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Synthesis and Multinuclear NMR Characterizations of Some [3.3]Diselena- and [4.4]Tetraselenacyclophanes.

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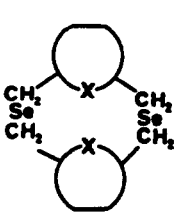
Summary: Several symmetrical and unsymmetrical bis-selenacyclophanes were prepared and characterized by multinuclear (^{1}H, $^{13}C\{^{1}H\}$ and $^{77}Se\{^{1}H\}$) NMR. The symmetrical cyclophanes of phenyl, furyl, pyridyl and thiophenyl appear to exist in predominantly syn conformation in solution at room temperature. VT-^{1}H NMR of some cyclophanes indicate that the equilibrium between the syn conformers which differ in the disposition of the bridge seleniums (symmetric about mirror plane⟷symmetric about inversion center) can be slowed at low temperatures. Interesting $^{13}C\{^{1}H\}$ shifts are observed in unsymmetrical cyclophanes containing 2,2'-biphenyl, pyridine and furan. The $^{77}Se\{^{1}H\}$ chemical shifts appear to be related to the size of the cavity of the cyclophanes.

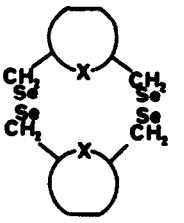
Introduction: Cyclophanes due to their rigid geometry and interesting conformational characteristics are ideal molecules for studying questions of strain energy, transannular π-electron interactions and bonding.[1] Their synthesis, conformation, electronic structure and host-guest chemistry have been subjects of many investigations.[2] Although heterophanes containing nitrogen, oxygen and sulfur have been widely studied,[2] only a few reports of cyclophanes containing selenium in the bridge have appeared.[3]

Selenium containing cyclophanes are attractive due to the large covalent radius and greater polarizability of selenium compared to oxygen, nitrogen and sulfur which could influence the conformational as well as complexation properties of these compounds and also due to the accessibility of ^{77}Se-NMR for the investigation of structural properties of selenium containing cyclophanes. We have initiated a systematic study of selenacyclophanes which involves their synthesis, conformational properties, complexation with metal ions and conductivity behavior. We have reported the synthesis, structural, complexation and conductivity properties of 2,11-diselena[3.3]-2,6-pyridinophane.[4] We now wish to report the synthesis and multinuclear NMR properties of a number of selenium macrocyclic com-

pounds with general structures I and II,



(I)



(II)

Where: X= C-H, N, O and S
ring = Benzene (o, m and p), Pyridine (2,6-), Furan (2,5-), Thiophene (2,5-), Biphenyl (2,2'-), Mixed Aromatic Rings (unsymmetrical cyclophanes)

Figure 1

Experimental Approach: The earliest attempts to synthesize a bis-selenide, 2,11-diselena[3.3]metacyclophane involved treatment of α,α'-dibromo-m-xylene with sodium selenide following the method for the synthesis of thiacyclophanes which provided a mixture of products with the desired selenacyclophane being obtained in less than 10% yields.[3a] Misumi proposed a method which provided much higher yields of the selenacyclophanes.[3b] We have modified Misumi's procedure and have prepared a number of symmetrical and unsymmetrical bis-selenides in excellent yields. The first step in the synthesis of selenacyclophanes involves the conversion of an appropriate benzylic dihalide (3) to its bis(selenocyanatomethyl) derivative (4) with potassium selenocyanate in degassed acetone under an inert atmosphere. The resulting mixture was filtered and the filtrate was concentrated to obtain (4) in quantitative yields as shown in scheme 1. 2,5-Bis(chloromethyl)-furan (3d) and 2,6-Bis(chloromethyl)pyridine (3f) were prepared from the commercially available dimethanol derivatives and PBr_3. 2,5-Bis(chloromethyl)thiophene (3e) was prepared by chloromethylation of thiophene with HCHO/HCl.[5] 2,2'-Bis(chloromethyl)biphenyl (3g) was prepared by lithiation of 2,2'-dibromobiphenyl with n-BuLi followed by the treatment with CO_2 and hydrolysis to the corresponding dicarboxylic acid, esterification, reduction and finally treatment with phosphorus tribromide.

The symmetrical bis-selenides were prepared from bis-selenocyanatomethyl derivatives (4) and the corresponding benzylic dihalide (3) under high dilution conditions,[6] in a mixture of degassed THF and ethanol in the presence of an excess of sodium borohydride.[4] The preparations of 2,6-bis(selenocyanatomethyl)pyridine and 2,11-diselena[3.3]-2,6-pyridinophane

are described as examples of the procedures utilized. The melting points, elemental analysis and spectral characteristics of the bis-selenocyanomethyl derivatives 4a-g are given along with the preparation of 2,6-bis-(selenocyanatomethyl)pyridine. The corresponding data for the bis-selenides 1a-q are given in Table 1 and Figure 2.

2,6-bis(selenocyanatomethyl)pyridine (3f): To a stirred solution of 5.1 g (0.02 mole) of 2,6-bis(bromomethyl)pyridine in 150 mL of degassed acetone was added a solution of 7.2 g (0.05 mole) of KSeCN in 200 mL of degassed acetone dropwise under an argon atmosphere at room temperature over a period of 4 h. KBr was filtered off, and the solution concentrated to yield 5.8 g of 2,6-bis(selenocyanatomethyl)pyridine as pale yellow crystals (98%), mp 81 °C; ^{1}H NMR ($CDCl_3$): δ 4.46 (s, C$\underline{H}_2$, $^2J_{SeH}$ = 16.7 Hz), 7.26 and 7.29 (d, 1:1, Ar$\underline{H}$, J_{HH} = 7.8 Hz), 7.7, 7.73 and 7.76 (t, 1:2:1, Ar$\underline{H}$, J_{HH} = 7.8 Hz); IR (KBr): ν(S-CN) 1650 cm^{-1}. Anal. Calcd. values in parenthesis. $C_9H_7Se_2N_2$. C: 35.8(35.9); H: 2.3(2.3); N: 9.1(9.3); Se: 52.0(52.5).

1,2-bis(selenocyanatomethyl)benzene(3a): $C_{10}H_8Se_2N_2$(100%, 79-80 °C); C: 38.1(38.2); H: 2.7(2.6); N: 8.4(9.0); Se: 49.4(50.3); ^{1}H NMR ($CDCl_3$): δ 4.26 (s, C$\underline{H}_2$, $^2J_{SeH}$= 15.9 Hz), 7.3 -7.37 (m, Ar$\underline{H}$). IR (KBr): ν(SCN) 1651 cm^{-1}.

1,3bis(selenocyanatomethyl)benzene(3b): $C_{10}H_8Se_2N_2$(100%, 99-100 °C); C: 38.3(38.2); H: 2.6(2.6); N: 8.5(8.9); Se: 49.6(50.3); ^{1}H NMR($CDCl_3$): δ 4.4 (s, C$\underline{H}_2$, $^2J_{SeH}$= 14.7 Hz), 7.13,7.23&7.36 (Ar$\underline{H}$); IR (KBr): ν(SCN) 1652 cm^{-1}.

1,4-bis(selenocyanatomethyl)benzene(3c): $C_{10}H_8Se_2N_2$(98%, 149 °C); C: 38.1(38.2); H: 2.5(2.6); N: 8.7(8.9); Se: 49.2(50.3). ^{1}H NMR($CDCl_3$): δ 4.4 (s, C$\underline{H}_2$, $^2J_{SeH}$= 18.3 Hz), 7.46 (s, Ar$\underline{H}$); IR (KBr): ν(SCN) 1651 cm^{-1}.

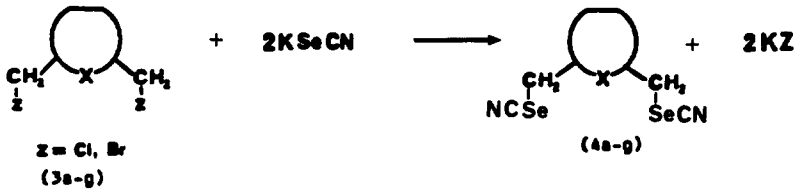
2,5-bis(selenocyanatomethyl)furan(3d): $C_8H_6Se_2N_2O$ (100%, 45 °C, decomp.); C: 31.5(31.6); H: 2.0(1.97); N: 8.6(9.2); Se: 51(52); O: 5.8(5.3); ^{1}H NMR: δ 4.44 (s, C$\underline{H}_2$, $^2J_{SeH}$= 19 Hz); IR(KBr): ν(SCN) 1649cm^{-1}.

2,5-bis(selenocyanatomethyl)thiophene(3e): $C_8H_6Se_2N_2S$ (100%, 137 °C, decomp.). C: 30.1(30); H: 1.8(1.9); N: 8.1(8.8); S: 9.2(10); Se: 48.7(49.4); ^{1}H NMR($CDCl_3$): 4.46(s, C$\underline{H}_2$, $^2J_{SeH}$= 16.5Hz), 6.97 (s,Ar$\underline{H}$); IR (KBr): ν(SCN) 1650 cm^{-1}.

2,2'-bis(selenocyanatomethyl)biphenyl(3g): $C_{16}H_{12}Se_2N_2$ (100%, oil); C: 49.3(49.2); H: 3.0(3.1); Se: 39.8(40.5); N: 6.5(7.2); ^{1}H NMR($CDCl_3$): δ 4.08, 4.13, 4.3 and 4.34 (AB, C$\underline{H}_2$, J_{AB} = 12 Hz, $\Delta\nu_{AB}$ = 52.2 Hz), 7.28 - 7.65 (m, Ar$\underline{H}$); IR(neat): ν(SCN) 1653 cm^{-1}.

2,11-Diselena[3.3]-2,6-pyridinophane(1f): 2,6-Bis(selenocyanatomethyl)pyridine (1.5 g, 0.005 mole) and 2,6-bis(bromomethyl)pyridine (1.3 g, 0.005 mole) were each dissolved separately in a mixture of 80% freshly distilled peroxide free THF and 20% absolute ethanol to a total volume of 200 mL and thoroughly degassed with Ar. They were added separately but

simultaneously from two constant addition funnels over 20 h into 950 mL of freshly distilled peroxide-free THF and 50 mL of absolute ethanol containing an excess (1.5 g) of $NaBH_4$ at room temperature under Ar. The resulting solution was filtered and concentrated to dryness. The solid was treated with 100 mL of freshly distilled benzene. The benzene solution was evaporated to dryness to yield a white crystalline solid which was recrystallized from $CHCl_3$ (1.75 g, 96%).



$$(3a\text{-}g) + (4a\text{-}g) \xrightarrow[THF/EtOH]{NaBH_4} (1a\text{-}g)$$

Scheme 1

The unsymmetrical macrocycles (1h-q) were prepared using the above method by treatment of the bis(selenocyanatomethyl) compounds (4) and an appropriate benzylic dihalide to obtain the corresponding mixed cyclophanes in high yields (Table 1 and Figure 2).

2,3,18,19-[4.4]-Tetraselena-2,2'-biphenyl(1r): This compound was prepared by the base hydrolysis of the corresponding bis(selenocyanatomethyl) derivative (3g).[7] 1.17 g (0.003 mole) of 2,2'-Bis(selenocyanatomethyl)biphenyl (3g) was dissolved in 100 mL of freshly distilled THF. Potassium hydroxide (0.003 mole, 0.17 g) in 100 mL of freshly distilled methanol was added to (3g) under Ar over a period of 4 h at room temperature. The solution was filtered and concentrated to obtain an orange powder. It was recrystallized from $CHCl_3$. This is the only case where the base hydrolysis provided the tetraselenide in reasonable yields without leading to a mixture of products. This method is not a reliable route for the synthesis of tetraselenacyclophanes and we are currently investigating methods of obtaining these compounds in better yields. The bis-selenides and the tetraselenide are shown in Figure 2 with their yields and melting points.

All NMR data were obtained on a Brucker WM-250 instrument in the FT mode in $CDCl_3$ solvent. For proton and carbon NMR the solvent peaks were used as reference. $(CH_3)_2Se$ was used as an external standard for selenium NMR. IR spectra were recorded on a Perkin-Elmer FT-1800 instrument either as neat samples or as KBr pellets. Mass spectra were recorded with a

Hewlett-Packard Model 5930A dodecapole mass spectrometer. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tn. Melting points were recorded with a AcuLab melting point apparatus in open capillary tubes and are uncorrected.

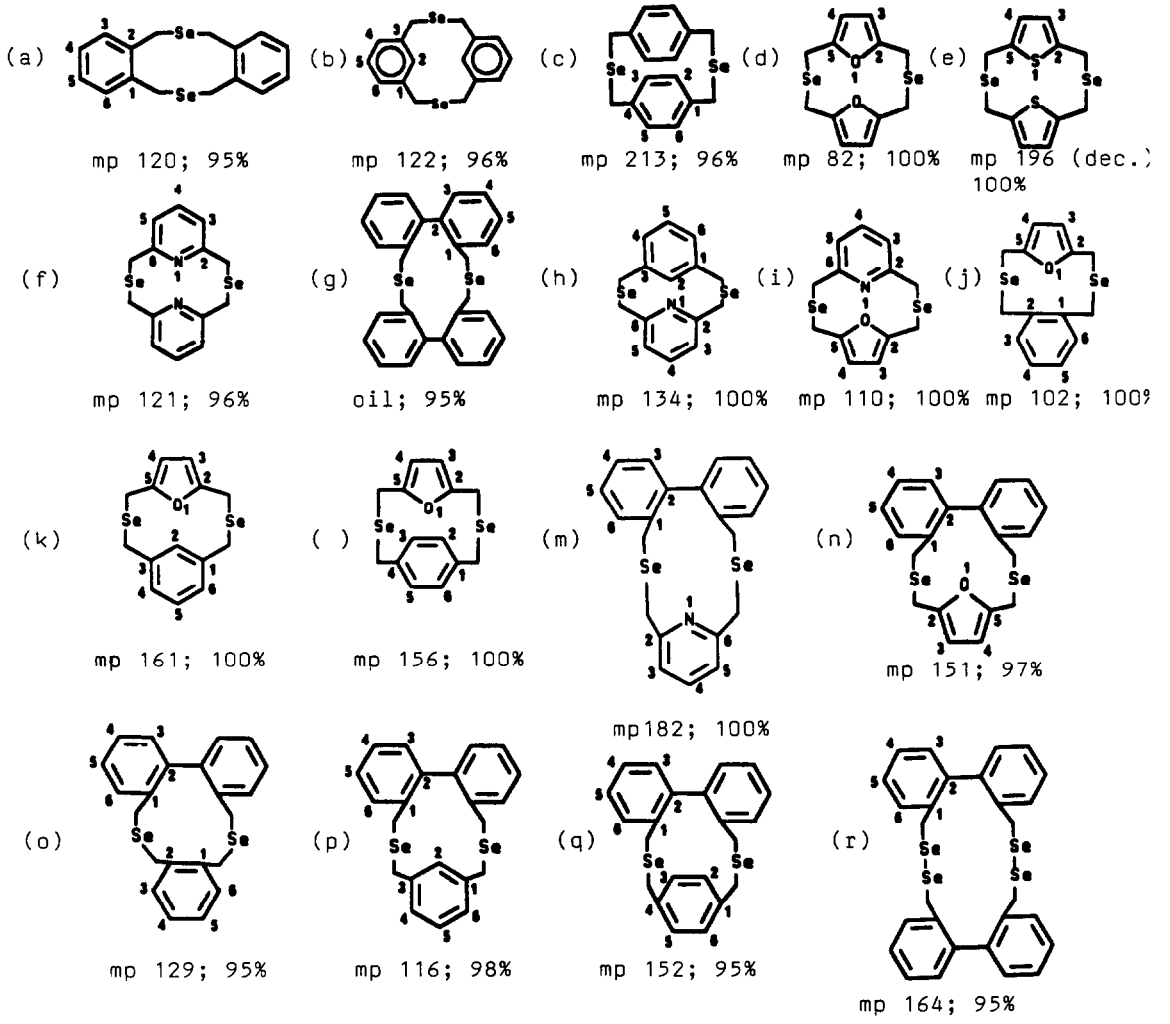


Figure 2

Table 1. Spectral Properties of Bis-selenides and the Tetraselenide.

Compd.	^{1}H-NMR[a]	^{13}C-NMR[a]	^{77}Se-NMR[a]
(1a)	3.78(s, C$\underline{H}_2$);17.75 7.04, 7.07(d, H3,6) 7.09, 7.12(d, H4,5)	27.82 (C$\underline{H}_2$) 128.6(C3,6), 131.4, (C4,5), 137.65(C1,2)	l.s.[b]
(1b)	3.66(s, C$\underline{H}_2$); 16.5 7.13(s, H2), 7.19, 7.22(d, H4,6), 7.47,7.5,7.53(t, H3,5)	22.06 (C$\underline{H}_2$) 127.3 (C4,6), 130.3, (C5), 130.6 (C2), 137.5(C1,3)	l.s.[b]
(1c)	3.75(s, C$\underline{H}_2$); 17.3 7.16(s, Ar$\underline{H}$)	32.19 (C$\underline{H}_2$) 129.11 (C2,3,5,6), 137.7 (C1,4)	341.8
(1d)	3.67(s, C$\underline{H}_2$); 17.3 5.85(s, Ar$\underline{H}$)	19.14 (C$\underline{H}_2$); 65; 107.7 (C3,4), 151.4, (C2,5)	314.4
(1e)	3.62(s, C$\underline{H}_2$); 21.4 6.28(s, Ar$\underline{H}$)	23.04 (C$\underline{H}_2$) 126.5 (C3,4), 143.9 (C2,5)	l.s.[b]
(1f)	3.95(s, C$\underline{H}_2$); 17.7 6.87, 6.9(d, H3,5) 7.12, 7.15, 7.18(t, H4)	30.2 (C$\underline{H}_2$); 65.5; 120.7 (C3,5), 136.4 (C4),157.8 (C2,6)	358.2
(1g)	3.53, 3.57, 3.86, 3.9 (AB, C$\underline{H}_2$);14.5; J_{AB} = 11.4Hz; $\Delta\nu_{AB}$ = 82.2 7.19-7.67 (m, Ar$\underline{H}$)	22.42 (C$\underline{H}_2$); 55.7; 127.05 (C4), 127.61 (C5), 127.96 (C3), 128.44 (C6), 136.29 (C2), 140.1 (C1)	445.1
(1h)	3.79 (s, ph C$\underline{H}_2$); 17.0 3.95 (s, Py C$\underline{H}_2$); 17.7 6.83, 6.87(d, H2,4) 6.86, 6.89, 6.92(t, H3, Py$\underline{H}$);6.88(s, H2), 6.95, 6.98(d, H4,6), 7.22, 7.25, 7.28(t, H5, ph$\underline{H}$)	29.2 (Py $\underline{C}H_2$) 24.5 (ph $\underline{C}H_2$) 120 (C2,4), 137.1 (C3), 158.9 (C1,5, Py); 127 (C4,6), 130.5 (C5), 130.7 (C2), 137.6 (C1,3, ph)	298.9
(1i)	3.8 (s, Furyl C$\underline{H}_2$);18.9 3.89 (s, Py C$\underline{H}_2$); 16.7 5.88 (s, Furyl^2$\underline{H}$); 6.93 & 6.96 (d, H3,5, Py$\underline{H}$); J_{HH} = 7.7 Hz 7.33, 7.36 & 7.39 (t, H4, Py$\underline{H}$); J_{HH} = 7.5 Hz	19.19 (Furyl,$\underline{C}H_2$);66; 29.26 (Py, $\underline{C}H_2$); 66; 108.7 (C3,4), 150.07 (C2,5 Furyl); 120.4 (C3,5),136.6(C4),159.04 (C2,6, Py)	346.23
(1j)	3.82(s, Furyl C$\underline{H}_2$);18.4 3.99 (s, Py C$\underline{H}_2$); 17.8 5.94 (s, Furyl^2$\underline{H}$); 7.1, 7.13(d, H3,6) 7.23, 7.26(d, H4,5,ph$\underline{H}$)	18.6 (Furyl, $\underline{C}H_2$) 27.9 (ph,$\underline{C}H_2$) 108.5 (C3,4), 150.8 (C2,5 Furyl); 126.3 (C3,6), 128 (C4,5), 138.8 (C1,2, ph)	
(1k)	3.8 (s, Furyl C$\underline{H}_2$) 3.87 (s, ph C$\underline{H}_2$) 6.02 (s, Furyl^2$\underline{H}$); 6.98 (s, H2), 7.02 -	20.3 (Furyl, $\underline{C}H_2$) 24.6 (ph, $\underline{C}H_2$) 107.9 (C3,4), 152.6 (C2,5 Furyl);127.1(C4,6),	

	7.045(d, H4,6), 7.055, 7.09, 7.12(t, H5, ph)	127.3 (C5),131 (C2), 136.8 (C1,3, ph)	
(1ℓ)	3.61 (s, Furyl CH_2);204 (s, ph CH_2); 19.7 5.83(Furyl H); 7.42(ph H)	17.06 (Furyl,CH_2) 29.04 (ph, CH_2) 107.4 (C3,4), 152.5 (C2,5 Furyl);129(C2,3, 5,6), 138 (C1,4, ph)	
(1m)	3.50, 3.55, 3.62 & 3.67 (AB, Py CH_2);17.5;J_{AB} = 12.7Hz; $\Delta\nu_{AB}$ = 25Hz 3.76, 3.82, 4.10 & 4.16 (AB, Biph CH_2); 22; J_{AB} =15.1Hz; $\Delta\nu_{AB}$= 85Hz 7.03-7.06 & 7.34-7.89 (Biph H);6.96, 6.99 (d, H3,5), 7.21, 7.24, 7.27(t, H4, Py H)	26.14 (CH_2, Py & Biph); 75.5Hz 119.87 (C3,5), 134.56 (C4), 160.34 (C2,6,Py); 126.14 (C4), 127.75 (C5), 129.67 (C3), 130.25 (C6), 137.2 (C2), 141.19 (C1, Biph)	260.9
(1n)	3.18, 3.24, 3.34 & 3.41 (AB, Furyl CH_2); 17.5 J_{AB}= 14.1Hz; $\Delta\nu_{AB}$= 39Hz 3.67, 3.73, 4.09 & 4.15 (AB, Biph CH_2); 16.0 J_{AB} = 15Hz; $\Delta\nu_{AB}$= 104Hz 5.71 (Furyl H); 6.96-7.92 (m, Biph H)	15.4 (Furyl CH_2) 26.2 (Biph CH_2) 88Hz (both) 105.86 (C3,4), 154.1 (C2,5, Furyl); 127.8 (C5), 128.23 (C4),130.27 (C3), 131.05 (C6),133.9 (C2), 140.2 (C1, Biph)	274.2
(1o)	3.53, 3.59, 3.65 & 3.70 (AB, ph CH_2);J_{AB}=12.6Hz; $\Delta\nu_{AB}$= 26.0Hz;3.31, 3.37 3.88 & 3.94(AB,Biph CH_2) J_{AB}= 14.4Hz; $\Delta\nu_{AB}$= 143Hz 7.04, 7.07(d, H3,6), 7.10, 7.13(d,H4,5,ph H); 7.06-7.78 (Biph H)	25.13 (ph CH_2) 26.2 (Biph CH_2) 129.9 (C3,6), 130.16 (C4,5),139.1 (C1,2, ph); 126 (C4), 126.9 ((C5), 127.7 (C3), 128.3 (C6), 135 (C2), 139.53 (C1, Biph)	
(1p)	3.38, 3.42, 3.58 & 3.63 (AB, ph CH_2);J_{AB}=11.1Hz; $\Delta\nu_{AB}$ = 51Hz;3.76, 3.81, 3.91 & 3.96(AB,Biph CH_2) J_{AB}= 10.1Hz; $\Delta\nu_{AB}$= 36Hz 6.9(s, H2), 7.18, 7.21, (d, H4,6), 7.34, 7.37, 7.4(t, H5, ph H); 7-7.25(Biph H)	25.2 (ph CH_2) 26 (Biph CH_2) 126.9 (C4,6), 129.7 (C5),130.34 (C2), 131 (C1,3, ph);125.8 (C4), 127.2 (C5),127.8 (C3), 128.1 (C6),136.7 (C2), 138.7 (C1, Biph)	
(1q)	3.76(s, ph CH_2); 3.77, 3.81, 3.85 & 3.89 (AB, Biph CH_2) J_{AB}= 11.1Hz;$\Delta\nu_{AB}$= 17Hz 6.8(s, ph H); 6.87-7.6(m, Biph H)	24.5 (ph CH_2) 25.9 (Biph CH_2) 129.4 (C2,3,5,6), 136 (C1,4, ph);125.6 (C4), 127.3 (C5),129 (C3), 129.81 (C6),134.9 (C2), 138.75 (C1, Biph)	
(1r)	3.69, 3.74, 3.94, 3.98 (AB, CH_2);J_{AB} = 10.8; $\Delta\nu_{AB}$ = 59.5;3.24, 3.29, 3.49, 3.53(AB, CH_2) J_{AB} = 11.5, $\Delta\nu_{AB}$ = 59.7	22.8, 29.21 (CH_2); 94.34 and 83.86 126.6 - 140.5 (phenyl C)	381.2

a. Chemical shifts in δppm. Coupling constants $^{2}J_{SeH}$ and $^{1}J_{SeC}$ in Hz. b. Low solubility. ph = phenyl, Py = pyridine, Biph = biphenyl, Ar = aromatic.

Elemental Analysis. Calculated Values in Parenthesis.

(1a). $C_{16}H_{16}Se_2$: C: 52.4(52.45); H: 4.4(4.37); Se: 42.8(43.16)
(1b). $C_{16}H_{16}Se_2$: C: 52.5(52.45); H: 4.3(4.37); Se: 43.3(43.16)
(1c). $C_{16}H_{16}Se_2$: C: 52.3(52.45); H: 4.4(4.37); Se: 43.1(43.16)
(1d). $C_{12}H_{12}O_2Se_2$: C: 41.5(41.60); H: 3.5(3.46); Se: 45(45.66); O: 9(9.25)
(1e). $C_{12}H_{12}S_2Se_2$: C: 38(38.09); H: 3.1(3.17); S: 16.5(16.93); Se: 40.9(41.8)
(1f). $C_{14}H_{14}N_2Se_2$: C: 45.4(45.65); H: 3.7(3.8); N: 7.5(7.6); Se: 41.4(42.93)
(1g). $C_{28}H_{24}Se_2$: C: 64.9(64.86); H: 4.6(4.63); Se: 30.2(30.5)
(1h). $C_{15}H_{15}NSe_2$: C: 48.9(49.05); H: 4.1(4.09); N: 3.6(3.81); Se: 42.5(43.05)
(1i). $C_{13}H_{13}ONSe_2$: C: 43.6(43.7); H:3.6(3.64); O:4.1(4.5); N:3.7(3.92); Se: 43.5(44.2)
(1j). $C_{14}H_{14}OSe_2$: C: 47.1(47.19); H: 3.9(3.93); O: 4.1(4.45); Se: 43.5(44.38)
(1k). $C_{14}H_{14}OSe_2$: C: 47.4(47.19); H: 3.8(3.93); O: 4.2(4.45); Se: 43.8(44.38)
(1ℓ). $C_{14}H_{14}OSe_2$: C: 47.3(47.19); H: 4.0(3.93); O: 4.0(4.45); Se: 43.6(44.38)
(1m). $C_{21}H_{19}NSe_2$: C: 56.6(56.88); H: 4.4(4.29); N: 2.7(3.2); Se: 34.5(35.6)
(1n). $C_{20}H_{18}OSe_2$: C: 55.8(55.56); H: 4.1(4.17); O: 4.1(3.7); Se: 35.8(36.57)
(1o). $C_{22}H_{20}Se_2$: C: 59.6(59.73); H: 4.6(4.52); Se: 35.3(35.75)
(1p). $C_{22}H_{20}Se_2$: C: 59.8(59.73); H: 4.4(4.52); Se: 35.7(35.75)
(1q). $C_{22}H_{20}Se_2$: C: 59.5(59.73); H: 4.4(4.52); Se: 35.5(35.75)
(1r). $C_{28}H_{24}Se_4$: C: 49.6(49.70); H: 3.7(3.55); Se: 46.1(46.75)

Mass Spectral Data. Percent Relative Intensities in Parenthesis.

(1a). 368(26), 367(6), 366(PI[C], 28), 364(15), 287(6), 183(15), 105(100), 91(26), 78(22).
(1b). 368(5), 367(1), 366(PI, 4), 364(2), 264(24), 184(50), 183(75), 104(100), 78(30), 51(13).
(1c). 368(10), 367(6), 366(PI, 9), 264(30), 184(60), 183(49), 104(100), 103(52), 78(25), 51(10).
(1d). 348(1), 347(0.5), 346(PI, 1), 238(14), 188(3), 174(4), 162((12), 160((40), 158(33), 94(100), 66(14), 50(5).
(1e). 382(2), 380(4), 378(PI, 4), 111(15), 109(11), 79(6), 78(17), 66(20), 45(17).
(1f). 370(15), 369(3), 368(PI, 13), 291(20), 290(19), 289(100), 287(49), 209(20), 185(19), 168(6), 119(6), 107(28), 104(32), 65(32).
(1g). 520(2), 519(0.5), 518(PI, 2), 260(67), 179(100), 165(69), 89(1), 76(2), 63(1).
(1h). 367(19), 366(8), 367(PI, 19), 289(20), 194(32), 187(23), 183(100), 145(6), 104((93), 91(21), 78(28), 51(34).
(1i). 359(12), 358(2), 357(PI, 11), 356(4), 265(14), 199(96), 185(17), 170(18), 156(36), 105(91), 94(100), 78(31), 65(37), 51(25).
(1j). 358(36), 357(6), 356(PI, 31), 355(11), 183(25), 104(100), 94(60), 78(20), 65(13), 51(12).
(1k). 358(21), 357(4), 356(PI, 20), 355(7), 183(4), 104(100), 94(54), 78(36), 65(20), 51(24).
(1ℓ). 358(21). 357(4). 356(PI, 19), 355(12), 353(5), 184(7), 105(15), 104(100), 95(45), 94(97), 91(9), 78(16), 51(12).
(1m). 445(1), 444(0.2), 443(PI, 1), 335(1), 285(2), 260(33), 207(23),

185(17), 179(87), 165(54), 147(20), 119(13), 107(58), 91(65), 83(30), 78(30), 69(41), 57(88), 55(100), 50(24).

(1n). 432(PI, 1), 339(4), 260(25), 179(100), 165(39), 152(9), 94(34), 89(11), 76(9), 65(9), 51(7).

(1o). 444(16), 443(4), 442(PI, 14), 283(11), 260(18), 179(100), 165(37), 104(27), 89(9), 78(9), 51(4).

(1p). 444(1), 443(0.2), 442(PI, 1), 260(86), 183(48), 179(100), 152(12), 115(3), 103(10), 89(10), 78(6), 51(5).

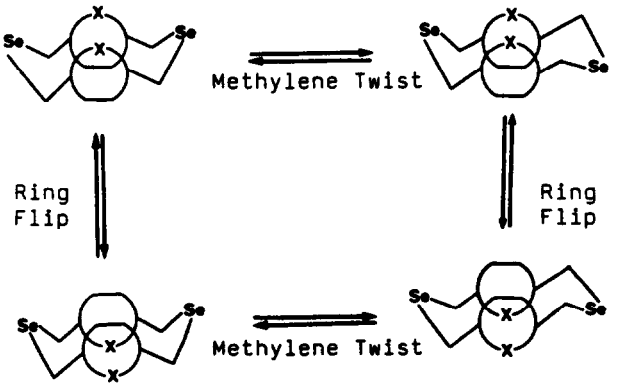
(1q). 444(11), 443(3), 442(PI, 10), 339(14), 336(5), 260(7), 184(50, 179(100), 166(37), 165(54), 152(9), 104(49), 91(6), 78(10), 63(4), 52(3).

(1r). 338(1/2 PI, 9), 260(84), 180(51), 178(100), 167(11), 166(91), 152(17), 139(5), 126(3), 89(16), 87(2), 78(2), 76(11), 63(5), 51(3).

c. PI = Parent Ion.

Results and Discussion:

^{1}H-NMR: The above compounds were identified based on their mass spectra, ^{1}H-NMR, ^{13}C-NMR and elemental analysis and in some cases in combination with their ^{77}Se-NMR spectra (Table 1). We have reported the spectral properties of (1f) in detail.[4] The ^{1}H-NMR chemical shifts of this compound were very similar to those for the thia analog reported by Newkome.[8] This indicated that the predominant conformation of (1f) is syn. Using the same argument, it can be concluded that both (1h) and (1b) are also predominantly in syn conformation in solution at room temperature. The crystal structure of (1b) has been determined by Mitchell and is syn in the solid state.[9] Variable temperature (VT) proton NMR studies of (1b) failed due to its low solubility.[3b] We have performed VT ^{1}H-NMR on both (1f) and (1h) and showed that the syn forms arising from twist of bridge methylenes can be differentiated by the non-equivalency of the bridge protons,[4] as shown below (Scheme 2) and also observed in the thia analog.[8]



Scheme 2

The replacement of one pyridine ring in (1f) by the corresponding phenyl ring to yield (1h) lowers the activation energy $\Delta G^{\neq}$ by 3.5 kJ mol^{-1} (Tc = 168°) in the latter. From this experiment we estimated that the activation energy for (1b) to be 30.4 kJ mol^{-1} (Tc = 150°). CPK model indicated that 1a is predominantly in syn conformation with the bridge methylenes and seleniums symmetric about a vertical mirror plane which is perpendicular to the plane of the phenyl ring. This accounts for the observed ^{1}H-NMR spectrum. CPK model also shows that the barrier for syn⟷anti equilibrium is small. The ^{1}H-NMR spectrum of (1c) is consistent with a syn conformation in which the bridge CH_2 and Se are symmetrical about an inversion center as evident from the CPK model of this compound. The $^{2}J_{SeH}$ can be determined from the selenium satellite peaks which accompany the methylene ^{1}H-NMR peak and are of the order of 16-20 Hz. The compounds (1d) and (1e), namely, 2,10-diselena[3.3]-2,5-furanophane and 2,10-diselena[3.3]-2,5-thiophenophane which exhibit a singlet for methylene protons and a singlet for the aromatic protons could be either syn or anti in solution. They probably undergo the conformational transformations in Scheme 2. X-ray crystallographic and VT-NMR studies are underway for these compounds to determine the predominant conformation. Replacing one of the furan rings with either a pyridine moiety or a phenyl ring, i.e, (1i-ℓ), does not alter the chemical shifts of the aromatic and bridge CH_2 protons significantly indicating a similar motion exists in the above unsymmetrical macrocycles as well.

Among the biphenyl derivatives, the CPK models consistent with the ^{1}H-NMR data indicates that compounds (1g), (1m), (1n), (1p) and (1q) are all in forms where the bridge seleniums are symmetrical about a vertical mirror plane while in (1o) they are symmetrical about an inversion center. The biphenyl rings are not coplanar in all cases as evident from the complexity of the proton signals of the biphenyl moieties. The methylene protons are AB quartets due to restricted rotation of the biphenyl moieties. When 2,2′-biphenyl is mixed with other aromatic systems like 2,6-pyridine (1m), 2,5-furyl (1n), 1,2-phenyl (1o), and 1,3-phenyl (1p) an AB pattern is observed for the CH_2 moiety of these aromatic rings as well, but the CH_2 of 1,4-phenyl when this is mixed with the biphenyl (1q) is a singlet. CPK models of these compounds clearly indicate that the CH_2 protons are equivalent in the case of 1,4-phenyl mixed with 2,2′-biphenyl and inequivalent in the case of the other aromatic rings mixed with 2,2′-biphenyl.

$^{13}C\{^{1}H\}$-NMR: The ^{13}C-NMR chemical shifts are shown in Table 1. The

chemical shifts of the syn selena compounds are similar to those of syn thia analogs where a comparison is possible.[3,9] The chemical shifts of the methylene bridge carbons of the selenaphanes in general are somewhat to the higher field compared to the thiaphanes.[3b] When furyl or pyridyl is mixed with biphenyl interesting shifts in ^{13}C position of the CH_2 are observed. When furyl is mixed with biphenyl, CH_2 of furyl moves upfield by 3.7 ppm (19.1 to 15.4) and biphenyl CH_2 moves downfield by 3.8 ppm (22.4 to 26.2). In other words the sum of the chemical shifts of the CH_2 carbons is the same in the symmetrical and unsymmetrical cyclophanes. This has an interesting effect in the case of pyridine mixed with biphenyl. The pyridine CH_2 moves upfield by 4.1 ppm (30.2 to 26.1 ppm) and the biphenyl CH_2 moves downfield by roughly same amount (22.4 to 26.1) which results in an accidental coincidence of the chemical shifts resulting in a single CH_2 line in ^{13}C-NMR. The only mixed cyclophanes whose sum of ^{13}C chemical shifts of CH_2 is not approximately the same as the sum of the shifts of the corresponding symmetrical ones are (1k), (1ℓ), (1p) and (1q). Interestingly in the mixed cyclophanes containing biphenyl moiety the CH_2 of the biphenyl occurs at around 26 ppm in every case.

$^{77}Se\{^1H\}$-NMR: The ^{77}Se-NMR chemical shifts for some of the selenacyclophanes are also listed in Table 1. A single signal was observed for ^{77}Se chemical shifts in all cases, indicating the equivalency of the selenium atoms in the compounds. The chemical shifts of the bridge Se also exhibit an interesting phenomenon. The chemical shifts move downfield as the cavity size increases as evident from the symmetrical cyclophanes of furyl, pyridyl and biphenyl. CPK space filling models indicate clearly an increase in the size of the cavity in these three symmetrical cases. When unsymmetrical cyclophanes are formed by mixing two different ring moieties this trend is still preserved. Thus mixing meta phenyl and pyridyl moves the ^{77}Se chemical shift from 358 ppm of the symmetrical pyridyl (1f), to 299 ppm in (1h), due to crowding in the cavity by an introduction of the phenyl proton. Similarly mixing biphenyl with furyl and pyridyl causes an upfield shift of ^{77}Se indicating crowding of the cavity, also observed by CPK models. VT-$^{77}Se\{^1H\}$ NMR of (1f) and (1h) showed a single peak even at the coalescence temperature for the methylene protons. This is consistent with the equilibrium in Scheme 2. VT-^{77}Se NMR of (1g) exhibited no splitting in the peak down to 160 °K in CD_2Cl_2 indicating that this compound is frozen in one conformation as evident from CPK models and VT-^1H NMR.

The position of the methylene protons and aromatic protons are essentially unaffected by the formation of unsymmetrical cyclophanes. Similarly

the position of $^{13}C\{^{1}H\}$ chemical shifts of the aromatic ring is unaffected. The values of $^{2}J_{SeH}$ fall between 17 and 21 Hz while $^{1}J_{SeC}$ values fall between 50 and 90 Hz in magnitude. The sign of $^{1}J_{SeC}$ cannot be determined by simple FT NMR. McFarlane and co-workers have shown by nuclear double resonance experiments that $^{1}J_{SeC}$ in alkyl selenides is negative and that if the magnitude of $^{1}J_{SeC}$ is $\geq$ 45 Hz it is indicative of a direct Se-C bond.[10] The $^{1}J_{SeC}$ values of the selenacyclophanes are probably negative by comparison and their magnitudes indicate a direct Se-C bond. More detailed interpretations of the values of $^{2}J_{SeH}$ and $^{1}J_{SeC}$ are difficult.

X-ray crystallographic studies of the symmetrical and mixed selenacyclophanes mentioned above are underway in order to determine their predominant conformations and understand their NMR spectra better.

Conclusion: Several [3.3]diselenacyclophanes and one [4.4]tetraselenacyclophane were prepared in high yields from the corresponding bis(selenocyanatomethyl) derivatives. Mass spectral data, ^{1}H, ^{13}C and ^{77}Se-NMR were used to characterize these compounds. Variable temperature ^{1}H, ^{13}C and ^{77}Se-NMR was performed for some compounds in order to determine their conformational behavior. Synthesis, chemical shift assignments and structural properties of these compounds were discussed.

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References:

1. Y. Sekine and V. Boekelheide, J. AM. Chem. Soc, 103, 1777 (1981).
2. a. "Cyclophanes," Vol. I and II, edited by P. M. Keehn and S. M. Rosenfeld, Academic Press (NY) 1983. b. "Topics in Current Chemistry," 113 (pp 1-183), edited by F. Vogtle, Springer-Verlag (Berlin) 1983. c. "Topics in Current Chemistry," 115 (pp 1-156), edited by F. Vogtle, Springer-Verlag (Berlin) 1983.
3. a. H. Higuchi and S. Misumi, Tetrahedron Lett., 23, 5571(1982). b. R. H. Mitchell, Can. J. Chem., 58, 1398 (1980).
4. S. Muralidharan, M. Hojjatie, M. Firestone and H. Freiser, J. Org. Chem., Accepted, to appear in January 1989 issue.
5. J. M. Griffin and L. F. Salisbury, J. Am. Chem. Soc., 70, 3416 (1948).
6. F. Vogtle and L. Schunder, Chem Ber., 102, 2677 (1969).
7. A. Biezais-Ziruis and A. Fredga, Acta Chim. Scand., 25, 1171 (1971).
8. G. R. Newkome, S. Pappalardo and F. R. Fronczek, J. Am. Chem. Soc., 105, 5152 (1983).
9. W. Anker, G. W. Bushnell and R. H. Mitchell, Can. J. Chem., 57, 3080 (1979).
10. W. McFarlane, D. S. Roycroft and C. J. Turner, Bull. Soc. Chim. Belg., 86, 457 (1977).