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Breathing Vibration of Cyclohexane Ring in Cyclohexanol

Yoshiko TAKEOKA
Department of Chemistry, Otsuma Women's University, Sanban-cho, Chiyoda-ku, Tokyo 102

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It was found that the wave numbers of the bands due to the breathing vibration of the cyclohexane ring in the e-conformer are higher than 802 cm^{-1} in the monosubstituted cyclohexane-derivatives having substituents Cl, Br, I, SH, SD and SCH_3, while lower than 802 cm^{-1} in cyclohexanol and fluorocyclohexane. The effect of introducing OH group to the cyclohexane ring upon this band was studied.

The Raman band of cyclohexane due to the breathing vibration of the cyclohexane ring, namely A_{1g} C–C stretching vibration, has been found at 802 cm^{-1} by the studies of fundamental vibration.[1,2] In the Raman spectrum of cyclohexane-derivatives, we can assign a strong band near 800 cm^{-1} to the breathing vibration of the cyclohexane ring, because the Raman band of this vibration is expected to possess the lowest wave number among C–C stretching vibrations and also the strong intensity due to the highest symmetry of this vibration mode. By studying several halogen-derivatives of cyclohexane, it has been found that the wave numbers of the breathing vibration of the ring having substituents in the a-position or the a,a-positions do not remarkably shift from that of cyclohexane, namely, 802 cm^{-1}, and are always lower than that having substituents in the e-position or the e,e-position.[3] This fact could be explained by considering that, in the a- or the a,a-conformer, the carbon–halogen bond is situated nearly vertically to the cyclohexane ring and contributes slightly to the breathing vibration; on the other hand that, in the e- or the e,e-conformer, the carbon–halogen bond is located almost in the same plane as the cyclohexane ring and possesses an important effect upon the breathing vibration.

We have made conformational studies on cyclohexanol,[4] *trans*-2-halocyclohexanols[5] and *trans*-4-halocyclohexanols[6] by infrared spectroscopy. The existence of two mutually convertible isomers, namely the e- and the a-conformers, was found in these molecules as in halogen derivatives of cyclohexane. However, the bands of the breathing vibration for the cyclohexane ring in these molecules were not assigned except *trans*-4-chlorocyclohexanol. It would be interesting to find the bands of the breathing vibration of the ring in these molecules having OH group.

Experimental

The infrared spectra were measured by JASCO model A-302 and Perkin-Elmer model 112 spectrometers. Commercial cyclohexanol was purified by desiccation with calcium oxide and subsequent distillation.

The sample of cyclohexanol was cooled with the mixture of Dry Ice and ethanol. The supercooled solid (phase I) in a cell with potassium bromide windows changed gradually to the ordered solid (phase III) by cooling for about three hours.

Results and Discussion

We have studied the conformational isomers of cyclohexanethiol[7] which is structurally similar to cyclohexanol. It is known that the bands of C–SH stretching vibration have similar wave numbers to those of C–Cl stretching vibration, because of their similar mass. We found that only the e-conformer exists in the true solid of cyclohexanethiol as in that of chlorocyclohexane.

As shown in Table 1, some cyclohexane derivatives having monosubstituent Cl, Br, I, SH, SD and SCH_3

TABLE 1. BANDS OF THE BREATHING VIBRATION IN THE MONOSUBSTITUTED CYCLOHEXANE-DERIVATIVES (cm^{-1})

	Substituente	a-Conformer	e-Conformer	Ref.
Chlorocyclohexane	Cl	807	818 *	3, 8
Bromocyclohexane	Br	806	812 *	9
Iodocyclohexane	I	801	806 *	4, 9
Cyclohexanethiol	SH	802	817 *	7
Cyclohexanethiol-*d*	SD	802	819 *	7
Cyclohexyl methyl sulfide	SCH_3	801	818 *	9
Cyclohexanol	OH		789 *	
Fluorocyclohexane	F		793 *	10

* This band remained in the true solid.

possess the bands of the breathing vibration in the similar wave number region.

The F atom of fluorocyclohexane has a mass similar to OH of cyclohexanol, and the C–F stretching vibration have the bands in the similar region to those of the C–OH stretching vibration. Christian *et al.* showed by the infrared spectra that fluorocyclohexane possesses the e- and the a-conformers in the liquid, while almost only the e-conformer in the true solid (ordered anisotropic phase).[10]

As for cyclohexanol, many studies have been made.[4,9,12,13] It has been known that cyclohexanol has a supercooled plastic solid (disordered phase, phase I) and two true solids (ordered phases, phase II has the transition point at −7.9 °C and the phase III at −28.4 °C).[11]

It is very probable, in view of the results on fluorocyclohexane and cyclohexanethiol, that only or almost only the e-conformer exist in the true solid. However it seems that there is not yet conclusive evidence whether the true solid of cyclohexanol has only one conformer or two conformers. The infrared spectra of cyclohexanol has the very strong bands at 968 cm^{-1} and 1068 cm^{-1} in the true solid (phase II and phase III) and it has been pointed out that the C–O stretching bands for the a- and the e-conformer appear near 960 cm^{-1} and 1060 cm^{-1} respectively in the derivatives of cyclohexanol.[11,13]

The a- and the e-conformers of cyclohexanol exist in the phase I as in the liquid. There are many differences between the infrared spectra of the phase III and that of the phase I.

As shown in Table 2, the infrared spectra of cyclohexanol and fluorocyclohexane have the similarity in the 780 cm^{-1}—1070 cm^{-1} region. Around the 800 cm^{-1} region of the infrared spectra, cyclohexanol has the bands at 789 (m) cm^{-1}, 835 (w) cm^{-1}, 844 (m) cm^{-1}, and 863 (w) cm^{-1} in the liquid, while in the true solid (phase III and according to Ref. 13 also phase II) the bands at 835 cm^{-1} and 863 cm^{-1} disappear, the bands at 789 cm^{-1} and 844 cm^{-1} persist.

TABLE 2. THE SIMILARITY IN THE INFRARED SPECTRA OF CYCLOHEXANOL AND FLUOROCYCLOHEXANE (cm^{-1})

Cyclohexanol		Fluorocyclohexane (Data of Ref. 10)
Liquid	Solid (phase III)	Liquid
789 (m)	787 (m)	793 (m)
835 (w) *		830 (m) *
844 (m)	845 (m)	844 (m)
863 (w) *		865 (m) *
889 (s)	888 (s)	892 (m)
925 (w)	922 (vw)	924 (sh)
		938 (vs) *
	963 (sh)	948 (sh)
968 (vs)	973 (vs)	962 (vs)
1024 (s)	1026 (s)	1016 (vs)
		1024 (vw)
1033 (sh) *		1031 (m) *
	1049 (w)	
1068 (vs)	1067 (vs)	1049 (vs)

* This band disappeared in the true solid.

According to Ref. 10, in the same region of the infrared spectra, fluorocyclohexane has the bands at 793 (m) cm^{-1}, 830 (m) cm^{-1}, 844 (m) cm^{-1}, and 865 (m) cm^{-1} in the liquid, however in the true solid the bands at 830 cm^{-1} and 865 cm^{-1} disappear, the bands at 793 cm^{-1} and 844 cm^{-1} persist like in cyclohexanol. In the true solid of fluorocyclohexane almost only the e-conformer exists as mentioned above, the bands at 793 cm^{-1} and 844 cm^{-1} are assigned to the e-conformer and the bands at 830 cm^{-1} and 865 cm^{-1} to the a-conformer.

By the similarity of the infrared spectra in near 800 cm^{-1} region for cyclohexanol and fluorocyclohexane, the bands at 789 cm^{-1} and 844 cm^{-1} which exist in the true solid of cyclohexanol may belong to the e-conformer and the bands at 835 cm^{-1} and 863 cm^{-1} which disappear in the true solid to the a-conformer. It is very probable that only the e-conformer exists in the true solid of cyclohexanol.

Near 960 cm^{-1} cyclohexanol has one infrared band at 968 (vs) cm^{-1} in the liquid, but according to Ref. 10, fluorocyclohexane has three bands at 962 (vs) cm^{-1}, 948 (sh) cm^{-1}, and 938 (vs) cm^{-1} in the liquid, and only the 938 cm^{-1} band disappears in the true solid. As shown in Fig. 1, the shape of the 968 cm^{-1} band in the liquid cyclohexanol is largely changed in the CS_2 solution from that in the true solid. According to the similarity of the infrared spectra of cyclohexanol to that of fluorocyclohexane, it is very probable that the 968 cm^{-1} band of cyclohexanol consists of three bands in the CS_2 solution and in the liquid, while two bands in the true solid. The 968 cm^{-1} band in the liquid splits in the CS_2 solution and the lower wave number band probably consists of two bands, one of them disappear in the true solid (phase III). Then the band disappearing in the true solid may be assigned to the C–O stretching vibration for the a-conformer of cyclohexanol.

The 789 cm^{-1} band of cyclohexanol and the 793 cm^{-1} band of fluorocyclohexane in the infrared spectra have the very strong intensities in the Raman liquid spectra[10,12] and their intensities are the most strong in each near 800 cm^{-1} region. Therefore the bands at 789 cm^{-1} and 793 cm^{-1} may be assigned to the breathing vibration of cyclohexane ring in the e-conformers of cyclohexanol and fluorocyclohexne respectively.

As shown in Table 1, the wave numbers of the bands due to the breathing vibration of the e-conformer are higher than 802 cm^{-1} in the mono-substituted cyclohexane-derivatives having substituente Cl, Br, I, SH, SD and SCH_3, while lower

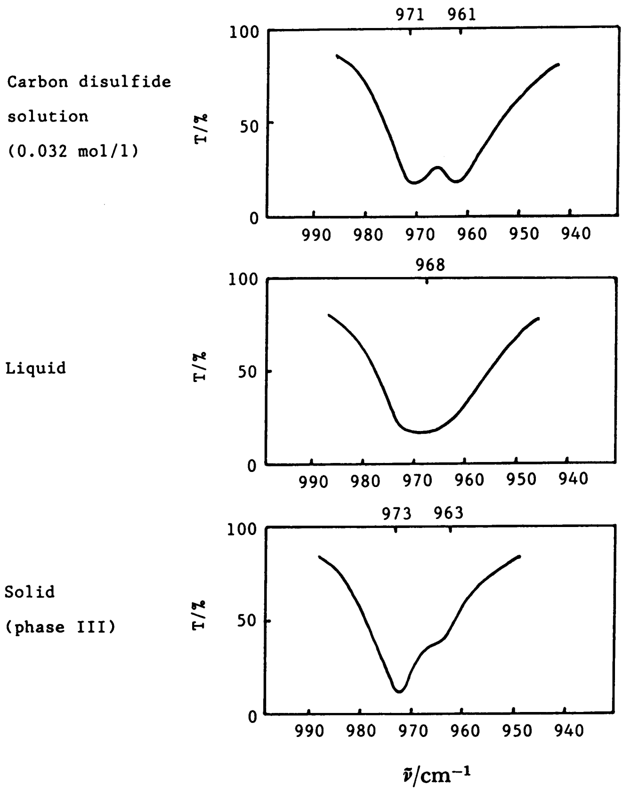

Fig. 1. Change of the 968 cm^{-1} band shape in the infrared spectra of cyclohexanol.

than 802 cm^{-1} in cyclohexanol and fluorocyclohexane. This difference may be due to the fact that the wave numbers for the bands of the C–O and C–F stretching vibrations are higher than 802 cm^{-1}, namely the band of the C–O stretching vibration at 1068 cm^{-1} and the C–F stretching vibration probably at 1049 cm^{-1} in the e-conformer, on the other hand those of the bands of C–Cl, C–Br, C–I, and C–S stretching vibrations are lower than 802 cm^{-1}, namely C–Cl at 733 cm^{-1}, C–Br at 688 cm^{-1}, C–I at 655 cm^{-1}, and C–SD at 757 cm^{-1} in the e-conformers.

As for the breathing vibration, the wave numbers of the bands for the e-conformer differ from those of the band for the a-conformer by about 5—15 cm^{-1} as shown in Table 1. However in the infrared spectra of the liquid, near the 789 cm^{-1} band of cyclohexanol and near the 793 cm^{-1} band of fluorocyclohexane, there are no bands which may be assigned to the breathing vibration for the a-conformers. In these moleculs, the bands at 793 cm^{-1} and 789 cm^{-1} may belong to both the e- and the a-conformer because of the small difference of the wave numbers in the a- and the e-band.

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