



# Synthesis, structural characterization and quantum chemical studies of silicon-containing benzoic acid derivatives



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## ABSTRACT

The present paper is concerned with the synthesis and molecular structure investigation of two new benzoic acid derivatives having trimethylsilyl tails, 4-((trimethylsilyl)methoxy) and 4-(3-(trimethylsilyl)propoxy)benzoic acids. The structures of the novel compounds have been confirmed by X-ray crystallography, Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$  NMR). The theoretical studies of molecules were conducted by using the quantum chemical methods, such as Density Functional Theory (DFT B3LYP/6-31 + G\*\*), Hartree-Fock (HF/6-31 + G\*\*) and semi-empirical computations (PM3, PM6 and PM7). The optimized molecular geometries have been found to be in good agreement with experimental structures resulted from the X-ray diffraction. The maximum electronic absorption bands observed at 272–287 nm (UV–vis spectra) have been assigned to  $\pi \rightarrow \pi^*$  transitions, which were in reasonable agreement with the time dependent density functional theory (TD-DFT) calculations. The computed vibrational frequencies by DFT method were assigned and compared with the experimental FTIR spectra. The mapped electrostatic potentials revealed the reactive sites, which corroborated the observation of the dimer supramolecular structures formed in the crystals by hydrogen-bonding. The energies of frontier molecular orbitals (HOMO and LUMO), energy gap, dipole moment and molecular descriptors for the new compounds were calculated and discussed.

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## 1. Introduction

Benzoic acid derivatives are versatile compounds used as chemicals, pharmaceuticals, agrochemicals and consumer products [1]. Benzoic acid inhibits bacterial development and its substituted compounds are very important for the development of new materials in food and pharmaceutical industries [2]. In the last years, considerable efforts have been devoted to theoretically and experimentally study of the benzoic acid derivatives [1–14]. Thus, a number of these compounds were investigated: *p*-hydroxybenzoic, *m*-anisic, vanillic, and syringic acids [1]; 4-butyl benzoic acid [2]; methyl- and methoxybenzoic acids [3]; *m*-trifluoromethylbenzoic acid [4]; 4-(2,5-di-2-thienyl-1H-pyrrol-1-yl)benzoic acid [5]; *p*-(*p*-hydroxyphenoxy)benzoic acid [6]; toluic acid [7]; 2-(4-hydroxyphenylazo)benzoic acid [8]; 2-amino-5-bromo-benzoic acid methyl ester [9]; 4-(trimethylammonium)benzoic acid

chloride [10]; 2,3,4-tri-fluoro-benzoic acid dimer [11]; 2-[(2-hydroxyphenyl)carbonyloxy]benzoic acid [12]; Cu(II) complex with 4-[(Z)-[(2-hydroxybenzoyl)hydrazono]methyl]benzoic acid [13] and 4-[(substituted phenyl)imino]methyl]benzoic acids [14]. All of the above mentioned molecules were mainly modeled by density functional theory (DFT), and the simulation outcomes were compared with the available experimental results (e.g. X-ray crystallography; FTIR, Raman, UV–vis and NMR spectra).

The current work aims to report on the synthesis pathway, molecular structure characterization and theoretical quantum chemical investigations of two novel benzoic acid derivatives having trimethylsilyl (TMS) tails, i.e. 4-((trimethylsilyl)methoxy) and 4-(3-(trimethylsilyl)propoxy)benzoic acids as potential ligands for the metal ions. The presence of TMS groups creates premises for obtaining metal complexes with increased solubility in non-polar media, such as supercritical carbon dioxide (scCO<sub>2</sub>), a non-toxic, non-flammable, eco-friendly and relatively cheap solvent, where they can act as homogeneous catalyst for different reactions. The number of metal complexes that are soluble in this environment is

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very limited [15]. In addition, due to the higher hydrophobicity of the trimethylsilyl group, these compounds have a high potential for application as bioactive compounds in enzymatic reactions [16].

Previously published articles described the experimental investigations regarding the synthesis and characterization of benzoic acid derivatives containing organosilicon groups [17–19]. However, to the best of our knowledge no report has been focused, until now, on both theoretical and experimental investigations of the molecular structures of silicon-containing benzoic derivatives [20]. Molecular modeling is an extremely useful tool to complement experimental techniques providing a potential structural context for understanding the experimental results [21]. Note that, some organosilicon compounds have been tested as pharmaceuticals [20].

## 2. Experimental

### 2.1. Materials

4-Hydroxybenzoic acid (Aldrich), (chloromethyl)trimethylsilane 98% (Aldrich), (3-chloropropyl)trimethylsilane 97% (Aldrich), anhydrous  $K_2CO_3$  (Aldrich),  $Na_2SO_4$  (Aldrich), dimethylformamide (Aldrich), chloroform (Aldrich) were used as received.

### 2.2. Methods

Fourier transform infrared (FT-IR) measurements were carried out using a Bruker Vertex 70 FT-IR spectrometer. Spectra were recorded in the transmission mode in the range 400–4000  $cm^{-1}$  at room temperature with a resolution of 2  $cm^{-1}$  and accumulation of 32 scans.

The NMR spectra were recorded on a Bruker Avance DRX 400 MHz Spectrometer equipped with a 5 mm QNP direct detection probe and Z-gradients. Spectra were recorded in  $CDCl_3$ , at room temperature. The chemical shifts are reported as  $\delta$  values (ppm). The assignments of all the signals in the 1D NMR spectra were done using 2D NMR experiments like H,H-COSY, H,C-HMQC and H,C-HMBC.

UV–vis absorption spectra measurements were carried out in  $CHCl_3$  and DMSO solutions on a Specord 200 spectrophotometer.

X-Ray crystallographic measurements for **1** and **2** were carried out with an Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo- $K\alpha$  radiation. Single crystals were positioned at 40 mm from the detector and 848, and 208 frames were measured each for 25, and 40 s over 1° scan width for **1**, and **2**, respectively. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction [22]. The structures were solved by direct methods using Olex2 [23] and refined by full-matrix least-squares on  $F^2$  with SHELXL-97 [24]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. All H atoms were introduced in idealized positions ( $d_{CH} = 0.96 \text{ \AA}$ ) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. The molecular plots were obtained using the Olex2 program. The crystallographic data and refinement details are quoted in Table 1, while bond lengths, interatomic angles and dihedral angles are summarized in ESI (Tables B1–B6).

CCDC-1438222 (**1**), CCDC-1438223 (**2**) contain the supplementary crystallographic data for this contribution. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.ca.ac.uk](mailto:deposit@ccdc.ca.ac.uk)).

### 2.3. Synthesis

#### 2.3.1. Synthesis of **1**

In a 100 mL round bottom flask equipped with magnetic stirring and reflux condenser protected with  $CaCl_2$  tube, 4-hydroxybenzoic (0.98 g, 7 mmol) and (trimethylsilyl)chloromethylsilane (0.86 g, 1 mL, 7 mmol) were dissolved together in DMF (15 mL). Anhydrous  $K_2CO_3$  (1.45 g, 10.5 mmol) was added to the resulting solution and the mixture was stirred under argon atmosphere at 110 °C for 8 h. The resulting precipitate was filtered off and the filtrate was poured into water (60 mL) and extracted with chloroform ( $3 \times 15$  mL). The combined organic phases were dried ( $Na_2SO_4$ ) and evaporated under reduced pressure. The resulted beige solid product was dried in vacuo. X-ray diffraction-quality single crystals were obtained by recrystallization from methanol, washed with methanol and diethylether and dried in air at room temperature. Yield: 1.2 g, 75%. Anal. Calcd for  $C_{11}H_{16}O_3Si$  ( $M_r$  224.33): C, 58.89, H, 7.19. Found: C, 58.67, H, 7.23.

$IR\nu_{max}$  (KBr),  $cm^{-1}$ : 3551w, 3474w, 3416w, 2957w, 2901w, 2882w, 2822w, 1688s, 1601vs, 1578s, 1506s, 1421m, 1292s, 1250s, 1215m, 1157s, 1130vw, 1109w, 1007m, 858vs, 847vs, 775m, 758w, 706w, 636m, 619m, 604w, 546w, 513w, 505w, 480vw, 451vw, 378vw.

$^1H$  NMR ( $CDCl_3$ , 400.13 MHz,  $\delta$ , ppm): 9.87 (s, 1H,  $-COOH$ ), 7.82 (d,  $J = 8.7$  Hz, 2H, Ar-H), 7.05 (d,  $J = 8.7$  Hz, 2H, Ar-H), 3.66 (s, 2H,  $-CH_2-$ ), 0.16 (s, 9H,  $-Si-CH_3$ ).

$^{13}C$  NMR ( $CDCl_3$ , 100.16 MHz,  $\delta$ , ppm): 190.88 ( $-COOH$ ), 166.72 (Ar-C), 131.91 (Ar-C), 129.63 (Ar-C), 114.53 (Ar-C), 61.78 ( $-CH_2-$ ),  $-3.20$  ( $-Si-CH_3$ ).

UV–vis ( $CHCl_3$ ),  $\lambda_{max}$  ( $\epsilon$ ,  $L M^{-1}cm^{-1}$ ): 272 (21816); UV–vis (DMSO),  $\lambda_{max}$  ( $\epsilon$ ,  $L M^{-1}cm^{-1}$ ): 275 (20823).

#### 2.3.2. Synthesis of **2**

In a 100 mL round bottom flask equipped with magnetic stirrer and reflux condenser protected with  $CaCl_2$  tube, 4-hydroxybenzoic (0.83 g, 6 mmol) and (trimethylsilyl)chloropropylsilane (0.88 g, 1 mL, 6 mmol) were dissolved together in DMF (15 mL). Anhydrous  $K_2CO_3$  (1.45 g, 10.5 mmol) was added to the resulting solution and the mixture was stirred under argon atmosphere at 110 °C for 8 h. The resulting precipitate was filtered off and the filtrate was poured into water (60 mL) and extracted with chloroform ( $3 \times 15$  mL). The combined organic phases were dried ( $Na_2SO_4$ ) and evaporated under reduced pressure. The solid product was dried in vacuo. X-ray diffraction-quality single crystals were obtained by recrystallization from chloroform/methanol (1:2, v:v), washed with methanol and diethylether and dried in air at room temperature. Yield: 1.3 g, 86%. Anal. Calcd for  $C_{11}H_{16}O_3Si$  ( $M_r$  252.38): C, 61.87, H, 7.99. Found: C, 61.67, H, 8.13.

$IR\nu_{max}$  (KBr),  $cm^{-1}$ : 3366m, 3289m, 3155w, 3119w, 3074m, 3040w, 2951vs, 2895s, 2878s, 2826s, 2904s, 2735s, 2573w, 2515vw, 2428vw, 2012w, 1936vw, 1906w, 1693vs, 1601vs, 1578vs, 1510vs, 1470s, 1427s, 1393s, 1313s, 1250vs, 1215vs, 1184s, 1159vs, 1109s, 1063s, 1047s, 1009s, 895s, 854vs, 835vs, 787s, 758s, 694s, 650s, 617s, 606s, 515s, 453w, 436w, 422w, 382w.

$^1H$  NMR ( $CDCl_3$ , 400.13 MHz,  $\delta$ , ppm): 9.86 (s, 1H,  $-COOH$ ), 7.82 (d,  $J = 8.7$  Hz, 2H, Ar-H), 6.97 (d,  $J = 8.7$  Hz, 2H, Ar-H), 3.98 (t,  $J = 6.8$  Hz,  $-CH_2-CH_2-CH_2-$ ), 1.84–1.77 (m, 2H,  $-CH_2-CH_2-CH_2-$ ), 0.63–0.58 (m, 2H,  $-CH_2-CH_2-CH_2-$ ), 0.02 (s, 9H,  $-Si-CH_3$ ).

$^{13}C$  NMR ( $CDCl_3$ , 100.16 MHz,  $\delta$ , ppm): 190.85 ( $-COOH$ ), 164.24 (Ar-C), 132.00 (Ar-C), 129.68 (Ar-C), 114.72 (Ar-C), 70.99 ( $-CH_2-CH_2-CH_2-$ ), 23.66 ( $-CH_2-CH_2-CH_2-$ ), 12.50 ( $-CH_2-CH_2-CH_2-$ ),  $-1.79$  ( $-Si-CH_3$ ).

UV–vis ( $CHCl_3$ ),  $\lambda_{max}$  ( $\epsilon$ ,  $L M^{-1}cm^{-1}$ ): 285 (28235); UV–vis (DMSO),  $\lambda_{max}$  ( $\epsilon$ ,  $L M^{-1}cm^{-1}$ ): 287 (26176).

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