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

On New Mesomorphic Sequences in Some Polar 2 or 3 Chlorodibenzoates

C. Destrade [a], F. Hardouin [a] & Nguyen Huu Tinh [a]
[a] Centre de Recherche Paul Pascal, Université de Bordeaux I, Domaine Universitaire, 33405, Talence Cédex, France
Version of record first published: 20 Apr 2011.

To cite this article: C. Destrade , F. Hardouin & Nguyen Huu Tinh (1984): On New Mesomorphic Sequences in Some Polar 2 or 3 Chlorodibenzoates, Molecular Crystals and Liquid Crystals, 116:1-2, 47-56

To link to this article: http://dx.doi.org/10.1080/00268948408072495

Mol. Cryst. Liq. Cryst., 1984, Vol. 116, pp. 47–56
0026-8941/84/1162–0047/$15.00/0

Printed in the United States of America

On New Mesomorphic Sequences in Some Polar 2 or 3 Chlorodibenzoates†

C. DESTRADE, F. HARDOUIN and NGUYEN HUU TINH

Centre de Recherche Paul Pascal, Université de Bordeaux I, Domaine Universitaire, 33405 Talence Cédex, France

(*Received March 12, 1984; in final form May 29, 1984*)

Four series of 4-alkoxyphenyl 4'cyano or nitrobenzoyloxy 2″ or 3″-chlorobenzoates have been synthesized and various mesophases have been identified. A discussion of the relationships between the general molecular structure (relative direction of the different permanent dipoles) and the polymorphism is given. These series provide some interesting sequences including the first example of a S_{A_2}–S_{A_d} transition directly observable through a microscope.

I. INTRODUCTION

We report on four series of mesogenic 4-alkoxyphenyl 4'-cyano or nitrobenzoyloxy 2″ or 3″-chlorobenzoates which derive from the general formula:

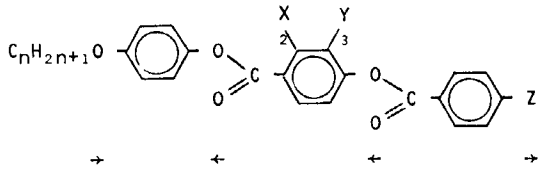


FIGURE 1 Structural formulae and acronyms of the different studied series.

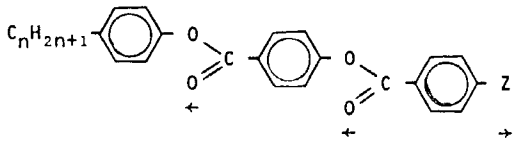
†Presented at the Ninth International Liquid Crystal Conference, Bangalore India, 1982.

where $Z = NO_2$ or CN

$X = H$, $Y = Cl$ DB n O NO_2 3Cl or DB n O CN 3Cl

$X = Cl$, $Y = H$ DB n O NO_2 2Cl or DB n O CN 2Cl

These four series have basically a structure similar to those of the well known DBn series. The dipole moments of the two esters groups are opposite to the one of the end cyano or nitro group:

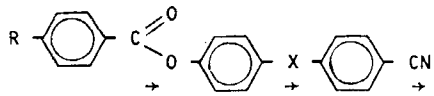


(structure I)

The DBn cyano[1,2] or nitro[2] ($X = Y = H$) compounds have shown a rich variety of smectic A phases:[3] S_{A_1} (monolayer), S_{A_d} (partially bilayer), S_{A_2} (bilayer) for instance which come out from the antiparallel overlap of the polar end groups of neighbor molecules. We recall too the existence of the so-called $S_{\tilde{A}}$ *antiphase*[4] in some of these systems.[5]

These ones are formed by non-tilted molecules, but a very recent extension of this special polymorphism to the biaxal smectic C phases has been achieved: discovery of a S_{C_2},[6,7] S_{C_d}[6,8,9] and evidence for a ribbon $S_{\tilde{C}}$ phase.[10]

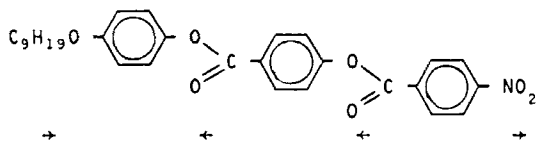
On an other hand molecules of the type:



(structure II)

(in this case all the dipolar moments are parallel to that of the cyano group) have been extensively investigated and most of them give rise to reentrant nematic phases.[2]

Close to these two classes of molecular structures I and II a rather exciting sample has been recently reported: the so-called DB_9ONO_2 with the formula:



which exhibits a remarkable mesomorphic sequence:[11]

$$K\ 109\ [S_{C_2}\ 96]\ S_{\tilde{C}}\ 118\ S_{A1}\ 124\ N_{re}\ 127\ S_{A_{dre}}$$

$$138\ N_{re}\ 156\ S_{A_d}\ 195\ N\ 224\ I$$

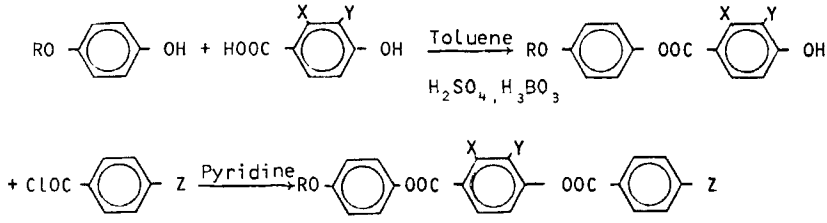
Furthermore the only published cyano compound with the structure I (DB_n) but substituted by a chlorine on the central benzene ring[1] provides another interesting $S_?$–S_{C_2}–S_{A_2} sequence in which the $S_?$ is a novel fluid biaxial smectic phase.[7]

Taking into account all these results we have explored four series of 4-alkoxyphenyl 4′-cyano or nitrobenzoyloxy-2″ or 3″-chlorobenzoates in order to test the influence of the position of the lateral substituted chlorine on the mesomorphic polymorphism.

The structural formula and acronyms of the different synthesized series are shown in figure 1.

II. EXPERIMENTAL

The synthesis of the four series follows the same scheme:



All the products are purified by chromatography on silica gel with benzene as the eluting solvent followed by recrystallization from ethanol. The purities of the samples have been checked by thin layer chromatography and elemental analysis.

The transition temperatures were determined using a Mettler FP5 hot stage in conjunction with a polarizing microscope as well as through DSC (DUPONT 990). The X-ray studies, the details of which will be published elsewhere,[12] were made using a high temperature Guinier camera (Hüber).

III. RESULTS AND DISCUSSION

The transition temperatures and (when available) the heats of transition are given in Table I (DB n O CN 3Cl), Table II (DB n O NO_2 3Cl), Table III (DB n O CN 2Cl) and Table IV (DB n O NO_2 2Cl).

1. DB n O CN 3Cl. Three derivatives have been synthesized in this series which prove a rather poor polymorphism with *only* a S_C, S_A and nematic phase (Table I).

Yet, S_{A_2}–S_{A_d} transition could have been expected if one consider the large S_A domain and the molecular analogy with the methyl derivatives published by MADHUSUDANA et al:[13]

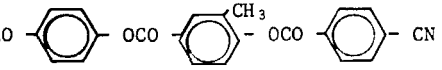


TABLE I

Transition temperature of the DB O_n CN 3Cl compounds

R	*K*		S_C	S_A		*N*		*I*
C_9H_{19}	·	118	—	·	137	·	186	·
$C_{10}H_{21}$	·	118	(.106)	·	160	·	183	·
$C_{11}H_{23}$	·	116	(.110)	·	169.5	·	179	·

( ) indicate monotropic transitions

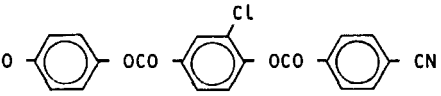


TABLE II

Transition temperature of the DB10 ONO_2 3Cl

R	*K*		$S_{\tilde{C}}$	S_A	N_{re}		S_A		*N*		*I*
$C_{10}H_{21}$	·	80	(.67.5)	(.68)	·	102.5	·	140	·	170	·

$S_{\tilde{C}}$ tilted smectic with a ribbon structure
( ) indicate monotropic transitions

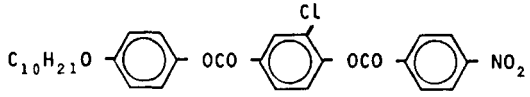


TABLE III

Transition temperature of the DB O_n CN 2Cl compounds

R	K	$S_?$	S_{C_2}	S_A[a]	N	I
C_6H_{13}	· 112	—	(.111)	· 143	· 197	·
C_7H_{15}	· 120	(. 99)	.115	· 155	· 190	·
C_8H_{17}	· 111	(.106)	.119	· 166.5	· 186	·
C_9H_{19}	· 100	.106	.121	· 173	· 182	·
	4.9	*0.089*	*0.010*	*0.12*	*0.22*	
$C_{10}H_{21}$	· 96	(. 95)	.122.5	· 176	· 179	·
$C_{11}H_{23}$	· 95	—	.123	· 178	—	·
$C_{12}H_{25}$	· 100	—	.126	· 178	—	·

$S_?$ biaxial bilayered fluid mesophase
S_{C_2} bilayer smectic C phase
[a] a S_{A_2}–S_{A_d} transition has been detected ~150°C, see ref. 12
( ) indicate monotropic transition
For $r = C_9H_{19}$ the heat of transition (Kcal.mole^{-1}) are given in italic

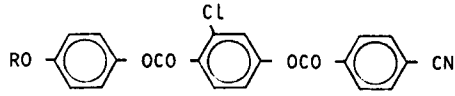
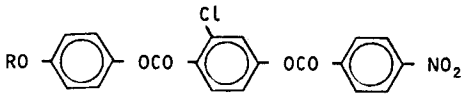


TABLE IV

Transition temperature of the DB O_n NO_2 Cl compounds

R	K	S_{A_2}		S_{A_d}	N	I
C_6H_{13}	· 109	—		—	· 175	·
C_7H_{15}	· 106	—		(. 98)	· 171	·
C_8H_{17}	· 109.5	—		.115	· 166.5	·
C_9H_{19}	· 106.5	(.105)	0.21[a]	.135	· 165	·
$C_{10}H_{21}$	· 105	.110	0.19[a]	.152	· 163	·
$C_{11}H_{23}$	· 103	.112	0.24[a]	.159.5	· 162	·

S_{A_2} bilayer smectic A phase
S_{A_d} partially bilayered smectic A phase
( ) indicates monotropic transition
[a] enthalpies (Kcal.mole^{-1}) of the S_{A_2}–S_{A_d} transitions



2. DB n O NO_2 3Cl. Within this series one derivative ($n = C_{10}H_{21}$) is of special interest (Table II) with a reentrant nematic and a reentrant S_A. Moreover another smectic modification is readily detected on cooling which leads to a texture closely related to the $S_{\tilde{C}}$ texture. This series give another example of reentrant phases in pure nitro derivatives. Furthermore this compound provides an intermediate between the now classical $S_A N_{re} S_A N$ and the unique $S_{C_2} S_{\tilde{C}} S_{A_1} N_{re} S_{A_{d_{re}}} N_{re} S_{A_d} N$ new sequence.

3. DB n O CN 2Cl. This series provides other examples of S_{A_2}–S_{C_2} (Figures 2b and 2c) and S_{A_2}–S_{A_d} transitions. The former is clearly characterized through all the techniques used; for example the S_{C_2} phase gives rise to a schlieren texture in the previously homeotropic areas of the S_A phase. However the determination of the S_{A_d}–S_{A_2} transition temperature is much more difficult, especially for long chains ($n \geqslant C_{10}H_{21}$) for which a heat peak is no more noticeable; but the thermal variation of the layer thickness still exhibits a slope change which suggest a possible S_{A_d}–S_{A_2} transition. At last this series provides a new example of the uncommun $S_?$ phase. For example in the C_9 derivative (Table III) a sudden textural change makes the $S_{C_2} \rightarrow S_?$ transition obvious (Figures 2c and 2d) which corresponds to a clear *DSC* peak, however the molecular order in this bilayered phase still remain unknown.

4. DB n O NO_2 2Cl. This last new series provide the first evidence for a S_{A_2}–S_{A_d} transition in nitro series. Interestingly a transient textural change is observed under microscope (Figures 3a and 3b), this peculiar behaviour is obviously connected to a straightforward enhancement of the layer spacing and to a rather strong heat of transition (Table IV).

CONCLUSION

Four series of 4-alkoxyphenyl 4′cyano or nitrobenzoyloxy 2″ or 3″-chlorobenzoates have been synthesized. According to the direction of the various dipole moment, all of these series belong to the DB_n family. Anyway the presence of a chlorine atom on the central benzene ring obviously enhance structure I (Cl in the 2 position) or the mesomorphic tendancies of structure II (Cl in the 3 position).

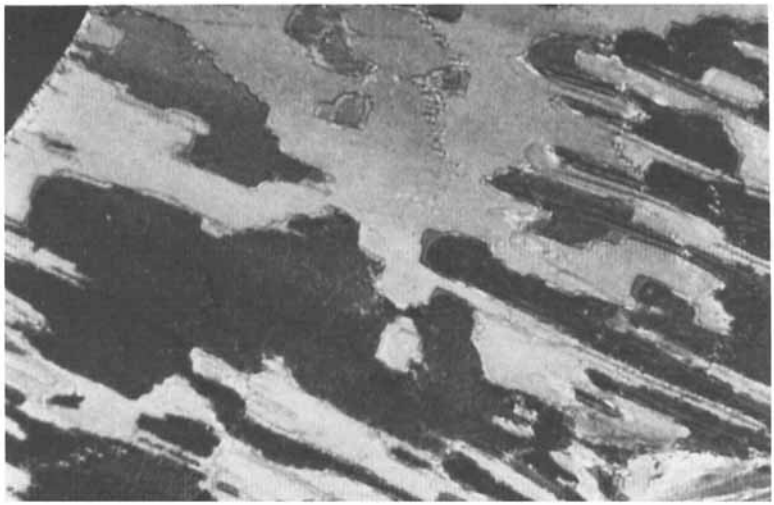
— In the position 3 the chlorine leads to reentrant nematic and for nitro derivative to the $S_{\tilde{C}}$ modification.

— In the position 2 the chlorine leads to novel examples of S_{A_2}–S_{A_d}, S_{C_2}–S_{A_2} transitions and the second example of the uncom-

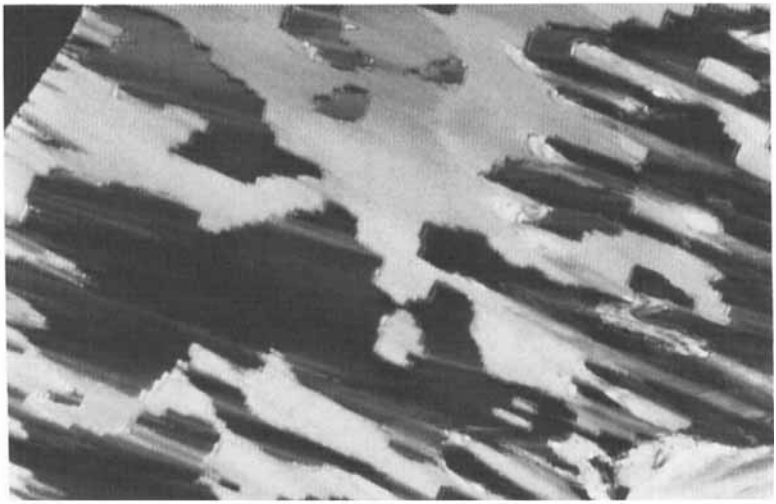
(a)
See Color Plate I

(b)
See Color Plate II

FIGURE 2 Optical textures of DB_9 O CN 2C1 between crossed polarizers: a) 180° nematic phase, b) 120° S_A phase (same area), c) 110° S_{C_2} phase (same area), d) 100° $S_?$ phase (same area).
See Color Plates I-IV, Vol. 116 (3/4).



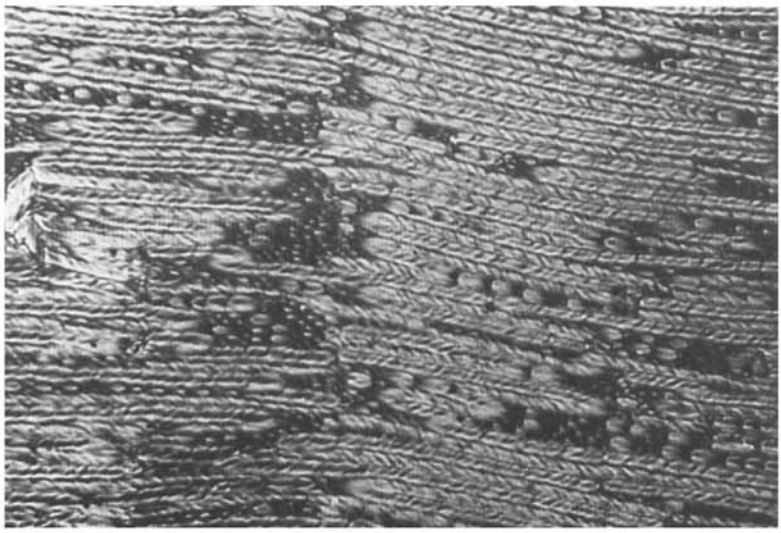
(c)
See Color Plate III



(d)
See Color Plate IV

FIGURE 2 (*continued*)

(a)



(b)

FIGURE 3 Optical textures of DB_{10} O NO_2 2C1 between crossed polarizers: a) 115° S_{A_d} phase, b) 106° S_{A_2} phase (same area).

mon $S_?$ phase (cyano derivatives). At last nitro series provides the first example of a directly observable $S_{A_2} - S_{A_d}$ transition with a transient texture change observed under microscope.

References

1. J. P. Van Meter, R. T. Klingbiel, and D. J. Genova, *Solid State Commun.* **16**, 315 (1975).
2. Nguyen Huu Tinh, *J. Chim. Phys.* **80**, 83 (1983).
3. See for example: F. Hardouin, A. M. Levelut, M. F. Achard, and G. Sigaud, *J. Chim. Phys.* **80**, 53 (1983).
4. G. Sigaud, F. Hardouin, M. F. Achard, and A. M. Levelut, *J. de Physique*, **42**, 107 (1981).
5. F. Hardouin, G. Sigaud, Nguyen Huu Tinh, and M. F. Achard, *J. de Physique*, **42**, L-63 (1981).
6. Nguyen Huu Tinh, F. Hardouin, C. Destrade, and H. Gasparoux, *J. de Physique*, **42**, L-739 (1982).
7. F. Hardouin, Nguyen Huu Tinh and A. M. Levelut, *J. de Physique Lett.* **43**, L 779 (1982).
8. G. Pelz, S. Diele, A. Wiegeleben, and D. Demus, *Mol. Cryst. Liq. Cryst. Lett.* **64**, 163 (1981).
9. Nguyen Huu Tinh, F. Hardouin, C. Destrade, and A. M. Levelut, *J. de Physique*, **43**, L-33 (1982).
10. F. Hardouin, Nguyen Huu Tinh, M. F. Achard, and A. M. Levelut, *J. de Physique*, **43**, L 327 (1982).
11. Nguyen Huu Tinh, F. Hardouin, and C. Destrate, *J. de Physique*, **43**, 1127 (1982).
12. F. Hardouin, M. F. Achard, C. Destrate, and Nguyen Huu Tinh, *J. de Physique*, **45**, 765 (1984).
13. N. V. Madhusudana, B. S. Srikanta, and M. Subramanya Raj Urs, *Mol. Cryst. Liq. Cryst.* **97**, 49 (1983).