Heteroatom Chemistry
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Synthesis of 6aλ^4-Thia-1,6-diselena-3,4-diazapentalenes, 1,6,6aλ^4-Triselena-3,4-diazapentalenes, 6aλ^4-Thia-1,3,4,6-tetraazapentalenes, and 6aλ^4-Selena-1,3,4,6-tetraazapentalenes from Cyclic Thioureas and Selenoureas*

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ABSTRACT

*Imidazolidine-2-thione (**7a**) and the corresponding 2-selone (**7b**), hexahydropyrimidine-2-thione (**7c**) and 2-selone (**7d**), and hexahydro-1H-1,3-diazepine-2-thione (**7e**) and 2-selone (**7f**) reacted with 2,4-dinitrobenzyl chloride to give the 2-(2,4-dinitrobenzylthio) and 2-(2,4-dinitrobenzylseleno) derivatives (**8a**)–(**8f**) of 4,5-dihydroimidazolium chloride, 1,4,5,6-tetrahydropyrimidinium chloride, and 4,5,6,7-tetrahydro-1H-1,3-diazepinium chloride. Deprotonation of the chlorides (**8a**)–(**8f**) gave, respectively, 2-(2,4-dinitrobenzylthio)- and 2-(2,4-dinitrobenzylseleno)-4,5-dihydroimidazole (**9a**) and (**9b**), 2-(2,4-dinitrobenzylthio)- and 2-(2,4-dinitrobenzylseleno)-1,4,5,6-tetrahydropyrimidine (**9c**) and (**9d**), and 2-(2,4-dinitrobenzylthio)- and 2-(2,4-dinitrobenzylseleno)-4,5,6,7-tetrahydro-1H-1,3-diazepine (**9e**) and (**9f**). The bases (**9a**)–(**9f**) reacted with isoselenocyanates with elimination of 2,4-dinitrotoluene and concomitant addition of two molecules of the isoselenocyanate to give 1,6,6aλ^4-triheterapentalenes of two structural types, depending on the size of the heteroring in the bases (**9a**)–(**9f**). The imidazoles (**9a**) and (**9b**) gave 6aλ^4-thia-1,6-diselena-3,4-diazapentalenes (**10a**)–(**10j**) and 1,6,6aλ^4-triselena-3,4-diazapentalenes (**11a**)–(**11h**), respectively. The sulfur-containing bases (**9c**) and (**9e**) gave 6aλ^4-thia-1,3,4,6-tetraazapentalenes (**12a**)–(**12j**) and (**14a**)–(**14d**), respectively, and the selenium-containing bases (**9d**) and (**9f**) gave 6aλ^4-selena-1,3,4,6-tetraazapentalenes (**13a**)–(**13j**) and (**15a**)–(**15d**). Heteroatom–heteroatom covalent bond energies have been estimated for representative members of the series (**10**)–(**14**) by using the Huggins equation and experimentally determined bond lengths. © 1997 John Wiley & Sons, Inc.*

INTRODUCTION

We have shown in recent articles [1,2] that 3-methyl-6,7-dihydro-5*H*-1,2,4-thiadiazolo[4,5-*a*]pyrimidine (**1**) and 3-methyl-5,10-dihydrobenzo[*e*]-1,2,4-thiadiazolo[4,5-*a*][1,3]diazepine (**2**) react with isocyanates RNCO, isothiocyanates RNCS, and isoselenocyanates RNCSe with elimination of acetonitrile and accompanying addition of two molecules of the het-

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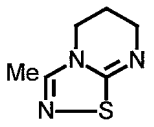
erocumulene to give 6aλ^4-thia-1,3,4,6-tetraazapentalene derivatives (**3a**), whose members constitute six groups of hypervalent heterocyclic compounds. The presence of the corresponding symmetrical isomers (**4a**) was not detected in any of these reactions. In contrast, the reaction of the isothiuronium salt (**5**) with phenyl isothiocyanate in the presence of sodium hydrogen carbonate had previously given the diazatrithiapentalene (**6**), whose structure corresponds to (**4**) [3]. The structure of compound (**6**) was established by X-ray crystallography [4]. The generality of this synthesis was not investigated. In continuation of our work on new structural variations in the triheterapentalene series, we required a general synthetic procedure that would provide compounds possessing structure (**3**) or (**4**) in which *X*, *Y*, and the size of the ring incorporating *Z* could be varied. We now give details of a general synthesis of triheterapentalenes possessing structure (**3**) or (**4**) that starts from five-, six-, and seven-membered cyclic thioureas and selenoureas (7a)–(7f).



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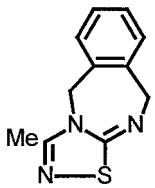

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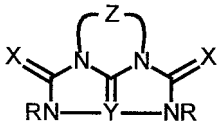

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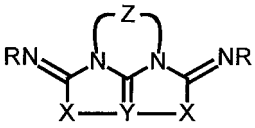
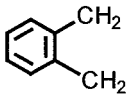


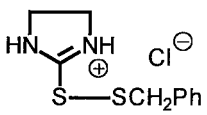
(4)

(3a), (4a) X = O, S, Se

Y = S

Z = $[CH_2]_3$,





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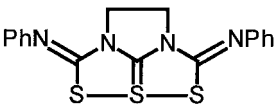

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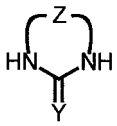
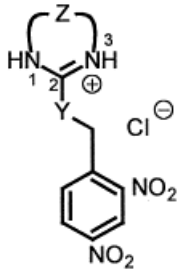


(7)

(7a)	Y = S,	Z = $[CH_2]_2$
(7b)	Y = Se,	Z = $[CH_2]_2$
(7c)	Y = S,	Z = $[CH_2]_3$
(7d)	Y = Se,	Z = $[CH_2]_3$
(7e)	Y = S,	Z = $[CH_2]_4$
(7f)	Y = Se,	Z = $[CH_2]_4$



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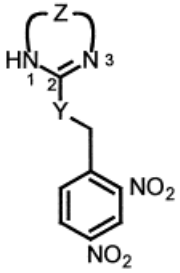
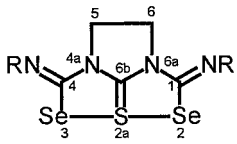


(9)

	Y	Z
(8a), (9a)	S	$[CH_2]_2$
(8b), (9b)	Se	$[CH_2]_2$
(8c), (9c)	S	$[CH_2]_3$
(8d), (9d)	Se	$[CH_2]_3$
(8e), (9e)	S	$[CH_2]_4$
(8f), (9f)	Se	$[CH_2]_4$

(8g) Y = S, Z = $[CH_2]_2$, ClO_4 for Cl



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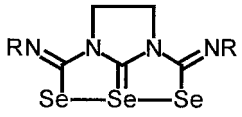


(11)

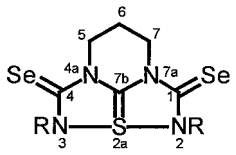
(10a)	R = Et	**(11a)**	R = Et
(10b)	R = n-Bu	**(11b)**	R = n-C_4H_9
(10c)	R = c-C_6H_{11}	**(11c)**	R = c-C_6H_{11}
(10d)	R = $PhCH_2$	**(11d)**	R = $PhCH_2$
(10e)	R = $Ph[CH_2]_2$	**(11e)**	R = 4-MeC_6H_4
(10f)	R = 4-MeC_6H_4	**(11f)**	R = 4-$MeOC_6H_4$
(10g)	R = $MeOC_6H_4$	**(11g)**	R = 3-$EtOC_6H_4$
(10h)	R = 4-BrC_6H_4	**(11h)**	R = 2-$EtOC_6H_4$
(10i)	R = 3-$EtOC_6H_4$		
(10j)	R = 2-$EtOC_6H4$		

RESULTS AND DISCUSSION

The cyclic thioureas and selenoureas (**7a**)–(**7f**) reacted readily with 2,4-dinitrobenzyl chloride in boiling ethanol to give, respectively, the chloride (**8a**) as an oil and the chlorides (**8b**)–(**8f**) as crystalline solids in high yield. The chloride (**8a**) was converted into the perchlorate (**8g**) for characterization. Treatment of the chlorides (**8a**)–(**8f**) with aqueous sodium carbonate gave the corresponding bases (**9a**)–(**9f**). The imidazoline (**9a**) was a stable solid and was fully characterized. The pyrimidine (**9c**) and the diazepine (**9e**) were obtained as solids that were characterized by their ^{1}H- and ^{13}C-NMR spectra but could not be obtained analytically pure. The selenium-containing bases (**9b**), (**9d**), and (**9f**) decompose slowly at ambient temperatures to multicomponent red materials and were used for further reaction immediately after preparation.

The imidazoline (**9a**) reacted readily with isoselenocyanates, rapidly in boiling toluene or more slowly in dichloromethane at ambient temperatures. Addition of two molecules of the isoselenocyanate took place with accompanying elimination of 2,4-dinitrotoluene to give the thiadiselenadiazapentalenes (**10a**)–(**10j**). The 2,4-dinitrotoluene was isolated and identified in selected reactions. In a similar manner, the imidazoline (**9b**) reacted with isoselenocyanates in dichloromethane at ambient temperatures to give the triselenadiazapentalenes (**11a**)–(**11h**). The structures of the triheterapentalenes (**10**) and (**11**) were established by X-ray crystal structure determinations of the respective representative members (**10f**) [5] and (**11a**) [6].

The pyrimidines (**9c**) and (**9d**) reacted with isoselenocyanates in dichloromethane at ambient temperatures to give, respectively, the 6aλ^4-thia-1,3,4,6-tetraazapentalene diselones (**12a**)–(**12j**) and the 6aλ^4-selena-1,3,4,6-tetraazapentalene diselones (**13a**)–(**13g**). The majority of the 6aλ^4-thia-1,3,4,6-tetraazapentalenes, namely, (**12a**)–(**12h**), had previously been obtained [2] by reaction of the base (**1**) with the relevant isoselenocyanate, and the structure of (**12c**) had been determined by X-ray crystallography [7]. The structure of the 6aλ^4-selena-1,3,4,6-tetraazapentalenes (**13**) has been established by an X-ray crystal structure determination of the representative member (**13a**) [6].



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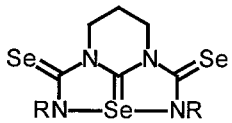
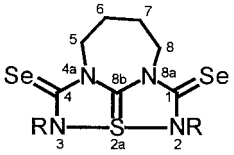


(13)

(12a)	R = Et	**(13a)**	R = Et
(12b)	R = n-C_4H_9	**(13b)**	R = n-C_4H_9
(12c)	R = c-C_6H_{11}	**(13c)**	R = c-C_6H_{11}
(12d)	R = $PhCH_2$	**(13d)**	R = $PhCH_2$
(12e)	R = $Ph[CH_2]_2$	**(13e)**	R = 4-MeC_6H_4
(12f)	R = 4-MeC_6H_4	**(13f)**	R = 4-$MeOC_6H_4$
(12g)	R = $MeOC_6H_4$	**(13g)**	R = 3-$EtOC_6H_4$
(12h)	R = 2-$EtOC_6H_4$		
(12i)	R = 3-$EtOC_6H_4$		
(12j)	R = 4-BrC_6H4		

The diazepines (**9e**) and (**9f**) reacted slowly with isoselenocyanates in dichloromethane to give the 6aλ^4-thia-1,3,4,6-tetraazapentalene diselones (**14a**)–(**14d**) and the 6aλ^4-selena-1,3,4,6-tetraazapentalene diselones (**15a**)–(**15d**), respectively. The presence of the 6aλ^4-thia-1,3,4,6-tetraazapentalene ring system in the diselones (**14**) was confirmed by an X-ray crystal structure determination of the diphenyl derivative (**14b**) [8]. The assigned structure of the diselones (**15a**)–(**15d**) rests on comparative ^{13}C-NMR spectral evidence. The ^{13}C-NMR spectra of the N–S–N diselones (**14a**)–(**14d**) show two diagnostic low-field sig-

nals below δ = 160 arising from C-8b (range δ = 161.7–164.3) and C-1(4) (range δ = 169.2–170.4). Two low-field signals are also present in the ^{13}C-NMR spectra of the N–Se–N diselones (**15a**)–(**15d**) in the ranges δ = 166.3–167.4 and δ = 170.1–172.0, which we attribute to C-8b and C-1(4), respectively. The alternative structure to the diselone structure (**15**), namely (**4**; X = Y = Se, Z = $[CH_2]_4$), contains the C=N moiety that would give rise to a ^{13}C signal at ca. δ = 150. For comparison, the thiadiselenapentalenes (**10**) and the triselenapentalenes (**11**) show ^{13}C signals arising from C=N in the ranges δ = 146.8–152.8 and δ = 146.8–153.0, respectively.



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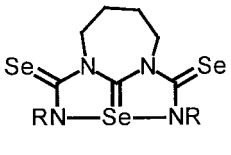
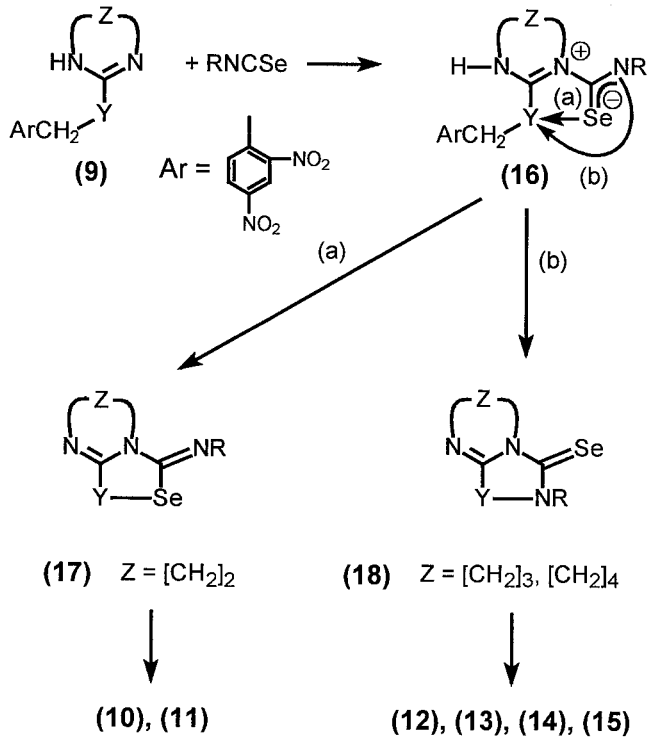


(15)

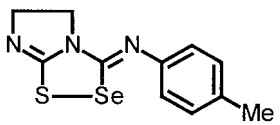
(14a)	R = $PhCH_2$	**(15a)**	R = $PhCH_2$
(14b)	R = Ph	**(15b)**	R = Ph
(14c)	R = 4-MeC_6H_4	**(15c)**	R = 4-MeC_6H_4
(14d)	R = 4-$MeOC_6H_4$	**(15d)**	R = 4-$MeOC_6H_4$

A possible route from the bases (**9**) to the triheterapentalenes (**10**)–(**15**) is given in Scheme 1. Reaction of the bases (**9**) with the isoselenocyanate RNCSe gives the zwitterions (**16**) in which intramolecular nucleophilic attack by selenium [path (a)] or nitrogen [path (b)] results in the formation of (**17**) or (**18**), respectively, and concomitant elimination of 2,4-dinitrotoluene. Breaking of the $ArCH_2$–Y bond is assisted by the stability of the 2,4-dinitrobenzyl anion. Subsequent reaction of (**17**) with the excess of the isoselenocyanate would give the triheterapentalenes (**10**) or (**11**), and reaction of (**18**) with the isoselenocyanate would lead to the products (**12**), (**13**), (**14**), or (**15**).

Evidence for the intermediacy of heterocycles having structure (**17**) or (**18**) was obtained by following the reactions of the base (**9a**) with isoselenocyanates spectroscopically. The ^{1}H-NMR spectrum of a freshly prepared solution of (**9a**) and 4-methylphenyl isoselenocyanate (2:3 molar ratio) in $CDCl_3$ showed three singlets at δ = 2.72, 3.64, and 4.56 arising from the Me group in 2,4-dinitrotoluene, the CH_2 groups in (**9a**), and the CH_2 groups in the product (**10f**), respectively, together with two triplets of equal intensity at δ = 4.05 and 4.48. After 2 hours, the concentration of 2,4-dinitrotoluene had increased, and some of the thiadiselenapentalene (**10f**) had separated from the solution. It seems likely that the triplets arise from the CH_2 groups of the intermediate (**19**) or its isomer (**20**). Experiments to isolate and characterize compounds having structure (**17**) or (**18**) are in progress.



SCHEME 1 SCHEME 1



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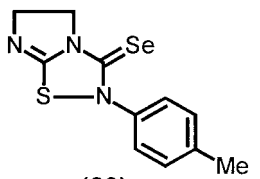
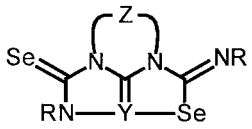


(20)

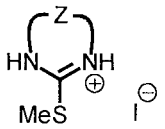
The reaction of the bases (**9**) with isoselenocyanates gave invariably the C_{2v}-symmetrical products (**10**)–(**15**), and there was no evidence for the presence of isomers possessing the less symmetrical structures (**21**). Nevertheless, the possibility that compounds (**21**) are present as intermediates in solution at low concentration cannot be discounted at present.



(21)

Y = S, Se

Z = $[CH_2]_2$, $[CH_2]_3$, $[CH_2]_4$



(22a) Z = $[CH_2]_2$

(22b) Z = $[CH_2]_3$

(22c) Z = $[CH_2]_4$

The reactions of the five-membered ring bases (**9a**) and (**9b**) with isoselenocyanates result in the eventual formation of triheterapentalenes (**10**) and (**11**) in which Y–Se bonds (Y = S, Se) have been formed, whereas the reactions of the six- and seven-membered ring bases (**9c**)–(**9f**) with isoselenocyanates leads to the triheterapentalenes (**12**)–(**15**) in which Y–N bonds have been formed. We postpone a discussion to rationalize the difference in outcome of these reactions until we have prepared the presumed intermediate bases (**17**) and/or (**18**) and studied their reactions with isoselenocyanates.

Compounds (**10f**), (**11a**), (**12c**), (**13a**), and (**14b**) show in the heteroatom moieties Se–S–Se, Se–Se–Se, N–S–N, and N–Se–N the structural features characteristic of the hypervalent three-center four-electron system in 1,6,6aλ^4-triheterapentalenes. First, the S–Se, Se–Se, S–N, and Se–N bonds are long. Their lengths are greater by more than 9% than the corresponding two-center two-electron bond lengths based on the sum of the covalent radii of the respective heteroatoms (Table 1). Second, the internal bond angle of the heteroatom sequence is large, ranging from 159.4° in (**13a**) to 174.3° in (**10f**) (Table 1). This is a consequence of the heteroatom sequence tending to adopt the colinear arrangement preferred energetically by the atoms in a three-center four-electron system [10]. Further details of the structures of (**10f**), (**11a**), (**12c**), (**13a**), and (**14b**) and discussions are given in the references cited.

The strength of a covalent bond *A–B* can be estimated by using the Huggins equation [11]

$$D_{A-B} = 10^2(r_A^* + r_B^* - d_{A-B}),$$

where D_{A-B} is the bond dissociation energy in kcal mol^{-1}, d_{A-B} is the observed bond length, and r_A^* and r_B^* are the calculated constant energy radii for the atoms *A* and *B*. Using this equation, we have calculated the bond dissociation energy *D* for each of the three-center heteroatom bonds in (**10f**), (**11a**), (**12c**), (**13a**), and (**14b**). The results, summarized in Table 1, show that the three-center bonds in these compounds are weak, being of the order of 20 kcal mol^{-1} for the S–N and Se–N bonds and 11 kcal mol^{-1} for the S–Se and Se–Se bonds.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H-NMR spectra were determined at 200.13 MHz, and ^{13}C-NMR spectra at 50.32 MHz with a Bruker AC200 spectrometer. ^{1}H- and ^{13}C-NMR spectra were obtained using solutions in $CDCl_3$, unless otherwise stated. ^{1}H-NMR chemical shifts are given in parts per million downfield from tetramethylsilane as internal reference. Unless otherwise stated, δ values refer to singlet absorptions. Data are given in the following order: δ value, number of protons, multiplicity (d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet; br, broad), *J* (Hz), and assignment. ^{1}H-NMR signals assigned to the pairs of *o* and *m* protons of *p*-substituted phenyl groups correspond to the midpoints between the two most intense signals in the *AA′* and *BB′* multiplets. ^{13}C-NMR chemical shifts are given relative to the central deuteriochloroform peak taken as δ = 77.00 and are proton-decoupled values.

Extracts were dried over sodium sulfate. Solvents were removed from extracts and chromatographic eluates with a rotary evaporator. Ether denotes diethyl ether. Acetonitrile, benzene, chloroform, dichloromethane, ethanol, hexane, methanol, and toluene were dried by standard procedures and distilled before use. Solvent mixtures are described in ratios by volume. Triethylamine was refluxed over calcium hydride and then distilled before use. Column chromatography was carried out with silica (85–200 mesh).

Preparation of Triethylammonium Hydrogen Selenide in Ethanol

Hydrogen selenide was generated slowly by dropwise addition of water (30 mL) over 30 minutes and 3M sulfuric acid (37.5 mL) over a further 30 minutes to crushed aluminum selenide (17.34 g, 60 mmol) in a nitrogen atmosphere and carried in a slow stream of nitrogen into a solution of triethylamine (40 mL, 287 mmol) in ethanol (250 mL). The resulting solution contained ca. 0.15 mole of triethylammonium hydrogen selenide.

Preparation of the Cyclic Thioureas and Selenoureas (**7**)

Imidazolidine-2-thione (**7a**) was obtained from commercial sources. Hexahydropyrimidine-2-thione

TABLE 1 Heteroatom–heteroatom Bond Lengths, Bond Angles, and Bond Dissociation Energies in the Triheterapentalenes (**10f**), (**11a**), (**12c**), (**13a**), and (**14b**)

Compound	Bond		Bond Lengths (Å)	% Bond Elongation[a]		Bond Angle (deg)	Bond Dissociation Energy D (kcal mol^{-1})	Reference
(**10f**)	S–Se	(*A*)[b]	2.504(4)	13.3	(*A*)[b]	Se–S–Se	11.8	[5]
			2.532(4)	14.6		174.0(1)	10.4	
		(*B*)[b]	2.500(4)	13.1	(*B*)[b]	Se–S–Se	12.0	
			2.566(4)	16.1		174.3(1)	8.9	
(**11a**)	Se–Se		2.597(2)	11.0		Se–Se–Se	13.4	[6]
			2.658(2)	13.6		167.5(1)	10.1	
(**12c**)	S–N		1.931(7)	11.0		N–S–N	19.9	[7]
			1.935(7)	11.2		164.8(3)	19.5	
(**13a**)	Se–N		2.044(8)	9.3		N–Se–N	20.5	[6]
			2.053(7)	9.8		159.4(4)	19.7	
(**14b**)	S–N	(*A*)[b]	1.899(3)	9.1	(*A*)[b]	N–S–N	23.0	[8]
			1.910(3)	9.8		166.1(1)	21.9	
		(*B*)[b]	1.901(3)	9.3	(*B*)[b]	N–S–N	22.8	
			1.907(3)	9.6		165.6(1)	22.2	

[a]Relative to the corresponding two-center two-electron covalent bond length based on the sum of the relevant covalent radii (S–Se, 2.21 Å; Se–Se, 2.34 Å; S–N, 1.74 Å; Se–N, 1.87 Å) [9].
[b]Two molecules (*A*) and (*B*) in the unit cell.

(**7c**) [12,13] and hexahydro-1*H*-1,3-diazepine-2-thione (**7e**) [13] were prepared according to the references cited.

Imidazolidine-2-selone (**7b**). This selenourea was obtained (90%) from 4,5-dihydro-2-methylthioimidazolium iodide (**22a**) [13,14], as described by Klayman and Shine [15]. ^{1}H NMR [$(CD_3)_2SO$]: δ 3.52 (4H, 4.5-CH_2), 8.47 (2H, 1,3-NH). ^{13}C NMR [$(CD_3)_2$ SO]: δ 44.6 (4,5-CH_2), 176.8 (CSe).

Hexahydropyrimidine-2-selone (**7d**). A solution of triethylammonium hydrogen selenide in ethanol, prepared according to the foregoing procedure using aluminum selenide (17.45 g), triethylamine (40 mL), and ethanol (250 mL), was added to a stirred suspension of 1,4,5,6-tetrahydro-2-methylthiopyrimidinium iodide (**22b**) (19.36 g, 75 mmol) [12,13] in ethanol (50 mL) under nitrogen, and the resulting mixture was stirred until all the iodide had dissolved. The solution was then kept in the dark with exclusion of air for 3 days. The solid that had crystallized was filtered off and washed with ether (2 × 20 mL). The mother liquor was concentrated at reduced pressure to ca. 150 mL, then cooled to 0–5°C to yield a second crop of product. Recrystallization of the combined crops of solid from ethanol under nitrogen gave hexahydropyrimidine-2-selone (**7d**) (7.18 g, 59%) as white plates, mp 216–218°C (decomposition); ^{1}H NMR [$(CD_3)_2SO$]: δ 1.76 (2H, quint, 5-CH_2), 3.09 (4H, t, 4,6-CH_2), 8.27 (2H, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 18.5 (C-5), 39.9 (C-4, C-6), 168.6 (CSe). Anal. calcd for $C_4H_8N_2Se$: C, 29.46; H, 4.94; N, 17.18. Found: C, 29.49; H, 4.87; N, 17.24%.

Hexahydro-1H-1,3-diazepine-2-selone (**7f**). 4,5,6,7-Tetrahydro-2-methylthio-1*H*-1,3-diazepinium iodide (**22c**) was prepared (85%) from the thiourea (**7e**) [13] as described by McKay and Krelig [13]. ^{1}H NMR [$(CD_3)_2SO$]: δ 1.74 (4H, quint, 5,6-CH_2), 2.60 (3H, SMe), 3.43 (4H, brs, 4,7-CH_2), 9.39 (2H, 1,3-NH). ^{13}C NMR [$(CD_3)_2SO$]: δ 15.1 (C-5, C-6), 25.2 (SMe), 45.5 (C-4, C-7). The iodide (**33c**) (13.61 g, 50 mmol) was added to a stirred solution of sodium hydrogen selenide that had been prepared from selenium (6.0 g, 76 mmol) and sodium borohydride (3.18 g, 84 mmol) in ethanol (250 mL) under nitrogen according to the procedure of Klayman and Shine [15]. The mixture was stirred for 2 hours or until all the iodide had dissolved, then it was kept for 3 days with exclusion of air. The selone (**7f**) (7.08 g, 80%) that had crystallized was filtered off, washed with ether (2 × 20 mL), and dried. A sample for characterization was recrystallized from methanol under nitrogen and obtained as white needles, mp 192–200°C (decomposition); ^{1}H NMR [$(CD_3)_2SO$]: δ 1.63 (4H, brs, 5,6-CH_2), 3.12 (4H, brs, 4,7-CH_2), 8.18 (2H, brs, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 26.5 (C-5, C-6), 45.0 (C-4, C-7), 180.9 (CS). Anal. calcd for $C_5H_{10}N_2Se$: C, 33.91; H, 5.69; N, 15.82. Found: C, 33.85; H, 5.64; N, 15.82%.

Reactions of the Thioureas and Selenoureas (**7a**)–(**7f**) *with 2,4-Dinitrobenzyl Chloride: Preparation of the Salts* (**8a**)–(**8f**)

2-(2,4-Dinitrobenzylthio)-4,5-dihydroimidazolium Chloride (**8a**). A mixture of imidazolidine-2-thione (**7a**) (2.55 g, 25 mmol) and 2,4-dinitrobenzyl chloride (5.42 g, 25 mmol) in ethanol (30 mL) was boiled for 75 minutes. The solution was cooled, solvent was removed at reduced pressure, and ether (200 mL) was added gradually to the residual oil with swirling. The chloride (**8a**) formed a lower oily layer that did not crystallize. The upper ether layer was decanted, and the lower oily layer of the salt was dissolved in water (50 mL) for conversion into the base (**9a**), as subsequently described.

2-(2,4-Dinitrobenzylseleno)-4,5-dihydroimidazolium Chloride (**8b**). A mixture of imidazolidine-2-selone (**7b**) (3.73 g, 25 mmol) and 2,4-dinitrobenzyl chloride (5.42 g, 25 mmol) in ethanol (30 mL) was boiled in a nitrogen atmosphere for 15 minutes. The solution was cooled, and ether (200 mL) was added to complete the precipitation of the solid that had partly crystallized. The solid was filtered off, washed with ether (2 × 10 mL), and dried, giving the pure chloride (**8b**) (9.75 g, 96%). A sample for characterization was recrystallized from acetonitrile–ether and obtained as pale yellow plates, mp 165–168°C; ^{1}H NMR [$(CD_3)_2SO$]: δ 3.87 (4H, 4,5-CH_2), 5.03 (2H, $SeCH_2$), 8.25 (1H, d, *J* 8.6, 6-H of Ar), 8.55 (1H, dd, *J* 8.6 and 2.4, 5-H of Ar), 8.74 (1H, d, *J* 2.4, 3-H of Ar), 11.06 (2H, brs, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 26.3 ($SeCH_2$), 45.4 (C-4, C-5), 120.7, 128.3, 133.7 (C-3, C-5, C-6 of Ar), 140.0 (C-1 of Ar), 146.8, 147.2 (C-2, C-4 of Ar), 163.4 (C-2). Anal. calcd for $C_{10}H_{11}ClN_4O_4Se$: C, 32.85; H, 3.03; N, 15.32. Found: C, 32.90; H, 2.99; N, 15.35%.

2-(2,4-Dinitrobenzylthio)-1,4,5,6-tetrahydropyrimidinium Chloride (**8c**). A mixture of hexahydropyrimidine-2-thione (**7c**) (2.91 g, 25 mmol) and 2,4-dinitrobenzyl chloride (5.42 g, 25 mmol) in ethanol (30 mL) was boiled for 75 minutes. Ether (30 mL) was added gradually to the cooled solution, and the solid that crystallized was filtered off, washed with ether (2 × 5 mL), and dried. The chloride (**8c**) (8.06 g, 97%) was thus obtained as pale yellow plates, mp 188–189°C after recrystallization from acetonitrile–ether; ^{1}H NMR [$(CD_3)_2SO$]: δ 1.82 (2H, quint, 5-CH_2), 3.35 (4H, t, 4,6-CH_2), 5.08 (2H, SCH_2), 8.17 (1H, d, *J* 8.6, 6-H of Ar), 8.60 (1H, dd, *J* 8.6 and 2.4, 5-H of Ar), 8.80 (1H, d, *J* 2.4, 3-H of Ar), 10.67 (2H, brs, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 17.9 (C-5), 31.8 (SCH_2), 39.9 (C-4, C-6), 120.7, 128.1, 133.5 (C-3, C-5, C-6 of Ar), 138.0 (C-1 of Ar), 147.0, 147.5 (C-2, C-4 of Ar), 159.0 (C-2). Anal. calcd for $C_{11}H_{13}ClN_4O_4S$: C, 39.71; H, 3.94; N, 16.68. Found: C, 39.66; H, 3.85; N, 17.07%.

2-(2,4-Dinitrobenzylseleno)-1,4,5,6-tetrahydropyrimidinium Chloride (**8d**). A mixture of hexahydropyrimidine-2-selone (**7d**) (4.08 g, 25 mmol) and 2,4-dinitrobenzyl chloride (5.42 g, 25 mmol) in ethanol (25 mL) and methanol (25 mL) was refluxed in a nitrogen atmosphere for 15 minutes. Solvent was removed at reduced pressure from the cooled solution, and ether (30 mL) was added to the residue. The chloride (**8d**) that precipitated was filtered off, washed with ether, and dried (9.01 g, 95%). Recrystallization of a sample from acetonitrile–ether gave (**8d**) as pale yellow plates, mp 157–161°C; ^{1}H NMR [$(CD_3)_2SO$]: δ 1.85 (2H, quint, 5-CH_2), 3.37 (4H, t, 4,6-CH_2), 4.99 (2H, $SeCH_2$), 8.12 (1H, d, *J* 8.6, 6-H of Ar), 8.58 (1H, dd, *J* 8.6 and 2.4; 5-H of Ar), 8.79 (1H, d, *J* 2.4, 3-H of Ar), 10.62 (2H, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 17.9 (C-5), 26.9 ($SeCH_2$), 40.4 (C-4, C-6), 120.6, 128.1, 133.7 (C-3, C-5, C-6 of Ar), 140.4 (C-1 of Ar), 146.6, 147.2 (C-2, C-4 of Ar), 154.5 (C-2). Anal. calcd for $C_{12}H_{13}ClN_4O_4Se$: C, 34.80; H, 3.45; N, 14.76. Found: C, 34.55; H, 3.32; N, 14.65%.

2-(2,4-Dinitrobenzylthio)-4,5,6,7-tetrahydro-1H-1,3-diazepinium Chloride (**8e**). A mixture of hexahydro-1*H*-1,3-diazepine-2-thione (**7e**) (3.26 g, 25 mmol) and 2,4-dinitrobenzyl chloride (5.42 g, 25 mmol) in methanol (75 mL) was refluxed for 20 minutes. The chloride (**8e**) (7.01 g) that had crystallized from the cooled solution was filtered off, washed with ether (25 mL), and dried. The methanol filtrate was concentrated to low volume, acetone (20 mL) was added, and the solid (1.01 g) that remained undissolved was filtered off, washed with ether (2 × 5 mL), and combined with the first crop of chloride (**8e**) (total yield 8.02 g, 93%). A sample recrystallized from methanol–ether for characterization was obtained as pale yellow plates, mp 194–195°C; ^{1}H NMR [$(CD_3)_2SO$]: δ 1.66 (4H, brs, 5,6-CH_2), 3.35 (4H, brs, 4, 7-CH_2), 5.02 (2H, SCH_2), 8.08 (1H, d, *J* 8.5, 6-H of Ar), 8.60 (1H, dd, *J* 8.5 and 2.4, 5-H of Ar), 8.81 (1H, d, *J* 2.4, 3-H of Ar), 10.36 (2H, brs, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 25.1 (C-5, C-6), 33.2 (SCH_2), 45.5 (C-4, C-7), 120.8, 128.2, 133.7 (C-3, C-5, C-6 of Ar), 138.1 (C-1 of Ar), 147.1, 147.6 (C-2, C-4 of Ar), 166.7 (C-2). Anal. calcd for $C_{12}H_{15}ClN_4O_4S$: C, 41.56; H, 4.36; N, 16.15. Found: C, 41.89; H, 4.23; N, 16.19%.

2-(2,4-Dinitrobenzylseleno)-4,5,6,7-tetrahydro-1H-1,3-diazepinium Chloride (**8f**). The procedure was identical with that of the preceding experiment,

with the selone (**7f**) (4.43 g, 25 mmol) in place of the thione (**7e**). The chloride (**8f**) (9.01 g, 92%) was obtained as pale yellow plates, mp 186–187°C; ^{1}H NMR [$(CD_3)_2SO$]: δ 1.70 (4H, brs, 5,6-CH_2), 3.42 (4H, brs, 4,7-CH_2), 4.95 (2H, $SeCH_2$), 8.05 (1H, d, *J* 8.6, 6-H of Ar), 8.58 (1H, dd, *J* 8.6 and 2.4, 5-H of Ar), 8.79 (1H, d, *J* 2.4, 3-H of Ar), 10.37 (2H, brs, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 25.2 (C-5, C-6), 28.2 ($SeCH_2$), 46.0 (C-4, C-7), 120.8, 128.1, 133.7 (C-3, C-5, C-6 of Ar), 140.4 (C-1 of Ar), 146.8, 147.3 (C-2, C-4 of Ar), 163.2 (C-2).

Preparation of the Bases (**9a**)–(**9f**) *from the Corresponding Salts* (**8a**)–(**8f**)

2-(2,4-Dinitrobenzylthio)-4,5-dihydroimidazole (**9a**). Sodium carbonate (5 g, 47.2 mmol) was added to a solution of the oily chloride (**8a**) in water (50 mL), prepared from the thiourea (**7a**) (2.55 g, 25 mmol) and 2,4-dinitrobenzyl chloride (5.42 g, 25 mmol), as described previously. The resulting solution was swirled (effervescence), then extracted with dichloromethane (3 × 200 mL). Solvent was removed at reduced pressure from the combined dried extracts. Recrystallization of the residual solid from hexane–benzene (4:1) gave the base (**9a**) (6.17 g, 87%) as pale yellow plates, mp 101–102°C; ^{1}H NMR: δ 3.65 (4H, 4,5-CH_2), 4.46 (1H, vbrs, NH), 4.67 (2H, SCH_2), 8.08 (1H, d, *J* 8.6, 6-H of Ar), 8.40 (1H, dd, *J* 8.6 and 2.4, 5-H of Ar), 8.84 (1H, d, *J* 2.4, 3-H of Ar); ^{13}C NMR: δ 31.8 (SCH_2), 50.6 (vbrs, C-4, C-5), 120.3, 127.2, 134.3 (C-3, C-5, C-6 of Ar), 141.1 (C-1 of Ar), 146.8, 147.9 (C-2, C-4 of Ar), 162.2 (C-2). Anal. calcd for $C_{10}H_{10}N_4O_4S$: C, 42.55; H, 3.57; N, 19.85. Found: C, 42.41; H, 3.50; N, 19.74%.

Perchloric acid (70–72% w/w, 1 mL) in acetonitrile (4 mL) was added to a solution of the base (**9e**) (564 mg, 2 mmol) in dichloromethane (3 mL). Addition of ether (50 mL) to the resulting solution precipitated 2-(2,4-dinitrobenzylthio)-4,5-dihydroimidazolium perchlorate (**8g**), which was filtered off, washed with much ether, and dried *in vacuo* at room temperature. The salt (**8g**) (736 mg, 96%) was thus obtained as pale yellow plates, mp 141–143°C after recrystallization from acetone–ether (1:5); ^{1}H NMR [$(CD_3)_2SO$]: δ 3.90 (4H, 4,5-CH_2), 4.90 (2H, SCH_2), 8.08 (1H, d, *J* 8.6, 6-H of Ar), 8.62 (1H, dd, *J* 8.6 and 2.4, 5-H of Ar), 8.82 (1H, d, *J* 2.4, 3-H of Ar), 10.32 (2H, 1,3-NH); ^{13}C NMR [$(CD_3)_2SO$]: δ 32.0 (SCH_2), 45.2 (4,5-CH_2), 120.7, 128.4, 133.1 (C-3, C-5, C-6 of Ar), 137.1 (C-1 of Ar), 147.2, 147.8 (C-2, C-4 of Ar), 167.6 (C-2). Anal. calcd for $C_{10}H_{11}ClN_4O_8S$: C, 31.38; H, 2.90; N, 14.64. Found: C, 31.11; H, 2.78; N, 14.75%.

2-(2,4-Dinitrobenzylthio)-1,4,5,6-tetrahydropyrimidine (**9c**). Sodium carbonate (5 g, 47.2 mmol) was added to a solution of the chloride (**8c**) (8.06 g, 24.2 mmol) in water (50 mL). The resulting mixture was swirled to expel carbon dioxide, then extracted with dichloromethane (3 × 200 mL). Solvent was removed at reduced pressure from the dried extracts, and the residual solid was recrystallized from hexane–dichloromethane (5:1). The base (**9c**) (5.93 g, 83%) was obtained as pale yellow plates, mp 91–92°C; ^{1}H NMR: δ 1.73 (2H, quint, 5-CH_2), 3.3 (4H, t, 4,6-CH_2), 4.50 (2H, brs, SCH_2), 4.62 (1H, vbrs, NH), 7.92 (1H, d, *J* 8.6, 6-H of Ar), 8.32 (1H, dd, *J* 8.6 and 2.4, 5-H of Ar), 8.78 (1H, d, *J* 2.4, 3-H of Ar); ^{13}C NMR: δ 21.4 (C-5), 30.4 (SCH_2), 43.0 (C-4, C-6), 120.0, 126.8, 134.1 (C-3, C-5, C-6 of Ar), 142.2 (C-1 of Ar), 146.4, 148.1 (C-2, C-4 of Ar), 151.1 (C-2). Due to slow decomposition in solution, the base (**9c**) could not be crystallized with sufficient purity for elemental analysis.

2-(2,4-Dinitrobenzylthio)-4,5,6,7-tetrahydro-1H-1,3-diazepine (**9e**). The chloride (**8e**) (3.47 g, 10 mmol) was added to a saturated solution of sodium carbonate in water (20 mL). The mixture was swirled and then extracted with dichloromethane (2 × 30 mL). Solvent was removed at reduced pressure from the dried extracts, and the residual solid was dissolved in benzene (30 mL). The benzene was removed at reduced pressure, and the residual solid was redissolved in dichloromethane (10 mL). Addition of hexane (50 mL) to the solution precipitated the base (**9e**) (1.86 g, 60%) as red needles that could not be purified further due to gradual decomposition in solution. The product was characterized by NMR spectroscopy. ^{1}H NMR: δ 1.60 (4H, brs, 5,6-CH_2), 3.22 (4H, brs, 4,7-CH_2), 4.29 (1H, vbrs, NH), 4.49 (2H, SCH_2), 7.91 (1H, d, *J* 8.6, 6-H of Ar), 8.35 (1H, dd, *J* 8.6 and 2.3, 5-H of Ar), 8.78 (1H, d, *J* 2.3, 3-H of Ar); ^{13}C NMR: δ 28.5 (C-5, C-6), 32.9 (SCH_2), 48.7 (C-4, C-7), 120.1, 126.8, 134.0 (C-3, C-5, C-6 of Ar), 142.3 (C-1 of Ar), 146.5, 148.2 (C-2, C-4 of Ar), 156.3 (C-2).

The 2,4-dinitrobenzylseleno bases (**9b**), (**9d**), and (**9f**) obtained by deprotonation of the corresponding salts (**8b**), (**8d**), and (**8f**) are unstable in solution, could not be obtained pure for characterization, and gradually became deep red on standing at room temperature. The deprotonation products containing (**9b**), (**9d**), and (**9f**) were therefore used for further reaction immediately after preparation, as described in the following sections.

Reactions of 2-(2,4-Dinitrobenzylthio)-4,5-dihydroimidazole (**9a**) *and 2-(2,4-Dinitrobenzylseleno)-4,5-dihydroimidazole* (**9b**) *with Isoselenocyanates: Synthesis of the 6aλ^4-Thia-1,6-diselena-3,4-diazapentalenes* (**10a**)–(**10j**) *and the 1,6-6aλ^4-Triselena-3,4-diazapentalenes* (**11a**)–(**11h**)

The following general procedures A–C were used. Experimental details, physical properties, and analytical data are given in Table 2.

Procedure A. A solution of the dihydroimidazole (**9a**) (565 mg, 2 mmol), the isoselenocyanate (8 mmol), and triethylamine (0.5 mL, 3.6 mmol) in toluene (25 mL) was refluxed in a nitrogen atmosphere for 30 minutes. Solvent was removed at reduced pressure and dichloromethane (15 mL) and acetonitrile (30 mL) were added in succession to the residue to precipitate the triheterapentalene that was filtered off, washed with acetonitrile (2 × 2mL), and recrystallized from acetonitrile–dichloromethane (ca. 5:1).

Procedure B. A solution of the dihydroimidazole (**9a**) (565 g, 2 mmol) and the alkyl isoselenocyanate (8 mmol) in dichloromethane (20 mL) was kept in darkness for 24 hours. Solvent was removed at reduced pressure, and the residual solid was recrystallized from acetonitrile–dichloromethane (ca. 5:1).

Procedure C. Sodium carbonate (5 g, 47.2 mmol) was added to a solution of the chloride (**8b**) (731 mg, 2 mmol) in water (20 mL). The mixture was swirled and then extracted with dichloromethane (2 × 20 mL). Solvent was removed from the combined dried extracts, and the residue was redissolved in benzene (10 mL). The benzene was removed at reduced pressure from a flask kept below 30°C, and the residual solid containing the dihydroimidazole (**9b**) was dissolved in a solution of the isoselenocyanate (8 mmol) in dichloromethane (20 mL). The resulting solution was kept in darkness for 48 hours. The triheterapentalene (**11**) that crystallized was filtered off and washed with acetonitrile. Compounds (**11**) obtained from alkyl isoselenocyanates were recrystallized from acetonitrile–dichloromethane (3:1), and those obtained from aryl isoselenocyanates were recrystallized from the solvent indicated in Table 2.

Reactions of 2-(2,4-Dinitrobenzylthio)-1,4,5,6-tetrahydropyrimidine (**9c**) *with Isoselenocyanates; Synthesis of the 6aλ^4-Thia-1,3,4,6-tetraazapentalenes* (**12a**)–(**12j**)

The following general procedures A and B were used.

Procedure A. A solution of the pyrimidine (**9c**) (592 mg, 2 mmol) and the isoselenocyanate (8 mmol) in dichloromethane (25 mL) was kept in darkness for 24 hours. Solvent was removed from the solution at reduced pressure, and the residue was dissolved in dichloromethane (20 mL). Addition of acetonitrile (30 mL) to the solution precipitated the triheterapentalene (**12**), which was filtered off and recrystallized from acetonitrile–dichloromethane (1:1). These products were shown to be identical with the triheterapentalenes previously obtained [2] by reaction of the pyrimidine (**7**) with the corresponding isoselenocyanates, on the basis of mp and mixed mp determinations and by comparison of TLC behavior and ^{1}H-NMR spectra. The following triheterapentalenes were obtained, all as pale yellow crystals.

2,3-Diethyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12a**). From ethyl isoselenocyanate; yield 66%; mp 208–210°C (Ref. [2] mp 208–210°C).

2,3-Dibutyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12b**). From butyl isoselenocyanate; yield 48%; mp 173–174°C (Ref. [2] 170–172°C).

2,3-Dicyclohexyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12c**). From cyclohexyl isoselenocyanate; yield 57%; mp gradual decomposition >160°C (Ref [2] mp 172–180°C).

2,3-Dibenzyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12d**). From benzyl isoselenocyanate; yield 64%; mp gradual decomposition >210°C (Ref. [2] mp gradual decomposition >210°C).

2,3-Di-(2-phenylethyl)-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4-(3H)-diselone (**12e**). From 2-phenylethyl isoselenocyanate; yield 69%; mp 193–198°C (Ref. [2] mp 193–199°C).

2,3-Di-(4-methylphenyl)-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12f**). From 4-methylphenyl isoselenocyanate; yield 66%; mp 148–154°C (Ref. [2] mp 148–152°C). Solvent was removed from the acetonitrile–dichloromethane filtrate from which (**12f**) had crystallized, and the residue was chromatographed on silica (20 × 2.2 cm) with benzene. The eluates (ca. 200 mL) yielded 2,4-dinitrotoluene (237 mg, 65%), very pale yellow needles from hexane–dichloromethane (4:1), mp and mixed mp with an authentic sample 69–70°C.

TABLE 2 Preparation, Physical Properties, and Analytical Data of Compounds (**10a**)–(**10j**) and (**11a**)–(**11h**)

						Found (*%*) (*Required*)		
Compound[a]	*Procedure*	*RNCSe*	*Yield* (*%*)	*Mp* (°*C*)	*Formula*	*C*	*H*	*N*
(**10a**)	B	EtNCSe	34	145–146	$C_9H_{14}N_4SSe_2$	29.22 (29.36)	3.73 (3.83)	15.15 (15.22)
(**10b**)	A	*n*-BuNCSe	28	156–160	$C_{13}H_{22}N_4SSe_2$	36.65 (36.80)	5.20 (5.23)	13.28 (13.20)
(**10b**)	B[b]	*n*-BuNCSe	48[c]	156–160				
(**10c**)	A	c-C_6H_{11}NCSe	15	177–179	$C_{17}H_{26}N_4SSe_2$[d]	42.71 (42.86)	5.52 (5.50)	11.81 (11.76)
(**10c**)	B	c-C_6H_{11}NCSe	39	177–179				
(**10d**)	A	$PhCH_2NCSe$	65	198–199	$C_{19}H_{18}N_4SSe_2$	46.05 (46.35)	3.59 (3.68)	11.44 (11.38)
(**10e**)	A	$Ph[CH_2]_2NCSe$	50	167–171	$C_{21}H_{22}N_4SSe_2$	48.42 (48.42)	4.16 (4.26)	10.82 (10.77)
(**10f**)	A	4-MeC_6H_4NCSe	75	185–198 (decomp.)	$C_{19}H_{18}N_4SSe_2$	46.16 (46.35)	3.51 (3.68)	11.39 (11.38)
(**10g**)	A[e]	4-$MeOC_6H_4NCSe$	84[f]	198–201	$C_{19}H_{18}N_4O_2SSe_2$	43.38 (43.52)	3.43 (3.46)	10.75 (10.68)
(**10h**)	A	4-BrC_6H_4NCSe	67	242–244	$C_{17}H_{12}Br_2N_2SSe_2$	32.56 (32.82)	1.83 (1.94)	8.92 (9.01)
(**10i**)	A	3-$EtOC_6H_4NCSe$	50	148–150	$C_{21}H_{22}N_4O_2SSe_2$	45.50 (45.66)	3.95 (4.01)	10.05 (10.14)
(**10j**)	A	2-$EtOC_6H_4NCSe$	46	107–110	$C_{21}H_{22}N_4O_2SSe_2$	45.50 (45.66)	3.97 (4.01)	10.09 (10.14)
(**11a**)	C	EtNCSe	86	175–178	$C_9H_{14}N_4Se_3$[g]	26.10 (26.04)	3.33 (3.40)	13.50 (13.50)
(**11b**)	C	*n*-BuNCSe	58	182–183	$C_{13}H_{22}N_4Se_3$	33.10 (33.14)	4.66 (4.71)	11.89 (11.89)
(**11c**)	C	c-C_6H_{11}NCSe	76	201–202	$C_{17}H_{26}N_4Se_3$	39.04 (39.02)	5.05 (5.01)	10.70 (10.77)
(**11d**)	C	$PhCH_2NCse$	62	209–211	$C_{19}H_{18}N_4Se_3$	42.35 (42.32)	3.20 (3.36)	10.36 (10.39)
(**11e**)	C[h]	4-MeC_6H_4NCSe	89[i]	232–234[j]	$C_{19}H_{18}N_4Se_3$	42.62 (42.32)	3.26 (3.36)	10.34 (10.39)
(**11f**)	C	4-$MeOCH_6H_4NCSe$	89	209–211[k]	$C_{19}H_{18}N_4O_2Se_3$	40.03 (39.95)	3.02 (3.18)	9.80 (9.81)
(**11g**)	C	3-$EtOC_6H_4NCSe$	81	172–174[l]	$C_{21}H_{22}N_4O_2Se_3$	42.08 (42.09)	3.59 (3.70)	9.33 (9.35)
(**11h**)	C	2-$EtOC_6H_4NCSe$	65	193–195[m]	$C_{21}H_{22}N_4O_2Se_3$	42.11 (42.09)	3.68 (3.70)	9.33 (9.35)

[a]Compounds (**10a**)–(**10e**) were obtained as yellow crystals. Compounds (**10f**)–(**10j**) and (**11a**)–(**11h**) were obtained as orange crystals.
[b]The mother liquor was chromatographed on silica (20 × 2.2 cm) with benzene. The eluates (200 mL) yielded 2,4-dinitrotoluene as pale yellow crystals [hexane-dichloromethane (4:1)], identified by comparison with an authentic sample by mp and mixed mp (69–70°C), TLC behavior, and ^{1}H-NMR spectrum.
[c]Yield of 2,4-dinitrotoluene 153 mg (42%).
[d]Found: Se, 33.04. Required: 33.15%.
[e]The mother liquor was chromatographed on silica (16 × 2.2 cm) with benzene. The eluates (150 mL) gave 2,4-dinitrotoluene, mp 69–70°C, identified by comparison with an authentic sample by mp, mixed mp, and TLC behavior.
[f]Yield of 2,4-dinitrotoluene 254 mg (70%).
[g]Found: Se, 56.96. Required: Se, 57.06%.
[h]The mother liquor was chromatographed on silica (18 × 2.2 cm) with benzene. The eluates (150 mL) yielded 2,4-dinitrotoluene, mp and mixed mp with an authentic sample 69–70°C.
[i]Yield of 2,4-dinitrotoluene 245 mg (67%).
[j]Solvent $CHCl_3$–toluene (1:1).
[k]Solvent MeCN–CH_2Cl_2 (3:1).
[l]Solvent hexane–$CHCl_3$ (2:1).
[m]Solvent hexane–CH_2Cl_2 (2:1).

2,3-Di-(4-methoxyphenyl)-6,7-dihydro-5H-2aλ⁴-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12g**). From 4-methoxyphenyl isoselenocyanate: yield 68%; mp 172–175°C (Ref. [2] mp 171–173°C).

Procedure B. The reaction was carried out according to procedure A. The residue obtained after removal of the reaction solvent was dissolved in dichloromethane (20 mL), and cyclohexane (30 mL) was added. The precipitated triheterapentalene was filtered off and recrystallized from hexane–dichloromethane (1:1). The following compounds were obtained as yellow crystals.

2,3-Di-(2-ethoxyphenyl)-6,7-dihydro-5H-2aλ⁴-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12h**). From 2-ethoxyphenylisoselenocyanate; yield 79%; mp 144–146°C (Ref. [2] mp 143–146°C).

2,3-Di-(3-ethoxyphenyl)-6,7-dihydro-5H-2aλ⁴-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12i**). From 3-ethoxyphenyl isoselenocyanate; yield 71%; mp 108–114°C (decomposition). Anal. calcd for $C_{22}H_{24}N_4O_2SSe_2$: C, 46.65; H, 4.27; N, 9.89. Found: C, 46.65; H, 4.26; N, 9.93%.

2,3-Di-(4-bromophenyl)-6,7-dihydro-5H-2aλ⁴-thia-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**12j**). From 4-bromophenyl isoselenocyanate; yield 33%; mp 142–143°C. Anal. calcd for $C_{18}H_{14}Br_2N_4SSe_2$: C, 33.99; H, 2.22; N, 8.81. Found: C, 33.81; H, 2.12; N, 8.79%.

Satisfactory ^{1}H- and ^{13}C-NMR spectra of compounds (**12h**)–(**12j**) could not be obtained due to some decomposition in $CDCl_3$.

Reactions of 2-(2,4-Dinitrobenzylseleno)-1,4,5,6-tetrahydropyrimidine (**9d**) *with Isoselenocyanates: Synthesis of the 6aλ⁴-Selena-1,3,4,6-tetraazapentalenes* (**13a**)–(**13g**)

General Procedure. Sodium carbonate (5 g, 47.2 mmol) was added to a solution of the pyrimidinium chloride (**8d**) (759 mg, 2 mmol) in water (20 mL). The mixture was swirled and then extracted with dichloromethane (2 × 20 mL). Solvent was removed from the dried extracts, and the residue was dissolved in benzene (10 mL). The benzene was removed at reduced pressure from the solution kept below 30°C, and the residual solid containing the pyrimidine (**9d**) was dissolved in a solution of the isoselenocyanate (10 mmol) in dichloromethane (30 mL). The resulting solution was kept in darkness for 48 hours. Solvent was removed at reduced pressure, and the residual solid was recrystallized from hexane–dichloromethane (3:1). The following selenatetraazapentalenes were obtained by this procedure as yellow crystals.

2,3-Diethyl-6,7-dihydro-5H-2aλ⁴-selena-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**13a**). From ethyl isoselenocyanate; yield 68%; mp 195–196°C; ^{1}H NMR: δ 1.40 (6H, t, J 7.3, *Me*CH_2), 2.39 (2H, quint, 6-CH_2), 3.96 (4H, q, Me*CH_2*), 4.66 (4H, t, 5, 7-CH_2); ^{13}C NMR: δ 14.4 (*Me*CH_2), 20.2 (C-6), 45.2 (Me*CH_2*), 49.3 (C-5, C-7), 159.4 (C-7b), 167.4 (C-1, C-4). Anal. calcd for $C_{10}H_{16}N_4Se_3$: C, 27.99; H, 3.76; N, 13.06. Found: C, 27.96; H, 3.70; N, 13.01%.

2,3-Dibutyl-6,7-dihydro-5H-2aλ⁴-selena-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**13b**). From butyl isoselenocyanate; yield 37%; mp 157–159°C; ^{1}H NMR: δ 0.99 (6H, t, J 7.3, *Me*$[CH_2]_3$), 1.44 (4H, sext, Me*CH_2* $[CH_2]_2$), 1.78 (4H, quint, $MeCH_2$*CH_2*CH_2), 2.40 (2H, quint, 6-CH_2), 3.90 (4H, t, J 7.5, $Me[CH_2]_2$*CH_2*), 4.65 (4H, t, 5, 7-CH_2); ^{13}C NMR: δ 13.8 (*Me*$[CH_2]_3$), 20.2 (C-6), 20.4 (Me*CH_2*$[CH_2]_2$), 30.9 ($MeCH_2$*CH_2*CH_2), 49.3 (C-5, C-7), 50.1 ($Me[CH_2]_2$*CH_2*), 159.4 (C-7b), 167.6 (C-1, C-4). Anal. calcd for $C_{14}H_{24}N_4Se_3$: C, 34.65; H, 4.99; N, 11.55. Found: C, 34.61; H, 5.01; N, 11.53%.

2,3-Dicyclohexyl-6,7-dihydro-5H-2aλ⁴-selena-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4-(3H)-diselone (**13c**). From cyclohexyl isoselenocyanate; yield 44%; mp 180–182°C; ^{1}H NMR: δ 1.22–2.30 (20H, m, 10 × CH_2 of cyclohexyl), 2.37 (2H, quint, 6-CH_2), 4.47–4.57 (2H, m, 2,3-CH), 4.67 (4H, t, 5,7-CH_2); ^{13}C NMR: δ 20.1 (C-6), 25.4 (4-CH_2 of cyclohexyl), 25.5 (3,5-CH_2 of cyclohexyl), 33.3 (2,6-CH_2 of cyclohexyl), 48.8 (C-5, C-7), 62.3 (C-1 of cyclohexyl), 159.5 (C-7b), 166.1 (C-1, C-4). Anal. calcd for $C_{18}H_{26}N_4Se_3$: C, 39.02; H, 5.01; N, 10.77. Found: C, 39.04; H, 5.05; N, 10.70%.

2,3-Dibenzyl-6,7-dihydro-5H-2aλ⁴-selena-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H),4-(3H)-diselone (**13d**). From benzyl isoselenocyanate; yield 82%; mp 158–160°C; ^{1}H NMR: δ 2.37 (2H, quint, 6-CH_2), 4.63 (4H, t, 5,7-CH_2), 4.89 (4H, Ph*CH_2*), 7.19–7.42 (10H, m, *Ph*CH_2); ^{13}C NMR: δ 20.0 (C-6), 49.3 (C-5, C-7), 55.2 (Ph*CH_2*), 128.3 (C-4 of Ph), 128.8, 129.2 (C-2, C-3 of Ph), 135.9 (C-1 of Ph), 160.3 (C-7b), 168.2 (C-1, C-4). Anal. calcd for $C_{20}H_{20}N_4Se_3$: C, 43.41; H, 3.65; N, 10.13. Found: C, 43.28; H, 3.63; N, 10.02%.

2,3-Di-(4-methylphenyl)-6,7-dihydro-5H-2aλ⁴-se-

lena-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H), 4(3H)-diselone (**13e**). From 4-methylphenyl isoselenocyanate; yield 70%; mp 154–156°C. Anal. calcd for $C_{20}H_{20}N_4Se_3$: C, 43.41; H, 3.65; N, 10.13; Se, 42.81. Found: C, 43.51; H, 3.74; N, 10.02; Se, 42.86%.

2,3-Di-(4-methoxyphenyl)-6,7-dihydro-5H-2aλ^4-selena-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H), 4(3H)-diselone (**13f**). From 4-methoxyphenyl isoselenocyanate; yield 69%; mp 176–177°C. Anal. calcd for $C_{20}H_{20}N_4O_2Se_3$: C, 41.04; H, 3.45; N, 9.57. Found: C, 40.68; H, 3.33; N, 9.45%.

2,3-Di-(3-ethoxyphenyl)-6,7-dihydro-5H-2aλ^4-selena-2,3,4a,7a-tetraazacyclopenta[cd]indene-1(2H), 4(3H)-diselone (**13g**). From 3-ethoxyphenylisoselenocyanate; yield 72%; mp 157–159°C. Anal. calcd for $C_{22}H_{24}N_4O_2Se_3$: C, 43.38; H, 3.94; N, 9.13. Found: C, 43.31; H, 3.82; N, 9.07%.

Because of instability of compounds (**13e**)–(**13g**) in $CDCl_3$, satisfactory ^{1}H- and ^{13}C-NMR spectra were not obtained.

Reactions of the 2-(2,4-Dinitrobenzylthio)-4,5,6,7-tetrahydro-1H-1,3-diazepine (**9e**) *and 2-(2,4-Dinitrobenzylseleno)-4,5,6,7-tetrahydro-1H-1,3-diazepine* (**9f**) *with Isoselenocyanates: Synthesis of the 6aλ^4-Thia-1,3,4,6-tetraazapentalenes* (**14a**)–(**14d**) *and the 6aλ^4-Selena-1,3,4,6-tetraazapentalenes* (**15a**)–(**15d**)

The following general procedures A and B were used. Experimental details, physical properties, and analytical data are given in Table 3.

Procedure A. A solution of the diazepine (**9e**) (621 mg, 2 mmol) and the isoselenocyanate (8 mmol) in dichloromethane (10 mL) was kept in darkness for 48 hours. The small amount of solid that had precipitated was filtered off and discarded, and solvent was removed from the filtrate at reduced pressure. The residue was triturated with acetonitrile unless otherwise stated (Table 3), and the mixture was kept in darkness for 1 hour. The solid that had precipitated was filtered off, washed with ether (2 × 5mL), and recrystallized from acetonitrile–dichloromethane (3:1).

Procedure B. The diazepinium chloride (**8f**) (787 mg, 2 mmol) was added to a saturated solution of sodium carbonate in water (20 mL), and the resulting mixture was extracted with dichloromethane (2 × 30 mL). Solvent was removed from the combined dried extracts kept below 30°C, and the residue was dissolved in benzene (20 mL). The benzene was removed at reduced pressure from the solution kept below 30°C, and the residual solid containing the diazepine (**9f**) was redissolved in dichloromethane (10 mL). The isoselenocyanate (8 mmol) was added to the solution, and the resulting solution was kept in darkness for 48 hours. A small amount of solid that had precipitated was filtered off and discarded, and solvent was removed from the filtrates at reduced pressure. The residue was triturated with the solvent specified (Table 3), and the mixture was kept in darkness for 1 hour. The triheterapentalene (**15**) that crystallized was filtered off, washed with acetonitrile (2 × 5 mL), and dried.

^{1}H NMR Spectroscopic Examination of the Reaction of 2-(2,4-Dinitrobenzylthio)-4,5-dihydroimidazole (**9a**) *with 4-Methylphenyl Isoselenocyanate*

The ^{1}H-NMR spectrum of a solution of the dihydroimidazole (**9a**) (56.5 mg, 0.2 mmol) and 4-methylphenyl isoselenocyanate (58.8 mg, 0.3 mmol) in $CDCl_3$ (0.5 mL), obtained immediately after preparation of the solution, showed a strong singlet at δ 3.64 arising from 4- and 5-CH_2 in (**9a**), a weak singlet at δ 2.64 from the methyl group in 2,4-dinitrotoluene, and a weak singlet at δ 4.56 arising from 5- and 6-CH_2 in the thiadiselenadiazapentalene (**10f**). The ratio of (**9a**):2,4-dinitrotoluene:(**10f**) was 14:1:1. Additionally, two very weak triplets were present at δ 4.05 and 4.37, which we attribute tentatively to the nonequivalent CH_2 groups in the imine (**19**) or the selone (**20**). After a further 2 hours, the ratio of (**9a**):2,4-dinitrotoluene :(**10f**) had changed to 6:10:1, much of the triheterapentalene (**10f**) had crystallized from the solution, and the triplets at δ 4.05 and 4.37 had become very weak.

^{1}H and ^{13}C-NMR Spectral Data for the 6aλ^4-Thia-1,6-diselena-3,4-diazapentalenes (**10**) *and the 1,6,6aλ^4-Triselena-3,4-diazapentalenes* (**11**)

1,4-Bis-ethylimino-5,6-dihydro-2aλ^4-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]indene-1(2H),-4(3H)-diselone (**10a**). ^{1}H NMR: δ 1.20 (6H, t, J 7.3, *Me*CH_2), 3.21 (4H, q, Me*CH_2*), 4.38 (4H, 5,6-CH_2). ^{13}C NMR: δ 15.1 (Me), 45.6 (C-5, C-6), 51.3 (Me*CH_2*), 149.1 (C-1, C-4), 171.7 (C-6b).

1,4-Bis-butylimino-5,6-dihydro-2aλ^4-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]indene-1(2H),-4(3H)-diselone (**10b**). ^{1}H NMR: δ 0.92 (6H, t, J 7.2, *Me*$[CH_2]_3$), 1.37 (4H, sext, Me*CH_2*$[CH_2]_2$), 1.59 (4H, quint, $MeCH_2$*CH_2*CH_2), 3.16 (4H,t,*J*6.90, $Me[CH_2]_2$*CH_2*), 4.37 (4H, 5,6-CH_2). ^{13}C NMR: δ 13.5

TABLE 3 Preparation, Physical Properties, and Analytical Data of Compounds (**14a**)–(**14d**) and (**15a**)–(**15d**)

						Found (%) (*Required*)		
Compound[a]	*Procedure*	*RNCSe*	*Yield* (%)	*Mp* (°*C*)	*Formula*	*C*	*H*	*N*
(**14a**)	A[bc]	$PhCH_2NCSee$	23	174–176	$C_{21}H_{22}N_4SSe_2$	48.49 (48.48)	4.06 (4.26)	10.71 (10.77)
(**14b**)	A	PhNCSe	87	159–160	$C_{19}H_{18}N_4SSe_2$[d]	46.43 (46.35)	3.57 (3.68)	11.37 (11.38)
(**14c**)	A	$4\text{-}MeC_6H_4NCSe$	78	150–153	$C_{21}H_{22}N_4SSe_2$	48.22 (48.38)	4.38 (4.26)	10.86 (10.77)
(**14d**)	A	$4\text{-}MeOC_6H_4NCSe$	73	132–135	$C_{21}H_{22}N_4O_2SSe_2$	45.63 (45.64)	3.90 (4.01)	10.23 (10.15)
(**15a**)	B[be]	$PhCH_2NCSe$	26	158–159	$C_{21}H_{22}N_4Se_3$	44.41 (44.46)	3.75 (3.91)	10.01 (9.88)
(**15b**)	B[f]	PhNCSe	29	159–160	$C_{19}H_{18}N_4Se_3$	42.25 (42.32)	3.22 (3.36)	10.42 (10.39)
(**15c**)	B[g]	$4\text{-}MeC_6H_4NCSe$	48	160–163	$C_{21}H_{22}N_4Se_3$	44.26 (44.46)	3.83 (3.91)	10.03 (9.88)
(**15d**)	B[g]	$4\text{-}MeOC_6H_4NCSe$	44	135–136	$C_{21}H_{22}N_4O_2Se_3$	41.75 (42.09)	3.67 (3.70)	9.45 (9.35)

[a]Compounds (**14a**)–(**14d**) and (**15a**)–(**15d**) were obtained as yellow crystals.
[b]12 mmol isoselenocyanate used.
[c]Residue triturated with 10 mL MeCN–ether (1:1).
[d]Found: Se, 32.05. Required: Se, 32.07%.
[e]Residue triturated with 20 mL MeCN–ether (1:1).
[f]Residue triturated with 20 mL hexane–ether (4:1).
[g]Residue triturated with MeCN.

(Me), 20.5 (Me*CH*$_2$), 32.3 ($MeCH_2$*CH*$_2CH_2$), 45.6 (C-5, C-6), 58.5 (Me[CH_2]$_2$*CH*$_2$), 149.1 (C-1, C-4), 171.5 (C-6b).

1,4-Bis-cyclohexylimino-5,6-dihydro-2aλ^4*-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]indene-1*(*2H*)*,4*(*3H*)*-diselone* (**10c**). ^{1}H NMR: δ 1.25–1.80 (20H, m, 10 × CH_2 of cyclohexyl), 2.95 (vbrs, CHN), 4.35 (4H, 5,6-CH_2). ^{13}C NMR: δ 24.6 (3,5-CH_2 of cyclohexyl), 25.7 (4-CH_2 of cyclohexyl), 33.0 (2,6-CH_2 of cyclohexyl), 45.6 (C-5, C-6), 65.9 (1-CH of cyclohexyl), 146.8 (C-1, C-4), 171.8 (C-6b).

1,4-Bis-benzylimino-5,6-dihydro-2aλ^4*-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]indene-1*(*2H*)*,4*(*3H*)*-diselone* (**10d**). ^{1}HNMR: δ4.38(4H, 5,6-CH_2), 4.47 (4H, Ph*CH*$_2$), 7.32–7.37 (10H, m, Ph).

1,4-Bis-(*2-phenylethylimino*)*-5,6-dihydro-2a*λ^4*-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]indene-1*(*2H*)*,4*(*3H*)*-diselone* (**10e**). ^{1}H NMR: δ 2.90 (4H, t, *J* 7.0, Ph*CH*$_2$), 3.42 (4H, t, $PhCH_2$*CH*$_2$), 4.32 (5,6-CH_2), 7.16–7.36 (10H, m, Ph). ^{13}C NMR: δ 36.5 (Ph*CH*$_2$), 45.6 (C-5, C-6), 58.1 ($PhCH_2$*CH*$_2$), 126.1 (C-4 of Ph), 128.3, 128.9 (C-2, C-6, C-3, C-5 of Ph), 140.1 (C-1 of Ph), 150.2 (C-1, C-4), 171.1 (C-6b).

1,4-Bis-(*4-methylphenylimino*)*-5,6-dihydro-2a*λ^4*-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]indene-1*(*2H*)*,4*(*3H*)*-diselone* (**10f**). ^{1}H NMR: δ 2.33 (6H, Me), 4.60 (4H, 5,6-CH_2), 6.91 (4H, *o* protons of Ar), 7.15 (4H, *m* protons of Ar). ^{13}C NMR: δ 21.0 (Me), 46.0 (C-5, C-6), 120.4 (C-2, C-6 of Ar), 129.7 (C-3, C-5 of Ar), 134.4 (C-4 of Ar), 147.5 (C-1 of Ar), 151.8 (C-1, C-4), 173.0 (C-6b).

1,4-Bis-(*4-methoxyphenylimino*)*-5,6-dihydro-2a*λ^4*-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]-indene-1*(*2H*)*,4*(*3H*)*-diselone* (**10g**). ^{1}H NMR: δ 3.80 (6H, MeO), 4.61 (4H, 5,6-CH_2), 6.89 (4H), 6.99 (4H) (*o*, *m* protons of Ar).

1,4-Bis-(*3-ethoxyphenylimino*)*-5,6-dihydro-2a*λ^4*-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]indene-1*(*2H*)*,4*(*3H*)*-diselone* (**10i**). ^{1}H NMR: δ 1.41 (6H, t, *J* 7.0, Me), 4.03 (4H, q, Me*CH*$_2$), 4.56 (4H, 5,6-CH_2), 6.54–6.71 (6H, m, 2,4,6-H of Ar), 7.20–7.26 (2H, m, 5-H of Ar). ^{13}C NMR: δ 14.8 (Me), 46.0 (C-5, C-6), 63.4 (Me*CH*$_2$), 106.6, 111.2, 112.7 (C-2, C-4, C-6 of Ar), 129.9 (C-5 of Ar), 151.3 (C-1 of Ar), 152.3 (C-1, C-4), 159.6 (C-3 of Ar), 173.1 (C-6b).

1,4-Bis-(*2-ethoxyphenylimino*)*-5,6-dihydro-2a*λ^4*-thia-2,3-diselena-4a,6a-diazacyclopenta[cd]ind-ene-1*(*2H*)*,4*(*3H*)*-diselone* (**10j**). ^{1}H NMR: δ 1.39 (6H, t, *J* 7.0, Me), 4.04 (4H, q, Me*CH*$_2$), 4.56 (4H, 5,6-CH_2), 6.88–7.12 (8H, m, 3,4,5,6-H of Ar). ^{13}C NMR: δ 14.9 (Me), 46.0 (C-5, C-6), 64.1 (Me*CH*$_2$), 113.2,

120.6, 120.8, 125.5 (C-3, C-4, C-5, C-6 of Ar), 139.7 (C-1 of Ar), 149.7 (C-2 of Ar), 152.8 (C-1, C-4), 172.8 (C-6b).

1,4-Bis-ethylimino-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11a**). ^{1}H NMR: δ 1.22 (6H, t, J 7.3 *Me*CH_2), 3.23 (4H, q, Me*CH_2*), 4.39 (4H, 5,6-CH_2). ^{13}C NMR: δ 15.2 (Me), 47.0 (C-5, C-6), 51.0 (Me*CH_2*), 149.4 (C-1, C-4), 171.6 (C-6b).

1,4-Bis-butylimino-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11b**). ^{1}H NMR: δ 0.93 (6H, t, J 7.2, *Me*$[CH_2]_3$), 1.38 (4H, sext, Me*CH_2*$[CH_2]_2$), 1.60 (4H, quint, MeCH_2*CH_2*CH_2), 3.18 (4H,t,*J*7.0, Me$[CH_2]_2$*CH_2*), 4.38 (4H, 5,6-CH_2). ^{13}C NMR: δ 14.0 (Me), 20.6 (Me*CH_2*), 32.9 (MeCH_2*CH_2*CH_2), 46.9 (C-5, C-6), 56.3 (Me$[CH_2]_2$*CH_2*), 149.2 (C-1, C-4), 171.4 (C-6b).

1,4-Bis-cyclohexylimino-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11c**). ^{1}H NMR: δ 1.21–1.75 (20H, m, 10 $\times$ CH_2 of cyclohexyl), 3.08 (2H, vbrs, CHN), 4.36 (4H, 5,6-CH_2). ^{13}C NMR: δ 24.6 (3,5-CH_2 of cyclohexyl), 25.8 (4-CH_2 of cyclohexyl), 32.9 (2,6-CH_2 of cyclohexyl), 46.9 (C-5, C-6), 65.3 (1-CH of cyclohexyl), 146.8 (C-1, C-4), 171.5 (C-6b).

1,4-Bis-benzylimino-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11d**). ^{1}H NMR: δ 4.39 (4H, 5,6-CH_2), 4.49 (4H, Ph*CH_2*), 7.32–7.35 (10H, m, Ph).

1,4-Bis-(4-methylphenylimino)-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11e**). ^{1}H NMR: δ 2.33 (6H, Me), 4.62 (5,6-CH_2), 6.92 (4H, *o* protons of Ar), 7.16 (4H, *m* protons of Ar).

1,4-Bis-(4-methoxyphenylimino)-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11f**). ^{1}H NMR: δ 3.81 (6H, MeO), 4.63 (4H, 5,6-CH_2), 6.89 (4H), 7.00 (4H) (*o*, *m* protons of Ar).

1,4-Bis-(3-ethoxyphenylimino)-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11g**). ^{1}H NMR: δ 1.41 (6H, t, J 7.0, Me), 4.02 (4H, q, Me*CH_2*), 4.60 (4H, 5,6-CH_2), 6.55–6.72 (6H, m, 2,4,6-H of Ar), 7.21–7.29 (2H, m, 5-H of Ar). ^{13}C NMR: δ 14.9 (Me), 47.4 (C-5, C-6), 63.5 (Me*CH_2*), 106.5, 111.1, 112.7 (C-2, C-4, C-6 of Ar), 129.9 (C-5 of Ar), 151.4 (C-1 of Ar), 152.6 (C-1, C-4), 159.7 (C-3 of Ar), 173.6 (C-6b).

1,4-Bis-(2-ethoxyphenylimino)-5,6-dihydro-2,2aλ⁴,3-triselena-4a,6a-diazacyclopenta[cd]indene-1(2H),4(3H)-diselone (**11h**). ^{1}H NMR: δ 1.39 (6H, t, J 7.0, Me), 4.03 (4H, q, Me*CH_2*), 4.54 (4H, 5,6-CH_2), 6.89–7.13 (8H, m, 3,4,5,6-H of Ar). ^{13}C NMR: δ 14.9 (Me), 47.3 (C-5, C-6), 64.1 (Me*CH_2*), 113.3, 120.7, 120.8, 125.3 (C-3, C-4, C-5, C-6 of Ar), 139.7 (C-1 of Ar), 149.5 (C-2 of Ar), 153.0 (C-1, C-4), 173.3 (C-6b).

^{1}H and ^{13}C-NMR Spectral Data for the 6aλ⁴,-Thia-1,3,4,6-tetraazapentalenes (**14**) *and the 6aλ⁴-Selena-1,3,4,6-tetraazapentalenes* (**15**)

2,3-Dibenzyl-5,6,7,8-tetrahydro-2aλ⁴-thia-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**14a**). ^{1}H NMR: δ 2.23 (4H, quint, 6,7-CH_2), 4.89 (4H, Ph*CH_2*), 5.08 (4H, brt, 5,8-CH_2), 7.30 (10H, Ph). ^{13}C NMR: δ 23.6 (C-6, C-7), 51.7 (C-5, C-8), 52.3 (Ph*CH_2*), 127.9 (C-4 of Ph), 128.6, 129.0 (C-2, C-3 of Ph), 135.4 (C-1 of Ph), 161.7 (C-8b), 169.2 (C-1, C-4).

2,3-Diphenyl-5,6,7,8-tetrahydro-2aλ⁴-thia-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**14b**). ^{1}H NMR: δ 2.39 (4H, quint, 6,7-CH_2), 5.25 (4H, brs, 5,8-CH_2), 7.29–7.50 (10H, m, Ph). ^{13}C NMR: δ 23.7 (C-6, C-7), 52.5 (C-5, C-8), 126.1, 129.6 (C-2, C-3, C-4, C-5 of Ph), 128.1 (C-4 of Ph), 138.3 (C-1 of Ph), 162.9 (C-8b), 170.4 (C-1, C-4).

2,3-Di-(4-methylphenyl)-5,6,7,8-tetrahydro-2aλ⁴-thia-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**14c**). ^{1}H NMR: δ 2.34 (4H, 6,7-CH_2), 2.36 (6H, Me), 5.23 (4H, brs, 5,8-CH_2), 7.13–7.26 (8H, m, *o* and *m* protons of Ar). ^{13}C NMR: δ 20.6 (Me), 23.0 (C-6, C-7), 51.7 (C-5, C-8), 125.1, 129.3 (C-2, C-3, C-5, C-6 of Ar), 135.0 (C-4 of Ar), 137.2 (C-1 of Ar), 162.1 (C-8b), 169.3 (C-1, C-4).

2,3-Di-(4-methoxyphenyl)-5,6,7,8-tetrahydro-2aλ⁴-thia-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**14d**). ^{1}H NMR: δ 2.35 (4H, brs, 6,7-CH_2), 3.80 (6H, MeO), 5.21 (4H, brs, 5,8-CH_2), 6.95 (4H, *m* protons of Ar), 7.23 (4H, *o* protons of Ar). ^{13}C NMR: δ 23.7 (C-6, C-7), 52.5 (C-5, C-8), 55.5 (MeO), 114.6 (C-3, C-5 of Ar), 127.2 (C-2, C-6 of Ar), 130.9 (C-1 of Ar), 159.1 (C-4 of Ar), 162.5 (C-8b), 170.1 (C-1, C-4).

2,3-Dibenzyl-5,6,7,8-tetrahydro-2aλ⁴-selena-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**15a**). ^{1}H NMR: δ 2.22 (4H, quint, 6,7-CH_2), 4.88 (4H, Ph*CH_2*), 5.11 (4H, brt, 5,8-CH_2), 7.19–7.34 (10H, m, Ph). ^{13}C NMR: δ 23.5 (C-6, C-7), 53.9 (C-5, C-8), 55.7 (Ph*CH_2*), 128.2 (C-4 of Ph), 128.7, 129.1 (C-2, C-3 of Ph), 135.5 (C-1 of Ph), 166.3 (C-8b), 170.1 (C-1, C-4).

2,3-Diphenyl-5,6,7,8-tetrahydro-2aλ⁴-selena-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**15b**). ^{1}H NMR: δ 2.37 (4H, quint, 6,7-CH_2), 5.26

(4H, brs, 5,8-CH_2), 7.26–7.49 (10H, m, Ph). ^{13}C NMR: δ 23.6 (C-6, C-7), 54.7 (C-5, C-8), 125.8, 129.5 (C-2, C-3, C-5, C-6 of Ph), 127.8 (C-4 of Ph), 140.5 (C-1 of Ph), 167.4 (C-8b), 172.0 (C-1, C-4).

2,3-Di-(4-methylphenyl)-5,6,7,8-tetrahydro-2aλ^4-selena-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**15c**). ^{1}H NMR: δ 2.36 (10H, brs, 2 $\times$ Me and 6,7-CH_2), 5.30 (4H, brs, 5,8-CH_2), 7.15 (4H), 7.24 (4H) (*o*, *m* protons of Ar). ^{13}C NMR: δ 21.2 (Me), 23.6 (C-6, C-7), 54.6 (C-5, C-8), 125.4, 130.1 (C-2, C-3, C-5, C-6 of Ar), 137.7 (C-1, C-4 of Ar), 167.3 (C-8b), 171.7 (C-1, C-4).

2,3-Di-(4-methoxyphenyl)-5,6,7,8-tetrahydro-2aλ^4-selena-2,3,4a,8a-tetraazacyclopenta[cd]azulene-1,4-diselone (**15d**). ^{1}H NMR: δ 2.35 (4H, quint, 6,7-CH_2), 3.81 (6H, MeO), 6.95 (4H, *m* protons of Ar), 7.20 (4H, *o* protons of Ar). ^{13}C NMR: δ 23.6 (C-6, C-7), 54.7 (C-5, C-8), 55.4 (MeO), 114.6 (C-3, C-5 of Ar), 126.8 (C-2, C-6 of Ar), 133.1 (C-1 of Ar), 158.8 (C-4 of Ar), 167.0 (C-8b), 171.7 (C-1, C-4).

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