

## Communications

### Synthesis and Structure of Tetrahomodioxo *p*-Phenylcalix[4](aza)biscrowns

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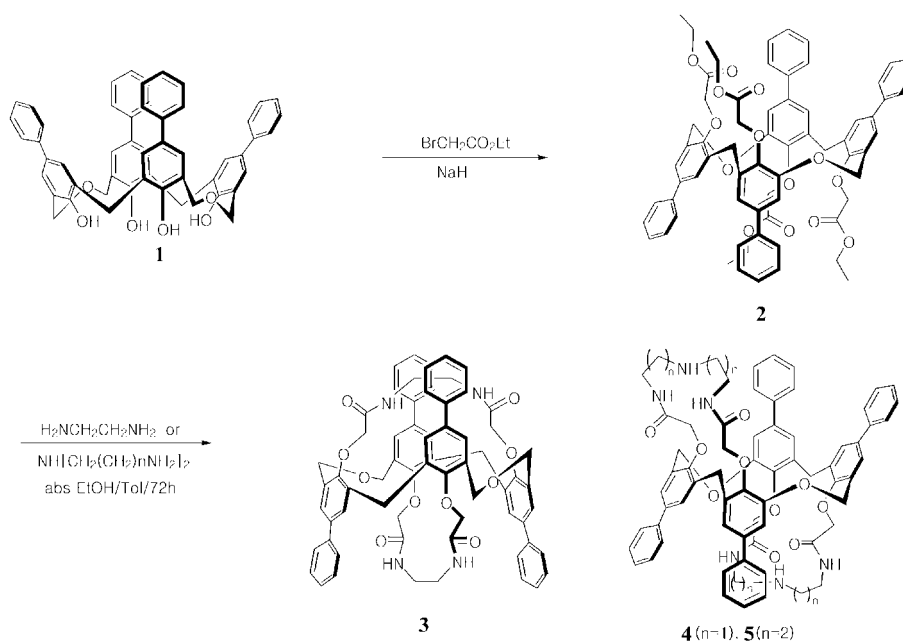
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Calixarenes have been intense interest as complexation hosts for ions and molecules.<sup>1-3</sup> Tetrahomodioxacalix[4]-arenes which contain two extra oxygen atoms in the macrocyclic ring, however, have been rarely studied due to their synthetic difficulty.<sup>4-8</sup> Previously, we reported that C-1,2-alternate<sup>9</sup> *N,N*-diethyltetrahomodioxacalix[4]arene tetraamide showed Pb<sup>2+</sup> ion selectivity.<sup>10</sup> In the case of *monoalkyl* amide, however, the conformation changes to 1,3-alternate conformation because of the strong hydrogen bonding, reflecting weak extractability for metal cations.<sup>9</sup>

Calix[4]crown ethers in which the proper-sized crown

rings are incorporated into the calix[4]arene framework have been also attracted as a specific metal-selective extractant.<sup>11</sup> 1,3-Alternate calix-*bis*-crowns have particularly interesting molecular features including the cation- $\pi$  interaction as well as the electrostatic interaction in cation complexation.<sup>12</sup> The family of calix[4](aza)crowns refer to molecules combining calix[4]arene elements and aza-crown units in their framework. They are constructed with aza-ethylene chains attached to the phenolic oxygen atoms of the calix via acetamido functions, which may serve as linking functions and also as chelating groups. The first 1,3-calix[4](aza)crowns were



Scheme 1

prepared by reaction of either calix dimethyl ester or calix diacid chloride with the appropriate diamine,  $\text{NH}_2\text{-R-NH}_2$ , and were shown to complex divalent and trivalent metal cations using FAB-mass spectrometry.<sup>13</sup> After pioneering study of Rheinholdt, Bitter and Vicens research groups reported the synthesis and complexation studies of *p-tert*-butylcalix[4]-(aza)crown derivatives.<sup>14</sup> However, crown or azacrown derivatives of homooxalix[4]arene were not reported yet.

In a continuation of the homooxalixarene, we synthesized tetrahomodioxo-*p*-phenylcalix[4](aza)biscrowns of which conformations are 1,3- and C-1,2-alternate. The synthetic route for homooxalix[4](aza)biscrowns is depicted in Scheme. Reaction of **2**<sup>10</sup> having a C-1,2 alternate conformation with ethylenediamine and dialkylenetriamine in absolute ethanol and toluene gave **3**, **4** and **5**, respectively. Judging from <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, **3** was found in the 1,3-alternate conformation and **4** and **5** in the C-1,2-alternate conformation, respectively.

In the <sup>1</sup>H NMR spectrum of **3**,<sup>15</sup> the dimethylenoxy protons of the  $\text{ArCH}_2\text{OCH}_2\text{Ar}$  bridge showed AB doublets at 4.28 and 4.13 ( $\Delta\nu = 60$  Hz) with a *geminal* coupling constant of 14.1 Hz. In addition, a singlet peak for the methylene protons of  $\text{ArCH}_2\text{Ar}$  appeared at 4.06. The <sup>13</sup>C NMR spectrum showed one peak at 68.93 ppm for the  $\text{ArCH}_2\text{O}$  of bridge methyleneoxy carbons and one peak at 37.85 ppm for the  $\text{ArCH}_2\text{Ar}$  bridge carbons implying that two adjacent benzene rings are in an *anti* orientation. These NMR data confirms that **3** is in 1,3-alternate conformation.

For **4**,<sup>16</sup> in the <sup>1</sup>H NMR spectrum, the dimethylenoxy protons of the  $\text{ArCH}_2\text{OCH}_2\text{Ar}$  bridge showed AB doublets at 4.38 and 3.80 ( $\Delta\nu = 232$  Hz) with a *geminal* coupling constant of 14.0 Hz. In addition, a doublet peaks for the methylene protons of  $\text{ArCH}_2\text{Ar}$  appeared at 4.52 and 3.58 ( $\Delta\nu = 376$  Hz) with a *geminal* coupling constant of 13.2 Hz. The <sup>13</sup>C NMR spectrum showed one peak at 73.59 ppm for the  $\text{ArCH}_2\text{O}$  of bridge methyleneoxy carbons and one peak at 30.17 ppm for the  $\text{ArCH}_2\text{Ar}$  bridge carbons implying that two adjacent benzene rings are in an *syn* orientation. So, it is in the C-1,2-alternate conformation. The NMR spectral data of **5**<sup>17</sup> were similar with the those of compound **4**, the protons of the  $\text{ArCH}_2\text{OCH}_2\text{Ar}$  and  $\text{ArCH}_2\text{Ar}$  bridge showed AB doublets. The <sup>13</sup>C NMR spectrum showed one peak at 73.66 ppm for the  $\text{ArCH}_2\text{O}$  bridge methyleneoxy carbons and one peak at 31.42 ppm for the  $\text{ArCH}_2\text{Ar}$  bridge carbons which is also indicating that two adjacent benzene rings are in a *syn* orientation (C-1,2-alternate conformation).

Further works on complexation experiments with **3**, **4** and **5** as ligand are in progress.

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- 3**: 63%; mp 282 °C (decompose); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.41-7.34 (m, 24, ArH), 7.29-7.25 (m, 4, ArH), 5.89 (br. d, 4, NH,  $J = 5.5$  Hz), 4.81 (d, 4,  $\text{OCH}_2\text{CO}$ ,  $J = 12.9$  Hz), 4.33 (d, 4,  $\text{OCH}_2\text{CO}$ ,  $J = 12.9$  Hz), 4.28 (d, 4,  $\text{ArCH}_2\text{O}$ ,  $J = 14.1$  Hz), 4.13 (d, 4,  $\text{ArCH}_2\text{O}$ ,  $J = 14.1$  Hz), 4.06 (s, 4,  $\text{ArCH}_2\text{Ar}$ ), 3.18 (br. q, 4,  $\text{NCH}_2$ ,  $J = 6.3$  Hz), 2.30 (br. q, 4,  $\text{NCH}_2$ ,  $J = 6.3$  Hz). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  167.89 (C=O), 152.57, 139.61, 138.92, 133.55, 130.82, 129.25, 128.97, 127.98, 127.15, 126.48 (Ar), 69.18 ( $\text{OCH}_2\text{CO}$ ), 68.93 ( $\text{ArCH}_2\text{O}$ ), 39.05 ( $\text{NCH}_2$ ), 37.85 ( $\text{ArCH}_2\text{Ar}$ ). Anal. Calcd. For  $\text{C}_{66}\text{H}_{60}\text{O}_{10}\text{N}_4$ : C, 74.14; H, 5.66. Found: C, 74.41; H, 5.48.
- 4**: 55%; mp 290 °C (decompose); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.60 (d, 8, ArH,  $J = 7.7$  Hz), 7.53 (br. s, 8, ArH), 7.47 (t, 8, ArH,  $J = 7.7$  Hz), 7.38 (t, 4, ArH,  $J = 7.4$  Hz), 6.84 (br. 6, NH), 4.94 (d, 4,  $\text{OCH}_2\text{CO}$ ,  $J = 11.0$  Hz), 4.52 (d, 2,  $\text{ArCH}_2\text{Ar}$ ,  $J = 13.2$  Hz), 4.38 (d, 4,  $\text{ArCH}_2\text{O}$ ,  $J = 14.0$  Hz), 4.23 (d, 4,  $\text{OCH}_2\text{CO}$ ,  $J = 11.0$  Hz), 3.80 (d, 4,  $\text{ArCH}_2\text{O}$ ,  $J = 14.0$  Hz), 3.58 (d, 2,  $\text{ArCH}_2\text{Ar}$ ,  $J = 13.2$  Hz), 2.90 (br. m, 4,  $\text{NCH}_2$ ), 2.45 (br. m, 4,  $\text{NCH}_2$ ), 2.23 (br. m, 4,  $\text{NCH}_2$ ), 2.19 (br. m, 4,  $\text{NCH}_2$ ). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  167.51 (C=O), 154.30, 139.62, 138.03, 134.91, 130.27, 129.79, 129.64, 128.96, 127.66, 127.05 (Ar), 73.59 ( $\text{ArCH}_2\text{O}$ ), 67.77 ( $\text{OCH}_2\text{CO}$ ), 45.94, 37.75 ( $\text{NCH}_2$ ), 30.17 ( $\text{ArCH}_2\text{Ar}$ ). Anal. Calcd. For  $\text{C}_{76}\text{H}_{70}\text{O}_{10}\text{N}_6$ : C, 72.77; H, 6.11. Found: C, 72.51; H, 6.08.
- 5**: 46%; mp 274 °C (decompose); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.51-7.29 (m, 34, ArH, & NH), 4.88 (d, 2,  $\text{ArCH}_2\text{Ar}$ ,  $J = 14.6$  Hz), 4.60 (s, 8,  $\text{OCH}_2\text{CO}$ ), 4.06 (br. d, 4,  $\text{ArCH}_2\text{O}$ ,  $J = 12.0$  Hz), 3.79 (d, 4,  $\text{ArCH}_2\text{O}$ ,  $J = 12.0$  Hz), 3.51 (d, 2,  $\text{ArCH}_2\text{Ar}$ ,  $J = 14.6$  Hz), 3.18 (br. 4,  $\text{NCH}_2$ ), 3.07 (br. 4,  $\text{NCH}_2$ ), 2.26 (br. 4,  $\text{NCH}_2$ ), 2.22 (br. 4,  $\text{NCH}_2$ ), 1.38 (br. 8,  $\text{CH}_2$ ). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  168.27 (C=O), 154.92, 139.64, 137.58, 134.64, 130.44, 130.08, 129.18, 128.95, 127.82, 126.94 (Ar), 73.66 ( $\text{ArCH}_2\text{O}$ ), 68.10 ( $\text{OCH}_2\text{CO}$ ), 45.48, 36.12 ( $\text{NCH}_2$ ), 31.42 ( $\text{ArCH}_2\text{Ar}$ ), 28.71 ( $\text{CH}_2$ ). Anal. Calcd. For  $\text{C}_{74}\text{H}_{78}\text{O}_{10}\text{N}_6$ : C, 73.37; H, 6.49. Found: C, 73.11; H, 6.28.