

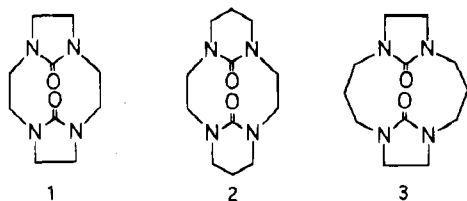
## Synthesis and Structures of Tricyclic Diureas

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Macrocyclic compounds which contain heteroatoms such as ethers, amines, or carbonyl groups are of considerable interest because of their ability to form complexes with a variety of cations. The coordinating groups in these molecules are tethered by spacers which play a role in defining their properties. In cryptands and crown ethers, for example, oxygen and/or nitrogen atoms are linked with flexible carbon chains such as dimethylene or trimethylene units, which allow the molecules to form stable complexes. Rigid spacers, such as phenylene or xylylene units that occur in spherands, hemispherands, or cryptaspherands contain constrained cavities which are capable of selective complexation.<sup>1</sup> Urea units and cyclic derivatives thereof are known to possess powerful ligating abilities which are due primarily to their highly polarized carbonyl groups.<sup>1,2</sup> Cram's group has published extensively on complexation chemistry<sup>1</sup> and some of these studies have dealt with polycyclic compounds having five- or six-membered cyclic urea units linked with rigid spacers.<sup>2-5</sup> Meth-Cohn's group has also reported the synthesis of N-bridged cyclic bisbenzimidazolones, tethered by flexible chains (penta- to decamethylene groups)<sup>6</sup> and has examined their complexing properties. These data suggest that shorter carbon chains in tethers result in stronger complexing abilities.<sup>7</sup> In this paper we wish to report the synthesis and structures of some simple macrocyclic diureas which contain flexible carbon spacers composed of five- or six-membered cyclic urea and di- or trimethylene units (1-3).



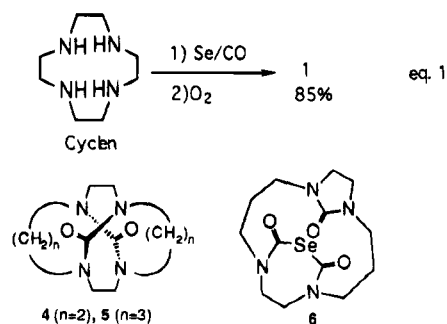
## Results and Discussion

In an earlier paper, we reported that secondary amines react with selenium and carbon monoxide under mild conditions to yield ammonium carbamoselenoates, which

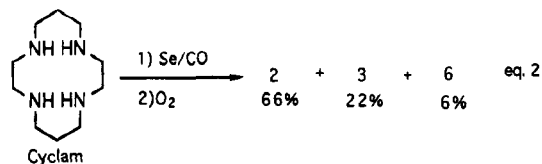
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- (1) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039.
- (2) Bryant, J. A.; Ho, S. P.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 5837 and references cited therein.
- (3) Cram, D. J.; Dicker, I. B.; Lein, G. M.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 6827.
- (4) Cram, D. J.; Dicker, I. B.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 6828.
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afford ureas upon oxidation via biscarbamoyl diselenides.<sup>8a</sup> Using this reaction, a variety of cyclic ureas were synthesized from the corresponding diamines.<sup>8b-d</sup> This methodology has been applied to the carbonylation of 1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,8,11-tetraazacyclotetradecane (cyclam). The selenium-assisted carbonylation was carried out in dilute solution in the presence of an excess of selenium and a small amount of LiHBEt<sub>3</sub>.<sup>9</sup> In a typical experiment, a suspension of cyclen, selenium, and LiHBEt<sub>3</sub> in THF was stirred at 20 °C in an atmosphere of carbon monoxide. After the carbonylation reaction, the carbon monoxide was replaced by oxygen, and the stirring was continued. The suspension was then filtered, the filtrate was evaporated and, after column chromatography, **1** was obtained in 85% yield (eq 1). Compound **4**, an isomer, expected to be formed via crossed carbonylation between 1- and 7-nitrogens and between 4- and 10-nitrogens, was not observed.



For the case of cyclam, carbonylative cyclization can take place between three different pairs of nitrogens, giving rise to **2**, **3**, and/or **5**. Although the crossed carbonylation product **5** was not formed, a mixture of **2** (66%), **3** (22%), and **6** (6%) was obtained from cyclam under these conditions (eq 2). These products were separated in pure form by preparative HPLC and were fully characterized by spectral and X-ray analyses. An attempt to prepare diureas from cyclam using 1,1'-carbonyldiimidazole as a carbonylating agent resulted in formation of a complex mixture.



ORTEP views of **1**, **2**, **3**, and **6** are shown in Figures 1-4.<sup>10</sup> The two cyclic urea units in each diurea 1-3 are disposed in an anti orientation. All diureas have crystallographic C<sub>i</sub> symmetry, but the structure of **2** is very close to C<sub>2h</sub>. For example, an interatomic distance of O1-C2\* in **1** is shorter than the corresponding O1-C3\* distance by 0.08 Å, whereas the difference of interatomic distances between O1-C2\* and O1-C4\* in **2** is only 0.01 Å.<sup>11</sup> This

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(9) When a stoichiometric amount of selenium was used or when LiHBEt<sub>3</sub> was not added, uptake of carbon monoxide was very slow.

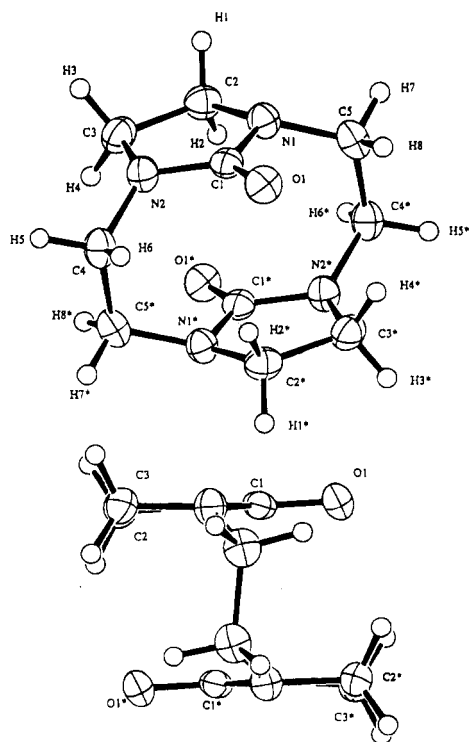


Figure 1. ORTEP views of 1.

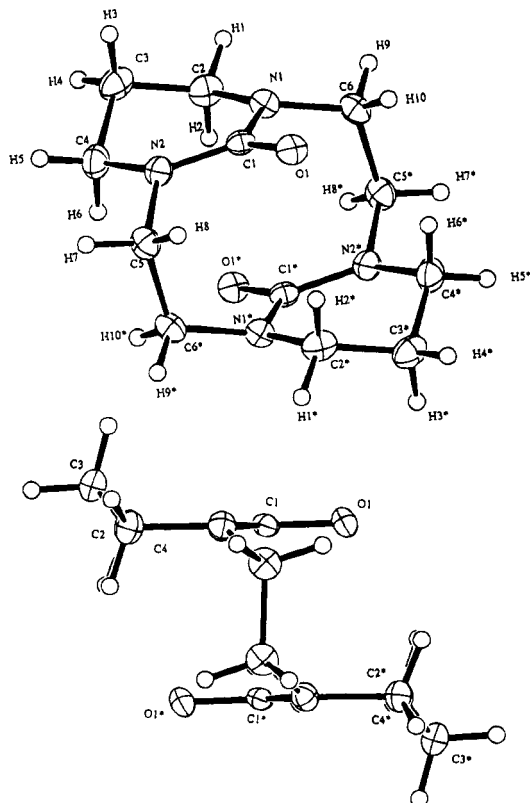


Figure 2. ORTEP views of 2.

is in accord with a  $^1\text{H}$  NMR spectrum of **1** which shows four sets of clear AB patterns.<sup>12</sup> Since the central methylene protons in the trimethylene units of **3** appear as a normal quintet, the trimethylene units flip rapidly in solution at room temperature on the NMR time-scale.

Two cyclic urea units in **1**, **2**, and **3** are located parallel to each other, and the distances between the planes, as defined by C1-N1-N2 and C1\*-N1\*-N2\*, are 2.83,

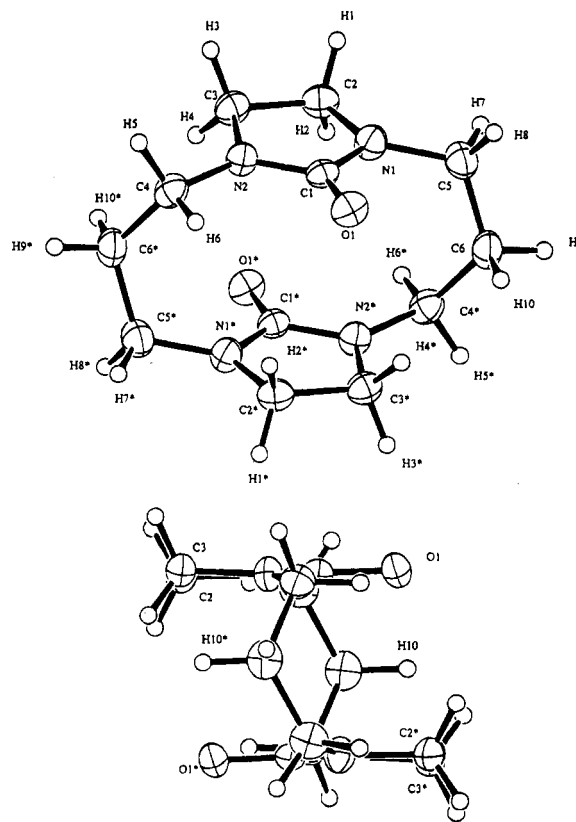


Figure 3. ORTEP views of 3.

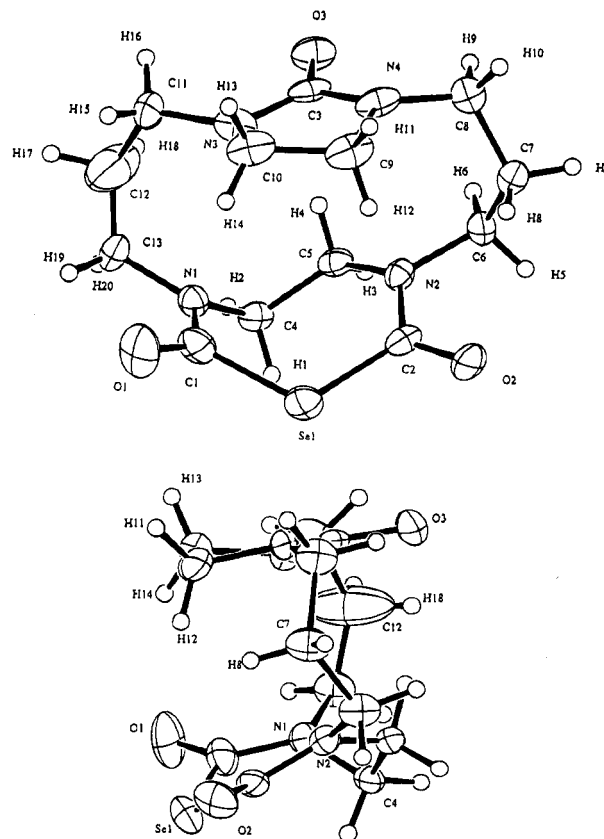
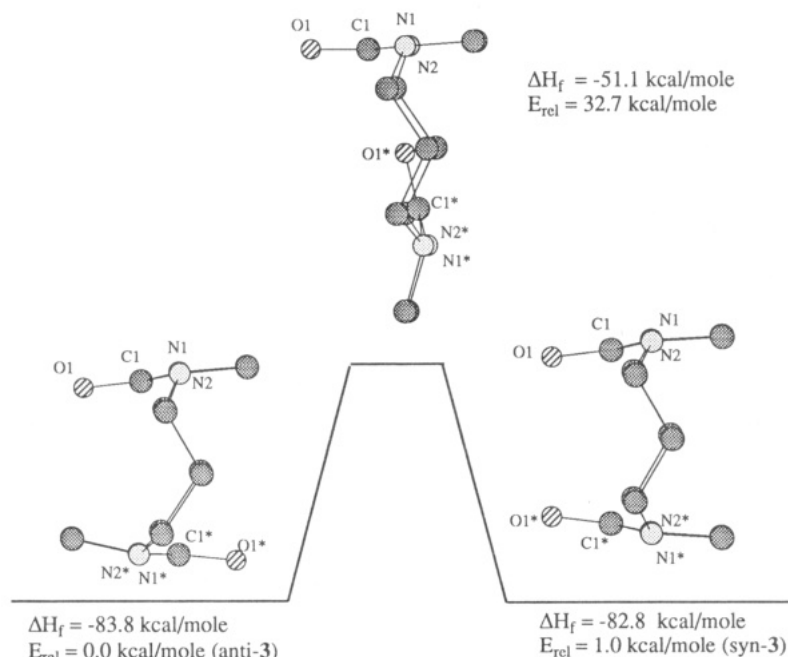


Figure 4. ORTEP views of 6.

2.77, and 2.94 Å, respectively. The distance between the planes of **3** tethered by trimethylene units is the largest, but it does not differ significantly from **1** and **2** in which the planes are tethered by only two methylene carbon



**Figure 5.** An energy diagram for the conversion of *anti*-**3** to *syn*-**3** calculated at PM3 level.  $E_{rel}$  refers to the relative energy based on *anti*-**3**. Hydrogen atoms were omitted for clarity.

atoms. The nitrogen atoms of **3** are nearly planar, but those of **1** and **2** are appreciably distorted.<sup>13</sup>

An analogous diurea compound, a trimethylene linked five-membered diurea has also been synthesized from cyclam by reaction with (dimethoxymethyl)dimethylamine followed by oxidation.<sup>14</sup> Although detailed analytical data for this compound were not reported, it appears to be the *syn* isomer of **3**, since it has a different melting point (c.a. 205 °C, dec) from that of the *anti* form obtained in this study (278–280 °C, dec). It is also noteworthy that it forms chelation complexes with rhodium and zinc.<sup>14</sup>

By using PM3 calculations, the relative energy of *anti* and *syn* forms of **3** and the activation energy for isomerization between these two isomers were estimated. Optimized structures of the *anti* form and transition state have  $C_s$  symmetry and the *syn* form has  $C_{2v}$  symmetry instead of  $C_i$ .<sup>15</sup> The energy diagram is shown in Figure 5. The *anti* and *syn* forms are energetically similar and

differ by only 1.0 kcal/mol in favor of *anti*-**3**. The isomerization barrier, however, was estimated to be 32.7 kcal/mol. When similar calculations were performed including a lithium cation, some interesting results were obtained (Figure 6).<sup>15</sup> *syn*-**3** chelates lithium to two O-atoms but *anti*-**3** coordinates lithium to only one. The former is more stable than the latter by 19 kcal/mol. Furthermore the isomerization barrier from *anti* to *syn* is reduced to 23.6 kcal/mol. It is presently not clear that *anti*-**3** is capable of isomerization to the *syn* isomer with or without metal cations but this cannot be ruled out, since *anti*-oriented diureas tethered by longer flexible spacers, such as  $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ , are known to isomerize to the *syn* form on complexation.<sup>16</sup> PM3 calculations also revealed that **3** is more stable than **2** by 4.7 kcal/mol suggesting that the preferred formation of **2** over **3** from cyclam is kinetically controlled.

Byproduct **6** includes a five-membered cyclic urea and a seven-membered biscarbamoyl selenide moiety disposed in an *anti* orientation (Figure 4). It has no molecular symmetry owing to the distorted seven-membered ring. Figure 4 shows that C12 has large thermal vibration in the crystal state. Although biscarbamoyl selenides are known to yield the corresponding ureas upon heating (with elimination of selenium and carbon monoxide),<sup>17</sup> **6** does not appear to be a precursor of **3** because **3** is not formed from **6** at the conditions employed in carbonylation experiments.<sup>18</sup> Formation of **6** can be explained if selenocarboxylation took place at three of four nitrogen

(10) Crystal data for **1** ( $\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}_2$ ): FW = 224.36,  $P2_1/c$ ,  $a = 6.5381$  (5) Å,  $b = 11.7060$  (6) Å,  $c = 7.2125$  (5) Å,  $\beta = 113.234$  (4)°,  $V = 507.24$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc} = 1.468$  g/cc,  $R = 0.031$ ,  $R_w = 0.032$ ; for **2**: ( $\text{C}_{12}\text{H}_{20}\text{N}_4\text{O}_2$ ), FW = 252.32,  $P2_1/c$ ,  $a = 6.7592$  (9) Å,  $b = 7.837$  (1) Å,  $c = 11.385$  (1) Å,  $\beta = 97.61$  (1)°,  $V = 597.8$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc} = 1.402$  g/cc,  $R = 0.043$ ,  $R_w = 0.045$ ; for **3** ( $\text{C}_{12}\text{H}_{20}\text{N}_4\text{O}_2$ ): FW = 252.32,  $P2_1/c$ ,  $a = 6.642$  (1) Å,  $b = 10.940$  (1) Å,  $c = 8.763$  (1) Å,  $\beta = 108.11$  (1)°,  $V = 605.2$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc} = 1.384$  g/cc,  $R = 0.041$ ,  $R_w = 0.050$ . For **6** ( $\text{C}_{13}\text{H}_{20}\text{N}_4\text{O}_3\text{Se}$ ): FW = 359.29,  $P2_1/n$ ,  $a = 9.253$  (3) Å,  $b = 9.093$  (2) Å,  $c = 18.170$  (1) Å,  $\beta = 96.20$  (1)°,  $V = 1519.8$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_{calc} = 1.570$  g/cc,  $R = 0.072$ ,  $R_w = 0.069$ . Total numbers of observed reflections for **1**, **2**, **3**, and **6** are 691, 1163, 862, and 2213, respectively. The authors have deposited the atomic coordinates for all structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(11) In case of **3**, an interatomic distance of O1–C2\* is longer than that of corresponding O1–C3\* by 0.14 Å.

(12) <sup>13</sup>C NMR of **1**, **2**, **3**, and **6** afforded equilibrated spectra showing only 3, 4, 4, and 7 peaks, respectively.

(13) Dihedral angles of C1–C2–N1–C5 and C1–N2–C3–C4 in **3** are 170.4° and 178.3°, respectively, although those of C1–C2–N1–C5 and C1–N2–C3–C4 are 146.8° and 150.4° in **1**, and those of C1–C2–N1–C6 and C1–N2–C4–C5 in **2** are 153.9° and 152.1°, respectively.

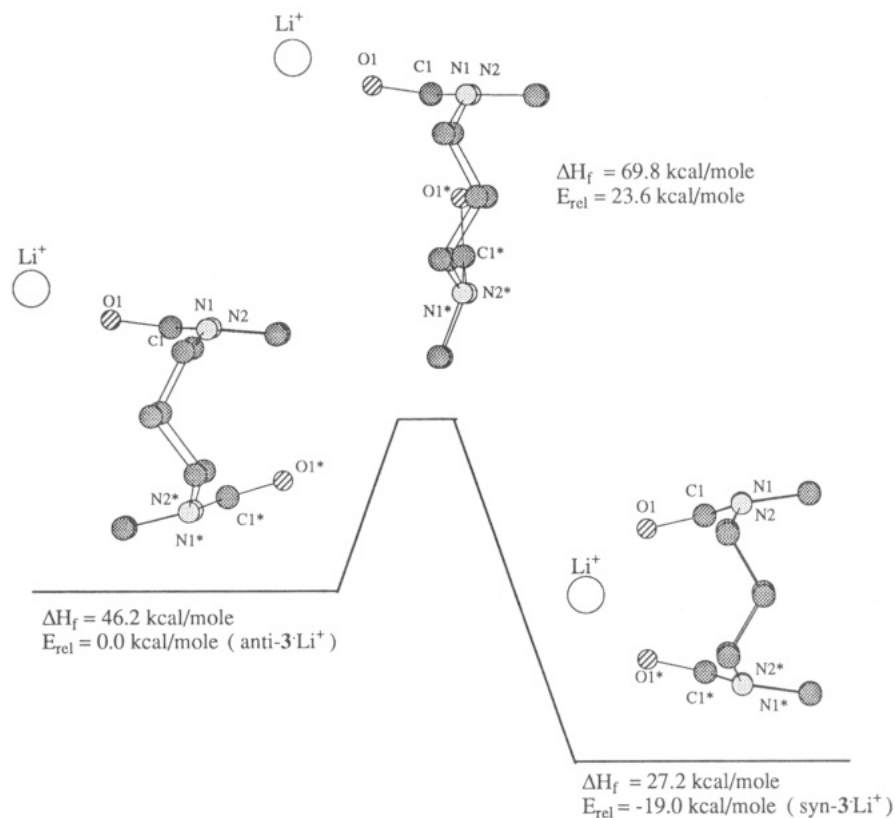
(14) Hitchcock, P. B.; Lappert, M. F.; Terreros, P.; Wainwright, K. P. *J. Chem. Soc., Chem. Commun.* **1980**, 1180.

(15) Structure optimization of an *anti* form of **3** with  $C_i$  symmetry led to a local minima which is similar to the crystal structure shown in Figure 3. But its energy is 1.1 kcal/mol higher than that of the  $C_s$  structure. All other structures shown in Figures 5 and 6 also have  $C_s$  symmetry except *syn*-**3** which has  $C_{2v}$ , and it was confirmed that these have a lower energy than alternative conformations arising from flipping of the trimethylene spacers in **3**.

(16) Rosser, M.; Parker, D.; Ferguson, G.; Gallagher, J. F.; Howard, J. A. K.; Yufit, D. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1267.

(17) Kondo, K.; Sonoda, N.; Yoshida, K.; Koishi, M.; Tsutsumi, S. *Chem. Lett.* **1972**, 401.

(18) Stirring **6** in THF for 24 h in the presence of cyclam and selenium at 25 °C did not afford **3**.



**Figure 6.** An energy diagram for the conversion of *anti*-3·Li<sup>+</sup> to *syn*-3·Li<sup>+</sup> calculated at PM3 level.  $E_{rel}$  refers to the relative energy based on *anti*-3·Li<sup>+</sup>. Hydrogen atoms were omitted for clarity.

atoms of cyclam, with one carbamoselenoate moiety reacting intramolecularly with the remaining amino group giving a cyclic urea unit, and with the other two carbamoselenoate moieties leading to a cyclic biscarbamoyl selenide unit on oxidation.

### Conclusion

New simple tricyclic diureas **1–3** and a biscarbamoyl selenide **6** have been synthesized from cyclen and cyclam by the selenium-mediated carbonylation with carbon monoxide. X-ray crystal analysis of these compounds revealed (i) diureas **1–3** have  $C_i$  symmetry with carbonyl groups disposed in an anti orientation relative to one another, (ii) distances between urea units in **1–3** are not significantly different, but the nitrogens in **1** and **2** are largely distorted from planarity although those in **3** are nearly planar, (iii) **6** has no molecular symmetry and the C12 atom has considerable thermal vibration in its crystal state. PM3 calculations showed **3** is more stable than **2** by 4.6 kcal/mol, suggesting that the preferred formation of **2** over **3** is kinetically controlled. PM3 calculations also indicate that *anti*-**3** is slightly more stable than *syn*-**3** (by 1.0 kcal/mol) and that the addition of a lithium cation not only stabilizes *syn*-3·Li<sup>+</sup> in comparison to *anti*-3·Li<sup>+</sup> owing to chelation, but it also causes a substantial decrease of the isomerization barrier between the anti and syn forms.

### Experimental Section

**General.** Mass spectroscopy was performed at Analysis Center of Faculty of Engineering of Osaka University. THF was distilled from Na-benzophenone, and t-BuOH from CaH<sub>2</sub>. Metallic selenium was ground with a mortar and pestle. The starting cyclic tetraamines were purchased from commercial sources.

Crystallographical measurements were made on a RIGAKU AFC-5R diffractometer with monochromated Mo K $\alpha$  radiation for **2** and **6** and zirconium-filtered Cu K $\alpha$  radiation for **1** and **3**, respectively. All structures were solved<sup>10</sup> using the TEXSAN crystallographic software package.<sup>19</sup>

Theoretical calculations were done at PM3 level of theory by using Spartan Ver. 2.1 or Ver. 3.1.2 GL packages.<sup>20</sup>

**1,4,7,10-Tetraazatricyclo[8.2.1.1<sup>4,7</sup>]tetradecane-13,14-dione (1).** 1,4,7,10-Tetraazacyclododecane (53 mg, 0.31 mmol), powdered selenium (98 mg, 1.2 mmol), and THF (20 mL) were placed in a 200 mL round bottom flask. The flask was flushed several times with CO, and LiHBET<sub>3</sub> (1 M in THF, 0.02 mmol) was added.<sup>9</sup> The suspension was stirred at 20 °C under CO at 1 atm for 12 h. Uptake of CO (14 mL) was observed and the suspension became pale grey in color. The flask was then evacuated, and oxygen was introduced. The mixture was stirred under an O<sub>2</sub> atmosphere for 18 h at 20 °C. The reaction mixture was filtered, the selenium was washed with MeOH (recovered in 92% yield), and the combined washings and the filtrate were evaporated to give a pale yellow solid (63 mg). This material was purified by elution from a silica gel column (2 cm × 1 cm) with 30 mL of CHCl<sub>3</sub> and afforded 59 mg of pure **1** (85%) as a white powder. Colorless transparent crystals suitable for X-ray analysis were obtained from a saturated solution of **1** in CHCl<sub>3</sub> (1 mL) by the addition of THF (10 mL) as a precipitant, followed by standing for 3–4 weeks at room temperature: mp 215–220 °C dec; <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  2.67 (d,  $J$  = 12.0 Hz, 2H), 2.74 (d,  $J$  = 12.0 Hz, 2H), 3.27 (d,  $J$  = 5.8 Hz, 2H), 3.29 (d,  $J$  = 5.8 Hz, 2H), 3.86 (d,  $J$  = 5.4 Hz, 2H), 3.88 (d,  $J$  = 5.4 Hz, 2H), 4.19 (d,  $J$  = 12.2 Hz, 2H), 4.26 (d,  $J$  = 12.2 Hz, 2H); <sup>13</sup>C-NMR (68 MHz, CDCl<sub>3</sub>)  $\delta$  41.3, 41.7, 165.2; IR (KBr, cm<sup>-1</sup>) 1698, 1496, 1481, 1441, 1429; EI-mass (70 eV),  $m/z$  (relative intensity) 224 (M<sup>+</sup>, 71), 154 (56), 138 (89), 126 (68), 113 (67), 112 (62); HRMS calcd for C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> 224.1273, found 224.1264. Anal. Calcd for C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>: C, 53.57; H, 7.19; N, 24.99. Found: C, 53.02; H, 7.08; N, 24.36.

(19) TEXSAN Crystal Structure Analysis Package, Molecular Structure Corp. (1985 & 1992).

(20) Spartan Ver. 2.1 and Ver. 3.1.2 GL, Wavefunction Inc, Irvine CA.

**Synthetic Procedure for 2, 3, and 6.** 1,4,8,11-Tetraazacyclotetradecane (200 mg, 1 mmol), powdered selenium (395 mg, 5 mmol), THF (80 mL), and *t*-BuOH (27 mL) were placed in a 200 mL round bottom flask, which was then flushed several times with CO. The mixture was stirred for 30 h at 25 °C under 1 atm of CO after addition of LiHBEt<sub>3</sub> (1 M in THF, 0.05 mmol). The flask was then evacuated and oxygen was introduced. The mixture was stirred under an O<sub>2</sub> atmosphere for 25 h at 25 °C. After removal of selenium by filtration (recovered in 91% yield), the filtrate was dried over MgSO<sub>4</sub> and concentrated to give a pale yellow solid (276 mg). The crude products were chromatographed on a silica gel column (5 cm × 1.5 cm) using 50 mL of CHCl<sub>3</sub> and were purified by HPLC to give **2** (166 mg, 66%, white powder), **3** (55 mg, 22%, white powder), and **6** (21 mg, 6%, pale yellow powder). Crystals suitable for X-ray analysis were obtained by slow recrystallization as described for compound 1.

**1,4,8,11-Tetraazatricyclo[9.3.1.1<sup>4,8</sup>]hexadecane-15,16-dione (2):** white powder; mp 240–244 °C dec; <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 1.90–2.11 (m, 4H), 2.39 (d, *J* = 12.0 Hz, 2H), 2.46 (d, *J* = 12.0 Hz, 2H), 2.93–2.98 (m, 4H), 3.89–3.98 (m, 4H), 4.71 (d, *J* = 10.5 Hz, 2H), 4.78 (d, *J* = 10.5 Hz, 2H); <sup>13</sup>C-NMR (68 MHz, CDCl<sub>3</sub>) δ 22.1, 45.3, 46.4, 161.1; IR (KBr cm<sup>-1</sup>) 1636, 1491, 1444; EI-mass (70 eV), *m/z* (relative intensity) 252 (M<sup>+</sup>, 100), 152 (100), 140 (35), 126 (60); HRMS calcd for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub> 252.1586, found 252.1582. Anal. Calcd for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: C, 57.12; H, 7.99; N, 22.21. Found: C, 56.72; H, 7.97; N, 22.26.

**1,4,8,12-Tetraazatricyclo[10.2.1.1<sup>5,8</sup>]hexadecane-15,16-dione (3):** white powder; mp 278–280 °C dec; <sup>1</sup>H-NMR (270 MHz,

CDCl<sub>3</sub>) δ 1.95 (quintet, *J* = 5.9 Hz, 4H), 2.80 (t, *J* = 6.1 Hz, 2H), 2.86 (t, *J* = 6.1 Hz, 2H), 3.17–3.22 (triplet like, 4H), 3.72–3.81 (m, 8H); <sup>13</sup>C-NMR (68 MHz, CDCl<sub>3</sub>) δ 21.2, 41.3, 43.0, 159.9; IR (KBr, cm<sup>-1</sup>) 1698, 1515, 1272; EI-mass (70 eV), *m/z* (relative intensity) 252 (M<sup>+</sup>, 100), 139 (20), 127 (30), 113 (15); HRMS calcd for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub> 252.1586, found 252.1574. Anal. Calcd for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: C, 57.12; H, 7.99; N, 22.21. Found: C, 56.21; H, 7.68; N, 22.04.

**1,5,8,12-Tetraza-14-selenatricyclo[10.3.2.1<sup>5,8</sup>]octadecane-13,15,18-trione (6):** colorless crystals; mp 204–208 °C dec; <sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 1.78–1.89 (m, 2H), 2.16–2.29 (m, 2H), 2.83–2.98 (m, 4H), 3.14–3.19 (m, 2H), 3.51–3.56 (m, 2H), 3.60–3.71 (m, 2H), 3.87–3.98 (m, 4H), 4.27 (dd, *J* = 8.3, 2.0 Hz, 1H), 4.32 (dd, *J* = 7.8, 1.5 Hz, 1H); <sup>13</sup>C-NMR (68 MHz, CDCl<sub>3</sub>) δ 23.4, 43.0, 44.2, 51.4, 52.1, 161.0, 163.7; IR (KBr, cm<sup>-1</sup>) 1684, 1671, 1636; CI-mass, *m/z* (<sup>80</sup>Se, relative intensity) 361 (M<sup>+</sup> + 1, 8), 332 (5), 253 (100); HRMS calcd for C<sub>13</sub>H<sub>21</sub>N<sub>4</sub>O<sub>3</sub>Se (<sup>80</sup>Se) 361.0779 (M<sup>+</sup> + 1), found 361.0788 (M<sup>+</sup> + 1). Anal. Calcd for C<sub>13</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>Se: C, 43.46; H, 5.61; N, 15.59. Found: C, 42.83; H, 5.52; N, 15.43.

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