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Note

STUDIES ON AMINE HYDROTHIOCYANATES. III. HEATS OF FUSION

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Although amine hydrothiocyanates are not new [1], very few physical data have been reported [2—5]. Consequently, we have begun a series of studies to provide certain basic physical data for several of these compounds that we have found most useful [2,4]. We report here some heats of fusion as determined by DSC studies.

EXPERIMENTAL

The amine hydrothiocyanates used in this work were prepared by the reaction of the appropriate amine with ammonium thiocyanate [1,2]. The compounds studied include piperidine hydrothiocyanate (HpipSCN), piperazine hydrothiocyanate (HpipzSCN), ethylenediamine dihydrothiocyanate ($H_2en(SCN)_2$), and the dihydrothiocyanate of 1,3-diaminopropane ($H_2pn(SCN)_2$). In the case of the 1 : 1 compounds, equimolar amounts of the reactants were used while in the case of the dihydrothiocyanates a slightly greater than 2 : 1 ratio of ammonium thiocyanate to amine was used [1,5]. Table 1 shows the analytical data for these compounds.

DSC studies to determine the heats of fusion were carried out using a Perkin-Elmer DSC Model 1B. Procedures used were similar to those previously published [6]. In general, 5—10 determinations were made on each compound.

TABLE 1

Analytical data for the amine hydrothiocyanates

Compound	M.p. (°C)	C (%)		H (%)		N (%)	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
HpipSCN	92—94	49.96	50.46	8.41	8.18	19.41	19.18
HpipzSCN	167—169	41.35	41.92	7.65	7.58	28.92	28.85
$H_2en(SCN)_2$	144—145	26.95	27.09	5.67	5.75	31.41	31.50
$H_2pn(SCN)_2$	109—111	31.23	31.50	6.30	6.12	29.12	29.04

TABLE 2

Heats of fusion of some amine hydrothiocyanates

Compound	ΔH (kJ mole^{-1})	
	Mean	Std. dev.
HpipSCN	27.44	2.59
HpipzSCN	34.39	1.38
$H_2en(SCN)_2$	35.27	2.76
$H_2pn(SCN)_2$	32.59	1.76

RESULTS AND DISCUSSION

The heats of fusion of the amine hydrothiocyanates are shown in Table 2. Some of these compounds gave excellent uniformity with the standard deviation being as low as about 4% of the mean. In other cases, such as HpipSCN, a total of 10 samples was used, but the standard deviation is about 9% of the mean. No reason for this difference in uniformity could be found.

Somewhat surprisingly, all of the heats of fusion are about the same magnitude except that of HpipSCN. In this case, there are fewer possibilities for hydrogen bonding in the lattice than in the other cases. There seems to be no real difference in the size of $Hpipz^+$ and $Hpip^+$, but there is a difference in hydrogen bonding capability which may cause a lower ΔH_{fusion} for HpipSCN.

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