



Weak hydrogen bonding interaction $S-H \cdots O=C$ studied by FT-IR spectroscopy and DFT calculations



Agnieszka Mielcarek, Anna Dołęga*

Department of Inorganic Chemistry, Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

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ABSTRACT

Interactions between the thiolate group of tri-*tert*-butoxysilanethiol (TBST) and carbonyl group of acetone are described. With the use of FT-IR spectroscopy the formation of weak hydrogen bond has been detected in the TBST – acetone system. The interaction results in the change of the frequency of donor $S-H$ stretching vibration (ν_{S-H}). To confirm the interpretation of spectral results hydrogen bonded system has been studied with the use of DFT calculations. General energies of solutions components, stabilization energies of hydrogen bonds in solution, geometrical parameters of TBST and acetone, energies of molecular orbitals HOMO and LUMO of donor and acceptor molecules engaged in the formation of hydrogen bonds have been analyzed.

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1. Introduction

Thiol and thiolate groups play significant roles in biological systems. Thiol group can be found in almost all aspects of cell functioning [1]. It is present in many biologically essential compounds such as cysteine, glutathione or dihydrolipoic acid (Scheme 1). Tripeptide glutathione is commonly found in plant and animal cells as an intracellular nutrient and nonspecific coenzyme and a regulator of oxidation-reduction potential within the cell. As an antioxidant, glutathione regenerates thiol groups which were oxidized to disulfide bonds or sulfonic groups in proteins [1]. Coenzyme A, another biologically important sulfur-containing compound, participates in the transport of acyl groups, containing up to twenty four atoms of carbon [1]. The molecule of dihydrolipoic acid contains two thiol moieties. This compound is a product of the reduction of lipoic acid – a coenzyme taking part in the oxidation of pyruvic and α -glutaric acids. Dihydrolipoic and lipoic acids are antioxidant agents which neutralize reactive oxygen species. They take part in the recycling of other antioxidant agents, like vitamins C and E [2].

There are both thiol and thiolate moieties in active sites of enzymatic proteins. Cysteine residues ensure the correct structure of protein polymers; they are responsible for coordination of metal

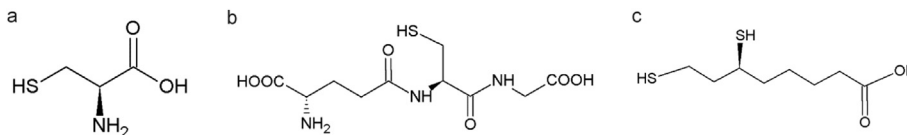
ions and regulation of catalytic activity [3]. There is a difference in the pK_a between cysteine residue and cysteine zwitterion; for cysteine residue embedded in protein scaffold this value is usually lower than for zwitterion [4,5]. For this reason, cysteine residue is a good electron donor in proteins. Electrostatic interactions between cysteine and surrounding amino acid residues influence electron density on sulfur atom and acidity of cysteine. These interactions often include the formation of hydrogen bonding. Oxidoreductases, transferases (including desulfurases, phosphatases and sulfo-transferases), hydrolases (especially cysteine proteases) and protein isomerases are examples of enzymes that contain cysteine residue within their active sites [3].

It is a recent finding that hydrogen sulphide is produced within a mammalian body by endogenous enzyme systems. Similar to two other gaseous signaling molecules: CO and NO it exerts a number of physiological actions [6]. As a result of this discovery a growing number of papers is dedicated to the interactions and methods of detection of small amounts of hydrogen sulphide (eg. Ref. [7]) and moreover polysulfides [8] in biological samples.

Hydrogen bonds (HBs) involving sulfur-containing functional groups are much less investigated compared to hydrogen bonds with the participation of oxygen atoms. Nevertheless as early as over 60 years ago the formation of dimers in solutions of thiols was detected [9] and 50 years ago the association constants for several thiols in diluted carbon tetrachloride solutions were determined by proton NMR [10]. More systematic and detailed studies have been undertaken only very recently by Wategaonkar [11–13]. The

* Corresponding author.

E-mail address: anndoleg@pg.gda.pl (A. Dołęga).



Scheme 1. Examples of natural compounds containing sulfhydryl group: a) cysteine; b) glutathione; c) dihydrolipoic acid.

hydrogen-bonding properties of S–H donor in several simple HSH \cdots OR₂ complexes were investigated by means of infrared predissociation spectroscopy and computationally at various levels of theory [13].

For the purpose of detection of the formation of O or S-containing HBs, infrared [9,11,14–17] and Raman [15,17–20] spectroscopies are widely applied. Infrared spectroscopy is one of the most important methods for examination of hydrogen bonds in solution. The frequency of the donor X–H stretching vibration ($\Delta\nu_{X-H}$) is a good parameter to follow hydrogen bond formation. For most polar X–H groups it can be easily identified in the IR spectra and its frequency is very sensitive to hydrogen bond formation [21].

Various theoretical methods such as DFT and *ab initio* [11,15,17–20] or natural bond orbital (NBO) analysis [22,23] are also widely used to examine weak bonding. Several computational programs offer calculations of harmonic vibration frequencies to simulate the IR spectrum of the examined system. However the calculated harmonic vibration frequencies are usually systematically different from measured experimental frequencies due to several factors such as anharmonicity, lack of correlation or insufficiency of the basis set [15].

Frequency shifts resulting from the interactions of thiol group with DMF and THF were thoroughly studied for a series of silanethiols [24]. We have previously observed weak intramolecular SH $\cdots\pi$ interaction in aryloxysilanethiols [16]. In this paper we examine a weak hydrogen-bonding type interaction between SH function of tri-*tert*-butoxysilanethiol (TBST) and carbonyl group of acetone by means of FT-IR measurements and DFT calculations. The steric hindrance at the silicon atom in TBST molecule allows the formation of relatively simple adducts between TBST and hydrogen bond acceptors. Moreover pK_a of TBST (8.0), unlike other silanethiols, is similar to the pK_a of organic thiols especially cysteine [25,26].

2. Experimental

Solvents: carbon tetrachloride and acetone were purchased from commercial sources and stored over 3A molecular sieves. TBST was synthesized as described [27].

2.1. Physical measurements

Infrared transmission spectra were recorded using Nicolet iS50 FT-IR spectrometer with Omnic computer software in range 4000–1000 cm^{-1} . Measurements were performed for mixtures of TBST-acetone- CCl_4 of various concentrations. CaF_2 cuvette 0.154 cm thick was used for measurements. CCl_4 was used as background. Experiment was repeated twice.

2.2. Computational details

DFT calculations: geometry optimization and calculations of frequencies, were performed using ADF program (version 2014.01) [28–30] with GGA BLYP-DXC potential [31,32] and TZP basis in SCF model as implemented in ADF. The calculated frequencies were

neither scaled nor ZPE corrected. The NPA and NBO analyses were carried at BLYP/6-31G(d,p) level with the use of Gaussian 98 program. All calculations were performed *in vacuo*.

3. Results and discussion

3.1. Experimental vibrational spectra

Low intensity band connected with stretching vibrations of thiol group is observed within the range 2500–2600 cm^{-1} [11,14–16,24–26,33]. In the solution of TBST in CCl_4 this band was previously observed at 2592 cm^{-1} which is now confirmed [24]. Shifts due to the formation of hydrogen bonds between thiols and various acceptors are generally between one and several dozens of cm^{-1} [11,15,16,24,33]. For the equimolar mixture of TBST, acetone and carbon tetrachloride, a difference band $\nu_{S-H\cdots O=C}$ resulting from the interaction between molecules of silanethiol and acetone is observed at 2561 cm^{-1} (Fig. 1). We could observe the phenomenon due to the relatively low intensity of the studied band since the shift is visible only at large concentrations of the interacting species (0.6–1.6 M). The experiment was repeated for the decreasing concentrations of TBST and acetone in carbon tetrachloride. On dilution the absorbance of the difference band at 2561 cm^{-1} decreased and for the solution of 0.49 M TBST and 0.49 M acetone in CCl_4 the band was no longer observed. This is illustrated in Fig. 2.

The complete table of assignments for the spectra of TBST and acetone is given in Supporting information (Table 1S part a, b, c).

3.2. Calculated vibrational spectra

Computed FT-IR bands of TBST, acetone and TBST-acetone are shown in Fig. 3. The calculated diagnostic frequency of S–H of TBST

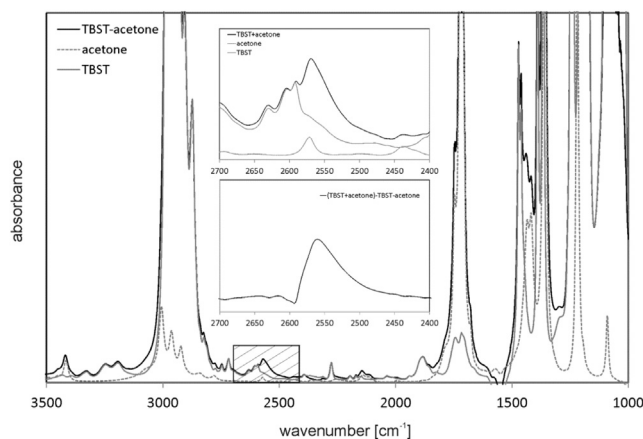


Fig. 1. Experimental FT-IR frequencies of TBST, acetone; TBST +acetone system in CCl_4 in range 3500–1000 cm^{-1} . Upper insert shows the enlarged region of the SH stretching mode (crosshatched in the main figure), lower insert shows the difference band [(TBST + acetone)-TBST-acetone] interpreted as ν_{S-H} of the thiol group interacting with carbonyl group.

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