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N-trimetylsilyl carboxamides RC(O)NHSiMe$_3$ (R = Me, CF$_3$, Ph): X-ray, DFT and FTIR study

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ABSTRACT

The X-ray single-crystal structures of N-trimetylsilyl acetamide $CH_3CONHSiMe_3$ (**1**), N-trimethylsilyl trifluoroacetamide $CF_3CONHSiMe_3$ (**2**) and N-trimethylsilyl benzamide $PhCONHSiMe_3$ (**3**) have been determined. Quantum chemical calculations (B3LYP/6-311+G**, NBO analysis) were performed for gas phase optimized structures, proton affinities and N–H bond dissociation energies of amides **1**–**3** and their isostructural carbon analogs **4**–**6**. The effect of silicon atom on structural features and intermolecular electron interactions was determined. Types of self-associates which can be formed by amides **1**–**3** in CCl_4 solution were studies by infrared spectroscopy.

1. Introduction

Amide functional group plays an important role in organic chemistry. It is an essential building block both for biological polymers (proteins and peptides) and a series of synthetic polyamides which are widely used in industry and medicine. Despite the fact that the synthesis, chemical structure and properties of amides have been adequately described in the 70s of the last century [1,2], numerous papers on amides are being published annually. Of particular interest is the ability of amides to form hydrogen bonds [1,3–15] which are the most important noncovalent interactions allowing some biochemical and catalytic reactions to proceed. Proton transfer and H-bonding processes are well studied by IR spectroscopy and DFT calculations [16–21]. Depending on the structure and the acid-base properties, amides are involved in hydrogen bond formation as donors or acceptors of proton [1]. The center of basicity in the amide group can be either the oxygen or nitrogen atom [9,11,22–27]. For some amides a linear dependence of the proton affinity on the hydrogen bond enthalpy was established [28–30]. Due to amphoteric nature amides can form self-associates in non-polar solvents via C=O···H–N bonding [31–39].

The first representatives of N-trimethylsilyl amides of carboxylic acids were synthesized in the middle of the last century and have been used as the major trimethylsilyl group donors. Introduction of the silicon atom into the molecule results in a significant alteration in its stereoelectronic structure and chemical properties. According to the NMR data, in solution N-trimethylsilylcarboxamides exist as amide-imidat tautomers due to the silyl group migration from nitrogen to oxygen atom (energy barrier to migration ~10–20 kcal/mol). Each tautomer can exist as a configurational *cis*- or *trans*-isomer because of hindered rotation about the C–N bond having partial double-bond character (Scheme 1) [40–53].

The existence of hydrogen bonds in N-TMS amides of carboxylic acids was proved only in a few cases. For example, N-trimethylsilyl acetamide was shown to form π-complexes with aromatic compounds [54], and the presence of intermolecular hydrogen bonds C=O···H-N in the crystal of N-(trimethylsilyl)pyridine-3-carboxamide was proved by X-ray diffraction study [55]. No discussion about the existence of intra- or intermolecular H-bonding in solutions of N-TMS-carboxamides was found in the literature. Considering a widespread use of these compounds in organic and organometallic synthesis, we believe that investigation of the propensity of amides to form H-bonds is an interesting and

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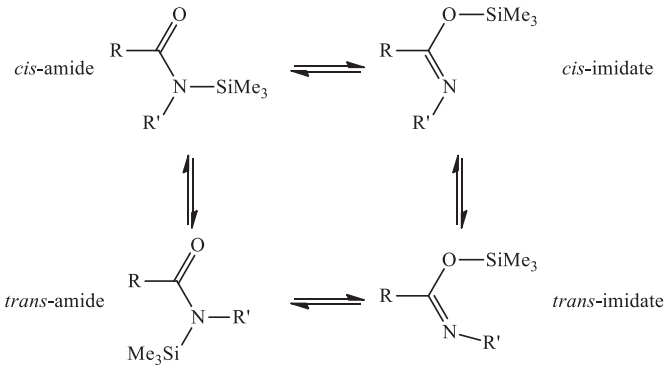


Scheme 1. Tautomerism of N-trimethylsilylcarboxamides.

important problem the solution of which will provide us with a better understanding of the effect of the N-TMS group on the acid-base properties of the amide moiety and the reactivity of these compounds. The aim of the present work is to investigate the structure, acid-base properties and ability to form self-associates of N-trimethylsilyl amides of carboxylic acids. N-(Trimethylsilyl)amides of acetic, trifluoroacetic and benzoic acids $RC(O)NHSiMe_3$ (R = Me, **1**; CF_3, **2**; Ph, **3**) were chosen as the objects of this study. The structure of compounds **1**–**3** in the crystals was studied by X-ray analysis. Quantum chemical methods (B3LYP/6-311+G**, NBO-analysis) were employed to calculate the structure, proton affinity and dissociation energy of molecules **1**–**3** and their isostructural carbon analogs - N-tert-butylamides of the corresponding acids $RC(O)NHCMe_3$ (R = Me, **4**; CF_3, **5**; Ph, **6**) (Scheme 2). The formation of self-associates of N-TMS amides was studied by FTIR spectroscopy (Scheme 2).

2. Experimental

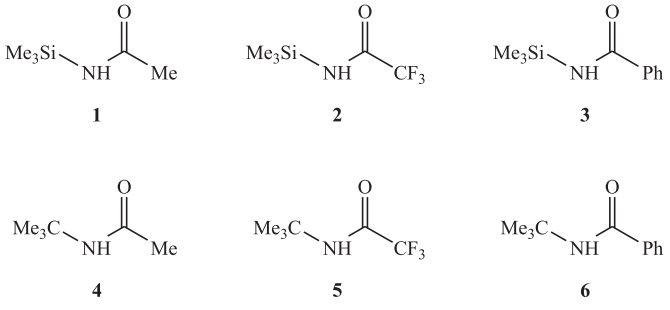
2.1. Synthesis and crystallization

Acetamide, benzamide, trifluoroacetic anhydride and hexamethyldisilazane were commercial products. N-trimethylsilyl acetamide **1** and N-trimethylsilyl benzamide **3** were prepared according to the procedures given in Ref. [56].

2.1.1. N-trimethylsilyl trifluoroacetamide (2)

Trifluoroacetic anhydride $(CF_3CO)_2O$ (8.7 g, 41 mmol) was added dropwise to cooled (~6°C) hexamethyldisilazane $(Me_3Si)_2NH$ (6.69 g, 41 mmol) with stirring. After the addition was complete, the final reaction mixture was slowly warmed to ~50°C and stirred for 6 h. The crude product was distilled under atmospheric pressure to give **2** (7.2 g–95%) as a colorless liquid. Bp. 142–144°C. ^1H NMR ($CDCl_3$, δ, ppm): 0.32 (9H, s, CH_3), 5.7 (1H, br. s., NH). ^{13}C NMR ($CDCl_3$, δ, ppm): −1.16 (Me), 116 (CF_3, J = 320.2 Hz), 161.6 (C=O).

Important! Compounds **1**–**3** were purified by distillation and were obtained as a colorless viscous liquids, which solidifies at room themperature to give colorless crystals suitable for a single crystal X-ray diffraction study.



Scheme 2. The objects of study : N-trimethylsilylcarboxamides **1**–**3** and N-*tert*-butylcarboxamides **4**–**6**.

2.2. X-ray study and refinement

Crystal data were collected on a Bruker D8 Venture diffractometer with MoKa radiation (λ = 0.71073) using the φ and ω scans.The structures were solved and refined by direct methods using the SHELX programs set [57]. Data were corrected for absorption effects using the multi-scan method (SADABS). Non-hydrogen atoms were refined anisotropically using SHELX [57] (Sheldrick, 2008). Crystal data, data collection and structure refinement details are summarized in Table 1. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3. Quantum chemical calculations

All calculations were performed using the Gaussian 09 suite of programs [58] with full optimization of all variables without any symmetry restrictions imposed on the initial structures. DFT calculations with 6-311+G** basis set were used for the monomer and dimers of N-trimethylsilyl amides **1**–**3**. All calculated structures correspond to minima on the potential energy surface (PES) as proved by positive eigenvalues of the corresponding Hessian matrices. All energies were calculated with the ZPE correction. The NBO analysis [59,60] as implemented into the Gaussian 03 package was performed using the 6–311++G** basis set on the previously DFT optimized structures.

2.4. NMR spectroscopy

NMR spectra were registered for 20% solutions in $CDCl_3$ on a Bruker 400 MHz instrument with cyclohexane as an internal standard.

2.5. IR spectroscopy

The FT-IR spectra were taken on an FT-IR Spectrometer Varian 3100. For neutral compounds the spectra were recorded in KBr pellets. The spectra of the H-bonded self-associates of compounds **1**–**3** were registered in CCl_4 solution with different concentration (0.02 mol l^{-1} – 0.1 mol l^{-1}).

3. Results and discussion

3.1. Structural analysis

The X-ray single-crystal structure of amides **1**–**3** has been determined. Crystal data, data collection and structure refinement details are summarized in Table 1. Principal bond distances, bond angles and torsion angles are presented in Table 2. Like in the majority of secondary amides [1] the substituent R at the carbonyl oxygen and the N-trimethylsilyl group in **1**–**3** are trans to each other with respect to the N–C_2 bond (Fig. 1).

The C=O bond lengths in compound **1** and its carbon analog N-tert-buthylacetamide **4** are very similar (1.2325 Å and 1.2320 Å [61], respectively), while the C–N bond compound **1** is by ~0.02 Å longer. In comparison with the unsubstituted acetamide [62] the C–N bond in **1** is 0.013–0.018 Å longer and the C=O bond is 0.015–0.017 Å shorter. The trimethylsilyl group virtually does not affect the geometrical characteristics of the molecule of N-