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# Redetermination of Piperidinium Hydrogen Sulfide Structure

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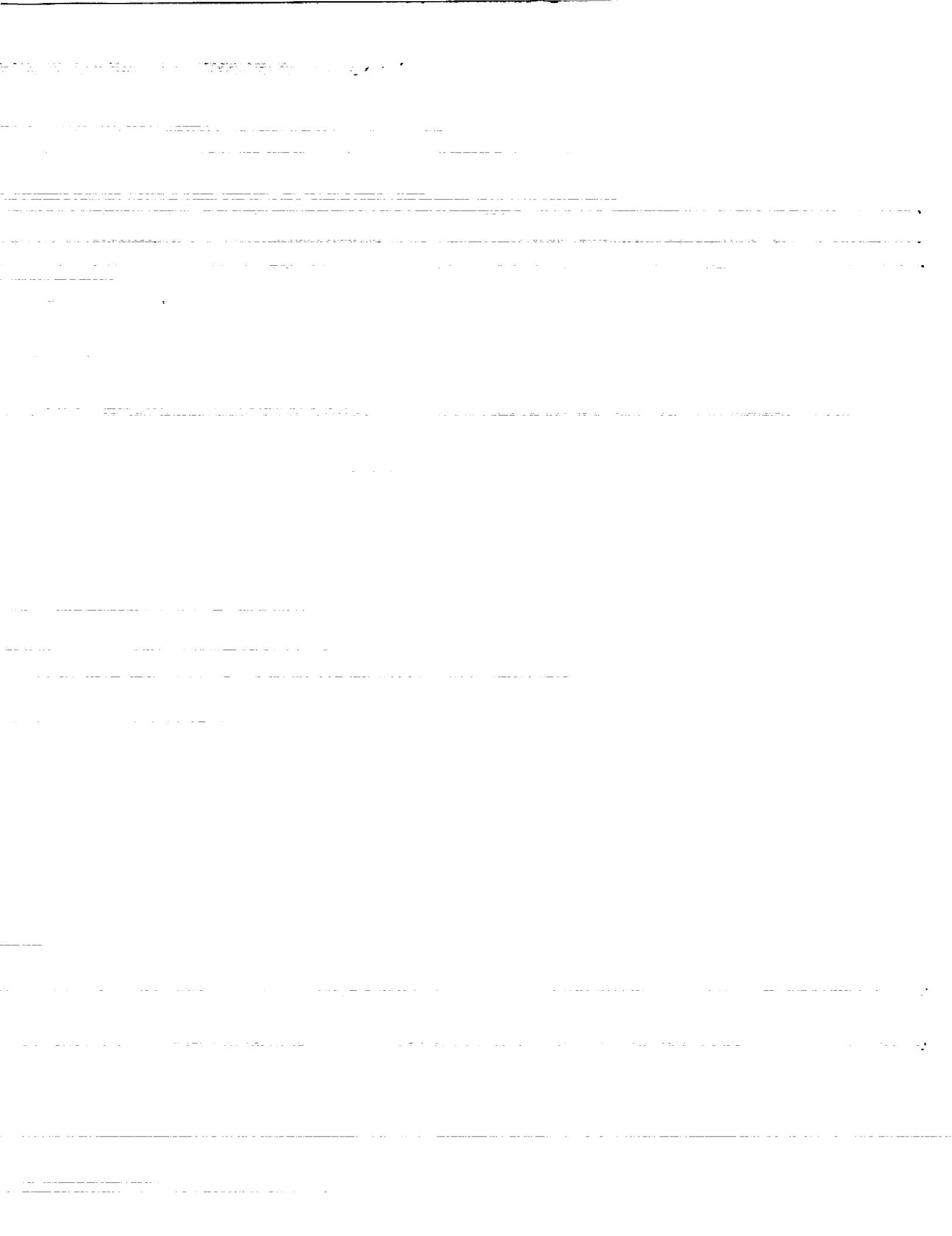
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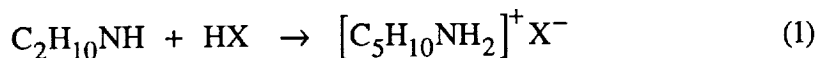
## ABSTRACT

The presence of adventitious water in a reaction between dicyclopentamethylenethiuram-disulfide ( $C_5H_{10}NCS_2$ )<sub>2</sub> and a picoline solution of tricyclopentadienylindium(III) ( $C_5H_5$ )<sub>3</sub>In resulted in the formation of piperidinium hydrogen sulfide ( $C_5H_{13}NS$ ). The piperidinium hydrogen sulfide produced in this way was unambiguously characterized by X-ray crystallography. The structure determination showed that the piperidinium hydrogen sulfide crystal (MW = 119.23 g/mol) has an orthorhombic (*Pbcm*) unit cell whose parameters are:  $a = 9.818(2)$ ,  $b = 7.3720(1)$ ,  $c = 9.754(1)$  Å,  $V = 706.0(3)$  Å<sup>3</sup>,  $Z = 4$ .  $D_x = 1.122$  g cm<sup>-3</sup>, Mo K $\alpha$  ( $\lambda = 0.71073$  Å),  $\mu = 3.36$  cm<sup>-1</sup>,  $F(000) = 264.0$ ,  $T = 293$  K,  $R = 0.036$  for 343 reflections with  $F_o^2 > 3\sigma(F_o^2)$  and 65 variables. The compound consists of [ $C_5H_{10}NH_2$ ]<sup>+</sup> cations and [ $SH$ ]<sup>-</sup> anions with both species residing on crystallographic mirror planes. N-H ··· S hydrogen bonding contributes to the interconnection of neighboring piperidinium components of the compound.

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## Introduction

Pyridinium and piperidinium salts and their derivatives have been of interest for a number of years because of their physico-chemical properties. Of particular interest is their behavior as low temperature (sometimes even room temperature) melts. These compounds are most commonly prepared by treating a pyridine or piperidine derivative with the appropriate acid as is shown for piperidine in equation 1. In the course of carrying out reactions in pyridine and picoline (4-methylpyridine) solvent systems, we have observed the production of salts of this type through different routes.



For example, reacting tetraethylthiuram disulfide  $[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2$  with a picoline ( $\text{C}_6\text{H}_7\text{N}$ ) solution of copper(I) bromide dimethylsulfide  $[\text{CuBr} \cdot \text{S}(\text{CH}_3)_2]$  in the absence of rigorous drying produces picolinium bromide (Andras et. al., 1993). In a similar vein, we now report that reacting dicyclopentamethylenethiuram disulfide  $(\text{C}_5\text{H}_{10}\text{NCS}_2)_2$  with a picoline solution of tricyclopentadienylium(III)  $[(\text{C}_5\text{H}_5)_3\text{In}]$  in the absence of rigorous drying gives piperidinium hydrogen sulfide  $[\text{C}_5\text{H}_{10}\text{NH}_2]\text{HS}$ . This product was unambiguously characterized by X-ray crystallography. This preparation and X-ray crystallographic analysis of piperidinium hydrogen sulfide are detailed in the following sections.

## Experimental

Piperidinium hydrogen sulfide crystals were prepared in the following manner. Under argon, a solution of tricyclopentadienylium(III),  $(\text{C}_5\text{H}_5)_3\text{In}$ , (0.25 g, 0.806 mmol) and dicyclopentamethylenethiuram disulfide,  $(\text{C}_5\text{H}_{10}\text{NCS}_2)_2$  (0.62 g, 1.61 mmol) in 35 mL of 4-methylpyridine was stirred for six days at 20° C. Subsequent filtration and layering of the 4-methylpyridine solution with hexanes afforded colorless crystals of the piperidinium salt.

A crystal of dimensions 0.32 x 0.25 x 0.25 mm was sealed inside a glass capillary and mounted on an Enraf-Nonius CAD-4 diffractometer which produced graphite-monochromated Mo  $\text{K}\alpha$  radiation. Cell constants were determined from least-squares refinement of 25 reflections having  $13 < \theta < 19^\circ$ . Intensity data were collected with the  $\omega$ - $2\theta$  scan technique with  $4 < 2\theta < 45^\circ$ ; the scan rate varied from 1 to 16°  $\text{min}^{-1}$ . Three standard reflections measured every 5000 sec. revealed no significant intensity loss. Intensities were corrected for Lorentz and polarization effects; an absorption correction was not applied. Within index ranges ( $0 \leq h \leq 10$ ,  $0 \leq k \leq 10$ ,  $0 \leq l \leq 7$ ), 572 unique reflections were collected of which 343 are classified as observed,  $F_o^2 > 3\sigma(F_o^2)$ . Calculations were performed on a VAX computer using Enraf-Nonius *MolEN* (Enraf-Nonius, 1990). All non-H atoms were located using SHELX-86 (Sheldrick, 1986). The H atoms were located from a difference map and refined isotropically.

The structure was refined by full-matrix least-squares on  $F$  and the function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ . The weight,  $w$ , was defined by the Killean and Lawrence method with terms of 0.020 and 0.1 (Killean & Lawrence, 1969). The final refinement parameters are:  $R = 0.036$ ,  $wR = 0.044$ ,  $S = 1.364$ ,  $(\Delta/\sigma)_{\max} = 0.06$ . The maximum residual peak in the final difference Fourier map was  $0.16 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors were taken from Cromer and Waber (1974). Anomalous dispersion effects were included in  $F_c$  (Ibers & Hamilton, 1964); the values for  $f'$  and  $f''$  were those of Cromer (1974). Plots of  $w(|F_o| - |F_c|)^2$  versus  $|F_o|$  reflection order in data collection,  $\sin \theta/\lambda$  and various classes of indices showed no unusual trends.

Further details of the crystallographic analysis are given as supplemental material in Appendix A.

## Results and Discussion

The crystallographic analysis of the product of the reaction between tricyclopentadienylindium(III) and dicyclopentamethylenethiuram disulfide produced the ORTEP (Johnson, 1965) drawing of the piperidinium hydrogen sulfide molecule shown in Fig. 1. Final positional and equivalent isotropic thermal parameters are listed in Table 1. Bond distances and angles are listed in Table 2. The structure of piperidinium hydrogen sulfide consists of chains of piperidinium hydrogen sulfide connected by  $\text{N-H} \cdots \text{S}$  hydrogen bonding. Both the cationic and anionic species of the compound reside on crystallographic mirror planes with the S, N, H(N), C(3), H(1), H(31) and H(32) atoms located in these planes. The piperidinium ring adopts the chair conformation in this structure. The structural data clearly indicates that the compound which was isolated from the reaction between tricyclopentadienylindium(III) and dicyclopentamethylene-thiuram disulfide is piperidinium hydrogen sulfide. Furthermore, the data is consistent with that for piperidinium hydrogen sulfide prepared by a different route (Smail & Sheldrick, 1973).

## Conclusions

This technical memorandum describes the formation of piperidinium hydrogen sulfide in a reaction quite different from the reactions usually used to produce this type of compound. The piperidinium hydrogen sulfide product was characterized by X-ray crystallography. Although crystallographic data for the title compound were previously reported (Smail & Sheldrick, 1973):  $Pmab$ ,  $a = 9.77$  (1),  $b = 7.30$  (2),  $c = 9.84$  (1)  $\text{\AA}$ ,  $R = 0.075$  and  $wR = 0.078$ , we have included a description of the structure determination because it describes a more accurate determination of the structure of this compound.

## Acknowledgements

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TABLE 1

Positional and Equivalent Isotropic Thermal Parameters  
with e.s.d.'s for [C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>][SH].

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*a_i \cdot a_j.$$

	$x$	$y$	$z$	$B_{eq} (\text{\AA}^2)$
S	0.1731(1)	0.0373(2)	1/4	3.96(2)
N	0.1358(4)	0.0446(6)	3/4	3.96(9)
C(1)	0.1941(4)	-0.0358(5)	0.6236(4)	5.30(9)
C(2)	0.3456(4)	-0.0071(5)	0.6229(5)	6.8(1)
C(3)	0.4090(6)	-0.0875(9)	3/4	8.5(2)
H(1)	0.153(5)	0.310(7)	1/4	8(1)*
H(N)	0.035(6)	0.033(7)	3/4	7(1)*
H(11)	0.146(4)	0.040(5)	0.547(4)	8(1)*
H(12)	0.168(3)	-0.184(5)	0.628(4)	7.2(9)*
H(21)	0.361(3)	0.143(5)	0.616(4)	7.3(9)*
H(22)	0.387(5)	-0.081(6)	0.532(4)	11(1)*
H(31)	0.397(6)	-0.233(9)	3/4	10(2)*
H(32)	0.499(8)	-0.09(1)	3/4	12(2)*

\* Refined isotropically

TABLE 2

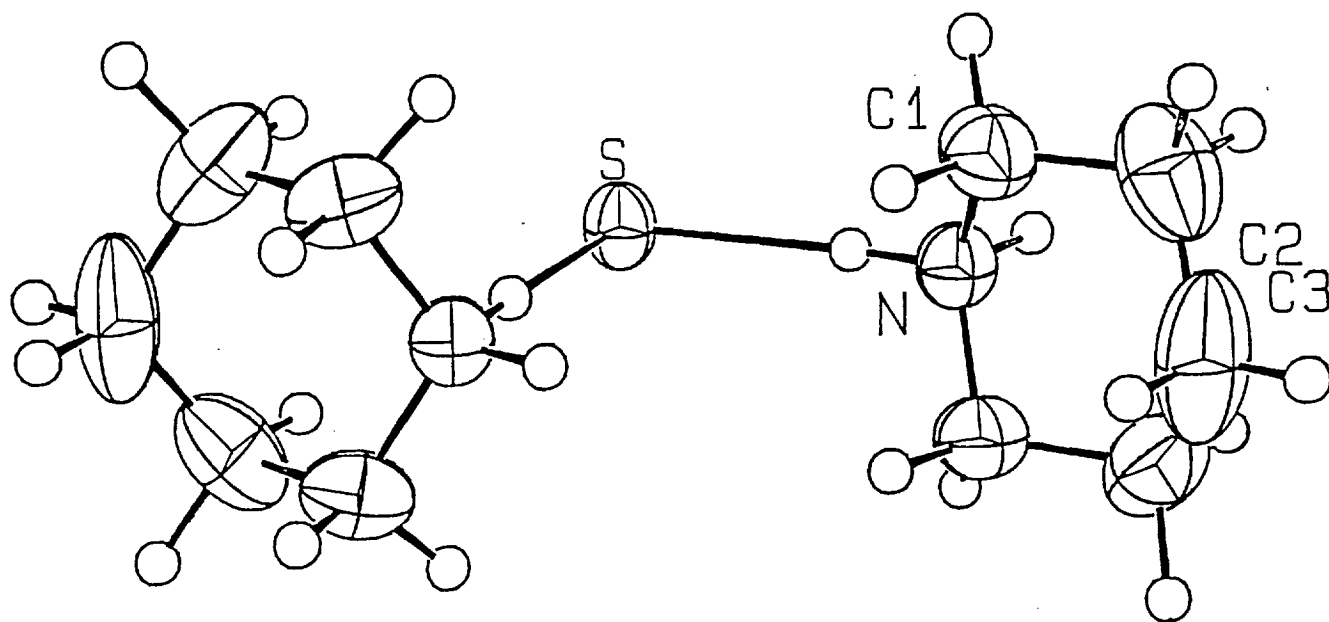
Bond lengths (Å) and angles (°) with e.s.d.'s  
for [C<sub>5</sub>H<sub>10</sub>NH<sub>2</sub>][SH].

S-H(1)	2.02(7)	C(1)-H(12)	1.12(4)
S-H(N)	2.11(7)	C(2)-C(3)	1.508(7)
N-C(1)	1.482(5)	C(2)-H(21)	1.12(5)
N-H(1)	1.09(7)	C(2)-H(22)	1.11(5)
N-H(N)	0.99(7)	C(3)-H(31)	1.08(8)
C(1)-C(2)	1.503(7)	C(3)-H(32)	0.9(1)
C(1)-H(11)	1.05(5)		
H(1)-S-H(N)	99(2)	C(11)-C(2)-H(21)	106(2)
C(1)-N-C(1)'	112.5(5)	C(1)-C(2)-H(22)	107(3)
C(1)-N-H(1)	110(1)	C(3)-C(2)-H(21)	113(2)
C(1)-N-H(N)	111(2)	C(3)-C(2)-H(22)	108(3)
H(1)-N-H(N)	104(4)	H(21)-C(2)-H(22)	113(3)
N-C(1)-C(2)	109.3(4)	C(2)-C(3)-C(2)'	110.6(6)
N-C(1)-H(11)	102(3)	C(2)-C(3)-H(31)	110(2)
N-C(1)-H(12)	106(2)	C(2)-C(3)-H(32)	115(3)
C(2)-C(1)-H(11)	112(3)	H(31)-C(3)-H(32)	94(7)
C(2)-C(1)-H(12)	111(2)	S-H(1)-N	177(5)
H(11)-C(1)-H(12)	116(3)	S-H(N)-N	171(5)
C(1)-C(2)-C(3)	110.4(5)		



FIGURE 1

ORTEP (Johnson, 1965) drawing of the  $[C_5H_{10}NH_2][SH]$  compound showing the atomic-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by sphere of arbitrary size.



## Appendix A

Supplemental data from the structural determination of  $[C_5H_{10}NH_2][SH]$ .  
 $10 \cdot F_{obs}$  and  $10 \cdot F_{calc}$

10\*Fobs and 10\*Fcalc for [NC5H12](HS)

Page 1

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
0	2	0	1083	1322	8	4	0	64	64	1	2	2	238	233	1	2	3	89	92
0	4	0	406	406	8	5	0	83	83	1	3	2	235	219	1	3	3	337	323
0	6	0	64	65	9	0	0	114	109	1	4	2	127	124	1	5	3	141	142
1	0	0	144	141	9	2	0	79	77	1	5	2	210	210	2	1	3	193	181
1	2	0	194	194	0	2	1	382	359	1	7	2	143	141	2	3	3	91	90
1	3	0	121	120	0	4	1	303	297	2	0	2	171	167	2	4	3	54	48
1	4	0	123	127	0	6	1	183	179	2	1	2	226	224	2	6	3	49	54
1	5	0	137	142	1	1	1	285	329	2	2	2	152	149	3	1	3	219	214
1	7	0	104	111	1	2	1	82	85	2	3	2	324	304	3	2	3	27	27
2	0	0	657	685	1	6	1	49	55	2	4	2	90	92	3	3	3	80	79
2	1	0	215	218	2	1	1	400	376	2	5	2	233	234	3	4	3	106	104
2	2	0	463	457	2	2	1	110	106	2	7	2	123	126	3	6	3	86	88
2	3	0	347	357	2	3	1	178	169	3	0	2	550	538	4	1	3	245	238
2	4	0	215	215	2	4	1	145	149	3	1	2	44	44	4	2	3	35	35
2	5	0	250	244	2	6	1	123	124	3	2	2	404	376	4	3	3	168	165
2	6	0	60	58	3	1	1	252	253	3	3	2	27	32	4	5	3	66	65
2	7	0	125	115	3	2	1	167	163	3	4	2	166	166	5	1	3	240	236
3	0	0	624	612	3	3	1	45	50	4	0	2	277	277	5	2	3	86	86
3	1	0	36	36	3	4	1	173	169	4	1	2	46	48	5	3	3	145	146
3	2	0	412	394	3	6	1	136	144	4	2	2	171	171	5	4	3	97	95
3	4	0	158	161	4	1	1	167	167	4	3	2	130	129	5	5	3	62	68
3	7	0	37	24	4	2	1	25	25	4	4	2	56	58	5	6	3	60	60
4	0	0	584	601	4	3	1	184	178	4	5	2	149	153	6	1	3	164	163
4	2	0	329	318	4	5	1	88	91	4	7	2	116	115	6	2	3	38	32
4	3	0	61	61	5	2	1	201	202	5	0	2	227	226	6	3	3	102	99
4	4	0	110	113	5	4	1	197	202	5	1	2	86	83	6	4	3	75	74
4	5	0	113	113	5	6	1	124	124	5	2	2	144	150	6	5	3	43	36
4	7	0	95	95	6	2	1	47	49	5	3	2	163	160	6	6	3	82	76
5	0	0	404	413	6	4	1	103	104	5	4	2	41	56	7	1	3	263	265
5	1	0	90	91	6	6	1	112	112	5	5	2	145	145	7	3	3	159	159
5	2	0	242	243	7	1	1	165	173	6	0	2	196	194	7	5	3	57	54
5	3	0	176	175	7	3	1	83	88	6	2	2	172	172	8	2	3	51	51
5	4	0	84	76	8	1	1	85	90	6	4	2	109	109	8	4	3	79	73
5	5	0	143	144	8	2	1	80	84	7	0	2	126	124	9	1	3	62	67
6	0	0	407	396	8	3	1	84	88	7	1	2	59	57	9	2	3	49	57
6	1	0	51	50	8	4	1	107	109	7	2	2	85	82	9	3	3	57	53
6	2	0	325	319	8	5	1	50	51	7	3	2	109	110	10	1	3	108	109
6	3	0	78	81	9	1	1	49	48	7	5	2	102	97	0	0	4	173	179
6	4	0	201	200	9	2	1	63	63	8	0	2	69	70	0	2	4	126	121
6	5	0	56	51	9	3	1	44	46	8	2	2	59	61	0	6	4	37	47
6	6	0	79	73	9	4	1	74	77	8	3	2	45	46	1	0	4	239	233
7	1	0	53	51	10	1	1	121	123	9	0	2	132	126	1	1	4	142	140
7	3	0	100	104	0	0	2	876	940	9	2	2	103	97	1	2	4	221	214
7	5	0	86	86	0	2	2	543	521	0	2	3	100	97	1	3	4	270	264
8	0	0	125	129	0	4	2	171	171	0	4	3	110	104	1	4	4	118	117
8	2	0	107	111	1	0	2	261	256	0	6	3	68	70	1	5	4	246	248
8	3	0	59	62	1	1	2	107	103	1	1	3	579	572	1	6	4	39	37

Appendix A (cont.)

Supplemental data from the structural determination of  $[C_5H_{10}NH_2][SH]$ .  
 $10 \cdot F_{obs}$  and  $10 \cdot F_{calc}$

$10 \cdot F_{obs}$  and  $10 \cdot F_{calc}$  for [NC5H12](HS)

Page 2

H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc	H	K	L	Fobs	Fcalc
3	3	5	45	45	6	0	6	162	160	6	0	8	140	135					
3	4	5	79	83	6	2	6	135	134	6	2	8	115	111					
3	6	5	70	75	6	4	6	77	76	0	4	9	73	71					
4	1	5	199	201	7	0	6	73	75	2	1	9	39	47					
4	3	5	137	137	7	2	6	60	57	2	2	9	33	36					
4	5	5	60	54	7	3	6	58	57	2	3	9	31	37					
5	1	5	138	140	8	0	6	74	67	3	2	9	34	36					
5	2	5	59	56	8	2	6	60	58	4	1	9	51	47					
5	3	5	100	97	0	2	7	70	74	0	0	10	102	104					
5	4	5	73	69	0	4	7	97	104	0	2	10	78	81					
5	5	5	50	48	1	2	7	29	23	1	0	10	56	51					
6	1	5	144	146	2	1	7	81	83	1	2	10	46	41					
6	3	5	95	93	2	2	7	44	53	2	0	10	40	40					
6	4	5	56	59	2	3	7	63	61	3	0	10	88	90					
6	5	5	40	34	2	4	7	76	73										
7	1	5	166	170	2	5	7	34	30										
7	3	5	106	103	3	2	7	71	71										
9	1	5	43	47	3	4	7	92	91										
0	0	6	375	374	4	1	7	104	97										
0	2	6	270	268	4	3	7	74	74										
0	4	6	116	122	4	5	7	43	35										
1	0	6	153	153	5	2	7	63	61										
1	1	6	71	68	5	4	7	83	80										
1	2	6	127	129	6	2	7	36	41										
1	3	6	140	143	6	3	7	34	16										
1	4	6	70	66	7	1	7	51	56										
1	5	6	137	138	0	0	8	316	321										
2	0	6	132	138	0	2	8	243	244										
2	1	6	73	70	0	4	8	123	122										
2	2	6	118	116	1	0	8	95	94										
2	3	6	134	132	1	2	8	73	75										
2	4	6	65	67	1	3	8	48	48										
2	5	6	120	122	1	4	8	31	35										
3	0	6	252	252	1	5	8	53	52										
3	2	6	201	200	2	0	8	153	147										
3	4	6	95	96	2	1	8	30	28										
4	0	6	127	128	2	2	8	124	117										
4	1	6	35	36	2	3	8	67	70										
4	2	6	86	89	2	4	8	62	61										
4	3	6	84	85	3	0	8	174	179										
4	4	6	33	35	3	2	8	134	139										
4	5	6	91	92	3	4	8	64	65										
5	0	6	77	77	4	0	8	85	94										
5	1	6	44	46	4	2	8	70	72										
5	2	6	54	57	5	0	8	103	103										
5	3	6	97	96	5	2	8	82	81										
5	5	6	95	93	5	3	8	49	54										

Appendix A (cont.)

Supplemental data from the structural determination of  $[C_5H_{10}NH_2][SH]$ .

Table of Atomic Multiplicities

Name	Multiplicity	Name	Multiplicity	Name	Multiplicity
----	-----	----	-----	----	-----
S	1.000	N	1.000	C(1)	2.000
C(2)	2.000	C(3)	1.000	H(1)	1.000
H(N)	1.000	H(11)	2.000	H(12)	2.000
H(21)	2.000	H(22)	2.000	H(31)	1.000
H(32)	1.000				

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Appendix A (cont.)

Supplemental data from the structural determination of  $[C_5H_{10}NH_2][SH]$ .

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
H(N)	N	C(1)	C(2)	176.77 ( 2.68)
H(N)	N	C(1)	H(11)	58.48 ( 3.44)
H(N)	N	C(1)	H(12)	-63.49 ( 3.18)
N	C(1)	C(2)	C(3)	56.92 ( 0.45)
N	C(1)	C(2)	H(21)	-65.11 ( 1.91)
N	C(1)	C(2)	H(22)	174.46 ( 2.43)
H(11)	C(1)	C(2)	C(3)	168.79 ( 2.22)
H(11)	C(1)	C(2)	H(21)	46.76 ( 2.91)
H(11)	C(1)	C(2)	H(22)	-73.68 ( 3.28)
H(12)	C(1)	C(2)	C(3)	-59.53 ( 1.96)
H(12)	C(1)	C(2)	H(21)	178.44 ( 2.69)
H(12)	C(1)	C(2)	H(22)	58.00 ( 3.11)
C(1)	C(2)	C(3)	H(31)	65.04 ( 3.02)
C(1)	C(2)	C(3)	H(32)	170.27 ( 4.93)
H(21)	C(2)	C(3)	H(31)	-177.19 ( 3.53)
H(21)	C(2)	C(3)	H(32)	-71.96 ( 5.28)
H(22)	C(2)	C(3)	H(31)	-51.92 ( 3.90)
H(22)	C(2)	C(3)	H(32)	53.31 ( 5.52)

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13. ABSTRACT (Maximum 200 words)  The presence of adventitious water in a reaction between dicyclopentamethylene thiuram-disulfide (C <sub>5</sub> H <sub>10</sub> NCS <sub>2</sub> ) <sub>2</sub> and a picoline solution of tricyclopentadienylindium(III) (C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> In resulted in the formation of piperidinium hydrogen sulfide (C <sub>5</sub> H <sub>13</sub> NS). The piperidinium hydrogen sulfide produced in this way was unambiguously characterized by X-ray crystallography. The structure determination showed that the piperidinium hydrogen sulfide crystal (MW = 119.23 g/mol) has an orthorhombic (Pbcm) unit cell whose parameters are: a = 9.818(2), b = 7.3720(1), c = 9.754(1) Å, V = 706.0(3) Å <sup>3</sup> , Z = 4, D <sub>x</sub> = 1.122 g cm <sup>-3</sup> , Mo Kα (λ = 0.71073), μ = 3.36 cm <sup>-1</sup> , F(000) = 264.0, T = 293 K, R = 0.036 for 343 reflections with F <sub>o</sub> <sup>2</sup> > 3σ (F <sub>o</sub> <sup>2</sup> ) and 65 variables. The compound consists of [C <sub>5</sub> H <sub>10</sub> NH <sub>2</sub> ] <sup>+</sup> cations and [SH] <sup>-</sup> anions with both species residing on crystallographic mirror planes. N-H...S hydrogen bonding contributes to the interconnection of neighboring piperidinium components of the compound.			
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