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MOLECULAR AND CRYSTAL STRUCTURE OF α-NAPHTHYLPHENYLFLUOROMENTHOXYSILANE

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Summary

The crystal and molecular structure of α-naphthylphenylfluoromenthoxysilane was solved from three dimensional X-ray diffraction data by direct methods and refined by full-matrix least-squares calculations to a final unweighted R of 0.039, excluding zeroes. The crystal is monoclinic, space group $P2_1$, with a 8.814(4), b 16.465(7), c 9.271(4) Å, β 119.73(5)°, $Z = 2$. 2023 independent reflexions recorded at 22°C with Ni-filtered Cu-K_α radiation were used. The absolute configuration was determined.

Introduction

The reaction of *l*-menthol with α-naphthylphenylfluorosilane leads quantitatively to a diastereoisomeric mixture. Through fractional crystallization, Corriu et al. [1] separated one of the diastereoisomers, ($[\alpha]_D$ —54.7°, pentane, m.p. 99°C). As it was one of the first examples of an optically active fluoroalkoxysilane, crystalline samples of α-naphthylphenylfluoromenthoxysilane were subjected to X-ray analysis in order to determine the absolute configuration. Thus, by reference to this particular compound, absolute configurations of some other compounds can be inferred.

Experimental

Crystal data. $Si(C_{10}H_7)(C_6H_5)(F)(OC_{10}H_{19})$. Molecular weight: 406.08, monoclinic, a 8.814(4), b 16.465(7), c 9.271(4) Å, β 119.73(5)°, V 1168.3 Å^3, $Z = 2$, $d_c = 1.155$. Systematic absences: $0k0$, $k \neq 2n$. Space group: $P2_1/m$ or $P2_1$ ($P2_1$ confirmed by structure analysis). μ 10.4 cm^{-1} (λ(Cu-K_α) 1.5418 Å). $F(000) = 436$.

A 0.40 × 0.55 × 0.40 mm crystal was selected, Weissenberg photographs were used to determine lattice constants and space group. 2322 intensities were collected at 22°C up to θ 66.8° on an Enraf-Nonius CAD-3 automatic diffractometer with θ—2θ scan mode, at a rate of $1/6°$ sec^{-1}. Each scan is 1.20° wide at θ 0° and an increment, $\Delta(\theta) = 0.30° \tan\theta$ is added, to take into account spectral dispersion; background was measured at each end in fixed position with a total counting time equal to the scanning time.

The intensities of two standard reflexions (0 10 0 and 0 0 7) were alternately measured every 40 reflexions and remained constant to within ±3%.

Standard deviations were calculated from

$$\sigma(I) = \{I + I_1 + I_2 + [0.02(I - I_1 - I_2)]^2\}^{1/2}$$

where I_1 and I_2 are the background and I the peak counts.

163 reflexions were redundant due to space-group equivalence and 136 reflexions having $I \leqslant 2\sigma(I)$ were considered unobserved and then omitted. The remaining 2023 reflexions were used for solving the structure. Corrections were applied for Lorentz and polarization factors but not for absorption.

Structure determination

From statistics on normalized structure factors, the structure was solved in the non-centrosymmetric space group $P2_1$. It was determined by direct methods using MULTAN [2]. All atoms but hydrogens were located by repeating structure factor calculations and Fourier process. The structure was refined isotropically to the conventional R factor of 0.136. The scattering factors of heavy atoms were taken from Cromer and Mann tables [3]. The real and imaginary parts of Si, F and O atoms were included [4]. With anisotropic thermal parameters R dropped to 0.089. The 31 hydrogen atoms were located on a difference synthesis. They were given the scattering factor taken from Stewart et al. [5] and the isotropic temperature factor of their atom of attachment. Their positional parameters were refined, all other parameters being held constant. The R factor dropped to 0.054.

At this stage the absolute configuration was determined. In $P2_1$, $|F(hkl)| = |F(h\bar{k}\bar{l})|$ when there is no violation of the Friedel's law. The structure factors were calculated for both enantiomers and the R factors were $R^+ = 0.054$ and $R^- = 0.060$, indicating that the molecule has the correct absolute configuration. To confirm it, 216 reflexions were selected for which $F_0 \geqslant 20.0$ and the magnitude of the calculated Bijvoet difference [6] defined as $([F(hkl) - F(h\bar{k}\bar{l})])/(\frac{1}{2}[F(hkl) + F(h\bar{k}\bar{l})])$ was >0.05. The R factors were respectively $R^+ = 0.050$ and $R^- = 0.089$. For nine pairs of reflexions the ratios of observed and calculated structure amplitudes are the following:

h	k	l	F_0^+/F_0^-	F_c^+/F_c^-
0	14	0	1.19	1.07
0	14	2	1.19	1.08
0	2	3	1.28	1.24
0	9	3	1.12	1.05
0	12	3	1.13	1.05
0	5	4	1.22	1.13
0	10	7	1.13	1.04
1	3	8	1.06	1.06
1	4	8	1.07	1.06

TABLE 1

NON-HYDROGEN ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS ($\times 10^4$) IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
Si	5712(1)	2500	7001(1)	2.86(0.03)
F	5350(3)	2586(1)	8525(2)	4.32(0.08)
O	6998(3)	1740(1)	7296(3)	3.06(0.09)
C(1)	6931(5)	3420(2)	7028(4)	3.1(0.1)
C(2)	6504(6)	4173(2)	7427(5)	4.4(0.2)
C(3)	7384(7)	4871(3)	7416(6)	5.6(0.2)
C(4)	8642(6)	4848(3)	7014(6)	5.6(0.2)
C(5)	9125(7)	4115(3)	6623(7)	5.8(0.2)
C(6)	8251(6)	3421(3)	6654(6)	4.9(0.2)
C(7)	3499(4)	2389(2)	5138(4)	3.2(0.1)
C(8)	2032(5)	2485(3)	5292(5)	4.6(0.2)
C(9)	337(5)	2434(4)	3900(6)	5.9(0.2)
C(10)	94(5)	2292(3)	2362(6)	5.4(0.2)
C(11)	1325(6)	2067(3)	508(5)	5.2(0.2)
C(12)	2717(7)	2000(3)	289(5)	5.2(0.2)
C(13)	4411(6)	2045(3)	1642(5)	4.6(0.2)
C(14)	4683(5)	2157(2)	3212(4)	3.7(0.1)
C(15)	3254(4)	2247(2)	3509(4)	3.3(0.1)
C(16)	1537(5)	2196(2)	2115(5)	4.0(0.1)
C(17)	6577(5)	884(2)	7113(4)	3.2(0.1)
C(18)	6035(5)	632(2)	8368(5)	4.0(0.2)
C(19)	5695(6)	—285(2)	8331(5)	4.8(0.2)
C(20)	7293(7)	—748(2)	8531(6)	5.4(0.2)
C(21)	7777(6)	—499(2)	7252(6)	4.9(0.2)
C(22)	8201(5)	420(2)	7370(5)	3.7(0.1)
C(23)	8872(6)	687(2)	6209(6)	4.7(0.2)
C(24)	10754(6)	396(3)	6858(8)	6.8(0.2)
C(25)	7766(6)	441(3)	4414(6)	5.5(0.2)
C(26)	5255(8)	—503(3)	9678(8)	7.2(0.3)

TABLE 2

HYDROGEN ATOMIC COORDINATES ($\times 10^3$) WITH ESTIMATED STANDARD DEVIATIONS ($\times 10^3$) IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
H(C2)	559(5)	422(2)	765(4)	H1(C18)	509(5)	89(2)	820(4)
H(C3)	710(5)	541(3)	771(5)	H2(C18)	712(4)	84(2)	960(4)
H(C4)	949(5)	537(3)	716(5)	H1(C20)	700(5)	—133(3)	840(5)
H(C5)	1005(6)	411(3)	647(5)	H2(C20)	811(5)	—69(3)	946(5)
H(C6)	860(5)	289(2)	639(5)	H1(C21)	690(5)	—62(3)	613(5)
H(C8)	224(4)	257(3)	631(4)	H2(C21)	870(5)	—68(3)	742(5)
H(C9)	—42(5)	258(3)	411(5)	H1(C24)	1149(6)	63(3)	789(5)
H(C10)	—107(5)	223(3)	143(5)	H2(C24)	1134(6)	71(3)	615(5)
H(C11)	22(5)	204(3)	—31(5)	H3(C24)	1074(5)	—3(3)	671(5)
H(C12)	257(5)	188(3)	—76(5)	H1(C25)	683(5)	55(3)	404(5)
H(C13)	527(5)	186(3)	147(5)	H2(C25)	776(5)	—6(3)	422(5)
H(C14)	569(4)	217(2)	403(4)	H3(C25)	805(5)	75(2)	355(5)
H(C17)	550(4)	81(2)	605(4)	H1(C26)	484(5)	—113(3)	962(5)
H(C19)	477(5)	—40(3)	735(5)	H2(C26)	437(6)	—8(3)	977(5)
H(C22)	924(4)	54(2)	858(4)	H3(C26)	652(5)	—46(3)	1097(5)
H(C23)	884(5)	116(2)	609(4)				

TABLE 3

NON-HYDROGEN THERMAL PARAMETERS ($Å^2 \times 10^4$) IN THE FORM: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2\,hka^*b^*U_{12} + 2\,hla^*c^*U_{13} + 2\,klb^*c^*U_{23})]$ WITH ESTIMATED STANDARD DEVIATIONS ($\times 10^4$) IN PARENTHESES

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si	474(4)	285(4)	357(4)	20(2)	114(2)	8(2)
F	796(14)	496(13)	496(11)	6(7)	216(5)	—4(6)
O	441(14)	234(12)	468(14)	13(5)	105(6)	1(5)
C(1)	532(24)	264(17)	352(18)	4(8)	96(8)	—4(7)
C(2)	621(29)	363(21)	715(30)	18(20)	173(12)	—24(10)
C(3)	920(38)	272(21)	887(34)	—15(11)	207(15)	—61(11)
C(4)	851(36)	445(25)	776(32)	—92(12)	180(14)	—5(12)
C(5)	796(36)	642(33)	963(40)	—92(14)	286(17)	—34(14)
C(6)	857(33)	358(21)	815(30)	—31(11)	279(14)	—60(11)
C(7)	442(17)	312(19)	487(18)	14(7)	119(7)	30(8)
C(8)	581(21)	586(24)	661(23)	29(13)	187(9)	34(13)
C(9)	451(21)	821(34)	998(35)	—1(13)	191(11)	37(17)
C(10)	445(22)	625(31)	747(30)	—30(10)	59(10)	41(11)
C(11)	797(31)	414(23)	451(22)	—63(11)	33(11)	—9(9)
C(12)	988(37)	442(25)	433(23)	—28(12)	130(12)	—28(9)
C(13)	816(30)	506(26)	502(24)	23(11)	186(12)	—2(10)
C(14)	527(21)	431(19)	413(19)	18(9)	102(9)	—4(8)
C(15)	467(19)	271(16)	438(19)	—5(7)	88(8)	16(7)
C(16)	523(22)	307(17)	539(22)	—22(8)	67(9)	10(8)
C(17)	447(23)	276(18)	420(20)	—7(8)	76(9)	—5(7)
C(18)	682(26)	330(20)	591(24)	24(9)	184(11)	42(9)
C(19)	778(30)	364(22)	614(25)	—46(10)	139(12)	37(10)
C(20)	950(36)	280(20)	726(30)	30(11)	175(14)	40(10)
C(21)	832(31)	257(19)	770(31)	28(10)	191(13)	—29(9)
C(22)	538(22)	254(17)	573(23)	16(8)	119(10)	—37(8)
C(23)	658(28)	371(22)	815(32)	5(10)	198(13)	—52(11)
C(24)	680(20)	730(34)	1188(46)	8(14)	244(16)	—176(16)
C(25)	757(30)	682(31)	729(30)	61(13)	211(13)	—23(13)
C(26)	1187(48)	601(32)	1138(48)	3(16)	366(21)	144(16)

At the end of the refinement the following weighting scheme was used: $w = (3.398 + 0.0458|F_0|)^{-1}$, where $w = 1/\sigma^2$.

Refinement was terminated when the maximum shift in any parameter was $<0.15\ \sigma$.

The final R values are $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.039$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2} = 0.047$.

Positional and thermal parameters are listed in Tables 1, 2 and 3.

A list of the structure factors may be obtained from the authors on request.

Results and discussion

The projection of the structure in the plane ab is shown in Fig. 1 with atom numbering. The environment of silicon atom is given in Fig. 2. The interatomic distances and bond angles are given in Fig. 3 for the menthoxy group and in Fig. 4 for the naphthyl and phenyl groups. The average standard deviations are 0.004 Å on O—C, 0.007 Å on C—C and 0.04 Å on C—H distances; 0.2° on Si—O—C, 0.3° on Si—C—C and O—C—C angles, 0.4° on C—C—C, 3° on C—C—H and 4° on H—C—H angles.

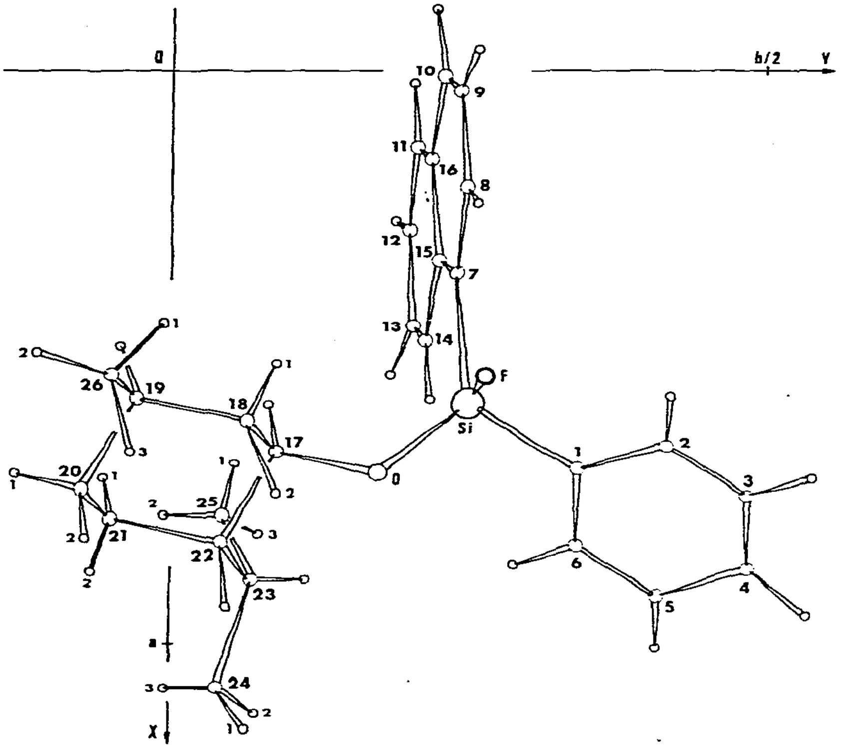

Fig. 1. Projection of the structure in the plane *ab*.

The deviations (Å) of atoms from the least-squares planes are the following in the phenyl and naphthyl groups (* denotes atoms not included in the calculation of the planes):

Phenyl group:	C(1)	0.004(3)	C(4)	0.007(5)
	C(2)	−0.001(5)	C(5)	0.001(6)
	C(3)	−0.006(5)	C(6)	−0.008(5)
	Si*	0.0501(7)		
Naphthyl group:	C(7)	−0.004(3)	C(12)	0.020(4)
	C(8)	0.022(5)	C(13)	0.021(4)
	C(9)	0.017(6)	C(14)	−0.008(4)
	C(10)	−0.006(5)	C(15)	−0.013(3)
	C(11)	−0.007(4)	C(16)	−0.018(4)
	Si*	0.0681(1)		

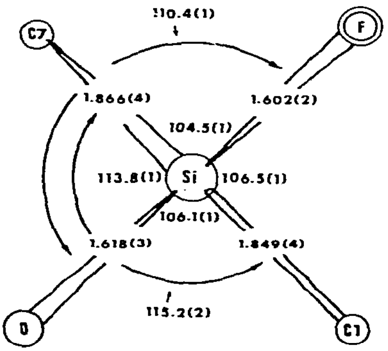

Fig. 2. Environment of the silicon atom with bond lengths (Å) and angles (°) and their estimated standard deviations in parentheses.

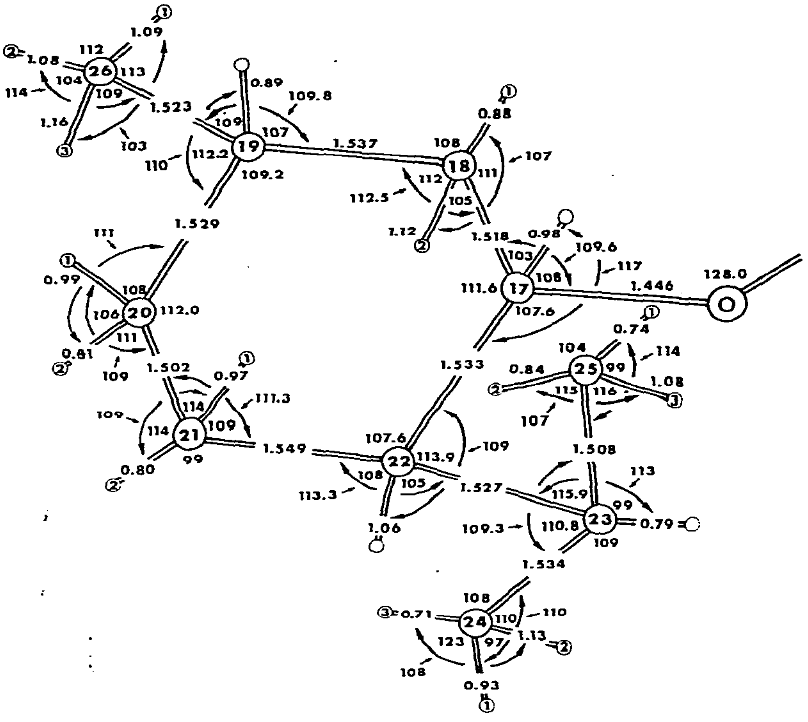

Fig. 3. Bond lengths (Å) and angles (°) in menthoxy group.

The angle between the two rings of the naphthyl group is 1.6°, so that there is no significant distortion from planarity of the naphthyl group, such as that observed in (+)-α-(1-naphthylphenylmethylsilyl)benzyl *p*-bromobenzoate [7]. It can be seen that the silicon atom is slightly out of the plane of its attached phenyl ring, as in the complex (+)-*trans*-[PtCl{SiMe(1-$C_{10}H_7$)Ph}(PMe_2Ph)$_2$] [8].

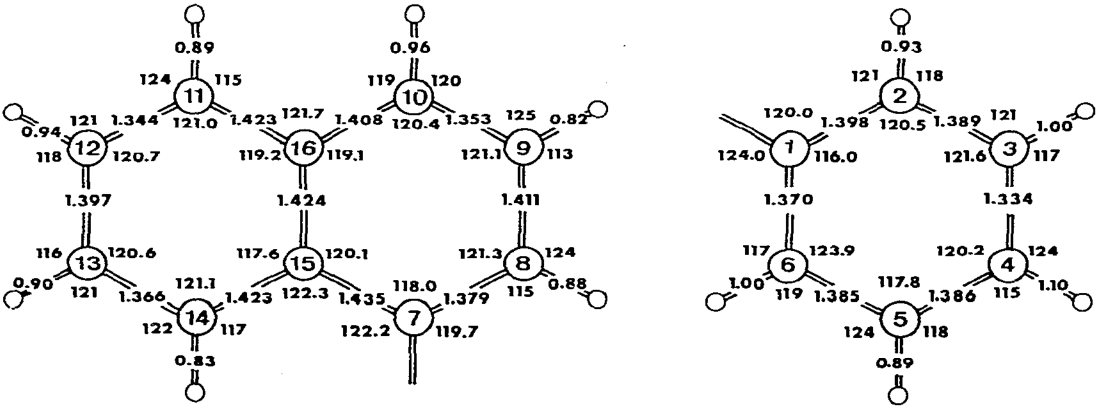

Fig. 4. Bond lengths (Å) and angles (°) in naphthyl and phenyl groups.

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