

# Synthesis and Conformational Analysis of a Small *meta*-Cyclophane, Bis(5-carbomethoxy-1,3-phenylene)-14-crown-4

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**ABSTRACT:** A small cyclophane, bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (BCMP14C4, **3**) and its diacid, bis(5-carboxy-1,3-phenylene)-14-crown-4 (**4**), were synthesized and characterized. The solid-state molecular structures of **3** and **4** were determined by X-ray crystallography as ladder or stepped conformations in which the two aromatic rings are antiparallel to each other without overlap and the ethylene tethers both take *trans*-conformations. Diester **3** is formed in the lowest cyclization yield (under the same reaction conditions) and exhibits the highest melting point compared to its larger ring (20-, 26- and 32-membered) analogs. In CD<sub>2</sub>Cl<sub>2</sub> solution, diester **3** exists predominantly as a nonplanar *gauche-gauche* structure as deduced by <sup>1</sup>H NMR studies. © 2008 Wiley Periodicals, Inc. *Heteroatom Chem* 19:48–54, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20393

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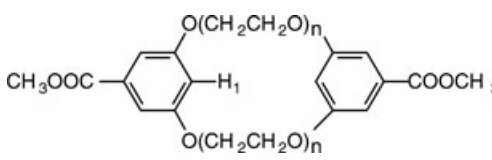
## INTRODUCTION

Previously, we synthesized a series of *meta*-cyclophanes, i.e., bis(5-carbomethoxy-1,3-phenylene)-(3*x* + 2)-crown-*x* (*x* = 6, 8, 10) [1,2] and used these to prepare pseudorotaxanes [3,4] “self-threaded” poly(amide crown ethers) [5], polyesters with macrocyclic repeat units [6], polyurethanes with macrocyclic repeat units [7], a cylindrical bis(crown ether) [8], self-assembled supramolecular polymers [9], and cryptands [10]. To complete this series of *meta*-cyclophanes, we sought the previously unknown bis(5-carboxy-1,3-phenylene)-14-crown-4 (BCMP14C4, **3**), whose cavity is too small to be threaded according to the early work of Schill et al. [11] and Harrison [12].

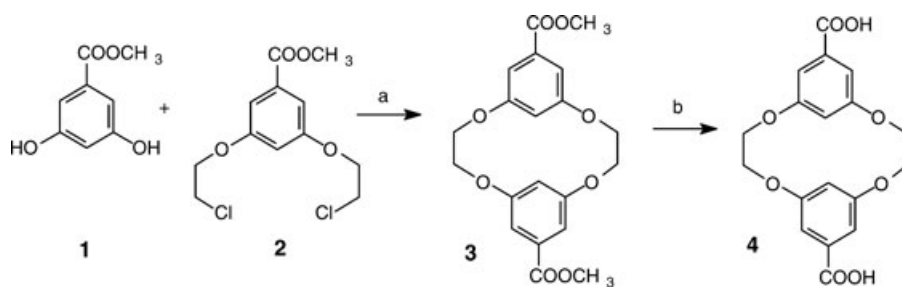
## RESULTS AND DISCUSSION

### Synthesis

BCMP14C4 (**3**) was synthesized by cyclization of methyl 3,5-dihydroxybenzoate (**1**) and methyl 3,5-bis(chloroethoxy)benzoate (**2**) under high-dilution conditions (Scheme 1) [1,13]. The yield of **3** (19%) was lower than that (27%) for dibenzo-14-crown-4 [14] and those of the larger ring bis(*m*-phenylene) crown analogs under the same cyclization conditions (Table 1). This can be explained by the rigidity of the *m*-phenylene linkages, the small ring size of **3**, the lack of templation, and the propensity for

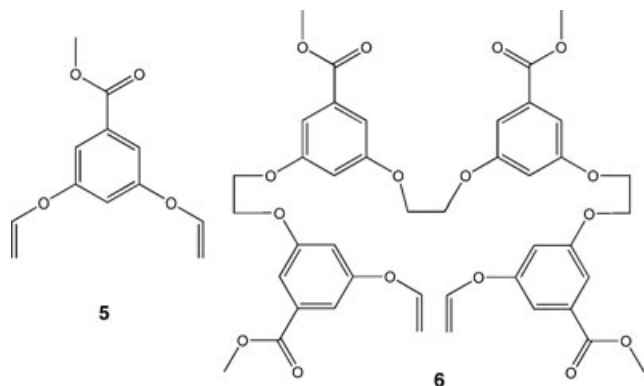
**TABLE 1** Comparison of Bis(5-carbomethoxy-1,3-phenylene) Crown Ethers


Crown Ether	Cyclization Yield (%)	Mp (°C)	$\delta$ of H <sub>1</sub> <sup>a</sup> (ppm)	Cavity size <sup>b</sup> (Å)
BCMP32C10, <i>n</i> = 4 [1d]	43	107	6.71	4.9 × 7.8 [2]
BCMP26C8, <i>n</i> = 3 [1c]	46	132	6.68	2.6 × 7.0 [2]
BCMP20C6, <i>n</i> = 2 [1c]	58	186	6.67	—
BCMP14C4, <i>n</i> = 1	19	252	5.81	2.1 × 3.6

<sup>a</sup>In CDCl<sub>3</sub>.<sup>b</sup>From crystal structure taking van der Waals radii into account.**SCHEME 1** Preparation of **3** and **4**; reagents and conditions: (a) DMF, K<sub>2</sub>CO<sub>3</sub>, *n*-Bu<sub>4</sub>NI, 10 days at 110°C; (b) THF, LiOH, water, reflux, 4 days.

dehydrochlorination, leading to byproducts **5** and **6** (Scheme 2), identified by H NMR and mass spectrometry.

Dicarboxy crown ether **4** was prepared (91%) by hydrolysis of **3**. The higher (by 66°C) melting point of **3** relative to its larger homologs (Table 1) is viewed as being reflective of its greater rigidity. Likewise, the melting point of **4** (390°C) is substantially higher than those of its homologs, the 32-, 26- and 20-membered diacids: 171°C, 260°C, and 310°C, respectively.

**SCHEME 2** Byproducts of the synthesis of **3**.

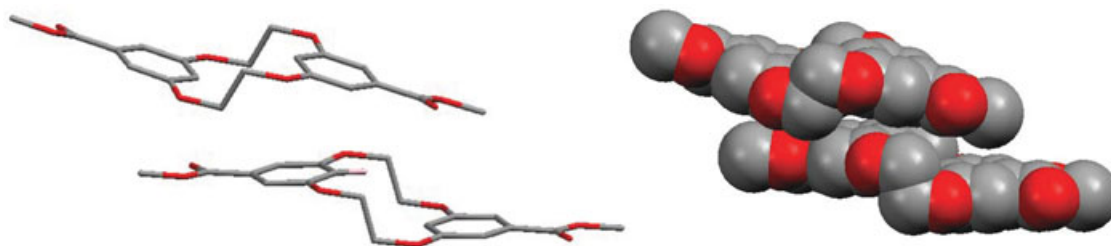
### Crystal Structures

In the crystal **3** exists in a “stepped” conformation (Fig. 1) similar to that observed in the 26- and 32-membered analogs [2], dibenzo-14-crown-4 [14], the parent bis(*m*-phenylene)-14-crown-4 [15] and most cyclophanes [16]. The two aromatic rings are antiparallel to each other, whereas the two aromatic protons (H<sub>1</sub>) included in the cavity nest with each other, and the ethylene units are both in the *trans* conformation, as was observed in the unsubstituted analog [15]. The cavity size of **3** is 2.1 × 3.6 Å, which is too small to be threaded by another organic molecule.

The crystal structure of diacid **4** is shown in Fig. 2. Like **3**, in the solid state, **4** takes a conformation with an antiparallel arrangement of the two aromatic rings. The carboxy groups in **4** are involved in hydrogen bonding with DMF (crystallization solvent).

### Solution Phase Conformational Analysis of **3** by NMR

At ambient temperature, the NMR signal for aromatic proton H<sub>1</sub> ( $\delta$  5.81 ppm) of **3** appears significantly (>0.8 ppm) upfield compared to the



**FIGURE 1** Structure of bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (**3**) in the crystal: (a) stick structure, (b) full van der Waals space-filling structure. The aromatic rings of **3**  $\pi$ - $\pi$  stack in the solid state; the distance between the centroids of the two stacked aromatic rings is 4.00 Å and the angle between the planes of the aromatic rings is 2.6°. The O—C—C—O dihedral angles are 170.6° and 171.3°.

analogous 20-, 26-, and 32-membered crown ethers, (Table 1) [1]. This indicates that the two aromatic rings of **3** are very close to each other, so that H<sub>1</sub> is shielded by the opposite aromatic ring.

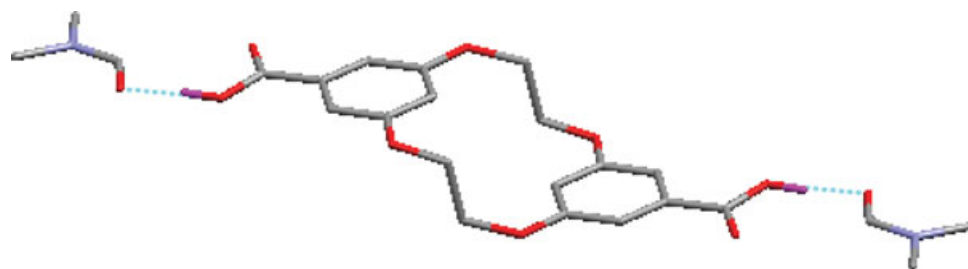
Variable temperature <sup>1</sup>H NMR spectra of **3** in CD<sub>2</sub>Cl<sub>2</sub> are compiled in Fig. 3. The aromatic H<sub>3,5</sub> doublet ( $\delta$  7.24 ppm at 23°C) gets broader as the temperature is decreased, starts to decoalesce at -88°C, and then splits into two peaks ( $\delta$  7.20 and 7.12 ppm,  $\Delta\delta = 0.08$  ppm) with equal intensity. This indicates that either two conformers with the same energy or one conformer with unsymmetric H<sub>3</sub> and H<sub>5</sub> protons exist (s) in the low-temperature solution. The TOCSY spectrum (Fig. 4) reveals that the protons of the two H<sub>3</sub> and H<sub>5</sub> peaks are coupled to each other, demonstrating that they result from a single species, i.e., one conformer.

Likewise, the single peak ( $\delta$  4.38 ppm at 23°C) attributed to ethylene protons H<sub>c</sub> decoalesces into four nonequivalent ethylene signals ( $\delta$  4.63, 4.42, 4.31, 3.96 ppm) at -88°C (Fig. 1). The TOCSY spectrum (Fig. 4) reveals that all four ethyleneoxy protons are coupled to each other, i.e., arise from one conformer. Furthermore, this demonstrates that the two ethyleneoxy units have the same conformation. A simulated spectrum with three relatively large couplings (12.5–14.5 Hz) and three small couplings (3.4–3.6 Hz) matches the experimental spectrum very

well (Fig. 5). An activation barrier of 9.09 ( $\pm 0.06$ ) kcal/mol was calculated for the interconversion of conformers based on the coalescence temperature of -88°C.

Our molecular mechanics (MM3) calculations indicate that the trans-trans (t-t) conformer of **3** is lowest in energy, the gauche-trans (g-t) conformer is 1.98 kcal/mol higher and the gauche-gauche (g-g) conformer is 6.61 kcal/mol higher (Fig. 6). Density functional theory (DFT) indicates that g-t and g-g isomers are 3.58 and 3.05 kcal/mol higher in energy than t-t, respectively.

To assign the structure (s) of the species in solutions of **3**, we keep in mind the fact that solvation effects are not included in our calculations; furthermore, we note that conformations of cyclophanes in solution often do not conform to those in the solid state nor theoretically predicted, as shown for other systems [17–19]. And we again note that the stepped t-t conformation observed in the crystal structure of **3** would render H<sub>3</sub> and H<sub>5</sub> equivalent and produce only two types of ethyleneoxy protons, contrary to the experimental results. Indeed the observation of three large and three small coupling constants for the ethyleneoxy protons rules out the t-t conformation completely; such a structure would lead to two large geminal couplings and two large vicinal couplings. The experimental results point,



**FIGURE 2** Structure of bis(5-carboxy-1,3-phenylene)-14-crown-4 (**4**) in the crystal. Two solvent (DMF) molecules bind to the carboxy groups by H-bonding (O—H 0.97(8), H...O 1.64(8), O...O 2.609(6) Å, O—H...O 173 (7)°).

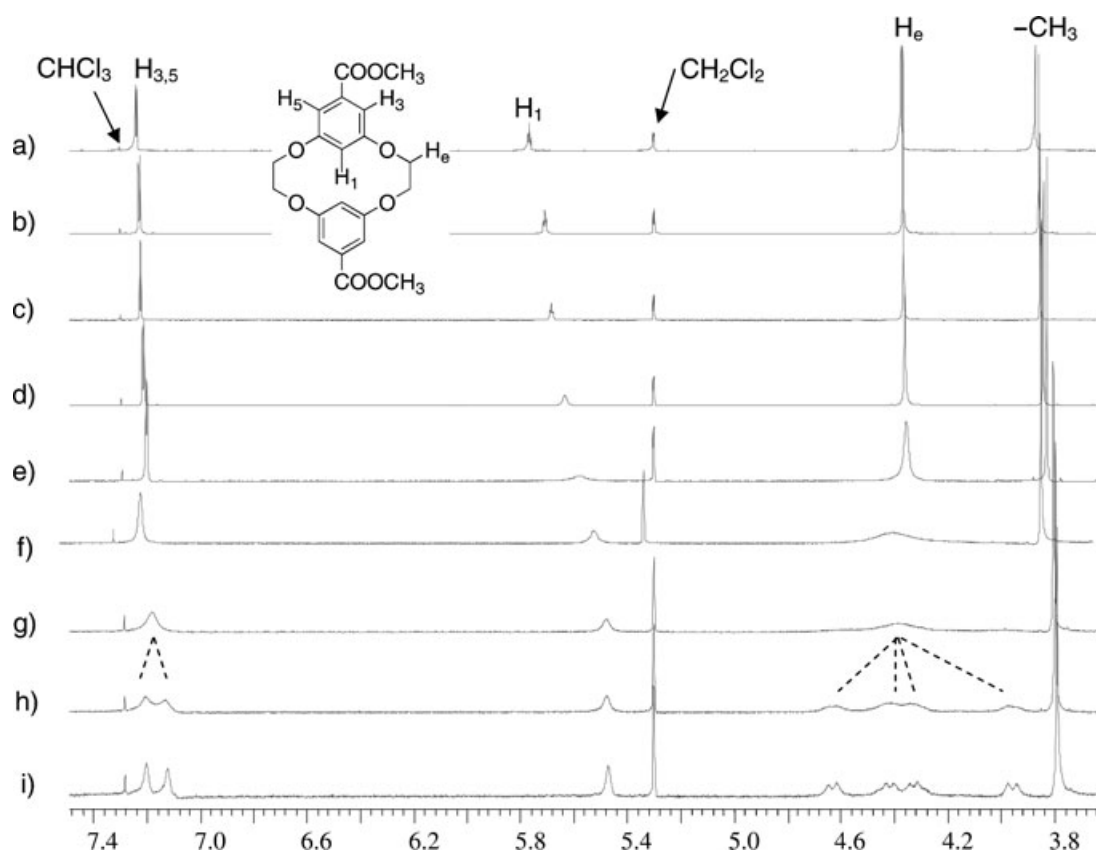


FIGURE 3 400 MHz  $^1\text{H}$  NMR spectra of bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (**3**) in  $\text{CD}_2\text{Cl}_2$  at (a) 23°C, (b) 0°C, (c) -10°C, (d) -30°C, (e) -50°C, (f) -70°C, (g) -80°C, (h) -90°C, (i) -98°C.

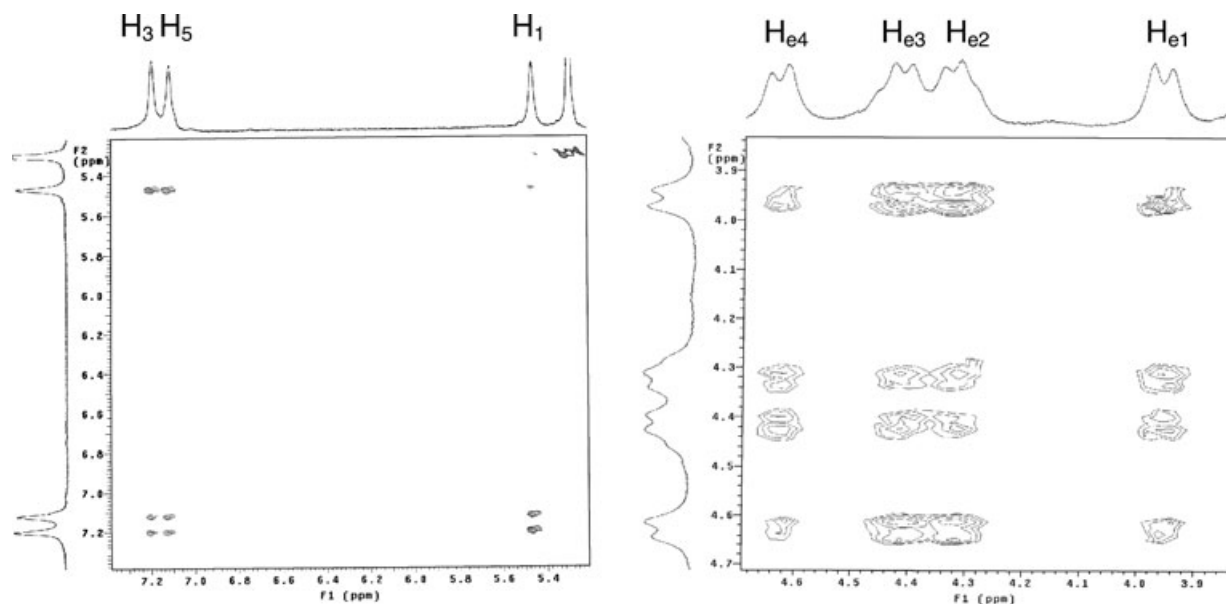
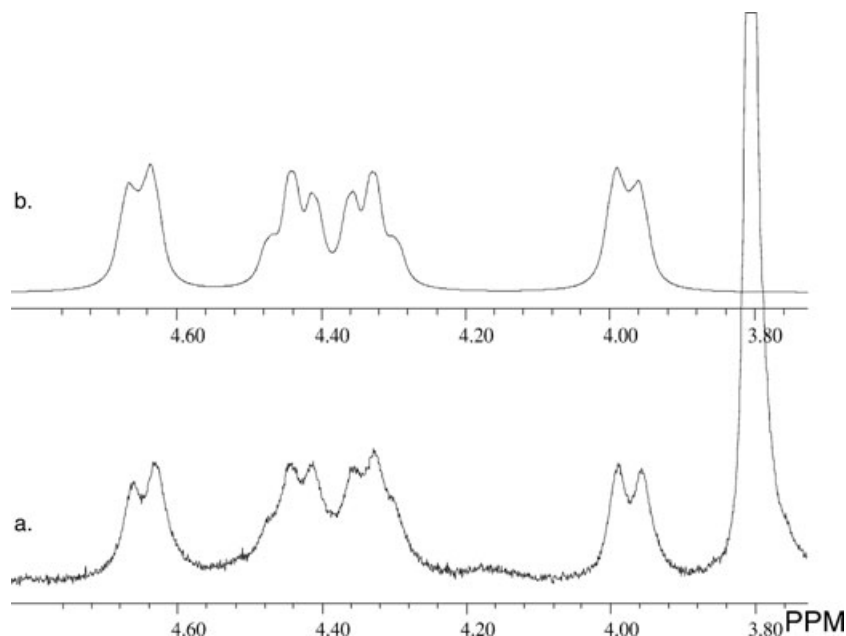


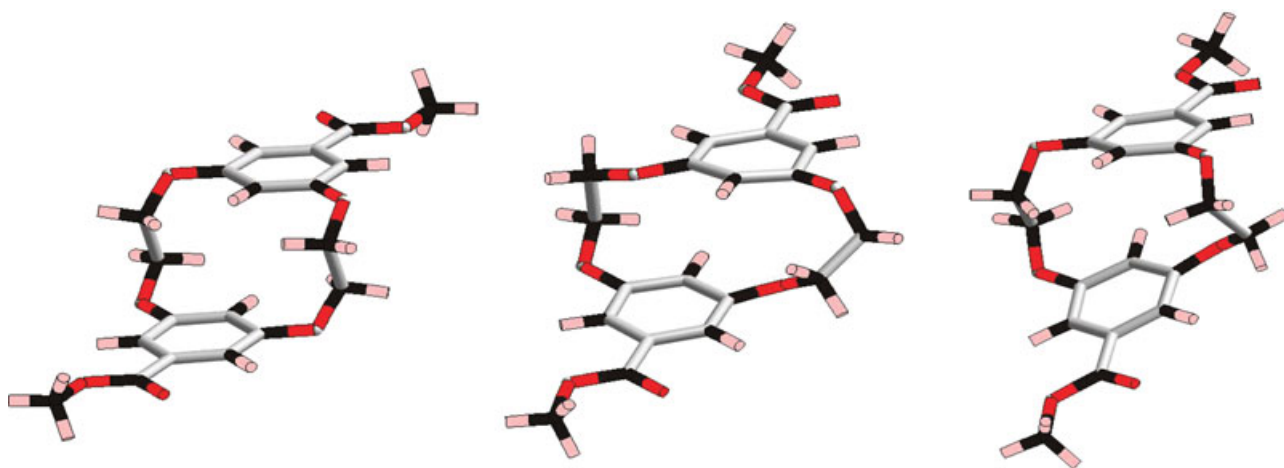
FIGURE 4 400 MHz TOCSY spectra of bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (**3**) in  $\text{CD}_2\text{Cl}_2$  at -98°C.



**FIGURE 5** (a) Experimental CH<sub>2</sub> region of the <sup>1</sup>H NMR spectrum of **3** in CD<sub>2</sub>Cl<sub>2</sub> at -98°C. (b) Simulated <sup>1</sup>H NMR spectrum of the CH<sub>2</sub> region of the gauche-gauche conformer of **3**. Simulation parameters: δ<sub>e1</sub> = 3.957, δ<sub>e2</sub> = 4.313, δ<sub>e3</sub> = 4.425, δ<sub>e4</sub> = 4.629 ppm; J<sub>e1-e2</sub> = 3.4, J<sub>e1-e3</sub> = 14.5, J<sub>e1-e4</sub> = 3.6, J<sub>e2-e3</sub> = 12.5, J<sub>e2-e4</sub> = 14.1, J<sub>e3-e4</sub> = 3.6 Hz.

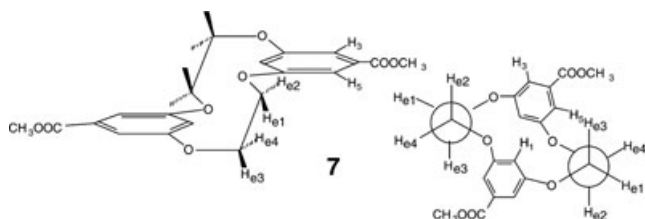
therefore, to a gauche conformation in both ethyleneoxy units. This can be understood in the following way. The H<sub>1</sub>/H<sub>1</sub> interaction can be minimized by rotations about the O-CH<sub>2</sub> and CH<sub>2</sub>-CH<sub>2</sub> bonds, yielding the g-g isomer with noncoplanar aromatic rings, while maintaining their parallel arrangement with an offset with respect to the long axes; this preserves the equivalence of the H<sub>1</sub> protons, but produces four nonequivalent H<sub>e</sub> protons, designated H<sub>e1</sub>-H<sub>e4</sub> in **7**. The strictly antiparallel arrangement of the ester dipoles main-

tains a low-overall dipole moment. Note that on each aromatic ring one O-CH<sub>2</sub> bond is directed toward H<sub>1</sub> and the other toward H<sub>5</sub>, thus rendering H<sub>3</sub> and H<sub>5</sub> nonequivalent. The approximate angles of the vicinal ethyleneoxy protons are 60°, 60°, and 180°, as shown in structure **7**, consistent with the observed coupling constants. On the basis of their NMR conformational studies, Newkome et al. reported that bis(2,6-pyridyl-14-crown-4) exists in solution as the conformer in which the ethyleneoxy units are both trans [17], but unlike most



**FIGURE 6** Minimized structures (MM3) of three conformers of bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (**3**): trans-trans (left), gauche-trans (center), and gauche-gauche (right).

cyclophanes [16] assumes a planar zig-zag state, rather than a stepped structure, and that the two equivalent structures interconvert with an activation barrier of 13.5 ( $\pm 0.3$ ) kcal/mol. Fukazawa et al. concluded that bis(*m*-phenylene)-14-crown-4 exists in CD<sub>2</sub>Cl<sub>2</sub> solution as a nearly equal mixture of *t-t* and *t-g* conformers [19].



The interconversion of the mirror image forms of **7** presumably occurs via the planar *t-t* conformation, which places the H<sub>1</sub> protons in a deshielding environment relative to the out-of-plane *g-g* conformation; this is why the signal for H<sub>1</sub> shifts downfield as the interconversion rate increases at higher temperatures.

## CONCLUSIONS

We report the synthesis and characterization of a small crown ether diester **3** and its diacid analog **4**. CPK models and the crystal structures of **3** and **4** show that the cavity is too small to be threaded; **3** exists as a stepped conformation in the crystal. Conformational analysis reveals that in solution **3** exists as a noncoplanar *g-g* conformer (**7**), which interconverts with its mirror image with an activation energy of 9.09 kcal/mol.

## EXPERIMENTAL

### Bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (**3**)

To a vigorously stirred suspension of K<sub>2</sub>CO<sub>3</sub> (31.0 g, 224 mmol) and tetrabutylammonium iodide (0.80 g, 2.2 mmol) in DMF (2.00 L) at 110°C, a solution of methyl 3,5-dihydroxybenzoate [**1**] (**1**; 3.671 g, 21.8 mmol) and methyl 3,5-di( $\beta$ -chloroethoxy)benzoate [13] (**2**; 6.399 g, 21.8 mmol) in DMF (50 mL) was added via syringe pump at 0.60 mL/h. After the addition, the suspension was stirred 10 days at 110°C, cooled to room temperature and filtered through a pad of Celite 545. The brown solution was concentrated by rotoevaporation in vacuo to give a brown viscous oil, which was subjected to flash column chromatography (silica gel column, eluent: chloroform) to yield three fractions, all yielding single spot TLCs: **5**, 40 mg (1%) of yellow

liquid; **6**, 100 mg (0.6%) of white solid, mp 87.2°C–89.1°C; **3**, 1.46 g (18.6%) of white solid, mp 251.0°C–252.0°C.

**5**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.39 (d,  $J = 2.4$ , 2H), 6.85 (t,  $J = 2.4$ , 1H), 6.65 (dd,  $J = 6.1$ ,  $J = 13.7$ , 2H), 4.85 (dd,  $J = 1.7$ ,  $J = 13.7$ , 2H), 4.54 (dd,  $J = 1.7$ ,  $J = 6.1$ , 2H) ppm. HR MS (FAB) calcd. for C<sub>12</sub>H<sub>13</sub>O<sub>4</sub> (M + H)<sup>+</sup>:  $m/z$  221.0814, found:  $m/z$  221.0777 (M + H)<sup>+</sup>.

**6**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.35 (dd,  $J = 1.3$ ,  $J = 2.3$ , 2H), 7.31 (dd,  $J = 1.3$ ,  $J = 2.3$ , 2H), 7.23 (m, 4H), 6.81 (t,  $J = 2.3$ , 2H), 6.71 (t,  $J = 2.3$ , 2H), 6.65 (dd,  $J = 5.9$ ,  $J = 13.6$ , 2H), 4.83 (dd,  $J = 1.9$ ,  $J = 13.6$ , 2H), 4.51 (dd,  $J = 1.9$ ,  $J = 5.9$ , 2H), 4.36 (s, 8H), 3.91 (s, 12H), 3.83 (s, 4H) ppm; MS (FAB)  $m/z$  402.1 [(M/2) + H]<sup>+</sup>.

**3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.28 (d,  $J = 2.5$ , 4H), 5.81 (t,  $J = 2.5$ , 2H), 4.40 (s, 8H), 3.92 (s, 6H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  166.53, 158.64, 132.01, 111.68, 111.02, 67.57, 52.39 ppm; MS (CI)  $m/z$  389 (M + H)<sup>+</sup>, 357 (M–OCH<sub>3</sub>)<sup>+</sup>; MS (EI)  $m/z$  388 M<sup>+</sup>, 357 (M–OCH<sub>3</sub>)<sup>+</sup>; HR MS (FAB) calcd. for C<sub>20</sub>H<sub>21</sub>O<sub>8</sub> (M + H)<sup>+</sup>:  $m/z$  389.1237; found:  $m/z$  389.1256.

### Bis(5-carboxy-1,3-phenylene)-14-crown-4 (**4**)

To **3** (0.50 g, 1.3 mmol) stirred in THF (35 mL), a solution of LiOH·H<sub>2</sub>O (0.41 g, 9.8 mmol) in 5.3 mL of water was added. The suspension was heated at reflux to give a clear light yellow solution. After 4 days, the solvents were removed by rotoevaporation. The residue was treated with water, and insoluble solid was removed by filtration. The filtrate was acidified with 2 N HCl to pH = 3. The white precipitate was collected by filtration and dried in vacuum, 0.42 g (91%), mp 390°C (dec.); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>)  $\delta$  13.11 (s, 2H), 7.13 (d,  $J = 2.6$ , 4H), 6.08 (t,  $J = 2.6$ , 2H), 4.38 (s, 8H) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  166.92, 158.45, 132.78, 110.51, 109.57, 66.27 ppm; MS (FAB)  $m/z$  359 (M – H)<sup>–</sup>; anal. calcd for C<sub>18</sub>H<sub>16</sub>O<sub>8</sub>·1/3H<sub>2</sub>O: C, 59.02; H, 4.59. Found: C, 59.31; H, 4.53.

### Crystallization of **3** and **4**

The crystals were grown via a vapor diffusion method. A small vial containing a solution of **3** in chloroform (or **4** in DMF) was placed in a large-capped bottle containing pentane (or hexane for **4**) at ambient temperature. After several days, a crystal formed in the solution.

CCDC deposition numbers for crystal structures reported in "Synthesis and Conformational Analysis of a Small *meta*-Cyclophane, Bis(5-carbomethoxy-1,3-phenylene)-14-crown-4." (1) bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (**3**):

CCDC 205224 and (2) bis(5-carboxy-1,3-phenylene)-14-crown-4 (**4**): CCDC 20552.

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*Supporting Information:* General methods, <sup>1</sup>H NMR spectra of **2**, **5**, and **6**; mass spectra of **2** and **3**; crystal data for **3** and **4**. Detailed information are available by contacting the corresponding author at hwgibson@vt.edu.

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