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Synthesis of the BCAC4ND2 Ionophore from *p*-*t*-Butylcalix[4]arene Ethylester

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Abstract

Research on the synthesis of the BCAC4ND2 ionophore from p-t-butylcalix[4]arene ethylester has been carried out. This study aims to synthesize the BCAC4ND2 ionophor from p-t-butylcalix[4]arene ethylester. The BCAC4ND2 ionophore is synthesized by hydrolyzing p-t-butylcalix[4]arene ethylester in aqueous KOH-ethanol of 95%. The hydrolysis reaction of these base-promoted esters are refluxed for 28 hours at 78 ^{o}C. The BCAC4ND2 ionophore was identified and characterized by melting point, thin layer chromatography (TLC), FTIR, ^{1}H-NMR, and ^{13}C-NMR spectrometers. The BCAC4ND2 ionophore obtained was in the form of white solid (62.38% recovery), a melting point 326-328 ^{o}C, and TLC (SiO_2, ethanol : ethylacetate = 1 : 1 v/v, R_f = 0.93).

Keywords: synthesis, BCAC4ND2 ionophore, calix[4]arene, hydrolysis, esters, carboxylic acid

Abstrak

Penelitian tentang sintesis ionofor BCAC4ND2 dari p-t-butilkaliks[4]arena etilester telah dilakukan. Penelitian ini bertujuan untuk mensintesis ionofor BCAC4ND2 dari p-t-butilkaliks[4]arena etilester. Ionofor BCAC4ND2 disintesis dengan cara menghidrolisis p-t-butilkaliks[4]arena etilester dalam larutan KOH-etanol 95%. Reaksi hidrolisis ester terpromosi basa ini direfluks selama 28 jam pada suhu 78 ^{o}C. Ionofor BCAC4ND2 diidentifikasi dan dikarakterisasi dengan titik leleh, kromatografi lapis tipis (KLT), spektrometer FTIR, ^{1}H-NMR, dan ^{13}C-NMR. Ionofor BCAC4ND2 yang diperoleh berupa padatan putih (perolehan 62,38%), titik leleh 326-328 ^{o}C, dan KLT (SiO_2, etanol : etilasetat = 1 : 1 v/v, R_f = 0,93).

Kata Kunci: sintesis, ionofor BCAC4ND2, kaliks[4]arena, hidrolisis, ester, asam karboksilat

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I. Introduction

Calixarene is included in the group of macrocyclic molecules. Calixarene is composed of aromatic units connected by a methylene bridge. Calixarene can be synthesized and modified widely, so that we can produce different types and quantities of aromatic units, methylene bridges, and different functional groups [1].

Calixarene is a vase-shaped flower that has a variety of cavity diameters. This geometric shape causes calixarene can be used in the host-guest system, where calixarene acts as a host and ions or other molecules act as guest [1]. The ability of calixarene in forming host-guest interactions makes the use of calixarene in chemistry more extensive.

Calixarene can be used as an ionophore because it has a cavity and two functional groups, namely the functional groups above and below the annulus ring. Both of these functional groups can be modified to produce ionophores that are selective about compounds or metal ions [2] [3] [4]. For example, modification of the *t*-butyl group over the annular ring with a tetramer or hexamer group produces an ionophore that is selective to the cations of Rb, Sr, Cs, alkali metals, and alkaline earth metals [5]. Modification of hydroxyl groups under the annulus ring with carboxylic, sulfonato, alkenyl, and haloalkyl groups produces ionophores that are selective to the cations of Fe^{3+}, Ni^{2+}, Pb^{2+}, and Cr^{3+} [6] [7] [8].

One of the derivative compounds of calix[4]arenes that can be modified into ionophores is the *p*-*t*-butylcalix[4]arene ethylester compound. Ionofor BCAC4ND2 can be synthesized by hydrolyzing *p*-*t*-butylcalix[4]arene ethylester in 96% KOH-ethanol solution [9]. In the hydrolysis reaction of this base-promoted ester, the ethylester group under the annulus ring in the *p*-*t*-butylcalix[4]arene compound is converted to a carboxylic group.

II. Experiment

Tools and Materials

A set of reflux devices consisting of 100 mL three-neck round bottom flask, ball coolers, thermometers (100 °C), 1 cm magnetic stirrers, heating mantles, and funnels. Spectrometers used included the FTIR Prestige-21 Shimadzu and FTNMR JEOL ECX500. Other supporting tools are desiccator, analytical balance (Explorer Ohaus), Electrothermal 9100, dropper pipette (Pyrex), measuring cup (Pyrex), chemical beaker (Pyrex), stirring rod, and chamber.

The raw material, *p*-*t*-butylcalix[4]arene ethylester (synthesized) [8], potassium hydroxide (Merck), ethanol (Merck), hydrochloric acid (Merck), chloroform (Merck), distilled water, and

TLC plate. All solvents were obtained from commercial sources and used without further treatment.

Synthesis of the BCAC4ND2 Ionophore

The raw material (2.0 g, 0.0027 mol) is put into a 100 mL three-neck round bottom flask equipped with a ball cooler. Furthermore, a solution of KOH (0.5 g, 0.0089 mol) in 100 mL ethanol of 95% was added to the three-neck round bottom flask. The solution was refluxed for 28 hours at 78 ^{o}C and every 8 hours the solution was tested TLC. After cooling, the solution is acidified with 1M HCl. The precipitate formed was filtered and then washed with 2 x 2.5 mL of 1M HCl solution and 3 x 2.5 mL of water. The solids formed are dried in a desiccator, then recrystallized with ethanol to form a white powder (BCAC4ND2 ionophore). Furthermore the BCAC4ND2 ionophore was dried in a desiccator and then characterized by TLC, melting point, FTIR, ^{1}H-NMR, and ^{13}C-NMR spectrometers [10].

Determination of the BCAC4ND2 Ionophore Structure

The BCAC4ND2 ionophore structure was determined using spectroscopic techniques, namely FTIR and FTNMR 1-D (^{1}H and ^{13}C). The physical data and spectrum of FTIR, ^{1}H and ^{13}C-NMR of the BCAC4ND2 ionophore are as follows. Yield: 1.2476 g (62.38 %); mp 326 – 328 ^{o}C; TLC (SiO_2, ethanol : ethyl acetate = 1 : 1 v/v, R_f = 0.93). FTIR spectrum (KBr) ν_{max} (cm^{-1}): 3450,65 (OH acid), 1739,79 (C=O acid), 1244,09 (COC alkyl aryl ether), 1089,78 (RCO alkyl aryl ether), 1637,56 (C=C aromatic), 1201,65 (C-O aromatic), 817,82 and 711,73 (CH OOP aromatic), 2956,87, 2920,23, and 2850,79 (CH saturated aliphatic), 1455,09 (CH_3 aliphatic), 1465,9 (CH_2 aliphatic). ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) δ_H (ppm): 10,3353 [(s, 1**H**) (O**H**-1*)], 7,0484 [(s, 1**H**) (Ar**H-**22/24)], 4,4776 [(s, 2**H**) (C$\mathbf{H_2}$O-2”)], 4,2474 [(d, 2**H,** *J* = 12,9 Hz) (ArC$\mathbf{H_2}$Ar-20, *endo*)], 3,3939 [(d, 2**H,** *J* = 12,9 Hz) (ArC$\mathbf{H_2}$Ar-2, *ekso*)], 1,2556 [(s, 9**H**) (C(C$\mathbf{H_3}$)$_3$-2’)]. ^{13}C-NMR spectrum (500 MHz, $CDCl_3$) δ_C (ppm): 170,3153 [(**C**O_2H) (**C**-1”)], 146,8503 [(**C**O aryl) (**C**-25)], 144,5516 [(**C**-*para* aryl) (**C**-23)], 127,8691 [(**C**-*ortho* aryl) (**C**-1/**C**-21)], 126,1236 [(**C**-*meta* aryl) (**C**-22/**C**-24)], 73,1351 [(O**C**H_2CO_2H) (C-2”)], 34,1932 [(**C**(CH_3)$_3$) (**C**-1’)], 31,5892 [(C(**C**H_3)$_3$) (**C**-2’)], and 30,2348 [(Ar**C**H_2Ar) (**C**-2/**C**-20)].

III. Results and Discussion

The ionophore BCAC4ND2 was obtained by hydrolyzing *p-t*-butylcalix[4]arene ethylester in aqueous

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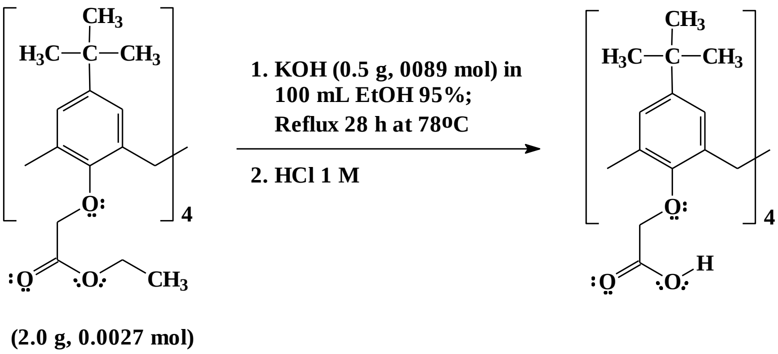
KOH-ethanol of 95% (Figure 1) [9]. The BCAC4ND2 ionophore was obtained as a white solid substance (62.38% recovery), a melting point of 326-328 ^{o}C, and R_f 0,93 on TLC (SiO_2, ethanol : ethylacetate = 1 : 1 v/v). The melting point of the BCAC4ND2 ionophore is in accordance with the melting point of compounds obtained by Kadir [6] and Maming [11].



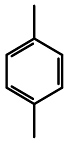
***p-t*-Butylcalix[4]arene ethylester**
(Raw Material)

***p-t*-Butylcalix[4]arene carboxylicacid**
(Ionophore BCAC4ND2)

Figure 1. Synthesis of the BCAC4ND2 ionophore from *p-t*-butylcalix[4]arene ethylester

In the base-promoted ester hydrolysis reaction above (Figure 1) it appears that the ethyl ester group (-$CO_2CH_2CH_3$) in *p-t*-butylcalix[4]arene ethylester is converted to a carboxylic group (-CO_2H) on the BCAC4ND2 ionophore. The success of the base-promoted ester hydrolysis reaction is supported by FTIR spectra data of synthesis products (BCAC4ND2 ionophore). From FTIR spectrum data (Table 1) it appears that the BCAC4ND2 ionophore does not show a strong and sharp absorption band at 1743.65 cm^{-1} of the carbonyl group (C=O) ester and strong absorption band at 671.23 cm^{-1} from bending O-C-O ester. According to Lambert [13] strong absorption bands in the range of 675-575 cm^{-1} are typical for bending O-C-O esters. The presence of wide and strong absorption bands at 3450.65 cm^{-1} and strong absorption bands at 1739.79 cm^{-1} indicates that the BCAC4ND2 ionophore contains hydrogen-bonded O-H groups and carbonyl groups (C=O) of carboxylic acids. These four FTIR spectrum data indicate that the reaction of the base-promoted ester hydrolysis has taken place.

Table 1. The FTIR spectrum of the *p*-*t*-butylcalix[4]arene ethylester (raw material) and the BCAC4ND2 ionophore

No	Frequency (cm^{-1}) and Intensities		Frequency Ranges (cm^{-1}) and Intensities*	Group or Class	Remarks
	Raw Material	BCAC4ND2Ionophore			
1	-	3450,65 (vs)	3400-2400 (s)	Carboxylic Acids RCOOH	OH stretch
2	-	1739,79 (vs)	1730-1700 (vs)		C=O stretch
3	1743,65 (vs)	-	1765-1720 (vs)	Esters RCOOR’	C=O stretch
4	671,23 (s)	-	675-575 (s)		O-C-O bend
5	1244,09 (s)	1244,09 (s)	1280-1220 (s)	Ethers ROR’	C-O-C stretch in alkyl aryl ethers
6	1066,64 (m)	1089,78 (s)	1075-1020 (s)		R-C-O stretch in alkyl aryl ethers
7	1604,77 (vs)	1637,56 (s)	1630-1430 (v)	Aromatic ArH 	C=C aromatic ring stretching
8	1201,65 (vs)	1201,65 (vs)	1300-1000 (s)		C-O aromatic ring stretching
9	877,61 (w)	817,82 (w)	900-650 (s)		Out-of-plane C-H deformation 1,4-disubstituted
10	846,75 (s)	711,73 (w)			
11	2958,8 (w)	2956,87 (w)	2970-2850 (s)	Aliphatic RH	C-H stretch from saturated $(CH_3)_3C$-
12	2924,09 (w)	2920,23 (vs)			
13	2854,65 (w)	2850,79 (s)			
14	1435,04 (s)	1455,09 (m)	1450-1375 (s)	*t*-Butyl $(CH_3)_3C$-	C-H stretch from CH_3-
15	1485,19 (w)	1465,9 (m)	1485-1450 (m)	Methylene -CH_2-	C-H stretch from –CH_2-

◦Notes: vs = *very strong*; v = *variable*; s = *strong*; m = *medium*; w = *weak.*

*Sources: [12] [13] [14]

The success of the base-promoted ester hydrolysis reaction is also supported by the BCAC4ND2 ionophore ^{1}H-NMR spectrum data. From the ^{1}H-NMR spectrum data (Table 2) it appears that the BCAC4ND2 ionophore does not show any signal at δ_H 4.2045 ppm (2**H**, *q*, *J* = 6.7 Hz) of the methylene ethoxy proton (OC**H**$_2$CH$_3$-1*) next to the neighboring methyl ethoxy proton (OCH$_2$C**H**$_3$-2*) which appears at δ_H 4,2045 ppm (2**H**, *q*, *J* = 6.7 Hz). The presence of a signal at δ_H 10.3353 ppm (1**H**, *s*) indicates that the BCAC4ND2 ionophore contains carboxylic acid proton (O**H**-1*). According to Kemp [14] OH carboxylic acid protons in the ^{1}H-NMR spectrum appear at δ_H 10 – 13 ppm.

Table 2. The NMR (^{1}H, ^{13}C) spectrum of the *p*-*t*-butylcalix[4]arene ethylester (raw material) and the BCAC4ND2 ionophore

C Position	δ_C (ppm)		Groups	H Position	δ_H (ppm)		Groups
	Raw Material	BCAC4ND2 Ionophore			Raw Material	BCAC4ND2 Ionophore	
1, 21	132,9455	127,8691	**C**-*o* aryl		-	-	-
22, 24	125,5032	126,1236	**C**-*m* aryl	22, 24	6,5283 (1**H**, *s*)	7,0484 (1**H**, *s*)	Ar**H**
23	146,6711	144,5516	**C**-*p* aryl		-	-	-
25	153,1262	146,8503	**C**O aryl		-	-	-
1’	34,3669	34,1932	$\mathbf{C}(CH_3)_3$		-	-	-
2’	31,4291	31,5892	$C(\mathbf{CH_3})_3$	2’	1,0467 (9**H**, *s*)	1,2556 (9**H**, *s*)	$C(C\mathbf{H_3})_3$
20	31,7629	30,2348	$Ar\mathbf{C}H_2Ar$	2	4,8548 (2**H**, *d*, *J* = 12,9 Hz)	4,2474 (2**H**, *d*, *J* = 12,9 Hz)	$ArC\mathbf{H_2}Ar$, *endo*
2					3,1925 (2**H**, *d*, *J* = 12,9 Hz)	3,3939 (2**H**, *d*, *J* = 12,9 Hz)	$ArC\mathbf{H_2}Ar$, *ekso*
	169,6680	-	**C**=O			-	-
1”	-	170,3153	$\mathbf{C}\text{-}O_2H$	1”	-	10,3353 (1**H**, *s*)	$CO_2\mathbf{H}$
2”	70,7127	73,1351	$O\mathbf{C}H_2CO_2$	2”	4,7344 (2**H**, *s*)	4,4776 (2**H**, *s*)	$C\mathbf{H_2}O$
1*	61,0646	-	$CO_2\mathbf{C}H_2CH_3$	1*	4,2045 (2**H**, *q*, *J* = 6,7 Hz)	-	$OC\mathbf{H_2}CH_3$
2*	14,4127	-	$CO_2CH_2\mathbf{C}H_3$	2*	1,2478 (3**H**, *t*, *J* = 6,7 Hz)	-	$OCH_2C\mathbf{H_3}$

The ^{13}C-NMR spectrum data of the BCAC4ND2 ionophore also strengthen the results of the FTIR and ^{1}H-NMR spectrum analysis above. From the ^{13}C-NMR spectrum data (Table 2) it appears that the BCAC4ND2 ionophore does not show any signal at δ_C 61.0646 ppm (**C**-1*) of methylene ethoxy carbon (O**C**H$_2$CH$_3$), signal at δ_C 14.4127 ppm (**C**-2*) from methyl ethoxy carbon (OCH$_2$**C**H$_3$), and the signal at δ_C 169.6680 ppm (**C**-1") from carbon carbonyl (**C**=O) esters. The presence of a signal at δ_C 170.3153 ppm (**C**-1") indicates that the BCAC4ND2 ionophore contains carbonyl carbon (**C**=O) carboxylic acid (**C**-O$_2$H). This shows that the hydrolysis reaction of the *p*-*t*-butylcalix[4]arene ethylester forming the BCAC4ND2 ionophore has taken place.

The results of the ^{13}C-NMR data analysis (Table 2) also provide a number of signals that fit into the BCAC4ND2 ionophore carbon framework. The signals of the aryl carbon atom (**C**-aryl) are scattered into four values of δ_C. First, the **C**-25 carbon atom shows the most downfield signal at δ_C 146.8503 ppm (**C**O aryl) compared to the other aryl carbon because this **C**-25 atom binds directly oxygen from the OCH$_2$CO$_2$H group. Second, the **C**-23 carbon absorption signal at δ_C 144.5516 ppm which binds to the *tert*-butyl group in the *para* (**C**-*para* aryl) position. Third, the **C**-1/**C**-21 carbon absorption signal at the *ortho* position appears at δ_C 127.8691 ppm (**C**-*ortho* aryl). Fourth, the **C**-22/**C**-24 carbon absorption signal at the *meta* position appears at δ_C 126.1236 ppm (**C**-*meta* aryl). The more upfield carbon uptake groups are derived from alkyl groups. The methylene carbon (O**C**H$_2$CO$_2$H) absorption signal appears at δ_C 73.1351 ppm (**C**-2"). The three strong absorption signals at δ_C 34.1932, 31.5892, and 30.2348 ppm were respectively derived from the carbon resonance quarterners of *t*-butyl (**C**-1'), -**C**H$_3$ (**C**-2'), and Ar**C**H$_2$Ar (**C**-2/**C**-20). This sequence is based on the electronegativity effect of the atom bound by the carbon atom to the value of δ_C and the relative intensity of the carbon absorption signal in the spectrum. Thus, the absorption that appears in the range of δ_C 0 – 170 ppm in the ^{13}C-NMR spectrum of the synthesized product is in accordance with the carbon framework of 5,11,17,23-tetracis(1,1-dimethylethyl)-25,26,27,28-tetra(carboxymethoxy)calix[4]arene or the BCAC4ND2 ionophore (Figure 2).

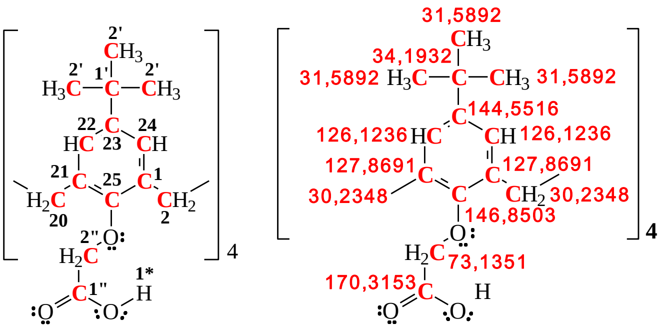


Figure 2. The position of the chemical shift value of ^{13}C-NMR on the carbon framework of the BCAC4ND2 ionophore

The ^{1}H-NMR spectrum of the BCAC4ND2 ionophore (Table 2) shows that the proton absorption band of the aryl group (Ar**H**) appears as a singlet at δ_H 7.0484 ppm, the methylene bridge proton absorption band (ArC$\mathbf{H_2}$Ar) appears as two doublets at δ_H 4.2474 ppm and 3.3939 ppm, and the *t*-butyl proton absorption band [-C(C$\mathbf{H_3}$)$_3$] appears as a singlet at δ_H 1.2556 ppm. The pattern of these absorption bands indicates that the conformational form of the BCAC4ND2 ionophore is a cone (Figure 3) [15] [16]. The ^{13}C-NMR spectrum of the BCAC4ND2 ionophore (Table 2) also strengthen that the conformational form of the BCAC4ND2 ionophore is cone (Figure 3). This can be seen by the presence of carbon absorption bands from the methylene bridge group (Ar**C**H$_2$Ar) that appear at δ_C 30.2348 ppm (≈ 31 ppm). This means that the orientation of two adjacent aryl groups is *syn* (a plot) with each other [17] [18].

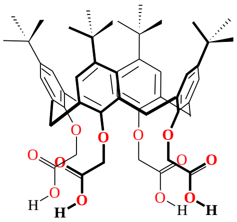


Figure 3. Cone conformation of the BCAC4ND2 ionophore

IV. Conclusion

Synthesis of the BCAC4ND2 ionophore from *p*-*t*-butylcalix[4]arene ethylester as the raw material has been successfully carried out through the reaction stage of base-promoted ester hydrolysis.

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Synthesis product was obtained as a white solid (62.38% recovery), a melting point of 326-328 °C, TLC (SiO_2, ethanol:ethyl acetate = 1:1 v/v, R_f = 0.93). The results of the synthesis product analysis with FTIR, ^1H and ^{13}C-NMR spectrometers showed that the synthesis product is 5,11,17,23-tetracis(1,1-dimethylethyl)-25,26,27,28-tetra(carboxymethoxy)calix[4]arene or the BCAC4ND2 ionophore.

V. Acknowledgements

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