



Substituted phenyl urea and thiourea silatranes: Synthesis, characterization and anion recognition properties by photophysical and theoretical studies



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ABSTRACT

A series of functionalized phenyl unsymmetrical urea and thiourea possessing silatranes **3–8** were synthesized in good yields by the rearrangement reaction of electrophiles 1-isocyanato-4-nitrobenzene, 1-isothiocyanato-4-nitrobenzene, 1-isocyanato-4-methoxybenzene, 1-isothiocyanato-4-methoxybenzene, 1-isothiocyanatobenzene with primary amines 3-aminopropylsilatrane **1** and 3,7,10-trimethyl substituted 3-aminopropylsilatrane **2** acting as nucleophiles. All the compounds were characterized by elemental analysis, spectroscopic techniques and X-ray diffraction analysis in the case of **3**, **6** and **8**. The functionalized phenyl unsymmetrical urea and thiourea possessing silatranes **3–8** are categorized into three sub series depending upon the electron withdrawing or releasing effect of the groups attached to the silatrane's axial position and based on these observations, we describe the effect of each category on the electronic properties via solution state studies i.e. photophysical studies (UV–Vis absorption and fluorescence emission spectra). The geometries of all the compounds are optimized at the DFT/6-31+G(d) level using quantum mechanical calculations for supporting the photophysical studies.

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1. Introduction

Silatranes and their derivatives constitute a class of neutral pentacoordinate silicon compounds with the notable feature of the transannular interaction between the silicon center and the nitrogen group [1–3]. These compounds are significant because of the stereoelectronic effect of silatranyl group in shaping the reactivity of exocyclic functional groups apical to the transannular bond [4,5]. The contemporary chemists have boosted this work on the modification of exocyclic functional groups due to enhanced biological and material science application of modified silatranes [6,7].

3-Aminopropylsilatrane and its derivatives are well known precursors for the modification of silatranes at axial position which is very helpful for the incorporation of properties of both silatrane and its axial group [8,9]. One of the important derivatization reaction of 3-aminopropylsilatrane is rearrangement reaction with isocyanates and isothiocyanates for the synthesis of urea and thiourea derivatives. As urea and thiourea derivatives are notable

choices for researchers due to their considerable industrial and biological importance, so integrating silatranes with urea and thiourea groups may lead to incorporation of some novel properties [10–13]. So, we herein report the synthesis of substituted phenyl urea and thiourea silatranes **3–8** by the reaction of isocyanates and isothiocyanates with compounds containing nitrogen–hydrogen bonds i.e. 3-aminopropylsilatrane **1** and 3,7,10-trimethyl substituted 3-aminopropylsilatrane **2**.

Urea and thiourea are very promising building blocks for anion receptors as firstly they contribute two relatively strong hydrogen-bonding sites resulting in stable hydrogen bonded complexes and secondly urea and thiourea possessing compounds can be simply synthesized from commercially available reagents by a single-step reaction [14–16]. Nowadays, several urea and thiourea derivatives are widely used as spacer units bearing anion binding sites that proved to be an efficient signature linker for anion sensors [17–20]. Prompted by these observations, our research is focused on the synthesis of new compounds involving both “metal coordination chemistry” and its young sister “anion coordination chemistry”. To assess their anion recognition properties, photophysical studies are carried out against various anions which have demonstrated selective sensing of six silatranes towards acetate ions.

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2. Experimental

2.1. Materials and methods

All the reactions were carried out under a dry nitrogen atmosphere using vacuum glass line. The organic solvents were dried and freshly distilled under an inert atmosphere according to standard procedures and stored under nitrogen. Triethanolamine (Aldrich), triisopropanolamine (Aldrich), 1-isothiocyanato-4-methoxybenzene (Aldrich), 1-isocyanato-4-methoxybenzene (Aldrich), 1-isothiocyanato-4-nitrobenzene (Aldrich), 1-isocyanato-4-nitrobenzene (Aldrich), 1-isothiocyanatobenzene (Aldrich) were used as supplied. The silatranes **1** and **2** were synthesized according to reported methods [9]. Infrared spectrum was obtained as Neat on a Thermo Scientific Fischer spectrometer. C, H and N analyses of samples were performed on a FLASH-2000 organic element analyzer while Si content was estimated gravimetrically [21]. ^1H and ^{13}C NMR spectra were recorded in DMSO/ CDCl_3 solution using a 400 MHz (Bruker 400) instrument. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer. Fluorescence spectroscopy was performed on Perkin Elmer LS 55 Fluorescence Spectrometer. The UV–Vis spectra were recorded with a JASCO V-530 double beam spectrophotometer.

2.2. X-ray crystallography

Measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Suitable crystals were mounted on MiTeGenMicromounts™ and these samples were used for data collection. Data were collected with a BrukerD8 Venture (100 K) diffractometer. The data were processed with APEX2 program [22] and corrected for absorption using SADABS [23]. The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. These atoms were refined on F^2 by a full-matrix least-square procedure using anisotropic displacement parameters [24]. All hydrogen atoms were located in different Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atom. Geometric calculations were carried out with PLATON [25] and drawings were produced with Olex2 [26] and MERCURY [27]. Additional crystal data and more information about the X-ray structural analyses are shown in Tables 1–3.

2.3. Anion recognition properties of **3–8**

All the anion recognition studies were performed at $25 \pm 1^\circ\text{C}$ and before recording any spectrum sufficient time was given for shaking to ensure the uniformity of the solution. UV–Vis titrations were performed on $1.0 \times 10^{-5}\text{ M}$ solutions of **3–8** in CH_3CN . The freshly prepared 0.01 (M) Bu_4NX ($\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$ and CH_3COO^-) standard solutions were added successively and the UV–Vis spectra of the samples were recorded. The fluorescence spectra of **3–8** were recorded with excitation wavelengths 390, 405, 335, 300, 290 and 300 nm for **3–8** ($1.0 \times 10^{-5}\text{ M}$) respectively in CH_3CN and the anion recognition behavior was evaluated from the changes in fluorescence spectrum of silatranes upon addition of tetrabutylammonium salts of anions.

2.4. Theoretical studies

The quantum mechanical calculations were performed on the Gaussian 03 series programs [28]. Geometries were optimized at Density Functional Theory (DFT), using Becke's three parameter

hybrid exchange functional and the correlation functional of Lee, Yang and Parr (B3LYP) with basis set at 6-31G*(d) level.

2.5. Syntheses

2.5.1. 1-(3-(2,8,9-Trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propyl-3-(4-nitrophenyl)urea (**3**)

3-Aminopropylsilatrane **1** (0.70 g, 3.01 mmol) was dissolved in chloroform and solution of 1-isocyanato-4-nitrobenzene (0.49 g, 3.01 mmol) in 5 mL chloroform was added dropwise with stirring. The mixture was stirred and refluxed for 4 h. Upon cooling, the solvent was evaporated under vacuum and yellow colored solid was extracted with hexane. The crystals of compound **3** were grown in chloroform-hexane mixture. Yield: 0.85 g (71%). M.p.: 192–194 °C. *Anal. Calc.* for $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_6\text{Si}$ (396): C, 48.48; H, 6.06; N, 14.14; Si, 7.07. Found: C, 48.12; H, 5.86; N, 13.92; Si, 6.97%. IR (cm^{-1}) = 582 m (ν N → Si), 1097 s (ν Si–O), 1483 s (ν N–O), 1655 s (ν C=O), 2874, 2927 m (ν CH_2), 3339 m (ν NH). ^1H NMR (400 MHz, DMSO- d_6 / CDCl_3): δ (ppm) = 0.30 (t, 2H, $J = 8.2$ Hz, SiCH_2), 1.54 (m, 2H, CCH_2C), 2.82 (t, 6H, $J = 5.7$ Hz, NCH_2), 3.09 (m, 2H, CCH_2N), 3.70 (t, 6H, $J = 5.7$ Hz, OCH_2), 6.23 (s, 1H, NHCH_2), 7.58–8.07 (m, 4H, Ar–H), 9.16 (s, 1H, NHAr). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6 / CDCl_3): δ (ppm) = 13.67 (SiCH_2), 25.24 (CCH_2C), 42.39 (CCH_2N), 50.22 (NCH_2), 56.88 (OCH_2), 116.22–140.16 (Ar–C), 147.12 (CNO_2), 154.43 (C=O). MS: m/z (relative abundance (%), assignment) = 132 [11.6, ($\text{HSi}(\text{OCH}_2\text{CH}_2)_2\text{NH}^+$), 150 [16.4, ($\text{HOCH}_2\text{CH}_2)_3\text{NH}^+$], 174 [7.0, $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}^+$], 192 [18.3, $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}^+\cdot\text{NH}_3$], 216 [34.7, $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$], 397 [15.8, (M+H) $^+$], 419 [100, (M+Na) $^+$].

2.5.2. 1-(3-(2,8,9-Trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propyl-3-(4-nitrophenyl)thiourea (**4**)

Silatrane **4** was synthesized following a similar procedure as described for silatrane **3** except 1-isothiocyanato-4-nitrobenzene (0.54 g, 3.01 mmol) was used instead of 1-isocyanato-4-nitrobenzene. The yellow colored product was obtained by the extraction with diethyl ether. Yield: 1.02 g (82%). M.p.: 203–205 °C. *Anal. Calc.* for $\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_6\text{SSi}$ (412): C, 46.60; H, 5.82; N, 13.59; S, 6.79; Si, 7.76. Found: C, 46.21; H, 5.65; N, 13.38; S, 6.42; Si, 7.28%. IR (cm^{-1}) = 580 m (ν N → Si), 1081 s (ν Si–O), 1491 s (ν N–O), 1580 s (ν C=S), 2872, 2922 m (ν CH_2), 3361 m (ν NH). ^1H NMR (400 MHz, DMSO- d_6 / CDCl_3): δ (ppm) = 0.44 (t, 2H, $J = 8.2$ Hz, SiCH_2), 1.53 (m, 2H, CCH_2C), 2.80 (t, 6H, $J = 5.7$ Hz, NCH_2), 3.16 (m, 2H, CCH_2N), 3.69 (t, 6H, $J = 5.7$ Hz, OCH_2), 6.91 (s, 1H, NHCH_2), 7.57 (s, 1H, NHAr), 8.05–8.20 (m, 4H, Ar–H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6 / CDCl_3): δ (ppm) = 12.98 (SiCH_2), 24.53 (CCH_2C), 44.67 (CCH_2N), 56.81 (NCH_2), 57.56 (OCH_2), 122.59–128.33 (Ar–C), 154.00 (CNO_2), 178.32 (C=S). MS: m/z (relative abundance (%), assignment) = 132 [13.7, ($\text{HSi}(\text{OCH}_2\text{CH}_2)_2\text{NH}^+$), 150 [35.3, ($\text{HOCH}_2\text{CH}_2)_3\text{NH}^+$], 174 [55.2, $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}^+$], 192 [16.9, $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}^+\cdot\text{NH}_3$], 216 [21.3, $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$], 413 [11.3, (M+H) $^+$], 435 [100, (M+Na) $^+$].

2.5.3. 1-(3-(2,8,9-Trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propyl-3-(4-methoxyphenyl)urea (**5**)

Silatrane **5** was synthesized following a similar procedure as described for silatrane **3** except 1-isocyanato-4-methoxybenzene (0.39 g, 3.01 mmol) was used instead of 1-isocyanato-4-nitrobenzene. The white colored product was obtained upon addition of diethyl ether. Yield: 0.85 g (71%). M.p.: 168–170 °C. *Anal. Calc.* for $\text{C}_{17}\text{H}_{27}\text{N}_3\text{O}_5\text{Si}$ (381): C, 53.54; H, 7.08; N, 11.02; Si, 7.34. Found: C, 53.25; H, 6.93; N, 10.85; Si, 7.03%. IR (cm^{-1}) = 586 m (ν N → Si), 1099 s (ν Si–O), 1682 s (ν C=O), 2874, 2922 m (ν CH_2), 3275 m (ν NH). ^1H NMR (400 MHz, DMSO- d_6 / CDCl_3): δ (ppm) = 0.23 (t, 2H, $J = 8.2$ Hz, SiCH_2), 1.46 (m, 2H, CCH_2C), 2.80 (t, 6H, $J = 5.7$ Hz, NCH_2), 3.03 (m, 2H, CCH_2N), 3.65 (t, 6H, $J = 5.7$ Hz,

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