The Crystal Structure of the Hydrogen Bonded 2:1 Complex of Pentafluorophenol with Dioxane

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The 2:1 pentafluorophenol−dioxane complex forms colourless crystals. They are monoclinic with a=7.951(2), b=10.279(2), c=10.195(2) Å, β=94.76(2)°, Z=2, space group $P2_1/c$. The structure, determined from diffractometer data at −135 °C was refined by full-matrix least-squares methods to R=0.033 for 1991 observed reflections. Both oxygens of the dioxane molecule are hydrogen bonded to an OH group of an adjacent pentafluorophenol molecule, resulting in centrosymmetric trimolecular complexes. The hydrogen bonds have an O---O distance of 2.647(1) Å; the O−H---O angle is 170(2)°.

As part of an investigation of hydrogen bonding between pentafluorophenol, PFP, and proton acceptors such as ethers, ketones, and phosphoryl compounds, the 2:1 complex formed between PFP and 1,4-dioxane has been studied by X-ray methods.

EXPERIMENTAL

Synthesis of the complex. Under nitrogen atmosphere PFP was slowly added with stirring to 1,4-dioxane. At a molar ratio 1:3 the addition of PFP was stopped and excess dioxane distilled off under vacuum. The solid residue was sublimed at 40 °C and 0.8 mm Hg pressure yielding colourless crystals, m.p. 47−48 °C (lit. 50 °C, Refs. 1 and 2); Equiv. wt. 455.0, req. 456.2. The equivalent weight was determined by titration with aqueous sodium hydroxide.

X-Ray data. An Enraf-Nonius CAD-4 diffractometer with graphite monochromated MoKα radiation was used for the determination of unit cell dimensions ($\lambda\alpha_1$=0.70926, $\lambda\alpha_2$=0.710354 Å) and recording of intensity data ($\lambda\alpha$=0.71069 Å). The temperature at the crystal site was −135 °C. Unit cell parameters are based on least squares fits to the diffractometer settings of 23 general reflections. The space group is $P2_1/c$ (No. 14) with a=7.951(2), b=10.279(2), c=10.195(2) Å, β=94.76(2)°, d_{calc}=1.825 g cm^{-3}, Z=2, μ(MoKα)=1.92 cm^{-1}. The crystal used had approximate dimensions 0.3×0.3×0.25 mm^3. Intensity data were recorded using the ω-scan technique, constant scan rate of 4° min^{-1}, and minimum scan width 1.80° including background scans of 0.30° at the beginning and the end of the scans. The orientation of the crystal was checked at intervals of 200 recordings. Three standard reflections were remeasured every 2 h. and the intensities later corrected according to the variation of these. Corrections according to the variation of the standard reflections were calculated by interpolating between the nearest standard reflections, in terms of time, after having corrected those to zero time. The ratio between maximum and minimum correction factors was 1.07, average correction 1.00. All 1991 crystallographically independent reflections with $2\theta \leqslant 56°$ were measured, of these 1798 were considered observed and 193 unobserved, $I \leqslant 2\sigma(I)$. The computer programs used throughout this investigation are supplied by ENRAF-NONIUS (SDP-plus 1983 and CAD4-OS11).

Table 1. Positional parameters and their estimated standard deviations.[a]

Atom	x	y	z	$B(\text{Å}^2)$
C1	0.2605(1)	0.1585(1)	0.4128(1)	1.40(2)
C2	0.2068(1)	0.0360(1)	0.4494(1)	1.39(2)
C3	0.2715(1)	−0.0242(1)	0.5641(1)	1.45(2)
C4	0.3935(1)	0.0369(1)	0.6457(1)	1.42(2)
C5	0.4497(2)	0.1585(1)	0.6115(1)	1.48(2)
C6	0.3834(2)	0.2183(1)	0.4977(1)	1.48(2)
O1	0.2006(1)	0.22135(8)	0.30269(9)	1.79(2)
H1	0.161(2)	0.169(2)	0.246(2)	3.2(4)*
F2	0.08871(9)	−0.02699(7)	0.37090(7)	1.90(1)
F3	0.2161(1)	−0.14292(7)	0.59452(7)	2.05(1)
F4	0.45971(9)	−0.02145(7)	0.75585(7)	1.89(1)
F5	0.57275(9)	0.21620(7)	0.68839(7)	2.05(1)
F6	0.4411(1)	0.33649(7)	0.46710(7)	2.08(1)
O2	0.0752(1)	0.07958(8)	0.10100(8)	1.71(1)
C7	−0.1050(2)	0.0716(1)	0.0763(1)	1.90(2)
C8	0.1503(2)	−0.0420(1)	0.0671(1)	1.96(2)
H2	−0.146(2)	0.001(2)	0.131(2)	2.3(3)*
H3	−0.149(2)	0.156(2)	0.102(2)	2.5(3)*
H4	0.108(2)	−0.112(2)	0.122(2)	2.2(3)*
H5	0.271(2)	−0.035(2)	0.085(2)	2.7(4)*

[a] Starred atoms were refined isotropically. For anisotropically refined atoms are given the equivalent isotropic thermal parameter defined as:
$(\frac{4}{3})[a^2 B(1,1)+b^2 B(2,2)+c^2 B(3,3)+ab\cos\gamma\,B(1,2)+ac\cos\beta\,B(1,3)+bc\cos\alpha\,B(2,3)]$.

STRUCTURE DETERMINATION

The intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved using direct methods (MULTAN). The solution was refined by standard full matrix least squares iterations. The refinement was concluded when the shifts in parameter values became less than one hundredth of the associated standard deviations. The function minimized is $\Sigma w(\Delta F)^2$. The intensities were recorded with constant scan rate and the attributed weights were calculated according to $w=(\sigma(F)^2+(0.02F)^2+5.0)^{-1}$. Thermal parameters for hydrogen atoms, were refined isotropically, for all others anisotropically. The refinement converged giving $R=\Sigma|\Delta F|/\Sigma\Delta|F_o|=0.033$, $R_w=[\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}=0.046$, $S=[\Sigma w(\Delta F)^2/N-n]^{\frac{1}{2}}=1.51$, and a final Fourier difference synthesis showed a maximum of 0.35 e/Å^3.

RESULTS AND DISCUSSION

Atomic positional parameters are listed in Table 1, bond distances and angles in Table 2 and molecular planes and interplanar angles in Table 3. Complementary data are available from one of the authors (K.M-M).

Fig. 1 shows the geometry of the hydrogen-bonded complex and the labelling of the atoms. The 1,4-dioxane molecule is situated around a crystallographic center of symmetry, the ring has chair form and both oxygen atoms are hydrogen bonded to hydroxyl groups on

Table 2. Bond distances and angles.[a]

Bond distances in Ångström

C1	C2	1.391(1)	C4	F4	1.342(1)	O2	C8	1.439(1)
C1	C6	1.393(1)	C5	C6	1.378(1)	C7	C8	1.507(1)
C1	O1	1.348(1)	C5	F5	1.340(1)	C7	H2	0.986(15)
C2	C3	1.383(1)	C6	F6	1.345(1)	C7	H3	0.984(15)
C2	F2	1.348(1)	O1	H1	0.83(2)	C8	H4	0.986(14)
C3	C4	1.377(1)	O1	O2	2.647(1)	C8	H5	0.966(14)
C3	F3	1.343(1)	H1	O2	1.82(2)			
C4	C5	1.382(1)	O2	C7	1.436(1)			

Bond angles in degrees

C2	C1	C6	116.60(9)	C5	C4	F4	120.23(9)	O2	C7	H2	108.4(8)
C2	C1	O1	124.22(9)	C4	C5	C6	120.45(9)	O2	C7	H3	106.0(8)
C6	C1	O1	119.18(9)	C4	C5	F5	119.21(9)	C8	C7	H2	109.9(8)
C1	C2	C3	122.05(9)	C6	C5	F5	120.31(9)	C8	C7	H3	112.3(8)
C1	C2	F2	119.33(8)	C1	C6	C5	121.73(9)	H2	C7	H3	110.(1)
C3	C2	F2	118.62(8)	C1	C6	F6	119.28(9)	O2	C8	C7	109.73(8)
C2	C3	C4	120.05(9)	C5	C6	F6	118.98(9)	O2	C8	H4	109.0(8)
C2	C3	F3	119.71(9)	C1	O1	H1	111.(1)	O2	C8	H5	108.3(9)
C4	C3	F3	120.23(9)	O1	H1	O2	170.(2)	C7	C8	H4	109.7(8)
C3	C4	C5	119.11(9)	C7	O2	C8	109.65(8)	C7	C8	H5	110.6(9)
C3	C4	F4	120.64(9)	O2	C7	C8	109.66(8)	H4	C8	H5	110.(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 3. Molecular planes and interplanar angles (°).

No. of plane	Atoms included	Max. deviation of atoms/Å	Interplanar angles	
1	C1,C2,C3,C4,C5,C6,O1	0.004	1–2	64.1
2	C7,O2,C8	0	1–3	82.7
3	C7,C8,C7′,C8′	0	2–3	54.2

Distances of atoms from planes (Å) with standard deviations.

1 H1, 0.31(2); F2, 0.015(1); F3, 0.006(1); F4, 0.021(1);
   F5, 0.053(1); F6, 0.004(1); O2, 1.014(1); C7, 0.106(1)
2 O1, −1.308(1); H1, −0.99(2); C7′ and C8′, 1.223(1);
   H2, −0.82(2); H3, −0.02(2); H4, −0.81(2); H5, −0.01(2).
3 O2, 0.672(1); H2, −0.93(2); H3, 0.49(2); H4, −0.93(2); H5, 0.46(2).

PFP molecules, thus forming a centrosymmetric 1:2 molecular complex. The directions of the hydrogen bonds relative to the dioxane ring are roughly equatorial. The interatomic distances relevant to the hydrogen bonding are O1–H1=0.83(2); H1···O2=1.82(2); O1···O2=2.647(1) Å. The angles involved are $\angle$C1–O1–H1=111(1)° and $\angle$O1–H1···O2=170(2)°. This implies a relatively strong hydrogen bond and dioxane is known to partake in such, especially with water, with O···O distances varying from 2.5 to 2.8 Å.[3,4,6,7,9] Fig. 1 illustrates that the plane through the aromatic ring and the plane defined by the carbon atoms of the dioxane molecule are qualitatively perpendicular to each other.
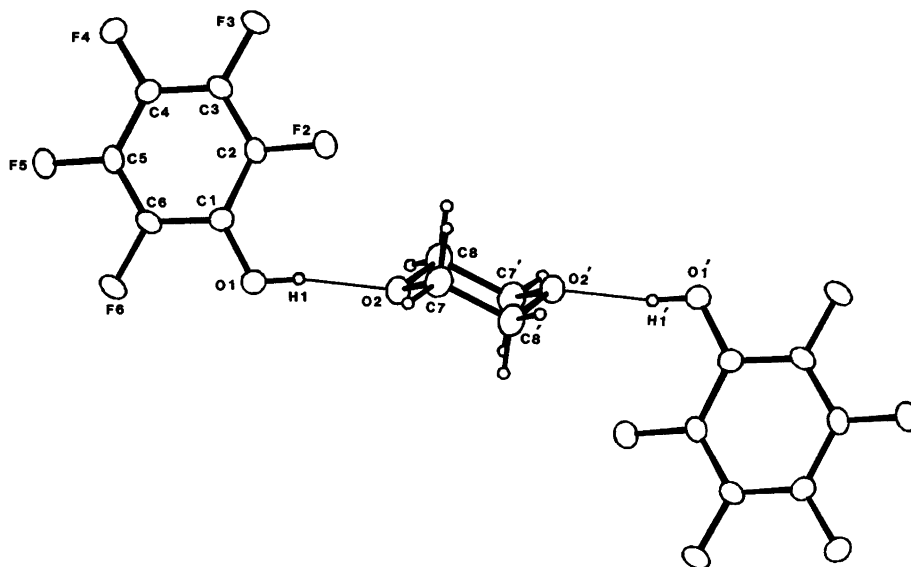
Fig. 1. The centrosymmetric 2:1 PFP−dioxane complex seen 80° off normal to the central C7,C8,C7′,C8′ plane of the dioxane molecule. It can clearly be seen that the benzene rings are at nearly right angles to this plane.

The bond lengths and angles within the dioxane molecule agree well with the values reported in other investigations.[3,13] The geometry of the dioxane molecule seems unaffected under varying crystallographic situations.

The oxygen and carbon atoms of the PFP molecule are coplanar, the fluorine atoms, however, are observed at varying distances from this plane and lying to the same side of the plane. Conf. Table 3. The C−C, C−F and C−O bond lengths in PFP agree with previously found values.[15-19]

The angle C−CO−C, being 116.6°, the shortness of the C−O bond and the length of the C−CO bonds relative to the other C−C bond lengths of the aromatic ring, conf. Table 2,
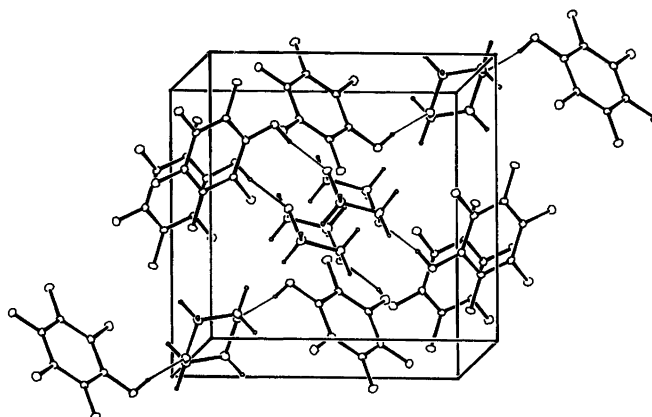

Fig. 2. The molecular packing of the complex in the unit cell.

indicate some double bond character in the C–O bond in the PFP molecule. This may well be due to the electron withdrawing effect of the fluorine atoms.[19] The notable difference between the angles C2–C1–O1 (124.2°) and C6–C1–O1 (119.2°) may be caused by interaction between the OH group and F2(F2---H=2.48(2) Å).

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