Condensation of 5-aminothieno[2,3-*c*]pyridazine-6-carbaldehyde with aliphatic primary amines. Synthesis of new heterocyclic 2,6,9-triazabicyclo[3.3.1]nonane derivatives

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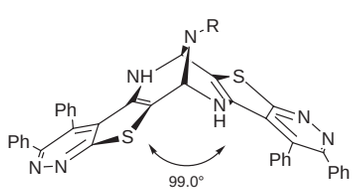
5-Amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carbaldehyde (**2**) undergoes condensation with aliphatic primary amines to give the corresponding 2,6,9-triazabicyclo[3.3.1]nonane derivatives **1** with different substituents at position 14. The molecular and crystal structure of **1b** (R = Bu) have been determined by X-ray analysis. A suitable mechanism for the formation of **1** is proposed.

Introduction

It has long been known that a number of aromatic *o*-aminoaldehydes have wide utilization in the annelation of heterocyclic fused ring systems due to their remarkable versatility as starting materials.[1] In particular, polymeric self-condensation products of *o*-aminobenzaldehyde have received considerable attention due to the fact that the character of the polymer is strongly dependent upon the experimental reaction conditions.[2] Nitrogen-containing heterocycles bearing amino substituents are of broad pharmaceutical interest and this justifies continuing efforts in the development of structure–activity relationships of new compounds in this series and of new synthetic strategies.[3] In connection with our ongoing interest in exploring new synthetic routes for the formation of heterocyclic compounds of biological interest we were interested in the preparation of some *o*-aminoimine derivatives for use as starting materials in continued efforts directed towards the synthesis of tricyclic compounds containing a thienopyrimidine or thienopyridazine system.[4]

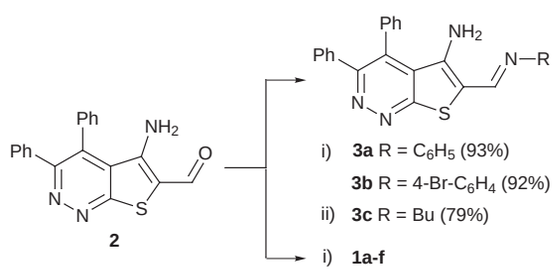


1	R	Yield (%)
a	Pr	42
b	Bu	87
c	C_5H_{11}	67
d	Pr^i	39
e	Bu^i	40
f	Bn	39

The synthesis of the 2,6,9-triazabyciclo[3.3.1]nonane system is not well documented. A substituted 2,6,9-triazabyciclo[3.3.1]-nonane was previously prepared by Katritzky *et al.*,[5] from crotonaldehyde and methylamine, and the 3,7-dioxo derivative was isolated from the thermolysis of β-aminocrotonamide.[6] The dimer of 2-(methyliminomethyl)aniline was found, on the evidence of the IR, UV, and NMR spectra, to be 6,12-epimethylimino-5*H*,11*H*-dibenzo[*b*,*f*][1,5]diazocine.[7] Its 9-aryl analogues have been prepared[8] from *o*-[(triphenylphosphoranyliden)-amino]benzaldehyde and primary amines. Also, it has been reported that the reaction of *o*-(tosylamino)benzaldehyde with ammonium acetate, methyl- and ethylamine afforded the corresponding 1,5-ditosyl-6,12-epimethyliminodibenzo[*b*,*f*]-[1,5]diazocines.[9] To the best of our knowledge, the synthesis of [*b*,*f*][1,5]diazocines **1** is the first example of a 2,6,9-triazabicyclo[3.3.1]nonane incorporating an annelated heterocyclic system.

Results and discussion

The expected imine derivatives **3** were obtained in high yields by reaction of 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carbaldehyde[10] (**2**) with aromatic primary amines in refluxing EtOH–AcOH (15:1); however, when the reaction was carried out with aliphatic primary amines under the same reaction conditions, compounds **1** containing the [*b*,*f*][1,5]diazocine ring system were isolated (Scheme 1). The use of PTSA or piperidine instead of acetic acid yielded the imine compounds **3** as the only reaction product with both aliphatic and aromatic primary amines.



Scheme 1 *Reagents and conditions*: i) RNH_2, EtOH–AcOH (15:1), reflux; ii) butylamine, piperidine, EtOH, reflux.

In Scheme 2 a suitable mechanism for the conversion **2**→**1** is represented. In order to exclude alternative pathways compound **2** was refluxed in EtOH–AcOH (15:1), but the starting material was recovered unaltered. This result eliminates the possibility that the reaction involves initial formation of the eight-membered ring followed by a cross-addition of the amino group on the aldimine bonds. This suggests that the initial reaction of the *o*-aminoaldehyde **2** and the corresponding primary amino group producing the imine derivative **3** which undergoes reaction with a second equivalent of aminoaldehyde **2** to give, through a [4+2] cycloaddition, the key intermediate **4** with a pyrimidine ring. The subsequent intramolecular nucleophilic attack of the terminal amino nitrogen atom to the 4-carbon determines the closure of the nine-membered triazabicyclo-[3.3.1] to give **1**.

Structural elucidation of [1,5]diazocine derivatives **1** was accomplished from analytical, spectral data, and X-ray analysis. The FAB-MS spectra showed the expected molecular ion peaks and the ^{1}H NMR spectra exhibited signals at δ = 3.78–3.84 ppm (2H, d, *J* 3.4–4.4) (exchangeable with D_2O) for the

Table 1 Selected bonds (Å) and angles (°) for compound **1b**[a]

N(4)–C(38)	1.468(3)	C(38)–N(4)–C(19)	107.8(2)
N(4)–C(19)	1.451(3)	N(5)–C(19)–C(15)	110.6(2)
C(37)–C(38)	1.506(3)	C(15)–C(16)–N(3)	121.2(3)
N(5)–C(20)	1.391(3)	N(4)–C(19)–C(15)	106.3(2)
N(3)–C(16)	1.399(3)	C(39)–N(4)–C(38)	113.9(2)
C(15)–C(19)	1.505(3)	C(16)–C(15)–S(1)	114.3(2)
N(3)–C(38)	1.455(3)	N(3)–C(38)–C(37)	109.0(2)
C(19)–N(5)	1.464(3)	N(3)–C(38)–N(4)	111.2(2)

[a] Crystallographic numbering scheme, see Fig. 1.

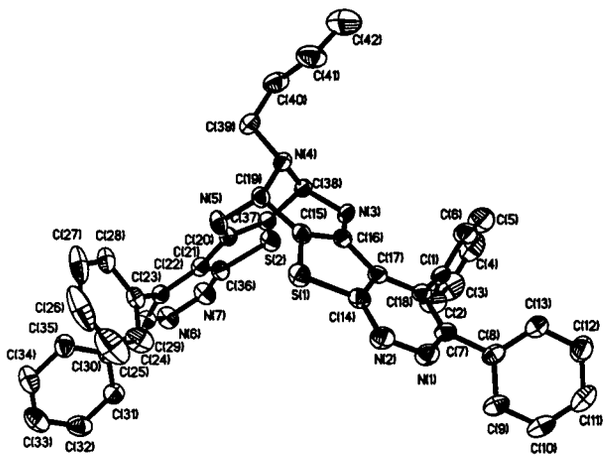
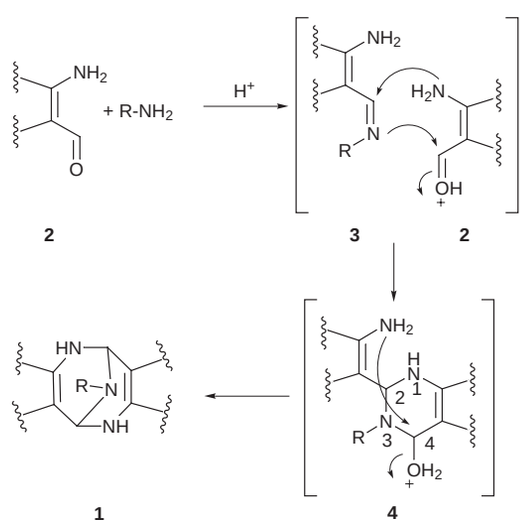


Fig. 1 ORTEP diagram of compound **1b** showing the numbering scheme used in the crystallographic study.



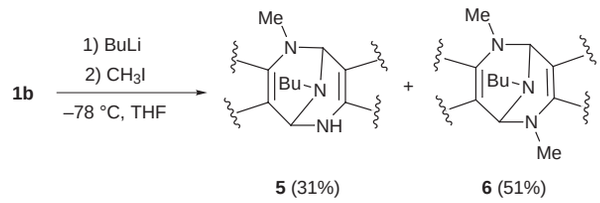
Scheme 2

NH groups and δ = 4.84–5.24 (2H, d, J 3.4–4.4) for the 6-H and 13-H. The most salient features of the ^{1}H NMR and ^{13}C NMR spectra are given in the Experimental section.

X-Ray structural analysis of a single crystal of **1b** (Fig. 1) has been carried out, which confirmed our earlier assignments. The V-shaped geometry of **1** is reminiscent of the form of Tröger's base. The angle between the two thienopyridazino rings fused to the bicycle system (99.0°) is similar to the 6,12-epiminodibenzo[*b*,*f*][1,5]diazocines previously described,[8,9] whereas the dihedral angle between the phenyl rings in compounds with Tröger's base moiety shows a great deal of flexibility, lying in the range 79.0–104.0°.[11] The CH–NBu–CH angle for compound **1b** is 107.8° whereas the N–CH_2–N angle in Tröger's base compounds ranges from 110.2 to 112.6°.[9] The main features of the molecular and crystal structure of compound **1b** are listed in Table 1.

The rigid, concave, sharply folded geometry of compounds **1** could make these molecules attractive in the design of molecular receptors or solvating agents, and they could interact with DNA in the same way as a Tröger's base analogue incorporating a heterocyclic derivative,[12] and be used as hosts for hydrogen bond donor compounds.

Finally, treatment of **1b** with BuLi and methyl iodide gave compounds **5** and **6** in 1 : 1.7 ratio (Scheme 3) which were isolated by flash chromatography and characterized by microanalysis and spectral data.



Scheme 3

We have demonstrated here that some substituted epiminodipyridazinodithieno[1,5]diazocines **1** can be prepared rapidly from aminoaldehyde **2**. These compounds could provide relatively rigid chiral frameworks for the construction of chelating and biomimetic systems, because of their close analogy with Tröger's bases.[12,13] Further detailed investigations with other heterocyclic *o*-aminoaldehydes are in process.

Experimental

Melting points were determined on a Büchi 510 apparatus and are uncorrected. IR spectra were recorded as potassium bromide disks on a Perkin-Elmer 783 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 200F instrument at room temperature for $CDCl_3$ solutions. Chemical shifts are reported in δ values and coupling constants (J) in Hz. Mass spectra were obtained on a VG QUATTRO spectrometer. The silica gel 60 $HF_{254+366}$ used for analytical thin layer chromatography and the silica gel 60 (230–400 mesh) employed for flash chromatography were purchased from Merck. Visualization was done under UV (254 and 365 mn) radiation. Microanalyses for C, H and N were performed by the Elemental Analysis General Service of the University of La Coruña.

Preparation of 14-alkyl-5,6,12,13-tetrahydro-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′ : 4,5]thieno)-[3,2-*b* : 3,2-*f*][1,5]diazocines 1a–f

To a solution of 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carbaldehyde **2** (0.100 g, 0.302 mmol) in anhydrous EtOH (10 cm^3), glacial acetic acid (0.66 cm^3) and the appropriate amine (0.453 mmol) were added. The reaction mixture was refluxed for 4 h (**1f**: 1 h) but the work-up for the isolation of the products was dependent on the amine used in the reaction. Thus, compounds **1b** and **1c** precipitated from the reaction mixture and were recrystallized from acetone–CH_2Cl_2, while for isolation of compounds **1a**, **1d**, **1e** and **1f** it was necessary to concentrate the resulting solutions to dryness and the resulting crude products were then chromatographed on a silica gel column using dichoromethane–ethyl acetate (25 : 1) (**1e**: 9 : 1) as eluent, and recrystallized from acetone–CH_2Cl_2.

14-Propyl-5,6,12,13-tetrahydro-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′ : 4,5]thieno)[3,2-*b* : 3,2-*f*][1,5]diazocine 1a. 42% Yield; mp 185–187 °C (Found: C, 71.7; H, 4.6; N, 14.2. Calc. for $C_{41}H_{31}N_7S_2$: C, 71.8; H, 4.6; N, 14.3%); ν_{max}(KBr)/cm^{-1} 3410 and 3380 (NH), 1560, 1440, 1300, 1200, 760 and 700; δ_H(200 MHz; $CDCl_3$) 0.86 (3 H, t, J 7.3, CH_3), 1.51 (2 H, sextet, J 7.3, CH_2CH_3), 2.28–2.61 (2 H, m, NCH_2), 3.84 (2 H, d, J 4.4, NH), 4.97 (2 H, d, J 3.9, 6-H and 13-H) and 7.16–7.49 (20 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 11.7 (CH_3), 20.9

(CH_2), 51.0 (NCH_2), 63.1 (6-C and 13-C), 120.6, 125.5, 127.8, 128.0, 128.3, 128.9, 129.7, 130.2, 131.8, 133.7, 136.6, 154.8 and 162.0; *m*/*z* (FAB) 686 [$(MH)^+$, 20%], 642 (26), 383 (73), 341 (85), 304 (100), 221 (55) and 207 (62).

14-Butyl-5,6,12,13-tetrahydro-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′:4,5]thieno)[3,2-*b*:3,2-*f*][1,5]diazocine 1b. 74% Yield; mp 252–254 °C (Found: C, 71.8; H, 4.7; N, 14.2. Calc. for $C_{42}H_{33}N_7S_2$: C, 72.1; H, 4.75; N, 14.0%); ν_{max}(KBr)/cm^{-1} 3380 and 3320 (NH), 1560, 1440, 1300, 1200, 760 and 700; δ_H(200 MHz; $CDCl_3$) 0.86 (3 H, t, *J* 7.3, CH_3), 1.22–1.37 (2 H, m, CH_2), 1.41–1.56 (2 H, m, CH_2), 2.32–2.64 (2 H, m, NCH_2), 3.80 (2 H, d, *J* 3.9, NH), 4.96 (2 H, d, *J* 4.4, 6-H and 13-H) and 7.16–7.47 (20 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 13.8 (CH_3), 20.4 (CH_2), 29.8 (CH_2), 48.9 (NCH_2), 63.4 (6-C and 13-C), 120.6, 125.5, 127.8, 128.0, 128.3, 129.0, 129.7, 130.2, 133.7, 136.6, 154.8 and 162.0; *m*/*z* (FAB) 700 [$(MH)^+$, 28%], 642 (12), 524 (25), 496 (45), 397 (17), 353 (100), 341 (22), 325 (66), 316 (23), 304 (24) and 288 (23).

14-Pentyl-5,6,12,13-tetrahydro-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′:4,5]thieno)[3,2-*b*:3,2-*f*][1,5]diazocine 1c. 67% Yield; mp 238–240 °C (Found: C, 72.45; H, 5.0; N, 13.6. Calc. for $C_{43}H_{35}N_7S_2$: C, 72.3; H, 4.9; N, 13.7%); ν_{max}(KBr)/cm^{-1} 3380 and 3320 (NH), 1560, 1440, 1310, 1200, 760 and 700; δ_H(200 MHz; $CDCl_3$) 0.85 (3 H, t, *J* 6.6, CH_3), 1.23–1.28 (4 H, m, CH_2), 1.47–1.55 (2 H, m, CH_2), 2.32–2.64 (2 H, m, NCH_2), 3.80 (2 H, d, *J* 3.9, NH), 4.97 (2 H, d, *J* 3.9 6-H and 13-H) and 7.17–7.48 (20 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 13.9 (CH_3), 22.4 (CH_2), 27.4 (CH_2), 29.4 (CH_2), 49.2 (NCH_2), 63.4 (6-C and 13-C), 120.6, 125.5, 127.8, 128.0, 128.4, 129.2, 129.7, 130.2, 131.8, 133.7, 136.6, 154.8 and 162.0; *m*/*z* (FAB) 714 [$(MH)^+$, 100%], 643 (22), 412 (41), 341 (43), 304 (53) and 181 (80).

14-Isopropyl-5,6,12,13-tetrahydro-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′:4,5]thieno)[3,2-*b*:3,2-*f*][1,5]diazocine 1d. 39% Yield, mp 253–255 °C (Found: C, 72.0; H, 4.50; N, 14.1. Calc. for $C_{41}H_{31}N_7S_2$: C, 71.80; H, 4.6; N, 14.3%); ν_{max}(KBr)/cm^{-1} 3380 and 3320 (NH), 1560, 1440, 1310, 1210, 760 and 700; δ_H(200 MHz; $CDCl_3$) 1.15 (6 H, t, *J* 5.9, CH_3), 2.73 [1 H, quintet, *J* 6.2, C*H*(CH_3)$_2$], 3.78 (2 H, d, *J* 3.4, NH), 5.24 (2 H, d, *J* 3.4, 6-H and 13-H) and 7.17–7.48 (20 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 21.1 (CH_3), 21.7 (CH_3), 47.0 [*C*H(CH_3)$_2$], 61.0 (6-C and 13-C), 120.7, 125.5, 127.9, 128.1, 128.4, 129.1, 129.7, 130.2, 131.8, 132.3, 133.7, 136.6, 154.9 and 162.0; *m*/*z* (FAB) 686 [$(MH)^+$, 90%], 642 (30), 341 (100) and 304 (62).

14-Isobutyl-5,6,12,13-tetrahydro-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′:4,5]thieno)[3,2-*b*:3,2-*f*][1,5]diazocine 1e. 40% Yield; mp 209–211 °C (Found: C, 71.8; H, 4.9; N, 14.2. Calc. for $C_{42}H_{33}N_7S_2$: C, 72.1; H, 4.75; N, 14.0%); ν_{max}(KBr)/cm^{-1} 3380 and 3320 (NH), 1550, 1440, 1300, 1200, 760 and 700; δ_H(200 MHz; $CDCl_3$) 0.85 (3 H, d, *J* 3.4, CH_3), 0.89 (3 H, d, *J* 3.4, CH_3), 1.75 [1 H, septet, *J* 6.8, C*H*(CH_3)$_2$], 2.15 (1 H, dd, *J* 12.7 and 7.3, NCH_2), 2.40 (1 H, dd, *J* 12.7 and 6.8, NCH_2), 3.79 (2 H, d, *J* 3.9, NH), 4.90 (2 H, d, *J* 3.9, 6-H and 13-H) and 7.04–7.50 (20 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 20.7 (CH_3), 20.9 (CH_3), 26.6 [*C*H(CH_3)$_2$], 57.0 (CH_2), 63.9 (6-C and 13-C), 121.0, 125.6, 127.9, 128.0, 128.3, 129.0, 129.7, 130.3, 131.8, 131.9, 133.7, 136.7, 154.9, 162.0; *m*/*z* (FAB) 700 [$(MH)^+$, 51%], 642 (45), 398 (41), 341 (100), 304 (78) and 207 (50).

14-Benzyl-5,6,12,13-tetrahydro-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′:4,5]thieno)[3,2-*b*:3,2-*f*][1,5]diazocine 1f. 39% Yield; mp 244–246 °C (Found: C, 73.5; H, 4.1; N, 13.6. Calc. for $C_{45}H_{31}N_7S_2$: C, 73.6; H, 4.3; N, 13.4%); ν_{max}(KBr)/cm^{-1} 3360 and 3280 (NH), 1560, 1440, 1310, 1200, 760 and 700; δ_H(200 MHz; $CDCl_3$) 3.60, 3.70 (4 H, AA′BB′ system, *J* 12.9, CH_2), 3.79 (2 H, d, *J* 3.9, NH), 4.84 (2 H, d, *J* 3.9, 6-H and 13-H) and 7.20–7.99 (25 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 53.6 (CH_2), 62.9 (6-C and 13-C), 120.4, 125.5, 127.9, 128.1, 128.4, 128.7, 129.1, 129.6, 130.2, 131.8, 133.7, 136.3, 136.6, 154.9 and 162.1; *m*/*z* (FAB) 734 [$(MH)^+$, 41%], 642 (40), 539 (13), 431 (32), 341 (100) and 304 (96).

Preparation of 6-aryliminomethyl-5-amino-3,4-diphenylthieno-[2,3-*c*]pyridazine 3a,b

To a solution of 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carbaldehyde **2** (0.100 g, 0.302 mmol) in anhydrous EtOH (10 cm^3), glacial acetic acid (0.66 cm^3) and the appropriate aromatic amine (0.362 mmol) were added. The reaction mixture was refluxed for 2 h. The precipitate obtained was filtered off, washed with cold EtOH and recrystallized from acetone.

6-Phenyliminomethyl-5-amino-3,4-diphenylthieno[2,3-*c*]-pyridazine 3a. 93% Yield; mp 257–259 °C (Found: C, 73.6; H, 4.8; N, 13.45. Calc. for $C_{25}H_{18}N_4S$: C, 73.9; H, 4.5; N, 13.8%); ν_{max}(KBr)/cm^{-1} 3440 (NH), 1540, 1480, 1460, 1360, 1080, 760 and 700; δ_H(200 MHz; $CDCl_3$) 6.31 (2 H, br s, NH_2), 7.14–7.46 (15 H, m, C_6H_5) and 8.62 (1 H, s, NCH); δ_C(50 MHz; $CDCl_3$) 110.8, 120.8, 125.1, 126.2, 127.9, 128.0, 128.1, 128.8, 129.3, 129.6, 129.7, 130.3, 133.4, 136.5, 142.1, 150.9, 154.4 (NCH) and 155.0; *m*/*z* (FAB) 316 [$(M + H - NPh)^+$, 82%] and 288 (100).

6-(4-Bromophenyliminomethyl)-5-amino-3,4-diphenylthieno-[2,3-*c*]pyridazine 3b. 92% Yield; mp 250–252 °C (Found: C, 62.0; H, 3.3; N, 11.3. Calc. for $C_{25}H_{17}N_4SBr$: C, 61.9; H, 3.5; N, 11.5%); ν_{max}(KBr)/cm^{-1} 3430, 3280 and 3180 (NH_2), 1630, 1540, 1480, 1080, 760, 700; δ_H(200 MHz; $CDCl_3$) 6.32 (2 H, br s, NH_2), 7.04 (2 H, d, *J* 8.9, C_6H_4), 7.19–7.32 (12 H, m, C_6H_5 and C_6H_4), 8.58 (1 H, s, NCH); δ_C(50 MHz; $CDCl_3$) 110.5, 119.6, 122.5, 124.9, 127.9, 128.1, 128.8, 129.3, 129.5, 130.3, 132.3, 133.3, 135.3, 136.4, 142.5, 149.7, 154.6 (NCH), 155.0 and 163.3; *m*/*z* (FAB) 316 [$(M + H - NPhBr)^+$, 65%] and 288 (100).

6-Butyliminomethyl-5-amino-3,4-diphenylthieno[2,3-*c*]-pyridazine 3c

To a solution of 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carbaldehyde **2** (0.100 g, 0.302 mmol) in anhydrous EtOH (10 cm^3), piperidine (1 cm^3) and butylamine (0.035 cm^3, 0.362 mmol) were added. The reaction mixture was refluxed for 6 h. The solvent was evaporated and the crude product was recrystallized from acetone to give **3c** (79%); mp 155–157 °C (Found: C, 71.4; H, 5.9; N, 14.3. Calc. for $C_{23}H_{22}N_4S$: C, 71.5; H, 5.7; N, 14.5%); ν_{max}(KBr)/cm^{-1} 3440, 3310 and 3200 (NH_2), 1630, 1600, 1440, 1220, 770 and 700; δ_H(200 MHz; $CDCl_3$) 0.92 (3 H, t, *J* 7.1, CH_3), 1.28–1.46 (2 H, m, CH_2), 1.56–1.70 (2 H, m, CH_2), 3.58 (2 H, t, *J* 6.8, NCH_2), 6.95 (2 H, br s, NH_2), 7.18–7.42 (10 H, m, C_6H_5) and 8.38 (1 H, s, NCH); δ_C(50 MHz; $CDCl_3$) 13.8 (CH_3), 20.4 (CH_2), 33.5 (CH_2), 61.8 (NCH_2), 120.6, 125.4, 127.8, 128.0, 128.6, 129.0, 129.6, 130.3, 133.0, 133.6, 136.7, 140.7, 154.8 (NCH) and 163.0; *m*/*z* (FAB) 386 [$(MH)^+$, 100%] and 331 (18).

Preparation of 14-butylbis(pyridazinothieno)[1,5]diazocine derivatives 5 and 6

To a solution of compound **1b** (0.100 g, 0.143 mmol) in dry THF (5 cm^3) under argon at −78 °C a solution of BuLi (2.5 M in hexanes, 0.1 cm^3, 0.357 mmol) was added dropwise and the reaction mixture was stirred at that temperature for 0.5 h. Then, methyl iodide (0.1 cm^3, 1.712 mmol) was added and the reaction mixture was allowed to reach room temperature (1.5 h). The solvent was removed, CH_2Cl_2 was added and the solution was washed with H_2O, dried with Na_2SO_4 and the solvent was evaporated. The resulting crude products were then chromatographed on a silica gel column using CH_2Cl_2–AcOEt (70:1) as

eluent and recrystallized from acetone to yield **5** and **6** in 1 : 1.7 ratio.

14-Butyl-5,6,12,13-tetrahydro-5-methyl-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′ : 4,5]thieno)[3,2-*b* : 3,2-*f*]-[1,5]diazocine 5. 31% Yield; mp 198-200 °C (Found: C, 72.0; H, 5.1; N, 13.8. Calc. for $C_{43}H_{35}N_7S_2$: C, 72.3; H, 4.9; N, 13.7%); ν_{max}(KBr)/cm^{-1} 3380 (NH), 1540, 1440, 1360, 1310, 1200, 1150, 1000, 760 and 700; δ_H(200 MHz; $CDCl_3$) 0.87 (3 H, t, *J* 7.1, CH_3), 1.22–1.51 (4 H, m, CH_2), 1.98 (3 H, s, NCH_3), 2.28–2.41 (1 H, m, NCH_2), 2.55–2.69 (1 H, m, NCH_2), 3.80 (1 H, d, *J* 3.4, NH), 4.51 (s, 1 H, H-6 or H-13), 5.05 (1 H, d, *J* 3.4, H-13 or H-6) and 7.20–7.48 (20 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 13.8 (CH_3), 20.3 (CH_2), 29.7 (CH_2), 39.2 (NCH_3), 48.3 (NCH_2), 63.7, 72.1 (6-C and 13-C), 118.6, 127.3, 127.8, 127.9, 128.0, 128.4, 128.5, 129.1, 129.6, 130.0, 130.2, 130.4, 131.0, 133.1, 133.9, 135.2, 136.7, 137.2, 137.8 and 154.7; *m*/*z* (FAB) 714 [$(MH)^+$, 20%], 656 (22), 397 (58) and 341 (100).

14-Butyl-5,6,12,13-tetrahydro-5,12-dimethyl-3,4,10,11-tetraphenyl-6,13-epiminobis(pyridazino[4′,3′ : 4,5]thieno)[3,2-*b* : 3,2-*f*][1,5]diazocine 6. 51% Yield; mp 289–291 °C (Found: C, 72.45; H, 5.0; N, 13.7. Calc. for $C_{44}H_{37}N_7S_2$: C, 72.6; H, 5.1; N, 13.5%); ν_{max}(KBr)/cm^{-1} 1530, 1440, 1360, 1280, 1100, 980 and 700; δ_H(200 MHz; $CDCl_3$) 0.86 (3 H, t, *J* 7.1, CH_3), 1.23–1.67 (4 H, m, CH_2), 2.07 (6 H, s, NCH_3), 2.55–2.68 (1 H, m, NCH_2), 2.79–2.93 (1 H, m, NCH_2), 4.84 (2 H, s, 6-H, 13-H) and 7.16–7.43 (20 H, m, C_6H_5); δ_C(50 MHz; $CDCl_3$) 13.8 (CH_3), 20.2 (CH_2), 30.4 (CH_2), 40.5 (NCH_3), 51.0 (NCH_2), 72.0 (6-C and 13-C), 127.0, 127.5, 127.6, 127.8, 127.9, 128.5, 130.4, 132.8, 133.7, 136.1, 137.3, 155.5 and 162.4; *m*/*z* (FAB) 728 [$(MH)^+$, 11%], 669 (13), 391 (100) and 351 (70).

X-Ray crystallographic analysis of 1b

Crystal data: $C_{42}H_{33}N_7S_2$, $M_r = 699.89$, monoclinic, space group $P2_1/n$ with $a = 10.080$ (1), $b = 34.633$ (2), $c = 10.593$ (1) Å, $\beta = 99.375$ (1), $V = 3648.5$ (3) Å^3, $Z = 4$, $D_c = 1.274$ Mg m^{-3} and $\mu = 0.187$ mm^{-1}. A colourless block-like crystal (dimensions: 0.80 × 0.40 × 0.30 mm) was used for the structure determination. The chosen crystal was mounted on a glass fiber using an epoxy resin. Data was collected using a Siemens SMART CCD area detector single crystal diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) operating at 298(2) K, $2.59 < \theta < 33.13°$. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in ω) scans. A total of 1255 frames of intensity data were collected with a frame width of 0.3° per frame in ω and counting time of 30 s per frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using a orientation matrix determined from the narrow frame scans and refined using Siemens SAINT[14] software on all observed reflections. Absorption correction was applied using SADABS[15] program. The integration process yielded 30277 reflections, of which 13098 were independent ($R_{int} = 0.1136$). The structure was solved using the Siemens SHELXTL-PC[16] software by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. The final *R* indices [$I > 2\sigma(I)$] were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0634$ and $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{\frac{1}{2}} = 0.1418$ where $w = 1/\sigma^2(F_o)$.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/267.

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