Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

X-Ray Study of the Mesophase-Mesophase Transition of Octaalkyloxyorthocyclophanes

S. Dai [a] , N. Spielberg [a] & H. Zimmermann [b]

[a] Physics Department, Liquid Crystal Institute, Kent State U., Kent, OH, 44242, USA

[b] Max Planck Inst. f. Med. Forsch., AG Molekülkristalle, Jahnstrasse 29, 6900, Heidelberg, Germany

Version of record first published: 04 Oct 2006

To cite this article: S. Dai, N. Spielberg & H. Zimmermann (1997): X-Ray Study of the Mesophase-Mesophase Transition of Octaalkyloxyorthocyclophanes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 97-101

To link to this article: http://dx.doi.org/10.1080/10587259708039411

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 97–101
Reprints available directly from the publisher
Photocopying permitted by license only

X-RAY STUDY OF THE MESOPHASE-MESOPHASE TRANSITION OF OCTAALKYLOXYORTHOCYCLOPHANES

S.DAI, N.SPIELBERG
Physics Department and Liquid Crystal Institute, Kent State U., Kent, OH, 44242, USA

H. ZIMMERMANN
Max Planck Inst.f.Med.Forsch., AG Molekülkristalle, Jahnstrasse 29, 6900 Heidelberg, Germany

Abstract Previous studies of the mesomorphic octaether derivatives of cyclotetraveratrylene, CTTV-I- *n* (*n* is the number of carbon atoms per ether chain), have shown two columnar mesophases for $9<n<16$. In the higher temperature mesophase the columns are packed in a two-dimensional hexagonal unit cell, while in the lower phase the packing is two-dimensional centered rectangular. DSC showed no heat of transition between the two mesophases. For $n=13$, the transition occurred over a wide temperature range. We find this wide transition region is a third mesophase, with an oblique net intermediate between the other two. The upper boundary of this phase marks breaking of hexagonal symmetry by the appearance of a unit cell having $\gamma=120°$, but with $a \neq b$. With decreasing temperature, b is essentially constant while a and γ increase until $-2b\cos\gamma=a$, marking the transition to the primitive cell for the two dimensional centered rectangular net. Similar behavior is observed for $n=14$.

INTRODUCTION

Previous optical microscope and x-ray studies[1] of the mesomorphic octaether derivatives of cyclotetraveratrylene, CTTV-I- *n*, where *n* is the number of carbon atoms per ether chain, have shown that there are two columnar mesophases for $9<n<16$. No heat of transition was detected for the transition between the two mesophases. The microscope measurements showed the higher temperature mesophase to be optically uniaxial and the lower phase optically biaxial. X-ray powder diffraction data for the higher temperature uniaxial phase was indexed on the basis of a two dimensional hexagonal unit cell. The data for the lower temperature phase were indexed on the basis of a two dimensional

centered rectangular unit cell, for which the primitive cell had the same area as the hexagonal cell. For the compound having n=13, the transition between these two phases was examined by studying the (10) reflection for the hexagonal cell and the (11) and (02) reflections of the centered rectangular cell as a function of temperature. This study seemed to show that the transition between the two phases took place over a wide temperature range (~20°C), which implied a puzzling coexistence region for the two mesophases.

The present work presents results of a more detailed study of the x-ray powder diffraction pattern in the transition region between the two columnar mesophases. This study shows evidence that the wide transition region is really a third mesophase, with an oblique lattice having different symmetry than the hexagonal and centered rectangular cells of the other two phases.

EXPERIMENTAL.

The measurements were carried out on a computer controlled powder diffractometer, with transmission specimen and monochromated Cu Kα radiation (weighted wavelength 1.5418 Å).[2] The specimen materials used were from the same batch as the earlier work.[1]

Measurements were made of the complete diffraction pattern of the compound n=13 at temperatures of 120°C, 112 to 92°C in 2° steps, and 88°C. This range of temperatures extends from well within the higher temperature hexagonal phase to well within the lower temperature rectangular phase. To obtain satisfactory counting statistics, repeated scans were made over specific portions of the diffraction pattern. The raw data were smoothed using a five-point moving average, and background corrections applied. Overlapping lines were resolved using empirical line shapes derived from the line profiles obtained from the diffraction pattern of specimens in the hexagonal phase. Figure 1 shows the extreme case for which the "parent" 11 and 20 reflections of the hexagonal cell became noticeably broader when the temperature of the specimen was just inside the transition region to the centered rectangular cell. For the 11 reflection the width increased from .35° to .42° 2θ. This broadening signals the breakup of the 11, 20 hexagonal reflections into unresolved $2\bar{1}$, $1\bar{2}$, $20/2\bar{2}$, 02 reflections resulting from the

change to oblique symmetry. (If it were possible to obtain data from single domains, these reflections would be spatially separate.) Further into the transition region, the

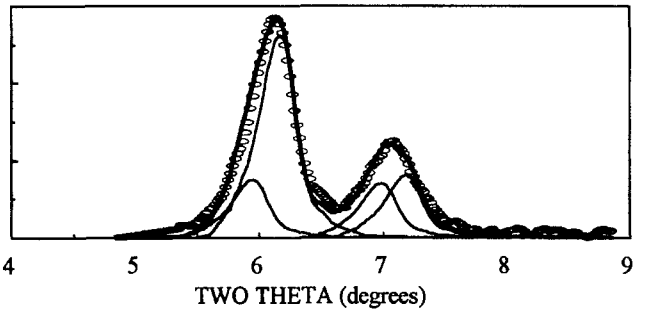

FIGURE 1 Constituent components of broad diffraction lines.

breakup of the 11 and 20 reflections is much more apparent, as shown in previous work.[1] In the figure, the corrected experimental data are shown by open circles, the component reflections by light lines and their sum by the heavy line.

RESULTS AND DISCUSSION

Table I presents values of the two-dimensional lattice parameters obtained from the analysis of the observed diffraction patterns. At temperatures of 108°C and higher, the observed diffraction pattern consisted of three lines corresponding to d-spacings of approximately 24, 14, and 12Å respectively, which could be indexed on the basis of a two-dimensional hexagonal unit cell. At 106°C, the latter two diffraction lines become noticeably broader, and can be decomposed into four diffraction lines, corresponding to splitting of the 14 and 12Å d-spacings, as shown in figure 1, thus signaling a change of structure. These four lines and the line at 24Å can be indexed assuming an oblique lattice with γ=120°, as for a uniaxial hexagonal cell, but with *different* repeat distances along the axes. Such a lattice must be biaxial. The assumed lattice also results in a splitting of the 24Å d-spacing, but by an amount too small to be detected by our instrument.

TABLE I Two-dimensional lattice parameters for n=13.

Temp. (°C)	a(Å)	b(Å)	γ (°)	$-2b\cos\gamma$	symmetry
120	28.57	28.57	120	28.57	hexagonal
112	28.44	28.44	120	28.44	hexagonal
110	28.58	28.58	120	28.58	hexagonal
108	28.58	28.58	120	28.58	hexagonal
106	29.20	28.57	120	28.57	oblique
104	29.00	28.15	120	28.15	oblique
102	29.10	28.67	120	28.67	oblique
100	29.35	28.54	122	30.25	oblique
98	29.44	28.58	123	31.13	oblique
96	30.20	27.73	123	30.21	rectangular
94	30.50	27.62	124	30.89	rectangular
92	30.76	27.49	124	30.74	rectangular
88	30.83	27.24	124	30.48	rectangular

At 102°C, a barely perceptible broadening of the 24Å diffraction line is observed, while at 100°C the 24Å line is markedly broader. At this temperature, the data can be indexed on the basis of an oblique lattice with $\gamma = 122°$. At temperatures of 98°C and lower, the splitting of the 24Å line is sufficiently large that it is clearly apparent in the diffraction pattern. At 96°C and lower temperatures, the values of the lattice parameters determined by indexing the pattern are such that $-2b\cos\gamma \approx a$. This means that the structure can be described as centered rectangular, corresponding to the lower temperature rectangular mesophase identified in the earlier work,[1] for which the primitive cell has values a=31.29Å, b=28.02Å, γ=124°.

From Table I, it is apparent that the uniaxial (hexagonal) mesophase D_2 has its lower temperature boundary between 108 and 106°C; while the biaxial (rectangular) mesophase D_1 has its upper temperature boundary between 98 and 96°C. It seems reasonable to assign the structure in the region between 106 and 98°C to an oblique (biaxial) mesophase, i.e., with symmetry which is neither hexagonal nor rectangular. Because the temperature increments in this experiment are not very small, it is not

possible to say whether the lattice parameter changes at the transition temperatures to this oblique phase are continuous or discrete. The changes are small enough to explain the failure to detect an enthalpy of transition by conventional DSC.

TABLE II Two-dimensional lattice parameters for n=14.

Temp. (°C)	a(Å)	b(Å)	γ(°)	-2b cosγ	Symmetry
110	29.87	29.87	120	29.87	hexagonal
100	29.80	29.80	120	29.80	hexagonal
99	30.40	29.20	120	29.20	oblique
98	30.80	28.80	120	28.80	oblique
97	30.44	28.88	120	28.88	oblique
96	30.42	28.20	120	28.20	oblique
95	30.62	28.17	120	28.17	oblique
94	30.60	27.90	120	27.90	oblique
93	31.35	28.76	122	30.48	oblique
92	31.60	28.44	122	30.14	oblique
91	31.84	28.42	123	30.96	oblique
90	31.73	28.30	124	31.65	rectangular
89	31.62	28.20	124	31.54	rectangular

Table II shows similar results for the compound having n=14. The upper temperature boundary for the oblique phase lies between 99 and 100°C, while the lower boundary lies between 91 and 90°C, making this region about 10° wide, as is the case for n=13. For the compound n=12, the transition region, if it exists, is less than 1° wide, and we were not able to study it with our apparatus. Similar difficulty was experienced for n=15, for which the temperature range of the lower mesophase is only 1.8°.[1]

REFERENCES

1. N.Spielberg, M.Sarkar, Z.Luz, R.Poupko, J.Billard, H.Zimmermann, Liq. Cryst, 15, 311 (1993).
2. M.Sarkar, N.Spielberg, K.Praefcke, H.Zimmermann, Mol. Cryst. Liq. Cryst, 203, 159 (1991).