Crystal Structure of a 2-Biphenyl-2-yl-1,1,3,4-tetraphenyl-1H-silole

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Crystals of silole (silole = silacyclopentadiene) analogue, 2-biphenyl-2-yl-1,1,3,4-tetraphenyl-1H-silole, were grown from a dichloromethane/hexane solution and the crystal structure was determined. The crystal belongs to the monoclinic system with space group of $P2_1/c$. There is an intramolecular π - π interaction in an asymmetric unit, and the shortest distance between one of the phenyl rings in the biphenyl and the phenyl ring at the 3-position of silole is about 3.643 Å. This silole can be used as a potential building block for generating linear polymers containing the silole moiety owing to the labile nature of the proton attached at the 2-position.

(Received March 12, 2004; Accepted April 26, 2004; Published on Web June 17, 2004)

Of a variety of the organosilicon compounds, silole (silole = silacyclopentadiene) derivatives have attracted much attention in material science owing to their various applications to conductors, OLEDs (organic light-emitting diodes) and non-linear optics.¹ By introducing various functional groups at the 2 and 5 positions, siloles have been shown to have unique electronic properties and novel molecular structures. Based on previous reports, a series of siloles with the same functional group at the 2 and 5 positions were prepared readily by a Pd-mediated one-step reaction *via* intramolecular reductive cyclization when employing bis(alkyl or arylethynyl)silanes.² Although the crystal structures and optical properties of 2,5-disubstituted siloles, containing the same group at the 2 and 5 positions, have been well described in the past several years, the number of analyzed structures of silole with different groups at those positions, such as 2-alkyl-5-arylsilole, 2-halo-5-alkyl(or aryl)silole and 2-alkyl(or aryl)-5H-silole *etc.*, still remains limited. In our ongoing development of silole derivatives,³ we found that mono-substituted siloles at the 2 or 5 position were formed as major components, depending on reaction conditions. Herein, we describe the structure of mono-substituted silole, 2-biphenyl-2-yl-1,1,3,4-tetraphenyl-1H-silole (Fig. 1), based on an X-ray crystal analysis.

Fig. 1 Chemical structure.

2-Biphenyl-2-yl-1,1,3,4-tetraphenyl-1H-silole was prepared by a slight modification of the synthetic methodology reported by Tamao's group.² Pale-yellow crystals suitable for X-ray crystallography were grown by slow evaporation from dichloromethane/hexane at room temperature. The crystal and experimental data are depicted in Table 1. The structure was solved by a direct method. The bond length of C2-C18 is 1.498(6)Å, which is slightly longer than those of other 2,5-diarylsiloles, such as 1,1-dimethyl-2,5-bis(*p*-nitrophenyl)-3,4-diphenylsilole (1.475(2)Å), 1,1-dimethyl-2,5-bis(*p*-

Table 1 Crystal and experimental data

Formula: C ₄₀ H ₃₀ Si	
Formula weight = 538.73	
Temperature: 173(2)K	
Crystal size: 0.40 × 0.20 × 0.10 mm	
Crystal color: pale-yellow	
Crystal description: plate	
Crystal system: monoclinic	
Space group: $P2_1/c$	$Z = 4$
$a = 17.719(2)$ Å	
$b = 11.9761(15)$ Å	$\beta = 107.774(2)^\circ$
$c = 14.9394(19)$ Å	
$V = 3018.9(7)$ Å ³	
$D_x = 1.185$ g/cm ³	
Radiation: 0.71073 (Mo K_α)	
$2\theta_{\max} = 56.63^\circ$	
$R = 0.0712$	
$wR = 0.1549$	
Goodness-of-fit = 0.885	
$(\Delta\sigma)_{\max}$ final cycle: 0.000	
$(\Delta\rho)_{\max} = 0.570$ eÅ ⁻³	
$(\Delta\rho)_{\min} = -0.576$ eÅ ⁻³	
No. of reflections used = 7069	
No. of parameters = 371	
Diffraction: Bruker SMART CCD system	
Monochromator: graphite	
Structure determination: SHELXTL	
Refinement: full-matrix least-squares	

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Fig. 2 Crystal structure of the titled compound with the atomic-numbering scheme for Table 2. Displacement ellipsoids are drawn at the 50% probability level.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U(eq)
Si(1)	1324(1)	2110(1)	1112(1)	31(1)
C(2)	2034(3)	1798(3)	441(3)	30(1)
C(3)	2609(2)	2591(3)	647(3)	28(1)
C(4)	2508(2)	3496(3)	1296(3)	29(1)
C(5)	1929(3)	3321(3)	1710(3)	33(1)
C(6)	341(3)	2628(3)	352(3)	31(1)
C(7)	314(3)	3496(4)	-269(4)	49(1)
C(8)	-386(3)	3961(4)	-808(4)	52(1)
C(9)	-1104(3)	3577(4)	-711(3)	50(1)
C(10)	-1096(3)	2705(4)	-118(3)	46(1)
C(11)	-388(3)	2247(4)	425(3)	37(1)
C(12)	1194(2)	901(4)	1832(3)	29(1)
C(13)	1402(3)	922(4)	2810(3)	42(1)
C(14)	1321(3)	-32(5)	3318(4)	51(1)
C(15)	1029(3)	-994(4)	2859(4)	46(1)
C(16)	815(3)	-1037(4)	1896(4)	43(1)
C(17)	904(3)	-106(4)	1400(3)	36(1)
C(18)	1986(3)	819(4)	-198(3)	29(1)
C(19)	1302(3)	737(4)	-972(3)	39(1)
C(20)	1213(3)	-123(4)	-1618(4)	47(1)
C(21)	1801(4)	-924(4)	-1492(4)	50(2)
C(22)	2468(3)	-870(4)	-711(4)	45(1)
C(23)	2570(3)	-23(4)	-45(3)	32(1)
C(24)	3281(3)	-49(4)	796(4)	38(1)
C(25)	3221(3)	54(4)	1700(4)	44(1)
C(26)	3893(3)	17(4)	2484(4)	52(1)
C(27)	4632(3)	-111(4)	2377(4)	57(2)
C(28)	4701(3)	-223(4)	1479(4)	52(2)
C(29)	4035(3)	-192(4)	691(4)	43(1)
C(30)	3318(3)	2594(3)	296(3)	29(1)
C(31)	4065(3)	2773(4)	914(4)	40(1)
C(32)	4730(3)	2790(4)	620(4)	46(1)
C(33)	4639(3)	2626(4)	-333(4)	58(2)
C(34)	3903(3)	2441(4)	-965(4)	51(2)
C(35)	3244(3)	2417(4)	-644(3)	35(1)
C(36)	2935(2)	4578(4)	1403(3)	31(1)
C(37)	3142(3)	5151(4)	2272(3)	38(1)
C(38)	3445(3)	6226(4)	2342(4)	48(1)
C(39)	3557(3)	6754(4)	1560(4)	52(2)
C(40)	3369(3)	6191(4)	718(4)	51(1)
C(41)	3068(3)	5120(4)	638(4)	41(1)

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

Si1 - C12	1.860(4)	Si1 - C5	1.862(4)
Si1 - C2	1.870(4)	Si1 - C6	1.872(6)
C4 - C5	1.365(5)	C2 - C18	1.498(6)
C3 - C4	1.501(6)	C2 - C3	1.357(6)
C2 - Si1 - C5	91.71(18)	C6 - Si1 - C12	110.60(19)
Si1 - C5 - C4	107.7(3)	Si1 - C2 - C3	108.6(3)
Si1 - C2 - C18	125.5(3)	C2 - C3 - C4	115.0(4)

methoxyphenyl)-3,4-diphenylsilole (1.480(2) $\text{\AA}$), 1,1-dimethyl-2,5-bis(*p*-methylphenyl)-3,4-diphenylsilole (1.479(2) $\text{\AA}$) and 1,1-dimethyl-2,5-bis(*p*-trifluoromethylphenyl)-3,4-diphenylsilole (1.473(3) $\text{\AA}$).³ Notably, the shortest distance (C24-C30) between one of the phenyl rings in the biphenyl and the phenyl ring at the 3-position of silole is about 3.257 $\text{\AA}$, indicating that there is an intramolecular π - π interaction in an asymmetric unit, as shown in Fig. 2. These two phenyl rings (C24-C29 and C30-C35) are almost parallel with a dihedral angle of 12.37(8) $^\circ$, while the two phenyl rings between biphenyl (C18-C23 and C24-C29) are significantly tilted by an angle of 49.75(15) $^\circ$. This result can be explained by a steric repulsion between C18 and H25 attached at C25 (atropisomerism). The H-atoms were calculated geometrically, 0.95 $\text{\AA}$ from the corresponding atoms, and refined using a riding model. The atomic coordinates and the selected geometric parameters are presented in Tables 2 and 3, respectively. There are no significant intermolecular interactions (*e.g.* π - π stacking) in the crystal packing. The large positive (0.57 $\text{e\AA}^{-3}$) and negative (-0.58 $\text{e\AA}^{-3}$) difference Fourier peaks are located at short distances from C32 (0.69 $\text{\AA}$) and H31A (1.37 $\text{\AA}$), respectively; these peaks can be attributed to ghosts.

Acknowledgements

The support of Kangwon National University is gratefully acknowledged.

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