Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Reentrant phenomenon in cyanoaryl alkylthioxybenzoates and cyanobenzoyloxyphenyl alkylthiobenzoates

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To cite this Article Nguyen, H. T. , Destrade, C. , Twieg, R. J. and Betterton, K.(1990) 'Reentrant phenomenon in cyanoaryl alkylthioxybenzoates and cyanobenzoyloxyphenyl alkylthiobenzoates', Liquid Crystals, 8: 3, 419 — 427
To link to this Article: DOI: 10.1080/02678299008047357
URL: http://dx.doi.org/10.1080/02678299008047357

LIQUID CRYSTALS, 1990, VOL. 8, NO. 3, 419–427

Reentrant phenomenon in cyanoaryl alkylthioxybenzoates and cyanobenzoyloxyphenyl alkylthiobenzoates†

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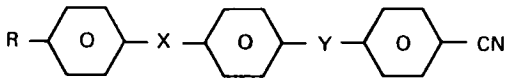
(*Received 15 January 1990; accepted 30 March 1990*)

Three new series of cyanoaryl 4-alkylthioxybenzoates have been synthesized and characterized. The 4-cyanophenyl series displays only transient mesomorphic properties while the 6-cyano-2-naphthyl and 4-cyanobiphenyl series exhibit the classical nematic and smectic A phases; a reentrant nematic phase is also found in the latter. Two other new series in which the position of the sulphur atom in the central rigid core has been varied were also prepared: the 4-[4′-cyanobenzoyloxy]-phenyl 4-alkylthiobenzoates and 4-[4′-alkylbenzoyloxy]phenyl 4-cyanothiobenzoates. As in the analogous benzoate series, the reentrant phenomenon with the sequence C, $S_{A_{re}}$, N_{re}, S_A, N, I is observed with the nonyl derivatives. Comparisons between the alkoxybenzoates and the alkylthioxybenzoates are given.

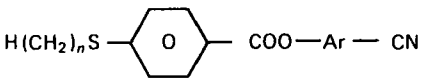
1. Introduction

It is now well established that polar molecules with three phenyl rings with the general formula



possess a rich polymorphism with a number of reentrant sequences and new fluid smectic modifications [1–5]. While the influence of R = alkyl, alkoxy, alkanoyloxy on the reentrant phenomenon [6] has been intensively studied, the mesomorphic properties of the alkylthioxy group require more investigations. Since the phenyl thiobenzoate core [7, 8] is well known to induce smectic phases it is interesting to study the behaviour of this core with the cyano group on the reentrant phenomenon.

In order to study the influence of the sulphur in the chain and in the central group (X, Y), we have synthesized two different polar series,

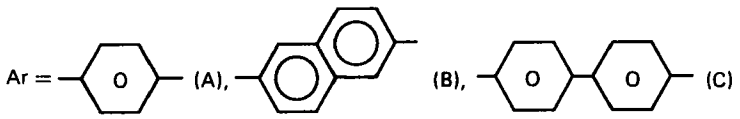


I

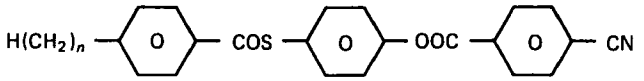
† Presented at the Twelfth International Liquid Crystal Conference, 15–19 August 1988, University of Freiburg, F.R. Germany.

0267-8292/90 $3.00

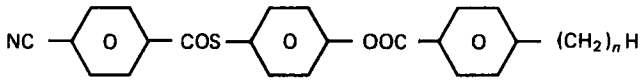
with



and



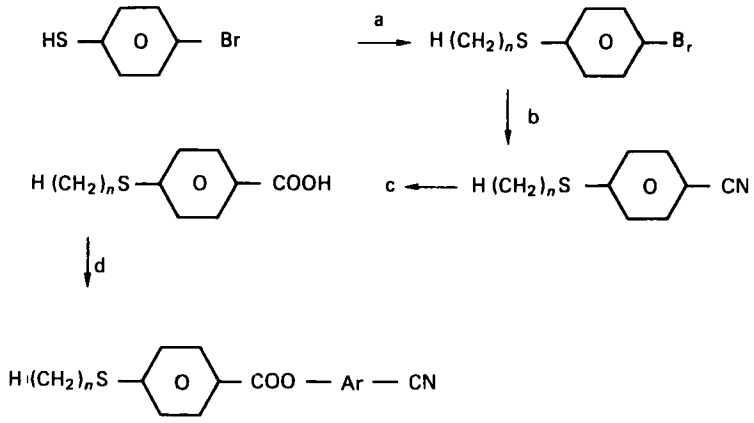
IIA



IIB

2. Synthesis

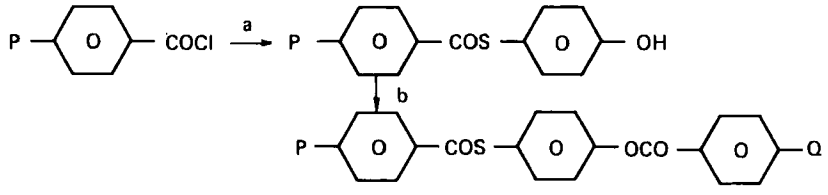
The compounds of these two series **I** and **II** were prepared following schemes 1 and 2. All of the final compounds were purified by chromatography on silica gel with toluene as eluent and recrystallized from absolute ethanol.



I

Scheme 1.

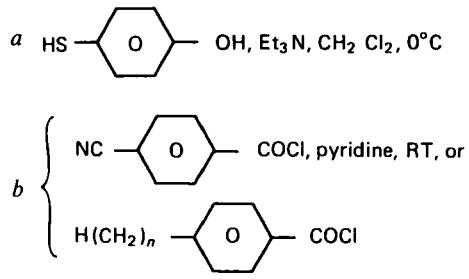
a RBr, KOH, EtOH; *b* CuCN, DMF, 200°C;
c H_2SO_4 50 per cent, 140°C; *d* $SOCl_2$, HO–Ar–CN, pyridine.



II

Scheme 2.

$$\begin{cases} P = H(CH_2)_n;\ Q = CN\ (A) \\ P = CN;\ Q = H(CH_2)_n\ (B) \end{cases}$$



3. Results and discussion

Most of the compounds prepared are mesogenic. The phase transitions were studied by polarizing microscopy (Mettler FP 5) and by miscibility. The transition temperatures and mesophases types are given in tables 1 to 6.

3.1. *Series* I

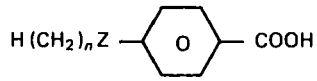
3.1.1. *4-Alkylthioxybenzoic acids*

Due to dimer formation, the 4-alkoxybenzoic acids are mesogenic and the mesophases observed are first nematic, then nematic and smectic C as the chain length is increased. The mesomorphic range is wide, around 50°C (see table 1). When the oxygen is replaced by sulphur in the chain, the transverse dipolar moment decreases, the intermolecular interaction also decreases, and the mesomorphism of the 4-alkylthioxybenzoic acids is weaker than the corresponding alkoxy acids. The clearing temperatures are also lower and the odd–even effect is observed in this series. When n is even, most of the mesophases are enantiotropic (except $n = 10$) but with a very short range and when n is odd, all of the mesophases are monotropic.

3.1.2. *4-cyanophenyl 4'-alkylthioxybenzoates* IA

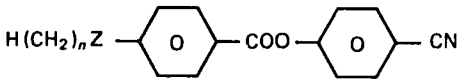
The lower aptitude of the alkylthioxy chains to generate mesophases relative to the alkoxy chain is more pronounced in series **IA** as clearly shown in table 2 (compare

Table 1. Transition temperatures of the compounds



n	Z	C		S_C		N		I	Ref.
6	O	●	105°C	—		●	153	●	[9]
6	S	●	103°C	—		●	111	●	
7	O	●	92°C	●	98	●	146	●	[9]
7	S	●	112°C	—		(●)	102)	●	
8	O	●	101°C	●	108	●	147	●	[9]
8	S	●	105°C	—		●	108·5	●	
9	O	●	94°C	●	117	●	143	●	[9]
9	S	●	113°C	—		(●)	102)	●	[10]
10	O	●	97°C	●	122	●	142	●	[9]
10	S	●	109°C	(●)	101)	(●)	107)	●	
11	O	●	84·5°C	●	128	●	139·5	●	[9]
11	S	●	110°C	(●)	102)	(●)	106)	●	
12	O	●	95°C	●	129	●	137	●	[9]
12	S	●	106°C	●	107·5	●	108	●	[10]

Table 2. Transition temperatures of the compounds



n	Z	C		S_A		N		I	Ref.
6	O	●	70·5°C	—		●	81	●	[9(b)]
6	S	●	75°C	—		(●	)†	●	
7	O	●	71·6°C	—		●	82	●	[9(b), 11]
7	S	●	87°C	—		—		●	
8	O	●	75·6°C	—		●	88	●	[9(b), 11]
8	S	●	77°C	—		(●	)†	●	
9	O	●	62°C	(●	59)	●	84	●	[11]
9	S	●	79°C	—		—		●	
10	O	●	79°C	(●	78)	●	86	●	[11]
10	S	●	78°C	(●	)†	—		●	[11]
11	S	●	84°C	(●	)†	—		●	
12	S	●	82°C	(●	76)	—		●	

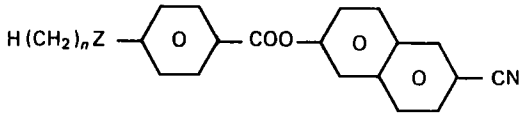
† Observed when quickly cooled from the isotropic phase.

X = S and X = O compounds). Only one compound, the dodecylthioxy derivative, exhibits a monotropic S_A phase. All others are either not mesomorphic or exhibit a strongly metastable mesophase when cooled quickly from the isotropic phase.

3.1.3. *6-cyano-2-naphthyl 4'-alkylthioxybenzoate* **IB**

In the molecule with the longer core, the mesophases are enantiotropic. They are nematic for short chains (n = 6, 7), nematic and smectic A for medium ones (n = 8, 9) and only smectic A for the longer ones (n = 10–12). In this series (see table 3) the reentrant phenomenon is not observed as in the alkoxy analogues in which the S_A phase is only observed when n = 10 with the sequence C (N_{re}) S_A N I. This

Table 3. Transition temperatures of the compounds



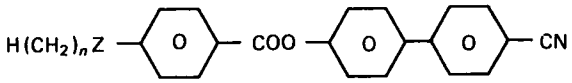
n	Z	C		N_{re}		S_A		N		I	Ref.
6	O	●	95°C	—		—		●	160	●	[12]
6	S	●	88°C	—		—		●	134	●	
7	O	●	95°C	—		—		●	161	●	[11]
7	S	●	100°C	—		—		●	129	●	
8	O	●	92·8°C	—		—		●	156	●	[12]
8	S	●	99°C	—		●	109·5	●	129·5	●	
9	O	●	92°C	—		—		●	153	●	[11]
9	S	●	107°C	—		●	122	●	127	●	
10	O	●	78°C	(●	72°C)	●	139	●	152	●	[11]
10	S	●	100°C	—		●	128·5	—		●	
11	O	●	79°C	—		●	146	●	149·5	●	[11]
11	S	●	100°C	—		●	130·5	—		●	
12	S	●	104°C	—		●	133	—		●	

indicates, that for polar molecules the alkylthioxy groups favour the S_A phase more than the alkoxy ones and consequently the nematic phase is suppressed.

3.1.4. *4-cyanobiphenyl 4'-alkylthioxybenzoates* **IC**

This specific behaviour of the alkylthioxy groups is confirmed in series **IC** where the S_A phase appears from $n = 7$ while in the alkoxy series, it is observed from $n = 8$ (see table 4). Consequently the derivative of **IC** displays a reentrant nematic phase with a shorter chain than the alkoxy ones. This monotropic N_{re} phase is only observed for one derivative. The sequence C (N_{re}) S_A N I of the heptylthioxy derivative is miscible with that of the octyloxy compound (see figure 1). As for 4-alkylthioxy benzoic acids, the clearing temperatures of compounds **IA**, **IB**, **IC** are lower than those of the alkoxy analogues.

Table 4. Transition temperatures of the compounds



n	Z	C		N_{re}		S_A		N		I	Ref.
6	O	●	103°C	—		—		●	246	●	[13]
6	S	●	107°C	—		—		●	218	●	
7	O	●	89°C	—		—		●	246	●	[13]
7	S	●	104°C	(●	91)	●	155	●	211	●	
8	O	●	97°C	●	120	●	201	●	240	●	[12, 13]
8	S	●	108°C	—		●	186	●	206	●	
9	O	●	96°C	(●	71)	●	217	●	232	●	[13]
9	S	●	109°C	—		●	193	●	201	●	
10	O	●	100°C	—		●	224	●	230	●	[13]
10	S	●	103°C	—		●	196·5	●	197·5	●	
11	O	●	104°C	—		●	224	●	225	●	[13]
11	S	●	107°C	—		●	197	—		●	
12	O	●	102°C	—		●	224	—		●	[13]
12	S	●	105°C	—		●	197	—		●	

3.2. *Series* **II**

Here, the sulphur atom is in the central linkage. The electronegativity of sulphur (2·8) is smaller than that of oxygen (3·5), and it is significantly larger than oxygen (van der Waals radii are 1·85 Å and 1·4 Å respectively). Consequently the sulphur is more favourable to the resonance of the COS group than the oxygen in –COO–, the molecules are more rigid and the transverse dipolar moment of –COS– is larger than that of –COO–. So, the intermolecular interaction is higher with COS and the clearing points are also higher than those of the –COO– derivatives.

3.2.1. *4-alkylbenzoylthioxyphenyl 4'-cyanobenzoates* **IIA**

This series displays the same mesomorphic properties as the benzoate analogues. We observe N and probabily S_{A_1} phases for short chains ($n = 7, 8$). A double reentrant sequence, C $S_{A_{re}}$ N_{re} S_A N I, is obtained with the nonyl derivative. This sequence is entirely miscible with that of the octylbenzoate analogue (see table 5, figure 2).

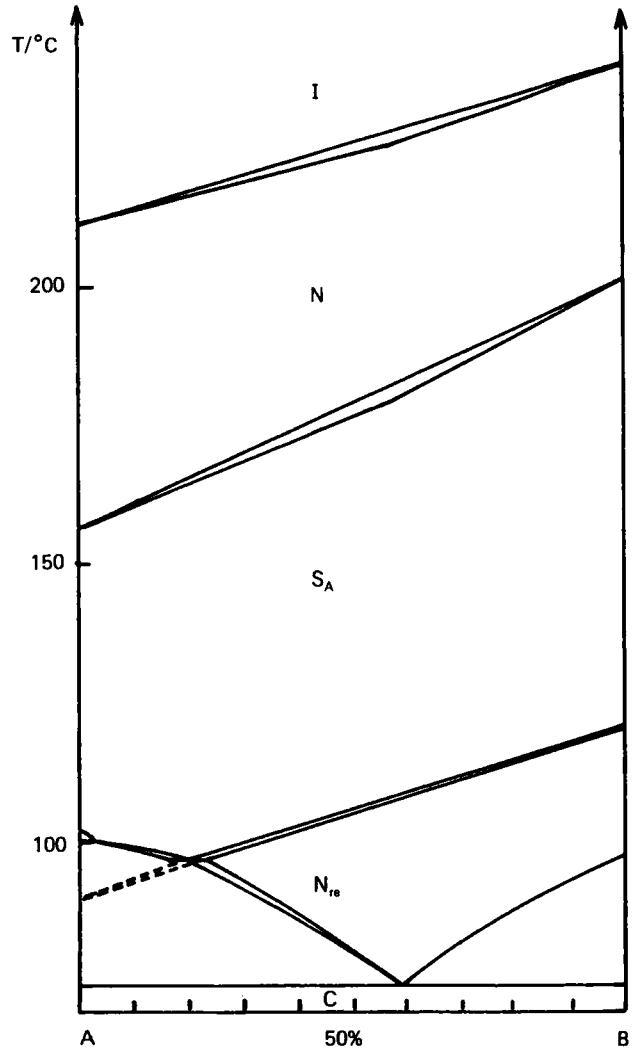
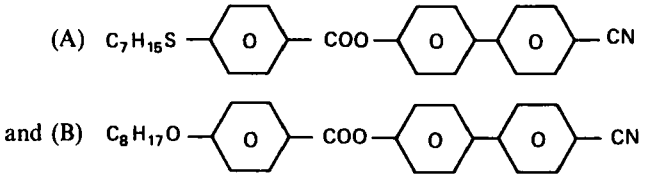


Figure 1. Diagram of isobaric state for the mixtures of



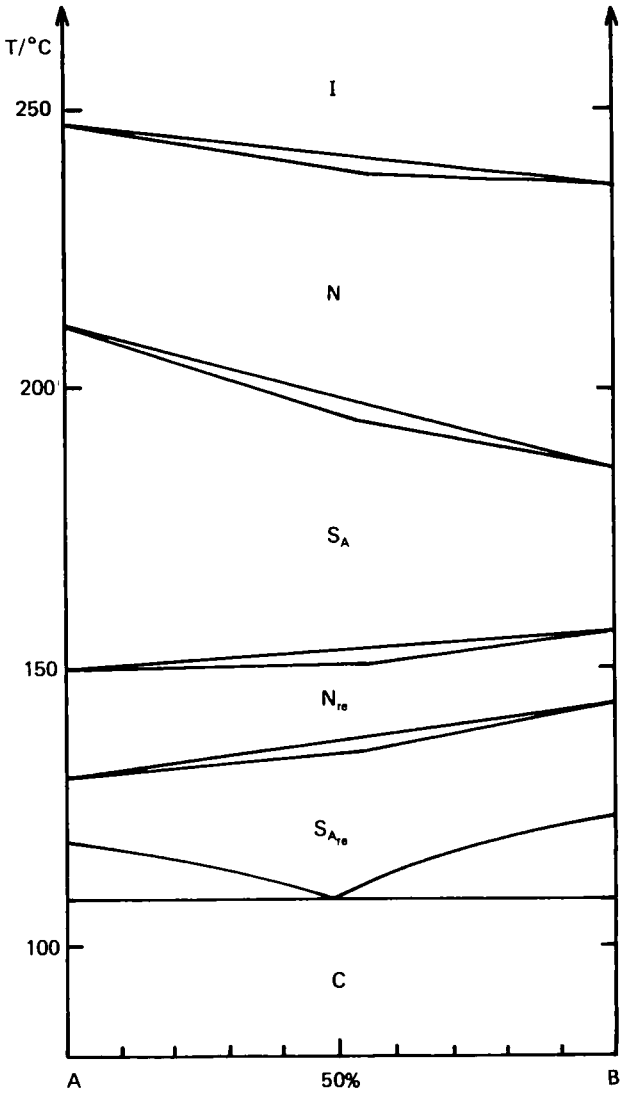


Figure 2. Diagram of isobaric state for the mixtures of

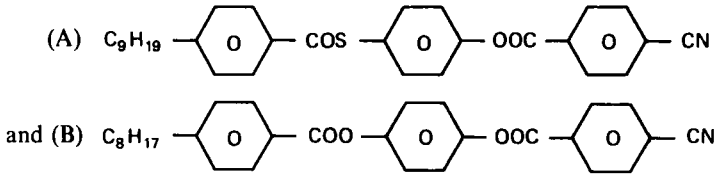
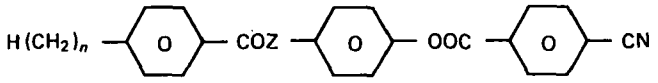


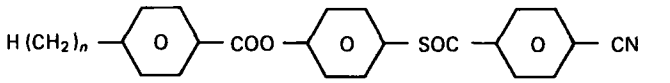
Table 5. Transition temperatures of the compounds



IIA

n	Z	C		S_{A_1}		N_{re}		S_A		N		I	Ref.
7	O	●	121°C	●	153	—		—		●	245	●	[14]
7	S	●	125°C	●	156	—		—		●	255	●	
8	O	●	125°C	●	142	●	157	●	186	●	238	●	[14]
8	S	●	121°C	●	157	—		—		●	250	●	
9	O	●	126°C	—		—		●	213	●	233	●	[14]
9	S	●	119°C	●	130	●	150	●	211	●	246	●	
10	O	●	125·5°C	—		—		●	218	●	227	●	[14]
10	S	●	115°C	—		—		●	226	●	240	●	
11	S	●	116°C	—		—		●	227	●	236	●	
12	S	●	105°C	—		—		●	197	—		●	

Table 6. Transition temperatures of the compounds



IIB

n	C		S_A		N_{re}		S_A		N		I
7	●	113°C	●	122	—		—		●	255	●
8	●	119°C	(●	109)	—		—		●	248	●
9	●	114°C	(●	98)	●	136	●	206	●	242	●
10	●	114°C	—		—		●	222	●	237	●

3.2.2. *4-alkylbenzoyloxyphenyl 4'-cyanothiobenzoates* **IIB**

A little difference between series **IIA** and **IIB** is observed due to the difference of longitudinal dipolar moment of -COS- and -COO- in the cores. In series **IIB** (see table 6) the low temperature S_A phase is less favoured than the nematic phase and we also obtain the reentrant sequence but the reentrant S_A phase is monotropic.

4. Conclusion

Five new polar series containing a sulphur atom in the chains or in the core have been synthesized. Three of them display reentrant mesomorphism. Two important influences of sulphur are emphasized (i) alkylthioxy chains are less favourable for mesomorphic properties than the alkoxy, and (ii) in contrast the thiocarboxylate in the central group favours the formation of mesophases and especially smectic phases.

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