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INFLUENCE OF THE SUBSTITUENT ON THE REENTRANT PHENOMENON

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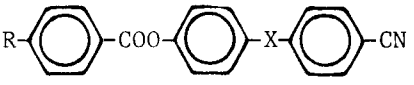
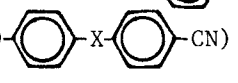
ABSTRACT: Three new series of compounds exhibiting nematic and smectic A reentrant mesophases at atmospheric pressure are presented: 4-alcanoyloxybenzoyloxy-4'-cyanobiphenyl series, 4-alcanoyloxybenzoyloxy-4'-cyanostilbene series and 4-alcanoyloxybenzoyloxy-4'-cyanoazobenzene series. The influence of the alkyl, alkoxy and alcanoyloxy terminal substituents on the reentrant phenomenon is discussed.

INTRODUCTION: Reentrant N and S_A phases have been observed for pure compounds at atmospheric pressure.[1-7] All the molecules inducing this phenomenon have the general formula:



The relation between the molecular structure and the influence of the X group and of the attracting electron terminal groups such as CN, NO_2, and Br have been largely discussed;[8] however, concerning the R substituent only alkyl and alkoxy derivatives have been described. We report here the results obtained with another type of substituent, R=$C_nH_{2n+1}COO$-, of particular interest because of its large polarizability, and along with X being a single bond (biphenyls), a double bond -N=N- (azobenzenes) or -CH=CH- (stilbenes). We attempted to determine whether the nature of the substituent has any influence on the reentrant phenomenon.

EXPERIMENTAL: All the products where prepared by esterification between R'COO-  -COCl and the corresponding cyanophenol (HO-  -CN) in pyridine. They were purified

by chromatography on silica gel, eluted with benzene, and recrystallized from absolute ethanol. The purity of the products was checked by elemental analysis and thin layer chromatography. Transition temperatures were determined using a DSC (DuPont 990). The textures were observed with a polarizing microscope equipped with a heating stage (Mettler FP 5).

RESULTS: In the three series which were prepared, the reentrant nematic phase is always observed. In two cases, a smectic A reentrant phase is also observed. All the results are collected in Table I. The nature of the phases was systematically verified using the contact method by their isomorphy with a known reference compound. The four phases N, S_A, N, S_A of the N°10 compound are miscible with those of 4-octyloxybenzoyloxy-4'-cyanostilbene[1,2] (Fig. 1) and with those of the N°9 compound (Fig. 2).

TABLE I

Transition Temperatures of Compounds Belonging to the Series C_nH_{2n+1}-COO-⟨⟩-COO-⟨⟩-X-⟨⟩-CN

N°	X	n	K	S_A	N	S_A	N	I
1	-	5	. 94	. (75)	-	-	. 280	.
2	-	6	. 94	-	-	-	. 262	.
3	-	7	. 96	-	-	-	. 246	.
4	-	8	. 94	-	. 107	. 185	. 240	.
5	-	9	. 91	-	-	. 212	. 233	.
6	-	10	. 81	-	-	. 217	. 230	.
7	-	11	. 82	-	-	. 219	. 229	.
8	N=N.	8	. 104	. (102)	-	-	. 260	.
9	N=N.	9	. 108	. (87)	. 130	. 211	. 258	.
10	CH=CH	8	. 104	. (103)	. 177,5	. 214,5	. 281	.
11	CH=CH	9	. 96,7	-	. 105	. 252	. 280	.

DISCUSSION: Let us recall that, in the series already known, the reentrant phase appears:

- for the alkoxy group with $C_8H_{17}O$ and $C_9H_{19}O$
- for the alkyl group, only in two series: the

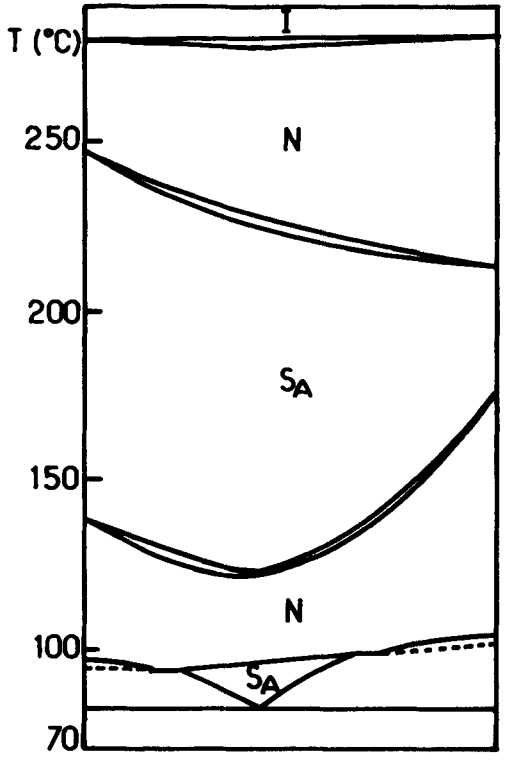


FIG. 1 : Isobaric phase diagram of the compound n°10 (on right) and the 4-octyloxybenzoyloxy-4' cyanostilbene (on left)

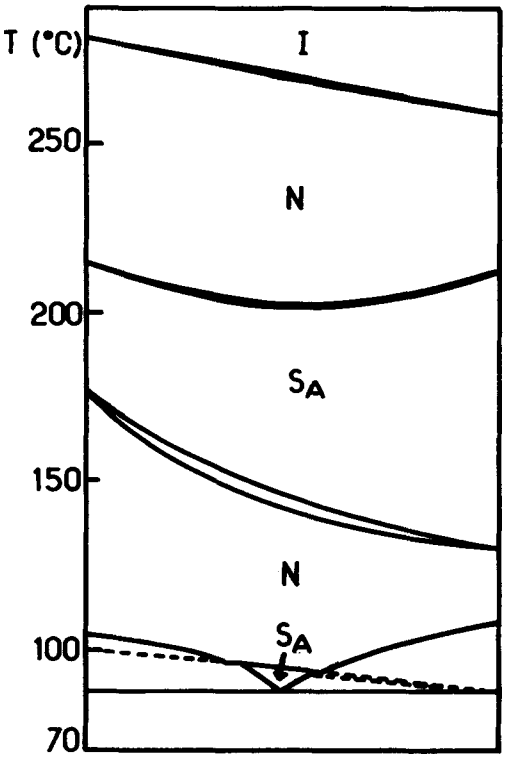
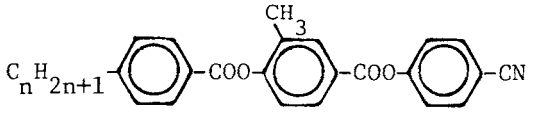


FIG. 2 : Isobaric phase diagram of the compound n°9 (on right) and the compound n°10 (on left)

tolanes[4] starting with $C_{10}H_{21}$ and the dibenzoates[9]



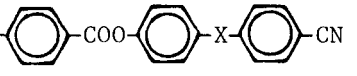
starting with $C_{11}H_{23}$. Therefore, the alkoxy group appears to be more suitable to induce the reentrant phenomenon than the alkyl group. In Table II, we report, for the three central rigid cores studied, the results obtained with the alkyl and alkoxy groups, for two lengths of the aliphatic chains. It is seen clearly that the alcanoyloxy group favors the appearance of the reentrant phenomenon. It may be thought that this ability is related to the polarizability of the different R groups, which can be classified in the increasing order:[10]

$$C_nH_{2n+1}- < C_nH_{2n+1}O- < C_nH_{2n+1}COO-$$

agreeing with the dipole moment of CH_3-, CH_3O, and CH_3COO- groups, which are respectively 0.37 D, 1.2 D and 1.83 D[11] when they are related to an aromatic carbon. On the other

Table II

Transition Temperatures of the Compounds of the series



X	R	K	S_A	N	S_A	N	I
-	C_8H_{17}-	. 70	-	-	. 184	. 217	.
-	$C_8H_{17}O$-	. 97	-	. 120	. 201	. 240	.
-	$C_8H_{17}COO$-	. 94	-	. 107	. 185	. 240	.
N=N	$C_9H_{19}O$-	. 90	. (72)	. 118	. 214	. 253	.
N=N	$C_9H_{19}COO$-	. 108	. (87)	. 130	. 211	. 258	.
CH=CH	C_8H_{17}-	. 105	-	-	-	. 265	.
CH=CH	$C_8H_{17}O$-	. 96	. (94.5)	. 138	. 248	. 281	.
CH=CH	$C_8H_{17}COO$-	. 104	. (103)	. 177,5	. 214,5	. 281	.
CH=CH	C_9H_{19}-	. 86	-	-	. 232	. 254	.
CH=CH	$C_9H_{19}O$-	. 97	. (63)	. (93,7)	. 261	. 275,3	.
CH=CH	$C_9H_{19}COO$-	. 97	-	. 105	. 252	. 280	.

hand, the reentrant phenomenon seems to be related to the length of the substituent. That is the reason why we prepared especially compounds with n=8 and n=9.

A closer look at Table II shows that:

- in the case of high polarizability groups $C_nH_{2n+1}O-$ and $C_nH_{2n+1}COO-$, the reentrant nematic phase is observed for the compounds whose aliphatic chain contains the same number of carbon atoms; for instance, $C_8H_{17}O-$ and $C_8H_{17}COO-$ for the biphenyls and the stilbenes or $C_9H_{19}O-$ and $C_9H_{19}COO-$ for the azobenzenes and the stilbenes. Except in the cases of the biphenyls, this phase is more stable with $C_nH_{2n+1}COO-$ than with $C_nH_{2n+1}O-$

- for the S_A reentrant phase, these two groups are almost equivalent.

- concerning the other transition temperatures:

. the nematic-isotropic transition temperature (T_{NI}) increases with the group polarizability;[10] indeed, $T_{NI}(RCOO) > T_{NI}(RO) > T_{NI}(R)$:

. the S_AN highest transition temperature is such as $T_{S_{A-N}}(RCOO) < T_{S_{A-N}}(RO)$

- the nature of the S_A phase observed in the n° 1 compound (Table I) has been discussed by Heppke et al.,[7] for the 4-alkoxybenzoyloxy-4'-cyanoazobenzenes. This low temperature S_A phase exhibits a maximum when the aliphatic chains vary from pentyloxy to helptyloxy, in the series studied[2,4,7]. In our series, it seems to be at its maximum with the product n°1 (pentyl chain) and it is not surprising to see that this S_A phase disappears with longer chains (compounds n°2 and 3, Table I).

CONCLUSION: We have synthesized three series of new compounds. Four of these compounds present a reentrant nematic phase at atmospheric pressure, and two of them exhibit moreover a reentrant smectic A phase. A comparison with the homologous alkyl and alkoxy derivatives is reported. It shows that this group is particularly suitable to induce the reentrant phenomenon and may shed some light in its understanding.

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