

The Crystal Structure and Absolute Configuration of (+)- α -(1-Naphthylphenylmethylsilyl)benzyl *p*-Bromobenzoate

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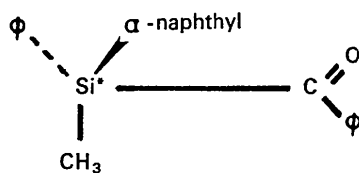
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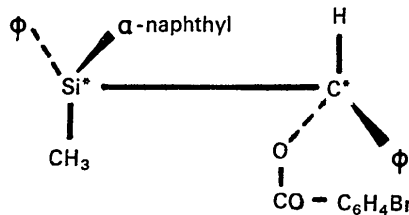
The crystal structure and absolute configuration of (+)- α -(1-naphthylphenylmethylsilyl)benzyl *p*-bromobenzoate, $C_{31}H_{25}O_2SiBr$, which contains both an asymmetric Si atom and an asymmetric C atom, has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic, space group $P2_12_12_1$, with $Z=4$, and with unit-cell dimensions $a=12.936$ (5), $b=19.953$ (8), $c=10.165$ (4) Å. The intensities of 2080 observed reflexions were measured on an automatic four-circle diffractometer. Intensities of Friedel-related pairs of reflexions were not measured, but the absolute configuration was determined by making allowance for the anomalous dispersion of Cu $K\alpha$ by O, Si and Br and calculating which enantiomorph gave the lower residual. The residuals resulting from the least-squares refinement of the two enantiomorphs were 0.047 and 0.038. The absolute configuration at Si is as expected, but that at C* is opposite to that predicted by the application of Cram's rule to the reduction of the related acylsilane. The molecule exhibits distortions remarkably similar to those found in some other acylsilanes.

Introduction

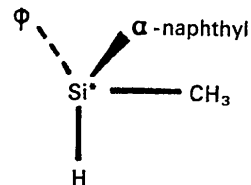
The structural interest in (+)- α -(1-naphthylphenylmethylsilyl)benzyl *p*-bromobenzoate (II) lies in the absolute configuration at C*, when the compound is prepared by Grignard reduction of the acylsilane (+)-benzoyl-1-naphthylmethylsilane (I).



(I)



(II)



(III)

X-ray analysis was undertaken to test Cram's rule concerning the configuration at C* (Cram & Abd Elhafez, 1952). The absolute configuration of the silane (III) is known from X-ray analysis (Okaya & Ashida, 1966), and (I) has been prepared from (III) by a chemical route known to cause inversion at Si (Brook & Limburg, 1963).

The preparation of (II) by reduction of (I), followed by esterification, leaves the configuration at Si unchanged so that (II) and (III) should have opposite absolute configurations at Si. The present analysis confirms this and shows, in addition, that the configuration at C* is opposite to that predicted by application of Cram's rule to the reduction of the related acylsilane (I). A detailed account of the chemical implications of this work has been published (Brook & Pascoe, 1971).

Colourless crystals were obtained from n-hexane solution. The crystal used for the structure determination was tabular (110) and prismatic *c*, the other faces observed being (110) and the form {001}. For data collection a crystal of dimensions $0.27 \times 0.15 \times 0.58$ mm was mounted about its longest dimension, which was along the *z* axis.

Crystal data

The crystal system is orthorhombic.
 $a=12.936$ (5), $b=19.953$ (8), $c=10.165$ (4) Å.
 (Cu $K\alpha_1=1.5405$, $K\alpha_2=1.5443$, $K\alpha_{mean}=1.5418$ Å)
 Space group $P2_12_12_1$, No. 19, uniquely determined from systematic absences ($h00$ absent for $h=2n+1$, $0k0$ for $k=2n+1$, $00l$ for $l=2n+1$).
 $F.W.$ for $C_{31}H_{25}O_2SiBr=537.54$
 $D_c=1.361$ g.cm⁻³ for $Z=4$. (D_m not measured).
 Linear absorption coefficient μ (Cu $K\alpha$) 29.8 cm⁻¹.

Data collection

X-ray intensity data were collected on a Picker automatic four-circle diffractometer, using Ni-filtered Cu $K\alpha$ radiation, to a limit of $\sin \theta=0.93$. The scan range was 1.4° at $2\theta=0$, increasing with 2θ (Arndt & Willis, 1966). The scan rate was 1° min⁻¹, with a total background counting time of 80 sec per reflexion. 2571 re-

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flexions from one octant of *R* space were measured, of which 2080 were considered observed according to the criterion $I > 2\sigma(I)$. For estimating $\sigma(I)$, counting statistics and an Abrahams factor of 0.008 were used (Abrahams & Bernstein, 1965). Empirical absorption corrections were applied based on the ϕ -sweep curves for the 002 and 004 reflexions (North, Phillips & Mathews,

1968). These two curves were found to be identical within experimental error. The octant of *R* space chosen for data collection was the one where absorption was least, the maximum correction applied to any intensity being 1.09. The cell dimensions and standard deviations quoted above were obtained by a least-squares refinement using both positive and negative

Table 1. $10 \times |F_o|$ and $10 \times |F_c|$

h	k	l	$10 \times F_o $	$10 \times F_c $
0	0	0	0	0
0	0	1	10	10
0	0	2	20	20
0	0	3	30	30
0	0	4	40	40
0	0	5	50	50
0	0	6	60	60
0	0	7	70	70
0	0	8	80	80
0	0	9	90	90
0	0	10	100	100
0	0	11	110	110
0	0	12	120	120
0	0	13	130	130
0	0	14	140	140
0	0	15	150	150
0	0	16	160	160
0	0	17	170	170
0	0	18	180	180
0	0	19	190	190
0	0	20	200	200
0	0	21	210	210
0	0	22	220	220
0	0	23	230	230
0	0	24	240	240
0	0	25	250	250
0	0	26	260	260
0	0	27	270	270
0	0	28	280	280
0	0	29	290	290
0	0	30	300	300
0	0	31	310	310
0	0	32	320	320
0	0	33	330	330
0	0	34	340	340
0	0	35	350	350
0	0	36	360	360
0	0	37	370	370
0	0	38	380	380
0	0	39	390	390
0	0	40	400	400
0	0	41	410	410
0	0	42	420	420
0	0	43	430	430
0	0	44	440	440
0	0	45	450	450
0	0	46	460	460
0	0	47	470	470
0	0	48	480	480
0	0	49	490	490
0	0	50	500	500
0	0	51	510	510
0	0	52	520	520
0	0	53	530	530
0	0	54	540	540
0	0	55	550	550
0	0	56	560	560
0	0	57	570	570
0	0	58	580	580
0	0	59	590	590
0	0	60	600	600
0	0	61	610	610
0	0	62	620	620
0	0	63	630	630
0	0	64	640	640
0	0	65	650	650
0	0	66	660	660
0	0	67	670	670
0	0	68	680	680
0	0	69	690	690
0	0	70	700	700
0	0	71	710	710
0	0	72	720	720
0	0	73	730	730
0	0	74	740	740
0	0	75	750	750
0	0	76	760	760
0	0	77	770	770
0	0	78	780	780
0	0	79	790	790
0	0	80	800	800
0	0	81	810	810
0	0	82	820	820
0	0	83	830	830
0	0	84	840	840
0	0	85	850	850
0	0	86	860	860
0	0	87	870	870
0	0	88	880	880
0	0	89	890	890
0	0	90	900	900
0	0	91	910	910
0	0	92	920	920
0	0	93	930	930
0	0	94	940	940
0	0	95	950	950
0	0	96	960	960
0	0	97	970	970
0	0	98	980	980
0	0	99	990	990
0	0	100	1000	1000

diffractometer 2θ values of axial reflexions. At low θ , a mean Cu $K\alpha$ wavelength was used; for three higher-angle reflexions, the positions of both the $K\alpha_1$ and $K\alpha_2$ reflexions were measured. All measurements were made at 20°C.

Structure determination and refinement

The structure was solved by routine application of the heavy-atom method, using the position of the bromine atom obtained from the Patterson function. The first heavy-atom phased Fourier map clearly revealed nine additional atoms, and the second Fourier map, the whole structure. Refinement was carried out by full-matrix least-squares procedures, using program *XFLS* (Ellison, 1962). The unobserved reflexions were excluded from the refinement and are not listed in Table 1. The scattering curves used in the structure factor calculations were evaluated from Hartree-Fock wave functions, using coefficients given by Cromer & Mann (1968) and, in the case of Si(0.2e) and Br(-0.9e), corrected for the real part of the anomalous scattering of Cu $K\alpha$. The hydrogen scattering factor used was that of Stewart, Davidson & Simpson (1965). Refinement was uneventful. All hydrogen atom positions, apart from those at the methyl group, were obtained from a difference synthesis and these latter three hydrogen atoms were easily found from a further difference synthesis, in which 22 of the 25 hydrogen atoms were included in F_c . The observed hydrogen positions were very close to those expected, and all hydrogen atoms were included in subsequent structure factor calculations at their predicted positions, and with isotropic temperature factors of 5.0 Å². These parameters were not subsequently refined. At this stage, with R at 0.043₂, the imaginary part of the anomalous dispersion was included for O(0.1e), Si(0.4e) and Br(1.5e) atoms (*International Tables for X-ray Crystallography*, 1962). R for the assumed structure fell to 0.039₈, whereas for the enantiomorphic structure it rose to 0.046₈ (Ibers & Hamilton, 1964). Application of the Hamilton \mathcal{R} test (Hamilton, 1965) indicates that the expected ratio of residuals at the ½% significance level ($\mathcal{R}_{1,1763,0.005}$) is

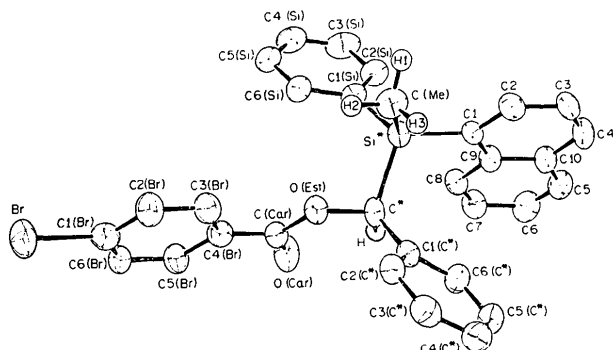


Fig. 1. The molecule with 30% probability thermal ellipsoids, shown in absolute configuration (calculated by *ORTEP*; Johnson, 1965).

Table 2. (a) Atomic fractional coordinates with standard deviations in parentheses (for Br and Si, $\times 10^5$, otherwise $\times 10^2$) and (b) atomic fractional coordinates of hydrogen atoms (unrefined) $\times 10^3$

	X/a	Y/b	Z/c
Br	19639 (7)	14556 (4)	-98987 (8)
Si	895 (11)	37244 (6)	-25120 (14)
C(meth)	7 (5)	2819 (3)	-2098 (7)
C(1)	31 (4)	4242 (2)	-979 (5)
C(2)	-144 (5)	3919 (3)	191 (6)
C(3)	-141 (5)	4246 (4)	1420 (6)
C(4)	77 (6)	4917 (4)	1473 (6)
C(5)	494 (5)	5979 (3)	347 (7)
C(6)	653 (6)	6326 (3)	-746 (8)
C(7)	571 (5)	6012 (3)	-1991 (7)
C(8)	382 (4)	5341 (3)	-2070 (5)
C(9)	218 (4)	4953 (2)	-943 (5)
C(10)	266 (4)	5279 (3)	316 (5)
C(1) (Br)	1840 (5)	2125 (3)	-8590 (6)
C(2) (Br)	1596 (5)	1937 (3)	-7318 (6)
C(3) (Br)	1510 (5)	2416 (3)	-6356 (5)
C(4) (Br)	1671 (4)	3096 (3)	-6662 (5)
C(5) (Br)	1907 (5)	3268 (3)	-7961 (5)
C(6) (Br)	1987 (5)	2789 (3)	-8924 (5)
C(car)	1616 (4)	3625 (3)	-5670 (5)
O(car)	1726 (4)	4213 (2)	-5889 (4)
O(est)	1398 (3)	3387 (2)	-4462 (3)
C*	1405 (4)	3851 (2)	-3350 (5)
C(1) (C*)	2323 (4)	3691 (2)	-2493 (5)
C(2) (C*)	2809 (5)	3066 (3)	-2521 (6)
C(3) (C*)	3655 (5)	2939 (3)	-1746 (6)
C(4) (C*)	4041 (5)	3418 (4)	-906 (6)
C(5) (C*)	3557 (5)	4043 (3)	-869 (6)
C(6) (C*)	2719 (5)	4175 (3)	-1648 (6)
C(1) (Si)	-942 (4)	3946 (3)	-3729 (6)
C(2) (Si)	-1654 (5)	4458 (3)	-3478 (7)
C(3) (Si)	-2451 (5)	4595 (3)	-4382 (9)
C(4) (Si)	-2540 (5)	4226 (4)	-5524 (8)
C(5) (Si)	-1884 (5)	3716 (4)	-5782 (6)
C(6) (Si)	-1076 (4)	3576 (3)	-4889 (6)
H[C(2)]	-28	339	15
H[C(3)]	-30	398	232
H[C(4)]	10	516	242
H[C(5)]	54	626	125
H[C(6)]	85	685	-62
H[C(7)]	65	629	-290
H[C(8)]	37	512	-303
H[C(2), Br]	147	142	-707
H[C(3), Br]	132	225	-538
H[C(5), Br]	203	378	-823
H[C(6), Br]	216	293	-992
H[C(2), Si]	-159	475	-259
H[C(3), Si]	-300	499	-418
H[C(4), Si]	-313	434	-623
H[C(5), Si]	-200	343	-667
H[C(6), Si]	-55	317	-509
H[C(2), C*]	252	268	-316
H[C(3), C*]	403	246	-178
H[C(4), C*]	470	330	-30
H[C(5), C*]	383	444	-23
H[C(6), C*]	237	466	-159
H(C*)	147	436	-368
H(1) (meth)	-66	266	-170
H(2) (meth)	11	248	-284
H(3) (meth)	54	266	-145

1.0023. The observed ratio of 1.175 is very significantly greater than this, and serves to establish the absolute configuration of the molecule which is shown diagram-

Table 3. Atomic thermal parameters with standard deviations in parentheses (for Br and Si, $\times 10_5$, otherwise $\times 10^4$)

Temperature factor: $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	1221 (6)	606 (3)	1930 (11)	122 (4)	110 (7)	-489 (5)
Si	106 (5)	26 (1)	173 (8)	0 (2)	-1 (1)	8 (3)
C(meth)	768 (9)	248 (3)	1009 (12)	17 (5)	-1 (9)	9 (6)
C(1)	70 (4)	31 (1)	92 (5)	-2 (2)	9 (4)	1 (2)
C(2)	85 (4)	40 (2)	120 (6)	-1 (2)	9 (5)	10 (3)
C(3)	88 (5)	53 (2)	103 (6)	4 (3)	18 (4)	9 (3)
C(4)	100 (5)	58 (3)	95 (6)	13 (3)	-9 (5)	-9 (3)
C(5)	104 (5)	41 (2)	151 (8)	7 (3)	-19 (5)	-27 (4)
C(6)	127 (6)	33 (2)	185 (10)	7 (3)	-19 (6)	-18 (4)
C(7)	110 (5)	31 (2)	163 (8)	7 (2)	4 (6)	-5 (3)
C(8)	87 (4)	29 (1)	109 (6)	4 (2)	10 (4)	-2 (2)
C(9)	77 (4)	30 (1)	96 (5)	7 (2)	-1 (4)	-7 (2)
C(10)	88 (4)	38 (2)	100 (6)	9 (2)	-7 (4)	-15 (3)
C(1) (Br)	67 (4)	47 (2)	141 (7)	8 (2)	0 (5)	-11 (3)
C(2) (Br)	107 (5)	34 (2)	142 (7)	6 (2)	1 (5)	-11 (3)
C(3) (Br)	89 (4)	32 (1)	112 (6)	2 (2)	1 (4)	4 (3)
C(4) (Br)	67 (3)	32 (1)	100 (5)	2 (2)	-1 (4)	4 (2)
C(5) (Br)	90 (4)	40 (2)	102 (5)	-1 (2)	2 (4)	4 (3)
C(6) (Br)	82 (4)	51 (2)	101 (6)	0 (3)	-1 (4)	-5 (3)
C(car)	81 (4)	29 (2)	93 (5)	1 (2)	0 (3)	8 (2)
O(car)	180 (5)	28 (1)	122 (4)	-9 (2)	12 (4)	8 (2)
O(est)	93 (3)	25 (1)	91 (4)	-1 (1)	4 (2)	0 (1)
C*	91 (4)	23 (1)	88 (4)	4 (2)	-2 (4)	-5 (2)
C(1) (C*)	79 (3)	27 (1)	89 (4)	4 (2)	11 (4)	4 (2)
C(2) (C*)	90 (4)	30 (1)	114 (6)	5 (2)	-3 (4)	3 (3)
C(3) (C*)	93 (5)	39 (2)	134 (7)	13 (2)	6 (5)	17 (3)
C(4) (C*)	80 (4)	57 (3)	131 (7)	1 (3)	-6 (5)	12 (4)
C(5) (C*)	98 (5)	45 (2)	118 (6)	-5 (3)	-13 (5)	-7 (3)
C(6) (C*)	89 (4)	34 (2)	120 (6)	-4 (2)	-5 (4)	-4 (3)
C(1) (Si)	71 (4)	29 (1)	126 (6)	0 (2)	-6 (4)	2 (2)
C(2) (Si)	85 (4)	31 (2)	190 (9)	6 (2)	-6 (5)	-7 (3)
C(3) (Si)	88 (5)	36 (2)	259 (12)	9 (3)	-15 (7)	18 (4)
C(4) (Si)	94 (5)	44 (2)	184 (10)	-7 (3)	-36 (6)	25 (4)
C(5) (Si)	93 (4)	48 (2)	128 (6)	13 (3)	-16 (5)	4 (3)
C(6) (Si)	77 (4)	39 (2)	124 (6)	1 (2)	2 (4)	. (3)

Table 4. Bond lengths and standard deviations

Br—C(1) (Br)	1.892 (6) Å	Si—C(1) (Si)	1.872 (6) Å
C(1) (Br)—C(2) (Br)	1.383 (9)	C(1) (Si)—C(2) (Si)	1.398 (8)
C(2) (Br)—C(3) (Br)	1.372 (8)	C(2) (Si)—C(3) (Si)	1.409 (8)
C(3) (Br)—C(4) (Br)	1.407 (7)	C(3) (Si)—C(4) (Si)	1.379 (10)
C(4) (Br)—C(5) (Br)	1.398 (7)	C(4) (Si)—C(5) (Si)	1.351 (10)
C(5) (Br)—C(6) (Br)	1.372 (8)	C(5) (Si)—C(6) (Si)	1.413 (8)
C(1) (Br)—C(6) (Br)	1.381 (9)	C(1) (Si)—C(6) (Si)	1.403 (8)
C(4) (Br)—C(car)	1.461 (7)	C*—C(1) (C*)	1.508 (7)
C(car)—O(car)	1.203 (6)	C(1) (C*)—C(2) (C*)	1.396 (7)
C(car)—O(est)	1.347 (6)	C(2) (C*)—C(3) (C*)	1.373 (9)
O(est)—C*	1.462 (6)	C(3) (C*)—C(4) (C*)	1.374 (8)
Si—C(1)	1.872 (5)	C(4) (C*)—C(5) (C*)	1.398 (8)
C(1)—C(2)	1.372 (7)	C(5) (C*)—C(6) (C*)	1.367 (7)
C(2)—C(3)	1.410 (9)	C(1) (C*)—C(6) (C*)	1.390 (7)
C(3)—C(4)	1.369 (9)		
C(1)—C(9)	1.439 (7)		
C(4)—C(10)	1.402 (9)		
C(5)—C(10)	1.427 (9)		
C(5)—C(6)	1.326 (10)		
C(6)—C(7)	1.416 (9)		
C(7)—C(8)	1.363 (8)		
C(8)—C(9)	1.400 (7)		
C(9)—C(10)	1.437 (7)		
Si—C(meth)	1.857 (5)		
Si—C*	1.920 (6)		

Non-bonded atoms:
H(C*)—O(car) 2.29 Å

All C—H bond lengths are in the range 1.01–1.08 Å (unrefined).

atically as (I) and in Fig. 1. The F_c 's were then taken to be error free, and a value of $\sigma(F)$ was calculated for a number of ranges of F . Assuming $\sigma(F)$ to be of the form $A F_o + B + C/F_o$, a least-squares fit established $A = 0.01965$, $B = 0.2182$, and $C = 1.122$. This showed that our previous weighting of the weaker reflexions had been too large. Use of the new $\sigma(F)$ relation for weighting the data gave a slightly lower residual of 0.038_3 .

Final positional and thermal parameters are given in Tables 2 and 3.

Table 5. Bond angles with standard deviations

C*—Si—C(meth)	106.2 (3) ^o
C*—Si—C(1) (Si)	107.9 (2)
C*—Si—C(1)	109.4 (2)
C(1)—Si—C(meth)	110.2 (3)
C(1) (Si)—Si—C(1)	113.0 (2)
C(1) (Si)—Si—C(meth)	109.8 (3)
Si—C*—C(1) (C*)	114.5 (3)
Si—C*—O(est)	104.7 (3)
C(1) (C*)—C*—O(est)	108.6 (4)
C*—O(est)—C(car)	118.7 (4)
O(est)—C(car)—O(car)	122.5 (5)
O(est)—C(car)—C(4) (Br)	112.6 (4)
O(car)—C(car)—C(4) (Br)	124.9 (5)
C(car)—C(4) (Br)—C(3) (Br)	122.5 (5)
C(car)—C(4) (Br)—C(5) (Br)	119.0 (5)
C(3) (Br)—C(4) (Br)—C(5) (Br)	118.5 (5)
C(2) (Br)—C(3) (Br)—C(4) (Br)	120.2 (5)
C(1) (Br)—C(2) (Br)—C(3) (Br)	119.7 (6)
C(6) (Br)—C(1) (Br)—C(2) (Br)	121.5 (6)
Br—C(1) (Br)—C(2) (Br)	119.5 (5)
Br—C(1) (Br)—C(6) (Br)	119.1 (5)
C(1) (Br)—C(6) (Br)—C(5) (Br)	118.8 (5)
C(4) (Br)—C(5) (Br)—C(6) (Br)	121.3 (5)
C*—C(1) (C*)—C(2) (C*)	122.1 (4)
C*—C(1) (C*)—C(6) (C*)	120.0 (4)
C(2) (C*)—C(1) (C*)—C(6) (C*)	117.9 (5)
C(1) (C*)—C(2) (C*)—C(3) (C*)	120.8 (5)
C(2) (C*)—C(3) (C*)—C(4) (C*)	121.1 (6)
C(3) (C*)—C(4) (C*)—C(5) (C*)	118.4 (6)
C(4) (C*)—C(5) (C*)—C(6) (C*)	120.7 (6)
C(5) (C*)—C(6) (C*)—C(1) (C*)	121.0 (5)
Si—C(1) (Si)—C(2) (Si)	121.4 (5)
Si—C(1) (Si)—C(6) (Si)	121.2 (4)
C(2) (Si)—C(1) (Si)—C(6) (Si)	117.2 (5)
C(1) (Si)—C(2) (Si)—C(3) (Si)	120.3 (6)
C(2) (Si)—C(3) (Si)—C(4) (Si)	120.4 (6)
C(3) (Si)—C(4) (Si)—C(5) (Si)	120.9 (6)
C(4) (Si)—C(5) (Si)—C(6) (Si)	119.3 (6)
C(5) (Si)—C(6) (Si)—C(1) (Si)	121.8 (5)
Si—C(1)—C(2)	118.0 (4)
Si—C(1)—C(9)	123.9 (4)
C(2)—C(1)—C(9)	118.0 (5)
C(1)—C(2)—C(3)	123.4 (5)
C(2)—C(3)—C(4)	119.2 (5)
C(3)—C(4)—C(10)	120.5 (5)
C(10)—C(5)—C(6)	121.7 (5)
C(5)—C(6)—C(7)	120.3 (6)
C(6)—C(7)—C(8)	120.1 (5)
C(7)—C(8)—C(9)	121.5 (5)
C(8)—C(9)—C(10)	118.1 (4)
C(8)—C(9)—C(1)	123.4 (5)
C(10)—C(9)—C(1)	118.4 (5)
C(9)—C(10)—C(4)	120.4 (5)
C(9)—C(10)—C(5)	118.1 (5)
C(4)—C(10)—C(5)	121.4 (5)

Discussion

The molecule is shown with its correct configuration in Fig. 1; bond lengths and angles are given in Tables 4 and 5. Standard deviations were calculated from program *ORFFE* (Busing, Martin & Levy, 1964).

The plane of the naphthyl group lies at about 9° to the C(Me)—Si—C(1) plane, so that the hydrogen atom on C(2) lies midway between H(1) and H(3) of the methyl group.

The naphthyl group and its attached Si atom exhibit significant distortions, remarkably similar to those reported by Okaya & Ashida (1966) for α -naphthylphenylmethylsilane (hereafter called R_3SiH) and for R_3SiF , even though, as will be seen, the intramolecular environment of the naphthyl group is quite different. In all three compounds, the Si—C(1) bond makes 7° with the naphthyl plane defined by C(3), C(4), C(5), C(6), C(9), and C(10) (plane 2, Table 6). The distortions of the remaining naphthyl atoms away from plane 2 are extraordinarily similar in all three cases.* This close similarity is illustrated in Fig. 2.

In no case are the distortions simply explained by intramolecular forces. In the present structure, the hydrogen atom on C(8) is close (2.18 \AA) to that on C* and would be even closer if C(8) were to lie in plane 2. However, the hydrogen atom on C(7) is not as close as that on C(8) to the hydrogen atom on C* although C(7) is further displaced from plane 2 than is C(8). Not only are the distortions from planarity of the naphthyl group in these compounds remarkably similar, but the bond lengths also vary in the same way, particularly the short C(5)—C(6) distance of 1.326 \AA found here compared with 1.323 and 1.329 \AA in R_3SiH and R_3SiF .

That the distortion of the naphthyl group cannot be simply explained in intramolecular terms is illustrated by Fig. 3(a) and (b). Here, part of the present molecule and part of R_3SiH are viewed on the same scale along Si—C(1); to compare them, one has to take the R_3SiH enantiomorph of opposite hand to that studied by Okaya & Ashida. This then brings our molecule and that of R_3SiH to the same configuration about Si* (phenyl to methyl being clockwise in the diagram). In our molecule, there has been a rotation of Si—C(1) of about 120° to bring the methyl group to where the phenyl group is in R_3SiH . Hence the environment of the naphthyl group is quite different in the two cases. The close correspondence in geometry of the naphthyl groups themselves can be seen from Fig. 3; this correspondence is even more impressively made by a 'best molecular fit' analysis (Nyburg, unpublished). This analysis superimposes two molecules, or corresponding parts of them, and minimizes the sum-of-squares of displacements $\sum d^2$ between corresponding atoms.

* The displacement of $+0.043 \text{ \AA}$ for C(7) (our numbering) in R_3SiF given by Okaya & Ashida should have its sense reversed.

When the carbon framework of the present compound is matched with R₃SiH, $\sum \Delta^2 = 0.0042 \text{ \AA}^2$, whereas when it is matched with naphthalene (Cruickshank, 1957), $\sum \Delta^2 = 0.0168 \text{ \AA}^2$.

Thus it seems unlikely that intramolecular forces could be responsible for the observed geometry. Equally, it seems unlikely that intermolecular forces are responsible. Although R₃SiH and R₃SiF are isostructural and thus subject to very similar intermolecular forces, the present compound has quite a different molecular packing. (The fact that the present compound, like R₃SiH and R₃SiF, belongs to *P*2₁2₁2₁ with *b* close to 19.9 Å, appears to be fortuitous.) Accordingly, we are forced to conclude that the distortions are an intrinsic property of the molecule and not due to its environment. We have been unable to find other cases where Si attached directly to an aryl group lies out-of-plane from it.

No other features of the molecule appear to warrant

special comment. Best least-squares planes for various parts of the molecule are given in Table 6. There are no exceptionally short intermolecular contacts.

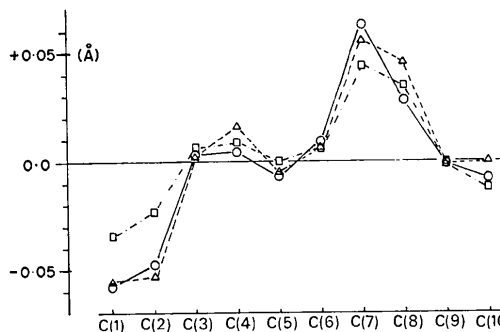


Fig. 2. Deviations of carbon atoms in the naphthyl group from plane 2 in three crystal structures. (○ present structure; △ R₃SiH; □ R₃SiF. Our numbering of atoms throughout.)

Table 6. Planes of best fit (least squares)

(a) Coefficients. Each plane is represented by $AX + BY + CZ = D$, where *X*, *Y*, *Z* are coordinates in Å referred to crystallographic axes.

Plane	Description	A	B	C	D
1	Whole naphthyl radical	-0.9787	0.1960	-0.0615	1.7171
2	Part of naphthyl radical	-0.9759	0.2085	-0.0646	1.8484
3	<i>p</i> -bromophenyl radical	-0.9743	0.0968	-0.2033	-0.1271
4	Phenyl on C*	0.6059	0.3259	-0.7258	6.0595
5	Phenyl on Si*	0.5966	0.6425	-0.4809	6.1454
6	Ester group	-0.9784	0.0873	-0.1873	-0.3312

(b) Deviations from planes. A distance in parentheses indicates the atom was not included in the calculation of the plane.

Plane No.	1	2	3	4	5	6
Br			(-0.022)			
Si	(-0.217)	(-0.247)		(-1.714)	(0.074)	
C(1)	-0.036	(-0.058)				
C(2)	-0.014	(-0.048)				
C(3)	0.034	0.003				
C(4)	0.017	0.004				
C(5)	-0.026	-0.007				
C(6)	-0.022	0.009				
C(7)	0.036	(0.063)				
C(8)	0.018	(0.028)				
C(9)	0.003	-0.001				
C(10)	-0.008	-0.008				
C(1) (Br)			-0.006			
C(2) (Br)			0.002			
C(3) (Br)			0.004			
C(4) (Br)			-0.004			
C(5) (Br)			0.000			
C(6) (Br)			0.005			0.000
C(car)			(-0.038)			-0.003
O(car)			(-0.018)			0.001
O(est)			(-0.058)			0.002
C*				(0.017)	(1.514)	(0.139)
C(1) (C*)				0.001		
C(2) (C*)				-0.004		
C(3) (C*)				0.004		
C(4) (C*)				-0.002		
C(5) (C*)				-0.002		
C(6) (C*)				0.002		
C(1) (Si)					0.010	
C(2) (Si)					-0.007	
C(3) (Si)					-0.004	
C(4) (Si)					0.013	
C(5) (Si)					-0.009	
C(6) (Si)					-0.002	

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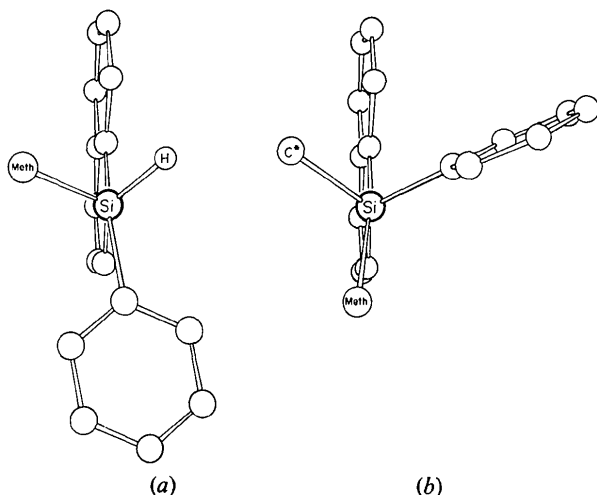


Fig. 3. (a) A view down the Si- α C bond in Okaya & Ashida's (1966) R_3SiH , but for the enantiomorph of opposite hand. The hydrogen position was calculated by assuming sp^3 hybridization on silicon, and an Si-H bond length of 1.48 Å. (b) The same view of the present structure. The diagrams show the same distortion of the naphthyl radical, despite the completely different location of neighbouring groups.

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Structural Studies of Synthetic Analgetics. I. The Crystal and Molecular Structure of (\pm)- γ -Promedol Alcohol

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The crystal structure of (\pm)- γ -1,2,5-trimethyl-4-phenylpiperidin-4-ol, the alcohol of the least active promedol isomer, has been determined by the direct method, and has been refined by least-squares to $R=0.048$ for the 1565 observed reflexions. The piperidine ring has the chair form, with the phenyl and three methyl substituents in equatorial positions, and the hydroxyl group axial. The phenyl ring is oriented at 73.7° from the mean plane of the piperidine ring, and its *ortho* hydrogen atoms make rather short intramolecular contacts $H \cdots H = 2.07$ and $H \cdots O = 2.39$ Å. Intermolecular hydrogen bonds of the type $O-H \cdots N$ link molecules of opposite chirality which are related by glide planes to form infinite chains along *c*. The space group is $P2_1/c$, and the unit-cell parameters are $a = 10.806$, $b = 11.569$, $c = 10.460$ Å, $\beta = 98.75^\circ$.

Introduction

The isomeric prodines (I) and the isomeric promedols, (II) are powerful synthetic analgetics with wide application in medicine, because they combine high potency

and relatively low toxicity. The analgetic activity varies widely among the isomers of both the prodines and the promedols. It is important to correlate these variations with the molecular structures in order to establish the rules of these systems and to enhance the understanding of their biological action. The potency of the different isomers of (I) and (II), in terms of

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