

Short Note

# 2-Hydroxy-3-(4-oxy(2,2,6,6-tetramethylpiperidin-1-oxyl)butoxy)benzaldehyde

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**Abstract:** Salen-type complexes with transition metals and corresponding polymers attract great scientific interest due to their high electrochemical properties and potential for use as part of next generation organic energy storage devices. Because of their good conductivity but relatively low capacity, energy-intensive additives such as quinones or TEMPO fragments can significantly enhance the capacitive characteristics of the electrode materials. Herein, we report a preparation of precursor for a modified Salen-type complex, the substituted 2,3-Dihydroxybenzaldehyde by butoxy linkers with TEMPO fragment using alkylation reaction. The resulting product was characterized by the  $^1\text{H}$  and  $^{13}\text{C}$ , COSY, HMBC, HSQC nuclear magnetic resonance (NMR), ESI-high resolution mass spectrometry (ESI-HRMS), and Fourier-transform infrared spectroscopy (FTIR). The reported approach opens the way for easy modification of Salen-type complexes in order to increase their specific characteristics.

**Keywords:** TEMPO; linkers; Salen precursor; alkylation



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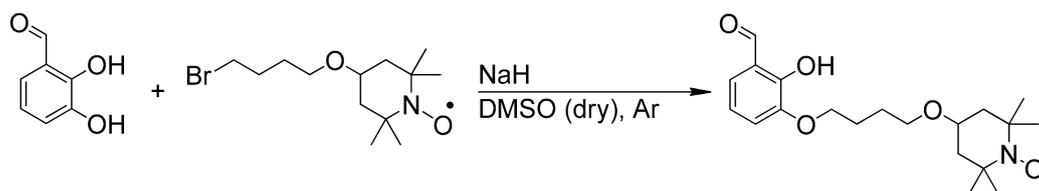
## 1. Introduction

Polymeric metal complexes with Salen-type Schiff base ligands, poly[M(Schiff)] might be promising candidates for the creation of highly conducting polymer-based electrodes for energy storage devices [1–6]. The availability of modification for poly[M(Schiff)] precursors by changing the chemical structure of substitutes opens the path to the targeting adjustment of material performance. Usage of different substitutes significantly changes the properties of obtained polymers [7–9], even if the differences in the substituent structures are minimal [10]. Considering the relatively low capacity of poly[M(Schiff)] material, they can be combined with an energy bearing group such as TEMPO or quinone compound and used as a conductive polymer framework [11]. Evidence of the synergistic action of polymeric Ni-Salen with the nitroxyl polymer PTMA in a composite has been demonstrated [11]; however, such modification complicates the production material process due to the need for the exact ratio of the components. To avoid this, the direct modification of Salen complex precursors allow the monocomponent product to be obtained, which combines the advantages of several classes [12]. Usage of different linkers also allows the properties of the materials to be regulated [13,14].

Herein, we report the synthesis of a Ni-Salen precursor with butoxy TEMPO-containing fragment, namely 2-hydroxy-3-(4-oxy(2,2,6,6-tetramethylpiperidin-1-oxyl)butoxy)benzaldehyde, by the alkylation of 2,3-dihydroxybenzaldehyde with TEMPO-containing butyl bromide. The obtained product was characterized with nuclear magnetic resonance (NMR), high resolution mass spectrometry (HRMS) and Fourier-transform infrared spectroscopy (FTIR) spectra.

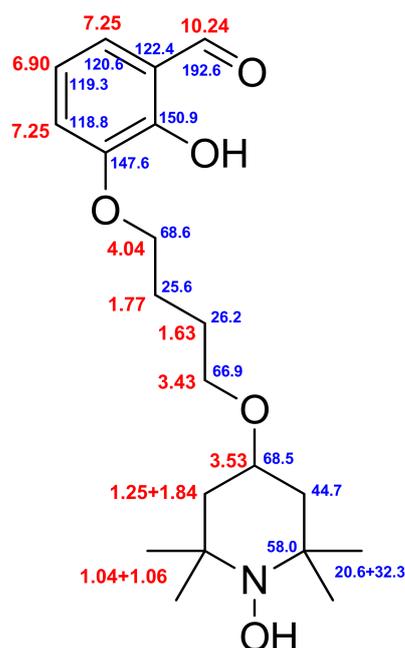
## 2. Results

The desired product was obtained by alkylation of 2,3-dihydroxybenzaldehyde with 4-(4-bromobutoxy)2,2,6,6-tetramethylpiperidine-1-oxyl (Scheme 1) using the typical alkylation conditions [15].



**Scheme 1.** Reaction conditions for the alkylation of 2,3-dihydroxybenzaldehyde with 4-(4-bromobutoxy) 2,2,6,6-tetramethylpiperidine-1-oxyl.

It is noteworthy that the product was purified by simple crystallization from a hexane–Et<sub>2</sub>O (3:1) mixture. Due to the paramagnetic nitroxyl fragment, NMR spectra could only be obtained after the reductive quenching of the radical center with ascorbic acid. The <sup>1</sup>H-NMR spectrum of the product (Figure S1) shows a set of TEMPO-related signals: a multiplet around 3.53, two doublets at 1.84 and 1.25 and a pair of singlets at 1.06 and 1.04 ppm, along with the butoxy triplets at 4.04, 3.43, 1.77 and 1.63 ppm, aromatic signals at 7.25 and 6.9 ppm, accompanied by an aldehyde singlet at 10.24 ppm. The <sup>13</sup>C-NMR spectrum (Figure S2) contains a complete set of signals attributed to the proposed structure of the product: linker signals at 25.6, 26.2, 66.9 and 68.6 ppm, TEMPOL peaks at 20.6, 32.3, 44.7, 58.0 and 68.5 ppm, aryl signals at 118.8, 119.3, 120.6, 122.4, 147.6, and 150.9 ppm, and a carbonyl carbon peak at 192.6 ppm. An unambiguous attribution of the signals was made on the basis of the COSY, HSQC and HMBC correlation spectra (Figure 1, Figures S3–S6).



**Figure 1.** Attribution of the chemical shifts for 2-hydroxy-3-(4-oxy(2,2,6,6-tetramethylpiperidin-1-oxyl)butoxy)benzaldehyde.

The exact mass of [M+Na]<sup>+</sup> ion, determined by ESI–HRMS (Figure S7), was found to be 387.2016 (387.2016 as calcd. for C<sub>20</sub>H<sub>30</sub>NO<sub>5</sub>Na<sup>+</sup>). The FTIR spectrum recorded in KBr (Figure S8) contains a strong peak at 1652 cm<sup>−1</sup> (C=O). Vibration of the phenolic O–H, which typically occurs about 3400 cm<sup>−1</sup>, is shifted to ca. 3000 cm<sup>−1</sup> due to the strong hydrogen bonding.

### 3. Materials and Methods

#### 3.1. General Consideration

Reagents of “reagent grade” purity were purchased from Sigma–Aldrich (Darmstadt, Germany). 4-(4-bromobutoxy)-2,2,6,6-tetramethylpiperidine-1-oxyl was obtained using a known method [16] with minor modifications. The Fourier transform infrared spectra were recorded on a Shimadzu IRAffinity-1 FTIR spectrophotometer (Shimadzu Europa GmbH, Kyoto, Japan) in KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were acquired on a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in  $\text{DMSO-}d_6$ , as well as COSY, HMBC and HSQC 2D NMR spectra. Before NMR analysis, the paramagnetic center of nitroxyl radical residues was reduced in situ by ascorbic acid. The HRMS spectrum was recorded using electrospray ionization on a Bruker microTOF apparatus (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) in positive mode.

#### 3.2. Synthesis of 2-Hydroxy-3-(4-oxy(2,2,6,6-tetramethylpiperidin-1-oxyl)butoxy)benzaldehyde

To a stirred suspension of NaH (60% susp. in oil, 1 g, 25 mmol) in 25 mL of dry DMSO, 2,3-dihydroxybenzaldehyde (1.381 g, 10 mmol) was added (in one portion under Ar) dissolved in 5 mL of dry DMSO, and then, the mixture was stirred at RT for 1 h. At this point, 4-(4-bromobutoxy) 2,2,6,6-tetramethylpiperidine-1-oxyl (2.94 g, 9.5 mmol) dissolved in 2 mL dry DMSO was added in one portion and the mixture was stirred overnight at RT. Then, the mixture was poured into ice water (100 mL), acidified with 1M HCl solution (pH~3) and extracted with  $\text{Et}_2\text{O}$ . The organic layer was washed with 1% NaOH, the aqueous layer was acidified with 1M HCl solution and again, extracted with DEE, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated by rotary evaporation in vacuum. Residue was purified by using crystallization from hexane- $\text{Et}_2\text{O}$  (3:1 v/v) solution in a fridge (+4 °C). The crystalline precipitate was separated by decantation and dried in a vacuum using an oil pump. The desired product is a pink-orange crystalline solid (0.8 g, 2.2 mol, 23%).

$^1\text{H}$ -NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ , ppm: 10.24 (s, H, -CH=O), 7.22–7.25 (m, 2H, Ar), 6.87–6.91 (t, 1H, Ar), 4.04 (t, 2H, -CH<sub>2</sub>-), 3.5 (m, 1H, -CH-), 3.43 (t, 2H, -CH<sub>2</sub>-), 1.84 (d, 2H, -CH<sub>2</sub>-), 1.77 (t, 2H, -CH<sub>2</sub>-), 1.63 (t, 2H, -CH<sub>2</sub>-), 1.25 (d, 2H, -CH<sub>2</sub>-), 1.06 (s, 6H, -CH<sub>3</sub>), 1.04 (s, 6H, -CH<sub>3</sub>),  $^{13}\text{C}$ -NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$ , ppm: 192.6 (C=O), 150.9 (Ar), 147.6 (Ar), 122.4 (Ar), 120.6 (Ar), 119.3 (Ar), 118.8 (Ar), 68.6 (alkyl linker), 68.5 (alkyl TEMPO), 66.9 (alkyl linker), 58.0 (alkyl TEMPO), 44.7 (alkyl TEMPO), 32.3 (alkyl TEMPO), 26.2 (alkyl linker), 25.6 (alkyl linker), 20.6 (alkyl TEMPO). FTIR (KBr)  $\tilde{\nu}$ ,  $\text{cm}^{-1}$ : 2850–3000 (O-H, C-H), 1652 (C=O). HRMS (ESI)  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{30}\text{NO}_5\text{Na}^+$  387.20, found 387.2016.

### 4. Conclusions

Substituted salicylaldehyde is a typical precursor to Salen-type materials, which is widely used in energy storage devices and electrocatalysis systems. We demonstrate the possibility for the direct alkylation of 2,3-dihydroxybenzaldehyde with 4-(4-bromobutoxy) 2,2,6,6-tetramethylpiperidine-1-oxyl, which provides the possibility to easily immobilize materials with TEMPO by using different linkers. Such approach allows significant change and improves the properties of materials, which is vital for the development of organic electrodes.

**Supplementary Materials:** The following are available online,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra, COSY, HMBC, HSQC, HRMS and FTIR data for 2-hydroxy-3-(4-oxy(2,2,6,6-tetramethylpiperidin-1-oxyl)butoxy)benzaldehyde.

**Author Contributions:** Conceptualization: D.A.L.; synthesis: A.A.V. and J.V.N.; writing—original draft preparation: A.A.V.; writing—review and editing: D.A.L.; Validation: A.Y.K.; visualization: D.A.L., A.A.V.; supervision: D.A.L.; funding acquisition: A.A.V. All authors have read and agreed to the published version of the manuscript.

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