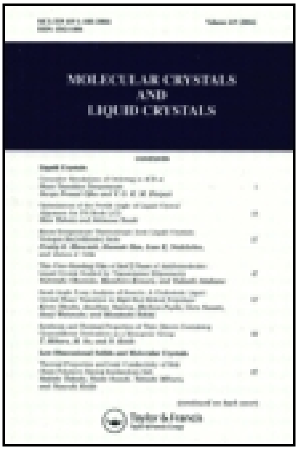
This article was downloaded by: [University of Haifa Library]
On: 20 August 2012, At: 10:51
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Further Investigation of Mesophase of Pyramidic Liquid Crystal by X-Ray Transmission Diffractometry

M. Sarkar [a] , N. Spielberg [b] & H. Zimmermann [c]

[a] Tennessee State University, Nashville, TN, 37209-1561

[b] Kent State University, Kent, OH, 44242

[c] Max Planck Inst. f. Medizinische Forschung, D-6900, Heidelberg, Germany

Version of record first published: 04 Oct 2006

To cite this article: M. Sarkar, N. Spielberg & H. Zimmermann (1998): Further Investigation of Mesophase of Pyramidic Liquid Crystal by X-Ray Transmission Diffractometry, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 312:1, 45-53

To link to this article: http://dx.doi.org/10.1080/10587259808042430

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

Mol. Cryst. Liq. Cryst., 1998, Vol. 312, pp. 45–53
Reprints available directly from the publisher
Photocopying permitted by license only

© 1998 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license
under the Gordon and Breach Science
Publishers imprint.
Printed in India.

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

Further Investigation of Mesophase of Pyramidic Liquid Crystal by X-Ray Transmission Diffractometry

M. SARKAR[a,]*, N. SPIELBERG[b] and H. ZIMMERMANN[c]

[a]*Tennessee State University, Nashville, TN 37209-1561;*
[b]*Kent State University, Kent, OH 44242;*
[c]*Max Planck Inst. f. Medizinische Forschung, D-6900 Heidelberg, Germany*

(Received 9 June 1997; In final form 12 August 1997)

Further X-ray powder diffractometer measurements have been made on compound II-9 of the columnar liquid crystal series hexaalkanoyloxytribenzocyclononene. For this compound the transition temperature between the solid and the columnar phase is 26°C. Data have been collected at several temperatures from 2°C to 52°C. We compare results obtained from II-9 with results published for II-10, 12, 13 and 15. Unlike these other compounds, in the mesophase the diffraction patterns show a large number of lines, with at least four high angle lines superposed on the broad hump arising from scattering by the disordered hydrocarbon side chains. This indicates a more highly ordered structure than for the other compounds in this series.

Keywords: Pyramidic; mesophase; columnar; liquid crystal; X-ray; diffraction

INTRODUCTION

We report X-ray measurements on the pyramidic liquid crystal II-9, a homologue of the hexaalkanoyloxytribenzocyclononene series (II-*n*) [1–9]. (We follow the nomenclature of reference 9 in designating this and other pyramidic compounds). The phase diagram for this series is shown in Figure 1, along with a representation of the molecular geometry of II-*n* [1, 9]. Pyramidic liquid crystals are of interest because the polar nature of the central core of their constituent molecules might make possible columnar arrangements exhibiting ferroelectric or antiferroelectric properties [10].

---

*Corresponding author.

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

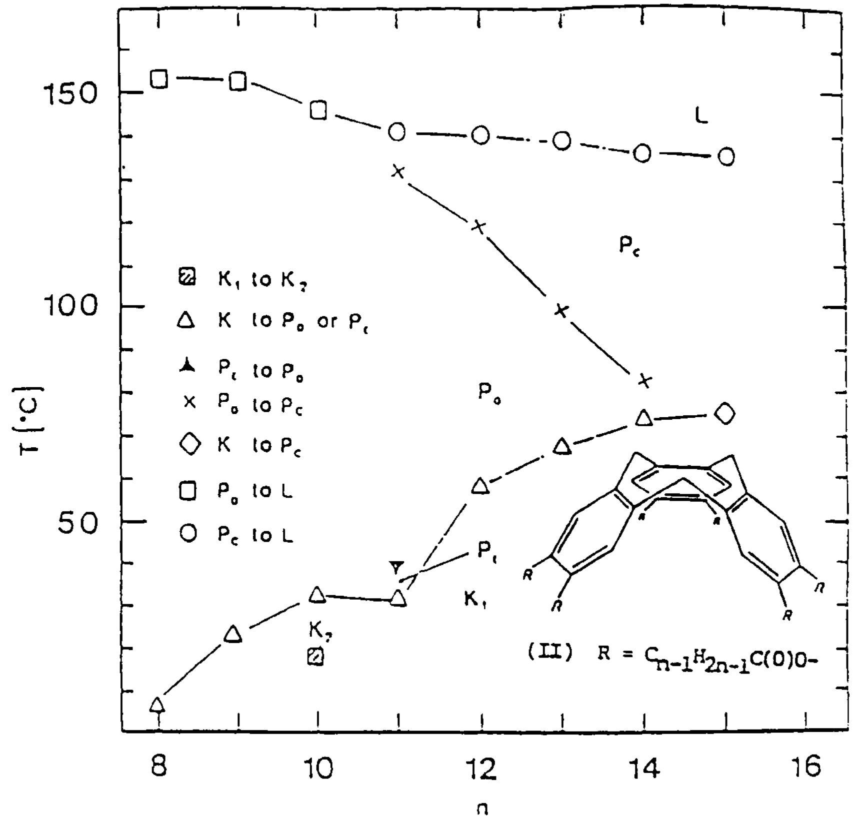


FIGURE 1 Schematic representation of the phase transition temperatures for the hexaalkanoyloxytribenzocyclononene (II-*n*) homologues.

X-ray measurements have been reported previously on four other members of this series: *n* = 10, 12 [3]; *n* = 13 [9]; and *n* = 15 [11]. Unlike those compounds, the x-ray diffraction pattern for compound II-9 is very rich in diffraction lines, with several very strong lines superposed on the diffraction region associated with scattering from the disordered hydrocarbon chains.

X-RAY MEASUREMENTS

Samples of II-9 were hermetically sealed in disc-shaped specimens, 0.4 mm thick and covered at top and bottom with 25 micron thick aluminium foil. A modified vertical scanning Philips diffractometer with transmission specimen holder and focusing LiF(200) monochromator adjusted for CuK_α

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

(weighted wavelength 1.5418 Å) radiation was used for the powder x-ray measurements. The x-ray tube was operated at 32 kV, 20 mA for all data. To minimize temperature gradients in the sample, the sample holder temperature was controlled from both above and below with thermoelectric devices. Data collection and operation of the instrument was computer controlled. Measurements were made at 2, 3, and 20°C in the crystalline phase region and at 26, 38, 48, and 52°C in the mesophase region.

Data points were recorded as counts per 300 second time interval at 0.05 deg 2θ steps over a 25 deg range beginning at 1 deg 2θ. The raw data were smoothed using a five point moving average.

ANALYSIS

Figure 2 shows the diffraction pattern obtained at 48°C. The feature from 1 to about 3 degrees represents the "tail" of the "zero" angle undiffracted beam. This tail actually extends to about 6 deg 2θ. There are several diffraction peaks in the range from 3 to 6 deg and a number of weaker peaks

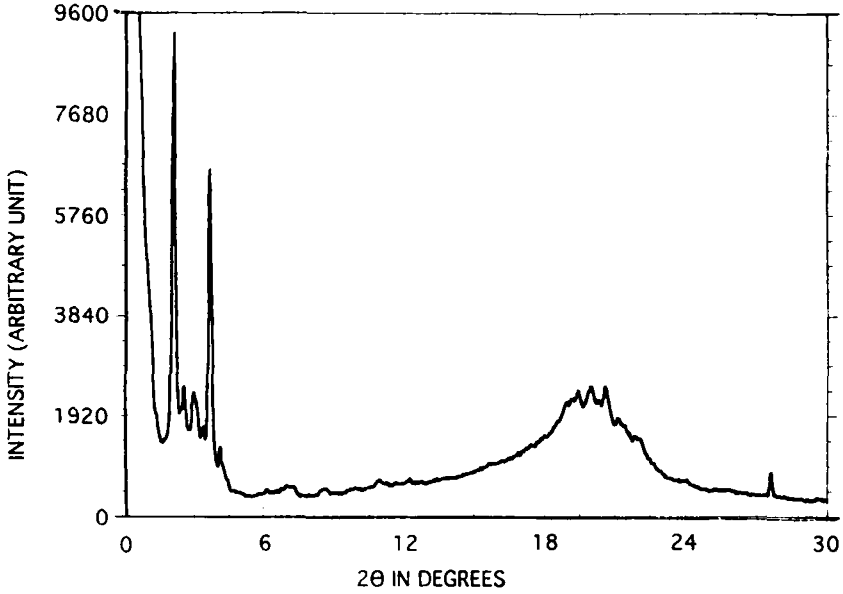


FIGURE 2 Intensity vs 2θ diffraction pattern at 48 degree celcius.

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

in the range from 6 to 26 deg, some of which are superposed on a broad "hump" stretching from about 16 to about 25 deg. The hump represents scattering from the long hydrocarbon chains [12]. This pattern is typical for columnar discotic mesophases, with the exception of the 4 or 5 peaks superposed on the hump. Usually, if the stacking of the molecules along the length of the discotic columns is disordered, there are no peaks superposed on the hump. If the stacking along the length of the column is ordered, then there is a wide diffraction peak superposed on the hump at a 2θ value corresponding to the stacking distance [5]. The significance of the several peaks on the hump in this case will be discussed further below.

The pattern was analyzed by stripping the zero angle beam and the hump from the smoothed data, using repeated subtraction of straight line segments. The resulting diffraction peaks were fitted with model profiles empirically derived from strong well resolved diffraction peaks. This made it possible to resolve a number of overlapping peaks. Figure 3 shows the result for a particular instance. The open circles represent the stripped data, the light lines the fitted model profiles, and the heavy line the pattern synthesized by adding the various model profiles. (The apparent unfitted peak just below 3 deg 2θ is an artifact of the stripping procedure.)

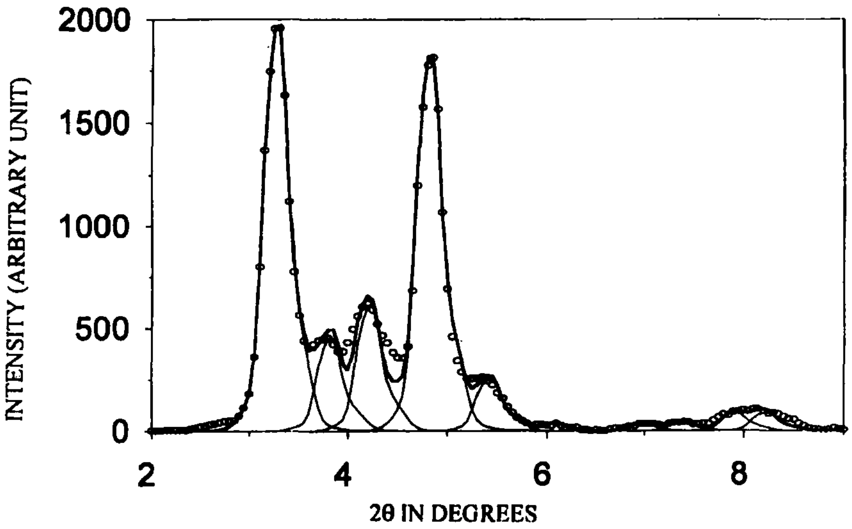


FIGURE 3 Diffraction Peaks at 52°C. The open circles represent the stripped data, the light lines the fitted model line profiles, and the heavy line the pattern synthesized by adding the various profiles.

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

RESULTS AND DISCUSSION

The diffraction patterns obtained at 2, 3 and 20°C, within the solid crystalline phase region were essentially all the same. At 26°C, the pattern changed, signaling the known transformation to the mesophase (Fig. 1). The results obtained at 38°C were essentially unchanged from those at 26 deg., with 38 diffraction lines and the broad hump. Three of the diffraction features superposed on the hump were comparable in intensity to the strong low angle lines. At 48°C, the number of diffraction lines decreased to 27 and at 52°C, 26 diffraction lines were identified. At 52°C, the intensity of the features superposed on the hump was much less than that of the strong low angle lines.

The number of diffraction lines found is much larger than for the other homologues of this series, approaching the number of powder diffraction lines in the crystalline phase. For example, for compound II-13, 11 diffraction lines were found in the biaxial columnar mesophase, and 6 lines in the uniaxial columnar mesophase [9]. As already noted, the intensity of the lines superposed on the hump, corresponding to *d*-spacings in the neighborhood of 4 Å, is surprisingly large.

The x-ray diffraction pattern of the biaxial phase of compound II-10 can be interpreted on the basis of a 2-dimensional oblique lattice of columns with either 2 or 8 columns/cell [3, 9]. Similarly, the present compound, II-9, can also be indexed on the basis of a 2-dimensional oblique lattice with 2 or 8 columns/cell, but for II-9 it is necessary to use very high values for the Miller indices *h* and *k* (upto 10 or 11) for those diffraction lines having *d*-spacings of the order of 3 or 4 Å. Such high values of *h* and *k* imply at least 200 pairs of values of *hk*. This then leads to the question as to why so many lines having smaller and intermediate values for *h* and *k* are not observed, even after allowing for multiplicity and/or failure to resolve very close lines. Although it might be supposed that various extinction rules are operative, this would imply an unusually special symmetry and large coherence length (for liquid crystals) of packing of columns within the 2-dimensional net.

It seems more plausible to index the pattern on the basis of a 3-dimensional lattice, using Miller indices *hkl*, but restricting 1 to values of 0, 1, or 2, while assuming a monoclinic lattice with a judiciously chosen value of the lattice parameter *c*. The results of such an indexing scheme are given in Table I for the data taken at 52°C. (Tab. I assumes the equivalent of 8 columns/cell. It is also possible to assume 2 columns/cell with the *a* and *b* lattice parameters being about half those given in Tab. I).

Table II summarizes the lattice parameters for the three temperatures 38, 48 and 52°C. The 3-dimensional indexing scheme, of course, implies

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

TABLE I Indexed lines and d-spacings at 52°C for oblique cell with $a=53.44$, $b=45.99$, $c=8.69$, $\gamma=95°$

h	k	l	d_{calc}	d_{exp}	*diff*	*exp.err*	h	k	l	d_{calc}	d_{exp}	*diff*	*exp.err*	h	k	l	d_{calc}	d_{exp}	*diff*	*exp.err*
2	0	0	26.62	26.37	0.25	0.39	5	−2	1	6.56	6.55	0.01	0.02	6	5	2	3.54	3.55	−0.01	.001
0	2	0	22.91	22.66	0.25	0.29	0	7	0	6.54	6.55	−0.01	0.02	2	7	2	3.56	3.55	0.01	.001
1	2	0	20.40	20.55	−0.15	0.24	3	−4	1	6.57	6.55	0.02	0.02	7	−5	2	3.54	3.55	−0.01	.001
2	−2	0	18.16	18.26	−0.10	0.19	7	3	0	6.58	6.55	0.03	0.02	6	−6	2	3.53	3.55	−0.02	.001
3	1	0	16.08	16.10	−0.02	0.15								7	4	2	3.54	3.55	−0.01	.001
							4	5	1	5.57	5.57	−0.00	0.02							
3	−2	0	14.66	14.51	0.15	0.12	5	−5	1	5.57	5.57	0.00	0.02							
1	3	0	14.35	14.51	−0.16	0.12	3	−6	1	5.57	5.57	−0.00	0.02							
							2	6	1	5.53	5.57	−0.04	0.02							
4	1	0	12.49	12.56	−0.07	0.09	7	5	0	5.62	5.57	0.05	0.02							
4	−2	0	11.97	11.88	0.09	0.08	6	6	0	5.55	5.57	−0.02	0.02							
							6	−4	1	5.60	5.57	0.03	0.02							
4	2	0	11.09	11.08	0.01	0.07														
3	3	0	11.11	11.08	0.03	0.07	5	5	1	5.29	5.32	−0.03	0.02							
1	4	0	11.00	11.08	−0.08	0.07	6	4	1	5.32	5.32	0.00	0.02							
							3	6	1	5.36	5.32	0.04	0.02							
5	0	0	10.65	10.68	−0.03	0.06	6	−5	1	5.29	5.32	−0.03	0.02							
5	−3	0	9.12	9.18	−0.06	0.05	6	5	1	5.00	5.02	−0.02	0.01							
0	5	0	9.16	9.18	−0.02	0.05	7	−5	1	5.00	5.02	−0.02	0.01							
1	−5	0	9.16	9.18	−0.02	0.05														
							0	1	2	4.33	4.34	−0.01	0.01							
0	0	1	8.69	8.69	0.00	0.04	0	0	2	4.34	4.34	0.00	0.01							
							1	0	2	4.33	4.34	−0.01	0.01							
1	−2	1	8.07	8.02	0.05	0.04														
6	−3	0	7.98	8.02	−0.04	0.04	2	−2	2	4.23	4.22	0.01	0.01							
1	2	1	7.99	8.02	−0.03	0.04	2	2	2	4.20	4.22	−0.02	0.01							
6	2	0	8.04	8.02	0.02	0.04	3	0	2	4.22	4.22	0.00	0.01							
							3	−1	2	4.21	4.22	−0.01	0.01							
5	−5	0	7.27	7.30	−0.03	0.03														
3	2	1	7.30	7.30	0.00	0.03	3	−3	2	4.09	4.10	−0.01	0.01							

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

4	5	0	7.26	7.30	−0.04	0.03	2	3	2	4.11	4.10	0.01	0.01
4	−1	1	7.24	7.30	−0.06	0.03	4	1	2	4.10	4.10	0.01	0.01
3	−6	0	7.25	7.30	−0.05	0.03	4	−2	2	4.08	4.10	−0.02	0.01
4	0	1	7.28	7.30	−0.02	0.03	4	−1	2	4.12	4.10	0.02	0.01
2	−3	1	7.35	7.30	0.05	0.03							
6	−4	0	7.33	7.30	0.03	0.03	4	−3	2	4.01	3.99	0.02	0.01
							3	−4	2	3.99	3.99	−0.00	0.01
7	2	0	7.04	6.99	0.05	0.03	2	4	2	4.00	3.99	0.01	0.01
4	−2	1	7.03	6.99	0.04	0.03	5	1	2	4.00	3.99	0.01	0.01
							5	−2	2	3.98	3.99	−0.01	0.01
2	−4	1	6.79	6.75	0.04	0.03							
5	−1	1	6.71	6.75	−0.04	0.03	5	−4	2	3.84	3.85	−0.01	0.01
3	6	0	6.80	6.75	0.05	0.03	4	4	2	3.85	3.85	0.00	0.01
4	−3	1	6.69	6.75	−0.06	0.03	5	3	2	3.86	3.85	0.01	0.01
5	0	1	6.73	6.75	−0.02	0.03	3	−5	2	3.86	3.85	0.01	0.01
6	4	0	6.74	6.75	−0.01	0.03	6	−2	2	3.87	3.85	0.02	0.01
							2	5	2	3.86	3.85	0.01	0.01

TABLE II Lattice parameters at three temperatures in the mesophase for 8 columns/cell

Temp(°C)	*a(A)*	*b(A)*	*c(A)*	*γ(deg)*
38	59.79	45.41	8.88	94
48	58.28	50.33	8.17	104
52	53.44	45.99	8.69	95

Downloaded by [University of Haifa Library] at 10:51 20 August 2012

3-dimensional order. The question then arises as to how a 3-dimensionally ordered columnar liquid crystal differs from the usual crystalline solid. It should be noted that 3-dimensional ordering in columnar liquid crystalline phases has been reported previously. Three-dimensional ordering in a pyramidic liquid crystal with benzene rings in the hydrocarbon chains was ascribed to an overall spiral configuration of the hydrocarbon chains [3]. Measurements on oriented thin strands of the columnar mesophases of hexa-hexylthiotriphenylene have been interpreted in terms of a three-column superlattice and a resulting longitudinal correlation of adjacent columns [12]. More recently [13], mixing trifluoroacetic acid with a non-mesogenic member of the hexaalkyloxytribenzocyclononene series I-*n* induced mesomorphism. The powder x-ray diffraction pattern of the mixture could not be interpreted in terms of 2-dimensional packing of disordered columns. It was suggested that the pattern could be interpreted in terms of longitudinal correlation between adjacent columns.

It is tempting to apply a similar interpretation to the present results, ascribing a temperature dependence to this longitudinal correlation. Some support for this interpretation can be inferred from the decreased number of diffraction lines observed as the temperature of the sample increased. Further measurements at higher temperatures within the mesophase would help explore this possibility further.

References

[1] H. Zimmermann, R. Poupko, Z. Luz and J. Billard, *Z. Naturf.*(a), **40**, 149 (1985).
[2] J. Malthete and A. Collet, *Nouv. J. Chim.*, **9**, 151 (1985).
[3] A. M. Levelut, P. Oswald, A. Ghanem and J. Malthete, *J. Physi.* (Paris), **45**, 745 (1984); A. M. Levelut, J. Malthete and A. Collet, *J. Phys.* (Paris), **47**, 351.
[4] H. Zimmermann, R. Poupko, Z. Luz and J. Billard, *Z. Naturf.*(a), **41**, 1137 (1986).
[5] J. Malthete, A. M. Levelut and N. H. Tinh, *Phys. Lett.*, **46**, L-875 (1985).
[6] Lin Lei, Wuli, **11**, 171 (1982); *Mol. Cryst. Liq. Cryst.*, **146**, 41 (1987); Leung, K. M. and Lin Lei, *Mol. Cryst. Liq. Cryst.*, **146**, 71 (1987).
[7] A. Collet, *Tetrahedron*, **4.3**, 5725 (1987).
[8] J. Malthete and A. Collet, *J. Am. Chem. Soc.*, **109**, 7544 (1987).
[9] R. Poupko, Z. Luz, N. Spielberg and H. Zimmerman, *J. Am. Chem. Sco.*, **111**, 6094 (1989).

[10] H. Zimmerman, R. Poupko, Z. Luz and J. Billard, *Liquid Crystals*, **3**(6 and 7), 759–770 (1988).

[11] M. Sarkar, N. Spielberg, K. Praefeke and H. Zimmerman, *Mol. Cryst. Liq. Cryst.*, **203**, 159–169 (1991).

[12] Ernest Fontes, Paul A. Heiney and Wim H. de Jeu, *Phys. Rev. Lett.*, **61**, 1202–1205 (1988).

[13] L. Calucci, , H. Zimmermann, , E. J. Wachtel, , R. Poupko and Z. Luz, *Liquid Crystals* (in press, accepted for publication).

Downloaded by [University of Haifa Library] at 10:51 20 August 2012