SHORT PAPER

J. Chem. Research (S),
2000, 528–529

Synthesis and photochemical properties of 2,2′-silaspirobiindan and related compounds[†]

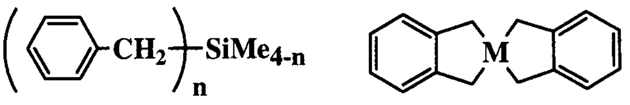
Yohtaro Inoue, Akira Sugimoto and Kazuhiko Mizuno*

Department of Applied Chemistry, Graduate School of Engineering,
Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

2,2′-Silaspirobiindan and several related compounds containing group 14 elements are synthesised and characterised. The absorption and fluorescence spectra of the spiro compounds do not show any π–π interaction between two aryl groups, although di-, tri-, tetra-benzyl substituted silanes show the typical intramolecular excimer fluorescence.

In the last three decades, much attention has been focused on the photochemical reactions of group 14 element compounds because of their characteristic properties and reactivities.[1–3] Kira and Sakurai have previously reported the photorearrangement of benzyltrimethylsilane (**1a**) and (acyloxy)-methyl-substituted benzylsilanes via C–Si photo-cleavage.[4] Very recently, Hiratsuka *et al*. have clarified the photophysical and photochemical processes of **1a** at 77 K and the molecular structure of its excited state by MNDO-PM3 calculations.[5] However, little is known about the synthesis and photochemical behaviour of 2,2’-silaspirobiindan and its related group 14 element compounds,[6] although spiro conjugated compounds having two perpendicular π-electron systems have been widely investigated.[7–9] We now report the synthesis and photochemical behaviour of 2,2′-sila- and germa-spiro compounds and their related compounds.

The benzyl-substituted silanes (**1a–d**) and the spirocompounds **2a–c** were prepared by the Grignard method or the literature method (see Scheme 1).[6,10] For example, 2,2′-silaspirobiindan **2b** was obtained by treatment of the Grignard reagent of *o*-xylylenedichloride with tetrachlorosilane in THF in a 52 % isolated yield.[11] The product was purified by flash column chromatography on silica gel using hexane eluent and repeated recrystallisation from methanol. Similarly the related group 14 element compounds were synthesised in good yields. The results are summarised in Table 1.



1a: n = 1
1b: n = 2
1c: n = 3
1d: n = 4

2a: M = C
2b: M = Si
2c: M = Ge
2d: M = Sn

Scheme 1

The structures of these spiro compounds were determined by their spectral properties. The benzylic protons of **2a–c** showed singlets at δ 2.97, 2.31, and 2.54 ppm, respectively. These values are similar to those of 1,2-diphenylethane (δ 2.88 ppm), **1a** (δ 2.00 ppm), and benzyltrimethylgermane (δ 2.22 ppm). The UV spectra of **2a–c** did not show any π–π interaction between two benzene rings. From these results, both π–ring systems should be mutually perpendicular and not interact with each other. In fact, the two benzene rings are almost perpendicular from the X-ray crystallographic analysis of **2c**.[12]

The spiro compounds **2a–c** in cyclohexane showed almost the same fluorescence maximum at 291 ± 2 nm, although the relative intensity decreased in the order **2a** > **2b** > **2c**. The fluorescence lifetimes of **2a–c** in cyclohexane are 9.6, 6.3, and < 1 ns, respectively. The lifetime of **2b** is quite similar to those of 2,2-dimethyl-2-silaindan (6.2 ns) and *o*-bis(trimethylsilylmethyl) benzene (7.4 ns). These results clearly show that (1) the mutually perpendicular π–aryl systems do not interact with each other, (2) the weak fluorescence and the shorter lifetime of **2c** are attributable to the heavy atom effect of the germanium atom.

The fluorescence intensity of **2b** in cyclohexane was *ca*. 4 times stronger than that of **1a**, which was intramolecularly quenched by the trimethylsilyl group.[5] In addition, the monomer fluorescence intensity of **1a–d** at 290 nm decreased with increase of the number of benzyl groups, accompanying an increase of the excimer fluorescence at 345 nm (Figure 1).

It is well-known that group 14 element compounds act as excellent electron donors in the photoinduced electron transfer

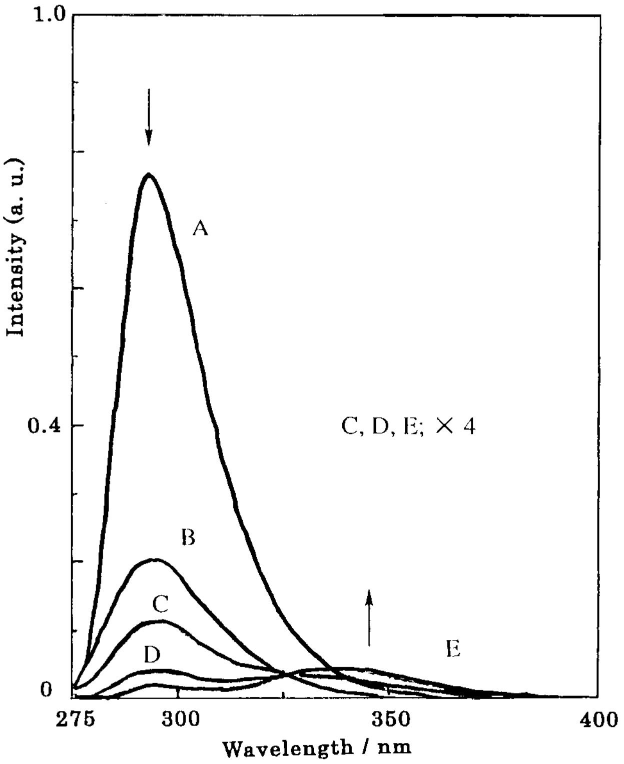


Fig. 1 Fluorescence spectra of **1a–d** and **2b** in cyclohexane: A, **2b**; B, **1a**; C, **1b**; Dm **1c**; E, **1d**; [**1a–d**] = [**2b**] = 4.4×10^{-4} mol/dm^3

---

* To receive any correspondence. Email:mizuno@chem.osakafu-u.ac.jp

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Synthesis of benzylsilanes and spiro compounds and their spectral and physical properties

Compound	M.p./°C (B.p./°C)	Yield/%	^{1}H NMR[a] δ CH_2/ppm	^{13}C NMR[a] δ CH_2/ppm	UV[b] λ_{max}/nm (e)	Fluorescence[b] λ_{max}/nm	Lifetime[b] τ/ns
1a	(190–191)	77	2.09	27.4	267.5 (560)	285	nd[c]
1b	56–58	70	2.10	25.6	267.5 (940)	285, 335	nd[c]
1c	96–97	43	2.11	23/6	267.5 (1300)	285, 335	nd[c]
1d	124–125	40	2.10	21.8	267.5 (1800)	285, 335	nd[c]
2a[d]	55–56	30	2.97	45.8	274 (2210)	289	9.6
2b	79–80	52[e]	2.31	19.4	277 (2810)	293	6.3
2c	130–131	30[e]	2.54	20.8	277 (2010)	292.5	0.4
2d	171 (decomp)[f]	31[f]	2.21[f]	16.9[f]	nr[g]	nr[g]	nr[g]

[a]In $CDCl_3$ using TMS as an internal standard. [b]In aerated cyclohexane. [c]Not determined. [d]C.f. ref. 10. [e]Isolated yields based on $SiCl_4$ and $GeCl_4$ used. [f]Data from ref. 6. [g]The spectra data were not reported.

reactions.[3b] Therefore, we have examined the photochemical behaviour of **2a–c** in the presence of 1,4-dicyanonaphthalene (DCN).[13]

The fluorescence of DCN in cyclohexane was efficiently quenched by **2b-c**. In the case of **2b**, an exciplex emission was observed, accompanied by an isoemissive point at 390 nm. However, the fluorescence of DCN was not quenched appreciably by **2a**, but shifted to longer wavelength. The shifted emission is due to an exciplex emission between DCN and **2a**, and this is supported by its longer lifetime (15.0 ns) compared with that of DCN (2.1 ns) in cyclohexane.[14]

In conclusion, we have demonstrated the characteristic photochemical and spectral properties of 2,2′-silaspirobiindan (**2b**) and its related compounds compared with benzyltrimethylsilane (**1a**).

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 (270MHz) spectrometer for solution in $CDCl_3$. Infrared spectra was obtained on JASCO FT/IR-230 spectrometer, fluorescence spectra on a JASCO FP-500 spectrofluorimeter, and fluorescence lifetime on a HORIBA NAES-550 nanosecond fluorimeter.

2, 2′-Silaspirobiindan (**2b**): In a 300ml. three-necked, round-bottomed flask, equipped with a reflux condenser and a dropping funnel, were placed 1.50 g (61.7 mmol) of magnesium powder and 20ml of dry THF, and were cooled to 0°C. A solution of 2.51 g (14.3 mmol) of *o*-xylylenedichloride and 1.18 g (6.95 mmol) of tetrachlorosilane in 150 ml of THF was added dropwise over 2 h, and the mixture was stirred for 2 h at room temperature, and then was refluxed over night. After the usual work-up, the crude product was purified by column chromatography on silica gel (eluent hexane), and was recrystallized from methanol to give 0.85 g (3.61mmol, yield 52%) of **2b**.: m.p. 79–80°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.31(s, 8H), 7.11 (dd, 4H, *J*=5.5, 3.7Hz), 7.27 (dd, 4H. *J*=5.5, 3.7Hz); ^{13}C NMR (67 MHz, $CDCl_3$) δ 19.4, 125.9, 141.6; IR(KBr) 794, 845, 1128, 1210, 1475, 2894, 3010, 3053 cm^{-1}; UV(C_6H_{12}) λ_{max}= 277 nm (ε 2810). Anal Calcd for $C_{16}H_{16}Si$: C, 81.55; H, 6.80. Found: C, 81.30; H, 6.82.

We are indebted to Dr. Kunio Oka at Osaka Prefecture University for measurements of ^{29}Si NMR spectrum of **2b**. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

Received 3 June 2000; accepted 1 November 2000
Paper 00/345

References and Notes

1 (a) A.G. Brook, in *The Chemistry of Organosilicon Compounds*, S. Patai and Z. Rappoport John Wiley & Sons, New York 1989, Part 2, Chapter 15; (b) G. Raabe and J. Michl, *ibid*., Part 2, (eds) Chapter 17.

2 (a) M. Ishikawa and M. Kumada, *Adv. Organomet. Chem*., 1981, **19**, 51; (b) R.D. Miller and J. Michl, *Chem. Rev*., 1989, **89**, 1359; (c) M. G. Steinmetz, *ibid*., 1995, **95**, 1527.

3 (a) K. Mizuno and Y. Otsuji, Top. Curr. Chem., 1994, **169**, 301; (b) K. Mizuno, T. Tamai, A. Sugimoto, and H. Maeda, in *Advances in Electron Transfer Chemistry*, Vol. 6. P. Mariano, (ed.) JAI Press, Greenwich, 1999, pp. 131–165.

4 M. Kira, H. Yoshida, and H. Sakurai, *J. Am. Chem. Soc.*, 1985, **107**, 7767.

5 H. Hiratsuka, Y. Kadokura, H. Chida, M. Tanaka, S. Kobayashi, T. Okutsu, M. Oba and K. Nishiyama, *J. Chem. Soc., Faraday Trans*., 1996, **92**, 3035.

6 Synthesis of 2,2′-stannaspirobiindan (**2d**) was reported by Lappert *et al*. M.F. Lappert, W.-P.Leung, C.L. Ratson, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans*., 1992, 775.

7 H.E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, 1967, **89**, 5208.

8 H. Duller and R. Gleiter, *Angew. Chem. Int. Ed. Engl*., 1978, **17**, 559; R. Gleiter and J. Uschmann, *J. Org. Chem*., 1986, **51**, 370; J. Spanget-Larsen, J. Uschmann, and R. Gleiter, *J. Phys. Chem*., 1990, **94**, 2334 and references cited therein.

9 W. Setaka, C. Kabuto, and M. Kira, *Chem. Lett*., 1999, 317; K. Ueda, M. Yamanoha, T. Sugimoto, H. Fujita, A. Ugawa, K. Yakushi, and K. Kano, *Chem. Lett*., 1997, 461 and references cited therein.

10 Y. Sakata, S. Nakashima, Y. Goto, H. Tatemitsu, S. Misumi, T. Asahi, M. Hagihara, S. Nishikawa, T. Okada, and N. Mataga, *J. Am. Chem. Soc*., 1989, **111**, 8979.

11 ^{29}Si NMR spectra of **2b** and 2,2-dimethyl-2-silaindan in $CDCl_3$ showed singlets at 33.3 and 17.1ppm.

12 Crystal data for **2c**: $C_{16}H_{16}Ge$, monoclinic, a = 14.177(3), b = 11.173(2), c = 8.247(2) Å, β = 103.84(2)°, V = 1268.3(5) Å^3, space group *C2*/c(#15), *D*c = 1.471 g/cm^3, Z = 4, μ(Mo-Kα) = 23.88 cm^{-1}. 1468 (I > -10.0σ(I)) reflections were used in the structure determination with 78 parameters. Final refinements converged to R (Rw) = 0.059 (0.067). S = 1.52. Dihedral angle between least squares planes (benzene rings); 87.05(8)°. Details will be published elsewhere.

13 Irradiation of **2b** in benzene or acetonitrile did not give any product and **2b** was recovered quantitatively. On the other hand, irradiation of an acetonitrile solution containing **2b** and *p*-dicyanobenzene in the presence of phenanthrene as a redox photosensitizer gave *o*-xylene and 1,2-bis(*o*-methylphenyl)ethane as C-Si bond cleavage products and (*p*-cyanophenyl)(*o*-methylphenyl)methane as a substitution product in 15, 9, and 13% yields, respectively. These results clearly showed that **2b** served as an electron donor in the photoinduced electron transfer reactions. Cf. K. Mizuno, M. Ikeda, and Y. Otsuji, *Tetrahedron Lett*., 1985, **26**, 461; K. Nakanishi, K. Mizuno, and Y. Otsuji, *Bull. Chem. Soc. Jpn*., 1993, **66**, 2371.

14 H.F. Davis, S.K. Chattopadhyay, and P.K. Das, *J. Phys. Chem*., 1984, **88**, 2798; Y. Masaki, S. Yanagida, and C. Pac, *Chem. Lett*., 1988, 1305; Y. Masaki, Y. Uehara, S. Yanagida, and C. Pac, *Chem. Lett*., 1990, 1339; K. Nakanishi, K. Mizuno, and Y. Otsuji, *J. Chem. Soc., Chem. Commun*., 1991, 90; T. Tamai, K. Mizuno, I. Hashida, and Y. Otsuji, *Bull. Chem. Soc. Jpn*., 1993, **66**, 3747.