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Reentrant Behavior and Cyano Substituted Aryl *p*-Alkoxycinnamates

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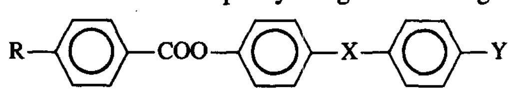
Several new homologous series of cyano substituted aryl *p*-alkoxycinnamates have been synthesized. The reentrant behavior of these series is compared with those of the *p*-alkoxybenzoates series. The influence of the length of the conjugated system on the reentrant phenomenon is studied.

INTRODUCTION

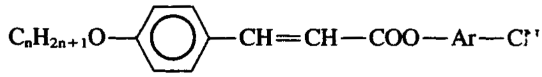
After the first observation of an enantiotropic reentrant nematic phase at atmospheric pressure in pure compounds of the series 4-alkoxybenzoyloxy-4′-cyanostilbenes,[1,2] many new homologous series have been published.[3-20] The series with three phenyl rings have the general formula:



With this structure, we have found that the substitution of the polar group Y=CN by others such as —NO_2, —Br... causes the reentrant phases to disappear.[12] Weissflog *et al.*[15] have recently agreed with us. Moreover, we have shown that the molecules with three benzene rings constitute the optimal condition for the formation of reentrant phases at atmospheric pressure.

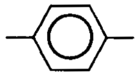
We present several new homologous series of cyano substituted aryl *p*-alkoxycinnamates and we discuss the minimum and maximum length of the rigid core allowing the occurrence of reentrant phases at atmospheric pressure.

The general formula of these substances is as follows:

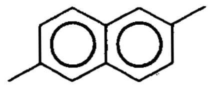


(1)

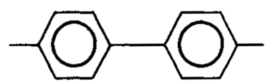
with Ar=



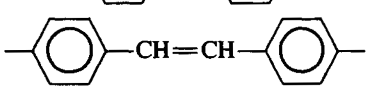
(1a)



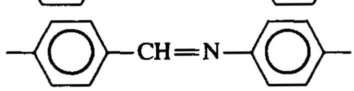
(1b)



(1c)

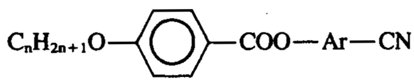


(1d)



(1e)

The reentrant behaviors of these series are compared with these of the *p*-alkoxybenzoates series:

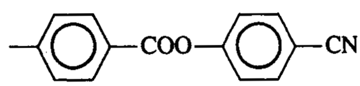


(2 a-e)

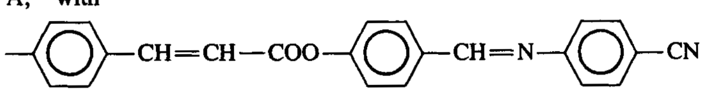
RESULTS AND DISCUSSION

The transition temperatures and types of mesophases of these derivatives are given in Tables I to X.

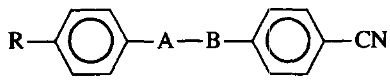
The compounds of the series **1** differ from that of **2** by the introduction of a—CH=CH—group. Consequently, we have different cores with polar cyano end group for which the length of this core (hereafter noted d_C) varies from the shortest:

d_C = 13.6 Å, with  to the longest

d_C = 22.4 Å, with



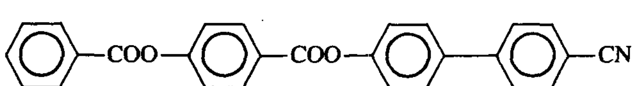
In the homologous series **2a** (Table VI) with the shortest core, the reentrant nematic phase can not be found in a pure derivative, but the mixture of octyloxy and nonyloxy derivatives exhibits a metastable reentrant nematic domain. The same behavior has been reported in a mixture of two cyano derivatives with two benzene rings primary where Cladis[21] discovered the reentrant nematic phase; and then in a mixture of two cyanobiphenyls. It comes out that the derivatives following the formula:



(2)

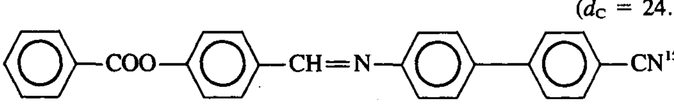
where A—B is —COO—, —CH=N—, —CH=CH—... do not exhibit alone a reentrant nematic phase at atmospheric pressure.

The nonyloxy derivative of **1a** (Table I) exhibits a very metastable reentrant nematic phase. Probably the core ⟨◯⟩-CH=CH—COO-⟨◯⟩-CN (d_C = 16 Å) is the shortest for which a long chain derivative exhibits a reentrant nematic phase at atmospheric pressure. The core of **2b** is slightly longer (d_C = 16.1 Å), and the decyloxy of **2b** (Table VII) presents the sequence N S_A N_{re}; but with these two cores, in each series one can find only one derivative which exhibits this phenomenon. When the mesomerism between the cyano group and the aromatic ring is favored by introducing a —CH=CH— group, the transition temperatures and the clearing temperatures strongly increase, which is also the case when the core length is longer. In the series **1b** (Table II) the length of the core is now d_C = 18.3 Å, the nonyloxy derivative possesses a nearly stable reentrant nematic phase, and the decyloxy derivative exhibits a sequence K N_{re} S_C S_A N I[10]. It is the third compound which is not a Schiff's base but leads to this kind of polymorphism. The difference between **1c** (Table III) and **2c** (Table VIII) or **1d** (Table IV) and **2d** (Table IX) is clear. In the series **2c** and **2d**, there are two or three compounds exhibiting reentrant phenomenon, while in each series **1c** and **1d**, only one derivative or none presents the sequence N S_A N_{re} S_{Are}. On the other hand, these two series exhibit very ordered smectic S_B phase. This is, perhaps, due to the fact that the core of **1c** and **1d** is stiffer. The only perfect resemblance was observed with two series, **1e** (Table V) and **2e** (Table X). In each series, one can find the reentrant nematic phase in three compounds: octyloxy, nonyloxy, and decyloxy. The two decyloxy are the two first compounds which exhibit the sequence I N S_A S_C N_{re} K. The core of **1e** (d_C = 22.4 Å) seems the longest core allowing one to observe the reentrant phenomenon at atmospheric pressure; with longer core such as:



(d_C = 24.1 Å)

or

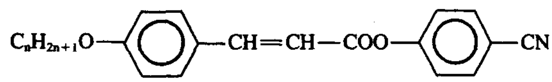


[15]

the reentrant nematic phase disappears.

TABLE I

Transition temperatures of compounds of **1a**



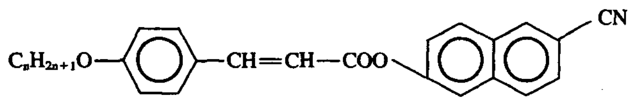
(1a)

n	K		N_{re}	S_A		N		I	Ref.
6	·	73	–	–		·	134	·	24
7	·	72	–	–		·	129	·	24
8	·	84	–	–		·	135	·	
9	·	72	(· 28)	·	117	·	129	·	
10	·	73	–	·	125	·	127	·	

Transition temperatures in this and all other Tables are in °C.

TABLE II

Transition temperatures of compounds of **1b**



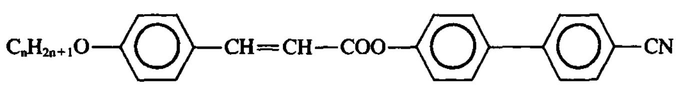
(1b)

n	K		N_{re}	S_C	S_A		N		I
7	·	89	–	–	–		·	204	·
8	·	74	–	–	–		·	202	·
9	·	87	(· 87)	–	·	174	·	197	·
10*	·	83	(· 71)	(· 79)	·	186	·	195	·
11	·	78	–	(· 64)	·	187	·	189	·

*K_2 70 N_{re} 72 S_C 79 S_A 186 N 195 I

TABLE III

Transition temperatures of compounds of **1c**

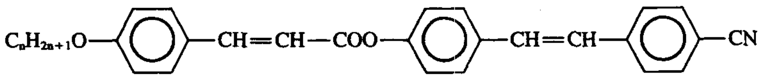


(1c)

n	K		S_B	$S_{A_{re}}$	N_{re}		S_A		N		I
7	·	131	–	(· 118)	·	162	·	202	·	>300	·
8	·	135	(· 93)	–	–		·	247	·	>290	·
9	·	119	(· 87)	–	–		·	256	·	279	·
10	·	117	–	–	–		·	260	·	264	·

TABLE IV

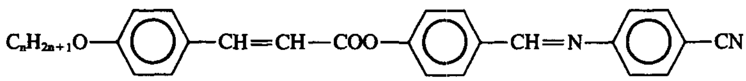
Transition temperatures of compounds of **1d**


(1d)

n	K		S_B	S_A		N		I
6	·	141	(. 104)	·	161	·	>300	·
7	·	133	(. 112)	·	245	·	>300	·
8	·	120	(. 108)	·	282	·	>300	·

TABLE V

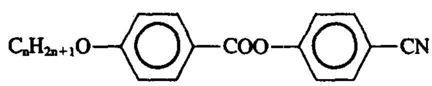
Transition temperatures of compounds of **1e**


(1e)

n	K		N_{re}	S_C	S_A	N		I
6	·	120	–	–	(. 92)	·	>285	·
7	·	92	–	–	.124	·	>285	·
8	·	99	.152.5	–	.223	·	281	·
9	·	93	(. 74)	–	.244	·	272	·
10	·	100	(. 70)	(. 87)	.257	·	267	·
11	·	95	–	(. 66)	.260	·	264	·

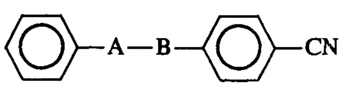
TABLE VI

Transition temperatures of compounds of **2a**


(2a)

n	K		S_A	N		I	Ref.
6	·	70	–	·	81	·	24
7	·	71.6	–	·	82	·	24
8	·	75.6	–	·	88	·	24
9	·	62	(. 59)	·	84	·	
10	·	80	(. 78)	·	85	·	

In conclusion (Figure 1): for the existence of the reentrant nematic phase, at atmospheric pressure:

*Core:  (d_C = 13.6 Å) (Table VI)

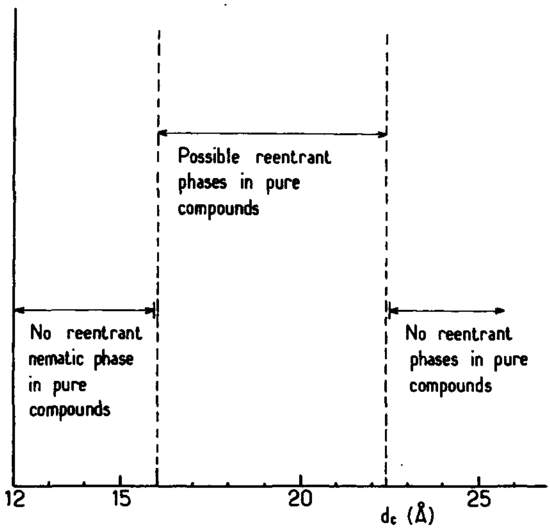
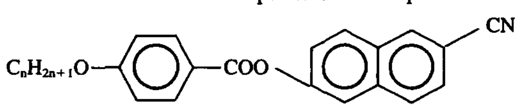


FIGURE 1 Existence of reentrant nematic phase at atmospheric pressure against the length of the cores.

TABLE VII

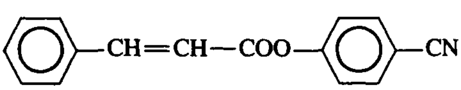
Transition temperatures of compounds of **2b**



(2b)

n	K		N_{re}	S_A		N		I	Ref.
7	·	95	–	–		·	161	·	
8	·	92.8	–	–		·	156	·	25
9	·	92	–	–		·	153	·	
10	·	78	(. 72)	·	139	·	152	·	
11	·	79	–	·	146	·	149.5	·	

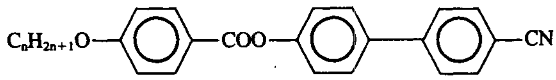
Comments: No reentrant phase found. This phase has been observed in binary mixtures or in pure materials but at high pressure.

*Core:  (d_C = 16 Å) (Table I)

Comments: Possible reentrant phase. Actually, only three two ring compounds in the three different series[5,22] are known to exhibit monotropic

TABLE VIII

Transition temperatures of compounds of **2c**

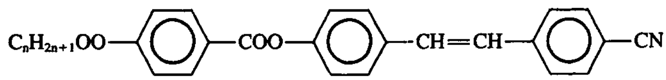


(2c)

n	K		N_{re}	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	–		·

TABLE IX

Transition temperatures of compounds of **2e**

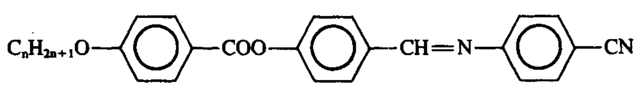


(2d)

n	K		$S_{A_{re}}$	N_{re}	S_A		N		I
6	·	100.5	. 143,5	–	–		·	310	·
7	·	99	. 127	–	–		·	293	·
8	·	96	(. 94,5)	. 138	·	248	·	283	·
9	·	97	(. 63)	(. 93.7)	·	261	·	275	·
10	·	96.5	–	(. 78)	·	265	·	270	·
12	·	98	–	–	·	258	–		·

TABLE X

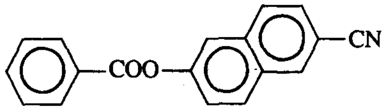
Transition temperatures of compounds of **2d**



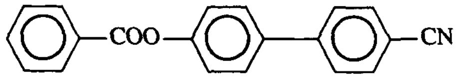
(2e)

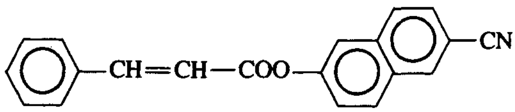
n	K		S_A	N_{re}		S_C	S_A		N		I	Ref.
6	·	115	(. 91)	–		–	–		·	274	·	10, 11
7	·	115	(. 70)	–		–	–		·	264	·	10, 11
8	·	108	–	·	153	–	·	197.5	·	255	·	10, 11
9	·	96	(. 40)	(. 92)		–	·	228	·	251	·	10, 11
10	·	100	–	(. 66)		(. 79)	·	232	·	242	·	10

reentrant nematic phase with the long chain $C_9H_{19}O$ or $C_{10}H_{21}$. It is the shortest core for which the derivatives can exhibit this phenomenon.

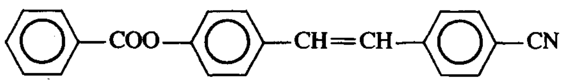
*Core:  (d_C = 16.1 Å) (Table VII)

Comments: Possible reentrant phase. Monotropic reentrant nematic phase with the long chain $C_{10}H_{21}O$.

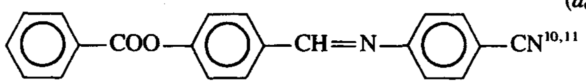
*Cores:  (d_C = 17.9 Å) (Table VIII)

 (d_C = 18.3 Å) (Table II)

Comments: Possible reentrant phase. Two compounds in each series with chain $C_8H_{17}O$, $C_9H_{19}O$ or $C_{10}H_{21}O$

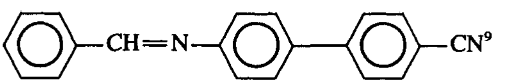
*Cores:  (Table IX)

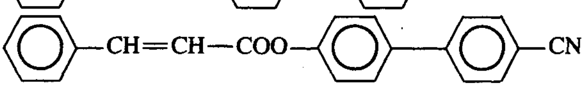
(d_C = 20.2 Å)

 (Table X)

Comments: Possible reentrant phases. Three compounds of each series with chain from $C_8H_{17}O$ to $C_{10}H_{21}O$

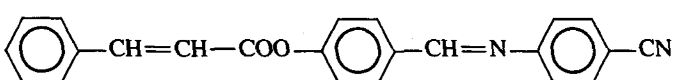
*Cores more rigid such as:

 (d_C = 17.9 Å)

 (d_C = 20.2 Å)

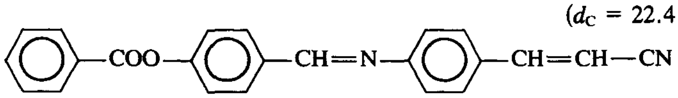
(Table III)

Comments: Possible reentrant phases. One compound with short chain $C_7H_{15}O$.

*Cores: 

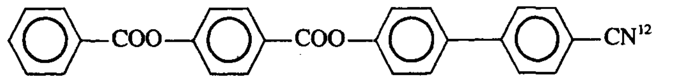
(Table V)

(d_C = 22.4 Å)

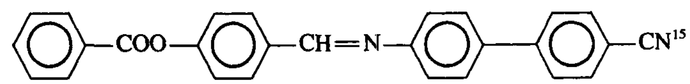


Comments: Possible reentrant phase. These two cores seem the longest core for which one can build up a derivative which still exhibits the reentrant phenomenon at atmospheric pressure.

*Cores:



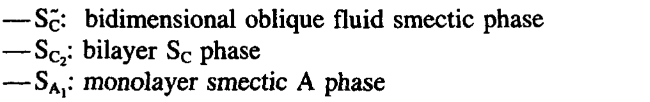
(d_C = 24.1 Å)



Comments: No reentrant phase found. This phenomenon may, perhaps, be observed at low pressure.

We claim that it is possible to generate a reentrant phase with a length of the core comprised between 16 Å and 22 Å. But if it seems to be a necessary condition, we add that it is not sufficient, and the chemical structure of the core, the position, and the sense of the dipolar linking groups between the phenyl rings have a crucial importance.

In this paper, we have been interested only in compounds with a polar group Y=CN which appeared to be very favorable to get the reentrant nematic phase. But is has been already shown that the NO_2 terminal group (which has roughly the same dipolar moment than CN ≈ 4 debyes) may also lead to the nematic reentrance . . . and more. As an example, we recall the recent discovery we have reported regarding the following compound:



which exhibits the novel and remarkable sequence:

$$\begin{array}{l} K\ 109\ S_{\tilde{C}}\ 118\ S_{A_1}\ 124\ N_{re}\ 127\ S_{A_{re}}\ 138\ N_{re}\ 156\ S_{A_d}\ 195\ N\ 224\ I \\ \quad\quad\ \ \uparrow\downarrow 96 \\ \quad\quad\ \ [S_{C_2}] \end{array}$$

where—$S_{\tilde{C}}$: bidimensional oblique fluid smectic phase
—S_{C_2}: bilayer S_C phase
—S_{A_1}: *monolayer smectic* A *phase*
—S_{A_d}: partially bilayer smectic A phase

Very new results indicate that in mixture, a strong dipole is not necessary to obtain a reentrant nematic phase.[23] Surely such advances will stimulate new synthetic works in the future.

Acknowledgments

The author is indebted to Drs. C. Destrade, F. Hardouin, and especially Dr. G. Sigaud for discussions and helpful comments.

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