00\bar{2}$) monitored every 120 min of exposure time showed a 6.1% intensity variation over the total period of 46.5 h. The crystal had well defined faces at the beginning of the data collection. At the end of the data collection, the faces had become etchy and could not be indexed due to sublimation. Data processing, structure solution and refinements were carried out using the *NRCVAX* crystal structure programs running on a SUN 3/80 workstation (Gabe, Le Page, Charland, Lee & White, 1989). An empirical absorption correction (North, Phillips & Mathews, 1968) was applied using a $360^\circ \psi$ scan for nine reflections in the θ range 12.7 – 38.1° . The maximum and the minimum transmission factors were 0.6217 and 0.5764, respectively. Equivalent reflections were averaged, $R_{\text{int}} = 0.015$, to give 2282 unique reflections of which 1510 were considered observed [$I \geq 2.5\sigma(I)$]. From systematic absences, the space group was deduced to be $P2_1/c$.

The structure was solved and refined by full-matrix least-squares methods on F . Scattering factors

for neutral non-H atoms were taken from Cromer & Waber (1974) and those for H atoms were taken from Stewart, Davidson & Simpson (1965). The real component of anomalous scattering was included for all non-H atoms (Cromer & Liberman, 1970). The F and O atoms were refined with anisotropic thermal parameters. All six H atoms were located on a difference map; methylene H atoms were allowed to ride on the appropriate C atoms [$U(H) = 1.1 \times U_{eq}(C)$, C—H = 1.08 Å]. The positional and isotropic thermal parameters of the two hydroxy H atoms were refined in the least-squares fit. The final refinement on F employed 181 parameters using unit weights and converged at $R_f = 0.073$, $wR = 0.063$ and $S = 2.93$. A relatively high R_f value may be due to sublimation of the crystal during data collection. The final difference Fourier synthesis had electron density fluctuations ranging from 0.45 to 0.30 e Å⁻³. The secondary-extinction coefficient was refined to 1.514 (74) (Larson, 1970) and maximum $\Delta/\sigma = 0.001$. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.*

Discussion. An ORTEP (Johnson, 1971) diagram of the structure, with atom labelling, is shown in Fig. 1, and a PLUTO (Motherwell & Clegg, 1978) view of the unit-cell contents is displayed in Fig. 2. Bond distances, angles and intramolecular hydrogen-bond geometry are given in Table 2.

The dihydroxy ketone consists of discrete molecules in which intramolecular type I hydrogen bonding links each OH group to the carbonyl function, forming two fused six-membered rings in a somewhat distorted chair form. O...O bond distances of 2.764 (6) and 2.690 (6) Å are close to the value of 2.75 Å found in ice at 123 K (Peterson & Levy, 1957). The three O atoms in (2) are nearly collinear, with an O...O...O angle of 175.5 (2)°. We have previously reported very similar O...O distances, in the range 2.746 (4)–2.792 (5) Å, in a complex where ethanol and water are hydrogen bonded to a coordinated ionized and fluorinated diol (Bradford, Hynes, Payne & Willis, 1990). The C—OH bonds in (2), at 1.402 (6) and 1.391 (6) Å, show the slight shortening which is usual in fluorinated alcohols (Willis, 1988, and references therein), while the ketonic C=O bond length is normal, 1.202 (6) Å. Molecules of (2) are arranged in pairs with the functional groups directly opposed to each other (Fig. 2). The closest intermolecular contacts are O(2)...H(3) (1 - x, 2 - y, -z)

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55639 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1006]

Table 1. Atomic positional ($\times 10^4$) and thermal parameters (Å²)

B_{eq} for non-H atoms is the mean of the principal values for the anisotropic mean displacement tensor, U_{ij} , multiplied by $8\pi^2$.

	x	y	z	B_{eq}
F(1)	231 (3)	1756 (4)	4727 (4)	7.69 (21)
F(2)	846 (4)	1146 (5)	3143 (4)	9.29 (24)
F(3)	1822 (4)	756 (4)	4854 (4)	9.2 (3)
F(4)	110 (4)	4214 (5)	3946 (4)	9.4 (3)
F(5)	1586 (4)	5041 (5)	3450 (5)	11.2 (3)
F(6)	676 (4)	3571 (6)	2395 (4)	10.6 (3)
F(7)	2105 (4)	7178 (5)	7557 (5)	11.1 (3)
F(8)	2340 (4)	6990 (5)	5719 (4)	10.0 (3)
F(9)	3210 (5)	8457 (4)	6828 (5)	11.6 (3)
F(10)	3739 (4)	6106 (5)	9196 (3)	10.3 (3)
F(11)	4746 (5)	7681 (5)	8679 (4)	11.0 (3)
F(12)	5348 (5)	5759 (6)	8684 (4)	12.3 (3)
O(1)	2745 (3)	2624 (5)	3620 (4)	5.96 (21)
O(2)	3701 (3)	4692 (4)	4997 (3)	5.40 (18)
O(3)	4703 (4)	6570 (5)	6466 (4)	6.36 (23)
C(1)	1817 (4)	2912 (5)	4214 (5)	4.42 (11)
C(2)	2181 (4)	3375 (5)	5527 (5)	4.44 (11)
C(3)	3113 (4)	4381 (5)	5725 (5)	4.11 (10)
C(4)	3391 (5)	4884 (6)	7006 (5)	5.69 (13)
C(5)	3855 (4)	6281 (5)	7153 (5)	4.43 (11)
C(6)	1175 (6)	1638 (7)	4219 (6)	6.07 (14)
C(7)	1054 (6)	3956 (7)	3485 (6)	6.18 (14)
C(8)	2890 (7)	7263 (8)	6836 (7)	7.28 (17)
C(9)	4431 (7)	6433 (8)	8447 (7)	7.47 (17)

Table 2. Selected bond distances (Å), angles (°) and hydrogen-bond geometry (Å, °)

O(1)—C(1)	1.402 (6)	O(2)—C(3)	1.202 (6)
O(3)—C(5)	1.391 (6)	C(1)—C(2)	1.555 (7)
C(1)—C(6)	1.509 (9)	C(1)—C(7)	1.547 (9)
C(2)—C(3)	1.494 (7)	C(3)—C(4)	1.527 (8)
C(4)—C(5)	1.533 (8)	C(5)—C(8)	1.514 (9)
C(5)—C(9)	1.522 (10)	F(1)—C(6)	1.334 (7)
F(2)—C(6)	1.320 (8)	F(3)—C(6)	1.319 (8)
F(4)—C(7)	1.325 (8)	F(5)—C(7)	1.279 (9)
F(6)—C(7)	1.307 (8)	F(7)—C(8)	1.330 (9)
F(8)—C(8)	1.354 (9)	F(9)—C(8)	1.282 (9)
F(10)—C(9)	1.310 (9)	F(11)—C(9)	1.347 (10)
F(12)—C(9)	1.270 (10)	O(1)—H(1)	0.83 (6)
O(3)—H(3)	0.84 (7)		
O(1)—C(1)—C(2)	114.4 (4)	O(1)—C(1)—C(6)	104.2 (5)
O(1)—C(1)—C(7)	108.3 (5)	O(2)—C(3)—C(2)	124.5 (5)
O(2)—C(3)—C(4)	120.5 (5)	O(3)—C(5)—C(4)	114.3 (5)
O(3)—C(5)—C(8)	107.4 (5)	O(3)—C(5)—C(9)	105.9 (5)
C(2)—C(1)—C(6)	108.7 (5)	C(2)—C(1)—C(7)	110.2 (5)
C(6)—C(1)—C(7)	110.9 (5)	C(1)—C(2)—C(3)	115.8 (4)
C(2)—C(3)—C(4)	114.5 (5)	C(3)—C(4)—C(5)	115.9 (5)
C(4)—C(5)—C(8)	111.0 (5)	C(4)—C(5)—C(9)	107.1 (5)
C(8)—C(5)—C(9)	110.9 (5)	C(1)—O(1)—H(1)	104 (4)
C(5)—O(3)—H(3)	109 (5)	F(1)—C(6)—F(2)	107.3 (5)
F(1)—C(6)—F(3)	105.7 (5)	F(2)—C(6)—F(3)	107.3 (6)
F(4)—C(7)—F(5)	106.3 (6)	F(4)—C(7)—F(6)	105.0 (6)
F(5)—C(7)—F(6)	109.0 (6)	F(7)—C(8)—F(8)	106.9 (6)
F(7)—C(8)—F(9)	107.4 (7)	F(8)—C(8)—F(9)	106.6 (6)
F(10)—C(9)—F(11)	107.3 (6)	F(10)—C(9)—F(12)	108.4 (7)
F(11)—C(9)—F(12)	106.3 (7)	F(1)—C(6)—C(1)	111.9 (5)
F(2)—C(6)—C(1)	113.6 (5)	F(3)—C(6)—C(1)	110.7 (5)
F(4)—C(7)—C(1)	112.0 (5)	F(5)—C(7)—C(1)	112.2 (5)
F(6)—C(7)—C(1)	112.0 (6)	F(7)—C(8)—C(5)	112.1 (6)
F(8)—C(8)—C(5)	107.9 (6)	F(9)—C(8)—C(5)	115.5 (6)
F(10)—C(9)—C(5)	112.1 (6)	F(11)—C(9)—C(5)	110.5 (6)
F(12)—C(9)—C(5)	112.0 (6)	O(1)...O(2)...O(3)	175.5 (2)
H(1)...O(2)...H(3)	161 (3)		
D—H...A	D...A	H...A	D—H...A
O(1)—H(1)...O(2)	2.764 (6)	2.06 (6)	144 (6)
O(3)—H(3)...O(2)	2.690 (6)	1.96 (7)	144 (7)

2.51 (8) Å and O(3)···H(1) ($1-x$, $2-y$, $-z$) 2.54 (6) Å. These distances between O atoms in one molecule and hydroxy H atoms in the adjacent molecule suggest a weak dipole-dipole attraction, rather than intermolecular hydrogen bonding.

From previous results, it may be assumed that intramolecular hydrogen bonding in (2) lowers the C=O stretching frequency, but a 'shift' cannot be demonstrated experimentally because the interaction is always present. The frequencies for (2) and (1) are 1711 (nujol mull) and 1730 cm^{-1} (liquid film), respectively; $(\text{CH}_3)_2\text{C}=\text{O}$ in hexane has a frequency of 1721.5 cm^{-1} and in $(\text{CF}_3)_2\text{CHOH}$ gives 1688 and 1702.5 cm^{-1} (doublet) (Symons & Eaton, 1985).

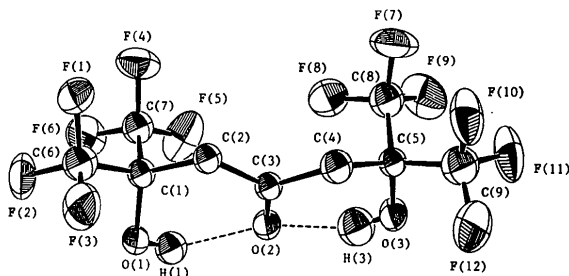


Fig. 1. ORTEP view of compound (2) showing the atom-numbering scheme (50% thermal ellipsoids). The methylene H atoms have been omitted for clarity.

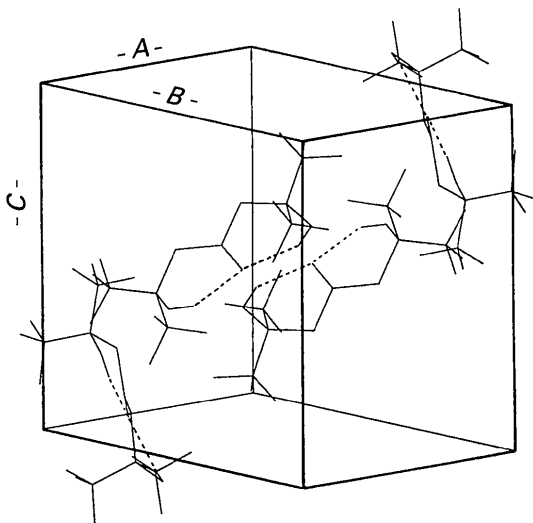


Fig. 2. Unit cell of (2), showing the molecular packing.

This structural determination demonstrates unequivocally that a ketonic carbonyl group may simultaneously hydrogen bond to the hydroxy groups of two fluorinated alcohols. While the geometry of (2) is particularly favorable to such an interaction, it would seem likely that it may be found in other systems.

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