Compounds with Bridgehead Nitrogen. Part 43.[1] The Reaction between *trans*-2-Aminocycloalkanethiols and Formaldehyde

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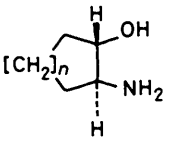
trans-2-Aminocyclopentanethiol condenses with formaldehyde to give *rel*-(3a*R*,6a*R*,9a*R*,12a*R*)-6,12-methanoperhydrodicyclopentano[*d*,*i*][1,6,3,8]dithiadiazecine whereas *trans*-2-aminocyclohexanethiol and *trans*-2-aminocycloheptanethiol give 1 : 1 mixtures of diastereoisomeric bis(perhydrocycloalkanothiazol-3-yl)methanes.

The condensation between *trans*-2-aminocycloalkanols (1) and formaldehyde leads to either a bis(perhydrocycloalkaoxazol-3-yl)methane (2) or a *NN'*-methanoperhydrocycloalka-[*d*,*i*][1,6,3,8]dioxadiazecine (3) depending on the size of the cycloalkane ring. Thus whereas (1; $n = 1$) and (1; $n = 2$) yield (3; $n = 1,2$), (1; $n = 3,4,5$) yields (2; $n = 3,4,5$).[2] In contrast to the reaction of (1; $n = 2$), the reaction between *trans*-2-aminocyclohexanethiol (4; $n = 2$) and formaldehyde has been reported [3] to yield the bis(perhydrobenzothiazol-3-yl)methane (5; $n = 2$). Since the alternative structure (6; $n = 2$) had not been considered [3] a reinvestigation of this work was undertaken. In addition, in order to investigate the effect of the cycloalkane ring size in 2-aminocycloalkanethiols on the type of dimer formed with formaldehyde, the condensation reactions between *trans*-2-aminocyclopentanethiol and *trans*-2-aminocycloheptanethiol with formaldehyde were selected for study. The assignment of the two possible structures (5) and (6) to the products of the condensation reactions must rest on a comparison of J_{gem} values for the NCH_2S protons in the ^1H n.m.r. spectra of the products and of model 1,3-thiazolidines as shown below and accordingly the synthesis of such compounds was also undertaken.



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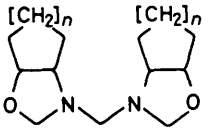

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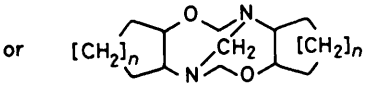

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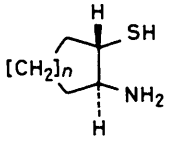

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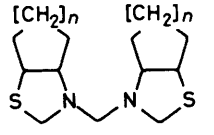

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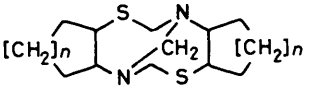

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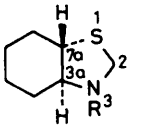


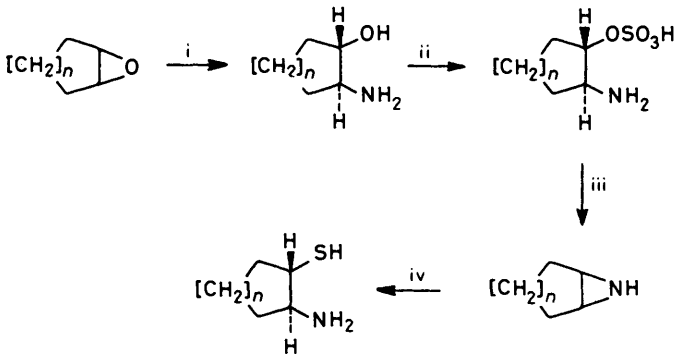
(7) R = Hexyl
(8) R = Cyclohexyl
(9) R = Bu
(10) R = Bu^t
(11) R = CH_2Ph

Synthesis and N.m.r. Spectra of Model 1,3-*Thiazolidines*.—Cyclohexene episulphide, prepared [4,5] by treatment of cyclohexene oxide with potassium thiocyanate, was heated under reflux with the appropriate amine for 1—2 days to give *trans*-2-*N*-alkylaminocyclohexanethiols which on condensation with aqueous formaldehyde gave the model 1,3-thiazolidines (7)—(11).

The ^1H n.m.r. spectra (Table 1) of the 1,3-thiazolidines showed a single AB quartet for the SCH_2N methylene protons, with J_{gem} in the range −6.7 to −9.5 Hz, in agreement with previously recorded [6] values (−6.0 to −9.0 Hz) for NCH_2S protons in five-membered rings.

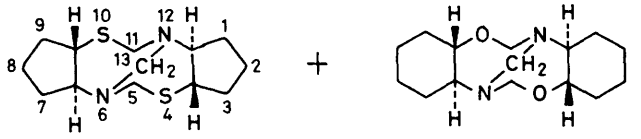
The ^{13}C n.m.r. spectrum (Table 3) of *N*-benzylperhydrobenzo[*d*][1,3]thiazole (11) showed absorption for the NCH_2S carbon nucleus at δ 57.9 [$J(C^{13}-H)$ 155 Hz], with two doublets at δ 50.7 [$J(^{13}C-H)$ 134 Hz] and δ 73.9 [$J(^{13}C-H)$ 127 Hz] assigned to the bridgehead carbons C-7a and C-3a respectively.

Synthesis and Structure of the Dimers (5) *and* (6).—*trans*-2-Aminocyclohexanethiol (4; $n = 2$), *trans*-2-aminocyclopentanethiol (4; $n = 1$), and *trans*-2-aminocycloheptanethiol (4; $n = 3$) were prepared as outlined in the Scheme.[7] Cyclopentene and cycloheptene oxides were prepared from the cycloalkenes by treatment with *N*-bromosuccinimide followed by ring closure of the resultant bromohydrin with sodium hydroxide.[8] Reaction between the cycloalkene oxides and concentrated aqueous ammonia under pressure and at elevated temperatures yielded the *trans*-2-aminocycloalkanols [9] which were converted into the imines by reaction with chlorosulphonic acid followed by sodium hydroxide. Hydrogen sulphide gas bubbled through a cooled ethanolic solution of the imine formed the *trans*-2-aminocycloalkanethiols [7] which



Scheme. Synthesis of *trans*-2-aminocycloalkanethiols

Reagents: i, NH_4OH aq. 140 °C *ca.* 20 atm; ii, $ClSO_3H$; iii, NaOH; iv, H_2S



(12) (13)

were converted into the dimers (5) or (6) by treatment with 40% aqueous formaldehyde.

The Reaction between trans-2-*Aminocyclopentanethiol* (4; n = 1) *and Formaldehyde.*—The reaction between *trans*-2-aminocyclopentanethiol (4; $n = 1$) and formaldehyde gave white crystals, m.p. 114—115 °C (M^+, 270) with a molecular formula of $C_{13}H_{22}N_2S_2$ consistent with the dimeric structures (5; $n = 1$) or (6; $n = 1$).

The ^1H n.m.r. spectrum (Table 2) of the dimer showed a coupling constant of −13.8 Hz for the NCH_2S protons. This eliminates structure (5; $n = 1$) since J_{gem} for thiazolidines are in the range −6.7 to −9.5 Hz (Table 1). The rather negative J_{gem} of −13.8 Hz for the NCH_2S protons is consistent with the presence of the NCH_2S moiety in the seven-membered ring in (6; $n = 1$) since J_{gem} values for NCH_2S protons in six-membered rings [10] and in eight-membered rings [11] have been reported as −13.8 Hz and from −14.6 to −15.2 Hz respectively.

The presence of only one AB quartet (δ 4.2 and 3.65) equivalent to four protons, assigned to the NCH_2S protons, and of a two-proton singlet at δ 4.1 assigned to the NCH_2N protons indicates a single isomer of (6; $n = 1$) symmetrical about a plane containing the N–C–N atoms as depicted in (12).

The ^{13}C n.m.r. spectrum (Table 3) shows the presence of seven carbon nuclei consistent with the symmetrical structure (12). The triplet at lowest field [δ 72.8, $J(^{13}C–H)$ 145 Hz] was assigned to the NCH_2N carbon nucleus {*cf.* δ 67.9, $J(^{13}C–H)$ 146 Hz for the NCH_2N carbon nucleus in 7,14-methanoperhydrobenzo[*d,i*][1,6,3,8]dioxadiazecine (13) [2]}. The bridgehead carbon nuclei C-6a (C-12a) and C-3a (C-9a) absorbed as single doublets at δ 70.5 [$J(^{13}C–H)$ 144 Hz] and δ 45.7 [$J(^{13}C–H)$ 138 Hz] respectively and the NCH_2S carbon nuclei absorbed as a single triplet at δ 59.4 [$J(^{13}C–H)$ 155 Hz].

The Reaction between trans-2-*Aminocyclohexanethiol* (4; n = 2) *and an Excess of Formaldehyde.*—The reaction between *trans*-2-aminocyclohexanethiol (4; $n = 2$) and an excess of formaldehyde gave a white crystalline solid, m.p. 93—94.5 °C, of molecular formula $C_{15}H_{26}N_2S_2$ (M^+, 298), in agreement either with the previously reported [3] bis(perhydrobenzothiazol-3-yl)methane structure (5; $n = 2$) or with the 7,14-methanoperhydrodibenzo[*d,i*][1,6,3,8]dithiadiazecine structure (6; $n = 2$).

The ^1H n.m.r. spectrum (Table 2) of the crystalline material showed two sets of signals for the NCH_2N protons; a singlet at δ 3.00 and an AB quartet at δ 3.21 and 2.95 (J_{gem} −9.5 Hz), together with two AB quartets for the NCH_2S protons at δ 4.40 and 3.90 (J_{gem} −8.6 Hz) and at δ 4.40 and 3.80 (J_{gem} −8.6 Hz).

The doubling of signals in the ^1H n.m.r. spectrum (including those from the CHN and CHS angular protons) together with the intensity measurements indicate the presence of two isomers in equimolar proportions.

The value of −8.6 Hz for the J_{gem} of the NCH_2S protons is inconsistent with the perhydrodithiadiazecine structure (6; $n = 2$) [*cf.* −13.8 Hz for (12)] but is in the range (−6.7 and −9.5 Hz) expected (Table 1) for the thiazolidine structure (5; $n = 2$). The structures of the two isomers may therefore be assigned as (14; $n = 2$) and (15; $n = 2$) with (14; $n = 2$) corresponding to the compound giving rise to the AB quartet for the NCH_2N protons and (15; $n = 2$) to the compound showing a singlet for the NCH_2N protons in the respective ^1H n.m.r. spectra.

Preparation of a single isomer of the dimer was achieved by a modification of the published method.[3] The reaction between (±)-*trans*-2-aminocyclohexanethiol and D-glucose in aqueous solution gave a mixture of 2-(D-*gluco*-1,2,3,4,5-pentahydroxypentyl)-*trans*-perhydrocyclohexa[*d*][1,3]-thiazoles. Fractional recrystallisation of the mixture from ethanol gave the (−)-diastereoisomer (m.p. 152 °C), which on

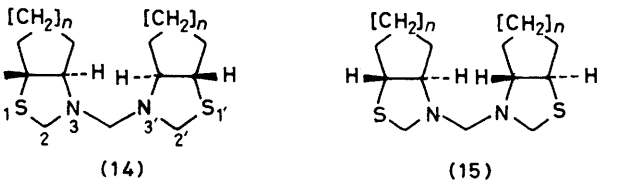


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Table 1. ^1H N.m.r. spectra of *N*-alkylperhydrobenzo[*d*][1,3]thiazoles (7)—(11)

Compound	Solvent	Chemical shifts (δ) NCH_2S		J_{gem} (Hz) NCH_2S
(7)	C_6D_6	4.8	4.45	−9.5
(8)	C_6D_6	4.0	3.8	−6.7
(9)	$CDCl_3$	4.15	3.9	−8.0
(10)	$CDCl_3$	4.2	4.0	−9.0
(11)	C_6D_6	3.95	3.8	−8.1

Table 2 ^1H N.m.r. spectra ($CDCl_3$) of 6,12-methanoperhydrodicyclopenta[*d,i*][1,6,3,8]dithiadiazecine (12), the bis(perhydrobenzothiazol-3-yl)methanes (14 and 15; $n = 2$), and the bis(perhydrocycloheptathiazol-3-yl)methanes (14 and 15; $n = 3$)

Compound	Chemical shifts (δ) NCH_2S		NCH_2N		J_{gem} (Hz) NCH_2S	NCH_2N
(12)	4.20	3.65	4.10		−13.8	—
(14; $n = 2$)	4.40	3.80	3.21	2.95	−8.6	−9.5
(15; $n = 2$)	4.40	3.90	3.00		−8.6	—
(14; $n = 3$)	4.16	3.93	3.22	3.03	−8.0	−5.0
(15; $n = 3$)	4.23	4.0	3.25		−8.0	—

Table 3. ^{13}C N.m.r. spectra ($CDCl_3$) of *N*-benzylperhydrobenzo[*d*][1,3]thiazole (11), 6,12-methanoperhydrodicyclopenta[*d,i*][1,6,3,8]dithiadiazecine (12), and the bis(perhydrobenzothiazol-3-yl)methanes (14 and 15; $n = 2$)

	Chemical shifts (δ)				
Compound	NCH_2S	NCH_2N	CHN	CHS	Other carbon nuclei
(11)	57.9 [$J(^{13}C-H)$ 155 Hz]	—	73.9	50.7	25.1 (t), 26.2 (t), 29.7 (t), 32.6 (t), 53.5 (t, NCH_2Ph), 127.1 (d), 128.0 (d), 128.4 (d), 139.0 (s)
(12)	59.4 [$J(^{13}C-H)$ 155 Hz]	72.8 [$J(^{13}C-H)$ 145 Hz]	70.5	45.7	23.9 (t), 32.6 (t), 34.1 (t)
(14; $n = 2$)	56.3 [$J(^{13}C-H)$ 154 Hz]	65.9 [$J(^{13}C-H)$ 140 Hz]	71.9	51.0	25.0 (t), 26.2 (t), 29.5 (t), 31.7 (t)
(15; $n = 2$)	57.3 [$J(^{13}C-H)$ 157 Hz]	63.2 [$J(^{13}C-H)$ 135 Hz]	72.3	51.0	25.1 (t), 26.2 (t), 29.0 (t), 32.1 (t)

treatment with aqueous formaldehyde gave a single isomer m.p. 116—117 °C) corresponding to (15; $n = 2$) or its enantiomer. The ^1H n.m.r. spectrum of this isomer showed a single AB quartet at δ 4.40 and 3.90 (J_{gem} −8.6 Hz) arising from the NCH_2S protons and a singlet at δ 3.0 attributed to the NCH_2N protons.

The ^{13}C n.m.r. spectra of the bis(perhydrobenzothiazol-3-yl)methanes (14 and 15; $n = 2$) are summarised in Table 3.

The Reaction between trans-2-*Aminocycloheptanethiol* (4; n = 3) *and an Excess of Formaldehyde.*—The reaction between *trans*-2-aminocycloheptanethiol (4; $n = 3$) and excess formaldehyde gave a colourless viscous oil with M^+ 326 and an empirical formula of $C_{17}H_{30}S_2N_2$ consistent with a dimeric structure (5 or 6; $n = 2$). The ^1H n.m.r. spectrum (Table 2) showed the presence of a 1 : 1 mixture of two isomers. The magnitudes of the J_{gem} values for the AB quartets at δ 4.16, 3.93 (J_{gem} −8.0 Hz) and δ 4.23, 4.0 (J_{gem} −8.0 Hz) indicated the bis(perhydrocycloheptanothiazol-3-yl)methane structure as in (14; $n = 3$) and (15; $n = 3$). The AB quartet at δ 3.22 and 3.03 (J_{gem} −5.0 Hz) and a singlet at δ 3.25 were assigned to the NCH_2N methylene protons in (14; $n = 3$) and (15; $n = 3$) respectively.

Discussion

Whereas *trans*-2-aminocyclopentanethiol condenses with formaldehyde to give *rel*-(3a*R*: 6a*R*: 9a*R*: 12a*R*)-6,12-methanoperhydrodicyclopentano[*d,i*][1,6,3,8]dithiadiazecine (12), *trans*-2-aminocyclohexanethiol and *trans*-2-aminocycloheptanethiol gave 1 : 1 mixtures of dimers (14 and 15; $n = 2$, $n = 3$), containing 1,3-thiazolidine rings. This difference in the direction of cyclisation may be interpreted in terms of ring-fusion strain in the two types of dimer. The conversion of *trans*-2-aminocyclopentanethiol into bis(perhydrocyclopentanethiazol-3-yl)methane (5; $n=1$) is not expected since *trans*-fusion between two five-membered rings will involve considerable strain.[12] The *trans*-fusion between a five- and a seven-membered ring will be relatively strain free and, accordingly, the formation of (12) is favoured.

The condensation between *trans*-2-aminocyclohexanethiol and formaldehyde gives the bis(perhydrobenzothiazol-3-yl)-methanes (14 and 15; $n = 2$) in contrast to the formation of 7,14-methanoperhydrobenzo[*d,i*][1,6,3,8]dioxadiazecine (13) from the condensation between *trans*-2-aminocyclohexanol and formaldehyde.[2] It has been suggested [2] that formation of (13) rather than (2; $n = 2$) is favoured because of the ring fusion strain present in the *trans*-fused 5/6 ring system (*cf.* ring-fusion strain in *trans*-hydrindane [12]). The strain present in the bis(perhydrobenzoxazol-3-yl)methanes (2; $n = 2$) however may be reduced by the substitution of sulphur for oxygen, due to the presence of the long C–S bond (1.82 Å) (*cf.* C–O bond length of 1.43 Å) and in this case the formation of bis(perhydrobenzothiazol-3-yl) methane is favoured.

Experimental

Elemental analyses were carried out by the Analytical Section, Department of Chemistry, Portsmouth Polytechnic, and Butterworth Micro-Analytical Consultancy, Teddington, Middlesex. The ^1H n.m.r. spectra were recorded on Varian T60 and Brüker WH 270 spectrometers, as 10% solutions with tetramethylsilane as internal reference. ^{13}C N.m.r. spectra were obtained from the P.C.M.U. at Harwell on a Brüker 90 FT spectrometer operating at 25.2 MHz; spectral width 6 024 Hz (decoupled) and 3 012 Hz (coupled) with 4 096 memory points; pulse width 11 μs; pre-delay time 143 μs; number of scans accumulated 1 000—2 000 (decoupled) or 20 000—40 000 (coupled). Samples were dissolved in equal volumes of $CDCl_3$ with $SiMe_4$ as internal reference.

trans-2-N-*Alkylaminocyclohexanethiols.*—Cyclohexene episulphide [4] (0.2 mol, 22.8 g) was heated under reflux with the appropriate amine (0.2 mol), hexylamine, cyclohexylamine, t-butylamine or benzylamine for 24—48 h. The product was distilled under reduced pressure to yield trans-2-N-*hexylaminocyclohexanethiol* (40%), b.p. 108—110 °C at 1.6 mmHg (Found: C, 66.6; H, 11.9; N, 6.4. $C_{12}H_{25}NS$ requires C, 66.9; H, 11.7; N, 6.5%), *trans*-2-*N*-cyclohexylaminocyclohexanethiol (29%), b.p. 140—141 °C at 0.25 mmHg (lit.,[13] 117—118 °C at 1.0 mmHg) (Found: C, 67.4; H, 11.2; N, 6.5. Calc. for $C_{12}H_{23}NS$: C, 67.6; H, 10.9; N, 6.6%), trans-2-N-*t-butylaminocyclohexanethiol* (15%), b.p. 83 °C at 0.30 mmHg (Found: C, 63.6; H, 10.8; N, 7.9. $C_{10}H_{21}NS$ requires C, 64.1; H, 11.3; N, 7.5%), and trans-2-N-*benzylaminocyclohexanethiol* (35%), b.p. 143—145 °C at 0.9 mmHg (Found: C, 71.0; H, 8.8; N, 6.4. $C_{13}N_{19}NS$ requires C, 70.5; H, 8.6; N, 6.3%).

N-*Alkylperhydrobenzo*[d][1,3]*thiazoles.*—*trans*-2-*N*-Cyclohexyl-, *trans*-2-*N*-benzyl- and *trans*-2-N-t-butylaminocyclohexanethiol (0.03 mol) were dissolved in benzene (50 ml) and heated under reflux with paraformaldehyde (0.033 mol, 1.0 g) using a Dean and Stark water separator to remove water formed during the reaction. When no further water separated out the solvent was removed by distillation and the residue distilled under reduced pressure to yield N-*cyclohexylperhydrobenzo*[d][1,3]*thiazole* (29%), b.p. 150—156 °C at 1.0 mmHg (Found: C, 69.5; H, 10.1; N, 6.4. $C_{13}H_{23}NS$ requires C, 69.3; H, 10.3; N, 6.2%), N-*benzylperhydrobenzo*[d][1,3]-*thiazole* (76%), b.p. 145—147 °C at 0.55 mmHg (Found: C,

72.4; H, 7.9; N, 6.1. $C_{14}H_{19}NS$ requires C, 72.1; H, 8.2; N, 6.0%), N-*t-butylperhydrobenzo*[d][1,3]*thiazole* (25%), b.p. 150—152 °C at 0.45 mmHg (Found: C, 66.0; H, 10.3; N, 7.2. $C_{11}H_{21}NS$ requires C, 66.3; H, 10.6; N, 7.0%).

N-*Hexylperhydrobenzo*[d][1,3]*thiazole*.—*trans*-2-*N*-Hexylaminocyclohexanethiol (0.17 mol, 36 g) was shaken with 40% aqueous formaldehyde solution (0.173 mol, 13 ml) for 0.5 h. The mixture was basified with 50% aqueous sodium hydroxide and extracted with ether. The combined ether extracts were dried (Na_2SO_4), the ether removed by distillation, and the product purified by distillation under reduced pressure to yield N-*hexylperhydrobenzo*[d][1,3]*thiazole* (4.9 g, 13%), b.p. 95—97 °C at 0.2 mmHg (Found: C, 68.5; H, 10.8; N, 6.1. $C_{13}H_{25}NS$ requires C, 68.7; H, 11.1; N, 6.2%).

N-*Butylperhydrobenzo*[d]]1,3]*thiazole*.—Cyclohexene episulphide (0.2 mol, 22.8 g) and butylamine (0.4 mol, 29.2 g) were dissolved in benzene (100 ml) and heated in a high-pressure stainless-steel autoclave at 120 °C for 0.5 h. The reaction mixture was transferred to a round bottomed flask and heated under reflux with paraformaldehyde (0.2 mol, 6 g) using a Dean and Stark water separator to separate the water formed. When no more water separated out the solvents were removed by distillation and the residue distilled under reduced pressure to yield N-*butylperhydrobenzo*[d][1,3]thiazole (10.2 g, 25%), b.p. 101—103 °C at 0.08 mmHg (Found: C, 65.9; H, 10.4; N, 7.1. $C_{11}H_{21}NS$ requires C, 66.3; H, 10.6; N, 7.0%).

trans-2-*Aminocyclopentanethiol*, trans-2-*Aminocyclohexanethiol*, *and* trans-2-*Aminocycloheptanethiol*.—These compounds were prepared by an adaptation of the published method for the preparation of *trans*-2-aminocyclohexanethiol.[7] *trans*-2-Aminocyclopentanol (0.5 mol, 50.5 g), *trans*-2-aminocyclohexanol (0.5 mol, 57.5 g), or *trans*-2-aminocycloheptanol (0.5 mol, 64.5 g) were dissolved in carbon tetrachloride (250 ml) and heated to 60 °C in a water-bath. Freshly distilled chlorosulphonic acid (30 ml) was added drop by drop with constant stirring the temperature being kept at 60 °C. The solid ester which formed was filtered off, washed with fresh carbon tetrachloride (3 × 30 ml), and dried *in vacuo*. The resulting solid was dissolved in 30% aqueous sodium hydroxide (1.8M; 250 ml) by adding the sodium hydroxide solution slowly to the solid. The mixture was then distilled until *ca.* 200 ml of distillate was collected. Sodium hydroxide (50 g) was added to the distillate which was then extracted with ether. The combined extracts were dried (Na_2SO_4) and solvent removed to yield an oil which was distilled under reduced pressure to give cyclopenteneimine, cyclohexeneimine, and cycloheptenimine respectively. Hydrogen sulphide gas was bubbled through an ice-cooled solution of the imine in absolute ethanol (200 ml). The white precipitate formed was filtered off and recrystallised from absolute ethanol to yield trans-2-*aminocyclopentanethiol* (6.1 g, 10%), m.p. 68—70 °C (Found: C, 51.4; H, 9.3; N, 11.8. $C_5H_{11}NS$ requires C, 51.3; H, 9.5; N, 12.0%), *trans*-2-aminocyclohexanethiol (9.2 g, 14%), m.p. 78—79 °C (lit.,[7] 79—81 °C) (Found: C, 54.6; H, 9.6; N, 10.3. Calc. for $C_6H_{13}NS$, C, 54.9; H, 10.0; N, 10.6%) and trans-2-*aminocycloheptanethiol* (1.6 g, 2%), m.p. 86—87 °C (Found: C, 57.4; H, 10.3; N, 9.4. $C_7H_{15}NS$ requires C, 57.9; H, 10.4; N, 9.6%).

6,12-*Methanoperhydrodicyclopentano*[d,i][1,6,3,8]*dithiadiazecine*.—*trans*-2-Aminocyclopentanethiol (0.047 mol, 5.5 g) was dissolved in water (10 ml) and 40% aqueous formaldehyde solution (0.07 mol, 5.2 ml) was added drop by drop with constant stirring. The mixture was shaken for 0.5 h, basified with 50% aqueous sodium hydroxide solution, and extracted with ether. The combined ether extracts were dried (Na_2SO_4), the ether removed, and the resulting oil allowed to crystallise. The crystals were filtered off and recrystallised from absolute ethanol to yield 6,12-*methanoperhydrodicyclopentano*[d,i]-[1,6,3,8]*dithiadiazecine* (2.3 g, 36%), m.p. 114—115 °C (Found: C, 57.6; H, 8.1; N, 10.2. $C_{13}H_{22}N_2S_2$ requires C, 57.7; H, 8.2; N, 10.4%).

Bis(*perhydrocycloheptathiazol*-3-*yl*)*methane*.—*trans*-2-Aminocycloheptanethiol (0.01 mol, 1.5 g) was dissolved in water (5 ml) and 40% aqueous formaldehyde solution (2 ml) was added drop by drop with constant stirring. The mixture was shaken for 0.5 h, basified with 50% aqueous sodium hydroxide, and extracted with ether. The combined ether extracts were dried (Na_2SO_4) and the ether removed by distillation. The resulting oil was distilled under reduced pressure to yield *bis*(*perhydrocycloheptathiazol*-3-*yl*)*methane* (0.4 g, 29%), b.p. 146—148 °C at 10 mmHg (Found: C, 62.3; H, 9.4; N, 8.7. $C_{17}H_{30}N_2S_2$ requires C, 62.5; H, 9.3; N, 8.6%).

The Resolution of Racemic trans-2-*Aminocyclohexanethiol*.—Separation of racemic *trans*-2-aminocyclohexanethiol was achieved by a modification of the published method.[3] *trans*-2-Aminocyclohexanethiol (0.1 mol, 13.5 g) was dissolved in water (40 ml) and heated under reflux with D-glucose (0.1M; 18.5 g). The solution was allowed to cool and kept at 5 °C for 16 h. The white precipitate was filtered off and an equal volume of ether added to the filtrate. The mixture was left for 16 h and the white precipitate formed was filtered off and recrystallised from ethanol to yield 2-(D-*gluco*-1,2,3,4,5-pentahydroxypentyl)-(−)-*trans*-perhydrocyclohex[*d*][1,3]thiazole (4.4 g, 14%), m.p. 151—152 °C (lit.,[3] m.p. 152—153 °C).

rel-(3*a*R,3′*a*R,8*a*R,8′*a*R)-*Bis*(*perhydrobenzothiazol*-3-*yl*)-*methane*.—2-(D-*gluco*-1,2,3,4,5-Pentahydroxypentyl)-(−)-*trans*-perhydrocyclohexa[*d*][1,3]thiazole (0.02M, 6.3 g) was shaken with 40% aqueous formaldehyde (0.27M; 20 ml) for 0.5 h. The mixture was set aside for 3 days and then basified with 40% aqueous sodium hydroxide and extracted with ether. The combined ether extracts were dried (Na_2SO_4), the ether removed by distillation, and the resulting solution set aside. Crystals slowly precipitated out and were filtered off to give rel-(3*a*R,3′*a*R,8*a*R,8′*a*R)-*bis*(*perhydrobenzothiazol*-3-*yl*)-*methane* (0.3 g, 9%), m.p. 116—117 °C (Found: C, 60.5; H, 8.7; N, 9.2. $C_{15}H_{26}N_2S_2$ requires C, 60.4; H, 8.8; N, 9.4%).

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