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## Crystal and Molecular Structure of $\beta$ -1-Phenylsilatrane, $C_{12}H_{17}O_3NSi$

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(Received 20 May 1974; accepted 24 May 1974)

Two crystalline modifications of 1-phenylsilatrane are reported. The  $\beta$  form is orthorhombic, space group  $Pna2_1$ , with  $a = 15.855$ ,  $b = 6.648$ ,  $c = 11.635$  Å. The  $\gamma$  form is monoclinic, space group  $P2_1/n$ . The structure of the  $\beta$  form was determined by direct methods with phases generated from the partially known structure and recycled into the tangent formula. The structure was refined to  $R = 0.076$  for 1103 observed reflexions and 0.079 for all 1134 reflexions. The Si–N bond length is 2.156 (4), the Si–C 1.908 (5) Å. The mean Si–O bond distance is 1.657 Å. The N–Si–C angle is 177.0°, the average N–Si–O, C–Si–O and O–Si–O angles are 83.3°, 96.8° and 118.6°. The carbon atoms  $\alpha$  to the nitrogen are bent out of the plane of the five-membered rings.

### Introduction

The crystal structure of  $\alpha$ -1-phenylsilatrane,  $C_6H_5Si(OCH_2CH_2)_3N$ , was determined by Turley & Boer (1968). The structure is disordered. By recrystallization from acetone we could isolate two other crystalline modifications, called the  $\beta$  and  $\gamma$  forms. These can be easily separated by their shapes. Infrared

spectra of the three modifications in KBr pellets were recorded. While the spectra of the  $\alpha$  and  $\gamma$  forms were similar, and practically identical with the spectrum published by Voronkov (1966), the spectrum of the  $\beta$  form showed large differences.\* In the present paper we give an account of the structure of the  $\beta$  form.

\* Unpublished results.

## Experimental

The title compound was recrystallized from acetone in the form of well developed prisms. The  $\gamma$  form also occurred as colourless needles elongated along  $b$ . Crystal data of the two forms were determined from precession photographs.

## Crystal data

$C_{12}H_{17}O_3NSi$ ,  $M = 251.36$

$\beta$  Form: orthorhombic, m.p. 208°C

$a = 15.855$  (4),  $b = 6.648$  (1),  $c = 11.635$  (3) Å

$V = 1226.38$  Å<sup>3</sup>,  $Z = 4$

$D_m = 1.351$  g cm<sup>-3</sup> (by flotation),  $D_x = 1.361$  g cm<sup>-3</sup>

$F(000) = 536$ ; space group  $Pna2_1$  (No. 33)

$\mu$  for Cu  $K\alpha$  ( $\lambda = 1.5418$  Å) 16.58 cm<sup>-1</sup>.

$\gamma$  Form: monoclinic, m.p. 207°C

$a = 8.475$  (1),  $b = 12.949$  (2),  $c = 11.122$  (4) Å

$\beta = 90.86$  (2)°

$V = 1220.69$  Å<sup>3</sup>,  $Z = 4$

$D_m = 1.364$  g cm<sup>-3</sup> (by flotation),  $D_x = 1.364$  g cm<sup>-3</sup>

$F(000) = 536$ ; space group  $P2_1/n$  (No. 14)

$\mu$  for Cu  $K\alpha$  ( $\lambda = 1.5418$  Å) 16.75 cm<sup>-1</sup>.

The crystal used was approximately 0.25 × 0.30 × 0.35 mm. Intensities were collected on a Stoe two-circle semi-automatic diffractometer in the equi-inclination arrangement for the  $hk0 \rightarrow hk10$  layers by the  $\omega$ -scanning method with Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) and a scintillation counter (Ni filter and pulse-height discriminator). Intensities measured at over 10 000 c.p.s. were remeasured with Ni filters in the direct beam. 31 of the 1134 reflexions with  $I - 1.5\sigma(I) < 0$  were taken as unobserved with a value of  $I_o = 0.5\sigma(I)$ . After data reduction an absolute scale factor and overall temperature factor ( $\bar{B} = 2.95$  Å<sup>2</sup>) were determined by Wilson's method. No absorption correction was made.

## Determination of the structure

The structure was determined by direct methods with the program *MULTAN* (Main, Woolfson & Germain, 1971). 217 reflexions with  $E$  values greater than 1.30 were used. The figures of merit of the different sets were almost the same and rather high. The calculated phases showed a distribution about 360 and 180°. The molecule could not be recognized in the  $E$  map calculated from the different phase sets. Every  $E$  map contained one peak of very high intensity at  $x = 0.32$ ,  $y = 0.66$ ,  $z = 0.25$ . This centrosymmetric solution was presumably due to the position of the silicon atom at  $z = \frac{1}{4}$  resulting in a pseudo-mirror plane. Therefore the high peak was assigned as a silicon atom. This could

Table 1. Phases used for recycling into the tangent formula

The phases were generated with the following atomic positions: Si ( $x = 0.32$ ,  $y = 0.66$ ,  $z = 0.25$ ), A ( $x = 0.41$ ,  $y = 0.69$ ,  $z = 0.13$ ), B ( $x = 0.22$ ,  $y = 0.57$ ,  $z = 0.37$ ).

$h$	$k$	$l$	$\phi^0$	$\phi$	WT	$h$	$k$	$l$	$\phi^0$	$\phi$	WT
10	0	1	183°	184°	1.0	14	4	2	175°	192°	0.8
6	0	4	359	3	0.8	6	4	4	360	169	1.0
11	1	0	360	360	1.0	0	5	3	343	9	0.81
5	1	4	354	334	1.0	14	0	2	343	329	0.79
10	1	6	185	263	0.64	8	0	6	5	1	0.64
10	1	10	175	213	0.88	6	1	3	193	232	0.87
1	2	10	2	22	1.0	18	1	4	182	192	1.0
7	3	3	10	11	1.0	6	1	7	160	161	0.61
3	3	6	180	188	1.0	11	2	3	182	195	0.80
11	3	8	186	184	1.0	11	3	0	180	180	0.94
15	3	3	193	174	1.0	11	1	8	350	351	0.76
1	3	7	13	24	1.0	15	2	6	181	159	0.9
3	3	10	179	169	1.0	3	3	2	180	166	1.0
15	4	2	35	25	0.87	5	3	4	184	204	1.0
4	4	5	2	344	0.71	7	3	7	347	354	1.0
4	5	6	346	349	1.0	13	4	0	0	0	1.0
4	0	3	360	8	0.99	4	4	3	175	163	0.61
8	0	10	356	328	0.69	4	5	0	180	180	1.0
14	1	3	352	312	0.79	4	5	10	9	1	1.0
15	1	5	182	184	0.76						

Table 2. The final atomic parameters ( $\times 10^4$ ) with their e.s.d.'s in parentheses

Anisotropic thermal parameters are given in the form  $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ . The  $z$  coordinate of Si was fixed throughout the structure refinement.

	$x/a$	$y/b$	$z/c$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
Si	3193 (1)	-3494 (2)	2500	24 (1)	205 (3)	27 (1)	-14 (2)	-1 (2)	14 (4)
O(2)	2439 (3)	-2345 (9)	1757 (5)	24 (2)	361 (14)	44 (4)	-12 (8)	5 (4)	76 (13)
C(3)	1585 (4)	-2145 (12)	2169 (7)	25 (2)	334 (18)	55 (7)	18 (12)	1 (6)	102 (16)
C(4)	1395 (5)	-3800 (15)	2949 (9)	33 (3)	395 (22)	67 (7)	-27 (13)	-6 (7)	88 (20)
N	2158 (3)	-4188 (8)	3633 (6)	29 (2)	227 (12)	29 (4)	-11 (8)	7 (5)	15 (12)
C(6)	2269 (6)	-2887 (14)	4619 (9)	42 (3)	376 (22)	56 (7)	-66 (14)	24 (7)	-57 (22)
C(7)	3191 (5)	-2428 (16)	4735 (8)	41 (3)	396 (24)	30 (6)	-34 (13)	10 (6)	-80 (21)
O(8)	3582 (3)	-2323 (8)	3634 (5)	32 (2)	293 (11)	39 (4)	-52 (7)	2 (5)	-21 (12)
O(9)	3274 (3)	-5974 (7)	2418 (6)	46 (2)	206 (9)	63 (4)	-22 (7)	45 (5)	-35 (15)
C(10)	2681 (5)	-7298 (11)	2895 (8)	44 (3)	216 (15)	74 (8)	-3 (12)	24 (7)	4 (17)
C(11)	2276 (5)	-6346 (12)	3930 (8)	46 (3)	252 (15)	66 (8)	-19 (13)	30 (8)	46 (19)
C(12)	4069 (4)	-2866 (10)	1434 (7)	21 (2)	225 (13)	51 (5)	0 (9)	-14 (6)	-6 (15)
C(13)	4400 (4)	-4284 (11)	667 (7)	30 (2)	276 (16)	29 (5)	-7 (10)	6 (5)	-31 (16)
C(14)	4947 (5)	-3784 (13)	-217 (8)	28 (2)	349 (19)	52 (7)	32 (12)	4 (7)	-10 (21)
C(15)	5196 (5)	-1777 (13)	-348 (8)	28 (2)	364 (21)	45 (6)	8 (12)	16 (6)	67 (19)
C(16)	4903 (5)	-356 (12)	426 (8)	30 (2)	300 (18)	65 (7)	-2 (11)	4 (7)	91 (18)
C(17)	4353 (4)	-885 (12)	1297 (7)	30 (2)	257 (15)	54 (6)	-8 (10)	14 (6)	51 (16)

be verified by the strongest vectors of the Patterson map. Other maxima which would satisfy atomic positions in agreement with chemical evidence were then considered. Two peaks assigned as nitrogen together with the silicon atom gave an  $R$  of 0.465. Phases generated by these positions were recycled into part III (FASTAN) of the program MULTAN as suggested by Karle (1970). These phases were weighted as  $WT = F(H)_c/[pF(H)_o]$ , where  $H$  stands for the indices  $h, k, l$  and  $p$  is the scaling factor. 39 reflexions with  $WT \geq 0.61$  (all figure at the end of the convergence mapping) were recycled and fixed during the phase refinement with the tangent formula. The recycled phases ( $\varphi_0$ ) and their values after the refinement of the structure ( $\varphi$ ) together with their weights (WT) are listed in Table 1. In the  $E$  map calculated after the recycling, 13 atoms were located and the subsequent structure-factor calculation ( $R=0.340$ ) and Fourier synthesis gave the positions of the missing four non-hydrogen atoms. At this stage  $R$  was 0.229.

### Refinement of the structure

Refinement of the atomic parameters was carried out by block-diagonal least-squares calculations with the program of Albano, Domenicano & Vaciego (1966). The function minimized was

$$\Phi = \sum_h w_h (|F_{oh}| - 1/G|F_{ch}|)^2$$

where  $G$  is the scaling factor,  $w_h$  is the weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961):  $w_h = (1.1 + 1.0F_o + 0.01F_o^2)^{-1}$ . After two cycles of isotropic refinement ( $R=0.152$ ) all the hydrogen atoms were generated geometrically assuming the proper  $sp^2$  and  $sp^3$  hybridization of the carbon atoms. The isotropic thermal parameters of the hydrogen atoms were approximated by those of the carbon atoms. Five anisotropic cycles reduced  $R$  to the final value of 0.076 for observed and 0.079 for all re-

Table 3. Fractional coordinates ( $\times 10^3$ ), isotropic temperature parameters ( $\text{\AA}^2$ ) and bond distances ( $\text{\AA}$ ) for the hydrogen atoms

	$x/a$	$y/b$	$z/c$	$B_i$	C-H distances
H(3a)	153	-84	257	3.8	1.00
H(3b)	121	-214	149	3.8	0.99
H(4a)	92	-344	347	5.0	0.99
H(4b)	125	-504	250	5.0	1.00
H(6a)	207	-353	533	4.6	0.98
H(6b)	197	-157	450	4.6	1.01
H(7a)	347	-350	519	4.4	0.99
H(7b)	329	-116	515	4.4	0.98
H(10a)	295	-857	310	3.7	0.97
H(10b)	224	-756	230	3.7	1.00
H(11a)	266	-646	459	3.9	0.98
H(11b)	172	-696	407	3.9	0.99
H(13)	425	-570	79	3.3	0.98
H(14)	516	-484	-73	4.0	0.98
H(15)	557	-136	-99	3.9	1.00
H(16)	510	104	36	3.8	0.98
H(17)	416	18	184	3.4	1.00

flexions. At this stage the maximum shifts in the atomic coordinates were less than  $0.5\sigma_{av}$ . No hydrogen parameters were refined. The atomic parameters for the non-hydrogen atoms are given in Table 2 and the hydrogen

Table 4. Observed and calculated structure factors ( $\times 10$ )

Reflexions indicated by an asterisk have an intensity less than the threshold value for an observed reflexion.

$h$	$k$	$l$	$F_o$	$F_c$	$F_o/F_c$	$F_o$	$F_c$	$F_o/F_c$	$F_o$	$F_c$	$F_o/F_c$
0	0	0	1000	1000	1.00	0	0	0	0	0	0
0	0	1	1000	1000	1.00	0	0	0	0	0	0
0	0	2	1000	1000	1.00	0	0	0	0	0	0
0	0	3	1000	1000	1.00	0	0	0	0	0	0
0	0	4	1000	1000	1.00	0	0	0	0	0	0
0	0	5	1000	1000	1.00	0	0	0	0	0	0
0	0	6	1000	1000	1.00	0	0	0	0	0	0
0	0	7	1000	1000	1.00	0	0	0	0	0	0
0	0	8	1000	1000	1.00	0	0	0	0	0	0
0	0	9	1000	1000	1.00	0	0	0	0	0	0
0	0	10	1000	1000	1.00	0	0	0	0	0	0
0	0	11	1000	1000	1.00	0	0	0	0	0	0
0	0	12	1000	1000	1.00	0	0	0	0	0	0
0	0	13	1000	1000	1.00	0	0	0	0	0	0
0	0	14	1000	1000	1.00	0	0	0	0	0	0
0	0	15	1000	1000	1.00	0	0	0	0	0	0
0	0	16	1000	1000	1.00	0	0	0	0	0	0
0	0	17	1000	1000	1.00	0	0	0	0	0	0
0	1	0	1000	1000	1.00	0	0	0	0	0	0
0	1	1	1000	1000	1.00	0	0	0	0	0	0
0	1	2	1000	1000	1.00	0	0	0	0	0	0
0	1	3	1000	1000	1.00	0	0	0	0	0	0
0	1	4	1000	1000	1.00	0	0	0	0	0	0
0	1	5	1000	1000	1.00	0	0	0	0	0	0
0	1	6	1000	1000	1.00	0	0	0	0	0	0
0	1	7	1000	1000	1.00	0	0	0	0	0	0
0	1	8	1000	1000	1.00	0	0	0	0	0	0
0	1	9	1000	1000	1.00	0	0	0	0	0	0
0	1	10	1000	1000	1.00	0	0	0	0	0	0
0	1	11	1000	1000	1.00	0	0	0	0	0	0
0	1	12	1000	1000	1.00	0	0	0	0	0	0
0	1	13	1000	1000	1.00	0	0	0	0	0	0
0	1	14	1000	1000	1.00	0	0	0	0	0	0
0	1	15	1000	1000	1.00	0	0	0	0	0	0
0	1	16	1000	1000	1.00	0	0	0	0	0	0
0	1	17	1000	1000	1.00	0	0	0	0	0	0
0	2	0	1000	1000	1.00	0	0	0	0	0	0
0	2	1	1000	1000	1.00	0	0	0	0	0	0
0	2	2	1000	1000	1.00	0	0	0	0	0	0
0	2	3	1000	1000	1.00	0	0	0	0	0	0
0	2	4	1000	1000	1.00	0	0	0	0	0	0
0	2	5	1000	1000	1.00	0	0	0	0	0	0
0	2	6	1000	1000	1.00	0	0	0	0	0	0
0	2	7	1000	1000	1.00	0	0	0	0	0	0
0	2	8	1000	1000	1.00	0	0	0	0	0	0
0	2	9	1000	1000	1.00	0	0	0	0	0	0
0	2	10	1000	1000	1.00	0	0	0	0	0	0
0	2	11	1000	1000	1.00	0	0	0	0	0	0
0	2	12	1000	1000	1.00	0	0	0	0	0	0
0	2	13	1000	1000	1.00	0	0	0	0	0	0
0	2	14	1000	1000	1.00	0	0	0	0	0	0
0	2	15	1000	1000	1.00	0	0	0	0	0	0
0	2	16	1000	1000	1.00	0	0	0	0	0	0
0	2	17	1000	1000	1.00	0	0	0	0	0	0
0	3	0	1000	1000	1.00	0	0	0	0	0	0
0	3	1	1000	1000	1.00	0	0	0	0	0	0
0	3	2	1000	1000	1.00	0	0	0	0	0	0
0	3	3	1000	1000	1.00	0	0	0	0	0	0
0	3	4	1000	1000	1.00	0	0	0	0	0	0
0	3	5	1000	1000	1.00	0	0	0	0	0	0
0	3	6	1000	1000	1.00	0	0	0	0	0	0
0	3	7	1000	1000	1.00	0	0	0	0	0	0
0	3	8	1000	1000	1.00	0	0	0	0	0	0
0	3	9	1000	1000	1.00	0	0	0	0	0	0
0	3	10	1000	1000	1.00	0	0	0	0	0	0
0	3	11	1000	1000	1.00	0	0	0	0	0	0
0	3	12	1000	1000	1.00	0	0	0	0	0	0
0	3	13	1000	1000	1.00	0	0	0	0	0	0
0	3	14	1000	1000	1.00	0	0	0	0	0	0
0	3	15	1000	1000	1.00	0	0	0	0	0	0
0	3	16	1000	1000	1.00	0	0	0	0	0	0
0	3	17	1000	1000	1.00	0	0	0	0	0	0
0	4	0	1000	1000	1.00	0	0	0	0	0	0
0	4	1	1000	1000	1.00	0	0	0	0	0	0
0	4	2	1000	1000	1.00	0	0	0	0	0	0
0	4	3	1000	1000	1.00	0	0	0	0	0	0
0	4	4	1000	1000	1.00	0	0	0	0	0	0
0	4	5	1000	1000	1.00	0	0	0	0	0	0
0	4	6	1000	1000	1.00	0	0	0	0	0	0
0	4	7	1000	1000	1.00	0	0	0	0	0	0
0	4	8	1000	1000	1.00	0	0	0	0	0	0
0	4	9	1000	1000	1.00	0	0	0	0	0	0
0	4	10	1000	1000	1.00	0	0	0	0	0	0
0	4	11	1000	1000	1.00	0	0	0	0	0	0
0	4	12	1000	1000	1.00	0	0	0	0	0	0
0	4	13	1000	1000	1.00	0	0	0	0	0	0
0	4	14	1000	1000	1.00	0	0	0	0	0	0
0	4	15	1000	1000	1.00	0	0	0	0	0	0
0	4	16	1000	1000	1.00	0	0	0	0	0	0
0	4	17	1000	1000	1.00	0	0	0	0	0	0
0	5	0	1000	1000	1.00	0	0	0	0	0	0
0	5	1	1000	1000	1.00	0	0	0	0	0	0
0	5	2	1000	1000	1.00	0	0	0	0	0	0
0	5	3	1000	1000	1.00	0	0	0	0	0	0
0	5	4	1000	1000	1.00	0	0	0	0	0	0
0	5	5	1000	1000	1.00	0	0	0	0	0	0
0	5	6	1000	1000	1.00	0	0	0	0	0	0
0	5	7	1000	1000	1.00	0	0	0	0	0	0
0	5	8	1000	1000	1.00	0	0	0	0	0	0
0	5	9	1000	1000	1.00	0	0	0	0	0	0
0	5	10	1000	1000	1.00	0	0	0	0	0	0
0	5	11	1000	1000	1.00	0	0	0	0	0	0
0	5	12	1000	1000	1.00	0	0	0	0	0	0
0	5	13	1000	1000	1.00	0	0	0	0	0	0
0	5	14	1000	1000	1.00	0	0	0	0	0	0
0	5	15	1000	1000	1.00	0	0	0	0	0	0
0	5	16	1000	1000	1.00	0	0	0	0	0	0
0	5	17	1000	1000	1.00	0	0	0	0	0	0
0	6	0	1000	1000	1.00	0	0	0	0	0	0
0	6	1	1000	1000	1.00	0	0	0	0	0	0
0	6	2	1000	1000	1.00	0	0	0	0	0	0
0	6	3	1000	1000	1.00	0	0	0	0	0	0
0	6	4	1000	1000	1.00	0	0	0	0	0	0
0	6	5	1000	1000	1.00	0	0	0	0	0	0
0	6	6	1000	1000	1.00	0	0	0	0	0	0
0	6	7	1000	1000	1.00	0	0	0	0	0	0
0	6	8	1000								

Table 5 (cont.)

In ethoxy bridges			
Si—O(2)—C(3)	122.99 (48)	O(9)—C(10)—C(11)	109.80 (66)
Si—O(8)—C(7)	122.13 (52)	C(3)—C(4)—N	107.37 (70)
Si—O(9)—C(10)	123.36 (50)	C(7)—C(6)—N	108.12 (74)
O(2)—C(3)—C(4)	109.42 (65)	C(10)—C(11)—N	105.89 (74)
O(8)—C(7)—C(6)	110.78 (74)		
In the phenyl group			
Si—C(12)—C(13)	122.64 (53)	C(12)—C(13)—C(14)	123.08 (70)
C(13)—C(14)—C(15)	119.09 (77)	C(14)—C(15)—C(16)	118.98 (79)
C(15)—C(16)—C(17)	120.98 (77)	C(16)—C(17)—C(12)	121.66 (70)
C(17)—C(12)—C(13)	116.13 (65)	C(17)—C(12)—Si	120.89 (54)

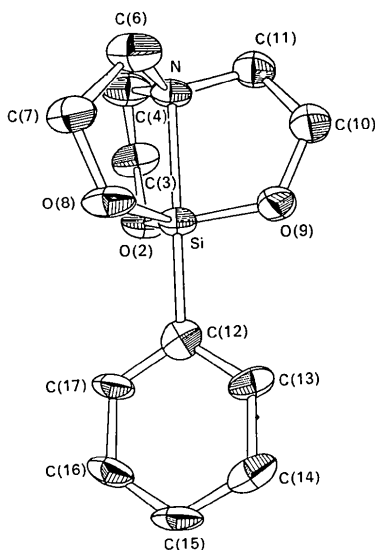
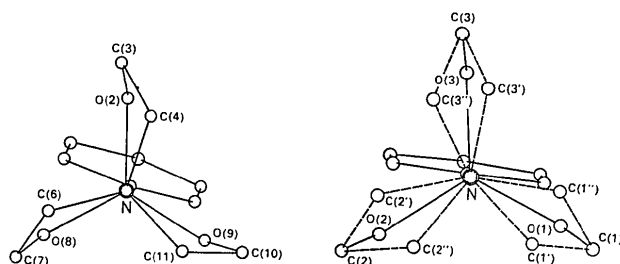


Fig. 1. ORTEP diagram of the title compound.

Fig. 2. The  $\beta$  and the  $\alpha$  structures viewed down the N-Si axis.

atomic coordinates and isotropic thermal parameters in Table 3. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).  $F_o$  and  $F_c$  values are listed in Table 4.

### Discussion

The bond lengths and angles are given in Table 5. Fig. 1 shows the ORTEP diagram of the molecule.

The molecular geometry is a distorted trigonal bipyramid similar to that in the  $\alpha$  form (Turley & Boer, 1968). The length of the transannular Si  $\leftarrow$  N dative bond [2.156 (4) Å] is shorter by 0.037 Å than that found in the  $\alpha$  form, but substantially longer than in the *m*-nitrophenyl derivative [2.116 (8) Å, Turley & Boer, 1969]. C(12) of the other apical ligand (the phenyl group) is 1.908 (5) Å from the silicon, which is the same as in the *m*-nitrophenyl compound [1.904 (9) Å] and somewhat longer than in the  $\alpha$  form [1.882 (6) Å]. The N-Si-C(12) angle is 177.0°, the average N-Si-O angle is 83.3°, and the average C(12)-Si-O angle is 96.8°. The O-Si-O angles show approximate threefold symmetry about the Si-N bond axis with a mean of 118.6°. The plane of the three oxygen atoms is 0.195 Å above the silicon, towards the nitrogen atom. This is shorter by *ca* 0.01 Å than in the  $\alpha$  form. The bond lengths and angles for the oxygen atoms seem to be affected by the asymmetric position of the phenyl group (Fig. 2). The aliphatic C-C distances are shorter (mean 1.487 Å) than the theoretical value (1.54 Å) of the C( $sp^3$ )-C( $sp^3$ ) single bond. It is noteworthy that in the  $\alpha$  form the three carbon atoms linked to the nitrogen are disordered and two kinds of C-C bond length are reported with average values 1.451 Å

Table 6. Equations of planes with respect to the crystallographic axes

X, Y and Z are in Å.

Atoms forming the plane	Normal distance of atoms not forming the plane (Å)	Equation of the plane
O(2), O(8), O(9)	Si -0.195	$-0.7512X - 0.2129Y + 0.6248Z = -1.2961$
C(4), C(6), C(11)	N -0.379	$-0.7616X - 0.2166Y + 0.6107Z = 0.9585$
C(3), C(7), C(10)		$-0.7484X - 0.2254Y + 0.6238Z = 0.0140$
Atoms of the phenyl group	Mean deviation of the phenyl group atoms from the plane is 0.01 Å	$0.7759X - 0.1734Y + 0.6066Z = 6.3650$

[for C(1')-C(1), C(2'')-C(2) and C(3'')-C(3)] and 1.545 Å [for C(2')-C(2), C(3')-C(3) and C(1'')-C(1)]. Other bond lengths and angles are comparable to the values found in the  $\alpha$  modification.

The planes formed by C(3), C(7), C(10) and by C(4), C(6), C(11) are inclined to the plane of the oxygens by 1.02 and 0.73°, respectively. The angle between the plane of the phenyl group and that of the oxygen atoms is 99.6°. The phenyl group is planar within experimental error. The equations of the planes are listed in Table 6.

The average C-C bond length in the phenyl ring is 1.393 Å, which agrees with that in crystalline benzene (Cox, Cruickshank & Smith, 1958). An unusual C-C-C angle of 116.1° is found at C(12), as in the  $\alpha$  form (115.9°).

The  $\alpha$  and  $\beta$  structures are shown in Fig. 2 viewed down the N-Si axis. In the title compound each carbon atom  $\alpha$  to the nitrogen [namely C(4), C(6) and C(11)] is bent out of the plane formed by the N, Si and the proper O and C atoms, in accordance with the rule assumed by Boer & Turley (1969) for similar structures containing short (2.1-2.2 Å) dative Si  $\leftarrow$  N bonds.

We thank Dr K. Sasvári and Dr A. Kálmán for stimulating discussions and Mr Cs. Kertész for help with the data collection.

*Acta Cryst.* (1974). B30, 2332

## The Crystal Structure of the Complex Dibromobis-[5-(2-hydroxyethyl)-4-methylthiazole]cobalt(II)

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(Received 28 May 1974; accepted 31 May 1974)

The crystal structure of the title compound has been solved by direct methods and refined by full-matrix least-squares calculations to  $R=0.061$  for 1696 independent reflexions. The monoclinic unit cell, space group  $P2_1/c$ , with  $a=16.993$  (8),  $b=7.794$  (5),  $c=14.807$  (7) Å,  $\beta=112.1$  (2)°, contains four molecules. The cobalt atom is tetrahedrally bound to two bromine atoms and the nitrogen atoms of the substituted thiazoles. The overall molecular symmetry is approximately twofold and the hydroxyethyl side chains have similar atomic environments. All but one of the hydrogen atoms have been located in difference syntheses. Short S...O and Br...O contacts are observed, the latter indicating O-H...Br hydrogen bonding.

### Introduction

The reaction between transition metal halides and organic molecules containing the thiazole entity produces both ionic structures and organometallic complexes. Compounds of the former class have recently been studied by X-ray diffraction. Among these are 3-(2-diethylammoniumethoxy)-1,2-benzisothiazole tetrachlorocobaltate (Bonamartini, Nardelli & Palmieri,

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1972), the corresponding Cu compound (Bonamartini, Nardelli, Palmieri & Pelizzi, 1971) and more recently, (protonated thiamine)<sup>2+</sup>(CuCl<sub>4</sub>)<sup>2-</sup> (Caira, Fazakerley, Linder & Nassimbeni, 1973). In the structure reported here, there is direct bonding between the metal atom and the thiazole ligand. Much enzymic activity depends on transition-metal-thiazole interaction and it is therefore of interest to establish the binding site in this heterocyclic system. In addition the ligand 5-(2-hydroxy-