Preparation and Properties of 2,2-Bissilyl-1,3-dithia-2-silacyclopent-4-enes and Related Compounds

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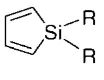
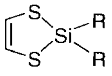
Several 1,3-dithia-2-silacyclopent-4-ene (dithiasilole) derivatives were prepared by the reactions of *cis*-NaS–HC=CH–SNa with the corresponding dichlorosilanes. The compounds formed charge-transfer (CT) complexes with tetracyanoethylene in CH_2Cl_2. The UV–vis spectra of the CT complexes indicated that the ionization potential of 2,2-bis(trimethylsilyl)dithiasilole was smaller than that of 2,2-dimethyldithiasilole. The results were explained by the σ(Si–R)–π interactions resulting in a higher HOMO level. Ab initio MO calculations supported the experimental results.

Silacyclopentadienes (siloles) have been receiving attention for their unique photophysical properties, which originate from low-lying LUMOs due to the interaction between σ(Si–R) and π*(diene) orbitals.[1,2] However, the chemistry of 1,3-dithia-2-silacyclopent-4-ene (dithiasilole) derivatives has rarely been investigated.[3] Only 2,2-dimethyldithiasilole was prepared by Satgé et al. in 1988.[3]



silole

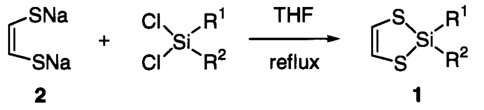


dithiasilole

It was assumed that dithiasilole did not have low-lying LUMOs because the σ*–π* interaction was not allowed by the symmetry of molecular orbitals. However, the orbital interaction between the π(S–C=C–S) system and σ(R–Si–R) bonds was thought to raise the HOMO level of the compound. We will report here the preparation and properties of 2,2-bis(trimethylsilyl)dithiasilole and their related compounds. Ab initio MO calculations were also made to investigate the characteristics of the compounds.

The reactions of *cis*-NaS–HC=CH–SNa (**2**) with the corresponding 2,2-dichlorotrisilanes in THF under reflux gave 2,2-bis(*t*-butyldimethylsilyl)dithiasilole (**1a**)[4] and 2,2-bis(trimethylsilyl)dithiasilole (**1b**)[5] in 44% and 37% yields, respectively, as shown in Scheme 1. Disilanes **1c**[6] and **1d**[7] and monosilane **1e**[3] were also obtained in a similar manner. The compounds **1a–e** gradually decomposed in air, but can be kept without decomposition under an argon atmosphere for several weeks.

Scheme 1.



1a ($R^1 = R^2 = SiMe_2(t\text{-}Bu)$, 44%)
1b ($R^1 = R^2 = SiMe_3$, 37%)
1c ($R^1 = SiMe_3$, $R^2 = t\text{-}Bu$, 74%)
1d ($R^1 = SiMe_3$, $R^2 = Me$, 41%)
1e ($R^1 = R^2 = Me$, 28%)

The UV spectra of **1a–e** in cyclohexane are shown in Figure 1. Except for monosilane **1e**, the compounds exhibited broad absorption at 250–300 nm. The bathochromic shift was ascribed to the rise of the HOMO levels of the compounds due to the σ(Si–Si)–π interaction described above. It is notable that **1a** showed a significant red-shifted absorption at 278 nm, which was tailed into 380 nm. The steric hindrance between the two bulky silyl groups would increase the Si–Si–Si angle and reinforce the σ–π interaction.

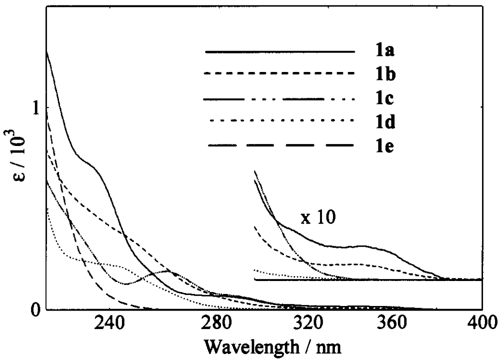


Figure 1. UV spectra of **1** in cyclohexane.

It is well-known that oligosilanes form charge-transfer (CT) complexes with tetracyanoethylene (TCNE),[8,9] and their CT energies have a linear relationship with the ionization potentials (IPs) of oligosilanes (eq 1).[9]

$$h\nu_{CT} / eV = 0.77\ IP - 3.72 \quad (eq\ 1)$$

To estimate the IPs of **1a–e**, the absorption maxima of the CT complexes of **1a–e** with TCNE in CH_2Cl_2 were measured (Figure 2). IP_{est}s of **1a–e** were estimated using eq 1 and summarized in Table 1. IP_{est} increased in the order **1a** < **1b** < **1c** < **1d** < **1e**. This means that the introduction of silyl substituents into the dithiasilole skeleton was effective in raising the HOMO levels. The higher IP_{est} of **1a** than that of **1b** should stem from the more effective interactions between σ(Si–Si) bond and π orbital in **1a** due to the steric effects described above.

Non-empirical MO calculations of the dithiasilole derivatives were made at the B3LYP/6-31G* level. The calculated structure of the 5-membered ring in **1e** was almost planar. However, slightly deformed, envelope-type structures were found in **1b** and **1d**. The S–Si–S–C dihedral angles were 7.3°, 12.2°, and 0.0° for **1b**, **1d**, and **1e**, respectively. Figure 3 shows

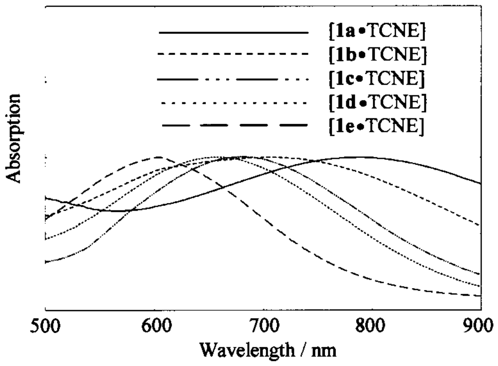


Figure 2. Absorption spectra of [**1** •TCNE] complexes in CH_2Cl_2.

Table 1. Charge-transfer absorption maxima of complexes of TCNE with **1** in CH_2Cl_2 at rt

1	λ_{max} / nm	IP_{est} / eV^a	IP_{calcd} / eV^b
1a	793	6.86	——
1b	705	7.10	6.69
1c	676	7.21	——
1d	657	7.27	7.16
1e	603	7.49	7.42

[a] Estimated using $h\nu_{CT}$ / eV = 0.77 IP_{obsd} - 3.72. [b] OVGF method at B3LYP/6-31G* geometry.

the HOMOs of **1e** and **1b**. Apparently, the contribution of the σ(Si–Si) orbitals in **1b** was larger than that of the σ(Si–Me) orbitals in **1e**.

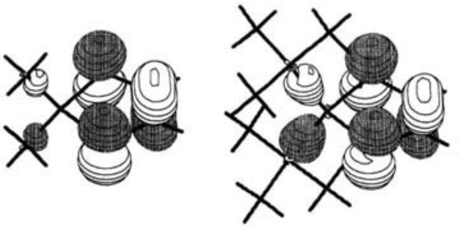


Figure 3. MOLDEN pictorial presentations of the HOMOs of **1e** (left) and **1b** (right), the threshold level being 0.05.

The IPs and electron affinities (EAs) of **1b**, **1d**, and **1e** were calculated using ab initio MO method with the Outer Valence Green's Function (OVGF) propagator method.[9,10] The results are listed in Table 1. Compound **1a** was too large to calculate the IP and EA at the same level of calculation under our computational conditions. Although the LUMO levels of **1b**, **1d**, and **1e** were almost the same (0.90–0.91 eV), the HOMO levels rose when the silyl substituent was introduced into the dithiasilole ring. This is consistent with the IP_{est} values experimentally obtained from the CT complexes with TCNE.

We expect that the π-systems including 2,2-bis(silyl)dithiasilole will be useful materials with high-lying HOMO levels. Further experimental and theoretical studies are in progress.

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References and Notes

1 For recent reviews on siloles, see: J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, **90**, 215 (1990); E. Colomer, R. J. P. Corriu, and M. Lheureux, *Chem. Rev.*, **90**, 265 (1990); K. Tamao and S. Yamaguchi, *Pure Appl. Chem.*, **68**, 139 (1996); J. Jubac, C. Guérin, and P. Meunier, in "The Chemistry of Organic Silicon Compounds," ed. by Z. Rappoport and Y. Apeloig, Wiley & Sons, Chichester (1998), Vol. 2, Chap. 34, pp. 1961–2036; S. Yamaguchi and K. Tamao, J. *Chem. Soc., Dalton Trans.*, **1998**, 3693; J. Hermanns and B. Schmidt, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 81.

2 S. Yamaguchi and K. Tamao, *Bull. Chem. Soc. Jpn.*, **69**, 2327 (1996).

3 H. Lavayssiere, G. Dousse, and J. Satgé, *Recl. Trav. Chim. Pays-Bas*, **107**, 440 (1988).

4 **1a**: A pale yellow oil; bp 150–180 °C / 1 mmHg; ^1H NMR ($CDCl_3$, δ) 0.22 (s, 12H), 1.00 (s, 18H), 6.15 (s, 2H); ^{13}C NMR ($CDCl_3$, δ) –5.50, 18.95, 27.75, 122.34; ^{29}Si NMR ($CDCl_3$, δ) –1.67, 21.36; HRMS *m/z* found: 348.1237. calcd for $C_{14}H_{32}S_2Si_3$: 348.1251.

5 **1b**: A colorless oil; bp 115–135 °C / 1.5 mmHg; ^1H NMR (CDCl3, δ) 0.25 (s, 18H), 6.16 (s, 2H); ^{13}C NMR ($CDCl_3$, δ) –2.06, 121.93; ^{29}Si NMR ($CDCl_3$, δ) –13.60, 22.82; HRMS *m/z* found: 264.0305. calcd for $C_8H_{20}S_2Si_3$: 264.0314.

6 **1c**: A pale yellow oil; bp 70–130 °C / 1 mmHg; ^1H NMR ($CDCl_3$, δ) 0.30 (s, 9H), 0.93 (s, 9H), 6.19 (s, 2H); ^{13}C NMR ($CDCl_3$, δ) –0.49, 24.42, 24.59, 120.64; ^{29}Si NMR ($CDCl_3$, δ) –15.58, 38.94; HRMS *m/z* found: 236.0532. calcd for $C_8H_{20}S_2Si_2$: 236.0544.

7 **1d**: A colorless oil; bp 70–120 °C / 1 mmHg; ^1H NMR ($CDCl_3$, δ) 0.27 (s, 9H), 0.53 (s, 3H), 6.23 (s, 2H); ^{13}C NMR ($CDCl_3$, δ) –2.09, 5.32, 120.29; ^{29}Si NMR ($CDCl_3$, δ) –16.04, 34.58; HRMS *m/z* found: 206.0073. calcd for $C_6H_{14}S_2Si_2$: 206.0076.

8 V. F. Traven and R. West, *J. Am. Chem. Soc.*, **95**, 6824 (1973).

9 H. Sakurai, M. Kira, and T. Uchida, *J. Am. Chem. Soc.*, **95**, 6826 (1973).

10 Ab initio MO calculations were performed using the Gaussian 98[11] program on a vector-parallel computer, Fujitsu VPP700E, at RIKEN. The geometries were fully optimized at the B3LYP/6-31G* level.

11 M. J. Frish, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrezewski, J. A. Mongomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayali, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M.A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, GAUSSIAN 98 (Revision A.1), Gaussian Inc., Pittsburgh, PA, 1998.