Kurze Mitteilungen

Bis am 20. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht. Es werden auch Manuskripte aus dem Ausland angenommen

Chemistry of Sulfur Compounds. Part IV: The Vibrational Spectroscopic Studies of Some Aliphatic Sulfur Containing Compounds***

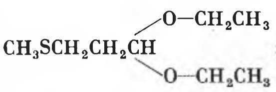
Abstract

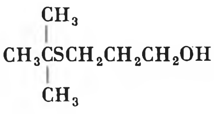
The infra-red spectra between 4000–400 cm^{-1} of several aliphatic sulfur containing compounds were recorded and analyzed. Assignments for the observed frequencies are proposed with special attention to the internal rotation, the CH_3(–S) and CH_3(–C) stretching, deformation and rocking, the C–S stretching, the CH_2 wagging, twisting and rocking, and the CH stretching and bending. The synthesis of the compounds studied is briefly described.

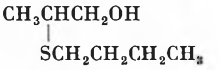
Thompson and Trotter[1] were among the first to report on the infra-red spectra of organo-sulfur compounds. Subsequently, several investigations were undertaken to assign characteristic frequencies to C–S, S–H, and S–S links[2, 3, 4]. In the past few years, the interest in the infra-red spectroscopy of organosulfur compounds was renewed by investigating the absorptions occurring in the 700–300 cm^{-1} region and numerous detailed studies of the spectra of thiols and mono or disulfides were made[5, 6, 7, 8, 9, 10]. Our study of the infrared spectra of several organosulfides was reported in a preceding paper[11] and the concern of this work is to extend this discussion to the infra-red spectra of the following compounds:

[I] $CH_3SCH_2CH_2CH_2SCH_3$;

[II] 
$CH_3SCH_2CH_2C(=O)H$

[III] 
;

[IV] 
$CH_3C(CH_3)_2SCH_2CH_2CH_2OH$

[V] 
$CH_3CH(SCH_2CH_2CH_2CH_3)CH_2OH$

1,3-di (methylthio)-propane [I]

The infra-red spectrum of [I] is given in Table A. The very strong band at 2905 cm^{-1} can be assigned to the CH_2(S) antisymmetric stretching since the same vibration in ethyl methylsulfide occurs at 2907 cm^{-1} [6] and in ethyl dimethylsulfonium iodide at 2909 cm^{-1} [5]. The highest band in the spectrum (2960 cm^{-1}) must be the CH_3(–S) antisymmetric stretch and the one below at 2935 cm^{-1} could be the CH_2 antisymmetric or CH_3 symmetric stretch. The C–H deformations are not resolved and give rise to a very strong and broad absorption with a maximum at 1425 cm^{-1}. The assignment for CH_2 wagging and twisting is made with reference to earlier studies[6, 11, 12]. Thus the band at 1339 cm^{-1} is

Table A. Infra-red spectrum (4000–400 cm^{-1}) of 1,3-di (methylthio)-propane

cm^{-1}	Motions	cm^{-1}	Motions
2960 m	C–H symmetric and assymmetric stretching	1140 w	
2935 sh		1118–25 w	
2905 v.s		1040 sh	CH_3(–S) rock or C–C stretching
		1020 m	Skeletal stretching
2825 s	Overlap of a CH deformation[5]	951 s	CH_3(–S) rock
		925 sh	CH_2 rock *(trans)*
		845 m	CH_2 rock *(gauche)*
1425 v.s	C–H deformation	825 m	CH_2 rock *(gauche)*
1339 m	CH_2 wag *trans* + *gauche*	770 m	CH_2 rock *(trans)*
1312 m	CH_2 (–S) symmetric deformation	719 m	CH_3–S stretching
1294 s	CH_2 twist *trans* or wag *gauche* or 2 × 642	690 w	CH_3–S stretching
1256 v.s	CH_2 wag *trans*	668 w	CH_2–S stretching
1242 s	CH_2 twist *gauche*	642 w	CH_2–S stretching
1198 m	CH_2 twist *trans*	555 v.w	
1178 w		430 w	

---

* Part III: K.S. Boustany and A. Jacot-Guillarmod, *Chimia 23* (1969) 1, 31.

** Received July 28, 1969.

[1] H.W. Thompson and I.F. Trotter, *J. Chem. Soc. 1946*, 481.

[2] N. Sheppard, *J. Chem. Physics 17* (1949) 79–83; D.W. Scott, H. L. Finke, J.P. McCullough, M.E. Gross, K.D. Williamson, G. Waddington and H. M. Huffman, *J. Amer. Chem. Soc. 73* (1951) 261.

[3] N. Sheppard, *Trans. Faraday Soc. 46* (1950) 229; *ibid. 51* (1955) 1465.

[4] D.W. Scott and J.P. McCullough, *J. Amer. Chem. Soc. 80* (1958) 3553.

[5] W.O. Georges, J.H.S. Green and D.J. Harrison, *Spectrochim. Acta 24 A* (1968) 367.

[6] K.G. Allum, J. A. Creighton, J. H. S. Green, G. J. Minkoff and L. J. S. Prince, *Spectrochim Acta 24 A* (1968) 927; J.H.S. Green and D.J. Harrison, *ibid.* 599.

[7] J.H.S. Green, *Spectrochim. Acta 18* (1962) 39; *ibid. 24 A* (1968) 1627.

[8] G.A. Growder and D.W. Scott, *J. Mol. Spectr. 16* (1965) 122.

[9] F. Bentley, L.D. Smithson and A.L. Rozek, *Infra-red Spectra and Characteristic Frequencies ~ 700–300 cm^{-1}*, Interscience Publishers, New York 1968.

[10] Ingo W. May and E.L. Pace, *Spectrochim. Acta 24 A* (1968) 1605.

[11] K.S. Boustany and A. Jacot-Guillarmod, *Chimia 23* (1969) 1, 31.

[12] N. Sheppard and D.M. Simpson, *Quart. Rev. 7* (1953) 19.

attributed to CH_2 wagging[12], the one at 1294 cm^{-1} to CH_2 twist *(trans)* or wag *(gauche)* and the one at 1198 cm^{-1} to CH_2 twisting also. The region 1150–1000 cm^{-1} is the one of ill defined and unresolved absorptions due to skeletal modes. The band at 951 cm^{-1} is the $CH_3(S)$ rocking[11]. The intensities and positions of the four bands at 926 cm^{-1}, 845 cm^{-1}, 825 cm^{-1} and 770 cm^{-1} require their assignments to the CH_2 rocking modes. *n*-Butyl bromide and *n*-propyl bromide exhibit similar bands in this region and were assigned to the CH_2 rocking *(gauche* and *trans)*[14]. The two sets of absorptions, one at 719 cm^{-1} and 690 cm^{-1} and the other at 668 cm^{-1} and 642 cm^{-1} are, respectively, the CH_3–S and the CH_2–S stretching. They reveal also the presence of the two rotational isomers *(trans* and *gauche)*.

Methylthio-3-propanal [II]

The assignments for the absorption bands in cm^{-1} of this compound are made in the light of the above and earlier discussions[11] and of the known motions of aldehydes[9, 13] and alkylhalides[14]: 3420 m; 2965 sh; 2918 v.s; 2830 v.s; 2725 v.s (CH stretching); 1720 v.s (C=O); 1435 sh; 1422 v.s (CH_2 symmetric deformation, same band is present at 1423 cm^{-1} in propionaldehyde[13], at 1430 cm^{-1} in 2-chloropropionitrile and 1415 cm^{-1} in 2-bromopropionitrile); 1405 s; 1384 s (CH bending, same band is present at 1395 cm^{-1} in propionaldehyde); 1338 sh; 1330 m (CH_2 wag *trans* and *gauche); 1315 sh (CH_3–S symmetric deformation); 1305 sh; 1275 s (CH_2 wag *gauche* or twist *trans* or C–S overlap)[5]; 1200 w (CH_2 twist *gauche*, same band present at 1208 cm^{-1} and 1200 cm^{-1} in *n*-propylchloride and *n*-propylbromide respectively)[14]; 1170 s (CH_2 twist *trans)*; 1100 w.br (C–C stretching); 1050 s (CH_3–S rock or C–C stretching); 1035 sh and 1025 (C–C stretching); 955 s (CH_3–S rock); 885 m and 845 s (CH_2 rock); 808 m (CH wag, same band present at 791 cm^{-1} in propionaldehyde); 716 w and 690 v.w (CH_3–S stretching); 665 sh and 656 w.br (CH_2–S stretching); 612 s; 515 s (C–C=O in plane bending). The frequency band at 2725 cm^{-1} is assigned to the aldehydic C–H stretching vibration and the higher band at 2830 cm^{-1} to the first overtone of the aldehydic in plane C–H bending vibration[15]. The CH_2 wag in *trans* 2-chloropropionitrile and *trans* 2-bromopropionitrile are at 1336 cm^{-1}, 1308 cm^{-1} and 1329 cm^{-1}, 1276 cm^{-1}. The CH_2 twist is at 1183 cm^{-1} and 1150 cm^{-1}, respectively, and the CH_2 rock at 919 cm^{-1}, 885 cm^{-1} and 896 cm^{-1} and 822 cm^{-1}, respectively[16].

Methylthio-3-propanal diethylacetal [III]

The IR spectrum shows the following maxima: 2970 v.s; 2915 s; 2870 sh; 1468 sh; 1438 s; 1425 sh; 1398 sh; 1385 sh; 1368 s; 1342 m (CH_2 wag); 1312 w; 1275 m; 1222 m; 1150 sh; 1130 v.s.br; 1055 v.s.br; 960 s (CH_3–S rock); 918 w (probably CH_3–C rock); 879 w; 852 m; 815 w; 795 w; 755 w.br; 695 w; 668 w; 660 w; 555 m; 540 m.

The CH_3(–C) symmetric deformation, the CH_3(–S) symmetric deformation and rock, the CH_2 wag and twist and the C–S stretching are easily recognizable.

The IR of the acetal [III] differs from the IR of the corresponding aldehyde [II] by the absence of the C–H stretching at 2725, the C=O stretching, the C–C=O in plane bending and by the presence of the strong doublet at 1130 and 1055 cm^{-1} characteristic of the C–O–C–O–C stretching[17]. It differs from the infrared of butanal diethylacetal [VI] by the following only: The CH deformation at around 1450 cm^{-1} are unresolved and shifted by ~ -20 cm^{-1}; the presence in [III] of the CH_3S symmetric deformation at 1312 cm^{-1}; absence of the strong band present at 992 cm^{-1} in [VI]; presence in [III] of three bands at 695 cm^{-1} (C–S stretch), 555 cm^{-1} and 540 cm^{-1}.

t-Butylthio-3-propanol-1 [IV]

The IR absorptions of this compounds are given in Table B. The assignments for the *t*-butylthio group are made with reference to those of *t*-butyldisulfide[6] and for the propanol chain by comparison with methylthio-3-propanol-1[11]. The OH out of plane bending is present as a strong broad band with a maximum at 600 cm^{-1}.[9]

n-Butylthio-2-propanol-1 [V]

The IR spectrum of this compound is as follows: 3390 v.s.br; 2955 v.s; 2925 v.s; 2870 s; 2725 v.w; 1465–55 v.s.br; 1421 sh; 1390 sh; 1378 s; 1338 v.w; 1290 w; 1272 m; 1248 sh; 1222 m; 1198 m; 1110 s; 1068 m (OH deformation); 1022 v.s.br (C–O stretching α branched primary alcohol); 972 m; 912 m (CH_3 rock) 893 w; 875 w; 785 w; 741 m; 720 sh; 685 w (CH_2–S stretching) w; 495 w. The bands between 1338 cm^{-1} and 1198 cm^{-1} are the CH_2 wagging and twisting and the band at 912 cm^{-1} is the CH_3(–C) rocking.

The absorptions due to the *n*-butylthio group can be recognized easily by comparison with the spectrum of *n*-butyldisulfide given in[6] and the absorptions due to the α substituted propanol by comparison with methylthio-2-propanol-1[11].

---

[13] E. F. Worden, *Spectrochim. Acta 18* (1962) 1125.

[14] J. K. Brown and N. Sheppard, *Trans. Faraday Soc. 50* (1954) 1164 and *Faraday Soc. Disc. 1950*, 9, 144.

[15] E. L. Saier, L. R. Cousins and M. R. Basila, *J. Physic. Chem. 66* (1962) 232.

[16] P. Klaboe and J. Grundnes, *Spectrochim. Acta 24 A* (1968) 1905.

[17] L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Methuen & Co., London 1958, 2nd Ed.

Table B. Infrared spectrum (4000–400) of *t*-buthylthio-3-propanol

Frequencies	Motions	Frequencies	Motions
3360–30 v.s.br	OH stretching	1265 m	CH_2 wag or twist
2955 v.s		1208 w	CH_2 twist
2935 sh		1162 v.s	CH_3 rock + OH deformation
2922 sh		1050 v.s.br	C—O stretching
2985	(1471 + 1459)	1015 sh	CH_3 rock or OH deformation
2860	(2 × 1458)	931 sh	CH_3 rock + C—C stretching
2745			
2715	(2 × 1365)	901 sh	CH_2 rock
1630 w.br		810 w	CH_2 rock or C—C stretching
1471 s	CH_3 assymmetric deformation		
1458 v.s	CH_3 assymmetric deformation	590 m	$-\overset{|}{\underset{|}{C}}-S$ stretching
1440 sh		480 w.br	Skeletal deformation
1389 m	CH_3 symmetric deformation		
1365 v.s	CH_3 symmetric deformation		
1285 w			

Starting Materials and Procedure

The spectra were recorded using a Perkin-Elmer spectrophotometer model 521. The materials were examined as liquid capillary films and 0.025 or 0.050 mm liquid mulls (Abbreviations: v.s = very strong; s = strong; m = medium; w = weak; v.w = veryy weak; sh = shoulder; br = broad).

[I] was obtained by addition of methane thiol to allyl chloride in presence of UV light and by reacting the adduct with sodium methylmercaptide followed by a fractional distillation. [II] and [III] were described in an earlier paper[18]. [IV] was obtained by free radical addition of *t*-butylmercaptan to allyl alcohol[19] and [V] by addition of *n*-butyl mercaptan to allyl alcohol in presence of sulfur according to[20]. All compounds were examined by GLC on two different columns and gave a single peak. The N.M.R. confirmed the structure of [IV] and [V]. The measured physical constants of compounds [I] → [V] are given in Table C.

Table C. Physical Properties of Compounds [I] to [V]

Compounds	b.p. °C/mm Hg	*n*°C	D4°C
[I]	80/10	1.5180^{23}	1.009^{22}
[II]	61/14	1.4850^{20}	1.036^{20}
[III]	91/12	1.4525^{20}	0.960
[IV] *	47.5–49/0.5	1.4756^{26}	
[V] **	86–88/4	1.4793^{23}	

* % S found 21.10; % S calculated = 21.55.
** % S found 21.84; % S calculated = 21.54.

Acknowledgements: The authors thank C. Ghirardi for the synthesis of compound [I].

By Kamel S. Boustany
Monsanto Company, Organic Chemicals Division,
Rubber Chemicals Research Laboratories, Akron (Ohio)

and André Jacot-Guillarmod
Department of Chemistry, Neuchâtel University, Switzerland

---

[18] K. S. Boustany, *J. Chem. U. A. R. 9* (1966) 3, 317.

[19] T. Hoshimo and K. Yamegishi, *Japan 2060* (1955); *Chem. Abstr. 51* (1957) 8779 c.

[20] K. S. Boustany, C. Ghirardi and A. Jacot-Guillarmod, *Chimia 22* (1968) 8, 337.