The Vibrational Spectra and the Stable Conformers of 1-Propanethiol

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The infrared spectra of 1-propanethiol in the vapour phase, as a liquid, and as a solid were recorded, and the Raman spectrum of the liquid obtained. This molecule exists as a mixture of predominantly two conformers in the vapour and in the liquid. The more stable conformer in the liquid (probably the *trans*) is present in the crystalline solid at low temperatures. Tentative assignments for most of the fundamental frequencies have been proposed.

We have for some time been interested in the vibrational spectra of the propanes, and our results regarding the 2-halo-[1] and the 2,2-dihalo-propanes [2] have recently been reported. These studies have been extended to the propyl derivatives for which the spectra are complicated by a conformational equilibrium in the gaseous and liquid states. In the present communication we shall report our data for 1-propanethiol (propyl mercaptan). This molecule has already been studied in some detail by vibrational spectroscopy. The infrared [3] and the Raman [4,5] spectra reported for the liquid were used by Pennington et al.[6] to make a tentative assignment of the fundamental frequencies. Later Hayashi and co-workers [7] published new infrared data for this molecule and very recently Scott and El-Sabban [8] tested the earlier assignments with a valence force field calculation.

The previous spectroscopic work on 1-propanethiol was restricted by the very uncertain attributions of the fundamental frequencies to the respective conformers, since this distinction was based upon rather small band intensity variations with temperature. However, we have succeeded in recording the infrared spectrum of 1-propanethiol in the crystalline state at low temperature. Various absorption bands which were present in the vapour and the liquid spectra disappeared in those of the solid. Thus, a number of fundamental frequencies can unambiguously be ascribed to one or the other conformer.
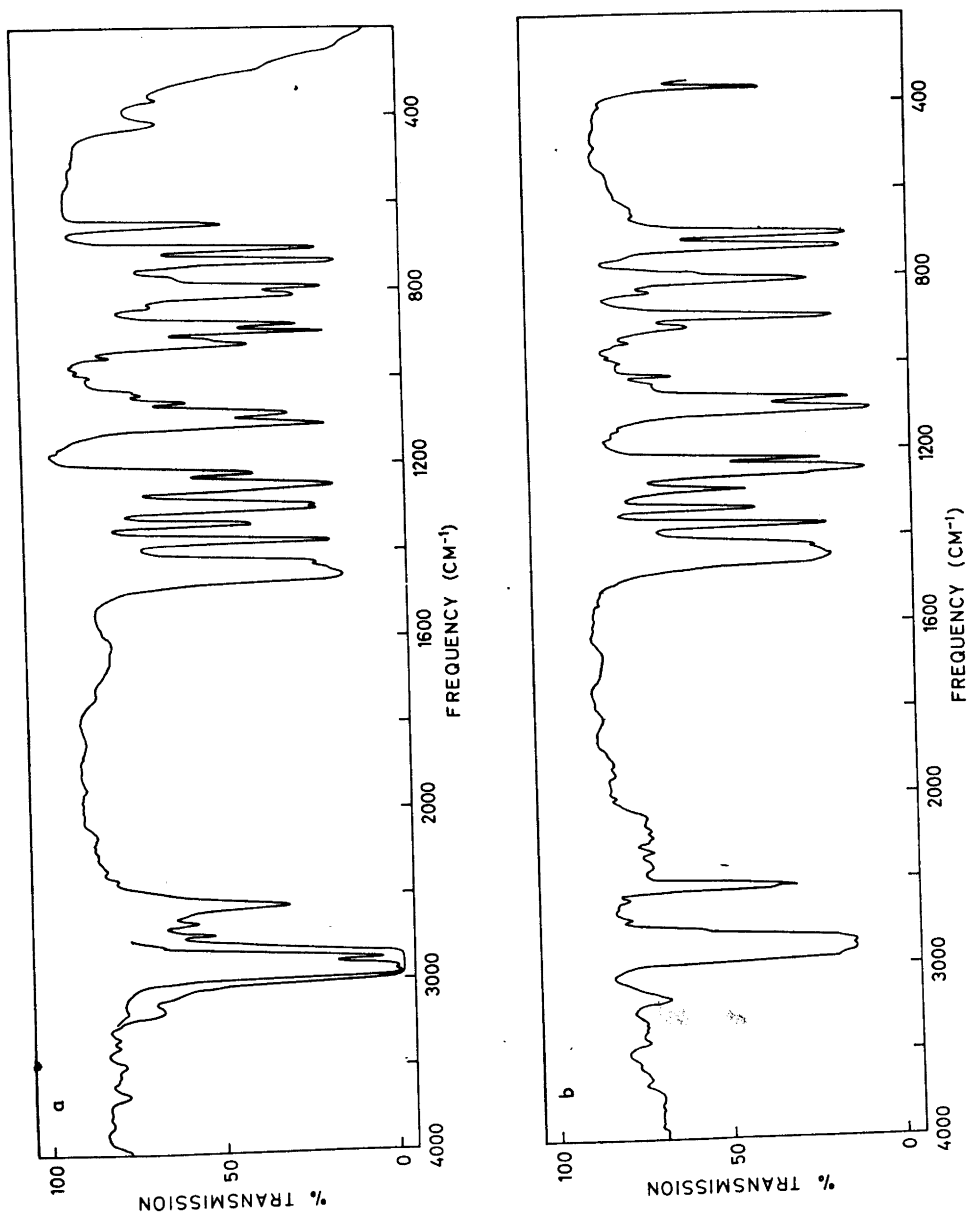
Fig. 1. a. The infrared spectrum of 1-propanethiol in the liquid state at −60°. b. The infrared spectrum of 1-propanethiol in the crystalline state at −160°.

EXPERIMENTAL

1-Propanethiol from British Drug Houses was purified by repeated fractionation in a Vigreux column. No impurity peaks were detected by gas chromatographic analysis.

The infrared spectra were recorded with a Perkin-Elmer model 225 spectrometer. A 9 cm cell with KRS-5 windows was used to study the vapour, whereas the liquid was filled in sealed cells of various thicknesses, having windows of KBr, CsI, and poly-ethylene. The low temperature spectra of the liquid as well as the spectrum of the crystal-line solid were recorded in a commercial cell from RIIC, using liquid nitrogen as the refrigerant. Contrary to the experience of the earlier workers,[7] the sample froze readily and no elaborate annealing was necessary to obtain a truly crystalline film.

The Raman spectrum of the liquid was recorded with a Cary 81 Raman spectrometer equipped with a Spectra Physics model 125 helium-neon laser. A capillary cell was used in the axial illumination, and because of the low symmetry no polarization data were measured.

RESULTS AND DISCUSSION

The infrared absorption curves recorded from liquid 1-propanethiol at ambient temperature and of a polycrystalline sample at $-160°$ are shown in Figs 1a and b, respectively. The measured infrared frequencies as observed in the three states of aggregation are listed in Table 1. These data are much more complete than the work reported by the earlier workers [3,6,7] which was confined to the liquid state frequencies in the rock salt region $(4000-650 \text{ cm}^{-1})$. Among the observed Raman frequencies included in Table 1, we have detected some bands not described previously [5] while a few reported lines were not verified.

It appears from Figs. 1a and b and from Table 1 that certain infrared bands present in the vapour and in the liquid are absent in the solid as expected in molecules with conformational equilibria.[9,10] There are seven certain cases of infrared bands vanishing in the crystal, fitted with an asterisk in Table 1. In other cases there are some doubt regarding which bands in the liquid spectra have counterparts in the crystal. It is a well known fact that intramolecular vibrational modes may split up into several components in the crystal because of the interaction from neighbouring molecules. Doublets observed at 2534 and 2517 cm^{-1}, at 1945 and 1915 cm^{-1}, and at 1257 and 1245 cm^{-1} in the solid spectra are obvious examples.

Compared with the total number of infrared or Raman bands observed, the number that vanishes is rather small. Therefore, the majority of bands observed in the vapour and in the liquid are due to coinciding vibrational modes for two or more conformers. However, with the high resolution of the modern spectrometers, some doublets were observed (e.g. 1298 and 1290 cm^{-1}) not detected in the earlier work.[7] Particularly the CH stretching and deformation frequencies may be situated at nearly the same frequencies for all the conformers. The low frequency skeletal stretching and bending vibrations are likely to be more influenced by the different geometrical arrangement of the conformers and therefore appear as separate bands. The recent force constant calculation [8] on 1-propanethiol is in agreement with these predictions. In the region $3000-200 \text{ cm}^{-1}$ they have calculated [8] 8 instances for which a fundamental in the *trans* conformer is separated more than 10 cm^{-1} from that of the *gauche*. For the remaining 20 fundamentals the corresponding

Table 1. Infrared and Raman spectral data ^{a} of 1-propanethiol.

Vapour	Infrared Liquid	Solid	Raman Liquid	Conformer	Interpretation ^{b}
	3980 w ^{c}	3960 w			
	3660 w	3656 w			
	3490 vw	3470 w			
3183 w	3175 w	3172 w			
3090 w	3090 w,sh				
2960 vs	2954 vs	2940 vs	2968 m		
2945 vs	2925 vs	2902 vs	2933 s		
2848 s	2872 s	2890 s	2877 s	t,g ^{d}	CH₃ and CH₂
2838 s	2852 s,sh	2860 vs	2863 m		stretch
2800 w	2797 m,sh	2793 m,sh			
2746 w					
2736 w	2726 w		2740 w		
2678 w	2660 w				
2598 m,sh	2558 m	2534 s,sh	2577 vs	t,g	SH stretch
2589 m		2517 s			
2485 vw					
2420 vw					
	2400 vw	2396 vw			
2270 vw		2320 w			
2150 vw	2145 vw				
	1950 vw	1945 vw			
		1915 vw			
	1447 vs		1455 s		CH₃ asym def
1456 vs,bd	1438 vs	1450 vs,bd	1444 s	t,g	CH₂ scissor
	1423 vs		1435 s		
1391 s					
1384 s A	1377 s	1368 s		t,g	CH₃ sym def
1378 s					
1351 m					
1343 m A	1337 m	1329 s	1335 w	t,g	CH₂ wag
1335 m					
1310 w,sh					
1305 vs	1298 s	* ^{e}		g	CH₂ wag
1300 vs	1290 s	1289 m	1296 w	t	CH₂ wag
1295 w,sh					
1254 s B		1257 s,sh			
1243 s	1246 s	1245 s	1252 w	t,g	CH₂ twist
	1217 w	1222 s	1219 w	t,g	CH₂ twist
1117 w,sh					
1105 s	1105 s	1105 s	1110 m	t,g	CC stretch
1090 w					
	1084 m	1080 s	1082 w	t,g	CH₃ rock
	1058 w	*	1064 sh	g	CC stretch
	1032 vw	1028 w	1035 s	t	CC stretch
	953 vw	960 w			
933 vw					
930 w	922 w	*	920 w	g	CH₃ rock
926 w					
923 w					
918 w	915 w,sh	915 w		t	CH₃ rock
914 w					
900 m	893 m	890 s		t	CH₂ rock

Table 1. Continued.

887 m ⎫ 879 m ⎬ 872 w ⎭	A	878 m	*		881 m	g	CH$_3$ rock
		836 w	833 w				
820 vw ⎫ 814 w ⎬ 808 vw ⎭	A	809 m	807 s		814 w	t	CSH def
799 vw ⎫ 791 w ⎬ 788 vw ⎭	A	791 m	*		778 w	g	CSH def
742 m ⎫ 736 m ⎬ 728 m ⎭	A	730 m	730 s		735 m	t,g	CH$_3$ rock
714 w ⎫ 707 w ⎬ 700 w ⎭		703 m	701 s		710 m	t	CS stretch
663 m ⎫ 656 m ⎬ 649 m ⎭		650 m	*		655 s	g	CS stretch
		525 vw					
420 vw ⎫ 410 vw ⎭		415 w	*		415 vw	g	CCC def
		362 w	363 m		368 m	t	CCC def
		286 m,sh	*		295 vw	g?	CCS def
		242 s,sh	241 vw		248 vw	t?	CCS def

[a] The weakest bands are omitted.

[b] Bands not interpreted are assigned as combinations or overtones.

[c] The following abbreviations have been used: s, strong; m, medium; w, weak; v, very; sh, shoulder and bd, broad.

[d] t and g denotes *trans and gauche* relative to the C−C bond, respectively.

[e] Bands equipped with an asterisk are absent in the crystalline spectrum.

separation is less than 10 cm^{-1} and they are therefore likely to overlap in the spectra.

Among the five theoretically possible conformations of 1-propanethiol Scott and El-Sabban [8] considered the *trans-gauche* and *gauche-gauche*, but Hayashi et al.[7] assumed the *trans-trans* and the *gauche-trans* conformations to be the more stable (referring to the conformations around the C−C and the C−S bonds, respectively). However, the geometrical arrangement around the C−S bond should mostly affect the S−H stretching and the CSH bending frequencies. Since only one infrared band was observed at 2558 cm^{-1} in the liquid, definitely assigned to the S−H stretching mode, it seems reasonable that one single CSH arrangement is stable. Hence, as an approximation we may take into account only rotamers around the C−C bond and the descriptions of the previous authors [6-8] will be reduced to the same *trans* and *gauche* conformations.

Our own infrared measurements at lower temperatures as well as those of Hayashi et al.[7] revealed that the bands which are enhanced at lower temperatures and therefore belong to the more stable conformer are those which persist in the crystal. Various arguments [7,8,11] strongly suggest that the more stable

conformer is the *trans* form (C_s-symmetry) in 1-propanethiol as reported for the *n*-propylhalides.[12] Since the *trans* and the *gauche* conformers have different principal moments of inertia, an unambiguous distinction between them should be feasible from the vapour phase band contours. However, although several P and R shoulders were observed in the vapour spectrum, the band separations were too uncertain to allow any definite conclusions.

The infrared bands vanishing in the crystalline state are attributed to the *gauche* conformer, whereas those present in the crystal are pure *trans* bands which eventually overlap with *gauche* bands in the liquid. Our assignments are listed in Table 1, and they agree fairly well with the previous research, although there are a number of discrepancies. The two torsional modes and the lowest skeletal bending mode are probably situated below 250 cm^{-1} as suggested from the force constant calculations.[8] However, no Raman bands were observed below 240 cm^{-1} whereas the infrared spectrum was not scanned below 200 cm^{-1}.

When applied to the six pairs of bands, the $\sum \nu^2$ rule gives 5.469×10^6 and 5.468×10^6 for the *gauche* and the *trans* conformers, respectively. The listed group frequency description should be considered as highly approximative since these modes are strongly mixed for this molecule.

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