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Table 1 (Continued)

Gaseous Room Temp.	Liquid Room Temp.	CS ₂ soln. Room Temp.	Solid		Assignment ^{b)}
			Unannealed	Annealed	
(1378 s 1368 s)	1366 s	1365 s	(1367 m 1364 s)	(1372 s 1363 s)	$\delta_{\text{CH}_3}^s$
(1329 w 1323 w)	1321 w	1319 w	1328 w	1328 vw	
(1316 w 1308 w)	1313 w	1312 w	1316 w	1318 m	$\delta_{\text{CH}_3}^s$
1285 sh, vw	~1280 sh, vw	~1280 sh, vw	1282 sh, w	—	
1276 sh, w	1275 sh, m	1275 sh, m	1275 w	1276 m	
1270 sh, w	1268 sh, m	1268 sh, m	—	—	
1265 sh, w	1263 m	1263 s	—	—	
(1256 vs 1249 vs 1242 vs)	1244 vs	1243 vs	1245 vs	1245 vs	
1230 sh, vw	1229 sh, vw	1227 sh, vw	—	—	
(1167 s 1162 s 1155 s)	1159 s	1157 s	(1159 s 1155 sh, s)	(1161 sh, s 1158 s)	
1115 vw	1113 w	1114 w	1113 w	1113 vw	
1108 vvw	1108 sh, vw	1108 sh, vw	—	—	
(1075 sh, m 1068 m)	1064 s	1063 s	1060 s	1059 s	
(1060 m 1054 sh, m)	1059 s	1057 s	1057 sh, w	—	
~1025 vvw	1038 sh, vvw	1038 sh, vvw	—	—	
1015 vvvw	1015 vvw	1015 vvw	—	—	
	~990 vvw	~990 vvw	992 vw	994 vw	
	~985 sh, vw	~985 sh, vw	—	—	
975 sh, w	980 sh, vw	980 sh, vw	—	—	
970 sh, w	970 sh, w	970 sh, w	969 sh, s	—	
965 m	965 sh, m	965 sh, m	966 s	966 s	
(958 sh, m 955 m)	957 s	955 s	959 m	—	
952 sh, m	952 sh, m	951 sh, m	952 m	952 w	
940 sh, w	941 sh, vw	940 sh, vw	944 sh, vw	945 m	
925 vw	927 w	927 w	927 w	932 m	
920 vw	920 sh, vw	920 sh, vw	921 sh, vvw	—	
	918 sh, vvw	917 sh, vvw	918 sh, vvw	—	
885 w, br	884 w	884 w	884 w	884 m	
725 vw	725 w	725 w	727 w	727 m	$\nu_{\text{C-S}}$
690 vw	690 vvvw	690 vvvw	—	—	
(647 w 638 w 630 w)	637 m	637 m	637 m	638 m	$\nu_{\text{C-S}}$
610 vw	610 w	610 w	—	—	$\nu_{\text{C-S}}$
	537 vvw, br	—	—	—	
	456 vvvw	—	—	—	
	427 vw	—	426 w	429 w	δ_{skel}
	420 sh, vw	—	419 sh, vw	—	
	349 vw	—	353 vw	~355 vw	δ_{skel}
	334 vw	—	337 sh, vw	338 vw	δ_{skel}
	327 vw	—	329 vvw	—	
	323 sh, vvw	—	325 sh, vvw	—	
	276 vvw	—	—	—	
	255 vvw	—	—	—	
	234 vvvw	—	~235 vvw	~235 vvw	δ_{skel}
	217 vvw	—	217 vvw	217 vvw	δ_{skel}

s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

a) Above 3000 cm⁻¹ and 2800—1500 cm⁻¹ regions are omitted.b) ν , stretching; δ^d , degenerate deformation; δ^s , symmetrical deformation; δ_{skel} , skeletal deformation (including torsions).

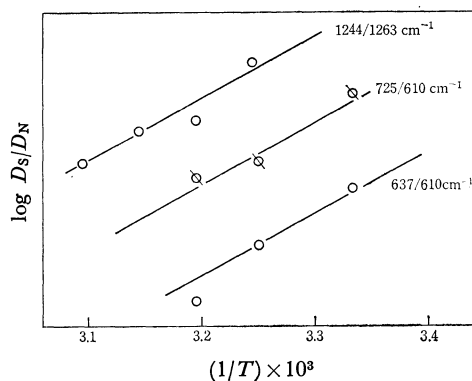


Fig. 1. Plots of $\log D_S/D_N$ vs. $1/T \times 10^3$ of the three liquid-band pairs of methyl isopropyl sulfide. D_S : Stable form, D_N : Less stable form.

in the liquid state and five bands remain in the annealed state. Thus, in the liquid or gaseous spectra in the C-S stretching and skeletal deformation regions, there are bands which correspond to two forms. In the annealed state, this sulfide may exist in one form.

In order to confirm the existence of the rotational isomers, we attempted to make an experiment on the solvent effects. We took up the bands at 637 and 610 cm^{-1} and used cyclohexane and acetone as the solvents. In this species, however, it seems that the difference in the dipole moment between the two conformations, C_s and C_1 , is not very much. In the observed spectra, we cannot see any clear difference.

We have, then, tried to determine the temperature dependence of the liquid bands at temperatures of $27\text{--}50^\circ\text{C}$. Figure 1 shows the plots of $\log D_S/D_N$ vs. $1/T \times 10^3$ of the three liquid-band pairs. In Fig. 1, D_S means the stable forms and D_N means the less stable forms. The origin of $\log D_S/D_N$ is different in each case. The pairs of bands at $1244/1263$, $725/610$, and at $637/610\text{ cm}^{-1}$ show nearly the same temperature dependence. From these slopes, we can see the enthalpy difference between two rotational isomers; the order of ΔH is evaluated to be *ca.* $1\text{--}1.5\text{ kcal/mol}$. We cannot, however, determine an exact value, since our obtained data are not sufficient.

From the obtained infrared data, therefore, we can postulate for this sulfide that: a) two conformations coexist in the liquid and gaseous states (energy difference $\Delta H \approx 1\text{--}1.5\text{ kcal/mol}$), and b) one form exists in the crystalline state.

Experimental

The methyl isopropyl sulfide was prepared by the method of McAllan *et al.*,³⁾ bp $84\text{--}85^\circ\text{C}/760\text{ mmHg}$ (reported bp³⁾ $84.8^\circ\text{C}/760\text{ mmHg}$). The purity of this sulfide was checked by means of gas chromatography. The methods of infrared recording and instrument used were described previously.⁴⁾

3) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, **73**, 3627 (1951).

4) M. Ohsaku, Y. Shiro, and H. Murata, *This Bulletin*, **45**, 954 (1972).