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# Conformationally Locked Bridged Bicyclic Diselenides: Synthesis, Structure, Se···O Interaction, and Theoretical Studies

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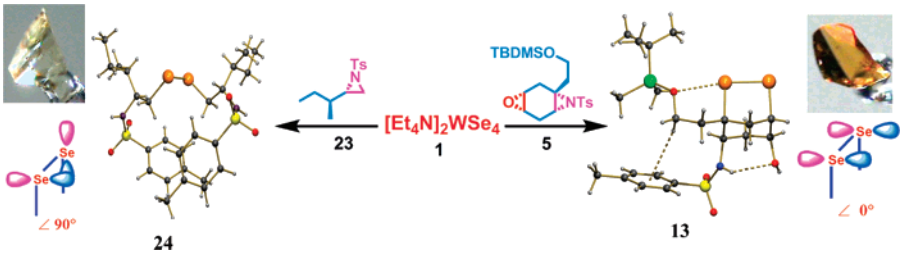


A general synthetic methodology has been developed for the synthesis of a conformationally locked, bridged diselena-bicyclo[3.2.1]octane skeleton by regio- and stereospecific tandem nucleophilic ring opening of *cis*-1,4-aziridino-epoxides with tetraethylammonium tetraselenotungstate $[Et_4N]_2WSe_4$, **1**, in a one-pot synthesis. Some correlations have been made on the physicochemical characteristics of the diselenides with a change in the dihedral angles.

## Introduction

Bridged disulfides are of great interest because of their rigid bicyclic framework, which forces the dihedral angle of the sulfur−sulfur bond close to 0°. The preferred conformation of acyclic disulfides has a dihedral angle of about 90°, which minimizes the interaction between the two pairs of 3p nonbonding electrons on the sulfur atoms. When the dihedral angle is close to 0°, the chemistry of these molecules changes dramatically. While the physicochemical properties of the conformationally locked disulfides have been studied extensively,[1] not much attention has been paid to the corresponding selenium analogues. This has mainly been due to the nonavailability of general synthetic protocols for the synthesis of the conformationally locked diselenides and the relative instability of this class of molecules. Although the synthesis of bridged disulfides was first reported by Davis et al.[2] and Harpp et al.,[3] there are not many reports in the literature for the synthesis of selenium analogues except the one by Strakovs[4] Recently from our laboratory we reported the synthesis of chiral $\beta$-sulfonamidodiselenides from chiral aziridines using tetraethylammonium tetraselenotungstate[5] $[Et_4N]_2WSe_4$, **1**, as an efficient selenium transfer reagent.[6] In this article, we report a general synthetic methodology for the synthesis of a conformationally locked, bridged diselena-bicyclo[3.2.1]octane skeleton by regio- and stereospecific tandem nucleophilic ring opening of *cis*-1,4-aziridino-epoxides with **1** in a one-pot synthesis as well as reporting some physicochemical characteristics of these molecules.

## Results and Discussion

**Reaction of *cis*-Aziridino-epoxide 2 with Tetraselenotungstate 1.** It was of interest to study the nucleophilic ring opening reaction of *cis*-1,4-bis-aziridines,[7] *cis*-1,4-bis-epoxides,[8] and *cis*-

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(1) (a) Barltrop, J. A.; Hayes, P. M.; Calvin, M. *J. Am. Chem. Soc.* **1954**, *76*, 4348−4367. (b) Beecham, A. F.; Fridrichsons, J.; Mathieson, A. M. *Tetrahedron Lett.* **1966**, *7*, 3131−3138. (c) Bergson, G.; Sjoberg, B.; Tweit, R. C.; Dodson, R. M. *Acta Chem. Scand.* **1960**, *14*, 222−223.

(2) Wilson, R. M.; Buchanan, D. N.; Davis, J. N. *Tetrahedron Lett.* **1971**, *12*, 3919−3922.

(3) (a) Folkins, P. L.; Harpp, D. N. *J. Org. Chem.* **1991**, *56*, 904−906. (b) Folkins, P. L.; Harpp, D. N. *J. Org. Chem.* **1992**, *57*, 2013−2017.

(4) Tonkikh, N.; Duddeck, H.; Petrova, M.; Neilands, O.; Strakovs, A. *Eur. J. Org. Chem.* **1999**, 1585−1588.

(5) (a) Saravanan, V.; Porhiel, E.; Chandrasekaran, S. *Tetrahedron Lett.* **2003**, *44*, 2257−2260. (b) Bhat, R. G.; Porhiel, E.; Saravanan, V.; Chandrasekaran, S. *Tetrahedron Lett.* **2003**, *44*, 5251−5253. (c) O'Neal, S.; Kollis, J. W. *J. Am. Chem. Soc.* **1998**, *110*, 1971−1973. (d) Muller, A.; Diemann, E.; Jostes, R.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934−955.

(6) Sureshkumar, D.; Gunasundari, T.; Saravanan, V.; Chandrasekaran, S. *Tetrahedron Lett.* **2007**, *48*, 623−626.

(7) There are no synthetic procedures reported in the literature for the synthesis of *cis*-1,4-bis-aziridines.

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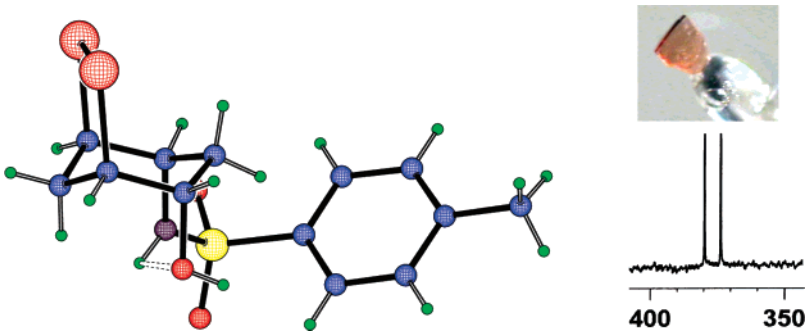



**FIGURE 1.** X-ray platon diagram with intramolecular N—H···O hydrogen bonding, crystal color, and $^{77}$Se NMR of **3**.

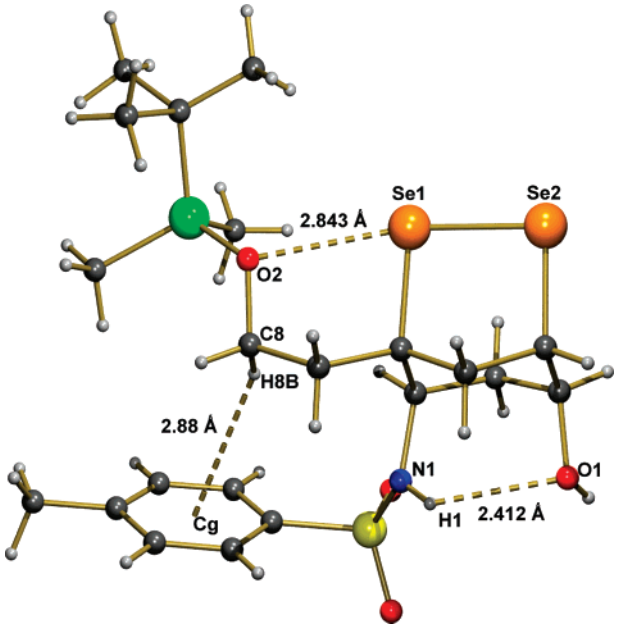
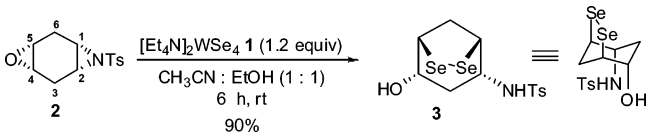



**FIGURE 2.** X-ray structure of **13** with Se···O, C—H···$\pi$ interaction, and intramolecular N—H···O hydrogen bonding.

**SCHEME 1. Regio- and Stereospecific Ring Opening of *cis*-Aziridino-epoxide 2 with 1**




1,4-aziridino-epoxides.[9] However, in the preliminary experiments, *cis*-aziridino-epoxide **2** was chosen as the substrate to study a nucleophilic ring opening reaction with tetraselenotungstate **1** as the diselenide equivalent. The choice is based on the increased reactivity of the aziridine ring, which could be exploited to modulate the reaction in a tandem fashion to form conformationally locked diselenides in a selective manner with efficiency. Treatment of **2** with **1** (1.2 equiv; $CH_3CN$/EtOH; 1:1, 28 °C, 6 h) furnished the bicyclic diselenide **3** as the only product as wine red crystals in 95% yield (Scheme 1).

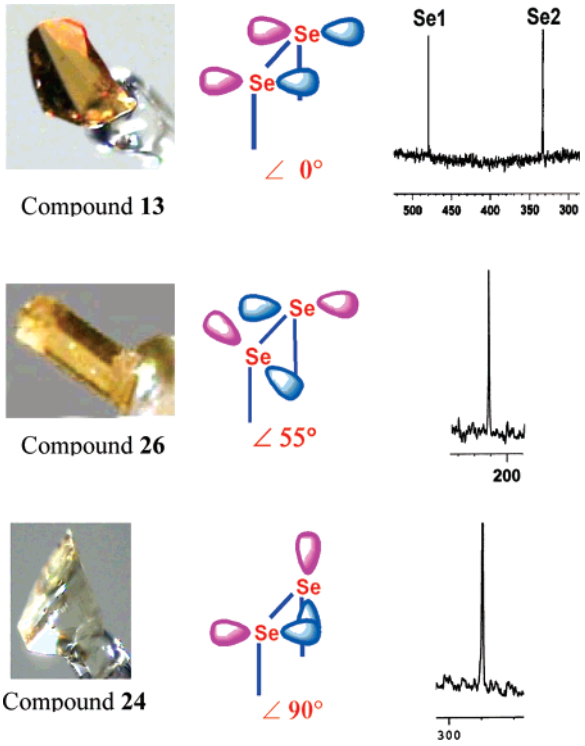



**FIGURE 3.** Color of the crystals, orbital diagrams, and $^{77}$Se NMR of **13**, **24**, and **26**.

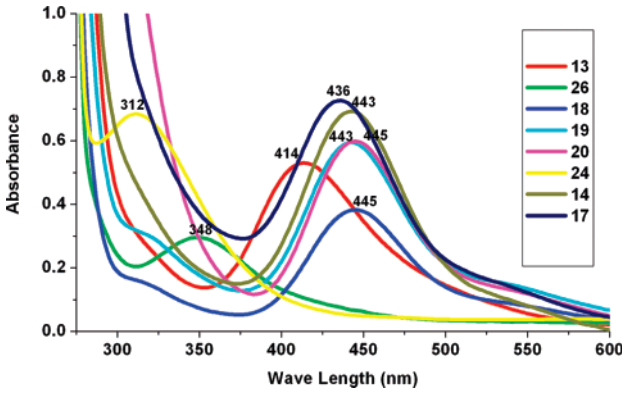
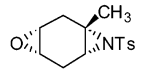
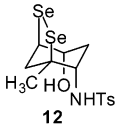
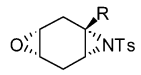
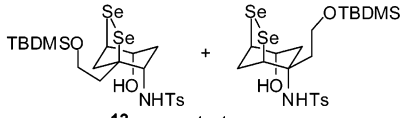
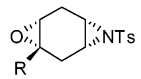
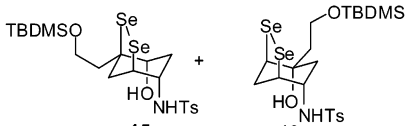
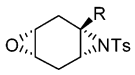
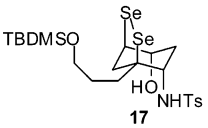
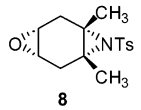
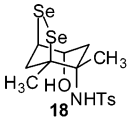
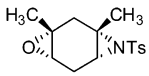
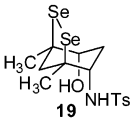
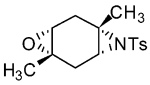
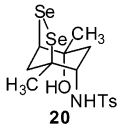
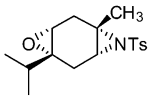
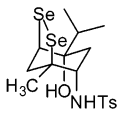



**FIGURE 4.** UV—vis spectrum of acyclic, cyclic, and representative locked diselenides.

(8) Treatment of *cis*-1,4-bis-epoxides with tetraselenotungstate **1** (1.2 equiv, $CH_3CN$/EtOH; 1:1, 28 °C) failed to give locked diselenides even under sonication conditions. This is due to a lack of reactivity of **1** towards epoxides.

(9) (a) Brien, O. P.; Pilgram, C. D. *Org. Biomol. Chem.* **2003**, *1*, 523—534. (b) Sureshkumar, D.; Maity, S.; Chandrasekaran, S. *J. Org. Chem.* **2006**, *71*, 1653—1657.

**TABLE 1. Conformationally Locked Bridged Bicyclic Diselenides**

| Entry | *cis*-Aziridinoepoxides | Bridged Diselenides | Time (h) | Yield(%) |
|---|---|---|---|---|
| 1 |  **4** |  **12** | 6 | 92 |
| 2 |  **5** |  **13** 4 : 1 **14** | 7 | 91 |
| 3 |  **6** |  **15** 1 : 1 **16** | 7 | 83 |
| 4 |  **7** |  **17** | 8 | 85 |
| 5 |  **8** |  **18** | 9 | 88 |
| 6 |  **9** |  **19** | 8 | 90 |
| 7 |  **10** |  **20** | 7 | 89 |
| 8 |  **11** |  **21** | 9 | 90 |

The structure of **3** was confirmed by $^{1}$H, $^{13}$C, $^{77}$Se, and COSY NMR and HR-MS studies, and the solid-state structure was proven by single-crystal X-ray analysis (Figure 1). This methodology was then extended to study the reactivity of a number of di, tri, and tetra substituted *cis*-aziridino-epoxides[9] **4**−**11** (Table 1).

**Study of Ring Opening of Different *cis*-Aziridino-epoxides with Tetraselenotungstate 1.** Interestingly, in the tri and tetra substituted *cis*-aziridino-epoxides **4**−**11**, aziridine ring opening always takes place by an attack of the selenium nucleophile at the more substituted carbon site,[10] whereas in the case of epoxide, the ring opening takes place by attack at the less substituted carbon as well as at the more substituted carbon center depending on the substrate (Table 1, entries 4−8). It was anticipated that by introducing a bulky substituent at C1, it would be possible to facilitate the ring opening at the less substituted site. However, in the reaction of **5** with **1**, the major product was still **13**, resulting from ring opening at the more substituted carbon. Reaction of **7** with **1** gave **17** as the exclusive product. In the reaction of **9** with **1**, the only product formed was the diselenide **19** arising out of the ring opening of aziridine and epoxide rings from the more substituted site. In the case of **10** and **11**, aziridine ring opening occurs from the more hindered site, while the epoxide ring opens from the less substituted site to form diselenides **20** and **21**, respectively. The attack of the

(10) (a) Lin, P.; Bellos, K.; Stamm, H.; Onistschenko, A. *Tetrahedron* **1992**, *48*, 2359−2372. (b) Tanner, D. *Angew. Chem., Int. Ed.* **1994**, *33*, 599−619. (c) Stamm, H. *J. Prakt. Chem.* **1999**, *341*, 319−331. (d) Davis, F. A.; Coull, S. M. *Synthesis* **2000**, 1347−1365. (e) Hu, X. E. *Tetrahedron* **2004**, *60*, 2701−2743. (f) Sureshkumar, D.; Koutha, S.; Chandrasekaran, S. *J. Am. Chem. Soc.* **2005**, *127*, 12760−12761. (g) Li, P.; Forbeck, E. M.; Evans, C. D.; Joullie, M. M. *Org. Lett.* **2006**, *8*, 5105−5107.

(11) Chao, B.; Dittmer, D. C. *Tetrahedron Lett.* **2001**, *42*, 5789−5791.

**SCHEME 2. Tentative Mechanism for Formation of 3**

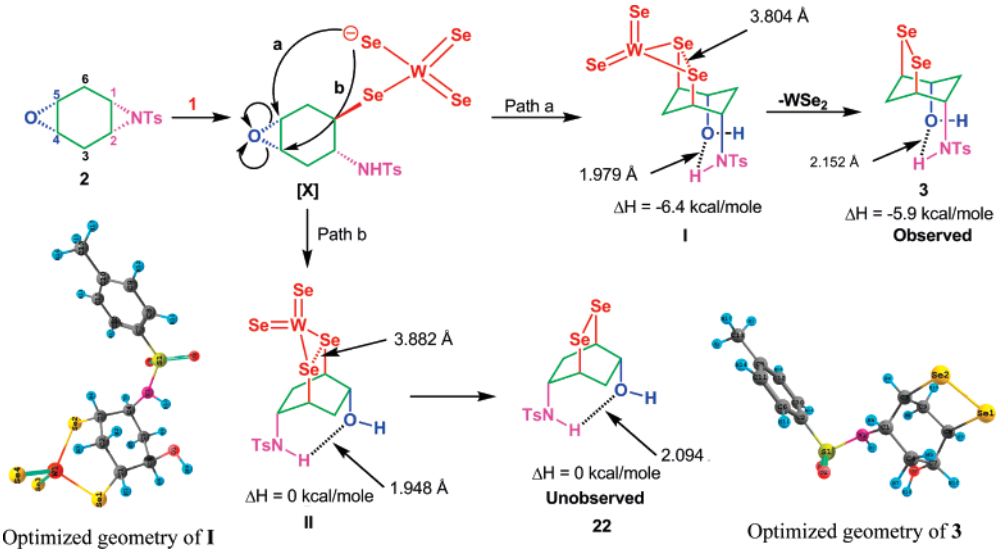


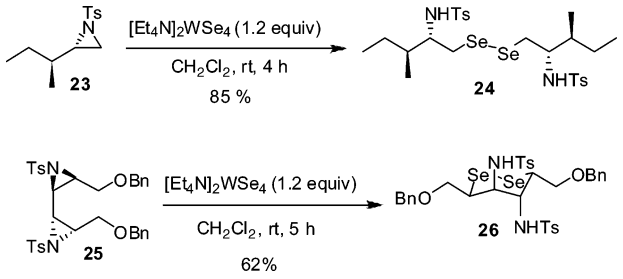

**TABLE 2. Experimental and Calculated Torsion Angle and Intramolecular N—H···O Hydrogen Bonding of Different Diselenides**

| | | torsion angle of −C−Se−Se−C− | | N—H···O intra H-bonding | | | Se−Se bond length | |
|---|---|---|---|---|---|---|---|---|
| entry | diselenides | exptl | calcd | exptl | calcd | exptl | calcd | $\lambda_{max}$ $n \rightarrow \sigma^*$ | $\epsilon$ ($M^{-1}$ $cm^{-1}$) |
| 1 | **3** | 0.3 | −0.1 | 2.366 | 2.152 | 2.372 | 2.392 | 443 | 130 |
| 2 | **12** | −4.0 | −2.6 | 2.125 | 2.099 | 2.356 | 2.386 | 443 | 143 |
| 3 | **13** | −1.9 | | 2.412 | | 2.372 | | 414 | 141 |
| 4 | **14** | 0.1 | | 2.203 | | 2.367 | | 443 | 161 |
| 5 | **17** | | | | | | | 436 | 143 |
| 6 | **18** | 1.3 | 1.6 | 1.947 | 1.963 | 2.351 | 2.382 | 445 | 177 |
| 7 | **19** | 0.9 | −1.0 | 2.130 | 2.087 | 2.354 | 2.380 | 443 | 145 |
| 8 | **20** | 3.6 | 4.5 | 2.041 | 2.058 | 2.355 | 2.382 | 445 | 195 |
| 9 | **21** | 1.7 | 5.7 | 2.261 | 2.080 | 2.364 | 2.383 | 442 | 179 |
| 10 | **24** | −96.5 | | | | 2.316 | | 312 | 506 |
| 11 | **26** | −54.9 | | | | 2.319 | | 348 | 293 |

selenium nucleophile at the more substituted carbon atom of the tosyl-aziridine is probably related to the stabilization of carbocationic character at this position when a good electron withdrawing group like NTs is present.[11] The regio- and stereochemical outcome of the reaction was confirmed by X-ray analysis of compound[12] **13** (Figure 2; see Supporting Information for other new compounds).

**Tentative Mechanism and Theoretical Investigation of Tandem Multistep Reactions with *cis*-Aziridino-epoxides Mediated by Tetraselenotungstate 1.** It is possible to visualize the nucleophilic attack of **1** at C1 of the aziridine ring to generate the intermediate [**X**]. The selenium nucleophile in **X** can then open the epoxide ring either at C5 (path a) to generate intermediate **I** or at C4 (path b) to give intermediate **II**. The intermediates (**I** or **II**) can undergo an internal redox process,[13] leading to selenium−selenium bond formation with the elimination of $WSe_2$.[13a,14] This process could lead to the formation of diselena-bicyclo[3.2.1]octane **3** or diselena-bicyclo[2.2.2]octane **22** (Scheme 2). To explain the exclusive formation of **3** over **22**, DFT calculations were carried out on proposed intermediates **I** and **II** using the B3LYP[15] method and LanL2DZ level basis set.[16] A recent comparison of density functional methods and molecular orbital methods with a variety of basis sets has shown that the B3LYP/6-31G(d) method yields reliable geometries for organoselenium compounds.[17] Furthermore, this level of theory

**SCHEME 3. Regio- and Stereospecific Ring Opening of Aziridines 23 and 25 with 1**




(12) CCDC 292058 (**3**), CCDC 610604 (**12**), CCDC 610605 (**13**), CCDC 610606 (**14**), CCDC 610607 (**16**), CCDC 610608 (**18**), CCDC 610609 (**19**), CCDC 610610 (**20**), CCDC 610611 (**21**), CCDC 610612 (**24**), and CCDC 292060 (**26**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallography Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

(13) (a) Kruhlak, N. L.; Wang, M.; Boorman, P. M.; Parvez, M. *Inorg. Chem.* **2001**, *40*, 3141−3148. (b) Boorman, P. M.; Wang, M.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1995**, 999−1000. (c) Gea, Y.; Greaney, M. A.; Coyle, C. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun.* **1992**, 160−161 and references cited therein.

(14) $WSe_2$ was identified as one of the major inorganic byproducts after reaction.

(15) (a) B3LYP is Becke's three parameter hybrid method using the LYP correlation functional. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (c) Vosoko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(16) Calculations were performed using the Gaussian 98 program. For further reference, see the Supporting Information.

(17) Pearson, J. K.; Ban, F.; Boyd, R. J. *J. Phys. Chem. A* **2005**, *109*, 10373−10379 and references cited therein.

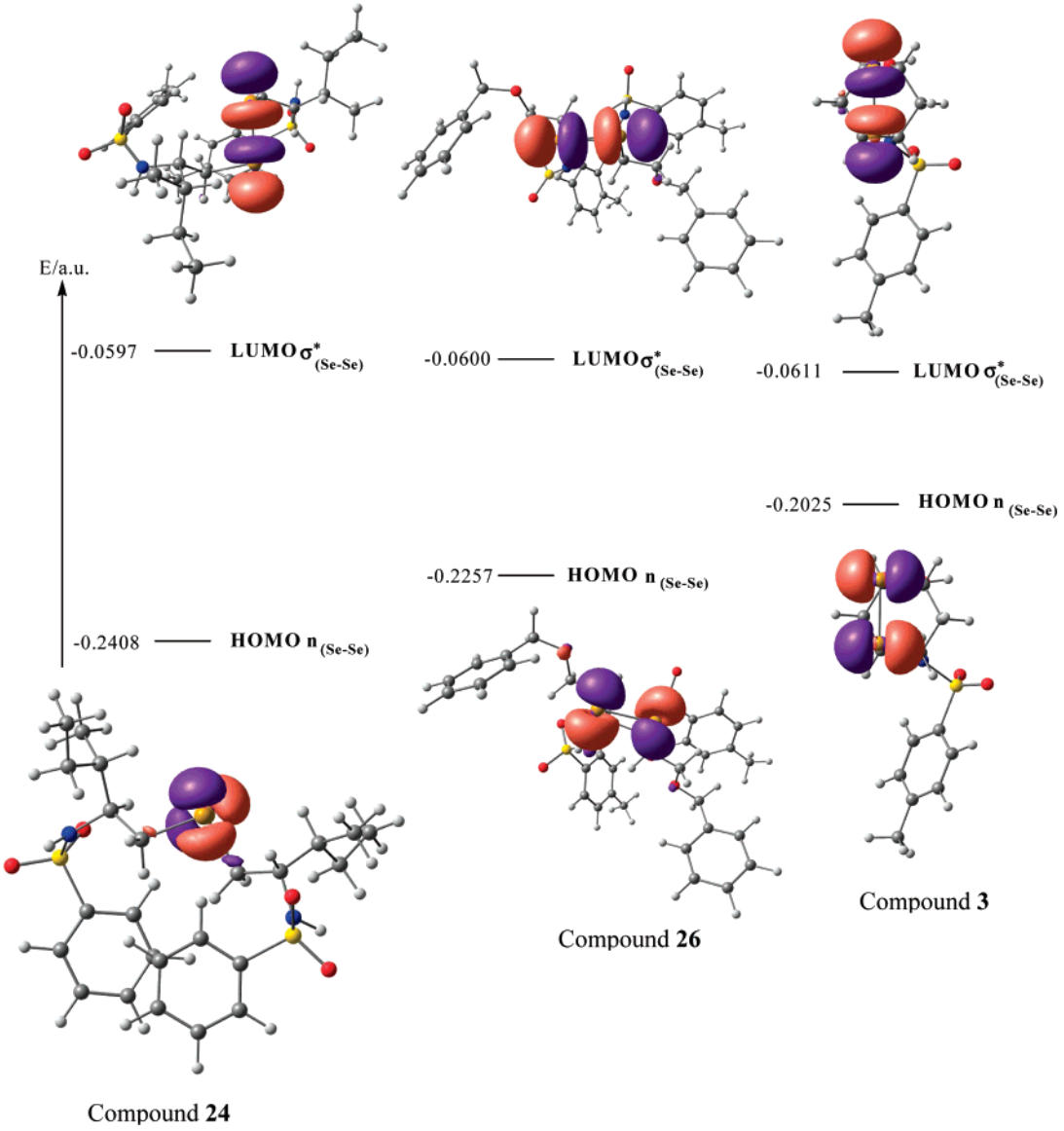



**FIGURE 5.** Kohn−Sham HOMO and LUMO orbital of **24**, **26**, and **3** at the B3LYP/6-31G(d) level.

has been used successfully to model reaction mechanisms and can be expected to yield reliable relative energies.[18] The calculations clearly suggest that the six membered intermediate **I** is 6.4 kcal/mol more favorable than the corresponding seven membered intermediate **II** (Scheme 2). The structures of diselenide **3** and **22** were optimized using the B3LYP method and 6-31G(d) level, which also clearly suggests that **3** is more stable by 5.9 kcal/mol than the corresponding diselenide **22** (Scheme 2).

Experimental and calculated values of torsion angles, intramolecular N−H···O hydrogen bonding distances, and UV−vis absorption maxima of all the diselenides are summarized in Table 2. The diselenides (**3** and **12**−**21**) with smaller dihedral angles absorb light at longer wavelengths (414−445 nm, $n \rightarrow \sigma^*$) and as a result are wine red in color (Figures 1 and 3) and have lower ionization potentials.

Interestingly, the UV−vis spectrum of **13** shows a blue shift (414 nm, Figure 4). The $^{77}$Se NMR of **13** shows a difference of 147 ppm between the two selenium signals, whereas the difference between the selenium signals in other conformationally locked diselenides is only 10−70 ppm (Figures 1 and 3), which is due to an Se···O (Se1···O2, 2.843 Å and Se2−Se1···O2, 166.4°) nonbonding interaction[19] in **13** (Figure 2).

**Synthesis of Acyclic Diselenide 24 and Cyclic Diselenide 26.** To compare the behavior of diselenides having larger dihedral angles, we synthesized the acyclic diselenide[6] **24** and cyclic diselenide[12] **26** by regio- and stereospecific ring opening of aziridine[20] **23** and bis-aziridine[21] **25**, respectively, with **1** (1.2 equiv; $CH_3CN$, 28 °C, 4−5 h) as the selenium transfer reagent (Scheme 3).

Since diselenides **24** and **26** have larger dihedral angles (−96.5 and −54.9°, respectively), the interaction between the two pairs of 4p nonbonding electrons on the selenium atoms becomes much less. As a result, they absorb light at shorter wavelengths in the ultraviolet region and are orange and yellow,-

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respectively, as compared to conformationally locked diselenides **3** and **12**−**21** (Figure 3).

On the other hand, bridged diselenides have an enhanced interaction between the two pairs of 4p nonbonding electrons on the selenium atoms, and therefore, they have a longer selenium−selenium bond length as compared to simple diselenides **24** and **26** (Table 2). To further understand how color, UV absorption, and Se−Se bond length change with the dihedral angle, we carried out DFT calculations on locked bridged diselenides **3**, **12**, and **18**−**21** using the B3LYP method and at the 6-31G(d) level basis set. The bond lengths and bond angles are in good agreement with the experimental data (see Supporting Information). The Kohn−Sham HOMO and LUMO calculations for **3**, **24**, and **26** show that the energy gap between HOMO and LUMO of diselenides increases with an increase in the dihedral angle (Figure 5) and that the Se−Se bond length increases with a decrease in the dihedral angle (Table 2).

## Conclusion

In conclusion, we have demonstrated an easy and efficient synthesis of conformationally locked diselenides in a single step starting from *cis*-1,4-aziridino-epoxides. These compounds serve as useful precursors for the synthesis of selenium substituted amino-cyclohexanol derivatives in a highly regio- and stereocontrolled manner. Some correlations have been made on the physicochemical characteristics of the diselenides with changes in the dihedral angles.

## Experimental Section

**General Procedure for Aziridine Ring Opening.** To a stirred solution of *cis*-aziridino-epoxide **2** (0.1 g, 0.38 mmol) in $CH_3CN$/EtOH (1:1; 5 mL), tetraethylammonium tetraselenotungstate **1** (0.346 g, 0.46 mmol) was added at room temperature (28 °C). After completion of the reaction (TLC, 6 h), the solvent was removed in vacuo, and the black residue was extracted with $CH_2Cl_2$−$Et_2O$ (1:4, 5 × 20 mL) and filtered through a Celite pad. The filtrate was concentrated, and the crude product was purified by flash column chromatography on silica gel (230−400 mesh, eluting with hexane/ethyl acetate 8:2) to obtain **3** as wine red crystals (0.146 g, 90%). $R_f$ = 0.70 (hexanes/EtOAc, 7:3). mp: 172 °C. IR (neat) $\nu_{max}$: 3464, 3309, 1422, 1324, 1285, 1155, 1080, 1054, 1020, 668 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.75 (d, $J$ = 8.1 Hz, 2H), 7.33 (d, $J$ = 8.1 Hz, 2H), 6.29 (d, $J$ = 8.4 Hz, 1H), 4.36−4.28 (m, 2H), 4.09 (bs, 1H), 4.00 (bs, 1H), 3.50 (t, $J$ = 1.6 Hz, 1H), 2.67 (td, $J$ = 15.2, 4.0 Hz, 1H), 2.56 (bs, 1H), 2.45 (s, 3H), 2.06 (td, $J$ = 14.0, 3.6 Hz, 1H), 1.33 (dd, $J$ = 15.2, 2.0 Hz, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 143.4, 137.8, 129.8, 126.9, 71.3, 54.1, 48.8, 48.5, 37.9, 28.5, 21.5. $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ 380.2, 374.2. HR-MS $m/z$: calcd for $C_{13}H_{17}NO_3SSe_2$ [M + $Na^+$]: 449.9157; found: 449.9156. Anal. Calcd for $C_{13}H_{17}NO_3SSe_2$: C, 36.72; H, 4.03; N, 3.29; S, 7.54. Found: C, 36.55; H, 4.12; N, 3.38; S, 7.66.

**Compound 12.** $R_f$ = 0.70 (hexanes/EtOAc, 7:3); Yield: 0.201 g, 92%; mp: 166 °C; IR (neat) $\nu_{max}$: 3481, 3287, 1597, 1418, 1325, 1158, 813, 668 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.76 (d, $J$ = 8.1 Hz, 2H), 7.33 (d, $J$ = 8.1 Hz, 2H), 6.23 (d, $J$ = 8.8 Hz, 1H), 4.01−3.96 (m, 2H), 3.85 (dd, $J$ = 10.8, 2.0 Hz, 1H), 3.47−3.44 (m, 1H), 2.76−2.71 (m, 1H), 2.44 (s, 3H), 2.14 (dd, $J$ = 14.3, 3.5 Hz, 1H), 1.71 (s, 3H), 1.32−1.15 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 143.4, 137.4, 129.9, 126.9, 71.1, 60.8, 59.2, 49.0, 44.7, 30.2, 23.3, 21.5; $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ 453.4, 401.1; HR-MS $m/z$: calcd for $C_{14}H_{19}NO_3SSe_2$ [M + $Na^+$]: 463.9314; found: 463.9299. Anal. Calcd for $C_{14}H_{19}NO_3SSe_2$: C, 38.28; H, 4.36; N, 3.19; S, 7.30. Found: C, 38.41; H, 4.23; N, 3.24; S, 7.36.

**Compound 13.** $R_f$ = 0.60 (hexanes/EtOAc, 8:2); Yield: 0.213 g, 73%; mp: 178 °C; IR (neat) $\nu_{max}$: 3486, 3255, 1597, 1423, 1330, 1255, 1156, 1064, 836, 779, 671 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.72 (d, $J$ = 8.1 Hz, 2H), 7.32 (d, $J$ = 8.1 Hz, 2H), 6.19 (d, $J$ = 9.3 Hz, 1H), 4.10−3.95 (m, 2H), 3.83−3.69 (m, 3H), 3.60 (d, $J$ = 9.3 Hz, 1H), 2.73−2.57 (m, 2H), 2.48 (s, 3H), 2.13−1.99 (m, 3H), 0.95 (s, 9H), 0.13 (s, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 143.6, 137.6, 129.9, 127.1, 72.1, 61.1, 58.1, 55.5, 45.8, 45.1, 39.7, 29.2, 26.2, 21.6, 18.4, −5.2, −5.3; $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ 480.2, 333.7; HR-MS $m/z$: calcd for $C_{21}H_{35}NO_4SSe_2Si$ [M + $Na^+$]: 608.0284; found: 608.0283. Anal. Calcd for $C_{21}H_{35}NO_4SSe_2Si$: C, 43.22; H, 6.05; N, 2.40; S, 5.49. Found: C, 43.36; H, 6.23; N, 2.46; S, 5.52.

**Compound 14.** $R_f$ = 0.70 (hexanes/EtOAc, 8:2); Yield: 0.052 g, 18%; mp: 161 °C; IR (neat) $\nu_{max}$: 3478, 3259, 1153, 1087, 835, 777, 665 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.76 (d, $J$ = 8.1 Hz, 2H), 7.29 (d, $J$ = 8.1 Hz, 2H), 6.55 (s, 1H), 4.64 (bs, 1H), 4.38 (d, $J$ = 14.7 Hz, 1H), 4.10 (bs, 1H), 4.03 (bs, 1H), 3.46−3.38 (m, 1H), 3.30−3.23 (m, 1H), 2.42 (s, 3H), 2.39 (dd, $J$ = 17.7, 3.3 Hz, 1H), 2.18−2.06 (m, 3H), 1.82 (d, $J$ = 15.3 Hz, 1H), 0.82 (s, 9H), −0.06 (s, 3H), −0.07 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): 143.2, 139.9, 129.6, 126.9, 71.9, 63.2, 58.6, 54.4, 48.6, 39.9, 39.5, 34.1, 25.9, 21.5, 18.2, −5.5, −5.4; $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ 453.8, 402.4; HR-MS $m/z$: calcd for $C_{21}H_{35}NO_4SSe_2Si$ [M + $Na^+$]: 608.0284; found: 608.0312. Anal. Calcd for $C_{21}H_{35}NO_4SSe_2Si$: C, 43.22; H, 6.05; N, 2.40; S, 5.49. Found: C, 43.16; H, 6.26; N, 2.32; S, 5.44.

**Procedure for Ring Opening of Simple Aziridine 23 with 1.** To a stirred solution of aziridine **23** (0.101 g, 0.4 mmol) in $CH_2Cl_2$ (3 mL), tetraethylammonium tetraselenotungstate **1** (0.364 g, 0.48 mmol) was added at room temperature (28 °C). After completion of the reaction (TLC, 4 h), the black residue was extracted with $CH_2Cl_2$−$Et_2O$ (1:4, 5 × 20 mL) and filtered through a Celite pad. The filtrate was concentrated, and the crude product was purified by flash column chromatography on silica gel (230−400 mesh, eluting with hexane/ethyl acetate 9:1) to obtain **24** as a yellow solid (0.226 g, 85%). $[\alpha]^{26}_D$ = +37.83 ($c$ = 6.0, $CH_2Cl_2$); mp: 103 °C; IR (neat) $\nu_{max}$: 3286, 1402, 1165, 1095, 816, 742, 666 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.77 (d, $J$ = 8.1 Hz, 4H), 7.29 (d, $J$ = 8.1 Hz, 4H), 5.09 (d, $J$ = 8.1 Hz, 1H), 3.39−3.35 (m, 1H), 3.04 (d, $J$ = 5.7 Hz, 2H), 2.43 (s, 3H), 1.38−1.22 (m, 1H), 1.02−0.92 (m, 1H), 0.79 (t, $J$ = 7.5 Hz, 3H), 0.75 (d, $J$ = 6.9 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 143.3, 137.8, 129.6, 127.1, 58.6, 37.7, 32.8, 24.8, 21.6, 14.8, 11.5; $^{77}Se$ NMR (76 MHz, $CDCl_3$): $\delta$ 290.2; HR-MS $m/z$: calcd for $C_{26}H_{40}N_2O_4S_2Se_2$ [M + $Na^+$]: 707.0397; found: 707.0389. Anal. Calcd for $C_{26}H_{40}N_2O_4S_2Se_2$: C, 46.84; H, 6.05; N, 4.20; S, 9.62. Found: C, 46.98; H, 6.28; N, 4.30; S, 9.86.

**Procedure for Ring Opening of Bis-aziridine 25 with 1.** To a stirred solution of aziridine[21] **25** (0.252 g, 0.4 mmol) in $CH_3CN$ (5 mL), tetraethylammonium tetraselenotungstate **1** (0.364 g, 0.48 mmol) was added at room temperature (28 °C). After completion of the reaction (TLC, 5 h), the solvent was removed in vacuo, and the black residue was extracted with $CH_2Cl_2$−$Et_2O$ (1:4, 5 × 20 mL) and filtered through a Celite pad. The filtrate was concentrated, and the crude product was purified by flash column chromatography on silica gel (230−400 mesh, eluting with hexane/ethyl acetate 9:1) to obtain **26** as a yellow solid (0.196 g, 62%). $[\alpha]^{26}_D$ = −137.00 ($c$ = 1.0, $CHCl_3$); mp: 152 °C; IR (neat) $\nu_{max}$: 3293, 1402, 1160, 1090, 814, 736, 665 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.81 (d, $J$ = 8.1 Hz, 4H), 7.39−7.17 (m, 7H), 5.49 (d, $J$ = 3.9 Hz, 1H), 4.19 (bs, 1H), 4.11 (dd, $J$ = 38.1, 12.0

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Hz, 2H), 3.87 (d, $J$ = 4.2 Hz, 1H), 3.36 (dd, $J$ = 9.6, 5.4 Hz, 1H), 2.76 (dd, $J$ = 9.6, 3.0 Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 143.7, 136.8, 135.8, 129.6, 128.5, 127.9, 127.6, 127.3, 73.1, 72.1, 56.7, 38.8, 21.6; $^{77}$Se NMR (76 MHz, $CDCl_3$): $\delta$ 211.3; HR-MS *m*/*z*: calcd for $C_{34}H_{38}N_2O_6S_2Se_2$ [M + $Na^+$]: 817.0399; found: 817.0421. Anal. Calcd for $C_{34}H_{38}N_2O_6S_2Se_2$: C, 51.51; H, 4.83; N, 12.11; S, 8.09. Found: C, 51.63; H, 4.96; N, 12.41; S, 8.23.

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**Supporting Information Available:** Spectral data of other new compounds, copy of $^1$H, $^{13}$C, and DEPT spectra for all new compounds, and X-ray structural details of compounds 3, 12−14, 16, 18−21, 24, and 26. This material is available free of charge via the Internet at http://pubs.acs.org.

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