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# Synthesis, characterization, and antioxidant activity of some organotin(IV) 2-nitrobenzoate using the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) method

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**Abstract.** Synthesis, characterization, and antioxidant activity of diphenyltin(IV) di-2-nitrobenzoate (**2**), dibutyltin(IV) di-2-nitrobenzoate (**4**), and triphenyltin(IV) 2-nitrobenzoate (**6**) using the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) method has been successfully carried out. All compounds were well characterized by some spectroscopy techniques of UV, IR, NMR and based on physical technique by microelemental analysis. The result showed that diphenyltin(IV) di-2-nitrobenzoate was the most active in the antioxidant activity test, with an IC<sub>50</sub> value of 8.6 µg/mL compared to the other compounds in which the dibutyltin(IV) di-2-nitrobenzoate and triphenyltin(IV) 2-nitrobenzoate have IC<sub>50</sub> values of 12.29 µg/mL and 27.28 µg/mL, respectively, which indicated that compounds **6** and **9** were categorized active antioxidant activity. However the IC<sub>50</sub> values of these compounds were higher than the positive control, ascorbic acid with IC<sub>50</sub> value of 0.66 µg/mL.

**Keywords:** antioxidant activity, DPPH method, organotin(IV) 2-nitrobenzoate, synthesis.

## 1. Introduction

Organotin compounds are compounds that contain at least one direct covalent bond between the carbon atom (C) of the organic group which is attached to the central Sn atom. Organotin compounds have been known to have wide range of applications and are among the most widely used of organometallic compounds. Organotin(IV) compounds have been reported to show many biological activities [1-4]. Among the various organotin(IV) complexes with biological molecules, organotin(IV) carboxylate complexes have received special attention because these compounds have better biological activity compared to other organotin(IV) complexes with various ligands [5-14].



Antioxidants are compounds that can fight or reduce the negative effects of oxidants. Antioxidants work by contributing one electron to an oxidant compound so that the activity of the oxidant compound can be inhibited [15]. Antioxidant compounds can play a role in reducing oxidative damage associated with aging, cardiovascular disease, cancer, inflammation, skin diseases, and malaria, prompting some searches for metal-based antioxidant drug compounds, especially organotin(IV) to be developed [15-17].

Based on the reactivity of organotin compounds, many researches have been attempted to utilize them in some biological activities, one of them is as an antioxidant. Therefore, in this paper, we reported the antioxidant activity of some organotin(IV) 2-nitrobenzoate using the DPPH method.

## 2. Experimental

### 2.1. Materials and characterisation

All reagents used were AR grade. Diphenyltin(IV) oxide ( $[(C_6H_5)_2SnO]$ ) (**1**), dibutyltin(IV) oxide ( $[(C_6H_5)_2SnO]$ ) (**3**) and triphenyltin(IV) oxide ( $[(C_6H_5)_3SnCl]$ ) (**5**), 2-nitrobenzoic acid were obtained from Sigma, sodium hydroxide (NaOH) and methanol ( $CH_3OH$ ) were JT Baker products, and the control ascorbic acid were from Sigma-Aldrich. All chemical were used as received without further purification.

The measurement of IR spectra were conducted using Bruker VERTEX 70 FT-IR spectrophotometer in the range  $4000-400\text{cm}^{-1}$  with KBr pellets. The UV spectra was measured with a UV-Shimadzu UV-245 Spectrophotometer on UV region. The measurement was performed in 1mL quartz-cells. The solvent used was methanol and sample concentration of  $1.0 \times 10^{-5}\text{M}$  were prepared. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AV 600 MHz NMR (600 MHz for  $^1\text{H}$  and 150 MHz for  $^{13}\text{C}$ ). DMSO- $D_6$  was used as solvent in the experiments and measured at 298K. The number of runs used for  $^1\text{H}$  experiments were 32 with reference at DMSO signal at 2.5 ppm, while the  $^{13}\text{C}$  were 1000-4000 scans with the reference of DMSO signal at 39.5 ppm. The microelemental analysis (CHNS) was carried out using Fision EA 1108 series elemental analyser.

### 2.2. Preparation of organotin(IV) 2-nitrobenzoate

The organotin(IV) 2-nitrobenzoate compounds used in this work were prepared based on the procedures previously reported [8, 9, 11-13]. These procedures were obtained as adaptation from the work available in the literature [10]. For example the procedure in the preparation of diphenyltin(IV) di-2-nitrobenzoate was as follows:

0.4605 g (1.5 mmol) compound **1** in 20 mL of methanol was added with 2 mole equivalents of 2-nitrobenzoic acid (0.498 g) and was refluxed for 4 hours at  $60 - 61^\circ\text{C}$ . After removal of the solvent by rotary evaporator, the compound  $[(C_6H_5)_2Sn(2-OOCC_6H_4(NO_2))_2]$  (**2**) was obtained as white solid and was dried *in vacuo* until they are ready for analysis and further use for antioxidant activity test. The yield was 0.835 g (92 %). The same procedure was also adapted in the preparation of dibutyltin(IV),  $[(C_4H_9)_2Sn(2-OOCC_6H_4(NO_2))_2]$ . For the triphenyltin(IV) derivatives,  $[(C_6H_5)_3Sn(OOCC_6H_4(NO_2))]$ , one mole equivalent of 2-nitrobenzoic acid was added.

### 2.3. Antioxidant Activity Test

Antioxidant activity test by DPPH method was performed according to method used by others [15-17]. Briefly, the compounds to be tested were dissolved in methanol at concentrations of 2; 4; 8; 16, and 32  $\mu\text{M}$ . To each test solution, DPPH (0.1 mM in methanol) was added and mixed thoroughly. The solution was left aside for 30 min. The absorbance of the mixture at a wavelength of 517 nm was measured using a UV-vis spectrophotometer. Antioxidant activity was calculated as the percentage of inhibition against DPPH. Percentage inhibition or percentage of DPPH radical capture activity was calculated using Equation 1:

$$\text{Percentage inhibition} = \left\{ \frac{\text{Control absorbance} - \text{Sample absorbance}}{\text{Control absorbance}} \right\} \times 100\%. \quad (1)$$

The  $IC_{50}$  of each sample concentration was calculated using the linear regression equation. The sample concentration was plotted in the X axis and percentage of inhibition in the y axis. From the equation  $y = a + bx$ , the value of  $IC_{50}$  was calculated using Equation 2.

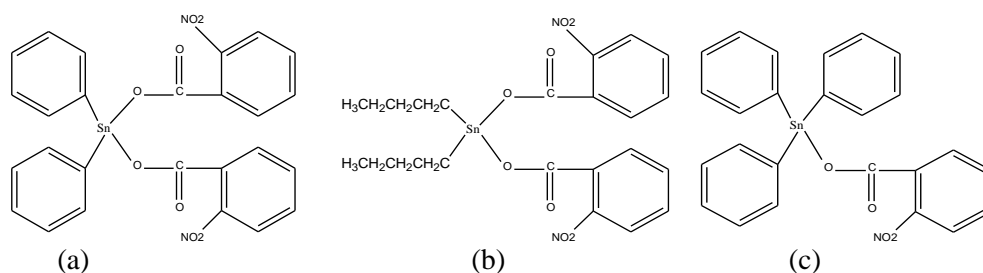
$$IC_{50} = \frac{50 - a}{b}, \quad (2)$$

where y is the percentage inhibition (50), a is the intercept (intersection of lines the y axis), b is the slope, and x is the concentration.

### 3. Results and discussion

#### 3.1 Characterisation of compounds

All synthesised compounds were well characterized with some spectroscopy techniques of UV, IR, NMR ( $^1H$  and  $^{13}C$ ) as well as based on the microelemental analysis. The results of each analysis are tabulated on Tables 1-4. The structure of the compounds which have been prepared are shown in Figure 1.



**Figure 1.** (a) diphenyltin(IV) di-2-nitrobenzoate; (b). dibutyltin(IV) di-2-nitrobenzoate; (c). triphenyltin(IV) 2-nitrobenzoate

**Table 1.** The microanalytical data of the organotin(IV) compounds synthesized

Compound	Elemental analysis found (calculated)		
	C	H	N
$[(C_6H_5)_2Sn(o-C_6H_4(NO_2)COO)_2]$ ( <b>2</b> )	51.40 (51.57)	2.96 (2.98)	4.57 (4.63)
$[(n-C_4H_9)_2Sn(o-C_6H_4(NO_2)COO)_2]$ ( <b>4</b> )	46.63 (46.73)	3.12 (3.19)	4.89 (4.96)
$[(C_6H_5)_3Sn(o-C_6H_4(NO_2)COO)]$ ( <b>6</b> )	58.08 (58.14)	3.65 (3.68)	2.67 (2.71)

**Table 2.**  $^1H$  and  $^{13}C$  spectra of the compounds synthesized

Compounds	H in butyl or phenyl (ppm)	H in benzoate (ppm)	C in butyl, phenyl and benzoate (ppm)
$[(C_6H_5)_2Sn(o-C_6H_4(NO_2)COO)_2]$ ( <b>2</b> )	$H_2$ & $H_6 = 7.61$ (d, 4H); $H_3$ & $H_5 = 7.50$ (t, 4H); $H_4 = 7.39$ (t, 2H)	$H_{10-13} = 7.82 - 7.95$ (m)	C(phen) $C_{2 \& 6} = 131.8$ , $C_{3 \& 5} = 129.7$ , $C_4 = 127.1$ ; $C_7 = 166.1$ ; $C_8 = 138.9$ ; $C_9 = 139.2$ , $C_{10} = 132.5$ ; $C_{11} = 128.9$ , $C_{12} = 128.1$ ; $C_{13} = 130.2$ ;

$[(n\text{-C}_4\text{H}_9)_2\text{Sn}(o\text{-C}_6\text{H}_4(\text{NO}_2)\text{COO})_2]$ ( <b>4</b> )	$\text{H}_\alpha$ & $\text{H}_\beta=1.41\text{-}1.62$ (m); $\text{H}_\gamma=1.30$ (m); $\text{H}_\delta=0.95$ (t)	7.35-7.85 (m)	$\text{C}_\alpha=26.3$ ; $\text{C}_\beta=24.6$ ; $\text{C}_\gamma=22.9$ ; $\text{C}_\delta=14.2$ ; $\text{C}_7=166.6$ ; $\text{C}_8=138.3$ ; $\text{C}_9=138.8$ ; $\text{C}_{10}=131.7$ ; $\text{C}_{11}=128.1$ ; $\text{C}_{12}=127.6$ ; $\text{C}_{13}=129.7$
$[(\text{C}_6\text{H}_5)_3\text{Sn}(o\text{-C}_6\text{H}_4(\text{NO}_2)\text{COO})]$ ( <b>6</b> )	$\text{H}_2$ & $\text{H}_6=7.58$ (d, 6H); $\text{H}_3$ & $\text{H}_5=7.45$ (t, 6H); $\text{H}_4=7.31$ (t, 3H)	7.86 - 7.92 (d)	C (phen) $\text{C}_{2\&6}=131.1$ ; $\text{C}_{3\&5}=129.4$ , $\text{C}_4=127.5$ ; $\text{C}_7=167.8$ ; $\text{C}_8=137.6$ ; $\text{C}_9=138.1$ ; $\text{C}_{10}=131.1$ ; $\text{C}_{11}=129.3$ ; $\text{C}_{12}=128.0$ ; $\text{C}_{13}=129.9$

**Table 3.** The characteristic and important IR bands of the organotin(IV) compounds ( $\text{cm}^{-1}$ ) synthesized

Compound	<b>2</b>	<b>4</b>	<b>6</b>	References
Sn-O	594.2	435.9	765.61	800-400
Sn-O-C	1243.1	1028.3	1243.42	1050-900
Sn-Bu	-	678.4	-	740-660
CO <sub>2</sub> asym	1532.7	1418.7	1558.9	1600-1400
CO <sub>2</sub> sym	1661.1	1560.9	1631.47	1700-1550
C-H aliphatic	-	2955 – 2868	-	2960 – 2850
Phenyl	1467.8; 751.5	-	1429.2; 729.6	1450, 730

**Table 4.** The  $\lambda_{\text{max}}$  of the UV-Vis spectra of the organotin(IV) compounds

Compound	$\lambda_{\text{max}}$ (nm)
$[(\text{C}_6\text{H}_5)_2\text{Sn}(o\text{-C}_6\text{H}_4(\text{NO}_2)\text{COO})_2]$ ( <b>2</b> )	236 and 278
$[(n\text{-C}_4\text{H}_9)_2\text{Sn}(o\text{-C}_6\text{H}_4(\text{NO}_2)\text{COO})_2]$ ( <b>4</b> )	235 and 275
$[(\text{C}_6\text{H}_5)_3\text{Sn}(o\text{-C}_6\text{H}_4(\text{NO}_2)\text{COO})]$ ( <b>6</b> )	237 and 282

An example of characterization of the products obtained was analyzed using FT-IR spectroscopy in the frequency range  $4000 - 400 \text{ cm}^{-1}$ . The characteristic vibration of starting material (compound **1**) is the present of the main absorption of the Sn-O bond in the region  $440\text{-}390 \text{ cm}^{-1}$  and it was observed that in **1** appeared at a frequency of  $417.4 \text{ cm}^{-1}$ . When compound **1** is converted into compound **2**, the strong band  $417.4 \text{ cm}^{-1}$  is disappeared and a new main absorption appears at  $594.2 \text{ cm}^{-1}$  which is a typical absorption. from the appearance of the Sn-O bond in compound **2** where oxygen from carboxylic group has bound to Sn atom. While the absorption of phenyl and C = C vibrations are still appeared as expected. Upon formation of compound **2**, the present very strong vibration band in the region of  $1661.1 \text{ cm}^{-1}$  is a typical of C=O bond vibration in compound **2**. The presence of vibration from Sn-O-C bond at  $1243.1 \text{ cm}^{-1}$  supported the analysis. The same observations were also observed in the formation of compound **4** and **6**, and these data are agreed to the reported values in the literature [8, 9, 11-13, 18]. The results of analysis with UV and NMR also indicated that all compounds prepared are in agreement with similar compounds reported in the literature [5, 8, 9, 11-13, 18-20]

### 3.2 Antioxidant activity test

In the antioxidant activity test using the DPPH method, the three synthesized compounds were tested in concentration variation of 2, 4, 8, 16, 32  $\mu\text{M}$ . After the absorbance in each measurement is obtained, the % inhibition can be calculated and the data are shown in Tables 5, 6, and 7. From these tables, then the  $\text{IC}_{50}$  (Inhibitory Concentration of 50%) value can be calculated.

**Table 5.** The results of the antioxidant activity test for diphenyltin(IV) di-2-nitrobenzoate

No	Concentration $\mu\text{M}$	Sample Absorbance	Control Absorbance	% Inhibition
1.	2	0.534	0.959	45.5102
2.	4	0.521	0.959	46.83673
3.	8	0.506	0.959	48.36735
4.	16	0.493	0.959	49.69388
5.	32	0.386	0.959	60.61224

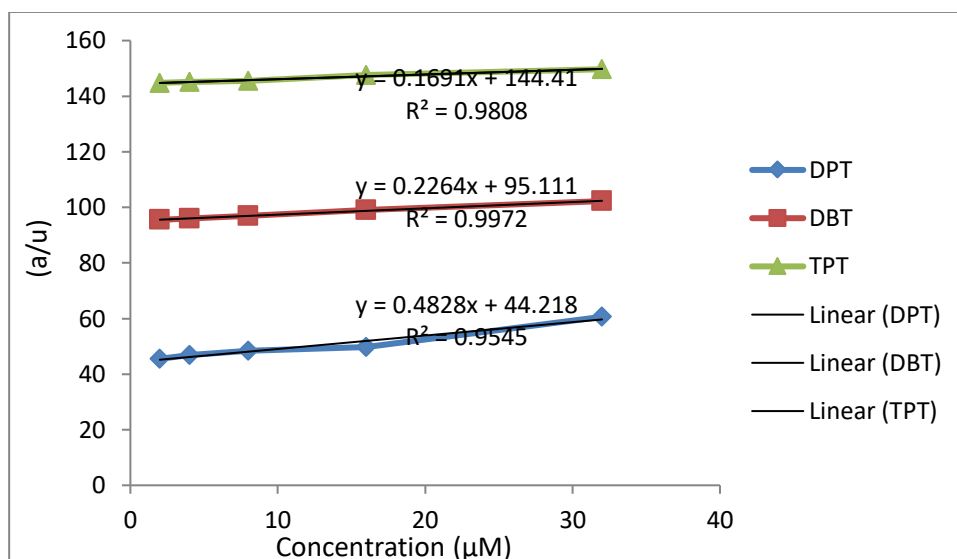
**Table 6.** The results of the antioxidant activity test of the compound dibutyltin(IV) di-2-nitrobenzoate

No	Concentration $\mu\text{M}$	Sample Absorbance	Control Absorbance	% Inhibition
1.	2	0.512	0.959	47.7551
2.	4	0.510	0.959	47.95918
3.	8	0.505	0.959	48.46939
4.	16	0.495	0.959	49.4898
5.	32	0.479	0.959	51.12245

**Table 7.** The results of the antioxidant activity test of the triphenyltin(IV) 2-nitrobenzoate compound

No	Concentration $\mu\text{M}$	Sample Absorbance	Control Absorbance	% Inhibition
1.	2	0.507	0.959	48.26531
2.	4	0.506	0.959	48.36735
3.	8	0.505	0.959	48.46939
4.	16	0.498	0.959	49.18367
5.	32	0.491	0.959	49.89796

To find out the value of IC, the % inhibition value is inserted to the linear regression equation curve and the line equation  $y = 50$  (50% inhibition) is generated in the equation and the value of  $x$  (concentration) is obtained. The minimum concentration is the  $x$  value of the test compound which can be used to inhibit radicals by 50%. The results on the antioxidant activity of the synthesized compounds compared to ascorbic acid are presented in Table 8 and the linear regression curve in Figure 2.



**Figure 2.** Linear regression curve for antioxidant activity test of all compounds tested DPT = diphenyltin(IV); DBT = dibutyltin(IV); TPT = triphenyltin(IV)

**Table 8.** The results of the antioxidant activity test using the DPPH method.

Compound	IC <sub>50</sub> (µM)	IC <sub>50</sub> (µg/mL)
[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Sn( <i>o</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )COO) <sub>2</sub> ] ( <b>2</b> )	14.21	8.6
[( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Sn( <i>o</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )COO) <sub>2</sub> ] ( <b>4</b> )	21.68	12.29
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sn( <i>o</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )COO)] ( <b>6</b> )	27.28	27.28
Ascorbic acid	3.74	0.66

Based on the data in Table 8, the IC<sub>50</sub> value for compounds **2**, **4** and **6** are 8.6; 12.29; 27.28 µg/mL, respectively. Therefore, compound **2** is categorized as to be very active while compound **4** and **6** categorized as active compound. This is based on categorization stated by Phongpaichit *et al.* [21] that compound having IC<sub>50</sub> value <10 µg/mL is very active compound as antioxidants and IC<sub>50</sub> value of 10-50 µg/mL is an active compound as antioxidant. However, the IC<sub>50</sub> values for the compounds reported are still less active compared to the positive control, ascorbic acid which IC<sub>50</sub> of only 0.66 µg/mL.

#### 4. Conclusions

Based on the results of this study, it can be concluded that the three compounds synthesized are potential to be developed as antioxidant although their antioxidant activities are below properties with the following order of activity: diphenyltin (IV) di-2-nitrobenzoate > dibutyltin(IV) di-2-nitrobenzoate > triphenyltin(IV) 2-nitrobenzoate.

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#### References

- [1] Affan MA, Foo SW, Jusoh I, Hanapi S and Tiekink ERT 2009 *Inorg. Chim. Acta.* **362** 5031
- [2] Alama A, Tasso B, Novelli F and Sparatore F 2009 *Drug Discov. Today* **14** 500
- [3] Kang W, Wu X and Huang J 2009 *J. Organometal. Chem.* **694** 2402
- [4] Wu X, Kang W, Zhu D, Zhu C and Liu S 2009 *J. Organo. Chem.* **694** 2981
- [5] Pellerito L and Nagy L 2002 *Coor. Chem. Rev.* **224** 111

- [6] Gleeson B, Claffey J, Ertler D, Hogan M, Müller-Bunz H, Paradisi F, Wallis D and Tacke M 2008 *Polyhedron* **27** 3619
- [7] Rehman W, Badshah A, Khan S and Tuyet LTA 2009 *Eur. J. Med. Chem.* **44** 3981
- [8] Hadi S, Rilyanti M 2010 *Orient. J. Chem.* **26** 775
- [9] Hadi S, Rilyanti M and Suharso 2012 *Indo. J. Chem.* **12** 172
- [10] Szorcsik A, Nagy L, Gadja-Schranz K, Pellerito L, Nagy E and Edelmann ET 2002 *J. Radioanal. Nucl. Chem.* **252** 523
- [11] Kurniasiah H, Nurissalam M, Iswantoro B, Afriyani H, Qudus HI and Hadi S 2015 *Orient. J. Chem.* **31** 2377
- [12] Hadi S, Afriyani H, Anggraini WD, Qudus HI and Suhartati T 2015 *Asian J. Chem.*, **27** 1509
- [13] Hadi S, Noviany and Rilyanti M 2018 *Maced. J. Chem. Chem Eng.* **37** 191
- [14] Hansch C and Verma RP 2009 *Eur. J. Med. Chem.* **44** 260
- [15] González A, Gómez E, Cortés-Lozada A, Hernández S, Ramírez-Apan T, Nieto-Camacho A. 2009 *Chem Pharm Bull* (Tokyo). **57** 5
- [16] Devi J, Yadav J, Singh N. 2019 *Res. Chem. Intermed.* **45** 3943
- [17] Sari W, Qudus H I, Hadi S. 2020 *Rev. Chim.* **71** (10) **in press**.
- [18] Sudjadi, The Structure Determination of Organic Compounds. Ghalia Publishers, 1985. (In Indonesian).
- [19] Hadi S, Appleton TG and Ayoko GA 2003 *Inorg. Chim. Acta.* **352** 201
- [20] Hadi S and Appleton TG 2010 *Russ. J. Inorg. Chem.* **55**, 223
- [21] Phongpaichit S, Nikom J, Rungjindamai N and Sakarajoy J.2008 *FEMS Immunol. Med. Microbiol.* **51** 517