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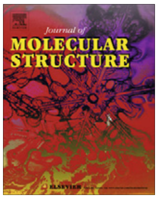

Synthesis, characterization and structural aspects of 3-azidopropylsilatrane

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ABSTRACT

Reaction of 3-chloropropyltriethoxysilane (**1**) with sodium azide (**2**) in the presence of phase transfer catalyst, tert-butylammonium bromide provided 3-azidopropyltriethoxysilane (**3**). This undergoes transesterification reaction with triethanolamine in the presence of KOH to form a new silatrane 3-azidopropylsilatrane (**4**). Multinuclear NMR (^{1}H, ^{13}C and ^{29}Si), IR and elemental analyses support the structure of novel silatrane **4**. ^{29}Si NMR indicates the presence of penta-coordinated silicon atom, which is supported by X-ray studies. It revealed that Si is present in distorted trigonal bipyramidal environment with three O atoms in equatorial positions and N atom at one of the apical positions. The second axial position is occupied by long alkyl chain bearing azide moiety. The interaction of Si with N forms a trans-annular bond having 2.176 Å bond length.

1. Introduction

More than a century after their discovery organic azides have received renewed interest in synthetic chemistry and are becoming established as an important and versatile class of chemical compounds [1–3]. In particular, in the past two decades an increasing interest in organic azides could be observed due to their vast synthetic utility in conjunction with easy accessibility via various synthetic routes. Among others, organic azides are currently considered as powerful precursors for reactive species such as nitrenes and nitrenium ions as well as nitrogen – rich compounds such as aziridines, azirines, triazoles, triazolines and triazenes. Moreover, organic azides can be easily transformed into amines, isocyanates and other functional molecules. More recently, these compounds received an increasing interest as valuable and versatile reagents within the concept of ‘Click Chemistry’ [4,5]. However, alongside their huge utility in organic synthesis the potential hazardous properties of organic azides must be carefully taken into account. Many organic compounds containing azido groups have not found wide application as practical energetic materials because of their high sensitivity to heat and shock stimuli. This poor thermal and mechanical stability of many organic azides is probably the most crucial property that has prevented chemists in the past from extending their research on azido compounds. Organic and inorganic azides are energy-rich molecules that often exhibit explosive properties. Azido group is a highly energetic functional group because N_3 π-bond can be easily polarized, which consequently results in strong exothermic dissociation reactions with the release of molecular nitrogen and reactive nitrene groups. In general, the introduction of an azido group into an organic compound increases its energy content by approx. 290–355 kJ/mol [6,7]. This is one of the reasons, why organic azides are considered and partly used as energetic materials such as energetic polymers or high-energy–density-materials (HEDM) in explosives or propellant formulations [8,9].

Among organosilanes, 3-chloropropyltriethoxysilane is considered as one of the important precursor, especially for the synthesis of ionic liquids [10–12], chloropropylsilatrane [13], siloxanes [14] and hybrid materials [15–17]. Recently, SiMCM-41 was successfully modified by using 3-aminopropyltrimethoxysilane and 3-chloropropyltriethoxysilane to give organic group modified samples [18]. A mesoporous and amorphous silica, chemically modified by using 3-chloropropyltriethoxysilane and organic reagents, have been utilized for the adsorption of toxic metal ions such as Cr(VI) and Hg(II) from aqueous samples [19,20].

Herein, we report synthesis of novel 1-(3-azido-propyl)-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecane with the structural characterization in solid state by X-ray crystallography, multinuclear NMR (^{1}H, ^{13}C and ^{29}Si), IR, elemental analysis and mass spectroscopy. The results obtained from X-ray crystallography are compared with theoretical studies such as DFT and HF methods.

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2. Experimental

2.1. Materials

All the syntheses were carried out under a dry nitrogen atmosphere using vacuum glassline. Organic solvents used were dried and purified according to standard procedures and stored under nitrogen. 3-Chloropropyl(triethoxy)silane (Aldrich), sodium azide (Acros organics) and triethanolamine (Merck) were used as such.

2.2. Instruments and measurements

Infrared spectra were routinely obtained as thin films or Nujol mulls and KBr pellet on a Perkin–Elmer RX-I FT IR Spectrophotometer. Mass spectral measurements (EI, 70 eV) were carried out on a VG Analytical (70-S) spectrometer. C, H and N analyses were obtained on a Perkin–Elmer Model 2400 CHN elemental analyzer. The solution ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Jeol and Bruker FT NMR (AL 300 MHz and 400 MHz) spectrometer using $CDCl_3$ as the solvent. Chemical shifts in ppm were determined relative to internal $CDCl_3$ and external tetramethylsilane (TMS).

2.3. Synthesis of 3-azidopropyltriethoxysilane (**3**)

To a dried 100 mL single-neck round-bottom flask equipped with reflux condenser, 3-chloropropyltriethoxysilane (4 g, 16.6 mmol), sodium azide (2.16 g, 33.2 mmol) and tetrabutyl ammonium bromide (1.288 g, 4 mmol) were added in dry acetonitrile (50 mL), under nitrogen atmosphere. The reaction mixture was then brought to stirr under reflux for 18 h. After completion of the reaction, the solvent was removed under reduced pressure. The crude mixture was diluted in dry hexane and the suspension was filtered under vacuum. Solvent was removed from the resulting filtrate and the crude oil obtained was distilled under reduced pressure to give 3-azidopropyltriethoxysilane as a colorless liquid. Yield: 3.02 g, 74%. IR (Neat, KBr plates cm^{-1}): 2098 ($\text{—N=N}^+\text{=N}^-\text{—}$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.60 (t, 2H, CH_2Si), 1.15 (t, 9H, CH_3), 1.64 (q, 2H, CCH_2C), 3.19 (t, 2H, CH_2N_3), 3.77 (q, 6H, OCH_2); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.38 ($SiCH_2$), 18.41 (CCH_2C), 22.45 (CH_2N_3), 53.54 (NCH_2), 58.58 (OCH_2).

2.4. Synthesis of 3-azidopropylsilatrane (**4**)

To a dried 100 mL single-neck round-bottom flask fitted with Dean Stark apparatus, 3-azidopropyltriethoxysilane (2.22 g, 8.98 mmol) and triethanolamine (1.34 g, 8.98 mmol) was added in dry benzene. The contents were refluxed for 5 h in the presence KOH in catalytic amount. Benzene was removed under vacuum and dry diethylether was added when white solid was separated out. The contents were further stirred for 1 h at room temperature. The solid was filtered under vacuum, washed twice with diethylether (2 × 10 mL) and dried. M.pt. 55–57 °C; yield: 1.95 g, 84%. Anal. Calcd for $C_9H_{18}N_4O_3Si$: C, 41.84; H, 7.02; N, 21.69; found: C, 41.10; H, 6.89; N, 21.20; IR (CCl_4, KBr plates, cm^{-1}): 2093 vs. ν ($\text{—N=N}^+\text{=N}^-\text{—}$), 583 m ν (Si ← N), 612 m δ_s (SiO_3), ν_s (Si–C), 936 s, 1087 s, 1105 vs. 1130 vs. ν (Si–O–C–C), 1180 m τ (CH_2O), 1278 m ω (CH_2O), 1352 m, 1454 m ω (CH_2N); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (t, CH_2Si), 1.66 (q, CCH_2C), 2.75 (t, NCH_2), 3.12 (t, CH_2N_3), 3.70 (t, OCH_2); ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.32 ($SiCH_2$), 24.78 (CCH_2C), 54.63 (CH_2N_3), 51.00 (NCH_2), 57.62 (OCH_2); ^{29}Si (300 MHz, $CDCl_3$); −70.24 ppm; MS: m/z (relative abundance, %): 132 (48), 150 (89), 172 (71), 174 (60), 192 (100), 216 (23), 233 (91).

2.5. X-ray structure determination

Single crystal X-ray diffraction data for **4** was collected on a Nonius Kappa CCD diffractometer equipped with a CCD detector and graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). All intensities were corrected for Lorentz and polarization. The structure was solved by direct methods using SIR97 program [21] and refined on F^2 by full-matrix least-square methods. Crystal data is given in Table 1 and ORTEPIII [22] view along with atomic labelling (thermal ellipsoids are drawn at 40% probability) of **4** is shown in Fig. 1. Non hydrogen atoms were refined anisotropically apart from N4 and C2, which were found disordered over two almost equivalent positions and refined isotropically. The other disordered atoms C4 and C6 were refined anisotropically with a fixed occupancy factor of 0.5 (Fig. 1). H atoms were included on calculated positions. All calculations were performed using SHELXL-97 [23], and PARST [24], as implemented in the WINGX [25] system of programs.

2.6. Theoretical studies

The quantum mechanical calculations were carried out using the GAUSSIAN 03 series of programs. Geometries were fully optimized at both the Restricted Hartree–Fock (RHF) and Density Functional Theory level (DFT), using Becke's three parameter hybrid exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP) with 3-21 + G^* and 6-31$G^*(d)$ basis sets.

3. Results and discussion

3.1. Synthesis

3-Azidopropyltriethoxysilane can be prepared from 3-chloropropyltriethoxysilane and sodium azide by using two alternate methods, either in the presence or in the absence of catalyst. In the absence of catalyst, reaction has been carried out by refluxing the reactants in butanone for 72 h [26]. On the other hand, use of catalyst such as tetrabutylammonium bromide reduces the reaction time to 18 h [27].

In the present work, 3-azidopropyltriethoxysilane (**3**) was synthesized in high yield by nucleophilic substitution reaction of 3-chloropropyltriethoxysilane (**1**) and sodium azide (**2**) in the presence of tetrabutylammoium bromide as catalyst and acetonitrile as solvent. The compound was isolated as a colorless liquid after distillation under reduced pressure, which can be used as a precursor for the synthesis of new silatrane (**4**). Transesterification of compound (**3**) with triethanolamine in the presence of a catalytic

Table 1
X-ray crystal data and structure refinement of 4.

Chemical formula	$C_9H_{18}N_4O_3Si$
M_r	258.36
Crystal system, space group	Orthorhombic, $Pna2_1$
a, b, c (Å)	13.2149 (2), 12.0619 (3), 8.1850 (3)
V (Å^3)	1304.66 (6)
Z	4
Radiation type	Mo Kα
μ (mm^{-1})	0.18
Crystal size (mm)	0.41 × 0.37 × 0.29
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2700, 2700, 2279
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.063, 0.200, 1.04
No. of reflections	2700
No. of parameters	171
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.50