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Short Communication

Synthesis and Characterization of Silatranes Possessing Biphenylcarboxylate as Exocyclic Substituent

Gurjaspreet Singh* and Amandeep Saroa

*Department of Chemistry, Punjab University, Chandigarh 160014, **INDIA**

Email: gurjaspreet@gmail.com

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ABSTRACT

*(4-biphenylcarboxlate)triethoxysilane **2** was synthesized by the reaction of chlorotriethoxysilane **1** and 4-biphenylcarboxylic acid. New silatranes possessing 4-biphenylcarboxlate as exocyclic substituent **3-6** were prepared by the transesterification reaction of silane **2** with different tripodal ligands. The structures of these silatranes **3-6** have been established by elemental analyses, spectroscopic techniques (IR, ^{1}H and ^{13}C NMR) as well as by mass spectrometry.*

Keywords: Silatranes, Silane, Biphenylcarboxylate, Chlorotriethoxysilane.

INTRODUCTION

The self-assembled metal-organic frameworks containing metal ions and organic building blocks are rapidly expanding in recent years due to potential applications in the areas of nonlinear optics, catalysis, magnetism, gas storage, and electrical conductivity and diverse topologies [1-4]. The carboxylate ligands have been proven to be excellent candidates owing to their diversified coordination modes and interesting structures [5,6]. To best of our knowledge, silatranes possessing carboxlate group as exocyclic group are reported less. Prompted by these studies, we have synthesized silane and its silatranes incorporating biphenylcarboxylate group at axial position in this manuscript. Silatranes are studied extensively due to structural aspects, especially N→Si transannular bond in distorted trigonal bipyramid geometry at silicon atom [7-10]. These compounds are important because of the stereoelectronic effect of silatranyl group in shaping the reactivity of exocyclic functional groups apical to the transannular bond [11-12]. The modern chemists have boosted work on the modification of exocyclic functional groups due to enhanced biological and material science application of modified silatranes [14-16].

MATERIALS AND METHODS

All the syntheses were carried out under nitrogen atmosphere using the Schlenk technique. Toluene, tetrahydrofuran, ether and hexane were distilled over sodium pieces. Silicon tetrachloride (Aldich), ethanol (Aldich), trisisopropanolamine (Aldich), triethanolamine (Aldich), tris(2-aminoethyl)amine (Aldich), 2,4-dimethylphenol (Aldich) and 4-biphenylcarboxylic acid (SDFCL) were used without any purification.

Infrared spectra were obtained with a Thermo Nicolet Nexus 670 spectrometer. C, H and N analyses of samples were performed on a FLASH-2000 organic element analyzer while Cl and Si contents were estimated gravimetrically. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using a 300 MHz (JEOL AL 300) FT NMR instrument. Chemical shifts for the protons were reported using tetramethylsilane (TMS) as an internal reference. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer. The chlorotriethoxysilane **1** was synthesized as reported in literature [17].

SYNTHESIS

1-(4-biphenylcarboxlate)triethoxysilane (2): In two neck round bottom flask, mixture of 4-biphenyl carboxylic acid (1g, 5.05 mmol) and triethylamine (0.80 mL, 5.97 mmol) in 20 mL THF was stirred at 0-5 ^{o}C and chlorotriethoxysilane (1.00 mL, 5.05 mmol) was added dropwise with stirring. The reaction mixture was stirred at room temperature for 20 h. Triethylammonium chloride salt was filtered off and filtrate was evaporated under vacuum. Colorless oil was obtained. Yield: (1.65 mL, 91%). IR (KBr, cm^{-1}) = 719 s, 765 s (υ_s Si-O), 1075 vs (υ_{as} Si-O), 1128 vs (υ C-O), 1705 m (υ_s C=O), 1768 s (υ_{as} C=O), 2882, 2927 s (υ_s CH_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.19 (t, 9H, *J* = 7.2 Hz, CH_3), 3.83 (t, 6H, *J* = 7.2 Hz, OCH_2), 7.38-8.12 (m, 9H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 18.14 (CH_3), 51.62 (OCH_2), 129.47-139.23 (Ar-C), 164.91 (C=O).

1-(4-biphenylcarboxylate)-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3.]undecane (3): A solution of tri ethanolamine (0.36 g, 2.77 mmol) in anhydrous benzene was stirred for 5 min and silane **2** (1.00 mL, 2.77 mmol) was added drop wise. The solution was refluxed for 4 h in a flask fitted with Dean-Stark apparatus. The solvent was evaporated under vacuum and dry ether (10 ml) was added. The white color solid was obtained. Yield: 0.89 g (84%). M.p.: > 220 °C. Anal. Calcd for $C_{20}H_{24}NO_5Si$ (386): C, 62.15; H, 6.26; N, 3.62; Si, 7.27. Found: C, 61.96; H, 6.19; N, 3.49; Si, 7.12. IR (cm^{-1}): 582 m (υ N→Si), 709 s, 755 s (υ_s Si-O), 1096 vs (υ_{as} Si-O), 1124 vs (υ C-O), 1719 m (υ_s C=O), 1764 s (υ_{as} C=O), 2879, 2929 s (υ_s CH_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.81 (t, 6H, *J* = 5.8 Hz, NCH_2), 3.64 (t, 6H, *J* = 5.8 Hz, OCH_2), 7.57-8.13 (m, 9H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 50.81 (NCH_2), 57.61 (OCH_2), 129.87-140.39 (Ar-C), 165.10 (C=O). MS: *m/z* (relative abundance (%), assignment): 150 (7.4), 174 (21.5), 387 (100, $M+H)^+$.

1-(4-biphenylcarboxylate)-3,7,10-trimethyl-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3.]undecane (4): This silatrane **4** was synthesized following a similar procedure as described for silatrane **2** except trisisopropanolamine (0.53 g, 2.77 mmol) was used instead of triethanolamine. Yield: 0.92 g (77 %). M.p.: >220 °C. Anal. Calcd for $C_{23}H_{30}NO_5Si$ (427): C, 64.46; H, 7.06; N, 3.27; Si, 6.55. Found: C, 64.21; H, 6.92; N, 3.13; Si, 6.43. IR (cm^{-1}): 578 m (υ N→Si), 720 s, 761 s (υ_s Si-O), 1087 vs (υ_{as} Si-O), 1113 vs (υ C-O), 1717 m (υ_s C=O), 1766 s (υ_{as} C=O), 2881, 2926 s (υ_s CH_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.17 (m, 9H, CH_3), 2.62 (m, 6H, NCH_2), 3.78 (t, 3H, *J* = 5.8 Hz, OCH), 7.57-8.29 (m, 9H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 20.21, 20.45, 20.52 (CH_3), 61.63, 61.78, 61.87 (NCH_2), 65.24, 65.41, 66.67 (OCH), 127.36-141.74 (Ar-C), 165.29 (C=O). MS: *m/z* (relative abundance (%), assignment) = 192 (13.4), 216 (33.53), 428 (100).

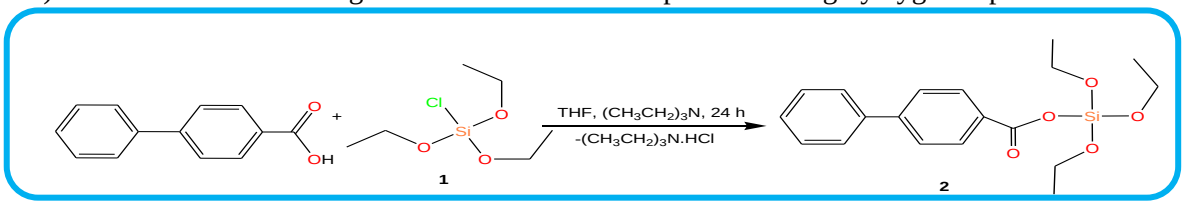
1-(4-biphenylcarboxylate)-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4',6'-dimethylbenzo)[4.4.4.0]tri cyclo-tetradecane (5): This silatrane **5** was synthesized following a similar procedure as described for silatrane **2** except tris(2-hydroxy-3,5-dimethylbenzyl)amine (1.16 g, 2.77 mmol) was used instead of triethanolamine. Yield: 1.40 g (78%). M.p.: >240 °C. Anal. Calcd for $C_{40}H_{39}NO_5Si$ (641): C, 74.62; H, 6.42; N, 2.18; Si, 4.36. Found: C, 74.36; H, 6.29; N, 2.60; Si, 4.14. IR (Nujol, KBr, cm^{-1}) = 593 m (υ N→Si), 1089 (Si-O), 1132 (C-O), 1723 m (υ_s C=O), 1759 s (υ_{as} C=O), 2879, 2925 s (υ_s CH_2). ^{1}H NMR (300 MHz, DMSO/$CDCl_3$): δ (ppm) = 2.15 (s, 9H, Ar-CH_3), 2.20 (s, 9H, Ar-CH_3), 4.23 (s, 6H, NCH_2), 6.82 (s, 3H, Ar-H), 6.91 (s, 3H, Ar-H), 7.34-8.13 (Ar-H). ^{13}C NMR (75 MHz, DMSO/$CDCl_3$): δ (ppm) =

17.82 (Ar-***C***H_3)**,** 19.58 (Ar-***C***H_3), 51.14 (NCH_2), 116.92-150.75 (Ar-C), 166.79 (C=O). MS: *m/z* (relative abundance (%), assignment) = 642 (42.80, $M+H)^+$.

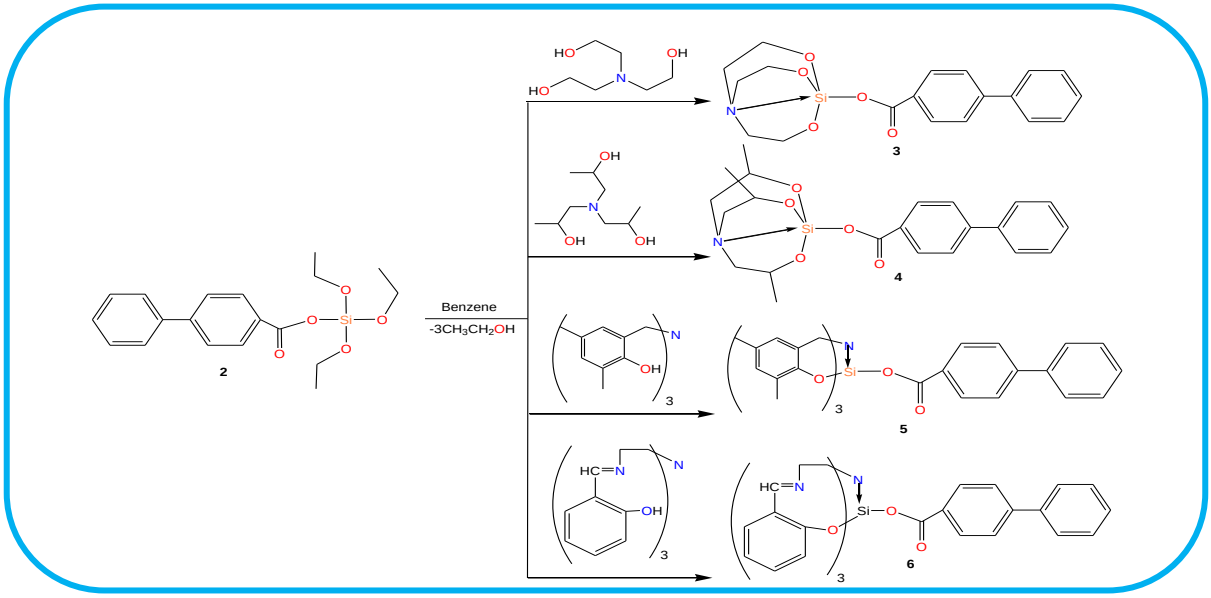
1-(4-biphenylcarboxylate)-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(benzylideneethyleimine)[4.4.4.0]tricyclo-tetradecane (6): This silatrane **6** was synthesized following a similar procedure as described for silatrane **2** except tris(2-hydroxybenzylideneethylimine)amine (1.27 g, 2.77 mmol) was used instead of triethanolamine. Yield: 1.32 g (70 %). M.p.: >240 °C. Anal. Calcd for $C_{40}H_{36}N_4O_5Si$ (680): C, 70.36; H, 5.61; N, 8.20; Si, 4.11. Found: C, 69.85; H, 5.50; N, 7.90; Si, 4.02. IR (Nujol, KBr, cm^{-1}) = 590 m (υ N→Si), 1092 (Si-O), 1125 (C-O), 1640 (C=N),1718 m (υ_s C=O), 1757 s (υ_{as} C=O), 2884, 2932 s (υ_s CH_2). ^{1}H NMR (75 MHz, DMSO/$CDCl_3$): δ (ppm) = 3.12 (t, 6H, NCH_2), 3.84 (t, 6H, NCH_2), 7.31-8.02 (m, 21H, Ar-H), 8.27 (s, 3H, CH=N). ^{13}C NMR (75 MHz, DMSO/$CDCl_3$): δ (ppm) = 42.57 (NCH_2), 52.26 (NCH_2), 120.38-143.56 (Ar-C), 162.70 (CH=N). MS: *m/z* (relative abundance (%), assignment) = 681 $(49.78, M+H)^+$.

RESULTS AND DISCUSSION

The silane **2** was prepared by the reaction of chlorotriethoxysilane **1** with 4-biphenycarboxlyic acid at 0 ^oC in the presence of slightly excess triethylamine base as depicted in scheme 1. The triethylammonium chloride salt and silane **2** are separated on the basis of solubility in THF. In this series, silatrane **3-6** were synthesized by transesterification reaction of silane **1** with different tripodal ligands i.e. triethanolamine, trisisopropanolamine, tris(2-hydroxy-3,5-dimethylbenzyl)amine and tris(2-hydroxybenzylidene ethyl imine)amine as shown according to the scheme 2. All compounds are highly hygroscopic.



Scheme 1. Synthesis of biphenylcarboxylatetriethoxysilane **2**.



Scheme 2. Synthesis of 4-biphenylcarboxylatesilatranes **3-6**.

IR Spectroscopy: The absorption peaks of significance are those of C=O, Si-O and Si→N bonds for silatranes **3-6**. Si-O stretching vibration is assigned to the bands present 1095-1060 cm^{-1}. In addition, symmetric deformational vibration of the silatranyl skeleton with a predominant contribution from the N→Si bond is observed in the region 590-570 cm^{-1}. The typical absorption band for C=O is assigned in the region 1730-1710 cm^{-1} for symmetric stretching and 1770-1655 cm^{-1} for anti-symmetric stretching .

NMR spectroscopy: Multinuclear (^1H and ^{13}C) NMR spectra are consistent with the structure of prepared compound. The silane **2** depicts triplet and quartet for ethoxy group which are replaced by atranyl moiety formed by tripodal ligands. The atrane moiety i.e. $Si(OCH_2CH_2)_3N$ in compound **3** contains two triplets at 2.81 and 3.84 ppm. It is noteworthy that each CH_3 group of $Si(CH_2CH(O)CH_3)_3N$ moiety in case compound **4** shows own doublet due to steric factors. Therefore, ^1H NMR shows three doublets at this region due to CH_3 group. The downfield shifts are observed for CH_2 and CH group in compound **4** as compared to compound **3** as in ^1H NMR spectra. For compound **5**, silatrane contains six membered ring i.e. $N[(CH_2(Me_2C_6H_2)O]_3Si$ possessing three singlets at 4.23, 6.82 and 6.91 ppm for NCH_2 and aromatic protons of atrane ring respectively. The compound **6** shows a singlet at 8.27 ppm for CH=N. In ^{13}C NMR, alkoxy carbons of silane **2** appeared more shielded at 18.14 and 51.62 ppm than atranyl moiety carbons appeared at 50.81 and 57.81 ppm for compound **3**. Same trend in chemical shifts is observed for ^{13}C NMR in case of compound **4** as observed in ^1H NMR. On comparing the ^1H and ^{13}C NMR spectra of the silatranes with that of the silane **2**, a downfield shift for the protons and carbon atoms of the CH_2N moiety in all compounds are observed which supports desired compound synthesis. The least shielded carbons appeared for >C=O in range of $\delta \approx 165.20$-166.50 ppm.

Mass spectrometry: Mass spectra of the all compound **3-6** have shown the common features of silatrane and the respective molecular ion peaks appears in spectra. Besides the molecular ion peak, a silatranyl ion at m/e=174 and m/e=216 peaks observed which are corresponded to characteristic feature of mass spectrum of C-substituted silatrane involving the fragmentation of X-Si bond for silatranes **3** and **5** respectively. The molecular ion peak was more abundant as compared as compared to silatranyl ion peak.

APPLICATIONS

- 1-Chloro-methylsilatrane prevents the loss of calcium from the bones of skeleton and manifests by an increase in permeability of connective tissues, blood vessels and follicles in animals [18].
- Hypervalent silicon complexes like 3`-O-(trimethyl)silatranylthymidine and 3'-O-silatranylthymidine have been found to be active for treating cancers of breast, central nervous system and lung. Hypervalent silicon complexes produced by incorporating a 5-fluorouracil moiety are also active for treating cancer [19].
- 1-Ethoxysilatrane is used for improving productivity of farm animals, birds and beneficial insects. Toxicity of hypervalent silicon compounds has been examined and a rodenticide 1-(3-chlorophenyl)silatrane has been commercialized [20].
- Hypervalent silicon compounds have found application in the production of silicon containing polymer based compositions for electric insulating coating films having suitable uniform thickness and good dielectric constants [21].
- A silatrane with moiety $p\text{-}FcC_6H_4COOSi(OCH_2CH_2)_3N$ is found to be active against bacteria such as *Gibberella saubinetii*, *Cladosporium fulvum*, and *Isariopsis clavispor* [22]. Metal complexes of 3-formylchromoniminopropylsilatrane show antimicrobial activity against various bacteria such as *K. pneumoniae, S. aureus, E. coli and B. subtilis* [23].

CONCLUSIONS

4-Biphenylcarboxylate incorporating silatranes have been reported in good yield. The spectroscopic techniques have supported structure of compounds. These silatranes would be very useful in biological and

material science applications. 4-Biphenylcarboxylate silatranes could act as coordinating agent with other metals.

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