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The Vibrational Assignment and Rotational Isomerism of *n*-Propyl Mercaptan

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The infrared and Raman spectra of *n*-propyl mercaptan have been measured and vibrational assignments made with 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, TT and GT molecular forms have been confirmed to exist. An appreciable energy difference in the isomers has been found even in the liquid state. The TT form has a lower energy than the GT form. The CH_2 hydrogen deformation frequencies of CH_2CH_2 groups in molecules similar to *n*-propyl mercatpan have been listed and discussed in relation to their molecular forms.

In a series of studies[1,2] we have studied the Raman and infrared spectra of molecules containing sulfur atoms in relation to the rotational isomerism. As a continuation of this reseach, we shall now report on the vibrational spectra of *n*-propyl mercaptan. This is the third of this series of papers.

For this substance, Scott et al.[3] pointed out the possibility of rotational isomers and gave a brief assignment of the observed spectra as a mixture of the trans and the gauche isomers around the C–C bond. This assignment, unfortunately, requires many improvements when a comparison is made with other members of the series of molecules we have studied.

In the previous papers, we pointed out a tendency toward hydrogen deformation frequencies in molecules containing sulfur atoms. In this paper, we will summarize the results of all the studies of this series of molecules.

Experimental

The sample used for the measurements was commercial *n*-propyl mercaptan which had been carefully redistilled. B. p. 67°C; n_D^{20} 1.4351.

The spectra were obtained by the same apparatus and under the same conditions as we have described in the previous papers. We attempted to measure the infrared spectra in the crystalline state for a sample cooled by liquid nitrogen at about -120°C. However, we could not make the sample in the crystalline state, though we could measure the spectra in a very viscous liquid state. The observed spectra in the liquid state were in a good agreement with those reported by Scott et al.

Rotational Isomerism

Though the spectra in the crystalline state are not available, the infrared spectra recorded at about -120°C have shown large changes in their relative absorption intensities.

Around 800 cm^{-1}, we have three bands, at 815, 793 and 779 cm^{-1}, of which the one at 779 cm^{-1} appears as a shoulder of the strongest band at 793 cm^{-1} at room temperature, while at a low temperature, the one at 815 cm^{-1} becomes the

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[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] R. E. Pennington, D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, I. A. Hossenlopp and G. Waddington, *J. Am. Chem. Soc.*, **78**, 3266 (1956).

TABLE I. OBSERVED SPECTRA OF *n*-PROPYL MERCAPTAN IN cm^{-1}

Infrared			Raman	
Gas	Liquid (Room temp.)	Liquid[a] (Low temp.)	Liquid	Assignment[b]
			233	Skeletal def. (G), C–SH torsion (T, G)
			290	CH_3 torsion (T)
			363	Skeletal def. (T)
			417	Skeletal def. (G)
655 s	655 s		651	CS str. (G)
710 s	706 m	706 vs	701	CS str. (T)
735 m	736 m	736 vs	736	CH_2 rock. (T)
780 w	779 sh	780 w	779	CH_2 rock. (G)
793 s	793 s	790 sh	805	CSH def. (G)
815 w	815 w	810 s		CSH def. (T)
880 sh	880 m	880 sh	880	CH_2 rock. (G)
890 s	892 s	891 vs	905	CH_2 rock. (T)
920 w	925 w	918 w		CH_3 rock. (G)
961 vw	961 m	960 w	964	CH_3 rock. (T)
1032 w	1032 w	1030 m	1032	CC str. (T, G)
1060 w	1060 sh	1062 m		CH_3 rock. (G)
1085 s	1088 s	1082 m		CH_3 rock. (T), CC str. (G)
1105 m	1105 s	1108 s	1103	CC str. (T)
1210 w	1208 sh		1205	CH_2 twist. (G)
1225 sh	1225 sh	1221 s		CH_2 twist. (T)
1240 s	1246 s	1249 s	1256	CH_2 wag. (T), CH_2 twist. (G)
1298 s	1298 s	1297 s	1294	CH_2 twist. (T), CH_2 wag. (G)
1340 w	1339 m	1340 m	1330	CH_2 wag. (T, G)
1380 s	1380 s	1380 m		CH_3 sym. def. (T, G)
1450 s	1440 s	1440 s	1440	CH_2 bend. (T, G)
	1458 s	1458 s		CH_3 deg. def. (T, G)
2565 s	2564 s	2560 s	—[c]	SH str. (T, G)
2950 br.	2950 br.	2950 br.	—[c]	CH str. (T, G)

a) Measured at about −120°C.
b) Molecular forms around the C–C bond are shown in parentheses.
c) Not measured.

strongest band, and the band at 793 cm^{-1} appears as a shoulder of a weak band at 779 cm^{-1}.

Around 900 cm^{-1}, three bands are seen at room temperature, at 925, 892 and 880 cm^{-1}, with weak, strong and medium intensities respectively, while at a low temperature, the band at 892 cm^{-1} becomes much more intense, that at 925 cm^{-1} shifts to 918 cm^{-1} and that at 880 cm^{-1} appears as a shoulder of 892 cm^{-1}. At 1225 cm^{-1}, we have a shoulder of a strong band at 1246 cm^{-1} at room temperature, while at a low temperature, this shoulder gains in intensity and appears as a doublet with that at 1246 cm^{-1}.

There are too many observed spectra for unique molecular form, and, as Scott et al. have pointed out, we may also conclude that for this substance rotational isomers exist which have different energies even in the liquid state. The skeletal deformation frequencies have been calculated as a four-body problem using the reported values[1,4] of the force constants in the Urey-Bradley force field. The calculations have been carried out for seven different isomers around the C–C bond. It has been found that a Raman line observed at 363 cm^{-1} belongs to the trans isomer, while the lines at 233 and 417 cm^{-1} belong to the gauche isomer around the C–C bond.

When the molecular form around the C–S bond is taken into consideration, we would expect five different isomers, TT, TG, GT, GG and GG′ in the notation described in the previous papers, where the first symbol refers to the molecular form around the C–C bond, and the second, to those around the C–S bond. In the second paper of this series, we mentioned that the molecular form of the CH_2CH_2SH part of the molecule affects strongly only the CSH deformation frequencies, while its influence is negligible for the other vibrational modes. For β-chloroethyl mercaptan, a refinement of the normal vibration calculation has shown that CSH deformation frequencies for five different isomers would be arrayed in the sequence

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4) S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953).

of GG′, TG, TT and GT ranging from the higher frequencies to the lower frequencies. The highest frequency for β-chloroethyl mercaptan is 928 cm^{-1}, whie the lowest is 860 cm^{-1}.

For *n*-propyl mercaptan CSH deformation mode would be expected at a frequency region lower than those of β-chloroethyl mercaptan for two reasons; (1) the lack of C–Cl stretching modes in the lower frequency region, and (2) the introduction of the CH$_3$ rocking modes at the frequency region higher than the region where the CSH deformations would be expected.

We have five infrared bands, at 925, 892, 880, 815 and 793 cm^{-1}, of which those at 925, 880 and 793 cm^{-1} may be attributed to the gauche bands around the C–C bond on the basis of intensity measurements at different temperatures. The bands at 925, 892 and 880 cm^{-1} are assigned to the CH$_3$ rocking modes on the basis of a comparison of the spectra with those of propane which Takahashi[5] reported. The bands at 815 and 793cm^{-1} might be the CSH deformation frequencies, of which that at 815 cm^{-1} arises from the trans isomer around the C–C bond. A refinement of the normal vibration calculation, which will be described below, indicates that these should be attributed to TT and GT molecular forms. As for the other three isomers (GG′, GG and TG), since the CH$_3$ rocking modes might overlap in the region expected, we could not confirm their existence.

A Refinement of the Normal Vibration Calculation

In the previous papers we attempted to test the set of force constants in a modified Urey-Bradley force field, considering all the vibrational freedoms which we obtained from the observed frequencies of 1, 2-ethanedithiol in the first paper of this series. (The details of the modifications of the Urey-Bradley force field were described in that paper.) For *n*-propyl mercaptan, we have also attempted to find the transferability of the set of force constants. All the force constants are listed in Table II. To make the treatment simple, the C–H and S–H stretching modes were split out from the ***G*** and ***F*** matrices by the high-frequency splitting technique. Thirty force constants are required, of which twenty can be transferred from the set obtained from 1, 2-ethanedithiol, while ten can be transferred from propane, for which Takahashi reported the force constants.[5] The calculation has been carried out on the assumption that the molecular forms are TT and GT. The results are shown in Table III, with forty-one observed frequencies. The assignments have been found to be very satisfactory (average error, 1.9%). In the table we have also added brief descriptions of the potential energy distributions. For the other molecules of this series, we found that all the vibrational modes have relatively well-localized potential energy distributions. However, we found,

TABLE II. FORCE CONSTANTS

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

K(C–S)	md./Å	1.9	κ(CH$_2$)	md.·Å	0.058
K(C–C)	md./Å	2.2	l(CH$_2$)	md.·Å	0.057
K(C–H)	md./Å	4.33	t(CH$_2$CH$_2$)	md.·Å	0.136
K(S–H)	md./Å	3.46	g(CH$_2$CH$_2$)	md.·Å	−0.051
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
H(CSH)	md./Å	0.086	F(CSH)	md./Å	0.620
Y(CH$_2$CH$_2$)	md.·Å	0.15	Y(CH$_2$SH)	md.·Å	0.052

Force constants transferred from the set reported for propane by Takahashi.

H(HCH)	md./Å	0.37	F(HCH)	md./Å	0.2
H(HCC)	md./Å	0.186	F(HCC)	md./Å	0.54
H(CCC)	md./Å	0.275	F(CCC)	md./Å	0.335
κ(CH$_3$)	md.·Å	0.008	Y(CH$_3$CH$_2$)	md.·Å	0.15
t(CH$_3$CH$_2$)	md.·Å	0.118	g(CH$_3$CH$_2$)	md.·Å	0.0

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

l; Interaction term within the CH$_2$ groups

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

Y; Force constant for torsional vibration

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[5] H. Takahashi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 978 (1962).

TABLE III. OBSERVED AND CALCULATED FREQUENCIES OF *n*-PROPYL MERCAPTAN IN cm^{-1} c)

Trans form (TT)a)			Gauche form (GT)a)		
Obs.	Calcd.	Interpretationb)	Obs.	Calcd.	Interpretationb)
1458	1457	CH_3 deg. def. (80)	1458	1453	CH_3 deg. def. (80)
1458	1449	CH_3 deg. def. (80)	1458	1445	CH_3 deg. def. (80)
1440	1437	CH_2 bend. (90)	1440	1423	CH_2 bend. (90)
1440	1421	CH_2 bend. (90)	1440	1421	CH_2 bend. (90)
1380	1371	CH_3 sym. def. (95)	1380	1373	CH_3 sym. def. (95)
1339	1334	CH_2 wag. (70)	1339	1333	CH_2 wag. (70)
1298	1277	CH_2 twist. (90)	1298	1279	$\underline{\mathrm{CH_2\ wag.}}$ (60), CH_2 twist. (20)
1246	1266	CH_2 wag. (70)	1246	1236	$\underline{\mathrm{CH_2\ twist.}}$ (50), CH_2 wag. (20)
1225	1232	$\underline{\mathrm{CH_2\ twist.}}$ (60), CH_3 rock. (30)	1208	1199	CH_2 twist. (70)
1105	1101	$\underline{\mathrm{CC\ str.}}$ (40), CH_3 rock. (35)	1088	1062	$\underline{\mathrm{CC\ str.}}$ (50), CH_2 rock. (30)
1088	1081	$\underline{\mathrm{CH_3\ rock.}}$ (60), CH_2 twist. (30)	1060	1051	$\underline{\mathrm{CH_3\ rock.}}$ (45), CH_2 wag. (45)
1032	1031	CC str. (90)	1032	1019	$\underline{\mathrm{CC\ str.}}$ (60), CH_2 twist. (20)
961	947	$\underline{\mathrm{CH_3\ rock.}}$ (30), CC str. 20) CSH def. (30)	925	940	$\underline{\mathrm{CH_3\ rock.}}$ (30), CC str. (30) CSH def. (30)
892	860	$\underline{\mathrm{CH_2\ rock.}}$ (40), CH_3 rock. (50)	880	870	$\underline{\mathrm{CH_2\ rock.}}$ (40), CH_3 rock. (40)
815	829	$\underline{\mathrm{CSH\ def.}}$ (50), CC str. (30)	793	821	$\underline{\mathrm{CSH\ def.}}$ (50), CC str. (30)
736	715	CH_2 rock. (80)	779	750	CH_2 rock, (90)
706	694	CS str. (80)	655	644	CS str. (90)
363	358	$\underline{\mathrm{CCS\ def.}}$ (60), CC str. (20)	417	435	CCS def. (80)
290	298	CH_3CH_2 torsion (90)	—	313	$\underline{\mathrm{CH_3CH_2\ torsion}}$ (70), CCC def. (20)
233	240	CH_2SH torsion (90)	233	243	CH_2SH torsion (80)
—	211	CCS def. (100)	233	222	$\underline{\mathrm{CCC\ def.}}$ (60), CH_2CH_2 torsion (40)
—	130	CH_2CH_2 torsion (90)	—	123	$\underline{\mathrm{CH_2CH_2\ torsion}}$ (80), CCC def. (20)

a) Trans form (TT); the trans form around the C–C bond and the trans form around the C–S bond.
Gauche form (GT); the gauche form around the C–C bond and the trans form around the C–S bond.

b) Diagonal elements of the potential energy distributions for mainly contributing internal coordinates are added in parentheses in %, and the underlines indecate the assignments of the spectra.

c) CH and SH stretching modes were split out in the treatments. The averaged difference between the observed and the calculated frequencies is 1.9% and the maximum difference is 6.0%.

as special features of *n*-propyl mercaptan, that some of the vibrational modes are largely mixing and that their potential energy distributions are not localized in special internal coordinates.

The Energy Difference between the Isomers

We determined the change in the absorption intensities of the spectra at a lower temperature and used it as one of the most important data for the assignment of the observed spectra to different rotational isomers.

Since these changes were observed in the liquid state, the rotational isomers are shown to have different energies, even in the liquid state. For this molecule we would think the electrostatic interaction might not depend on the molecular forms so strongly. Therefore, it seems natural to expect that the energy difference is not large in either the liquid or the gaseous state, as in the works by Mizushima and his co-workers.6) However, Scott et al. reported that, in the gaseous state, the trans isomer around the C–C bond has an energy about 400 cal./mol. lower than the gauche isomer. We also found that there is some energy difference in the liquid state, and that the trans has a lower energy than the gauche isomer. We have no idea at present how to explain this fact.

The Assignment of the Spectra

As we have mentioned above, a mixing of the vibrational modes sometimes makes the assignments of the observed spectra difficult. For example, the band at 880 cm^{-1} has almost equal contributions from the CH_3 and CH_2 rocking modes of the gauche isomer. However, we will call this band a CH_2 rocking mode, since we can find the bands at 1060 and 925 cm^{-1} for two CH_3 rocking modes, and since this band corresponds well to a CH_2 rocking mode for the other molecules of the

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6) S. Mizushima "Structure of Molecules and Internal Rotation," Academic Press, New York (1964).

series which we previously reported on. In the table, the underlining indicates the names of vibrations given in this way.

Scott et al. did not report the spectra at a lower temperature, and they did not notice that the spectra show appreciable changes in their absorption intensities. Furthermore, they took *n*-propyl bromide as the sample for comparison, while we have taken 1, 2-ethanedithiol and *β*-halogenoethyl mercaptan, in assigning the observed spectra. When we compare the infrared spectra of these substances, we immediately find that the spectra of *n*-propyl mercaptan resemble those of 1, 2-ethanedithiol and *β*-halogenoethyl mercaptan, but that they are different from those of *n*-propyl bromide both in the shapes of the bands and in their frequency values. Therefore, our choice of the sample for comparison would be much better than theirs. Therefore, we believe that our assignments are better than theirs.

Actually, we have the sum rule of $\sum\nu^2(\mathrm{TT})=8.949\times10^7$ and $\sum\nu^2(\mathrm{GT})=8.925\times10^7$ (0.3% difference), in which the CH and SH stretching frequencies are excluded from the calculation, while they reported a 1.25% difference between the sums. The most appreciable difference in the assignments between ours and theris may be those of the CH_2 rocking frequencies, which would have a great influence on the assignments of the other spectra. They took 767 and 1105 cm^{-1} for the trans isomer and 793 and 1105 cm^{-1} for the gauche isomer. It seems to us, according to this assignment, that the frequency differences between the two CH_2 rockings are too large, and also that the frequency differences between different isomers are too small. As we will discuss again below, when we take the ratio of the frequencies of different isomers, we would expect that it would be around 0.65, while it is 0.89 according to their assignments. Therefore, we think their assignments are not acceptable.

CH_2 Hydrogen Deformation Frequencies in Relation to Molecular Forms

It is well known that the CH_2 hydrogen deformation frequencies for molecules with the $-CH_2CH_2-$ structures are strongly influenced by molecular forms around the C–C bond. Especially, the frequency difference between two CH_2 rocking frequencies for the trans isomer is found, in general, to be much larger than those for the gauche isomer. In Table IV we have listed the CH_2 rocking frequencies of the molecules with rotational isomers. In the tenth column of Table IV, we have added the ratio of the frequency differences for the trans and the gauche isomers in order to make the above tendencies clear. From the table, it can be seen that this ratio is less than unity; we always have a larger ratio for the molecules containing sulfur atoms than for the typical example, 1, 2-dichloroethane. Larger ratios are also obtained for molecules which do not contain sulfur atoms. For example, it is 0.62 for succinonitrile.[7] The averages

TABLE IV. CH_2 ROCKING FREQUENCIES OF THE MOLECULES (XCH_2CH_2Y) (cm^{-1})

Molecule[a]	Trans isomer[b]				Gauche isomer[b]				Ratio[e]	Ref.
	ν_1^T	ν_2^T	Av.[c]	Dif.[d]	ν_1^G	ν_2^G	Av.[c]	Dif.[d]		
(HS, SH)	1027	718	873	309	972	769	871	203	0.66	1
(HS, Cl)	1021	724	873	297	967	778	872	189	0.64	2
(HS, Br)	1022	710	866	311	962	764	863	198	0.64	2
(HS, SCH_3)	1019	728	873	291	963	778	871	185	0.64	8
(CH_3S, SCH_3)	1010	739	875	271	958	840	899	118	0.43	9
(CH_3S, Cl)	1005	746	876	259	957	845	901	112	0.43	8
(CH_3S, Br)	1015	738	878	278	958	838	898	120	0.43	8
(HS, CH_3)	892	736	814	156	880	779	830	101	0.65	This work
(Cl, Cl)	989	768	879	221	943	881	912	62	0.28	6
(Cl, Br)	955	761	858	194	921	861	891	60	0.31	6
(Cl, CH_3)	863	729	796	134	856	788	822	68	0.51	6
(Br, Br)	934	747	841	187	897	838	868	59	0.32	6
(Br, CH_3)	849	737	793	112	838	777	808	61	0.54	6
(CN, CN)	1005	762	884	243	963	813	888	150	0.62	7

a) The formulas of the molecules are abridged. For example, (HS, SH) means $HSCH_2CH_2SH$.
b) The trans and the gauche isomers around the C–C bonds.
c) The averaged frequency values of two CH_2 rocking frequencies.
d) The differences in two rocking frequencies.
e) The ratio of the frequency differences for the trans and the gauche isomers. That is, dif.(gauche)/dif. (trans).

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[7] T. Fujiyama, K. Tokumaru and T. Shimanouchi, *Spectrochim. Acta*, **20**, 415 (1964).

[8] M. Hayashi, Y. Shiro, T. Kawakita and H. Murata, to be published.

[9] M. Hayashi, Y. Shiro, T. Oshima and H. Murata, This Bulletin, **39**, 118 (1966).

of two CH_2 rocking frequencies for the trans isomers of molecules containing sulfur atoms are found to be nearly $872\ cm^{-1} \pm 10\ cm^{-1}$, except for *n*-propyl mercaptan, while for the other molecules the averages are far from the above range.

If we arrange the molecules in the sequence of X, which stands for SH, CH_3, SCH_3, Br and Cl, we find that the ratio is strongly influenced by the exchange of X, as is shown in Table V.

For $HSCH_2CH_2X$, the ratio decreases slightly as X changes. For four other series of molecules, that is, for the $CH_3CH_2CH_2X$, $CH_3SCH_2CH_2X$, $BrCH_2CH_2X$ and $ClCH_2CH_2X$ series, the ratio decreases appreciably. In general, this ratio is largest when X is SH, becomes smaller as X changes to CH_3, SCH_3 Br and Cl successively, and is smallest when X is Cl.

TABLE V. RATIO OF FREQUENCY DIFFERENCES IN TWO CH_2 ROCKING FREQUENCIES

Y=	SH	CH_3	SCH_3	Br	Cl
$HSCH_2CH_2Y$	0.66	0.65	0.64	0.64	0.64
$CH_3CH_2CH_2Y$	0.65	—	—	0.54	0.51
$CH_3SCH_2CH_2Y$	0.64	—	0.43	0.43	0.43
$BrCH_2CH_2Y$	0.64	0.54	0.43	0.32	0.31
$ClCH_2CH_2Y$	0.64	0.51	0.43	0.31	0.28

Table VI is a similar table given for the CH_2 wagging frequencies. The frequency differences in two wagging frequencies are, in general, much smaller than those of the CH_2 rocking frequencies. Therefore, a large uncertainty is introduced into the ratio of the frequency differences of isomers. However, when X and Y stand for one of the groups, SH, CH_3, Br or Cl, the ratio of the frequency diffrences for the XCH_2CH_2Y molecule always takes a value between those of the XCH_2CH_2X and YCH_2CH_2Y molecules.

We believe, then, that the above tendencies for the CH_2 rocking and wagging frequencies will be useful in the assignment of the observed spectra.

TABLE VI. CH_2 WAGGING FREQUENCIES OF THE MOLECULES (XCH_2CH_2Y) (cm^{-1})

Molecule	Trans isomer			Gauche isomer			Ratio[a)]	Ref.
	ν_1^T	ν_2^T	Dif.	ν_1^G	ν_2^G	Dif.		
(HS, SH)	1292	1220	72	1292	1273	19	0.26	1
(HS, Cl)	1298	1222	76	1306	1281	25	0.33	2
(HS, Br)	1291	1199	92	1291	1260	31	0.34	2
(HS, SCH_3)	1290	1215	75	1290	1271	19	0.25	8
(CH_3S, SCH_3)	1285	1209	76	1285	1267	19	0.25	9
(CH_3S, Cl)	1294	1217	77	1294	1272	22	0.29	8
(CH_3S, Br)	1295	1213	82	1295	1270	25	0.31	8
(HS, CH_3)	1339	1246	93	1339	1298	41	0.44	This work
(Cl, Cl)	1304	1230	74	1304	1264	40	0.54	6
(Cl, Br)	1300	1203	97	1295	1258	37	0.38	6
(Cl, CH_3)	1338	1258	80	1338	1304	34	0.43	6
(Br, Br)	1284	1190	94	1284	1252	32	0.34	6
(CN, CN)	1359	1272	87	1339	1322	17	0.20	7

a) The ratio of the frequency differences for the trans and the gauche isomers.