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Chirality in Polar Mesogens: Reentrant Cholesteric and New Smectic Phases†

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Several chiral polar mesogens are described. The existence of the reentrant cholesteric phase is discussed from a molecular structure point of view (chain length, central cores). Compound 1c (n = 3) provides the first example of a double reentrant sequence: K-S_A-N^*_{re}-S_A-N^*-I. In addition, we have obtained the chiral variant of some new smectic modifications: $S^*_{C_2}$, S_{C^*} . . .

INTRODUCTION

We recently reported several chiral polar elongated molecules exhibiting a reentrant cholesteric phase[1] at atmospheric pressure. Here we describe new studies on this topic, using different chiral chains R* coupled to the same terminal asymmetric center.

Several polar cyano or nitro mesogenic cores are well known for their aptitude in giving reentrant nematics[2,3] (series 1* and 2*)

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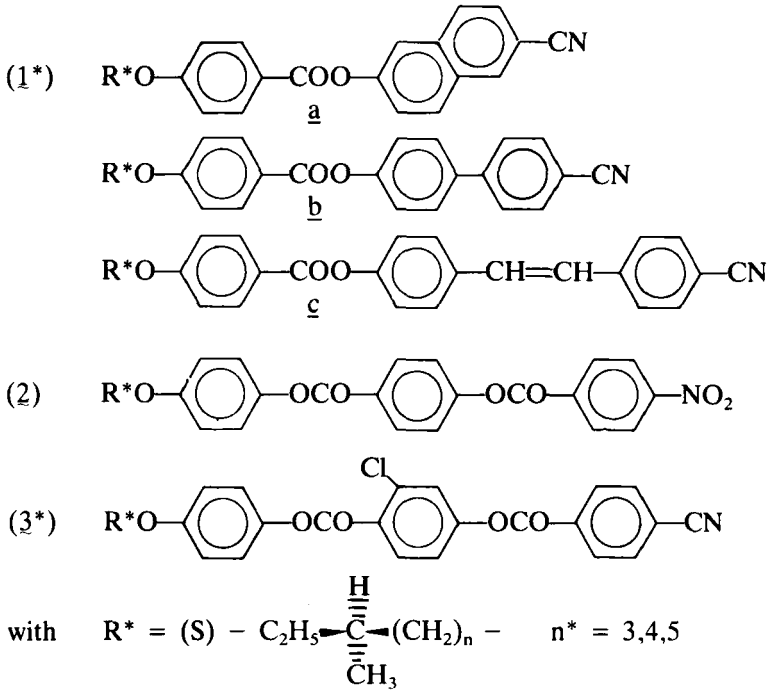
and novel smectic modifications: S_{C_2}, $S_{\tilde{C}}$ . . . (series 2* and 3*). One of our aims was to check the relation between the chiral chain length and rigid core structure for reentrant phenomena as previously investigated for achiral systems.

Three different chiral series have been investigated: 1* a, b, c, 2* and 3*



RESULTS AND DISCUSSION

SERIES 1

Table I* shows the transition temperatures obtained for the chiral 6-cyanonaphthyl-2 (1a*), 4-cyanobiphenyl-4′ (1b*), 4-cyanostilbene-4′ (1c*) *p*-(S)-alkoxybenzoates.

In series 1a*, no reentrant phenomena were observed for the pure compounds but it did occur for the mixture 1a* (n^* = 4) and 1a* (n^* = 5) (Figure 1).

In series 1b*, only one compound (n^* = 3) exhibits a reentrant cholesteric phase, but in series 1c* this phase is observed for two compounds (n^* = 3 and 4), the former being the first example of a

TABLE I*

Transition temperatures of compounds 1*a, b, c

	n^*	K	S_3^*	S_C^*	S_A	N_{re}^*	S_A	N^*	I
1a*	4	. 65	—	—	—	—	—	. 129	.
	5	. 80	—	—	—	—	. 122	. 135	.
1b*	3	. 74	—	—	—	. 99	. 178	. 231	.
	4	. 66	—	—	—	—	. 202	. 223	.
	5	. 72	—	(. 42)	—	—	. 214	. 220	.
1c*	3	. 88	—	—	. 112	. 131	. 217	. 275	.
	4	. 70	(. 63)	—	—	(. 67)	. 243	. 266	.
	5	. 70	(. 54)	(. 64)	—	—	. 247	. 258	.

TABLE I[2]

Transition temperatures of compounds 1a, b, c

	n	K	S_A	N_{re}	S_A	N	I
1a	9	. 92	—	—	—	. 155	.
	10	. 78	—	(. 72)	. 139	. 152	.
	11	. 79	—	—	. 146	. 149.5	.
1b	8	. 97	—	. 120	. 201	. 240	.
	9	. 96	—	(. 71)	. 217	. 232	.
	10	. 100	—	—	. 224	. 230	.
1c	8	. 96	(. 95)	. 138	. 248	. 283	.
	9	. 97	(. 63)	(. 94)	. 261	. 275	.
	10	. 96	—	(. 78)	. 265	. 270	.

double reentrant sequence: K S_A N_{re}^* S_A N^* I (Figure 2). This tetramesomorphism is entirely miscible with that of achiral T8[2] (Figure 3). Derivatives 1c* (n = 4) and 1c* (n = 5) exhibit an evidently biaxial smectic modification at low temperature, the structure of which is not yet known, although its optical textures are rather similar to the bidimensional smectic phase recently described in some chlorodibenzoates[4] (Figure 4).

As a comparison Table I with the data for some of the corresponding achiral derivatives, i.e. with R = normal paraffinic chain. Several features are apparent:

- The chiral branched chains inducing reentrant cholesteric phases are systematically shorter than the normal ones leading to reentrant phenomena.
- The longer the polar rigid core, the greater the tendency towards reentrant phenomena. Again we find that three benzene ring systems are particularly suitable for this kind of phenomenon.

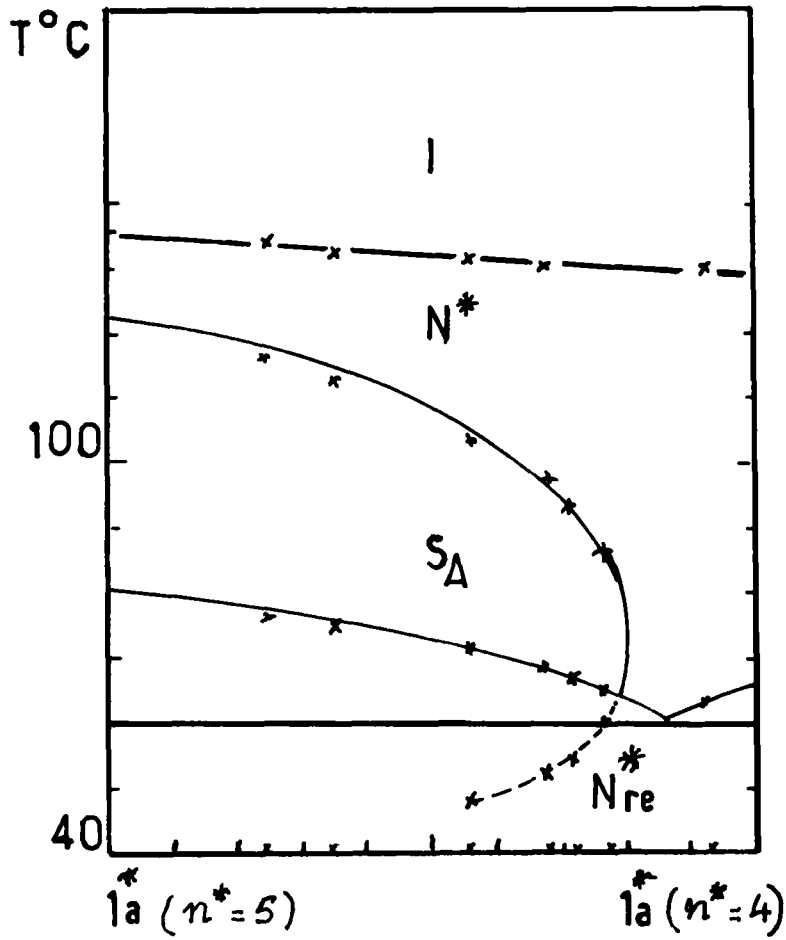


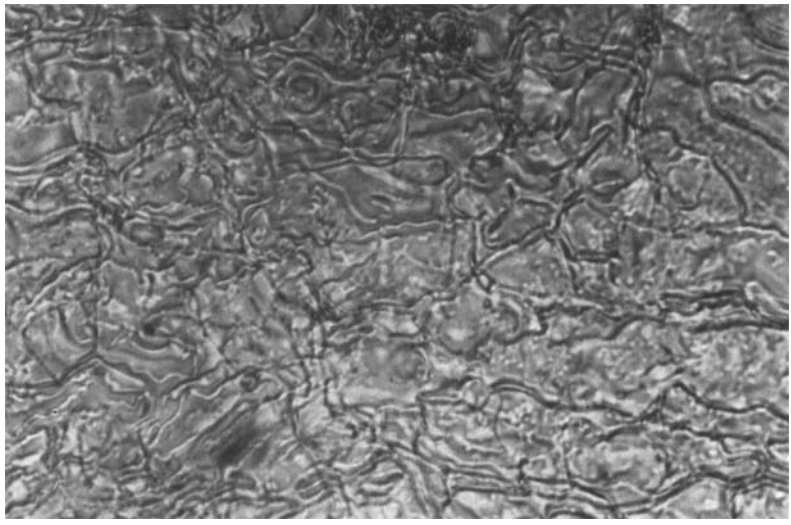
FIGURE 1 Diagram of isobaric state of the mixture of $1^*a(n^* = 5)$ (left) and $1^*a(n^* = 4)$ (right).

• Finally it is apparent (see Table I* and I) that branched chains are less favourable than normal ones in this respect, but smectic C properties are injected into the chiral series 1b* and 1c*.

SERIES 2*

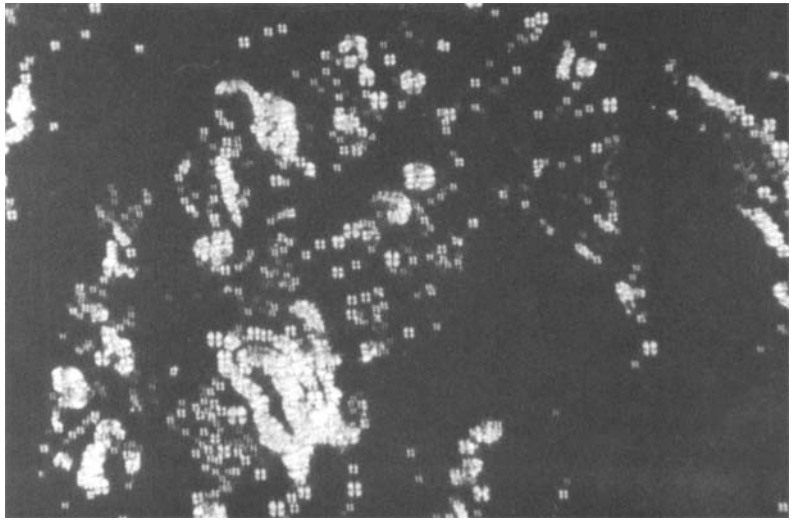
Table II* summarizes the transition temperatures of chiral 4-(S)-alkoxyphenyl 4′-(4″-nitrobenzoyloxy)benzoates.

In this chiral series, all the pure compounds are devoid of reentrant properties. However, a reentrant cholesteric phase is observed in a



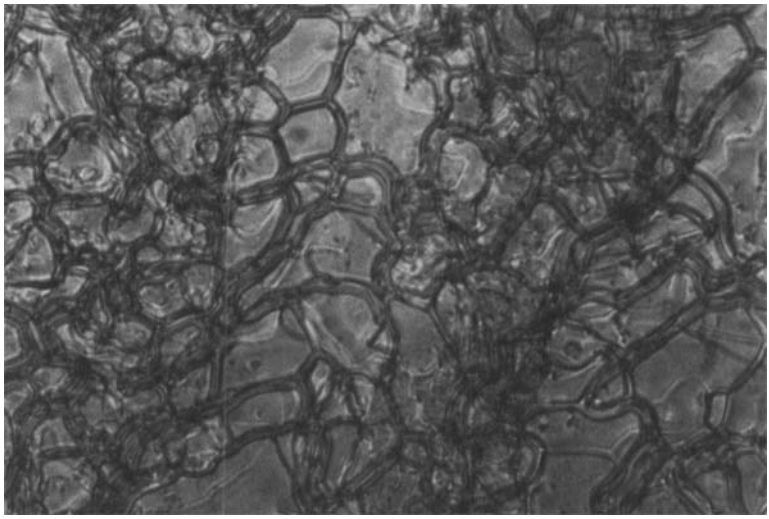
(a)

See Color Plate XXV, located in the final volume of these conference proceedings.



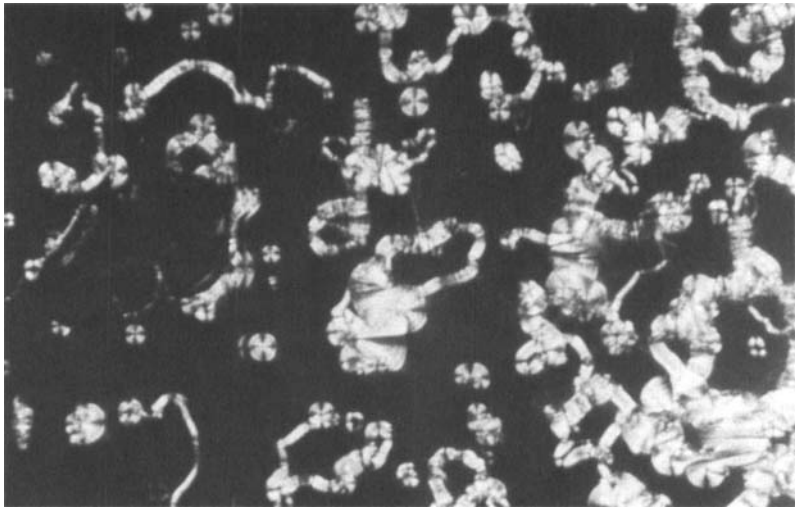
(b)

FIGURE 2 Optical textures of the compound 1c^*(n^* = 3): (a) Cholesteric phase at 220°C; (b) Smectic A phase at 200°C; (c) Reentrant cholesteric phase at 117°C; (d) Reentrant smectic A phase at 91°C.
See Color Plate XXVI, located in the final volume of these conference proceedings.



(c)

See Color Plate XXVII, located in the final volume of these conference proceedings.



(d)

See Color Plate XXVIII, located in the final volume of these conference proceedings.

FIGURE 2 (*Continued*)

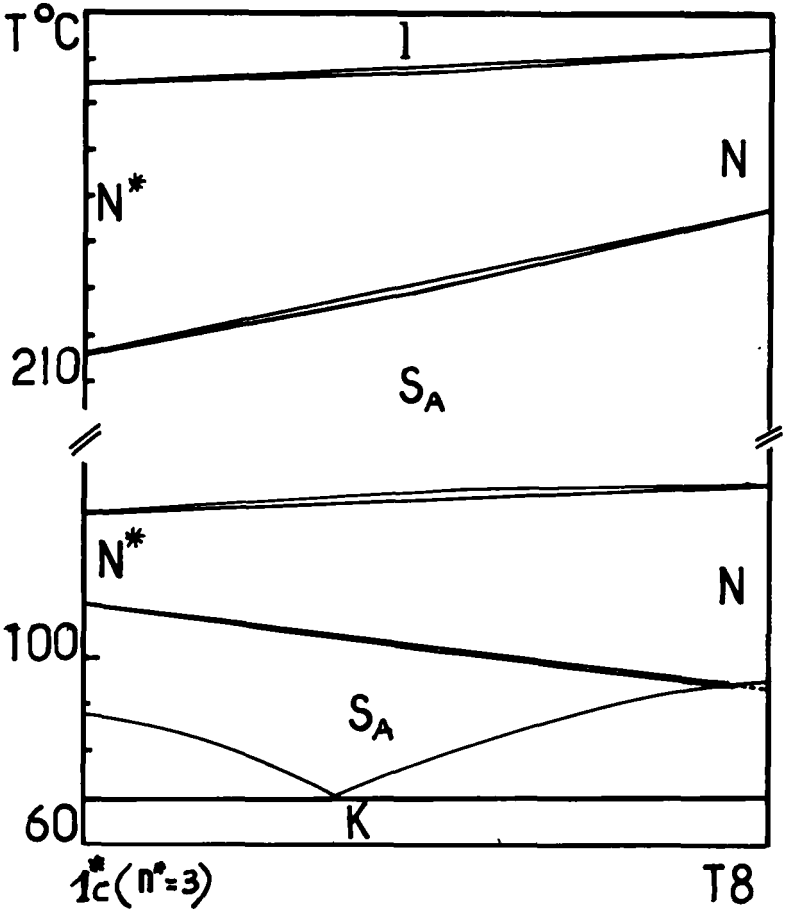
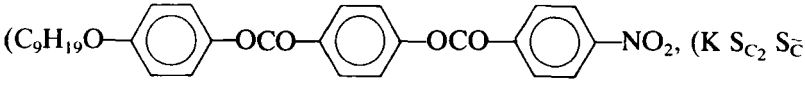


FIGURE 3 Diagram of isobaric state of the mixture of 1*c(n^* = 3) (left) and T_8 (right).

mixture of 2* (n^* = 4) and 2* (n^* = 5). The corresponding binary diagram will be detailed elsewhere. Taking into account the comparison between series 1* and 1, the absence of reentrance is perhaps not surprising in series 2* since the corresponding achiral series 2 shows only one example of a reentrant sequence



S_A N_{re} S_A N_{re} S_A N I).[5] The ability of a chiral branched chain in conferring reentrant properties seems to be lower than that of a

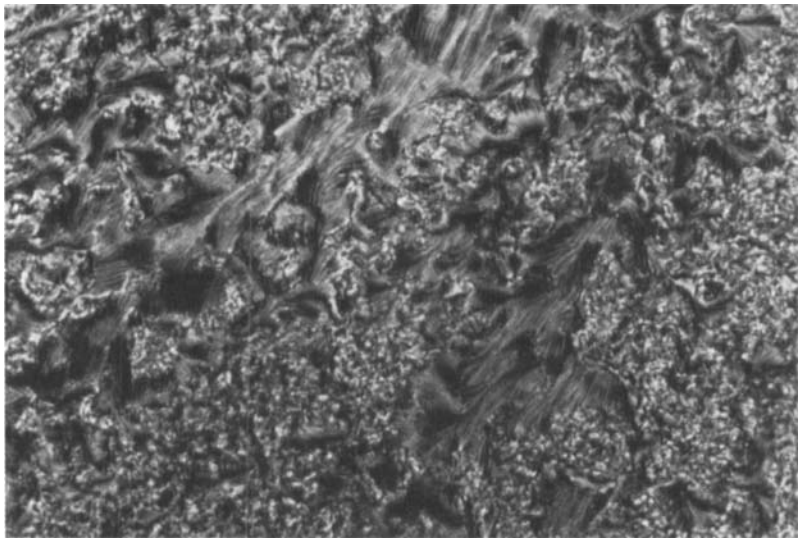


FIGURE 4 Optical textures of $S_{\tilde{C}}^{*}$ phase of $1c^{*}(n^{*} = 5)$. See Color Plate XXIX, located in the final volume of these conference proceedings.

TABLE II*
Transition temperatures of 2* compounds

2*	n^{*}	K	$S_{\tilde{C}}^{*}$	S_A	N*	I
	3	. 107	—	. 111	. 216	.
	4	. 106	—	. 108	. 213	.
	5	. 107	. 108	. 196	. 212	.

FIGURE 5 Optical textures of $S_{\tilde{C}}^{*}$ phase of $2^{*}(n^{*} = 5)$.
See Color Plate XXX, located in the final volume of these conference proceedings.

TABLE III*

Transition temperatures of 3* compounds

3*	n^*	K	$S_?^*$	$S_{C_2}^*$	S_A	N*	I
	3	. 120	(. 115)	—	. 147	. 169	.
	4	. 115	(. 112)	. 117	. 155	. 168	.
	5	. 110	. 120	. 123	. 165	. 168	.

normal chain. Furthermore this series provided the first example of the chiral variant of the so-called $S_{\tilde{C}}$ with optical textures (Figure 5) similar to those of a D_{hd} columnar phase.

SERIES 3*

We have synthesized some of the chiral homologues of the 4-alkoxyphenyl-4′-(4″-cyanobenzoyloxy)2′-chlorobenzoates. Full details of the transition temperatures of these compounds are given in Table III*.

The polymorphism of these substances is similar to that of the achiral series and provides the new chiral $S_{C_2}^*$ and $S_?^*$ phases.

CONCLUSION

A number of related chiral systems have been studied and some of them have been shown to exhibit reentrant cholesteric phases and new chiral smectic phases. A striking feature is that in all cases branched chains are less favourable than normal ones in inducing reentrant phenomenon: with the same core, the chiral reentrant compounds are fewer than the normal chain ones. In addition, we have obtained the chiral variant of new smectic phases in pure compounds in order to help the structural studies of these systems as well as potential applications.

References

1. a) Nguyen Huu Tinh, C. Destrade, J. Malthête and J. Jacques, *Mol. Cryst. Liq. Cryst. Lett.*, **72**, 195 (1982);
b) J. Malthête, Nguyen Huu Tinh and C. Destrade, *9th Intern. Conf. of Liq. Cryst., India*, Bangalore (1982).
2. Nguyen Huu Tinh, *J. Chim. Phys.*, **80**, 83 (1983).

3. Nguyen Huu Tinh, H. Gasparoux, J. Malthête and C. Destrade, *Proceedings of the 4th Winter European Conf. Yugoslavia,* Bovec (1984).
4. a) F. Hardouin, Nguyen Huu Tinh and A. M. Levelut, *J. Phys. (Paris),* **43**, L-779 (1982);
b) C. Destrade, F. Hardouin and Nguyen Huu Tinh, *Mol. Cryst. Liq. Cryst.* (in press).
5. Nguyen Huu Tinh, F. Hardouin and C. Destrade, *J. Phys. (Paris),* **43**, 1127 (1982).