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Synthesis and structural characterization of functionalized cyclotetrasiloxane rings [4-$RC_6H_4Si(O)OR'$]$_4$ (R = Cl, Br, CH=CH_2, CH_2Cl; R′ = Na, $SiMe_3$) as scaffolds for the synthesis of models of a silica bound monolayer of fluorescent or second order NLO active organic chromophores

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Prof. Gyula Pályi in honour of his 70th birthday.

Abstract

A series of sodium arylcyclotetrasiloxanolates properly functionalized in the *para* position of the aromatic ring, like [4-$RC_6H_4Si(O)ONa$]$_4$ and the corresponding (trimethylsiloxy)cyclotetrasiloxanes [4-$RC_6H_4Si(O)OSiMe_3$]$_4$ (R = Cl, Br, CH=CH_2, CH_2Cl), were prepared as scaffolds for anchoring second order NLO active or fluorescent organic chromophores. Such cyclic molecules can be regarded as 2D models reproducing supramolecular organizations as monolayers. The crystalline structures of some of the compounds synthesized in this work were characterized by single crystal X-ray diffraction analysis at low temperature. All the compounds have phenyl rings in an all-*cis* arrangement with respect to the tetrasiloxane cycle which, in the trimethylsiloxy derivatives, is quite planar. In these latter compounds the phenyl rings are almost parallel one to the other, although not orthogonal to the ring.

Keywords: Silica surface; Models; X-ray structures; Cyclotetrasiloxanolates

1. Introduction

A topic of current interest is the preparation, by new growth or self-assembly techniques, of functional nanoscale multimolecular organizations (e.g. thin films, multilayers, molecular wires, etc.) with an efficient translation of the functional molecular properties into the macroscopic properties of a nanostructured material. However, full control of the macroscopic properties of nanomaterials, such as their optoelectronic, electrical, charge transport or magnetic properties, can only be achieved if there is a high level of control on the nanometer scale [1].

Approaches to such preparation include crystal engineering, nano-organization by the Langmuir–Blodgett technique [2], self-assembly and self-organization guided by hydrogen bonding and ionic interactions [3]. Indeed, particular interest today lies in the development of efficient synthetic approaches that lead to a step by step growth of ordered superlattices [1,3,4].

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A silica surface is an attractive substrate for the preparation of layer-by-layer, or even monolayer, siloxane based organizations [5]. Indeed, an approach to nanomaterials with non-linear optical or luminescent properties is through the guided preparation of an ordered assembly of organic chromophores bound to a flat surface of silica. However, the anchoring of organic chromophores to a silica surface first requires the grafting of the silica surface with bifunctional coupling layer groups that can be linked to both the surface and the organic chromophores [1a,5].

One interesting question not yet explained is the effect, on the optical properties, of the possible non-bonding electronic interaction of chromophores closely packed on the layer. One way to investigate the effect on the functional properties of the closeness of so many chromophores bound to the substrate is the synthesis, and investigation, of the functional properties of a simple model of a fragment of silica surface with only a few closely assembled and covalently bound chromophores.

A generation of potential models based on cyclosiloxane rings has been developed to imitate fragments of a silica surface [6]. The first examples of phenylcyclooligometallasiloxanolates were reported in the early 1990s by the pioneering work of Shchegolikhina et al. [7]; their structures consisted in stereoregular phenylsiloxane macrocycles such as $[C_6H_5Si(O)O^-]_n$ ($n = 3,4,6,8,12$), linked to alkaline and/or transition metals [8].

More recently, such cyclic phenylsiloxanes have been obtained without stabilizing the stereoregular macrocycle by a metal [9].

Indeed, when the ring is small enough to be sufficiently rigid ($n = 3,4$), these macrocycles can be considered a 2D model of a silica surface fragment. In addition, as in monolayers, when $n = 3,4$ the aromatic moieties are in an all-*cis* arrangement with respect to the oligosiloxane cycle, the alignment among them being almost parallel [9c]. Therefore, by binding covalently second order NLO active, or luminescent, organic chromophores to these macrocycles a suitable model of a covalently assembled monolayer can be obtained. A preliminary step in the synthesis of such models is the synthesis of cyclic molecules with the phenyl ring substituted by a reactive group in the *para* position, so as to generate a building block that acts as the scaffold of the monolayer model. Therefore, in this paper we report the synthesis of a series of sodium phenylcyclotetrasiloxanolates ($n = 4$) properly functionalized in the *para* position of the aromatic rings, $[4\text{-}RC_6H_4Si(O)ONa]_4$, and of the corresponding trimethylsiloxy derivatives, $[4\text{-}RC_6H_4Si(O)\text{-}OSiMe_3]_4$ (R = Cl, Br, CH=CH$_2$, CH$_2$Cl). Attempts to obtain these compounds by simply following the procedure reported by Shchegolikhina et al. for unsubstituted phenyl derivatives [9c] failed. In fact, the synthesis of these cyclic molecules is so sensitive to a combination of experimental factors (e.g. water content, solvent nature, base amount, etc.) that simply starting from a *para* substituted phenyltriethoxysilane we produced a complex mixture of oligomers and resin materials. After careful investigation, the sodium salts of the expected cyclotetrasiloxane rings were obtained only by slow separation from the reaction solution. This means that the selective synthesis of such salts is controlled by their solubility under specific reaction conditions. Here we report the optimized synthesis of many sodium arylcyclotetrasiloxanolates $[4\text{-}RC_6H_4Si(O)ONa]_4$ and their trimethylsiloxy derivatives $[4\text{-}RC_6H_4Si(O)OSiMe_3]_4$ (R = Cl, Br, CH=CH$_2$, CH$_2$Cl). Moreover, we investigated the X-ray single-crystal structures of some of them in an effort to understand whether the *para* substitution of the phenyl ring can influence the crystalline packing, and the potential interactions of the phenyl rings of the building blocks.

2. Results and discussion

2.1. Synthesis

Compounds $[4\text{-}RC_6H_4Si(O)ONa]_4$ (R = Cl, Br, CH=CH$_2$, CH$_2$Cl) were prepared by controlled alkaline hydrolysis of the corresponding triethoxysilane, as proposed by Shchegolikhina et al. [9c] for the synthesis of the unsubstituted compound $[C_6H_5Si(O)ONa]_4$. However, the presence of a substituent in the *para* position of the aromatic ring forced us to introduce some modifications to the synthetic procedure in order to obtain selectively, and in good yield, the expected compounds, which could then be used without further purification (see Section 4).

Reactions of *para* substituted phenyltriethoxysilanes with NaOH (Si/NaOH = 1/1) were performed in the presence of water (Si/H$_2$O = 1/1) using EtOH as solvent with a 1.5 M concentration of the aryltriethoxysilane according to Scheme 1.

Differently from Shchegolikhina et al. [9c], as starting material we used only the triethoxy derivative, working in ethanol. In fact, moving from the triethoxy to the tributoxy derivative and working in *n*-butanol we were unable to obtain the sodium salts **1**–**4** in acceptable purity and yield. It appears that solvent volatility is an important requirement, since the reaction must be carried out at room temperature under nitrogen stream for 1 h to slowly reduce the volume to one half. Under these conditions the pure

$$4\,[4\text{-}RC_6H_4Si(OEt)_3] + 4\,NaOH + 4\,H_2O \xrightarrow[EtOH,\ r.t.]{N_2} [4\text{-}RC_6H_4Si(O)ONa]_4 \cdot nEtOH$$

R = Cl **1**; R = Br **2**; R = CH=CH$_2$ **3**; R = CH$_2$Cl **4**

Scheme 1.

compounds **1**–**4** were separated out as white crystalline powders in good to high yield (40–80%).

The starting reagent 4-(triethoxysilyl)bromobenzene was prepared in good yield (66%) from 1,4-dibromobenzene, making some modifications to the known general procedure (see Section 4) [10]. Equally the 4-(triethoxysilyl)styrene was prepared in high yield (75%) from 4-bromostyrene, making some modifications to the known procedure (see Section 4) [11]. During the final distillation *in vacuo*, some 3,5-di-*tert*-butylcatechol was added in order to prevent polymerization.

Reacting the sodium salts **1**–**4** with Me_3SiCl in the presence of pyridine, as reported by Shchegolikhina et al. [9c], but with a larger excess of Me_3SiCl (1/20), the corresponding (trimethylsiloxy)cyclotetrasiloxanes were obtained in excellent yield, according to Scheme 2.

This latter step is useful in view of the further reactions of these *para* substituted phenylcyclosiloxane rings with organic chromophores. In fact, the trimethylsiloxy derivatives are not only much more soluble than the corresponding sodium salts, but they also present only one potential reactive group in the *para* position of the phenyl ring, and can be easily purified by chromatography on silica gel. Therefore, trimethylsiloxy derivatives are better scaffolds for covalently anchoring organic chromophores.

All the compounds were characterized by ^1H and ^{29}Si NMR spectra and elemental analyses. We were also able to define the nuclearity of our cyclic compounds by determining the parent peak of the trimethylsiloxy derivatives **5**–**8** by mass spectrometry, using the electrospray ionization source (ESI) (see Section 4). This is a significant result since up to now the nuclearity of these phenylcyclosiloxanes has been determined only by X-ray crystallography, and therefore only when suitable crystals could be obtained.

2.2. NMR and mass spectra

^1H NMR spectra of sodium salts **1**–**4** in DMSO are characterized by a sharp AA′BB′ system around 7 ppm and confirm the presence of some EtOH molecules. When the ^1H NMR spectrum is carried out on a pure crystalline sample, obtained directly by precipitation from the ethanol reaction solution without drying, the signals of the AA′BB′ system, typical of the *para* substitution, are very neat. When the same sample is dried *in vacuo* for some hours there is the loss of some EtOH molecules, as confirmed by the elemental analyses of the dried compound which becomes amorphous. The amount of EtOH left after drying is always different, so it is very difficult to reproduce a sample with the same 'after drying' composition.

$$[4\text{-}RC_6H_4Si(O)ONa]_4 \cdot n\text{EtOH} \xrightarrow[\substack{n\text{-hexane, }\Delta \\ -\text{ NaCl}}]{Me_3SiCl,\ py} [4\text{-}RC_6H_4Si(O)OSiMe_3]_4$$

R = Cl **5**; R = Br **6**; R = CH=CH$_2$ **7**; R = CH$_2$Cl **8**

Scheme 2.

These differences are reflected in the ^1H NMR spectrum as small AA′BB′ system changes, such as doubling of doublets or broadening of the signals, particularly of protons close to the substituent in the *para* position. This effect could be due to the decrease in the number of EtOH molecules, which produces some polycondensation or oligomerization, since the complex hydrogen bonding system (see later) stabilizing the cyclotetrasiloxane ring is destroyed.

^{29}Si NMR spectra of **1**–**4** show a single signal around −70 ppm, as expected for the 4 equivalent Si atoms of the siloxanolate ring. This signal remains unchanged on moving from the crystalline material separated out from the reaction solution to the amorphous dried compound, thus evidencing that the signal broadening observed in the ^1H NMR spectrum is probably due to the formation of some oligomers which cannot be detected by ^{29}Si NMR spectroscopy. In fact, we have found that such oligomers do not give a well defined signal in the ^{29}Si NMR spectrum.

^1H NMR spectra of trimethylsiloxy derivatives **5**–**8**, performed in $CDCl_3$ solution, are characterized by an AA′BB′ system like the corresponding sodium salts **1**–**4**, but with a slight downfield shift from the aromatic protons. Such a shielding effect can be interpreted in terms of a solvent effect, or a ring-current effect, exerted by each aryl moiety on the protons belonging to the others. In fact, in their X-ray structure (see later) the aryl moieties of trimethylsiloxy derivatives are in a more parallel position than the corresponding sodium salts. The expected strong singlet of the methyl protons of the trimethylsilyl fragment is at around 0.2 ppm, with the appropriate integral ratio compared with the aromatic protons.

In order to investigate the possible presence, in solution, of conformers of the trimethylsiloxy derivatives that involve aromatic moiety rotation around the aryl–Si bond, we performed some variable temperature experiments.

The low temperature ^1H NMR spectra of the trimethylsiloxy derivative **5** show the strong dependence of the doublets of the AA′BB′ system on the nature of the solvent, but we did not observe any signal splitting, as can be expected when different conformers are present. In toluene-d_8, decreasing the temperature to 183 K caused the signal of the aromatic protons *ortho* to the chlorine substituent of **5** to shift to high field ($\Delta ppm = 1.25$), whereas the protons *ortho* to the silicon atom did not move, so the two doublets became separated. On the contrary, in the $CDCl_3/CD_2Cl_2$ mixture, decreasing the temperature to 173 K caused the aromatic protons *ortho* to the silicon atom to shift to high field ($\Delta ppm = 0.8$) while the protons *ortho* to the chlorine substituent did not move so that the two doublets came closer together. Such behaviour in aromatic moieties is probably the result of completely different solute–solvent interactions due to the different steric and polar properties of the solvent [12].

The ^{29}Si spectra of (trimethylsiloxy)cyclotetrasiloxanes **5**–**8** show the expected two signals at about −80 ppm due

to silicon atoms of the ring, and at 11 ppm due to silicon atoms of the $OSiMe_3$ groups.

Mass spectra which, due to the low solubility of the sodium salts **1**–**4**, were performed only on the trimethylsiloxy derivatives **5**–**8** using an electrospray ionization source (ESI), clearly show the presence of the molecular peak $[M+Na]^+$, in agreement with a tetrameric species, with the expected isotopic distribution. Unfortunately, since the ESI technique is a soft method with relatively few fragmentations, it is useful to determine the parent peak, but in our experimental conditions it was not possible to evidence further fragmentation patterns.

2.3. Single crystal X-ray structural characterization

The crystalline structures of $[(4\text{-}BrC_6H_4)Si(O)OSiMe_3]_4$ (**6**) and $[4\text{-}RC_6H_4Si(O)ONa]_4 \cdot 9EtOH$ (R = Cl, **1**; Br, **2**; CH=CH_2, **3**) were determined by single crystal X-ray diffraction at low temperature (see Section 4).

Suitable crystals for X-ray diffraction of compounds **1**, **2** and **3** were obtained directly at room temperature by slow evaporation of the reaction solvent. Suitable crystals of compound **6** were obtained by evaporation of the reaction solvent to obtain an oily material and subsequent slow crystallization of the oil at −22 °C.

4-Bromophenyl(trimethylsiloxy)cyclotetrasiloxane $[(4\text{-}BrC_6H_4)Si(O)OSiMe_3]_4$ (**6**) (Fig. 1), crystallizes with a weakly interacting molecular packing, differing from the corresponding sodium cyclosiloxanolate **2** which shows extended ionic interactions.

The cyclic molecule of **6** is based on a slightly distorted planar skeleton of Si atoms connected by exo-cyclic oxygen bridges. Such kinds of molecules of the formula $[RSi(O)OR']_4$ (R = aryl, alkyl; R′ = H, alkyl) usually assume a *crown* conformation of eight-membered rings (instead of the *boat–boat* or the *boat–chair*) [13a], however, conformational analysis on the structure of **6** reveals an intermediate situation that does not allow clear classification [13b]. All the structures known in the literature (as isolated tetrameric units or as part of condensed polycycles or polyhedra) are in all-*cis* configuration. The only exceptions are represented by 1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane (synthesized in all the possible configurations, namely all-*cis*, all-*trans*, *cis–trans–cis* and *cis–cis–trans* [14a]) and by some tricyclic silsesquioxanes in *cis–trans–cis* configurations [14b,14c].

The conformation of the aryl and alkyl groups bonded to the Si atoms is clearly dictated by the need to minimize the mutual hindrance, therefore the four aryls not only have different torsions with respect to the Si–O bond (see Fig. 1 and Table 1), but also the angle of the Si_4O_4 average plane and the Si–Ar bonds is larger than 90°, being in the range 102–142°. There is only a modest influence of the crystalline environment (at most, very weak C–H···O contacts may be detected), with no stacking of the aryl groups. The crystal packing is dominated by the segregation of cyclotetrasiloxane molecules in layers (perpendicular to the *c*-axis of the monoclinic lattice). Each layer is separated from its neighbors by facing the R and R′ groups of the molecules, producing a weak "hook and loop" interpenetration on the side of the aryl moieties (Fig. 2). A similar packing motif was observed for the "parent" $[C_6H_5Si(O)OH]_4$ molecule [15], though characterized by stronger (Si)–O–H···O intermolecular hydrogen bonds.

It is interesting to compare the corresponding sodium derivative **2**, which crystallizes with solvent molecules, $[(4\text{-}BrC_6H_4)Si(O)ONa]_4 \cdot 9EtOH$.

As one can appreciate from Fig. 3a and b and Table 1, much larger distortions occur in the tetraanionic $[(4\text{-}BrC_6H_4)Si(O)O^-]_4$ moiety which deviates substantially from a square arrangement of Si atoms and where the conformation becomes closer to *boat–boat*. Therefore, the four Si atoms are further away from their least average plane, and two sets of aryls can be clearly identified: two have Si–Ar bonds almost perpendicular to the Si_4O_4 average plane and two are quite bent (ca. 145°) (see Table 1). Coupling the bending angle of the aryls with their orientation, the overall volume occupied by the $[(4\text{-}BrC_6H_4)Si(O)O^-]_4$

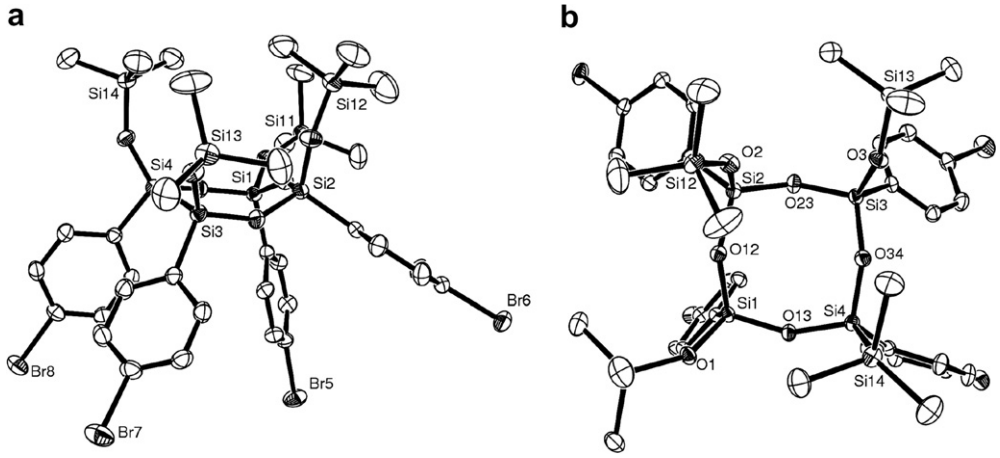

Fig. 1. Two views of the $[(4\text{-}BrC_6H_4)Si(O)OSiMe_3]_4$ (**6**) as characterized by X-ray single crystal diffraction (a: side view and b: upper view).

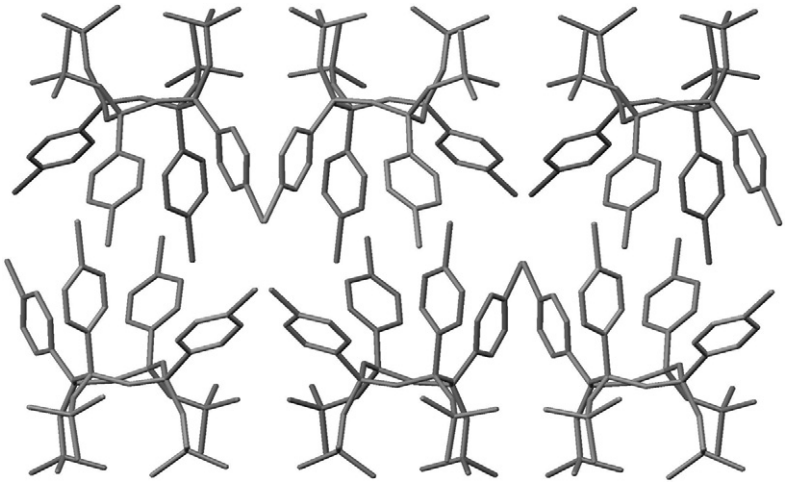

Fig. 2. View along crystallographic *a*-axis of the $[(4\text{-}BrC_6H_4)Si(O)OSiMe_3]_4$ (**6**).

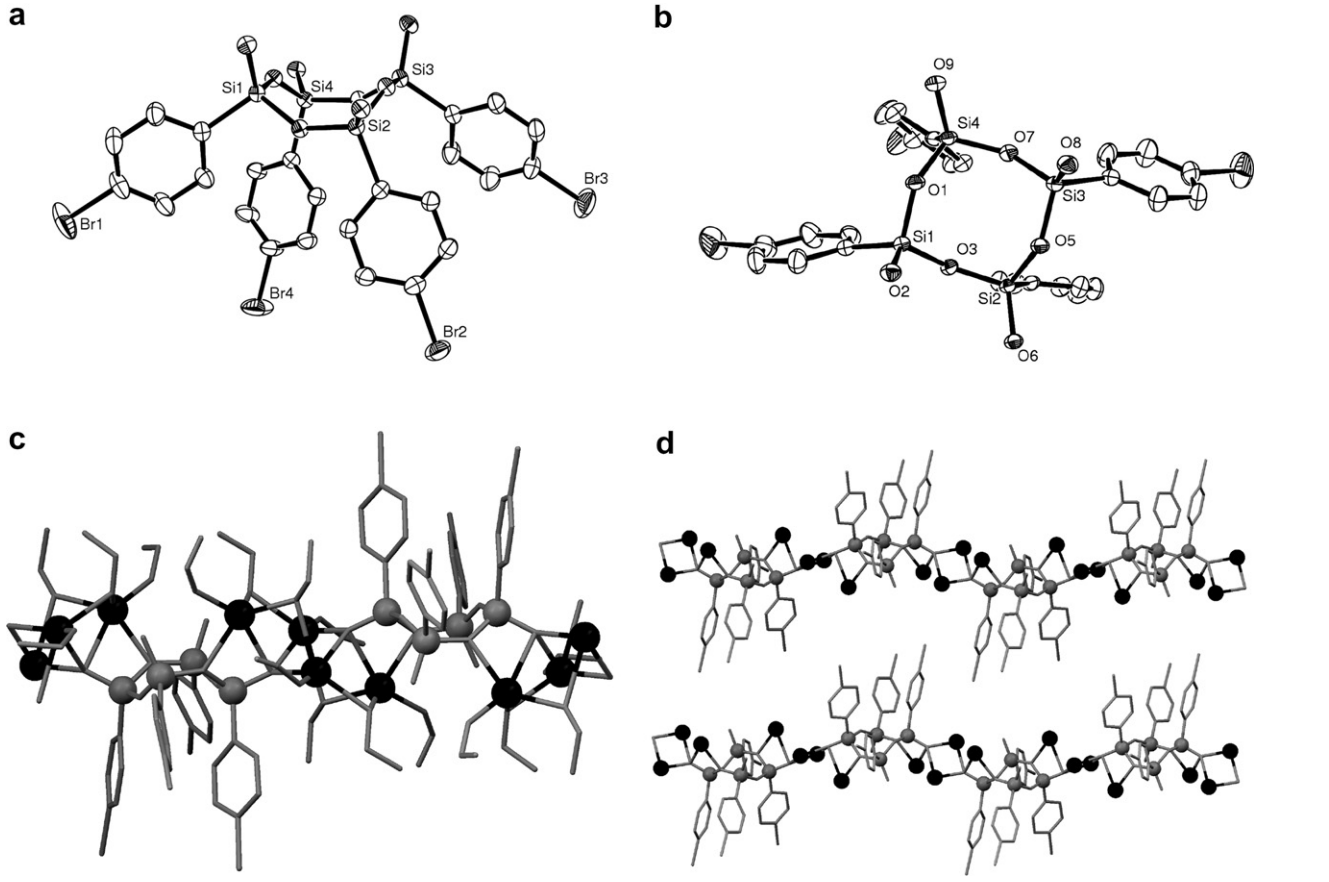

Fig. 3. ORTEP view of the anionic structure (a: side view and b: upper view) and of the corresponding crystalline packing (c and d) of $[4\text{-}RC_6H_4Si(O)ONa]_4 \cdot 9EtOH$ (R = Cl, **1**; Br, **2**). Hydrogen atoms are omitted for clarity as well as structurally disordered solvent molecules; $[4\text{-}RC_6H_4Si(O)O^-]$ units are in solid sticks, Si atoms are gray spheres, Na atoms are black spheres, EtOH molecules are represented with sticks in (c), but omitted for clarity in (d).

unit in **2** is much larger than that occupied by the tetracyclic moiety in **6** (see Figs. 1 and 3a and b for a visual comparison).

The crystal structure is dictated by the linkage of two opposite O^- anionic atoms of each $ArSi(O)O^-$ unit to three cations of a Na_4 cluster, which are held together by solvent molecules. Four ethanol molecules are terminally linked to each Na^+ cation and four others bridge two cations each, while a ninth solvent molecule is hydrogen bonded to one uncoordinated O^- atom and to another ethanol molecule

Table 1
Principal structural parameters of the $[4\text{-}RC_6H_4Si(O)OR']_4$ compounds (R′ = Na, R = Cl **1**, Br **2**, CH=CH_2 **3**; R′ = $SiMe_3$, R = Br **6**) investigated in this paper and those reported in the literature for the parent compound $[C_6H_5Si(O)ONa]_4 \cdot 8BuOH$ [9b]

	1	**2**	**3**	**6**	$[C_6H_5Si(O)ONa]_4 \cdot 8BuOH$
Si···Si	3.077	3.079	3.007	3.065	3.081
	3.078	3.081	3.067	3.124	3.084
	3.090	3.095	3.080	3.144	3.107
	3.124	3.128	3.087	3.156	3.108
Si···Si···Si	85.1	85.0	85.9	87.5	86.7
	86.1	86.1	86.5	89.2	86.8
	86.9	86.9	87.1	89.4	86.8
	87.6	87.6	88.2	90.0	86.9
$\langle Si–O_{(bridging)}\rangle$	1.63(1)	1.64(1)	1.64(1)	1.613(4)	1.638
$\langle Si–O_{(terminal)}\rangle$	1.583(5)	1.579(1)	1.59(1)	1.601(1)	1.584
$\langle Na\cdots O_{(alcohol)}\rangle$	2.41(12)	2.41(12)	2.39(10)	–	2.36(10)
$\langle Na\cdots O_{(silox.)}\rangle$	2.37(16)	2.37(15)	2.35(12)	–	2.46(18)
Si–O-Si	138.6	138.3	135.3	142.8	139.5
	139.2	139.4	136.7	150.6	139.9
	141.0	141.2	137.9	154.7	143.9
	147.9	147.9	142.0	157.1	144.4
Ar conformation[a]	15.1	16.0	16.4	62.3	6.4
	52.6	52.8	41.1	93.5	24.8
	105.5	104.5	105.4	148.3	119.0
	145.4	143.8	136.4	171.2	137.8
Si–Ar vs. Si_4O_4[b]	144.5	144.5	145.6	142.6	146.5
	140.0	140.5	136.2	119.8	145.3
	99.9	99.7	115.3	129.8	100.6
	94.2	95.0	97.8	102.9	100.6

Bond lengths are given in Å and bond angles in °.
[a] The aryl conformation is evaluated by the torsion of the aryl group with respect to the $Si–O_{terminal}$.
[b] The angle between the Si–C bond of each aryl group (in the same order of the Ar conformation) and the average plane of Si_4O_4 is reported.

(Fig. 3c). Overall, the Na^+ cations are penta-coordinated, counting also the interaction with one oxygen bridge of the cyclosiloxanolate unit. This crystalline network, controlled mainly by ionic interactions and hydrogen bonding, produces parallel chains of alternating cluster cations and cyclic anions elongated in one crystallographic direction (namely, the *c*-axis of the triclinic $P\bar{1}$ lattice, see Fig. 3c). Interestingly, in the chain two adjacent anionic cyclosiloxane units have an *anti* disposition of their bromophenyl groups, due to the crystallographic inversion centers located along the chains.

Also the inter-chain packing is at variance with what occurs in the neutral (trimethylsiloxy)cyclotetrasiloxane **6**. In fact, in **2** the aryl groups do not "interact", they are mutually shifted so that a $[(4\text{-}BrC_6H_4)Si(O)O^-]_4$ moiety of a chain is facing a $Na_4(EtOH)_8$ cluster of the other chain (see Fig. 3d).

The inter-chain packing in **2** is, however, even less tight than the inter-layer chain in **6** and this clearly affects the overall diffraction of the crystals, which is quite poor. In addition, on removal from their mother liquor the crystals quickly lose part of the ethanol molecules, collapsing into an amorphous phase. Therefore, it is also possible that during the X-ray diffraction investigation the crystals of **1**–**3** may have lost some of their solvent molecules, although this did not affect the solution of these crystal structures dramatically.

Interestingly, **2** has many structural similarities with the first example of such structures, namely $[C_6H_5Si(O)ONa]_4 \cdot 8BuOH$ [9b]. Despite the different nature and number of solvent molecules, and the presence of a bulky bromine atom in the aryl moieties of **2**, the two structures are isomorphous and therefore display the same packing motif (Table 1 gives, for the sake of comparison, the main structural parameters). The analogous compound $[(4\text{-}ClC_6H_4)Si(O)ONa]_4 \cdot 9EtOH$ (**1**) is, as expected, isomorphous and iso-structural to **2** with only negligible differences (Table 1). On the contrary, compound $[(4\text{-}CH_2{=}CHC_6H_4)Si(O)ONa]_4 \cdot 9EtOH$ (**3**), crystallizes in a different space group (monoclininc *C*2/*c*). Although there is a very similar structure of the chains (Fig. 4a), their packing is quite different, as the layers of chains directed along (1 1 0) and (1 −1 0) alternate. Thus, the interaction between two chains is quite different and more complex than in **1** or **2** (see Fig. 4b).

It can be concluded that the main feature of the $[ArSi(O)ONa]_4$ species is a chain made by cyclotetrasiloxane anionic units and Na_4 cationic clusters, controlled by ionic interaction and hydrogen bonding of the solvent molecules. Replacing the nature of the alkyl group of the solvent does not affect the chain network and its packing, while a bulky substituent in the *para* position may induce a different arrangement of the chains in the crystal.

Based on the structural investigation of this work, we can also predict that the chain motif of this class of compounds must be inherently centro-symmetric. In fact, it seems quite reasonable that two adjacent $[4\text{-}RC_6H_4Si(O)O^-]_4$ units arrange their bulky parts in opposite

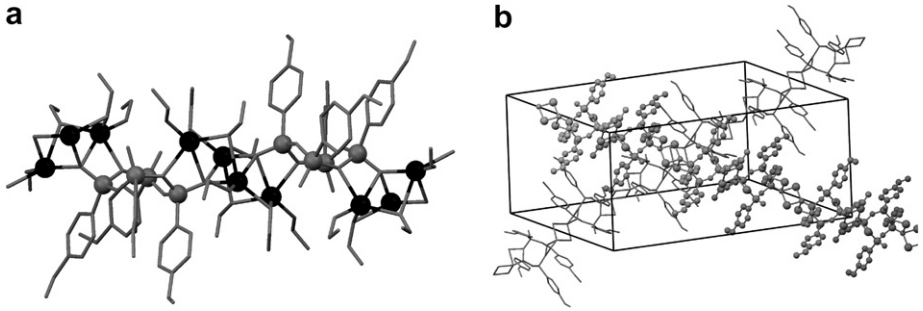

Fig. 4. The chain generated in $[(4\text{-}CH_2{=}CHC_6H_4)Si(O)ONa]_4 \cdot 9EtOH$ (**3**) (Si atoms are gray spheres, Na atoms are black spheres; EtOH molecules are represented with sticks in (a), but omitted for clarity in (b)) and corresponding packing of two chains in the monoclinic crystals (the front chain is represented by small spheres, the back one by sticks).

directions, thus favoring the formation of a crystallographic inversion center.

For the neutral compound **6**, and other related molecules, the reasoning is different since there is no special effect hampering their crystallization in non-centrosymmetric space groups. However, in the absence of specific intermolecular driving forces which could be introduced by specific substituents in the *para* position, this compound and the related molecules generally prefer a centrosymmetric packing.

This tendency towards centrosymmetric packing suggests that even the attachment of NLO active chromophores at the *para* position of the trimethylsiloxy derivative aryl moieties would not result in a NLO active crystalline material, even though at the molecular level in solution NLO activity would still be maintained.

3. Conclusions

In this paper we report an optimized synthetic methodology for the preparation, in good yield, of the cyclotetrasiloxane rings of general stoichiometry $[4\text{-}RC_6H_4Si(O)ONa]_4$ ($R = Cl$, Br, $CH{=}CH_2$, CH_2Cl) and the corresponding trimethylsiloxy derivatives $[4\text{-}RC_6H_4Si(O)OSiMe_3]_4$. In all compounds the phenyl moiety carries, in the *para* position, a reactive group suitable for anchoring a second order NLO active or a fluorescent organic chromophore.

This synthetic work is not at all trivial as the preparation and isolation of these products requires well defined conditions, quite different from those reported for the corresponding cyclotetrasiloxanes carrying an unsubstituted phenyl group [9b].

It can be seen that to obtain the products in good yield and high purity, they must separate out from the reaction solution as crystalline materials containing 9 ethanol molecules for each cyclotetrasiloxane unit. Just by drying under vacuum reduces the number of ethanol molecules controlling the crystalline network, thus producing amorphous materials which contain variable amounts of ethanol molecules for each cyclotetrasiloxane unit (usually three molecules).

Interestingly, we also identified a suitable mass spectrometry method to determine the parent peak of the trimethylsiloxy derivatives (in our case compounds **5**–**8**), thus allowing an easy definition of the nuclearity of these cyclotetrasiloxane rings which up to now was possible only in the case of suitable crystals for X-ray structural determination.

Finally, we have shown that by going from the ionic compounds to the related neutral compounds with trimethylsiloxy groups linked to the O^- anionic part of the cycle, we have a more planar structure of the cyclotetrasiloxane ring, and thus a closer packing of the *para*-substituted phenyl rings. In addition trimethylsiloxy derivatives are much more soluble than the corresponding sodium salts and can be easily purified by chromatography on silica gel.

In conclusion the trimethylsiloxy derivatives synthesized here can be considered better scaffolds for monolayer models of organic chromophores bound to a silica surface, although the aryl moieties are not orthogonally linked to the cyclotetrasiloxane ring.

Of course this model is limited by the presence of a hole at the center of the ring (Figs. 1b and 3b), so that the packing of the aryl moieties is probably less close than on a monolayer of organic molecules linked to a silica surface.

In any case, just in terms of aryl moiety packing, this is a more suitable 2D model of the silica surface than, for instance, the 3D silsesquioxanes usually used as excellent models for organometallic species involved in surface organometallic chemistry [16].

Bearing in mind that a relatively simple model cannot reproduce the complex and various topology of a silica surface [17] we are now extending our investigation. Our aim is to anchor various organic chromophores showing second harmonic generation or fluorescent emission to the aryl ring via the reactive group in the *para* position. Thus we hope to clarify whether the relatively close packing of these chromophores can introduce any significant variation into their absorption or emission properties, compared to their monomeric molecular counterparts.

4. Experimental

All reagents, anhydrous solvents and the 4-(triethoxysilyl)chlorobenzene were obtained from commercial sources (Aldrich) and used without additional purification. Pyridine was distilled under nitrogen. All reactions were performed under nitrogen atmosphere. The 4-(triethoxysilyl)bromobenzene [10] and 4-(trietoxysilyl)styrene [11] were prepared making some modifications to the procedure reported in the literature, 4-(triethoxysilyl)chloromethylbenzene was prepared by the correspondent trimethoxysilyl derivative by exchange reaction with anhydrous EtOH [18].

^{1}H and ^{29}Si NMR spectra were recorded with a Bruker Avance DRX 400 and DRX 500 spectrometers in $CDCl_3$ and DMSO-d_6 as solvents. Elemental analyses were carried out with a Perkin–Elmer CHN 2400 instrument in the Analytical Laboratories of the Department of Inorganic Metallorganic and Analytical Chemistry of Milan University. Mass spectra were collected with a Thermo-Finnigan apparatus with an Ion Trap analyzer (positive mode) and an Electrospray ionization source (ESI) using a LCQ-Advantage instrument.

4.1. X-ray crystallographic determination

The crystals were mounted on a glass fiber and collected on a Bruker SMART 1K (**2**), a Bruker SMART-APEX1 (**1** and **3**) and a Bruker SMART APEX2 (**6**) CCD area-detector diffractometers, all equipped with Oxford cryosystem LN cryostreams. Compounds **1**–**3** easily lost the included solvent and this required rapid mounting. The samples of species **3** underwent some degradation even under cold nitrogen stream, thus it was essential to carry out rapid data collection to prevent it (on the other hand, it was not possible to use a lower temperature because of crystal breaking below 200 K).

Graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation was used with the generator working at 50 kV and 30 mA (but for **2**, when 45 kV and 40 mA were set). Orientation matrixes were initially obtained from least-squares refinement on ca. 300 reflections measured in three different ω regions, in the range $0° < \theta < 23°$; cell parameters were optimized on the position, determined after integration, of all reflections above 10 $\sigma(I)$ level. Details of data collections are given in Table 2. An empirical absorption correction was applied (SADABS) [19]. The diffraction of species **1** and **3** was quite poor and therefore the data used for solution and refinement of the structure were limited to a lower resolution level.

The structures were solved by direct methods using SIR-97 [20] within the WINGX suite of programs [21], and were subsequently refined with full-matrix least-squares on F^2 on the basis of the independent reflections, reported in Table 2, with the program SHELX-97 [22]. Hydrogens were riding on their carbon and oxygen atoms (except for some EtOH molecules that had an ambiguous hydrogen

Table 2
Crystallographic data for the four crystalline systems investigated by X-ray diffraction analysis

Compound	**1**	**2**	**3**	**6**
Molecular formula	$[Cl_4C_{24}H_{16}O_8Si_4][Na]_4[C_2H_6O]_9$	$[Br_4C_{24}H_{16}O_8Si_4][Na]_4[C_2H_6O]_9$	$[C_{32}H_{28}O_8Si_4][Na]_4[C_2H_6O]_9$	$[Br_4C_{36}H_{52}O_8Si_8]$
Temperature (K)	200(2)	200(2)	200(2)	200(2)
Wavelength	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/a$
Unit cell dimensions				
a (Å)	13.628(4)	13.7228(6)	34.55(1)	11.19555(9)
b (Å)	13.548(4)	13.6882(6)	16.489(2)	21.173(2)
c (Å)	19.444(5)	19.4356(8)	24.114(6)	22.055(2)
α (°)	90.501(7)	90.307(1)		
β (°)	102.507(6)	102.167(1)	104.418(8)	95.688(1)
γ (°)	117.771(6)	117.846(1)		
Volume (Å^3)	3076.2(1)	3132.7(2)	13305(2)	5202(1)
Z	2	2	8	4
D_{calc} (g cm^{-3})	1.28	1.45	1.16	1.48
Absorption coefficient (mm^{-1})	0.357	2.73	0.173	3.321
Crystal size (mm)	$0.2 \times 0.1 \times 0.1$	$0.2 \times 0.2 \times 0.1$	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$
Crystal color	Transparent	Transparent	Transparent	Transparent
Diffractometer	SMART APEX1	SMART CCD 1K	SMART CCD	SMART APEX 2
Number of frames, time per frame	2400, 20 s	1800, 30 s	300, 50 s	1800, 30 s
Maximum θ data collection (°)	27	27	27	29
Reflections collected/unique	32362/12528	28992/12901	24228/10965	47075/13419
R_{int}	0.0474	0.0297	0.1008	0.0524
Data/restrain/parameters	12528/24/637	12390/24/637	10965/19/675	13419/0/505
Goodness-of-fit on F^2	1.11	1.027	0.921	0.994
R indices $[I > 2\sigma(I)]$	$R_1 = 0.1082$, $wR_2 = 0.3242$	$R_1 = 0.0592$, $wR_2 = 0.1610$	$R_1 = 0.0982$, $wR_2 = 0.2452$	$R_1 = 0.0502$, $wR_2 = 0.0992$
Largest difference in peaks and holes (e Å^{-3})	1.15 and −0.78	1.1 and −1.29	0.56 and −0.43	0.80 and −0.75

location, therefore they were omitted). Also the results of the refinements are reported in Table 2. If the refinement was stable, anisotropic temperature factors were assigned to non-hydrogen atoms, but for some carbon atoms of the solvent molecules this was not possible. Moreover, geometry restraints were necessary to refine sensible EtOH molecule positions. The large vibrational amplitudes of these groups are certainly related to their high volatility (see above), and probably reflect the presence of some vacancies which very likely occurred during the crystal manipulation.

4.2. Synthesis

4.2.1. Synthesis of 4-(triethoxysilyl)bromobenzene

To a stirring solution of 1,4-dibromobenzene (7.0 g, 29.7 mmol) in Et_2O (100 ml) at 0 °C, a 1.6 M solution of *n*-BuLi in *n*-hexane (18.5 ml, 29.7 mmol) was added. After 2 h the solution was added via cannula to a stirring solution of $ClSi(OEt)_3$ (12 ml, 59.4 mmol) in Et_2O (140 ml) at 0 °C, and LiCl immediately precipitated as a white powder. The reaction was allowed to warm to room temperature and was left overnight under stirring. The suspension was filtered off through Celite using a G3 filter. The solvent was removed and the residue was distilled under vacuum affording 6.12 g of the pure product as a colorless liquid (66% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.55 (m, 4H, *o*-C_6H_4Si, *m*-C_6H_4Si), 3.88 (q, 6H, CH_2), 1.26 (t, 9H, CH_3). ^{29}Si NMR (79.5 MHz, $CDCl_3$), δ, ppm: −58.3 (s).

4.2.2. 4-(Triethoxysilyl)styrene

A solution of 4-bromostyrene (6.54 ml, 50 mmol) in THF (5 ml) was added dropwise in 1 h, under rigorous water free conditions, to a 250 ml round bottom flask, under N_2 atmosphere, containing magnesium turnings (1.34 g, 55 mmol) in THF (60 ml). After addition, the reaction mixture was stirred for 1 h, then it was stopped to allow a black precipitate to settle from the solution of styrylmagnesium bromide. The Grignard reagent was added via cannula in a dropping funnel and was dropped in a solution of $ClSi(OEt)_3$ (19.6 ml, 100 mmol) in THF (50 ml) in half an hour. The resulting mixture was stirred overnight, then the solvent was removed *in vacuo* and the product extracted with *n*-hexane and filtered off on Celite to eliminate the magnesium salts. The solution was evaporated to dryness and the residue was distilled *in vacuo*, affording the pure product as a colorless liquid (10 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.67 (d, 2H, *o*-C_6H_4Si, $J_{H-H} = 7.9$ Hz), 7.45 (d, 2H, *m*-C_6H_4Si, $J_{H-H} = 7.9$ Hz), 6.74 (m, 1H, CH=, $J_{cis} = 10.9$ Hz, $J_{trans} = 17.6$ Hz), 5.83 (d, 1H, CH_2=, $J_{trans} = 17.6$ Hz), 5.30 (d, 1H, CH_2=, $J_{cis} = 10.9$ Hz), 3.90 (q, 6H, CH_2O), 1.27 (t, 9H, CH_3).

4.3. Synthesis of sodium cyclotetrasiloxanolates 1–4

Cyclotetrasiloxanolates **1**–**4** were synthesized according to the following general procedure: in a typical preparation, to a mixture of anhydrous EtOH, NaOH and H_2O, the amount of *para* substituted phenyltriethoxysilane [4-$RC_6H_4Si(OEt)_3$] was added in order to obtain a 1.5 M solution (silane/NaOH/H_2O = 1/1/1). The solution was left under nitrogen stream until the solvent was reduced to half volume (about 1 h) and compounds **1**–**4** precipitated from the solution. The residue was washed and centrifuged three times with anhydrous *n*-hexane and dried *in vacuo*, affording pure products **1**–**4**.

4.3.1. Sodium 4-chlorophenylcyclotetrasiloxanolate 1

Starting from (4-ClC_6H_4)$Si(OEt)_3$ (2.004 g, 7.29 mmol) in EtOH (4.9 ml) with NaOH (291 mg, 7.29 mmol) and H_2O (0.13 ml, 7.29 mmol), the pure product **1** (1.10 g, 77.6% yield) was obtained as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6), δ, ppm: 7.62 (d, 2H, *o*-C_6H_4Si), 7.18 (d, 2H, *m*-C_6H_4Si); ^{29}Si NMR (79.5 MHz, DMSO-d_6), δ, ppm: −70.3 (s). Anal. Calc. for $C_{24}H_{16}Cl_4Na_4O_8Si_4 \cdot 3EtOH$: C, 39.29; H, 3.71. Found: C, 39.45; H, 3.89%.

4.3.2. Sodium 4-bromophenylcyclotetrasiloxanolate 2

Starting from (4-BrC_6H_4)$Si(OEt)_3$ (2.10 g, 6.57 mmol) in EtOH (4.4 ml) with NaOH (263 mg, 6.57 mmol) and H_2O (0.12 ml, 6.57 mmol), the pure product **2** (650 mg, 41.4% yield) was obtained as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6), δ, ppm: 7.56 (d, 2H, *o*-C_6H_4Si), 7.38 (d, 2H, *o*-C_6H_4Si); ^{29}Si NMR (79.5 MHz, DMSO-d_6), δ, ppm: −70.0 (s). Anal. Calc. for $C_{24}H_{16}Br_4Na_4O_8Si_4 \cdot 3EtOH$: C, 32.9; H, 3.10. Found: C, 32.22; H, 3.23%.

4.3.3. Sodium 4-styryl-phenylcyclotetrasiloxanolate 3

Starting from (4-CH_2=CHC_6H_4)$Si(OEt)_3$ (2.015 g, 7.57 mmol) in EtOH (5.0 ml) with NaOH (303 mg, 7.57 mmol) and H_2O (0.135 ml, 7.57 mmol), the pure product **3** (998 mg, 71% yield) was obtained as a cream colored powder. ^{1}H NMR (400 MHz, DMSO-d_6), δ, ppm: 7.67 (d, 2H, *o*-C_6H_4Si, $J_{H-H} = 7.7$ Hz), 7.29 (d, 2H, *m*-C_6H_4Si, $J_{H-H} = 7.7$ Hz), 6.68 (m, 1H, CH=, $J_{cis} = 10.9$ Hz, $J_{trans} = 17.4$ Hz), 5.77 (d, 1H, CH_2=, $J_{trans} = 17.4$ Hz), 5.17 (d, 1H, CH_2=, $J_{cis} = 10.9$ Hz); ^{29}Si NMR (79.5 MHz, DMSO-d_6), δ, ppm: −70.23 (s). Anal. Calc. for $C_{32}H_{28}Na_4O_8Si_4 \cdot 2EtOH$: C, 51.65; H, 4.78. Found: C, 51.05; H, 4.60%.

4.3.4. Sodium 4-(chloromethyl)-phenylcyclotetrasiloxanolate 4

Starting from (4-$ClCH_2C_6H_4$)$Si(OEt)_3$ (3.90 g, 13.5 mmol) in EtOH (9.0 ml) with NaOH (541 mg, 13.5 mmol) and H_2O (0.24 ml, 13.5 mmol), the pure product **4** (2.28 g, 80.85% yield) was obtained as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6), δ, ppm: 7.67 (d, 2H, *o*-C_6H_4Si), 7.24 (d, 2H, *m*-C_6H_4Si), 4.69 (s, 2H, CH_2); ^{29}Si NMR (79.5 MHz, DMSO-d_6), δ, ppm: −69.88 (s). Anal. Calc. for $C_{28}H_{24}Cl_4Na_4O_8Si_4 \cdot 2EtOH$: C, 36.49; H, 3.09. Found: C, 36.82; H, 3.09%.

4.4. Synthesis of (trimethylsiloxy)cyclotetrasiloxanes 5–8

In a typical procedure: to the suspension of the sodium salts **1**–**4** in anhydrous *n*-hexane, Me_3SiCl and pyridine were added (sodium salt/Me_3SiCl/py = 1/20/10). The suspension was refluxed for 2 h under nitrogen atmosphere and, after cooling, NaCl and pyridinium chloridrate were filtered off and washed with anhydrous *n*-hexane. The *n*-hexane solution was washed with water until it was chloride-free, it was dried over $MgSO_4$ and, after filtration, the solvent was removed *in vacuo* affording the product as an oil that is purified by column chromatography.

4.4.1. 4-Chlorophenyl(trimethylsiloxy)cyclotetrasiloxane 5

Starting from **1** (2.08 g, 2.68 mmol) in anhydrous *n*-hexane (60 ml) with Me_3SiCl (6.8 ml, 53.6 mmol) and pyridine (2.3 ml, 26.8 mmol), the crude product **5** was obtained as a colorless oil. The compound was purified by column chromatography (silica gel, *n*-hexane/$CHCl_3$ = 9/1) affording 838 mg (64.4% yield) of pure **5** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.29 (d, 2H, *o*-C_6H_4Si, J_{H-H} = 8.24 Hz), 7.21 (d, 2H, *m*-C_6H_4Si, J_{H-H} = 8.24 Hz), 0.27 (s, 9H, $SiMe_3$); ^{29}Si NMR (79.5 MHz, $CDCl_3$), δ, ppm: 11.53 (s, $OSiMe_3$), −79.97 (s, $O_3SiC_6H_4Cl$). MS-ESI$^+$: m/z = 1001.8 $[M+Na]^+$.

4.4.2. 4-Bromophenyl(trimethylsiloxy)cyclotetrasiloxane 6

Starting from **2** (622 mg, 0.65 mmol) in anhydrous *n*-hexane (15 ml) with Me_3SiCl (1.65 ml, 13 mmol) and pyridine (0.55 ml, 6.5 mmol), the crude product **6** was obtained as a colorless oil. The compound was purified by column chromatography (silica gel, *n*-hexane/$CHCl_3$ = 9.4/0.6) affording 300 mg (68.2% yield) of pure **6** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.32 (d, 2H, *o*-C_6H_4Si, J_{H-H} = 8.1 Hz), 7.13 (d, 2H, *m*-C_6H_4Si, J_{H-H} = 8.1 Hz), 0.197 (s, 9H, $SiMe_3$); ^{29}Si NMR (79.5 MHz, $CDCl_3$), δ, ppm: 11.57 (s, $OSiMe_3$), −79.97 (s, $O_3SiC_6H_4Br$). Anal. Calc. for $C_{36}H_{52}Br_4O_8Si_8 \cdot 1.5n$-hexane: C, 41.98; H, 5.67. Found: C, 43.00; H, 5.64%. MS-ESI$^+$: m/z = 1180.7 $[M+Na]^+$.

4.4.3. 4-Styryl(trimethylsiloxy)cyclotetrasiloxane 7

Starting from **3** (768 mg, 1.03 mmol) in anhydrous *n*-hexane (25 ml) with Me_3SiCl (2.6 ml, 20.6 mmol) and pyridine (0.87 ml, 10.3 mmol), the crude product **7** was obtained as a colorless oil. The compound was purified by column chromatography (silica gel, *n*-hexane/$CHCl_3$ = 8/2) affording 212 mg (36% yield) of pure **7** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.35 (d, 2H, *o*-C_6H_4Si, J_{H-H} = 8.1 Hz), 7.22 (d, 2H, *m*-C_6H_4Si, J_{H-H} = 8.1 Hz), 6.71 (m, 1H, CH=, J_{cis} = 10.9 Hz, J_{trans} = 17.6 Hz), 5.78 (d, 1H, CH_2=, J_{trans} = 17.6 Hz, J_{gem} = 0.91 Hz), 5.29 (d, 1H, CH_2=, J_{cis} = 10.9 Hz, J_{gem} = 0.91 Hz), 0.274 (s, 9H, $SiMe_3$); ^{29}Si NMR (79.5 MHz, $CDCl_3$), δ, ppm: 10.64 (s, $OSiMe_3$), −79.51 (s, $O_3SiC_6H_4CH{=}CH_2$). MS-ESI$^+$: m/z = 967.7 $[M+Na]^+$.

4.4.4. 4-(Chloromethyl)phenyl(trimethylsiloxy)cyclotetrasiloxane 8

Starting from **4** (2.19 g, 2.63 mmol) in anhydrous *n*-hexane (70 ml) with Me_3SiCl (6.63 ml, 52.5 mmol) and pyridine (2.23 ml, 26.3 mmol), the crude product **8** was obtained as a pale yellow oil. The compound was purified by column chromatography (silica gel, *n*-hexane/$CHCl_3$ = 8/2) affording 1.1 g (58% yield) of pure **8** as a white oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.28 (d, 2H, *o*-C_6H_4Si, J_{H-H} = 8.0 Hz), 7.15 (d, 2H, *m*-C_6H_4Si, J_{H-H} = 8.0 Hz), 4.54 (s, 2H, CH_2Cl), 0.21 (s, 9H, $SiMe_3$) ^{29}Si NMR (79.5 MHz, $CDCl_3$), δ, ppm: 11.04 (s, $OSiMe_3$), −79.9 (s, $O_3SiC_6H_4CH_2Cl$). MS-ESI$^+$: m/z = 1058.2 $[M+Na]^+$. Anal. Calc. for $C_{40}H_{45}Cl_4O_8Si_8$: C, 46.40; H, 5.84. Found: C, 46.46; H, 5.97%.

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Appendix A. Supplementary material

CCDC 615086, 615087, 615088 and 615089 contain the supplementary crystallographic data for **1**, **2**, **3** and **6**. These data can be obtained free of charge via http://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 e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.007.

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