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X-ray Diffraction of Some Organic Substances in the Solid and liquid States

By

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Abstract

Of five organic substances, powder patterns were compared with liquid patterns. The results are as follows; (1) Corresponding to the intense lines in the crystal patterns, there appear liquid bands, (2) If these crystal lines keep at moderate distances from one another, we get separate liquid bands corresponding to each of them, (3) If these crystal lines lie close together, corresponding to them we get a broad and diffuse band in the liquid state. From these characters it may be concluded that the crystal planes which produce the intense reflection seem to maintain their properties when the crystal becomes liquid.

Investigations of the relations between the crystal and liquid patterns have already been performed with many substances. Eastman¹ investigated them with benzene, Herzog and Jancke² with more than twenty organic substances. P. Krishnamurti³ also investigated them with some di-substituted benzene derivatives and some other aromatic hydrocarbons and he pointed out some relations between the crystal dimensions and data derived from the liquid patterns.

The object of the present investigation is to study how the crystal lines are related to the liquid bands, by which means the structure of a liquid seems likely to be cleared up in some degree. The deeper investigation of the subject has, however, been left for the future.

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1. Eastman, J. Amer. Chem. Soc., **46**, 917, 1924.
 2. Herzog and Jancke, ZS. f. Phys., **45**, 194, 1927.
 3. P. Krishnamurti, Ind. J. Phys., **3**, 225, 1928; also **5**, 543, 1930.

Experiment and Results

The experimental apparatus and working conditions were almost the same as in the previous experiment.¹ The Shearer metal tube with copper anticathode was now evacuated with the mercury diffusion-pump and excited at about 55 kilovolts, the current through the tube being 3.2—4.2 milliamperes. The time of exposure was 4—6 hours for solids, and 6—9 hours for liquids. The sample was sealed in a thin glass tube 1 mm. in diameter. Many photographs corresponding to various temperatures were taken with samples in the solid state, all of which showed that the crystal lines did not change their appearance until the melting point was reached. The liquid patterns were photographed at the temperature of 10—20°C above the melting point. The substances now studied were Phenanthrene^K, α -Naphthol^M, β -Naphthol^K, α -Naphthylamine^M and β -Naphthylamine^{K2}. The spacings corresponding to the important crystal lines and liquid bands were calculated from Bragg's formula and are shown in the tables given below.

*Phenanthrene*³: In the powder photographs, there can be seen one intense line near the direct incident ray, and apart from this, three intense lines lying close together and keeping almost equal distances. There are two liquid bands; both are very broad and diffuse and are observed with difficulty. The inner band, with the maximum intensity at the spacing 8.55 A.U., corresponds to the crystal line near the direct incident ray, and the outer band, with the maximum intensity at the spacing 4.50 A.U., covers the range from 5.07 A.U. to 3.45 A.U. in the powder pattern. The other fainter lines in the powder pattern are lost in the general scattering in the case of the liquid one.

α - and β -Naphthol: For the α -Naphthol there appear two fairly sharp liquid bands, corresponding to the two intense crystal lines. Besides, at a small angle, there seems to exist a third faint band.

β -Naphthol has an intense line in the crystal pattern and shows only one liquid band, the sharpness of which is nearly equal to that of the band of α -Naphthol. There is, also, a moderate amount of scattering at small angles in the liquid pattern.

1. Tanaka and Tsuji, These Memoirs, **13**, 337. 1930.

2. The letters attached to the names of the samples mean "Merck" and "Kahlbaum", the manufacturers.

3. P. Krishnamurti, loc. cit. (the latter)

In the tables we use the following abbreviations :

v.s.=very strong, s.=strong, m.s.=medium strong,
w.=weak, v.w.=very weak.

Table 1. Phenanthrene

Powder		Liquid		
Spacing(A.U.)	Intensity	Angle of Diffraction	Spacing(A.U.)	Intensity
9.63	m.s.	10°22'	8.55	s.
5.59	v.w.	16°51'	5.23	Inner limit of outer band.
5.07	v.s.			
4.50	v.w.	19°39'	4.50	m.s.
4.10	s			
3.45	s	27°20'	3.26	Limit of general Scattering.
2.57	v.w.			

Table 2. α - and β -Naphthol

Sample	State	Powder		Liquid		
		Spacing(A.U.)	Intensity	Angle of Diffraction	Spacing(A.U.)	Intensity
α -Naphthol		5.80	s.	14°21'	6.18	s.
		4.59	v.w.	22°29'	4.03	m.s.
		4.01	w.			
		3.80	s.	17° 6'	5.18	s.
		3.24	w.			
		2.97	v.w.			
		2.74	v.w.			
	8.11	w.	23°16'			
β -Naphthol		5.10		w.		
		4.53	v.s.			
		4.15	m.s.			
		3.72	w.			
		3.35	w.			
		2.68	v.w.			

α - and β -Naphthylamine: α -Naphthylamine has again two liquid bands of fair sharpness which correspond to two intense crystal lines. Besides, the liquid pattern seems to have a third faint band at the position corresponding to that of the crystal line 10.41 A.U. in spacing, though this cannot be definitely stated.

β -Naphthylamine has characters analogous to those of β -Naphthol. It has only one liquid band, which is more diffuse at the outer side than at the inner.

Table 3. α - and β -Naphthylamine

State Sample	Powder		Liquid		
	Spacing(A.U.)	Intensity	Angle of Diffraction	Spacing(A.U.)	Intensity
α -Naphthylamine	10.41	m.s.	14°53'	5.93	m.s.
	6.13	w.			
	4.90	s.			
	4.12	w.	22°40'	3.93	w.
	3.67	s.			
	3.13	v.w.			
β -Naphthylamine			17° 7'	5.17	m.s.
	4.76	s.	24°28'	3.64	Limit of general Scattering
	4.24	w.			
	3.78	w.			
	3.44	m.s.			
	2.90	w.			
2.48	v.w.				

Summary

From the data above mentioned we can deduce the following conclusions:

1. A substance which shows only one intense crystal line gives one fairly sharp band in the liquid pattern. (β -Naphthol).
2. One which gives two intense crystal lines moderately separated, gives two corresponding liquid bands of fair sharpness. (α -Naphthol).

3. When two or more intense crystal lines lie close together, we get a broad band in the liquid state which has its maximum intensity at the position corresponding to that of the most intense crystal line, and which is more diffuse at the side where the less intense lines are situated. (β -Naphthylamine, Phenanthrene).

4. Even when two intense crystal lines lie pretty close together, we have two separate liquid bands, if they are of the same intensity. (α -Naphthylamine).

5. The spacing corresponding to the position of the maximum intensity in the liquid band is generally greater than that of the corresponding crystal line except in the case of phenanthrene.

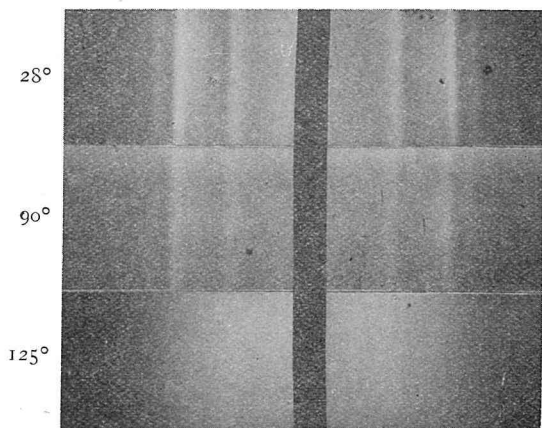
6. It may be concluded that the crystal planes which produce the intense reflection seem to maintain their properties when the crystal becomes liquid.

In conclusion the writers wish to express their hearty thanks to Prof. M. Ishino for the interest he has taken in the research.

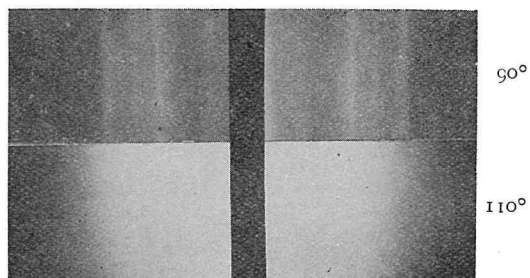
Physical Laboratory,
The Osaka University of Engineering,
January 16, 1931.

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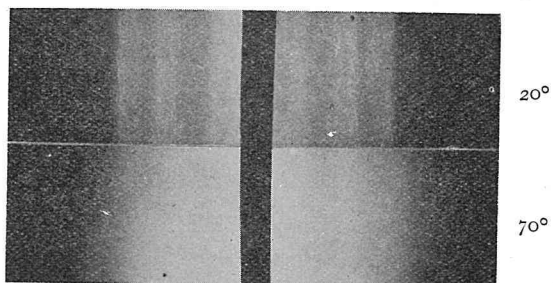
α -Naphthol



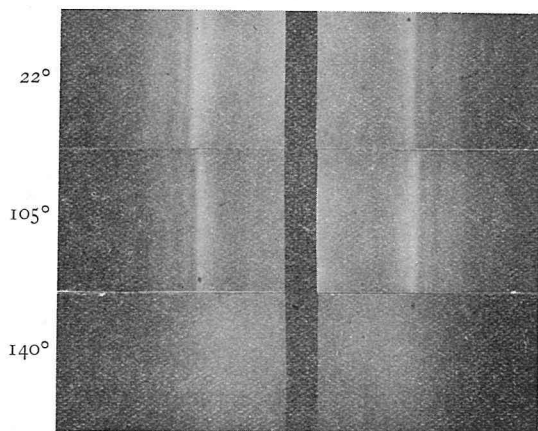
Phenanthrene



α -Naphthylamine



β -Naphthol



β -Naphthylamine

