

PREPARATION AND STRUCTURE OF (R)-(-)- AND
(S)-(+)-2, 2'-(2, 2-DIMETHYL-2-SILAPROPANE-1, 3-DIYL)-1, 1'-BINAPHTHALENE

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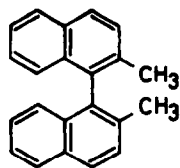
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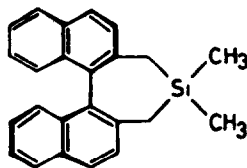
Summary. The title axially dissymmetric organosilicon compound is obtainable in optically pure form by synthesis of the racemate followed by resolution with a chiral poly(triphenylmethyl methacrylate) column. The structure has been established by spectroscopic and single crystal X-ray diffraction methods.

Axially dissymmetric molecules are of great significance from both stereochemical¹ and preparative²⁻⁵ point of view. Particularly biaryls which show atropisomerism occupy a central place in this area. Despite recent revolutionary development of organosilicon chemistry,⁶ chiral organosilicon compounds have been limited to those possessing an asymmetric silicon atom⁷ or a centro-dissymmetric alkyl substituent. We have prepared for the first time an axially dissymmetric tetraalkylsilane in a chiral form.

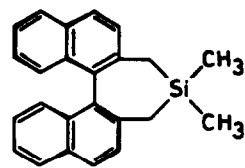
Synthesis of the racemic organosilicon compound, 2, possessing a C_2 axis is simply based on the condensation of a dilithio derivative of (\pm)-2, 2'-dimethyl-1, 1'-binaphthyl (1) and a dichlorosilane. Thus treatment of (\pm)-1 with 3 equiv of *n*-butyllithium/*N,N,N',N'*-tetramethylethylenediamine in hexane (-20 °C, 24 h) followed by exposure to 3 equiv of dichlorodimethylsilane (0 °C, 1 h) produced the desired (\pm)-2, mp 163-165 °C, in 50% yield. The



(\pm)-1



(R)-(-)-2



(S)-(+)-2

spectral and analytical data were consistent with the assigned structure.⁸

This organosilane possesses only aliphatic and aromatic hydrocarbon groupings and lacks obvious functionalities for optical resolution. Fortunately, however, the recently developed chiral poly(triphenylmethyl methacrylate) (PTrMA) column⁹ provides a powerful tool for optical resolution of racemates of this type. Thus when (\pm)-**2** was subjected to high-pressure liquid chromatography (HPLC) on a column of (+)-PTrMA coated on macroporous silica gel (Chiralpak OT)¹⁰ by using methanol as eluant, the complete resolution was attained (Figure 1).¹¹ Preparative separation followed by plug filtration through silica gel and recrystallization from methanol afforded analytical sample of (+)-**2** and (-)-**2** as colorless prisms. The circular dichroism (CD) curve of the levorotatory enantiomer, ¹² mp 169–171 °C, $[\alpha]_D^{22}$ -324° (c 0.089, dioxane), resembled closely those of the known related (R)-2,2'-bridged 1,1'-binaphthyl derivatives¹³ (Figure 2), and thus assigned to have the R configuration.

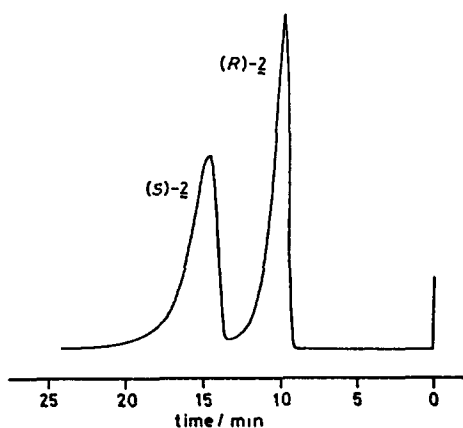


Figure 1. HPLC chromatogram for the resolution of racemic **2** on a Chiralpak OT column.

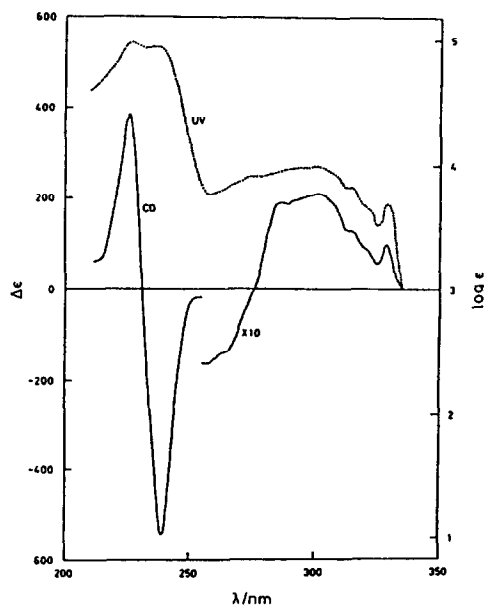


Figure 2. CD and UV spectra of (R)-(-)-**2** (dioxane).

The molecular structure of the levorotatory **2** has been determined by the X-ray crystal structure analysis (Figure 3).¹⁴ The absolute configuration was firmly established to be R. Some bond lengths and angles of interest are listed in Table I. The mean Si—CH₃ bond length [1.861(4) Å] is normal,^{15–17} but the lengths of the Si—C(11) and Si—C(11') bonds [1.884(3) and 1.893(3) Å, respectively] are rather long and the C(11)—Si—C(11') angle is

narrowed to $103.7(1)^\circ$. The angle between the least-squares planes through the two naphthyl groups is 65.5° .¹⁸

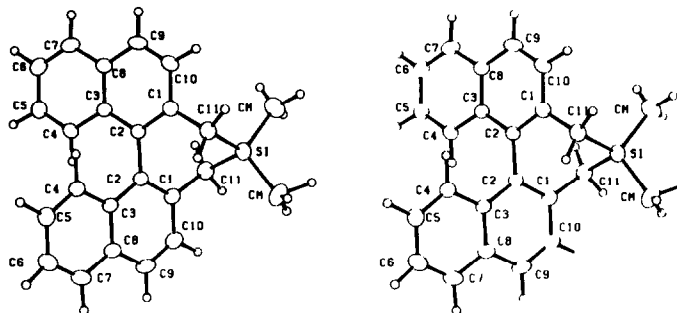


Figure 3. Stereoscopic view of (R)-(-)-2.

Table I. Selected Bond Lengths (\AA) and Angles (Deg) for (R)-(-)-2

$\text{S1}-\text{C(M)}$	1.861(3)	$\text{C(M)}-\text{S1}-\text{C(M')}$	110.4(2)
$\text{S1}-\text{C(M')}$	1.861(4)	$\text{C(M)}-\text{S1}-\text{C(11)}$	110.8(1)
$\text{S1}-\text{C(11)}$	1.884(3)	$\text{C(M)}-\text{S1}-\text{C(11')}$	111.0(2)
$\text{S1}-\text{C(11')}$	1.893(3)	$\text{C(11)}-\text{S1}-\text{C(11')}$	103.7(1)
$\text{C(2)}-\text{C(2')}$	1.492(3)	$\text{C(M')}-\text{S1}-\text{C(11)}$	109.4(1)
		$\text{C(M')}-\text{S1}-\text{C(11')}$	111.4(1)

Obviously the achiral synthesis/resolution sequence described herein allows an easy entry to various organic and organometalloid compounds having related chiral structures. Further application of this technique is in progress.

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7. L. H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, New York, 1965. See also Chapter Z and Z' in the books given in footnote 1b.
8. ^1H NMR (benzene with tetramethylsilane) δ -0.10 (s, 6H, CH_3), ^13C NMR (CDCl_3 , $J_{\text{AB}} = 13$ Hz, 4H, CH_2), 7.8-8.8 (m, 12H, aromatic). solvent signal taken as $\delta = 77.1$) δ 3.5 (CH_3), 23.9 (CH_2), 124.2, 125.8, 126.5, 127.8, 128.0, 131.8, 132.3, 132.3, 132.8, 137.1 (aromatic). IR (CCl_4) 3050-2900, 1640, 1580, 1510 cm^{-1} . UV^{dioxane} ($\epsilon \times 10^{-4}$) 227 (9.26), 237 (8.48), 302 (0.97), 315 (0.67, shoulder), 329 (0.49) nm . MS m/z 338 (M^+). Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{Si}$: C, 85.15, H, 6.55. Found: C, 84.93, H, 6.74.
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10. Optically active, isotactic PTrMA coated on LiChrospher Si 1000. Commercially available from Japan Spectroscopic Co. Ltd., Ishikawa-cho, Hachioji, Tokyo, Japan.
11. Waters 6000A instrument equipped with a JASCO UVIDEC-100 ultraviolet detector (292 nm). Column, 25 cm x 0.46 cm; eluant, methanol, flow rate, 1 mL/min, temp, 16 $^\circ\text{C}$.
12. λ^{dioxane} ($\Delta\epsilon$) 340 (0.0), 329 (+10.4), 325 (+6.0), 314 (+14.1, shoulder), 307 (+20.2, shoulder), 301 (+21.9), 289 (+19.8), 287 (+20.1), 263 (-14.4, shoulder), 254 (-16.5, shoulder), 240 (-558), 224 (+395), 210 (+56.5) nm, (c 3.54×10^{-5}).
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14. The crystals are colorless prisms. Intensities of the reflections were measured on a Rigaku AFC-5 diffractometer with $\text{Cu K}\alpha$ radiation up to $2\theta = 135^\circ$. The crystallographic data are $\text{SiC}_{24}\text{H}_{22}$, $M_r = 338.52$, orthorhombic, $P2_12_12_1$, $a = 12.441(1)$, $b = 20.331(1)$, $c = 7.581(1)$ A , $V = 1917.5(3)$ A^3 , $D_x = 1.173$ g cm^{-3} , $Z = 4$, and $\mu(\text{Cu K}\alpha) = 21.21$ cm^{-1} . The structure was solved by a direct method (MULTAN) and refined by block-diagonal least-squares calculations including hydrogen atoms. The final R and R_w values were 0.040 and 0.049, respectively, for a total of 3089 (1783 hkl and 1306 hkl)^w reflections with $|F_o| > 3\sigma(|F_o|)$. The enantiomeric structure refined under identical conditions gave R and R_w values of 0.046 and 0.057, respectively. The R configuration was also confirmed by comparison of the observed intensity relations between hkl and hkl reflections with the calculated relations. X-ray data (Tables of atomic coordinates, temperature factors, structure factors, bond lengths, and angles) have been deposited with the Cambridge Crystallographic Data Centre.
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18. Correspondence about X-ray crystallography should be made to T.I. among the authors.

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