Structure of (−)-(1R,4S,5R)-8-Phenyl-5-menthyl (S)-1,2,3,4-Tetrahydro-4-oxo-2-triphenylsilyl-1-pyridinecarboxylate

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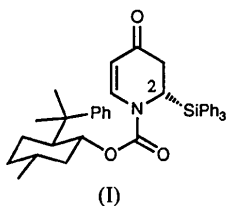
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Abstract. $C_{40}H_{43}NO_3Si$, $M_r = 613\cdot88$, orthorhombic, $P2_12_12_1$, $a = 10\cdot516\,(4)$, $b = 14\cdot693\,(5)$, $c = 22\cdot582\,(8)$ Å, $V = 3489\,(2)$ Å^3, $Z = 4$, $D_x = 1\cdot17$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 1\cdot00$ cm^{-1}, $F(000) = 1312$, $T = 298$ K, $R = 0\cdot0491$ for 3182 reflections [$F_o \geq 4\sigma(F_o)$]. From the known configuration of the (−)-8-phenyl-1-menthoxycarbonyl moiety the absolute configuration of the molecule is inferred to be as given in the title.

Experimental. The synthesis of the title compound (I) is reported elsewhere (Killpack, 1990).

(I)

Colorless crystals were grown by slow cooling of a concentrated solution of the compound in a 5% ethyl acetate–hexane mixture. A crystal of dimensions $0\cdot55 \times 0\cdot47 \times 0\cdot43$ mm was used to collect X-ray diffraction data on a Nicolet $R3m/\mu$ diffractometer equipped with a graphite monochromator utilizing Mo $K\alpha$ radiation. Cell-dimensions were obtained by a least-squares refinement of the setting angles of 15 reflections. Intensity data for 4501 reflections in the range $3 \leq 2\theta \leq 55°$ were collected by the ω-scan method at variable scan speeds between $3\cdot9$ and $29\cdot3°$ min^{-1} depending upon intensity; range in *hkl*: $0 \leq h \leq 13$, $0 \leq k \leq 19$, $0 \leq l \leq 29$. Backgrounds were measured by the stationary-crystal–stationary-counter method on each side of a peak for one-half of scan time. Two reflections were measured as standards after every 48 reflections. Their intensities varied by ±2·2% during data collection. Intensities were corrected for background and for Lorentz and polarization effects but not for absorption.

The structure was solved by the random tangent refinement technique (Yao, 1981) using 428 reflections with $E > 1\cdot71$, and refined using 3182 reflections with intensities $I \geq 2\sigma(I)$. The non-H atoms were refined with anisotropic thermal parameters and all H atoms, except H(22) and H(23), were placed in calculated positions and were allowed to move in the riding mode. H atoms H(22) and H(23) were found from a difference Fourier map and not refined. An extinction parameter was also refined, the final value of the extinction coefficient being $3\cdot2\,(4) \times 10^{-6}$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was $w = 1/[\sigma F^2 + 0\cdot001F^2]$, in which the factor 0·001 is used to downweight strong reflections and to account for instrument instability. Final $R = 0\cdot0491$ and $wR = 0\cdot0674$ for 415 variable parameters, goodness-of-fit parmeter, $S = 1\cdot29$. Maximum $\Delta/\sigma = 0\cdot5$ and the maximum and minimum difference Fourier peaks were $+0\cdot25$ and $-0\cdot18$ e Å^{-3}, respectively. Scattering factors were taken from Cromer & Waber (1974). All computations were performed on a Data General desktop computer (Micro-eclipse) with the program package *SHELXTL* (Sheldrick, 1985), which has a blocked-cascade least-squares algorithm for structure refinement (Sparks, 1961). Fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1, and the bond lengths, bond angles involving non-H atoms and selected torsion angles in Table 2.* The atom-labeling scheme is shown in Fig. 1.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52956 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
Si	0·4350 (1)	0·4818 (1)	1·0948 (1)	0·043 (1)
C(1)	0·3091 (4)	0·5826 (3)	1·1863 (2)	0·050 (1)
C(2)	0·2973 (4)	0·6480 (3)	1·2307 (2)	0·061 (1)
C(3)	0·4026 (5)	0·7009 (3)	1·2454 (2)	0·069 (2)
C(4)	0·5154 (4)	0·6874 (3)	1·2173 (2)	0·065 (1)
C(5)	0·5265 (4)	0·6212 (3)	1·1742 (2)	0·057 (1)
C(6)	0·4244 (4)	0·5675 (2)	1·1568 (1)	0·044 (1)
C(7)	0·2919 (4)	0·3598 (3)	1·1682 (2)	0·056 (1)
C(8)	0·2052 (4)	0·2908 (3)	1·1796 (2)	0·064 (1)
C(9)	0·1506 (4)	0·2445 (3)	1·1338 (2)	0·066 (2)
C(10)	0·1851 (5)	0·2633 (3)	1·0767 (2)	0·069 (2)
C(11)	0·2706 (4)	0·3327 (3)	1·0656 (2)	0·063 (1)
C(12)	0·3247 (4)	0·3847 (3)	1·1110 (2)	0·049 (1)
C(13)	0·7031 (4)	0·4934 (4)	1·0709 (2)	0·069 (2)
C(14)	0·8266 (4)	0·4578 (5)	1·0637 (2)	0·095 (2)
C(15)	0·8461 (6)	0·3651 (5)	1·0704 (2)	0·111 (3)
C(16)	0·7464 (6)	0·3103 (5)	1·0838 (2)	0·101 (3)
C(17)	0·6273 (5)	0·3453 (3)	1·0914 (2)	0·074 (2)
C(18)	0·6013 (4)	0·4371 (3)	1·0850 (2)	0·054 (1)
C(19)	0·3743 (3)	0·5356 (3)	1·0224 (2)	0·044 (1)
C(20)	0·2763 (4)	0·6111 (3)	1·0317 (2)	0·063 (1)
C(21)	0·3341 (4)	0·6996 (3)	1·0514 (2)	0·065 (2)
O(1)	0·2742 (4)	0·7548 (2)	1·0807 (2)	0·096 (1)
C(22)	0·4602 (4)	0·7185 (3)	1·0286 (2)	0·061 (1)
C(23)	0·5197 (4)	0·6591 (2)	0·9926 (2)	0·048 (1)
N	0·4768 (3)	0·5708 (2)	0·9838 (1)	0·041 (1)
C(24)	0·5331 (3)	0·5122 (3)	0·9439 (1)	0·041 (1)
O(2)	0·5009 (3)	0·4338 (2)	0·9378 (1)	0·057 (1)
O(3)	0·6244 (2)	0·5548 (2)	0·9144 (1)	0·046 (1)
C(25)	0·7075 (3)	0·5043 (2)	0·8743 (1)	0·044 (1)
C(26)	0·7181 (3)	0·5595 (3)	0·8168 (1)	0·044 (1)
C(27)	0·8288 (4)	0·5207 (3)	0·7805 (2)	0·061 (1)
C(28)	0·9519 (4)	0·5129 (3)	0·8147 (2)	0·064 (1)
C(29)	0·9361 (4)	0·4516 (3)	0·8685 (2)	0·061 (1)
C(30)	0·8306 (4)	0·4905 (3)	0·9067 (2)	0·055 (1)
C(31)	1·0604 (5)	0·4395 (4)	0·9030 (2)	0·094 (2)
C(32)	0·5910 (4)	0·5666 (3)	0·7813 (2)	0·053 (1)
C(33)	0·6157 (5)	0·6148 (4)	0·7218 (2)	0·077 (2)
C(34)	0·5383 (5)	0·4707 (3)	0·7682 (2)	0·085 (2)
C(35)	0·5223 (4)	0·7137 (3)	0·8303 (2)	0·061 (1)
C(36)	0·4367 (5)	0·7695 (3)	0·8578 (2)	0·080 (2)
C(37)	0·3155 (5)	0·7386 (4)	0·8696 (2)	0·095 (2)
C(38)	0·2836 (5)	0·6530 (4)	0·8541 (2)	0·089 (2)
C(39)	0·3699 (4)	0·5961 (4)	0·8266 (2)	0·069 (2)
C(40)	0·4928 (4)	0·6247 (3)	0·8143 (2)	0·049 (1)

Table 2. Bond lengths (Å), bond angles (°), and selected torsion angles (°)

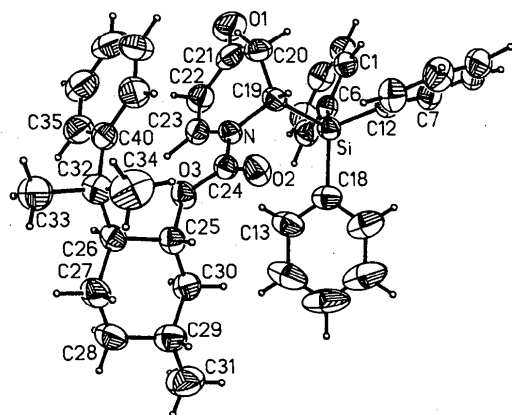|			
Si—C(6)	1·887 (4)	Si—C(12)	1·875 (4)
Si—C(18)	1·881 (4)	Si—C(19)	1·926 (4)
C(1)—C(2)	1·394 (5)	C(1)—C(6)	1·401 (5)
C(2)—C(3)	1·393 (6)	C(3)—C(4)	1·360 (7)
C(4)—C(5)	1·381 (6)	C(5)—C(6)	1·389 (5)
C(7)—C(8)	1·387 (6)	C(7)—C(12)	1·387 (5)
C(8)—C(9)	1·363 (6)	C(9)—C(10)	1·368 (7)
C(10)—C(11)	1·383 (6)	C(11)—C(12)	1·397 (6)
C(13)—C(14)	1·410 (6)	C(13)—C(18)	1·390 (6)
C(14)—C(15)	1·385 (10)	C(15)—C(16)	1·356 (10)
C(16)—C(17)	1·365 (8)	C(17)—C(18)	1·383 (7)
C(19)—C(20)	1·529 (6)	C(19)—N	1·479 (4)
C(20)—C(21)	1·503 (6)	C(21)—O(1)	1·221 (6)
C(21)—C(22)	1·450 (7)	C(22)—C(23)	1·346 (5)
C(23)—N	1·388 (5)	N—C(24)	1·380 (4)
C(24)—O(2)	1·208 (5)	C(24)—O(3)	1·326 (4)
O(3)—C(25)	1·461 (4)	C(25)—C(26)	1·534 (5)
C(25)—C(30)	1·502 (5)	C(26)—C(27)	1·533 (5)
C(26)—C(32)	1·563 (5)	C(27)—C(28)	1·511 (5)
C(28)—C(29)	1·521 (6)	C(29)—C(30)	1·517 (6)
C(29)—C(31)	1·532 (6)	C(32)—C(33)	1·541 (6)
C(32)—C(34)	1·542 (6)	C(32)—C(40)	1·533 (5)
C(35)—C(36)	1·367 (7)	C(35)—C(40)	1·392 (6)
C(36)—C(37)	1·379 (8)	C(37)—C(38)	1·348 (8)
C(38)—C(39)	1·381 (7)	C(39)—C(40)	1·388 (6)
C(6)—Si—C(12)	109·1 (2)	C(6)—Si—C(18)	112·0 (2)
C(12)—Si—C(18)	109·4 (2)	C(6)—Si—C(19)	109·7 (2)
C(12)—Si—C(19)	105·8 (2)	C(18)—Si—C(19)	110·6 (12)
C(2)—C(1)—C(6)	121·9 (4)	C(1)—C(2)—C(3)	119·0 (4)
C(2)—C(3)—C(4)	120·0 (4)	C(3)—C(4)—C(5)	120·4 (4)
C(4)—C(5)—C(6)	122·2 (4)	Si—C(6)—C(1)	120·7 (3)
Si—C(6)—C(5)	122·9 (3)	C(1)—C(6)—C(5)	116·4 (3)
C(8)—C(7)—C(12)	121·9 (4)	C(7)—C(8)—C(9)	120·1 (4)
C(8)—C(9)—C(10)	120·1 (4)	C(9)—C(10)—C(11)	119·5 (4)
C(10)—C(11)—C(12)	122·3 (4)	Si—C(12)—C(7)	122·4 (3)
Si—C(12)—C(11)	121·6 (3)	C(7)—C(12)—C(11)	116·0 (4)
C(14)—C(13)—C(18)	121·0 (5)	C(13)—C(14)—C(15)	119·3 (5)
C(14)—C(15)—C(16)	119·6 (6)	C(15)—C(16)—C(17)	120·9 (6)
C(16)—C(17)—C(18)	122·4 (5)	Si—C(18)—C(13)	122·3 (3)
Si—C(18)—C(17)	120·8 (8)	C(13)—C(18)—C(17)	116·9 (4)
Si—C(19)—C(20)	113·8 (2)	Si—C(19)—N	113·6 (2)
C(20)—C(19)—N	108·6 (3)	C(19)—C(20)—C(21)	113·4 (3)
C(20)—C(21)—O(1)	121·8 (4)	C(20)—C(21)—C(22)	115·5 (4)
O(1)—C(21)—C(22)	122·4 (4)	C(21)—C(22)—C(23)	121·0 (4)
C(22)—C(23)—N	122·8 (4)	C(19)—N—C(23)	118·7 (3)
C(19)—N—C(24)	118·5 (3)	C(23)—N—C(24)	122·5 (3)
N—C(24)—O(2)	123·3 (3)	N—C(24)—O(3)	110·1 (3)
O(2)—C(24)—O(3)	126·5 (3)	C(24)—O(3)—C(25)	120·3 (3)
O(3)—C(25)—C(26)	107·4 (3)	O(3)—C(25)—C(30)	106·4 (3)
C(26)—C(25)—C(30)	114·9 (3)	C(25)—C(26)—C(27)	108·1 (3)
C(25)—C(26)—C(32)	114·0 (3)	C(27)—C(26)—C(32)	113·5 (3)
C(26)—C(27)—C(28)	113·9 (3)	C(27)—C(28)—C(29)	111·0 (3)
C(28)—C(29)—C(30)	108·2 (3)	C(28)—C(29)—C(31)	112·4 (4)
C(30)—C(29)—C(31)	112·2 (3)	C(25)—C(30)—C(29)	113·8 (3)
C(26)—C(32)—C(33)	109·5 (3)	C(26)—C(32)—C(34)	110·2 (3)
C(33)—C(32)—C(34)	108·2 (3)	C(26)—C(32)—C(40)	111·3 (3)
C(33)—C(32)—C(40)	106·4 (3)	C(34)—C(32)—C(40)	111·1 (3)
C(36)—C(35)—C(40)	122·3 (4)	C(35)—C(36)—C(37)	120·0 (5)
C(36)—C(37)—C(38)	119·1 (5)	C(37)—C(38)—C(39)	121·2 (5)
C(38)—C(39)—C(40)	121·3 (5)	C(32)—C(40)—C(35)	120·0 (4)
C(32)—C(40)—C(39)	123·8 (4)	C(35)—C(40)—C(39)	116·1 (4)
C(26)—C(32)—C(40)—C(35)	56·7 (5)	C(26)—C(25)—O(3)—C(24)	134·4 (3)
C(25)—O(3)—C(24)—N	173·1 (3)	O(3)—C(24)—N—C(19)	−178·6 (3)
C(24)—N—C(19)—Si	87·5 (3)	C(19)—Si—C(6)—C(1)	81·5 (3)
C(19)—Si—C(12)—C(7)	−145·7 (3)	C(19)—Si—C(18)—C(13)	62·0 (3)

Fig. 1. View of the title compound (40% thermal ellipsoids) showing the S configuration at C(19). Only two atoms of each phenyl group are labeled for clarity.

Related literature.

The title compound is the first 2-triarylsilyl-2,3-dihydro-4(1H)-pyridinone prepared in non-racemic form. Racemic 1-acyl-2-alkyl-2,3-dihydro-4(1H)-pyridinones have been prepared by the addition of Grignard reagents to 1-acylpyridinium salts (Comins & Brown, 1986; Brown, Foley & Comins, 1988). The absolute configuration at C(2) of the dihydro-4(1H)-pyridinone ring is established from the known configuration of the 8-phenyl-menthoxycarbonyl moiety of the compound.

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Structure of 4,4',5,5'-Tetranitro-2,2'-biimidazole Dihydrate*

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Abstract. $C_6H_2N_8O_8.2H_2O$, $M_r = 350\cdot16$, monoclinic, $P2_1/n$, $a = 5\cdot031$ (2), $b = 8\cdot478$ (1), $c = 15\cdot362$ (1) Å, $\beta = 97\cdot18$ (2)°, $V = 650\cdot1$ Å^3, $Z = 2$, $D_x = 1\cdot789$ Mg m^{-3}, λ(Mo $K\alpha_1$) = 0·70926 Å, $\mu = 0\cdot16$ mm^{-1}, $F(000) = 316$, room temperature, final $R = 0\cdot034$ for 859 observed reflections $[I > 2\sigma(I)]$ out of 1133 independent reflections. The molecule lies on a center of symmetry. The hydrogen on the ring nitrogen is strongly hydrogen bonded to the water oxygen [N···O = 2·656 (3) Å], but the water hydrogens are only weakly bonded to the nitro-group O atoms [O···O = 3·137 (4), 3·073 (3) Å]. There are no unusual intramolecular distances.

Experimental. Title compound prepared by nitration of 2,2'-biimidazole by $NaNO_3$ in concentrated H_2SO_4. Crystals grown by evaporation of water solution. Selected crystal *ca* 0·43 × 0·27 × 0·16 mm. CAD-4 diffractometer, θ–2θ scan. Scan range $(1\cdot0 + 0\cdot34\tan\theta)°$. Scan speed 1·0 to 5·5° min^{-1}. Background first and last 1/6 of scan. Graphite-monochromated Mo $K\alpha$ radiation. Unit cell, 25 reflections $12 < \theta < 24°$. No absorption corrections. $[(\sin\theta)/\lambda]_{max} = 0\cdot596$ Å^{-1}. Index range $-5 \le h \le 5$, $0 \le k \le 10$, $-18 \le l \le 18$, 1635 reflections measured and averaged to yield 1138 unique reflections of which 859 were observed with $I > 2\sigma(I)$, merging $R_F = 0\cdot010$. Standard reflections $\overline{1}5\overline{5}$ and $14\overline{6}$ showed no significant variation. Least-squares refinement

minimized $\Sigma w(\Delta F)^2$ with $w = [\sigma_c^2(F) + 0\cdot03F^2]^{-1}$, $\sigma_c^2(F)$ based on counting statistics. Structure solved by *MULTAN* (Germain, Main & Woolfson, 1971), hydrogens by difference Fourier. Scale factor, isotropic type II extinction parameter (Larson, 1969), positional parameters, anisotropic thermal parameters for C, N, O, and isotropic thermal parameters for H were refined. Final $R = 0\cdot034$, $wR = 0\cdot046$, $S = 2\cdot1$. Max. $\Delta/\sigma = 0\cdot05$. Final ΔF Fourier synthesis $-0\cdot16 < \Delta\rho < 0\cdot19$ e Å^{-3}. Scattering factors f (RHF for C, N, O and SDS for H), f', f'' from *International Tables for X-ray Crystallography* (1974). Calculations on CRAY-1 using the Los Alamos crystal structure system developed primarily by A. C. Larson.

Fig. 1 is an *ORTEP* (Johnson, 1965) drawing of the molecule showing the atomic numbering scheme.
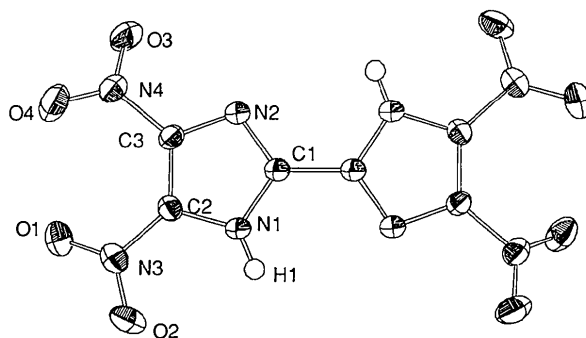

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule to show the atomic numbering scheme. Thermal ellipsoids are 30% probability. Hydrogen size is arbitrary.