848. *The Infrared and Ultraviolet Spectra of Some Dialkylthiomethanes and 1,2-Dialkylthioethanes.*

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The ultraviolet and infrared (1500—500 cm.$^{-1}$) spectra of the compounds RS·[CH_2]$_2$·SR, where R = H, Me, Et, Pr^i, or Bu^t, and R′S·CR″$_2$·SR′, where R′ = Me or Et and R″ = H or Me, have been examined. All the compounds possess rotational isomers, notably those containing the S·[CH_2]$_2$·S unit. The wagging modes of vibration of the *trans*-S·[CH_2]$_2$·S and the S·CH_2·S unit give characteristic and distinguishable strong infrared bands near 1200 cm.$^{-1}$. Both series of compounds can be compared with the equivalent chloro-compounds. In particular, the spectrum of ethane-1,2-dithiol is similar in many respects to that of 1,2-dichloroethane.

The ultraviolet spectra of compounds containing an S·CR″$_2$·S unit have well-formed maxima near 42,500 cm.$^{-1}$ (235 mμ). Compounds containing the S·[CH_2]$_2$·S unit give only an inflection in the same region.

THE infrared spectra of most sulphides and disulphides with CH_2 groups next to a sulphur atom contain a CH_2 wagging band of enhanced intensity between 1230 and 1300 cm.$^{-1}$. For ethyl groups this range can be reduced to 1250—1275 cm.$^{-1}$. We recently found [1] an additional strong band near 1200 cm.$^{-1}$ in the spectrum of 1,2-diethylthioethane. The present paper shows that the 1200 cm.$^{-1}$ band is due to a CH_2 wagging mode in compounds containing S·[CH_2]$_2$·S and S·CH_2·S units. It does not occur where $n > 2$ in S·[CH_2]$_n$·S. We shall report later on molecules containing more than two internal CH_2 groups.

As Sheppard [2] pointed out, the infrared spectra of sulphides and chlorides are similar in many ways. That of ethane-1,2-dithiol can be compared directly with that of 1,2-dichloroethane, which has been described by Brown and Sheppard [3] and by Mizushima and his co-workers.[4] Both molecules exist in two rotationally isomeric forms, and the assignments of the bands for the *trans*-isomer of the dithiol are almost identical with those of the *trans*-isomer of 1,2-dichloroethane. The scheme for the assignment of bands for the dithiol, based on the existence of different rotational isomers, can be extended throughout the series of compounds containing the S·[CH_2]$_2$·S unit.

Mizushima has shown [5] that rotational isomerism is not confined to compounds of the type X·[CH_2]$_2$·X but is common in most molecules similar to paraffins.[6] Sweeney, Mizushima, and Quagliano [7] refer briefly to only one of the compounds that we have examined, MeS·[CH_2]$_2$·SMe, and their results agree with ours. One of Mizushima's co-workers, Miyake,[8] discusses the CH_2 rocking frequencies of compounds containing the X·[CH_2]$_2$·X unit in relation to the structure of polyethylene glycol.

Mizushima [5,9] has suggested a convention for the nomenclature of rotational isomers which we shall observe. If we consider the middle of the bond about which the rotation occurs, the *trans*-isomer (T) has its skeleton lying along the plane of the bond in the same way as a *trans*-isomer of an olefin. The two *gauche*-isomers can be formed by rotating one

[1] Welti and Whittaker, *J.*, 1962, 3955.
[2] Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429.
[3] Brown and Sheppard, *Trans. Faraday Soc.*, 1952, **48**, 128.
[4] (*a*) Nakagawa, *J. Chem. Soc. Japan*, 1954, **75**, 178; (*b*) Nakagawa, *J. Chem. Soc. Japan*, 1953, **74**, 53; Nakagawa and Mizushima, *J. Chem. Phys.*, (*c*) 1953, **21**, 2195; (*d*) 1954, **22**, 759; (*e*) Nakagawa, Mizushima, Ichishima, and Miyazawa, *ibid.*, p. 1614; (*f*) Kuratini, *Rep. Inst. Sci. Tech. Univ. Tokyo*, 1952, **6**, 221; (*g*) Ichishima, Kamiyama, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1958, **29**, 1190; (*h*) Mizushima, Shimanouchi, Nakagawa, and Miyake, *ibid.*, 1953, **21**, 215.
[5] Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, 1954.
[6] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.
[7] Sweeney, Mizushima, and Quagliano, *J. Amer. Chem. Soc.*, 1955, **77**, 6521.
[8] Miyake, *J. Amer. Chem. Soc.*, 1960, **82**, 3040.
[9] Simanouti and Mizushima, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1943, **40**, 467.

part of the molecule about the bond in a clockwise direction (G') or in an anticlockwise direction (G). Neu and Gwinn [10] have confirmed the presence of two *gauche*-forms, as opposed to one *cis*-form, by obtaining twice the number of Raman bands from a partly deuterated molecule.

The first member of the series $RS{\cdot}CH_2{\cdot}SR$, methanedithiol, is difficult to isolate,[11] although Cairns and his co-workers [12] have identified it as a reaction product of formaldehyde and hydrogen sulphide. From the resemblance of the relevant features of the spectrum of dimethylthiomethane to that of dichloromethane,[13] it is probable that the spectra of methanedithiol and dichloromethane would be very similar.

After describing the preparation of the compounds and the spectroscopic apparatus, we shall discuss the individual spectra and suggest assignments for some of the bands. We have also made use of the band assignments for the vibrational modes of some alkyl sulphides which have been suggested by Scott and McCullogh,[14] Sheppard,[2] and Hayashi and his co-workers.[15] Our results need to be confirmed by an examination of the corresponding Raman spectra.

The ultraviolet spectra of the series $R'S{\cdot}CR''_2{\cdot}SR'$ show a well-formed peak near 42,500 cm.$^{-1}$ (235 mμ), while those of the series $RS{\cdot}[CH_2]_2{\cdot}SR$ show only an inflection. Some related compounds have already been examined by Fehnel and Carmack.[16] There are no certain correlations between the ultraviolet and the infrared spectra, although the subject will be discussed below.

Experimental

Preparation of Compounds.—The sulphides have been prepared by two methods: (*a*) reaction of the dihalide with a solution of the sodium derivative of the appropriate thiol in methanol; (*b*) reaction of the thiol with the aldehyde or ketone in the presence of a catalytic amount of hydrochloric acid.[17]

With the exception of 1,2-*di-isopropylthioethane* and 1,2-*di-t-butylthioethane*, all the compounds appearing in Table 1 have been described previously.

Table 1.

Preparation and properties of the sulphides.

Compound	Method of prep.	M. p.	B. p./mm.	Calc. (%) C	Calc. (%) H	Found (%) C	Found (%) H
$EtS{\cdot}[CH_2]_2{\cdot}SEt$	*a*	−35—36°	48—54°/0·2	48·0	9·3	48·0	9·6
$Pr^iS{\cdot}[CH_2]_2{\cdot}SPr^i$	*a*	—	82—84°/3	54·0	10·1	54·0	10·6
$Bu^tS{\cdot}[CH_2]_2{\cdot}SBu^t$	*a*	7—9	120—122°/2	58·3	10·7	58·4	10·8
$CH_2(SMe)_2$	*a*	−20·5	148—150°/760	33·3	7·4	33·5	7·4
$CH_2(SEt)_2$	*a*	—	74—76°/11	44·2	8·8	44·4	8·9
$CHMe(SMe)_2$	*b*	—	157—159°/760	39·4	8·2	39·9	8·5
$CHMe(SEt)_2$	*b*	—	80°/10	48·0	9·3	48·1	9·6
$CMe_2(SMe)_2$.....	*b*	−18	34—36°/0·4	44·2	8·8	44·3	9·3
$CMe_2(SEt)_2$	*b*	—	43—47°/8	51·2	9·8	51·2	10·1
$(MeS{\cdot}CH_2)_2S$	*a*	−30·5	100—103°/3·5	31·2	6·5	31·2	6·9
$(EtS{\cdot}CH_2)_2S$	*a*	−37—38	110°/6	39·5	7·8	39·4	8·2

Analysis on a Pye argon gas–liquid chromatograph shows that they are all at least 97% pure. The column packing was 15% of polyethylene glycol adipate on 50—100 mesh Celite. The flow rate was 40 ml. of argon per min., and the temperature was 100°.

Samples of ethane-1,2-dithiol (m. p. −43·5°; cf. lit.,[11] m. p. −41·2°) and 1,2-dimethylthioethane (m. p. 5·7°) were obtained from L. Light & Co.

[10] Neu and Gwinn, *J. Chem. Phys.*, 1950, **18**, 1642.
[11] Hall and Reid, *J. Amer. Chem. Soc.*, 1943, **65**, 1466.
[12] Cairns, Evans, Larchar, and McKusik, *J. Amer. Chem. Soc.*, 1952, **74**, 3982.
[13] Plyler and Benedict, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 202.
[14] Scott and McCullogh, *J. Amer. Chem. Soc.*, 1958, **80**, 3554.
[15] Hayashi, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1957, **26**, 608.
[16] Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84.
[17] Levi, *Gazetta*, 1932, **42**, 775.

Spectroscopic Apparatus.—The infrared spectra were recorded, linearly in $cm.^{-1}$, between 500 and 1500 $cm.^{-1}$ with a Unicam S.P. 100 double-beam spectrometer equipped with a sodium chloride prism-grating double monochromator [1500 lines per in. (650—2150 $cm.^{-1}$)] operated under dry nitrogen. From 500 to 650 $cm.^{-1}$ the instrument was opeated as a single monochromator, with a potassium bromide prism. The instrument was calibrated with carbon dioxide, ammonia, and water vapour, polystyrene being used for routine checks. The spectra were scanned at 190 $cm.^{-1}$ per min. with the grating and 24 $cm.^{-1}$ per min. with the potassium bromide prism. Owing to the comparatively fast scanning speeds, we cannot quote a consistent accuracy of better than ± 2 $cm.^{-1}$, although it was generally better than that.

The liquid spectra were obtained for films. The solid spectra were obtained by freezing the film between two blanks which were held on to a brass probe. The probe descends through the middle of a reinforced Perspex liquid-nitrogen container and into a cylindrical cell. This cell is similar to a 10 cm. gas-cell and can be evacuated. Compounds frozen by this method were: ethane-1,2-dithiol; 1,2-dimethylthioethane; 1,2-diethylthioethane; 1,2-di-t-butylthioethane, and dimethylthiomethane. The other compounds were more difficult to freeze. In their cases, the probe, with the filled blanks attached, was initially dipped into a Dewar flask filled with liquid nitrogen. Compounds measured in this way were: 1,2-di-isopropylthioethane, diethylthiomethane, di(methylthiomethyl) sulphide, and di(ethylthiomethyl) sulphide. The solid spectra were not obtained below 650 $cm.^{-1}$.

The ultraviolet spectra were recorded on a Unicam S.P. 700 spectrophotometer. This instrument was calibrated against hydrogen and mercury lines, and a spot test was carried out with each set of spectra. In the region 44,000—40,000 $cm.^{-1}$ the accuracy was within ± 100 $cm.^{-1}$, but as further errors may be introduced by the choice of position of broad maxima, we have quoted the values of the maxima to the nearest 100 $cm.^{-1}$. The spectra were measured in solutions in 96% ethanol. Except for the tests on maxima above 48,000 $cm.^{-1}$ (*ca.* 210 mμ), ordinary 10-mm. silica cells were used.

Results

(*a*) *Infrared Band Frequencies.*—The band frequencies, in $cm.^{-1}$, are given below for all the spectra, with the exception of those of three early members of the two main series of compounds, which are given in the Discussion.

The band intensities are not quoted on an absolute scale, being relative to each other only within each spectrum.

The spectra of the liquids are being submitted for inclusion in the D.M.S. reference spectra, commencing from No. 9780.

Ethane-1,2-dithiol. See tables under Discussion.

1,2-*Dimethylthioethane.* See table under Discussion.

1,2-*Diethylthioethane.* Solid: 654w, 671ms, 721ms, 739ms, 784ms, 892ms, 1025w, 1053ms, 1145s, 1209s, 1239m, 1264s, 1374ms, 1418s, 1440s, 1448s, 1455s, 1464s. Liquid: 615sh, 654wm, 688infl, 716ms, 756infl, 763wm, 783wm, 853w, 970m, 980infl, 1051wm, 1058wm, 1115infl, 1129wm, 1201s, 1260infl, 1266s, 1375ms, 1424s, 1452s.

1,2-*Di-isopropylthioethane.* Solid: 708m, 713infl, 728m, 740w, 759vw, 882wm, 924wm, 927wm, 952w, 1020vw, 1046ms, 1054infl, 1096wm, 1113vw, 1133m, 1155s, 1205s, 1250s, 1267wm, ~1280infl, 1312w, 1328vw, 1364m, 1380ms, 1420s, 1444sh, 1451s, 1456infl, 1462s. Liquid: 615vw, 636wm, 648vw, 716m, 853w, 882w, 927w, 953vw, 1022vw, 1051ms, 1099vw, 1112vw, 1131w, 1157s, 1201s, 1246s, 1263m, ~1280infl, ~1290infl, 1314w, 1367s, 1382s, 1426m, 1447sh, 1455s, 1462sh.

1,2-*Di-t-butylthioethane.* Solid: 722wm, 762w, 775w, 817w, 935w, 1024w, 1119wm, 1167s, 1191sh, 1203ms, ~1220infl, 1366ms, 1390wm, 1440—60infl, 1462ms, 1473ms. Liquid: 590wm, 714wm, 736infl, 758w, 814w, 933w, 1023w, 1113w, 1161s, ~1180infl, 1195m, 1213wm, 1269w, 1364s, 1389wm, 1423sh, 1459ms, 1472m.

Dimethylthiomethane. See table under Discussion.

Diethylthiomethane. Solid: 656w, 670w, 701w, 718w, sh, 735s, ~745infl, 789m, 792m, 835m, 901vw, 975sh, 983ms, 1035wm, 1061m, 1086wm, 1115wm, 1121wm, 1148wm, 1205s, 1232wm, 1273s, 1377m, 1389wm, 1438sh, 1449s, 1458s, 1469m. Liquid: 640infl, 655w, 661infl, 698vw, 732s, 747infl, 783w, 831wm, 897vw, 970m, 979sh, 1037sh, 1053wm, 1086w, 1121w, 1150w, 1201s, 1251infl, 1269ms, 1377m, 1391m, 1424m, 1453ms.

1,1-*Dimethylthioethane*. Liquid: 516vw, 528vw, 577vw, 608m, 632vw, 650vw, 688ms, 727m, 754vw, 778vw, 838w, 855w, 883vw, 901vw, 947ms, 959sh, 979m, 1009vw, 1057s, 1069infl, 1103m, 1123w, 1182ms, 1194ms, 1260wm, 1319w, 1344wm, 1372ms, 1398m, 1424s, 1435s, 1445s.

1,1-*Diethylthioethane*. Liquid: 603w, 629vw, 643vw, 669w, 701ms, 715infl, 760wm, 782wm, 849vw, 942w, 970w, 978infl, 1020w, 1035infl, 1055infl, 1062m, 1100w, 1113vw, 1151vw, 1177m, 1191m, 1267ms, 1375ms, 1426sh, 1450s, 1457sh.

2,2-*Dimethylthiopropane*. Liquid: 538wm, 566vw, 666ms, 725w, 951m, 962m,sh, 1008w, 1113s, 1154ms, 1203vw, 1315w, 1362ms, 1379m, 1422ms, 1439ms, 1461m.

2,2-*Diethylthiopropane*. Liquid: 543wm, 676ms, 695w, sh, 753w, 785wm, 976m, 1032w, 1050m, 1112s, 1153ms, 1264ms, 1361ms, 1377ms, 1450s, 1457sh.

Di(methylthiomethyl) sulphide. Solid: 663wm, 698vs, 713ms, 742vs, 778ms, 782ms, 806vw, 842sh, 846wm, 880w, 898w, 918w, 925w, 935w, 959s, 974infl, 978s, 984sh, ~1020infl, 1028ms, 1078m, ~1100infl, ~1110infl, 1135ms, 1153vw, 1188wm, 1196s, 1216w, 1238w, 1282w, 1297w, 1309wm, 1313wm, 1384ms, 1421s, 1435s. Liquid: 643sh, 660wm, 697s, 710m, 739s, 776m, 833w, 841w, 881w, 899w, 919vw, 928vw, 958m, 972m, 1018w, 1036wm, 1082wm, 1133w, 1159vw, 1192s, 1218wm, ~1280infl, ~1305infl, 1317wm, 1379m, 1423ms, 1435ms.

Di(ethylthiomethyl) sulphide. Solid: 670m, 733vs, ~750infl, ~785infl, 796m, 859m, 885vw, 903w, 930vw, 971m, 983sh, 1001vw, 1035m, 1055wm, 1083m, 1135w, 1165w, 1191s, 1221w, 1254w, sh, 1266ms, 1309vw, 1381ms, 1427m, 1452ms, 1458m. Liquid: 653sh, 668m, 732vs ~750infl, 791m, 831infl, 853m, 882vw, 900w, 929vw, 970m, 979sh, 1006w, 1035m, 1050wm, 1082m, 1128w, 1161sh, 1192s, 1215m,sh, 1266ms, 1307w, 1380ms, 1423m, 1450ms, 1458sh.

(*b*) *Ultraviolet Band Frequencies*.—The frequencies of the maxima below 45,000 cm.$^{-1}$ and their $\log_{10}\varepsilon$ values are given in Table 2.

TABLE 2.

Ultraviolet band maxima (cm.$^{-1}$) and extinction coefficients.

Compound	ν max.	Compound	ν max.	$\log_{10}\varepsilon$	Compound	ν max.	$\log_{10}\varepsilon$
HS·$[CH_2]_2$·SH ...	(42,500) *	$CH_2(SMe)_2$ ...	42,400	2·79	$CMe_2(SMe)_2$ ...	42,500	2·94
MeS·$[CH_2]_2$·SMe ...	(42,500) *	$CH_2(SEt)_2$ ...	42,300	2·84	$CMe_2(SEt)_2$ ...	41,900	2·94
EtS·$[CH_2]_2$·SEt ...	(42,500) *	$CHMe(SMe)_2$ ...	42,500	2·82	$(MeS·CH_2)_2S$ ...	42,600	2·96
$Pr^iS·[CH_2]_2·SPr^i$ ...	(42,500) *	$CHMe(SEt)_2$	42,600	2·84	$(EtS·CH_2)_2S$ ...	42,600	3·03
$Bu^tS·[CH_2]_2·SBu^t$	(42,500) *						

* Values for inflections are in parentheses.

DISCUSSION

Infrared Spectra of 1,2-Dialkylthioethanes.—(*a*) *Ethane-1,2-dithiol*. The infrared spectra of both the solid and the liquid state of ethane-1,2-dithiol can be compared directly with those of 1,2-dichloroethane described by Brown and Sheppard [3] and Mizushima.[4c] They attribute the spectrum of the liquid to both the *trans*- and *gauche*-rotational isomers, but assign the spectrum of the frozen solid compound to the *trans*-form alone. Subtraction of the solid spectrum from that of the liquid spectrum should leave a spectrum that can be associated with the *gauche*-isomer. Brown and Sheppard carried this out successfully with 1,2-dichloroethane, but we have found too much overlapping of liquid and solid spectra of the dithiol to be able to recognise the bands of the *gauche*-isomer with certainty.

The spectra of the *trans*-form of 1,2-dichloroethane and the solid form of ethane-1,2-dithiol are so similar that, with the exception of the SH bands, the bands of ethane-1,2-dithiol can be assigned from the same symmetry types and selection rules as for 1,2-dichloroethane. To maintain the same symmetry, C_{2h}, the SH groups of the dithiol must stay in the plane of the molecule, and both must be in the *cis*- or both in the *trans*-position with respect to the C–C bond. It is unlikely that they will exist in the *cis*-form, as by observation of models, the hydrogen of the SH group will be much nearer to, and would probably be repelled by, the CH_2 groups in the *cis*-form.

The symmetry types and selection rules for the solid dithiol are given in Table 3. Of the twenty-four fundamental modes of vibration, we can expect six to be infrared-active between 500 and 1500 cm.$^{-1}$. The allocations of the bands and their comparative strengths are given in Table 4.

TABLE 3.

Symmetry types and selection rules for the vibrations of the solid form of $HS{\cdot}[CH_2)_2{\cdot}SH$. Symmetry C_{2h}.

Vibration	A_g	A_u	B_g	B_u	Vibration	A_g	A_u	B_g	B_u
CH stretching	ν_1	ν_9	ν_{14}	ν_{18}	CH_2 rocking	—	ν_{11}	ν_{16}	—
SH stretching.....	ν_2	—	—	ν_{19}	C–C stretching	ν_6	—	—	—
CH_2 bending	ν_3	—	—	ν_{20}	C–S stretching	ν_7	—	—	ν_{23}
CH_2 wagging	ν_4	—	—	ν_{21}	SH bending (out-of-plane)	—	ν_{12}	ν_{17}	—
CH_2 twisting	—	ν_{10}	ν_{15}	—	C–C–S bending	ν_8	—	—	ν_{24}
SH bending (in-plane)	ν_5	—	—	ν_{22}	torsion	—	ν_{13}	—	—

Selection rules: A_g Raman-polarised. A_u Infrared. B_g Raman-depolarised. B_u Infrared.

TABLE 4.

Infrared frequencies ($cm.^{-1}$) and vibrational assignments of $HS{\cdot}[CH_2]_2{\cdot}SH$ in the solid state. Symmetry C_{2h}.

Frequency	Species	Assignment Mode		Frequency	Species	Assignment Mode	
687s	B_u	ν_{23}	C–S str	1153s	A_u	ν_{10}	CH_2 twt
704w, sh	A_g	ν_7	C–S str	1225m	B_u	ν_{21}	CH_2 wag
711m 719m	A_u	ν_{11}	CH_2 rck	1418m 1428m	B_u	ν_{20}	CH_2 bnd
882m, sh 888m	B_u	ν_{22}	SH bnd (in-plane)				

Here and elsewhere: str = stretching; rck = rocking; twt = twisting; wag = wagging; bnd = bending.

The only doubt about the allocation might occur between the bands chosen for the CH_2 rocking and the SH bending mode of vibration. However, the value of 882 $cm.^{-1}$ would be rather high for the CH_2 rocking mode,[8] and both Sheppard [2] and Scott and McCullogh [14] give values between 800 and 900 $cm.^{-1}$ for a C–SH bending vibration.

The splitting of the CH_2 bending and rocking vibrations and the SH in-plane bending vibration might be due to coupling between more than one molecule in the unit cell, or to the change of formally Raman-active and infrared-inactive vibrations to infrared-active ones by a less-than-centro-symmetric " site " symmetry, *i.e.*, by intermolecular distortion. The first-order selection rules of the isolated molecule would still be approximately correct.

The infrared spectrum shows, therefore, that the $S{\cdot}[CH_2]_2{\cdot}S$ unit is in the *trans*-form, and that a single isolated molecule has a centre of symmetry, with the probability of its being in an all-*trans*-form.

When the bands in the spectrum of the solid state are subtracted from the spectrum of the liquid dithiol, the situation becomes confused as a large part of the two spectra overlap badly. The difficulty in separating the *trans*- and the *gauche*-isomer is accentuated by the probability that the *trans*-form of the $S{\cdot}[CH_2]_2{\cdot}S$ skeleton is not completely centro-symmetric in the liquid state owing to different staggered conformations of the SH group. Probable allocations for the liquid spectrum are given in Table 5.

The two CH_2 wagging bands and the C–C stretching band of the *gauche*-isomer compare well with those in the spectrum of the *gauche*-isomer of 1,2-dichloroethane, but the *gauche* CH_2 bending and twisting bands overlap with those from the spectrum of the solid. In the spectra of the dichloroethane, the ν_{12} CH_2 twisting band of the *gauche*-isomer is weaker than the ν_8 CH_2 twisting band of the *trans*-isomer. By analogy, the 1159 $cm.^{-1}$ inflection in the liquid spectrum of the dithiol is due to the *gauche* ν_{15} twisting vibration and the 1147 $cm.^{-1}$ band is due to the *trans* ν_{10} twisting vibration. The C–S stretching bands also overlap, but the *gauche*-form is probably associated with the bands at 638 and 668 $cm.^{-1}$. The two *gauche*-dichloroethane bands are also much weaker than the main *trans*-C–Cl stretching band.

In the spectrum of *gauche*-1,2-dichloroethane, the two rocking bands at 944 and

TABLE 5.

Infrared frequencies (cm.$^{-1}$) of HS·$[CH_2]_2$·SH in the liquid state.

Frequencies		Assignment		Frequencies		Assignment	
638m	$\nu_{7'}$	C–S str	*gauche*	1030w	$\nu_{6'}$	C–C str	*gauche*
655infl.		C–S str?		1147m	ν_{10}	CH_2 twt	*trans*
666w	$\nu_{23'}$	C–S str	*gauche*	1159 infl	$\nu_{15'}$	CH_2 twt	*gauche*
693s	ν_{23}	C–S str	*trans*	1202 infl		?	
713w, sh	ν_{11}	CH_2 rck	*trans*	1219s	ν_{21}	CH_2 wag	*trans*
737w, sh		?		1274s	$\nu_{21'}$	CH_2 wag	*gauche*
766wm		?		1293m	$\nu_{4'}$	CH_2 wag	*gauche*
805w	$\nu_{12'}$	SH bnd	*gauche*	1420s	ν_{20}	CH_2 bnd	*gauche*
892wm	ν_{12}	SH bnd	*trans*	1430s	ν_{20}	CH_2 bnd	*trans*
942w	Two	$\nu_{15'}$	CH_2 rck	*gauche*			
956wm, sh	are	$\nu_{11'}$	CH_2 rck	*gauche*			
974wm							

880 cm.$^{-1}$ are medium-to-strong compared with the rest of the spectrum. None of the bands which would possibly be assigned to CH_2 rocking vibrations of the *gauche*-isomer of the dithiol is of a comparable strength. However, to some extent, these CH_2 rocking modes of the *gauche*-form are probably coupled with the C–X frequencies, and in the chlorides the vibrations of the more polar C–Cl bonds may contribute considerably to the intensities of the CH_2 rocking modes.

The relative strengths of the bands from equally intense spectra of the dithiol and dichloroethane agree well with each other. Any differences in the strengths of the bands in our spectra compared with those in Brown and Sheppard's spectra [3] are due to the different intensities of the whole spectra.

(*b*) 1,2-*Dimethylthioethane*. The differences between the spectra of the liquid and the solid state of this molecule show the presence of rotational isomers in the liquid state.

By comparison with ethane-1,2-dithiol, the spectrum of the solid indicates that the S·$[CH_2]_2$·S unit is in the *trans*-form in the solid state. As in the dithiol, the 1269 and 1286 cm.$^{-1}$ CH_2 wagging bands disappear on freezing, leaving the *trans*-1211 cm.$^{-1}$ band. The comparatively few bands in this spectrum indicate that the molecule must be predominantly in a rotational configuration with a higher symmetry, C_{2h}, point group rather than in a C_2, C_s, or C_i point group. This implies that the MeS groups must continue the *trans*-relation throughout the molecule. There would be a repulsion between the CH_3 and CH_2 groups if the CH_3 groups were in *cis*-positions with respect to the C–C bond. The *gauche*-form would have a lower symmetry.

The band frequencies and assignments for the spectrum of both the solid and the liquid state are given in Table 6.

TABLE 6.

Infrared frequencies (cm.$^{-1}$) and band assignments of MeS·$[CH_2]_2$·SMe.

Frequency		Assignment		Frequency		Assignment	
Liquid	Solid			Liquid	Solid		
635infl		C–S str?		1023infl		?	
649vw, sh		C–S str	*gauche*	1038infl		?	
683m	683s	C–S str	*trans*	1119infl		CH_2 twt	*gauche?*
714vw		C–S str?		1132m	1141m	CH_2 twt	*trans*
	729ms	CH_2 rck	*trans*	1204s	1211ms	CH_2 wag	*trans*
735m	736ms	C–S str	*trans* and *gauche*	1269m		CH_2 wag	*gauche*
844w		CH_2 rck	*gauche*	1286wm, sh		CH_2 wag	*gauche*
885vw		CH_2 rck	*gauche?*	1320wm	1316w	CH_3 sym bnd	
915vw	or	CH_2 rck	*gauche?*		1324w		
958ms	967s	CH_3 rck		1432s	1420m, sh	CH_2 bnd and	
977w, sh				1437s, sh	1439s	CH_3 antisym bnd	
1010w		C–C str	*gauche*				

In the spectrum of the liquid the bands due to the CH_2 and CH_3 bending modes of the *trans*- and the *gauche*-isomer overlap.

Our values and assignments agree well with the incomplete assignments of Sweeney, Mizushima, and Quagliano [7] who mention the bands at 729 and 736 cm.$^{-1}$ in the spectrum of the solid, at 845, 1010, and 1270 cm.$^{-1}$ in the spectrum of the liquid, and near 1430 and 950 cm.$^{-1}$ in the spectra of both the liquid and the solid. They assign the second *gauche* rocking frequency to a band at 900 cm.$^{-1}$. Our spectrum has no band at 900 cm.$^{-1}$ but it has two very weak bands at 885 and 915 cm.$^{-1}$. Either of these could be assigned to the CH_2 rocking vibration as, in the spectra of some 1,2-dimethylthioethane metal co-ordination compounds, Sweeney, Mizushima, and Quagliano found that the rocking band varies between 885 and 915 cm.$^{-1}$. They considered from this evidence that in the solid state the molecule existed in the extended *trans*-form. Our assignments for the spectrum of the liquid, particularly those below 1100 cm.$^{-1}$, could be confirmed by a Raman spectrum.

A C–S stretching band at 683 cm.$^{-1}$ compares well with the ethane-1,2-dithiol *trans*-C–S stretching band at 687 cm.$^{-1}$. As this C–S stretching band would be affected by the external C–S bond, the similarity could be taken as a point in favour of an all-*trans*-structure.

In the spectrum of the liquid, the 1204 cm.$^{-1}$ *trans*-CH_2 wagging band is much stronger than the equivalent *gauche*-band at 1269 cm.$^{-1}$, which could indicate that the *trans*-form predominates in the liquid state. Here again the *gauche*-CH_2 rocking bands are weaker than would be expected.

(*c*) 1,2-*Diethylthioethane*. The band frequencies of the spectra of the solid and liquid states are given under the subheading (*a*) of Results.

The presence of a band at 1209 cm.$^{-1}$ in the spectrum of the solid and at 1201 cm.$^{-1}$ in that of the liquid suggests that the *trans*-form of the S·$[CH_2]_2$·S unit exists in both the solid and liquid state. Unfortunately, the ethyl CH_2 group next to a sulphur atom gives a CH_2 wagging band near 1265 cm.$^{-1}$, and we cannot be certain whether the *gauche*-S·$[CH_2]_2$·S unit disappears from the solid state, or even whether it exists in the liquid state. Mizushima uses the CH_2 rocking and C–C stretching bands to recognise the presence or absence of the *gauche*-forms. The C–C stretching band of the S·$[CH_2]_2$·S unit is generally weak and in this case there is no suitable band for its assignment between 1000 and 1050 cm.$^{-1}$ in the spectra of either the solid or the liquid. The CH_2 rocking band of the *trans*-S·$[CH_2]_2$·S unit is strong in both spectra, and the CH_2 rocking bands of the ethyl group appear in their usual positions in the spectrum of the liquid. This leaves either a weak band at 853 cm.$^{-1}$ or an inflection at 756 cm.$^{-1}$ for the *gauche*-CH_2 rocking bands of the S·$[CH_2]_2$·S unit. Both these bands disappear in the spectrum of the solid. The evidence as a whole suggests that the S·$[CH_2]_2$·S unit is in the *trans*-form in the solid and that the *trans*-isomer is the more abundant of the two in the liquid state. It also confirms that the *gauche*-CH_2 rocking bands of the S·$[CH_2]_2$·S unit are weak compared with those of 1,2-dichloroethane.

The spectrum of the solid possesses bands at 671, 739, and 1239 cm.$^{-1}$ which are additional to those appearing in the spectrum of the liquid. The band at 1452 cm.$^{-1}$ also splits into four components, at 1440, 1448, 1455, and 1464 cm.$^{-1}$. These changes are most readily explained by the configuration of the ethyl or ethylthio-groups which, in the solid state, are most likely to be fixed in either the *trans*- or the *gauche*-position with respect to *trans*-S·$[CH_2]_2$·S unit.

The *trans*-CH_2 rocking band near 720 cm.$^{-1}$ appears in the symmetrical molecules ethane-1,2-dithiol and 1,2-dimethylthioethane. Asymmetry outside the S·$[CH_2]_2$·S unit might be expected to allow the *trans*-CH_2 rocking band that would otherwise only appear in the Raman spectrum, to appear in the infrared. The spectra of 1,2-diethylthioethane do not possess such a band in the expected range 900—950 cm.$^{-1}$, although admittedly it would probably be weak. On the other hand it could be argued that ethyl groups giving either GG or G′G′ isomers, especially if the angles of rotation were small, might not alter the effective symmetry properties of the S·$[CH_2]_2$·S unit. Hayashi and his co-workers [15]

found that of the two rocking bands due to the CH_2 group in ethyl methyl sulphide, the 760 cm.$^{-1}$ band was due to the *trans*-isomer and the 783 cm.$^{-1}$ band was due to the *gauche*-isomer. These results have been confirmed by Brown and Sheppard.[18] They suggest that, as the 763 cm.$^{-1}$ band in the spectrum of 1,2-diethylthioethane disappears on solidification, the solid molecule must have *gauche*-ethyl or -ethylthio-groups.

In addition, there is no C–S stretching band near 685 cm.$^{-1}$ in the spectrum of the solid. This would also indicate that the solid compound does not take up the all-*trans*-configuration. However, an inflection at 688 cm.$^{-1}$ appears in the spectrum of the liquid, showing, according to this argument, that an all-*trans*-isomer exists in the liquid state, but that it is not the most stable isomeric form.

The evidence obtained so far is not strong enough to establish which configuration the ethyl groups take up with respect to the S·$[CH_2]_2$·S unit. Whichever configuration the solid molecule assumes, it shifts and strengthens a C–S stretching band to 671 cm.$^{-1}$ and introduces a new CH_2 rocking band at 739 cm.$^{-1}$ and a new CH_2 wagging band at 1239 cm.$^{-1}$.

(*d*) 1,2-*Di-isopropylthioethane*. The band frequencies of the spectra of the solid and liquid states are given in subsection (*a*) of Results.

The relative strengths of the *trans*- and *gauche*-CH_2 wagging bands are the same in both the liquid and the solid state, showing that the *trans*-form is predominant in both states. All the other *gauche*-bands are very weak or absent. The presence of the *gauche*-form in the solid can be explained by the formation of an amorphous rather than a crystalline solid. This was caused by the cooling technique of dipping the blanks containing the sample directly into liquid nitrogen. Under these conditions the size of the isopropyl groups would impede the reorientation of the molecule and the distribution of isomers would be unchanged in the glass structure. The higher-melting t-butyl compound can be cooled more slowly and loses the *gauche*-isomer in the solid state.

Some of the relative intensities of the bands change between the liquid and the solid state, but the biggest difference is in the 700—750 cm.$^{-1}$ region where the CH_2 rocking band splits into a number of components.

(*e*) 1,2-*Di-t-butylthioethane*. The band frequencies are given in subsection (*a*) of Results.

The 1269 cm.$^{-1}$ *gauche*-CH_2 wagging band is weak in the spectrum of the liquid and is missing from the spectrum of the solid. This shows that the *trans*-S·$[CH_2]_2$·S unit is predominant in the liquid and displaces the *gauche*-isomer completely in the solid. Except for the CH_2 bands the spectra were typical of t-butyl sulphides.[14]

TABLE 7.

Infrared frequencies (cm.$^{-1}$) and band assignments of MeS·CH_2·SMe.

Frequency			Frequency		
Liquid	Solid	Assignment	Liquid	Solid	Assignment
649w		C–S str	986ms	995ms	CH_3 rck
	658ms	C–S str	1084w	1085w	?
695s	695ms	C–S str	1123vw		?
723vw	726w	C–S str	1157w	1167wm	CH_2 twt
745s	747ms	C–S str	1205s	1214ms	CH_2 wag
756m, sh		?		1219ms	
	776vw	?	1319wm	1313w	CH_3 sym bnd
805m	809ms	CH_2 rck		1326w	
824w, sh		?	1387wm	1387m, sh	CH_2 bnd
901vw	901w	CH_3 rck or comb		1393m	
959ms	954ms	CH_3 rck	1425ms	1422s	CH_3 antisym bnd
	961ms		1437s	1442s	

The Infrared Spectra of Dialkylthiomethanes.—(*a*) *Dimethylthiomethane*. The band frequencies and assignments are given in Table 7. If we consider the rotation of the methylthio-groups about the central methylene group, the molecule could theoretically

[18] Brown and Sheppard, personal communication.

exist in nine rotationally isomeric forms. Some of the isomers are equivalent to each other and we need only consider the four different types represented by TT, TG, GG, and GG'. Of these types, the GG' isomer is unlikely to be stable, owing to repulsion between the methylthio-groups. The splitting of some of the CH_3 and CH_2 bands in the spectrum of the solid suggests the presence of a more symmetrical isomer than the TG isomer. This leaves the TT and GG types.

The GG isomer would have a C_2 point group, and all the thirty-three modes of vibration would give bands in the infrared region. The TT isomer would have a C_{2v} point group and twenty-seven of its modes of vibration would give infrared bands. The extent of this investigation is not sufficient to distinguish with certainty between the two symmetry types. The splitting of the in-plane CH_2 wagging and bending bands in the spectrum of the solid might, as in previous compounds, be due to intermolecular interactions in the crystal lattice.

The symmetry of the TT form is the same as that of dimethyl sulphide, and the methyl bands are very similar to those of dimethyl sulphide. By comparison with the spectra of the RS·$[CH_2]_2$·SR series of molecules, it is reasonable to assign the 1205 cm.$^{-1}$ band to the wagging mode and the 1157 cm.$^{-1}$ band to the twisting mode. The remaining bands at 1387 and 805 cm.$^{-1}$ can be assigned to the bending and rocking modes. The C–S stretching bands have frequencies that would be expected in a molecule containing methylthio-groups. Although we have not been able to study methanedithiol itself the methylene bands of dimethylthiomethane can be readily correlated with those of dichloromethane.[13]

The bands that disappear on freezing (1123, 824, and 756 cm.$^{-1}$) might be due to one of the other isomers.

The band contours [19] of the spectrum of the vapour (Table 8) can be used to determine the configuration of the vapour molecule. If we suppose, initially, that the compound is in the all-*trans*-form, then the ratio of the moments of inertia I_A/I_B (= ρ) would be very small. The CH_2 wagging vibration alters the dipole moment along the axis of least moment of inertia, so the infrared band would be of type *A* with a strong *Q* centre. The CH_2 rocking vibration alters the dipole moment along the axis of largest moment of inertia, so the infrared band would be of type *C* but resembling type *B*. These contours describe both the 1200 cm.$^{-1}$ CH_2 wagging band and the 800 cm.$^{-1}$ CH_2 rocking band that are found in the spectrum. In addition, the contour of the out-of-plane CH_3 rocking band between

TABLE 8.

Infrared frequencies (cm.$^{-1}$) of the maxima of the main bands of gaseous MeS·CH_2·SMe.

Frequency	Assignment	Frequency	Assignment	Frequency	Assignment	Frequency	Assignment
694sh	C–S str	800sh	CH_2 rck	956sh	CH_3 rck	1199	CH_2 wag
700		806		963sh		1205	
704		812		969		1213	
747sh	C–S str			984		1440	CH_3 + CH_2 bnd
752				992sh			
758							

950 and 1000 cm.$^{-1}$ resembles the CH_2 rocking band, and the two C–S stretching bands near 750 and 700 cm.$^{-1}$ are very similar to each other. From this evidence it is probable that the vapour molecule is in the all-*trans*-configuration. The same band contours would not be expected with a non-*trans*-configuration as the character of the type *C* band contours would change with an increase in ρ.

(*b*) *Diethylthiomethane.* The band frequencies are given in subsection (*a*) of Results.

[19] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand Co., Inc., New York, 1945, pp. 469—484.

It is hard to distinguish in which isomeric form the solid exists. As the liquid-nitrogen dipping technique was used, the substance was probably a glass. The spectra have some similarities to those of 1,2-diethylthioethane, as a band at 1232 $cm.^{-1}$ appears in the spectrum of the solid, and there are weak CH_2 (ethyl) rocking bands at 783 and 747 $cm.^{-1}$ in the spectrum of the liquid. In the spectrum of the solid, the 783 $cm.^{-1}$ band splits and shifts to 789 and 792 $cm.^{-1}$, and the inflection at 747 $cm.^{-1}$ becomes less conspicuous on the side of the C–S band which has shifted to 735 $cm.^{-1}$. A weak band at 670 $cm.^{-1}$ develops out of what was a faint inflection in the spectrum of the liquid, and a weak shoulder also appears at 720 $cm.^{-1}$.

It would be reasonable to assume that the ethyl groups take up the same configuration as they do in solid 1,2-diethylthioethane. Again the dominant features of the spectrum are the two CH_2 wagging bands at about 1270 and 1200 $cm.^{-1}$, which are predominantly associated with the external and internal CH_2 group, respectively. The 1150 $cm.^{-1}$ weak band has been assigned to the internal CH_2 twisting mode because of the similarity to the 1157 $cm.^{-1}$ band in dimethylthiomethane. The 732 $cm.^{-1}$ C–S stretching band is at a lower frequency than in the spectra of dimethylthiomethane, but it is higher than in the spectrum of, for instance, diethyl sulphide. The comparatively high frequency must be due to the central CH_2 group. Comparison of the C–S stretching bands with those of *trans-* and *gauche*-ethyl methyl sulphide might be misleading because of the interaction of C–S bonds across the lone methylene group.

(*c*) 1,1-*Dimethylthioethane.* The spectrum is similar in many ways to that of 1,1-dichloroethane. Band assignments for the spectrum of the liquid can be based, where relevant, on those for 1,1-dichloroethane.[20] The frequencies are given in subsection (*a*) of Results.

It is interesting that in this molecule also a CH bending band appears at 1194 and 1182 $cm.^{-1}$. The corresponding bending band of 1,1-dichloroethane is not split.

(*d*) 1,1-*Diethylthioethane.* The band frequencies for the spectrum of the liquid are given in subsection (*a*) of Results. The bands are those expected from a knowledge of the spectra of 1,1-dichloroethane, 1,1-dimethylthioethane and the bands of the ethylthio-group.

A CH bending mode again gives a split band at 1191 and 1177 $cm.^{-1}$.

(*e*) 2,2-*Dimethylthiopropane and* (*f*) 2,2-*diethylthiopropane.* The band frequencies of the spectra of these two molecules in the liquid state are given in subsection (*a*) of Results. The strong band near 1200 $cm.^{-1}$ is missing from the spectra of both.

(*g*) *Di*(*methylthiomethyl*) *sulphide and* (*h*) *di*(*ethylthiomethyl*) *sulphide.* The band frequencies of these molecules in both the liquid and the solid state are given in subsection (*a*) of Results. As the solids were formed by the liquid-nitrogen dipping technique, it is possible that they are both glassy mixtures.

The assignments of the bands near 1380 and 1190 $cm.^{-1}$ to internal CH_2 bending and wagging vibrations follow from knowledge of the dialkylthiomethanes. Some doubts occur as to the positions of the two internal CH_2 rocking and the two internal CH_2 twisting bands and the second internal CH_2 wagging band. All these have to be common to both molecules. The two bands near 780—800 and 840—860 $cm.^{-1}$ which are chosen for the internal CH_2 rocking vibrations are the stronger of the bands appearing in the same region as the rocking bands of the dialkylthiomethanes. Three possible bands near 1135, 1160, and 1215 $cm.^{-1}$ are suggested for the internal CH_2 twisting vibrations. The most probable is the 1160 $cm.^{-1}$ band. The two CH_2 groups must be *cis* with respect to each other, so the nearest similar molecule for comparison is a *gauche*-substituted ethane. This leads us to suggest the 1215 $cm.^{-1}$ band as the second twisting band. The variation in intensity of the 1135 $cm.^{-1}$ band cannot be explained. No band is suggested for the second CH_2 wagging vibration.

[20] Daasch, Liang, and Nielsen, *J. Chem. Phys.*, 1954, **22**, 1293.

Ultraviolet Spectra.—Fehnel and Carmack [16] reported a strong maximum near 210 mμ (47,600 cm.$^{-1}$) in the ultraviolet spectra of dialkyl sulphides, and Ley and Arends [21] could not find a maximum above 185 mμ in the spectrum of diethyl sulphide.

When measured under normal conditions without precautions against stray light, the spectra of the dialkylthio-methanes and -ethanes also showed maxima near 48,400 cm.$^{-1}$ (207 mμ). Their appearance suggested that they could be false peaks. We therefore carried out tests on two molecules. The first, 1,2-di-isopropylthioethane, was representative of the molecules at present under discussion, and the second, diethyl sulphide, was representative of normal alkyl monosulphides. In each case we both diluted the alcoholic solutions and reduced the path length of the " Suprasil " cells from 10 mm. through 2 to 1 mm. We then flushed out the cell housing, the lamp housing, the beam splitter, and the monochromator of the Unicam S.P. 700 spectrophotometer with nitrogen. The results given by both molecules were very similar. The 1,2-di-isopropylthioethane spectrum has two shallow shoulders, at 48,700 and 49,400 cm.$^{-1}$, and a maximum at 50,500 cm.$^{-1}$. The diethyl sulphide spectrum has an inflection with a maximum change of slope at 47,400 cm.$^{-1}$ and a maximum at 50,600 cm.$^{-1}$. It is probable that both the maxima are still false as the solvent absorption may be too large. If these molecules can be considered truly representative of their series, then we can say that sulphides do not have a maximum below 50,500 cm.$^{-1}$ (above 198 mμ).

In our results (Table 2) we have not tabulated any maximum or inflection above 45,000 cm.$^{-1}$.

The spectra of both dimethyl and diethyl sulphide have an inflection at 42,500 cm.$^{-1}$ (235 mμ) on the low-frequency side of the maximum lying above 50,000 cm.$^{-1}$. This inflection is reduced in the spectrum of isopropyl sulphide and disappears from that of t-butyl sulphide.[16]

The spectra of sulphides containing the S–C–S linkage have a maximum in the region of 42,500 cm.$^{-1}$ ($\log_{10}\varepsilon \sim 2{\cdot}9$). Fehnel and Carmack [16] report a similar band in the spectra of mercaptals, which they discuss both in terms of hyperconjugation involving the skeletal bonds of the S–C–S unit, and in terms of the interaction of the sulphur electrons in space. Baddeley [22] has discussed evidence from kinetic studies for this interaction of electrons.

The spectra of the 2,2-dialkylthiopropanes also show maxima having the same $\log_{10}\varepsilon$ value at 42,500 cm.$^{-1}$. As these molecules have a disubstituted carbon atom between the two sulphur atoms, and the substituents are electron-donor methyl groups, it is unlikely that the maxima can be caused by hyperconjugation.

The ultraviolet spectra of the 1,2-substituted ethanes (S–C–C–S) have inflections rather than maxima near 42,000 cm.$^{-1}$. Examination of models of the structures RS·CH_2·CH_2·SR shows that the sulphur atoms are well separated in the *trans*-rotational isomer, but that they contact each other before the *cis*-rotational isomer can be reached. The absence of strong absorption below 43,000 cm.$^{-1}$ indicates that the sulphur atoms in the *gauche*-isomer must be sufficiently far apart for any electronic interaction through space to be negligible. There is no correlation of the degree of inflection with the amount of *gauche*-isomer present in the liquid state, as shown by the infrared spectra. The ultraviolet spectra of these molecules are very similar to those of normal methyl and ethyl sulphide which cannot possibly have intramolecular interaction of electrons from two sulphur atoms.

Summary of the Infrared Band Assignments.—The infrared bands assigned to the external methyl, ethyl, isopropyl, and t-butyl groups next to a sulphur atom are the same as those assigned by previous authors.[2,14,15] We have not been able to assign a band to the ethyl CH_2 twisting mode.[14,15] No band appears regularly near 1300 cm.$^{-1}$ when an ethyl group is present in a molecule, and when one does appear it can generally be assigned to another group.

[21] Ley and Arends, *Z. phys. Chem.*, 1932, *B*, **15**, 311.
[22] Baddeley, *J.*, 1950, 663.

The internal CH_2 vibrations of substituted methanes and the *trans*-isomers of 1,2-disubstituted ethanes give bands which are summarised in Table 9.

TABLE 9.

Infrared frequencies ($cm.^{-1}$) of the internal CH_2 vibrations of the substituted methanes and the *trans*-isomers of the 1,2-disubstituted ethanes.

	Bending		Wagging		Twisting		Rocking	
	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
$(CH_2{\cdot}SH)_2$	1430s	1428m						711m
	1420s	1418m	1219s	1225m	1147m	1153s	713w, sh	719m
$(CH_2{\cdot}SMe)_2$	*	*	1204s	1211ms	1132m	1141m	(735)m ‡	729ms ‡
$(CH_2{\cdot}SEt)_2$	*	*	1201s	1209s	1129wm	1145s	716ms	721ms
$(CH_2{\cdot}SPr^i)_2$	*	*	1201s	1205s	1131w	1133m	716m	708—759w–m §
$(CH_2{\cdot}SBu^t)_2$ ...	*	*	(1180—1215) †	(1190—1220) †	1113w	1119wm	714wm	722wm
$CH_2(SMe)_2$	1387wm	1387m, sh 1393m	1205s	1219ms 1214ms	1157w	1167wm	805m	809ms
$CH_2(SEt)_2$	1391m	1389wm	1201s	1205s	1150w	1148wm	831wm	835m
$(MeS{\cdot}CH_2)_2S$ ...	1379m	1384ms	1192s	1196s	1159vw	1153vw	776m	778, 782 } ms
					1133w or 1218wm	1135ms or 1216w	841w	842, 846 } wm
$(EtS{\cdot}CH_2)_2S$ ...	1380ms	1381ms	1192s	1191s	1161w	1165w	791m	796m
					1128w or 1215msh	1135w or 1221w	853m	859m

* The bands are obscured by other $CH_2 + CH_3$ bending bands. † One of several bands in the range quoted. ‡ Partially overlapped by a C–S stretching band. § Five bands appear on freezing.

The spectra of the *gauche*-isomers have been more difficult to establish from the spectra of the liquids, and, sometimes, have been too weak to show an outstanding band other than the 1270 $cm.^{-1}$ CH_2 wagging band. The strong internal CH_2 wagging band near 1200 $cm.^{-1}$ is the most notable of the bands shown in Table 9 and is strong evidence for the presence of substituted methanes and 1,2-disubstituted ethanes when one is examining infrared spectra of unknown sulphur-containing molecules. The presence of the internal CH_2 bending band near 1380 $cm.^{-1}$ at the same time as the wagging band near 1200 $cm.^{-1}$ is good evidence for the presence of a substituted methane provided that no normal alkyl groups larger than methyl are also present. The internal CH_2 rocking band correlations are substantiated by their probability in the lower molecules of each series, and their reproducibility throughout the series. The internal CH_2 twisting bands also show a good reproducibility throughout the series.

The main C–S stretching bands of each molecule are given in Table 10. They follow the usual pattern of decreasing frequency with increasing size of the alkyl group.[2] The spectra of molecules containing the MeS group all have C–S stretching bands between 725 and 745 $cm.^{-1}$.

TABLE 10.

Infrared frequencies ($cm.^{-1}$) of the main C–S stretching bands (liquid spectra only).

Compound	Frequency	Compound	Frequency
$(CH_2{\cdot}SH)_2$	693s, 666w, 638m	$CH_2(SEt)_2$	732s, 655w
$(CH_2{\cdot}SMe)_2$	735m, 683m	$(EtS{\cdot}CH_2)_2S$	732vs, 668m
$(CH_2{\cdot}SEt)_2$	654wm	$CHMe(SEt)_2$	701ms, 669w, 603w
$(CH_2{\cdot}SPr^i)_2$	636wm	$CMe_2(SEt)_2$	676ms, 543wm
$(CH_2{\cdot}SBu^t)_2$	590wm		
$CH_2(SMe)_2$	745s, 695s, 649w		
$(MeS{\cdot}CH_2)_2S$	739s, 710m, 697s, 660wm		
$CHMe(SMe)_2$	727m, 688ms, 608m		
$CMe_2(SMe)_2$	725w, 666ms, 538wm		

In the 1,2-dialkylthioethanes the decrease in frequency of the C–S stretching bands is similar to that of normal sulphides (unless there is an additional weak C–S stretching band

hidden by the 720 cm.$^{-1}$ CH_2 rocking band). The higher frequencies found in the substituted methanes must be due to the C–S stretching bands associated with the internal CH_2 group. Further substitution on the internal carbon atom has little effect on the methylthio-compounds, reducing the frequency by 20 cm.$^{-1}$ for dimethyl substitution. With the ethylthio-compounds, whose C–S stretching frequencies are most increased by the internal CH_2 group, the decrease of 56 cm.$^{-1}$ is much greater. It is well known that adjacent branching lowers the frequencies of C–C stretching and C–Cl stretching bands, and it could very well be the reason for the lowering of the frequencies of the C–S stretching bands here. But in this case, as we are considering a possible hyperconjugated system in the dithio-substituted methanes, there is the possibility that the higher-frequency C–S stretching bands are raised by their partial double-bond character. This is reduced by successive substitution of two electron-donor methyl groups on the central carbon atom.

In molecules containing the S·$[CH_2]_2$·S unit, the *trans*-rotational form of that unit is preferred to the *gauche*-form in the solid state. As the externally substituted alkyl group increases in size it would seem that the *trans*-S·$[CH_2]_2$·S unit also becomes predominant in the liquid. Although confirmatory evidence is needed it is likely that the methylthio-compounds in both series have an all-*trans*-conformation. The full conformation of the ethylthio-compounds cannot be established, as there are arguments in favour of both *trans*- and *gauche*-ethyl or -ethylthio-groups.

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