CHEMISTRY LETTERS, pp. 1341-1344, 1987.

Air-Stable Tetrakis(2,4,6-triisopropylphenyl)disilene. Direct Synthesis of Disilene from Dihalomonosilane

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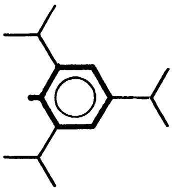
The most air-stable disilene, tetrakis(2,4,6-triisopropylphenyl)disilene was obtained by the direct treatment of dichloromonosilane, bis(2,4,6-triisopropylphenyl)dichlorosilane, with lithium naphthalenide. The Si=Si bond, the distance being 2.144 Å via X-ray structure analysis, was found to be sterically covered with the four bulky substituents.

The chemistry of disilenes is an intriguing subject of current interest because of their unusual structures and properties.[1-3] However, there are no reports on the successful isolation of air-stable disilene except one case in which only a moderately air-stable disilene, (E)-1,2-di-t-butyl-1,2-dimesityldisilene, has been prepared.[1c] Therefore, it is highly desired to produce much more stable disilene toward air for studying the disilene chemistry. In synthetic viewpoint, reductive coupling of dihalomonosilanes with alkali metal seems to be the most simple and convenient way for preparing disilene. Although a reported example along this line had been actually presented to obtain a disilene, tetramesityldisilene,[4] this reaction was later shown to be hardly reproducible, giving only the corresponding cyclotrisilane.[3] We should like to report on the synthesis of a substantially air-stable disilene directly from a dichlorosilane bearing bulky substituents. Thus, tetrakis(2,4,6-triisopropylphenyl)disilene, which was found to be the most air-stable among disilenes so far isolated, could be readily obtained in a good yield by the treatment of bis-

(2,4,6-triisopropylphenyl)dichlorosilane with lithium naphthalenide.

$$2Ar_2SiCl_2 \xrightarrow[DME]{Li/C_{10}H_8} \underset{1}{Ar_2Si{=}SiAr_2}$$

Ar =



Typically, a solution of bis(2,4,6-triisopropylphenyl)dichlorosilane (1.0 g, 2.0 mmol) in dimethoxyethane (DME) (10 ml) was added dropwise with stirring over 7 min to a cold, dark green solution (-58 °C) of lithium naphthalenide prepared from lithium (55 mg, 8.0 mmol) and naphthalene (0.51 g, 4.0 mmol) in DME (20 ml). The mixture was stirred for ca. 2 h at this temperature and then allowed to warm up to room temperature. After stirring for 1 h at room temperature, the mixture was passed through a silica gel column using petroleum-ether eluent under Ar. The resulting solution was concentrated slowly with a stream of Ar to form crystals which were collected on a filter under Ar. Thus, an analytically pure sample, identified as tetrakis(2,4,6-triisopropylphenyl)disilene (1), was obtained as deep-yellow glittering needles (0.44 g, 52%; mp 232-244 °C (sealed capillary)). Physical and spectral data for the sample were consistent with the proposed structure.$^{5)}$

In order to obtain further confirmation, the structure of the molecule was determined by X-ray diffraction (Fig. 1).$^{6)}$ It is shown from the analysis that there would exist three two-fold rotational axes if each para-isopropyl group on the aryl substituents is omitted. The silicon-silicon double bond distance (Si=Si) is 2.144 Å and similar to those of aryl substituted two analogues.$^{7)}$ It should be noted that the two silicon and the four carbon atoms are almost coplanar (the dihedral angle between the two C-Si-C planes is only 3°), and rotating angles of four aryl rings from the plane range from 52° to 61°. These facts indicate that the steric congestion of the four substituents is quite large and forces to minimize the steric repulsion between them in the space around the Si=Si bond.

It is interesting to note some physical and chemical properties for (1). Thus, as does tetramesityldisilene, the first disilene reported by West et al.,$^{1c)}$ compound 1 also undergoes reversible thermochromic transformation from an yellow

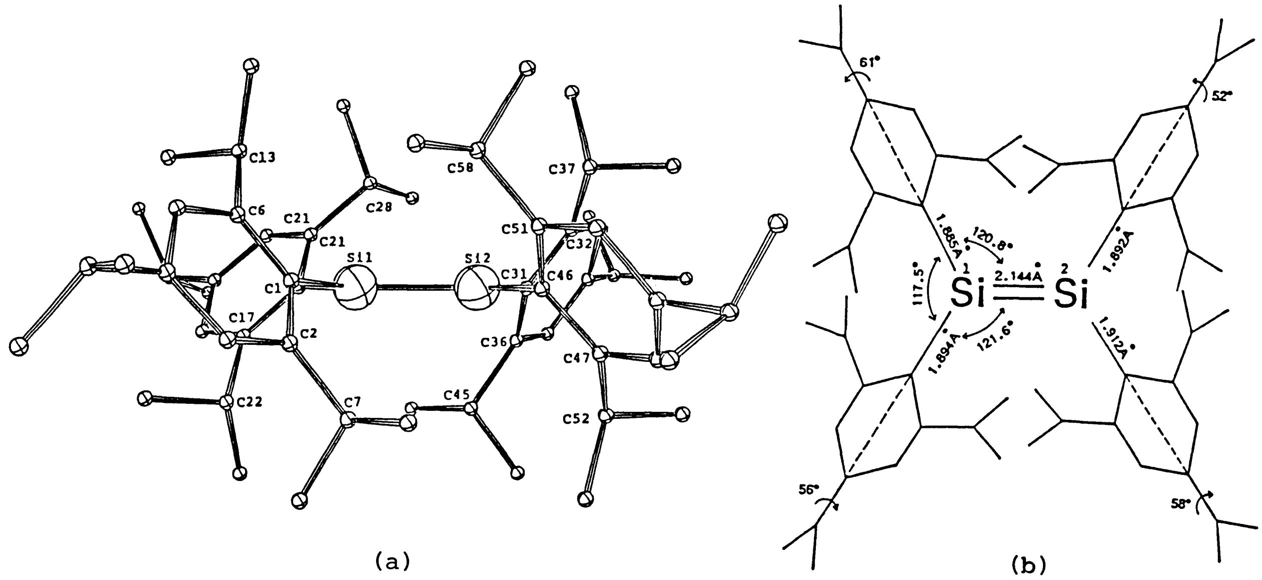


Fig. 1. Molecular structure of compound **1** by X-ray analysis.

to orange color when heated to near 250 °C, the resulting liquid decomposing at 300 °C into a colorless liquid. In air, compound **1** in crystal solid exhibits no change in color and in IR spectrum (KBr) for several hours, but on further standing for 1—2 days it altered gradually to a colorless solid. A cyclohexane solution (ca. 10^{-5} mol·l^{-1}), sealed in vacuo, remained intact for more than two years, showing no spectral change (UV), while on introduction of air the yellow color disappeared gradually with a half-lifetime of 17 min at 20 °C. Thus, the remarkably enhanced stability in air compared with other similar disilenes⁷⁾ can be ascribed to the steric covering with the bulky substituents around the Si=Si bond as can be envisioned from Fig. 1. Further investigation of physical and chemical properties of the compound is currently in progress.

References

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5) Elemental analysis, Found: C, 82.65%; H, 10.58%, Calcd for $C_{60}H_{92}Si_2$: C, 82.88%; H, 10.66%; UV and visible λ_{max} 266 nm(ε 14500), 347(9200), 432(17500) (n-C_6H_{14}); MW by MS 868 (Calcd 868); Isotopic pattern coefficients of molecular ions by electron impact (30 eV), Obs (Calcd) (M) 100(100), (M+1) ..(79), (M+2) 37(37); ^{1}HNMR (C_6D_6, TMS) δ 0.67(d, 12H), 0.70(d, 12H), 1.20(d, 24H), 1.44(d, 12H), 1.48(d, 12H), 2.77(sept, 4H), 3.87(sept, 4H), 4.60(sept, 4H), 7.02(d); 7.11(d)(8H); ^{13}CNMR (C_6D_6, TMS) δ 25.21(q), 25.79(q), 26.28(q), 35.76(d), 37.72 (d), 39.76(d), 122.51(d), 123.85(d), 135.07(s), 151.84(s), 156.17(s); ^{29}SiNMR (C_6D_6, TMS) δ +53.41; IR (KBr disk) 3040(m), 2950(s), 2860(s), 1765(m), 1598(s), 1550(m), 1540(sh), 1460(s), 1415(s), 1380(s), 1360(s), 1310(m), 1260(m), 1230 (m), 1190(m), 1160(m), 875(s), 835(m), 813(m), 790(s), 749(m), 739(m), 713(m) cm^{-1}; The first ionization potential by PES, 8.3 eV (see also Ref. 3, footnote; the first ionization potential of tetrakis(2,6-dimethylphenyl)disilene, 8.4 eV) (the authors are indebted to Prof. Y. Harada of The University of Tokyo for the measurement); Raman spectrum in solid (excitation: Ar^+ 514.5 nm/5 mW power, slit width: 150-200 μm, scan step: 1.0 cm^{-1}/step) 1598(w), 685(vs, νSi=Si),[8] 591(w) cm^{-1} (the authors are indebted to Prof. M. Tasumi at The University of Tokyo for the measurement of the spectrum which is available on request).

6) Crystal data for (**1**): $C_{60}H_{92}Si_2$; MW 869.575; Dimensions 0.2 mm x 0.2 mm x 0.5 mm; Triclinic $a = 13.621(1)$, $b = 13.013(1)$, $c = 21.223(2)$ Å, $\alpha = 70.33(1)°$, $\beta = 121.01(1)°$, $\gamma = 112.10(1)°$; $V = 2938.7(4)$ Å^3; Space group $P\bar{1}$; $Z = 2$; $\rho_c = 0.983$ g·cm^{-3}. In order to avoid air-contact during the data collection for the analysis, a small sample crystal was sealed under Ar in a glass capillary tube. Data were collected on a Rigaku-Denki Model AFC-4 diffractometer with Mo-Kα X-radiation (monochromated with graphite) using $\theta-2\theta$ scans (scan rate, 4 °/min). The structure was solved by direct method and all non-hydrogen atoms were refined anisotropically to $R = 0.084$ for 3563 reflections used ($|F_o| > 3\sigma|(F_o)|$, $3° \leqq 2\theta \leqq 50°$). Lists of the atomic coordinates and the other structural parameters are available from the authors as a supplementary material.

7) Tetrakis(2,6-diethylphenyl)disilene, 2.140 Å (Ref. 2g); tetramesityldisilene, 2.160 Å (Ref. 1b) ;(E)-1,2-di-t-butyl-1,2-dimesityldisilene, 2.140 Å (Ref. 9).

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(Received April 16, 1987)