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High-pressure freezing, crystal structure studies and Si–CF_3 bond polarizability of trimethyl(trifluoromethyl)silane

Anna Olejniczak [a], Andrzej Katrusiak [a,*], Ashwani Vij [b,**]

[a] *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland*
[b] *AFRL/RZSP, Edwards Air Force Base, 10 E. Saturn Boulevard, Building 8451, CA 93524, USA*

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ABSTRACT

Trimethyl(trifluoromethyl)silane, $(CH_3)_3SiCF_3$, has been *in situ* pressure frozen in a diamond anvil cell and its structure determined at 0.90(5) GPa/296 K by single-crystal X-ray diffraction. The crystal is monoclinic, space group $P2_1/m$, with the molecules lying on crystallographic mirror planes. The CH_3 and CF_3 groups assume the fully staggered conformation. The 14-fold coordination scheme of the molecules is similar to those in $(CH_3)_3SiCl$ polymorphs, but different from that in crystalline tetramethylsilane, $(CH_3)_4Si$ (TMS). The longest Si–C bond length of 1.943(12) Å observed in the crystal structure has been documented. The shortest intermolecular contacts in the structure of pressure-frozen $CF_3Si(CH_3)_3$ are observed between the hydrogen atoms, and those involving fluorine atoms are longer than sums of van der Waals' radii. These structural features explain the facile cleavage of Si–CF_3 bond for CF_3 group transfer in organic reactions.

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1. Introduction

Silanes are important chemical compounds, owing to their physical and chemical properties. They are widely applied, for example: in dentistry, medicine, construction technologies, synthesis, as adhesion promoters, coupling, cross-linking or dispersing agents and surface modifiers [1]. Trimethyl(trifluoromethyl)silane can be considered as a derivative of tetramethylsilane (TMS) where three hydrogen atoms of a methyl group are replaced by fluorine atoms. Generally, fluorination strongly changes intermolecular interactions and often desired physical and chemical properties for practical applications can be obtained [2]. Trimethyl(trifluoromethyl)silane, first synthesized in 1984 by Ruppert et al. [3] is commonly known as Ruppert's reagent. It is used in the syntheses of perfluorinated compounds and for introducing a trifluoromethyl group by nucleophilic substitution [4–7]. For these reasons the structural information about $(CH_3)_3SiCF_3$ are of particular interests and studies by gas phase electron diffraction, microwave spectroscopy and quantum-chemical calculations were performed [8]. The principal interest for these studies focused on the differences between Si–CF_3 and Si–CH_3 groups dimensions and their intermolecular interactions. Vibrational-spectroscopy studies on CF_3-silanes showed that the substitution of H-atoms with F-atoms lengthens and weakens the Si–CF_3 bond [9,10]. It is caused by the electronegative F-atoms withdrawing the electrons from C and Si-atoms, which results in electrostatic repulsion of their positive net-atomic charges, and a deficiency in the binding σ-electron pair. However, to the best of our knowledge, no solid-state crystal structure of $(CH_3)_3SiCF_3$ determined by X-ray or neutron powder diffraction has been reported so far. It was also established most recently, that the $Si(CH_3)_4$ (i.e. TMS) molecules in the crystalline state are distorted from the fully staggered conformation [11]. That result is consistent with the previous observation by electron-diffraction measurements for TMS vapor, and it was proposed that the twisted TMS conformation releases the intramolecular strains generated by interactions between H-atoms [12]. Thus the aim of this study was to provide the dimensions and conformation of $(CH_3)_3SiCF_3$ molecule embedded in the crystal structure, and also to investigate the influence of the fluorine atoms and the molecule polarization for the intermolecular interactions and crystal packing. All this information is essential to understand why this molecule does not spontaneously decompose to form a more stable molecule, $(CH_3)_3SiF$, with an explosive formation of difluorocarbene.

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[*] Corresponding author. Tel.: +48 61 8291443; fax: +48 61 8291505.
[**] Corresponding author. Tel.: +1 661 2756278; fax: +1 661 2755471.
E-mail addresses: katran@amu.edu.pl (A. Katrusiak), ashwani.vij@edwards.af.mil (A. Vij).

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2. Results and discussion

2.1. Molecular structure

In the pressure-frozen $(CH_3)_3SiCF_3$ structure, atoms Si(1), C(1), C(2), F(2) and H(2) of the molecule are located on a crystallographic mirror plane of space group $P2_1/m$ (Fig. 1).

The Si-atom is in a tetrahedral environment and is bonded to one CF_3 group and three CH_3 groups. However, the C–Si–C angles are significantly distorted from the ideal tetrahedral value, and range from 102.1(7)° to 113.9(3)° (Table 1). It is noteworthy, that the valency angles C–Si–C involving atom $C(1)F_3$ are considerably smaller than the C–Si–C valency angles between the methyl groups, which rules out the possibility of intramolecular steric hindrances between F- and H-atoms. Thus the Si–$C(1)F_3$ bond lengthening is purely due to the effect of the grouped highly electronegative fluorine atoms on electronic structure of the molecule. The lengths of three Si–CH_3 bonds (two of which are symmetry independent) are consistent within errors. The Si–$C(2)H_3$ bond to methyl group lying on the mirror plane is insignificantly longer than this to C(3) located in a general position (Table 1), whereas the Si–$C(1)F_3$ bond is by nearly 0.1 Å longer. This C–Si bond is significantly longer than any of Si–C bond length listed in the tables of molecular dimensions, even if the maximum values of Si–C in database are considered [13]. All these values agree well with the results of electron-diffraction studies in the gaseous phase and theoretical calculations for the isolated molecule [8]. The

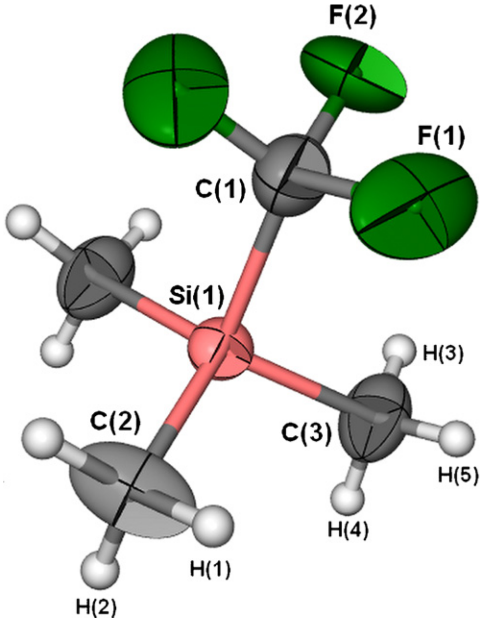

Fig. 1. The molecule of $(CH_3)_3SiCF_3$ at 0.90 GPa and 296 K, with displacement ellipsoids at 50% probability. Only the symmetry-independent atoms have been labeled in this drawing.

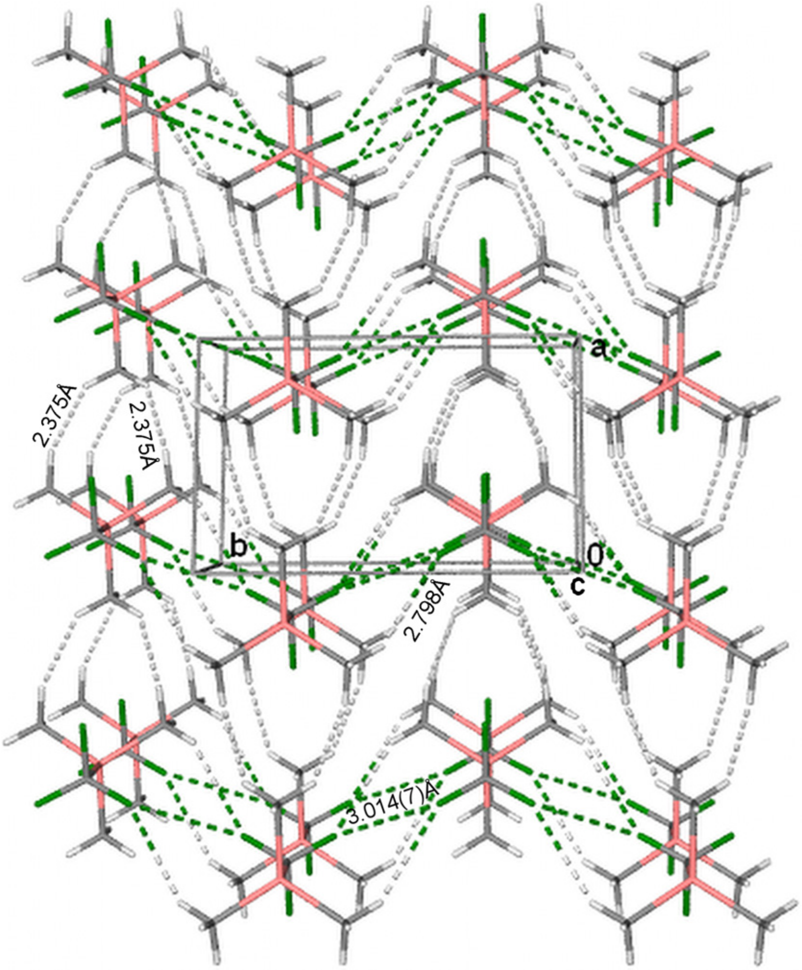

Fig. 2. The molecular packing of $(CH_3)_3SiCF_3$ with the shortest H···H, F···H and F···F contacts indicated as dashed lines.