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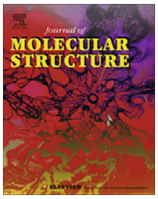

Structural characterization of a series of aryl selenoacetates

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HIGHLIGHTS

- ▶ A series of aryl selenoacetates has been investigated by XRD, DFT and FT-IR.
- ▶ Crystal structures of aryl selenoacetates have been measured for the first time.
- ▶ *Cis*-orientation of the carbonyl oxygen regarding the aryl moiety is a common feature for all investigated compounds.
- ▶ Torsion angle between the selenoacetate group and the aryl moiety is dominated by the packing effects.
- ▶ Strong IR bands at 1702–1722 cm^{-1} and 565–577 cm^{-1} are characteristic for the selenoacetate group.

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ABSTRACT

Se-mesityl ethaneselenoate, *Se*-4-(dimethylamino)phenyl ethaneselenoate, *Se*-anthracen-9-yl ethaneselenoate, and *Se*-(4′-cyanobiphenyl-4-yl) ethaneselenoate, potential building blocks for selenium-anchored self-assembled monolayers on metal surfaces, were examined and characterized using single crystal X-ray diffraction, Fourier-transform infrared (FT-IR) spectroscopy, and density functional theory (DFT) calculations. The molecules all adopt similar conformations with the selenoacetate unit being tilted between 61° and 78° with respect to the adjacent arene ring and binding angles of 97–100° at the selenium atom. An interesting feature is that the oxygen atom of the acetyl group always points toward the arene system, a feature correctly reproduced by the DFT calculations. The calculations could also predict the IR spectra of the compounds, making a detailed interpretation possible.

1. Introduction

Self-assembled monolayers (SAMs) play an important role in nanotechnology [1–4]. Aromatic thiolates on Au(111) substrates, the most frequently examined SAMs, have a great potential in the research and development of molecular electronics *inter alia* for molecular switches [5–9] or memory devices [10,11]. As first observed by Samant et al. selenols can be used instead of thiols to prepare SAMs on gold surfaces [12]. In our efforts to extend the knowledge on self-assembled monolayers, we investigated several selenolate-based SAM systems bearing alkyl as well as aryl groups. We were able to show that selenolate groups are in many aspects superior to thiolate groups as anchoring groups for SAMs on gold [13–20]. For the formation of aryl selenolate SAMs, the respective selenoacetates could be identified as suitable precursors [19]. In contrast to their parent selenols, aryl selenoacetates are inert to ambient oxygen, but become deprotected during monolayer preparation. Furthermore, in comparison to the corresponding diselenides, they exhibit a markedly higher solubility [21], which is a crucial parameter in SAM formation. Recently we developed a novel palladium-catalyzed selenium–carbon coupling procedure based on the selenium transfer reagent Cy_3SiSeH [22]. This method allows for a convenient one-pot access to these versatile SAM building blocks with selenium atoms as anchoring groups in high yields under very mild conditions.

In this paper, single crystal X-ray diffraction and Fourier-transform infrared (FT-IR) spectroscopy data of a series of such aryl selenoacetates, namely *Se*-mesityl ethaneselenoate (**1**), *Se*-4-(dimethylamino)phenyl ethaneselenoate (**2**), *Se*-anthracen-9-yl ethaneselenoate (**3**) and *Se*-(4′-cyanobiphenyl-4-yl) ethaneselenoate (**4**) obtained via the procedure described above, together with DFT calculation results are reported (Fig. 1). To the best of our knowledge, no structural data on aryl selenoacetates have been published until now.

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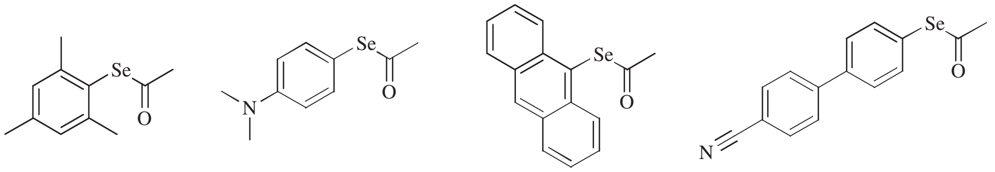

1 **2** **3** **4**

Fig. 1. Structural formulae of compounds **1**–**4**.

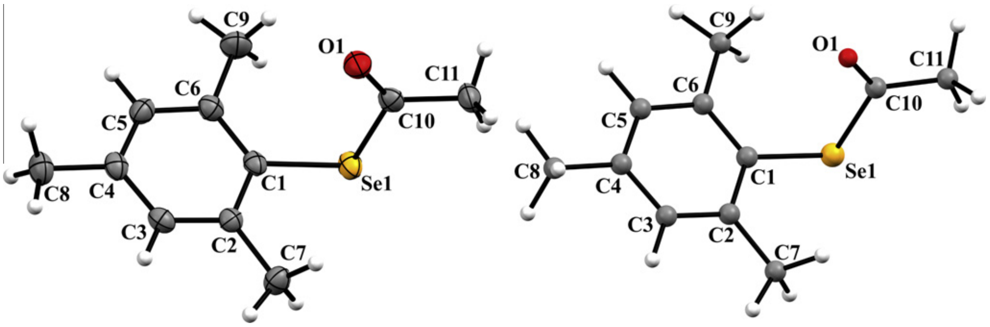

Fig. 2. *Left*: ORTEP plot of compound **1** at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii. *Right:* DFT-optimized structure of compound **1**. All atoms are drawn as spheres of arbitrary radii.

Table 1
Bond lengths (Å) and angles (°) for compound **1**.

Parameter	
Bond lengths	
Se(1)–C(1)	1.931(3)
Se(1)–C(10)	1.933(4)
C(1)–C(6)	1.398(5)
C(1)–C(2)	1.404(5)
O(1)–C(10)	1.210(4)
C(10)–C(11)	1.505(5)
C(6)–C(5)	1.388(5)
C(6)–C(9)	1.515(5)
C(5)–C(4)	1.381(5)
C(2)–C(3)	1.389(5)
C(2)–C(7)	1.514(5)
C(4)–C(3)	1.396(5)
C(4)–C(8)	1.512(5)
Bond angles	
C(1)–Se(1)–C(10)	99.70(15)
C(6)–C(1)–C(2)	121.3(3)
C(6)–C(1)–Se(1)	120.8(3)
C(2)–C(1)–Se(1)	117.8(3)
O(1)–C(10)–C(11)	124.4(3)
O(1)–C(10)–Se(1)	123.4(3)
C(11)–C(10)–Se(1)	112.2(2)
C(5)–C(6)–C(1)	118.0(3)
C(5)–C(6)–C(9)	119.5(3)
C(1)–C(6)–C(9)	122.4(3)
C(4)–C(5)–C(6)	122.6(3)
C(3)–C(2)–C(1)	118.1(3)
C(3)–C(2)–C(7)	119.2(3)
C(1)–C(2)–C(7)	122.8(3)
C(5)–C(4)–C(3)	117.9(3)
C(5)–C(4)–C(8)	121.8(3)
C(3)–C(4)–C(8)	120.3(3)
C(2)–C(3)–C(4)	122.1(3)

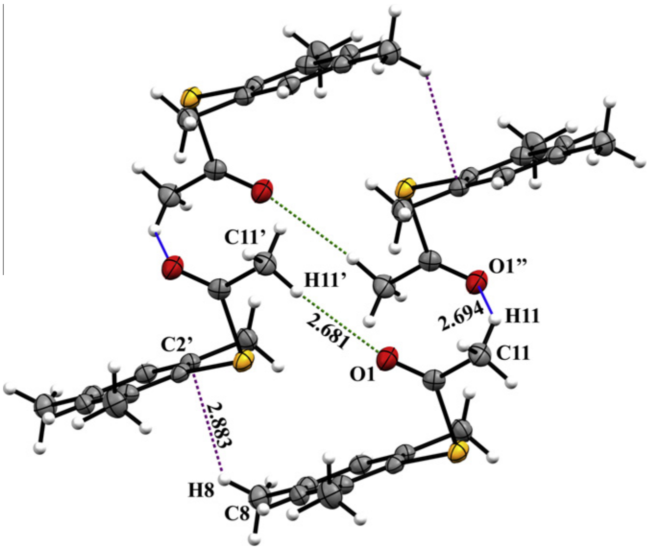

Fig. 3. Packing of compound **1**.

2. Experimental

Compounds **1**–**3** were synthesized as described in the literature [22]. Single crystals were obtained by gradient sublimation in high vacuum (~10^{-5} mbar) from samples locally heated to 100 °C.

Compound **4** was obtained in an analogous manner. Briefly, to a solution of 4-bromo-4′-cyanobiphenyl (258 mg) and lithium bis(trimethylsilyl)amide (1.1 mL of a 1 M soln in tetrahydrofuran) dry benzene (4 mL) a solution of $Pd(OAc)_2$ (11 mg) and 23 mg Ru-Phos [23] in benzene (1 mL) was added, followed by a solution of Cy_3SiSeH (357 mg) in benzene (5 mL). After stirring overnight, acetyl chloride (350 µl) and tetra-*n*-butylammonium fluoride (1.2 mL, 1 M in tetrahydrofuran) were added and stirring was continued for 3 h. Extraction with ethyl acetate, water, and brine yielded an organic phase that was evaporated onto silica (1.8 g). Chromatography (hexane/ethyl acetate 400/1 to 50/1) yielded a pink compound, which was recrystallized from methylcyclohexane to yield 180 mg (59%) crystals suitable for X-ray diffraction. Mp 130 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.72 (m, 4H), 7.60 (m, 4H), 2.51 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 196.3, 145.0, 140.0,