BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 118—121 (1966)

The Vibrational Assignment and Rotational Isomerism of 1, 2-Dithiamethyl Ethane

By Michiro HAYASHI, Yuji SHIRO, Toshiyuki OSHIMA and Hiromu MURATA
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received May 17, 1965)

The infrared and Raman spectra of 1, 2-dithiamethyl ethane have been measured in gaseous, liquid and solid states. Vibrational assignments have been made in relation to the rotational isomerism. The normal vibration calculation has been carried out in a modified Urey-Bradley force field. In the gaseous and liquid states, GTG′ and GGG molecular forms exist, while in the solid state the GTG′ form alone persists. The energy difference between GTG′ and GGG molecular forms has been found to be 1.1 kcal./mol. in the gaseous state and very small in the liquid state. The GTG′ form is more stable than the GGG form, in both the gaseous and liquid states.

In previous papers, we have dealt with the vibrational spectra of 1, 2-ethanedithiol,[1] β-halogenoethyl mercaptan[2] and *n*-propyl mercaptan[3] in relation to the rotational isomerism. The present work, the fourth of a series of papers, will deal with the vibrational spectra of 1, 2-dithiamethyl ethane. For this substance Sweeny et al.[4] discussed the possibility of rotational isomers in relation to its metal complex. However, they did not mention details of the vibrational assignments of the observed spectra, and they also did not consider the molecular forms around two C–S bonds.

In the present work, we will attempt assignments of the spectra and will consider the molecular forms around two C–S bonds as well as the C–C bond. The energy differences between the isomers will also be measured.

Experimental

1, 2-Dithiamethyl ethane was prepared by the reaction of 1, 2-dichloroethane with sodium methyl mercaptide in absolute alcohol. B. p. 84°C/20 mmHg; n_D^{20} 1.5297.

The spectra were obtained by the same apparatus and under the same conditions as we have described in the previous papers.

The infrared spectra in the crystalline state were recorded for a sample cooled with liquid nitrogen at about −120°C.

Rotational Isomerism

From a comparison of the observed spectra in the gaseous and the liquid states with those in the crystalline state, and also from a comparison of the spectra with those of 1,2-ethanedithiol which we reported in a previous paper, the following evidence of rotational isomers has been obtained.

The CH_2 wagging frequencies found for 1, 2-ethanedithiol at 1220, 1273 and 1292 cm^{-1} are also seen at 1202, 1273 and 1292 cm^{-1}, of which only 1202 cm^{-1} persists in the crystalline state. One C–C stretching frequency is seen at 1008 cm^{-1}; it disappears in the crystalline state. These are similar to those found for 1, 2-ethanedithiol. As Sweeny et al. pointed out, we may conclude that the isomer persisting in the crystalline state has the center of symmetry, which is the trans form around the C–C bond, while the other, which disappears in the crystalline state, might be the gauche form around the C–C bond.

The assignments of the observed spectra are easy from a comparison with those of 1, 2-ethanedithiol and β-halogenoethyl mercaptan. The assignments of the spectra are shown in Table I. It is important to note that there are no unassigned spectra over the spectral region obtained.

When we take the molecular forms around the two C–S bonds into consideration, ten different isomers may be expected for this substance. Four of them have the trans form, and six have the gauche form, around the C–C bond. We will use the symbols G and T for the molecular forms around each internal-rotation axis, as we did in the previous papers.

The actual molecular form in the crystalline state should be either TTT or GTG′ in this notation, because the observed spectra demonstrate the mutual exclusion rule between the infrared and the Raman spectra.

To get information on the detailed molecular form, the skeletal deformation frequencies have been calculated in the Urey-Bradley force field for

---

[1] M. Hayashi, Y. Shiro, T. Oshima and H. Murata, This Bulletin, **38**, 1734 (1965).

[2] M. Hayashi, Y. Shiro, M. Murakami and H. Murata, ibid., **38**, 1740 (1965).

[3] M. Hayashi, Y. Shiro and H. Murata, ibid., **39**, 112 (1966).

[4] D. M. Sweeny, S. Mizushima and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6521 (1955).

TABLE I. OBSERVED FREQUENCIES OF 1,2-DITHIAMETHYL ETHANE (cm^{-1})

Infrared			Raman	Assignment[a]
Gas	Liquid	Solid	Liquid	
			143 w	(G) skeletal def.
			235 m	(T)
			257 m	(G)
			340 s	(T, G)
	418 w		420 w	(G)
			644 w	CS str. (G)
	655 w	656 w	651 m	CS str. (T, G)
687 m	688 s	683 m	690 s	CS str. (T)
739 m	739 s	729 s	729 m	CH_2 rock. (T)
		739 s	735 m	CS str. (T)
840 w	840 w	—		CH_2 rock. (G)
960 s	960 s	—	965 w	CH_2 rock. (G), CH_3 rock. (T, G)
	972 sh	969 s		CH_3 rock. (T, G)
1010 w	1020 w	—	1026 vw	CC str. (T, G), CH_2 rock. (T)
	1130 sh	—		CH_2 twist. (G)
1137 s	1140 s	1137 m		CH_2 twist. (T)
1204 s	1200 sh	—	1200 vw	CH_2 twist. (G)
	1209 s	1206 s		CH_2 wag. (T)
1280 s	1268 s	—		CH_2 wag. (G), CH_2 twist. (G)
	1285 sh	—		CH_2 wag. (T, G)
1324 m	1320 m	1317 m 1322 sh	1325 vw	CH_3 sym. def. (T, G)
1435 s	1419 sh	1425 s	1429 m	CH_2 bend. (T, G)
	1432 vs	1435 vs		CH_3 deg. def. (T, G)
2900 s	2900 s	2900 s	2915 vs	CH str. (T, G)
2950 s	2950 s	2950 s	2951 m	CH str. (T, G)

a) Molecular forms around the C–C bond have been given in parentheses.

six different molecular forms as a four-body problem, using the reported values[1,5] of the six necessary force constants; these values are $K(CH_2\text{–}S)=2.60$, $K(CH_2\text{–}CH_2)=3.70$, $H(CH_2CH_2S)=0.15$, $H(CH_2SCH_3)=0.157$, $F(CH_2CH_2S)=0.50$ and $F(CH_2SCH_3)=0.211$ md./Å.

The results are shown in Fig. 1, where we have also added the observed Raman lines below 500 cm^{-1}. There are five observed Raman lines below 500 cm^{-1}, where the skeletal deformation frequencies are expected, while four skeletal deformation frequencies are calculated for a unique molecular form. If the form has the center of symmetry, two of the four frequencies become inactive in the Raman effect.

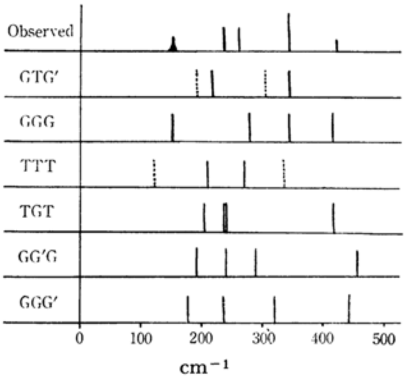

Fig. 1. Observed and calculated skeletal vibration frequencies below 500 cm^{-1}.
(……Raman inactive)

The calculated frequencies of the skeletal deformation modes show a strong dependance on the molecular forms, as we expected. The results suggest that the gauche forms for two C–S bonds are more favorable than the trans form for predicting the observed lines. Especially, the strong Raman line at 340 cm^{-1} should only belong to the frequencies for either GTG' or GGG, while the weak Raman line at 143 cm^{-1} should also only belong to the frequency for GGG. It may be noted that GTG' has the center of symmetry; this could be the molecular form in the crystalline state.

In general, the above treatment of normal vibrations is relatively uncertain, and there is difficulty in measuring weak Raman lines. Therefore, we could not determine whether GTG' is a unique molecular form in the crystalline state, and whether the other form exists in the gaseous and the

---

[5] M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **78**, 627 (1957).

liquid states in addition GTG′ and GGG. However, we believe that GTG′ and GGG are the main molecular forms for this substance.

The absorption intensity of the spectra were measured at ten different temperatures in the range from 50 to 140°C in the gaseous state, and at five different temperatures in the range from -20 to 50°C in the liquid state.

Three wagging frequencies around 1250 cm^{-1} were used in the measurements. From the observed optical densities, the energy difference of the isomers around the C–C bond has been computed to be 1.1 kcal./mol. in the gaseous state. In the liquid state, it has been found to be very small ($<$0.1 kcal./mol.).

A Refined Treatment of Normal Vibration Calculations

In the previous papers, we attempted to determine the force constants in a modified Urey-Bradley force field, considering all the vibrational freedoms. The purpose of this attempt was to determine a set of transferrable force constants which we could apply to every molecule with the $-$SCH$_2$CH$_2$S$-$ structure and, finally, to polyalkyl polysulfides.

In the first paper of this series, we determined a set from the observed spectra of 1, 2-ethanedithiol. In the second and the third papers, we tested it for the cases of β-halogenoethyl mercaptan and n-propyl mercaptan and found that the agreement between the observed and the calculated frequencies is quite satisfactory. In the present work, we have tried to apply the set to 1, 2-dithiamethyl ethane.

TABLE II. FORCE CONSTANTS

Force constants transferred from the set obtained from 1, 2-ethanedithiol

K(C–S)	md./Å	2.9	t(CH$_2$CH$_2$)	md·Å	0.136
K(C–C)	md./Å	2.0	g(CH$_2$CH$_2$)	md·Å	-0.051
K(C–H)	md./Å	4.33	l(CH$_2$)	md·Å	0.057
H(HCH)	md./Å	0.331	F(HCH)	md./Å	0.2
H(HCS)	md./Å	0.294	F(HCS)	md./Å	0.192
H(HCC)	md./Å	0.156	F(HCC)	md./Å	0.459
H(SCC)	md./Å	0.052	F(SCC)	md./Å	0.560
κ(CH$_2$)	md·Å	0.058	Y(CH$_2$CH$_2$)	md·Å	0.15

Force constants transferred from the set obtained from dimethyl sulfide

H(HCS)	md./Å	0.04	F(HCS)	md./Å	0.76
H(HCH)	md./Å	0.38	F(HCH)	md./Å	0.2
H(CSC)	md./Å	0.22	F(CSC)	md./Å	0.21
t(CH$_3$SC)	md·Å	0.07	g(CH$_3$SC)	md·Å	-0.07
Y(CH$_3$S)	md·Å	0.052	κ(CH$_3$)	md·Å	0.06
n(CH$_3$)	md·Å	0.03			

$F' = -(1/10)F$

l; Interaction term within the CH$_2$ group

t, g; Trans and gauche interaction terms for the CH$_2$CH$_2$ group and the CH$_3$SC group

Y; Force constants for torsional vibration

n; Interaction term within the CH$_3$ group

The force field adopted in the calculation is a modified Urey-Bradley force field, which has been described fully in the first paper of this series; it will also be described separately in a paper in which we will use dimethyl sulfide as an example.[6] All the force constants used are listed in Table II. To simplify the treatment, the C–H stretching modes were split from the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices by the high-frequency splitting technique.

Twenty-seven force constants are required, of which sixteen can be transferred from the set obtained from 1, 2-ethanedithiol, while eleven can be transferred from the set obtained from dimethyl sulfide. The calculations have been carried out on the assumption of two pairs of molecular forms. One of them is a pair (TTT and TGT) which have the trans form around two C–S bonds, while the other is a pair (GTG′ and GGG) which have the gauche form around two C–S bonds. The results are shown in Table III for fifty-one observed frequencies.

From the table, it may be seen that the influence of the molecular forms around two C–S bonds makes no essential difference in the calculated frequencies except in the frequencies of skeletal deformation modes. This indicates that we will have no chance to confirm the molecular forms around the C–S bond unless we examine the skeletal deformation modes. Though the observed Raman lines for the skeletal deformation frequencies are all relatively weak, the five observed Raman lines assigned to skeletal deformation modes can be much better predicted on the assumption of one pair (GTG′ and GGG) than on that of the other pair (TTT and TGT).

Therefore, we have concluded that GTG′ and GGG are the actual molecular forms for this substance; of these, GTG′ persists in the crystalline state.

The agreement between the calculated and the observed frequencies, assuming that the molecular forms are GTG′ and GGG, is quite satisfactory; the transferability of the set of force constants has also been proved for this substance.

The Assignment of CH$_2$ Rocking Frequencies

As is shown in Table I, there are several differences in the assignments of the observed spectra between ours and those reported by Sweeny et al. They reported that 840 and 900 cm^{-1} were two CH$_2$ rocking vibrations for the gauche isomer. We found a very weak band at 890 cm^{-1} at first. However, this disappeared after careful distillation, while that at 840 cm^{-1} remained unchanged.

---

[6] M. Hayashi, Y. Shiro and H. Murata, to be published.

TABLE III. OBSERVED AND CALCULATED FREQUENCIES OF 1, 2-DITHIAMETHYL ETHANE IN cm^{-1}

Trans form[a]			Gauche form[a]			
Obs.	Calcd.		Obs.	Calcd.		Assignment
	TTT	GTG′		TGT	GGG	
1432	1448	1448	1432	1447	1448	CH_3 deg. def.
1419	1426	1420	1419	1425	1428	CH_2 bend.
1321	1348	1348	1321	1347	1348	CH_3 sym. def.
1285	1296	1293	1268	1253	1254	CH_2 wag.
965	Ag 969	g 980	972	983	984	CH_3 rock.
1020	1020	1009	1020	997	1013	CC str.
735	726	713	651	654	647	CS str.
651	653	649	644	634	629	CS str.
340	281	344	143	A 245	A 138	CCS def.
235	208	214	340	204	340	CSC def.
1432	1447	1448	1432	1448	1448	CH_3 deg. def.
1140	1163	1159	1195	1180	1176	CH_2 twist.
959	961	964	972	981	980	CH_3 rock.
739	Au 717	u 724	960	960	959	CH_3 rock.
—	184	198	—	168	177	CH_3S torsion
—	110	77	—	84	110	CH_2CH_2 torsion
—	46	47	—	56	41	CH_2S torsion
1432	1450	1448	1432	1448	1448	CH_3 deg. def.
1419	1420	1420	1419	1423	1425	CH_3 deg. def.
1321	1347	1347	1321	1348	1348	CH_3 sym. def.
1209	1215	1211	1285	1298	1291	CH_2 wag.
972	Bu 986	u 985	972	983	980	CH_3 rock.
683	690	695	651	650	655	CS str.
655	646	660	644	648	642	CS str.
—	334	309	257	231	272	CSC def.
—	99	142	420	B 446	B 428	CCS def.
1432	1447	1448	1432	1448	1448	CH_3 deg. def.
1268	1282	1280	1130	1151	1151	CH_2 twist.
965	960	978	960	975	965	CH_3 rock.
1020	Bg 1023	g 1039	840	779	785	CH_2 rock.
—	176	169	—	176	170	CH_3S torsion
—	104	91	—	49	51	CH_2S torsion

a) Molecular form around the C–C bond.

Therefore, the band at 900 cm^{-1} may be caused by an impurity.

We regarded one of the CH_2 rocking modes as overlapping with a CH_3 rocking frequency at 960 cm^{-1}. For the trans isomer, since in the crystalline state the band at 739 cm^{-1} exists as a doublet, this band has two components, that is, one of the CH_2 rocking modes and one of the C–S stretching modes, as Sweeny et al. pointed out. The other CH_2 rocking modes for the trans isomer might be at 1020 cm^{-1}.

The frequency differences in the two CH_2 rocking modes are found to be 281 and 120 cm^{-1} for the trans and the gauche isomers respectively, while 221 and 62 cm^{-1} are found for 1, 2-dichloroethane, which Sweeny et al. chose as the standard. If the band at 900 cm^{-1} actually existed, the frequency differences for this substance could be close to those for 1, 2-dichloroethane. Since the band at 900 cm^{-1} does not exist, we have a large difference between these substances. However, when all the CH_2 rocking frequencies of the series of molecules which we studied are taken into consideration, the assignment of the two CH_2 rocking modes to 840 and 960 cm^{-1} for the gauche isomer is not only reasonable but inevitable.

The results of normal vibration calculations support the present assignment.

As we pointed out in the third paper of this series, we believe that this is a characteristic difference for the series of molecules containing sulfur atoms. It is worth noting that this improvement in the assignment does not have any influence on the discussions of the metal complex which Sweeny et al. reported on.