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Reactions of Fused Dihydro-1,2,4-Thiadiazoles with Isocyanates and Isothiocyanates to Give 6aλ^4-Thia-1,3,4,6-Tetraazapentalene Derivatives*

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ABSTRACT

3-Methyl-6,7-dihydro-5H-1,2,4-thiadiazolo[4,5-a]pyrimidine **4a** *reacted with isocyanates and isothiocyanates with elimination of acetonitrile and concomitant addition of two molecules of the heterocumulene to give the 2,3-disubstituted-6,7-dihydro-5H-2aλ^4-thia-2, 3, 4a, 7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-diones* **8a–8e** *and the corresponding dithiones* **9a–9h**, *respectively. 3-Methyl-5,10-dihydrobenzo[e]-1,2,4-thiadiazolo[4,5-a][1,3]diazepine* **5a** *likewise reacted with isocyanates and isothiocyanates to give the 2,3-disubstituted-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-diones* **10a–10f** *and the corresponding dithiones* **11a–11f**. *The base* **4a** *reacted with phenyl isocyanate, methyl isothiocyanate, and phenyl isothiocyanate in toluene at room temperature to give the zwitterions* **14a**, **14b**, *and* **14c**, *respectively, and the diazepine* **5a** *reacted with phenyl isothiocyanate to give the zwitterion* **17**.

INTRODUCTION

1,6,6aλ^4-Triheterapentalenes and their aza analogues comprise a large number of systems based on structure **1**, in which Y = S, Se, or Te and X and Z are O, S, Se, or NR. The essential structural feature of **1** is the heteroatom unit **2** in which Y is hypervalent and employs multicenter bonding. In the course of attempts to synthesise 1*H*,6*H*-3aλ^4-thia-1,3,4,6-tetraazapentalenes **3**, which are hitherto unknown variations of the triheterapentalene structure, we found [1] that 3-methyl-6,7-dihydro-5*H*-1,2,4-thiadiazolo[4,5-*a*]pyrimidine **4a** and 3-methyl-5,10-dihydrobenzo [*e*]-1,2,4-thiadiazolo[4,5-*a*][1,3]diazepine **5a** react with nitriles to give, respectively, the pyrimidines **4** (R = alkyl, aryl, heteroaryl) and the diazepines **5** (R = alkyl). We proposed [1] that these reactions take place (Scheme 1) via thiatetraazapentalenes **6**, which were not isolated or detected spectroscopically but are higher-energy intermediates in a reversible cycloaddition-elimination process. We now report that the bases **4a** and **5a** react with isocyanates and isothiocyanates to give stable derivatives of the 1*H*,6*H*-6aλ^4-thia-1,3,4,6-tetraazapentalene system **7**, which is isomeric with **3**.

RESULTS AND DISCUSSION

The pyrimidine **4a** reacted readily with isocyanates and isothiocyanates when heated in boiling toluene or when heated together in the absence of solvent. Elimination of acetonitrile took place with concomitant addition of two molecules of the isocyanate or isothiocyanate to give the diones **8a–8e** and the dithiones **9a–9h**, respectively. The diaze-

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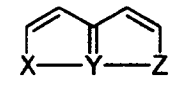

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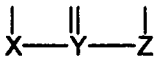

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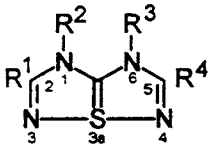

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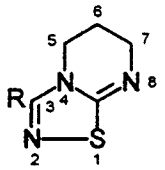
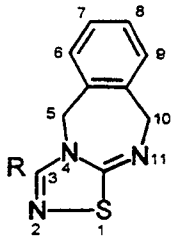


4

4a: R = Me



5

5a: R = Me

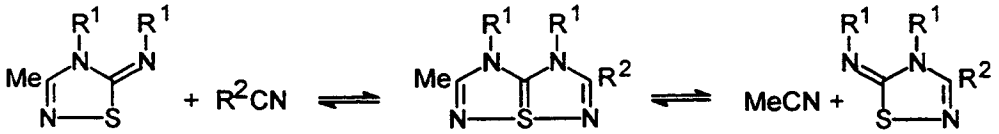
pine **5a** likewise reacted with isocyanates and isothiocyanates to give the corresponding diones **10a–10f** and the dithiones **11a–11f**. The diones **8d** [2–4] and **8f** [4] and the dithiones **9a** [2], **9b** [5,6], **9c**, [3,5], and **9g** [2] have previously been synthesized by other routes described in the references cited. The tetracyclic benzo[*e*]-1,2,4-thiadiazolo[4,5-*a*][1,3]diazepine system of compounds **10a–10f** and **11a–11f** is a new heterocyclic system.

The structures of the diones **8** and the dithiones **9** have previously been established by X-ray crystal structure determinations of the representative members **8d** [4,7], **8f** [4], and **9b** [5,6].

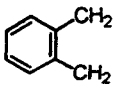
We assign structures **10a–10f** to the products from the reactions of the diazepine **5a** with isocyanates on the basis of their IR spectra, which show strong C=O absorption in the range 1690–1730 cm^{-1}, and their ^1H and ^{13}C NMR spectra, whose number and pattern of signals correspond to C_{2v}-symmetrical structures. The combined IR and NMR spectral data exclude the feasible alternative C_{2v}-symmetrical structures **12a** and the unsymmetrical structures **13a**.

The products from the reactions of the diazepine **5a** with isothiocyanates are assigned the dithione structures **11** on the basis of a comparison of their ^{13}C NMR spectra with those of the diones **8** and the dithiones **9**. The ^{13}C NMR spectra of compounds **11** show exactly the number of signals required by the C_{2v}-symmetrical structures **11** or **12b**. The diones **8** show only one signal below δ 151, namely, the C-7b signal which lies in the range δ 156–161. The C=O signal occurs in the range δ 148–151. The dithiones **9** on the other hand show two signals below δ 155, one of which is also in the range δ 156–161 and arises from C-7b. The second and lowest field signal lies in the range δ 167–169 and arises from 1(4)–C=S. Two low-field signals are also present in the ^{13} NMR spectra of the dithiones **11** in the ranges δ 159–161 and δ 168–171. They therefore arise from C-10b and from the thiocarbonyl groups at positions 1 and 4, respectively.

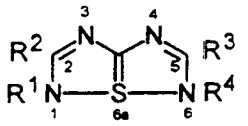
The base **4a** reacted rapidly with phenyl isocyanate, methyl isothiocyanate, and phenyl isothiocyanate in toluene at room temperature to give 1:1 addition products in almost quantitative yield. The low solubility in nonpolar solvents suggested that these adducts are the zwitterions **14a–14c** rather than the novel triheterapentalenes **15a–15c** or **16a–16c**. The structure of compound **14c** was confirmed by an X-ray crystal structure determination [8]. Only essential data are given here. The molecule is planar and the exocyclic nitrogen atom lies close to the extended ring N–S bond axis. The length of the ring N–S bond [1.687(9)Å] lies in the range found for the N–S bond in monocyclic 1,2,4-thiadiazolines [9], and the exocyclic N···S distance [2.298(9) Å] is much greater than the bond



6

R^1, R^1 = $[CH_2]_3$ or 

SCHEME 1



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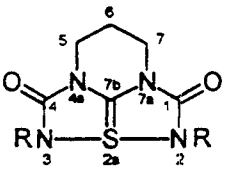

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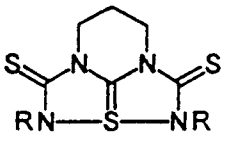


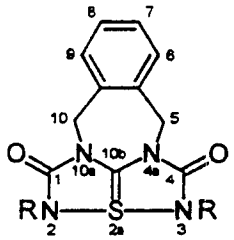
9

8a R = i-Pr
8b R = n-Bu
8c R = c-C_6H_{11}
8d R = Ph
8e R = 4-MeC_6H_4
8f R = Et

9a R = Me
9b R = Et
9c R = Allyl
9d R = n-Bu
9e R = c-C_6H_{11}
9f R = $PhCH_2$
9g R = Ph
9h R = 4-MeC_6H_4

lengths (range 1.83–1.98 Å) found [4–6,10] in triheterapentalenes containing the N–S–N sequence. These data thus exclude structures **15** and **16**.

The diazepine **5a** also reacted with phenyl isothiocyanate in dichloromethane at room temperature to give the zwitterion **17**. The zwitterion **14c** recrystallized from acetonitrile without change, but



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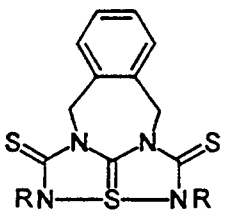
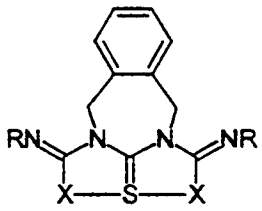


11

10a R = i-Pr
10b R = n-Bu
10c R = c-C_6H_{11}
10d R = $PhCH_2$
10e R = Ph
10f R = 4-MeC_6H_4

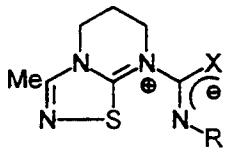
11a R = Me
11b R = n-Bu
11c R = Allyl
11d R = c-C_6H_{11}
11e R = $PhCH_2$
11f R = Ph



12

13

12a, 13a: X = O
12b, 13b: X = S



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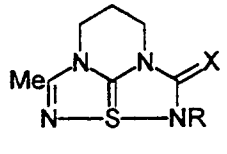

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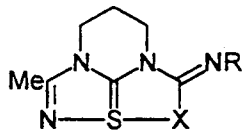
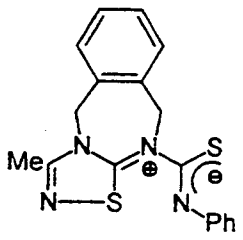


16

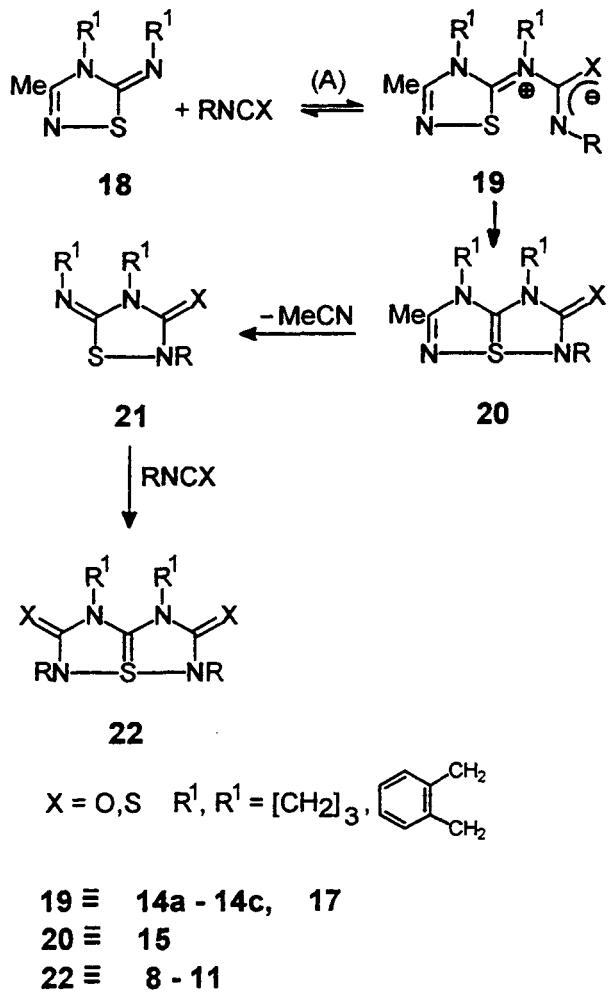
14a-16a: R = Ph, X = O
14b-16b: R = Me, X = S
14c-16c: R = Ph, X = S



17

the zwitterion **14b** disproportionated when heated briefly in boiling toluene or boiling acetonitrile to give a mixture of the triheterapentalene **9a** and the pyrimidine **4a**. The zwitterion **17** is unstable in solution. It dissolved in $CDCl_3$ to give a solution whose ^1H NMR spectrum showed that virtually complete reversion to the diazepine **5a** and phenyl isothiocyanate had occurred.

We interpret the foregoing results in terms of the reactions in Scheme 2. A reversible reaction [step (A)] takes place between the base **18** and the heterocumulene RNCX to give the zwitterion **19**. On being heated in the presence of an excess of RNCX, the zwitterion **19** is converted irreversibly into the thiadiazoline **21** via the transient unstable



SCHEME 2

triheterapentalene **20**. Reaction of **21** with RNCX gives the triheterapentalene **22**. Thus, in the presence of an excess of the heterocumulene RNCX, complete conversion of the base **18** into the triheterapentalene **22** takes place. In contrast, when the zwitterion **19** alone is heated in solution, the equilibrium (A) favors the formation of the reactants **18** and RNCX. Slow conversion of the zwitterion **19** into the thiadiazoline **21** followed by rapid reaction of **21** with RNCX drawn from the equilibrium (A) leads to the products **22** and **18** and non-isolation of the intermediate **21** among the reaction products.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained using solids dispersed in KBr discs. ^1H and ^{13}C NMR spectra were obtained using solutions in $CDCl_3$. ^1H NMR spectra were determined at 200.13 MHz and ^{13}C NMR spectra at 50.32 MHz with a Bruker AC 200 spectrometer. ^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; quin, quintet; m, multiplet; br, broad), J(Hz), assignment. ^{13}C NMR chemical shifts are given relative to the central deuteriochloroform peak taken as δ 77 and are proton-decoupled values.

Extracts were dried over sodium sulfate or magnesium sulfate. Solvents were removed from extracts and chromatographic eluates at reduced pressure with a rotary evaporator. Column chromatography was carried out with silica (85–200 mesh). Solvent mixtures are described in ratios by volume. Either denotes diethyl ether. The following solvents were dried by standard procedures and redistilled before use: acetonitrile, benzene, cyclohexane, dichloromethane, dimethylformamide, ether, hexane, and toluene.

Reactions of the Pyrimidine **4a** *with Isocyanates and Isothiocyanates: Synthesis of the Triheterapentalenes* **8a–8e** *and* **9a–9h**

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

Procedure A. A mixture of the pyrimidine **4a** (155 mg, 1 mmol) and the heterocumulene (20 mmol) was heated (oil bath) at 145°C for 15 minutes. The solid which crystallized from the cooled solution was filtered off, washed with a small volume of ether, and recrystallized from acetonitrile.

Procedure B. A solution of the pyrimidine **4a** (155 mg, 1 mmol) and the heterocumulene (10 mmol) in toluene (10 mL) was boiled for 15 minutes and cooled and solvent was removed at reduced pressure. The residue was triturated with acetonitrile (10 mL), and the resulting solid was filtered off and recrystallized from the solvent indicated in Table 1.

Procedure C. A solution of the pyrimidine **4a** (155 mg, 1 mmol) and the heterocumulene (10 mmol) in dichloromethane (20 mL) was kept at room temperature for 4 hours. Solvent was removed, ether (50 mL) was added, and the resulting solid was filtered off and recrystallized from acetonitrile.

Procedure D. A mixture of the pyrimidine **4a** (155 mg, 1 mmol) and the heterocumulene (10 mmol) was boiled for 15 minutes and cooled and hexane (30 mL) was added. The mixture was kept overnight in the refrigerator and the solid which

TABLE 1 Physical Properties and Analytical Data of Compounds **8** and **9**

Compound[a]	Procedure	RNCX	Yield (%)	mp (°C)	Formula	Found (%) (Required) C	H	N
8a	D	Me_2CHNCO	34	78–96 (decomp.)	$C_{12}H_{20}N_4O_2S$	50.74 (50.68	7.16 7.09	19.72 19.70)
8b	D	*n*-BuNCO	45	82–83	$C_{14}H_{24}N_4O_2S$	53.69 (53.81	7.86 7.74	17.95 17.94)
8c	B	*c*-$C_6H_{11}NCO$	74	130–145[b] (decomp.)	$C_{18}H_{28}N_4O_2S$	59.50 (59.31	7.86 7.74	15.47 15.37)
8d	A	PhNCO	80	209–212[c]	$C_{18}H_{16}N_4O_2S$	64.45 (61.35	4.50 4.58	15.97 15.90)
8e	A	4-MeC_6H_4NCO	72	217–218	$C_{20}H_{20}N_4O_2S$	63.15 (63.14	5.17 5.30	14.77 14.73)
9a	C	MeNCS	62	203–204[d]	$C_8H_{12}N_4S_3$	37.09 (36.90	4.50 4.64	21.64 21.52)
9b	B	EtNCS	64	202–204[f]	$C_{10}H_{16}N_4S_3$			
9c	A	CH_2=$CHCH_2NCS$	68	154–157	$C_{12}H_{16}N_4S_3$	45.86 (46.13	5.10 5.16	17.86 17.93)
9d	A	*n*-BuNCS	73	140–145	$C_{14}H_{24}N_4S_3$	48.63 (48.80	6.94 7.02	16.21 16.26)
9e[e]	B	*c*-$C_6H_{11}NCS$	56	183–185	$C_{18}H_{28}N_4S_3$	54.14 (54.51	7.22 7.12	14.28 14.13)
9f	A	$PhCH_2NCS$	87	207–208	$C_{20}H_{20}N_4S_3$	57.91 (58.22	4.83 4.89	13.54 13.58)
9g	A	PhNCS	61	175–182[g]	$C_{18}H_{16}N_4S_3$	56.05 (56.22	4.17 4.19	14.78 14.57)
9h[h]	A	4-MeC_6H_4NCS	37	175–179	$C_{20}H_{20}N_4S_3$	58.17 (58.22	4.83 4.89	13.47 13.58)

[a] White crystals unless otherwise stated.
[b] Solvent MeCN.
[c] Ref. [7] mp 210–212°C.
[d] Ref. [2] mp 203–205°C.
[e] Solvent MeCN–CH_2Cl_2 (4:1).
[f] Identical (mp, ^1H and ^{13}C NMR spectra) with an authentic sample (Ref. [6]).
[g] Ref. [2] mp 179–180°C.
[h] Pale yellow crystals.

had precipitated was filtered off, washed with hexane, and extracted with boiling hexane (4 × 75 mL). The combined extracts were concentrated at reduced pressure to ca. 40 mL solution from which the product crystallized.

Reactions of the Diazepine **5a** *with Isocyanates and Isothiocyanates: Synthesis of the Triheterapentalenes* **10a–10f** *and* **11a–11f**

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

Procedure A. A mixture of the diazepine **5a** (217 mg, 1 mmol) and the heterocumulene (10 mmol) was heated (oilbath) at 145°C for 15 minutes. The solid which had crystallized from the cooled mixture was filtered off, washed with a small volume of ether, and recrystallized from acetonitrile.

Procedure B. A solution of the diazepine **5a** (217 mg, 1 mmol) and the heterocumulene (10 mmol) in toluene (4 mL) was boiled for 15 minutes and cooled and solvent was evaporated at reduced pressure. The residual oily solid was recrystallized from the solvent indicated in Table 2.

Procedure C. A solution of the diazepine **5a** (217 mg, 1 mmol) and the heterocumulene (10 mmol) in dichloromethane (20 mL) was prepared and kept at room temperature for 4 hours. Solvent was then removed, ether (50 mL) was added, and the residual solid was filtered off, washed with ether, and recrystallized from acetonitrile.

Procedure D. A solution of the diazepine **5a** (217 mg, 2 mol) and the heterocumulene (10 mmol) in toluene (4 mL) was boiled for 15 minutes and cooled and solvent was removed at reduced pressure. The residual oily solid was dissolved in boiling hexane (20 mL), and the solution was kept in the refrigerator for 24 hours. The resulting solid was filtered

TABLE 2 Physical Properties and Analytical Data of Compounds **10** and **11**

Compound[a]	Procedure	RNCX	Yield (%)	mp (°C)	Formula	Found (%) (Required) C	H	N
10a	B	Me_2CHNCO	62	>87[b, c] (decomp.)	$C_{17}H_{22}N_4O_2S$	59.81 (58.94	6.41 6.40	16.22 16.17)
10b	B	*n*-BuNCO	73	>98[b, c] (decomp.)	$C_{19}H_{26}N_4O_2S$	60.88 (60.94	6.98 7.00	14.78 14.96)
10c	D	*c*-$C_6H_{11}NCO$	60	>132[b, d] (decomp.)	$C_{23}H_{30}N_4O_2S$	64.50 (64.76	7.12 7.10	12.98 12.98)
10d	A	$PhCH_2NCO$	20	162–163	$C_{25}H_{22}N_4O_2S$	67.61 (67.88	4.69 5.01	12.59 12.66)
10e	B	PhNCO	70	>170[b, e] (decomp.)	$C_{23}H_{18}N_4O_2S$	66.68 (66.65	4.32 4.38	13.52 13.52)
10f	A	4-MeC_6H_4NCS	39	185–187	$C_{25}H_{22}N_4O_2S$	67.51 (67.85	4.86 5.01	12.64 12.66)
11a	C	MeNCS	62	150–167 (decomp.)	$C_{13}H_{14}N_4S_3$	48.32 (48.42	4.40 4.38	17.43 17.37)
11b	A	*n*-BuNCS	39	126–127	$C_{19}H_{26}N_4S_3$	56.43 (56.12	6.33 6.44	13.78 13.78)
11c	D	$CH_2{=}CHCH_2NCS$	78	104–110 (decomp.)	$C_{17}H_{18}N_4S_3$	54.57 (54.52	4.87 4.84	15.03 14.96)
11d	D[f]	*c*-$C_6H_{11}NCS$	51	110–122[g] (decomp.)	$C_{23}H_{30}N_4S_3$		[h]	
11e	A	$PhCH_2NCS$	62	193–194	$C_{25}H_{22}N_4S_3$	63.48 (63.26	4.65 4.67	11.62 11.80)
11f[i]	B	PhNCS	68	>157[b, j] (decomp.)	$C_{23}H_{18}N_4S_3$	61.58 (61.86	4.02 4.06	12.42 12.54)

[a] White crystals unless otherwise stated.
[b] Melts gradually with decomposition above the temperature indicated.
[c] Solvent MeCN.
[d] Solvent hexane-CH_2Cl_2 (9:1).
[e] Solvent MeCN-CH_2Cl_2 (5:1).
[f] The solid which crystallized from hexane was chromatographed on silica (15 × 2.2 cm) with benzene. The eluates yielded an unstable clathrate (1 **11d**: $1C_6H_6$, ^1H NMR) which gradually loses solvent.
[g] Clathrate.
[h] Satisfactory analytical data could not be obtained.
[i] Pale yellow crystals.
[j] Solvent MeCN-CH_2Cl_2 (1:1).

off, washed with hexane, and recrystallized from hexane-CH_2Cl_2 (9:1).

Preparation of the Zwitterions **14a–14c** *and* **17**

1-(3-Methyl-6, 7-dihydro-5H-1, 2, 4-thiadiazolo-[4, 5-a] pyrimidin-8-ium-8-yl) -N-phenylformamidide **14a** Phenyl isocyanate (4.3 mL, 39.6 mmol) was added to a solution of the pyrimidine **4a** (776 mg, 5 mmol) in toluene (25 mL). The white precipitate which formed immediately was filtered off after 5 minutes, washed successively with toluene (50 mL) and ether (50 mL), and dried in vacuo. Compound **14a** (1.295 g, 94%) was thus obtained as a white powder, mp 137–139°C; IR, ν (C=O) 1661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (2H, quint, 6-CH_2), 2.40 (3H, 3-Me), 3.89 (2H, t, 7-CH_2), 4.11 (2H, t, 5-CH_2), 6.9–7.6 (5H, m, Ph). Anal. calcd for $C_{13}H_{14}N_4OS$: C, 56.92; H, 5.14; N, 20.42. Found: C, 56.61; H, 5.21; N, 20.22%.

1-(3-Methyl-6, 7-dihydro-5H-1, 2, 4-thiadiazolo-[4, 5-a]pyrimidin-8-ium-8-yl) -N-methylthioformamidide **14b**. The procedure was identical with that of the preceding experiment, with methyl isothiocyanate (3.5 mL, 51 mmol) in place of phenyl isocyanate. The zwitterion **14b** (1.111 g, 97%) was obtained as a white powder which decomposed gradually on being heated above 135°C. Owing to the low solubility of **14b** and its instability to heat a satisfactory ^1H NMR spectrum could not be obtained. Anal. calcd for $C_8H_{12}N_4S_2$: C, 42.08; H, 5.30; N, 24.54. Found: C, 42.36; H, 5.37; N, 24.18%.

1-(3-Methyl-6, 7-dihydro-5H-1, 2, 4-thiadiazolo-[4, 5-a]pyrimidin-8-ium-8-yl) -N-phenylthioformamidide **14c**. The procedure was identical with that of the two preceding experiments, with phenyl isothiocyanate (4.8 mL, 40 mmol) as the heterocumulene. The zwitterion **14c** (1.423 g, 98%) was ob-

tained as a white powder which, when recrystallized from acetonitrile, formed white plates, mp 153–155°C; ^{1}H NMR ($CDCl_3$) δ 2.30 (2H, quint, 6-CH_2), 2.45 (3H, 3-Me), 4.19 (2H, t, 5-CH_2), 4.42 (2H, t, 7-CH_2), 7.0–7.5 (5H, m, Ph). Anal. calcd for $C_{13}H_{14}N_4S_2$: C, 53.77; H, 4.86; N, 19.29. Found: C, 53.93; H, 4.92; N, 19.11%.

1-(3-Methyl-5,10-dihydrobenzo[e]-1,2,4-thiadiazolo[4,5-a][1,3]diazepin-11-ium-11-yl)-N-phenylthioformamidide **17**. Phenyl isothiocyanate (1.2 mL, 10 mmol) was added to a solution of the diazepine **5a** (217 mg, 1 mmol) in dichloromethane (25 mL). After 4 hours, the solvent was removed, ether (50 mL) was added to the residue, and the resulting solid was filtered off and washed with ether. The zwitterion **17** was thereby obtained (218 mg, 62%) as white prisms which decompose gradually on being heated above 130°C. The ^{1}H NMR spectrum ($CDCl_3$) consisted of the superimposed spectra of the diazepine **5a** and phenyl isothiocyanate; it showed signals at δ 2.30, 4.79, 5.04, 7.26–7.31 (m) (Ref. [1], **5a**: δ 2.29, 4.78, 5.03, 7.24–7.38). Anal. calcd for $C_{18}H_{16}N_4S_2$: C, 61.34; H, 4.58; N, 15.90. Found: C, 61.29; H, 4.53; N, 15.89%.

Action of Heat on Compound **14b**

In Toluene. Toluene (25 mL) containing the zwitterion **14b** (1.142 g, 5 mmol) in suspension was heated to the boiling point, at which temperature the solid had disappeared. The cooled solution deposited 2,3-dimethyl-6,7-dihydro-5*H*-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1(2*H*),4(3*H*)-dithione **9a** (647 mg, 49%) as white needles, identical (mp and mixed mp 203–205°C, ^{1}H NMR spectrum, TLC behavior) with the product from the reaction of the pyrimidine **4a** with methyl isothiocyanate. Solvent was removed from the toluene filtrates and the solid residue was sublimed at 120–130°C/0.4 mmHg, giving the pyrimidine **4a** (294 mg, 38%) as white crystals, identical (mp and mixed mp 72–73°C, TLC behavior) with an authentic sample (Ref. [1], mp 72–73°C).

In Acetonitrile. Acetonitrile (25 mL) containing the zwitterion **14b** (1.141 g, 5 mmol) in suspension was boiled for 3 minutes. The resulting clear solution on being cooled deposited a white solid which was recrystallized from acetonitrile (40 mL). Compound **9a** (542 mg) was obtained as white needles, identical (mp 204–205°C, mixed mp 203–205°C, TLC behavior) with an authentic sample. Solvent was removed from the combined acetonitrile filtrates, and the residual solid was chromatographed on silica (15 × 2.2 cm), giving the following eluates: (1) ether-methanol (19:1), 200 mL; (2) ether-methanol (19:1), 200 mL; (3) ether-methanol (19:1), 350 mL; (4) methanol, 1000 mL. Fraction (1) yielded a further quantity (48 mg) of compound **9a** (total yield 590 mg, 45%). The combined fractions (3) and (4) yielded the pyrimidine **4a** (250 mg, 32%), identical (mp, mixed mp, TLC behavior) with an authentic sample.

Spectral Data for the Triheterapentalenes **8–11**

2,3-Diisopropyl-6,7-dihydro-5H-2aλ^4-thia-2,3-4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-dione **8a**. IR: ν(C=O) 1685 cm^{-1} (s br). ^{1}H NMR: δ 1.34 (12H, d, *J* 6.7, 2,3-*Me*$_2$CH), 2.24 (2H, quint, 6-CH_2), 3.93 (4H, t, 5,7-CH_2), 4.04 (2H, sept, 2,3-Me$_2$C*H*). ^{13}C NMR: δ 17.62 (C-6), 20.94 (2,3-*Me*$_2$CH), 38.20 (C-5, C-7), 43.27 (2,3-Me$_2$CH), 148.65 (C-1, C-4), 158.23 (C-7b).

2,3-Dibutyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-dione **8b**. IR: ν(C=O) 1685 cm^{-1} (s br). ^{1}H NMR: δ 0.94 (6H, t, 2,3-[CH_2]$_3$*Me*), 1.28–1.46 (4H, m, 2,3-[CH_2]$_2$*C*H_2Me), 1.52–1.66 (4H, m, 2,3-CH_2*C*$H_2$$CH_2$Me), 2.24 (2H, quint, 6-$CH_2$), 3.32 (4H, t, 2,3-*C*$H_2$[$CH_2$]$_2$Me), 3.94 (4H, t, 5,7-$CH_2$). ^{13}C NMR: δ 13.59 (2,3-[CH_2]$_3$*Me*), 17.62 (C-6), 20.17 (2,3-[CH_2]$_2$*C*H_2Me), 31.89 (2,3-CH_2*C*$H_2$$CH_2$Me), 39.71 (5,7-$CH_2$), 40.22 (2,3-*C*$H_2$[$CH_2$]$_2$Me), 150.83 (C-1, C-4), 159.27 (C-7b).

2, 3-Dicyclohexyl-6, 7-dihydro-5H-2aλ^4-thia-2, 3, 4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-dione **8c**. IR: ν (C=O) 1680 cm^{-1} (s br). ^{1}H NMR: δ 1.17–2.02 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 2.23 (2H, quint, 6-CH_2), 3.56–3.71 (2H, m, 2,3-NCH), 3.92 (4H, 5,7-CH_2). ^{13}C NMR: δ 19.16 (C-6), 25.39, 25.67, 32.88 (CH_2 of 2,3-cyclohexyl), 39.62 (5,7-CH_2), 52.89 (2,3-NCH), 148.65 (C-1, C-4), 158.23 (C-7b).

2,3-Diphenyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-dione **8d**. IR: ν(C=O) 1690–1710 cm^{-1} (s br). ^{1}H NMR: δ 2.18 (2H, quint, 6-CH_2), 3.91 (4H, t, 5,7-CH_2), 7.12–7.48 (10H, m, 2,3-Ph). ^{13}C NMR: δ 19.10 (C-6), 40.25 (C-5, C-7), 122.74, 124.98, 129.26, 138.33 (2,3-Ph), 149.13 (C-1, C-4), 160.56 (C-7b).

2,3-Di-p-tolyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1(2H),4(3H)-dione **8e**. ^{1}H NMR: δ 2.23 (2H, quint, 6-CH_2), 2.33 (6H, 2 × Me), 3.97 (4H, t, 5,7-CH_2), 7.09–7.38 (8H, m, 2,3-Ar).

2,3-Dimethyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1 (2H) ,4(3H) -dithione **9a**. ^{1}H NMR: δ 2.35 (2H, quint, 6-CH_2), 3.02 (6H, 2,3-Me), 4.41 (4H, t, 5.7-CH_2).

2,3-Diethyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd] indene-1 (2H) ,4(3H) -dithione **9b**. ^{1}H NMR: δ 1.33 (6H, t, 2,3-CH_2*Me*), 2.35 (2H,

quint, 6-CH_2), 3.78 (4H, q, 2,3-CH_2Me), 4.41 (4H, t, 5,7-CH_2). ^{13}C NMR: δ 13.62 (2,3-CH_2*Me*), 19.94 (C-6), 39.88 (C-5, C-7), 44.58 (2,3-*C*H_2Me), 156.03 (C-7b), 168.53 (C-1, C-4).

2,3-Diallyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent [cd]indene-1 (2H),4(3H)-dithione **9c**. ^{1}H NMR: δ 2.36 (2H, quint, 6-CH_2) 4.42 (8H, m, 5,7-CH_2 + 2,3-CH_2CH=CH_2), 5.25 (4H, m, 2,3-CH_2CH=CH_2), 6.02 (2H, m, 2,3-CH_2C*H*=CH_2).

2,3-Dibutyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent [cd]indene-1 (2H),4(3H)-dithione **9d**. ^{1}H NMR: δ 0.74–1.84 (14H, m, 2,3-$CH_2[CH_2]_2$*Me*), 2.44 (2H, quint, 6-CH_2), 3.72 (4H, t, 2,3-C$H_2[CH_2]_2$Me), 4.41 (4H, t, 5,7-CH_2).

2,3-Dicyclohexyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent[cd]indene-1 (2H),4(3H)-dithione **9e**. ^{1}H NMR: δ 1.15–2.15 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 2.34 (2H, quint, 6-CH_2) 4.22–4.36 (2H, m, 2,3-CH), 4.42 (4H, t, 5,7-CH_2). ^{13}C NMR: δ 19.79 (C-6), 25.47, 25.61, 32.39 (CH_2 of 2,3-cyclohexyl), 44.38 (5,7-CH_2), 58.16 (2.3-CH), 156.49 (C-7b), 167.70 (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)-dithione **9f**. ^{1}H NMR: δ 2.38 (2H, quint, 6-CH_2), 4.40 (4H, t, 5,7-CH_2), 4.85 (4H, 2,3-CH_2Ph), 7.30 (10H, 2,3-CH_2*Ph*).

2,3-Diphenyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent [cd]indene-1 (2H),4 (3H)-dithione **9g**. ^{1}H NMR: δ 2.50 (2H, quint, 6-CH_2), 4.55 (4H, t, 5,7-CH_2), 7.39 (1OH, m, 2,3-Ph).

2,3-Di-p-tolyl-6,7-dihydro-5H-2aλ^4-thia-2,3,4a,7a-tetraazacyclopent [cd]indene-1 (2H),4 (3H)-dithione **9h**. ^{1}H NMR: δ 2.35 (6H, 2,3-*Me*C_6H_4), 2.50 (2H, quint, 6-CH_2), 4.51 (4H, t, 5,7-CH_2), 7.23 (8H, 4*o* and 4*m*—protons of 2,3-Ar).

2,3-Diisopropyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dione **10a**. IR: ν(C=O) 1690–1710 cm^{-1} (s br). ^{1}H NMR: δ1.33 (12H, d, *J* 7.3,2,3-*Me*$_2$CH), 3.93 (2H, sept, 2,3-Me$_2$C*H*), 5.46 (4H, 5,10-CH_2), 7.44 (4H, benzo-H). ^{13}C NMR: δ 22.09 (2,3-*Me*$_2$ CH), 44.51, 45.12 (C-5, C-10, 2,3-Me$_2$*C*H), 128.99, 129.72, 134.78 (benzo-C), 149.66 (C-1, C-4), 162.45 (C-10b).

2,3-Dibutyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dione **10b**. IR: ν(C=O) 1690–1710 cm^{-1} (s br). ^{1}H NMR: δ 0.93 (6H, t, 2,3-[CH_2]$_3$*Me*), 1.29–1.44 (4H, m, 2,3-[CH_2]$_2$CH_2Me), 1.50–1.84 (4H, m, 2,3-CH_2CH_2CH_2Me). 3.28 (4H, t, 2,3-CH_2[CH_2]$_2$Me), 5.46 (4H, 5,10-CH_2), 7.44 (4H, benzo-H). ^{13}C NMR: δ 13.62 (2,3-[CH_2]$_3$*Me*). 20.22 (2,3-[CH_2]$_2$*C*H_2Me), 31.72 (2,3-CH_2CH_2CH_2Me), 40.12 (2,3-*C*H_2[CH_2]$_2$Me), 45,12 (C-5, C-10), 129.04, 129.77, 134.70 (benzo-C), 150.49 (C-1, C-4), 162.13 (C-10b).

2,3-Dicyclohexyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dione **10c**. IR: ν(C=O) 1690–1710 cm^{-1} (s br). ^{1}H NMR: δ 1.15–1.91 (20H, m, 10 × CH_2 of 2,3-cyclohexyl), 3.52–3.64 (2H, m, 2,3-CH), 5.46 (4H, 5,10-CH_2), 7.43 (4H, benzo-H). ^{13}C NMR: δ 24.52, 25.75, 32.60 (CH_2 of 2,3-cyclohexyl), 44.56, 45.13 (C-5, C-10, 2,3-CH), 129.00, 129.71, 134.90 (benzo-C), 149.77 (C-1, C-4), 162.43 (C-10b).

2,3-Dibenzyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dione **10d**. ^{1}H NMR: δ 4.43 (4H, 2,3,-CH_2Ph), 5.42 (4H, 5,10-CH_2), 7.26 (10H, 2,3-CH_2*Ph*), 7.41 (4H, benzo-H).

2,3-Diphenyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dione **10e**. IR: ν(C=O) 1695–1730 cm^{-1} (s br). ^{1}H NMR: δ 5.51 (4H, 5, 10-CH_2), 7.14–7.52 (10H, m, 2,3-Ph), 7.47 (4H, benzo-H).

2,3-Di-p-tolyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dione **10f**. ^{1}H NMR: δ 2.32 (6H, 2,3-*Me*C_6H_4), 5.54 (4H, 5, 10-CH_2), 7.19–7.35 (8H, m, 2,3-MeC_6*H*$_4$), 7.47 (4H, benzo-H).

2,3-Dimethyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dithione **11a**. ^{1}H NMR: δ 3.17 (6H, 2, 3-Me), 6.25 (4H, br, 5, 10-CH_2), 7.32–7.68 (4 H, m, benzo-H).

2,3-Dibutyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dithione **11b**. ^{1}H NMR: δ 0.95 (6H, t, 2,3-[CH_2]$_3$*Me*), 1.38 (4H, sext, 2,3-[CH_2]$_2$CH_2Me), 1.74 (4H, quint, 2,3-CH_2CH_2CH_2Me), 3.67 (4H, t, 2,3-CH_2[CH_2]$_2$Me), 6.26 (4H, br, 5,10-CH_2), 7.36–7.65 (4H, m, benzo-H).

2,3-Diallyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dithione **11c**. ^{1}H NMR: δ 4.28–4.32 (4H, m, 2,3-CH_2CH=CH_2), 5.15–5.30 (4H, m, 2,3-CH_2CH=CH_2), 5.82–6.01 (2H, m, 2,3-CH_2C*H*=CH_2), 6.26 (br, 5, 10-CH_2), 7.26–7.57 (4H, m, benzo-H). ^{13}C NMR: δ 49.04, 49.86, (C-5, C-10, 2,3-CH_2), 118.05, 129.17, 130.18, 131.75, 134.39 (benzo-C, 2,3-CH_2CH=*C*H_2), 159.67 (C-10b), 169.91 (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-dithione **11d**. ^{1}H NMR: δ 1.12–2.12 (20H, m, 10 × CH_2 of 2,3-cyclohexyl, 4.14–4.34 (2H, m, 2,3-CH), 6.27 (4H, br, 5,10-CH_2), 7.22–7.58 (4H, m, benzo-

H), ^{13}C NMR: δ 25.51, 25.68, 32.17 (CH_2 of 2,3-cyclohexyl). 49.34, 50.17 (C-5, C-10, 2,3-CH), 129.13, 130.04, 134.64 (benzo-C), 159.66 (C-10b), 168.30 (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-dithione **11e**. ^1H NMR: δ 4.81 (4H, 2,3-CH_2Ph), 6.22 (4H, br, 5,10-CH_2), 7.27 (10H, 2,3-CH_2Ph), 7.38–7.62 (4H, m, benzo-H).

2,3-Diphenyl-5,10-dihydro-2aλ^4-thia-2,3,4a,10a-tetraazapentaleno[3,3a,4-gh]benzocycloheptene-1,4-dithione **11f**. Owing to instability in solution, satisfactory NMR spectra were not obtained.

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