Synthesis and Conformational Analysis of Substituted 4-Aminothianes

Pullachipatti K. Subramanian[1] and Kondareddiar Ramalingam*

Department of Chemistry, PSG College of Arts & Sciences, Coimbatore-641 014, India

Nagichettiar Satyamurthy and K. Darrell Berlin*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

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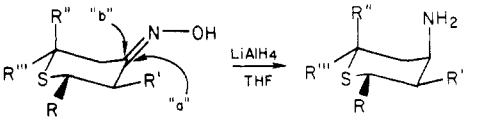
Reductions of substituted 4-thianone oximes by $LiAlH_4$ gave a mixture of epimeric 4-aminothianes. Separation of the epimeric mixture was achieved via column chromatography over neutral alumina. Independent syntheses of these amines by a stereospecific route starting from the tosylate of the corresponding 4-thianols that reacted with sodium azide in DMF followed by reduction of the azide with $LiAlH_4$ provided structure proofs for the amines. *N*-Acetyl derivatives were also prepared from the aminothianes. Conformational analysis of the amines was performed via an inspection of the ^1H and ^{13}C NMR spectra. These spectral data suggested twist conformations for 2,2-dimethyl-*trans*-6-phenyl-*r*-4-aminothiane and 2,2-dimethyl-*trans*-6-*p*-chlorophenyl-*r*-4-aminothiane.

Simple six-membered heterocyclic compounds containing nitrogen,[2-5] sulfur,[6-9] oxygen,[10-13] and selenium[14-18] are known to exist mostly in chair conformations. Conformations of heterocyclic systems show both similarities and differences with those of alicyclic systems.[19] A systematic study of the conformations of 2,6-diaryl-4-thianones, the corresponding epimeric alcohols, and the respective 1,1-dioxides has been reported recently from our laboratories.[20] Haller and co-workers[21] recorded the preparation of stereoisomeric 4-aminothianes. Baliah and Bhavani[22] prepared a few epimeric 4-aminothianes. Reduction of oximes of unsymmetrical cyclohexanones with sodium and ethanol gives the equatorial amines,[23-25] whereas catalytic hydrogenation in acid media generally yields the axial amines. Reduction of oximes of certain cholestanones by sodium and ethanol gave in each case a mixture of two epimeric amines rich in equatorial amines, whereas the $LiAlH_4$ reduction gave more of the axial amines.[26] A similar observation has been made simultaneously by Labler et al.[27] and also by Bannard and McKay.[28]

Conformational diagnosis of heterocyclohexylamines has not been made in extensio as in cyclohexane systems. As part of a study of the kinetics of quaternization and conformational analysis of substituted *N,N*-dimethyl-4-aminothianes, we prepared a number of 4-aminothianes. We now describe the preparation of these bases and data which bear on the configuration at the nitrogen center and conformation of these amines and of the corresponding *N*-acetyl derivatives.

Synthesis of 4-Aminothianes

The reduction of 4-thianone oximes **1a-f** with lithium



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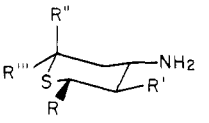

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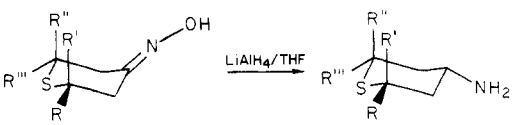
a, R = C_6H_5; R′ = H; R″ = H; R‴ = C_6H_5
b, R = *p*-ClC_6H_4; R′ = H; R″ = H; R‴ = *p*-ClC_6H_4
c, R = C_6H_5; R′ = CH_3; R″ = H; R‴ = C_6H_5
d, R = C_6H_5; R′ = C_2H_5; R″ = H; R‴ = C_6H_5
e, R = C_6H_5; R′ = H; R″ = CH_3; R‴ = CH_3
f, R = *p*-ClC_6H_4; R′ = H; R″ = CH_3; R‴ = CH_3

aluminum hydride afforded the axial amines with varying amounts of equatorial isomers. Reduction of oximes **4a** and **4b** with $LiAlH_4$ gave conformationally mobile amines



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a, R = H; R′ = H; R″ = H; R‴ = H
b, R = CH_3; R′ = CH_3; R″ = CH_3; R‴ = CH_3

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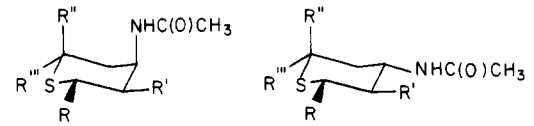
Table I. Substituted 4-Aminothianes and Corresponding *N*-Acetyl Derivatives[a]

compd	% yield	mp/bp, °C	formula	compd	% yield	mp/bp, °C	formula
2a[b]	68	128-129[c]	$C_{17}H_{19}NS$	5b	70	84-86 (1.6 mm)	$C_9H_{19}NS$
2b[b]	59	163-164[c]	$C_{17}H_{17}NSCl_2$	6a	91	223-225[e]	$C_{19}H_{21}NOS$
2c	59	141-142[c]	$C_{18}H_{21}NS$	6b	90	312-314[f]	$C_{19}H_{19}NOSCl_2$
2d	52	116-117[c]	$C_{19}H_{23}NS$	6c	92	295-297[f]	$C_{20}H_{23}NOS$
2e	44	71-72[c]	$C_{13}H_{19}NS$	6d	88	292-294[f]	$C_{21}H_{25}NOS$
2f	39	75-76[d]	$C_{13}H_{18}NSCl$	6e	91	130-131[e]	$C_{15}H_{21}NOS$
3a[b]	53	99-100[c]	$C_{17}H_{19}NS$	6f	88	172-73[e]	$C_{15}H_{20}NOSCl$
3b[b]	50	123-124[c]	$C_{17}H_{17}NSCl_2$	7a[g]	93	222-224[e]	$C_{19}H_{21}NOS$
3c	50	150-151[c]	$C_{18}H_{21}NS$	7b	89	248-250[e]	$C_{19}H_{19}NOSCl_2$
3d	41	110-112[c]	$C_{19}H_{23}NS$	7c	91	208-209[e]	$C_{20}H_{23}NOS$
3e	38	62-63[c]	$C_{13}H_{19}NS$	7d	87	180-182[e]	$C_{21}H_{25}NOS$
3f	36	70-71[d]	$C_{13}H_{18}NSCl$	7e	84	175-176[e]	$C_{15}H_{21}NOS$
5a	81	70-72 (1.9 mm)	$C_5H_{11}NS$	7f	82	179-180[e]	$C_{15}H_{20}NOSCl$

[a] Yield calculated for **2a-f** and **3a-f** was based on thian-*r*-4-ol as starting material; C, H, and N analyses agreed to within 0.3% of theoretical values. [b] Lit.[22] mp °C: **2a**, 121-122; **2b**, 154-155; **3a**, 87-88; **3b**, 95-97. [c] Recrystallized from petroleum ether (60-80 °C). [d] Recrystallized from petroleum ether (40-60 °C). [e] Recrystallized from ethanol/water. [f] Recrystallized from ethanol. [g] Lit.[21] mp 218 °C.

5a and **5b**, respectively. The heterocyclic bases obtained from the reduction of oximes **1a-f** were separated on neutral alumina. The axial amines were eluted in the initial fractions (petroleum ether–benzene) and the equatorial amines were eluted in the latter fractions (benzene–ether) (see Experimental Section). 2,2-Dimethyl-6-phenyl-4-thianone oxime (**1e**) and 2,2-dimethyl-6-(*p*-chlorophenyl)-4-thianone oxime (**1f**) were reduced with lithium aluminum hydride to afford *exclusively* the axial amines [C(4)-NH_2 axial] **2e** and **2f**, respectively. Physical constants for amines **2a-f**, **3a-f**, **5a**, and **5b** are given in Table I.

The *N*-acetyl derivatives **6a-f** and **7a-f** for the 4-



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a, R = C_6H_5; R′ = H; R″ = H; R‴ = C_6H_5
b, R = *p*-ClC_6H_4; R′ = H; R″ = H; R‴ = *p*-ClC_6H_4
c, R = C_6H_5; R′ = CH_3; R″ = H; R‴ = C_6H_5
d, R = C_6H_5; R′ = C_2H_5; R″ = H; R‴ = C_6H_5
e, R = C_6H_5; R′ = H; R″ = CH_3; R‴ = CH_3
f, R = *p*-ClC_6H_4; R′ = H; R″ = CH_3; R‴ = CH_3

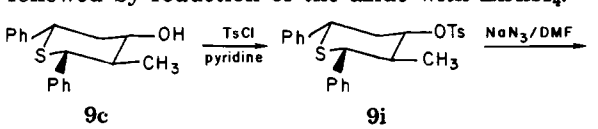
aminothianes were also synthesized (physical constants are given in Table I). The mixture composition of the bases formed from the reduction of oximes **1a-f** with lithium aluminum hydride in THF is given in Table II. In the reduction of oximes **1a-f**, the hydride ion is presumably transferred from the less hindered side "a" to give more of the less stable isomer [(4)-NH_2 axial]. Reduction of *r*-2,*cis*-6-diphenyl-4-thianone oxime (**1a**) with $LiAlH_4$ was first examined by Haller and Ziriakus[21] who, via acetylation and fractional crystallization, isolated and identified only **7a**, mp 218 °C. We find that reduction of oxime **1a** with lithium aluminum hydride and chromatography of the acetylated derivative led to **7a** with mp 222–224 °C. It appears that Haller's preparation was possibly contaminated with a difficulty separable impurity. Baliah and co-workers[22] reported the isolation of **2a** (mp 121–122 °C) and **3a** (mp, 87–88 °C) by the reduction of **1a** with $LiAlH_4$. The aminothianes **2b** (mp, 154–155 °C) and **3b** (mp, 95–97 °C) were also obtained by the reduction of *r*-2,*cis*-6-bis(*p*-chlorophenyl)-4-thianone oxime (**1b**) with $LiAlH_4$ in THF. It is obvious from Table I that the previously reported melting points of the bases **2a**, **2b**, **3a**, and **3b** do not agree with the results obtained in the present study. The lower melting points reported by the previous workers

Table II. Composition of the Products from the $LiAlH_4$ Reduction of Substituted 4-Thianone Oximes

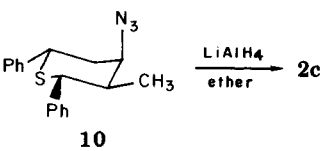
oxime reduced	total recov	% yield of epimeric 4-aminothianes		
		ax	eq	mixt
1a	85	53	12	20
1b	83	48	13	22
1c	81	43	20	18
1d	85	47	23	15
1e	72	72		
1f	68	68		

suggest that they did not isolate pure epimeric amines **2a**, **3a** and **2b**, **3b**. If the amines happen to be of dubious purity, assignment of configuration on the basis of chemical and physical properties is difficult.

Stereochemistry of 4-Aminothianes. In a perfect chair model of a thiane ring, the two syn-oriented bulky aryl groups, as in **2** and **3**, almost surely occupy only equatorial positons for maximum stability. Consequently, the epimeric amines **2a-f** and **3a-f** possess "pure" axial C–N and equatorial C–N bonds, respectively, because the thiane ring is biased due to the presence of the bulky aryl groups. These primary amines **2a-f** and **3a-f** were also synthesized by standard, stereospecific routes[29] from starting materials of established conformation[20] in order to prove unequivocally the configuration assigned to these epimeric amines. For example, the isomer **2c** (axial C–N bond) was obtained by a stereospecific route from tosylate **9i** of *cis*-2,6-diphenyl-*trans*-3-methylthian-*r*-4-ol (**9c**) via reaction of **9i** with sodium azide in dimethylformamide followed by reduction of the azide with $LiAlH_4$. The



9c **9i**



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physical constants and other information on the tosylates are given in Table III. The amine **2c** was found to be identical with the axial amine obtained from petroleum ether–benzene fractions in chromatography of the reduction ($LiAlH_4$) product of the oxime **1c**. Likewise, the amine

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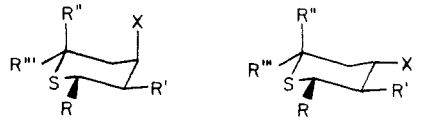
Table III. Substituted Thian-r-4-ol Tosylates

compd	% yield	mp,[a] °C	formula
8g	86	174-175	$C_{24}H_{24}O_3S_2$
8h	90	203-205	$C_{24}H_{22}O_3S_2Cl_2$
8i	84	138-140	$C_{25}H_{26}O_3S_2$
8j	84	160-161	$C_{26}H_{28}O_3S_2$
8k	80	113-114	$C_{20}H_{24}O_3S_2$
8l	78	124-125	$C_{20}H_{23}O_3S_2Cl$
9g	90	148-150	$C_{24}H_{24}O_3S_2$
9h	88	148-149	$C_{24}H_{22}O_3S_2Cl_2$
9i	86	168-169	$C_{25}H_{26}O_3S_2$
9j	82	172-174	$C_{26}H_{28}O_3S_2$
9k	81	123-124	$C_{20}H_{24}O_3S_2$
9l	82	135-137	$C_{20}H_{23}O_3S_2Cl$

[a] Recrystallized from 95% ethanol; C, H, and N analyses agreed to within 0.3% of theoretical values.

3c with an equatorial amino group was obtained from *trans*-2,6-diphenyl-*cis*-3-methylthian-*r*-4-ol (8c) (axial OH).



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a, R = C_6H_5; R′ = H; R″ = H; R‴ = C_6H_5; X = OH
b, R = *p*-ClC_6H_4; R′ = H; R″ = H; R‴ = *p*-ClC_6H_4; X = OH
c, R = C_6H_5; R′ = CH_3; R″ = H; R‴ = C_6H_5; X = OH
d, R = C_6H_5; R′ = C_2H_5; R″ = H; R‴ = C_6H_5; X = OH
e, R = C_6H_5; R′ = H; R″ = CH_3; R‴ = CH_3; X = OH
f, R = *p*-ClC_6H_4; R′ = H; R″ = CH_3; R‴ = CH_3; X = OH
g, R = C_6H_5; R′ = H; R″ = H; R‴ = C_6H_5; X = OTs
h, R = *p*-ClC_6H_4; R′ = H; R″ = H; R‴ = *p*-ClC_6H_4; X = OTs
i, R = C_6H_5; R′ = CH_3; R″ = H; R‴ = C_6H_5; X = OTs
j, R = C_6H_5; R′ = C_2H_5; R″ = H; R‴ = C_6H_5; X = OTs
k, R = C_6H_5; R′ = H; R″ = CH_3; R‴ = CH_3; X = OTs
l, R = *p*-ClC_6H_4; R′ = H; R″ = CH_3; R‴ = CH_3; X = OTs

^{1}H NMR Studies

The ^{1}H NMR spectra of the 4-aminothianes **2a–f** and **3a–f** proved useful in the configurational and conformational assignments (see Table IV). In general, two features of the spectra of epimeric amines deserve special mention: (i) the coupling constants of the signal due to H(2,6) and (ii) the shape and half-bandwidth[30] of H(4). The spectrum of amine **2b** shows a doublet of a doublet at δ 4.61 [$J_{2_a,3_a} = J_{5_a,6_a}$ = 11.0 Hz and $J_{2_a,3_e} = J_{5_e,6_a}$ = 4.0 Hz corresponds to benzylic protons H(2) and H(6)]. The vicinal coupling constants of ring protons indicate the chair conformation of the ring with the two aryl substituents in equatorial positions. The configuration of the aryl groups at C(2) and C(6) in **2c** is assigned on the basis of coupling constants of protons H(2) and H(6). The signals at δ 4.28 (d, J = 11.0 Hz) and 4.60 (dd, J = 11.0 and 4.0 Hz) for **2c** correspond to protons H(2) and H(6), respectively. The large coupling constants $J_{2_a,3_a}$ for **2c** suggest that the phenyl and methyl groups are in equatorial positions. The phenyl group at C(6) has been assigned an equatorial position based on the ^{1}H NMR data. H(6) in **2c** has one equatorial neighbor [H(5_e)] and one axial neighbor [H(5_a)] and therefore appears as a doublet of a doublet. The coupling constants of 11.0 and 4.0 Hz for $J_{6_a,5_a}$ and $J_{6_a,5_e}$, respectively, suggest the C(6)–C_6H_5 bond is equatorial. The ^{1}H NMR spectral signals of protons H(2) and H(6) in **2d**, **3c**, and **3d** are very similar to those of **2c**, which suggests that

(30) For a general review of the significance of $w_{1/2}$ in assigning proton signals for an axial or equatorial C–H bond, see Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; Chapter 4-2.

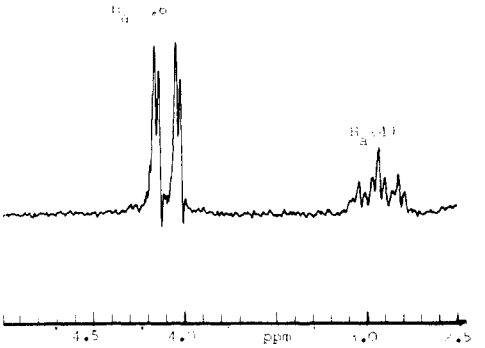


Figure 1. ^{1}H NMR spectra of **3a** (in $DCCl_3$).

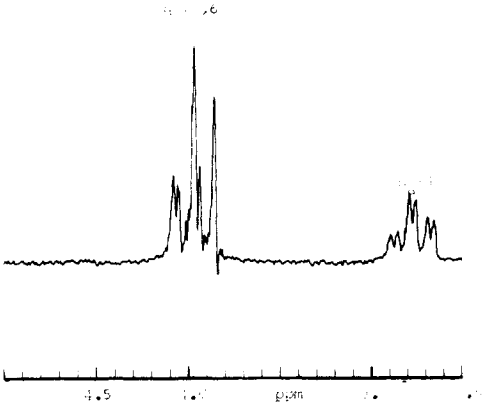


Figure 2. ^{1}H NMR spectra of **3d** (in $DCCl_3$).

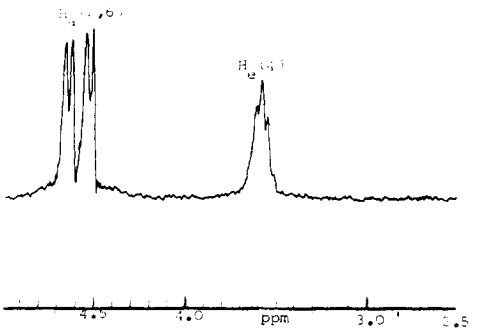


Figure 3. ^{1}H NMR spectra of **2a** (in $DCCl_3$).

3-alkyl substituted amines **2d**, **3c**, and **3d** have similar rigid chair conformations.

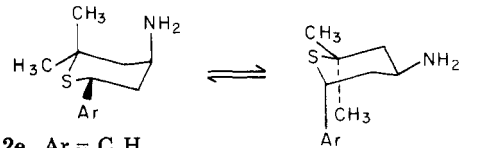
The aminothiane **3e** gave an H(6) proton signal at δ 4.04 which was fully resolved and appeared as a doublet of a doublet. The coupling constants of 12.0 and 3.0 Hz, $J_{6_a,5_a}$ and $J_{6_a,5_e}$, respectively, suggest that H(6) is in axial position and the heterocyclic ring exists in a rigid chair conformation. The signal for H(6) in the amine **3f** occurred essentially at the same position (δ 4.02) as in **3e** and was separated into a doublet of a doublet with J = 12.0 and 3.0 Hz. Thus, **3f** and **3e** quite likely have the same ring conformation. The H(6) resonance (δ 4.38) in **2e** was a doublet of a doublet due to its coupling with H(5_a) and H(5_e) ($J_{6_a,5_a}$ = 9.0 Hz and $J_{6_a,5_e}$ = 3.0 Hz). The coupling constants are somewhat abnormal in comparison with the constants found in other related thiane systems which exist in rigid chair conformations[20] and suggest a possible distorted chair or a twist conformation for **2e**. This is also supported by relatively large half-bandwidth ($w_{1/2}$ = 12 Hz) for H(4) for **2e**. The ^{1}H NMR spectral pattern and the coupling constant for H(6) in **2f** are very similar to those of **2e**, which indicates that amine **2f** may also have a distorted or a twist conformation. The possibility of a

twist conformation for **2f** gained further support from the observed $w_{1/2}$ value of the signal for H(4) (discussed in the following section).

The configuration of the amino group in **2a–f** and **3a–f** is strongly inferred from the half-bandwidth of the H(4) signal. The H(4) signal for **3a** appeared at δ 2.94 and was fully resolved as a triplet (separation 11.0 Hz = $J_{a,a}$), each component being a triplet (Figure 1, separation 4.0 Hz = $J_{a,e}$). Equally well resolved signal patterns for H(4) were also detected in the spectra of **3e** and **3f**. The signal profile at δ 2.78 for **3d** [a 1:2:1 triplet (J = 11.0 Hz), Figure 2] was due to coupling with two axial hydrogens at H(3) and H(5). Each component of the triplet was a doublet (J = 4.0 Hz) due to further coupling with the equatorial hydrogen at H(5). The H(4) signal in **3c** was also a triplet ($J_{a,a}$ = 11.0 Hz) and each component was a doublet ($J_{a,e}$ = 4.0 Hz). However, the H(4) resonance overlapped with the resonance pattern of ring protons H(3) and H(5).

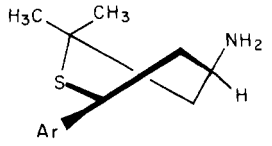
In all of the axial amines **2a–f**, the H(4) resonance was clearly observed downfield as a fairly narrow, unresolved peak (Figure 3). The lack of fine structure is presumably due to closeness in magnitude of $J_{a,e}$ and $J_{e,e}$.

Examination of the ^{1}H NMR data in Table IV indicates that the half-bandwidth ($w_{1/2}$) of the H(4) signal in the axial amines **2a**, **2b**, **2c**, and **2d** are 8.0, 8.0, 7.0, and 8.0 Hz, respectively, compared to 22.0, 21.0, 21.0, and 22.0 Hz, respectively, for the corresponding equatorial epimers [H-(4) axial]. 2,2-Dimethyl-*trans*-6-phenyl-*r*-4-aminothiane (**2e**) and 2,2-dimethyl-*trans*-6-(*p*-chlorophenyl)-*r*-4-aminothiane (**2f**) would be expected to exist primarily as



2e, Ar = C_6H_5
f, Ar = *p*-ClC_6H_4

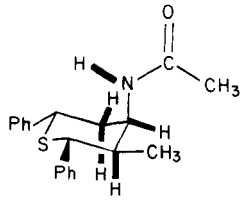
2e′, Ar = C_6H_5
f′, Ar = *p*-ClC_6H_4

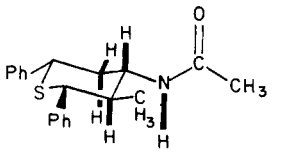


2e″, Ar = C_6H_5
f″, Ar = *p*-ClC_6H_4

the conformations **2e** and **2f**. The amines **2e** and **2f** show a somewhat broader, unresolved resonance for H(4) at δ 3.48 and 3.49, respectively. The H(4) resonance in amine **2e** has a half-bandwidth of 12.0 Hz (Figure 4), and **2f** has a half-bandwidth of 13.0 Hz, while amine **2a** (axial NH_2) shows a narrow resonance for H(4) (half-bandwidth of only 8.0 Hz). The larger half-bandwidth would lead to the reasonable conclusion that the contribution to the equilibrium by conformations **2e** and **2f** was small, and the bases largely exist in the alternate conformation **2e′** and **2f′**. However, CH_3–C_6H_5 diaxial interaction in **2e′** and **2f′** should be severe enough to make the chair conformation highly strained. Consequently, the chair forms could be distorted or the compounds might prefer a twist conformation **2e″** and **2f″**. Carbon-13 NMR spectral studies of **2e** and **2f** also led to similar conclusions.

The ^{1}H NMR data of the *N*-acetyl derivatives of **2a–f** and **3a–f** are also given in Table IV. The NH signal appeared downfield as a broad doublet (J = 7.0–9.0 Hz) in each case and suggests a NH–H(4) coupling.[21] *N*-Acetyl derivatives **7a–f** did not reveal the signals of H(4) which at δ 3.88–4.40 were hidden beneath the signal owing to H(2,6). However, the *N*-acetyl derivatives of **6a**, **6c**, and





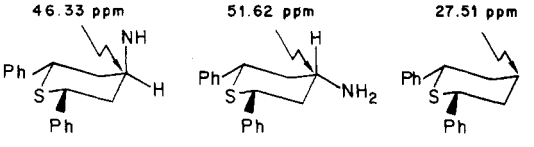
6d gave spectra in which H(4) signals were visible but showed no fine structure (unresolved broad signals observed). It was also interesting to note that the half-bandwidth of the 4(H) signal in the axial *N*-acetyl derivatives **6a**, **6c**, and **6d** were 14, 14, and 16 Hz, respectively, as compared with 8, 7, and 8 Hz, respectively, for corresponding primary amines **2a**, **2c**, and **2d**. This larger $w_{1/2}$ values for the H(4) signal in the *N*-acetyl derivatives **6a**, **6c**, and **6d** further confirms the NH–H(4) coupling. In general, acetylation of the amines **2a–f** and **3a–f** caused a deshielding of H(4) by about 1.1 ppm.

^{13}C NMR Studies

Following Grant's pioneering studies on cyclohexane derivatives,[31,32] the potential of ^{13}C NMR for elucidating configurational and conformational properties of cyclic systems has been applied in recent years to a number of six-membered heterocyclics.[33–38] In view of the pronounced dependence of ^{13}C shieldings on molecular geometry,[36] it was surprising that reports on substituted epimeric alicyclic amines were scant and ^{13}C chemical shift data on epimeric heterocyclic amines have been conspicuously missing. Carbon-13 chemical shifts for a number of substituted 4-aminothianes and the corresponding *N*-acetyl derivatives are given in Table V.

The carbon-13 spectra of the amines **2a–f** and **3a–f** and their *N*-acetyl derivatives **6a–f** and **7a–f** revealed that chemical shifts of the C(4) differed substantially for each epimeric pairs in this series. Shielding differences up to ~5 ppm were found between C(4) atoms bearing an axial vs. an equatorial amino group. In each case, the carbon with the axial amino group absorbed at a higher field (Table V). The pronounced sensitivity of ^{13}C shieldings to steric perturbations was apparent as has been established for epimeric 4-thianols,[33] 4-pyranols,[34] 4-piperidonols,[33] and 4-selenanols.[18]

For assessing the amino group substituent effect on the ring carbon shieldings of epimeric aminothianes **2a** and **2b**, the observed values for the specific carbons may be



2a **3a** **11**

compared with those for the corresponding carbon in *r*-2,*cis*-6-diphenylthiane (**11**). For example, C(4) in **11** absorbs at 27.51 ppm, while C(4) in **3a** appeared at 51.62

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Table IV. ^{1}H NMR Data for Substituted 4-Aminothianes and Corresponding *N*-Acetyl Derivatives (in $DCCl_3$)[e]

compd	H(2)	H(3)	H(4)	H(5)	H(6)	others
2a	4.61 [dd, J = Hz, J = 11 Hz, 2 H, H(2), H(6)]	1.83–2.38 [m, 4 H, H(3), H(5)]	3.60[a] ($w_{1/2}$ = 8 Hz)			1.12 (s, 2 H, NH_2), 7.04–7.50 (m, 10 H, ArH)
2b	4.61 [dd, J = 4 Hz, J = 11 Hz, 2 H, H(2), H(6)]	1.90–2.36 [m, 4 H, H(3), H(5)]	3.70[a] ($w_{1/2}$ = 8 Hz)			1.24 (s, 2 H, NH_2), 7.16–7.38 (m, 8 H, ArH)
2c	4.28 (d, J = 11 Hz)	2.05–2.58 [m, 3 H, H(3), H(5)]	3.42[a] ($w_{1/2}$ = 7 Hz)		4.60 (dd, J = 11 Hz, J = 4 Hz)	0.78 (d, 3 H, CH_3, J = 7 Hz), 1.13 (s, 2 H, NH_2), 7.02–7.64 (m, 10 H, ArH)
2d	4.28 (d, J = 11 Hz)	1.82–2.50 [m, 3 H, H(3), H(5)]	3.55[a] ($w_{1/2}$ = 8 Hz)		4.56 (dd, J = 4 Hz, J = 11 Hz)	0.72 (t, 3 H, CH_3, J = 8 Hz), 0.9–1.33 (m, 2 H, CH_2CH_3), 7.06–7.46 (m, 10 H, ArH)
2e		1.66–2.50 [m, 4 H, H(3), H(5)]	3.48 (q, $w_{1/2}$ = 12 Hz)		4.38 (dd, J = 4 Hz, J = 9 Hz)	1.16 (s, 3 H, CH_{3a}), 1.20 (s, 2 H, NH_2), 1.55 (s, 3 H, CH_{3e}), 7.12–7.54 (m, 5 H, ArH)
2f		1.68–2.54 [m, 4 H, H(3), H(5)]	3.49 (q, $w_{1/2}$ = 13 Hz)		4.38 (dd, J = 3 Hz, J = 9 Hz)	1.16 (s, 3 H, CH_{3a}), 1.32 (s, 2 H, NH_2), 1.56 (s, 3 H, CH_{3e}), 7.16–7.60 (m, 4 H, ArH)
3a	4.13 [dd, J = 3 Hz, J = 12 Hz, 2 H, H(2), H(6)]	1.60–2.48 [m, 4 H, H(3), H(5)]	2.94[b] ($w_{1/2}$ = 22 Hz, J_{aa} = 11 Hz, J_{ae} = 4 Hz)			1.47 (s, 2 H, NH_2), 7.12–7.60 (m, 10 H, ArH)
3b	4.07 [dd, J = 3 Hz, J = 12 Hz, 2 H, H(2), H(6)]	1.52–2.42 [m, 4 H, H(3), H(5)]	2.88[c] ($w_{1/2}$ = 21 Hz)			1.42 (s, 2 H, NH_2), 7.16–7.36 (m, 8 H, ArH)
3c	3.74 (d, J = 11 Hz)	1.69–2.45 [m, 3 H, H(3), H(5)]	2.58[d] ($w_{1/2}$ = 21 Hz, J_{aa} = 11 Hz, J_{ae} = 4 Hz)		4.12 (dd, J = 3 Hz, J = 11 Hz)	0.85 (d, 3 H, CH_3, J = 7 Hz), 1.31 (s, 2 H, NH_2), 7.12–7.42 (m, 10 H, ArH)
3d	3.92 (d, J = 11 Hz)	1.42–2.42 [m, 3 H, H(3), H(5)]	2.78[d] ($w_{1/2}$ = 22 Hz, J_{aa} = 11 Hz, J_{ae} = 4 Hz)		4.04 (dd, J = 3 Hz, J = 12 Hz)	0.67 (t, 3 H, CH_3, J = 8 Hz), 1.25 (s, 2 H, NH_2), 1.42–2.42 (m, 2 H, CH_2CH_3), 7.00–7.42 (m, 10 H, ArH)
3e		1.62–2.40 [m, 4 H, H(3), H(5)]	2.99[b] ($w_{1/2}$ = 22 Hz, J_{aa} = 11 Hz, J_{ae} = 4 Hz)		4.04 (dd, J = 3 Hz, J = 12 Hz)	1.31 (s, 3 H, CH_{3a}), 1.40 (s, 2 H, NH_2), 1.46 (s, 3 H, CH_{3e}), 7.14–7.44 (m, 5 H, ArH)
3f		1.51–2.40 [m, 4 H, H(3), H(5)]	2.98[b] ($w_{1/2}$ = 20 Hz, J_{aa} = 11 Hz, J_{ae} = 4 Hz)		4.02 (dd, J = 3 Hz, J = 12 Hz)	1.31 (s, 3 H, CH_{3a}), 1.42 (s, 2 H, NH_2), 1.45 (s, 3 H, CH_{3e}), 7.20–7.40 (m, 4 H, ArH)
6a	4.34 [dd, J = 3 Hz, J = 11 Hz, 2 H, H(2), H(6)]	1.90–2.48 [m, 4 H, H(3), H(5)]	4.54–4.85 (m, $w_{1/2}$ = 14 Hz)			2.08 (s, 3 H, $COCH_3$), 6.88–7.52 (m, 11 H, NH, ArH)
6b	4.16 [dd, J = 3 Hz, J = 11 Hz, 2 H, H(2), H(6)]	1.94–2.50 [m, 4 H, H(3), H(5)]	4.46–4.80 [m, overlapped with H(2)]			2.06 (s, 3 H, $COCH_3$), 5.74 (d, 1 H, NH, J = 9 Hz), 7.12–7.42 (m, 8 H, ArH)
6c	3.82 (d, J = 12 Hz)	2.24–2.62 [m, 3 H, H(3), H(5)]	4.48–4.78 (m, $w_{1/2}$ = 14 Hz)		4.20 (dd, J = 4 Hz, J = 11 Hz)	0.78 (d, 3 H, CH_3, J = 7 Hz), 2.12 (s, 3 H, $COCH_3$), 5.84 (d, 1 H, NH, J = 8 Hz), 6.94–7.46 (m, 10 H, ArH)

6d	3.87 (d, J = 12 Hz)	1.84–2.82 [m, 3 H, H(3), H(5)]	4.60–4.90 (m, $w_{1/2}$ = 16 Hz)	4.22 (dd, J = 3 Hz, J = 12 Hz)	0.80 (t, 3 H, CH_2CH_3, J = 5 Hz), 0.92–1.32 (m, 2 H, CH_2CH_3), 2.12 (s, 3 H, $COCH_3$), 5.74 (d, 1 H, NH, J = 8 Hz), 7.0–7.48 (m, 10 H, ArH)
6e		1.80–2.64 [m, 4 H, H(3), H(5)]	4.12–4.58 [m, overlapped with H(6)]	4.22 (dd, J = 4 Hz, J = 9 Hz)	1.13 (s, 3 H, CH_{3a}), 1.43 (s, 3 H, CH_{3e}), 1.98 (s, 3 H, $COCH_3$), 6.56 (d, 1 H, NH, J = 8 Hz), 7.04–7.56 (m, 5 H, ArH)
6f		1.78–2.66 [m, 4 H, H(3), H(5)]	4.20–4.46 [m, overlapped with H(6)]	4.11 (dd, J = 4 Hz, J = 9 Hz)	1.10 (s, 3 H, CH_{3a}), 1.38 (s, 3 H, CH_{3e}), 1.98 (s, 3 H, $COCH_3$), 5.92 (d, 1 H, NH, J = 7 Hz), 7.16–7.54 (m, 4 H, ArH)
7a	4.16 [dd, J = 3 Hz, J = 11 Hz, 2 H, H(2), H(6)]	1.60–2.60 [m, 4 H, H(3), H(5)]	3.88–4.32 [m, overlapped with H(2)]		1.92 (s, 3 H, $COCH_3$), 5.98 (d, 1 H, NH, J = 9 Hz), 7.06–7.50 (m, 10 H, ArH)
7b	4.13 [dd, J = 3 Hz, J = 12 Hz, 2 H, H(2), H(6)]	1.56–2.54 [m, 4 H, H(3), H(5)]	3.86–4.30 [m, overlapped with H(2)]		1.96 (s, 3 H, $COCH_3$), 5.56 (d, 1 H, NH, J = 8 Hz), 7.14–7.32 (m, 8 H, ArH)
7c	3.82 (d, J = 10 Hz)	1.86–2.62 [m, 3 H, H(3), H(5)]	3.76–4.28 [m, overlapped with H(2)]	4.18 (dd, J = 3 Hz, J = 12 Hz)	0.84 (d, 3 H, CH_3, J = 7 Hz), 1.96 (s, 3 H, $COCH_3$), 6.42 (d, 1 H, NH, J = 9 Hz), 7.02–7.48 (m, 10 H, ArH)
7d	3.90–4.40 [m, 3 H, H(2), H(4), H(6)]	1.74–2.62 [m, 3 H, H(3), H(5)]	3.90–4.40 [m, overlapped with H(2)]		0.74 (t, 3 H, CH_2CH_3, J = 8 Hz), 1.04–1.66 (m, 2 H, CH_2CH_3), 1.96 (s, 3 H, $COCH_3$), 6.33 (d, 1 H, NH, J = 9 Hz), 7.0–7.44 (m, 10 H, ArH)
7e		1.60–2.56 [m, 4 H, H(3), H(5)]	3.92–4.40 [m, overlapped with H(6)]	4.08 (dd, J = 3 Hz, J = 12 Hz)	1.29 (s, 3 H, CH_{3a}), 1.51 (s, 3 H, CH_{3e}), 1.94 (s, 3 H, $COCH_3$), 6.22 (d, 1 H, NH, J = 8 Hz), 7.0–7.46 (m, 5 H, ArH)
7f		1.60–2.50 [m, 4 H, H(3), H(5)]	3.94–4.24 [m, overlapped with H(6)]	4.06 (dd, J = 3 Hz, J = 12 Hz)	1.28 (s, 3 H, CH_{3a}), 1.50 (s, 3 H, CH_{3e}), 1.94 (s, 3 H, $COCH_3$), 6.18 (d, 1 H, NH, J = 8 Hz), 7.08–7.38 (m, 4 H, ArH)

[a] Center of multiplet. [b] Center of nonet. [c] Center of poorly resolved nonet. [d] Center of sextet. [e] Abbreviations used: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quintet.

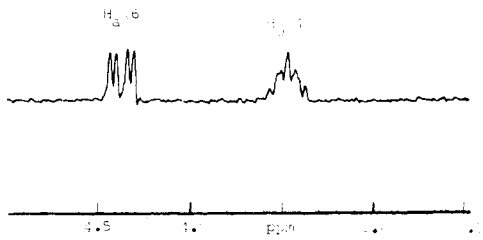

Figure 4. ^1H NMR spectra of **2e** (in $DCCl_3$).

ppm. The difference $\delta_{C(4)}^{RNH_2} - \delta_{C(4)}^{(RH)}$ of +24.11 ppm can be taken as the equatorial-NH_2 substituent effect at C(4) in amine **3a**. Similarly the NH_2 substituent effect at C(3) and C(2) has been calculated as +10.24 ppm and −1.15 ppm, respectively. The corresponding values for an axial amino group are +18.82, +6.07, and −7.75 ppm. The effect of the axial amino group corresponds to the similar 5.5-ppm shielding effect produced at the γ-carbon by an axial methyl group.[31] The effect of methyl substitution has been characterized in the methylcyclohexanes,[31] selected piperidines,[35] some 1,3-dioxanes,[36] and certain 1-hetera-2,6-diaryl-4-cyclohexanones[33] and 1-hetera-2,6-diaryl-4-cyclohexanols.[33] Downfield shifts of approximately 1–2 ppm were observed at the carbon site at which equatorial methyl substitution occurred, while a large downfield shift of 5–6 ppm was found at the adjacent β-positions [i.e., C(2)]. For example, a downfield shift of 6.06 ppm is observed for C(2) in **3c** compared to the corresponding signal in **3a**. The C(2) carbon resonance in **2c** is also shifted downfield (5.66 ppm) compared to C(2) signal in **2a**. An appreciable deshielding effect (5 ppm) recorded for C(4) in **2c** and **3c** compared to the corresponding resonances in **2a** and **3a** was apparently due to the β-effect of the equatorial methyl group.

The chemical shifts of the C(4) carbon in **2e** (45.86 ppm), **2f** (45.67 ppm), **3e** (47.40 ppm), and **3f** (47.28 ppm) are very close and provide useful conformational information. The upfield shift of the carbon bearing equatorial amino group (comparing **3e** and **3f** with **3a** and **3b**) is likely to be due to the gauche interaction between axial methyl at C(2) and the axial hydrogen H(4). On this basis, one would expect a greater upfield shift for C(4) in **2e** and **2f** relative to that found in **2a** and **2b**. It could be argued that these bases **2e** and **2f**, like their hydroxy analogues 2,2-dimethyl-6-phenyl-4-thianol[33] and 2,2-dimethyl-6-phenyl-4-piperidinol,[33] could probably exist in the twist conformations **2e″** and **2f″**. In such a case, steric interaction between quasi-axial methyl group at C(2) and quasi-axial NH_2 will be relieved to a large extent and this is reflected in the smaller upfield shift.

Experimental Section

General Data. Melting points were taken on a BOETIUS hot-stage microscope and are uncorrected. Proton magnetic resonance spectra were obtained on a Varian XL-100(15) high-resolution NMR spectrometer (with a time averaging computer accessory, C-1024) operating at 100.0 MHz and are expressed in δ values relative to internal standard Me_4Si. Proton-noise-decoupled ^{13}C NMR spectra were recorded at 25.2 MHz on a Varian XL-100(15) NMR spectrometer equipped with a Nicolet TT-100 Fourier transform accessory. Chemical shift data encompassing a 5000-Hz spectral region were collected into 8K data points. Single-frequency, off-resonance spectra were obtained by irradiation with a continuous-wave frequency at about δ −5 compared to Me_4Si in the proton spectrum. The samples were run as 0.3 M solutions in $DCCl_3$ containing Me_4Si as an internal reference. The spectra of all samples were recorded at 37 °C. Assignments have been made on the basis of signal multiplicity found in the off-resonance decoupled spectra and from the magnitude of the $^1J_{^{13}C-H}$ couplings.

1-(*p*-Chlorophenyl)-5-methyl-1,4-hexadien-3-one. To a mixture of 4-methyl-3-penten-2-one (30 g, 0.31 mol), *p*-chlorobenzaldehyde (43.6 g, 0.31 mol), hydroquinone (0.3 g), and piperidine (3 mL) was added glacial acetic acid (3 mL), and the mixture was gently boiled for 6 h (N_2 atmosphere). The brown mass obtained was extracted with ether (3 × 200 mL). The ether layer was washed with a saturated solution of bicarbonate and water and dried (Na_2SO_4). Removal of the solvent and vacuum distillation of the residue gave 17 g (25%) of 1-(*p*-chlorophenyl)-5-methyl-1,4-hexadien-3-one, bp 158–160 °C (1.7 mm), which solidified on standing. Further purification was achieved by recrystallization (petroleum ether, 60–80 °C) of the solid, mp 92–93 °C. Anal. Calcd fro $C_{13}H_{13}OCl$: C, 70.75; H, 5.94. Found: C, 70.92; H, 5.90.

2,2-Dimethyl-6-(*p*-chlorophenyl)-4-thianone. Into a boiling solution of sodium acetate trihydrate (40 g, 0.29 mol) and 1-(*p*-chlorophenyl)-5-methyl-1,4-hexadien-3-one (30 g, 0.14 mol) in ethanol (400 mL) was passed H_2S for 10 h.

The reaction mixture was then poured into water (1000 mL) which was extracted with ether (3 × 200 mL); the extracts were dried (Na_2SO_4). The solvent was removed and the residue was distilled to yield 21 g (61%) of 2,2-dimethyl-6-(*p*-chlorophenyl)-4-thianone, bp 154–156 °C (1.7 mm). The light yellow, viscous oil solidified upon standing and was recrystallized [petroleum ether; 60–80 °C]: mp 78–79 °C; ^1H NMR ($DCCl_3$) δ 1.42 [s, 6 H, CH_3(a), CH_3(e)], 2.40–2.96 [m, 4 H, H(3), H(5)], 4.32 [t, 1 H, H(6), J = 8 Hz], 7.22–7.40 (m, 4 H, ArH); ^{13}C NMR ($DCCl_3$) 28.54 [CH_3(a)], 30.64 [CH_3(e)], 44.27 [C(6)], 45.99 [C(2)], 49.87 [C(5)], 56.87 [C(3)], 207.94 [C(4)], 137.70, 133.47, 128.78, 128,54 ppm (CAr). Anal. Calcd for $C_{13}H_{15}OSCl$: C, 61.28; H, 5.93. Found: C, 61.44; H, 5.90.

2,2-Dimethyl-6-(*p*-chlorophenyl)-4-thianone Oxime (1f). A mixture of 2,2-dimethyl-6-(*p*-chlorophenyl)-4-thianone (1 g, 0.004 mol), hydroxylamine hydrochloride (1.5 g, 0.02 mol), sodium acetate trihydrate (3 g, 0.02 mol) and ethanol (50 mL) was boiled for 6 h. The solution was then poured onto crushed ice (500 g). The precipitated oxime **1f** (0.9 g, 85%) was filtered, washed with water, dried, and recrystallized (ethanol–water), mp 138–139 °C. Anal. Calcd for $C_{13}H_{16}NOSCl$: C, 57.87; H, 5.98; N, 5.19. Found: C, 57.98; H, 5.96; N, 5.22.

***r*-2,*cis*-6-Bis(*p*-chlorophenyl)-4-thianone Oxime (1b).** This oxime was prepared as described before from *r*-2,*cis*-6-bis(*p*-chlorophenyl)-4-thianone[39] and recrystallized (ethanol), mp 229–231 °C, yield 90%. Anal. Calcd for $C_{17}H_{15}NOSCl_2$: C, 57.96; H, 4.29; N, 3.98. Found: C, 57.82; H, 4.32; N, 3.96.

Thian-4-one Oxime (4a). Oximation of 4-thianone[40] gave **4a** in 90% yield. The oxime was recrystallized [petroleum ether; 60–80 °C], mp 84–86 °C. Anal. Calcd for C_5H_9NOS: C, 45.77; H, 6.92; N, 10.68. Found: C, 45.92; H, 6.89; N, 10.72.

2,2,6,6-Tetramethyl-4-thianone Oxime (4b). It was prepared as usual from 2,2,6,6-tetramethyl-4-thianone[41] and crystallized (ethanol–water); mp 126–127 °C, yield 86%. Anal. Calcd for $C_9H_{17}NOS$: C, 57.71; H, 9.15; N, 7.48. Found: C, 57.56; H, 9.11; N, 7.51.

The other oximes **1a**[42] and **1c–1e**[20] were prepared by known methods.

Reduction of 4-Thianone Oximes with Lithium Aluminum Hydride. To a well-stirred slurry of $LiAlH_4$ (0.05 mol) in dry tetrahydrofuran (40 mL) was added dropwise a solution of a thianone oxime (0.01 mol) in dry tetrahydrofuran (25 mL). The mixture was stirred under reflux for 8–12 h. Excess hydride was carefully destroyed by the dropwise addition of ice-cold water. The resultant mixture was extracted with ether (3 × 50 mL), and the ether solution was dried (Na_2SO_4). Evaporation of the solvent left a light yellow, viscous oil. This crude product was subjected to column chromatography.

Chromatographic Separation of the Mixture of Epimeric 4-Aminothianes. For 1 g of a mixture of epimeric amines, 20 g of Brockmann Grade neutral alumina (BDH) was used. The reduction product was dissolved in a minimum amount of benzene

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Table V. ^{13}C Chemical Shifts (δ) for Substituted 4-Aminothianes and Corresponding *N*-Acetyl Derivatives[a]

compd	C(2)	C(3)	C(4)	C(5)	C(6)	compd	C(2)	C(3)	C(4)	C(5)	C(6)
2a	41.32	40.24	46.33			6a	42.70	37.64	45.73		
2b	40.67	40.12	46.19			6b[b]					
2c	46.98	41.29	51.99	41.29	42.80	6c	49.14	40.21	50.19	39.83	42.87
2d	46.60	46.37	47.27	40.97	42.45	6d	48.70	45.93	46.60	39.60	42.66
2e	42.31	47.74	45.86	40.70	39.56	6e	42.08	44.45	42.08	40.39	36.80
2f	42.49	47.72	45.67	40.56	38.96	6f	42.26	44.60	44.04	39.95	36.53
3a	47.92	44.41	51.62			7a	47.74	41.09	49.29		
3b	47.12	44.12	51.30			7b	46.98	40.85	49.00		
3c	53.98	45.75	56.99	44.93	47.15	7c	54.30	43.64	54.48	42.84	47.39
3d	50.19	49.60	52.01	44.91	46.84	7d	50.72	47.71	50.95	43.07	47.27
3e	44.02	50.86	47.40	45.26	43.30	7e	43.02	45.79	47.18	43.75	41.52
3f	43.48	50.81	47.28	45.20	43.31	7f	42.93	46.87	45.55	43.10	41.15

[a] All data are given in parts per million downfield from Me_4Si; solutions used were 0.3 M in $DCCl_3$. [b] Not recorded due to poor solubility. All other signals for carbons in the systems are available in the Supplementary Material. *r*-2,*cis*-6-Diphenylthiane **11**: 49.07 [C-2,6], 34.17 (C-3,5), 27.51 (C-4), 141.87, 128.21, 127.17, 126.99 (CAr).

and fixed on the column. Elutions were carried out with petroleum ether (60–80 °C), petroleum ether–benzene (3:1, 1:1, 1:3), benzene, benzene–ether (3:1, 1:1, 1:3), and ether in the order given. Fractions (6) of 25 mL were collected for each eluant. The solvent was removed on a water bath. The contents of each flask were triturated with 1 mL of petroleum ether (60–80 °C) and left overnight whereupon solidification occurred. The yield and melting point of each solid from each fraction were determined. The fractions melting at the same temperature were combined and purified by crystallization from a suitable solvent. The axial amines were obtained from petroleum ether–benzene and benzene eluates and the equatorial amines from benzene ether and ether eluates. Details are furnished in Table II.

The 4-thianols **8a**,[39] **8b**,[39] **8c**,[20] **8d**,[20] **8e**,[20] **9a**,[39] **9b**,[39] **9c**,[20] **9d**,[20] and **9e**[20] were prepared by known methods.

2,2-Dimethyl-*trans*-6-(*p*-chlorophenyl)thian-*r*-4-ol (8f) and 2,2-Dimethyl-*cis*-6-(*p*-chlorophenyl)thian-*r*-4-ol (9f). These thianols were prepared from 2,2-dimethyl-6-(*p*-chlorophenyl)-4-thianone by reduction with $LiAlH_4$ in dry ether. The procedure adopted to reduce the thianone and to separate the epimeric alcohols by column chromatography over neutral alumina was similar to the previously described methods.[20] The axial isomer **8f** obtained (58%) was recrystallized (petroleum ether; 60–80 °C), mp 82–83 °C. Anal. Calcd for $C_{13}H_{17}SOCl$: C, 60.80; H, 6.67. Found: C, 60.96; H, 6.64.

A lesser amount (30%) of equatorial isomer **9f** was obtained and recrystallized (petroleum ether; 60–80 °C), mp 90–91 °C. Anal. Calcd for $C_{13}H_{17}SOCl$: C, 60.80; H, 6.67. Found: C, 60.72; H, 6.69.

Preparation of *p*-Toluenesulfonates. To a solution of the thianol **8a** (10.8 g, 0.04 mol) in dry pyridine (30 mL) was added a solution of *p*-toluenesulfonyl chloride (15.2 g, 0.08 mol) in dry pyridine (30 mL) at 0 °C; the solution was shaken well and set aside for 2 days at room temperature. It was then poured onto crushed ice with vigorous stirring and left overnight. The precipitated tosylate was filtered, washed with water, dried, and recrystallized from a suitable solvent. Similarly other tosylates were prepared. Relevant details are given in Table III.

Conversion of Tosylates into Amines. To a solution of the thianol tosylate (0.03 mol) and sodium azide (22.3 g, 0.34 mol) in dimethylformamide (120 mL) was added water (20 mL), and the solution was heated to 75–85 °C with stirring for 9–12 h. The mixture was then diluted with water (1000 mL) and extracted with ether (4 × 50 mL). The ether solution was washed with saturated brine (3 × 50 mL) and water and dried (Na_2SO_4). The solvent was removed in vacuum, and the residue was taken up in dry ether (30 mL) and added in the course of 20 min to a slurry of $LiAlH_4$ (3 g, 0.08 mol) in dry ether (50 mL). The mixture was stirred under reflux for 4 h. Excess hydride was carefully destroyed with wet ether and then ice-cold water; the resultant mixture was extracted with ether (4 × 50 mL). The ether solution was dried (Na_2SO_4) and dry HCl gas was passed into it. The precipitated amine hydrochloride was filtered, washed with dry ether, and dried. This salt was dissolved in a minimum amount of ethanol and the solution was basified with 1:1 ammonia. An oil separated and solidified upon standing. The solid was filtered, washed with water, dried, and recrystallized from a suitable solvent. Relevant details are given in Table I.

***N*-Acetyl Derivatives of the 4-Aminothianes.** A solution of the 4-aminothiane **2a** (0.40 g 0.0015 mol) in dry pyridine (2 mL) was treated with acetic anhydride (1.5 g, 0.015 mol). The reaction mixture was heated on a steam bath for 4 h and poured over crushed ice. The derivative obtained was crystallized from a suitable solvent. Other relevant data are given in Table I. This was the general procedure employed.

***r*-2,*cis*-6-Diphenylthiane (11).** A mixture of zinc powder (15 g, 0.23 mol), mercuric chloride (1.3 g, 0.005 mol), concentrated hydrochloric acid (2 mL), and water (15 mL) was well stirred for 5 min. The amalgamated zinc was washed with water and covered with ethanol (30 mL) and concentrated hydrochloric acid (20 mL). *r*-2,*cis*-6-Diphenylthian-4-one (5 g, 0.019 mol) was added, and the mixture was boiled for about 8 h with intermittent addition of concentrated hydrochloric acid and then left overnight. A yellow solid separated and was crystallized (methanol) to give **11**: 3.2 g (64%); mp 91–92 °C. Anal. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13. Found: C, 80.52; H, 7.17.

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Registry No. **1a**, 28144-11-8; **1b**, 70071-32-8; **1c**, 68226-75-5; **1d**, 68226-76-6; **1e**, 68226-78-8; **1f**, 78870-78-7; **2a**, 69832-20-8; **2b**, 70095-68-0; **2c**, 78837-43-1; **2d**, 78837-44-2; **2e**, 78837-45-3; **2f**, 78837-46-4; **3a**, 69832-19-5; **3b**, 70071-36-2; **3c**, 78918-40-8; **3d**, 78918-41-9; **3e**, 78837-47-5; **3f**, 78837-48-6; **4a**, 6309-59-7; **4b**, 78870-79-8; **5a**, 21926-00-1; **5b**, 78837-49-7; **6a**, 78961-94-1; **6b**, 78870-80-1; **6c**, 78870-81-2; **6d**, 78870-82-3; **6e**, 78870-83-4; **6f**, 78870-84-5; **7a**, 38132-32-0; **7b**, 78961-95-2; **7c**, 78961-96-3; **7d**, 78961-97-4; **7e**, 78870-85-6; **7f**, 78870-86-7; **8a**, 18456-46-7; **8b**, 32428-31-2; **8c**, 68296-31-1; **8d**, 68296-37-7; **8e**, 68226-25-5; **8f**, 78870-87-8; **8g**, 78870-88-9; **8h**, 78870-89-0; **8i**, 78870-90-3; **8j**, 78870-91-4; **8k**, 78870-92-5; **8l**, 78870-93-6; **9a**, 18456-47-8; **9b**, 32428-32-3; **9c**, 68226-14-2; **9d**, 68226-23-3; **9e**, 68226-24-4; **9f**, 78870-94-7; **9g**, 78961-98-5; **9h**, 79056-29-4; **9i**, 78961-99-6; **9j**, 78962-00-2; **9k**, 78870-95-8; **9l**, 78870-96-9; **11**, 54594-53-5; 4-methyl-3-penten-2-one, 141-79-7; *p*-chlorobenzaldehyde, 104-88-1; 1-(*p*-chlorophenyl)-5-methyl-1,4-hexadien-3-one, 77270-36-1; 2,2-dimethyl-6-(*p*-chlorophenyl)-4-thianone, 78870-97-0; *r*-2,*cis*-6-diphenylthian-4-one, 18456-44-5.

Supplementary Material Available: Expanded Tables I and III showing combustion analytical data and a table showing ^{13}C NMR data for the compounds listed in Table IV (6 pages). Ordering information is given on any current masthead page.