

Difference in the X-Ray Diffraction Patterns of some Isomers

By

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Abstract

The X-ray diffraction of some ordinary and optical isomers was examined by the photographic method. The former present remarkable difference with one another, the latter, however, no difference.

The effect of temperature which was also investigated, indicated the same result as above.

Introduction

The principal peak in the X-ray diffraction patterns of liquids is due to the interference between the separate molecules and the intensity distribution to the molecular forms. The principal object of this experiment is to find how the change in molecular forms of isomers affects their X-ray diffraction patterns.

Experiment

The apparatus employed is the same as that used by S. Tanaka and A. Tsuji which is described in detail elsewhere¹. The time of exposure was 1-3 hours for a long slit and 2-5 hours for a circular slit. The samples were extra pure ones manufactured by Kahlbaum or Merk, and only those selected which by test were not affected by such an exposure. Two or more photographs were taken of each sample by changing the distance between the sample and the photographic plate. The substances presently examined are *d* and *l* pinene and limonene for the optical isomers and many other isomers of the molecular formula $C_{10}H_{16}$, $C_{10}H_{16}O$ and $C_{10}H_{18}O$ etc.

1. S. Tanaka and A. Tsuji: These Memoirs, **13**, 169, (1930). and **13**, 338, (1930).

Result

Some of the photographs were reproduced in the annexed figures and the results were more exact than those reported before. The

Table 1.

Name of liquid	molecular formula	d
<i>d</i> -pinene	C ₁₀ H ₁₆	5.66 A. U.
<i>l</i> -pinene	"	5.66 "
<i>dl</i> -pinene	"	5.66 "
<i>d</i> -limonene	"	5.42 "
<i>l</i> -limonene	"	5.42 "
<i>dl</i> -limonene	"	5.42 "
Terpinolene	"	5.37 "
<i>dl</i> - α -phellandrene	"	5.08 "
<i>d</i> -camphene (solid)	"	5.59 "
<i>d</i> -pinene+ <i>dl</i> -limonene	"	5.54 "
<i>l</i> -menthone	C ₁₀ H ₁₈ O	5.01 "
Linalol	"	4.76 "
Geraniol	"	4.60 "
<i>dl</i> -fenchone	C ₁₀ H ₁₆ O	5.49 "
Citral	"	4.54 "
Eugenol	C ₁₀ H ₁₂ O ₂	5.42 "
Iso-eugenol	"	3.72 "
Safrol	C ₁₀ H ₁₀ O ₂	4.45 "
Iso-safrol	"	4.02 "

Table 2.

Name of liquid	Temperature	d
<i>d</i> -pinene	13.6°C	5.66 A. U.
	55.0°C	5.72 "
	110.0°C	5.80 "
	150.0°C	5.87 "
	163.0°C	5.92 "
<i>l</i> -pinene	19.6°C	5.66 "
	95.0°C	5.78 "
<i>dl</i> -pinene	25.0°C	5.66 "
	140.0°C	5.86 "
<i>dl</i> -fenchone	25.5°C	5.49 "
	176.0°C	5.98 "
	230.0°C	6.25 "
<i>l</i> -limonene	19.0°C	5.42
	57.0°C	5.50 "
	100.0°C	5.59 "
	125.0°C	5.65 "
	150°C-154°C	5.72 "
	175°C-180°C	5.82 "

results obtained at the room temperature are given in Table 1. and those for other temperatures in Table 2., where d was calculated simply by Bragg's equation $n\lambda = 2d \sin \theta$ corresponding to the intensity maxima of the principal halo.

We can see at once that there are variations in d excepting the case of the optical isomers which indicate not only d but also no difference in the form of the pattern. For instance the patterns of all pinenes are composed of a sharp principal halo accompanied by a secondary one in its inner side and those of limonenes give somewhat diffuser patterns showing, however, the similar intensity distribution. On the other hand the remarkable diminution of d for the ordinary isomers is always accompanied by the diffuseness of the patterns, and seems to indicate the connection between the phenomena and the side chain¹. i. e. the diminution of d and the increase of the diffuseness are parallel, in this case, to the degree of the unsymmetry of molecular forms. It is also noted that di-cyclic terpens and their derivatives give generally sharper haloes than mono-cyclic terpens and their derivatives.

Next we shall describe the effect of temperature upon the patterns. Attention must be paid to the chemical change which will occur by the elevation of the temperature. For instance the pinene will isomerise into dipentene by heating it over 200°C which can clearly be known by observing the change of the diffraction pattern.

Table 3.
d-pinene

	Temperature	d
Not heated		5.66 A. U.
After heating	180°C	5.66 "
"	200°C	5.60 "
"	250°C	5.42 "

This was shown in Table 3. All data were obtained with the photographs taken at room temperature by cooling the samples after heating about 2 hours. Pinenes having d of 5.66 A. U. at room temperature indicate, after heating 250°C, d of 5.42 A. U. which is equal to that of limonenes.

The elevation of the temperature always produces the diminution of d and the increase of the diffuseness. The same phenomena hold

1. S. Tanaka and A. Tsuji: These Memoirs, 13, 10, (1930).

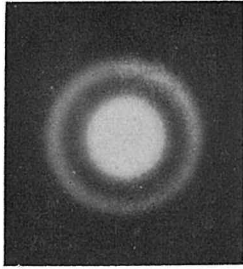
for the optical isomers, but, for ordinary isomers, there exist the characteristic properties. Thus we can not, in this case also, distinguish the diffraction patterns of the optical isomers, but it is otherwise for the ordinary ones.

In conclusion the writer's hearty thanks are due to Prof. M. Ishino of Kyoto Imperial University, for his interest in this research, and also to Prof. S. Tanaka, the director of this laboratory, for the guidance throughout the work.

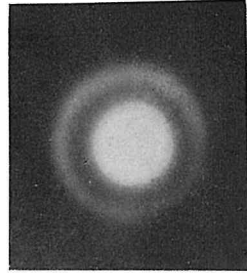
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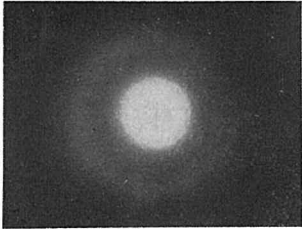
Plate I



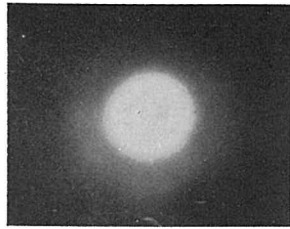
α -Pinene



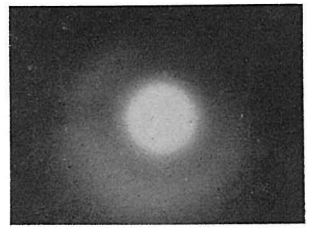
l-Pinene



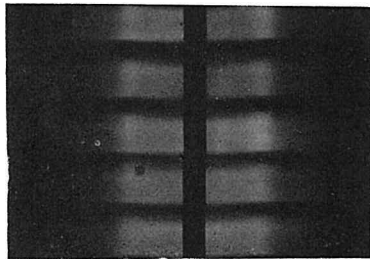
l-Limonene



Terpinolene



dl- α -Phellandrene



13.6°

55.0°

110.0°

150.0°

163.0°

α -Pinene