



# Proton transfer and hydrogen bonds in supramolecular, self-assembled structures of imidazolium silanethiolates. X-ray, spectroscopic and theoretical studies



Katarzyna Kazimierczuk\*, Anna Dołęga, Justyna Wierzbicka

Department of Chemistry, Gdańsk University of Technology, G. Narutowicza St. 11/12, 80-233 Gdańsk, Poland

## ARTICLE INFO

### Article history:

Received 14 March 2016

Accepted 16 April 2016

Available online 29 April 2016

### Keywords:

Hydrogen bonding

Silanethiolates

Imidazolium salts

Crystal structure

DFT studies

## ABSTRACT

The reaction of 1-methylimidazole, 2-ethyl-4-methylimidazole and 2-ethylimidazole with tris(2,6-diisopropylphenoxy)silanethiol (TDST) leads to the formation of three new salts, which have been characterized by elemental analyses, thermogravimetric analyses, FTIR spectroscopy, and their structures were determined by single-crystal X-ray diffraction. Structural analyses indicate that in all three compounds a proton transfer has occurred from the  $-SH$  group of TDST onto the imidazole nitrogen atom, giving charge-assisted  $(^+N-H \cdots S^{(-)})$  hydrogen bonds. The crystallographic characterization of the compounds reveals structural diversity. Compound **1** exhibit zero-dimensional (0-D) hydrogen bonded entities, while compounds **2** and **3** form one-dimensional (1-D) supramolecular networks. The transfer of the proton was confirmed by FTIR spectroscopy in the solid state. Computational studies on the compounds were carried out with the use of the density functional theory (DFT) method with the B3LYP functional at the TZV level.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

The design of new materials with predetermined spatial structures and properties is a very important area of research in materials science. Hydrogen bond formation between molecules and/or ions in a crystal is of a great advantage regarding the strength of intermolecular forces [1–3]. Self-assembly based on hydrogen bonding requires the complementarity of the substrates as well as the limited freedom of conformational and rotational movements, characteristics most commonly found in aromatic and heteroaromatic molecules. Another important feature of hydrogen bonds is their directional nature which determines the shape of the macromolecules as well as the specificity of their interactions [4–6]. That is why hydrogen bonds play a key role in the faithful replication of DNA, the folding of proteins into spatial structures and the enzymatic recognition [7,8].

The formation of  $S-H \cdots A$  hydrogen bonds in crystals is poorly documented, because the sulfhydryl group is a weak proton donor and forms hydrogen bonds of low energy [9–11]. Hydrogen bonds involving typical thiols were described in surprisingly few papers [12], despite the fact that the thiol group plays an important role in biology as a part of the semi-essential amino acid cysteine.

The thiol group of cysteine is one of the possible donors/acceptors of hydrogen bonds in proteins, particularly in the ionized form.

Due to its high reactivity, cysteine not only stabilizes the protein structure (disulfide bridges formed by oxidation of two cysteine residues), but also can be found in the active sites of enzymes. One possible way of cysteine activation in enzyme catalytic sites is to create a cysteine (thiolate)-imidazolium ion pair complex with a  $(^+N-H \cdots S^{(-)})$  hydrogen bond, which increases the nucleophilicity of the sulfur atom. Most likely, this type of complex is formed in the active center of a plant peptidase-papain [13], proteinases of Pikorna viruses (including many human and animal pathogens, such as polio and cold viruses) and papain-like protease of the SARS virus [14–16].

There are known experimental difficulties connected with the elaboration of thiol compounds. They have a very unpleasant odor, they are readily oxidized and most importantly difficult to crystallize. Therefore we decided to obtain and characterize thiolate-imidazolium pairs, using silanethiol that relatively easily forms crystalline compounds. Large steric hindrance at the silicon atom allows isolation of systems possessing defined, directional hydrogen bonding interactions between the thiol and imidazole groups.

In the context of our study on hydrogen bonding systems [17,18], we report herein the crystal structures of tris(2,6-diisopropylphenoxy)silanethiolate imidazolium salts, in which an  $(^+N-H \cdots S^{(-)})$  hydrogen bond is formed between the silanethiolate

\* Corresponding author. Tel.: +48 58 3472329; fax: +48 58 3472694.

E-mail address: [katarzyna.kazimierczuk@pg.gda.pl](mailto:katarzyna.kazimierczuk@pg.gda.pl) (K. Kazimierczuk).

anion and imidazolium cation. We describe the synthesis of three compounds and analyse of the nature of their hydrogen bonding interactions by spectroscopic, diffraction, thermochemical and theoretical methods.

## 2. Experimental

### 2.1. General procedures

The elemental CHNS analyses were performed on a CE Instruments model EA1108 elemental analyzer. The FTIR spectra were measured for crystalline compounds in the range 4000–700  $\text{cm}^{-1}$  with a Nicolet iS50 spectrometer equipped with the Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory. Spectral analysis was controlled by the OMNIC software package. The melting points of the new compounds were determined on an SMP3 apparatus (Stuart Scientific, UK) and are uncorrected. Thermal analysis coupled with IR Thermogravimetric analysis was performed using a Netzsch thermobalance TG 209 coupled with a Bruker IFS66 FTIR spectrometer under argon. The volatiles evolved from the heated sample were transported to the spectrometer chamber via a thermostated pipe in a stream of argon.

### 2.2. Descriptions of the syntheses

Tris(2,6-diisopropylphenoxy)silanethiol (TDST) was obtained according to procedures described previously by Dołęga [19]. All other reagents (Aldrich) were obtained commercially. The solvent was dried over Na/K and distilled under nitrogen prior to use. The imidazoles were used without further purification. All reactions and manipulations were carried in an inert atmosphere of argon employing standard Schlenk vacuum line techniques.

### 2.3. Synthesis of 1-methylimidazolium tris(2,6-diisopropylphenoxy)silanethiolate **1**

1-Methylimidazole (0.33 g, 4 mmol) was added dropwise to a solution of tris(2,6-diisopropylphenoxy)silanethiol (TDST) (1.2 g,

2 mmol) in toluene (5 mL). After standing for one week at 4 °C, colorless crystals of **1** formed, which were suitable for X-ray analysis. M.p.: 128–130 °C. Elemental analysis, Calc. for  $\text{C}_{47}\text{H}_{66}\text{N}_2\text{O}_3\text{SSi}$  (MW 767.17): C, 73.58; H, 8.67; N, 3.65; S, 4.18. Found: C, 72.00; H, 8.49; N, 3.81; S, 4.08%. Significant differences in the measured and calculated values result from the presence of the solvent in the crystalline structure, which could evaporate while performing measurements. FTIR (crystalline product,  $\text{cm}^{-1}$ ): 3139 (s), 3095 (m), 3023 (s), 2962 (vs), 2926 (vs), 2864 (vs), 2769 (m), 2704 (m), 2601 (m), 2457 (m), 1698 (w), 1576 (m), 1547 (m), 1494 (m), 1463 (vs), 1436 (vs), 1379 (m), 1359 (vs), 1330 (vs), 1295 (w), 1279 (m), 1255 (s), 1247 (s), 1196 (s), 1185 (vs), 1097 (s), 1081 (m), 1058 (m), 1043 (m), 967 (w), 936 (s), 916 (s), 896 (vs), 876 (s), 843 (w), 798 (m), 757 (vs), 747 (s), 734 (s).

### 2.4. Synthesis of 2-ethyl-4-methylimidazolium tris(2,6-diisopropylphenoxy)silanethiolate **2**

To a solution of TDST (1.2 g, 2 mmol) in toluene (5 mL), 2-ethyl-4-methylimidazol (0.44 g, 4 mmol) was added. A white precipitate formed immediately and this was dissolved by the addition of a portion of the solvent. Colorless small crystals of **2** separated from the solution after 2 weeks at 4 °C. M.p.: 130–131 °C. Elemental analysis, Calc. for  $\text{C}_{42}\text{H}_{62}\text{N}_2\text{O}_3\text{SSi}$  (MW 703.09): C, 71.75; H, 8.89; N, 3.98; S, 4.56. Found: C, 71.44; H, 8.76; N, 4.22; S, 4.54%. FTIR (crystalline product,  $\text{cm}^{-1}$ ): 3057 (s), 3021 (s), 2961 (vs), 2926 (vs), 2865 (vs), 2747(m), 2704 (m), 2620 (m), 2576 (m), 2514 (m), 1637 (m), 1604 (w), 1587 (m), 1495 (m), 1463 (s), 1438 (vs), 1379 (s), 1359 (m), 1341 (s), 1328 (s), 1295 (w), 1272 (m), 1249 (s), 1185 (vs), 1098 (s), 1057 (m), 1043 (s), 919 (vs), 881 (m), 806 (w), 796 (m), 755 (s), 731 (s).

### 2.5. Synthesis of 2-ethylimidazolium tris(2,6-diisopropylphenoxy)silanethiolate **3**

TDST (1.2 g, 2 mmol) was dissolved in toluene (5 mL). To the solution of tris(2,6-diisopropylphenoxy)silanethiol, a portion of 2-ethylimidazole (0.36 g, 4 mmol) in toluene (4 mL) was added.

**Table 1**  
Crystallographic data and structure refinement details for compounds **1–3**.

Compound reference	<b>1</b> (CCDC-1432622)	<b>2</b> (CCDC-1432623)	<b>3</b> (CCDC-1432624)
Empirical formula	$\text{C}_{47}\text{H}_{66}\text{N}_2\text{O}_3\text{SSi}$	$\text{C}_{42}\text{H}_{62}\text{N}_2\text{O}_3\text{SSi}$	$\text{C}_{46}\text{H}_{68}\text{N}_4\text{O}_3\text{SSi}$
$M$ ( $\text{g mol}^{-1}$ )	767.16	703.08	785.19
$T$ (K)	120(2)	120(2)	120(2)
$\lambda$ (Å)	0.71073 (Mo $K\alpha$ )	0.71073 (Mo $K\alpha$ )	0.71073 (Mo $K\alpha$ )
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$Pc$	$P2_1/c$
$a$ (Å)	12.4174(3)	10.9468(5)	20.1612(5)
$b$ (Å)	20.4796(5)	17.0409(7)	11.9967(3)
$c$ (Å)	19.3391(8)	13.2973(8)	38.1618(12)
$\alpha$ (°)			
$\beta$ (°)	110.965(3)	124.083(3)	93.493(2)
$\gamma$ (°)			
$V$ (Å <sup>3</sup> )	4592.4(3)	2054.43(19)	9213.0(4)
$Z$	4	2	8
$D_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.110	1.137	1.132
$F(000)$	1664	764	3408
$\theta$ (°)	2.26–25.5	2.25–25.5	2.276–25.5
Limiting indices	$-15 \leq h \leq 11$ $-24 \leq k \leq 13$ $-15 \leq l \leq 23$	$-13 \leq h \leq 13$ $-20 \leq k \leq 18$ $-13 \leq l \leq 16$	$-20 \leq h \leq 24$ $-9 \leq k \leq 14$ $-35 \leq l \leq 46$
Reflections collected/unique	17512/8528 [ $R_{\text{int}} = 0.0261$ ]	7492/5144 [ $R_{\text{int}} = 0.0233$ ]	36079/17154 [ $R_{\text{int}} = 0.0293$ ]
Completeness to $\theta_{\text{max}}/\%$	99.9	99.9	99.9
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	8528/1/505	5144/2/464	17154/2/1043
Goodness-of-fit (GOF) on $F^2$	1.032	0.939	0.965
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0447$ , $wR_2 = 0.1118$	$R_1 = 0.0382$ , $wR_2 = 0.0826$	$R_1 = 0.0456$ , $wR_2 = 0.1120$
$R$ indices (all data)	$R_1 = 0.0616$ , $wR_2 = 0.1177$	$R_1 = 0.0488$ , $wR_2 = 0.0851$	$R_1 = 0.0711$ , $wR_2 = 0.1204$
Largest difference peak and hole ( $\text{e Å}^{-3}$ )	0.394; $-0.382$	0.267; $-0.208$	0.655; $-0.366$

Download English Version:

<https://daneshyari.com/en/article/1336315>

Download Persian Version:

<https://daneshyari.com/article/1336315>

[Daneshyari.com](https://daneshyari.com)