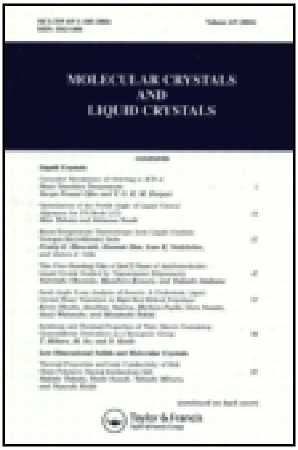

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

X-Ray Study on the Phase Transformation OP 1-BROMOOCTACOSANE

Naotake Nakamura[a]

[a] Department of Chemistry, Ritsumeikan University Tojiin, Kita-ku, Kyoto, Japan

To cite this article: Naotake Nakamura (1981): X-Ray Study on the Phase Transformation OP 1-BROMOOCTACOSANE, Molecular Crystals and Liquid Crystals, 64:9-10, 313-318

To link to this article: http://dx.doi.org/10.1080/01406568108072017

Mol. Cryst. Liq. Cryst. Vol. 64 (Letters), pp. 313-318
0140-6566/81/6409-0313$06.50/0

X-RAY STUDY ON THE PHASE TRANSFORMATION OF 1-BROMOOCTACOSANE

NAOTAKE NAKAMURA
Department of Chemistry,
Ritsumeikan University
Tojiin, Kita-ku, Kyoto, Japan

(Submitted for publication March 25, 1981)

ABSTRACT In the quenched samples, there was alternative disappearance of long spacing reflections. When the sample was kept for a long time, new reflections appeared at the positions between the long spacing reflections. The transformation studied here is related to the change of the period along the long axis.

Spontaneous transformation of the bromides containing 22, 24, 26 and 28 carbon atoms was studied by dielectric[1] and thermal[2] measurements, and the transformation was explained by the change of metastable form to stable one during the storage at room temperature for a certain period. But X-ray study on this transformation has not been reported yet. In the present work, X-ray study of the 1-bromooctacosane is made in order to obtain a structural information concerning this transformation.

The sample, 1-bromooctacosane, was synthesized in this laboratory. The bromide was purified and was confirmed to be pure by gas chromatography, IR, elemental analysis and melting point measurement. For the X-ray experiments, the bromide was filled in a thin walled glass capillary. The intensities of the reflections were estimated visually by a comparator.

The X-ray photograph of quenched sample showed two strong short spacing reflections and several long spacing ones*. Observed values of the short spacings and the long spacing are given in TABLE 1. From the intensity observations, it was obtained that the intensity of inner short spacing reflection was stronger than that of outer one. And the intensities of the long spacing reflections decayed gradually as the order of reflections increased. These results are shown in TABLE 2.

After a sample was quenched, X-ray photographs were taken at every 24 hours regularly. Storing temperature was about 30°C. New reflections appear at the intermediate positions between the long spacings. And the intensities of these reflections increased gradually with the increase of storage

---

* In the X-ray powder photographs of these long chain compounds, " long spacing reflections " are a general term for the inside rings, diffraction from the layers.

period. Intensity data of the long spacing reflections obtained from these photographs are listed in TABLE 3. The appearance of the new reflections shows a formation of a new structure. The rate of this transformation is fast in early stage and decreases gradually. This tendency is consistent with that observed in the previous dielectric 1) and thermal 2) studies.

The X-ray photograph of the stable bromide, which is stored about 1 year, showed two strong short spacing reflections and several long spacing ones. The intensity of the inner short spacing reflection was stronger than that of outer one as it has been observed in the quenched samples. The data of the short and long spacings are listed in TABLE 1 and intensity distribution of the long spacing reflections was given in TABLE 2 together with those of the quenched sample.

In TABLE 1, the short spacings of the quenched bromide are nearly equal to those of stored one. Then, it may be considered that the dimension of basal plane is very similar in both samples. And the intensity distribution is resembled in both the quenched sample and stored one. Therefore, the molecular disposal in lateral may be very similar to each other.

The remarkable difference was observed in the intensity distributions between the stored sample and the quenched one. As is shown in TABLE 2, the long spacing reflections alternately disappeared in the quenched sample. Then, it is obvious that

TABLE 1 The short spacings and the long spacings of the quenched sample and the stored one.

sample	short spacing (Å)		long spacing (Å)
quenched	4.11	3.74	34.8
stored	4.09	3.71	69.3

TABLE 2 The intensity distributions of the long spacings of the quenched sample and the stored one.

sample	the order from the inside						
	1	2	3	4	5	6	7
quenched		M		W		VW	
stored	VS	M	M	VW	W		VW

TABLE 3 The change of the long spacing intensity of the quenched 1-bromooctacosane.

the day elapsed(day)	the order from the inside					
	2	3	4	5	6	7
0	VS		M		W	
1	VS	W	M	VW	VW	
2	VS	M	M	W	VW	VW
3	S	M	W	W	VW	VW
4	S	M	W	M	VW	VW
5	S	M	W	W	VW	VW
6	VS	S	W	W	VW	VW
7	S	M	W	W	VW	VW
8	VS	S	W	M	VW	VW
9	VS	S	W	M	VW	VW

the molecular disposal along the long chain axis in the quenched crystal differs from that of stored one. This result shows that the identical structure of the terminal plane exists at the middle of a period of the long axis in the quenched crystal.

It is suggested from the single crystal structure analysis of this bromide, of which experiments are now in progress, that the length of the long axis is four molecules long as has been observed in β-form of 1-heptadecanol[3]. The long chain axis of the stored bromide may be of four molecular arrangement, because the structure of the stored sample can be considered to be the same as that of the single crystal. Then, (00ℓ) reflections are observed only in ℓ even. While, the quenched sample, the length of the long chain axis may be double molecular long, because the long spacing is one half of that of stored sample. Therefore, this transformation may relate to the change from double molecular disposal to a four molecular one. The similar transformation has been reported in long chain acids[4,5]. In the case of this type, some molecules in the quenched sample shift gradually along the long axis to make the stable disposal. On the other hand, gauche conformation of the terminal hydroxyl group had been observed in the structure of 1-heptadecanol[3]. If the similar gauche type molecules exist in this bromide, the mechanism of this transformation might be explained from the conformation change of terminal bromine atoms. The appearance of the new reflections may relate to the formation of a super-structure.

After being kept for 9 days, the intensity distribution of the long spacing reflections is not the same as that of stable sample. Then, the transformation may be not completely finished in this period.

When the crystal structure is analyzed perfectly, the mechanism of this transformation can be explained more clearly. The further investigation is being continued in this laboratory.

The author wishes to express his thanks to Professor Akira Watanabe for continued guidance and encouragement.

REFERENCES

1) N.Nakamura and A.Watanabe, Yukagaku, 25, 485 (1976)
2) N.Nakamura and A.Watanabe, Yukagaku, 27, 103 (1978)
3) T.Seto, Memoirs Coll.Sci.Univ.Kyoto, A30, 89 (1962)
4) T.R.Lomer, Nature, 176, 653 (1955)
5) T.R.Lomer, Acta Crystallogr., 16, 984 (1963)