Heteroatom Chemistry
Volume 7, Number 2, 1996

Reactions of Fused Dihydro-1,2,4-thiadiazoles with Isoselenocyanates Giving 6aλ^4-Thia-1,3,4,6-tetraazapentalene Derivatives and 5,10-Dihydro-1,2,4-thiaselenazolo[4,5-b][2,4] benzodiazepines*

Long-Li Lai** and David H. Reid†

Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

Received 15 September 1995

ABSTRACT

*3-Methyl-6,7-dihydro-5H-1,2,4-thiadiazolo[4,5-a]pyrimidine (**1**) reacted with isoselenocyanates with elimination of acetonitrile and concomitant addition of two molecules of the isoselenocyanate to give 2,3-disubstituted-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselones (**6a**)–(**6j**). 3-Methyl-5,10-dihydrobenzo[e]-1,2,4-thiadiazolo[4,5-a][1,3]diazepine (**3**) likewise reacted with alkyl isoselenocyanates to give the 2,3-dialkyl-5-10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselones (**9a**)–(**9h**), but reaction of (**3**) with aryl isoselenocyanates took place with elimination of acetonitrile and incorporation of one molecule of the aryl isoselenocyanate in the product to give 3-arylimino-5,10-dihydro-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepines (**10a**)–(**10h**). Structure (**10**) is a new heterocyclic system. The pyrimidine (**1**) and the diazepine (**3**) reacted with aryl isoselenocyanates at room temperature in solvents of low polarity to give zwitterion 1:1 addition compounds (**7**) and (**12**), respectively. NMR studies reveal that the thiaselenazoles (**10**) react in solution with aryl isoselenocyanates to give diaryl diselones (**11**) in a reversible process involving a Dimroth rearrangement.* © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

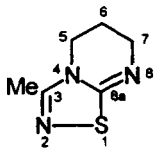
We have shown recently [1] that 3-methyl-6,7-dihydro-5*H*-1,2,4-thiadiazolo[4,5-*a*]pyrimidine (**1**) reacts with isocyanates RNCO and isothiocyanates RNCS with elimination of acetonitrile and concomitant addition of two molecules of the heterocumulene to give 2,3-disubstituted-6,7-dihydro-5*H*-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1(2*H*),4(3*H*)-diones (**2a**) and dithiones (**2b**), respectively. 3-Methyl-5,10-dihydrobenzo[*e*]-1,2,4-thiadiazolo[4,5-*a*][1,3]diazepine (**3**) likewise reacted with isocyanates and isothiocyanates to give 2,3-disubstituted-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno-[3,3a,4-*gh*]benzocycloheptene-1,4-diones (**4a**) and the corresponding dithiones (**4b**). These reactions constitute a new synthesis of stable derivatives (**2a**), (**2b**), (**4a**), and (**4b**) of the hypervalent 1*H*, 6*H*-6aλ^4-thia-1,3,4,6-tetraazapentalene system (**5**). We now report the results of an extension of this work involving the reactions of the bases (**1**) and (**3**) with isoselenocyanates.

*Studies of Heterocyclic Compounds. Part 34.

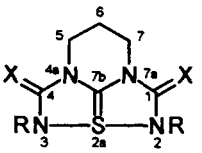
**Present address: Institute of Chemistry, Academia Sinica, Nankang, Taipei, 11529 R.O.C.

†To whom correspondence should be addressed.

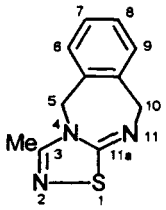
CCC 1042-7163/96/020097-13



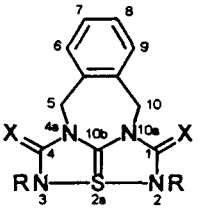
(1)



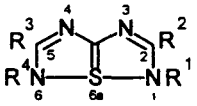
(2a) X = O
(2b) X = S



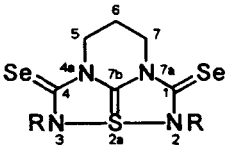
(3)



(4a) X = O
(4b) X = S



(5)



(6)

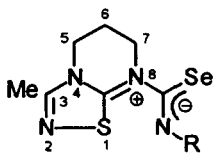
(6a) R = Et
(6b) R = n-Bu
(6c) R = c-C_5H_9
(6d) R = c-C_6H_{11}
(6e) R = c-C_7H_{13}
(6f) R = $PhCH_2$
(6g) R = $Ph[CH_2]_2$
(6h) R = 4-MeC_6H_4
(6i) R = 4-$MeOC_6H_4$
(6j) R = 2-$EtOC_6H_4$

RESULTS AND DISCUSSION

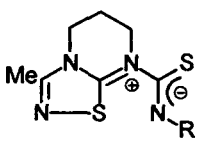
The pyrimidine (1) reacted readily with isoselenocyanates, rapidly in boiling toluene or more slowly in dichloromethane at ambient temperatures. Elimination of acetonitrile took place with concomitant addition of two molecules of the isoselenocyanate to give the diselones (6a)–(6j). The structure of the diselones (6) has been established by an X-ray crystal structure determination of the representative member (6d) [2]. Compound (6d) shows in the N–S–N moiety the structural features characteristic of the hypervalent three-center four-electron system in 1,6,6aλ^4-triheterapentalenes [3]. The S–N bonds in (6d) are long. Their lengths [1.935(7) and 1.931(7)Å] are greater by 11.2 and 11.0%, respectively, than the two-center two-electron covalent S–N bond length (1.74 A) based on the sum of the covalent radii of sulfur and nitrogen [4]. Also, the internal N–S–N bond angle is large [164.8 (3)°].

The pyrimidine (1) also reacted rapidly with phenyl isoselenocyanate, 4-methylphenyl isoselenocyanate, 3-ethoxyphenyl isoselenocyanate, and 3-chlorophenyl isoselenocyanate in toluene at room temperature to give 1:1 addition products that we formulate as the zwitterions (7a)–(7d). Compounds (7a)–(7d) have properties similar to those of the zwitterions (8) formed from the base (1) and isothiocyanates, whose structure has been established by X-ray crystallography of the derivative (8a) [1]. They are virtually insoluble in nonpolar solvents. Comparison of the ^{1}H NMR spectra of the zwitterions (7a)–(7d) and (8a) with the ^{1}H NMR spectrum of the base (1) [5] shows that all protons in the positively charged heterocyclic moiety of the zwitterions (7a)–(7d) and (8a) are substantially deshielded relative to the corresponding protons in the base (1). Thus the ranges for the chemical shift differences $\Delta\delta$ (ppm) between protons in the zwitterions (7a)–(7d) and the corresponding protons in (1) are as follows: 3-Me, $\Delta\delta$ 0.29–0.35; 5-CH_2, $\Delta\delta$ 0.34–0.39; 6-CH_2, $\Delta\delta$ 0.47–0.53; 7-CH_2, $\Delta\delta$ 1.28–1.33. The differences between the chemical shifts of protons in the zwitterion (8a) and those of the corresponding protons in the base (1) are: 3-Me, $\Delta\delta$ 0.25; 5-CH_2, $\Delta\delta$ 0.39; 6-CH_2, $\Delta\delta$ 0.38; 7-CH_2, $\Delta\delta$ 0.93.

The diazepine (3) reacted with alkyl isoselenocyanates in the same manner as the pyrimidine (1) to give the 2,3-disubstituted-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3, 3a,4-*gh*]benzocycloheptene-1,4-diselones (9a)–(9h). The assigned structure of the diselones rests on an X-ray crystal structure determination of the 1:1 clathrate of the diselone (9d) with benzene, which shows the presence of the N–S–N sequence in the heterocycles [6]. As is the case for the diselone (6d), the S–N bonds in the diselone (9d) are long [1.928 (12) and 1.887 (11) Å] and the internal bond angle is large [166.7 (5)°].



(7)



(8)

(7a) R = Ph
(7b) R = 4-MeC_6H_4
(7c) R = 3-$EtOC_6H_4$
(7d) R = 3-ClC_6H_4

(8a) R = Ph
(8b) R = Me

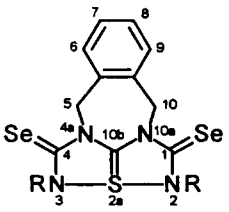
Compounds (9c), (9d), and (9e) crystallized from

benzene as stable 1:1 clathrates that retain the benzene guest molecules indefinitely at ambient temperatures. Compound (**9d**) also formed stable 1:1 clathrates with cyclohexane, toluene, and 1,2-dichloroethane; a 3 host:1 guest clathrate with diethyl ether; and a 4 host:3 guest clathrate with dichloromethane.

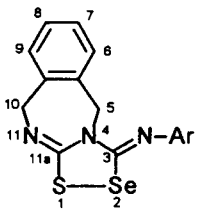
The diazepine (**3**) also reacted with aryl isoselenocyanates with elimination of acetonitrile but with incorporation of only one molecule of the isoselenocyanate in the product to give the 3-arylimino-5,10-dihydro-1,2,4-thiaselenazolo[4,5-*b*][2,4]benzodiazepines (**10a**)–(**10h**). The structure of the thiaselenazoles (**10a**)–(**10h**) was established by an X-ray crystal structure determination of the representative member (**10a**) [7]. The tricyclic 1,2,4-thiaselenazolo[4,5-*b*][2,4]benzodiazepine system of compounds (**10a**)–(**10h**) is a new heterocyclic system.

2,3-Diaryl analogues (**11**) of the diselones (**9**) were not detected by TLC in the reaction solutions that afforded the thiaselenazoles (**10**). Nevertheless NMR experiments indicated that the diaryl diselones (**11**) are formed reversibly in solutions containing the thiaselenazoles (**10**) and the isoselenocyanates. Thus the thiaselenazole (**10b**) and 4-methylphenyl isoselenocyanate (1:3 ratio) reacted slowly in $CDCl_3$ to establish an equilibrium in which the diaryl diselone (**11a**) and the thiaselenazole (**10b**) are present in a 3:2 ratio. No other product was present in detectable concentration. Similar experiments involving the reaction of compound (**10e**) with 3-ethoxyphenyl isoselenocyanate and compound (**10d**) with 4-bromophenyl isoselenocyanate gave the following equilibrium ratios: (**11b**):(**10e**), 1:1; (**11c**):(**10d**), 4:5.

The deduction that the thiaselenazoles (**10**) react with aryl isoselenocyanates to form the diaryl diselones (**11**) rests on ^1H and ^{13}C NMR evidence. The 5-CH_2 and 10-CH_2 proton signals of the thiaselenazoles (**10a**)–(**10h**) lie within the narrow ranges δ 5.37–5.47 and δ 4.85–4.87, respectively, whereas the 5(10)-CH_2 proton signals of the diselones (**9a**)–(**9h**) occur as broad singlets at much lower field over the range δ 6.36–6.47. The ^1H NMR spectra of solutions of the thiaselenazoles (**10b**) with 4-methylphenyl isoselenocyanate, (**10e**) with 3-ethoxyphenyl isoselenocyanate, and (**10d**) with 4-bromophenyl isoselenocyanate in $CDCl_3$ showed, in addition to the signals from 5-CH_2 and 10-CH_2 in (**10b**), (**10e**), and (**10d**), a broad singlet in the range δ 6.51–6.55 attributable to the 5(10)-CH_2 group of (**11a**), (**11b**), and (**11c**). The ^{13}C NMR spectra of the diselones (**9a**)–(**9h**) showed two diagnostic low-field signals in the ranges δ 158.61–159.40, arising from C-10b, and δ 166.13–168.80, arising from C-1(4). In contrast the two lowest field signals in the spectra of the thiaselenadiazoles (**10a**)–(**10h**) are present at considerably higher field in the ranges δ 150.39–151.52 and δ 151.91–152.51 and are provisionally assigned to C-3 and C-11a, respectively. The ^{13}C NMR spectra of solutions of (**10b**) with 4-methylphenyl isoselenocyanate, (**10e**) with 3-ethoxyphenyl isoselenocyanate, and (**10d**) with 4-bromophenyl isoselenocyanate in $CDCl_3$ showed, in addition to the signals from 5-CH_2 and 10-CH_2 in (**10b**), (**10e**), and (**10d**), two low-field signals in the ranges δ 160.21–160.40 and δ 169.56–170.26, which we assign to C-10b and C-1(4) in the diaryl diselones (**11a**), (**11b**), and (**11c**), respectively.



(**9**)



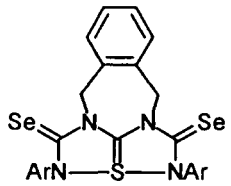
(**10**)

(**9a**)	R = Et	(**10a**)	Ar = Ph
(**9b**)	R = n-Bu	(**10b**)	Ar = 4-MeC_6H_4
(**9c**)	R = c-C_5H_9	(**10c**)	Ar = 4-MeOC_6H_4
(**9d**)	R = c-C_6H_{11}	(**10d**)	Ar = 4-BrC_6H_4
(**9e**)	R = c-C_7H_{13}	(**10e**)	Ar = 3-EtOC_6H_4
(**9f**)	R = PhCH_2	(**10f**)	Ar = 3-ClC_6H_4
(**9g**)	R = Ph[CH_2]$_2$	(**10g**)	Ar = 2-EtOC_6H_4
(**9h**)	R = Ph_2CHCH_2	(**10h**)	Ar = 2-BrC_6H_4

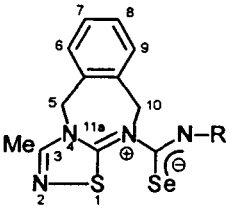
The diazepine (**3**) reacted rapidly with 4-methylphenyl isoselenocyanate and 3-ethoxyphenyl isoselenocyanate in dichloromethane at room temperature to give 1:1 addition products, namely the zwitterions (**12a**) and (**12b**), which could not be recrystallized owing to breakdown in solution. NMR studies showed that partial reversion to the diazepine (**3**) and the isoselenocyanate occurs immediately in solution. The ^1H NMR spectrum of a freshly prepared solution of (**12a**) in $CDCl_3$ showed singlet signals at δ 2.62, 5.53, and 6.58 arising from the 3-Me, 5-CH_2, and 10-CH_2 groups respectively in (**12a**), in addition to signals at the known positions for 3-Me (δ 2.32), 5-CH_2 (δ 5.03), and 10-CH_2 (δ 4.78) in the diazepine (**3**). The ratio of (**12a**):(**3**) was 2.3:1, but after 6 hours the ratio had changed to 2.7:1, and in addition to the signals from (**12a**) and (**3**) the spectrum showed weak signals at δ 4.84 and 5.39 arising from the incipiently formed thiaselenazole (**10b**). After several days the thiaselenazole (**10b**) had become the major component of the solution. The solution

also contained a small quantity of the diaryl diselone (**11a**) as evidenced by a signal at δ 6.54 arising from the 5(10)-CH_2 group in (**11a**), and also showed a strong signal at δ 2.00 from acetonitrile.

Zwitterions (**12**) are also intermediates in the reactions of the diazepine (**3**) with alkyl isoselenocyanates but could not be isolated owing to rapid conversion into the dialkyl diselones (**9**). A freshly prepared solution of the diazepine (**3**) and n-butyl isoselenocyanate (1:3 ratio) in $CDCl_3$ gave ^1H NMR signals corresponding to the presence of the diazepine (**3**), the zwitterion (**12c**), and the dibutyl diselone (**9b**) in a 1:5:1 ratio. The zwitterion (**12c**) gave identifying signals at δ 2.68 (3-Me), 5.62 (5-CH_2), and 6.51 (10-CH_2). After 30 minutes the ratio had changed to 1:3:10 and after 24 hours the diselone (**9b**) was the only detectable product.



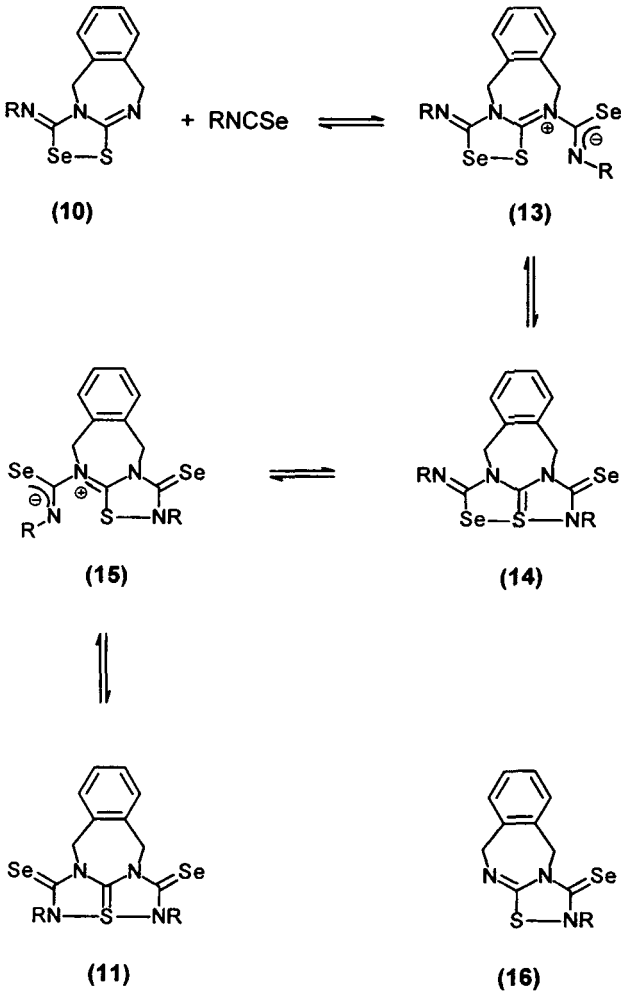
(**11**)



(**12**)

(11a)	Ar = 4-MeC_6H_4	**(12a)**	R = 4-MeC_6H_4
(11b)	Ar = 3-$EtOC_6H_4$	**(12b)**	R = 3-$EtOC_6H_4$
(11c)	Ar = 4-BrC_6H_4	**(12c)**	R = n-Bu

We propose that the pyrimidine (**1**) and the diazepine (**3**) react with isoselenocyanates to give respectively the zwitterions (**7**) and (**12**) and thence the diselones (**6**) and (**9**) or (**11**) via a series of steps that parallel those previously formulated for the reactions of (**1**) and (**3**) with isothiocyanates and isocyanates (see Ref. [1]). To account for the interconversion of the thiaselenazoles (**10**) and the diselones (**11**) we advance the mechanism in Scheme 1, which involves reversible addition of isoselenocyanate to (**10**) to give the transient zwitterion (**13**), ring-closure of (**13**) to give the intermediate triheterapentalene (**14**), and a Dimroth rearrangement of (**14**) that proceeds via the transient zwitterion (**15**) to give the diselone (**11**). The 1,2,4-selenadiazole-3-selones (**16**) that would result from reversible loss of isoselenocyanate from the intermediate zwitterions (**15**) are feasible intermediates or products but were not detected. The reason for the preference for formation of the thiaselenazoles (**10**) rather than the thiadiazoles (**16**) is not evident to us.



SCHEME 1

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were determined at 200.13 MHz and ^{13}C NMR spectra at 50.32 MHz with a Bruker AC200 spectrometer. ^1H and ^{13}C NMR spectra were obtained using solutions in $CDCl_3$, unless otherwise stated. ^1H 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; sept, septet; br, broad; s, strong), J (Hz), and assignment. ^1H NMR signals assigned to the pairs of *o*- and *m*-protons of the *p*-substituted phenyl group in 4-methylphenyl isonitrile, 4-methoxyphenyl isonitrile, 4-bromophenyl isonitrile, 4-methoxyphenyl isoselenocyanate, 4-bromophenyl isoselenocyanate,

and compounds (**6i**), (**10b**), and (**10d**) show an AA'BB' pattern. ^{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 at reduced pressure with a rotary evaporator. Ether denotes diethyl ether. Acetonitrile, benzene, carbon tetrachloride, chloroform, cyclohexane, 1,2-dichloroethane, dichloromethane, dimethylformamide (DMF), ether, hexane, tetrahydrofuran (THF), and toluene were dried by standard procedures and redistilled before use. Solvent mixtures are described in ratios by volume. Triethylamine was refluxed over powdered calcium hydride and then distilled before use. Column chromatography was carried out with silica (85–200 mesh).

Preparation of N-Substituted Formamides, Isonitriles, and Isoselenocyanates

All *N*-alkylformamides except *N*-benzylformamide were prepared by boiling a mixture of the alkylamine and ethyl formate (100% excess) for 4 hours, then removing the excess of ethyl formate at reduced pressure and purifying the residual *N*-alkylformamide by distillation at reduced pressure. *N*-Arylformamides and *N*-benzylformamide were prepared by boiling a mixture of the amine, 98–100% formic acid (100% excess), and toluene (100 mL/mole amine) for 4 hours. Toluene, water, and the excess of formic acid were removed at reduced pressure and the residual solid was distilled at reduced pressure to give the *N*-substituted formamide as a solid.

Isonitriles were prepared by reaction of *N*-substituted formamides with the following reagents according to the literature methods cited: (A) $SOCl_2$-DMF [8]; (B) Ph_3P-CCl_4 [9]; Ph_3PBr_2 [10]. Isonitriles prepared by method (A) were cyclopentyl isonitrile, cyclohexyl isonitrile, cycloheptyl isonitrile, benzyl isonitrile, 2-phenylethyl isonitrile, 2,2-diphenylethyl isonitrile, phenyl isonitrile, 4-methylphenyl isonitrile, 4-methoxyphenyl isonitrile, 4-bromophenyl isonitrile, 3-ethoxyphenyl isonitrile, 3-chlorophenyl isonitrile, 2-ethoxyphenyl isonitrile, and 2-bromophenyl isonitrile. Isonitriles prepared by method (B) were n-butyl isonitrile, 4-methylphenyl isonitrile, 4-methoxyphenyl isonitrile, and 3-ethoxyphenyl isonitrile. Isonitriles prepared by method (C) were ethyl isonitrile and 4-methoxyphenyl isonitrile. Spectral and analytical data are given in the following section.

Isoselenocyanates were prepared according to the literature method [11] by boiling a mixture of the isonitrile (25 mmol), triethylamine (2.5 mL, 17.9 mmol), and black selenium powder (2.96 g, 37.5 mmol) in THF (25 mL) under nitrogen for 3 hours (aryl isonitriles) or 6 hours (alkyl isonitriles). The excess of selenium was filtered off and solvent and triethylamine were removed from the filtrates in vacuo. The resulting isoselenocyanates were thus obtained in nearly quantitative yield and satisfactory state of purity and were used for subsequent reactions without further purification. They were characterized by their ^1H and ^{13}C NMR spectra.

Reactions of the Pyrimidine (**1**) *with Isoselenocyanates: Synthesis of the Triheterapentalenes* (**6a**)–(**6j**)

The following general procedures A–C were used. Experimental details, physical properties, and analytical data are given in Table 1.

Procedure A. A solution of the pyrimidine (**1**) (310 mg, 2 mmol) and the isoselenocyanate (10 mmol) in toluene (20 mL) was boiled in a nitrogen atmosphere for 30 minutes, cooled, and solvent was removed at reduced pressure. The residual oily solid was recrystallized from acetonitrile-dichloromethane (ca. 5:1).

Procedure B. Reaction was carried out according to procedure A. The residual oily solid was chromatographed on silica (16 × 2.2 cm). Elution with benzene brought through the excess of the isoselenocyanate and subsequent elution with dichloromethane gave homogeneous yellow eluates that yielded the product. Recrystallization of the product was from acetonitrile-dichloromethane (ca. 5:1).

Procedure C. A solution of the pyrimidine (**1**) (310 mg, 2 mmol) and the isoselenocyanate (8 mmol) in dichloromethane (10 mL) was kept at room temperature for 24 hours. The solid that had precipitated was filtered off, washed with acetonitrile (2 × 2 mL), and recrystallized from acetonitrile-dichloromethane (1:1).

Reactions of the Diazepine (**3**) *with Alkyl Isoselenocyanates: Synthesis of the Triheterapentalenes* (**9a**)–(**9h**)

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

Procedure A. A solution of the diazepine (**3**)

TABLE 1 Physical Properties and Analytical Data of Compounds (**6a–6j**)

Compound[a]	Procedure	RNCSe	Yield (%)	Mp (°C)	Formula	Found (%) (Required) C	H	N
						31.23	4.07	14.57
(**6a**)	C	EtNCSe	92	208–210	$C_{10}H_{16}N_4SSe_2$	(31.42)	(4.22)	(14.66)
						38.36	5.52	12.78
(**6b**)	C[b,c]	*n*-BuNCSe	96	170–172	$C_{14}H_{24}N_4SSe_2$[d]	(38.30)	(5.36)	(12.78)
(**6b**)	B	*n*-BuNCSe	93	170–172				
						41.58	5.19	12.05
(**6c**)	A	c-C_5H_9NCSe	69	>152[e]	$C_{16}H_{24}N_4SSe_2$	(41.56)	(5.23)	(12.12)
						44.16	5.74	11.52
(**6d**)	B	c-C_6H_{11}NCSe	83	172–180	$C_{18}H_{28}N_4SSe_2$	(44.08)	(5.76)	(11.42)
						46.60	6.21	10.75
(**6e**)	A	c-C_7H_{13}NCSe	77	162–165	$C_{20}H_{32}N_4SSe_2$	(46.33)	(6.22)	(10.81)
						47.48	4.05	11.12
(**6f**)	A	$PhCH_2$NCSe	95	>210[e]	$C_{20}H_{20}N_4SSe_2$	(47.44)	(3.98)	(11.06)
						49.47	4.42	10.40
(**6g**)	A	$Ph[CH_2]_2$NCSe	79	193–199	$C_{22}H_{24}N_4SSe_2$	(49.44)	(4.53)	(10.48)
						47.38	4.00	11.10
(**6h**)	A	4-MeC_6H_4NCSe	73	148–154	$C_{20}H_{20}N_4SSe_2$	(47.44)	(3.98)	(11.06)
						44.69	3.71	10.36
(**6i**)	B	4-$MeOC_6H_4$NCSe	45	171–173	$C_{20}H_{20}N_4O_2SSe_2$	(44.62)	(3.75)	(10.41)
						46.07	4.18	9.81
(**6j**)	A	2-$EtOC_6H_4$NCSe	80	143–146	$C_{22}H_{24}N_4O_2SSe_2$	(46.05)	(4.27)	(9.89)

[a]Compounds (**6a**)–(**6j**) were obtained as pale yellow crystals.
[b]6 Mmol isoselenocyanate used.
[c]Product chromatographed on silica (10 × 2.2 cm).
[d]Found: S, 7.32; Se, 36.03. Required: S, 7.33; Se, 35.80%.
[e]Melts with decomposition above the temperature indicated.

TABLE 2 Physical Properties and Analytical Data of Compounds (**9a–9h**)

Compound[a]	Procedure	RNCSe	Yield (%)	Mp (°C)	Formula	Found (%) (Required) C	H	N
						40.38	3.96	12.57
(**9a**)	D	EtNCSe	88	163–166	$C_{15}H_{18}N_4SSe_2$	(40.55)	(4.08)	(12.61)
						45.54	5.23	11.23
(**9b**)	C	*n*-BuNCSe	92	152–155	$C_{19}H_{26}N_4SSe_2$[b]	(45.60)	(5.24)	(11.20)
(**9b**)	D	*n*-BuNCSe	94					
						53.73	5.47	9.41
(**9c**)[c]	B	c-C_5H_9NCSe	45	95–99	$C_{21}H_{26}N_4SSe_2 + C_6H_6$	(53.82)	(5.35)	(9.30)
						55.14	5.71	8.90
(**9d**)[c]	B	c-C_6H_{11}NCSe	60	112–119	$C_{23}H_{30}N_4SSe_2 + C_6H_6$	(55.24)	(5.75)	(8.88)
						56.46	6.04	8.48
(**9e**)[c]	B	c-C_7H_{13}NCSe	51	94–103(decomp)	$C_{25}H_{34}N_4SSe_2 + C_6H_6$	(56.53)	(6.12)	(8.51)
						52.37	3.84	9.67
(**9f**)	A	$PhCH_2$NCSe	54	180–183	$C_{25}H_{22}N_4SSe_2$	(52.82)	(3.90)	(9.86)
						54.12	4.38	9.37
(**9g**)	A	$Ph[CH_2]_2$NCSe	87	168–169	$C_{27}H_{26}N_4SSe_2$	(54.37)	(4.40)	(9.40)
						62.10	4.51	7.35
(**9h**)	A	Ph_2CHCH_2NCSe	71	181–184	$C_{39}H_{34}N_4SSe_2$	(62.57)	(4.58)	(7.48)

[a]Compounds (**9a**)–(**9h**) were obtained as pale yellow crystals.
[b]Found: Se, 31.75. Required: Se, 31.56%.
[c]1:1 Clathrate with benzene.

TABLE 3 Physical Properties and Analytical Data of Compounds (**10a–10h**)

Compound[a]	Procedure	RNCSe	Yield (%)	Mp (°C)	Formula	Found (%) (Required) C	H	N
						53.55	3.56	11.87
(**10a**)	A	PhNCSe	71	>220[b]	$C_{16}H_{13}N_3SSe$	(53.62)	(3.66)	(11.73)
						54.62	3.92	11.16
(**10b**)	A[c]	4-MeC_6H_4NCSe	75	199–200	$C_{17}H_{15}N_3SSe$[d]	(54.84)	(4.06)	(11.29)
						52.49	3.86	10.73
(**10c**)	A	4-$MeOC_6H_4NCSe$	68	187–188	$C_{17}H_{15}N_3SSe$	(52.58)	(3.89)	(10.82)
						43.74	2.70	9.73
(**10d**)	A	4-BrC_6H_4NCSe	75	212–213	$C_{16}H_{12}BrN_3SSe$	(43.95)	(2.77)	(9.61)
						53.81	4.20	10.34
(**10e**)	A	3-$EtOC_6H_4NCSe$	30	152–160[e]	$C_{18}H_{17}N_3OSSe$	(53.73)	(4.26)	(10.44)
						48.76	2.98	10.69
(**10f**)	A	3-ClC_6H_4NCSe	40	181–184[e]	$C_{16}H_{12}ClN_3SSe$	(48.93)	(3.08)	(10.70)
						43.47	2.64	9.47
(**10g**)	B	2-BrC_6H_4NCSe	58	189–190[f]	$C_{16}H_{12}BrN_3SSe$	(43.95)	(2.77)	(9.61)
						53.81	4.20	10.34
(**10h**)	B	2-$EtOC_6H_4NCSe$	66	160–161[e]	$C_{18}H_{17}N_3OSSe$	(53.73)	(4.26)	(10.44)

[a]Compounds (**10a**)–(**10h**) were obtained as pale yellow crystals.
[b]Melts with decomposition above the temperature indicated.
[c]6 Mmol isoselenocyanate used.
[d]Found: Se, 21.42. Required: Se, 21.21%.
[e]Solvent cyclohexane-CH_2Cl_2 (ca. 5:1).
[f]Solvent MeCN–CH_2Cl_2 (ca. 5:1).

(434 mg, 2 mmol) and the alkyl isoselenocyanate (10 mmol) in toluene (30 mL) was boiled in a nitrogen atmosphere for 30 minutes, cooled, and solvent was removed at reduced pressure. The residual solid was recrystallized from acetonitrile-dichloromethane (5:1).

Procedure B. The reaction was carried out according to procedure A. The residue was chromatographed on silica (10 × 2.2 cm) with benzene. The initial colorless eluates brought through the excess of the isoselenocyanate and the succeeding yellow eluates afforded the product that was recrystallized from benzene.

Procedure C. The reaction was carried out according to procedure A, using redistilled butyl isoselenocyanate (6 mmol). The residual oily solid was chromatographed on silica (16 × 2.2 cm). Initial elution with benzene removed the excess of the isoselenocyanate and subsequent elution with dichloromethane brought through yellow eluates that yielded the product. Recrystallization was from acetonitrile-dichloromethane (5:1).

Procedure D. A solution of the diazepine (3) (434 mg, 2 mmol) and the isoselenocyanate (8 mmol) in dichloromethane (30 mL) was kept at room temperature for 24 hours. The solvent was removed at reduced pressure and the residue was recrystallized from acetonitrile-dichloromethane (ca. 5:1).

Reactions of the Diazepine (3) *with Aryl Isoselenocyanates: Synthesis of the 1,2,4-Thiaselenazolo[4,5-a][2,4]benzodiazepines* (10a)–(10h)

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 (3) (434 mg, 2 mmol) and the aryl isoselenocyanate (10 mmol) in toluene (30 mL) was boiled in a nitrogen atmosphere for 30 minutes, cooled, and solvent was removed at reduced pressure. The residue was chromatographed on silica (16 × 2.2 cm) with dichloromethane. The initial colorless eluates were discarded and the succeeding yellow eluates yielded the product that was recrystallized from acetonitrile-dichloromethane (ca. 5:1) unless otherwise indicated.

Procedure B. The reaction was carried out according to procedure A. The residue obtained after removal of the solvent was recrystallized directly from the solvent indicated (Table 3).

Preparation of Clathrates from the 1:1 (9d)-*Benzene Clathrate*

Procedure A. The 1:1 clathrate of (**9d**) with benzene (0.2 mmol) was dissolved in warm dichloromethane (5 mL) and the solution was chromatographed on silica (10 × 2.0 cm) with dichloromethane. The yellow eluates were concentrated to ca. 3 mL, then kept in darkness for 3 days. The 4:3 (**9d**)-CH_2Cl_2 clathrate (82%) crystallized as yellow crystals, mp 114–116°C; ^{1}H NMR: δ1.18–2.15 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 4.34–4.46 (2H, m, 2,3-CH), 5.29 (1.5H, CH_2Cl_2), 6.43 (4H, brs, 5,10-CH_2), 7.41–7.62 (4H, m, benzo-H). Anal. calcd. for $C_{23}H_{30}N_4SSe_2 \cdot 0.75\ CH_2Cl_2$: C, 46.29; H, 5.15; N, 9.09. Found: C, 46.24; H, 5.24; N, 9.06%.

Procedure B. The 4:3 clathrate of (**9d**) with CH_2Cl_2 (0.2 mmol) was dissolved in the guest solvent (20 mL), with warming if necessary, and solvent was removed from the solution at reduced pressure. The residual solid was redissolved in more (20 mL) of the solvent, and solvent was removed at reduced pressure from the solution. The residual solid was again dissolved in the solvent (20 mL) and the solution was concentrated to ca. 3 mL, then kept in darkness for 3 days while the clathrate separated from solution as yellow crystals. The following clathrates were obtained by this procedure.

1:1 (**9d**)-*1,2-Dichloroethane Clathrate* (*57%*). Mp 103–104°C. ^{1}H NMR: δ 1.18–2.16 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 3.74 (4H, $ClCH_2CH_2Cl$), 4.34–4.46 (2H, m, 2,3-CH), 6.43 (4H, brs, 5,10-CH_2), 7.41–7.62 (4H, m, benzo-H). Anal. calcd. for $C_{23}H_{30}N_4SSe_2 \cdot C_2H_4Cl_2$: C, 46.09; H, 5.26; N, 8.60. Found: C, 45.81; H, 5.22; N, 8.46%.

1:1 (**9d**)-*Cyclohexane Clathrate* (*78%*). Mp 118–120°C. ^{1}H NMR: δ 1.20–2.20 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 1.42 (12H, cyclohexane), 4.34–4.46 (2H, m, 2,3-CH), 6.43 (4H, brs, 5,10-CH_2), 7.40–7.62 (4H, benzo-H).

1:1 (**9d**)-*Toluene Clathrate* (*61%*). Mp 119–121°C. ^{1}H NMR: δ 1.18–2.20 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 2.34 (3H, Me of toluene), 4.34–4.46 (2H, m, 2,3-CH), 6.43 (4H, brs, 5,10-CH_2), 7.10–7.60 (9H, m, benzo-H + MeC_6H_4).

3:1 (**9d**)-*Diethyl Ether Clathrate* (*78%*). Mp 108–109°C. ^{1}H NMR: δ 1.21 (2H, t, Me of diethyl ether), 1.18–2.20 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 3.49 (1.33H, q, CH_2 of diethyl ether), 4.34–4.46 (2H, m, 2.3-CH), 6.43 (4H, brs, 5,10-CH_2), 7.40–7.60 (4H, m, benzo-H). Anal. calcd. for $C_{23}H_{30}N_4SSe_2 \cdot 0.33\ C_4H_{10}O$: C, 50.63; H, 5.82; N, 9.71. Found: C, 50.42; H, 5.75; N, 9.74%.

Reactions of 3-Arylimino-5,10-dihydro-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepines (**10b**), (**10e**), *and* (**10d**) *with Aryl Isoselenocyanates: Detection of Diaryl Diselones* (**11a**)–(**11c**) *in Solution by NMR Spectroscopy*

Solutions for NMR spectroscopic examination were prepared by dissolving the thiaselenazole (0.1 mmol) and the isoselenocyanate (0.3 mmol) in $CDCl_3$ (0.5 mL). Equilibrium ratios of (**11a**):(**10b**), (**11b**):(**10e**), and (**11c**):(**10d**) were determined after 6 days using proton signal integrals of 5(10)-CH_2 in (**11a**)–(**11c**) and 5-CH_2 and 10-CH_2 in (**10b**), (**10e**), and (**10d**).

Reaction of (**10b**) *with 4-Methylphenyl Isoselenocyanate.* The equilibrium ratio (**12a**):(**10b**) was 3:2. The diselone (**12a**) showed ^{1}H NMR signals at δ 2.34 (3H, Me) and 6.55 (2H, vbr, 5,10-CH_2) and ^{13}C NMR signals at δ 21.10 (Me), 53.51 (C-5, C-10), 160.21 (C-10b), and 169.56 (C-1, C-4).

Reaction of (**10e**) *with 3-Ethoxyphenyl Isoselenocyanate.* The equilibrium ratio (**12b**):(**10e**) was 1:1. The diselone (**12b**) showed a ^{1}H NMR signal at δ 6.51 (vbr, 5,10-CH_2) and ^{13}C NMR signals at δ 53.38 (C-5, C-10), 160.25 (C-10b), and 169.52 (C-1, C-4).

Reaction of (**10d**) *with 4-Bromophenyl Isoselenocyanate.* The equilibrium ratio (**12c**):(**10d**) was 4:5. The diselone (**12c**) showed a ^{1}H NMR signal at δ 6.52 (vbr, 5,10-CH_2) and ^{13}C NMR signals at δ 53.65 (C-5, C-10), 160.40 (C-10b), and 170.26 (C-1, C-4).

Preparation of the Zwitterions (**7a**)–(**7d**)

A solution of the pyrimidine (**1**) (155 mg, 1 mmol) in toluene (10 mL) was added to a solution of the isoselenocyanate (3 mmol) in toluene (5 mL) and the resulting solution was kept at room temperature for 1 hour. The solid that had precipitated was filtered off, washed with benzene (2 × 1 mL), and dried. The zwitterions could not be recrystallized owing to partial dissociation in solution that regenerated the base (**1**) and the isoselenocyanate, and the ^{1}H NMR spectra of the zwitterions (**7a**)–(**7d**) in $CDCl_3$ showed signals in the vicinity of δ 1.92, 2.20, 3.49, and 3.80 arising from (**1**) [5] in addition to the signals from the zwitterions.

1-(3-Methyl-6,7-dihydro-5H-1,2,4-thiadiazolo-[4,5-a]pyrimidin-8-ium-8-yl)-N-phenylselenoform amidide (**7a**). The zwitterion (**7a**) (241 mg, 72%)

was obtained as yellow plates, mp 160–162°C; ^{1}H NMR: δ 2.39 (2H, quint, 6-CH_2), 2.49 (3H, 3-Me), 4.14 (2H, t, 5-CH_2), 4.77 (2H, t, 7-CH_2), 7.20–7.50 (5H, m, Ph) [ratio of (**7a**):(1), 14:1]; ^{13}C NMR: δ 15.91 (Me), 20.12 (6-CH_2), 44.94, 46.57 (5-CH_2, 7-CH_2), 122.90, 124.34, 128.69 (C-2, C-3, C-4 of Ph). Anal. calcd. for $C_{13}H_{14}N_4SSe_2$: C, 46.29; H, 4.18; N, 16.61. Found: C, 46.38; H, 4.18; N, 16.32%.

1-(3-Methyl-6,7-dihydro-5H-1,2,4-thiadiazolo-[4,5-a]pyrimidin-8-ium-8-yl)-N-(4-methylphenyl)-selenoformamidide (**7b**). The zwitterion (**7b**) (239 mg, 68%) was obtained as yellow plates, mp 156–158°C; ^{1}H NMR: δ 2.35 (3H, C_6H_4*Me*), 2.43 (2H, quint, 6-CH_2), 2.52 (3H, 3-Me), 4.17 (2H, t, 5-CH_2), 4.81 (2H, t, 7-CH_2), 7.18–7.37 (4H, m, C_6*H*$_4$Me) [ratio of (**7b**):(1), 15:1]. Anal. calcd. for $C_{14}H_{16}N_4SSe$: C, 47.86; H, 4.59; N, 15.95. Found: C, 47.73; H, 4.57; N, 16.12%.

1-(3-Methyl-6,7-dihydro-5H-1,2,4-thiadiazolo-[4,5-a]pyrimidin-8-ium-8-yl)-N-(3-ethoxyphenyl) selenoformamidide (**7c**). The zwitterion (**7c**) (346 mg, 91%) was obtained as yellow plates, mp 170–172°C; ^{1}H NMR: δ 1.41 (3H, t, J_{Me,CH_2} 7.0, OCH_2*Me*), 2.40 (2H, quint, 6-CH_2), 2.50 (3H, 3-Me), 4.06 (2H, q, OCH_2Me), 4.14 (2H, t, 5-CH_2), 4.78 (2H, t, 7-CH_2), 6.67–6.73 (1H, m, 6-H of C_6H_4), 6.85–6.90 (1H, m, 4-H of C_6H_4), 6.93–6.95 (1H, m, 2-H of C_6H_4), 7.27 (1H, t, 5-H of C_6H_4) [ratio of (**7c**):(1), 12:1]. Anal. calcd. for $C_{15}H_{18}N_4OSSe$: C, 47.24; H, 4.76; N, 14.69. Found: C, 47.29; H, 4.76; N, 14.76%.

1-(3-Methyl-6,7-dihydro-5H-1,2,4-thiadiazolo-[4,5-a]pyrimidin-8-ium-8-yl)-N-(3-chlorophenyl) selenoformamidide (**7d**). The zwitterion (**7d**) (306 mg, 82%) was obtained as yellow plates, mp 184–185°C; ^{1}H NMR: δ 2.45 (2H, quint, 6-CH_2), 2.55 (3H, 3-Me), 4.19 (2H, t, 5-CH_2), 4.82 (2H, t, 7-CH_2), 7.10–7.32 (4H, m, C_6*H*$_4$) [ratio of (**7d**):(1), 15:1]. Anal. calcd. for $C_{13}H_{13}C\ell N_4SSe_2$: C, 42.00; H, 3.52; N, 15.07. Found: C, 41.74; H, 3.44; N, 15.12%.

Preparation of the Zwitterions (12a) *and* (12b)

1-(3-Methyl-5,10-dihydrobenzo[e]-1,2,4-thiadiazolo[4,5-a][1,3]diazepin-11-ium-11-yl)-N-(4-methylphenyl)selenoformamidide (**12a**). A solution of the diazepine (**3**) (217 mg, 1 mmol) in dichloromethane (25 mL) was added to a solution of 4-methylphenyl isoselenocyanate (588 mg, 3 mmol) in dichloromethane (5 mL) and the resulting solution was kept for 30 minutes. The solid that crystallized was filtered off, washed with benzene (2 mL), and dried in vacuo. The zwitterion (**12a**) (272 mg, 66%) was thus obtained as pale yellow plates, mp 139–140°C, which could not be recrystallized owing to partial breakdown in solution. Anal. calcd. for $C_{19}H_{18}N_4SSe$: C, 55.20; H, 4.39; N, 13.55. Found: C, 54.88; H, 4.35; N, 13.45%. A freshly prepared solution of (**12a**) in $CDCl_3$ showed ^{1}H NMR signals from (**12a**) at δ 2.30 (3H; *Me*C_6H_4), 2.62 (3H, 3-Me), 5.53 (2H, 5-CH_2), 6.58 (2H, 10-CH_2), 7.05–7.35 (8H, m, ArN and benzo-H), together with signals from the diazepine (**3**) at δ 2.32 (Me), 4.78 (10-CH_2), and 5.03 (5-CH_2) [5]. The ratio of (**12a**):(**3**) was 2.3:1. After 6 hours the ratio of (**12a**):(**3**) had increased to 2.7:1, and weak signals were present at δ 4.84 and 5.39 arising from the thiaselenazole (**10b**) which after several days became the major component of the solute mixture. The ^{13}C NMR spectrum of the freshly prepared solution showed signals from (**12a**) at δ 17.61 (3-Me), 21.02 (*Me*C_6H_4), 51.00, 51.62 (C-5, C-10), 164.10, 167.63 (C-3, C-11a).

1-(3-Methyl-5,10-dihydrobenzo[e]-1,2,4-thiadiazolo[4,5-a][1,3]diazepin-11-ium-11-yl)-N-(3-ethoxyphenyl)selenoformamidide (**12b**). A solution of the diazepine (**3**) (217 mg, 1 mmol) in dichloromethane (25 mL) was added to a solution of 3-ethoxyphenyl isoselenocyanate (678 mg, 3 mmol) in dichloromethane (5 mL) and the resulting solution was kept overnight. Solvent was removed at reduced pressure, the residue was redissolved in dichloromethane (10 mL), and ether (15 mL) and hexane (40 mL) were added in turn to the solution. The zwitterion (**12b**) (274 mg, 62%) crystallized as pale yellow plates, mp 133–134°C. Anal. calcd. for $C_{20}H_{20}N_4OSSe$: C, 54.17; H, 4.55; N, 12.63. Found: C, 53.75; H, 4.55; N, 12.51%. A freshly prepared solution of (**12b**) in $CDCl_3$ showed ^{1}H NMR signals arising from (**12b**) at δ 1.38 (3H, t, J 7.0, OCH_2*Me*), 2.60 (3H, 3-Me), 3.98 (2H, q, OCH_2Me), 5.51 (2H, 5-CH_2), 6.56 (2H, 10-CH_2), 6.65–7.81 (8H, m, ArN, and benzo-H), together with signals from the diazepine (**3**) at δ 2.29 (Me), 4.77 (10-CH_2), and 5.02 (5-CH_2). The ratio of (**12b**):(**3**) was 3:2. The ^{13}C NMR spectrum of the solution showed signals arising from (**12b**) at δ 14.89 (OCH_2*Me*), 17.71 (3-Me), 51.02, 51.77 (C-5, C-10), 63.36 (OCH_2Me), 164.31, 167.87 (C-3, C-11a).

Spectral Data for Isonitriles

The methods of preparation, yield, boiling point, and analytical data are appended to the NMR data for several previously unknown isonitriles.

Ethyl Isonitrile. ^{1}H NMR: δ 1.36 (3H, tt, J_{Me,CH_2} 7.3, Me), 3.40 (2H, tq, CH_2). ^{13}C NMR: δ 15.10 (Me), 36.41 (t, CH_2), 155.05 (t, N=C).

Cyclopentyl Isonitrile. ^{1}H NMR: δ 1.62–2.00 (8H, m, 4 × CH_2), 3.92 (1H, brs, CH). ^{13}C NMR: δ 22.84 (3,4-CH_2), 33.90 (2,5-CH_2), 53.26 (t, 1-CH), 154.10 (N=C).

Cycloheptyl Isonitrile. ^{1}H NMR: δ 1.43–2.01 (12H, m, 6 × CH_2), 3.78 (1H, m, CH). ^{13}C NMR: δ 22.79, 27.24 (3,4,5,6-CH_2), 34.83 (2,7-CH_2), 54.14 (t, 1-CH), 153.70 (t, N=C). Method (A) (57%). Bp 70–72°C/2 mm Hg. Anal. calcd. for $C_8H_{13}N$: N, 11.37. Found: N, 11.53%.

2-Phenylethyl Isonitrile. ^{1}H NMR: δ 2.91 (2H, tt, 2-CH_2), 3.53 (2H, tt, 1-CH_2), 7.17–7.36 (5H, m, Ph). ^{13}C NMR: δ 35.30 (2-CH_2), 42.69 (t, 1-CH_2), 126.95, 128.44, 128.50 (C-2, C-3, C-4 of Ph), 136.45 (C-1 of Ph), 156.32 (N=C).

Phenyl Isonitrile. ^{1}H NMR: δ 7.36 (s, Ph). ^{13}C NMR: δ 126.22, 129.19, 129.26 (C-2(6), C-3(5), C-4 of Ph), 126.80 (C-1 of Ph), 164.10 (N=C).

4-Methylphenyl Isonitrile. ^{1}H NMR: δ 2.35 (3H, Me), 7.16 (2H, 3, 5-H), 7.23 (2H, 2,6-H). ^{13}C NMR: δ 21.06 (Me), 123.78 (t, C-1), 125.88 (C-3 + C-5), 129.72 (C-2 + C-6), 139.44 (C-4), 163.00 (N=C).

4-Methoxyphenyl Isonitrile. ^{1}H NMR: δ 3.80 (3H, OMe), 6.86 (2H, 3,5-H), 7.27 (2H, 2,6-H). ^{13}C NMR: δ 55.25 (OMe), 114.25 (C-3 + C-5), 119.05 (t, C-1), 127.37 (C-2 + C-6), 159.57 (C-4), 162.42 (N=C).

4-Bromophenyl Isonitrile. ^{1}H NMR: δ 7.24 (2H, 2,6-H), 7.52 (2H, 3,5-H). ^{13}C NMR: δ 125.27 (t, C-1), 127.66 (C-2 + C-6), 132.52 (C-3 + C-5), 158.91 (C-4), 165.70 (N=C).

3-Ethoxyphenyl Isonitrile. ^{1}H NMR: δ 1.40 (3H, t, J_{Me,CH_2} 7.0, Me), 3.98 (2H, q, CH_2), 6.83–6.93 (3H, m, 2,4,6-H), 7.24 (1H, t, 5-H). ^{13}C NMR: δ 14.30 (Me), 63.57 (CH_2), 111.97, 115.75, 118.11 (C-2 + C-4 + C-6), 126.95 (t, C-1), 129.88 (C-5), 159.10 (C-3), 163.51 (N=C). Method (A) (57%), method (B) (65%). Bp 90–92°C/2 mm Hg. Anal. calcd. for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.81; H, 6.06; N, 9.55%.

3-Chlorophenyl Isonitrile. ^{1}H NMR: δ 7.26–7.44 (m, Ph). ^{13}C NMR: δ 124.60, 126.53, 129.78, 130.44 (C-2, C-4, C-5, C-6), 127.38 (t, C-1), 135.03 (C-3), 165.74 (N=C).

2-Ethoxyphenyl Isonitrile. ^{1}H NMR: δ 1.46 (3H, t, J_{Me,CH_2} 7.0, Me), 4.10 (2H, q, CH_2), 6.85–6.94 (2H, m, 3,5-H), 7.27–7.35 (2H, m, 4,6-H). ^{13}C NMR: δ 14.29 (Me), 64.30 (CH_2), 112.41, 120.03 (C-3, C-5), 115.89 (C-1), 127.28, 130.14 (C-4, C-6), 166.90 (N=C). Method (A) (55%), method (B) (69%). Bp 87–89°/2 mm Hg. Anal. calcd. for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.62; H, 6.22; N, 9.68%.

Spectral Data for Isoselenocyanates

Ethyl Isoselenocyanate. ^{1}H NMR: δ 1.42 (3H, t, J_{Me,CH_2} 7.2, Me), 3.70 (2H, q, CH_2). ^{13}C NMR: δ 14.61 (Me), 40.20 (CH_2), 121.0 (br, NCSe).

Butyl Isoselenocyanate. ^{1}H NMR: δ 0.97 (3H, t, J_{Me,CH_2} 7.3, Me), 1.42 (2H, sext, 3-CH_2), 1.74 (2H, quint, 2-CH_2), 3.64 (2H, t, $J_{1\text{-}CH_2,2\text{-}CH_2}$ 6.5, 1-CH_2). ^{13}C NMR: δ 12.92 (Me), 19.41 (3-CH_2), 31.04 (2-CH_2), 44.95 (1-CH_2), 121.5 (br, NCSe).

Cyclopentyl Isoselenocyanate. ^{1}H NMR: δ 1.58–2.04 (8H, m, 4 × CH_2), 4.16 (1H, quint, CH). ^{13}C NMR: δ 23.10 (3,4-CH_2), 33.70 (2,5-CH_2), 57.86 (CH).

Cyclohexyl Isoselenocyanate. ^{1}H NMR: δ 1.2–1.5 (4H, m) and 1.5–1.9 (6H, m) (5 × CH_2), 3.73 (1H, m, CH). ^{13}C NMR: δ 24.78 (4-CH_2), 22.98 (3,5-CH_2), 32.30 (2,6-CH_2), 55.48 (CH).

Cycloheptyl Isoselenocyanate. ^{1}H NMR: δ 1.45–2.04 (12H, m, 6 × CH_2), 4.00 (1H, quint, CH). ^{13}C NMR: δ 22.86, 27.18 (3,4,5,6-CH_2), 34.75 (2,7-CH_2), 58.23 (1-CH_2).

Benzyl Isoselenocyanate. ^{1}H NMR: δ 4.75 (2H, CH_2), 7.20–7.42 (5H, m, Ph). ^{13}C NMR: δ 48.77 (CH_2), 126.66, 128.38, 128.82 [C-2(6), C-3(5), C-4 of Ph], 132.64 (C-1).

2-Phenylethyl Isoselenocyanate. ^{1}H NMR: δ 2.95 (2H, t, J_{CH_2,CH_2}, 6.9, 2-CH_2), 3.72 (2H, t, 1-CH_2), 7.14–7.37 (5H, m, Ph). ^{13}C NMR: δ 35.80 (2-CH_2), 46.67 (1-CH_2), 127.21, 128.67, 128.75 [C-2(6), C-3(5), C-4 of Ph], 136.45 (C-1 of Ph).

4-Methylphenyl Isoselenocyanate. ^{1}H NMR: δ 2.34 (3H, Me), 7.15 (4H, s, 2,3,5,6-H). ^{13}C NMR: δ 21.21(Me), 125.72 (C-3 + C-5), 126.71 (C-1), 130.01 (C-2 + C-6), 138.38 (C-4).

4-Methoxyphenyl Isoselenocyanate. ^{1}H NMR: δ 3.81 (3H, OMe), 6.86 (2H, 3,5-H), 7.23 (2,6-H). ^{13}C NMR: δ 55.59 (OMe), 114.81 (C-3 + C-5), 122.15 (C-1), 127.41 (C-1), 127.41 (C-2 + C-6), 159.15 (C-4).

4-Bromophenyl Isoselenocyanate. ^{1}H NMR: δ 7.20 (2H, 2,6-H), 7.48 (3,5-H). ^{13}C NMR: δ 127.48 (C-2 + C-6), 128.78 (C-1), 132.76 (C-3 + C-5), 158.78 (C-4), 161.79 (NCSe).

3-Ethoxyphenyl Isoselenocyanate. ^{1}H NMR: δ 1.40 (3H, t, Me), 3.98 (2H, q, CH_2), 6.74–7.26 (4H, m, 2,4,5,6-H). ^{13}C NMR: δ 14.47 (Me), 63.64 (CH_2), 111.64, 114.85, 118.05 (C-2, C-4, C-6), 130.03 (C-5), 130.17 (C-1), 159.37 (C-3).

2-Ethoxyphenyl Isoselenocyanate. ^{1}H NMR: δ 1.46 (3H, t, Me), 4.07 (2H, q, CH_2), 6.81–7.27 (4H, m, 3,4,5,6-H). ^{13}C NMR: δ 14.44 (Me), 64.45 (CH_2), 112.20, 120.22 (C-3, C-5), 119.06 (C-1), 125.59, 128.87 (C-4, C-6), 155.47 (C-2).

^{1}H and ^{13}C NMR Spectral Data for the 3aλ^4-Thia-1,3,4,6-tetraazapentalene-2,5-diselones (6) *and* (9)

2,3-Diethyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6a**). ^{1}H NMR: δ 1.37 (6H, t, J 7.25, *Me*CH_2), 2.39 (2H, quint, 6-CH_2), 3.87 (4H, q, Me*CH_2*), 4.55 (4H, t, 5,7-CH_2). ^{13}C NMR: δ 13.99 (*Me*CH_2), 19.96 (C-6), 42.19 (Me*CH_2*), 47.46 (C-5, C-7), 155.86 (C-7b), 166.04 (C-1, C-4).

2,3-Dibutyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6b**). ^{1}H NMR: δ 0.98 (6H, t, J 7.24, *Me*$[CH_2]_3$, 1.42 (4H, sext, Me*CH_2*$[CH_2]_2$, 1.76 (4H, quint, Me-CH_2*CH_2*CH_2), 2.39 (4H, quint, 6-CH_2), 3.80 (4H, t, Me$[CH_2]_2$*CH_2*), 4.55 (4H, t, 5,7-CH_2). ^{13}C NMR: δ 13.55 (*Me*$[CH_2]_3$), 19.79 (C-6), 20.16 (Me*CH_2*$[CH_2]_2$), 30.19 (MeCH_2*CH_2*CH_2), 46.93 (Me$[CH_2]_2$*CH_2*), 47.33 (C-5, C-7), 155.54 (C-7b), 166.00 (C-1, C-4).

2,3-Dicyclopentyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6c**). ^{1}H NMR: δ 1.70–2.26 (16H, m, 8 × CH_2 of cyclopentyl), 2.38 (2H, quint, 6-CH_2), 4.57 (4H, t, 5,7-CH_2), 4.83–4.97 (2H, m, 2,3-CH). ^{13}C NMR: δ 19.80 (C-6), 24.33 (3,4-CH_2 of cyclopentyl), 31.90 (2,5-CH_2 of cyclopentyl), 47.41 (C-5, C-7), 62.14 (1-CH of cyclopentyl), 155.68 (C-7b), 165.98 (C-1, C-4).

2,3-Dicyclohexyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6d**). ^{1}H NMR: δ 1.23–2.20 (20H, m, 10 × CH_2 of cyclohexyl), 2.38 (2H, quint, 6-CH_2), 4.35–4.48 (2H, m, 2,3-CH), 4.57 (4H, t, 5,7-CH_2). ^{13}C NMR: δ 19.74 (C-6), 25.33, 25.48 (4-CH_2, 3,5-CH_2 of cyclohexyl), 32.47 (2,6-CH_2 of cyclohexyl), 47.13 (C-5, C-7), 60.56 (1-CH of cyclohexyl), 156.04 (C-7b), 165.04 (C-1, C-4).

2,3-Dicycloheptyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6e**). ^{1}H NMR: δ 1.59–2.02 (20H, m, 10 × CH_2 of cycloheptyl), 2.09–2.21 (4H, m, 2 × CH_2 of cycloheptyl), 2.37 (2H, quint, 6-CH_2), 4.56 (4H, t, 5,7-CH_2), 4.68 (2H, quint, 2,3-CH). ^{13}C NMR: δ 19.71 (C-6), 24.85; 27.95 (4,5-CH_2, 3,6-CH_2 of cycloheptyl), 34.48 (2,7-CH_2 of cycloheptyl), 47.21 (C-5, C-7), 155.90 (C-7b), 164.52 (C-1, C-4).

2,3-Dibenzyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6f**). ^{1}H NMR [$CDCl_3$ + DMSO-D_6 (3:1)]: δ 2.40 (2H, quint, 6-CH_2), 4.50 (4H, t, 5,7-CH_2), 4.94 (4H, Ph*CH_2*), 7.30 (10H, *Ph*CH_2).

2,3-Di-(2-phenylethyl)-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6g**). ^{1}H NMR: δ 2.34 (2H, quint, 6-CH_2), 2.93 (4H, t, Ph*CH_2*CH_2), 3.89 (4H, t, PhCH_2*CH_2*), 4.50 (4H, t, 5,7-CH_2), 7.19–7.37 (10H, m, *Ph*$[CH_2]_2$). ^{13}C NMR: δ 19.80 (C-6), 34.06 (Ph*CH_2*CH_2), 47.33 (C-5, C-7), 48.57 (PhCH_2*CH_2*), 126.59 (C-4 of Ph), 128.49, 128.92 (C-2, C-3 of Ph), 138.49 (C-1 of Ph), 155.51 (C-7b), 166.50 (C-1, C-4).

2,3-Di-(4-methylphenyl)-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6h**). ^{1}H NMR: δ 2.36 (6H, Me), 2.49 (2H, quint, 6-CH_2), 4.68 (4H, t, 5,7-CH_2), 7.24 (8H, *o*- and *m*-protons of Ar). ^{13}C NMR: δ 19.93 (C-6), 21.09 (Me), 47.93 (C-5, C-7), 125.44 (C-3, C-5 of Ar), 129.87 (C-2, C-6 of Ar), 135.29 (C-4 of Ar), 137.79 (C-1 of Ar), 156.96 (C-7b), 167.87 (C-1, C-4).

2,3-Di-(4-methoxyphenyl)-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diselone (**6i**). ^{1}H NMR: δ 2.43 (2H, 6-CH_2), 3.80 (6H, MeO), 4.62 (4H, t, 5,7-CH_2), 6.95 (4H, *m*-protons of Ar), 7.27 (4H, *o*-protons of Ar). ^{13}C NMR: δ 19.95 (C-6), 47.99 (C-5, C-7), 55.37 (MeO), 114.45 (C-3, C-5 of Ar), 126.81 (C-2, C-6 of Ar), 130.61 (C-1 of Ar), 156.77 (C-7b), 158.87 (C-4 of Ar), 167.89 (C-1, C-4).

2,3-Diethyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9a**). ^{1}H NMR: δ 1.32 (6H, t, J 7.20, *Me*CH_2), 3.82 (4H, q, Me*CH_2*), 6.42 (4H, brs, 5,10-CH_2), 7.43–7.63 (4H, m, benzo-H). ^{13}C NMR: δ 13.65 (*Me*CH_2), 42.78 (Me*CH_2*), 52.77 (C-5, C-10), 129.16, 130.22 (C-6, C-9 and C-7, C-8), 134.31 (C-5a, C-9a), 158.68 (C-10b), 166.99 (C-1, C-4).

2,3-Dibutyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9b**). ^{1}H NMR: δ 0.96 (6H, t, J 7.24,

Me[CH_2]$_3$), 1.38 (4H, sext, Me*C*$H_2$$CH_2$[$CH_2$]$_2$), 1.73 (4H, quint, $MeCH_2$*C*$H_2$$CH_2$), 3.75 (4H, t, Me[$CH_2$]$_2$*C*$H_2$), 6.42 (4H, brs, 5,10-$CH_2$), 7.44–7.63 (4H, m, benzo-H). ^{13}C NMR: δ 13.60 (*Me*[CH_2]$_3$), 20.22 ($MeCH_2$[CH_2]$_2$), 29.95 ($MeCH_2$*C*$H_2$$CH_2$), 47.46 (Me[$CH_2$]$_2$*C*$H_2$), 52.83 (C-5, C-10), 129.22, 130.25 (C-6, C-9 and C-7, C-8), 134.34 (C-5a, C-9a), 158.61 (C-10b), 167.27 (C-1, C-4).

2,3-Dicyclopentyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9c**). The following data refer to the 1:1 clathrate of (**9c**) with benzene. ^{1}H NMR: δ 1.63–1.92 (12H, m, 6 × CH_2 of cyclopentyl), 2.12–2.25 (4H, m, 2 × CH_2 of cyclopentyl), 4.79–4.89 (2H, m, 2,3-CH), 6.46 (4H, brs, 5,10-CH_2), 7.36 (6H, benzene), 7.43–7.64 (4H, m, benzo-H). ^{13}C NMR: δ 24.41 (3,4-CH_2 of cyclopentyl), 31.59 (2,5-CH_2 of cyclopentyl), 52.72 (C-5, C-10), 63.37 (1-CH of cyclopentyl), 128.22 (benzene), 129.17, 130.22 (C-6, C-9 and C-7, C-8), 134.42 (C-5a, C-9a), 158.72 (C-10b), 167.51 (C-1, C-4).

2,3-Dicyclohexyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9d**). The following data refer to the 1:1 clathrate of (**9d**) with benzene. ^{1}H NMR: δ 1.18–2.16 (20H, m, 10 × CH_2 of cyclohexyl), 4.34–4.46 (2H, m, 2,3-CH), 6.43 (4H, brs, 5,10-CH_2), 7.33 (6H, benzene), 7.41–7.62 (4H, m, benzo-H). ^{13}C NMR: δ 25.36, 25.55 (4-CH_2, 3,5-CH_2 of cyclohexyl), 32.28 (2,6-CH_2 of cyclohexyl), 52.24 (C-5, C-10), 61.93 (1-CH of cyclohexyl), 128.11 (benzene), 129.06, 130.07 (C-6, C-9 and C-7, C-8), 134.41 (C-5a, C-9a), 158.98 (C-10b), 166.46 (C-1, C-4).

2,3-Dicycloheptyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9e**). The following data refer to the 1:1 clathrate of (**9e**) with benzene. ^{1}H NMR: δ 1.56–1.89 (20H, m, 10 × CH_2 of cycloheptyl), 2.06–2.18 (4H, m, 2 × CH_2 of cycloheptyl), 4.59–4.71 (2H, m, 2,3-CH), 6.45 (4H, brs, 5,10-CH_2), 7.36 (6H, benzene), 7.43–765 (4H, m, benzo-H). ^{13}C NMR: δ 25.12, 28.00 (4,5-CH_2, 3,6-CH_2 of cycloheptyl), 34.50 (2,7-CH_2 of cycloheptyl), 52.54 (C-5, C-10), 128.26 (benzene), 129.22, 130.24 (C-6, C-9 and C-7, C-8), 134.51 (C-5a, C-9a), 159.15 (C-10b), 166.13 (C-1, C-4).

2,3-Dibenzyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9f**). ^{1}H NMR: δ 4.89 (4H, Ph*C*H_2), 6.40 (4H, brs, 5,10-CH_2), 7.28 (10H, *Ph*CH_2), 7.43–7.63 (4H, m, benzo-H). ^{13}C NMR: δ 52.46 (C-5, C-10), 53.22 (Ph*C*H_2), 127.95 (C-4 of Ph), 128.57, 128.95 (C-2, C-3 of Ph), 129.28, 130.39 (C-6, C-9 and C-7, C-8), 134.26 (C-5a, C-9a), 135.33 (C-1 of Ph), 159.40 (C-10b), 168.81 (C-1, C-4).

2,3-Di-(2-phenylethyl)-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9g**). ^{1}H NMR: δ 2.91 (4H, t, J 7.3, Ph*C*$H_2$$CH_2$), 3.84 (4H, t, Ph$CH_2$*C*$H_2$), 6.39 (4H, brs, 5,10-$CH_2$), 7.19–7.34 (10H, m, *Ph*[CH_2]$_2$), 7.44–7.64 (4H, m, benzo-H). ^{13}C NMR: δ 33.81 (Ph-*C*$H_2$$CH_2$), 49.09 (Ph$CH_2$*C*$H_2$), 52.89 (C-5, C-10), 126.65 (C-4 of Ph), 128.55, 128.98 (C-2, C-3 of Ph), 129.27, 130.37 (C-6, C-9 and C-7, C-8), 134.28 (C-5a, C-9a), 138.50 (C-1 of Ph), 158.61 (C-10b), 167.73 (C-1, C-4).

2,3-Di-(2,2-diphenylethyl)-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diselone (**9h**). ^{1}H NMR: δ 4.06 (4H, d, J 7.6, Ph_2CHC*H*$_2$), 4.55 (2H, t, Ph_2*C*HCH_2), 6.30 (4H, brs, 5,10-CH_2), 7.21–7.38 (20H, m, *Ph*$_2$CHCH_2), 7.42–7.61 (4H, m, benzo-H). ^{13}C NMR: δ 48.16, (Ph_2CHCH_2), 52.83 (C-5, C-10), 53.70 (Ph_2*C*HCH_2), 126.94 (C-4 of Ph), 128.39, 128.56 (C-2, C-3 of Ph), 129.19, 130.26 (C-6, C-9 and C-7, C-8), 134.16 (C-5a, C-9a), 141.36 (C-1 of Ph), 158.74 (C-10b), 168.53 (C-1, C-4).

^{1}H and ^{13}C NMR Spectral Data for the 5,10-Dihydro-3-arylimino-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepines (**10**)

5,10-Dihydro-3-phenylimino-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10a**). ^{1}H NMR: δ 4.86 (2H, 10-CH_2), 5.41 (2H, 5-CH_2), 6.97 (2H, d, J 7.0, 2*o*-protons of Ph), 7.15–7.46 (7H, m, 2*m*- + *p*-protons of Ph + 4 benzo-H). ^{13}C NMR: δ 50.58 (C-10), 52.70 (C-5), 120.96, 125.44, 127.87, 128.33, 128.91, 129.28, 129.69, 133.91, 139.83, 149.10 (Ph-C and benzo-C), 150.52 (C-3), 152.44 (C-11a).

5,10-Dihydro-3-(4-methylphenylimino)-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10b**). ^{1}H NMR: δ 2.35 (3H, Me), 4.85 (2H, 10-CH_2), 5.39 (2H, 5-CH_2), 6.85 (2H, *m*-protons of ArN), 7.16 (2H, *o*-protons of ArN), 7.24–7.42 (4H, m, benzo-H). ^{13}C NMR: δ 20.99 (Me), 50.51 (C-10), 52.65 (C-5), 120.70, 127.80, 128.27, 127.88, 129.21, 130.24, 133.90, 135.08, 139.81, 146.58 (Ar-C and benzo-C), 150.39 (C-3), 152.39 (C-11a).

5,10-Dihydro-3-(4-methoxyphenylimino)-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10c**). ^{1}H NMR: δ 3.81 (3H, OMe), 4.85 (2H, 10-CH_2), 5.40 (2H, 5-CH_2), 6.90 (4H, 2*o* + 2*m*-protons of ArN),

7.24–7.47 (4H, m, benzo-H). ^{13}C NMR: δ 50.51 (C-10), 52.62 (C-5), 55.40 (OMe), 114.79 (C-3, C-5 of ArN), 121.98 (C-2, C-6 of ArN), 127.79, 128.24, 128.85, 129.19, 133.87, 139.77 (benzo-C), 142.38 (C-1 of ArN), 150.83 (C-3), 152.44 (C-11a), 157.34 (C-4 of ArN).

5,10-Dihydro-3-(4-bromophenylimino)-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10d**). ^{1}H NMR: δ 4.86 (2H, 10-CH_2), 5.38 (2H, 5-CH_2), 6.85 (2H, *m*-protons of ArN), 7.25–7.43 (4H, m, benzo-H), 7.47 (2H, *o*-protons of ArN). ^{13}C NMR: δ 50.50 (C-10), 52.63 (C-5), 118.50 (C-4 of ArN), 122.76, 127.85, 128.32, 128.84, 129.30, 132.67, 133.65, 139.66 (C-2, C-3, C-5, C-6 of ArN and benzo-C), 147.93 (C-1 of ArN), 150.94 (C-3), 151.97 (C-11a).

5,10-Dihydro-3-(3-ethoxyphenylimino)-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10e**). ^{1}H NMR: δ 1.41 (3H, t, *J* 7.0, OCH_2*Me*), 4.02 (2H, q, OCH_2Me), 4.86 (2H, 10-CH_2), 5.40 (5-CH_2), 6.49–6.57 (2H, m, 4-H and 6-H of ArN), 6.73 (1H, ddd, 2-H of ArN), 7.21–7.46 (5H, 5-H of ArN and benzo-H). ^{13}C NMR: δ 14.76 (Me), 50.48 (C-10), 52.62 (C-5), 63.46 (OCH_2Me), 106.75, 112.07, 112.63, 127.80, 128.26, 128.85, 129.22, 130.46, 133.82, 139.74 (C-2, C-4, C-5, C-6 of ArN and benzo-C), 150.30 (C-1 of ArN), 150.58 (C-3), 152.33 (C-11a), 159.99 (C-3 of ArN).

5,10-Dihydro-3-(3-chlorophenylimino)-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10f**). ^{1}H NMR: δ 4.86 (2H, 10-CH_2), 5.37 (2H, 5-CH_2), 6.85–7.44 (8H, m, ArN and benzo-H). ^{13}C NMR: δ 50.50 (C-10), 52.64 (C-5), 119.08, 121.42, 125.37, 127.86, 128.33, 128.84, 129.31, 130.64, 133.64, 135.03, 139.65, 150.08 (C of ArN and benzo-C), 151.25 (C-3), 151.91 (C-11a).

5,10-Dihydro-3-(2-ethoxyphenylimino)-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10g**). ^{1}H NMR: δ 1.40 (3H, t, *J* 7.0, Me), 4.04 (2H, q, OCH_2Me), 4.85 (2H, 10-CH_2), 5.46 (2H, 5-CH_2), 6.89–7.47 (8H, m, ArN and benzo-H). ^{13}C NMR: δ 14.80 (Me), 50.41 (C-10), 52.52 (C-5), 64.28 (OCH_2Me), 113.64, 120.99, 121.42, 126.39, 127.69, 128.22, 128.85, 129.13, 133.85, 138.05, 139.78, 150.75 (C of ArN and benzo-C), 150.53 (C-3), 152.51 (C-11a).

5,10-Dihydro-3-(2-bromophenylimino)-1,2,4-thiaselenazolo[4,5-b][2,4]benzodiazepine (**10h**). ^{1}H NMR: δ 4.87 (2H, 10-CH_2), 5.47 (5-CH_2), 6.97–7.66 (8H, m, ArN and benzo-H). ^{13}C NMR: δ 50.50 (C-10), 52.59 (C-5), 117.22, 121.23, 126.50, 127.76, 128.40, 128.40, 128.96, 129.25, 133.56, 133.65, 139.65, 146.93 (C of ArN and benzo-C), 151.52 (C-3), 151.96 (C-11a).

REFERENCES

[1] L.-L. Lai, D. H. Reid, R. H. Nicol, J. B. Rhodes, *Heteroatom Chem., 5,* 1994, 149.

[2] D. G. Billing, J. C. A. Boeyens, L. Denner, M. D. Hellyar, L.-L. Lai, A. J. Matthee, D. H. Reid, *Acta Crystallogr. Sec. C, 47,* 1991, 2564.

[3] D. H. Reid, Y. Ding, L.-L. Lai, B. J. Luh, T.-H. Ngoi, *Bull. Soc. Chim. Belg., 103,* 1994, 539.

[4] L. Pauling: *The Nature of the Chemical Bond,* 3rd ed., Cornell University Press, Ithaca, NY, 1960.

[5] L.-L. Lai, T.-H. Ngoi, D. H. Reid, R. H. Nicol, J. B. Rhodes, *J. Chem. Soc. Perkin Trans. I,* 1993, 1753.

[6] D. G. Billing, J. C. A. Boeyens, L.-L. Lai, D. H. Reid, unpublished work.

[7] D. G. Billing, J. C. A. Boeyens, W. Haag, L.-L. Lai, D. H. Reid, *Acta Crystallogr. Sec. C, 49,* 1993, 1781.

[8] H. M. Walborsky, G. E. Niznik, *J. Org. Chem., 37,* 1972, 187.

[9] R. Appel, R. Kleinstück, K.-D. Ziehn, *Angew. Chem. Int. Ed. Eng., 10,* 1971, 132.

[10] H. J. Bestmann, J. Lienert, L. Mott, *Liebigs Ann. Chem., 718,* 1968, 24.

[11] E. Bulka, K.-D. Ahlers, E. Tućek, *Chem. Ber., 100,* 1967, 1367.