Journal of Organometallic Chemistry 808 (2016) 1–11

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Organo-functionalized trimethoxysilanes featuring thioester linkage: Synthetic and UV–Vis spectral investigations

Gurjaspreet Singh*, Sunita Rani, Amandeep Saroa, Aanchal Arora

*Department of Chemistry, Panjab University, Chandigarh, 160014, India*

ARTICLE INFO

*Article history:*
Received 27 November 2015
Received in revised form
5 February 2016
Accepted 8 February 2016
Available online 11 February 2016

*Keywords:*
Organosilanes
Thioester
Solvatochromism
Kamlet-Taft equation

ABSTRACT

The current work reveals a series of new organo-functionalized trimethoxysilanes (OfTMS) linked *via* a 3C tether to the thioester group along with the inclusion of versatile aromatic and heteroaromatic sequences. The synthetic procedure implicates the one-pot thioesterification reaction of the precursor carboxylic acids (**1a-r**) with 3-mercaptopropyltrimethoxysilane (MPTMS), stimulated by 1,1′-carbonyldiimidazole (CDI). The OfTMS have been attentively characterized by elemental analysis, infrared and [$^{1}$H, $^{13}$C] NMR spectroscopic techniques. The UV–Vis absorption behaviour demonstrates that the alkoxysilanes possess high sensitivity to the changes caused in the environment on account of different substitutions. Furthermore, the solvent effect on the absorption spectra has been scrutinized and quantified using the Kamlet-Taft approach. Importantly, the fabricated stable alkoxysilanes can be aspired for advance applications in the field of material science.



## 1. Introduction

Organically modified silanes, Y–$(CH_2)_3$–$SiX_3$ consist of the hydrolysable silyl bonds with alkoxy, amine, acyloxy, glycidyloxy or halogen units (X) and a substituent Y which provides structural malleability for the explicit functioning [1,2]. The organosilanes represent a fiercely developing branch of synthetic chemistry having the utmost importance in organic synthesis, metal complexes, catalysis, drug designing, polymers, analyte sensing and HPLC packing [3]. The assimilation of fascinating organic fragments with the trialkoxysilyl moiety is grabbing even more attention. This is because of their potential to react with both inorganic and organic substrates, adhesives, as well as other alkoxysilane derivatives to form multifarious organic-inorganic hybrids, dominant in nanomaterial and polymer science [4]. So far in the field of siliceous materials, alkoxysilanes have been the most common platform for the functionalization of metal oxide surface by siloxane bonding, along with an ease of handling and smooth reaction governance abilities [5].

The exploitation of smaller organic transformations that employ simple synthetic steps to provide maximum structural diversity within a single molecular framework is a deep-rooted area in the organosilicon chemistry [6]. However, more discreet measurements are required during the synthesis of organosilanes so that the organic moiety cannot interfere with the susceptible silyl part [7]. Conventional approaches to synthesize alkoxysilanes involve cross-coupling, hydrosilylation, transmetalation and replacement reactions [8]. The expensive metals involved, limited functional group tolerance, lower product yields, tedious isolation and purification techniques were the major shortcomings of these methodologies.

On the other hand, carboxylic acids are ubiquitous in the form of natural products, transition metal complexes, pharmaceutics and polymers etc. [9] The carboxyl group and its derivatized forms, for instance amide, ester, anhydride, carbamate etc. have been incorporated as an organic linker to the trialkoxysilyl moiety [7,10]. To-date, the blending of thioester unit with the silyl fragment is rarely reported and that too has been achieved by the complicated synthetic pathways [11]. The thioesters are biologically important motifs having vital roles in living cells, explicitly as intermediate for acyl group transfer reaction in metabolic processes and in the biosynthesis of polyketides and nonribosomal polypeptides [12]. Not only pharmacologically, these mono S-analogues of oxyesters are actively involved in organic synthesis such as asymmetric addition, aldol and Michael reactions etc. [13] Keeping the above perspectives in mind and extending our research interest on the alkoxysilanes [14], we have now designed an efficacious synthetic route in which atmospheric reaction conditions are employed. The rationale behind the synthesis of an array of compounds is to have a better visualization of the effect of incorporating different aromatic

* Corresponding author.
*E-mail address:* gjpsingh@pu.ac.in (G. Singh).

http://dx.doi.org/10.1016/j.jorganchem.2016.02.013
0022-328X/

rings (**3a-i**) as well as the electronic nature of the substituent attached at the phenyl ring (**3j-r**) on the UV–Vis absorption profiles and solvatochromic properties.

The paper is organized as follows: Firstly, the synthetic procedure and characterization of new OfTMS bearing thioester linkage are described. Secondly, we have discussed the UV–Vis spectra of the silanes and then continued with the investigation on the solvatochromic behaviour of these compounds where substitution effect is clearly observed. Finally in the end, an appropriate conclusion is presented to summarize the paper.

## 2. Experimental

### 2.1. Materials and equipments

All carboxylic acids (Aldrich), MPTMS (Avra) and CDI (Avra) were used directly as received. The $^1$H and $^{13}$C NMR spectra were recorded on a JEOL (AL 300 MHz) spectrometer using $CDCl_3$ as an internal reference and chemical shifts were reported relative to tetramethylsilane. Electronic spectral measurements were carried out using a JASCO V-530 UV–Vis spectrophotometer. The infrared spectra were recorded as neat spectra on a Thermo Scientific NICOLET IS50 spectrophotometer. Elemental analysis was obtained on Perkin Elmer Model 2400 CHNS elemental analyzer and Thermo Scientific Flash 2000 organic elemental analyzer.

### 2.2. General procedure for the synthesis of OfTMS (**3a-r**)

1 equiv. of the respective carboxylic acid (**1a-r**) and 1.20 equiv. of CDI were mixed in THF (20 ml) at room temperature in a round bottomed flask. The reaction mixture was heated to reflux for 1 h while evolution of the by-product carbon dioxide gas started within 10–15 min. After cooling to room temperature, the addition of MPTMS (1 equiv.) was carried out and heating was continued for 8 h. The reaction mixture was diluted with water and the aqueous layer was extracted with dichloromethane (15 ml). The combined organic layer was washed with brine (25%) and dried over anhydrous $Na_2SO_4$. The mixture was concentrated in *vacuo* to furnish highly viscous oil as the desired product.

#### 2.2.1. S-3-(trimethoxysilyl)propyl benzothioate (**3a**)

The quantities used were as follows: **1a** (0.50 g, 4.09 mmol), CDI (0.80 g, 4.91 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{13}H_{20}O_4SSi$: C, 51.97; H, 6.71; S, 10.67. Found: C, 51.91; H, 6.67; S, 10.59. IR (neat, $cm^{-1}$): 1648 ($\nu$ C=O), 1075 ($\nu$ Si–O), 684 ($\nu$ C–S). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.67 (m, 2H, $SiCH_2$), 1.69 (m, 2H, $CCH_2C$), 2.99 (t, 2H, $CH_2S$, $J$ = 7.3 Hz), 3.47 (s, 3H, $OCH_3$), 7.33 (t, 2H, $H^{3,5}$, $J$ = 8.1 Hz), 7.43 (d, 1H, $H^4$, $J$ = 8.3 Hz), 7.86 (d, 2H, $H^{2,6}$, $J$ = 8.0 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 8.64 ($SiCH_2$), 20.33 (C**C**H$_2$C), 31.44 ($CH_2S$), 50.09 ($OCH_3$), 127.03 ($C^{2,6}$), 128.27 ($C^{3,5}$), 132.87 ($C^4$), 137.19 ($C^1$), 191.02 (C=O).

#### 2.2.2. S-3-(trimethoxysilyl)propyl pyridine-2-carbothioate (**3b**)

The quantities used were as follows: **1b** (0.50 g, 4.06 mmol), CDI (0.79 g, 4.88 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{12}H_{19}NO_4SSi$: C, 47.81; H, 6.35; N, 4.65; S, 10.64. Found: C, 47.78; H, 6.33; N, 4.60; S, 10.59. IR (neat, $cm^{-1}$): 1653 ($\nu$ C=O), 1088 ($\nu$ Si–O), 688 ($\nu$ C–S). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.56 (m, 2H, $SiCH_2$), 1.62 (m, 2H, $CCH_2C$), 3.06 (t, 2H, $CH_2S$, $J$ = 7.3 Hz), 3.49 (s, 9H, $OCH_3$), 7.22 (m, 1H, $H^4$), 8.04–8.11 (m, 1H, $H^3$), 8.52 (d, 1H, $H^2$, $J$ = 4.7 Hz), 8.92 (s, 1H, $H^5$). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.37 ($SiCH_2$), 18.48 ($CCH_2C$), 37.98 ($CH_2S$), 57.66 ($OCH_3$), 123.29 ($C^2$), 131.43 ($C^4$), 135.42 ($C^3$), 147.88 ($C^5$), 151.49 ($C^1$), 190.69 (C=O).

#### 2.2.3. S-3-(trimethoxysilyl)propyl pyridine-3-carbothioate (**3c**)

The quantities used were as follows: **1c** (0.50 g, 4.06 mmol), CDI (0.79 g, 4.88 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{12}H_{19}NO_4SSi$: C, 47.81; H, 6.35; N, 4.65; S, 10.64. Found: C, 47.72; H, 6.28; N, 4.60; S, 10.59. IR (neat, $cm^{-1}$): 1655 ($\nu$ C=O), 1084 ($\nu$ Si–O), 680 ($\nu$ C–S). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.58 (m, 2H, $SiCH_2$), 1.64 (m, 2H, $CCH_2C$), 2.97 (t, 2H, $CH_2S$, $J$ = 7.3 Hz), 3.56 (s, 9H, $OCH_3$), 7.24 (t, 1H, $H^4$, $J$ = 5.5 Hz), 8.09 (t, 1H, $H^3$, $J$ = 5.7 Hz), 8.54 (d, 1H, $H^5$, $J$ = 4.7 Hz), 8.94 (s, 1H, $H^1$). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 8.84 ($SiCH_2$), 17.63 (C**C**H$_2$C), 31.26 ($CH_2S$), 50.25 ($OCH_3$), 120.24 ($C^4$), 127.32 ($C^2$), 136.82 ($C^3$), 149.04 ($C^5$), 152.32 ($C^1$), 193.07 (C=O).

#### 2.2.4. S-3-(trimethoxysilyl)propyl pyridine-4-carbothioate (**3d**)

The quantities used were as follows: **1d** (0.50 g, 4.06 mmol), CDI (0.79 g, 4.88 mmol), MPTMS (0.80 ml, 4.08 mmol). Anal. Calcd. for $C_{12}H_{19}NO_4SSi$: C, 47.81; H, 6.35; N, 4.65; S, 10.64. Found: C, 47.78; H, 6.39; N, 4.60; S, 10.59. IR (neat, $cm^{-1}$): 1657 ($\nu$ C=O), 1090 ($\nu$ Si–O), 683 ($\nu$ C–S). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.59 (m, 2H, $SiCH_2$), 1.65 (m, 2H, $CCH_2C$), 2.86 (t, 2H, $CH_2S$, $J$ = 7.3 Hz), 3.51 (s, 9H, $OCH_3$), 7.61 (d, 2H, $H^{2,5}$, $J$ = 5.8 Hz), 8.56 (d, 2H, $H^{3,4}$, $J$ = 5.8 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.35 ($SiCH_2$), 15.30 (C**C**H$_2$C), 37.20 ($CH_2S$), 60.94 ($OCH_3$), 150.44 ($C^1$), 165.64 ($C^{3,4}$), 191.59 (C=O).

#### 2.2.5. S-3-(trimethoxysilyl)propyl pyrazine-2-carbothioate (**3e**)

The quantities used were as follows: **1e** (0.50 g, 4.03 mmol), CDI (0.78 g, 4.83 mmol), MPTMS (0.79 ml, 4.03 mmol). Anal. Calcd. for $C_{11}H_{18}N_2O_4SSi$: C, 43.69; H, 6.00; N, 9.26; S, 10.60. Found: C, 43.62; H, 5.96; N, 9.29; S, 10.53. IR (neat, $cm^{-1}$): 1659 ($\nu$ C=O), 1087 ($\nu$ Si–O), 680 ($\nu$ C–S). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.69 (m, 2H, $SiCH_2$), 1.74 (m, 2H, $CCH_2C$), 2.99 (t, 2H, $CH_2S$, $J$ = 7.2 Hz), 3.48 (s, 9H, $OCH_3$), 8.56 (m, 1H, $H^4$), 8.71 (m, 1H, $H^3$), 9.06 (m, 1H, $H^2$). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.63 ($SiCH_2$), 20.92 ($CCH_2C$), 32.31 ($CH_2S$), 51.26 ($OCH_3$), 141.94 ($C^{2,3}$), 143.65 ($C^4$), 148.32 ($C^1$), 192.62 (C=O).

#### 2.2.6. S,S-bis(3-(trimethoxysilyl)propyl) pyridine-2,3-bis(carbothioate) (**3f**)

The quantities used were as follows: **1f** (0.50 g, 2.99 mmol), CDI (1.16 g, 7.18 mmol), MPTMS (1.17 ml, 5.97 mmol). Anal. Calcd. for $C_{19}H_{33}NO_8S_2Si_2$: C, 43.57; H, 6.35; N, 2.67; S, 12.24. Found: C, 43.51; H, 6.19; N, 2.62; S, 12.20. IR (neat, $cm^{-1}$): 1665 ($\nu$ C=O), 1075 ($\nu$ Si–O), 689 ($\nu$ C–S). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.63 (m, 4H, $SiCH_2$), 1.62 (m, 4H, $CCH_2C$), 2.85 (t, 2H, $CH_2S$, $J$ = 7.3 Hz), 3.05 (t, 2H, $CH_2S$, $J$ = 7.3 Hz), 3.43 (s, 9H, $OCH_3$), 3.47 (s, 9H, $OCH_3$), 7.57 (t, 1H, $H^4$, $J$ = 8.1 Hz), 7.77 (d, 1H, $H^5$, $J$ = 9.1 Hz), 8.79 (d, 1H, $H^3$, $J$ = 9.1 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 8.90 ($SiCH_2$), 15.98 ($CCH_2C$), 33.35 ($CH_2S$), 50.51 ($OCH_3$), 122.28 ($C^2$), 126.96 ($C^4$), 151.55 ($C^3$), 155.16 ($C^{1,5}$), 190.74 (C=O), 191.91 (C=O).

#### 2.2.7. S,S-bis(3-(trimethoxysilyl)propyl) pyridine-2,6-bis(carbothioate) (**3g**)

The quantities used were as follows: **1g** (0.50 g, 2.99 mmol), CDI (1.16 g, 7.18 mmol), MPTMS (1.17 ml, 5.97 mmol). Anal. Calcd. for $C_{19}H_{33}NO_8S_2Si_2$: C, 43.57; H, 6.35; N, 2.67; S, 12.24. Found: C, 43.49; H, 6.30; N, 2.63; S, 12.18. IR (neat, $cm^{-1}$): 1650 ($\nu$ C=O), 1070 ($\nu$ Si–O), 678 ($\nu$ C–S). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.59 (m, 4H, $SiCH_2$), 1.77 (m, 4H, $CCH_2C$), 3.03 (t, 4H, $CH_2S$, $J$ = 7.4 Hz), 3.46 (s, 18H, $OCH_3$), 7.96 (t, 1H, $H^3$, $J$ = 9.1 Hz), 8.26 (d, 2H, $H^{2,4}$, $J$ = 7.9 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 10.27 ($SiCH_2$), 16.85 ($CCH_2C$), 38.10 ($CH_2S$), 50.77 ($OCH_3$), 125.21 ($C^3$), 139.21 ($C^{2,4}$), 149.57 ($C^{1,5}$), 192.32 (C=O).

#### 2.2.8. S-3-(trimethoxysilyl)propyl furan-2-carbothioate (**3h**)

The quantities used were as follows: **1h** (0.50 g, 4.46 mmol), CDI (0.87 g, 5.37 mmol), MPTMS (0.87 ml, 4.44 mmol). Anal. Calcd. for