ELSEVIER

Journal of Fluorine Chemistry 73 (1995) 265-266

JOURNAL OF FLUORINE CHEMISTRY

Short Communication

Synthesis and X-ray crystal structure of 1,2,4,6,7,9-hexafluorodibenzo-*p*-dioxin

Ursula Haffer [a], Wolfgang Rotard [a], Joachim Pickardt [b,*]

[a] *Institut für Wasser-, Boden- und Lufthygiene des Bundesgesundheitsamtes, Corrensplatz 1, D-14195 Berlin, Germany*

[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany*

Received 27 September 1994, accepted 16 December 1994

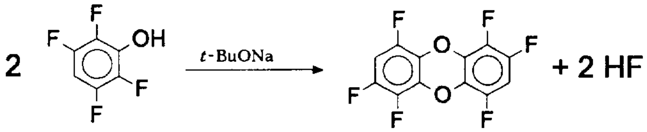
Abstract

1,2,4,6,7,9-Hexafluorodibenzo-*p*-dioxin was synthesized from 2,3,4,6-tetrafluorophenol in the presence of sodium-t-butylate. An X-ray structure analysis has been performed. The molecule is essentially planar and possesses a centre of inversion. The C–C bond distances range from 136.3(7) to 138.3(6) pm and the C–F distances from 133.8(5) to 134.5(6) pm. The C–O distances are 137.8(5) and 139.1(6) pm, respectively.

Keywords: Synthesis; X-Ray structure analysis; Hexafluorodibenzo-*p*-dioxin; Mass spectrometry; IR spectroscopy

1. Introduction

Polyhalogenated dibenzo-*p*-dioxins and -furans were well known as hazardous compounds. While much information is available about the occurrence and toxicity of chlorinated and brominated dioxins, little information exists about polyfluorinated dioxins ('PFDD'). To investigate the formation of PFDD, their physical and chemical properties, and their occurrence and behaviour in the environment, several PFDDs have been synthesized [1]. 1,2,4,6,7,9-Hexafluorodibenzo-*p*-dioxin was obtained from 2,3,5,6-tetrafluorophenol via nucleophilic aromatic substitution in the presence of a base (Scheme 1).



Scheme 1.

2. Results and discussion

The toxicity of a chemical substance depends on its molecular composition and on its chemical and biological activity, which means in many cases interaction with a receptor. This interaction is based on the molecular dimensions, arrangement, spacing and size of active groups. In this regard the crystal data of a compound can be very helpful in an assessment of its toxicity. The crystal structure of 1,2,4,6,7,9-hexafluorodibenzo-*p*-dioxin has therefore been determined, thus providing the first crystal data for a non-perfluorinated dioxin.

The atom coordinates are given in Table 1, and selected bond lengths and angles in Table 2. Fig. 1 shows the molecular structure. Since $Z=2$ for the space group $P2_1/n$, the centre of the molecule lies on a centre of symmetry in the unit cell and thus the symmetry of the molecule is C_i. This is also the case for dibenzo-*p*-dioxin [2], as well as for some of its chlorinated derivatives [3] and octafluorodibenzo-*p*-dioxin [4]. The molecule is nearly planar, the maximum deviations from the least-squares plane through the carbon atoms being 0.3 pm for C, and 1 pm for F and O, with a very slight indication of a chair configuration for the central ring. This was also found for the structures of the parent compound dibenzo-*p*-dioxin and of octafluorodibenzo-*p*-dioxin. The C–C bond distances in the benzene rings range from 136.3(7) to 138.3(6) pm with a mean of 137.5 pm, while the angles range from 117.4(4) to 123.4(4)°. Similar distances are also found in octafluorodibenzo-*p*-dioxin.

The C–F distances vary between 133.8(5) and 134.5(6) pm with a mean of 134.0; this value agrees well with the average C–F distances of 133.9 pm observed in 1,3,5-trifluorobenzene [5] and in octafluorodibenzo-*p*-dioxin.

The C–O distances are 137.8(5) and 139.1(6) pm respectively, with a mean value of 138.5 pm, which is comparable with the value of 138.3(8) pm found in dibenzo-*p*-

---

* Corresponding author.

SSDI 0022-1139(95)03236-3

Table 1
Atom coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	U_{eq} [a]
F(1)	0.1952(3)	0.4608(5)	0.4039(3)	0.0507(11)
F(2)	0.1142(3)	0.4576(6)	0.1427(3)	0.0912(14)
F(3)	−0.1719(3)	1.1665(5)	0.1833(3)	0.0764(11)
O	0.0985(3)	0.8140(6)	0.5580(3)	0.0617(11)
C(1)	0.0523(4)	0.8185(9)	0.4257(4)	0.0475(16)
C(2)	0.1050(5)	0.6347(9)	0.3487(4)	0.0532(17)
C(3)	0.0619(5)	0.6373(10)	0.2163(4)	0.0573(19)
C(4)	−0.0309(5)	0.8106(10)	0.1576(4)	0.0586(19)
C(5)	−0.0813(5)	0.9908(9)	0.2360(4)	0.0526(17)
C(6)	−0.0412(5)	0.9980(9)	0.3694(4)	0.0483(17)
H	−0.05869	0.78513	0.05164	0.06

[a] $U_{eq} = 1/3 \times$ trace of orthogonalized U [10^4 pm^2].

Table 2
Selected bond lengths (pm) and angles (°)

C1–C2	138.3(6)	C1–C2–C3	118.2(4)
C1–C6	138.0(6)	C1–C6–C5	119.1(4)
C2–C3	137.4(6)	C2–C3–C4	123.2(4)
C3–C4	136.3(7)	C3–C4–C5	117.4(4)
C4–C5	137.0(7)	C4–C5–C6	121.9(4)
C5–C6	137.9(6)	C1–C2–F1	119.9(4)
C2–F1	133.8(5)	C2–C3–F2	117.5(4)
C3–F2	134.5(6)	C4–C5–F3	119.9(4)
C5–F3	133.8(5)	C2–C1–O	117.2(4)
C1–O	137.8(5)	C5–C6–O′	118.2(4)
C6–O′	139.1(6)	C1–O–C6′	114.6(3)

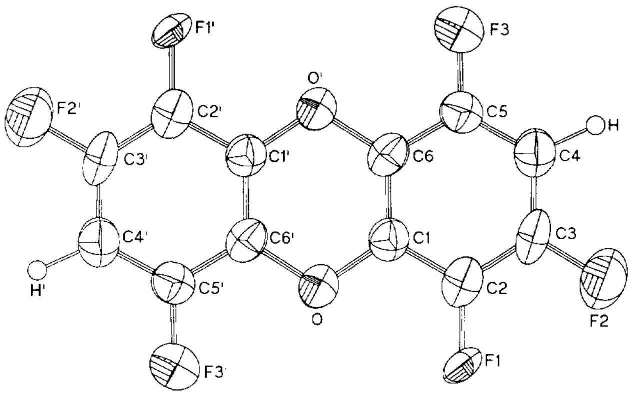


Fig. 1. Molecular structure of 1,2,4,6,7,9-hexafluorodibenzo-*p*-dioxin.

dioxin [2] and the C–O bond lengths of 137.3 and 137.6 pm observed in octafluorodibenzo-*p*-dioxin. There are no intermolecular contacts less than approx. 310 pm, except for a C4–H···F2 distance with H···F2 238(2) pm, C4–H 109(2) and C4···F2 340.4(6) pm, respectively, which may denote a weak hydrogen bridge but is too long for a typical hydrogen bond.

3. Experimental details

3.1. Preparation of 1,2,4,6,7,9-hexafluorodibenzo-p-dioxin

2,3,5,6-Tetrafluorophenol (2.0 g, 12.04 mmol), 0.58 g (6.03 mmol) of sodium t-butylate and 10 ml of tetramethylene sulphone were refluxed at 170 °C under N_2 for 3 d. After cooling, another 0.57 g (5.27 mmol) of sodium t-butylate were added. The mixture was heated to 170 °C for three more days. The cold dark mixture was poured over 25 g of activated silica gel and stirred well to effect homogenization. It was then transferred to a chromatographic column filled with 40 g of activated silica gel. The column was eluted with 380 ml of cyclohexane, yielding a colourless eluate. A product yield of 0.187 g (15%, m.p. 133–134 °C) was obtained after preparative thin-layer chromatography of the eluate (film thickness, 0.25 mm; silica gel 60; 20×20 cm; $R_f = 0.41$ with n-pentane).

1,2,4,6,7,9-Hexafluorodibenzo-*p*-dioxin: MS (70 eV), *m/z* (%): 292 (100) [M^+]; 264 (6.3) [$M^+ - CO$]; 236 (20.3) [$M^+ - C_2O_2$]; 245 (48.6) [$M^+ - COF$]; 216/217 (7.2/19.8) [$M^+ - C_2O_2(H)F$]; 164 (15.8) [M^{2+}]. IR (*o*-dichlorobenzene) ν (cm^{-1}): 1651 (w); 1539 (s); 1477 (s); 1408 (w) (C=C); 1269 (m); 1173 (m) (Ar–O–Ar); 1134 (w); 1084 (m) (δ Ar in plane); 1030 (m) (δ Ar aromatic ring breathing); 833 (w) (δ C–H out-of-plane).

3.2. Crystal data

$C_{12}H_2F_6O_2$ M = 292.14 g mol^{-1}; crystal size 0.12×0.15×0.23 mm; $a = 948.5(5)$, $b = 529.6(3)$, $c = 1026.8(6)$ pm, $\beta = 96.65(4)°$, $V = 512.3(5)$ 10^6 pm^3, D(calc.) = 1.89 g cm^{-3}; $\mu = 1.9$ cm^{-1}; $F(000) = 288$ e; $Z = 2$; crystal system monoclinic, space group $P2_1/n$ (No. 14), diffractometer Syntex P2$_1$, Mo Kα radiation, $\lambda = 0.71069$ Å, ω-scan, 1391 reflections measured ($\pm h, +k, -l$), [$(\sin\theta)/\lambda)]_{max} = 0.70$, 968 unique and 545 observed reflections [$I > 2\sigma(I)$], 94 refined parameters [6], direct methods [7], all atoms except H refined anisotropically, $R = 0.058$, $R_w = 0.054$ [$w = 1/\sigma^2(F_o)$], max. res. electron density 0.22 e 10^6 pm^3 [8].

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401003, the names of the authors, and the journal citation.

References

[1] U. Haffer, W. Rotard, W. Mailahn and G. Schulze, *Organohalogen Compd., 11* (1993) 87.
[2] P. Singh and J.D. McKinney, *Acta Crystallogr., B34* (1978) 2956.
[3] F.P. Boer, F.P. van Remoortere, P.P. North and M.A. Neuman, *Acta Crystallogr., B28* (1972) 1023.
[4] D. Rainville, R.A. Zingaro and E.A. Meyers, *Crystal Struct. Commun., 9* (1980) 771.
[5] A. Skancke, *Fluorine-Containing Molecules*, VCH, 1988, p. 45ff.
[6] G.M. Sheldrick, SHELX-76. *Program for Crystal Structure Determinations*, University of Cambridge, 1976.
[7] G.M. Sheldrick, SHELXS-86. *Program for Crystal Structure Solution*, University of Göttingen, 1986.