



ORIGINAL ARTICLE

Keto-enol tautomerism in new silatranes Schiff bases tailed with different substituted salicylic aldehyde

Alexandra Bargan^{*}, Mirela Fernanda Zaltariov, Angelica Vlad,
Ana-Maria-Corina Dumitriu, Alina Soroceanu, Ana-Maria Macsim,
Mihaela Dascalu, Cristian Dragos Varganici, Maria Cazacu, Sergiu Shova

“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, Iasi 700487, Romania

Received 31 August 2017; accepted 2 September 2018

Available online 8 September 2018

KEYWORDS

Aminopropylsilatrane;
Schiff base modified
silatranes;
Single crystal X-ray;
Azomethine;
Antimicrobial activity;
Surface properties

Abstract New Schiff base-type products starting from 1-(3-aminopropyl)silatrane and three derivatives of salicylaldehyde having as substituents 3,5-dichloro- (1), 3-methoxy- (2) and 3,5-di-*tert*-butyl- (3), respectively were obtained and isolated with high yields (78–87%) in pure, crystalline forms and their structures were established by different methods. The molecular electronic transitions of the compounds in solvents with various polarities were investigated by UV–Vis spectral analysis. Their thermal behavior was studied by thermogravimetric analysis and differential scanning calorimetry, results of the latter highlighting thermochromism of the compounds, proved by the appearance of IR absorption bands specific for enolic form at the temperature corresponding to each sample. The moisture sorption capacity and stability of the compounds in wet environment were investigated by vapor sorption analysis in dynamic regime and IR spectroscopy. The biological activity was assessed by specific tests. All results were discussed in correlation with the nature of substituents and structures formed. The chemical handling of the silatrane tail, by using different substituents on the silicon atom would allow fine tuning of the compounds properties.

© 2018 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Silatranes are heterocyclic, pentacoordinate silicon compounds (Tharmaraj et al., 2009; Puri et al., 2011) generally prepared by transesterification reaction between Si-substituted trialkoxysilanes and triethanolamine (Singh et al., 2015; Cozzi, 2004; Warncke et al., 2012; Seiller et al., 2007). Although known for over fifty years (Voronkov et al., 1982, 2012), these are a class of expanding high interest in the areas of material science (in sol–gel processes, in atomic force microscopy for DNA

^{*} Corresponding author at: Aleea Gr. Ghica Voda 41A, Iasi 700487, Romania.

E-mail address: anistor@icmpp.ro (A. Bargan).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

imaging, as surface agents, coupling, or adhesion promoters for curable silicone compositions, as covalent surface linkers to nanoparticulate metal oxide films for use in photoelectrochemical cells, etc.) but mainly due to their biological activity useful in medicine and pharmacology (pleiotropic, antitumor, anticancer, antibacterial, anti-inflammatory activity) and agriculture (fungicidal activity, stimulating effect in animal production and seed germination effects) (Puri et al., 2011; Brennan et al., 2009; Singh et al., 2016; Scheschkewitz, 2014).

Their special properties result from the steric structure and the electron density distribution (Voronkov et al., 1982), which is influenced by the nature and position of the substituents (Tharmaraj et al., 2009). The most interesting feature of silatranes consists in variation of the transannular dative Si←N bond length in dependence on the nature of the substituent on the silicon atom (Puri et al., 2011). The degree of interaction of the Si and N atoms increases with an increase in the electronegativity of the silicon substituent. Meanwhile, the hypervalent bond gives a high sensitivity of the nitrogen electron cloud and its immediate environment to the effects of substituents on the silicon (Brennan et al., 2009; Voronkov et al., 2012). In the same time, the silatranyl group has an important stereoelectronic influence in shaping the reactivity of the exocyclic functional group apical to the transannular bond (Sidorkin et al., 1980; Chuit et al., 1993; Iwamiyat and Maciel, 1993).

Different groups could be attached to the silicone, these coming from the alkoxysilane precursor or by subsequent chemical modification of the silatrane. Ones of the most frequently used precursors for silatranes are aminoalkyltrialkoxysilanes, which are of great importance due to a broad range of biological applications, ability to form hydrogen bonds and complex metallic species. In addition, they also allow chemical modification in a simple way leading to numerous N-derivative silatranes based on the reactivity of amino group with various reagents such as alkyl halides, aryl halides, phosphoryl halides, acid halides and carbonyl compounds (Singh et al., 2015, 2018). The condensation reaction with carbonyl group is one of the most important reactions of amino group leading to the compounds of Schiff base type containing azomethine group (Gungor et al., 2018; Acar et al., 2018). In the same time, Schiff base complexes containing hexa- and pentacoordinate silicon(IV) are of interest due to their catalytic, anti-viral, anti-cancer, antibacterial and anti-fungal activities (Seiller et al., 2007; Voronkov et al., 2012, 1982; Mutneja et al., 2016). Silatranes in particular are of interest both in terms of theoretical and experimental because their steric and electronic structures causing them special properties can be fine-tuned by the substituents attached to the silicon atom (Mutneja et al., 2016). There are reported in literature many Schiff bases derived from 3-aminoalkyl-silicon functional silatranes (i.e., N-(2-aminoethyl)-3-aminopropyl (Singh et al., 2015), aminopropyl (Tharmaraj et al., 2009; Warncke et al., 2012; Seiller et al., 2007) by reaction with different carbonylic compounds: salicylaldehyde, 2'-hydroxyacetophenone, pyrrole-2-carboxaldehyde, acetylacetone and ethyl acetoacetate (Singh et al., 2015), 3-formylchromone (Tharmaraj et al., 2009), 2-hydroxy-4-methoxybenzophenone (Warncke et al., 2012), pyrrole-2-carboxaldehyde and 2-hydroxy-1-naphthaldehyde (Seiller et al., 2007) etc. The flexibility in the length and structure of the tail attached to silicon

offers opportunities to build up larger ligand systems able to coordinate different metals (Voronkov et al., 2012) and to stabilize them in various oxidation states, useful for catalysis (Seiller et al., 2007).

In this work, we prepared three new Schiff base-functionalized propylsilatranes by reacting 1-(3-aminopropyl) silatrane with 3,5-dichlorosalicylaldehyde, 3-methoxysalicylaldehyde and 3,5-di-*tert*-butylsalicylaldehyde. The obtained structures were verified by elemental and spectral (FTIR, ^1H NMR, ^{13}C NMR and UV-Vis) analyses as well as by single-crystal X-ray diffraction. The effects of the substituents on the structural, thermal, biocidal and surface properties were investigated.

2. Experimental

2.1. Materials

1-(3-Aminopropyl)silatrane was prepared according to an already reported procedure (Dumitriu et al., 2012) consisting in treating (3-aminopropyl)triethoxysilane with triethanolamine in 1:1 M ratio, 10 vol% in a mixture of methanol:butanol:toluene (14:1:50 vol ratio), and 3 h stirring at 60 °C. The structure was established by elemental and spectral analyses as well as by X-ray single crystal diffraction.

3,5-Dichlorosalicylaldehyde, 3-methoxysalicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde, all of them of 99% purity, were purchased from Sigma Aldrich and used as such. Methanol, butanol, toluene were purchased from Chimopar-Romania, while acetonitrile was acquired from Sigma-Aldrich.

2.2. Equipments

Infrared spectra were recorded using a Bruker Vertex 70 FTIR spectrometer in the transmission mode (KBr pellets) between 4000 and 400 cm^{-1} at room temperature with a resolution of 2 cm^{-1} and accumulation of 32 scans.

The NMR spectra were recorded on a Bruker Avance DRX 400 MHz Spectrometer equipped with a 5 mm QNP direct detection probe and z-gradients. Spectra were recorded in DMSO d_6 at room temperature.

UV-Vis spectra of the samples **1–3** were registered on a Jenway 6505 Spectrophotometer (Watford, UK) in 10 mm optical path quartz cuvettes by using the chosen solvents (chloroform, methanol, acetonitrile and dimethylformamide) as references.

The carbon, hydrogen, and nitrogen contents were determined by standard methods.

The thermogravimetric analysis was performed on STA 449F1 Jupiter NETZSCH (Germany) equipment. The measurements were made in the temperature range 20–700 °C under a nitrogen flow (50 mL/min) using a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were conducted on a DSC 200 F3 Maia device (Netzsch, Germany). A mass of 15 mg of each sample was heated in pierced and sealed aluminum crucibles at a heating rate of 10 °C min^{-1} . Nitrogen atmosphere at a flow rate of 50 mL min^{-1} was used. The temperature against heat flow was recorded. The device was calibrated using indium according to standard procedures.

Water vapor sorption capacity of the samples have been measured by using the fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK).

The study of antimicrobial activity of the new synthesized compounds was carried out using three species of fungi (*Aspergillus fumigatus* ATCC 66567, *Penicillium chrysogenum* ATCC 20044, *Fusarium* ATCC 20327) from pure culture and two bacteria (*Pseudomonas* sp. ATCC 15780 and *Bacillus* sp. ATCC 31073) species according to previously reported standard procedures (Zaltariov et al., 2015).

2.3. X-ray crystallography

Crystallographic measurements were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer using graphite-monochromated Mo- K_α radiation. The crystals were placed 40 mm from the CCD detector. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction (CrysAlis RED, 2003). The structures were solved by direct methods using Olex2 (Dolomanov et al., 2009) software with the SHELXS structure solution program and refined by full-matrix least-squares method on F^2 with SHELXL-97 (Sheldrick, 2008). Disordered fragments in structure **3** were modeled using available tools of SHELXL97 (PART, DFIX and SADI) in combination with anisotropic/isotropic refinement of non-H atoms.

CCDC 1543444, CCDC 1543446 and CCDC 1543447 contain the supplementary crystallographic data for this contribution. These data obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The main crystallographic data together with refinement details are summarized in Table 1.

2.4. Procedure

2.4.1. Synthesis of compound 1

A solution of 1-(3-aminopropyl)silatrane (0.99 g, 4.26 mmol) in 15 mL methanol was added to a solution of 3,5-dichlorosalicylaldehyde (0.81 g, 4.62 mmol) in 10 mL methanol. The resulting mixture was stirred for 4 days at room temperature and refluxed 4 h at 50 °C. The solution was allowed to stand at room temperature. Small crystals of X-ray diffraction quality were separated by filtration, washed with methanol, and dried in air. Yield: 1.35 g, 78.57%. Calcd for $C_{16}H_{22}Cl_2N_2O_4Si$ ($M = 405.33$ g/mol), %: C, 47.40; H, 5.47; N, 6.91. Found, %: C, 47.50; H, 5.29; N, 6.90.

FT-IR (KBr pellet, cm^{-1}): 3437 s, 3049 w, 2963 m, 2620 s, 2874 m, 1641 vs, 1603 m, 1499 s, 1456 m, 1443 m, 1418 w, 1383 w, 1373 w, 1354 w, 1306 w, 1275 m, 1227 s, 1190 m, 1148 s, 1124 vs, 1097 vs, 1088 vs, 1051 s, 1016 s, 984 w, 935 m, 908 s, 883 m, 851 m, 806 s, 762 vs, 714 s, 679 m, 667 m, 623 m, 581 m, 561 w, 509 w, 492 w.

1H NMR (400 MHz, DMSO d_6 , δ -ppm): 14.64 (1H, s, OH), 8.51 (1H, s, H-10), 7.54 (1H, d, 2.8 Hz, H-14), 7.36 (1H, d, 2.7 Hz, H-12), 3.62 (6H, t, 5.9 Hz, H-1, H-3, H-5), 3.54 (2H, t, 6.6 Hz, H-9), 2.80 (6H, t, 5.9 Hz, H-2, H-4, H-6), 1.66 (2H, q, 6.9 Hz, H-8), 0.20 (2H, q, 5.3 Hz, H-7).

^{13}C NMR (400 MHz, DMSO d_6 , δ -ppm): 166.16 (C-11), 165.07 (C-10), 133.15 (C-14), 130.46 (C-12), 125.6 (C-16), 115.62 (C-15), 115.00 (C-13), 56.59 (C-1, C-3, C-5), 55.36 (C-9), 49.88 (C-2, C-4, C-6), 26.22 (C-8), 14.06 (C-7).

Table 1 Crystallographic data, details of data collection and structure refinement parameters for compounds **1**, **2** and **3**.

Compound	1	2	3
Empirical formula	$C_{16}H_{22}Cl_2N_2O_4Si$	$C_{17}H_{26}N_2O_5Si$	$C_{24}H_{40}N_2O_4Si$
Molecular weight	405.34	366.49	448.67
T [K]	293 (2)	173.05 (10)	293 (2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
a , [Å]	25.491 (5)	13.550 (2)	11.4952 (11)
b , [Å]	12.270 (3)	11.0080 (10)	20.4614 (13)
c , [Å]	14.470 (3)	13.839 (2)	11.1437 (8)
α , [°]	90	90	90
β , [°]	123.70 (3)	117.28 (2)	106.054 (8)
γ , [°]	90	90	90
V , [Å ³]	3765 (17)	1834.7 (6)	2518.9 (4)
Z	8	4	4
ρ (calcd.), [g cm ⁻³]	1.430	1.327	1.183
Crystal size [mm]	$0.4 \times 0.2 \times 0.1$	$0.15 \times 0.1 \times 0.02$	$0.5 \times 0.4 \times 0.2$
μ , [mm ⁻¹]	0.432	0.158	0.124
Reflections collected	7730	7711	9629
Independent reflections (R_{int})	3329 (0.0253)	3236 (0.0921)	4450 (0.0310)
R_1^a ($I > 2\sigma(I)$)	0.0453	0.0875	0.0855
wR_2^b (all data)	0.1160	0.2445	0.2277
GOF ^c	1.033	0.999	1.025
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ [e Å ⁻³]	0.30 and -0.27	0.55 and -0.44	0.76 and -0.69

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

^c GOF = $\{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

2.4.2. Synthesis of compound 2

A solution consisting in 0.460 g (1.97 mmol) 1-(3-aminopropyl)silatrane in acetonitrile/methanol 3:1 (28 mL) was added to a solution of 3-methoxysalicylaldehyde 0.304 g (1.99 mmol) in 10 mL acetonitrile, in a 50 mL one-necked round-bottom flask. The reaction mixture was stirred for 1 h at room temperature and refluxed 5 days at 50 °C. After that was allowed to stay at room temperature. Formation of orange crystals was observed after about 5 days. These were separated by filtration washed with diethyl ether, dried and analyzed further. Yield: 0.63 g, 87.26%. Calcd for $C_{17}H_{26}N_2O_5Si$ ($M = 366.49$ g/mol), %: C, 55.71; H, 7.15; N, 7.64. Found, %: C, 55.59; H, 7.13; N, 7.67.

FT-IR (KBr pellet, cm^{-1}): 3435 m, 3001 w, 2930 s, 2878 s, 1634 s, 1474 s, 1462 s, 1441 m, 1344 w, 1278 s, 1250 vs, 1175 m, 1126 vs, 1094 vs, 1053 m, 1036 m, 1020 s, 984 w, 961 m, 941 m, 910 m, 874 w, 839 w, 808 m, 775 s, 760 s, 741 s, 735 s, 716 s, 631 m, 579 w, 451 w.

1H NMR (400 MHz, DMSO d_6 , δ -ppm): 14.18 (1H, s, OH), 8.44 (1H, s, H-10), 6.97 (2H, d, 7.9 Hz, H-12, H-14), 6.70 (1H, t, 7.8 Hz, H-13), 3.76 (3H, s, H-17), 3.60 (6H, t, 5.9 Hz, H-1, H-3, H-5), 3.48 (2H, t, 6.7 Hz, H-9), 2.79 (6H, t, 5.9 Hz, H-2, H-4, H-6), 1.63 (2H, q, 6.9 Hz, H-8), 0.19 (2H, q, 5.1 Hz, H-7).

^{13}C NMR (400 MHz, DMSO d_6 , δ -ppm): 164.98 (C-10), 154.38 (C-11), 148.55 (C-15), 123.16 (C-14), 117.62 (C-16), 116.34 (C-13), 114.41 (C-12), 60.17 (C-9), 56.60 (C-1, C-3, C-5), 55.63 (C-17), 49.90 (C-2, C-4, C-6), 26.82 (C-8), 14.42 (C-7).

2.4.3. Synthesis of compound 3

A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.25 g, 1.07 mmol) in 10 mL methanol was added under stirring at room temperature to a solution of 1-(3-aminopropyl)silatrane (0.25 g, 1.06 mmol) in 10 mL methanol. The mixture was stirred 4 days at room temperature after that was stirred 4 h at 50 °C. The obtained solution was allowed to stand at room temperature. Small crystals of X-ray diffraction quality were separated by filtration after 24 h, washed with methanol, and dried in air. Yield: 0.40 g, 84.30%. Calcd for

$C_{24}H_{40}N_2O_4Si$ ($M = 448.67$ g/mol), %: C, 64.24; H, 8.98; N, 6.24. Found, %: C, 64.09; H, 8.96; N, 6.25.

FT-IR (KBr pellet, cm^{-1}): 3400 m, 2953 vs, 2893 s, 2874 s, 1632 s, 1597 m, 1476 s, 1443 s, 1387 m, 1362 m, 1275 m, 1248 m, 1200 m, 1184 m, 1177 m, 1130 vs, 1107 vs, 1086 s, 1053 s, 1016 s, 968 w, 937 m, 910 m, 880 m, 827 w, 810 m, 773 s, 760 s, 725 m, 700 m, 646 w, 623 m, 581 w, 446 w.

1H NMR (400 MHz, DMSO d_6 , δ -ppm): 14.46 (1H, s, OH), 8.46 (1H, s, H-10), 7.27 (2H, d, 2.4 Hz, H-12, H-14), 3.61 (6H, t, 5.8 Hz, H-1, H-3, H-5), 3.48 (2H, t, 6.2 Hz, H-9), 2.79 (6H, t, 5.8 Hz, H-2, H-4, H-6), 1.63 (2H, q, 6.4 Hz, H-8), 1.39 (9H, s, H-22, H-23, H-24), 1.27 (9H, s, H-18, H-19, H-20), 0.20 (2H, q, 4.6 Hz, H-7).

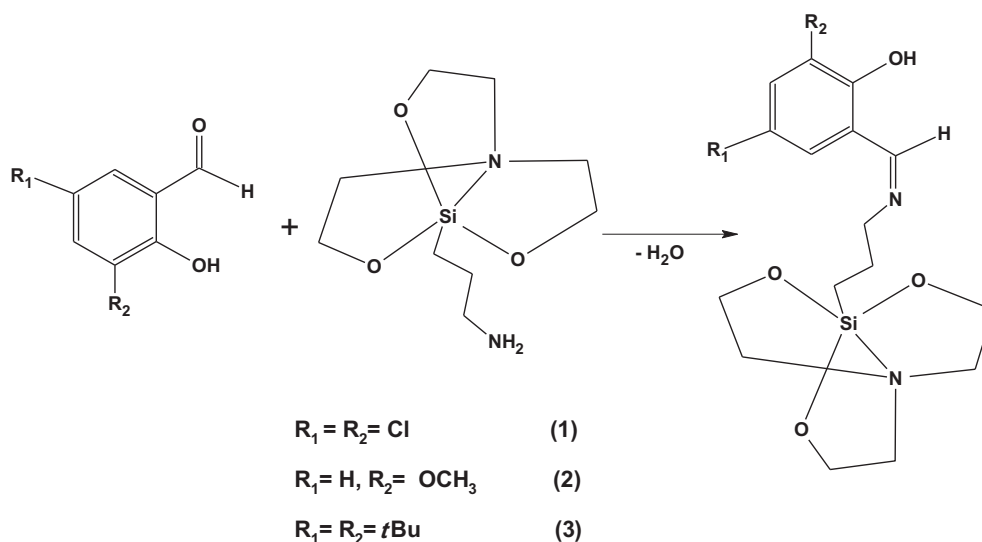
^{13}C NMR (400 MHz, DMSO d_6 , δ -ppm): 165.89 (C-10), 158.49 (C-11), 138.86 (C-15), 135.66 (C-13), 125.92 (C-12), 125.79 (C-14), 117.48 (C-16), 61.34 (C-9), 56.60 (C-1, C-3, C-5), 49.90 (C-2, C-4, C-6), 34.45 (C-21), 33.71 (C-17), 31.22 (C-18, C-19, C-20), 29.20 (C-22, C-23, C-24), 26.92 (C-8), 14.63 (C-7).

3. Results and discussion

1-(3-Aminopropyl)silatrane prepared according to an already reported procedure (Dumitriu et al., 2012) was treated in 1:1 M ratio, with three different substituted salicylaldehyde: 3,5-dichloro-, 3-methoxy- and 3,5-di-*tert*-butylsalicylaldehyde when corresponding Schiff bases, **1**, **2**, and **3**, respectively, were formed (Scheme 1). Depending on the type of aldehyde, each reaction was conducted under specific conditions in terms of solvent, concentration, thermal regime, established by preliminary testing and reaction monitoring by IR spectroscopy. In all cases, the reaction products separated as crystals in the reaction solution and were isolated in good yields by filtration.

3.1. Structural analysis

According to single-crystal X-crystallography, all Schiff bases have a molecular crystal structure built up by the corresponding neutral entities as shown in Figs. 1–3, without any co-crystallized solvent molecules. In all structures, the



Scheme 1 The general reaction pathway leading to the Schiff base-functionalized propylsilatranes.

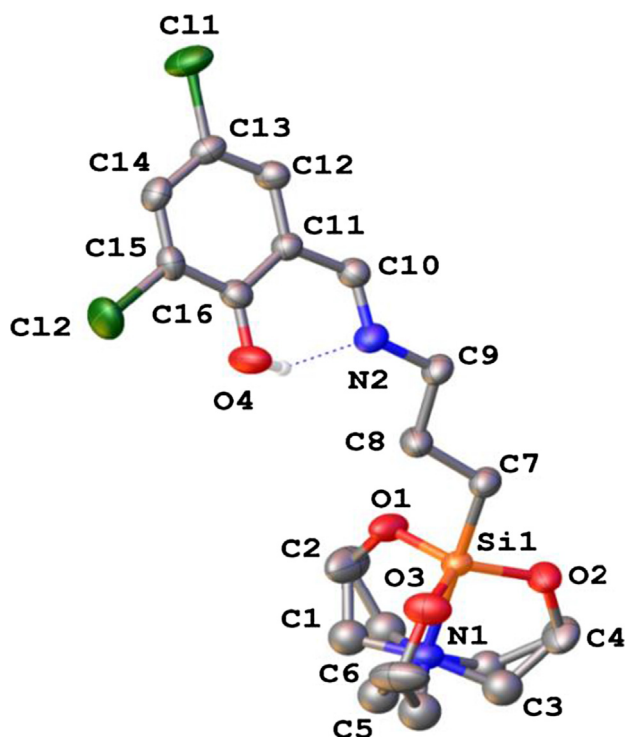


Fig. 1 X-ray molecular structure of compound **1** with atom labeling scheme and thermal ellipsoids at 50% probability level. Non-relevant H-atoms are omitted for clarity.

hydroxyl groups act as donor to the nitrogen atom of the imine group to form an intramolecular H-bond. The hydrogen bonding parameters are shown in Table 2.

Compound **1** crystallizes in monoclinic system in $C2/c$ space group. The molecular structure of **1** is given in Fig. 1. The molecule **1** is in enol-imine form. The hydrogen atom H4 is located closer to the O4 than to the nitrogen atom N2. The C16—O4 and C10—N2 bond distances are representative for these Schiff bases to determine the enol-imine and keto-amine tautomerism. The values C16—O4 (1.2981(3) Å) and C10—N2 (1.3159(3) Å) are in agreement with enol-imine form (Table 3) of compound **1**. In this conformer, the phenolic group hydrogen bonded to the nitrogen atom of the imine group, forming a six-membered ring with O4—H4...N2 length 1.81 Å. The bond angles C11—C10—N2 (122.0(3)°) and C10—N2—C9 (126.2(2)°) are also consistent with the sp^2 hybrid character for C10 and N2 atoms (Khalaji et al., 2011).

Compounds **2** and **3** crystallize in monoclinic system in $P2_1/c$ space group. The molecular structures are shown in Figs. 2 and 3. Both structures exhibit enol-imine tautomer form with the intramolecular hydrogen bond O4—H4...N2 at 1.79 Å for **2** and 1.85 Å for **3**. The large value of the H-bond is due to the presence of the *t*-butyl groups attached to the aromatic ring. The bond angles C11—C10—N2 (121.5(5)° for **2** and 123.7(4)° for **3**) and C10—N2—C9 (121.1(5)° for **2** and 118.5(4)° for **3**) are also consistent with the sp^2 hybrid character for C10 and N2 atoms and confirm the enol-imine character of the compounds **2** and **3**. The structural characteristics of the compounds **1–3** show a remarkable similarity with that found of another four Schiff bases containing silatrane fragment in the structure (Singh et al., 2013).

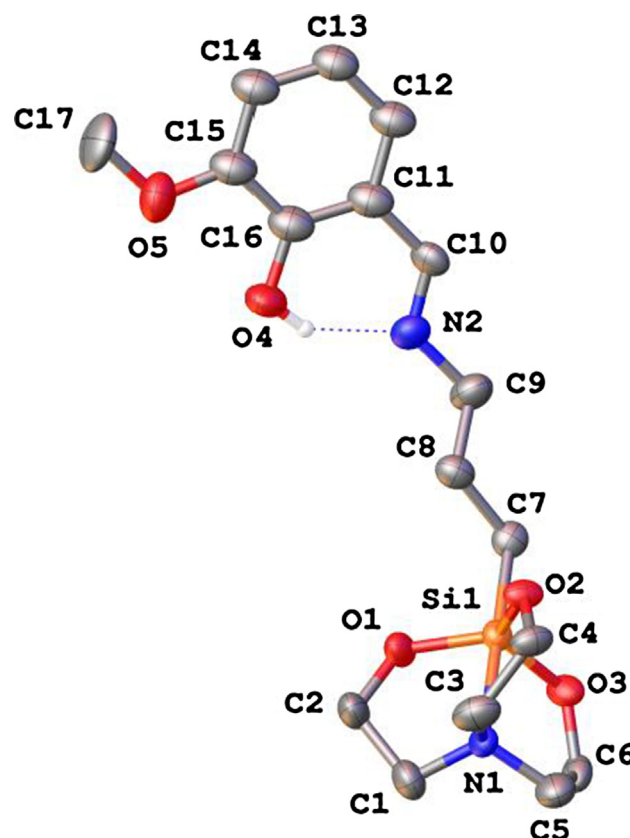


Fig. 2 X-ray molecular structure of compound **2** with atom labeling scheme and thermal ellipsoids at 50% probability level. Non-relevant H-atoms are omitted for clarity.

The X-ray single-crystal investigation revealed that in all synthesized compounds, the silicon exhibits a pentacoordinated environment with slightly distorted trigonal-bipyramidal geometry.

The formation of Schiff bases was verified by FTIR spectroscopy. The disappearance of the free amine group absorption bands (3294 cm^{-1} and 3192 cm^{-1}) and presence of the absorption band at 1632–1641 cm^{-1} is a proof for the azomethine (Gungor et al., 2018; Acar et al., 2018). The other bands characteristics for the silatrane can be found in spectra at about the same wavelength as in 1(3-aminopropyl)silatrane.

1H NMR and ^{13}C NMR spectra also confirm the structure found by X-ray structural analysis (Fig. 1S). In 1H NMR spectrum can be noticed the presence of the peak at 8.44–8.51 ppm assigned to imine proton, the presence of the peak at 14.17–14.45 ppm assigned to OH proton, besides to those belonging to aromatic protons and the displacement of the protons of the propyl group: from 0.19 to 0.21 ppm (2H, $-Si-CH_2-$), 1.62–1.66 ppm (2H, $-Si-CH_2-CH_2-CH_2-NH_2$); 3.54–3.60 ppm (2H, $-Si-CH_2-CH_2-CH_2-NH_2$); 2.51–2.78 ppm (6H, $N-CH_2-CH_2-O-$); 2.78–3.48 (6H, $N-CH_2-CH_2-O-$).

Aromatic protons from sample **1**: 7.36–7.54 ppm (2H).

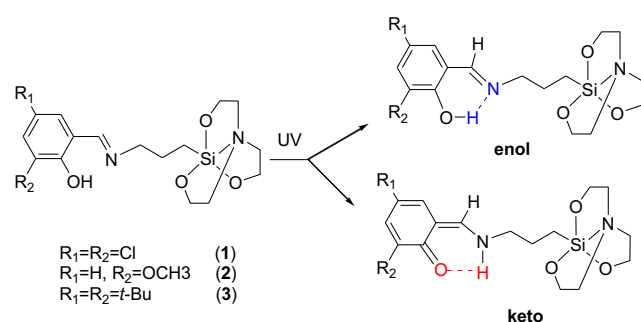
Aromatic protons from sample **2**: 6.7–6.96 ppm (3H) and methoxy protons 3.7 ppm (3H).

Aromatic protons from sample **3**: 7.24–7.29 ppm (2H), *tert*-butyl protons 1.27 ppm (9H) and 1.39 ppm (9H).

In ^{13}C NMR spectrum can be noticed the presence of the peak at 164.98–165.89 ppm assigned to imine carbon.

Table 4 Spectral characteristics of the compounds **1–3**.

Solvent	ϵ^a	λ_{abs} , nm			ϵ ($\text{M}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$)		
		1	2	3	1	2	3
Chloroform	4.8	284	297	328	14,166	10,785	14,400
		334	328	426	12,083	7000	1332
		366 _{sh}	424		6667	4286	
		428			8333		
Methanol	33.0	275	292	261	6625	25,785	26,547
		320 _{sh}	416	326	3625	11,240	9462
		418		416	3750		2063
Acetonitrile	36.6	262 _{sh}	260	261	9417	33,455	29,058
		280 _{sh}	295 _{sh}	326	7125	6838	10,493
		325	325		4750	4912	
		428	420		4542	2647	
DMF	36.7	334	328	326	13,250	33,198	25,785
		425	420	420	9667	10,169	2242

^a Dielectric constant.**Scheme 2** Molecular structures of **1**, **2** or **3** compounds in the corresponding tautomeric species discussed in the text.

separation of the aromatic rings (Zaltariov et al., 2015) and as a result the absence of the $S_2 \leftarrow S_0$ (π^* , π) transition in benzene ring in comparison with **1** and **2**.

It can be concluded that substitution with chloro, methoxy and *t*-Bu groups led to the stabilization in solution of enol tautomer species, depending on the polarity of the chosen solvents. Substitution with methoxy group or the presence of *t*-Bu substituents led to stabilization only of the enol tautomer in acetonitrile. The position of the absorption maximum of the enol species remains unchanged for **2** and **3**, while for **1** has a bathochromic shift (6–9 nm) in CHCl_3 and DMF, due to the different intermolecular interactions between solute and solvents: extended π - π stacking interactions (in CHCl_3) and the larger polarizability of DMF.

The absorption maxima are affected by both solvent polarity and the nature of the substituent (electron donating capability $\text{O}-\text{CH}_3 > \text{Cl} > t\text{-Bu}$). It has been demonstrated the decisive influence of the hypervalent $\text{Si} \leftarrow \text{N}$ bond (quite different from a covalent bond) on the physicochemical and spectroscopic characteristics of silatrane (Pedersen et al., 1998; Sidorkin et al., 1980; Singh et al., 2016).

3.3. Dynamic vapor sorption

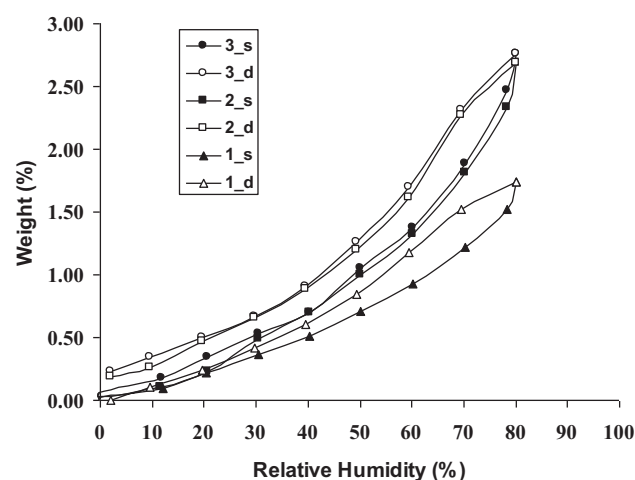
The behavior of the crystalline Schiff bases in the presence of the humidity was studied by registering sorption/desorption

isotherms in dynamic regime. In a special container, the samples were dried at 25 °C in flowing nitrogen (250 mL/min), until their weight was in equilibrium at a relative humidity $\text{RH} < 1\%$. After that, the relative humidity was increased step by step from 0 to 90%, in 10% humidity interval, having a pre-established equilibrium time between 3 and 5 min. The sorption equilibrium was obtained for all the steps. Then, the relative humidity was diminished and desorption curves were recorded (Fig. 4).

According to IUPAC classification, the sorption/desorption isotherms can be associated to type V curves describing sorption on hydrophobic/low hydrophilic material with weak sorbent–water interactions. The maximum sorption capacity value was 2.77 wt% at 25 °C. The desorption process occurs more slowly than sorption and about 0.18–0.22 wt% water is retained in samples **2** and respectively **3**.

3.4. Study of Schiff's bases stability in moist environment

As is known, literature data indicate the tendency of the azomethine bond toward hydrolytic cleavage (Bernardo

**Fig. 4** Water vapor sorption-desorption isotherms registered at room temperature.

et al., 2006), while the Si—O—C linkage and some silazane compounds tend to be hydrolytically unstable (Noshay and Matzner, 1974). Therefore to be handled properly, it is important to establish how our compounds are sensitive to moisture. The study of the stability of the Schiff base compounds **1–3** during sorption/desorption process was conducted to highlight the effect of water on the azomethine, Si—O and Si—N bonds.

Regarding the azomethine bond, its hydrolytic cleavage can be prevented when the nitrogen atom of the —CH=N— group is involved in hydrogen bond formation (Bernardo et al., 2006; Godoy-Alcantar et al., 2005). We thought it would be of interest to examine if the intramolecular H bond between aldehyde O—H group and the nitrogen atom from imine group could improve the resistance of the Schiff bases **1–3** toward hydrolytic cleavage that could take place in the presence of water vapors during the sorption process. Hydration competes with the azomethine formation so that its reversible character is of particular importance and actuality for consideration of the Schiff bases as ideal candidates for the dynamic combinatorial chemistry field (Noshay and Matzner, 1974).

Different methods are used to investigate the hydrolytic stability of the Schiff bases in aqueous media: ^1H NMR technique, UV–Vis, potentiometric measurements, etc.

In this study we used two different techniques: DVS and ATR-FTIR to check the stability of the Schiff bases **1–3**, measuring their moisture stability by DVS and the structural changes by IR spectroscopy.

In order to determine the changes that occur in the IR spectra of the samples after their exposure to a relative humidity of 90%, at room temperature for 5 h, ATR-FTIR technique was used.

The spectra were registered using a Bruker Vertex 70 FTIR spectrometer equipped with a ZnSe crystal. The measurements were performed in ATR (Attenuated Total Reflectance) mode in the 4000–600 cm^{-1} spectral range at room temperature with a resolution of 4 cm^{-1} and accumulation of 32 scans.

The 3700–2800 cm^{-1} spectral region of all samples is associated with the O—H groups of the adsorbed water and from aldehyde structure, and C—H from aromatic CH_3 and CH_2 groups (Fig. 5S).

The hydroxyl groups absorb strongly in the region 3300–3600 cm^{-1} . Broad bands are the result of the presence of intermolecular bonding. The precise position of the O—H bands is dependent on the strength of the H bonds and is difficult to establish exactly for these samples the dependence between the adsorbed water molecules and the intensity of the O—H broad band. The intramolecular H bonding (O—H...N=CH) also occurs in the case of Schiff bases, the resulting hydroxyl group absorption band being unaffected by concentration changes.

The modes of vibration of aromatic compounds are considered as separate C—H or ring C=C vibrations. In general, the bands are of variable intensity and are observed at 3100–3000 cm^{-1} for =C—H— stretching vibrations.

The asymmetric and symmetric vibrations of the methyl and methylene groups in the structure of the samples **1–3** occur between 3000 and 2800 cm^{-1} . The — CH_3 and — CH_2 — asymmetric stretching vibrations occur at 2962 cm^{-1} and 2924 cm^{-1} (**1**), 2973 cm^{-1} and 2927 cm^{-1} (**2**), 2952 cm^{-1} and 2923 cm^{-1} (**3**), while the symmetric one occurs at 2888 cm^{-1} and 2855 cm^{-1} (**1**), 2877 cm^{-1} and 2837 cm^{-1} (**2**), 2876 cm^{-1} and 2846 cm^{-1} (**3**). The position of the — CH_3 and — CH_2 —

stretching vibration bands is not altered by the exposure of the samples to water vapors (Fig. 5S).

The effect of exposure to water vapors on the azomethine group and Si—N or Si—O bonds of the analyzed compounds were studied by the deconvolution procedure of the IR spectra.

The 1700–1550 cm^{-1} , 1550–1200 cm^{-1} , 1200–950 cm^{-1} and 950–600 cm^{-1} spectral regions of the samples **1**, **2** and **3** were deconvoluted by a curve-fitting method, and the areas were calculated with a 50% Lorentzian and 50% Gaussian function. The curve-fitting analysis was performed with the OPUS 6.5 software. The procedure led to a best fit of the original curve with an error of less than 0.002.

Fig. 6S shows the 1700–1550 cm^{-1} spectral region of the samples **1–3** before and after the exposure to water vapors. This region is associated with the —CH=N— group at 1636 cm^{-1} (**1**), 1634 cm^{-1} (**2**) and 1630 cm^{-1} (**3**), the ring skeletal vibrations at 1599 and 1576 cm^{-1} (**1**), 1608 and 1582 cm^{-1} (**2**) and 1613 and 1598 cm^{-1} (**3**) and the adsorbed water vibrations after the sorption process at 1662 cm^{-1} (**2**) and 1677 cm^{-1} (**3**). These data are well correlated with DVS data, where the compounds **2** and **3** retain about 6.8% and 8% water after sorption-desorption processes (Fig. 4).

The IR spectra of the samples in 1550–1200 cm^{-1} spectral region revealed the presence of the aromatic C—C stretches variable in intensity at 1520–1470 and 1465–1430 cm^{-1} overlapped with those assigned to O—H deformation vibrations, to aliphatic — CH_2 — symmetric bending vibrations at 1430–1350 cm^{-1} and scissor and deformation vibrations at 1480–1440 cm^{-1} . The — CH_3 asymmetric bending in the case of compound **2** is evidenced by the band at 1440 cm^{-1} , while the *t*-butyl groups in compound **3** give rise to two bands assigned to the asymmetric — CH_3 deformation vibration at 1474 cm^{-1} and to — CH_3 symmetric bending vibration at 1354 cm^{-1} . The in-plane O—H deformation vibrations coupled with C—H wagging vibrations give rise to bands in the region 1440–1370 cm^{-1} which are overlapped with the aliphatic ones. The bands between 1300 and 1200 cm^{-1} are assigned to alkane C—C skeletal and to C—H in-plane deformation vibrations (Fig. 7S).

The 1200–950 cm^{-1} spectral region of the samples **1–3** revealed the presence of the asymmetric and symmetric stretches of the Si—O group, as much more intense bands due to the greater ionic character, at 1145 cm^{-1} and 1101 cm^{-1} (ν_{as}) and 1022 cm^{-1} (ν_{s}) (**1**), 1088 cm^{-1} and 1058 cm^{-1} (ν_{as}) and 1020 cm^{-1} (ν_{s}) (**2**), 1104 cm^{-1} and 1089–1050 cm^{-1} (ν_{as}) and 1014 cm^{-1} (ν_{s}) (**3**) and asymmetric stretching and — CH_2 — wagging (γ_{w}) vibrations of Si—C bond at 1215 cm^{-1} (ν_{as}) and 1192 cm^{-1} (γ_{w}) (**1**), 1174 cm^{-1} (ν_{as}) and 1124 cm^{-1} (γ_{w}) (**2**), 1209 cm^{-1} (ν_{as}) and 1179 cm^{-1} (γ_{w}) (**3**). The bands at 980–960 cm^{-1} and 970 cm^{-1} in the IR spectra of (**2**) and (**3**), respectively are characteristic for C—H in-plane deformation vibrations (Fig. 8S) (Socrates, 2001).

The IR spectra of the compounds **1–3** in the 950–600 cm^{-1} spectral region reveal the presence of the asymmetric and symmetric N—Si stretching vibrations at 859 cm^{-1} and 795 cm^{-1} in (**1**), 878 cm^{-1} and 804 cm^{-1} in (**2**), 880 cm^{-1} and 809 cm^{-1} in (**3**), — CH_2 — rocking vibrations between 774 and 680 cm^{-1} , a number of C—H in-plane deformation bands overlapped with O—H out-of-plane deformation vibrations between 940 and 626 cm^{-1} . Beside these, in the IR spectrum of (**1**) can be seen the characteristic band for C—Cl bond at 683 cm^{-1} (Fig. 9S) (Singh et al., 2015).

The ATR-FTIR technique was used to evidence if structural changes or chemical interactions occur after the exposure of the Schiff bases to water vapor. IR spectra revealed no structural modification, but only the sorption of water molecules onto the surface of solid samples **2** and **3** as a result of weak physically forces such as van der Waals or H bonds. The data are well correlated with the DVS results, where a slight retention of water of 6.8% and 8% for **2** and **3** respectively was registered. The azomethine bond was not affected by the sorption process mainly due to the intramolecular H bond which stabilizes their hydration cleavage.

No structural changes occurred in the composition of the Schiff bases due to the water vapor sorption, the Si—O and Si—N groups demonstrating a remarkable stability due to the structural packing of them in solid state on the one hand, and on the other hand to the ability of the lone electron pair of the nitrogen atom to interact with the empty orbitals of the silicon atom, that results in a shorter bond distance Si—N which is also an advantage in terms of chemical stability of these compounds.

Based on the results of this study, it can say that in the absence of other factors besides water vapor in the atmosphere of nitrogen, after exposure of 5 h, it is concluded that none of bonds susceptible to hydrolysis, Si—C, Si—N and CH=N are not affected.

3.5. Thermogravimetric analysis

Fig. 5A and B show the TGA and DTG curves of the Schiff bases. Characteristic data extracted from these curves are given in Table 5. All three azomethines exhibited three thermal decomposition stages with a maximum weight loss in the range of 261–420 °C. The first stage was assigned to loss of solvent molecules (methanol and acetonitrile) (7.23; 0.91; and 1.48 wt % for compounds **1**, **2**, and **3**). The second step, with initial temperatures between 206 and 255 °C, corresponds to the loss of ligand moiety, debuting with the azomethine linkage scission (—HC=N—) (Zaltariov et al., 2014; Kaya et al., 2008). An explanation for the different thermal decomposition pattern of the second stage corresponding to each sample would be due to structural bulkiness, substituents type and to the nature of solvents used in synthesis. The mentioned factors may generate symmetry disruption in the azomethine entity by hindering its structural packing (Al-Ghamdi et al., 2006). The more stable remaining structural entities thermally decompose in the third and last stage, in the range 279–548 °C leaving residue corresponding to the aminopropylsilatranyl moiety. Samples **1** and **2**, containing the substituents $R_1 = R_2 = \text{—Cl}$ and $R_1 = \text{H}$, $R_2 = \text{—OCH}_3$, left high comparable residue values of 52.48% and 51.01%. The *t*Bu substituent in sample **3**

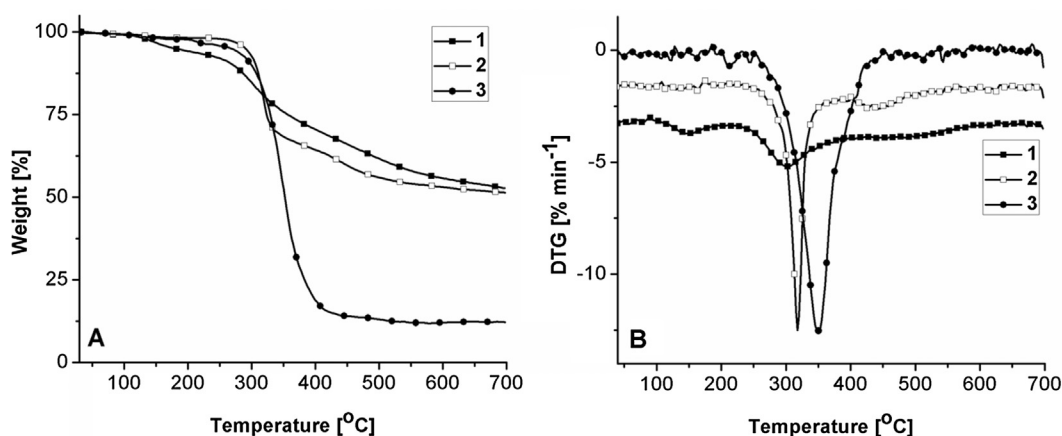


Fig. 5 TG (A) and DTG curves (B) of the studied structures.

Table 5 Thermal characteristics extracted from TG and DTG curves.

Sample	Stage	T_{onset} (°C)	T_{max} (°C)	T_{endset} (°C)	W_{m} (%)	W_{rez} (%)
1	I	110	146	177	7.23	52.48
	II	255	303	335	22.85	
	III	433	439	548	16.55	
2	I	122	165	171	0.91	51.01
	II	273	318	336	33.29	
	III	408	443	483	13.72	
3	I	103	122	131	1.48	11.63
	II	206	213	228	2.85	
	III	279	351	417	83.27	

T_{onset} is the onset thermal degradation temperature.

T_{max} is the temperature that corresponds to the maximum rate of decomposition for each stage evaluated from the peaks of the first derivative (DTG) curves.

T_{endset} is the endset thermal degradation temperature.

W_{m} is the mass loss rate corresponding to T_{max} values.

W_{rez} is the percent of residue remaining at the end of thermal degradation (700 °C).

generates more free radicals during thermal decomposition, hence lowering the sample's thermal stability and residue value (11.63%).

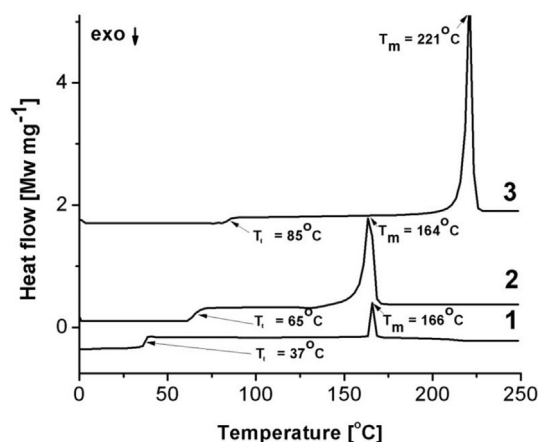


Fig. 6 DSC second heating curves of the studied structures.

Fig. 6 shows the DSC curves corresponding to second heating runs of the studied samples.

As expected, considering their crystalline form, the three compounds show melting transitions at 166 °C (1), 164 °C (2) and 221 °C (3). But, besides this, each of them shows an endothermic transition at lower temperatures, 37 °C (1), 65 °C (2) and 85 °C (3), attributed to the thermochromism phenomenon. It is supposed that a keto-enolic tautomerism occurs in solid state, as was also highlighted in solution in certain solvents (see above), as literature also reports (Zhu et al., 2016; Ogawa et al., 2001). In order to verify this, IR spectra were recorded at transition temperatures marked on DSC curves as T_t and comparatively shown with those recorded at room temperature in Fig. 7. It can be seen that indeed these transitions correspond to keto-enolic tautomerism.

3.6. Biological studies (antimicrobial and antifungal studies)

Aminopropylsilatrane and its derivatives are of a special interest as biologically active compounds, with various pharmaceutical applications as antitumor, antiviral and regulating plant growth. Their anticancer activity has been demonstrated in

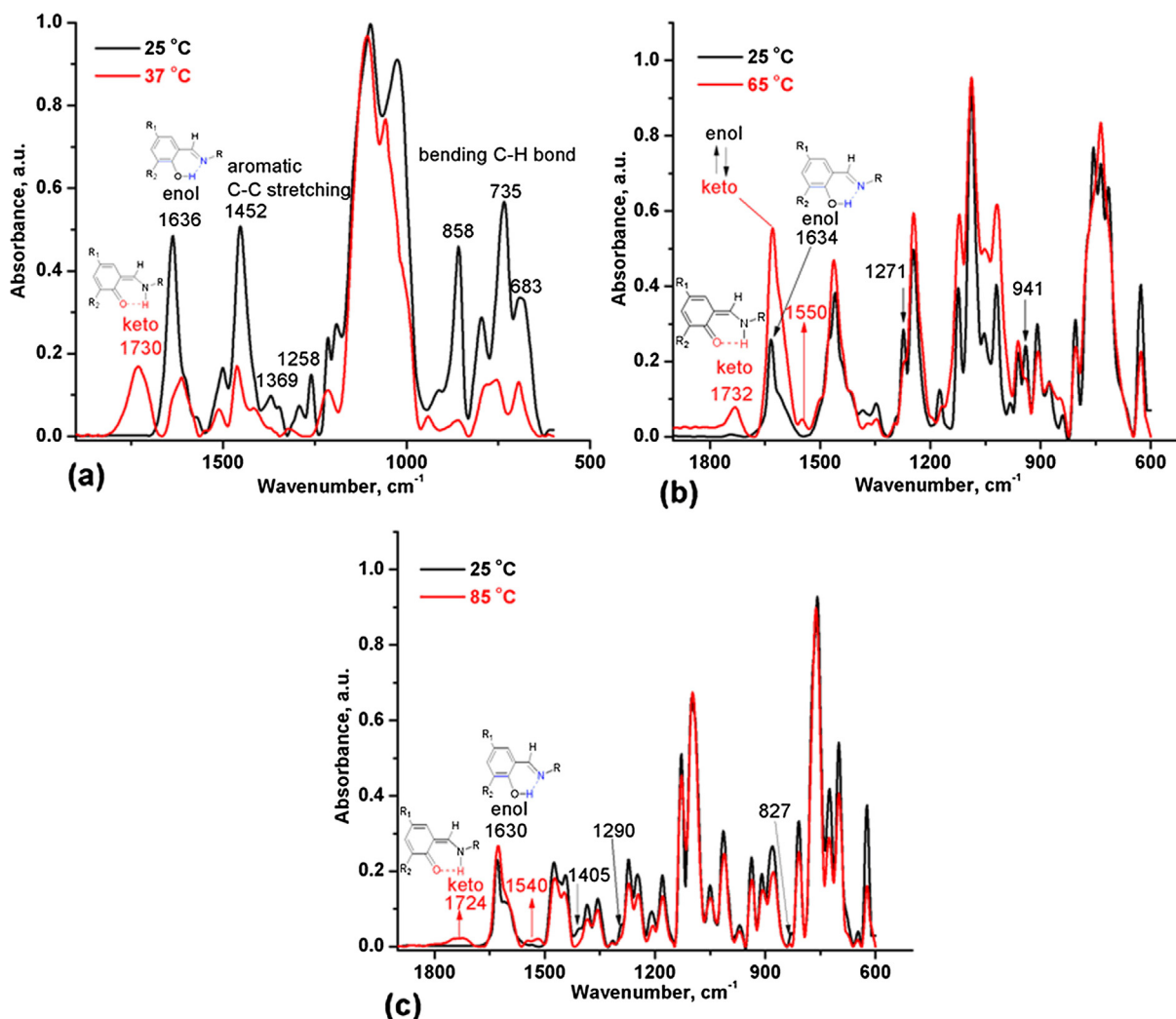


Fig. 7 IR spectra revealing keto-enolic tautomerization occurrence at temperatures T_t specific for each sample as identified on DSC curves, compared to those recorded at room temperature.

different cell lines by inhibiting tumor growth through few mechanisms (Ping et al., 2014).

A great importance on the antimicrobial activity of silatrane derivatives has their hydrophobicity mainly due to the alkyl groups favoring on the one hand the hydrolytically stability and on the other hand the direct diffusion through the lipid bilayer due to the lipophilicity (Hearn and Cynamon, 2004).

The antimicrobial efficacy of different biomolecules is dependent on many cellular routes as well as physico-chemical and metabolic characteristics of the various drugs (Fong, 2015). For the Schiff bases, many researches have indicated that their biological activity can be explained based on the structure of the azomethine $\text{CH}=\text{N}$ bond. These compounds possess N, O-donor atoms which can polarize the azomethine group improving its ability for hydrogen bonding and in this way the interaction with the cell membrane of the microorganisms. An important characteristic for the antimicrobial activity of biomolecules is their hydrophobic/hydrophilic balance which can have a large action on the transport across the cell membrane. The most important factors influencing the thermodynamics binding affinity between the drug and membrane transporter are lipophilicity and dipole moment of the drug.

The study of antimicrobial activity of the new synthesized compound was carried out using three species of fungi (*Aspergillus fumigatus* ATCC 66567, *Penicillium chrysogenum* ATCC 20044, *Fusarium* ATCC 20327) from pure culture and two bacteria (*Pseudomonas* sp. ATCC 15780 and *Bacillus* sp. ATCC 31073) species according to previously reported standard procedures (Zaltariov et al., 2015; Zaltariov et al., 2013).

The results of the antimicrobial activity as MIC values ($\mu\text{g/ml}$) for the analyzed compounds were compared with those of the standard ones: *Capsofungin* (MIC = 0.3 $\mu\text{g/ml}$) and *Kanamycin* (MIC = 4 $\mu\text{g/ml}$). The Schiff bases having chloro and *t*-Bu substituents, **1** and **3**, respectively, have no effect against bacteria and fungi (MIC > 128 $\mu\text{g/ml}$), while the Schiff base **2** with methoxy substituent on the aromatic ring showed a good antifungal activity (MIC = 0.08 $\mu\text{g/ml}$).

In the case of the Schiff bases, the antimicrobial activity can be explained based on the structure of the azomethine group, which can be polarized by the presence of different donor atoms N and O. In the case of **2** the presence of the methoxy substituent with electron-donor properties larger than chloro substituents contributes to the polarization of the imine group increasing its ability for hydrogen bonding with the membrane constituents, indicating their biological activity (Singh et al., 2018).

4. Conclusions

Three new Schiff base-functionalized propylsilatranes were prepared by reacting 1-(3-aminopropyl)silatrane with 3,5-dichlorosalicylaldehyde, 3-methoxysalicylaldehyde and 3,5-di-*tert*-butylsalicylaldehyde. The obtained structures were confirmed by elemental and spectral (FTIR, ^1H NMR, ^{13}C NMR and UV-Vis) analyses as well as by single-crystal X-ray diffraction. In all the structures, the silicon exhibits a pentacoordinated environment with slightly distorted trigonal bipyramidal geometry. The effect of the substituents on the

structural, thermal, biocidal and water vapor sorption properties were investigated. The substitution with chloro, methoxy and *t*-Bu groups led to the stabilization in solution of keto-enol tautomer species, mainly enol, depending on the polarity of the solvent. The absorption maxima are affected by: solvent polarity and the nature of the substituent.

In the absence of other factors besides water vapor in the atmosphere of nitrogen, after exposure of 5 h, the bonds susceptible to hydrolysis, $\text{Si}-\text{C}$, $\text{Si}-\text{N}$ and $\text{CH}=\text{N}$ are not affected. Thermal stability is strongly affected by the nature of the substituents on the aromatic ring. DSC studies showed, as expected melting transitions but also keto-enolic tautomerization at temperatures specific for each sample, the latter being supported by the IR studies. Only compounds with methoxy substituent at aromatic ring showed biological activity.

Acknowledgment

This work was supported by a grant of the Ministry of Research and Innovation, CNCS-UEFISCDI, project number PN-III-P4-ID-PCE-2016-0642 (Contract 114/2017), within PNCDI III. We sincerely thank Dr. N. Vornicu for biological tests.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.arabj.2018.09.001>.

References

- Acar, Y., Kara, H., Gungor, E., Coban, M.B., 2018. Catena-poly[[[2,4-dichloro-6-((2-hydroxyethyl)imino)methyl]phenolato- ^3N , O, O']-copper(II)]- μ -chlorido]monohydrate]: synthesis, structural, spectroscopic and luminescent properties. *Mol. Cryst. Liq. Cryst.* 664, 165–174.
- Al-Ghamdi, R.F., Fahmi, M.M., Mohamed, N.A., 2006. Reinforcement of dynamically vulcanized EPDM/PP elastomers using organoclay fillers. *Polym. Degrad. Stab.* 91, 1530–1544.
- Bernardo, P.D., Zanonato, P.L., Tamburini, S., Tomasin, P., Vigato, P.A., 2006. Complexation behaviour and stability of Schiff bases in aqueous solution. The case of an acyclic diimino(amino) diphenol and its reduced triamine derivative. *Dalton Trans.*, 4711–4721.
- Brennan, B.J., Keirstead, A.E., Liddell, P.A., Vail, S.A., Moore, T.A., Moore, A.L., Gust, D., 2009. 1-(3'-amino)propylsilatrane derivatives as covalent surface linkers to nanoparticulate metaloxide films for use in photoelectrochemical cells. *Nanotechnology* 20 (50). IOP Publishing Ltd..
- Chuit, C., Corriu, R.J.P., Reye, C., Young, J.C., 1993. Reactivity of penta- and hexacoordinate silicon compounds and their role as reaction intermediates. *Chem. Rev.* 93, 1371–1448.
- Cozzi, P.G., 2004. Metal-Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.* 33, 410–421.
- CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.34.76, 2003.
- Dolomanov, V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., Puschmann, H., 2009. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 42, 339–341.
- Dumitriu, A.M.C., Cazacu, M., Shova, S., Turta, C., Simionescu, B. C., 2012. Synthesis and structural characterization of 1-(3-aminopropyl)silatrane and some new derivatives. *Polyhedron* 33, 119–126.

- Fong, C., 2015. Anti-cancer properties of “hydrophilic and hydrophobic” statins and cyclin-dependent kinases (research report) Eigenenergy, Adelaide, Australia <hal-01368756>.
- Godoy-Alcantar, C., Yatsimirsky, A.K., Lehn, J.M., 2005. Structure-stability correlations for imine formation in aqueous solution. *J. Phys. Org. Chem.* 18, 979–985.
- Gungor, E., Coban, M.B., Kara, H., Acar, Y., 2018. Antiferromagnetic coupling in a new Mn(III) Schiff base complex with open-cubane core: structure, spectroscopic and luminescence properties. *J. Cluster Sci.* 29, 533–540.
- Hearn, M.J., Cynamon, M.H., 2004. Design and synthesis of antituberculars: preparation and evaluation against *Mycobacterium tuberculosis* of an isoniazid Schiff base. *J. Antimicrob. Chemother.* 53, 185–191.
- Iwamiyati, J.H., Maciel, G.E., 1993. Chemical shifts in silatrane and its derivatives: a study of the transannular interaction. *J. Am. Chem. Soc.* 115, 6835–6842.
- Kaya, I., Koyuncu, S., Çulhaoğlu, S., 2008. Studying the utilization of plastic waste by chemical recycling method. *Polymer* 49, 703–714.
- Khalaji, A.D., Mighani, H., Bijanzadeh, H.R., Gotoh, K., Ishida, H., 2011. One dimensional hydrogen bonded arrangement in new Schiff-base compound (E)-2-(2,5-dimethoxybenzylideneamino)phenol(1): synthesis, characterization, crystal structure and conformational studies. *J. Chem. Crystallogr.* 41, 1515–1519.
- Mitra, S., Tamai, N., 1999. A combined experimental and theoretical study on the photochromism of aromatic anils. *Chem. Phys.* 246, 463–475.
- Mutneja, R., Singh, R., Kaur, V., Wagler, J., Fels, S., Kroke, E., 2016. Schiff base tailed silatranes for the fabrication of functionalized silica based magnetic nano-pores possessing active sites for the adsorption of copper ions. *New J. Chem.* 40, 1640–1648.
- Noshay, A., Matzner, M., 1974. Hydrolytic stability of the Si-O-C linkage in organo-siloxane block copolymers. *Die Angew. Makromol. Chem.* 37, 215–218.
- Ogawa, K., Harada, J., Fujiwara, T., Yoshida, S., 2001. Thermochromism of salicylideneanilines in solution: aggregation-controlled proton tautomerization. *J. Phys. Chem. A* 105, 3425–3427.
- Pedersen, B., Wagner, G., Herrmann, Echert'98. Electronic Conference on Heterocyclic Chemistry, 29 June–24 July, 1998, <http://www.ch.ic.ac.uk/ectoc/echet98/pub/048/index.htm>.
- Ping, G., Yue-Wu, W., Xin-Tong, L., Xiao-Lu, Q., Le-Ping, H., Zi-Xin, X., Qing, Y.F., 2014. Synthesis, antitumor activity and SAR of N-substituted γ -aminopropylsilatrane derivatives. *Phosphorus, Sulfur Silicon Related Elements* 189, 511–518.
- Puri, J.K., Singh, R., Chahal, V.K., 2011. Silatranes: a review on their synthesis, structure, reactivity and applications. *Chem. Soc. Rev.* 40, 1791–1840.
- Scheschkewitz, D., 2014. Functional Molecular Silicon Compounds I: Regular Oxidation States, vol. 233. Springer, p. 8 <http://link.springer.com/book/10.1007%2F978-3-319-03620-5>.
- Seiller, O., Burschka, C., Fenske, T., Troegel, D., Tacke, R., 2007. Neutral hexa- and pentacoordinate silicon (IV) complexes with SiO (6) and SiO(4)N skeletons. *Inorg. Chem.* 46 (13), 5419–5424.
- Sheldrick, G.M., 2008. A short history of SHELX. *Acta Crystallogr. A* 64, 112–122.
- Sidorkin, V.F., Pestunovich, V.A., Voronkov, M.G., 1980. The physical chemistry of silatranes. *Russ. Chem. Rev.* 49, 414–427.
- Singh, G., Saroa, A., Girdhar, S., Rani, S., Choquesillo-Lazarte, D., Chandra Sahoo, S., 2015b. Incorporation of azo group at axial position of silatranes: synthesis, characterization and antimicrobial activity. *Appl. Organometal. Chem.* 29, 549–555.
- Singh, G., Saroa, A., Khullar, S., Mandal, S.K., 2015a. Schiff bases of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and its silatranes: synthesis and characterization. *J. Chem. Sci.* 127 (4), 679–685.
- Singh, G., Saroa, P.A., Singh, J., Sharm, R.P., Ferretti, V., 2016. Schiff base functionalized organopropylsilatranes: synthesis and structural characterization. *J. Chem. Sci.* 128 (2), 193–200.
- Singh, G., Kalra, P., Aora, A., Singh, A., Sharma, G., Maurya, I.K.S., Dutta, S., Munshi, P., Verma, V., 2018a. Acetylenic indole-encapsulated Schiff bases: synthesis, in silicon studies as potent antimicrobial agents, cytotoxic evaluation and synergistic effects. *Chem. Select* 3, 2366–2375.
- Singh, G., Kaur, G., Singh, J., 2018b. Progressions in hyper-coordinate silicon complexes. *Inorg. Chem. Commun.* 88, 11–20.
- Singh, R., Mutneja, R., Kaur, V., Wagler, J., Kroke, E., 2013. Derivatization of 3-aminopropylsilatrane to introduce azomethine linkage in the axial chain: synthesis, characterization and structural studies. *J. Organomet. Chem.* 724, 186–191.
- Socrates, G., 2001. Infrared and Raman Characteristic Group Frequencies. Tables and Charts. John Wiley & Sons, LTD, Chichester, pp. 76–146.
- Tharmaraj, P., Kodimunthiri, D., Sheela, C.D., Shanmuga Priya, C.S., 2009. Synthesis, spectral characterization, and antimicrobial activity of copper(II), cobalt(II), and nickel(II) complexes of 3-formylchromoniminopropylsilatrane. *J. Coord. Chem.* 62 (13), 2220–2228.
- Vargas, V., Amigo, L., 2001. A study of the tautomers of N-salicylidene-p-X-aniline compounds in methanol. *J. Chem Soc Perkin Trans. 2*, 1124–1129.
- Voronkov, M.G., Dyakov, V.M., Kirpichenko, S.V., 1982. Silatranes. *J. Organomet. Chem.* 233 (1), 1–147.
- Voronkov, M.G., Belyaeva, V.V., Abzaeva, K.A., 2012. Basicity of silatranes. *Chem. Heterocycl. Comp.* 47, 1330–1338.
- Warncke, G., Bohme, U., Gunther, B., Kronstein, M., 2012. Racemization versus retention of chiral information during the formation of silicon and tin complexes with chiral Schiff base ligands. *Polyhedron* 47, 46–52.
- Zaltariov, M.F., Cazacu, M., Vornicu, N., Shova, S., Racles, C., Balan, M., Turta, C., 2013. A new diamine containing disiloxane moiety and some derived Schiff bases: synthesis, structural characterization and antimicrobial activity. *Supramol. Chem.* 25 (8), 490–502.
- Zaltariov, M.F., Cazacu, M., Shova, S., Varganici, C.D., Vacareanu, L., Musteata, V., Airinei, A., 2014. A silicon-containing polyazomethine and derived metalcomplexes: synthesis, characterization and evaluation of the properties. *Des. Monom. Polym.* 17 (7), 668–683.
- Zaltariov, M.F., Cazacu, M., Avadanei, M., Shova, S., Balan, M., Vornicu, N., Vlad, A., Dobrov, A., Varganici, C.D., 2015b. Synthesis, characterization and antimicrobial activity of new Cu (II) and Zn(II) complexes with Schiff bases derived from trimethylsilyl-propyl-p-aminobenzoate. *Polyhedron* 100, 121–131.
- Zaltariov, M.F., Vlad, A., Cazacu, M., Avadanei, M., Vornicu, N., Balan, M., Shova, S., 2015a. Silicon-containing bis-azomethines: synthesis, structural characterization, evaluation of the photophysical properties and biological activity. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 138, 38–48.
- Zhu, S.P., Chen, Y., Sun, J., Yang, Y.T., Yue, C.J., 2016. Synthesis, characterization, thermochromism and photochromism of aromatic aldehyde hydrazone derivatives Article ID 8460462 *J. Chem.*, 8