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Fluorescence of Siloxy Substituted Cyclohexasilanes

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tert-Butyldimethylsiloxy cyclosilanes $\text{Si}_6\text{Me}_{12-n}(\text{OTBDMS})_n$ ($n=1,2$) were synthesised, their UV/Vis and fluorescence spectra measured and compared with the spectra of the according phenylsilanes.

Keywords: fluorescence; siloxanes; cyclohexasilanes

Introduction

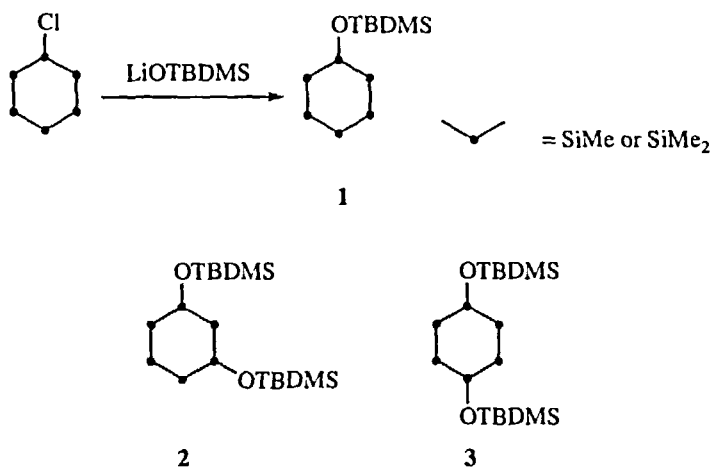
The fluorescence of arylidisilanes, has been investigated thoroughly in the recent years [1]. The strong fluorescence of Kautsky siloxene [2] encouraged our interest in cyclosilanes, because previous studies proved that only polymers derived from the hydrolysis of cyclic halosilanes show fluorescence, the ones from linear halosilanes do not [3,4].

Synthesis

$\text{Si}_6\text{Me}_{11}\text{OTBDMS}$ (**1**) is prepared by reacting $\text{Si}_6\text{Me}_{11}\text{Cl}$ with LiOTBDMS (see Scheme 1). In the same manner as **1** the disubstituted products $1,3\text{-Si}_6\text{Me}_{10}(\text{OTBDMS})_2$ and $1,4\text{-Si}_6\text{Me}_{10}(\text{OTBDMS})_2$ can be synthesised from the according chlorosilanes and two equivalents of

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LiOTBDMS. *cis*-1,3-Si₆Me₁₀(OTBDMS)₂ (**2**) and *trans*-1,4-Si₆Me₁₀(OTBDMS)₂ (**3**) crystallise as colourless solids from acetone solutions, Si₆Me₁₁OTBDMS is an oil at room temperature and is purified by chromatography over a RP-18 column.



Scheme 1

UV/Vis and Fluorescence Spectra

The UV/Vis (figure 1) and fluorescence (figure 2) spectra of **1-3**, *cyclo*-Si₆Me₁₂ (**4**) and the according phenylcyclohexasilanes Si₆Me₁₁Ph (**5**), *cis*-1,3-Si₆Me₁₀Ph₂ (**6**) and *trans*-1,4-Si₆Me₁₀Ph₂ (**7**) were measured at room temperature in cyclohexane and CH₂Cl₂ solutions. Although all compounds show fluorescence, there are significant differences in the spectra.

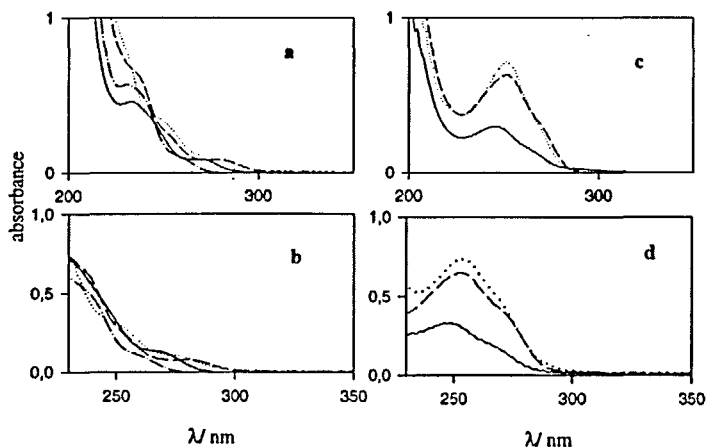


FIGURE 1 UV/ Vis spectra; left: —, 1, ..., 2, ---, 3, ---, 4, (a) in cyclohexane; (b) in CH_2Cl_2 , $c = 1.10^{-4}$ mol/L; right: —, 5, ..., 6, ---, 7, (c) in cyclohexane (d) in CH_2Cl_2 , $c = 2.10^{-5}$ mol/L

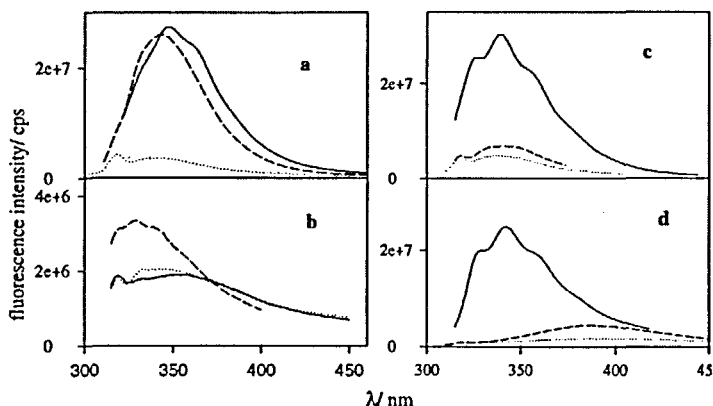


FIGURE 2 Fluorescence (excitation at 288 nm) spectra; left: —, 1, ..., 2, ---, 3 (a) in cyclohexane, (b) in CH_2Cl_2 , $c = 5.10^{-4}$ mol/L; right: —, 5, ..., 6, ---, 7 (c) in cyclohexane, (d) in CH_2Cl_2 , $c = 1.10^{-3}$ mol/L

For **1-4** the solvent has little influence on the UV spectra, while **5-7** show a small bathochromic shift in CH_2Cl_2 . The fluorescence intensity of **1-3** in cyclohexane is significant higher than in CH_2Cl_2 , for **4-7** the difference is negligible, **4** showing almost no fluorescence in both solvents.

Conclusions

Methylated cyclohexasilanes show fluorescence in the UV region, substitution by siloxy and phenyl groups reinforces this fluorescence, but does not influence the position of the maximum dramatically. Monosubstituted cyclohexasilanes (**1, 5**) show the greatest intensity, 1,3-substituted (**2, 6**) the lowest.

Acknowledgement

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