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199. **Masao Nishikawa**: Infrared Spectra of Thiourea and its Inclusion Compounds. II.*[1] Spectra of Guest Molecules.

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So-called "clathrate" or "inclusion compound" is an adduct in which one of the components wraps up some foreign molecules into a cage or a channel formed with its crystal lattice. The molecules which construct the crystal framework are designated as host molecules and those which are enclosed in it are named guest molecules.

There are many excellent investigations about the intermolecular interactions between host and guest molecules and about the mobilities of guest molecules in the cage. Meakins[1] has calculated the energy barriers of the rotation of long-chain molecules in urea occlusion compounds and concluded that the guest molecules were loosely held in the urea lattice. A study of magnetic susceptibility has been conducted by Evans and Richards.[2] They revealed that oxygen or nitric oxide molecules in β-hydroquinone clathrates have the same specific susceptibilities as those of the gas phase. Recently proton magnetic resonance work[3] has detected some free rotation and torsional oscillation of straight-chain hydrocarbons in a urea channel and less mobility of cyclohexane in a thiourea one.

Investigations on infrared spectra of guest molecules have also been published, for example, Drago and his coworkers[4] have shown that the bands due to out-of-plane vibrations of pyrrol and benzene trapped in dicyanoammine-nickel (II) appeared at somewhat different frequencies from those of liquid state but the absorptions of in-plane modes were similar between these two states within experimental error. The rotational motion of carbon dioxide has been found by Hexter and Goldbard[5] to be restricted in a hydroquinone (β-form) clathrate. Barlow and Corish[6] have investigated some normal fatty acids and diethyladipate enclosed in urea complexes and suggested that they took *trans*-zig-zag forms in a channel.

In the previous paper,*[1] infrared spectra of thiourea adducts were reported and the assignment of absorption bands due to the host molecule were determined by dichroismic investigations. The aim of the present work is to study the infrared spectra of guest molecules in thiourea adducts and to show that the infrared dichroism of the molecules which were able to form adducts with thiourea could be measured by orientating them in a hexagonal channel of thiourea.

Experimental

Thiourea used in this work was of special grade. 9-Oxocamphor-, turmerone-, and lipoic acid-thiourea adducts were prepared by H. Mima. The other adducts were obtained by the method described in the previous paper.*[1] Among the guest molecules employed, *trans*- and *cis*-decalin, 2,3-dimethylnaphthalene, and cyclohexanone were the guaranteed reagents of Tokyo Chemical Industries, Ltd. 2-Ethylanthracene was synthesized by K. Mizuno and was checked by elementary analysis.

Most spectrophotometric measurements were carried out on a Hitachi IR spectrophotometer Model

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*[1] Part I: This Bulletin, **10**, 1199(1962).

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1) R.J. Meakins: Trans. Faraday Soc., **51**, 953 (1955).

2) D.F. Evans, R.E. Richards: J. Chem. Soc., **1952**, 32.

3) D.F.R. Gilson, C.A. McDowell: Nature, **183**, 1183 (1959).

4) R.S. Drago, J.T. Kwon, R.D. Archer: J. Am. Chem. Soc., **80**, 2667 (1958).

5) R.M. Hexter, T.D. Goldbard: J. Inorg. and Nucle. Chem., **4**, 171 (1957).

6) G.B. Barlow, P.J. Corish: J. Chem. Soc., **1959**, 1706.

EPI-2 equipped with NaCl optics, an IR microscope attachment Model IM-2P being installed on it. Air absorptions were compensated by inserting a 1 m.-gas cell in the reference beam.

Ten or twenty single-crystals (needles) of thiourea adducts of about 2 mm. long and 50 μ in diameter were collected under a microscope and were arranged side by side on a thin NaCl plate ("deck glass"), the surface of which had been coated with Nujol or perfluorocarbon to make the arrangement easy. The deck glass was then placed on the IR microscope, orientating the crystals so that the image of them made on the slit took the angle of 45° to the slit. The polarized light, having the electric vector varallel or perpendicular to these crystals, were used to measure the dichroism of the guest molecules. Before measurements, the focus of the microilluminator should be readjusted by regulating the alignment of the condensing mirrors to minimize the transmittance at 3100 cm^{-1} where thiourea had a strong absorption band and also that of the upper mirrors to maximize the transmittance at 5000 cm^{-1} where it had no absorption. In this way, the absorption spectra of nearly the same background were obtained with the both polarized lights. Some guest molecules had too strong absorptions to be measured by this method, in which case thin orientated crystals were prepared by growing them on a NaCl plate using the technique described in the previous paper.*1

The frequencies of C=O stretching and aromatic C-H out-of-plane bending vibrations in various states were determined with a Perkin Elmer Model 221 IR spectrophotometer with prism-grating interchange assembly. The absorption bands of H_2O vapour near 1700 cm^{-1} and of NH_3 near 900 cm^{-1} were employed as frequency standards. The C=O stretching frequencies due to monomeric carboxylic acids were observed in 0.0005% CCl_4 solution. The other solution spectra were measured at the concentration of 5～0.5%. The solvents were all purified carefully by the standard methods.

Discussion

Most thiourea adducts crystallize in needles with lattice symmetry $R^{3\bar{2}}/_{c}—D^{6}_{3d}$.7,8) The needle axis coincides with a C-axis (optic axis) of crystal system and, accordingly, with the direction of the hexagonal channel formed by thiourea molecules. A unit cell consists of six thiourea molecules and some guest molecules enclathrated in the channel. The molar ratio of thiourea and its guest molecules are different from adducts to adducts depending on the size and shape of guest molecules.7) For example the ratio of 9-oxocamphor-thiourea is 3:1 and that of turmerone-thiourea is 6.2:1. If therefore, infrared spectra are determined on adducts by ordinary method, usually only the absorption bands attributable to the host molecules are obtained. However, these bands which come mostly from fundamental vibrations lie in the region between 3500 and 3000 cm^{-1}, 1650 and 1590 cm^{-1}, 1500 and 1050 cm^{-1}, and 730 and 690 cm^{-1}, and the other regions of the spectra are fairly transparent. So the absorptions due to guest molecules in the latter regions can be observed by the method described in the experimental part. Some of the results are shown in Figs. 1～5. In the figures, solid curves represent spectra obtained with polarized light parallel to the C-axis of the crystal and broken curves perpendicular to it. As a matter of course, the dichroisms of the absorption bands due to thiourea in these figures were all qualitatively the same with those observed with the thin film of adduct crystals grown on a sodium chloride plate using the technique of gradual evaporation of their methanolic solution under thermal gradient.

9-Oxocamphor (I), one of the compounds which form adducts with thiourea most easily, has been found by Mima9) to become quite stable once it was included in the thiourea channel. Its spectra determined by the aforesaid method is shown in Fig. 1(A). Two strong bands at 1745 and 1723 cm^{-1}, three weak bands between 1350 and 1230 cm^{-1}, and six bands of various intensities lying between 1060 and 770 cm^{-1}, arise from vibrations of the guest molecule. Among the bands at carbonyl region, the one at 1745 cm^{-1} would be assigned to the stretching vibration of the ring ketone and the

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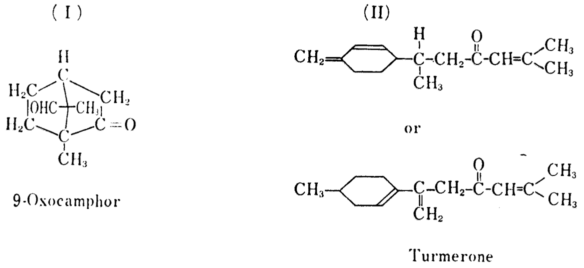
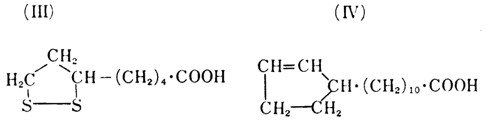
7) W. Schlenk: Ann., **573**, 142 (1951).
8) H.V. Lenne: Acta Cryst. **7**, 1 (1954).
9) H. Mima: Yakugaku Zasshi, **77**, 1196 (1957).



9-Oxocamphor

Turmerone



Lipoic acid

Hydnocarpic acid

Chart 1.

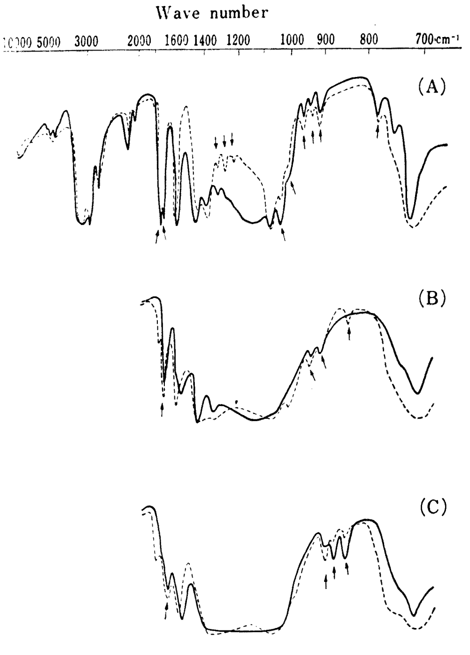


Fig. 1. Infrared Spectra of Thiourea Adducts

(A) 9-oxocamphor-thiourea
(B) camphor-thiourea
(C) cyclohexanone-thiourea
—— : electric vector parallel to the C-axis
······ : electric vector perpendicular to it

other at 1723 cm^{-1} to that of the aldehyde group, for the latter is absent in the spectrum of camphor.

Although it appears that some of the bands cited in the preceding paragraph exhibit dichroism, the phenomenon is not sure as these bands are all located on the foot of strong thiourea absorptions. The orientation of such spherical guest molecules to the definite direction, when enclosed in a thiourea channel, is however verified through the inspection of the spectra of camphor-thiourea adducts (Fig. 1(B)), in which the bands at 950 and 855 cm^{-1} show strong perpendicular dichroism against the C-axis. Similar results are obtained on the cyclohexanone-thiourea adduct (Fig. 1(C)). A band at 909 cm^{-1} is more intense when measured with the perpendicularly polarized light than with the parallel one, whereas the reverse is true to the bands at 890 and 865 cm^{-1}. These bands have been attributed to C–C stretching or CH_2 rocking vibrations[10,11] and if the mirror plane of cyclohexanone (C_s symmetry) is presumed to be parallel to the C-axis of the crystal, the former band might be assigned more likely to be A′ mode and the latter two bands to be A″ mode.

The situation is much clearer in case of *trans*-decalin-thiourea adduct. Comparing the shape of a *trans*-decalin molecule with that of a thiourea channel, one may arrive at the judgement that the guest molecule should be so arranged as the line connecting the centers of two cyclohexane rings are parallel to the C-axis of the crystal. This line is equal to the two fold axis of a *trans*-decalin molecule which belongs to symmetry group C_{2h}. According to the theory of molecular vibrations, a C_{2h} structure has four species of vibrations : A_g, B_g, A_u, and B_u. Of these, the gerade species are infrared inactive because of the presence of a center of symmetry. One of the infrared active species, A_u, has the polarization vector parallel to the two fold axis of a molecule and, consequently, parallel to the C-axis of the adduct crystal. On the other hand, the change of the dipole moment owing to B_u vibrations must be perpendicular to these axes. In Fig. 2(A) five absorption bands due to *trans*-decalin are illustrated by arrows, all exhibiting marked dichroism as expected. Four of them, situated at 970, 925, 840, and 825 cm^{-1}, match with the bands at 978, 924, 840, and 824 cm^{-1}, respectively, which are observed with liquid film of *trans*-decalin itself. And as the band at 840 cm^{-1} absorbs the polarized light parallel to the C-axis, the above consideration would assign this band to A_u species. The other three bands which show perpendicular dichroism, should belong to B_u species. Appearance of the remaining band at 880 cm^{-1}, could not be interpreted without ambiguity at this stage, but a possibilty exists that a Raman band[12] at 875 cm^{-1} might be altered to be infrared active on account of some distortion from C_{2h} symmetry forced by the thiourea framework. If this supposition is accepted, the band would be attributed to B_g species as deduced from its dichroismic behavior.

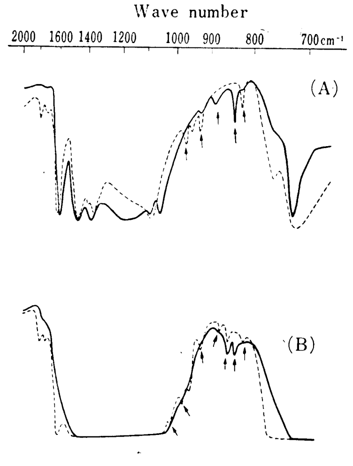


Fig. 2. Infrared Spectra of Decalins-Thiourea Adducts

(A) *trans*-decalin
(B) *cis*-decalin
—— : electric vector parallel to the C-axis
······ : electric vector perpendicular to it

The spectra of *cis*-decalin would be analyzed in the same manner. The molecule possesses C_{2v} symmetry, the axis of which is normal to the plane determined by two cyclohexane rings. In this case B_1 species is identified distinctly through its parallel polarization vector against the C-axis of the adduct crystal but A_1 and B_2 species can not be differentiated. In fact, all the seven absorptions found in the spectrum of liquid

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10) E. Billeter, Th. Burer, Hs. H. Gunthard : Helv. Chim. Acta, **40**, 2046 (1957).
11) Th. Burer, Hs. H. Gunthard : *Ibid.*, **40**, 2054 (1957).
12) G. Canquil, A. Delay, J. Lecomte : Bull. Soc. Chim. France, [5], **13**, 30 (1946).

cis-decalin in a region between 1020 and 820 cm^{-1} appear in either of the two spectra determined by the present method (Fig. 2 (B)), from which only the following assignment could be derived: the band at 835 cm^{-1} belongs to B_1 species and those at 1010, 967, 923, 870, and 825 cm^{-1} belong to either A_1 or B_2 species. The band at 852 cm^{-1} absorbs both polarized lights almost equally and, therefore, might be composed of two bands having different dichroism.

The results obtained from the similar experiments on thiourea adducts with aromatic compounds are just like they are anticipated. That is, the out-of-plane bending vibrations (B_2 species) of isolated ring hydrogen atoms at positions 1 and 4 in 2,3-dimethylnaphthalene which has C_{2v} pseudosymmetry appear at 874 cm^{-1} and absorbs perpendicularly polarized light more intensely than oppositely polarized one (Fig. 3 (A)). The same is true for the bands at 898, 888, and 809 cm^{-1} in 2-ethylanthracene (Fig. 3 (B)). In this case, the former two arise from isolated ring hydrogen atoms at positions 1, 9, and 10 and the latter from two adjacent atoms at positions 3 and 4. It must be noticed here that the feature of these bands resembles rather with that in the spectrum of solutions than of solid state (Figs. 3 (B) and 4).

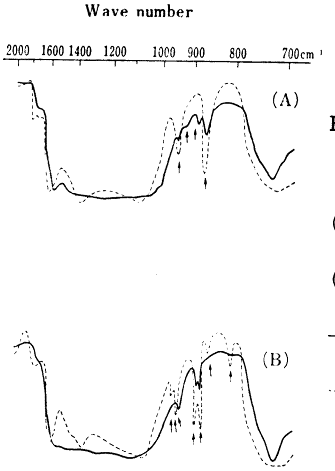

Fig. 3. Infrared Spectra of Thiourea Adducts with Aromatic Compounds

(A) 2,3-dimethylnaphthalene-thiourea
(B) 2-ethylanthracene-thiourea
—— : electric vector parallel to the C-axis
······ : electric vector perpendicular to it

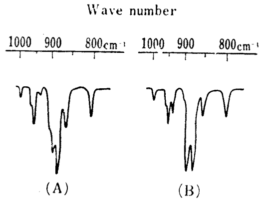

Fig. 4. Out-of-plane Bending Vibrations of 2-Ethylanthracene

(A) solid state
(B) CS_2 solution

Some other interesting observations revealed by the studies of this kind are shown in Figs. 5 (A) and (B). Turmerone (II),[13] an active constituent of curcuma oil, would direct its carbonyl group perpendicular to the long axis of the molecule as realized from Fig. 5 (A) when it is enclosed in a thiourea channel. This conformation corresponds with an extended form of the side chain attached to the cyclohexene ring.

Although lipoic acid (III)-thiourea adduct has been specified by Mima and his colaborators[14] to form a crystal of a different symmetry system, its infrared spectrum[14] and dichroismic behavior (Fig. 5 (B)) remain unchanged from other adducts. The fact suggests that the modification of crystal configuration would not be of great significance and the direction of a channel constructed by thiourea molecules would still coincides with a needle axis of the crystal. Further studies concerning with the asignment of lipoic acid in a thiourea channel were conducted assuming the crystal structure described above and the tail-to-tail or dimer configuration was ascertained from the following reasons. First, the band at 930 cm^{-1} (Fig. 5 (B)) seems to be a characteristic absorption due to the out-of-plane bending vibration of OH groups in a carboxylic acid dimer and,

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13) H. Mima: Yakugaku Zasshi, **79**, 644 (1959).
14) H. Mima, Y. Asahi, H. Okuto, T. Kanzawa: *Ibid.*, **80**, 1233 (1960).

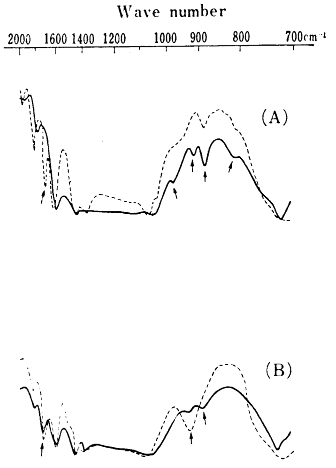

Fig. 5. Infrared Spectra of Thiourea Adducts

(A) turmerone-thiourea
(B) lipoic acid-thiourea
—— : electric vector parallel to the C-axis
······ : electric vector perpendicular to it

indeed, it exhibits strong perpendicular dichroism as shown in the figure. Secondly, the frequencies of C=O stretching vibrations of carboxylic groups were determined on lipoic acid- and hydnocarpic acid (IV)-thiourea adducts. The results are compared with those of carboxylic acid monomers in dioxane, acetonitrile or dilute carbon tetrachloride solutions and with those of dimers in chloroform or concentrated carbon tetrachloride solutions (Table I), indicating the dimer formation of the both acids in a thiourea channel. This conclusion agrees with the works carried out by Barlow and Corish⁽⁶⁾ on *n*-fatty acids-urea adducts.

Table I. Frequencies of C=O Stretching Vibrations of Carboxylic Acids in Various States

	State of carboxyl group	Lipoic acid (cm^{-1})	Hydnocarpic acid (cm^{-1})
Crystalline state	dimer	1688	1701
$CHCl_3$ soln.	〃	1709	1708
CCl_4 soln.	〃	1709	1709
	monomer	1755	1755
Dioxane soln.	〃 [a]	1734	1734
Acetonitrile soln.	〃 [a]	1734	1734
Thiourea adduct		1708	1709

a) Hydrogen bonded with solvent molecules.

The studies discussed above would propose a new method of investigations about infrared dichroism of organic molecules whose crystal structures have not yet been elucidated or whose dichroismic measurements are, with some other causes, difficult by ordinary methods. Certainly, the use of this method is restricted to the bands falling in limited frequency ranges and to the molecules of suitable size. However, the restrictions would be released to some extent by employing thiourea-d_4, urea or urea-d_4 as host molecules.

Finally, the similarity of spectra of guest molecules determined by the present method with those in solutions makes one think of "solvent effect" or environment effect upon guest molecule vibrations exerted by thiourea cage. It is well known that the frequencies of C=O stretching vibrations of carbonyl groups decrease with increasing dielectric constant or refractive index of solvents whereas the out-of-plane bending frequencies of aromatic compounds are related with these constants in inverse way. The state of guest molecules enclathrated in thiourea would not be exactly identical with that in solutions but surrounding thiourea molecules should have an analogous influence upon the guest molecules. In Table II it was contrasted with solvent effect. Such influence is of course not necessarily the same among the different guest molecules. It might depend upon the position occupied by functional groups of guest molecules in a thiourea channel and also upon the direction of dipole moment changes against the C-axis when the groups oscillate. These factors, however, have not been estimated at present and, roughly, neglecting them one recognizes through the data listed in the table that the effect exercised by thiourea upon both C=O stretching and aromatic C-H out-of-plane bending vibrations is comparable with that of the solvents having dielectric constants 2.5～5.5.

TABLE II. Environmental Effect

	Dielectric const. (20°C) (cm^{-1})	Menthone (cm^{-1})	Camphor (cm^{-1})	Cyclohexanone (cm^{-1})	2,3-Dimethylnaphthalene (cm^{-1})	2-Ethylanthracene		
						solo		duo
						(cm^{-1})		(cm^{-1})
Liquid or Solid		1706	1737[a)]	1709	877	907.5	894	813
CH_3CN soln.	37.45	1702	1737	1705	878			
$ClCH_2 \cdot CH_2Cl$ soln.	10.60	1704	1735	1705	872			
Tetrahydrofuran soln.	7.58	1709	1743	1714	872.5			
ϕ-Cl soln.	5.68	1706	1740	1711	873			
$CHCl_3$ soln.	4.80	1699	1735	1702	874.5	900	888.5	812
Et·O·Et soln.	4.34	1712	1746	1718	873			
CS_2 soln.	2.63	1710	1742	1713	871			
CCl_4 soln.	2.24	1711	1743	1715	872.5	898	886.5	
Decalin soln.	2.12	1714	1748	1720	871.5			
Cyclohexane soln.	2.03	1715	1751	1720	870.5	896	884.5	803
n-Hexane soln.	1.89	1715	1751	1722	870.5			
Vapour		1725	1762	1738				
Thiourea adduct		1710	1740	1714	874	898	888	809

a) These values are different from those determined by Josien, *et al.*[15] by 4 cm^{-1}.

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Summary

The infrared dichroismic behaviors of molecules enclosed in a thiourea channel were investigated with an infrared microscope by using oriented single crystals of adducts. The absorptions of guest molecules in the region between 3000 and 1650 cm^{-1}, 1590 and 1500 cm^{-1}, and 1050 and 730 cm^{-1} were found to be measurable with this technique. The vibrational species of some of these absorptions were determined, especially in case of *trans*- and *cis*-decalins. Molecules having carboxylic group were revealed to form dimers as in solutions when they were included in a thiourea channel. This technique would be used to study dichroism of some kinds of organic molecules under certain limitation. Environmental effect exerted by thiourea cage has been also estimated. The results showed that it is comparable with that of solvents of dielectric constant 2.5～5.5.

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15) L. Josien, J. Lascombe: J. Chim. Phys., **52**, 162 (1955).