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# Synthesis and Structure of 2,4,6-Tris[bis(trimethylsilyl)methyl]thiobenzaldehyde: The First Isolation of Rotational Isomers of Thiobenzaldehydes

Norihiro Tokitoh, Nobuhiro Takeda, and Renji Okazaki*

*Department of Chemistry*
*Graduate School of Science, The University of Tokyo*
*7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*

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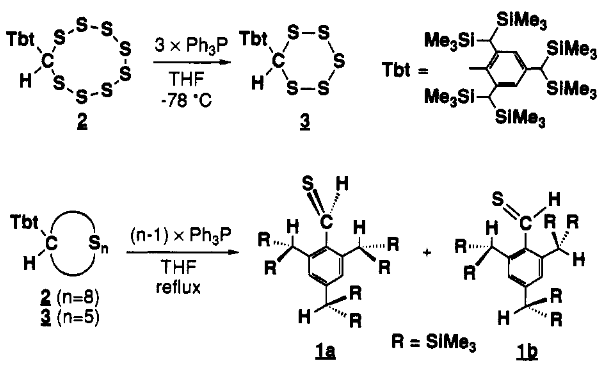
In recent decades, much attention has been focused on thioformyl compounds from the standpoints of not only their unique structure and chemical reactivities but also their potential biological activities.[1] Since our first successful isolation of kinetically stabilized 2,4,6-tri-*tert*-butylthiobenzaldehyde in 1982,[2] considerable progress has been made in the chemistry of thioaldehydes, which are highly reactive and unstable thiocarbonyl compounds under normal conditions. However, the intrinsic nature of this unique functional group has not been fully disclosed because of the limited examples of stable and isolable thioaldehydes.[3]

We have recently succeeded in the synthesis of novel metalanethiones of group 14 metals, Tbt(Tip)M=S (M = Si, Ge, or Sn; Tip = 2,4,6-triisopropylphenyl), as stable compounds[4] via the desulfurization of the corresponding cyclic tetrasulfides, Tbt(Tip)$MS_4$,[5] by taking advantage of a new and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl[6] (denoted as Tbt hereafter).[7] In this paper, we present the synthesis of the first example of rotational isomers of thioaldehydes **1a** and **1b** kinetically stabilized by the Tbt group together with their structural analysis both in the solid state and in solution.

When Tbt-substituted octathionane **2**[8] was treated with triphenylphosphine (1 equiv × 3) in THF at -78 °C, pentathiane **3**[9] was obtained in 64% yield (Scheme 1). On the other hand, desulfurization of **2** with $Ph_3P$ (7 equiv) in refluxing THF for 12 h resulted in the formation of two isomeric thiobenzaldehydes **1a** (purple crystals) and **1b** (green crystals) in 65 and 17% yields, respectively. Pentathiane **3** was also desulfurized with $Ph_3P$ (4 equiv) under similar reaction conditions to give **1a** and **1b** (72 and 17%). Since treatment of **2** with an excess amount of hexamethylphosphorous triamide (*ca.* 15 equiv) in THF at -78 °C afforded only **1a** (69%) as a desulfurized product, the formation of **1b** in the former reactions can be interpreted in terms of the thermal isomerization of **1a** in refluxing THF. The present desulfurization of cyclic polysulfides by trivalent phosphorus reagents represents a novel synthetic approach to thiocarbonyl compounds.

**Scheme 1**



Thioaldehydes **1a** and **1b** were separated and purified by flash column chromatography on silica gel at -20 °C. Both of them were found to be quite stable in the solid state even in the open air, while they underwent very slow decomposition in solution at room temperature (*ca.* 20 °C).

Both **1a** and **1b** showed satisfactory spectral and analytical data[9] characteristic of thiobenzaldehydes [$\delta_H$(CHS) 12.05 and 11.77, $\delta_C$(CHS) 234.1 and 229.8, $^1J_{CH}$(CHS) 162.4 and 156.9 Hz, $\lambda_{max}$(C=S) 587 ($\epsilon$ 30) and 604 (30) nm, for **1a** and **1b**, respectively], and X-ray crystallographic analysis definitively revealed their molecular geometries in the solid state as shown in Figures 1 and 2.[10]

In the case of **1a** both methine hydrogens of the *o*-bis(trimethylsilyl)methyl (disyl) groups confront the thioformyl group with the dihedral angle between the CH=S $\pi$-plane and the benzene ring being 48.7°, while the *o*-disyl groups of **1b** are unsymmetrically oriented toward the thioformyl group and the CH=S $\pi$-plane is almost coplanar with the benzene ring (dihedral angle is 10.6°), suggesting some conjugation between the two $\pi$-systems. The thioformyl hydrogen of **1b** lies between the two trimethylsilyl groups of the overturned *o*-disyl group, and its sulfur atom stands close to the methine hydrogen of the other *o*-disyl group. The thioformyl groups of **1a** and **1b** were found to have completely trigonal planar geometries and short C—S bond lengths [1.588(11) Å for **1a** and 1.602(7) Å for **1b**], which are in good agreement with the calculated C—S bond length for $H_2C$=S (1.599 Å).[11]

Molecular structures of **1a** and **1b** in solution were also investigated by a $^1H\{^1H\}$ nuclear Overhauser effect (NOE)

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[1] (a) Duss, F. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, p 373. (b) Okazaki, R. *Kagaku no Ryoiki* **1983**, *37*, 178. (c) Voss, J. *Houben-Weyl, Methoden der Organische Chemie*; Klamann, D., Ed.; George Thieme Verlag: Stuttgart, 1985; Band 11, p 188. (d) Okazaki, R. *Yuki Gosei Kagaku Kyokaishi* **1988**, *46*, 1149. (e) Usov, V. A.; Timokhina, L. V.; Voronkov, M. G. *Sulfur Rep.* **1992**, *12*, 95. (f) McGregor, W. M.; Sherington, D. C. *Chem. Soc. Rev.* **1993**, 199 and references cited therein.

[2] Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187.

[3] For kinetically stabilized thioaldehydes, see: (a) Vedejs, E.; Perry, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 1683. (b) Vedejs, E.; Perry, D. A.; Wilde, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 2985. (c) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Am. Chem. Soc.* **1987**, *109*, 279. (d) Ando, W.; Ohtaki, T.; Suzuki, T.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7782. See also ref 2. For thioaldehydes thermodynamically stabilized by a mesomeric effect, see ref 1 and references cited therein.

[4] (a) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065. (b) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (c) Tokitoh, N.; Matsuhashi, Y.; Goto, M.; Okazaki, R. *Chem. Lett.* **1992**, 1595. (d) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R. *Organometallics* **1993**, *12*, 2573. (e) Tokitoh, N.; Suzuki, H.; Okazaki, R. Xth International Symposium on Organosilicon Chemistry, Poznan, Poland, 1993; Abstract O-62.

[5] (a) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047. (b) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351.

[6] (a) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1987**, 2293. (b) Okazaki, R.; Unno, M.; Inamoto, N.; Yamamoto, G. *Chem. Lett.* **1989**, 493. (c) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1989**, 791.

[7] Since the abbreviation "Tb" for 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl, which we used so far in our previous papers, may confuse it with a symbol for an element (terbium), we denote this bulky aryl group hereafter as Tbt.

[8] Tokitoh, N.; Takeda, N.; Imakubo, T.; Goto, M.; Okazaki, R. *Chem. Lett.* **1992**, 1599.

[9] Physical properties of new compounds **1a**, **1b**, and **3** are detailed in the supplementary material.

[10] Crystallographic data, compound **1a**: $C_{28}H_{60}SSi_6$, $M$ = 597.35, triclinic, $a$ = 13.230(6) Å, $b$ = 16.658(3) Å, $c$ = 9.488(1) Å, $\alpha$ = 93.30(1)°, $\beta$ = 99.50(2)°, $\gamma$ = 102.92(2)°, $V$ = 2000(1) Å$^3$, $Z$ = 2, space group $P\bar{1}$, $D_c$ = 0.992 g cm$^{-3}$, $\mu$ = 2.68 cm$^{-1}$, final $R$ ($R_w$) = 0.058 (0.055) for 1622 reflections [$I > 3\sigma(I)$] and 316 variable parameters. Compound **1b**: $C_{28}H_{60}SSi_6$, $M$ = 597.35, triclinic, $a$ = 12.596(3) Å, $b$ = 17.866(4) Å, $c$ = 9.453(2) Å, $\alpha$ = 91.25(2)°, $\beta$ = 108.14(2)°, $\gamma$ = 102.38(2)°, $V$ = 1965.8(9) Å$^3$, $Z$ = 2, space group $P\bar{1}$, $D_c$ = 1.009 g cm$^{-3}$, $\mu$ = 2.72 cm$^{-1}$, final $R$ ($R_w$) = 0.057 (0.056) for 2737 reflections [$I > 3\sigma(I)$] and 320 variable parameters (the thioformyl hydrogen was isotropically refined together with the all non-hydrogen atoms). The intensity data ($2\theta < 50.1°$ for **1a** and $2\theta < 55.1°$ for **1b**) were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å), and the structures were solved by direct methods. All the non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were located in calculated positions otherwise noted.

[11] Calculated with HF/DZ (d, p). Nagase, S. Unpublished results.

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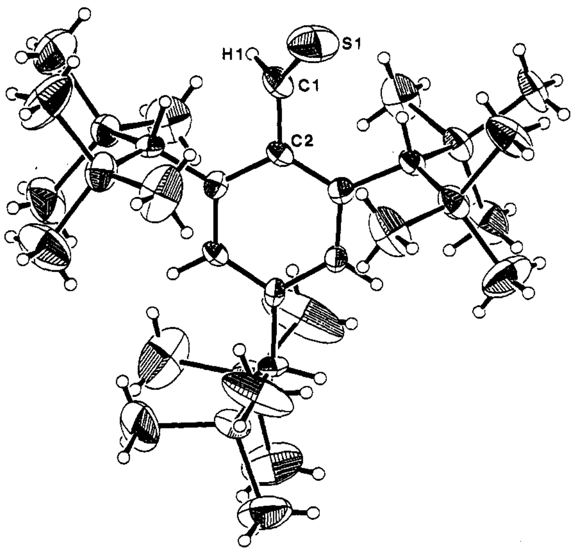

**Figure 1.** ORTEP drawing of TbtCHS (**1a**) with thermal ellipsoid plot (30% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): C(1)–S(1) 1.588(11), C(1)–C(2) 1.469(13), C(1)–H(1) 0.946(11), S(1)–C(1)–C(2) 131.5(9), C(2)–C(1)–H(1) 114(1), S(1)–C(1)–H(1) 114(1).

experiment. The observed difference NOEs for **1a** and **1b** and the absence of enhancement between the thioformyl proton and the methine protons of *o*-disyl groups in **1b** strongly suggested that their molecular structures in solution are essentially identical with those in the solid state.[12]

Of particular note among the chemical properties of these newly obtained thiobenzaldehydes is their thermal interconversion. When **1a** in toluene-$d_8$ was heated in a sealed NMR tube at 50.0 °C, it attained equilibrium with **1b** [$K$(**1b**/**1a**) = 0.271 as determined by $^1$H NMR spectroscopy]. Kinetic studies based on the rate constants for isomerization (**1a** → **1b**) (50.0–80.0 °C) and its equilibrium constants (50.0–140.0 °C) at several temperatures led to the following kinetic and thermodynamic parameters: $\Delta H^{\ddagger} = 21.5 \pm 0.4$ kcal mol$^{-1}$, $\Delta S^{\ddagger} = -13 \pm 1$ cal mol$^{-1}$ K$^{-1}$, $\Delta H^{\circ} = 0.27 \pm 0.02$ kcal mol$^{-1}$, and $\Delta S^{\circ} = -1.77 \pm 0.07$ cal mol$^{-1}$ K$^{-1}$. The value of $\Delta H^{\ddagger}$ is large enough for these two isomers to be isolated as stable and discrete thioaldehydes, and the $\Delta H^{\circ}$ value indicates that **1a** is thermodynamically more stable than **1b** as a result of more severe steric congestion around the thioformyl group of **1b** than that of **1a**.

We are aware that the isolation of **1a** and **1b** provides an interesting possibility of studying the reactivity of conformational isomers of thioaldehydes.[13] We have preliminarily found that competitive reaction of **1a** and **1b** (1:1 mixture) with an equimolar amount of hydrazine monohydrate in dichloromethane at 0 °C results in the quantitative formation of the corresponding hydrazone of **1a** with **1b** being completely recovered although **1b** alone undergoes slow but quantitative hydrazone formation under the identical conditions. Further investigation on the reactivity of the conformational isomers is currently in progress.

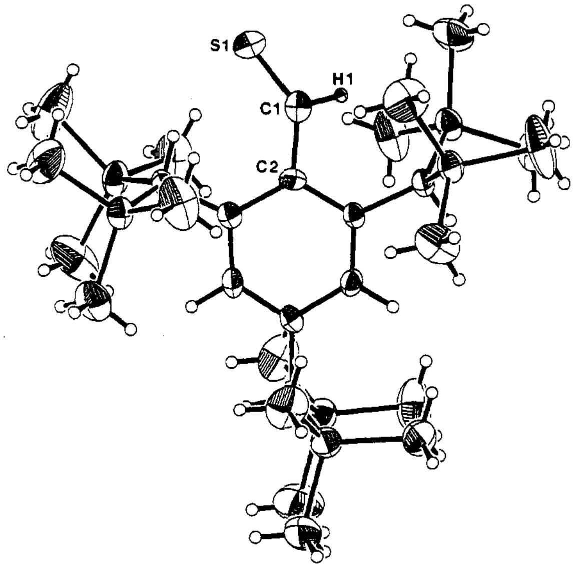

**Figure 2.** ORTEP drawing of TbtCHS (**1b**) with thermal ellipsoid plot (30% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): C(1)–S(1) 1.602(7), C(1)–C(2) 1.433(8), C(1)–H(1) 0.89(5), S(1)–C(1)–C(2) 137.6(6), C(2)–C(1)–H(1) 110(4), S(1)–C(1)–H(1) 112(4).

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**Supplementary Material Available:** Physical properties of compounds **1a**, **1b**, and **3**, schematic views of the observed NOEs for **1a** and **1b**, and crystallographic data with complete tables of bond lengths, angles, and thermal and positional parameters for **1a** and **1b** (48 pages); tables of observed and calculated structure factors for **1a** and **1b** (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[12] The results of the NOE experiments for **1a** and **1b** are listed in the supplementary material.

[13] For a review on the reactivity of conformational isomers, see: Oki, M. *Acc. Chem. Res.* **1984**, *17*, 154.