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

Polymorphism and X-Ray Diffraction of Some Cyano Biphenyl-Substituted Benzoates Exhibiting Reentrant Nematic Phases

F. Hardouin [a] , A. M. Levelut [a] , Nguyen Huu Tinh [b] & G. Sigaud [b]
[a] Laboratoire de Physique des Solides, Bat 510, 91405, ORSAY, France
[b] Centre de Recherche Paul Pascal Domaine Universitaire, 33405, Talence, Cedex, France

Version of record first published: 19 Apr 2011.

To cite this article: F. Hardouin , A. M. Levelut , Nguyen Huu Tinh & G. Sigaud (1979): Polymorphism and X-Ray Diffraction of Some Cyano Biphenyl-Substituted Benzoates Exhibiting Reentrant Nematic Phases, Molecular Crystals and Liquid Crystals, 56:2, 35-41

To link to this article: http://dx.doi.org/10.1080/01406567908071964

Mol. Cryst. Liq. Cryst. Vol. 56 (Letters), pp. 35-41
0140-6566/79/5602-0035$04.50/0

POLYMORPHISM AND X-RAY DIFFRACTION OF SOME CYANO BIPHENYL-SUBSTITUTED BENZOATES EXHIBITING REENTRANT NEMATIC PHASES

F. HARDOUIN*, A.M. LEVELUT
Laboratoire de Physique des Solides
Bat 510 - 91405 - ORSAY - France

NGUYEN HUU TINH, G. SIGAUD
Centre de Recherche Paul Pascal
Domaine Universitaire - 33405 Talence Cedex
France

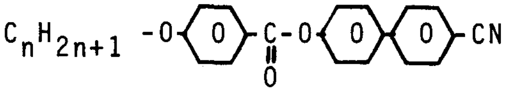
(Submitted for publication 23 July 1979)

ABSTRACT : The polymorphism of the 4 cyanobiphenyl-4'-n-alkoxy benzoate esters is investigated and a reentrant nematic phase is observed for the n = 8 and n = 9 homologues. X-Ray studies confirm this fact and show that in the reentrant phase the cybotactic groups are S_A-like at high temperature near the S_A phase while they appear S_C-like at lower temperatures.

INTRODUCTION : After the first observations of enantiotropic reentrant nematic phases at atmospheric pressure in pure compounds of two series : the 4-n- alkoxybenzoyloxy-4'-cyanostilbenes[1,2,3] and then the 4-n-alkoxybenzoyloxy-4'-cyanotolans[4], we have carried on the systematic study of such series with three phenyl rings in the rigid core and a cyano end group. In the present paper we examine the effect of replacing stilbene or tolan linkage by a simple biphenyl binding :

---

*Permanent adress : Centre de Recherche Paul Pascal, 33405 Talence



Some of these 4-cyanobiphenyl-4'-n-alkoxybenzoate esters were previously synthetized[5,6] and the reported polymorphism for the octyloxy member mentioned with decreasing temperature a nematic, smectic A and uncharacterized smectic[5] or smectic B[6] phases :

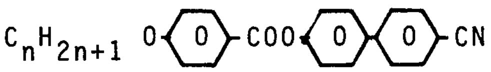
K 96.5 S 140 S_A 200 N 237 I [5]

K 97.3 S_B138.3 S_A 198.7 N 235.3 I [6]

Nevertheless, we have synthetized the members of this series from n = 7 to n = 12 and observed the textures of the different mesophases of each compound with a polarizing microscope. Then, these first identifications have been supported by means of isomorphism and X-Ray measurements.

MICROSCOPIC OBSERVATIONS : The different transition temperatures corresponding to the polymorphism deduced from texture characterization are given in the following table :

Table : Transition temperatures of the compounds of the series :



n	K		N		S_A		N		I
7	.	89	-		-		.	246	.
8	.	97	.	120	.	201	.	240	.
9	.	96	.	(71)	.	217	.	232	.
10	.	100	-		.	224	.	230	.
11	.	104	-		.	224	.	225	.
12	.	102	-		.	224	-		.

( ) = monotropic transition ; . = the phase exists ; - = the phase does not exist.

The main feature is of course that we conclude for the existence of a reentrant nematic phase for two compounds (n = 8 and n = 9) which is inconsistent with the results previously quoted. This result is confirmed by the complete miscibility of the lower temperature mesophases (for n = 8,9) with the reentrant nematic phases of two different compounds of the series previously described[1,4] :

the 4-n-decyloxy-benzoyloxy-4'-cyanotolan (Figure 1) and the 4-n-octyloxy-benzoyloxy-4'-cyanostilbene (Figure 2).
A point remains unclear : the important discrepancy between the transition temperature we observe for the S_A - reentrant nematic phase change of this octyloxy homologue (120°) and the S_A - S one yet reported (138°). At this last temperature our own calorimetric (Dupont 990 DSC) and microscopic studies do not detect any transition (while we reveal a very slight enthalpic peak at 120°C for the S_A - reentrant nematic transition). However, this difference with respect to earlier works[4,5] seems not to be due to the purity of the substance because the other transition temperatures we give are quite similar (Table).

X-RAY INVESTIGATIONS (n=8 HOMOLOGUE) : X-Ray patterns were taken after cooling the sample from the nematic phase in a magnetic field which gave, in the bulk, a smectic A single domain. We use a Cu Kα monochromatic beam reflected by a double bent pyrolitic graphite crystal and a flat film. The temperature of the sample is constant within ± 0.5° C . The X-Ray beam is perpendicular to the long molecular axis and the Figure 3 gives only the small angle region of the X-Ray patterns for identical exposure time. Nevertheless it is clear that, instead of the Bragg diffraction spots observed for smectic A phase (Figure 3-b), in high temperature nematic (Figure 3-a) or reentrant nematic (Figure 3-c) the X-Ray reflections become slightly more diffuse. Thus, the longitudinal long range order is undoubtedly destroyed in the lower temperature mesophase. Moreover we note that the high intensity and the sharpness of these diffuse spots in the high temperature nematic (Figure 3-a)

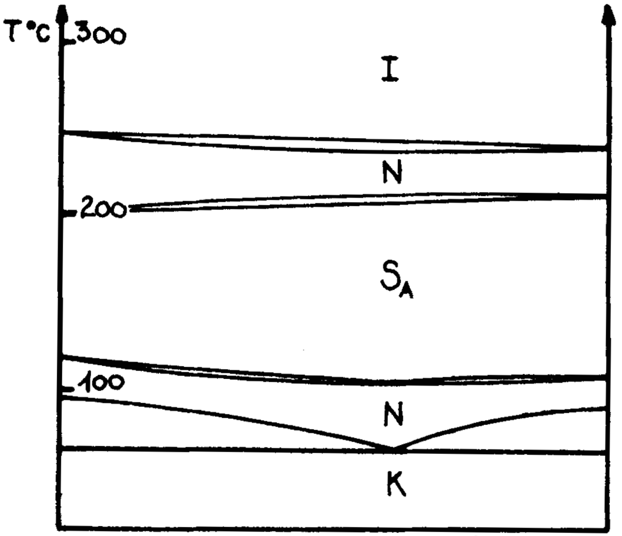
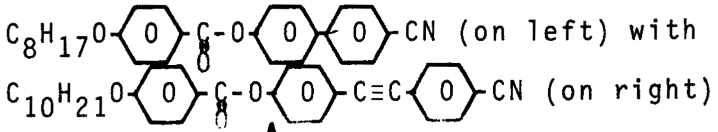


FIGURE 1 Binary isobaric diagram (contact method) of



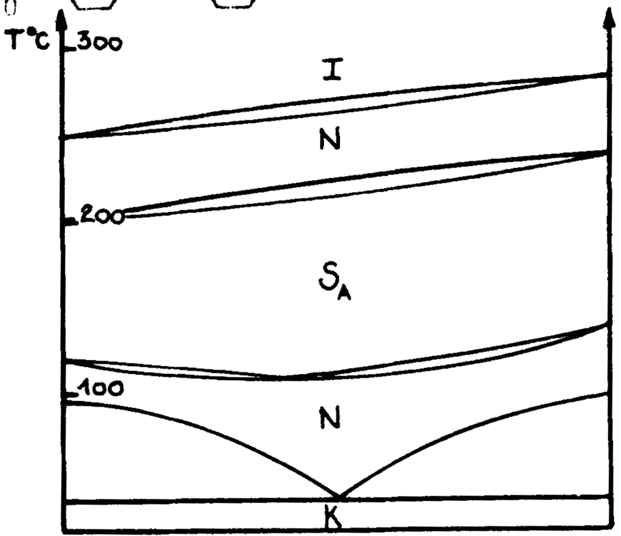
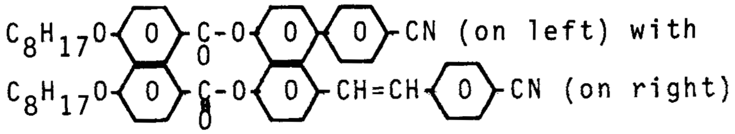


FIGURE 2 Binary isobaric diagram (contact method) of



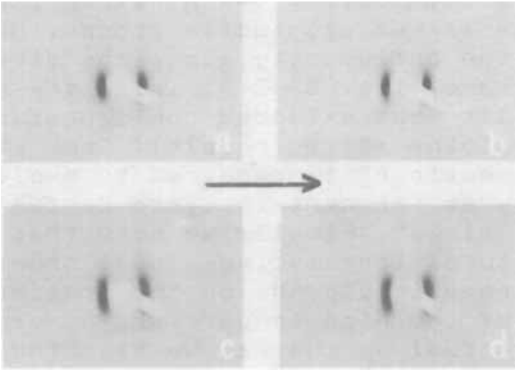


FIGURE 3 Small angle X-Ray patterns (n = 8 homologue) The arrow gives the magnetic field direction

a) Nematic phase 206° C

b) Smectic A phase 145° C

c) Reentrant nematic phase 115° C

d) Reentrant nematic phase 80° C (supercooled).

indicate the proximity of the N-S_A transition (cybotactic groups are rather large). In the low temperature nematic phase cybotactic groups appear to be smaller at 115° C (Figure 3-c) than in the high temperature one. In addition, on cooling down the sample in the reentrant phase the diffuse scattering intensity split progressively in two diffuse spots localized out of the symetry axis (magnetic field direction) (Figure 3-d). Thus the smectic A fluctuations of the nematic phase become smectic C fluctuations or so-called "skewed cybotactic groups"^{7} at low temperature. Considering in nematic phase tilt of the cybotactic layers with respect to the magnetic field direction resulting in a correlated logitudinal displacement of the molecules in that direction, we can roughly estimate the tilt angle in the cybotactic groups: 30° at 80° C. In the whole range of temperature we can measure the thickness of the layers in the

S_A phase and in the cybotactic groups. There is no important variation of this layer spacing with temperature (d = 33,2 ± 0.4 Å) except, of course, when we see skewed cybotactic groups. But even in this case the periodicity along the director remains the same, i.e. 33,2 Å, while the molecular length in its most extended configuration is 28,4 Å (Dreiding stereo models). Some kind of "bilayer smectic A" is required to explain this discrepancy as for certain cyano derivatives with two phenyl rings[8]. Finally we note that according to temperature, longitudinal local order in the reentrant nematic depends on the proximity respectively of the high temperature S_A or low temperature virtual S_C phases. We have the opportunity of seeing such a change because the reentrant nematic temperature range is rather large. Another direct evidence concerning the influence of high and low temperature smectic phases on reentrant nematic local order will be presented elsewhere[9] with results on the cyanostilbene homologue series.

CONCLUSION : We have undertaken the study of many different series exhibiting reentrant nematic phases with intending to specify the connections between structural or dipolar properties and the reentrant behavior. For this purpose it seems some times useful to proceed to the reexamination of certain series previously synthetized because the occurence of this phenomenon in pure compounds was established only a few months ago.

REFERENCES :

1. **F. HARDOUIN , G. SIGAUD , M.F. ACHARD and H. GASPAROUX.** Phys. Lett. 71A , 347, (1979)

2. **F. HARDOUIN , G. SIGAUD , M.F. ACHARD and H. GASPAROUX,** Solid State Comm. 30 , 265, (1979).

3. **J.C. DUBOIS , NGUYEN HUU TINH , A. ZANN and J. BILLARD,** Nouv. J. Chimie 2 , 647, (1978).

4. **NGUYEN HUU TINH and H. GASPAROUX,** Mol. Cryst. Liq; Cryst. Lett. 49, 287 (1979).

5. **J.C. DUBOIS and A. ZANN**, J. Phys. (Paris), Coll. C3 supp. 37 , C3-35, (1976).

6. **D. COATES and G.W. GRAY**, Mol. Cryst. Liq. Cryst. 37 , 249 , (1976).

7. **A DE VRIES** , Mol. Cryst. Liq. Cryst. 10 , 219 , (1970).

8. **A.J. LEADBETTER, J.C. FROST, J.P. GAUGHAN**, J. Phys. (Paris), 40 , 375 , (1979).

9. **F. HARDOUIN and A.M. LEVELUT** To be published.