UV Absorption and Fluorescence Properties of Pyrene Derivatives Having Trimethylsilyl, Trimethylgermyl, and Trimethylstannyl Groups

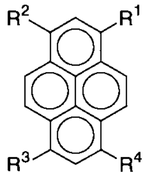
Hajime Maeda, Yohtaro Inoue, Hideki Ishida, and Kazuhiko Mizuno*
Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531

(Received October 9, 2001; CL-010981)

UV absorption maxima of trimethylsilyl-, trimethylgermyl-, and trimethylstannyl-substituted pyrenes shifted to longer wavelength than that of unsubstituted pyrene. Absorption maxima of mono-, bis-, tris-, and tetrakis(trimethylsilyl)pyrenes shifted to longer wavelength consecutively at intervals of 10 nm. Fluorescence intensities and lifetimes decreased in the order of $Me_3SiAr > Me_3GeAr > Me_3SnAr$. Fluorescence intensity of 1,3,6,8-tetrakis(trimethylsilyl)pyrene was the largest among those of a series of pyrenes.

Ground-state structures and electronic properties of silyl-substituted aromatic hydrocarbons such as naphthyl-,[1] anthryl-,[1f,2] phenanthryl-,[3] and pyrenylsilanes[3] have attracted much attention. Although the correlation between ground state structures and reactivities have been frequently discussed, photochemical studies with regard to UV absorption and fluorescence properties of arylsilanes are less known.[4–7] We report here the investigations of UV absorption and fluorescence behaviour of trimethylsilyl-, trimethylgermyl-, and trimethylstannyl-substituted pyrenes.

Synthesis of pyrene derivatives is as follows. 1-Bromopyrene[8] was lithiated with *tert*-BuLi in THF at –78 °C, then treated with Me_3SiCl to give 1-trimethylsilylpyrene (**1a**).[6b] 1-Trimethylgermylpyrene (**1b**) and 1-trimethylstannylpyrene (**1c**) were synthesized in a similar manner by use of Me_3GeCl[9] and Me_3SnCl instead of Me_3SiCl. Reaction of pyrene (**1d**) with 2 equiv of bromine in carbon tetrachloride gave a mixture containing 1,6- and 1,8-dibromopyrenes.[10] Lithiation and the following treatment with Me_3SiCl (2 equiv) gave a mixture of **1e** and **1f**. Further bromination of the mixture of 1,6- and 1,8-dibromopyrenes in nitrobenzene at 80 °C afforded a mixture of tri- and tetrabromopyrenes, which were silylated to give **1g** and **1h**. Bis-, tris-, and tetrakis(trimethylsilyl)pyrene (**1e–h**) could be isolated by recycling preparative HPLC.[11]



1a: $R^1 = SiMe_3$, $R^2 = R^3 = R^4 = H$
1b: $R^1 = GeMe_3$, $R^2 = R^3 = R^4 = H$
1c: $R^1 = SnMe_3$, $R^2 = R^3 = R^4 = H$
1d: $R^1 = R^2 = R^3 = R^4 = H$
1e: $R^1 = R^3 = SiMe_3$, $R^2 = R^4 = H$
1f: $R^1 = R^4 = SiMe_3$, $R^2 = R^3 = H$
1g: $R^1 = R^2 = R^3 = SiMe_3$, $R^4 = H$
1h: $R^1 = R^2 = R^3 = R^4 = SiMe_3$

Chart 1.

UV–vis absorption spectra of these compounds were measured in cyclohexane (ca. 10^{-5} M) (Table 1). Absorption maxima of trimethylsilyl-, trimethylgermyl-, and trimethylstannyl-substituted pyrenes shifted to bathochromic region than that of unsubstituted pyrene, although the absorption coefficients were almost unchanged. Absorption maxima of mono-, bis-, tris-, and tetrakis(trimethylsilyl)pyrenes shifted to longer wavelength consecutively at intervals of 10 nm (Figure 1). These results can be explained in terms of the energy gap between HOMO and LUMO of pyrene derivatives, which decreased with increasing the number of silyl-substitution. Silyl groups contribute to destabilization of HOMO and stabilization of LUMO by σ^*–π^* interaction.[2j,5–7,12]

Fluorescence spectra of pyrene and pyrene derivatives were taken in 10^{-5} M aerated cyclohexane solutions (Figure 2). Fluorescence intensity and fluorescence lifetime of monosilyl derivative **1a** were higher and longer than those of unsubstituted pyrene **1d**.[6b] Fluorescence intensities and lifetimes of germyl and stannyl derivatives **1b–c** were lower and shorter than those of **1a** due to the heavy atom effect. Emission maxima (λ_{max}) of **1a–c** shifted to longer wavelength than **1d**. It is interesting that the fluorescence intensities increased with increasing the number of silyl substitution (i.e. **1h** > **1g** > **1e** ~ **1f** > **1a**), however, fluorescence lifetimes decreased with increasing the number of silyl groups.

Table 1. Absorption, fluorescence properties, and calculated energy levels of HOMO and LUMO of silyl-, germyl-, and stannylpyrenes (**1a–h**)[a]

Compound	Absorption[a]		Eigenvalues / eV[b]			Fluorescence[a]		
	λ_{max} / nm	log ε	HOMO	LUMO	energy gap	λ_{max} / nm	τ (in air) / ns	τ (in argon) / ns
1a	344.5	4.71	–8.086	–0.909	7.177	393.5	19.3	107
1b	343.5	4.56	–8.130	–0.958	7.172	392.5	18.9	24.6
1c	344.0	4.70	–8.226	–1.023	7.203	392.5	14.5	21.2
1d	334.5	4.62	–8.249	–1.010	7.238	389.5	20.2	45.1
1e	354.5	4.69	–7.938	–0.818	7.120	403.0	18.7	84.7
1f	355.0	4.73	–7.940	–0.819	7.121	397.0	19.8	74.5
1g	365.0	4.74	–7.809	–0.744	7.065	388.5	17.7	27.9
1h	375.0	4.72	–7.689	–0.678	7.011	405.5	12.6	21.5

[a]In cyclohexane. [b]Calculated by MM3 // PM3.

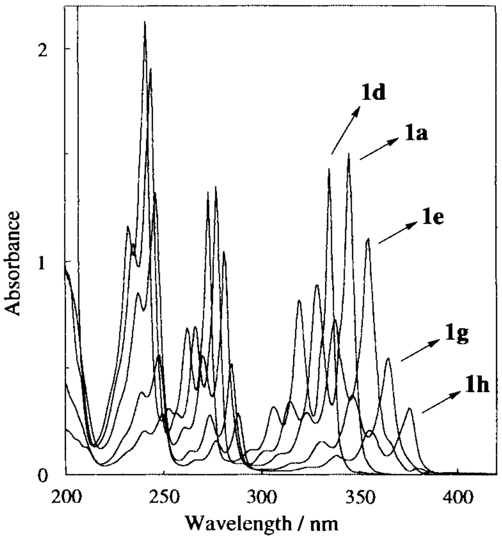


Figure 1. UV-vis spectra of **1a**, **1d**, **1e**, **1g**, and **1h** ([**1**] = (1–5) × 10^{-5} M) in cyclohexane.

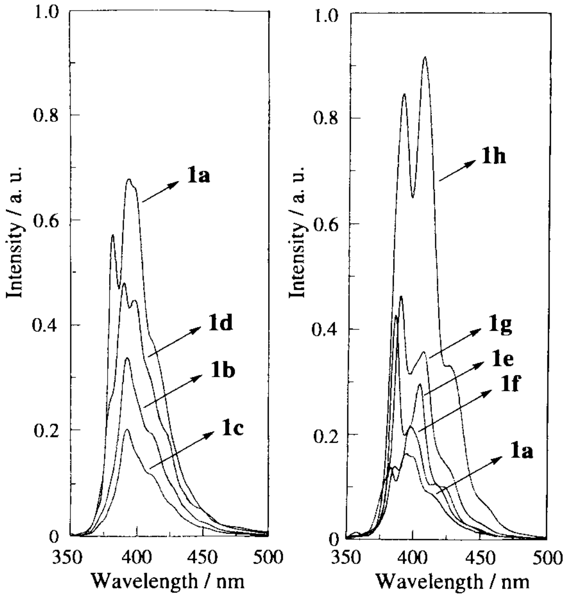


Figure 2. Fluorescence spectra of **1a–h** ([**1**] = 1 × 10^{-5} M) in cyclohexane.

In conclusion, UV absorption and fluorescence properties can be effectively controlled by the introduction of trimethylsilyl, trimethylgermyl, and trimethylstannyl substituents to the pyrene rings. Fluorescence intensities and lifetimes diminished in the order of Me_3SiAr > Me_3GeAr > Me_3SnAr. Fluorescence intensities increased with increasing the number of silyl groups, hence 1,3,6,8-tetrakis(trimethylsilyl)pyrene (**1h**) showed a highly emissive character.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

1 a) A. L. Allred and L. W. Bush, *J. Am. Chem. Soc.*, **90**, 3352 (1968). b) A. G. Evans, B. Jerome, and N. H. Rees, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 447. c) A. G. Evans, B. Jerome, and N. H. Rees, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 2091. d) H. J. Sipe, Jr. and R. West, *J. Organomet. Chem.*, **70**, 353 (1974). e) R. L. Funk and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, **1976**, 833. f) M. Bullpitt, W. Kitching, W. Adcock, and D. Doddrell, *J. Organomet. Chem.*, **116**, 161 (1976). g) W. Kaim, H. Tesmann, and H. Bock, *Chem. Ber.*, **113**, 3221 (1980). h) R. L. Funk and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **102**, 5245 (1980). i) M. Laguerre, J. Dunoguès, and R. Calas, *Tetrahedron Lett.*, **22**, 1227 (1981). j) T. Kitamura, N. Fukatsu, and Y. Fujiwara, *J. Org. Chem.*, **63**, 8579 (1998).

2 a) C. Eaborn, R. Eidenschink, and D. R. M. Walton, *J. Organomet. Chem.*, **96**, 183 (1975). b) H. Cho and R. G. Harvey, *J. Org. Chem.*, **40**, 3097 (1975). c) G. Felix, R. Lapouyade, H. Bouas-Laurent, and B. Clin, *Tetrahedron Lett.*, **1976**, 2277. d) H. Sakurai, K. Sakamoto, A. Nakamura, and M. Kira, *Chem. Lett.*, **1985**, 497. e) M. Daney, C. Vanucci, J.-P. Desvergne, A. Castellan, and H. Bouas-Laurent, *Tetrahedron Lett.*, **26**, 1505 (1985). f) H. Lehmkuhl, A. Shakoor, K. Mehler, C. Krüger, K. Angermund, and Y.-H. Tsay, *Chem. Ber.*, **118**, 4239 (1985). g) T. Alonso, S. Harvey, P. C. Junk, C. L. Raston, B. W. Skelton, and A. H. White, *Organometallics*, **6**, 2110 (1987). h) J.-P. Desvergne, N. Bitit, A. Castellan, M. Webb, and H. Bouas-Laurent, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1885. i) H. Suzuki, S. Satoh, Y. Kimata, and A. Kuriyama, *Chem. Lett.*, **1995**, 451. j) S. Kyushin, M. Ikarugi, M. Goto, H. Hiratsuka, and H. Matsumoto, *Organometallics*, **15**, 1067 (1996).

3 C. Eaborn, Z. Lasocki, and J. A. Sperry, *J. Organomet. Chem.*, **35**, 245 (1972).

4 Photochemistry of organosilicon compounds: a) M. G. Steinmetz, *Chem. Rev.*, **95**, 1527 (1995). b) M. Kako and Y. Nakadaira, *Coord. Chem. Rev.*, **176**, 87 (1998). c) K. Mizuno, T. Tamai, A. Sugimoto, and H. Maeda, "Advances in Electron Transfer Chemistry", ed. by P. S. Mariano, JAI Press, New York (1999), Vol.6, pp 131–165. d) M. Kako and Y. Nakadaira, *Bull. Chem. Soc. Jpn.*, **73**, 2403 (2000).

5 H. Shizuka, Y. Sato, Y. Ueki, M. Ishikawa, and M. Kumada, *J. Chem. Soc., Faraday Trans. 1*, **80**, 341 (1984).

6 a) D. Declercq, F. C. De Schryver, and R. D. Miller, *Chem. Phys. Lett.*, **186**, 467 (1991). b) D. Declercq, P. Delbeke, F. C. De Schryver, L. Van Meervelt, and R. D. Miller, *J. Am. Chem. Soc.*, **115**, 5702 (1993).

7 T. Karatsu, T. Shibata, A. Nishigaki, K. Fukui, and A. Kitamura, *Chem. Lett.*, **2001**, 994.

8 W. H. Gumprecht, *Org. Synth., Coll. Vol. V*, 147 (1973).

9 H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, **1966**, 5493.

10 J. Grimshaw and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1622.

11 **1e**: ^{1}H NMR (300 Mz, $CDCl_3$) δ 0.58 (s, 18 H), 8.09 (d, J = 9.1 Hz, 2 H), 8.15 (d, J = 9.1 Hz, 2 H), 8.19 (d, J = 9.1 Hz, 2 H), 8.36 (d, J = 9.1 Hz, 2 H). **1f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60 (s, 18 H), 8.04 (s, 2 H), 8.13 (d, J = 7.7 Hz, 2 H), 8.19 (d, J = 7.7 Hz, 2 H), 8.41 (s, 2 H). **1g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, 9 H), 0.60 (s, 9 H), 0.61 (s, 9 H), 7.36 (s, 1 H), 8.08 (d, J = 9.2 Hz, 1 H), 8.17 (t, J = 5.7 Hz, 2 H), 8.24 (d, J = 9.2 Hz, 2 H), 8.38 (d, J = 3.7 Hz, 2 H). **1h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60 (s, 36 H), 8.37 (s, 4 H), 8.39 (s, 2 H).

12 a) U. Weidner and A. Schweig, *J. Organomet. Chem.*, **39**, 261 (1972). b) C. G. Pitt and H. Bock, *J. Chem. Soc., Chem. Commun.*, **1972**, 28. c) C. G. Pitt, R. N. Carey, and E. C. Toren, Jr., *J. Am. Chem. Soc.*, **94**, 3806 (1972). d) C. G. Pitt, *J. Organomet. Chem.*, **61**, 49 (1973). e) W. Ensslin, H. Bock, and G. Becker, *J. Am. Chem. Soc.*, **96**, 2757 (1974). f) R. Gleiter, W. Schäfer, and H. Sakurai, *J. Am. Chem. Soc.*, **107**, 3046 (1985). g) H. Sakurai, *Pure Appl. Chem.*, **59**, 1637 (1987). h) C. A. van Walree, M. R. Roest, W. Schuddeboom, L. W. Jenneskens, J. W. Verhoeven, J. M. Warman, H. Kooijman, and A. L. Spek, *J. Am. Chem. Soc.*, **118**, 8395 (1996).