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Synthesis and Characterization of *Bis*-Dithiocarbamate Disubstituted Derivative of Calix[4]arene as a New Macrocyclic Ligand for Construction of Ion Selective Electrode

FATEMEH JAHANSHAHI-ANBOOHI[1,*] and GISA REZAIE[2]

[1]Lavasan Payame Noor University, No. 27, Daneshe 3, Moaalem Street, Emam Khomeini Boulvar, Lavasan, Iran
[2]Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

*Corresponding author: Tel/Fax: +98 21 22768957; E-mail: jahanshahifatemeh@yahoo.com

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In this communication, the synthesis and structure determining of 5,11,17,23-*tetrakis*(2,2,3,3-tetra methyl butyl)-25,27-*bis*(N,N diethyldithio carbamoyl propoxy)-26,28-dihydroxy calix[4]arene, which has selective complexing behaviour has been reported. According to substitutability at lower rim of calix[4]arene it can be possible to selective connecting of diethyl dithiocarbamate units at this position. The existence of calix[4]arene units in obtained molecule cause selective behaviour of dithiocarbamoyl part, so complexes are formed, which have special ion selective characteristics and are used in constructing of ion selective electrodes and electrochemical sensors. The structural properties and characteristics of obtained molecule are determined by different spectroscopic methods.

Key Words: Calix[4]arene, Dithiocarbamate, Ion selective electrode.

INTRODUCTION

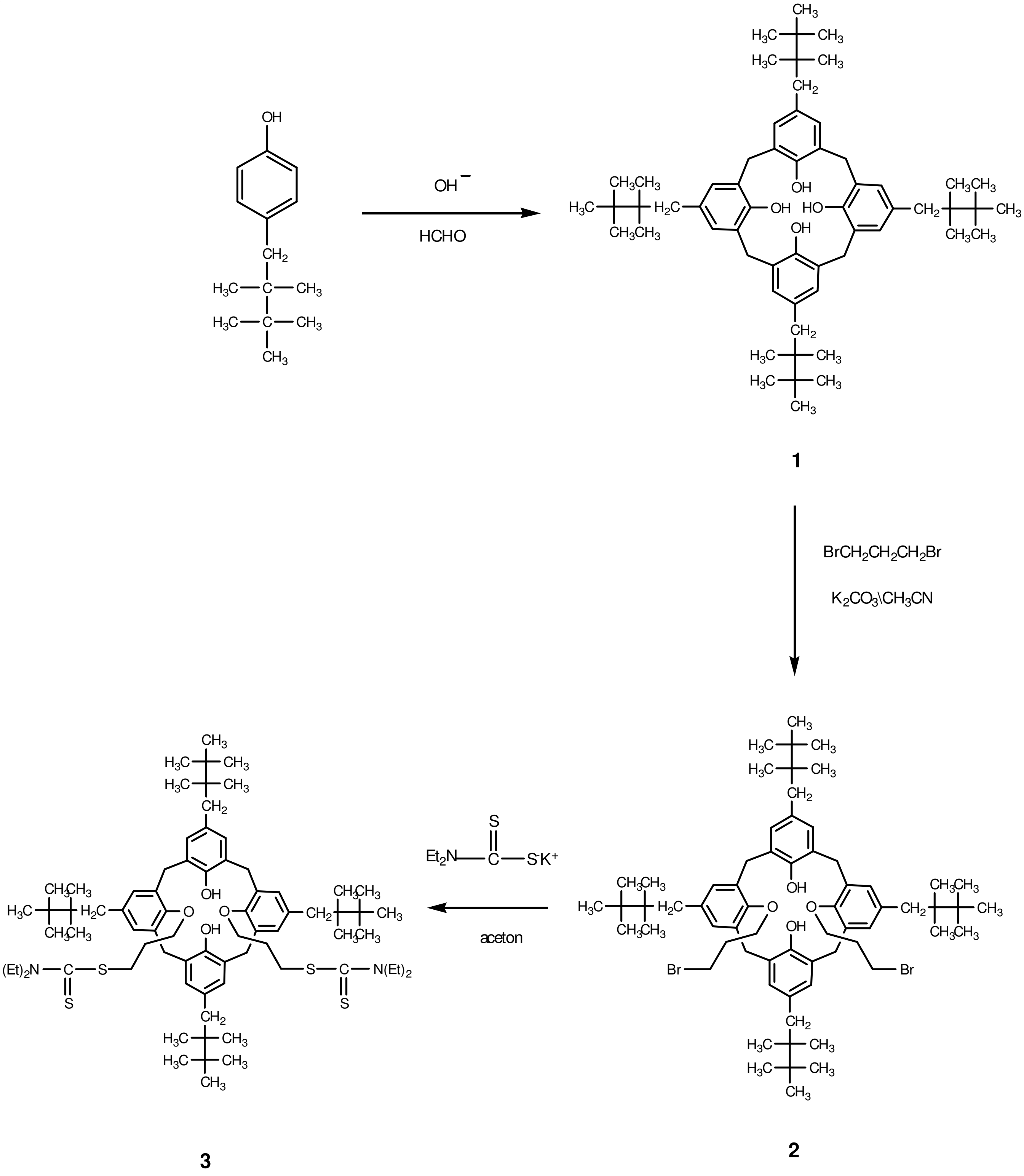
Calixarenes have attracted attention because of their potential for forming host-guest complexes in the supramolecular chemistry. They can be easily functionalized both at the phenolic -OH groups (lower rim) and after partial removal of tetra-butyl groups, at the *para* position of the phenyl rings (upper rim)[1-3].

The vast majority of these modifies calixarenes exist in the cone conformation in with there is a cavity suitable for reception of different ionic and neutral species[4]. Furthermore, the most significant feature of the chemistry of these molecules is their ability to bind selectively alkali and alkaline earth cations[5,6]. Calix[4]arenes have attracted considerable interest as building blocks for constructing selective host molecules[7]. Lower rim functionalized compounds can be obtained in a multi-step procedure from suitably substituted precursors[8]. Dithiocarbamate based ligands have an essential role in coordination chemistry. In this paper we would like to report the synthesis and characterization of a new dithiocarbamate derivative of calix[4]arene which can be applied as a selective ionophore both in carbamate and calixarene sections.

EXPERIMENTAL

Melting points are taken on a Buchi SMP-20 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-500 MHz in $CDCI_3$ with Me_4SI as an internal standard. IR spectra were recorded on a Bruker IFS-25 spectrophotometer.

Procedure for preparation of (*para*-2,2,3,3-tetra methyl butyl)calix[4]arene (1): A mixture of (10 g, 6 mmol) of *para*-2,2,3,3-tetra methyl butyl phenol, 6.2 mL of 37 % formaldehyde solution and (0.012 g, 0.43 mmol) of sodium hydroxide and 0.003 mL of water is placed in a three-necked, round-bottomed flask equipped with a mechanical stirrer. The contents of the open flask are allowed to stir for 15 min at room temperature and then heated for 2 h at 100-120 ºC by means of a heater mantle. Stirring is discontinued, the reaction vessel is removed from the heating and the reaction mixture is allowed to cool to room temperature. 80-100 mL of warm diphenyl ether is added to the flask and the continue are stirred, the process generally requiring at least 1 h and the contents of the flask are stirred and heated to 150-160 ºC for a few minutes and then at reflux for 3-4 h under a gentle flow of nitrogen. The reaction mixture is cooled to room temperature and the product is precipitated by the addition of 150 mL of ethyl acetate. The resulting mixture is stirred for 15-30 min and allowed to stand for at least 0.5 h. Filtration yields material that is washed twice with 10 mL portions of ethyl acetate, once with 20 mL of acetic acid, twice with 10 mL portions of water and twice with 5 mL portions of acetone. m.p. 241-245 ºC, ^{1}H NMR ($CDCl_3$) (δ, ppm): 10 (4H, s, OH), 7.04 (8H, s, ArH), 4.28 and 3.50 (8H, 2d, $ArCH_2Ar$), 11.58 (8H, s, CH_2), 1.27 (24H, s, CH_3), 0.56 (36 H, s, CH_3. IR (KBr, ν_{max}, cm^{-1}): 3168, 2955, 2901, 1583, 1485, 1276.



Scheme-I

Procedure for preparation of 5,11,17,23-*tetrakis* (2,2,3,3-tetra methyl butyl)-25,27-diboromo propoxy-26,28-dihidroxy calix[4]arene (2): A slurry of potassium carbonate (3.1 g, 31.6 mmol), diboromo propane (2.7 mL, 26.5 mmol), calix[4] arene **1** (1.7 g, 2 mmol) and 45 mL acetonitrile was stirred in reflux condition for 5 h. The reaction mixture was treated with dilute hydrochloric acid and then extracted by dichloro methane. The organic layer was separated, dried over magnesium sulfate and concentrated to half of mitral volume. With addition of methanol, **2** was percipitated and it was recrystillized in $CH_2Cl_2\backslash CH_3OH$ (2:1). Yield 61 %. m.p. 169-171 ºC, ^{1}H NMR ($CDCl_3$, 500 MHz) (δ, ppm): 7.77 (2H, s, OH), 7.01 (4H, s, ArH), 6.89 (4H, s, ArH), 4.28 (4H, d, *J* = 12.9 Hz, $ArCH_2Ar$), 4.14 (4H, t, CH_2), 4.07 (4H, t, CH_2), 3.37 (4H, d, *J* = 12.9 Hz, $ArCH_2Ar$), 2.57 (4H, m, CH_2), 1.74 (4H, s, CH_2), 1.39 (4H, s, CH_2), 1.37 (12H, s, CH_3), 1.15 (12H, s, CH_3), 0.81 (18H, s, CH_3), 0.24 (18H, s, CH_3), ^{13}C NMR ($CDCl_3$, 125 MHz); (δ, ppm), 30.8, 31.3, 31.4, 31.8, 31.9, 32.0, 32.4, 32.4, 32.8, 34.0, 38.1, 57.5, 58.0, 73.8, 126.3, 127.1, 127.6, 132.8, 141.0, 146.2, 148.7, 150.9. IR (KBr, ν_{max}, cm^{-1}): 3317, 2953, 1485, 1364, 1206.

Procedure for preparation of 5,11,17,23-*tetrakis*(2,2,3,3-tetra methyl butyl)-25,27-*bis*(3 N,N-diethyl-dithiocarbamoyl propoxy)-26,28-dihydroxy calix[4]arene (3): To solution of (0.5 g, 0.446 mmol) of **2** in 20 mL acetone was added (1.3 g, 5.77 mmol) N,N-dithiocarbamate sodium salt and put in at reflux condition for 7 h. The solvent was evaporated by rotary evaporator and 80 mL H_2O was added to remained crude and immediately was extracted with dichloromethane. The organic layer was resolved, evaporated and dried over magnesium sulfate. Compound **3** was purified by column chromatography (silica-gel/CH_2Cl_2: *n*-hexane, 1:2). Yield 24 %. m.p. 176-178 ºC, ^{1}H NMR ($CDCl_3$, 500 MHz) (δ, ppm): 7.94 (2H, s, OH), 7.06(H, s, ArH), 6.88 (4H, s, ArH), 4.29(4H, d, *J* = 15 Hz), 4.11 (4H, t, CH_2), 4.08 (4H, t, CH_2), 3.92 (4H, q, CH_2), 3.36 (4H, d, *J* = 15 Hz), 2.48 (4H, m, CH_2), 1.73 (4H, s, CH_2), 1.38 (4H, s, CH_2), 1.37 (12H, s, CH_3), 1.33 (12H, m, CH_3), 1.15 (12H, s, CH_3), 0.81 (18 H, s, CH_3, 0.24 (18 H, s, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) (δ, ppm): 12.1, 13.0, 30.3, 31.3, 31.4, 32.0, 32.4, 32.5, 32.8, 33.8, 38.1, 38.2, 47.2, 49.8, 57.5, 58.0, 75.1, 126.3, 127.0, 127.6, 132.8, 140.7, 145.9, 149.6,151.2, 196.1. IR (KBr, ν_{max}, cm^{-1}): 3347, 2953, 1596, 1487, 1417, 1270, 1207, 1144.

RESULTS AND DISCUSSION

For synthesis of considering molecule **3**, cone conformation of *bis*(bromo propoxy)-dihydroxy calix[4]arene **2**, as a key intermediate has been reacted with N,N-diethyl dithiocarbamate salt in acetone. **Scheme-I** shows the synthetic strategy of target molecule **3**. ^{1}H NMR spectra of compounds **2** and **3** in bridge methylen of calixarene zone (3-4.2 ppm) show two doublets according to highly symmetry of these molecules.

The difference between these 2d signals are more than 1 ppm (Δδ > ppm) and so establish the cone conformation of calixarene in all of derivatives. Free phenolic rings in compound **2** let us for substituting of 1,3-diboromoporopane in quantitative and selective reaction.

The free phenolic rings and also dithio carbamate sections in diastal positions can be afforded the best form for complexing of **3** with some soft transition metals, the complexation behaviour of **3** is under study in our research group.

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