Design, Synthesis, and Electrochemical Behavior of New Electron Donors Based on *β*-Effects of Group 14 Elements in Electron Transfer

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In a program aimed at new electron donors, we synthesized several silicon- and tin-substituted 1,3-benzodithioles which exhibited much lower oxidation potentials than 1,3-benzodithiole. This effect was supported by the molecular orbital calculations.

Since the high electrical conductivity in the charge-transfer (CT) complex of tetrathiafulvalene (TTF) with tetracyano-quinodimethane (TCNQ) was reported,[1] significant interest in organic conducting materials has been received by scientists of various fields. Although the largest body of work has been devoted to the study of TTF and its derivatives as electron donors,[2] developments of new types of donors are strongly needed. In this paper we wish to report preliminary results of the study directed toward new electron donors utilizing unique properties of group 14 elements such as silicon and tin.

Our approach is based on the following two concepts;

(1) Group 14 elements such as silicon and tin promote the electron transfer from a heteroatom and a π-system at β-position. Theoretical and experimental studies revealed that this effect is attributed to the rise of HOMO level by the interaction of a carbon-group 14 atom σ orbital with a nonbonding p orbital of the heteroatom.[3]

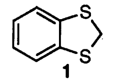
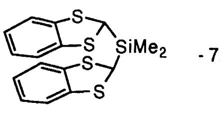
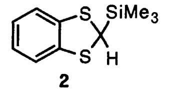
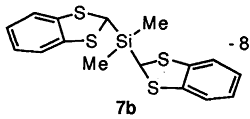
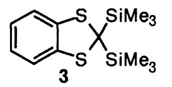
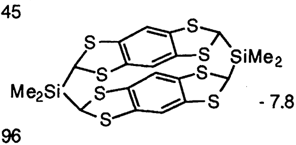
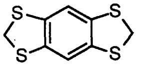
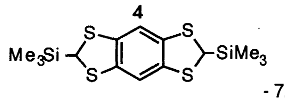
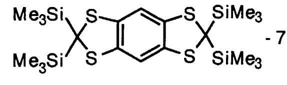
(2) Linking of donor π-systems with covalent bonds may be effective for the construction of artificial stackings.[4] It is well known that the stacking of donor molecules to make columns in the CT complexes is essential for the conductivity.[5] Longer C-Si and C-Sn bonds in comparison with C-C bonds seem to be suitable for linking π-systems to achieve artificial stacking.

Based on these concepts we envisioned that silicon and tin can be utilized for both enhancing the electron-donating ability of π-systems containing heteroatoms and linking the π-systems to construct artificial stackings.

As model compounds of electron donors based on this approach, we designed silicon-substituted 1,3-benzodithiole derivatives and related compounds. Semiempirical molecular orbital calculations using PM3 Hamiltonian indicate that the introduction of a silyl group onto the methylene carbon of 1,3-benzodithioles (**1** and **4**) causes significant increase of the HOMO level (**2** and **5**) (Table 1). The introduction of the second silyl group causes further increase of the HOMO level (**3** and **6**). Therefore, these results indicate that silicon has significant effect to promote the electron transfer from 1,3-benzodithioles. We also calculated the HOMO level of silicon-linked 1,3-benzodithiole (**7a**, **7b**, and **8**). The HOMO levels of the stacking compounds (**7a** and **8**) were found to be higher than that of the non-stacking analogs, suggesting that the electron transfer would be accelerated by the artificial stacking using silicon.

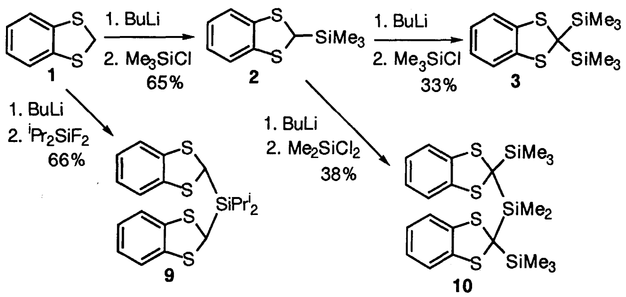
Some silicon-substituted 1,3-benzodithioles were synthesized according to Scheme 1. 1,3-Benzodithiole (**1**)[6] was easily deprotonated with butyllithium in THF at -23 — -30 °C.[7] The treatment of the resulting anion with chlorotrimethylsilane gave 2-(trimethylsilyl)-1,3-benzodithiole (**2**).[8] The second silyl group was introduced by the deprotonation of **2** with butyllithium followed by the reaction with chlorotrimethylsilane.

Table 1. HOMO level of silicon-substituted 1,3-benzodithioles[a]

compound	HOMO (eV)	compound	HOMO (eV)
 1	-8.57	 7a	- 7.92
 2	-8.18	 7b	- 8.12
 3	-7.84	 8	- 7.81
 4	-8.45		
 5	- 7.96		
 6	- 7.61		

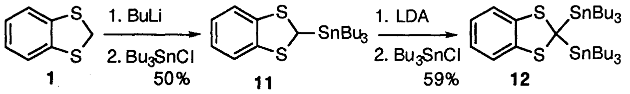
[a] The calculations were carried out using Spartan Ver 3.1 program using PM3 Hamiltonian.

Silicon-linked 1,3-benzodithioles (**9** and **10**) were prepared as follows: Deprotonation of 1,3-benzodithiole (**1**) followed by the treatment with difluorodiisopropylsilane gave **9** in 66% yield. Deprotonation of 2-(trimethylsilyl)-1,3-benzodithiole (**2**) followed by the reaction with dichloro-dimethylsilane afforded **10** in 38% yield.



Scheme 1. Synthesis of silicon-substituted 1,3-benzodithioles.

Tin-substituted 1,3-benzodithioles (**11** and **12**) were also synthesized in a similar fashion except that the deprotonation of the monostannyl derivative (**11**) was carried out with lithium disiopropylamide (LDA) (Scheme 2).



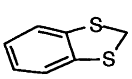
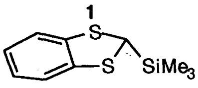
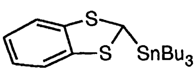
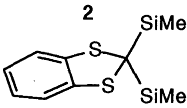
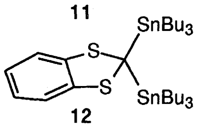
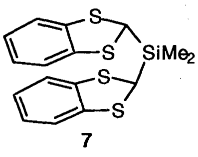
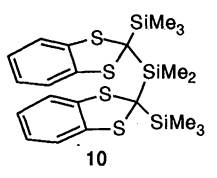
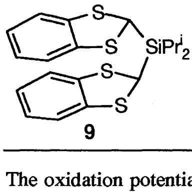
Scheme 2. Synthesis of tin-substituted 1,3-benzodithioles.

The oxidation potential of 2-(trimethylsilyl)-1,3-benzodithiole (**2**) was found to be less positive than that of 1,3-benzodithiole (**1**) (Table 2). The introduction of the second silyl group caused further decrease in the oxidation potential. These data indicate that silicon promotes the electron transfer from 1,3-benzodithiole. Probably the C-Si σ orbital interacts with the nonbonding p orbitals of two sulfur atoms effectively to cause the increase of the HOMO level.

The introduction of a stannyl group instead of a silyl group resulted in dramatic decrease in the oxidation potential. The larger effect of tin compared with silicon is attributed to the better interaction of the nonbonding p orbital of S with the C-Sn σ orbital than that with the C-Si σ orbital. This is probably because of smaller energy difference between the p orbital of S and the C-Sn σ orbital than that between the p orbital of S and the C-Si σ orbital.[9]

The oxidation potential of the dimeric 1,3-benzodithioles linked by silicon (compound **7**) was found to be comparable to those of the corresponding monomeric silyl-substituted 1,3-benzodithiole (**2**). Probably the non-stacking conformer (**7b**) is more stable than the stacking conformer (**7a**). The oxidation potential of compound **10** in which two silyl-substituted 1,3-benzodithiole units are linked by silicon, however, was found to be less positive than that of the corresponding monomeric compound (**3**). Probably, the population of the stacking conformer of **10** is larger than that for **7**,[10] and the contribution of such conformer in electron transfer reaction may cause the decrease in oxidation potential.

Table 2. The oxidation potentials of silicon-substituted 1,3-benzodithioles[a]

compound	Ed(V)	compound	Ed(V)
 1	1.07		
 2	0.83	 11	0.21
 3	0.65	 12	0.08
 7	0.80	 10	0.54
 9	0.86		

[a] The oxidation potentials (Ed: decomposition potentials) were determined with rotating disk electrode voltammetry using a glassy carbon working electrode in 0.1 M $LiClO_4/CH_3CN$ using a Ag/AgCl reference electrode.

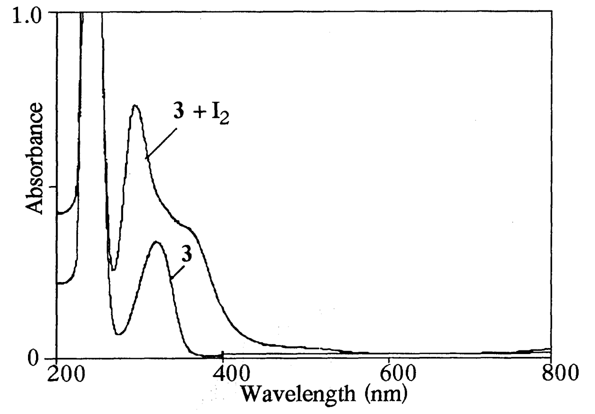


Figure 1. The absorption spectra of **3** and a 1:1 mixture of **3** and iodine.

Figure 1 shows the absorption spectra of **3** and a 1:1 mixture of **3** and iodine in CH_2Cl_2. The shifts of the absorption maxima for the latter from those of **3** suggests the formation of the CT complex of **3** and iodine.

The research reported above demonstrates the potentiality of new electron donors based on β-effects of group 14 elements in electron transfer. Further work is in progress to synthesize various types of silicon and tin-substituted π-systems to construct artificial stacking, and to explore the unique properties of such electron donors.

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References

1 J. Ferraris, D. O. Cowan, V. Waltka Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
2 For recent review articles see: a) M. R. Bryce, *Chem. Soc. Rev.*, **20**, 355 (1991); b) G. Schukat, A. M. Richter, and E. Fanghänel, *Sulfur Reports*, **7**, 155 (1987); c) M. Narita. and C. U. Pittman, *Synthesis*, **1976**, 489 .
3 a) J. Yoshida, T. Maekawa, T. Murata, S. Matsunaga, and S. Isoe, *J. Am. Chem. Soc.*, **112**, 1962 (1990); b) J. Yoshida, *Topics in Current Chemistry*, **170**, 39 (1994); c) J. Yoshida, Y. Ishichi, K. Nishiwaki, S. Shiozawa, and S. Isoe, *Tetrahedron Lett.*, **33**, 2599 (1992).
4 a) K. Matsuo, K. Takimiya, Y. Aso, T. Otsubo, and F. Ogura, *Chem. Lett.*, **1995**, 523; b) C. Kaes, M. W. Hosseini, R. Ruppert, A. D. Cian, and J. Fischer, *Tetrahedron Lett.*, **35**, 7233 (1994).
5 T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, *J. Chem.* Soc., *Chem. Comm.*, **1973**, 471.
6 J. Nakayama, K. Fujiwara, and M. Hoshino, *Bull. Chem. Soc. Jpn.*, **49**, 3567 (1976).
7 S. Ncube, A. Pelter, K. Smith, and P. Blatcher, and S. Warren, *Tetrahedron Lett.*, **26**, 2345 (1978).
8 ^1H NMR (300MHz, C_6D_6) δ 0.08 (s, 9H), 4.25 (s, 1H), 6.56-6.95 (m, 4H); ^{13}C NMR (75MHz, C_6D_6) δ 2.93, 39.31, 122.28, 125.59, 140.59; Anal. Calcd for $C_{10}H_{14}S_2Si$: C, 53.09; H, 6.24. Found: C, 53.11; H, 6.08.
9 a) R. S. Glass, A. M. Radspinner, and W. P. Singh, *J. Am. Chem. Soc.*, **114**, 4921 (1992); b) J. Yoshida, *J. Syn. Org. Chem. Jpn.*, **53**, 53 (1995).
10 This speculation is supported by PM3 calculations.