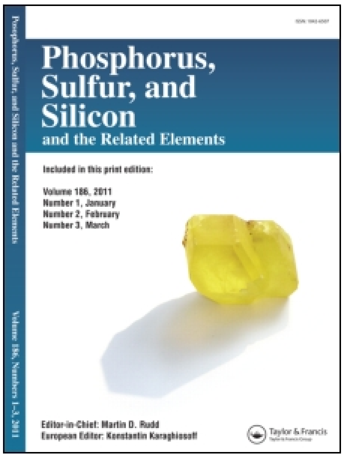

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SYNTHESIS OF AND CONFORMATIONAL STUDIES ON *N*-ALKYL-3-THIA-7-AZABICYCLO [3.3.1]NONAN-9-ONES AND DERIVATIVES. A SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 2,2,4,4-TETRAMETHYL-6,8-DIPHENYL-3-THIA-7-AZABICYCLO [3.3.1]-NONAN-9-ONE

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SYNTHESIS OF AND CONFORMATIONAL STUDIES ON *N*-ALKYL-3-THIA-7-AZABICYCLO [3.3.1]NONAN-9-ONES AND DERIVATIVES.
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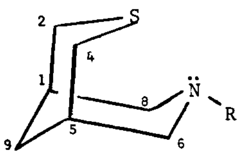
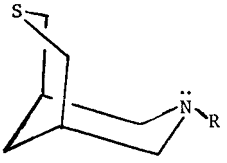
A series of *N*-alkyl-3-thia-7-azabicyclo[3.3.1]nonan-9-ones and derivatives have been prepared from the reaction of an appropriate 4-thianone, an aldehyde and an amine in a Mannich type condensation. Reduction of the ketones via Wolff–Kishner conditions produced bicyclic systems with the methylene bridging group. Addition of Grignard reagents to the ketones did yield the expected alcohols. Conformational analysis of the systems was performed via diagnosis of the ^{1}H and ^{13}C NMR spectra. A single crystal X-ray diffraction analysis of 2,2,4,4-tetramethyl-6,8-diphenyl-3-thia-7-azabicyclo[3.3.1]nonan-9-one was accomplished and revealed a boat conformer for the nitrogen-containing ring and a chair conformer for the sulfur-containing ring. The ketone crystallized in the triclinic space group $P\bar{1}$ ($Z = 2$) with $a = 6.216$ (3), $b = 10.507$ (5), $c = 15.335$ (6) Å, $\alpha = 86.64$ (4), $\beta = 86.66$ (4), and $\gamma = 98.51$ (5)° [Vol = 986.55 Å^3].

INTRODUCTION

3.7-Diheterabicyclo[3.3.1]nonanes and certain derivatives present quite interesting stereochemical features[1] as well as possess important biological activity when the heteroatoms are nitrogen and sulfur.[1,2] Both chair–chair (CC) and chair–boat (CB) forms have been recorded in the general family of heterocycles.[1–5] We report herein several new members with a variety of groups present on the nitrogen atom as well as at the C(9) position. The structures **1a**–**1c** illustrate the possible combinations of CC and CB forms that could exist for an (N,S) unit which would be labeled a 3-thia-7-azabicyclo[3.3.1]nonane system. A conformational analysis has been made of the compounds **2**–**4**.



1a



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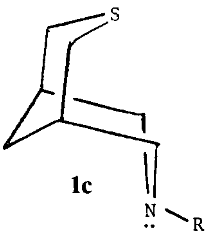

1c

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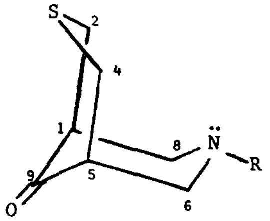
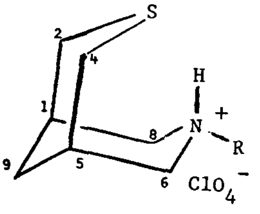
*Authors to whom all correspondence should be addressed.



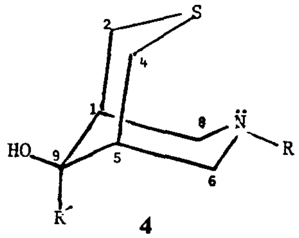
2

a. R = $PhCH_2$
b. R = *p*-$H_3COC_6H_4CH_2$
c. R = 3,4-$(H_3CO)_2C_6H_3CH_2$
d. R = $C_6H_5CH_2CH_2$
e. R = *p*-$H_3COC_6H_4CH_2CH_2$
f. R = 3,4-$(H_3CO)_2C_6H_3CH_2CH_2$



3

a. R - $PhCH_2$
b. R = *p*-$H_3COC_6H_4CH_2$
c. R = $C_6H_5CH_2CH_2$
d. R = 3,4-$(H_3CO)_2C_6H_3CH_2CH_2$

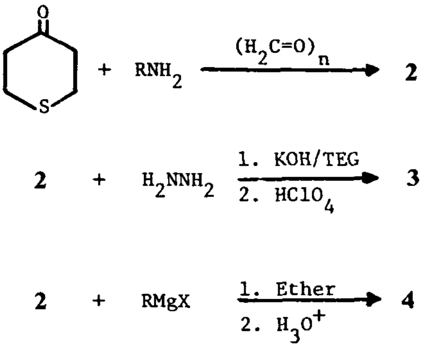


4

a. R = $PhCH_2$; R' = Ph
b. R = *p*-$H_3COC_6H_4CH_2$;
R' = Ph
c. R = $C_6H_5CH_2CH_2$;
R' = Ph
d. R = *p*-$H_3COC_6H_4CH_2CH_2$
R' = Ph
e. R = $C_6H_5CH_2CH_2$;
R' = H
F. R = $C_6H_5CH_2$; R' = CH_3

RESULTS AND DISCUSSION

The synthesis of members of **2** was achieved via a Mannich type of condensation involving 4-thianone and the appropriate amine along with paraformaldehyde. The general procedure is known[2] but variations in conditions are mandatory for maximizing yields of **2**. The Experimental Section describes the details for this preparation and Table I contains certain physical properties of the products. The yields ranged from excellent to very low since the dark reaction mixtures frequently gave polymeric like substances as observed during the workup. This was especially true in the preparation of members of **2**.



Reduction of members of **2** under Wolff–Kishner conditions produced amines which were converted to the perchlorates **3**. Addition of the appropriate Grignard reagent to **2** was the route employed to obtain members of **4**. The ^1H NMR spectral

TABLE I

Physical constants of members of **2**–**4**

				Analysis							
				Found			Calcd			M⁺(m/e)	
Compd.	Yield(%)	mp/bp°C	Formula	C	H	N	C	H	N	Calcd	Found
2a*	38	91–92	$C_{14}H_{17}NOS$								
2b	39	96–97	$C_{15}H_{19}NO_2S$							277.1136	277.1133
2c	6.5	81–83	$C_{16}H_{21}NO_3S$							307.1242	307.1243
2d	53	87–88	$C_{15}H_{19}NOS$	68.97	7.28	5.36	69.15	7.39	5.35	261.1187	261.1183
2e	21	79–80	$C_{16}H_{21}NO_2S$							291.1293	291.1302
2f	8.4	80.5–81	$C_{17}H_{23}NO_3S$							321.1399	321.1408
3a*	82	155–156	$C_{14}H_{15}ClNO_4S$								
3b	85	201–202	$C_{15}H_{22}ClNO_5S$	49.52	6.05		50.11	6.23			
3c	45	255–258	$C_{15}H_{20}ClNO_4S$							245.1238	245.1125**
3d	24	161–162	$C_{17}H_{27}ClNO_6S$	50.06	6.38		49.91	6.49			
4a*	100[‡]	112–113	$C_{20}H_{23}NOS$								
4b	66	131–132	$C_{21}H_{25}NO_2S$							234.0953	234.0933[‡‡]
4c	62	110–111	$C_{21}H_{25}NOS$							339.1657	339.1651
4d	72	133–134	$C_{22}H_{27}NO_2S$							248.1109	248.1109[§]
4e	56	99–101	$C_{14}H_{19}NOS$							249.1187	249.1209
4f	38	126–127	$C_{15}H_{21}NOS$							263.1344	263.1345
5	23	125–127	$C_{14}H_{17}NO_2S$							263.0980	263.0982
6	25	253–254	$C_{23}H_{27}NOS$							365.1813	365.1800

*Reported previously in reference 2.

**(M^+—$HClO_4$); in spite of all purification attempts and supportive spectral data, mass spectral data were not consistent.

[‡] This compound was reported in reference 2 and was obtained via neutralition of the hydroperchlorate.

[‡‡] [(M^+—C_8H_9O); thus the value for m/e found was for $C_{13}H_{16}NO_2S$; the calculated value for C_8H_9O (M^+—$C_{13}H_{16}NOS$) was: 121.0653; Found: 121.0665].

[§] [(M^+—C_8H_9O); thus the value found for m/e was for $C_{14}H_{18}NO_2S$; the calculated value for C_8H_9O (M^+—$C_{14}H_{18}NOS$) was: 121.0653; Found: 121.0653].

data are found in the Experimental Section but the ^{13}C NMR data are given in Table II. While the proton spectra were rather uninformative because of very severe overlap of signals of the ring protons, the ^{13}C signals were quite instructive and provided strong support for the major conformations present in the members of **2**–**4**.

As a starting point, we shall discuss the conformational aspects of members of **2**. In view of the X-ray diffraction analysis of **2a**,[2] the presence of a CB form in the solid state was suggested to persist also in solution on the basis of variable temperature NMR studies.[2] Consequently, the ^{13}C NMR shifts were interpreted for **2a** to describe a CB system with the sulfur atom in the boat form. Thus, it can be seen in Table II that signals for C(2, 4) and C(6, 8) do not differ significantly in any members of **2** (except for the hydroperchlorate **2á**). This seems to be very suggestive of a CB conformation for all of these compounds. It is also noteworthy that the C(9) resonance is essentially unaltered in **2a**–**f** which also implies that the carbonyl function is not influenced much by the substitution on the nitrogen atom. Likewise, signals for C(1, 5) are virtually identical in all examples. The ^{15}N shift (38.0 ppm) for **2b** was similar to that (37.3 ppm) for **2a**.[2]

Hydroperchlorates **3a**–**d** have very similar ^{13}C signals for corresponding carbons at all positions. Since **3a** has been shown to exist as a CC form in the solid state via

TABLE II

Selected ^{13}C chemical shifts for members of **2**–**4**

Compd*	Chemical shift in ppm from TMS			
	C(1,5)	C(2,4)	C(6,8)	C(9)
2a	47.1	34.6	58.4	212.8
2a' ($HClO_4$)**	37.3	29.0	54.7	88.5
2b	47.0	34.6	58.1	212.9
2c	47.0	34.8	58.1	212.7
2d	47.0	34.6	58.2	212.8
2e	47.0	34.6	58.4	212.7
2f	49.9	34.6	58.3	212.7
3a**	24.9	29.9	55.6	27.7
3b**	25.8	30.7	56.2	28.6
3c**	25.7	30.6	56.3	28.2
3d**	25.7	30.7	56.5	28.3
4a	35.6	29.2	55.5	71.2
4a' ($HClO_4$)**	33.4	27.3	55.1	67.4
4b	35.6	29.2	55.4	71.4
4c	35.3	29.3	59.8	71.4
4d	35.7	29.3	60.1	71.4
4e	33.4	26.5	58.2	70.9
4f	38.6	28.9	56.5	69.0
5	47.7	59.3	58.0	208.7
6	64.4	50.4	62.9	211.4

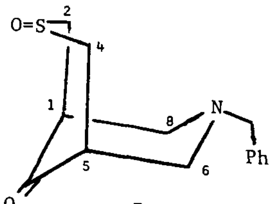
*Spectra recorded in $DCCl_3$ at approximately 20% solutions.
**Spectra recorded in DMSO-$\underline{d}_6$ at approximately 20% solutions.

X-ray diffraction analysis,[2] we intuitively reason that **3a**–**d** have similar conformations in solution. A comparison of ^{13}C signals for C(6, 8) in **2a**–**f** versus **3a**–**d** certainly supports a chair form containing the nitrogen atom in both series. In contrast, signals for C(2, 4) are shifted upfield in **3a**–**d** since C(9) is now a CH_2 group rather than a C=0 group as in **2a**–**f**. This upfield shift must be a result of the loss of the inductive effect of the C=0 group and the presence of a chair form for the thiane ring in members of **3a**–**f**.

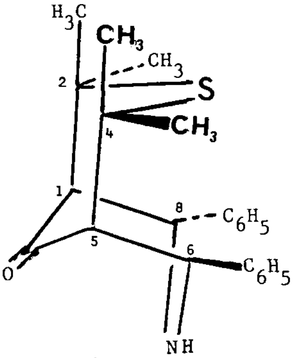
Alcohols **4a**–**f** are presumed to be CC forms since **4a'**, ($HClO_4$ derivative of **4a**) has been demonstrated to be a CC form in the solid state by X-ray analysis.[2] Again, differences in resonances for C(1, 5), C(2, 4), and C(6, 8) are small in **4a**–**f** as are signals for C(9) which adds credence to the supposition that these alcohols exist as CC forms. That the hydroxyl group is axial to the thiane ring is inferred for **4a**–**f** since the signal for C(6, 8) in **4e** (58.2 ppm) is essentially the same as in **2d** (58.2 ppm). Interestingly, the resonances for C(6, 8) in **4a** and **4f** are *upfield* from those in **2a** or **4e**, and we assume this is due to shielding by the phenyl and methyl groups, respectively.[2,4–6] These data again support a CC conformer for members of **4**.

The hydroperchlorate **2a'** is known to exist as a diol [at C(9)] with a CC conformer system.[7] Quite possibly this will be true for the other members of this family although such systems have not been prepared. The ^{13}C NMR data for **2a** as well as for **3a** and **4a** are included in Table II for the sake of completeness.

Mono-oxidation of sulfide **2a** to give sulfoxide **5** was achieved using $NaIO_4$ in H_2O/H_3COH at room temperature. Although the yield was modest, oxidation appears to have taken place at sulfur since the ^{13}C resonances for C(1, 5) and C(6, 8) were in essence the same in **5** [47.7 and 58.0 ppm, respectively] and **2a** [47.1 and 58.4 ppm, respectively]. A significant *downfield* shift was observed for C(2, 4) as expected, but, since the resonance for C(9) in **5** is upfield (208.7 ppm) compared to that for **2a** (212.8 ppm), we tentatively conclude that the thianone system is still a boat conformer and that the S → O bond is likely in a pseudo axial position as shown below.



5



6

Another area of interest regarding stereochemical consequences of large groups around the sulfur atom in these systems was examined in **6**. To date, our review of the literature has revealed that aryl groups attached to *alpha* carbons in 3- or 7-azabicyclo[3.3.1]nonanes and nonanones force the nitrogen-containing ring into a boat conformer.[2,4,5] Indeed, the synthesis of **6** involved a Mannich type reaction with 2,2,6,6-tetramethyl-4-thianone, benzaldehyde, and ammonium acetate in ethanol. The possible influence of such a process on the stereochemistry of the product has been discussed.[4,5,8] A solution ($DCCl_3$) of crystalline **6** gave a ^{13}C NMR spectrum which results in a significant *downfield* shift of all resonances for C(1, 5), C(2, 4), and C(6, 8). Since adequate models appeared to be lacking with which to compare the ^{13}C NMR spectrum,[10] an X-ray diffraction analysis was performed on a single crystal of **6**.

SINGLE CRYSTAL ANALYSIS OF 6

The 3-thia-7-azabicyclo[3.3.1]nonan-9-one backbone of **6** assumes a chair-boat (CB) conformation in the solid state with the thiane ring in a chair conformation and the piperidine ring in a boat conformation. The *gem*-dimethyl groups on C(2) and C(4) add strain to the thiane ring. The phenyl groups attached equatorially to C(6) and C(8) restrict the conversion of the piperidine ring to its chair form. The nitrogen has pyramidal geometry with its hydrogen attached equatorially. A perspective view of the molecule is presented in Figure 1. Table III contains pertinent data on the space group, unit cell dimensions, etc.

Bond distances and angles are given in Figures 2 and 3, respectively. The C—S bond lengths, 1.849(3) Å, are longer than both the value [1.817(5) Å] given by Sutton[9] as the mean distance for paraffinic C—S bonds and the range of 1.809 to

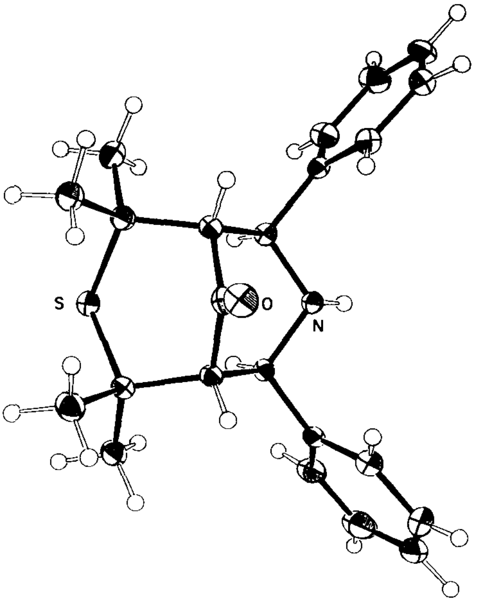


FIGURE 1 Perspective view of **6**.[23]

TABLE III

Crystal Data For Compound **6**

Mol. Formula	$C_{23}H_{27}NOS$
Mr	365.5
Linear absorption coefficient, cm^{-1}	1.36
Space group	$P\bar{1}$
Cell dimensions	
a, Å	6.216(3)
b, Å	10.507(5)
c, Å	15.3335(6)
α, deg	86.64(4)
β, deg	86.66(4)
γ, deg	98.51(5)
V, $Å^3$	986.55
Z	2
Density (calc), g cm^{-1}	1.23
Final R	0.048
R_w	0.046
No of observed reflections	2762

1.821 Å found in similar ring systems.[5,10] However, the C—S bonds in **6** are comparable to the bonds in compounds with adjacent *gem*-dimethyl groups (1.839 to 1.842 Å).[11,12] The C—N bond lengths [1.476(3) and 1.479(3) Å] agree well with the average 1.472(5) Å listed by Sutton for similar bonds.[13]

The conformational relationships in the bicyclo[3.3.1]nonane ring system are shown by the torsional angles given in Figure 4 and by the angles between selected planes given in Figure 5. Ideally the torsional angles in cyclohexane should be 56°,

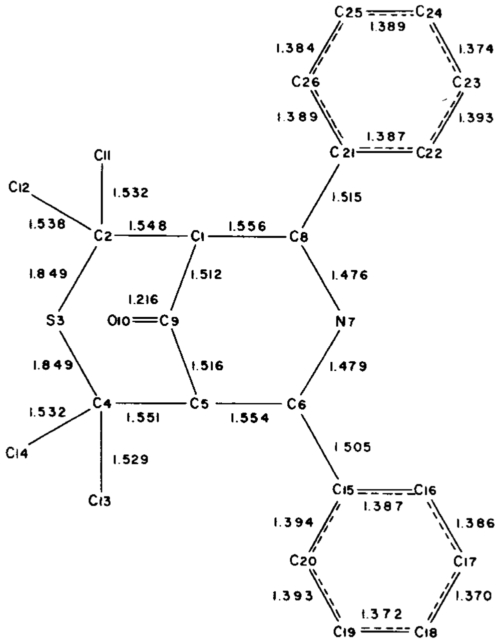


FIGURE 2 Bond distances (Å) in **6**. Estimated standard deviations are in the range 0.003 to 0.006 Å.

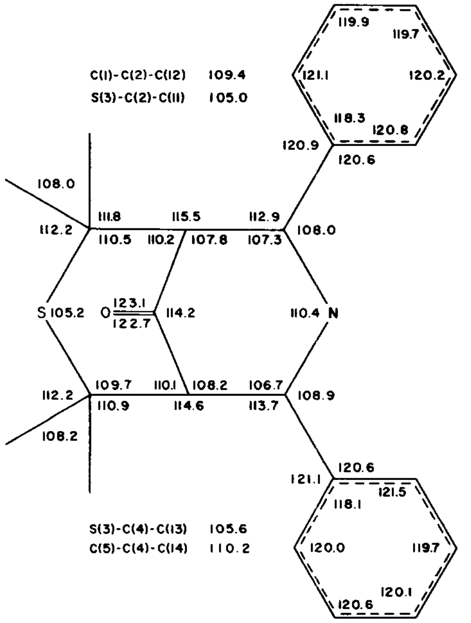


FIGURE 3 Bond angles (°) in **6**. Estimated standard deviations are in the range 0.2 to 0.3°.

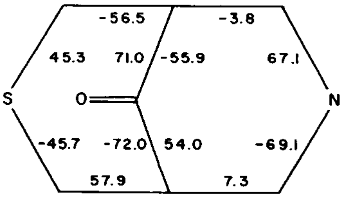


FIGURE 4 Selected torsion angles (°) in **6**. Estimated standard deviations are in the range 0.2 to 0.3°.

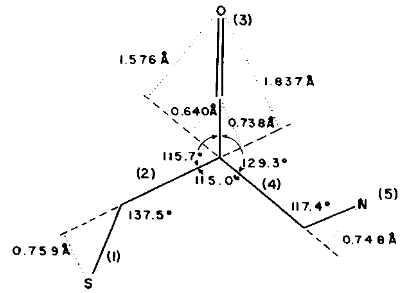


FIGURE 5 Selected interplanar angles (°). Estimated standard deviations of angles are in the range 0.1 to 0.2°. Distances to the indicated planes have estimated standard deviations of 0.001 to 0.003 Å.

and Macrosson and Ferguson predicted that angles between the three-atom and four-atom planes should be 125.25° when compared with values appropriate to a diamond lattice.[14] The torsional angles at the sulfur end of the boat ring, 45.3(2) and −45.7(2)°, and the corresponding interplanar angle, 137.5(1)°, show that this part of the ring system is significantly flattened. This flattening is due, in part, to repulsive interactions between the axial methyl groups on C(2) and C(4). The carbonyl plane leans somewhat towards the chair ring and away from the boat ring. Other bicyclo[3.3.1]nonan-9-ones with a CB conformation show a similar trend.[2,10,15]

The nitrogen end of the piperidine ring, having torsional angles of −69.1(2) and 67.1(2)°, is decidedly puckered. The bulky phenyl groups on C(6) and C(8) force the axial hydrogens together producing the puckered piperidine ring. The phenyl groups at C(6) and C(8) are at angles of −61.7(2) and 66.6(2)°, respectively, to the C(6), N(7), C(8) plane.

In previous studies of 3,7-diheterobicyclo[3.3.1]nonan-9-ones in a CB conformation, the carbonyl carbon, C(9), was found to be weakly attracted to the atom at the opposite end of the boat ring.[2,10,15] In those studies, C(9) was displaced from the C(1), C(5), 0 plane by from 0.026 to 0.039 Å. In **6**, this attraction does not exist because C(9) is only 0.007(2) Å from the C(1), C(5), 0 plane.

EXPERIMENTAL

General data. Melting points were taken on a Thomas–Hoover capillary apparatus and are uncorrected. Proton magnetic resonance spectra were recorded at 100.0 MHz on a Varian XL-100(15) high resolution NMR spectrometer and are reported in δ values relative to internal standard Me_4Si. Some proton spectra were recorded on a Varian XL-300 NMR spectrometer operating at 299.94 MHz. Carbon-13 spectra were recorded on the XL-100(15) equipped with a Nicolet TT-100 PFT accessory (at 25.2 MHz) or on the XL-300 spectrometer (at 75.42 MHz) and are reported in ppm relative from internal TMS. To aid in the carbon resonance assignments, single-frequency, off resonance spectra were obtained by irradiating with a continuous wave frequency at about δ -5 compared to TMS in the proton spectrum. The ^{15}N NMR spectra were recorded downfield from liquid ammonia (25°C) using formamide (neat: 112.4 ppm) in a capillary as an external standard. IR spectra were collected on a Perkin-Elmer 681 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Reactions were performed under nitrogen unless otherwise specified. All reagents were used directly without further purification unless indicated and all solvents were dried and distilled prior to use. 4-Thianone,[16] *cis*-2,6-diphenyltetrahydrothiopyran-4-one,[17] and 2,2,6,6-tetramethyl-thiopyran-4-one[18] were prepared by literature procedures as were **2a**,[2] **3a**,[2] and **4a**.[2] Hydrazine (Eastman, 95%), benzylamine (Eastman, bp 182–185°C), 2-phenethylamine (Matheson Coleman and Bell, bp 198–200°C), 4-methoxybenzylamine (Aldrich, bp 236–237°C), 2-(4-methoxyphenyl)ethylamine (Aldrich, bp 138–140°C/20 mm), 3,4-dimethyoxybenzylamine (Aldrich, bp 180°C/15 mm), 2-(3,4-dimethoxyphenyl)ethylamine (Aldrich, bp 154–158°C/12 mm), $HClO_4$ (Baker), $Na_2S \cdot 9H_20$ (Aldrich), H_2S (Matheson), phenylmagnesium chloride (Aldrich, 2 M in THF), methylmagnesium chloride (Aldrich, 2 M in THF), *N*-methyl-4-piperidone (Aldrich), and $NaBH_4$ (Matheson Coleman and Bell) were used as purchased.

General procedure for N-alkyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-ones (**2**). A mixture containing 25.9 mmol of an amine, 6.20 g (210 mmol) of paraformaldehyde and 90 mL of methyl alcohol was made acidic with 2.30 g (38 mmol) of gl acetic acid. In one portion, 3.00 g (25.9 mmol) of 4-thianone was added to the above mixture. The resulting mixture was heated under N_2 at reflux for 6–12 h. The solvent was removed from the red solution to give a red oil. This oil was diluted with 180 mL of H_2O and extracted with 2 × 40 mL of ether which was discarded. The aqueous layer was made basic by the addition of 4.3 g (77 mmol) of KOH pellets and extracted with 4 × 75 mL of ether.

The ether extracts were combined and dried (Na_2SO_4). The above solution was filtered, and the solvent was removed to give yellow-reddish brown oil or a solid. This oil (or solid) was distilled (or digested) in Skelly B (bp 60–68°C). This was followed by decantation of the hot solution, evaporation of the solvent and molecular distillation of the crude product in a sublimation apparatus. The details are given for each amine.

N-4-Methoxybenzyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-one (**2b**). Following the general procedure using 2.4 g (25.9 mmol) of 4-methoxybenzylamine and heating for 12 h gave a red solid. Digestion with 200 mL of Skelly B, followed by decantation of the hot solution and evaporation, gave a yellow solid. Molecular distillation in a sublimation apparatus at 140–145°C (oil bath)/10^{-4} mm gave 2.8 g (39%) of **2b**: mp 96–7°C; IR (KBr) 1720 (C=0) cm^{-1}; ^1H NMR ($DCCl_3$) δ 2.6–3.25 (m, 10 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.5 (s, 2 H, $ArC\underline{H}$), 3.78 (s, 3 H, $Ar—OC\underline{H}_3$); ^{13}C NMR ($DCCl_3$) ppm, see Table II and other signals are: 55.12 ($\underline{C}H_3—O$), 60.61 ($Ar—\underline{C}H_2$), 113.57, 129.71, 129.97, 158.63 ($Ar—\underline{C}$); ^{15}N NMR ($DCCl_3$) 38.02 ppm.

N-3-4-Dimethoxybenzyl-7-aza-3-thiabicyclo[3,3,1]nonan-9-one (**2c**). Following the general procedure using 4.40 g (26.5 mmol) of 3,4-dimethoxybenzylamine and heating for 12 h have an orange oil. Distillation of the oil through a 3-inch column at 185–200°C (head temp.)/10^{-4}–10^{-5} mm gave a clear oil which was dissolved in 15 mL of 95% ethanol. The resulting solution was placed in a freezer (−5°C) overnight. The white solid that crystallized was filtered off and dried at RT and 1 mm for 1 h. This procedure gave 0.53 g (6.5%) of **2c**: mp 81–83°C; IR (KBr) 1725 cm^{-1} (C=0); ^1H NMR ($DCCl_3$) δ 2.70–2.84 (m, 4 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.09–3.25 (m, 6 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.54 (s, 2 H, $ArC\underline{H}_2$), 3.90 (s, 3 H, $C\underline{H}_3—0$), 3.92 (s, 3 H, $C\underline{H}_3O$), 6.8–7.0 (m, 3 H, $Ar—\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 57.77 (*ortho* and *para* $\underline{C}H_3—O$), 60.90 [$Ar\underline{C}H_2$], 110.77, 111.62, 120.61, 130.64, 148.01, 148.77 ($Ar—\underline{C}$).

N-Phenethyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-one (**2d**). Following the general procedure using 3.1 g (25.9 mmol) of phenethylamine and heating for 12 h gave a reddish-yellow solid. This solid was digested with 200 mL of Skelly B for 10 min. The hot Skelly B solution was decanted and allowed to evaporate to give a white solid. Distillation in a sublimation apparatus at 100–140°C (oil bath)/10^{-4}–10^{-5} mm gave 2.4 g (53%) of **2d**: mp 87–88°C; IR (KBr) 1720 cm^{-1} (C=0); ^1H NMR ($DCCl_3$) δ 2.65–2.85 (m, 8 H, ring $C\underline{H}_2$ and $C\underline{H}$ and $Ar—C\underline{H}_2—C\underline{H}_2$), 3.1–3.26 (m, 6 H, ring $C\underline{H}_2$ and $C\underline{H}$ and $Ar-C\underline{H}_2—C\underline{H}_2$), 7.28 (m, 5 H, $Ar—\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm, see table II and the other signals are 34.74 ($Ar—\underline{C}H_2$), 58.36 [$Ar—CH_2—\underline{C}H_2$], 125.9, 128.2, 128.4, 139.7 ($Ar—\underline{C}$).

N-4-Methoxyphenethyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-one (**2e**). Following the general procedure using 3.9 g (25.9 mmol) of 4-methoxyphenethylamine and heating for 12 h gave a yellow oil. The oil was distilled through a 3-inch column at 180–200°C (head temp.)/10^{-2}–10^{-5} mm. The clear oil obtained was dissolved in 20 mL of ethanol (95%), and the solution was placed in a freezer (− 5°C) overnight. The white solid that crystallized was filtered off and gave 1.6 g (21%) of **2e**: mp 79–80°C; IR (KBr) 1725 cm^{-1} (C=O); ^{1}H NMR (DCCl$_3$) δ 2.6–2.9 (m, 8 H, ring C$\underline{H}_2$, C$\underline{H}$ and Ar—C$\underline{H}_2$—C$\underline{H}_2$), 3.1–3.2 (m, 6 H, ring C$\underline{H}_2$, C$\underline{H}$ and Ar—C$\underline{H}_2$—C$\underline{H}_2$), 3.75 (s, 3 H, C$\underline{H}_3$—O), 6.75–7.2 (q, 4 H, Ar—$\underline{H}$); ^{13}C NMR (DCCl$_3$) ppm, see Table II and the other signals are: 32.88 (Ar—$\underline{C}$H$_2$), 55.5 ($\underline{C}$H$_3$—O), 58.56 (Ar—CH$_2$—$\underline{C}$H$_2$), 113.68, 129.32, 131.78, 157.78 (Ar—$\underline{C}$).

N-3,4-Dimethoxyphenethyl-7-aza-3-thiabicyclo[*3.3.1*]*nonan-9-one* (**2f**). Following the general procedure using 4.7 g (25.9 mmol) of 3,4-dimethoxyphenethylamine and heating for 12 h gave a red oil. Distillation through a 3-inch column at 180–190°C(head temp.)/10^{-4}mm gave a yellow oil. This oil was distilled (short-path) and then dissolved in 20 mL of 95% ethanol, and the solution was placed in a freezer at − 5°C for 48 h. The solid that crystallized was filtered off and recrystallization (ethanol) gave 0.7 g (8.4%) of **2f**: mp 80.5–81°C; IR (KBr) 1725 cm^{-1} (C=O); ^{1}H NMR (DCCl$_3$) δ 2.7–2.95 (m, 8 H, ring C$\underline{H}_2$, C$\underline{H}$ and ArC$\underline{H}_2$—C$\underline{H}_2$), 3.1–3.3 (m, 6 H, ring C$\underline{H}_2$, C$\underline{H}$) and ArC$\underline{H}_2$), 3.85 (s, 6 H, *ortho* and *para* C$\underline{H}_3$—O), 6.85 (s, 3 H, Ar$\underline{H}$); ^{13}C NMR (DCCl$_3$), see Table II and the other signals are: ppm 33.28 (Ar—$\underline{C}$H$_2$), 55.68 (CH$_3$—O), 55.75 (CH$_3$—O), 58.43 (Ar—CH$_2$—$\underline{C}$H$_2$), 111.13, 111.88, 120.32, 132.46, 147.11, 148.54 (Ar—$\underline{C}$).

N-4-Methoxybenzyl-7-aza-3-thiabicyclo[*3.3.1*]*nonane hydroperchlorate* (**3b**). To a solution of 10 mL of triethylene glycol and 2 g (59.4 mmol) of hydrazine (95%) in a 25 mL flask equipped with a condenser, which had a fractional take off below the water jacket, was added 0.5 g (1.8 mmol) of **2b**. Then, 3.5 g (62.5 mmol) of KOH pellets were added and the resulting mixture was heated to 155–160°C (oil bath) under N$_2$ with magnetic stirring for 4 h. During this time, 1.5 mL of distillate was removed by way of the fractional take off. The solution was cooled to RT, diluted with 30 mL of H$_2$O, and extracted with ether (3 × 30 mL). The organic layers were combined and dried (Na$_2$SO$_4$). The solution was then filtered and cooled (ice bath). To the cooled solution, 2 mL of HClO$_4$ (60%) was added slowly. A white solid separated and was filtered and washed with 50 mL of fresh dry ether. Recrystallization (95% ethanol) gave 0.4 g (85%) of **3b**: mp 201–202°C; IR (KBr) 3450 (N—H), 1100 cm^{-1} (ClO$_4^-$); ^{1}H NMR (DMSO-$\underline{d}_6$) δ 1.80–3.60 (m, 12 H, ring C$\underline{H}_2$ and C$\underline{H}$), 3.80 (s, 3 H, C$\underline{H}_3$—O), 4.21 (s, 2 H, Ar—C$\underline{H}_2$), 7.08 (d, 2 H, J = 9 Hz, Ar—$\underline{H}$), 9.1 (s, 1 H, N—$\underline{H}$); ^{13}C NMR (DMSO-$\underline{d}_6$) ppm, see Table II and the other signals are: 55.12 (CH$_3$—O), 60.40 (Ar—$\underline{C}$H$_2$), 114.30, 121.54, 131.84, 159.83 (Ar—$\underline{C}$).

N-Phenethyl-7-aza-3-thiabicyclo[*3.3.1*]*nonane hydroperchlorate* (**3c**). To a solution of 10 mL of triethylene glycol and 2 g (59.4 mmol) of hydrazine (95%) in a 25 mL flask equipped with a condenser, which had a fractional take off below the water jacket, was added 0.5 g (1.9 mmol) of **2d**. Then, 3.5 g (62.5 mmol) of KOH pellets were added, and the resulting mixture was heated to 150–155°C (oil bath) under N$_2$ with magnetic stirring for 4 h. During this time, 1.5 mL of distillate was removed by way of the fractional take off. The solution was cooled to RT, diluted with 30 mL of H$_2$O and extracted with ether (3 × 30 mL). The organic layers were combined and dried (Na$_2$SO$_4$). The solution was then filtered and cooled (ice bath). To the cooled solution, 2 mL of HClO$_4$ (60%) was added slowly. A white solid separated and was filtered and washed with 50 mL of fresh dry ether. Recrystallization (95% ethanol) gave 0.3 g (45%) of **3c**: mp 255–258°C; IR (KBr) 3420 (N—H), 1600 (Ar, C=C), 1100 cm^{-1} (ClO$_4$ −); ^{1}H NMR (DMSO-$\underline{d}_6$) δ 1.85 [s, 2 H, H(9)], 2.25–3.5 (m, 12 H, ring C$\underline{H}_2$), C$\underline{H}$ and Ar—C$\underline{H}_2$), 3.85 (d, 2 H, Ar—CH$_2$—C$\underline{H}_2$), 7.33 (s, 5 H, Ar—$\underline{H}$), 9.0 (s, 1 H, N—$\underline{H}$); ^{13}C NMR (DMSO-$\underline{d}_6$) ppm, see Table II and the other signals are: 29.88 (Ar—$\underline{C}$H$_2$—CH$_2$), 59.03 (Ar—CH$_2\underline{C}$H$_2$), 126.67, 128.46, 136.33 (Ar—$\underline{C}$).

N-3,4-Dimethoxyphenethyl-7-aza-3-thiabicyclo[*3.3.1*]*nonane hydroperchlorate* (**3d**). To a solution of 10 mL of triethylene glycol and 2.0 g (59.4 mmol) of hydrazine (95%) in a 25 mL flask equipped with a condenser, which had a fractional take off below the water jacket, was added 0.50 g (1.6 mmol) of **2f**. Then, 3.50 g (62.5 mmol) of KOH pellets were added, and the resulting mixture was heated to 145–155°C (oil bath) under N$_2$ with magnetic stirring for 4 h. During this time, 1.5 mL of distillate was removed by way of the fractional take off. The solution was cooled to RT, diluted with 30 mL of H$_2$O, and extracted with ether (3 × 30 mL). The organic layers were combined and dried (Na$_2$SO$_4$). The solution was then filtered and cooled (ice bath). The cooled solution, 2 mL of HClO$_4$ (60%) was added slowly. An oil separated and the mixture was placed in the freezer (− 5°C) overnight during which time crystals formed. The solid was filtered and washed with dry ether (50 mL) to give 0.15 g (25%) of **3d**: mp 161–162°C; IR (KBr) 3400 (N—H), 1100 cm^{-1} (ClO$_4^-$); ^{1}H NMR (DMSO-$\underline{d}_6$) δ 1.7–3.5 (m, 16 H, ring C$\underline{H}_2$, C$\underline{H}$ and Ar—C$\underline{H}_2$—C$\underline{H}_2$), 3.74 (s, 3 H, *ortho* or *para* C$\underline{H}_3$—O), 3.78 (s, 3 H, *ortho* or *para* C$\underline{H}_3$—O), 6.9 (m, 3 H, Ar—$\underline{H}$); ^{13}C NMR (DMSO-$\underline{d}_6$) ppm, see Table II and the other signals are: 29.54 (Ar—$\underline{C}$H$_2$—), 55.39 ($\underline{C}$H$_3$—O), 59.30 (ArCH$_2$—$\underline{C}$H$_2$), 112.11, 112.44, 120.55, 128.51, 147.66, 148.73 (Ar—$\underline{C}$).

N-4-Methoxybenzyl-9-phenyl-7-aza-3-thiabicyclo[*3.3.1*]*nonan-9-ol* (**4b**). A solution of phenylmagnesium chloride (1.8 mL, 2 M in THF) was added dropwise to a stirred solution of 0.50 g (1.8 mmol) of **2b** in 35 mL of dry ether. The resulting mixture was stirred at RT for 12 h under N_2. Saturated aqueous NH_4Cl (2 mL) was slowly added to the mixture followed by stirring for 1 h. The ether solution was decanted from the white precipitate, and the precipitate was washed with ether (3 × 15 mL). The ether solutions were combined and dried (KOH). The solution was filtered, and the ether was evaporated to give a white solid. Recrystallization (95% ethanol) gave 0.42 g (66%) of **4b**: mp 131–132°C; IR (KBr) 3400 cm^{-1} (O-H); ^1H NMR ($DCCl_3$) δ 1.5–3.0 (m, 11 H, O—H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.25 (s, 2 H, Ar—$C\underline{H}_2$), 3.8 (s, 3 H, $C\underline{H}_3$—O), 6.75-7.6 (m, 10 H, Ar$\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 55.07 ($\underline{C}H_3O$), 61.45 (Ar—$\underline{C}H_2$), 113.28, 125.24, 127.43, 128.46, 129.27, 131.08, 144.50, 158.10 (Ar$\underline{C}$).

N-Phenethyl-9-phenyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-ol (**4c**). A solution of phenylmagnesium chloride (1.9 mL, 2 M in THF) was added dropwise to a stirred solution of 0.5 g (1.9 mmol) of **2d** in 35 mL of dry ether. The remaining procedure was identical to that used to obtain **4b**. Recrystallization (Skelly B, bp 60–68°C) of the crude solid gave 0.5 g (62%) of **4c**: mp 110–111°C; IR (KBr) 3420 cm^{-1} (O—H); ^1H NMR ($DCCl_3$) δ 2.2–2.9 (m, 11 H, OH, ring $C\underline{H}_2$, $C\underline{H}$ and Ar—$C\underline{H}_2$) 2.95–3.1 (m, 2 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.65-3.85 (m, 2 H, Ar—CH_2—$C\underline{H}_2$), 7.05–7.5 (m, 10 H, Ar$\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 33.38 (Ar—$\underline{C}H_2$), 56.23 (Ar—CH_2—$\underline{C}H_2$), 125.36, 125.53, 127.55, 127.95, 128.45, 140.47, 153.92 (Ar$\underline{C}$).

N-4-Methoxyphenethyl-9-phenyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-ol (**4d**). A solution of phenylmagnesium chloride (1.4 mL, 2 M in THF) was added dropwise to a stirred solution of 0.40 g (1.4 mmol) of **2e** in 35 mL of dry ether. The remaining procedure was the same as that for **4b**. Recrystallization (95% ethanol) of the crude solid gave 0.37 g (72%) of **4d**: mp 133–134°C; IR (KBr) 3400 cm^{-1} (OH); ^1H NMR ($DCCl_3$) δ 1.5–3.2 (m, 15 H, O$\underline{H}$, ring $C\underline{H}_2$, $C\underline{H}$, Ar—$C\underline{H}_2CH_2$), 3.8 (s, 3 H, $C\underline{H}_3$—O), 6.75–7.6 (m, 10 H, Ar$\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 32.42 (Ar$\underline{C}H_2$—CH_2), 55.04 ($\underline{C}H_3$—O), 56.24 (Ar—CH_2—$\underline{C}H_2$), 113.40, 125.34, 127.50, 128.46, 129.31, 132.57, 143.92, 157.41 (Ar$\underline{C}$).

N-Benzyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-ol (**4e**). A mixture of 48 mg (1.3 mmol) of $NaBH_4$ and 0.25 g (1 mmol) of **2a** in 10 mL of isopropyl alcohol was stirred at RT for 12 h. The solvent was removed and 20 mL of H_2O was added to the residue. The aqueous mixture was extracted with ether (4 × 30 mL), and the organic layers were combined and dried (Na_2SO_4). The ether solution was filtered and the solvent was removed to give a pale yellow oil. The oil was dissolved in 30 mL of boiling Skelly B (bp 60–68°C) and, the solution was allowed to cool to RT. White crystals formed and were filtered to give 0.14 g (56%) of **4e**: mp 99–101°C; IR (KBr) 3420 cm^{-1} (O—H); ^1H NMR ($DCCl_3$) δ 2.2–3.25 (m, 11 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.55 (s, 2 H, Ar—$C\underline{H}_2$), 3.75 (s, 1 H, O—$\underline{H}$), 7.25–7.5 (m, 5 H, Ar—$\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 62.21 (Ar—$\underline{C}H_2$), 126.65, 128.01, 128.42, 138.70 (Ar$\underline{C}$).

N-Benzyl-9-methyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-ol (**4f**). A solution of methylmagnesium chloride (2 mL, 3 M in THF) was added dropwise to a stirred solution of 0.5 g (2.0 mmol) of **2a** in 35 mL of dry ether. The resulting mixture was stirred at RT for 12 h under N_2. Saturated aqueous NH_4Cl (2 mL) was slowly added to the mixture followed by stirring for 1 h. The ether solution was decanted from the white precipitate, and the precipitate was washed with ether (3 × 15 mL). The ether solutions were combined and dried (Na_2SO_4). The solution was filtered, and the ether was evaporated to give a white solid. Recrystallization (Skelly B, bp 60–68°C) gave 0.2 g (38%) of **4f**: mp 126–127°C; IR (KBr) 3410 cm^{-1} (O—H); ^1H NMR ($DCCl_3$) δ 1.4 (s, 3 H, $C\underline{H}_3$), 1.8–3.5 (m, 10 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.6 (s, 2 H, Ar—$C\underline{H}_2$), 7.2–7.5 (m, 5 H, Ar$\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 27.72 ($\underline{C}H_3$), 62.36 (Ar—$\underline{C}H_2$), 126.68, 128.11, 128.45, 138.64 (Ar—$\underline{C}$).

N-Benzyl-7-aza-3-sulfoxidebicyclo[3.3.1]nonan-9-one (**5**). A solution of 0.90 g (4.2 mmol) of $NaIO_4$ in 5 mL of water was added to a stirred solution of 0.50 g (2.0 mmol) of **2a** in 25 mL of methanol under N_2. The resulting mixture was stirred at RT for 72 h at which time the solvent was removed to give a white solid. The solid was suspended in $HCCl_3$ (20 mL) and the insoluble material was filtered. Evaporation of the solvent gave a yellow solid. Recrystallization (ethyl acetate) gave 0.12 g (23%) of **5**: mp 125–127°C; ^1H NMR ($DCCl_3$) δ 2.35–3.20 (m, 8 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.60–3.82 (m, 2 H, ring $C\underline{H}_2$ and $C\underline{H}$), 3.68 (s, 2 H, Ar—$C\underline{H}_2$), 7.2–7.45 (m, 5 H, ArH); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 61.27 (Ar—$\underline{C}H_2$), 127.6, 128.5, 129.0, 136.5 (Ar—$\underline{C}$).

2,2,4,4-Tetramethyl-6,8-diphenyl-7-aza-3-thiabicyclo[3.3.1]nonan-9-one (**6**). A mixture of 0.45 g (5.8 mmol) of ammonium acetate, 1.23 g (11.6 mmol) of benzaldehyde, and 1.00 g (5.8 mmol) of 2,2,6,6-tetramethylthiapyran-4-one[18] in 10 mL of 95% ethanol was heated at reflux for 48 h under N_2. A white precipitate formed upon cooling to RT, and 0.5 mL of ether was added to the mixture which was then placed in the freezer (−10°C) for 1 h. The precipitated white solid was filtered and washed with 2 mL of ether. Recrystallization (95% ethanol) gave 0.53 g (25%) of **6**: mp 253–254°C; IR (KBr) 3325 (N—H), 1750 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 1.25 (s, 6 H, $C\underline{H}_{3a}$), 1.45 (s, 6 H, $C\underline{H}_{3e}$), 1.6 (s, 1 H, N$\underline{H}$), 2.6

TABLE IV

Fractional atomic coordinates (x, $y \times 10^4$, $z \times 10^5$) and anisotropic thermal parameters ($\times 10^4$ Å^2) with e.s.d.'s in parentheses for the nonhydrogen atoms of **6**

Atom	*x*	*y*	*z*	U11*	U22	U33	U23	U13	U12
C(1)	9554(4)	1874(2)	16501(16)	135(14)	194(13)	149(12)	1(10)	−31(11)	15(10)
C(2)	9358(4)	469(2)	20460(16)	186(15)	205(13)	188(13)	−23(10)	−23(11)	4(11)
S(3)	10499(1)	434(1)	31326(4)	243(4)	169(3)	202(3)	0(3)	−27(3)	49(3)
C(4)	9401(4)	1721(2)	37093(16)	207(15)	184(13)	147(12)	−14(10)	11(11)	25(11)
C(5)	9624(4)	2960(2)	30886(16)	155(15)	173(13)	141(12)	−17(10)	−2(10)	34(11)
C(6)	12011(4)	3575(2)	28070(15)	136(14)	155(12)	154(12)	−4(10)	−24(10)	16(11)
N(7)	12138(4)	3809(2)	18438(13)	128(13)	164(11)	159(11)	−15(8)	5(9)	−17(9)
C(8)	11921(4)	2576(2)	14195(16)	118(14)	165(12)	183(13)	−29(10)	−18(10)	36(10)
C(9)	8440(4)	2679(2)	22686(16)	106(14)	175(13)	202(13)	49(10)	0(11)	−39(10)
O(10)	6725(3)	3055(2)	21294(12)	123(11)	330(11)	292(10)	−27(8)	−34(8)	64(8)
C(11)	10699(5)	−338(3)	14924(20)	294(20)	200(15)	280(16)	−55(12)	−2(14)	1(13)
C(12)	6959(5)	−169(3)	20869(20)	252(18)	248(16)	247(15)	−31(12)	−15(13)	−76(13)
C(13)	10779(5)	1948(3)	44958(18)	244(18)	247(15)	183(14)	−2(11)	−39(12)	17(13)
C(14)	7019(5)	1312(3)	40520(19)	226(17)	284(16)	226(15)	−1(13)	18(13)	−3(13)
C(15)	12719(4)	4830(2)	32084(15)	197(15)	186(13)	131(12)	−12(10)	55(11)	−5(11)
C(16)	14608(5)	5009(3)	36541(18)	239(17)	329(16)	200(14)	−79(12)	8(12)	−43(13)
C(17)	15386(6)	6191(3)	39644(20)	406(23)	474(21)	243(16)	−122(14)	25(15)	−159(17)
C(18)	14281(7)	7212(3)	38275(20)	750(29)	262(17)	212(16)	−94(13)	81(17)	−201(18)
C(19)	12384(7)	7056(3)	34048(21)	810(30)	185(16)	284(17)	6(13)	73(18)	129(17)
C(20)	11583(6)	5869(3)	30951(18)	474(22)	225(15)	198(14)	−28(11)	−3(14)	84(14)
C(21)	12431(4)	2874(2)	4445(16)	188(15)	155(12)	166(12)	−48(10)	−21(11)	−13(10)
C(22)	14339(5)	2588(3)	389(18)	189(16)	310(16)	221(14)	−53(12)	−27(12)	15(13)
C(23)	14868(5)	2922(3)	−8487(19)	266(19)	377(17)	248(15)	−86(13)	81(14)	−50(14)
C(24)	13502(5)	3545(3)	−13351(18)	418(21)	307(16)	141(14)	−29(12)	27(13)	−100(14)
C(25)	11602(5)	3855(3)	−9350(18)	368(20)	226(15)	202(14)	−2(11)	−39(13)	−15(13)
C(26)	11077(5)	3514(3)	−544(17)	268(17)	203(14)	205(14)	−19(11)	−13(12)	29(12)

$*T = -2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^2U_{33}L^2 + b^*c^*U_{23}kL + a^*c^*U_{13}hL + a^*b^*U_{12}hk)$.

[d, 2 H, $J = 5$ Hz, H(6), H(8)] 7.2–7.5 (m, 10 H, Ar—H); ^{13}C NMR ($DCCl_3$) ppm, see Table II and the other signals are: 28.66 ($\underline{C}H_{3a}$), 32.45 ($\underline{C}H_{3e}$), 127.53, 127.69, 128.45, 144.47 (Ar—C); ^{15}N NMR ($DCCl_3$) 67.87 ppm.

Crystallographic experimental data. Colorless needles of **6** were formed by evaporation from a 95% ethanol solution. Data for calculating lattice constants and intensity data were measured on an Enraf-Nonius CAD-4 diffractometer fitted with a low-temperature apparatus. The cell parameters were determined from a least-squares fit to the $\pm 2\theta$ values of 48 reflections at 138 ± 2K using MoKα_1 ($\lambda = 0.70926$ Å) radiation. All unique reflections in the H ± k ± L octants with $2\theta < 53°$ were measured using MoKα radiation ($\lambda = 0.71069$ Å) and the θ–2θ scan technique. The intensities of three monitor reflections, which were remeasured after every 2 hours of X-ray exposure, had a maximum difference of only 2.3%. A total of 4062 unique reflections were measured of which 2762 were considered observed [$1 > 2\sigma(I)$]. All intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied ($\mu = 1.36$ cm^{-1}).

The structure was solved by heavy atom methods. The sulfur position was determined from a Patterson map. An electron density difference map, phased by the sulfur atom, revealed the positions of all remaining nonhydrogen atoms. After least-squares refinement of the heavy atoms, the positions of all hydrogen atoms were determined from an electron density difference map. All positional parameters, anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the hydrogens were refined by full-matrix least-squares methods using weights derived from counting statistics. The refinement converged to an $R = 0.048$ and $Rw = 0.046$ for 2762 observed data. The largest shift to error ratio on the last cycle of refinement was 0.094. A final difference map had maximum and minimum values of 0.31 and −0.29 e$^-$/Å^3, respectively. An analysis of the variance as a function of $\sin\theta/\lambda$ and Fo revealed no significant anomalies. Least-squares refinement and Fourier calculations were performed using the program SHELX.[19] The scattering factors for the heavy atoms were from Cromer and Mann[20] and Cromer and Liberman,[21] while hydrogen scattering factors were from Stewart, Davidson and Simpson.[22] Nonhydrogen coordinates have been placed in Table IV. Other data have been deposited with the CCDC.[24]

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24. The atomic coordinates for this work are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The following data are deposited: fractional coordinates ($x, y \times 10^4$, $z \times 10^5$) and anisotropic thermal parameters ($\times 10^4 Å^2$) with e.s.d.'s in parentheses for the nonhydrogen atoms of **6**, fractional coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^3 Å^2$) with e.s.d.'s in parentheses for the hydrogen atoms of **6**.